PROCEEDINGS
OF THE
CHEMICAL SOCIETY

APRIL 1959

---

# THE PLACE OF CHEMISTRY. X.* IN THE SCOTTISH UNIVERSITIES

By ANDREW KENT
(GLASGOW UNIVERSITY)

> "WHEN Galileo was promoting mechanical philosophy, Bacon was laying the foundation of Chemical.... The improvement of experimental knowledge was left to Boyle, who took up Chemistry where Bacon left it.... Boyle is almost the first chemist that is worth reading; but after him came many famous ones, particularly the great Newton.... Lastly came Boerhaave ... the chief reformer of the Method and Language of the Chemists (who) has made great discoveries in Chemistry, particularly in fire . . ."
> —William Cullen, Lectures.

Since St. Andrews, dating from 1413, is the oldest Scots university and Edinburgh, founded in 1582, the youngest, they have all at some time taught variants of the standard medieval curricula with a degree of emphasis on Aristotelian ideas of the structure of matter. Before a more modern approach to chemistry was anywhere attempted, two later influences had impinged effectively on the national outlook.

The Calvinist religion and politics of John Knox led to a general replacement of French cultural influence by Dutch. The Glorious Revolution of 1688 paved the way for the advent of a notably advanced and forward scientific outlook, stimulated largely by Isaac Newton's triumphant demonstration of the new natural philosophy. In the fluid situation of recovery and overhaul then prevalent in Scottish establishments novelties had more instant appeal than in the stabler south: as the northern universities in the eighteenth century replaced their antique "regent" system by a new and specialised professoriate, there was further opportunity for modernisation.

The impulse for the first provision of chemical curricula in Scotland came from the desire to provide, in continental fashion, university schools of instruction in medicine which would supplement existing facilities for the examination of intending physicians. Thanks to Paracelsus such plans in the eighteenth century inevitably included chemistry; and they were bound also to reflect the influence of Leyden's Boerhaave, whose *Elementa Chemiae* expounded his successful redaction of alchemy and iatro-chemistry to an empirical, factual recital.

Some sixty years after the appointment of D'Avisonne (né Davidson) at Paris, the town council of Edinburgh appointed in 1713 Dr. James Crawford (Crauford) as their first professor of Physic and Chemistry: and this project gained its second wind when in 1726 Dr. Andrew Plummer professed the chemical sector of a joint-chair at the College in Chemistry and Medicine. In 1747 Dr.

---

* For earlier articles in this series see: *Proc. Chem. Soc.*, 1957, 185, 190, 273, 276, 313; 1958, 93, 96, 135, 307; 1959, 52.

William Cullen filled the new lectureship in Chemistry at Glasgow: the regius chair was provided in 1818. Similar developments at St. Andrews were somewhat delayed by the lack of an adequate hospital and a concurrent shortage of cadavers;[1] but a course in Chemistry and Chemical Pharmacy under Dr. Robert Briggs was authorised in 1811, and a first appointment to the (Purdie) Chair of Chemistry duly transpired in 1840.

Crawford and Plummer were both pupils of Boerhaave. "Plummer's Pill"[2] still reminds us of their iatro-chemical interests although this doctor's status in science was well recognised. His own pupil Cullen was to become, in 1757, his successor as teacher of Chemistry and Medicine; but not before he had sounded, at Glasgow, a clear and compelling call to recognise the status of Chemistry as a separate branch of science. Thomas Thomson held him the first to do so and the first to lecture in Scots instead of Latin.[3] In curricula, exposition, and breadth of appeal Cullen and his successor Joseph Black set new standards, rapidly extended by their students to other institutions at home and in America. With their professional background and their academic purpose in medicine, they still contrived emphasis on Chemistry, not as a simple nurse of nostrums, but as a new and powerful physical science: and they opened their classes to every type of enthusiast.

### ORIGINAL APPROACHES

If such developments portrayed the response of medical science, events in Aberdeen underline the extent to which Galileo and Newton had energised all departments of Scots philosophy. In both universities of this city, various experiments in the teaching of chemistry were undertaken in the Faculties of Arts, before in 1793 Marischal College[4] announced Dr. George French—who had studied under Cullen at Edinburgh—as its first professor of Chemistry; and before Patrick Forbes provided a course on Chemistry and Mineralogy at King's College in 1817, which was also an Arts class and indeed a compulsory subject, superseding Willian Ogilvie's venture. If French was grandson to a litster (dyer), Forbes, like Ogilvie, was a professor of Humanity (Latin): and in early emphasis on the contribution of science to general culture these northernmost universities—whose union came only in 1860—together set a valuable precedent still echoed in the Arts curricula at Aberdeen. Both courses were of more immediate effect when a joint medical school was established in 1819.

