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Current Topics

Conference on the Application of Science & Technology to the Development of Asia

DURING the past two decades a number of international and regional conferences have been held bearing on the application of science and technology to the industrial development of nations. The earliest of the series was the United Nations Conference on the Conservation and Utilization of Resources held in 1948. A recent one of considerable significance to countries like India was the United Nations Conference on the Application of Science and Technology for the Benefit of the Less Developed Areas (UNCAST) held in Geneva in 1963. UNCAST called for continued attention by the United Nations to this subject and for the organization of regional conferences to study the needs of particular areas of the world. A major achievement of UNCAST lay in the fact that it provided for the first time information on various aspects of national development in different countries.

As a consequence of the recommendations of UNCAST, two regional conferences were convened. The first was the International Conference on the Organization of Research and Training in Africa in relation to the Study, Conservation and Utilization of National Resources held in Lagos, Nigeria, in 1964. The second was the Conference on the Application of Science and Technology to the Development of Latin America held in Santiago, Chile, in 1965. Many closely related problems concerning African and Latin American countries were discussed at these conferences.

The impact of these conferences on the peoples and governments of developing nations can be judged from the fact that during the past two decades an awareness has been created among them of the advantages of applying science and technology to solving national economic problems, the need for including science in the curriculum of education at all levels and the need for encouraging scientific research. The conferences emphasized the importance of trained manpower, the need for survey of natural resources, and the need for adopting a national science policy in harmony with the national plans for scientific development. Above all, these conferences have provided basic data on the progress made in different spheres of science and technology and have laid down the guiding principles for future development. It is largely because of these conferences, the United Nations Development Programme Special Fund Sector has, since 1959, approved over 700 projects, the majority of which involve the application of science and technology to the development of nations, and of these nearly 200 are in progress in Asia and the Far East.

The Conference on the Application of Science and Technology to the Development of Asia — third in the series since UNCAST — was convened in pursuance of a resolution adopted by the General Conference of Unesco and was organized in cooperation with the United Nations Economic Commission for Asia and the Far East. Twenty-five countries participated in the ministerial level conference which was held in New Delhi during 9-20 August 1968. Organizations of the United Nations and a number of inter-governmental and international non-governmental organizations and private foundations were also represented by observers. In all, 117 delegates and 35 observers attended the conference. The main objectives of the conference were to review the progress made since the earlier conferences and to consider action required to further the application of science and technology to the development of Asia.

Inaugurating the conference the Prime Minister, Shrimati Indira Gandhi, observed that CASTASIA was an important conference and its objective was to remove poverty in Asian countries and enable Asians to lead the kind of life which was today regarded as 'man's basic right'. The Prime Minister sought on behalf of India inter-Asian cooperation in the field of science and technology in a spirit of partnership and friendship. Dr Triguna Sen, the conference President, during the general debate, called upon the delegates to translate decisions into action for uplifting the millions of men, women and children ' who have not known the joy of living because science and technology have not yet brought to them the full consciousness of what it is to be fully alive '.

The conference adopted a 207-page report comprising the recommendations of the three commissions which respectively dealt with (i) Prerequisites for and promotion of the application of science and technology to development, (ii) Improvement of science education, and (iii) Science policy and its relation to economic planning. The recommendations of the conference are addressed to the member states and international and regional agencies (including Unesco and other UN agencies) and to the people at the working level.

An important recommendation of the conference concerns the targets for total national expenditure on research and development. The conference called upon the participating governments of Asian countries to achieve a minimum level of total national expenditure on R & D of 1 per cent of their gross national product as soon as possible, but not later than 1980; this figure comprises current

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and capital expenditures financed by both governmental and private sources.

The conference listed nine priority areas of action in Asia: (1) Full use of modern communication techniques, functional literacy programmes, science clubs and fairs, and cooperation with appropriate organizations, including women's organizations, to promote the appreciation of science with special emphasis on rural populations; (2) Improvement of expansion of science education at all levels by increasing the number and raising the qualifications of teachers with a parallel improvement of curricula, teaching materials and equipment; (3) Improvement of career prospects and possibilities of upgrading middle-level technicians, including agricultural technicians and technical school teachers; (4) Expansion and improvement of agricultural education in connection with the extension work and application of multi-disciplinary agricultural research programmes, both basic and problem-oriented; (5) Strengthening and linking of existing information and documentation centres, establishment of new centres and possibly regional information clearing houses, rationalization of existing systems through maximum use of modern techniques of reprography, abstracting and data processing; (6) Development of scientific and technological potential through improved training, employment and working conditions and equal educational opportunities for all; (7) Collaboration between universities and laboratories and creation of institutes for advanced studies to foster scientific research and technological development; (8) Formulation and implementation of national policies integrating education, research, technology and industry, based on the principle of endogenous development and integrated with development planning policies at the highest government level; and (9) Promotion of international and regional cooperation through exchange of information and scientific personnel, the pooling of resources and the transfer of appropriate technology.

On the subject of transfer of technology, the conference specifically recommended the setting up urgently of technology transfer and information centres charged with the functions as proposed by the UN Economic and Social Council's Advisory Committee on the Application of Science and Technology to Development, and with branches, wherever necessary, to provide assistance to enterprises in identifying their technological needs, the availability of external aid and in the negotiation of agreements. The UN Secretary-General would be invited to review the overall position of the work done in the transfer of technology by different UN bodies and to draw up a comprehensive plan and programme of action for operating the transfer of technology. The conference also recommended that the Unesco Director-General be invited to study ways and means of establishing in Asia, under Unesco's auspices and in collaboration with ECAFE and other international regional organizations, permanent machinery to keep under regular review, stimulate and facilitate the cooperation of member states represented at CASTASIA, so that its recommendations can be implemented.

The Unesco Director-General, Mr Rene Maheu, in his address at the final plenary session stressed the need for follow-up action and assured Unesco's cooperation to the Asian nations in implementing the recommendations. The Director-General summed up the post-conference programme under three heads: (i) Collection of information regarding the state of things in Asian countries, (ii) Analysis of the current position, and (iii) Future action. An important achievement of the conference is that it provided the basic premises for drawing up the blue-prints for scientific and industrial advancement of Asia for the coming two decades. The conference also laid emphasis on inter-Asian cooperation in the field of science and technology. India offered to share her experiences with other Asian countries in the application of science and technology. The conference impressed upon the participating countries the vital role of science and technology in lifting Asian countries from the morass of social and industrial backwardness. These objectives can be achieved only by a purposeful follow-up of the recommendations of the conference by the United Nations and its agencies and the countries of the region.

Radiostrontium in the Air & Surface Deposition

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R ADIOACTIVE contamination of the environment by fission products and induced radioactivity resulting from explosions of nuclear weapons constitute a source of human exposure to ionizing radiations. The seriousness of world-wide contamination from nuclear weapon tests was first clearly identified in 1953. Most of the high yield tests of nuclear weapons took place during the years 1957-62 which increased the world-wide contamination to a large extent. Studies on the behaviour of long-lived and potentially hazardous fission products such as Sr-90 are important in the evaluation of long-term hazards associated with such contamination and have to be pursued on a continuing basis as the nature of hazards is still a subject of extensive research. The present studies would be valuable for predicting the extent of future contamination by Sr-90 in the event of new weapon tests.

The programme of measurements of environmental radioactivity in India was started early in 1956 with the daily measurements of gross-beta activity of ground level air and surface deposition at Bombay and was extended to the measurements of Sr-90 in surface deposition and ground level air in 1957. From October 1961, the Sr-89 activity of the above samples was also estimated. Concentrations of Sr-90 in air and surface fallout were measured to obtain an idea of rate of deposition. From the Sr-89/Sr-90 ratios, the composition of fallout activity and the contribution of various test series to the activity of samples could be calculated. The production ratio of 176 for Sr-89/Sr-90 (ref. 1) for the fission of U-238 by 14 MeV. neutrons was assumed. This ratio was compared with the observed ratio for different test series. The present paper discusses some of the salient features of the measurements of Sr-89, Sr-90 activity in the samples.

Experimental Procedure

Ground level air was sampled at Bombay through HV-70 filters for 18-24 hr a day and daily filters were pooled together for one calendar month to get a total volume of 2000-3000 cu. m. of air. Surface deposition samples were collected at Bombay in a high-walled stainless steel pot of 30 cm. diameter, kept at a height of 1 metre from the ground. Details of sampling methods are given in an earlier report[2].

The samples were analysed for radiostrontium by the radiochemical method of Boni[3]. The radioactivity measurements were made with a low background GM counter using anticoincidence techniques[4]. After chemical separation strontium carbonate is first counted to obtain the sum of Sr-89 and Sr-90 activities and again counted after radioactive equilibrium is established between Sr-90 and Y-90. Yttrium is separated from strontium and counted to obtain Sr-90 activity. The Sr-89 activity is obtained by taking the difference of the two values.

Results and Discussions

Cumulative Deposition of Sr-90 at Bombay

Fig. 1 gives the cumulative deposition of Sr-90 at Bombay. The solid lines give the results of measurements and the dashed lines give the values estimated from the ground deposition values of gross-beta activity by using Dolan's[5] data.

Fig. 2 is a plot of the cumulative deposition of Sr-90 in mC./km.² against the cumulative precipitation in mm. for the period 1957-65 for Bombay. The nature of the plot indicates the approximate proportionality between the deposition of Sr-90 activity and the total rainfall. The slopes of the lines drawn for each year show the rate of deposition of Sr-90 fallout for that year. It can be concluded from the slopes of these lines that (i) the rate of Sr-90 deposition was lowest in the year 1957 and highest in 1963; (ii) the rate of Sr-90 fallout decreased in the year 1964 and dropped further in the year 1965 to almost the 1959 rate; and (iii) the rates of Sr-90 fallout during the test moratorium period from 1959 to 1961 also show decreasing trends.

The total annual Sr-90 deposition at Bombay and the percentage of the total deposition during the rainy season are presented in Table 1. It is evident from this table that most of the deposition of Sr-90 takes place in the rainy season.
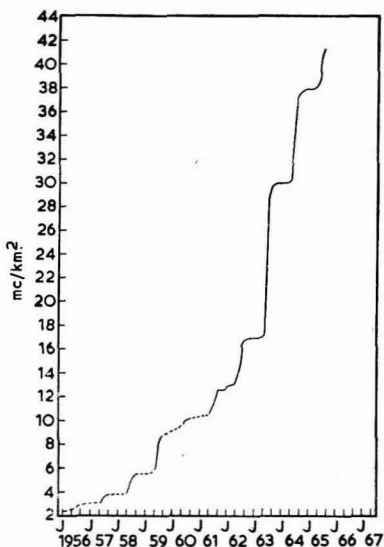
Fig. 1 — Cumulative deposition of Sr-90 at Bombay
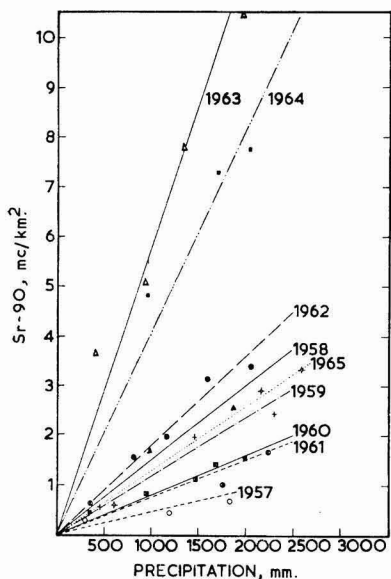
Fig. 2 — Variation of surface deposition of Sr-90 with rainfall

of the alternate years are compared to evaluate residence time. On the basis of these assumptions, we get

$$C_{(n+2)} = C_n e^{-\lambda_{st} \cdot t} \qquad \ldots(1)$$

where $C_{(n+2)}$ is the concentration of Sr-90 in $\mu\mu C./$litre of rain-water in $(n+2)$th year, C_n is the concentration in nth year, t is the time in years and here for this equation $t = 2$ years and $1/\lambda_{st}$ is stratospheric mean residence time. The value of C_{n+2} is corrected for radioactive decay for two years. The value of residence time so obtained for 1959-61 period is 2 years (Table 2). Similar calculations are made for the 1963-65 period because there was no major test series after the year 1962. The value of residence time for this period is approximately 1 year. Lower value of residence time for this period is due to the reason that most of the Sr-90 activity during 1961-62 test series was injected in polar regions. These values of residence time can be influenced to some extent by local and regional meteorological effects.

Sr-89/Sr-90 Ratios in Surface Fallout and Air

Fig. 3 gives a plot of Sr-89/Sr-90 ratio in surface deposition against time in days. Fig. 4 is a similar plot for ground level air. Levels of Sr-90 activity in ground level air are given in Table 3. Mean date for the 1961 USSR test series is taken as 20 October

TABLE 1 — ANNUAL DEPOSITION OF Sr-90 AT BOMBAY

Year	Deposition of Sr-90, mC./km.²	Fraction of total annual deposition in rainy season, %
1956	0·70	57·0
1957	0·76	95·5
1958	1·74	96·4
1959	3·48	86·3
1960	1·19	51·5
1961	2·31	90·8
1962	3·54	84·5
1963	12·48	97·0
1964	7·78	92·0
1965	3·60	87·0

TABLE 2 — MEAN AND HALF RESIDENCE TIME OF Sr-90 IN THE STRATOSPHERE

Period considered	Date of average conc. referred to in col. 3	Mean rain-water concentration in $\mu\mu C./$litre	λ_{st} in (years)⁻¹	Mean residence time $1/\lambda_{st}$ in years	Half residence time = $0·693/\lambda_{st}$ in years
1959-61	15 July 1959 15 July 1961	1·20 ⎫ 0·57 ⎭	0·347	2·89	2·0
1963-65	15 July 1963 15 July 1965	5·71 ⎫ 1·38 ⎭	0·682	1·47	1·0

Stratospheric Residence Time of Sr-90

The fact that no Sr-90 has been injected into the stratosphere after October 1958 till September 1961 can be used to calculate the stratospheric residence time of Sr-90. French atomic explosions of February and April 1960 have not contributed more than 0·1-0·2 per cent of the total Sr-90 in the stratosphere[6] and hence have been neglected in the present calculations. Under these conditions, the Sr-90 activity at ground level is controlled by the stratospheric burden and, therefore, can be said to be approximately proportional to stratospheric inventory of Sr-90. While using the observed ground level Sr-90 concentrations for calculating stratospheric residence time, one has to eliminate variations due to the annual seasonal cycle and this is done by comparing the levels of Sr-90 activity in the same periods of the year. The average activities of rain-water for the June-August period

Fig. 3 — Sr-89/Sr-90 activity ratio in surface deposition at Bombay

TABLE 3 — Sr-90 IN GROUND LEVEL AIR AT BOMBAY
(10^{-15} CURIES PER CU. M. OF AIR)

Month	1957†	1958†	1959†	1961	1962	1963
January				*	12·1	17·0
February	4·5	5·6	19·1	*	38·4	19·2
March				*	12·4	*
April				*	24·6	32·6
May	6·6	0·7	11·0	*	4·1	23·6
June				*	39·3	55·9
July				*	16·9	*
August	4·6	0·6	1·5	*	4·1	*
September				5·3	5·4	*
October				2·4	9·8	*
November	2·5	5·8	0·6	8·9	6·7	*
December				7·2	4·5	*

*Data not available.
†Air filter samples were pooled together for three months during 1957-59.

Fig. 4 — Sr-89/Sr-90 activity ratio in air filters at Bombay

1961, that for the 1962 USSR series as 15 October 1962 and that for the 1962 USA test series as 15 June 1962 (ref. 7). The activity ratios on these mean dates were compared with the production ratio of 176 to arrive at the following conclusions.

(i) The Sr-89/Sr-90 ratio for October 1961 to December 1961 period is about 50 on 15 October 1961. This shows that only 30 per cent of Sr-90 deposited in this period is from the 1961 test series. The remaining Sr-90 fallout is mainly from old stratospheric Sr-90.

(ii) The Sr-89/Sr-90 activity ratio for January 1962 to May 1962 decays with an approximate half-life of Sr-89; the same is true for January 1963 onwards for the whole year. This indicates that the activities from the various test series are in constant proportions. The activity ratios for these periods are 136 and 133 on the mean dates for the 1961 and 1962 autumn series. These ratios show that 77 per cent of fallout in 1962 and 75 per cent in 1963 are from the 1961 and 1962 autumn test series respectively. In the selection of an average date for the second period, an error is possible as polar tests were spread over a period of five months. A later average date than the one used here is likely. For example, if the average date is taken as 15 November 1962 (ref. 8), the contribution of 1962 autumn test series to Sr-90 deposition in 1963 could be about 50 per cent.

(iii) The peak in Sr-89/Sr-90 ratio in June 1962 (Fig. 4) in ground level air corresponds to the US Pacific tests of 1962. This is also supported by the shift of the points of activity ratio for July 1962 and August 1962 to the right-hand side of the decay line for the first half of 1962.

(iv) From September 1962 onwards, the Sr-89/Sr-90 ratio increases rapidly till the end of the autumn tests in December 1962, due to continuous influx of fresh activity from 1962 USSR test series. This rise reaches a maximum value in January 1963 for surface fallout and in December 1962 for air filter samples. The ratio then decreases with the half-life of Sr-89 for both the samples. Mean activity ratio
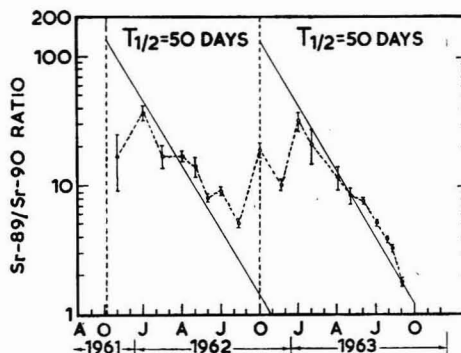
TABLE 4 — THE DEPOSITION VELOCITIES FOR Sr-89 AND Sr-90 ACTIVITIES

Period	V_g, cm./sec.		$\dfrac{(V_g)_{Sr-89}}{(V_g)_{Sr-90}}$
	Sr-89	Sr-90	
November 1961	0·02	0·03	0·66
January 1962	—	0·68	—
Feb.-March 1962	0·12	0·13	0·92
April 1962	0·04	0·05	0·80
19 Sept. to 14 Nov. 1962	0·09	0·13	0·69
14 Nov. 1962 to 1 Jan. 1963	0·06	0·29	0·21
January 1963	0·01	0·01	1·00
February 1963	0·06	0·07	0·85

for both the samples corrected to 15 October 1962 indicates that 75 per cent of Sr-90 fallout in 1963 was from 1962 autumn tests.

Peaks in Sr-89 activity (corrected for decay to mean dates for the respective test series) in April 1962 and April 1963 provide an evidence of the well-established spring peaks of stratospheric fallout.

Deposition Velocities of Sr-89 and Sr-90 Activities

The deposition velocity V cm./sec. is defined as

$$V = \frac{\text{rate of deposition in } \mu\mu C./cm.^2/sec.}{\text{concentration in air in } \mu\mu C./cm.^3}$$

The calculated deposition velocities of Sr-89 and Sr-90 are presented in Table 4. It is seen from this table that the deposition velocity of Sr-90 is in general more than that of Sr-89 during the period of fallout of recent origin (i.e. the period from November 1961 to February 1963). The ratio of the deposition velocity of Sr-89 to that of Sr-90 can be expressed as

$$\frac{V(Sr-89)}{V(Sr-90)} = \frac{\text{ratio of Sr-89/Sr-90 in surface fallout}}{\text{ratio of Sr-89/Sr-90 in air}}$$

$$\ldots(2)$$

Mamuro et al.[9] have shown that radioisotopes in highly radioactive particles in surface fallout fractionate more than those in air and that Sr-89 is impoverished to a large extent in such hot particles

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when compared to Sr-90 (ref. 10). In addition, Sr-90 from delayed fallout, which is not a part of highly radioactive particles of greater diameter found in fresh fallout, does not undergo severe fractionation as in the case of hot particles. Sr-89 comes from fresh fallout having a number of highly radioactive particles of greater diameter and is fractionated with reference to Sr-90 of recent origin. The overall effect is that there is greater fractionation of Sr-89 than that of Sr-90. This effect is more pronounced in surface fallout samples than in air filter samples. This explains the lower Sr-89 deposition velocity obtained by Eq. (2).

Summary

The results of measurements of radiostrontium in the air and surface deposition at Bombay for the period 1956-65 have been described. Some of the salient features of the measurements of Sr-89 and Sr-90 activities have been discussed. It is found that the rate of Sr-90 deposition was lowest in the year 1957 and highest in 1963. Sr-90 injected in polar latitude gets deposited at faster rate compared to equatorial injections. The study of the Sr-89/Sr-90 ratios shows that 77 per cent of fallout in 1962 and 75 per cent of fallout in 1963 were from 1961 and 1962 autumn test series respectively. Study of the deposition velocities of Sr-89 and Sr-90 activities indicates that the deposition velocity of Sr-90 is in general more than that of Sr-89 during the period of fallout of recent origin.

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Potential Energy Curves & Nature of Binding in Group IIIA Monohalides*

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POTENTIAL energy curves for different electronic states of diatomic molecules are of fundamental importance in understanding a number of molecular phenomena, e.g. dissociation energies, perturbations, etc. In addition, these curves form a basis for discussion of the nature of binding in the different states of a molecule. Thus a comparison of the true (experimental) potential curves with theoretical curves obtained using different type of valence structures can help in deciding the ionicity or polarity of the chemical bond. Even though the potential energy curves of a large number of diatomic molecules, in their various electronic states, have been lately constructed from the experimental data, no serious attempts have been made so far in the above direction. The work of Varshni and Shukla[1,2] on alkali hydrides and alkali halides is the only exception. The present paper extends this type of inquiry to the halides of Group IIIA.

Recent studies include the construction of potential energy curves based upon available experimental energy data for a large number of diatomic molecules[3-9]. In some cases, these curves have been used to discuss certain features of the observed spectra and dissociation energies of the molecules. To get an estimate of dissociation energies, the experimental potential energy curves have been compared with those obtained using an empirical potential function. The 3-parameter Lippincott function[10], which adequately represents the experimental curves of a large number of molecules[11-13], has been used for such comparison and has yielded satisfactory estimates of dissociation energies for many diatomic molecules. From a study of the potential energy curves and dissociation energies of diatomic molecules, it was found that values for dissociation energies obtained by this method of curve fitting, as indicated above, for the diatomic halides of Group IIIA elements are in great disagreement with the other reported values of dissociation energies.

The work reported in this paper was started with the above two objects in view. However, when a comparison of the experimental potential curves with empirical curves was started, it was found that the application of various empirical methods to the question of ionicity of these molecules would be quite interesting. Therefore, this paper not only includes the new results relating to the potential curves and Hellman curves obtained by the authors, but also discusses the various formulae suggested by earlier workers to determine the ionicity of the bond. A semi-empirical quantum mechanical method has also been discussed in brief.

Experimental Potential Energy Curves

The RKRV method used in the calculations of experimental potential energy curves was originally suggested by Rydberg[14] and Klein[15] and later modified by Rees[16] and Vanderslice et al.[17]. This method is a WKB procedure which starts with the experimental energy levels and finds out the classical turning points. This calculation has been done for various states of diatomic halides of Group IIIA elements. Table 1 lists the states and molecules for which the calculations have been performed as well as the molecular constants used in the calculations[18-44]. The results are summarized in Table 2.

Comparison of the RKRV Curves with Empirical Functions

A number of empirical potential functions were suggested by different workers before the RKRV method came in general use. These functions led to energy levels in reasonable agreement with the experimental observations. Steele et al.[12] compared these curves with RKRV curves for a large number of molecules. They found that the RKRV curves could be reproduced well by the Hulburt-Hirschfelder and the 5-parameter Lippincott functions. The 5-parameter Lippincott function can be reduced to a 3-parameter form without much loss in accuracy and can be made to depend on the dissociation energy in a simple way[10]. This simplified function, when compared with the RKRV curves, led to satisfactory estimates of the dissociation energies for various molecules. For the present group of molecules it leads to very low values of dissociation energy. However, application of the same method to excited states leads to a much better estimate.

The present sequence of molecules is known to be somewhat ionic. It was, therefore, thought worth while to investigate the behaviour of ionic potential functions. Of the various functions suggested, it was shown by Varshni and Shukla[1,2] that the functions suggested by Hellman[45] and Rittner[46] are the best. In the latter function, the two ions are supposed to introduce a polarization effect on the charge distribution of each other. It would be seen later that this polarization is not appreciable for TlCl, the only molecule of the group for which experimental dipole moment is known. In view of this, the Hellman function was chosen for comparison with the RKRV curve. It was seen that the Hellman curve approaches the experimental curve for the ground state, even for low values of r, in the neighbourhood of r_e. For the excited states, on the other hand, the experimental curve meets the ionic curve only for either very large or very small r values. This might be taken as an indication that the ionic contribution to the binding at $r \sim r_e$ is large for the ground state but quite small for the excited states. Another significant point concerning the separations of the ground state RKRV curve and the first excited state RKRV curve from the ionic curve was that in the lighter molecules like BF the Hellman curve is nearer to the first excited state than in

TABLE 1 — MOLECULAR CONSTANTS* USED IN CALCULATIONS

Molecule	State	T_e (cm.$^{-1}$)	ω_e (cm.$^{-1}$)	$\omega_e x_e$ (cm.$^{-1}$)	B_e (cm.$^{-1}$)	α_e (cm.$^{-1}$)	r_e (Å.)	Reference
BF	$X^1\Sigma^+$	0	1402·13	11·840	1·5107	0·01650	1·265	18-22
	$A^1\Pi$	51150·1	1264·96	12·530	1·4206	0·01650	1·305	
	$B^1\Sigma^+$	65334·8	1693·00	12·700	1·6583	0·01880	1·200	
	$a^3\Pi$	a	1323·86	9·200	1·4135	0·01580	1·308	
BCl	$X^1\Sigma^+$	0	839·12	5·110	0·6838	0·00646	1·716	23, 24
	$A^1\Pi$	36750·9	849·04	11·370	0·7054	0·00820	1·689	
BBr	$X^1\Sigma^+$	0	684·31	3·520	0·4900	0·00350	1·887	25, 26
	$A^1\Pi$	33935·3	637·63	17·580	0·5010	0·00900	1·866	
AlF	$X^1\Sigma^+$	0	801·52	4·700	0·5523	0·00483	1·655	27, 28
	$A^1\Pi$	43935·0	803·95	6·141	0·5566	0·00556	1·648	
	$B^3\Pi_0$	54273·0	862·00	7·000	0·5783	0·00471	1·617	
	$C^3\Pi_1$	57750·0	938·40	5·180	0·5901	0·00455	1·601	
AlCl	$X^1\Sigma^+$	0	481·30	1·950	0·2420	0·00200	2·133	29, 30
	$A^1\Pi$	38254·0	449·96	4·370	0·2590	0·00600	2·067	
AlBr	$X^1\Sigma^+$	0	378·00	1·280	0·1591	0·00085	2·296	31-33
	$A^3\Pi_0$	23647·0	411·20	1·750	0·1640	0·00100	2·260	
	$B^3\Pi_1$	23779·3	410·32	1·750	0·1640	0·00100	2·260	
	$C^1\Pi$	35879·5	297·20	6·400	0·1555	0·00216	2·322	
GaF	$X^1\Sigma^+$	0	623·80	3·400	0·3590	0·00280	1·775	34-36
	$A^3\Pi_0$	33096·2	661·00	3·400	0·3705	0·00302	1·747	
	$B^3\Pi_1$	33430·5	663·00	1·800	0·3715	0·00300	1·745	
	$C^1\Pi$	47362·3	542·80	9·700	0·3580	0·00530	1·778	
GaCl	$X^1\Sigma^+$	0	365·00	1·100	0·1489	0·00030	2·208	37, 38
	$A^3\Pi_0$	29524·1	395·30	2·300	0·1568	0·00115	2·152	
	$B^3\Pi_1$	29855·7	395·30	2·500	0·1572	0·00115	2·149	
InF	$X^1\Sigma^+$	0	534·70	2·560	0·2625	0·00186	1·985	34, 35, 39
	$A^3\Pi_0$	29935·6	575·70	3·660	0·2734	0·00202	1·945	
	$B^3\Pi_1$	31274·2	571·30	2·630	0·2738	0·00204	1·943	
	$C^1\Pi$	42807·5	463·90	77·350	0·2664	0·00500	1·970	
InCl	$X^1\Sigma^+$	0	317·40	1·010	0·1170	0·00090	2·420	38, 40, 41
TlF	$X^1\Sigma^+$	0	477·30	2·300	0·2231	0·00150	2·084	38, 42
	$A^3\Pi_0$	35180·7	360·65	12·250	0·2309	0·00274	2·049	
	$B^3\Pi_1$	36869·5	439·87	8·600	0·2249	0·00307	2·076	
TlCl	$X^1\Sigma^+$	0	287·47	1·240	0·0914	0·00039	2·485	38, 43
	$A^3\Pi$	31054·2	216·90	6·800	0·0923	0·00131	2·473	

*Most of the older data are from Herzberg[44].

heavier molecules. This indicates that the first excited states of lighter molecules have more ionic character than those of the heavier molecules whereas the reverse holds good for the ground states.

Dissociation Energies

The ground state of all the molecules in the present group is known to be $\pm a\ ^1\Sigma$ state and the lowest excited state is $a^3\Pi_{reg.}$, which changes in coupling from case a (case b) in BF to case c in heavier molecules. Above the $^3\Pi$ state there lies a $^1\Pi$ state. The dissociation products in these states are not higher than $M^*(^2P_{3/2})$ and $X^*\ (^2P_{1/2})$ in any of the molecules. The most widely used spectroscopic method for determining dissociation energies is form of the Birge-Sponer (BS) extrapolation. In the case of these molecules, the dissociation energies obtained from the ground state levels by this method are on the average only 0.7 ± 0.1 of the values obtained by thermochemical methods. Barrow[47] has recently discussed the dissociation energies of molecules of this group obtained from thermochemical and also from spectroscopic methods by extrapolations in the excited states, $^3\Pi$ and $^1\Pi$. These extrapolations lead to results in good agreement with thermochemical values except in case of lighter molecules.

Somayajulu[48] has shown that relation $k_e r_e/D_0 = S$, where S is a constant, holds either for a sequence of diatomic belonging to one column of the periodic table or when one of the atoms comes from one particular column and the other from another specified column. The results obtained for the present group of molecules were quite encouraging. However, in this sequence, BF, BCl and BBr were found to form a sub-group and obey the above relation with $S = 1.194$. All the other members of the sequence form another sub-group which has $S = 1.015$.

The failure of the BS extrapolation method as applied to the ground state may be attributed to the ionic contribution to the binding in the ground state. Of course other factors like sp-hybridization also have their effects. The reason as to why the BS method fails may be explained in the following manner. In the case of ions, the law of force between the atoms at large distances is approximately $1/r$ and as such the ΔG versus v curve becomes almost asymptotic to the v-axis. In all cases (except CsF) the limit of dissociation into ions lies above the limit for dissociation into normal atoms and, hence, even though the ground molecular states usually dissociate into normal atoms, excited states may dissociate into ions or at least have large ionic

TABLE 2 — RKRV CURVES FOR GROUP IIIA MONOHALIDES

State	v	U(cm.⁻¹)	$r_{min.}$ (Å)	$r_{max.}$ (Å)	T_e+U (cm.⁻¹)	State	v	U(cm.⁻¹)	$r_{min.}$ (Å)	$r_{max.}$ (Å)	T_e+U (cm.⁻¹)
			BF					BBr — *contd*			
$X^1\Sigma^+$	0	698.1	1.210	1.328	698.1	$X^1\Sigma^+$	9	6183.2	1.634	2.283	6183.2
	1	2077.6	1.174	1.379	2077.6		10	6797.1	1.623	2.309	6797.1
	2	3432.8	1.150	1.417	3432.8		11	7404.0	1.614	2.335	7404.0
	3	4767.9	1.132	1.451	4767.9		12	8003.8	1.604	2.360	8003.8
	4	6077.0	1.118	1.481	6077.0		13	8596.6	1.596	2.385	8596.6
	5	7364.5	1.105	1.509	7364.5		14	9182.4	1.588	2.410	9182.4
	6	8633.9	1.094	1.537	8633.9						
	7	9882.2	1.083	1.563	9882.2	$A^1\Pi$	0	314.5	1.798	1.948	34249.8
	8	11105.2	1.074	1.589	11105.2		1	919.3	1.755	2.020	34854.6
	9	12298.2	1.066	1.614	12298.2		2	1491.6	1.727	2.078	35426.9
	10	13483.2	1.058	1.638	13483.2		3	2026.0	1.703	2.136	35961.3
							4	2511.0	1.681	2.191	36446.3
$A^1\Pi$	0	629.4	1.247	1.371	51779.5		5	2929.4	1.647	2.269	36864.7
	1	1868.4	1.208	1.425	53018.5		6	3257.6	1.614	2.350	37192.9
	2	3079.5	1.184	1.466	54229.6						
	3	4262.1	1.164	1.503	55412.2				AlF		
	4	5413.3	1.148	1.536	56563.4						
	5	6534.6	1.134	1.568	57684.7	$X^1\Sigma^+$	0	399.6	1.596	1.720	399.6
	6	7620.5	1.121	1.599	58770.6		1	1192.1	1.558	1.772	1192.1
	7	8671.8	1.109	1.630	59821.9		2	1974.7	1.533	1.812	1974.7
	8	9681.8	1.098	1.660	60831.9		3	2748.6	1.514	1.845	2748.6
							4	3512.4	1.499	1.876	3512.4
$B^1\Sigma^+$	0	843.3	1.157	1.265	66178.1		5	4267.1	1.485	1.904	4267.1
	1	2509.7	1.125	1.312	67844.5		6	5013.0	1.473	1.931	5013.0
	2	4152.5	1.104	1.346	69487.3		7	5748.8	1.463	1.957	5748.8
							8	6479.1	1.454	1.982	6479.1
$a^3\Pi$	0	659.7	1.251	1.372	$a+659.7$		9	7199.2	1.445	2.006	7199.2
	1	1964.7	1.214	1.425	$a+1964.7$		10	7909.7	1.437	2.030	7909.7
	2	3250.4	1.190	1.465	$a+3240.4$		11	8611.5	1.429	2.053	8611.5
	3	4517.9	1.172	1.499	$a+4517.9$		12	9304.5	1.422	2.076	9304.5
	4	5757.8	1.157	1.530	$a+5757.8$		13	9988.9	1.416	2.099	9988.9
							14	10664.7	1.410	2.122	10664.7
			BCl								
$X^1\Sigma^+$	0	418.3	1.650	1.789	418.3	$A^1\Pi$	0	400.4	1.591	1.713	44349.4
	1	1247.1	1.607	1.849	1247.1		1	1192.9	1.554	1.766	45141.9
	2	2065.8	1.580	1.893	2065.8		2	2010.6	1.529	1.806	46959.6
	3	2874.3	1.558	1.932	2874.3		3	2777.2	1.510	1.842	46726.2
	4	3672.5	1.541	1.966	3672.5		4	3530.1	1.494	1.874	47479.1
	5	4460.5	1.526	1.999	4460.5		5	4270.0	1.481	1.904	48219.0
	6	5238.3	1.513	2.029	5238.3		6	4996.9	1.470	1.932	48945.9
	7	6005.9	1.501	2.059	6006.9		7	5709.5	1.459	1.960	49658.5
	8	6763.3	1.490	2.088	6763.3		8	6407.5	1.449	1.988	50356.5
	9	7510.4	1.480	2.116	7510.4		9	7083.2	1.439	2.017	51032.2
	10	8247.3	1.471	2.143	8247.3		10	7716.5	1.430	2.044	51665.5
	11	8974.0	1.463	2.170	8974.0		11	8364.5	1.422	2.069	52313.5
	12	9690.5	1.455	2.197	9690.5		12	8994.0	1.415	2.096	52943.0
	13	10396.8	1.448	2.223	10396.8		13	9603.9	1.407	2.124	53552.9
	14	11092.8	1.441	2.249	11092.8		14	10192.9	1.399	2.152	54141.9
$A^1\Pi$	0	421.7	1.625	1.763	37172.6	$B^3\Pi_0$	0	429.3	1.561	1.680	54702.3
	1	1247.9	1.582	1.825	37998.8		1	1276.8	1.523	1.730	55549.8
	2	2051.5	1.555	1.872	38802.4		2	2108.6	1.499	1.768	56381.6
	3	2832.3	1.533	1.913	39583.2		3	2926.3	1.479	1.801	57199.3
	4	3590.4	1.516	1.951	40341.3		4	3727.7	1.463	1.831	58000.7
	5	4325.7	1.500	1.988	41076.6		5	4512.2	1.449	1.860	58785.2
	6	5038.3	1.486	2.023	41789.2		6	5277.5	1.436	1.887	59550.5
	7	5728.2	1.473	2.058	42479.1		7	6022.8	1.424	1.914	60295.8
	8	6395.3	1.461	2.092	43146.2		8	6746.8	1.413	0.940	61019.8
	9	7039.7	1.450	2.126	43790.6						
	10	7661.3	1.439	2.161	44412.2				AlCl		
	11	8260.2	1.429	2.196	45011.1						
	12	8836.4	1.418	2.231	45587.3	$X^1\Sigma^+$	0	240.1	2.075	2.210	240.1
	13	9389.8	1.409	2.267	46140.7		1	718.0	2.032	2.269	718.0
	14	9920.5	1.399	2.303	46671.4		2	1190.3	2.006	2.312	1190.3
							3	1658.4	1.985	2.349	1658.4
			BBr				4	2124.7	1.969	2.382	2124.7
$X^1\Sigma^+$	0	341.3	1.819	1.962	341.3		5	2586.5	1.954	2.413	2586.5
	1	1018.5	1.773	2.022	1018.5		6	3043.3	1.942	2.442	3043.3
	2	1688.7	1.744	2.066	1688.7		7	3496.4	1.931	2.470	3496.4
	3	2351.9	1.721	2.104	2351.9		8	3945.6	1.921	2.498	3945.6
	4	3008.1	1.701	2.138	3008.1		9	4391.1	1.912	2.524	4391.1
	5	3657.2	1.685	2.170	3657.2		10	4832.7	1.904	2.549	4832.7
	6	4299.3	1.670	2.200	4299.3		11	5271.5	1.897	2.574	5271.5
	7	4934.3	1.657	2.229	4934.3		12	5705.9	1.890	2.599	5705.9
	8	5562.3	1.645	2.256	5562.3						

(*Contd*)

TABLE 2 — RKRV CURVES FOR GROUP IIIA MONOHALIDES (Contd)

State	v	U (cm.$^{-1}$)	$r_{min.}$ (A.)	$r_{max.}$ (A.)	$T_e + U$ (cm.$^{-1}$)
		AlCl			
$A^1\Pi$	0	223·9	2·006	2·147	38477·9
	1	661·2	1·972	2·219	38915·2
	2	1086·7	1·953	2·276	39340·7
	3	1503·6	1·941	2·328	39757·6
	4	1904·7	1·933	2·376	40158·7
	5	2294·7	1·927	2·425	40548·7
	6	2670·2	1·923	2·472	40924·2
	7	3027·1	1·919	2·523	41281·1
	8	3364·9	1·916	2·572	41618·9
		AlBr			
$X^1\Sigma^+$	0	188·7	2·232	2·365	188·7
	1	563·3	2·188	2·420	563·3
	2	935·6	2·160	2·461	935·6
	3	1305·1	2·138	2·495	1305·1
	4	1671·7	2·120	2·526	1671·7
	5	2034·8	2·104	2·554	2034·8
	6	2396·5	2·090	2·580	2396·5
	7	2755·2	2·078	2·606	2755·2
	8	3111·1	2·066	2·630	3111·1
	9	3466·3	2·056	2·653	3466·3
	10	3816·9	2·046	2·676	3816·9
$A^3\Pi_0$	0	205·2	2·200	2·328	23852·2
	1	612·8	2·159	2·382	24259·8
	2	1016·8	2·133	2·421	24663·8
	3	1416·7	2·112	2·455	25063·7
	4	1813·2	2·095	2·485	25460·2
	5	2205·3	2·080	2·513	25852·3
	6	2593·0	2·067	2·540	26240·0
	7	2978·1	2·056	2·565	26625·1
	8	3359·3	2·045	2·589	27006·3
	9	3736·4	2·035	2·613	27383·4
	10	4109·2	2·026	2·636	27756·2
$B^3\Pi_1$	0	204·7	2·200	2·328	23984·0
	1	613·0	2·159	2·382	24392·3
	2	1017·4	2·133	2·421	24796·7
	3	1415·0	2·112	2·455	25194·3
	4	1809·8	2·095	2·485	25589·1
	5	2205·9	2·081	2·512	25985·2
	6	2598·9	2·068	2·538	26378·2
$C^1\Pi$	0	147·0	2·253	2·404	36026·5
	1	429·7	2·207	2·477	36309·2
	2	694·8	2·177	2·535	36574·3
		GaF			
$X^1\Sigma^+$	0	311·0	1·718	1·839	311·0
	1	928·0	1·680	1·891	928·0
	2	1537·5	1·656	1·928	1537·5
	3	2142·2	1·637	1·961	2142·2
	4	2738·6	1·622	1·991	2738·6
	5	3328·4	1·608	2·018	3328·4
	6	3913·1	1·596	2·044	3913·1
	7	4492·7	1·586	2·069	4492·7
	8	5063·3	1·576	2·093	5063·3
$A^3\Pi_0$	0	329·6	1·692	1·810	33425·8
	1	982·6	1·656	1·860	34078·8
	2	1627·9	1·632	1·897	34724·1
	3	2265·0	1·614	1·929	35361·2
	4	2900·7	1·599	1·957	35996·9
$B^3\Pi_1$	0	331·0	1·690	1·807	33761·5
	1	988·4	1·654	1·857	34418·9
	2	1637·8	1·630	1·894	35068·3
	3	2280·3	1·611	1·927	35710·8
	4	2908·3	1·596	1·956	36338·8
	5	3520·8	1·582	1·984	36951·3
	6	4117·4	1·570	2·011	37547·9

State	v	U (cm.$^{-1}$)	$r_{min.}$ (A.)	$r_{max.}$ (A.)	$T_e + U$ (cm.$^{-1}$)
		GaF			
$C^1\Pi$	0	269·0	1·718	1·848	47631·3
	1	791·4	1·680	1·910	48153·7
	2	1288·7	1·656	1·957	48651·0
	3	1767·1	1·635	2·003	49129·4
	4	2204·2	1·617	2·046	49566·5
	5	2605·1	1·598	2·093	49967·4
	6	2965·1	1·581	2·140	50327·4
		GaCl			
$X^1\Sigma^+$	0	182·2	2·147	2·274	182·2
	1	545·1	2·104	2·323	545·1
	2	906·8	2·075	2·359	906·2
	3	1264·3	2·052	2·389	1264·3
	4	1619·4	2·032	2·415	1619·4
	5	1973·1	2·015	2·440	1973·1
	6	2324·5	1·999	2·462	2324·5
	7	2672·3	1·985	2·484	2672·3
	8	3018·4	1·971	2·504	3018·4
	9	3362·2	1·959	2·523	3362·2
	10	3703·6	1·947	2·542	3703·6
$A^3\Pi_0$	0	197·1	2·095	2·217	29721·2
	1	587·6	2·057	2·269	30111·7
	2	973·4	2·033	2·307	30497·5
	3	1354·7	2·014	2·341	30878·8
	4	1730·5	1·998	2·371	31254·6
	5	2101·3	1·984	2·399	31625·4
	6	2462·4	1·972	2·426	31986·5
$B^3\Pi_1$	0	197·0	2·092	2·214	30052·7
	1	587·2	2·054	2·266	30442·9
	2	972·2	2·029	2·305	30827·9
	3	1352·4	2·011	2·338	31208·1
	4	1727·4	1·995	2·368	31583·1
	5	2097·2	1·982	2·396	31952·9
	6	2461·3	1·969	2·423	32317·0
	7	2820·1	1·959	2·449	32675·8
	8	3174·3	1·949	2·474	33030·0
		InF			
$X^1\Sigma^+$	0	266·7	1·926	2·050	266·7
	1	794·0	1·886	2·103	794·0
	2	1319·6	1·861	2·142	1319·6
	3	1839·2	1·841	2·175	1839·2
	4	2354·0	1·825	2·205	2354·0
	5	2863·1	1·811	2·233	2863·1
	6	3367·8	1·799	2·259	3367·8
	7	3866·0	1·788	2·285	3866·0
	8	4359·4	1·778	2·309	4359·4
	9	4848·8	1·768	2·332	4848·8
	10	5331·8	1·760	2·355	5331·8
$A^3\Pi_0$	0	286·9	1·888	2·008	30222·5
	1	853·1	1·850	2·060	30788·7
	2	1411·6	1·826	2·098	31346·2
	3	1963·1	1·807	2·130	31898·7
	4	2509·0	1·791	2·160	32444·6
	5	3047·5	1·777	2·187	32983·1
	6	3576·9	1·765	2·214	33512·6
	7	4101·8	1·755	2·237	34037·4
	8	4616·0	1·746	2·261	34551·6
	9	5152·2	1·736	2·287	35087·8
	10	5628·0	1·727	2·310	35563·6
$B^3\Pi_1$	0	284·9	1·886	2·007	31559·1
	1	851·4	1·848	2·058	32125·6
	2	1409·1	1·824	2·096	32683·3
	3	1961·6	1·805	2·129	33235·8
	4	2508·6	1·790	2·159	33782·8
	5	3046·1	1·776	2·186	34320·3
	6	3577·5	1·764	2·213	34851·7
$C^1\Pi$	0	230·1	1·910	2·045	43037·6
	1	676·8	1·874	2·111	43484·3

(Contd)

TABLE 2 — RKRV CURVES FOR GROUP IIIA
MONOHALIDES (*Contd*)

State	v	U (cm.$^{-1}$)	$r_{min.}$(A.)	$r_{max.}$(A.)	T_e+U (cm.$^{-1}$)
			InF		
$C^1\Pi$	2	1104·7	1·852	2·164	43912·2
	3	1511·2	1·834	2·213	44318·7
	4	1892·9	1·820	2·261	44700·4
	5	2246·5	1·805	2·311	45054·0
	6	2568·1	1·792	2·362	45375·6
	7	2851·0	1·776	2·418	45658·5
	8	3089·9	1·762	2·472	45897·4
			InCl		
$X^1\Sigma^+$	0	158·4	2·259	2·385	158·4
	1	474·0	2·220	2·439	474·0
	2	787·4	2·196	2·479	787·4
	3	1098·5	2·177	2·513	1098·5
	4	1407·8	2·162	2·544	1407·8
	5	1714·8	2·149	2·573	1714·8
	6	2019·8	2·138	2·600	2019·8
	7	2323·3	2·128	2·626	2323·3
	8	2624·8	2·119	2·651	2624·8
	9	2923·9	2·112	2·675	2923·9
	10	3221·0	2·105	2·698	3221·0
	11	3516·2	2·098	2·722	3516·2
	12	3809·2	2·093	2·744	3809·2
			TlF		
$X^1\Sigma^+$	0	238·1	2·024	2·152	238·1
	1	709·2	1·983	2·206	709·2
	2	1175·6	1·957	2·245	1175·6
	3	1643·9	1·937	2·279	1643·9
	4	2102·3	1·920	2·309	2102·3
	5	2557·3	1·906	2·338	2557·3
	6	3011·0	1·893	2·364	3011·0
	7	3457·5	1·881	2·391	3457·5
	8	3894·8	1·870	2·416	3894·8
	9	4326·7	1·861	2·439	4326·7
	10	4757·6	1·852	2·463	4757·6
	11	5185·0	1·844	2·485	5185·0
	12	5610·3	1·836	2·507	5610·3
$A^3\Pi_0$	0	177·3	1·980	2·129	35358·0
	1	512·4	1·933	2·199	35693·1
	2	823·6	1·900	2·254	36004·3
$B^3\Pi_1$	0	216·8	2·015	2·419	37086·3
	1	642·4	1·976	2·212	37511·9
	2	1047·3	1·951	2·261	37916·8
	3	1435·4	1·932	2·305	38304·9
	4	1807·0	1·916	2·347	38676·5
	5	2160·9	1·901	2·388	39030·4
	6	2497·8	1·888	2·428	39367·3
	7	2816·8	1·882	2·458	39686·3
	8	3118·8	1·875	2·490	39988·3
			TlCl		
$X^1\Sigma^+$	0	143·4	2·425	2·550	143·4
	1	429·8	2·384	2·602	429·8
	2	710·9	2·357	2·640	710·9
	3	990·0	2·336	2·671	990·0
	4	1267·6	2·318	2·700	1267·6
	5	1542·6	2·302	2·726	1542·6
	6	1815·7	2·288	2·751	1815·7
	7	2085·7	2·275	2·774	2085·7
	8	2353·5	2·264	2·797	2353·5
	9	2619·1	2·253	2·819	2619·1
	10	2882·5	2·243	2·840	2882·5
	11	3143·7	2·234	2·860	3143·7
	12	3402·7	2·225	2·880	3402·7
	13	3659·5	2·216	2·900	3659·5
	14	3914·1	2·208	2·920	3914·1
$A^3\Pi$	0	106·7	2·407	2·553	31160·9
	1	310·8	2·364	2·625	31365·0
	2	500·3	2·336	2·682	31554·5
	3	676·5	2·313	2·736	31730·7
	4	842·1	2·292	2·789	31896·3

contribution. These usually lead to anomalous ΔG versus v curves for these excited states. The ground state extrapolations are, on the other hand, perfectly normal. As seen earlier, in the present group of molecules, the ground states are having more ionic character than the first excited states. Therefore, it is expected that more reliable results will be obtained from the excited state extrapolations than from the ground state extrapolation as is indeed the case[47]. In an attempt to study the behaviour of vibrational energy difference curve for ionic molecules, two ionic potentials were expanded in a Dunham series by Finn and Becke[49,50]. A study of the Dunham terms reveals that the convergence of vibrational levels is slower than the linear extrapolation would require in ionic molecules.