A third development was based neither on medicine nor on general culture but emphatically, if prematurely, on the values of a science-centred and inexpensive education. This was John Anderson's University, established without an official charter by those eighty-one trustees to whom this erstwhile Glasgow College professor had entrusted £1000 and his dream of a cultivated democracy. In 1796, within a few months of Anderson's death they appointed Thomas Garrett, later of the Royal Institution: he was followed by George Birkbeck, whose admiration of Glasgow's Mechanics Institute would fructify later as a constituent college of London University. So successful was the chemical section of their lectures on natural philosophy that already in 1804 the trustees appointed Andrew Ure as their first professor of Chemistry.

Thus early in the nineteenth century Scotland had six established courses in chemistry of university rank, apart from those in Mechanics Institutes, the powerful extra-mural schools in Edinburgh, or other teaching enterprises. It is clear that the ferment of science had proliferated headily in the century before. If David Gregory, Francis Hutcheson, Adam Smith, David Hume, and "Common-sense" Reid typified the more erudite devotees, there were few specialists in our sense of the term. Crawford, Edinburgh's first chemist, later accepted a chair of Hebrew: John Anderson had once professed Oriental Languages: Ogilvie and Forbes were Aberdeen divines: St. Andrew's first professor, Arthur Connell, had been trained as a lawyer. Yet were they all Newtonian.

The public response to their efforts was, and remains, astonishing. Nine hundred and seventy-two students enrolled in Garnett's third course of Chemistry. Andrew Ure took three classes in 1806, two of which had enrolments of some 400. Cullen's class at Edinburgh was nearly 150 strong, Black's was over 200, and Hope in 1827 issued tickets to 575. So late as 1878, the first Graham lecture promoted by the chemical section of Glasgow's Philosophical Society attracted an attendance of one thousand.

Three factors may be advanced in partial explanation of such statistics. First, it must be borne in mind that until about 1840 chemistry included, heat, light, electricity, and magnetism: as mineralogy it covered much of modern geology. Chemistry was almost the natural history of the inanimate, affording to its adepts wide and colourful fields of exposition.

Secondly, the startling facts of pneumatic chemistry, originating in Black's "Magnesia Alba" and still a world's wonder, shortly provoked the excitingly novel views of Mons. Lavoisier—translated and on

---

[1] Robert Walmsley, "Veterum Laudes," p. 121.

[2] A calomel ($Hg_2Cl_2$) confection, retained in the Pharmacopeias for more than two centuries.

[3] Thomas Thomson, "A History of Chemistry," Vol. I, London, 1830, p. 315.

[4] Marischal College and University, like the Town's College of Edinburgh, was a post-reformation foundation.

sale in Scotland within a few weeks—and then the astonishing atomism of Mr. Dalton. These were great days in which to be alive and to be an amateur of chemistry.

Finally and of special note to Scotland, partly ruined by the American War of Independance, there was wide interest in the industrial potential of this new knowledge. Black invested in an unlucky soda venture, but Watt turned his views on heat to massive account: James Hutton was enterprising in ammonium chloride provision (non-cameline): William Irvine was an expert on glass-manufacture. The MacIntoshes, Josias Gamble, Charles Tennant, and the rest became agents of a Chemical Revolution in industry. John Galt has written of Scotland in this era that "The minds of men were excited to new enterprises: a new genius, as it were, had descended upon the earth." Much of this drive originated in the new schools of chemistry whose vitality was expressed through some of the earliest chemical societies on record. The Chemical Society of Edinburgh University dates back to 1785. There was a shorter-lived Chemical Club in Glasgow College at the same time: this, and a second venture presided over by William Ramsay *grandpère*, had strong industrial associations. Such bodies catalysed the change of natural philosophers into chemical specialists.