Nature of Binding

A theoretical understanding of the nature of the bond between two atoms is approached in two different ways. The first method involves the use of hydrogen-like orbitals and a more or less approximate calculation leading to results which, from the mathematical difficulties involved, are of little conceptual value to the chemist. The other approach, as exemplified by Pauling, depends on the concept of electronegativity and available atomic bonding orbitals to describe the σ bond in a more qualitative or semi-empirical manner. Ionic character of chemical bonds presents a problem for which the first approach cannot yield a result and for which the second method is too qualitative or too far removed from a sound theoretical basis to be dependable.

Valence bond calculations for molecules are more suited for explaining the binding as partly covalent and partly ionic. Shull[51] has shown that the molecular orbital calculations can also give a good picture of the chemical bond regarding its ionic character if use is made of the natural orbital expansion. The present authors did not come across any valence bond calculations for any of the molecules in the sequence. Though some molecular orbital calculations for BF are available[52,53], no useful information regarding the ionic character of the bond could be extracted from them. In the absence of appropriate theoretical data, the chemical bond in the present sequence of molecules is discussed under two sub-heads. Under the first, the approach is semi-quantitative, mainly on the lines of Pauling. In the second, a semi-quantum mechanical model due to Barrow[54] is discussed.

Ionic Character and Electronegativity

In order to consider a molecule A-B in which atoms A and B are dissimilar and B more electronegative than A, a wave function $\Psi = \Psi_{covalent} + a\Psi_{ionic}$ is used to represent the chemical bond, the best value of a being that which makes the bond energy a maximum (i.e. minimizes the total energy of the molecule). Thus the energy of an actual bond between unlike atoms is greater than (or equal to) the energy of a normal covalent bond between these atoms. This additional energy is due to the ionic character of the bond. Pauling[55] defines the difference as

$$\Delta = D(A-B) - \tfrac{1}{2}[D(A-A) + D(B-B)]$$

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where D represents the dissociation energy as a measure of ionic character and Δ should be positive for bonding between unlike atoms. The latter is not true in some cases and hence the difference

$$\Delta' = D(A-B) - [D(A-A).D(B-B)]^{1/2}$$

has been defined by Pauling to be always greater than or equal to zero. It has been shown that the ionic character of a bond can be correlated more satisfactorily with the values of Δ' than with those of Δ.

Pauling found the relation $x_B - x_A = 0.208\sqrt{\Delta}$ to be true for a number of molecules. Here x_B is the electronegativity of the more electronegative atom B and x_A is that for the atom A. This simple relation gives an idea of the ionic character associated with an actual bond between atoms A and B. However, the method was too qualitative and, therefore, a number of empirical relations have been suggested from time to time which relate the ionic character of the bond with the electronegativity of the constituent atoms. The different relations available in the literature are summarized below.

Hannay and Smyth[56] gave the relation

$$\text{I.C.} = 0.16(x_B - x_A) + 0.035(x_B - x_A)^2 \quad ...(1)$$

Pauling[57] suggested

$$\text{I.C.} = 1 - \exp[-0.18(x_B - x_A)^2] \quad ...(2)$$

and according to Wilmshurst[58]

$$\text{I.C.} = \frac{x_B - x_A}{x_B + x_A} \quad ...(3)$$

Recently, Batsanov and Durakov[59] have modified the Pauling relation as follows:

$$\text{I.C.} = 1 - \exp[-0.20(x_B - x_A)^2] \quad ...(4)$$

The ionic characters of the present series of molecules determined from the above relations have been summarized in Table 1.

The ionic character was related to the dipole moment of the molecule by Pauling according to the relation I.C. $= \mu/er$, where μ is the dipole moment, e the electronic charge and r the bond length. In the group under study, only the dipole moment

of TlCl is experimentally known $(4.44 \times 10^{-18}$ e.s.u.$)$[60]. The value of ionic character for TlCl using the equilibrium internuclear separation comes out to be 37.2 per cent. This is in fair agreement with the values calculated from the other relations and summarized in Table 3. Rittner[46] has shown that the main cause of the failure of Pauling's relation (I.C. $= \mu/er$) in the alkali halides stems from the fact that it does not include the polarization deformation of ions. Considering the agreement in the present case, we can say that polarization deformations, if any, are very small for TlCl.

Wall[61] has given a method whereby the relative importance of the covalent and the ionic contribution in the normal state of a molecule can be estimated quantitatively from a knowledge of the actual potential energy curves and the idealized ionic and covalent curves. From this method, one obtains the value of a in the equation $\Psi = \Psi_{covalent} + a\Psi_{ionic}$ as

$$a^2 = \frac{W_c - W}{W_i - W}$$

where W_c is the energy corresponding to purely covalent bonding, W_i is the energy corresponding to purely ionic bonding and W is the actual binding energy for the molecule.

In the absence of exact value for W_c, Wall used the approximation

$$W_c(A-B) = \sqrt{W(A-A).W(B-B)}$$

For W_i he used the relation

$$W_i = -\frac{e^2}{r} + \frac{B}{r^n} + I_A - E_B$$

where I_A is the ionization potential of the metal atom and E_B is the electron affinity of the halogen atom. In the evaluation of W_i the authors used the value of the Hellman potential term

$$\frac{e^2}{r}\left[-1 + \frac{e^{-2(r-r_e)}}{1 + \lambda r_e}\right]$$

at the equilibrium internuclear separation instead of

TABLE 3 — ELECTRONEGATIVITIES AND IONIC CHARACTERS FOR GROUP IIIA MONOHALIDES

Molecule	$x_B + x_A$*	$x_B - x_A$	Percentage ionic character				
			From I	From II	From III	From IV	From $\frac{x_B - x_A}{5}$
BF	5·95	1·95	44·50	49·54	32·77	53·23	39·00
BCl	5·00	1·00	19·50	16·47	20·00	18·12	20·00
BBr	4·80	0·80	15·04	10·88	16·66	12·01	16·00
AlF	5·45	2·45	60·20	66·04	44·95	69·88	49·00
AlCl	4·50	1·50	31·87	33·30	33·33	36·23	30·00
AlBr	4·30	1·30	26·71	26·23	30·23	28·68	26·00
GaF	5·45	2·45	60·20	66·04	44·95	69·88	49·00
GaCl	4·50	1·50	31·87	33·30	33·33	36·23	30·00
InF	5·45	2·45	60·20	66·04	44·95	69·88	49·00
InCl	4·50	1·50	31·87	33·30	33·33	36·23	30·00
TlF	4·45	2·45	60·20	66·04	44·95	69·88	49·00
TlCl	4·50	1·50	31·87	33·30	33·33	36·23	30·00

*Electronegativity data from ref. 66.

$$\left[-\frac{\epsilon^2}{r}+B\,'r^n\right]$$

If Ψ_c and Ψ_i in the relation $\Psi=\Psi_c+a\Psi_i$ were orthogonal, following Wall, the dipole moment of the molecule can be expressed as

$$\frac{\mu}{cr}=\frac{a^2}{1+a^2}$$

under the assumption that the dipole moment is due entirely to the ionic contribution. However, Ψ_c and Ψ_i are not orthogonal but still it is reasonable to suppose that the dipole moment will be approximately proportional to a^2 especially when a^2 is small. In any case a equals the ratio of coefficients of Ψ_i and Ψ_c for the actual wave function and it gives a measure of the extent to which the bond is ionic. To calculate the ionic character of molecules, their a values were divided by the a value in case of CsF, which was assumed to be 100 per cent ionic. The results have been summarized in Table 4.

From Tables 3 and 4 it can be seen that the values of ionic characters as calculated using different relations do not differ much and they do give an indication that the sequence of molecules under study has considerable ionic character. Gordy[62] has given a linear relationship of the form I.C. $= \frac{1}{2}(x_B-x_A)$. In the present case, however, an approximate relation of this sort may be given only with a modified coefficient. The electronegativity differences should be divided by 5 or by a quantity slightly less than 5 in order to produce the value of I.C. in agreement with those obtained from other relations.

It can be seen from Tables 3 and 4 that the molecules form two distinct sub-groups so far as their ionic characters are concerned. The halides of boron falling in one sub-group and those of aluminium, gallium, indium and thallium in the other. The bonds involved in the first sub-group appear to be less ionic in the ground state than those in the second. The earlier observation from the Hellman potential curves that the first excited levels of lighter molecules are expected to be more ionic than those for the heavier molecules is in good agreement with the difficulty encountered by Barrow[47] in

obtaining the dissociation energies for the lighter molecules using BS extrapolation for the excited states. Somayajulu[48] also reached a similar conclusion in connection with the dissociation energy determinations. His value of S for the first sub-group is slightly more than that for the second sub-group and it is known that a low value of S is generally associated with a more ionic molecular bond. These evidences support the idea that the halides of boron are less ionic than the halides of other molecules of the group so far as the ground electronic state is concerned, but they are more ionic than the rest in the excited state.

The ionization potential of boron is 8·28 eV., that for aluminium 5·96 eV., for gallium 5·97 eV., for indium 5·76 eV. and for thallium 6·07 eV.[63]. The value for boron is the highest and those for the rest of the atoms lie within 0·3 eV. of each other. Thus, as one goes from boron to the sub-group formed by the rest of the atoms, there is an abrupt change of 2 eV. in the ionization potential. Radii of maximum radial charge density for various wave functions of the atoms as determined by self-consistent field calculations are given by Slater[64]. These values for boron, aluminium and gallium for the outermost ns and np wave functions are summarized below.

Element	n	Radius for ns in A.	Radius for np in A.
B	2	0·88	0·85
Al	3	1·16	1·21
Ga	4	0·92	1·13

From the above table it can be seen that the change in radii from ns to np shells in case of boron is in reverse order as compared to the other two atoms. These rather peculiar features of the boron atom lead to the conclusion that the differences obtained in the case of boron halides are attributable to the boron atom.

Quantum Mechanical Description of the Binding

Barrow[54] described the nature of bonding electrons in a single bond by a one-dimensional square well type potential model. This model represents

Molecule	W in kcal.*	W_c in kcal.†	W_i in kcal.	W_c-W in kcal.	W_i-W in kcal.	a	Percentage I.C.
BF	−185·0	−56·8	−137·2	128·2	47·8	1·637	31·63
BCl	−127·0	−53·7	−68·6	73·3	58·4	1·120	21·64
BBr	−103·5	−47·6	−47·9	55·9	55·6	1·002	19·36
AlF	−156·1	−49·1	−138·2	107·0	17·9	2·445	47·24
AlCl	−117·1	−46·4	−89·5	70·7	27·6	1·601	30·93
AlBr	−105·0	−41·1	−74·7	63·9	30·3	1·452	28·05
GaF	−143·9	−43·5	−125·6	100·4	18·3	2·342	45·25
GaCl	−113·5	−41·1	−84·0	72·4	29·5	1·566	30·26
InF	−125·9	−38·9	−114·8	87·0	11·1	2·799	54·08
InCl	−102·4	−36·8	−79·9	65·6	22·5	1·707	32·98
TlF	−109·6	−30·0	−100·3	79·6	9·3	2·925	56·52
TlCl	−89·6	−28·4	−68·6	61·2	21·0	1·707	32·98

TABLE 4 — IONIC CHARACTERS BY WALL'S FORMULA

*Data taken from ref. 47.
†Data from ref. 67.

the net Coulombic potential of the atomic nucleus and the core and the non-bonding electrons. When substituted in the Schrödinger equation it generates an atomic wave function which is used to describe the bonding to an adjacent atom. The combination of the bonding orbitals on the two atoms then leads in the LCAO approximation to a description of the bond. The relative depth of the potential wells is related to the electronegativity difference of the atoms by the equation $x_B - x = 0.0457 \, \Delta V$, where ΔV represents the difference in the well depths at the two nuclei. This electronegativity-well depth relationship has the important consequence of relating a basic parameter of quantum mechanical treatment to a familiar and useful atomic property.

The bond orbital for electrons 1 and 2 is defined by

$$\Psi = \frac{C_1}{\sqrt{2}}[\Psi_A(1)\Psi_B(2) + \Psi_A(2)\Psi_B(1)] + C_2[\Psi_B(1)\Psi_B(2)]$$

where Ψ_A and Ψ_B are atom-like orbitals associated with atoms A and B of which B is the more electronegative. The ionic character is defined by the relation

$$\text{I.C.} = \frac{C_2^2}{C_1^2 + C_2^2}$$

where C_1 and C_2 are the best values obtained by the variation method. The ionic characters for all the molecules in the present case have been obtained at equilibrium internuclear separations. Use has been made of the relation between the bond length and the ionic character given by Barrow. The results are summarized in Table 5 where V_1 represents the depth of the potential well associated with metal atom and V_2 that associated with the halogen atom. The values of ionic character obtained for different molecules from this model also have the same trend as was shown by other methods described earlier. The present calculation suffers particularly from the lack of adjustment of the atomic-like wave functions to the varying electronegativity of atoms. A more detailed calculation would allow for the use of less extended orbits for the more electronegative atoms.

A reliable source of information concerning molecular electronic structure is the nuclear quadrupole coupling constant eqQ where Q is a property of the nucleus, but q is directly related to the electronic charge distribution in the molecule. Townes and Daily[65] have discussed a semi-empirical relation between eqQ and approximate wave functions of the bonding electrons in a molecule. Assuming approximate values for s, p and d contribution to the bond Barrett and Mandel[38] have evaluated the ionic characters for these molecules. Their values are given in Table 6.

Conclusion

On the basis of the present considerations, it is seen clearly that the monohalides of Group IIIA elements are ionic to a considerable extent. No definite quantitative estimation, however, could be made. The values for ionic characters obtained from the quadrupole coupling constants by Barrett and

TABLE 5 — APPLICATION OF BARROW'S THEORY TO GROUP IIIA MONOHALIDES

Molecule	V_1 in eV.	V_2 in eV.	V in eV.	r_e in Å.	Percentage I.C.
BF	58·67	101·33	42·66	1·265	52·50
BCl	69·01	90·99	21·88	1·716	18·25
BBr	71·25	88·75	17·50	1·887	9·50
AlF	53·20	106·80	53·60	1·655	78·00
AlCl	63·59	96·41	32·82	2·133	39·50
AlBr	65·78	94·22	28·44	2·296	28·50
GaF	53·20	106·80	53·60	1·775	80·00
GaCl	63·59	96·41	32·82	2·208	40·00
InF	53·20	106·80	53·60	1·985	82·00
InCl	63·59	96·41	32·82	2·399	38·75
TlF	53·20	106·80	53·60	2·084	82·00
TlCl	63·59	96·41	32·82	2·485	37·00

TABLE 6 — IONIC CHARACTERS DETERMINED BY QUADRUPOLE COUPLING CONSTANTS (Ref. 38)

Molecule	Atom	Atomic eqQ in Mc/sec.	Molecular eqQ in Mc/sec.	Percentage I.C.
GaCl	Cl	−110	−20	79
GaBr	Br	770	134	80
GaI	I	−2292	−549	72
InCl	Cl	−110	−18	81
InBr	Br	770	138	79
TlCl	Cl	−110	−15·8	83
TlBr	Br	770	130	80
TlI	I	−2292	−537	72

Mandel[38] are considerably higher as compared to the values obtained from other methods. It is also found that the differences between the ionic character of chlorides and bromides are small as obtained by these authors. This may be due to the fact that they use the same value of s-character for all the halogens. Some suggestions for work to clarify this problem can be given. It is seen that none of the theoretical methods is completely unambiguous. What is needed is a reasonably complete quantum mechanical calculation on these molecules. The wave functions thus obtained, if analysed in terms of ionic and covalent character, would lead to reliable results. Till this is possible a search for better empirical parameters should continue.

Summary

The experimentally observed vibrational and rotational levels have been used to compute the true potential energy curves for a number of electronic states for the diatomic halides of Group IIIA. These curves have been compared with the empirical ionic curve suggested by Hellman. The difference between the actual dissociation energy and the value for D_e calculated by the BS extrapolation has been explained as being due to the contribution of ionic character to the binding in the ground state. The variation in this contribution as we go from B to Tl has been discussed and analysed. Various empirical and theoretical approaches to evaluation of percentage ionic character have been discussed.

Acknowledgement

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Stereochemistry of Five-Coordinated Complexes of Oxovanadium(IV) & Other Transition Metals*

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I N recent years many five-coordinated complexes of several transition metals have been reported. In the course of our extensive study of oxovanadium(IV) complexes it has been found that vanadium is either five- or six-coordinated[1]. The six-coordinated complexes of oxovanadium(IV) have a tetragonally distorted octahedral structure and the five-coordinated complexes have a tetragonal or square pyramidal rather than the expected trigonal bipyramidal structure. The conditions favouring square pyramidal and trigonal bipyramidal structures have not been discussed in a recent review on five-coordination[2]. This aspect has been dealt with in this paper. The stereochemistry of five-coordinated complexes of other transition metals, particularly of the 3d series, also discussed in this paper, is of general interest in understanding the stereochemistry of oxovanadium(IV) complexes.

Complexes of Oxovanadium(IV)

The six-coordinated complexes of oxovanadium(IV) have a tetragonally distorted octahedral structure. The stereochemistry of five-coordinated complexes, $VO(Ox).2H_2O$, $VO(Ox).2DMSO$, etc., needs consideration, as such compounds can have either a trigonal bipyramidal or a rectangular pyramidal arrangement[3]. A trigonal bipyramidal structure is preferred to a tetragonal pyramid for a five-coordinated complex from ligand-ligand repulsion considerations[4]. However, X-ray diffraction and electron spin resonance studies of five-coordinated bisacetylacetonato oxovanadium(IV)[5], $VO(acac)_2$, and bisoxalato oxovanadium(IV) ion[6], $VO(Ox)_2^{2-}$, show that they have a rectangular pyramidal structure. By close analogy of the electronic spectra of most of the other oxovanadium(IV) complexes[1,7-10] with these two compounds either in the solid state and/or in solution, it can be inferred that they also have a similar square pyramidal structure.

The ligand field stabilization energies for d^1 to d^9 system is less for a trigonal bipyramidal arrangement of ligands than for a square pyramidal arrangement[11] and this should favour the latter structure. However, interactions between the bonding electrons themselves may favour a trigonal bipyramid arrangement according to Gillespie[12]. Gillespie recently considered the stereochemistry of five-coordinated non-transition and transition metal compounds in terms of "valence shell electron pair repulsions". It is difficult to accept the views of Gillespie because of certain recent contradictory experimental observations or the availability of alternate explanations readily. Some of the complexes considered to be trigonal bipyramid

by Gillespie[12] in support of his theory are now considered to be nearer to square pyramidal structure in description.

In $VO(acac)_2$ which has a square pyramidal structure, the angle (α) which the multiply-bonded V-O makes with the other V-O bonds of acetylacetonate is 106°. Gillespie[12] is of the opinion that in $VO(acac)_2$, the extra repulsion produced by the multiply-bonded V-O causes the angle (α) to have a rather large value of 106° and that the interaction of the bond electron pairs with the single nonbonding d electron is sufficiently great to cause the square pyramidal structure to be preferred to a trigonal bipyramid. However, the multiple bond of V-O alone cannot be held responsible for the large angle (α) in the case of $VO(acac)_2$ since an angle (α) of 100° or more is observed in many other transition metal square pyramidal complexes such as bis(dimethylglyoximato) copper(II)[13], bis(NN'-di-n-propyldithiocarbamato) copper(II)[14], bisaquo-(acetylacetonato) copper(II) picrate[15], bisdimethyldithiocarbamato nitrosocobalt(II)[16], etc., with bidentate ligands in the square plane and not containing a strong bond in the axial direction. It is likely that the multiple bond of $V=O$ is responsible for the square pyramidal structure rather than the interaction of the bond electron pairs with the single nonbonding d electron as suggested by Gillespie[12]. The stabilization of square pyramid structure seems to be due to the interaction of the multiply-bonded $V=O$ electrons and the strongly bonded bidentate ligand electrons with the metal as discussed later. If the d^1 electrons were to be mainly responsible for the square pyramidal structure, titanium(III) also should favour the same structure, at least in some cases. In practice, titanium(III) generally forms octahedral complexes.

Trans-effect

Another factor influencing the five-coordination in oxovanadium(IV) compounds is the *trans*-effect[11] of the multiply-bonded vanadyl oxygen (bond order of V-O is nearly 2·4)[10] as distinct from other transition metal complexes. As a result of the *trans*-effect, the ligand in the site opposite to the vanadyl oxygen will either form a weak bond or be excluded during the process of solidification of the complex. The five-coordinated square pyramidal complexes in solution are expected to take a solvent molecule in the sixth place at a longer distance than the other ligands in the square plane. It may be noted that oxotitanium(IV) complexes of acetylacetone and fluoroacetylacetone containing multiply-bonded Ti-O (Ti-O stretching frequency occurs at 1030 cm.$^{-1}$)[17] are five-coordinated with square pyramidal structure. Trigonal bipyramidal structure is unlikely in oxovanadium(IV) complexes, since the ligand is likely to prefer a site other than that *trans*

to the vanadyl oxygen to form a strong bond and thus impart maximum stability to the complex.

Trans-effect, however, fails to explain the hexa-coordination normally observed with monodentate ligands like H_2O, CN^-, NCS^-, DMSO, etc. It is, therefore, worth noting that when two or all the four positions in the square plane are occupied by a bidentate ligand/ligands, the oxovanadium(IV) complexes are generally penta-coordinated. In general, it appears that square pyramidal complexes with monodentate ligands are rare. This indicates that the interaction of the ligands with the metal is of some importance in deciding the stereochemistry of the complexes.

Ligand-Metal and Ligand-Ligand Interactions

In general, with monodentate ligands, ligand-ligand repulsions are likely to be important and this may result in trigonal bipyramidal structure. But in chelates, the ligand-ligand repulsion is likely to be less important. The metal-ligand interaction is expected to be greater in chelates than in monodentate ligands. It is well known that the stability of the chelates is more than that of the monodentate complexes. The structures of $VO(acac)_2$ (ref. 5) and $(VOSO_4.4H_2O)H_2O$ (ref. 18) are known from single crystal X-ray diffraction studies and it is found that in the latter the metal atom is coplanar with the four water oxygens, while in the former the metal atom is above the plane formed by the oxygens of the acetylacetonate ligands as shown in (A) and (B).