## PRACTICAL INSTRUCTION

Chemistry's intrusion in the older academic fabric did not go quite unresisted by argument on expediency, legitimacy, or status. The universities were as poor as they were ambitious, and this new science came late to the table of endowments. Against the poverty of the new departments and the meagre equipment of the "preparation rooms" it is difficult to overestimate their research achievements or their sustained vitality. Edinburgh's first appointee was warned "not to expect any salary": Glasgow was launched on an unexpected windfall of £30, and forty years later the entire equipment was inventoried on a single sheet of notepaper. In Marischal College the early lectures were circumscribed because "we have not apparatus to fill up a much longer course": at the neighbouring King's the first graduating course was floated on the relics of earlier ventures, "the three-foot table with £20 and some glass, mostly broken." Sir James Irvine speaks of St. Andrew's first lecturer as "provided with no class-room, no laboratory, no apparatus and no place on the time-table": however, the United Colleges sent their Quaestor to a sale of Thomas Thomson's surplus apparatus where he procured a job-lot costing £40.[5] In chemistry our academic institutions were encountering with distaste the sharp and continuous cost of scientific education; yet worse was to come, for it later became evident that laboratory instruction of students was a pedagogic necessity at university levels.

Thomson had experimented with such instruction in his extra-mural work in Edinburgh: appointed professor at Glasgow he demanded an undergraduate laboratory and by 1820 had obtained it. Hope in Edinburgh soon followed suit. (Liebig's similar equipment was set up at Giessen in 1824.) Thomas Graham, at Anderson's, began a practical course in 1831. In the same year Thomson achieved the construction of a new department the "Shuttle Street Laboratories" of Glasgow University, specially designed for such teaching at a greatly grudged expenditure of £5,000.[6] His pupil, Thomas Clark, inaugurated practical chemistry at Marischal College in 1833: William Gregory followed up at King's in 1840, this member of his great academic clan having studied under Hope and Liebig. Largely for financial reasons, such equipment at St. Andrews had to await the appointment of Thomas Purdie in 1884; and he avoided the inevitable senate storms by financing the construction himself.

These changes implied some extra emphasis on the scientific students, a rapid rise in their quality and the production of a stream of young chemists, most notably from Glasgow and Edinburgh, who were of a new "professional" type, filling many posts of importance in the newer English institutions and industries. They played a notable part in the foundation of "The Chemical Society," first headed by a Scots professor, Graham of London University. Their intensive training underlined the need to reduce and homogeneate the syllabus. By 1840 heat had been transferred with similar intangibles to physics: interest in mineralogy died out slowly, perhaps because of private and profitable exercises in quantitative analysis; and a traditional attention to agricultural chemistry did nothing to improve the underdevelopment in organic studies. Prominent students like Gregory, Playfair, Ramsay, Crum Brown, Purdie, and Scott Couper had to look abroad for inspiration in this subject (and also for suitable scientific degrees). In the period *post* 1850 this deficiency continued. Moreover, organised research on fundamental topics was sporadic and of little significance: research schools in our modern sense were long unknown. A reasonable explanation, if a poor excuse, lay in the chronic financial shortages affecting staffing, building, and equipment.

## TEACHERS & TEXTS

There did result a powerful sequence of text-books

---

[5] Sir James Irvine, "Chemistry Centenary Lecture," a pamphlet, Edinburgh, 1941, p. 11.

[6] Andrew Kent, "Glasgow University Gazette," 1956, no. 25, p. 10.

based on the new modes of instruction. The later works of Thomas Thomson, those of Graham, Gregory, R. D. Thomson, and Greville Williams[6] were widely influential in mid-century and later, while the Scottish centres still maintained the degree of distinctiveness they had established in the previous century. Yet the influence of The Chemical Society, the broadened basis of the Royal Society, the activation of new departments in London and the provinces, all tended to fuse the northern schools into the general British field. Frederick Penny came to Anderson's from London in 1839; Brazier, appointed to the Chair at Aberdeen in 1862, was an early product of the Royal College of Chemistry. Even more suggestive was the appointment of Wm. Dittmar at Anderson's in 1874, only three years after his countryman Gustav Bischof had accepted the new Young appointment in Technical Chemistry at the same college.[7]

This second half-century was a period of great teachers. Gregory, Crum Brown, John Ferguson, Fyfe, Brazier, and Heddle could all claim pedagogic skill. Their academic status was effective in intramural policy: while the public status of the profession was enhanced by the activities of Sir Lyon Playfair, M.P., and the Master of the Mint. New opportunities occurred, not only at Anderson's but also when Carnelly of Owen's College became the first (Baxter) professor of Chemistry at University (Queen's) College, Dundee; and when the Heriot-Watt College in Edinburgh inducted W. H. Perkin, Jr., to a similar post in 1887.