A   B
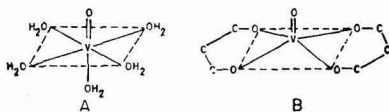
X-ray diffraction studies of many square pyramidal transition metal complexes have shown that the metal atom is situated above the rectangular plane formed by the donor atoms of the bidentate ligands[13-16]. When the vanadium atom is raised above the base of the pyramid, the effective approach of the ligand in the sixth position, *trans* to the vanadyl oxygen, is hindered as compared to the metal coplanar with the donor atoms in the square plane. The position of vanadium above the basal plane of the donor atoms together with the *trans*-effect of the multiply-bonded V=O is responsible for five-coordinated square pyramidal structure in oxovanadium(IV) complexes with one or two bidentate ligands. This is amply demonstrated by the formation of a large number of five-coordinated complexes[1,8], such as $VO(acac)_2$, $VO(bzac)_2$, $VO(dipy)_2^{2+}$, $VO(phen)_2^{2+}$, $VO(oxine)_2$, $VO(Ox)_2^{2-}$, $VO(malon)_2^{2-}$, $VO(mal)_2^{2-}$, $VO(sal.)_2$, $VO(DBM)_2$, $VO(dipy)F_2$, $VO(phen)F_2$, $VO(dipy)Ox$, $VO(phen)Ox$, $VO(Ox).2H_2O$, $VO(Ox).2DMSO$, etc. (acac = acetylacetonate, bzac = benzoylacetonate, dipy = dipyridyl, phen = o-phenonthroline, Ox = oxalate, malon = malonate, mal = maleate, sal. = salicylaldehyde, DBM = dibenzoylmethane and DMSO = dimethylsulphoxide).

Some exceptions are found to the above observations. For example, when the ligands are unidentate but bulky like antipyrine, triphenyl-phosphine oxide and triphenyl arsineoxide, the steric factors are likely to assume major part in deciding the stereochemical arrangement[10,19]. It is found that these ligands form complexes of the type $(VOL_4)(ClO_4)_2$ with square pyramidal arrangement. The X-ray diffraction study of a square pyramidal complex, $RuCl_2.3P(C_6H_5)_3$, has indicated the effective blocking of the sixth position of an octahedron by the bulky ligands[20]. Similar situation exists in $[(C_6H_5)_2CH_3A_5O]_4M(ClO_4)_2$, where M = Co, Mn, Fe, Ni or Zn (ref. 21); $MX_2.3PH(C_6H_5)_2$, M = Co or Ni and X = Br⁻ or I⁻ (ref. 22); and $PdI_2.3P(C_2H_5)_2C_6H_5$ (ref. 23), etc.

In the case of complexes like $VO(phen)_2Cl_2$, where all the four positions in the square plane are occupied by two bidentate ligands, it is found that one of the chloride ion is coordinated[8], giving a hexa-coordinated complex, $[VO(phen)_2Cl]Cl$. This may be attributed to the relatively smaller size of the chloride ion and its negative charge. In $VO(acac)_2$, the sixth position can be filled by more basic ligands[24] like pyridine, methylamine, piperidine, etc. These ligands are normally expected to hydrolyse oxovanadium(IV) complexes. Ligands like trimethylamine, 2,5-dimethylpyridine and acridine do not fill in the sixth position due to steric hindrance. It is found that the ligand occupying the sixth position in such compounds can be removed without much affecting the parent compound[24].

Complexes of Other Transition Elements

The stereochemistry of five-coordinated complexes of other transition metals, particularly of the $3d$ series, is considered here, which can be of general interest in understanding the stereochemistry of oxovanadium(IV) complexes. The factors, which are rather difficult to isolate completely from each other and may determine the square pyramidal or trigonal bipyramidal structure are discussed below.

The Nature of Ligand

Monodentate or polydentate nature of the ligands — charged or neutral — is likely to be an important factor in determining the stereochemistry of a complex formed. All nonbulky or partly nonbulky, charged or uncharged, monodentate ligands usually favour trigonal bipyramidal arrangement to a square pyramid. For example, $CoCl_3.2P(C_2H_5)_3$ (ref. 25), $Co(NCCH_3)_5^+$ (ref. 26), $MX_3.2N(CH_3)_3$ where M = Ti, V, Cr, and X = Cl⁻, Br⁻ (ref. 27-30), $CuCl_5^{3-}$ (ref. 31) and $Ni(CN)_3.3C_6H_5P(OC_2H_5)_2$ (ref. 32) have trigonal bipyramidal structure. This structure is adopted probably because the ligand-ligand repulsions are minimum for this arrangement. When bidentate or polydentate ligands are involved, the ligand-ligand repulsions may be small as compared to the ligand-metal interactions and consequently the trigonal bipyramidal arrangement may not be the preferred structure.

Although the donor property of the coordinating atom and the substituents on the ligand may have an influence on the formation of a compound with a particular coordination number, there is very little evidence to show that they influence the arrangements in a certain coordination number.

Thus, Meek et al.[33] have found that the ligands $P(O-C_6H_4SCH_3)_3$ and $P(O-C_6H_4SeCH_3)_3$ give stable trigonal bipyramidal complexes with nickel(II), whereas the arsine analogue $As(O-C_6H_4SCH_3)_3$ has no reaction with nickel(II), platinum(II) and palladium(II). The acetylacetoneamine complexes of cobalt(II), $Co(acaR)_2$ with $R = CH_3C_6H_4$, show no tendency to take up a molecule of pyridine even in pyridine, while with $R = ClC_6H_4$, the complex takes two molecules of pyridine to form a hexacoordinated complex[34]. This is due to the effect of the substituent on the ligand. It may be of interest to note that Clark et al.[35] have noted similar effects of the substituents during their study of a few eight-coordinated complexes of titanium(IV).

Crystal Field Stabilization Energy (CFSE)

As pointed out earlier, the crystal field stabilization energy (CFSE) is less for trigonal bipyramidal arrangement of ligands than for a square pyramid. This difference is more pronounced in the case of d^2, d^3, d^6, d^7 and d^8 systems. This alone is not an important factor in determining the stereochemical arrangement, as can be seen from the examples of chromium, cobalt and nickel complexes given above which have trigonal bipyramidal structure and not the preferred square pyramid from CFSE. The CFSE is about 4-6 Dq less for trigonal bipyramidal arrangement than for a square pyramid for complexes of d^2, d^3, d^6, d^7 and d^8.

π-Bonding between Ligand and Metal

One is tempted to consider whether the preference to a square pyramidal structure over a trigonal pyramid will involve any increased π-bonding from metal to ligand or vice versa. It is difficult to say definitely about this but the influence of π-bonding on the choice of the stereochemical arrangement is likely to be very small.

Steric Factors

The geometry of the ligand often determines the stereochemical arrangement of the complex. The quadridentate ligand, $N[CH_2CH_2N(CH_3)_2]_3$ ($= trenMe_6$), forms isomorphous five-coordinate complexes[36] of the type $[MtrenMe_6X]X$ where $M = Cr(II)$, $Co(II)$, $Ni(II)$ and $Cu(II)$ and $X = Cl^-$, Br^-, I^-, NO_3^- and ClO_4^-. Cobalt(II) and chromium(II) complexes were found to have trigonal bipyramidal arrangement by X-ray analysis[37]. The geometry of the ligand is such that the three dimethylamino groups are constrained to lie at the corners of an equilateral triangle with the metal atom at the centre. There is no room for another ligand in the plane of the dimethylamino groups and thus square pyramidal (or octahedral) structure cannot be obtained. The other coordination position available on the vertical axis is occupied by an anion. The complex, $[PtI(QAS)]^+$, where $QAS = tris(o-diphenylarsinophenyl)$ arsine, $As[O-C_6H_4As(C_6H_5)_2]_3$ has also trigonal bipyramidal structure[38]. The trigonal symmetry of the ligands helps in attaining the trigonal bipyramidal structure for these complexes. By constructing a model, it was shown that it is not possible to have all the four-coordinating groups of the tetradentate ligand, NN'-salicylidine-ethylene-diamine, at the four corners of a trigonal bipyramid[12]. It is found by X-ray studies that NN'-salicylidene-ethylenediamine zinc(II) monohydrate and NN'-disalicylidenepropylene-1,2-diamine copper(II) monohydrate have square pyramid structures[39,40].

Dichloro and dibromo (pyridine-2-aldehyde-2'-pyridyl-hydrazone) cobalt(II), $Co(PAPHY)X_2$ and isomorphous dihalogeno-2,2',2"-terpyridyl complexes of Mn, Co, Ni, Cu and Zn, $M(terpy)X_2$, have distorted tetragonal pyramid structure[41]. In these complexes the angle subtended at the metal atom by the donor atoms of the tridentate ligand is less than 90° (about 74°). As a consequence, it is said to favour the square pyramid structure which has basal bond angles (at the metal atom) of less than 90°. The interesting features of these PAPHY and terpy complexes normally observed are: a short basal metal-halogen bond, the basal halogen atom quite below and the metal atom slightly above the plane of the tridentate donor atoms. A very similar structure is also found for $NiBr_2.triarsine$[42] and $PdBr_2$ tris(2-phenylisophosphindoline)[43]. The structures of dibromo tris(diphenylphosphine) cobalt(II) and related complexes of cobalt iodide, nickel bromide and nickel iodide can also be described as distorted square pyramid in the same manner as $NiBr_2.triarsine$[42] and the depression of the basal halogen atom is larger. In the $CoBr_2$ complex, the basal bromine atom is depressed by nearly 46° below the plane as compared to 20° in $NiBr_2.triarsine$. The axial metal-halogen bonds are longer than the basal ones.

The metal-halogen bond distances in $Co(PAPHY)Cl_2$ are: basal, 2·28 A. and axial, 2·33 A., whereas in $NiBr_2.triarsine$ and $PdBr_2.triphosphine$, they are 2·37, 2·69 and 2·52, 2·93 A. respectively. For $Zn(terpy)Cl_2$, both the Zn-Cl bonds are reported to be equal[41]. The shorter basal metal-halogen bond and the depression of the halogen atom much below the plane of the tridentate ligand have been explained as indicating stronger π-bonding between the metal and the halogen atom[41]. It should, however, be noted that the differences in the metal-halogen bonds are much greater than can be explained by greater π-bonding in the case of nickel and palladium complexes. It is possible that the depression of the basal halogen atoms below the plane of the donor ligand atoms may be to minimize the greater ligand-ligand repulsion of the two halogen atoms.

Steric considerations may force a potentially tridentate ligand to a bidentate as in square pyramidal, $M(DEAS)_2$ (ref. 44), DEAS = 4-chloro-N-2-diethyl-salicylaldimine and $M = Co(II)$, $Ni(II)$. Square pyramidal complexes may be formed by blocking of the sixth position of an octahedron by bulky ligands as already discussed under oxovanadium(IV) complexes. In some cases steric repulsions in the molecule may determine a configuration which is intermediate between a square pyramid and a trigonal bipyramid as, for instance, in $Co(Me_5dien)Cl_2$ (ref. 45), $Me_5dien = CH_3N[CH_2N(CH_3)_2]_2$.

Packing Forces

Packing forces may play an important part in forcing the complex to acquire a certain structure.

The structure may be further stabilized by hydrogen bond formation in the crystal. N,N'-Disalicylidene-ethylenediamine zinc(II) monohydrate has a square pyramidal arrangement[39]. This complex has a number of intermolecular hydrogen bonds. The structure is very compact as found by relatively high density. In the case of the dihydrate and planar nonhydrate, the structures are said to be not so compact[39]. The structure of an analogous copper complex is similar[40]. The structures of some other transition metal complexes which have square pyramidal arrangement as a result of dimerization as in bisdimethylglyoximate[13] and bis-(NN'-di-n-propyldithiocarbamate) of copper(II)[14], NN' - disalicylidene-ethylenediamine copper(II)[46], bis(cis - 1,2 - difluoromethylethylene - 2,2 - dithiolate) cobalt(II)[47], [(CF$_3$)$_2$C$_2$S$_2$]$_2$Co, etc., may be looked upon in a similar fashion. Thus packing forces are likely to be an important factor.

Conclusion

From a careful consideration of the various factors discussed above, it is possible to predict in a five-coordinated complex, whether it would favour a trigonal bipyramidal or a square pyramidal structure. It is obvious that the five-coordination in 3d metals is achieved as a result of particular situations such as those listed above rather than any inherent tendency of the metal ion towards this coordination. It appears that the difference in stability between a square pyramid and a trigonal bipyramid is not too large. Gillespie has also pointed out that a square pyramid with $\alpha = 100°$ is not much less stable than a trigonal bipyramid[48]. Again, it may be noted here that in square pyramidal complexes with unidentate[21,49] and polydentate ligands, the metal atom is generally (0·2-0·5 A.) above the basal plane of the donor atoms, thus increasing α to over 90°. Unlike the transition metal complexes in five-coordinated nontransition metal compounds having square pyramidal geometry with the lone pair occupying the sixth position of an octahedron, the central atom would be usually below the basal plane of the four donor atoms as, for instance, BrF$_5$, IF$_5$ (ref. 48), [XeF$_5$]. [PF$_6$] (ref. 50), OSeCl$_2$.2-pyridine[51], etc.

Since all the characteristics favourable to one type of arrangement are very unlikely to be present in a given compound, one is likely to find departure from the idealized geometry and the distortion in some cases may be such that it may be difficult to say whether it is best represented as a trigonal bipyramid or a square pyramid. For example, the geometry of bisacetylacetonato zinc(II) monohydrate cannot be precisely defined, although the description of a distorted tetragonal pyramid may be acceptable[2]. In this connection, it may be noted that structures Zn(acac)$_2$.H$_2$O, Zn(terpy)Cl$_2$ and [Cu(dipy)$_2$I]$^+$, which were at one time said to be trigonal bipyramid[52-54], are now given the description of square pyramid[2,41,55] and the structures are considerably distorted from the idealized geometry. Similarly, dibromo tris(diphenylphosphine) cobalt(II) and related complexes of cobalt iodide and nickel bromide and iodide have structures intermediate between trigonal bipyramid and tetragonal

pyramid[22]. These structures can be described as distorted square pyramid, since they resemble NiBr$_2$.triarsine to some extent. From the existing structural data, it may be said that the weightage for attaining the square pyramidal structure is greater than the trigonal bipyramid particularly in chelates and tridentate ligands, where the geometry of the ligand does not necessarily restrict the stereochemical arrangement of the molecule.

If one were to consider the above factors, in addition to those discussed already, the stereochemical arrangement of oxovanadium(IV) complexes should obviously favour a square pyramidal arrangement of ligands to a trigonal bipyramid.

Note added in proof — The structures of [Cu-(tren)NCS]$^+$ (ref. 56), [Zn(tren)Cl]$^+$ (ref. 57) and [Zn(tren)NCS]$^+$ (ref. 58), where tren = tris(2-amino-ethyl)amine, have been found by X-ray diffraction to be trigonal bipyramid. Similarly, tris(o-diphenyl-phosphinophenyl)phosphinochlorocobalt(II)[59] and tris(o - diphenylarsinophenyl)phosphinocyanonickel - (II)[59] have been found to have trigonal bipyramid structure. These are similar to trenme$_6$ complexes[36] and the trigonal symmetry of the ligand is responsible for the trigonal bipyramidal structure of the complexes. The crystal structure of Cu(NH$_3$)$_2$Ag-(SCN)$_3$ has been found by X-ray analysis to be a trigonal bipyramid with two NH$_3$ groups in the axial positions and the three NCS$^-$ groups in the equatorial positions around copper[60].

In addition to the complexes referred to earlier, bisdithiodiketone complexes of iron(II) and cobalt(II) and their adducts[61], nitrosyliron(II) bis(NN-di-alkyldithiocarbamate)[62], monohalogenobisdialkyl-dithiocarbamato complexes of iron(III)[63], trans-bis-(triphenylphosphine)methyl di-iodorhodium(III)[64], bis(maleonitrile dithiolato)iron(III)[65], etc., have been found to have tetragonal pyramidal structure by X-ray analysis. In these compounds, the metal atom is situated above the tetragonal plane of the donor atoms, which is considered to impart stability to the tetragonal pyramidal arrangement, as also pointed out earlier.

The structure of dichloro-1,1,7,7-tetraethyl diethylene triaminecobalt(II)[66], Co(Et$_4$dien)Cl$_2$, is found to be similar to Ni(triarsine)Br$_2$ (ref. 42), which has a distorted tetragonal pyramidal structure. The distortion in the structure may be due to the ligand-ligand interactions. In the distorted tetragonal pyramidal series[67], Co(Et$_4$dien)X$_2$, where X = Cl$^-$, Br$^-$, NCS$^-$, N$_3^-$ and I$^-$, the complex Co(Et$_4$dien)I$_2$ is believed to have octahedral structure in dimethyl formamide, as a result of the formation of the complex, [Co(Et$_4$dien).3DMF]I$_2$. This is said to be due to the steric factors against five-coordination in solution[67].

An exception to the square pyramidal structure of oxovanadium(IV) complexes has been found in bis(trimethylamine)oxovanadium(IV) dichloride[68]. The coordination polyhedron in this complex is trigonal bipyramid with two amine molecules in the *trans* position perpendicular to the plane containing the two chlorines and the oxovanadium group. Although multiply-bonded VO is considered to stabilize the square pyramidal structure, it appears from this case that it is not the only factor

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responsible for the tetragonal pyramid structure, generally observed in oxovanadium(IV) complexes. In $VOCl_2.2Nme_3$, the V=O multiple bonding is considered to be insufficient to stabilize the tetragonal pyramidal structure. The trigonal bipyramidal arrangement of the complex is probably determined by the ligand-ligand repulsions. However, it may be noted that MOX_4^{2-}, where M=V, Mo, or Re and X=Cl⁻ or Br⁻, is square pyramidal[49,68,69].

Summary

The stereochemistry of five-coordinated complexes of oxovanadium(IV) and other transition metals, particularly of the $3d$ series, is discussed. Generally, with one or two bidentate ligands attached to oxovanadium(IV), five-coordinated square pyramidal complexes result, while with unidentate ligands six-coordinated distorted octahedral complexes are obtained. The stereochemistry of the oxovanadium(IV) complexes is explained in terms of the *trans*-effect of the multiply-bonded vanadyl oxygen and the interaction of the ligand with the metal. Some exceptions due to steric effects are pointed out. The importance of various factors like the nature of the ligand, coordinating properties of the donor atom, π-bonding between the metal and the ligand, crystal field stabilization energy, steric effects and packing forces that influence the stereochemical arrangement in five-coordinated transition metals is also discussed.

Acknowledgement

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Synthetic Heterocyclic Steroids*

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HETEROCYCLIC steroid is an expanding branch of organic chemistry. Present interest in this field is due to the potential biological activity of these compounds. In the last decade, the synthesis of a number of steroidal analogues containing nitrogen, oxygen and sulphur in the steroidal skeleton has been accomplished by two methods, viz. (i) modification of existing steroids and (ii) total synthesis. The first of these methods has been adequately reviewed in Djerassi's book[1] but the second method has not been reviewed. It is the object of this review to give a survey of the methods applied in the total synthesis of hetero-cyclic steroids. A literature survey of the compounds which contain heteroatom(s) in the cyclopenta (hexa)-(a)-phenanthrene unit and where the essential structural features associated with steroidal molecules such as the angular methyl groups, the oxygen function and particular stereochemical pattern has been retained, has been carried out.

Classification of Heterocyclic Steroids

To identify the type of heterocyclic steroid which is being discussed, a classification of these steroids is suggested. The numbering in the steroidal system as given in (I) is basically preserved. As it would be unwieldy to describe these steroids as 1-aza, 2-aza steroids, etc., they have been divided on the basis of the heteroatom(s) present and its (their) place(s) in the steroidal rings. Thus, if ring A of a steroid contains nitrogen atom (in any position corresponding to C_1, C_2, C_3, or C_4), it is denoted as an A_N steroid (II), the corresponding oxygen and sulphur analogues as A_O (III) and A_S (IV) steroids respectively. It is possible to denote steroids, e.g. of the type (V), with more than one heteroatom by this method. The steroids in which the nitrogen occupies the ring junction, say at C_8 or C_9 position corresponding to the carbocyclic analogues, can be denoted as BC_N type steroid, as examplified in (VI), showing that the nitrogen is common to both rings B and C. A further example of this notation is given in (VII).

In the present review, the steroids containing heteroatom in ring A will be discussed first, followed by those in rings B, C and D. Single heteroatom steroids will be covered first, followed by common heteroatom steroids (BC_N type) and then multiple heteroatom(s) steroids. The relevant spectroscopic data are given in the discussion. The structural formulae are drawn in this article to represent one of the enantiomers of the steroidal intermediates and it is understood that all the compounds are racemic; the ($\pm$) sign is omitted throughout.
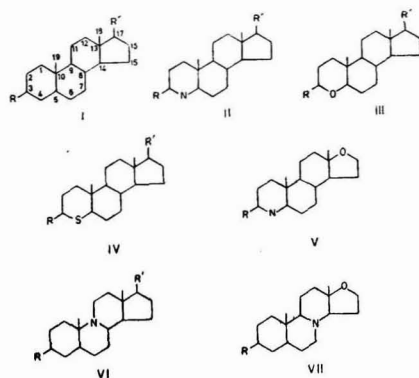
Modification of Existing Steroids and Their Derivatives

In the context of the discussion on the synthetic routes used in the total synthesis of heterocyclic steroids it is not out of place to give a short summary of the general methods applied to the modifications of natural steroids and their derivatives.

The oxa steroids exist as cyclic anhydrides, lactones and ethers. A synthetic method which is of particular interest is the oxidation of the corresponding ketones (either saturated or α,β-unsaturated) to the cyclic lactones; this can be accomplished by a variety of oxidizing agents. A second general method involves the cleavage of the ring in which the heteroatom is to be inserted. Oxidative cleavage of that ring results in γ- or δ-keto acid, which can cyclize under various dehydrating conditions to form an enol-lactone. The enol-lactones are usually reduced to cyclic ethers by complex metal hydrides.

Keto acids can also give rise to steroidal lactams when condensed with ammonia or an appropriate primary amine. Another general method of preparing cyclic lactams is by Beckmann rearrangement of the corresponding ketoximes or Schmidt reaction of the ketones. The resulting lactams can also be reduced to cyclic amines by complex metal hydrides.

The aza and oxa steroids are usually prepared by the above methods of modification but no thia steroid has yet been synthesized involving the modification of existing steroids.

Synthesis of Single Heteroatom Steroids

Ring A Heterocyclic Steroids

Sluyter et al.[2] have reported the preparation of the key intermediate (XIa) (Chart 1) in the synthesis of 4-aza steroids. This is the only total synthesis
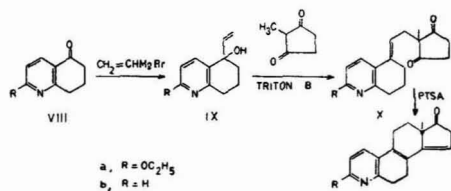
Chart 1 — Preparation of key intermediate (XIa) in the synthesis of 4-aza steroids
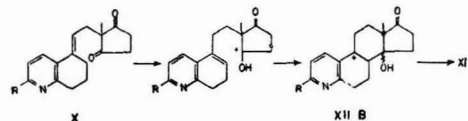

Chart 2 — Mechanism of cyclization of (X)

of a steroidal intermediate in which ring A is hetero-cyclic. The preparation involved the base catalysed condensation between 2-methylcyclopentane-1,3-dione and a vinyl alcohol derivative (IXa), which in itself incorporated the prefabricated rings A and B of the steroidal skeleton, leading to the tricyclic diketone (Xa). This method of preparing the tri-cyclic diketone of the type (Xa) is of general interest and has been previously used in the synthesis of carbocyclic[3] and other heterocyclic steroids. The tricyclic diketone (Xa) underwent a facile cycliza-tion to give an intermediate (XIa) but (Xb) did not cyclize under a variety of conditions. The mechan-ism suggested (Chart 2) for this cyclization explain this differing behaviour readily. The carbonium ion intermediate (XIIb) would be destabilized by the negative inductive effect of the neighbouring pyridine ring, but this effect is overshadowed by the electron donating properties of the ethoxy group in (XIIa), allowing the cyclization to occur, in that case.