Victorian prosperity had other useful repercussions. Public funds became available on an enlightened scale, though reaching a total of only £40,000 for all purposes in 1893. Professorial salaries were gradually made independent of fees: erstwhile "private" assistants were officially paid. The department at Edinburgh acquired new, "palatial" accommodation in 1884. Endowed lectureships in metallurgy and organic chemistry appeared before the century's end; yet Glasgow made the first such appointment in physical chemistry only in 1904, an opportunity furiously developed by Frederick Soddy.[8] (Scotland's academic appointments still lack a chair of physical chemistry.)

Probably the chief scientific event of this Victorian period was the appeal of Thomas Purdie at St. Andrews, in 1884, for student-and-other support of his proposed school of research. This disciple of Wislicenus and Edward Frankland founded the St. Andrews school of stereochemistry and, being Purdie, proceeded then to finance it and to achieve a properly equipped centre by 1905 which (Sir) James Irvine would inherit in 1909.

Further twentieth-century developments are mostly too recent for historical review. The Carnegie Trust from 1901 gave effective assistance at last with the financial burden of modern research: everywhere its largesse was welcome: the groups around Purdie, Soddy, Japp, and (Sir) James Walker had stimulus and support.[9]

The establishment of the first Universities Grants Commission in 1919 opened even wider horizons. In this same year of post-war reconstruction, T. S. Patterson became the first (Gardiner) professor of Organic Chemistry at Glasgow;[10] and Edinburgh's appointment of George Barger to a new chair of Chemistry in relation to Medicine neatly returned the courtesy of Dr. James Crawford's promotion some two centuries before—a full circle which must delimit this survey.

## A RECAPITULATION

In summary, then, chemistry in Scotland found its roots in iatro-chemistry and its inspiration in Galileo, Newton, and Boyle. There were some important scientific societies, but the nurture of modern science was a university achievement, assisted by a degree of disorganisation which provided a near *tabula rasa* for reformers of the early eighteenth century. In Aberdeen the cultural status, in Anderson's the social significance of the science was boldly set forth; the earlier and more general development was pursued in faculties of medicine, with a syllabus incorporating a substantial amount of physics and geology. This supervisory association persisted, despite the foundation of science faculties, until in the times of such as Japp and G. G. Henderson it had outlived its useful function; yet the sturdy attitude of Cullen and Black asserted from the beginning the full status of this new branch of physical science whose classes attracted every kind of enthusiast, including dissenters from New England, Ulster, and elsewhere.

The Newtonian fervour of Scottish philosophy in the eighteenth century was a major factor in the astonishing response to chemical praelection in the nineteenth. The departments, whose cost had been already lamented, now proceeded to the provision of

---

[7] Anderson's University, or Institution, was later incorporated in the Royal Technical College, Glasgow, now the Royal College of Science and Technology.

[8] Sir Alexander Fleck, "Biographical Memoirs of Fellows of the Royal Society," 1957, Vol. III, p. 206.

[9] "Record of Fellows, &c.," The Carnegie Trust, Edinburgh, 1935; A. Logan Turner, "History of University of Edinburgh, 1883—1933," Edinburgh, 1933, p. 47.

[10] In this same year (Sir) I. M. Heilbron occupied a similar chair at the Royal Technical College, Glasgow. Neither appointment has been continued, in the original form.

laboratory instruction against the heavy, prolonged resistance of economists and neo-scholastics. It was largely through chemistry that the northern universities were eventually reconciled to the cost of scientific teaching: and the new equipment, as in Shuttle Street, produced the first professional chemists. On the other hand, the following half-century was a period of consolidation, in which European progress in organic and physical chemistry or in the promotion of research schools was rather slowly followed up. The first years of this century saw provision of Carnegie finances to support research schools which now cover the whole spectrum of interests, in large and well-equipped departments. There are few populations which produce a similar proportion of university graduates in the subject, and this has relation to an old, still vigorous tradition of chemistry as a very important unit in the scientific sector of the national culture, which now enjoys both the prestige of departmental size and the dignity of long standing.