Bew and Clemo[4] reported a failure to form a 4-aza steroidal skeleton. The resulting product in the condensation of 8-aminoquinoline with 2-carb-ethoxycyclopentanone failed to undergo cyclization under a variety of conditions.

Ring B Heterocyclic Steroids

B_N type — A large number of steroids in this series have been synthesized. In 1963, Huisman et al.[5] reported the total synthesis of the inter-mediate (XVIa, X = N-tosyl; R = OCH₃) (Chart 3). 4-Keto-7-methoxy-1,2,3,4-tetrahydro-N-tosylquino-line (XIIIa, X = N-tosyl; R = OCH₃) was treated with vinyl magnesium bromide giving an alcohol (XIVa, X = N-tosyl; R = OCH₃). This gave an intermediate tricyclic ketone (XVa, X = N-tosyl; R = OCH₃) on being condensed with 2-methylcyclo-pentane-1,3-dione and it was cyclized using an acid catalyst to the intermediate (XVIa, X = N-tosyl; R = OCH₃). In the later publications[6,7], the modi-fication of this intermediate (XVIa) was reported and the stereochemical problems involved were discussed.

The compound (XVIa) was hydrogenated over palladium on calcium carbonate, but was found to yield predominantly the undesired 14β-isomer (XVIIa, X = N-tosyl; R = OCH₃). The presence of a C_{13}-methyl group was expected to direct the hydrogen to the α-surface. This unexpected result was attributed to the bulkiness of the N-tosyl group which in spite of its remoteness directed the hydro-gen to the β-surface. The required 14α-isomer (XVIIIa, X = N-tosyl; R = OCH₃) was prepared by first reducing the ketone (XVIa) to an alcohol (XIXa, X = N-tosyl; R = OCH₃) which was then catalytically hydrogenated to a 14α-isomeric alcohol (XXa, X = N-tosyl; R = OCH₃) and then sub-jecting this alcohol to Oppenauer oxidation. The treatment of (XXa) with sodium hydride gave a quinoline derivative (XXIa, X = N; R = OCH₃) along with a tetrahydroquinoline derivative, 6-azaestradiol-3-methyl ether (XXIIa, X = NH; R = OCH₃). Presumably, the two products origi-nated from (XXa) by two different reaction paths (Chart 4). The quinoline derivative (XXIa) could also be formed by the reaction of lithium aluminium hydride on the ketone (XVIIIa).

The alcohols (XXIa) and (XXIIa) were oxidized to 6-azaequilenin-3-methyl ether (XXIIIa, X = N; R = OCH₃) and 6-azaestrone-3-methyl ether (XXIVa, X = NH; R = OCH₃) respectively by Oppenauer oxidation. The ketone (XVIIIa, X = N-tosyl; R = OCH₃) could also be detosylated on treatment with 80 per cent sulphuric acid in the presence of arsenic pentaoxide. The demethylation of (XXIIIa, X = N; R = OCH₃) and (XXIVa, X = NH; R = OCH₃) led to 6-azaequilenin (XXIIIa, X = N; R = OH)
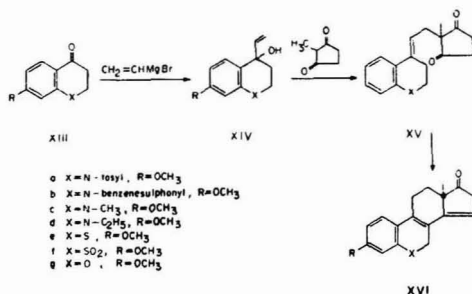

Chart 3 — Total synthesis of intermediate (XVIa, X = N-tosyl; R = OCH₃)
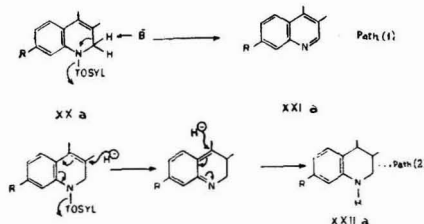

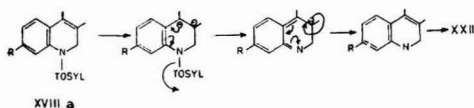Chart 4 — Generation of products (XXIa) and (XXIIa) from (XXa)

Chart 5 — Mechanism of reductive detosylation of (XVIIIa)

and 6-azaestrone (XXIVa, X=NH; R=OH) respectively. The reductive detosylation of the ketone (XVIIIa) with potassium in liquid ammonia led to the mixture of (XXIIIa) and (XXIIa). Variation of the reagent ratio gave (XXIIa) and (XXIa). The mechanism (Chart 5) put forward by the above workers is essentially the same as that described for the reduction of styrene bonds in several steroidal systems and is given below.
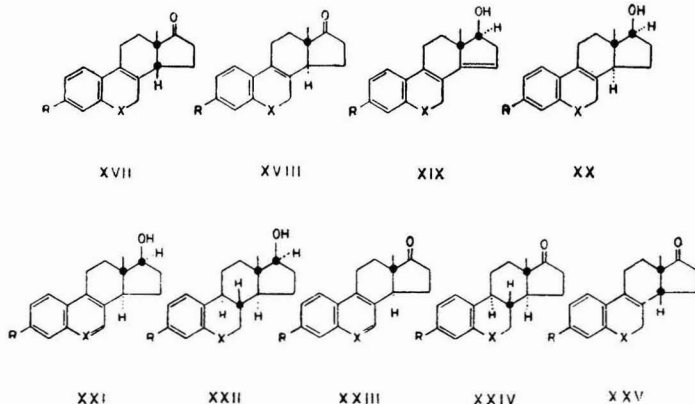
A similar set of reactions was carried out with 14β-isomer (XVIIa, X=N-tosyl; R=OCH₃) and 6-aza-isoequilenin-3-methyl ether (XXVa, X=N; R=OCH₃) and other related compounds were prepared.

The stereochemical assignment in (XVIIa) and (XVIIIa) at the C/D ring junction was based on the above sequence of reactions and also on the position of C_{13}-methyl resonances in the NMR spectra. The methyl signal in the ketone (XVIIIa) appears at 9·4 τ and in (XVIIa) at 9·16 τ. The 14α-isomer (XVIIIa) in which the C/D ring junction in *trans*, the C_{13}-methyl group is shielded by $\Delta^{8,9}$ while in the β-isomer it is not. The observed high field value for the methyl group in (XVIIIa), therefore, indicates that it is the 14α-isomer whereas (XVIIa) is the 14β-isomer. As further confirmation of these assignments, the NMR signals for C_{13}-methyl group in (XXIIIa, X=N; R=OCH₃) and in (XXVa, X=N, R=OCH₃) were compared. In (XXIIIa) it appeared at 9·25 τ while in (XXVa) it appeared at 8·93 τ. This observation that (XXIIIa) has a 14α-configuration as opposed to one in (XXVa) where it is 14β- is analogous to one in the carbocyclic series[8,9]. Pandit *et al.*[10] have put forward mass spectral evidence to substantiate the above assignments. The stereochemical assignments at the B/C ring junction in (XXIIa, X=NH; R=OCH₃) was made on the mass spectral evidence[10] and on the assumption

that the potassium/liquid ammonia reduction of (XVIIIa) would only lead to *trans* product such as (XXIIa). It was thus indicated that the stereochemistry in (XXIIa, X=NH; R=OCH₃ or OH) at the four ring junctions was 8β, 9α, 13β, 14α.

Smith *et al.*[11] have reported the preparation of the ketone (XVIb, X=N-benzenesulphonyl; R= OCH₃) by an analogous route. This compound was subjected to catalytic hydrogenation and these workers claimed to have obtained (XVIIIb, X=N-benzenesulphonyl; R=OCH₃) directly. No convincing proof of the stereochemistry at C/D ring junction was put forward. This claim appears to be contrary to that of Huisman and coworkers[7], who argued that the directing influence of the N-tosyl group was instrumental in the hydrogenation of Δ^{14} in (XVIa, X=N-tosyl; R=OCH₃) in spite of its remoteness. There is little difference in the volume between a benzenesulphonyl and toluene-p-sulphonyl group, and thus their directive influence should be more or less the same. In the light of a very convincing proof put forward by Huisman's school, and, in the absence of any comprehensive spectroscopic data, the claim of Smith *et al.*[11] does not seem to be valid. If their claim is true, there must be some other factor which governs the hydrogenation of (XVIa, X=N-tosyl; R=OCH₃) apart from the volume of the N-tosyl group.

Smith and coworkers reduced the ketone (to which they assigned the structure XVIIIb) to the corresponding alcohol (XXb, X=N-benzenesulphonyl; R=OCH₃), but both the ketone and the alcohol resisted the conversion to 6-azaestra-1,3,5(10)-triene derivatives (XXIVa, X=NH; R=OCH₃) and (XXIIa, X=NH; R=OCH₃) respectively. The ketone (XVIIIb) also failed to rearrange to (XXVIb, X=N-benzenesulphonyl; R=OCH₃). The alcohol (XXb) with lithium in liquid ammonia in the presence or absence of ethanol gave another alcohol (XXVII). The ultraviolet data for this compound are not consistent with that of either of pure isomers (XXIa, X=N; R=OCH₃) or its 14β-isomer mentioned by Huisman *et al.*[7]. It is rather doubtful if the compound (XXVII) was pure and it may be an isomeric mixture which originated in the hydrogenation of (XVIIIb).
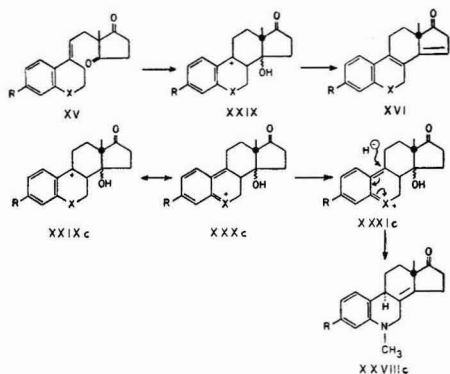

XVII   XVIII   XIX   XX

XXI   XXII   XXIII   XXIV   XXV

XV XXIX XVI

XXIXc XXXc XXXIc

XXVIIIc

Chart 6 — Mechanism of cyclization of (XVc) to (XXVIIIc)

XXVIIIc XXXIIc XXXIII

XXXIV XXXV

Chart 7 — Further evidence for the mechanism given in Chart 6

Quite recently Kessar et al.[12] have reported the preparation of the intermediate ketone (XVIb, X=N-benzenesulphonyl; R=OCH$_3$) by the same procedure.

Huisman's school[13] extended its work on 6-N-tosyl steroids to 6-N-methyl derivatives. The synthesis of 6-N-methyl steroids was planned on similar lines. But the tricyclic ketone (XVc, X = N-CH$_3$; R = OCH$_3$) on acid catalysed cyclization did not give the 'normal' product of the type (XVIa), but gave a new compound (XXVIIIc, X = N-CH$_3$; R = OCH$_3$) which in effect involved a net reduction of the system (XVIc, X = N-CH$_3$; R = OCH$_3$). In the absence of any reducing species, the reaction presumably proceeded via disproportionation involving hydride transfer at some stage of cyclization. The mechanism of the cyclization (Chart 6) of the tricyclic diketone of the type (XV) involves the formation of carbonium ion intermediate (XXIX) which undergoes rapid proton loss followed by dehydration to give the compounds of the type (XVI). In this case (XVc, X = N-CH$_3$; R = OCH$_3$), however, it was suggested that the availability of the lone pair of electrons increased the basicity of nitrogen resulting in additional stability of the species (XXIXc, X = N-CH$_3$; R = OCH$_3$) due to delocalization (XXIXc ⇌ XXc). The stabilized species such as (XXXc) could undergo dehydration leading to a more stabilized quaternary ion (XXXI) which abstracts a hydride from another molecule resulting in (XXVIIIc). Furthermore, Huisman suggested that the attack of the hydride would occur stereospecifically from the less hindered α-side at C$_9$. The above mechanism was substantiated independently by synthesizing the ketal of (XVId) and studying its acid hydrolysis (Chart 7). This resulted in the formation of (XXVIIId, X = N-C$_2$H$_5$; R = OCH$_3$) and not in the formation of (XVId, X=N-C$_2$H$_5$; R = OCH$_3$). The compound (XXVIIIc) was converted into its ketal (XXXIIc) and was subjected to reduction with lithium in methylamine. The resulting enol ether (XXXIII) was hydrolysed to ketone (XXXIV). The sodium borohydride reduction of (XXXIV) stereospecifically led to the
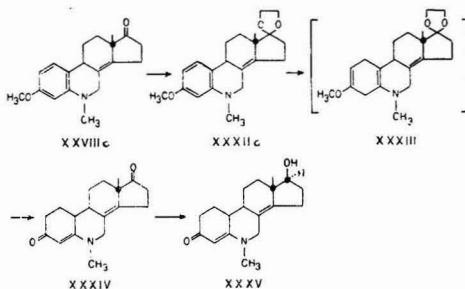
17β-isomeric alcohol (XXXV) which is 6-N-methyl-8(14)-dehydro-19-nor-testosterone.

Recently, it has been reported[14] that 6-N-benzyl-8(9)-dehydroestradiol-3-methyl ether can be converted into 6-azaestrone by a series of reactions involving potassium/liquid ammonia reduction and chromic acid oxidation.
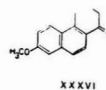
XXXVI

A total synthesis of equilenin has been reported by Johnson et al.[15]. In their synthesis, 1-keto-7-methoxy-1,2,3,4-tetrahydrophenanthrene (XXXVI) was the starting material. In the heterocyclic steroid series, their route has been applied by a number of workers with varying degrees of success.

In the B$_N$ series, successful total synthesis of 6-azaequilenin and 6-aza-isoequilenin (XXIIIa and XXVa respectively, X = N; R = OH) have been reported by Burkhalter and Watanabe[16]. Their starting material was 3-methoxy-7-oxo-7,8,9,10-tetrahydrophenanthridine (XXXVII). Successive steps (Chart 8) involving formylation, isoxazole formation and methylation led to α-cyanoketone (XXXVIII). This cyanoketone after Stobbe condensation and cyclization gave 6-aza-15-ethoxycarbonyl-14,15-dehydroequilenin-3-methyl ether (XXXIX). Banerjee

XXXVII XXXVIII XXXIX

XL XXIII A
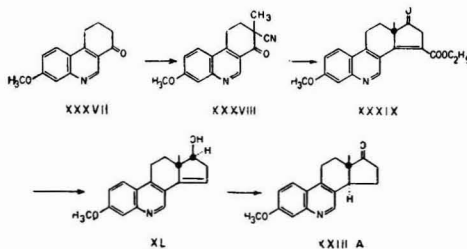
Chart 8 — Steps involved in the synthesis of 6-azaequilenin-3-methyl ether
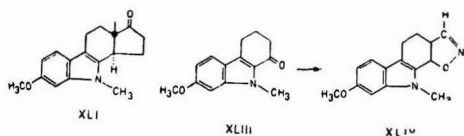
modification[17] of Johnson's method which involved the sodium borohydride reduction of (XXXIX) led exclusively to the 17β-alcohol (XL) which was hydrogenated to 6-azaestra-1,3,5(10),6,8-pentaene-17β-ol-3-methyl ether (XXIA, X = N; R = OCH₃). This compound was then oxidized back to 6-azaequilenin-3-methyl ether (XXIIIA, X = N; R = OCH₃).

Bhide *et al.*[18] have attempted the synthesis of B-nor-6-aza-6-methylequilenin (XLI), by applying Johnson's route. The starting material for this synthesis was 7-methoxy-1-oxo-1,2,3,4-tetrahydrocarbazole (XLII). This carbazole was first converted to the N-methyl derivative (XLIII), then to 9,10-dihydro-6-methoxy-4-methylcarbazole [2,1-*d*] isoxazole (XLIV), which was isomerized to the cyanoketone (XLV). The above workers reported the failure to methylate this cyanoketone to (XLVII). Instead, an enol ether was always obtained. It was inferred that the failure to obtain the 6-alkyl ketone (XLVII) was due to the strong enolizibility imparted to it by electron donating methoxy and the N-methyl groups. In the case of 1-oxo-9-methyl-1,2,3,4-tetrahydrocarbazole (XLVIII), only a poor yield of the C-methylated ketone (XIL) was reported, but this keto-nitrile (XIL) failed to undergo Stobbe condensation (Chart 9). This was attributed to the inaccessibility of the 1-oxo group, presumably because of the steric hindrance caused by the N-methyl group. A similar approach on the compound (L), the methylation gave only the O-methyl compound (LI) (Chart 9).

B_S type — Recently, Huisman's group at Amsterdam has reported[19] the synthesis of the intermediate (XVIe, X = S; R = OCH₃) by essentially the same procedure which had been previously used. The hydrogenation of the intermediate (XVIe) gave a 2:1 mixture of the *cis* and *trans* products (XVIIe and XVIIIe respectively, X = S; R = OCH₃). The reduction to the desired 14α-isomer (XVIII) could be

Chart 9 — Attempted synthesis of B-nor-6-aza-6-methylequilenin

accomplished on the corresponding alcohol (XIXe), which was oxidized to the ketone (XVIIIe) by Oppenauer oxidation (XVIe →XIXe →XVIIIe). In the same publication, the above workers reported the failure of the condensation of vinyl alcohol derivative (XIVf, X = SO₂; R = OCH₃) with 2-methylcyclopentane-1,3-dione. To overcome this, the intermediate tricyclic ketone (XVe, X = S; R = OCH₃) was oxidized to (XVf, X = SO₂; R = OCH₃), but this sulphone failed to undergo cyclization to (XVIf, X = SO₂; R = OCH₃). The instability of the tetracyclic ketone (XVIe, X = S; R = OCH₃) ruled out the possibility of its oxidation to the sulphone analogue (XVIf). The reason for the failure of the sulphone (XVf) to undergo cyclization might be the strong electronegativity of the sulphone group which prevents the stabilization of the intermediate carbonium ion (XXIXf, X = SO₂; R = OCH₃).

Mitra and Tilak[20] reported the synthesis of thiophene analogue of 3-desoxyequilenin (LII). They followed the Johnson route starting from 1-oxo-1,2,3,4-tetrahydrodibenzothiophene (LIII). The synthesis which was carried out without any difficulty resulted in two stereoisomers of (LII), viz. (i) a lower melting and (ii) a higher melting in 25 and 33 per cent yield respectively. The assignments of the configuration of these compounds was rather arbitrary: the lower melting and more stable (i) being designated as *trans* (13β-14α) isomer.
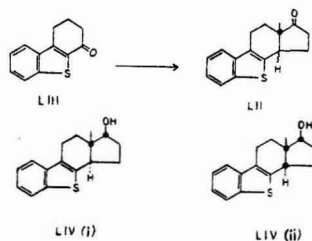
Collins and Brown[21] have also synthesized 3-desoxy-B-nor-6-thiaequilenin (LII) and assigned the lower melting variety the *cis* configuration L (LIV, ii).

Later on Tilak, Shastri, Jhina and Gogte (*Indian J. Chem.*, in press) prepared [LIV, (i); 14α-isomer] unambiguously by following Banerjee modification of Johnson route. It was found to be identical with the reduction product (ii) of the higher melting variety of (LII). The reduction product of the lower melting compound (i) of (LII) was different from them, as revealed by infrared spectrum and the mass spectral fragmentation data. The reduction product of the lower melting variety (i) of (LII) was also synthesized unambiguously. In view of the chemical and spectral evidence Tilak and colleagues later corrected their assignments. The lower melting variety (i) of (LII) was assigned as 14β-(isoequilenin) and the higher melting variety (ii) as 14α-isomer (equilenin).

Tilak and coworkers[22] have attempted the synthesis of B-nor-6-thiaequilenin. For this purpose, they converted 7-methoxy-4-oxo-1,2,3,4-tetrahydrodibenzothiophene (LV) into the keto-nitrile (LVI) following Johnson route. Compound (LVI) failed
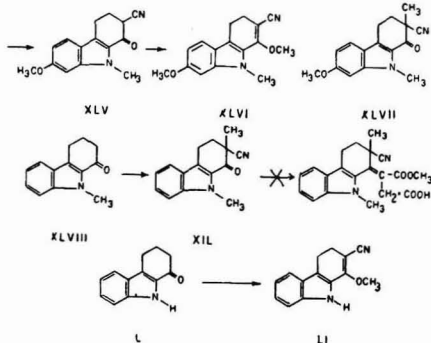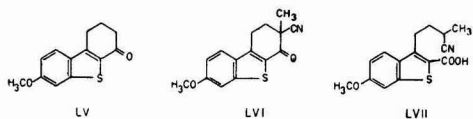
LV   LVI   LVII

XVI g   XVIII g

XXVI g   XXIV g   XXII g

LXII   LXIV   LXV

LXIII

LXVI   LXVII   LIX g

Chart 11 — Synthesis of 6-oxaestrone (XXIg, X = O; R = OH), its various transformations and structural assignments based on carbocyclic series

to undergo Stobbe condensation under a variety of conditions. Under mild conditions, the keto-nitrile (LVI) was obtained unchanged, whereas under severe conditions ring cleavage occurred to give 3-(3'-cyanobutyl)-2-carboxy-6-methoxythionaphthene (LVII).

Bhattacharjee and Tilak later synthesized B-nor-6-thiaequilenin by following Bachmann route starting from (LV) (*Indian J. Chem.*, in press). The assignment of the stereochemistry at the C/D ring junction in the final products is based on the analogy with the Bachmann route. No spectroscopic or chemical evidence is given for the assignments.

For the synthesis of a thiophene analogue of 3-desoxy-B-nor-6-thiaestrone (LX), Mitra and Tilak[23] started from the lower melting variety (*cis*) of the compound (LII) (Chart 10). It was first oxidized to the corresponding sulphone (LVIII) which was then catalytically hydrogenated to a mixture of two isomers of (LIX). One of these was presumably obtained pure but configurational assignments at the newly formed asymmetric centres at B/C ring junctions were not made. The crude mixture of isomers of (LIX) was directly subjected to lithium aluminium hydride reduction. Again two products were obtained. Of these, one was a thiophene analogue of 3-desoxyestradiol (LX) and its sulphone (LXI), both of which are presumably the mixtures of two stereoisomers.

B$_o$ type — Smith *et al.*[11] have synthesized 6-oxa-estrone (XXIVg, X= O; R = OH), starting from 7-methoxychroman-4-one by the route elaborated earlier for their synthesis of 6-aza steroidal systems (Chart 11). The tricyclic diketone (XVg, X = O; R = OCH$_3$) was subjected to cyclodehydration. This resulted in the intermediate ketone (XVIg, X = O; R = OCH$_3$). It was hydrogenated to 6-oxaestra-1,3,5(10),8(9)-tetraene (XVIIIg, X = O; R = OCH$_3$) in which the stereochemistry at the C/D ring junction was assumed to be *trans* (14α-H). Presumably, the C$_{13}$-methyl group directed the hydrogenation to the α-surface by analogy with the carbocyclic series. Ethanolic hydrogen chloride isomerized the compound (XVIIIg) to (XXVIg,

LII (i)   LVIII A

LIX

LX   LXI

Chart 10 — Synthesis of 3-desoxy-B-nor-6-thiaestrone

X = O; R = OCH$_3$). Subsequent hydrogenation over palladium on charcoal gave 6-oxaestrone-3-methyl ether (XXIVg, X = O; R = OCH$_3$), which was reduced to the 17β-alcohol (XXIIg, X = O; R = OCH$_3$) by sodium borohydride. Treatment of the above alcohol with lithium in liquid ammonia in the presence of ethanol yielded 3-methoxy-6-oxaestra-2,5(10)-diene-17-ol (LXII), which was hydrolysed with methanolic hydrochloric acid to 19-nor-6-oxatestosterone (LXIII). Oppenauer oxidation of (LXII) gave 3-methoxy-6-oxaestra-2,5(10)-diene-17-one (LXIV) which after treatment with lithium acetylide-ethylenediamine complex in dimethylacetamide and acid hydrolysis gave 17α-acetylene derivative of 6-oxaestrone (LXV). Exhaustive hydrogenation of the intermediate ketone (XVIg, X = O; R = OCH$_3$) gave 6-oxa-8α-estrone-3-methyl ether (LXVI) and converted by sodium borohydride to the corresponding alcohol (LXVII). The same compound has also been prepared from the ketone (XVIg) from its reduction to an alcohol (XIXg) followed by catalytic hydrogenation (Chart 11). The structural assignments were made by analogy to the reactions in the carbocyclic series.

Some experimental details of the above transformations have appeared in some recent patents[24-28].

Starting from 7-methoxy-4-oxo-1,2,3,4-tetrahydrobenzofuran (LXVIII), Bhide *et al.*[29] have synthesized B-nor-6-oxaequilenin (LXIX) by Johnson route (Chart 12). In this synthesis, it was found that once the cyclopentano(D) ring was formed, the compound showed instability to air, both in neutral and alkaline media. In the carbocyclic series, Johnson[15]

Chart 12 — Synthesis of B-nor-6-oxaequilenin and the structural assignments

has reported the formation of two double bond isomers (Δ^{14}- and Δ^{15}-) during the hydrolysis and decarboxylation after cyclization. In the 6-oxa-B-nor- series, however, the above workers reported the exclusive formation of one compound, viz. the Δ^{14}-derivative (LXIX). The structural assignment was supported by ul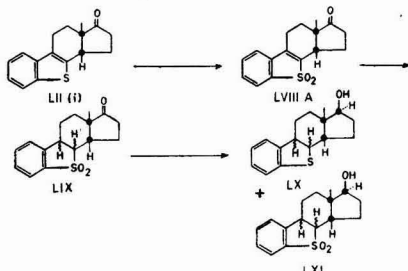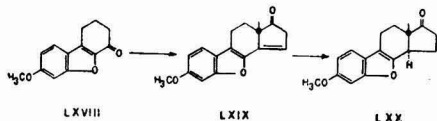traviolet spectrum. Compound (LXX) was assumed to be *trans*, by analogy with Johnson's observation in the carbocyclic series, but it was recognized that unambiguous proof is necessary for correct steric assignments.

Ring C Heterocyclic Steroids

Clemo and Mishra[30] condensed α-naphthylamine (LXXIa, R = R′ = H) with 2-carbethoxycyclopentanone (LXXII) and obtained a tricyclic ketone (LXXIIIa, R = R′ = H) which was cyclized to (LXXIVa). Catalytic reduction of this system failed, but sodium amalgam effected the reduction to (LXXV, R = R′ = H). Subsequent dehydrogenation l·d to the cyclopentanoazaphenanthrene (LXXVIa, R = R′ = H), but attempts to introduce an oxygen function either at C_{15} or C_{17} in this compound met with no success (Chart 13).
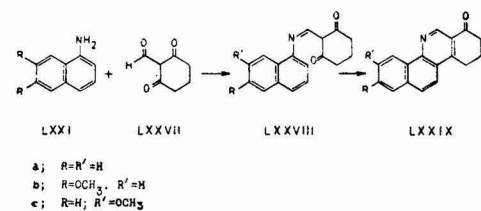
Kessar et al.[31] have reported the synthesis of 11-aza-D-homo steroidal derivatives (Chart 14). Their synthesis involved the condensation of α-naphthylamine derivative (LXXI) with 2-aldehydrocyclohexane-1,3-dione (LXXVII). This led to an anil (LXXVIII) which could be cyclized to the tetracyclic system (LXXIX).

Jones and Cross[32,33] have reported the synthesis of 11-aza-D-homo and 11-aza-C-nor-D-homo[33] steroidal intermediates (Chart 15). Treatment of 6-methoxy-1-naphthylamine (LXXIb) with 1-acetylcyclohexane-1,3-dione (LXXX) gave rise to a Schiff's base (LXXXI), which was cyclized in polyphosphoric acid, yielding 11-aza-D-homo steroidal system (LXXXII). However, catalytic reduction of a similar system obtained from the condensation of (LXXIa) with (LXXX) led to the compound (LXXXIII), in which ring A was saturated.

11-Aza-C-nor-D-homo steroidal compounds have been prepared by the above workers by a procedure involving Fischer-Indole synthesis. Treatment of 7-methoxytetralone with an appropriately substituted phenyl hydrazine, and then boiling the resulting hydrazone with ethanolic hydrochloric acid yielding the above system.

Kasturi and Damodaran[34] have reported the synthesis of 3-cyano-3-methyl-7-methoxychroman-4-one (LXXXIV) (Chart 16). When treated with ethyl formate, 7-methoxychroman-4-one (LXXXV) gave the corresponding formyl derivative which led to an isoxazole system (LXXXVI). This on treatment with potassium-t-butoxide and methyl iodide gave a cyanoketone (LXXXIV). The above workers hope to convert it into (LXXXVII), which might be considered as a prototype for C_0-steroids.

Apart from this, there are no reported attempts to make C_0-steroids. No ring D-steroids and C_s-steroids have yet been totally synthesized.

Chart 13 — Synthesis of cyclopentanoazophenanthrene (LXXVI)

a, R=R′=H
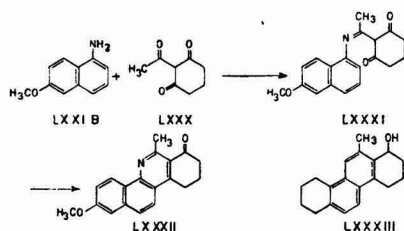
Chart 15 — Synthesis of 11-aza-D-homo and 11-aza-C-nor-D-homo steroidal intermediate

a; R=R′=H
b; R=OCH₃, R′=H
c; R=H; R′=OCH₃

Chart 14 — Synthesis of 11-aza-D-homo steroidal derivatives (LXXIX)
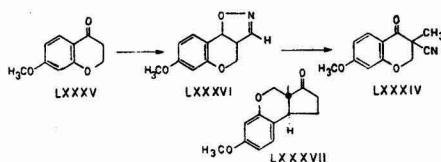
Chart 16 — Synthesis of 3-cyano-3-methyl-7-methoxychroman-4-one as a prelude to the synthesis of prototype of C_0-steroids

Synthesis of Common Heteroatom Steroids

Various ring junctions in the steroidal skeleton offer attractive sites for the introduction of tertiary nitrogen atom. No attempts have yet been made to introduce it at C_5 or C_{10} (A/B ring junction) but various successful and unsuccessful attempts have been reported for BC_N and CD_N type steroids and their homologues.

BC_N type — The first successful synthesis of an 8-aza steroidal system was reported by Meltzer *et al.*[35] in 1963, and later elaborated in a subsequent publication[36] (Chart 17). The reaction of 2-methyl-2-(β-carboxyethyl)-cyclopentane-1,3-dione (LXXXVIII) with *m*-methoxyphenethylamine (LXXXIX) led to the formation of the tricyclic lactam (XC) which, on cyclization with phosphorous oxychloride, gave an undesirable lactam (XCI). The catalytic reduction of (XC) yielded a single, saturated keto-lactam (XCII). This was also obtained when the amine (LXXXIX) and the acid (LXXXVIII) were subjected to reductive condensation, a byproduct being an amino acid (XCIII). This amino acid gave a single isomeric lactam (XCIV) on heating and this fact led these workers to assign a *trans*-lactam structure to the compound (XCIV). An alternative method of obtaining the *trans*-lactam (XCIV) in good yield has been developed. The unsaturated tricyclic lactam (XC) was first reduced to the corresponding alcohol (XCV) and catalytically hydrogenated to two epimeric lactam alcohols (XCVI and XCVII respectively) in which (XCVI) was predominant. Modification of the reaction conditions gave the lactam alcohol (XCVII) in good yield. The configuration of the hydroxyl group in the lactam alcohols (XCVI and XCVII) was established by independent synthesis of (XCV), which indicated a *cis* relationship between the hydroxyl and the angular methyl group.

When treated with phosphorous oxychloride the tricyclic saturated lactams (XCII and XCIV) gave quaternary salts, which were isolated as perchlorates (XCVIII and XCIX respectively). Catalytic reduction of (XCVIII) (C/D ring junction *cis*) gave a mixture C_9-isomeric* bases (C and CI) easily separable by fractional crystallization of the hydrobromide salts. But the quaternary salt (XCIX) (C/D ring junction *trans*) gave only one isomer (CII) analogous to the formation of lactam (XCIV). Demethylation of these two bases with 48 per cent hydrobromic acid gave three of four possible isomers of 8-azaestrone (Ca), (CIa) and (CIIa) respectively. Lithium aluminium hydride reduction of the estrone derivatives gave the corresponding 17-hydroxy compounds (CIII), (CIV) and (CV) respectively. The hydroxy compound (CV) arising from (CII) was assigned β-configuration while the other two were assigned α-configuration. These assignments for C_{17}-hydroxyl groups were based on the analogous reactions in the carbocyclic

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*The hydrogenation of perchlorates (XCVIII and XCIX) created an asymmetric centre at C_9. The configuration of the hydrogen situated at C_9 was related to C_{13}-methyl group. If both lie on the same side of the ring C, the configuration was denoted as *syn*- and when on the opposite side, it was denoted as *anti*-.
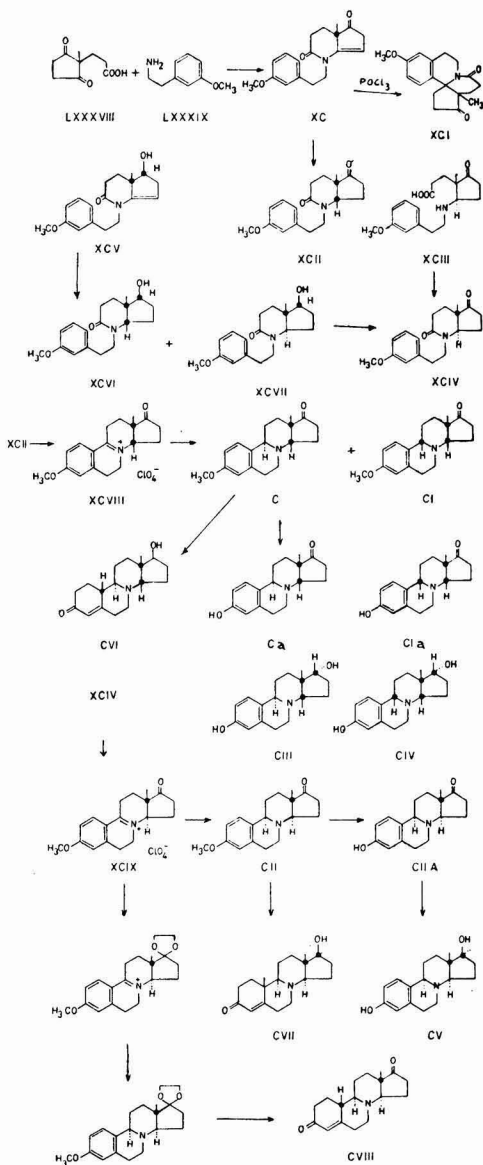
Chart 17 — Total synthesis of 8-aza steroidal derivative

series. Compound (CV) could also be prepared from the lactam alcohol (XCVII) directly.

Birch reduction of (C) and (CII) followed by acid hydrolysis gave two isomers of 8-aza-19-nor-testosterone (CVI and CVII). The sodium borohydride reduction of the ethylene-ketal of (XCIX), followed by its Birch reduction and acid hydrolysis, gave 8-aza-19-nor-androstane-3,17-dione (CVIII). In these

compounds the more stable β-configuration was assigned to the hydrogen at the newly created asymmetric centre at C_{10} based on the analogy to the carbocyclic series.

The above paper by Meltzer and coworkers also contained a discussion of the stereochemical problems involved in the synthesis. The C/D *trans*-fused products could only exist in three possible conformations (i, ii, iii) and the C/D *cis*-fused ones in six possible conformations (iv–ix). Of these nine conformations (i), (iv) and (vii) possess a *trans*-fused quinolizidine ring (i.e. the angular proton at C_9 is axial to both rings B and C) but in other available conformations it is *cis*. It was also observed that in (vi), (vii) and (viii), the C_{13}-methyl group is equatorial to ring C while in the others it is axial.
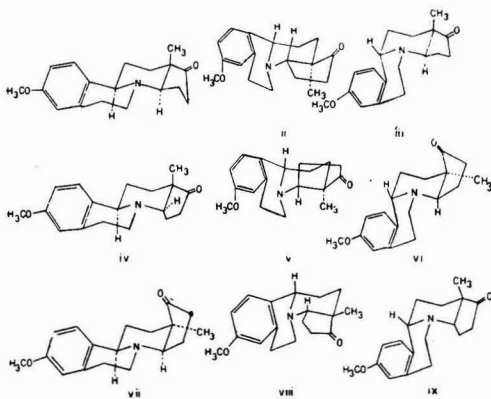
Preferable conformations for the isomers (C, CI and CII) were assigned on the basis of the infrared and nuclear magnetic resonance spectra. In the quinolizidine series, the appearance of at least two bands between 2700 and 2800 cm.$^{-1}$ in the infrared has been attributed[36] to the presence of at least two α-hydrogens, *trans* coplanar (diaxial) to the electron pair on the bridge-head nitrogen. These bands are called Bohlmann bands[37].

The compound (CII) has C/D ring *trans*-fused, so only conformations available for this compound are (i–iii). The appearance of two Bohlmann bands in its infrared spectrum suggested that conformation (i) is the only preferred one for this compound. This conclusion is in accord with the observation that the C_9-proton appears at higher field than usual in the NMR spectrum which is adequately explained by the shielding of this proton by the aromatic ring effected only in conformation (i).

The infrared spectrum of the compound (C) shows Bohlmann bands (at 2740 and 2790 cm.$^{-1}$). This compound must, therefore, incorporate a *trans*-fused quinolizidine ring, as in the previous case, thus limiting the choice of conformations for this compounds to conformations (iv) and (vii). There is yet another difference in these conformations. As pointed out earlier, in conformation (iv) the C_{13}-methyl group is axial to ring C, while in (vii) it is equatorial to ring C. Williams and Bhacca[38] have

correlated the chemical shifts of C_{13}-methyl groups, proximate to the carbonyl group, on passing from deuterochloroform to benzene as solvent. They have claimed that the ketones, in benzene solution, form a solute-solvent complex in which π electrons in the benzene ring interact with the positive end of carbonyl in such a way that the electrons are as far as possible from partial negative charge on the oxygen. The result is, in practice, that the axial methyl group or hydrogen in steroidal ketones are shielded in comparison with equatorial ones by dimagnetic anisotropy of the benzene ring. For the compound (C) the C_{13}-methyl group resonance signal moves upfield by 0·24 p.p.m., when recorded in benzene solution, indicating thereby that the C_{13}-methyl group is axial. Thus, out of the two conformations (iv) and (vii), conformation (iv) is assigned to compound (C).

The absence of Bohlmann bands in the infrared spectrum of (CI) indicated a *cis*-fused quinolizidine ring. The assignment of an *anti-cis* conformation, such as (iv) to the compound (C), leaves only conformations (viii) and (ix) for this compound. In conformation (viii), the C_9-hydrogen is axial to ring C and equatorial to ring B, while in (ix) it is axial to ring B and equatorial to ring C. The downfield shift for the NMR signal for C_9-hydrogen indicates its possible deshielding because of phenyl ring. This situation is more likely in conformation (viii) in comparison with (ix). Secondly, the NMR signal for the C_{13}-methyl group shows only a small downfield shift (0·04 p.p.m.) on passing from deuterochloroform to benzene as a solvent. This is consistent with an equatorial C_{13}-methyl group, thus ruling out the conformation (ix). However, the fact that mercuric acetate oxidation of (CI) to (XCVIII), though at a reduced rate compared with the oxidation of (C) indicated[39] that C_9-angular proton in (CI) is axial to both rings B and C, at least at the reaction temperatures. So far compound (CI), the conformation (vii) must also occur to an appreciable extent, though not enough to give Bohlmann bands in the infrared spectrum at the room temperature.

Meltzer and Brown[40-42] prepared a large number of compounds in this series by condensation of substituted phenylamines (of the type LXXXIX) with a suitable oxo-ester followed by cyclization of the condensation product.

Clarkson[43] has described a convenient stereospecific synthesis of 8-azaestrone (Chart 18). An amide (CIX), prepared from the condensation of (LXXXIX) and acryloyl chloride, added on dimethylamine to give a β-dimethylaminopropionamide (CX), which could be cyclized to a stable dihydroisoquinoline derivative (CXI). It was reacted with 2-methylcyclohexane-1,3-dione giving an enamine (CXII) and not the tricyclic diketone (CXIII). The catalytic hydrogenation of this enamine (CXII) gave 8-aza-D-homoestrone-3-methyl ether (CXIV). After removing (CXIV) by crystallization, the mother liquor was subjected to sodium borohydride reduction, from which the corresponding alcohol (CXV) was obtained, along with another ketone (CXVI), which could not be reduced to the alcohol, even after a prolonged contact with sodium borohydride at room temperature. The two ketones
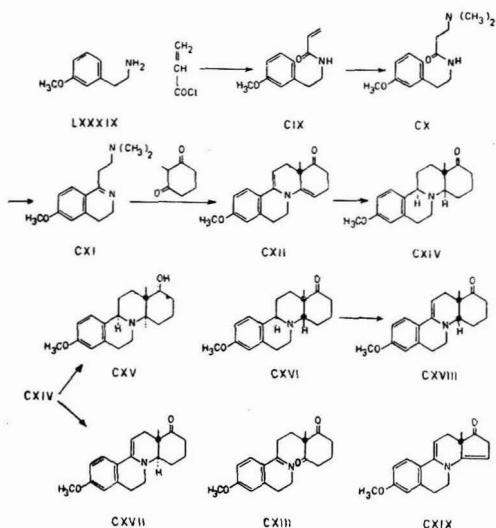
Chart 18 — Stereospecific synthesis of 8-azaestrone by Clarkson[43]

Chart 19 — Synthesis of 8-aza steroidal system by Meyers et al.[47]

(CXIV) and (CXVI), on mercuric acetate oxidation gave two different enamines (CXVII and CXVIII respectively) and hence, if ketone (CXIV) has the 14α-configuration, ketone (CXVI) must have a 14β-configuration. It was also found that the enamine (CXVIII) was a stronger base than (CXVII), and, on this basis, it was suggested that the enamine (CXVII) has the 14α-configuration and (CXVIII) has the 14β-structure. This suggestion was based on the analogy with carbocyclic compounds.

The reaction between (CXI) and 2-methylcyclopentane-1,3-dione also led to the corresponding dienamine (CXIX) which on catalytic hydrogenation gave 8-azaestrone (CIIa). Both Meltzer's and Clarkson's products have the same melting points, but comparison of other properties was not possible. It can be assumed that Clarkson's compound has the same stereochemistry (9α, 13β, 14α, anti-trans) as that of Meltzer's.

Though not indicated by Clarkson[43], it appears from the ease of mercuric acetate oxidation that the quinolizidine ring in these cases is trans-fused. Presumably, therefore, the ketone (CXIV) has the stereochemistry 9α, 13β, 14α (anti-trans) and the ketone (CXVI) has 9α, 13β, 14β (anti-cis).

Some patents[44-46] have been registered by the Imperial Chemical Industries, which involved the modification of 8-azaestrone to 8-aza analogues of testesterone, pregnenolone and their various alkyl derivatives.

In a preliminary publication, Meyers et al.[47] have described a method for the preparation of 8-aza and 9-aza steroidal derivatives.

In their approach to 8-aza steroids (Chart 19), phenylethyl chloride (CXXa) was condensed with ethyl cyanoacetate in presence of stannic chloride. The resulting isoquinoline derivative (CXXI) was catalytically hydrogenated to tetrahydroisoquinoline (CXXIIa). Cyclopentanone reacted with it to give an enamine (CXXIIIa) which was cyclized in hot ethylene glycol to an enaminoketone (CXXIVa). Reduction with lithium aluminium hydride gave a saturated ketone (CXXVa). The treatment of enaminoketone (CXXIVa) with excess of methyl iodide gave a C-alkylated compound (CXXVIa) which on catalytic reduction resulted in (CXXVIIa). Base catalysed equilibration of (CXXVa) suggested that C/D ring fusion was cis. In compound (CXXVIIa) also, the ring fusion was shown to be cis and the methyl group shown to occupy an axial position by measuring its upfield NMR shift in benzene as compared with chloroform. The appearance of Bohlmann bands[37] in the infrared spectrum of (CXXVa) and (CXXVIIa) at 2764 and 2804 cm.$^{-1}$ indicated that the systems incorporated the trans-quinolizidine ring.

This approach offered an excellent route to 8-aza steroids and is comparable to the approach of Clarkson, who used a similar method of reacting an isoquinoline derivative with suitable cyclic ketone.

Using the above method, Meyers and Sircar[48] have synthesized 8-azaestrone in good yield (Chart 20). They reacted (CXXIIb, R = OCH$_3$) with 2-methylcyclopentane-1,3-dione to get the corresponding enaminoketone (CXXVIII). An alcohol (CXXIX)
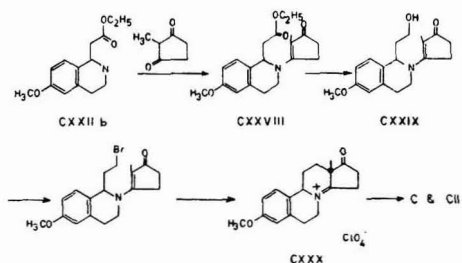
Chart 20 — Synthesis of 8-azaestrone by Meyers and Sircar[48]

prepared from the enaminoketone was converted into a bromide which was cyclized to (CXXX). It was hydrogenated to get a mixture of two isomers [14α-isomer (CII) and 14β-isomer (C)] of 8-azaestrone methyl ether which were readily separated by fractional crystallization.

The stereochemical assignments in (C) and (CII) were based on the infrared and NMR data as in the case of Meltzer's synthesis. Mayers and Sircar[48] have also condensed the isoquinoline derivative (CXXIIb) with cyclohexane-1,3-dione and the corresponding enaminoketone was cyclized and hydrogenated to get the D-homo steroidal system.

For preparing 9-aza steroidal compounds (Chart 21) Meyers and coworkers[47] reacted the isoquinoline derivative (CXXXI) with suitably substituted cyclohexanone (CXXXII) to get an enamine which cyclized in hot ethylene glycol to the corresponding enaminoketone (CXXXIII). The perchlorate of this enaminoketone (CXXXIV, $R_1 = R_2 = H$) gave upon addition with methyl magnesium iodide an angularly methylated derivative (CXXXVa, $R_1 = R_2 = H$; $R_3 = CH_3$). The treatment of the enaminoketone with excess of lithium aluminium hydride gave the ketone (CXXXVb, $R_1 = R_2 = R_3 = H$). On the basis of the field positions of C_8-proton in the NMR spectrum it was suggested that the compound (CXXXVa, $R_1 = R_2 = H$; $R_3 = CH_3$) possessed a *cis* quinolizidine ring. Similarly, in (CXXXVb, $R_1 = R_2 = R_3 = H$) it was indicated that the *trans*-fused ring was present.

CXXXI   CXXXII
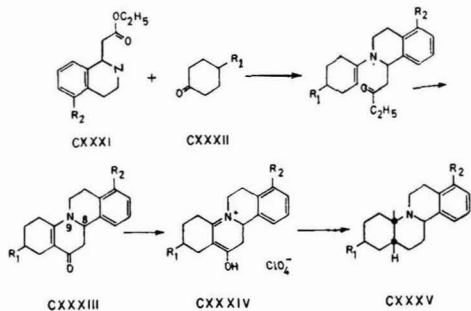

CXXXIII   CXXXIV   CXXXV

Chart 21 — Synthesis of 9-aza steroid by Meyers and co-workers[47]

The versatility of this approach was demonstrated by the above workers by the condensation of various 4-substituted cyclohexanone with isoquinoline esters followed by cyclization of the resulting enamines.

In a later publication[49], Meyers and colleagues concluded that ethylene glycol is not really necessary to achieve the cyclization in both 8-aza and 9-aza steroidal systems. It was observed that the reaction proceeds with or without acid catalyst, although the yields are higher and the reaction time shorter, when an acid catalyst is present. In the same publication was described the preparation of a number of ketones in the 8-aza steroidal series

with an oxygen function at C_3 and the size of the ring varying from 5 to 7 members.

There are some more recorded attempts at the synthesis of 9-aza steroids. The approaches of Jones and Wood[50] and of Schleigh and Popp[51] are based upon the Johnson method of equilenin synthesis, starting from an appropriate tricyclic ketone.

In Jones' approach (Chart 22), the quinoline derivative (CXXXVI, $R = CH_3$; $R' = OC_2H_5$) gave a keto-bromide (CXXXVII) which with Adams catalyst yielded benzoquinolizidine alcohol hydrobromide (CXXXVIII), which could not be oxidized to ketone (CXXXIX). Similarly, reduction of the semicarbazone or the oxime of the free base of (CXXXVII) was unsuccessful. The ketoester (CXL) was finally prepared and was found to be unstable to heat and to air. The hydrolysis of this ester (CXL) gave a ketone which was too unstable for further use. In the following publication[52], in this series, the synthesis of cyanoketones (CXLI) and (CXLII) from the cyclization of appropriate tetrahydroquinoline derivative was reported.
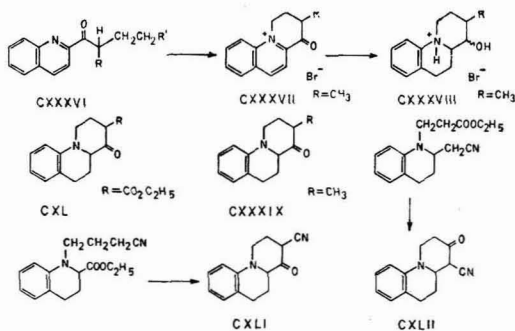
Chart 22 — Attempted synthesis of 9-aza steroidal system by Jones and Wood[50]

Schleigh and Popp[51] have also reported the synthesis of the ketoester (CXL), but the attempts to build ring D were abandoned, in view of the failures of analogous quinolizidine ketoester to undergo the reactions planned on the basis of Johnson's method.

CD_N type — 13-Aza steroids have been reported by two groups of workers. Birch and Subba Rao[53] have synthesized 13-azaequilenin-3-methyl ether (CXLVII) and 13-aza-D-homoequilenin-3-methyl ether (CXLVIII) (Chart 23). The potassium salt of succinimide (CXLIIIa, n = 2) or glutarimide (CXLIIIb, n = 3) was condensed with α-(6-methoxynaphthyl)-ethyl bromide (CXLIV) in dimethylsulphoxide, the resulting product (CXLVa or b) cyclized to (CXLVIa or b) and then catalytically hydrogenated to give (CXLVII) and (CXLVIII) respectively.

Kessar et al.[54] have synthesized (Chart 24) the compound (CXLVII) by a different route. They condensed α-(-6-methoxynaphthyl)-ethylamine
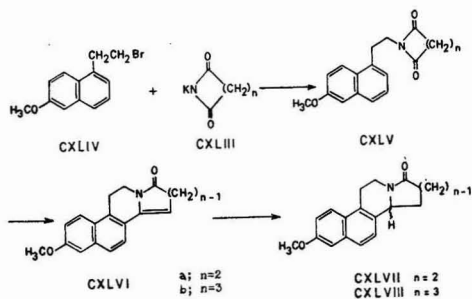
Chart 23 — Synthesis of 13-azaequilenin-3-methyl ether (CXLVII) and 13-aza-D-homoequilenin-3-methyl ether (CXLVIII)

Chart 25 — Synthesis of 14-aza steroidal system by Jones[55]

(CIL) with β-carbmethoxypropyl chloride (CL) and obtained an amide (CLI) which was cyclized with phosphorous oxychloride. The basic fraction in the above cyclization on hydrogenation and cyclization gave (CXLVII).

In both these publication, the stereochemistry of C_{14}-hydrogen with respect to lone pair on ring junction nitrogen is not discussed.

Chart 24 — Synthesis of compound (CXLVII) by Kessar et al.[54]

Chart 26 — Synthesis of 3-desoxy-18-nor-14-azaequileni (CLXI)

14-Aza steroids have been synthesized by various methods. In his approach (Chart 25), Jones[55] converted 6-methoxy-β-naphthylamine (CLII) into 3-ethoxycarbonyl-1-hydroxy-8-methoxybenzo(f)quinoline (CLIIIa, R = Cl) and was hydrogenated to (CLIIIc, R = H). This compound underwent Claisen condensation with ethyl acetate to give a k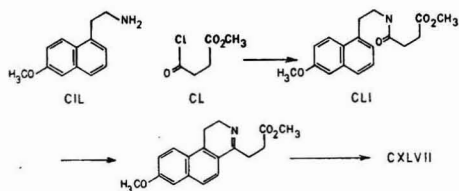etoester (CLIV) which was hydrogenated over platinum in ethanol to compound (CLV). However, this reduction, when carried out in acetic acid, gave a tetracyclic amide (CLVI) presumably by intra-molecular acylation of the compound (CLV). The tetracyclic amide (CLVI) could be reduced by a mixture of sodium borohydride and aluminium chloride, resulting in two isomers of 14-aza steroidal systems (CLVII).

The compound (CLIIIb, R = Cl) with hydrogen gave tetrahydrobenzo(f)isoquinoline derivative (CLVIII), which could be N-acetylated (CLIX). The N-acetyl derivative (CLIX) underwent base catalysed intramolecular ring closure to an amide (CLX) which was found to be a keto-enol tautomer (Chart 25).

Some more experimental details in the preparation of (CLVII) have appeared in recent patents[56].

Poirier et al.[57] have reported the preparation of 3-desoxy-18-nor-14-azaequilenin (CLXI) starting from β-naphthylamine (CLXII) and proceeding through benzo(f)quinoline (CLXIII) and tetrahydro-benzo(f)quinoline (CLXIV) intermediates. This synthesis of which no further details are available is summarized in Chart 26.

Logothetis[58], in his approach to 14-aza-D-homo steroids (Chart 27), used the Michael addition of 2-tetralone (CLXV) to 2-vinylpyridine (CLXVI) as his first step. The resulting tricyclic compound (CLXVII) was converted into a ketal (CLXVIII) and hydrogenated over Adams catalyst to give a piperidyl ketal (CLXIX). The corresponding ketone (CLXX) was cyclized with base to give a tetra-cyclic compound (CLXXI). Catalytic reduction of (CLXXI) gave an amine (CLXXII) which could also be obtained by direct reductive cyclization of (CLXVII) using Adams catalyst in ethanolic hydro-chloric acid. The stereochemistry at the B/C ring

CLXV CLXVI CLXVII

CLXVIII CLXIX

CLXX CLXXI CLXXII

CLXXIII

CLXXI CLXXV CLXXVI

Chart 27 — Synthesis of 14-aza-D-homo steroidal system and the assignment of stereochemistry

junction in the amine (CLXXII) has been assigned *cis* on the basis that catalytic hydrogenation of amines give *cis* product. The relations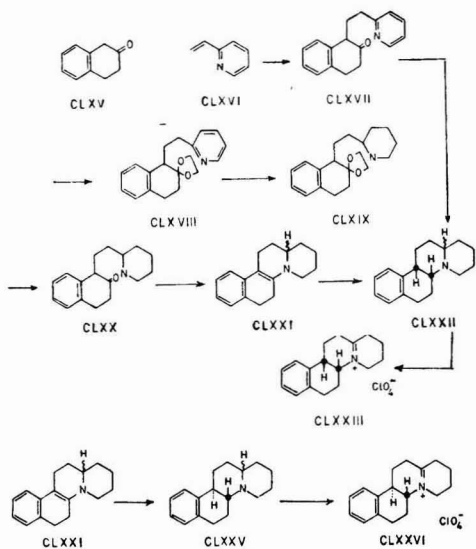hip of the hydrogens at the B/C ring junction could be either *syn-* or *anti-*. From the spread of melting point of the perchlorate of (CLXXII), he concluded that amine (CLXXII) was indeed a mixture of isomers. However, the oxidative destruction of the asymmetry at C_{13} by the use of mercuric acetate oxidation gave a single enamine (CLXXIII). The sodium borohydride reduction of the perchlorate (CLXXIV) of (CLXXI) followed by mercuric acetate oxidation gave another enamine (CLXXVI) isomeric with (CLXXIII) (Chart 27).

The preparation of two isomeric enamines (CLXXIII and CLXXVI) proved that both the methods of reduction were stereospecific. As pointed out earlier, the parent amine (CLXXII) of the perchlorate (CLXXIII) has been assigned *cis*-structure (at the B/C ring junction) so the other amine (CLXXV) obtained by sodium borohydride reduction of the perchlorate (CLXXIV) of (CLXXI) should have a *trans*-stereochemistry (at B/C ring junction) (Chart 27).

Synthesis of Multiple Heteroatom Steroids

Recently, Lehmann and coworkers[59] have reported the synthesis of A-nor-2,3-diaza steroidal ring system. They followed essentially the same method, which has been used in the total synthesis of carbocyclic steroids, viz. starting from an appropriate ketone, its condensation with vinyl magnesium bromide and treatment of the resulting tertiary alcohol with 2-methylcyclopentane-1,3-dione and cyclization. Thus they started with (CLXXVII) and arrived at

A-nor-2,3-diaza-3-phenylestra-1,5(10),8,14-tetraene-17-one (CLXXVIII) in good yields.

CLXXVII CLXXVIII
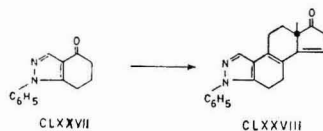
Jones[60] has described two more types of diaza steroidal systems. In order to prepare 6,8-diaza system (Chart 28), his approach was similar to that of Clarkson's[42]. A suitable Mannich base (CLXXIX) was prepared and subjected to base catalysed condensation with cyclic 1,3-diones. Thus Michael addition of (CLXXIX) to 2-methylcyclopentane-1,3-dione and 2-methylcyclohexane-1,3-dione gave (CLXXX) and (CLXXXI) respectively. Both these compounds could not be reduced. However, a similar compound, in which the angular methyl group was absent (CLXXXII), could be reduced and cyclized to 6,8-diaza-18,19-bis-nor-D-homo steroid system (CLXXXIII).

A 6,11-diaza-C-nor-D-homo steroidal analogue (CLXXXIV) (Chart 28) was prepared using Fischer-Indole reaction between 7-methoxy-4-keto-1,2,3,4-tetrahydroquinoline and suitably substituted phenyl hydrazine.

CLXXIX CLXXX n = 1 CLXXXI n = 2

CLXXXII CLXXXIII R

CLXXXIV R = R' = H R = H; R' = OCH₃
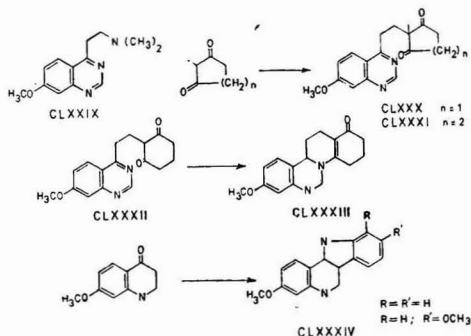
Chart 28 — Synthesis of 6,8-diaza (CLXXXII) and 6,11-diaza (CLXXXIV) steroidal systems

Burkhalter and Abramson[61] have reported the synthesis of 8,13-diaza steroidal system (Chart 29). They prepared 3-succinimido-N-(2-aryl-ethyl)-propionamide (CLXXXVa, R = H; and b, R = OCH_3), which yielded 3,4-dihydro-1-(2-succinimidoethyl)iso-quinoline (CLXXXVIa, R = H; and b, R = OCH_3). These isoquinoline derivatives were hydrolysed and catalytically reduced to 1-(2-aminoethyl)-1,2,3,4-tetrahydroisoquinoline (CLXXXVIIa, R = H; and b, R = OCH_3). Compound (CLXXXVII) was treated with 3-ethoxycarbonyl propionimidate hydrochloride to get 8,13-diaza steroidal system (CLXXXIX).

Williams *et al.*[62] have described a synthetic approach to 11,12-diaza steroidal skeleton (C_N-C_N type), by the addition of dimethylazodicarboxylate

365
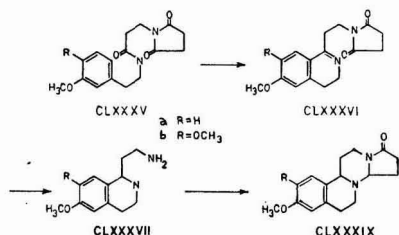
Chart 29 — Synthesis of 8,13-diaza steroidal systems (CLXXXIX)

Chart 30 — Synthetic approaches to 11,12-diaza steroidal skeleton

Chart 31 — Synthesis of 14,16-diazaequilenin and triaza-equilenin derivatives

(CXC) to a pseudo-diene followed by hydrolytic decarboxylation and oxidation. The pseudo-diene which were used were 2-(1-cyclopentenyl)-naphthalene (CXCI) and 2-(1-cyclohexenyl)-naphthalene (CXCII) derivatives (Chart 30). Compounds (CXCI) and (CXCII) were treated with (CXC) to 1,2-adducts (CXCIII and CXCIV respectively). On the basis of spectroscopic data, these two adducts were assigned two different structures. However, the above workers claimed that both of these adducts underwent hydrolytic decarboxylation on being refluxed with hydrazine hydrate followed by mercuric oxide oxidation. The resulting cinnolin derivatives (CXCV) and (CXCVI) might be used to prepare 11,12-diaza steroidal systems.

Jones[55] has obtained CD_N-D_N steroidal analogues of equilenin such as 14,16-diazaequilenin by treating compound (CLXIIIa, R = OC_2H_5) with urea in dimethylformamide (Chart 31). This reaction yielded the compound (CXCVII), which could also be obtained from the corresponding amide (CLXIIIb, R = NH_2) or hydrazide (CLXIIIc, R = $NHNH_2$) under 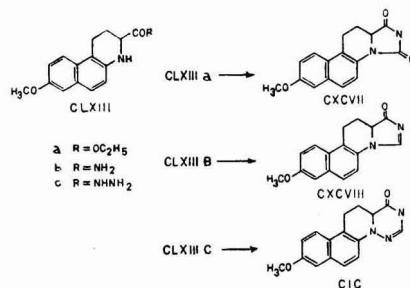similar conditions. The amide (CLXIIIb) could be converted into 14,16-diaza-15,16-dehydro-equilenin-3-methyl ether (CXCVIII) on boiling with

ethyl orthoformate. The hydrazide (CLXIIIc, R = $NHNH_2$) gave rise to a D-homo-triazaequilenin derivative (CIC).

The 9,15,16-triaza steroidal system (CC) was mentioned in the papers by Jones and Wood[50] and by Schleigh and Popp[51]. Jones obtained the above system by condensing the ketoester (CXL) with hydrazine.
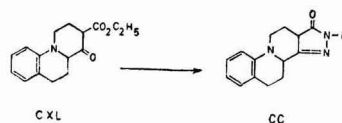
Summary

Though a number of heterocyclic steroidal skeletons have been synthesized, many of them are yet to be converted into the heterocyclic analogues of testosterone, pregnenolone, cortisone and progestin-estrogen preparations which are used in chemotherapy quite extensively. These conversions will open still another chapter which will be equally interesting both from biological and chemical points of view.

Acknowledgement

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REVIEWS

THE PLANETARIUM AND ATMOSPHERIUM by O. R. Norton (Naturegraph Publishers, Healdsburg, California, USA), 1968. Pp. viii+176. Price $ 2.75

The book is a very welcome one not only for those connected with the administration of planetaria, but also for anyone interested in knowing the planetarium and the successful way in which it has helped in popularizing the important and ancient science of astronomy. Rightly, the first chapter is devoted to a survey of the set-up of the starry heavens, the motions of the earth-rotation, revolution and precession of the planets and the moon, retrograde motions, etc. The next chapter deals with various early astronomical instruments, globes and orreries designed for the study of the celestial bodies. It describes the complex, mechanical Copernican planetarium set up at the Deutsches museum, Munich, in 1923. The Copernican planetarium was suspended from the ceiling of a circular room of 39 ft diameter with the sun (electric lamp) at the centre and the six planets up to Saturn (electric lamps) moving on rails with the satellites orbiting the planets.

The most spectacular and accurate presentation of the starry firmament was achieved only when the first Zeiss planetarium was set up at the Deutsches museum, Munich, in 1925. The project was taken up by Messrs Carl Zeiss at the suggestion of Dr Oscar Von Miller, Director, Deutsches museum, and his associate Dr Carl Bassler. The instrument was designed by Dr Bauersfeld of Zeiss. This instrument was designed for the projection of the stars on to the inside of a hemispherical dome and was made for the latitude of Munich. In Chapter 3, the author describes in detail several parts of the instrument and the 'planetary cage'. The second instrument set up at The Hague was capable of being tilted to any latitude from 49 degrees north to 68 degrees north. Further changes were soon introduced and the modern instrument can now present the starry sky as seen from any point on the surface of the earth. These developments are also explained in Chapter 3.

For more than 20 years the Zeiss planetarium dominated the field but still the facility of a planetarium was a 'million dollar operation'. With the development of space technology, educating students on space science became important and the author writes in sufficient detail in later chapters about the new types of planetaria designed in USA — the instrument at the Morrison planetarium (San Francisco), the Korkosz planetarium (Boston) and the different versions of the Spitz. The Spitz instruments are available commercially. In describing these instruments, the author explains how different techniques have been employed to get at the same results.

Presenting stars, planets, sun and moon alone do not constitute the entire fabric. Several astronomical phenomena have to be incorporated which the projector alone is not capable of handling. In Chapter 6, the author explains the various auxiliary equipments for eclipses, constellation symbols, lightnings, aurora, etc. Added to this is an interesting and important field: the atmospherium using special 180 degrees fish-eye lens systems that have been developed at the Fleischmann planetarium of the University of Nevada for presenting cloud formations, spacecraft sequence, earth orbit techniques, landscape scenes, etc. The book ends with a chapter with the title 'The curtain rises' where the author discusses a few typical programmes that could be carried out and has even suggested suitable background music.

Written in lucid style and printed and illustrated in a neat and pleasing way, the book will certainly be useful for any library.

R. SUBRAMANIAN

TRANSITION METAL INTERMEDIATES IN ORGANIC SYNTHESIS by C. W. Bird (Logos Press Ltd, London), 1967. Pp. vii+280. Price $ 13.00

Recent years have witnessed a tremendous surge of activity and interest in organometallic chemistry and the need for a general survey to familiarize chemists on the various aspects of organometallic compounds (apart from Grignard reagents) and to focus attention on the applicability of some of the elegant methods in synthetic organic chemistry has become pronounced over the past year or two. Dr C. W. Bird must be congratulated for bringing out this volume which covers in a lucid manner some of the above topics. He has done a good job in documenting the recent literature up to the time of publication of the book. In the first two chapters, he deals at length with numerous well-illustrated examples, the facile ease with which transition metal compounds bring about the oligomerization of acetylenes and olefins to long chain, cyclic and complex hydrocarbons, their capacity to dimerize, trimerize and polymerize the unsaturated compounds selectively depending upon the catalysts and conditions used and their ability to bring about Cope-like transformations in dienes. Pertinent reference has also been made of the breakthrough into the until recently elusive Dewar benzene-like structures using these complexes. Mention has also been made of their recent and widespread use in coupling reactions. In the chapter on hydrogen migrations, pointed reference has been drawn to the use of transition metal complexes to effect ring fissions. Of particular interest to synthetic organic chemists is the interesting isomerization of *cis*, *trans* cyclodeca-1,5-diene to *cis*, *cis* cyclodeca-1,6-diene (p. 78) and the reactions of carbanions on olefin-palladium complexes (p. 105). The hydroformylation, carboxylation and carbonylation reactions have been competently dealt with and the utility of metal complexes in the syntheses of certain acyclic, carbocyclic and heterocyclic compounds has been amply demons-

trated with a number of relevant examples. The decarboxylation reaction has been presented well with enough emphasis on the use of the recently discovered complex $(Ph_3P)_3RhCl$ in such reactions. Some of the matter presented in the book will be of interest to industrial chemists. Dr Bird has done a commendable job of the task that he had set before himself and his book will be welcomed not only by organometallic chemists and those who want to get initiated to this subject, but also by chemists working on synthesis who are avidly waiting for new aids in the synthesis of complex organic molecules.

T. R. GOVINDACHARI

COMPARATIVE BIOCHEMISTRY OF THE FLAVONOIDS by J. B. Harborne (Academic Press Inc., London), 1967. Pp. viii+383. Price 90s.

Dr Harborne, one of the pioneers in the study of biochemical and botanical aspects of the flavonoids, has written this book with specialized knowledge. The three main aims of the monograph are: (i) to outline the structural variations among the flavonoids and methods for their identification; (ii) to discuss in detail their distribution and potential systematic importance; and (iii) to review our present knowledge of their inheritance, biosynthesis, function and economic importance. These aims have been fulfilled admirably. The chemistry of the flavonoids has been rightly excluded in view of the publications of Geissman and Dean.

Every department of chemistry, biochemistry or botany will find this book an invaluable addition to its library, and no active worker on flavonoids can afford to be without a personal copy.

The first three chapters give a general account of anthocyanins, flavones and minor flavonoids, a special feature being the listing of R_f values. It is true, as the author states, that there is no other group of natural products in which the relationship between R_f value and structure is so clear cut, but it is difficult to agree with him that R_f values have played a large part in deducing the structures of new compounds. In fact, the present reviewer has always felt that one weakness in the otherwise very valuable work of Harborne and Bate-Smith is their almost complete dependence on R_f values for identification of specific flavonoids.

Chapters 4, 5, 6, 7 and 10 provide a detailed and comprehensive treatment of the distribution of the flavonoids and their uses as taxonomic markers. Chapters 8 and 9 give brief accounts of biosynthetic pathways and the function of the flavonoids. The last chapter on chemical taxonomy demonstrates how the flavonoids meet the requirements of chemical character to be of use in plant taxonomy or biochemical systematics.

A more comprehensive treatment of the physiological and pharmacological activity of the flavonoids would have been welcome. The statement: ' the only really important pharmacologically active group of flavonoids are the isoflavones ' needs to be revised. Catechin and a few flavones have been shown to have useful pharmacological properties and there is reason to believe that some of them and their derivatives have found clinical applica-

tion. In a subsequent edition, which will surely be called for in a few years, the author may find it possible to use the excellent background material which he has provided on the distribution of the flavonoids for a much more detailed review of their biosynthesis, physiological properties, and chemical taxonomy.

The following statements and structures need to be modified or corrected. ' Leucoanthocyanidins are really condensed tannins.' ' Most chromatographically mobile leucoanthocyanidins are dimers ' (p. 98). ' The structure of calycopterin (erroneous formula on p. 218) has not yet been confirmed by synthesis ' (p. 219). ' Citrinin in the ponderosa lemon . . .' (p. 177). ' Isoflavones are formed biosynthetically from the same chalcone precursor ' (p. 166). The structures of munetone (p. 168) and 6-hydroxyluteolin (p. 220). Structure 39 for a constituent of *Cedrus deodara* is only tentative (p. 122). The section on isoprenoid substituted flavonoids (p. 179) leaves out several of them, such as artocarpin and cycloartocarpin.

K.V.

INSTRUMENTATION IN BIOCHEMISTRY edited by T. W. Goodwin (Academic Press Inc., London), 1966. Pp. ix+113. Price 30s.

With the very rapid progress in biochemical research, instruments, especially those of the high precision type, are now being increasingly used for solving major biochemical problems. The present book is a collection of scientific papers on this topic presented at the Biochemical Society Symposia No. 26 held in London during April 1966. The contributors have dealt with some of the more sophisticated instrumentation techniques which have wide applicability in diverse fields of biochemical research.

The book covers six fields of instrumentation, namely laboratory centrifuges, microscale spectroscopy, applications of electron spin resonance, flow and relaxation techniques in rapid reaction studies, automated analysis in nutritional research, and application of digital computer for simulation of multi-enzyme systems. All these subjects are discussed by eminent authors who are intimately connected with the developments in the respective instrumentation techniques.

Although the book is not a descriptive one, the contributors have developed their topic from the basic principles underlying each technique. They have indicated how inherent limitations in instrumentation have been largely overcome by careful choice of material and precision design so as to make the techniques applicable even at the extreme scale of measurement.

The chapter on centrifuges discusses the design of different types of rotors with illustrations and gives useful information about the major types of commercially available ultracentrifuges. The topic of spectroscopy is discussed from the point of view of adaptation of commercially available instruments for experimental investigation of ultramicroscopic substances of biological significance. The application of electron spin resonance method of study of enzyme reactions is briefly discussed in one chapter. The limitations and advantages

of the developing methods in the study of fast biochemical reactions are dealt with in the chapter on flow and relaxation techniques. Automation in nutritional research problems, with examples of automatic analysis of a large number of constituents of blood, has been dealt with mainly for its importance in studies on clinical biochemistry. In the last chapter, the use of digital computer is explained with examples to indicate the application of this technique for kinetic studies of multi-enzyme systems.

The book, as a whole, gives a survey of important and fast developing areas which contribute to the present progress of biochemical research. The topics are presented in a simple style, easily understood by post-graduate students and research workers in biochemistry and biophysics. For those scientists, who are increasingly utilizing instrumentation in their research studies, the present book provides valuable information.

P. J. VITHAYATHIL & P. S. SARMA

COMBUSTION OF PULVERIZED COAL by M. A. Field, D. W. Gill, B. B. Morgan & P. G. W. Hawksley (British Coal Utilization Research Association, Leatherhead, UK), 1967. Pp. xv+413. Price 50s.

The book presents in an excellent manner the up-to-date information available for setting up of mathematical models for pulverized fuel fired combustors and charts out areas where further advances can be made and knowledge acquired on the subject.

The understanding of the combustion process in a p.f. fired combustor is a complicated matter and it is not feasible to work out any calculation without some degree of mathematical simplification of the system. The simplified representation of the system on which calculations can be made is referred to as a mathematical model. Models have been set up by different workers for varied purposes like calculating the effect on the rate burn-out of different degrees of swirl, showing the effect of recirculation combustion products on the rate of burn-out, ascertaining temperatures and compositions along the axis of combustors, etc.

In addition to known input conditions, the basic information needed for a model are pattern of gas flow and the rate of mixing of solid and gaseous reactants in the combustion chamber; the rates of heat transfer between the different parts of the combustion chamber and to the walls; and the rates of all reactions including devolatilization, combustion of gases and combustion of solid particles.

A survey on the main difficulties that are encountered in arriving at a proper understanding of the combustion process has been made at the outset of the book. In the two succeeding chapters, flow patterns and mixing of fuel and air, and methods for calculating rates of heat transfer and equilibrium temperature distribution in combustors are considered. Subsequently, topics on thermal decomposition of coal, combustion of coal and reaction rate of carbon particle are dealt with in separate chapters.

The isothermal combustion of a suspension of coal particles, which is discussed next, may be taken as the first step towards a mathematical model. The isothermal plug flow assumption makes the system largely simplified because of absence of heat transfer and mixing problems. For this simplified system the rate of carbon burn-out can be calculated, permitting prediction to be made for the effects of factors like fineness of grinding, amount of excess air or swelling on the time taken to burn the fuel. Finally, the authors deal with the problems of formulating models, review the models already constructed and suggest steps that might be helpful to make models better representations of combustion chambers. The authors are of opinion that if one-dimensional models can be replaced by three-dimensional ones and the radiant heat transfer in flame is taken into account in the construction of mathematical models, the models can be brought much closer to reality. The authors state further that important gaps in our knowledge on the mixing rate of gases in turbulent flow; general flow patterns in complex jet systems; estimation of absorption coefficient from the composition of the reactant stream; size changes undergone by a coal particle during combustion; sequence of events comprising devolatilization, ignition and volatiles and char burning and the extent to which these overlap; rate of reaction of carbon monoxide; precise values of the surface reaction rate coefficient; and dependence on fuel type and temperature would at present limit the application of a complete model.

Although the book is primarily concerned with combustion of pulverized coal, many of the topics discussed are useful for the combustion of liquid and gaseous fuels. Much of the subject matter of the book has been presented in the appendices and only the main conclusions from the appendices have been included in the text with the objective of presenting, in a concise and compact manner, the main themes of the book in the text.

The authors deserve to be congratulated for this nice publication and the book is recommended unhesitatingly to all who are interested in combustion of pulverized coal.

S. K. DAS GUPTA

Optical display using cold-cathode arrays

A system for optically displaying electronic signals that could lead to a practical 'flat' television tube has been developed at the Standard Telecommunication Laboratories, Harlow, UK. The system comprises an array of cold-cathode electron emitting elements, positioned behind a phosphor-coated display screen. Instead of a modulated electron beam scanning the screen to produce a picture, as in normal television, each element of the array is switched by the signals being read and emits electrons which produce light on collision with the screen. A picture can thus be built up on the screen from a series of point sources of light.

The cold-cathode elements consist of a layer of silicon oxide insulators 300-2000 A. thick, sandwiched between an upper metal electrode of gold and a lower one of aluminium. After a special electroforming process, a bias voltage applied across the electrodes produces 'hot' electrons in the insulator layer, some of which have sufficient energy to be emitted from the upper electrode. The phosphor screen, at a positive potential of 2 kV., is above this electrode and separated from it by a vacuum. The electrons produced are accelerated towards the screen to produce light on impact [*New Scientist*, **37** (1968), 491].

New tool for studying crystal structure

A new tool for studying crystal structure has been developed at Harwell [*New Scientist*, **37** (1968), 492]. The instrument, an addition to the existing electron and X-ray diffraction methods for studying crystal structure, bombards a crystal surface with a beam of protons to produce a shadow or 'blocked' pattern on a fluorescent screen. Unlike the interference patterns produced by other methods of crystal study, the pattern produced by the new instrument is instantly recognizable and does not require any lengthy interpretations.

The trajectories of the incident protons are obstructed by the closely packed rows and planes of atoms of the sample crystal, resulting in a back-scattering of protons. The back-scattered protons produce an image on a fluorescent screen with dark areas where protons have been deflected from the screen by the interference of the crystal structure, thereby producing a pattern corresponding exactly to the geometry of the crystal lattice.

Besides having the advantages of simple and rapid projection of the crystal lattice information, the method has the added advantage of not relying on transmission of the beam through the sample and can, therefore, be used to study thin crystal layers only tens of thousands of atoms thick, without removing them from a substrate.

Pseudo matrix isolation spectroscopy

A low temperature technique, pseudo matrix isolation spectroscopy, which provides a rapid and sensitive method of infrared quantitative analysis of mixtures of infrared absorbing gases and volatile liquids, has been reported [*Science, N.Y.*, **160** (1968), 196]. An added advantage of this technique based on cryogenic pulsed deposition is its capacity for distinguishing between molecular isotopes, and it requires no preanalytical separations.

In a typical experiment, three 0·46 m. moles of a 1 per cent mixture of d_2-ethylenes in nitrogen were condensed on a clear CsI window at 20°K., and the IR spectrum recorded. The matrix dispersion resulting from the controlled pulse deposition of a dilute solution and the low temperature help keep the intermolecular interactions small and the resulting bands narrow. The spectra were simple and the frequencies reproducible within 1 cm.$^{-1}$. 1,1-Ethylene-d_2 showed bands at 751 and 946 cm.$^{-1}$, *cis*-(1,2)-ethylene-d_2 at 847 cm.$^{-1}$ and *trans*-(1,2)-ethylene-d_2 at 725 and 991 cm.$^{-1}$. Beer's law plots drawn for the pure components at the wavenumbers characteristic of the species as seen from the spectrum were essentially linear.

Gas chromatography, due to its high selectivity, can be applied for the analysis of gas mixtures; but it requires preanalytical separations of the mixture or repeatedly chromatographing. In either case the distinguishability obtainable is much less. Another technique capable of analysing gas mixture is mass spectrometry, which involves complex analysis of spectral data. In view of these shortcomings, pseudo matrix isolation is of great significance, especially when one considers the easy access to a variety of X-ray equipment and cryogenic apparatus like Joule-Thomson refrigerators.

Spark source mass spectroscopy

Spark source mass spectroscopy (SSMS) is the latest of the tools to be made use of for the trace analysis of biological materials. Though complex and time-consuming, SSMS has the advantage over the earlier methods of enabling simultaneous analysis of about 60 elements at concentrations as low as a few parts per million. It will be particularly useful when limited amounts of samples are available. Plant leaves, animal and human tissues, blood plasma and bone have been analysed successfully with this technique.

In principle, the method consists in generating ions from solid samples by the use of vacuum discharge sparks and analysing them in a mass spectrometer. But there is a difficulty in applying this technique to biological materials; the sparks generate a complex mixture of organic and inorganic ion fragments which mask the spectral lines of the individual trace elements. The interference due to the organic part has been overcome by first getting rid of the organic matter

by ashing the specimen. The ash is blended with an equivalent weight of high purity graphite (to make it electrically conducting) and made into a pellet. The pellet is broken into two and the pieces placed close to each other in a spark chamber. After evacuating the chamber to 10^{-6} torr, radio frequency discharge is passed between the ash-graphite electrodes, when ions are produced. The ions are accelerated into a mass spectrometer slit system. A double focusing instrument with a Mattauch-Herzog geometry and a theoretical resolution of 6300 permits simultaneous focusing and photographic recording of the different ion masses.

The interference due to inorganic ion groups has been largely overcome by selecting an internal standard, which would compensate for fluctuations during the ionization and also provide a method for calibrating the emulsion used as a detector. The copper present in the samples, which could be accurately estimated by other techniques, was chosen as the internal standard. Alternatively, known quantities of a trace element not present in the sample being analysed could be added at the pellet-making stage, to serve as a standard [*Chem. Engng News*, **46** (No. 20) (1968), 38].

High pressure synthesis of PbCrO₃

A new compound, $PbCrO_3$, with a perovskite structure having chromium in Cr(IV) state, has been synthesized from mixtures in the system Pb-Cr-O using high pressure techniques. This is the first instance of finding Cr(IV) in an octahedral site in the cubic perovskite structure. The technique used is of general interest in the use of high pressure for studying reactions involving oxidation states of metals which may be unstable or metastable at normal pressure.

Equimolar mixtures of chemically pure yellow PbO and CrO_2 at 425°C. and 0·25 k bars oxygen pressure were used in 130 runs to plot a pressure-temperature diagram showing the perovskite stability region. The equilibrium nature of the $PbCrO_3$ phase was

confirmed by synthesis from other combinations of chemically pure oxides in Pb-Cr-O system.

The desired proportions of the oxides after thorough mixing were made into cylindrical pellets wrapped in thin platinum foil. The pellets were introduced into an internally heated cell, the pressure was raised to the desired value and the temperature raised at a programmed rate of 200°C./min. After 20-30 min., the sample was quenched at the rate of 400°C./sec. at the same pressure, the pressure released, and the sample taken out. The temperature was measured by the use of a watt-temperature plot established by earlier studies using Pt-Pt 10 Rh thermocouple. The phases formed were identified by X-ray powder diffraction and optical examination with transmitted light.

$PbCrO_3$ was formed above the pressure-temperature line extending from 50 k bars at 750°C. to 60 k bars at 1450°C. The $PbCrO_3$ phase can be quenched and retained at 1 atm., but decomposes if heated above 275°C. at the same pressure. It crystallizes primarily as black cubes with twinning on (111). Normally the crystals are of 30 μ size, but by growing the crystals in a large cell where a temperature gradient could be established, crystals as big as 0·1 mm. and flat plates as large as 0·25 mm. in the largest dimension were obtained. Instead of fast quenching if the $PbCrO_3$ phase was allowed to cool and the pressure released slowly, it decomposes to give Pb_2CrO_5, Cr_2O, and PbO, all of which could be identified [*J. Am. ceramic Soc.*, **51** (1968), 72].

Simple apparatus for rapid measurement of *p*H

The measurement of *p*H in as short a time as 0·003 sec. has become possible as a result of the development of a simple and inexpensive apparatus. The apparatus combines (i) a standard *p*H meter, (ii) a driving-mixing arrangement of the Hartridge-Roughton type and (iii) a specially designed glass microelectrode. The method is free from physical effects (e.g. streaming effects) and, hence, affords a precision of 0·005 *p*H unit, essential for most biochemi-

cal studies. However, the method does not give accurate results at low ionic strength due to (i) uncertainties in the liquid junction potential difference between the calibrating buffers and the buffers with unknown *p*H and (ii) the appearance of physical effects on *p*H readings (streaming potentials).

The apparatus comprises two all-glass thermostated syringes; two motor-driven plungers; a 12-jet mixing chamber; an observation tube (2·8 mm. in diameter); a glass electrode; a reference calomal electrode; and a thermostated outlet reservoir. The glass electrode is introduced into the observation tubes, and the distance between its sensitive tip and the mixing point is measured to ± 0·1 mm. by means of a vernier caliper and two fixed points, one on the electrode stem and one on the supporting Lucite block. After temperature equilibrium has been reached, the electrode is standardized by flowing two suitable buffers (usually borate at about *p*H 9·0 and phthalate at about *p*H 4·0). The calibrating buffers are usually stored inside thermostated bottles (capacity, 10 litres) and driven out by means of a positive gas pressure. The flow rates of the standardizing buffers used are comparable (to within 5 per cent) to those of the reaction mixture. The *p*H values of the buffers are separately determined by a radiometer microelectrode unit, type E 5021, with reference to standard phthalate, phosphate and borate buffers made up according to Bates method [*Determination of pH: theory and practice* (John Wiley & Sons Inc., New York), 1961]. The rapid flow electrode is standardized with a buffer having *p*H close to that of the solution under test. The *p*H reading of the second buffer is then noted. The procedure is repeated until constant readings for the two buffers are obtained. The outlet solenoid values of the two syringes and the motor are then simultaneously activated, and the *p*H of the reaction mixture is determined at a given distance from mixing. From the rate of discharge of the two syringes and the distance from mixing, the observation time can be calculated, with the assumption that (i) complete

mixing (97-98 per cent) has occurred in less than 2 mm. from the mixing point (2 msec.), (ii) the liquid, in turbulent flow, moves as a 'block' between the mixing and the observation point, (iii) the error due to the 'slit length' is negligible, and (iv) no significant stagnant layers of liquid are formed around the electrode [*J. biol. Chem.*, **243** (1968), 1297].

Fixation of atmospheric nitrogen by ruthenium compounds

Atmospheric nitrogen has been fixed for the first time as a coordinating ligand in a ruthenium(II) complex. Allen and Senoff's ion $[Ru(NH_3)_5N_2]^{2+}$ previously prepared from gaseous nitrogen [*J. Am. chem. Soc.*, **89** (1967), 5706] has now been synthesized from atmospheric nitrogen [*Can. J. Chem.*, **46** (1968), 469].

A $0.1M$ solution of $[Ru^{III}(NH_3)_5-Cl]Cl_2$ in $0.1M$ H_2SO_4 was reduced with amalgamated zinc under argon till the solution became neutral. A stream of air was drawn through the solution till it turned pink. The air was replaced by argon, more acid was added when all the air was flushed out, and the reduction continued. This cycle was repeated for 5-7 hr, when no pink colour developed when air was drawn in. Any remaining Ru(III) was reduced and zinc hydroxide dissolved by adding excess acid.

The electronic spectrum of the solution at this stage showed a strong band at 263 mμ and weak band at 221 mμ. When sodium fluoborate was added to this solution a yellow precipitate, mainly $[(NH_3)_5Ru-N_2-Ru(NH_3)_5]^{4+}$ as evidenced by the electronic spectra, was formed. When the precipitate was warmed with ammonia it was converted to $[(NH_3)_5RuN_2]^{2+}$ which was precipitated as fluoborates and identified spectrally. It is evident that molecular nitrogen is an effective nucleophile for ruthenium(II) even in competition with oxygen.

Adsorption of surfactants

Wetting agents and detergents have been distinguished for the first time by measuring their rates of adsorption on to graphitized carbon black. Earlier attempts at classifying surfactants from thermodynamic factors such as coareas at the air-water and oil-water interfaces and heats of adsorption were not successful.

Sodium salts of α-sulpho fatty esters, $RCH(SO_3Na)COOR'$, behave as wetting agents or detergents depending on the length of alkyl groups R and R'. If one of them is long and the other short, the surfactant behaves as a detergent; if both of them are of the same medium chain length then the surfactant is a wetting agent. The criteria employed in classifying compounds as wetting agents and detergents are the ability to displace air from solid surfaces and the ability to remove oily dirt from surfaces such as cotton, with a minimum efficiency.

For the adsorption study, sodium hexyl α-sulphopelargonate and its heptyl and octyl homologues were used as wetting agents and sodium methyl α-sulphomyristate, sodium methyl α-sulphopalmitate and sodium ethyl α-sulphopalmitate were used as detergents. Bulbs containing activated carbon were broken in a 0.2 per cent solution of the surfactant and the electrical conductance measured as a function of time. The plots of reduced conductance versus time showed a minimum conductance at 3-7 min. for wetting agents and at 20-25 min. for detergents. The wetting agents adsorb on to the carbon faster than the detergent. The reason for this could be the orientation of the molecules at the interface. Adsorption of a surfactant takes place with the hydrocarbon part orienting to the hydrophobic surface of the adsorbate and the bulk projected into the liquid phase. With different lengths of R and R', the proper orientation of the chains may be delayed [*Chem. Engng News*, **45** (No. 52) (1967), 52].

Plant Foods for Human Nutrition

This new quarterly journal, launched in May 1968 by the Pergamon Press Ltd, Oxford, collates and summarizes essential scientific information which can provide a basis for a rational world food programme. Annual subscription is £8 8s. 0d.

Regional Research Laboratory, Jammu

The annual report of the laboratory for the year 1966 records satisfactory progress under the scheme on the production of ergot with the objective of attaining national self-sufficiency in 3 years. Strains of *Claviceps purpurea* have been isolated, some of which produce mostly ergometrine and others mostly ergotamine in high yields. Strains of *Aspergillus niger* have been isolated locally which in submerged cultures (shake flasks) convert sucrose into citric acid in satisfactory yields. Methods worked out for the production of total belladonna alkaloids, atropine, hyoscine, homatropine and other salts have been taken up by the Drug Research Laboratory, Jammu, on a commercial scale. It is planned to manufacture enough of these drugs to meet the country's entire requirements. A process has been developed for the isolation of digoxin from *Digitalis lanata* leaves.

As a result of screening of plants for pharmacological action, three plants, viz. *Crotolaria agatiflora*, *C. mucronata* and *Piper peepuloides*, gave encouraging results. Madurensine and fulvine have been isolated from *C. madurensis*. Madurensine is a new alkaloid with OH substitution at C-6 in the pyrrolizidine nucleus and reported for the first time. Another new alkaloid, crosemperin, has been isolated from *C. wightiana*. The presence of isobutylamides in *Piper* sp. has been reported for the first time. Marked antitubercular and insecticidal activities have been exhibited by total extract and alkaloidal fractions of *P. peepuloides*.

A new ion-exchange method for the isolation of hyoscine from *Datura innoxia* has been standardized. Another method based on ion-exchange has been developed enabling economical utilization of poor quality raw material in the production of ephedrine.

A new method for the separation of individual alkaloids and estimation of total alkaloids of *W. somnifera* has been developed. The existence of 3 chemical races

in *Zingiber officinalis* has been established.

A technique has been developed whereby the pyrethrin contained within the cell walls of the marc are regenerated to the extent of over 90 per cent in free state.

Twenty heptanes having very high antifungal activities *in vitro* in the concentration range 0·5-2·0 μg./ml. have been isolated from *Streptomyces* cultures. Fifteen of these antibiotics constitute a new structural group of heptaenes. They contain the amino sugar, mycosamine and the aromatic moiety, *p*-aminobenzaldehyde, which is aldolically bound to the rest of the molecule. Two of these, X-2510 and X-2110, have been found to be new ones. Chantalmycin, a new polyene pentaene antifungal antibiotic, has been isolated; it shows a very high activity *in vitro* (conc. 0·5 μg./ml.) against various pathogenic fungi, *Mycobacterium tuberculosis* (1-2 μg./ml.) and strains of *Staphylococcus aureus* resistant to various antibiotics (0·5-2·0 μg./ml.). A new species belonging to the genus *Streptosporangium*, which produces polyene (pentaene) and heptaene type of antibiotics has been isolated.

A coumarin isolated from an indigenous plant showed interesting respiratory stimulant properties and is being clinically tested.

A new disease of *Solanum aviculare* has been observed on the plantation in Jammu, causing more than 40 per cent mortality. The causal organism has been found to be *Fusarium* sp. A new tip-blight disease of *Vinca rosea* caused by *Colletotricum dematium* has been observed. Two varieties of edible mushroom have been successfully cultivated in the laboratory.

Kalinga Prize, 1968

The £ 1000 Kalinga Prize for 1968 has been awarded to Prof. Fred Hoyle of UK in recognition of his efforts at popularization of science. Besides being an eminent scientist in the fields of astrophysics and cosmology, Prof. Hoyle is the author of 17 works on astronomy, philosophy and sociology of science in which he has dealt particularly with the problems relating to man's place in the universe and the conditions of his life on the earth. Some of his better known works are *The nature of the universe, Man in the universe* and *Frontiers of astronomy.*

Dr Bh. Subbaraju

Dr Bhupatiraju Subbaraju has been appointed Director, Central Road Research Institute, New Delhi. Dr Subbaraju (*b.* 21 March 1919) had his early education in the States of Andhra Pradesh and Madras. He took the degree of Bachelor of Engineering (Civil) in 1942 from the Madras University. Later, he obtained the degrees of Master of Science and Doctor of Philosophy in Highway Engineering in 1953 and 1955 respectively from the A. & M. University, USA. He was awarded the distinction of 'Phi-Kappa-Phi' at the A. & M. University.

Dr Subbaraju started his professional career with the Public Works Department of the Madras State in 1942, and worked there and with the PWD, Andhra Pradesh, for about 14 years in different capacities. During this period, he executed several highway projects involving different types of pavement constructions. While in the service of the Madras State, he conducted a few road experiments also and was associated with the establishment of the Highway Research Station at Madras.

Dr Subabraju joined the Central Road Research Institute in 1956 as the Head of the newly formed Roads Division. He developed this important wing of the institute from scratch to a full-fledged division. He held this post for a period of about ten years. During this period, he was responsible for giving technical advice to different organizations in the country on the design, construction, maintenance and investigation of failures, etc., of highway and airfield projects. He was also responsible for the construction and evaluation of a series of test tracks involving both flexible and rigid pavements. Dr Subbaraju's contributions in the field of basic research concern the development of a design method for flexible pavements applicable to Indian conditions.

In 1966, Dr Subbaraju was promoted as Scientist 'F' and made in-charge of the Indian Roads Congress Road Tests Project. This is the first project of its kind undertaken to evaluate comprehensively the relative efficacy and economics of different design and construction practices through road tests, so that more efficient and economical practices can be evolved for use in the planned road development programmes. In April 1958, Dr Subbaraju was deputed to USA on a UN fellowship for discussing the plans of the project.

Dr Subbaraju has about 50 reports and papers to his credit. He is a member of the Indian Roads Congress, Institution of Engineers (India), the Indian Society of Soil Mechanics and Foundation Engineering, and the International Association of Bridge and Structural Engineers. He has been actively engaged on the work of several committees of the Indian Roads Congress and the Indian Standards Institution. He has been the Secretary of the Research Organization Committee of the Indian Roads Congress for over six years.

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