It is little wonder that the Scots chemists have a bent to historical studies. They share a contact, thin yet clear, with the *Physica* of the classical quadrivium: a primary position in the practical manifestation of modern science, involving a long association with Medicine and Arts which antedated the Science faculties: a pioneering insistence upon expensive laboratories and quick proof of their profit in teaching and research; and a list of scientists who have added lustre for centuries to their subject and their colleges.

General references:

Alexander Findlay, "The Teaching of Chemistry in the Universities of Aberdeen," Aberdeen, 1935.

Andrew Kent (Ed.), "An Eighteenth Century Lectureship in Chemistry," Glasgow, 1950.

John E. Mackenzie, "The Chair of Chemistry in the University of Edinburgh," *J. Chem. Educ.*, 1935, **12**, 503.

John Read, "Men of Science, The Chemists," in "Veterum Laudes," (J. B. Salmond, Ed.), Edinburgh, 1950.

(For details of more recent developments see the articles "Schools of Chemistry in Great Britain," in *J. Roy. Inst. Chem.*, 1953-4.)

## NEWS AND ANNOUNCEMENTS

**New Members of Council.**—The following new appointments to the Council were announced at the Annual General Meeting:

*Vice-Presidents who have filled the Office of President*

Sir Robert Robinson

*Honorary Secretary*

Professor A. W. Johnson

*Vice-Presidents who have not filled the Office of President*

Professor F. Bergel

*Elected Ordinary Members of Council*

Constituency I:

Dr. C. B. Amphlett
Dr. H. T. Openshaw
Dr. W. A. Waters

Constituency II:

Professor C. H. Hassall

Constituency IV:

Dr. I. J. Faulkner
Professor G. E. Coates
Dr. A. H. Lamberton

**Corday-Morgan Medal and Prize.**—The Corday-Morgan Medal and Prize for 1957 has been awarded to Professor G. W. Kenner (Heath Harrison Professor of Organic Chemistry, University of Liverpool) in consideration of his contributions to synthetic organic chemistry, particularly in the field of peptide and nucleotide chemistry.

This Award, consisting of a Silver Medal and a monetary Prize of 200 Guineas, is made annually to the chemist of either sex and of British Nationality who, in the judgment of the Council of The Chemical Society, has published during the year in question the most meritorious contribution to experimental chemistry, and who has not, at the date of publication, attained the age of thirty-six years.

Copies of the rules governing the Award may be obtained from the General Secretary of the Society. Applications or recommendations in respect of the Award for the year 1958 must be received not later than December 31st, 1959, and applications for the Award for 1959 are due before the end of 1960.

**Election of New Fellows.**—118 Candidates, whose names were published in the *Proceedings* for February, have been elected to the Fellowship.

**Chemical Society Library.**—The Library will be closed for the Whitsun Holiday on May 18th and 19th, 1959.

**Elections to The Royal Society.**—The following Fellows of The Chemical Society have been elected to the Fellowship of The Royal Society:

*F. Bergel*, Professor of Chemistry in the University of London, at the Chester Beatty Research Institute of the Institute of Cancer Research, Royal Cancer Hospital. Distinguished for his work in synthetical organic chemistry in the field of vitamins and drugs.

*R. J. W. Le Fèvre*, Professor of Chemistry in the University of Sydney and Head of the School of

Chemistry. Distinguished for his studies of the physical properties of organic compounds.

*G. V. Raynor*, Feeney Professor of Physical Metallurgy in the University of Birmingham and Head of the Department of Physical Metallurgy. Distinguished for his research on the structure of metals and alloys.

*R. E. Richards*, Lecturer in Chemistry at the University of Oxford, Physical Chemistry Laboratory. Distinguished for his work on nuclear magnetic resonance and its application to chemical problems.

*R. Spence*, C.B., Chief Chemist and Head of Chemistry Division, Atomic Energy Research Establishment, Harwell. Distinguished for his work on the chemistry of radioactive elements, and for his leadership of the Chemistry Division of Harwell.

**The Chemical Council.**—The Chemical Council has elected Honorary Officers for 1959 as follows: Chairman, Dr. J. W. Cook, F.R.S., Vice-Chancellor of the University of Exeter; Vice-Chairman, Professor Harold Burton ; Honorary Treasurer, Dr. Frank Hartley; Honorary Secretary, Dr. J. Chatt.

**Conferences and Symposia.**—The 1959 Gordon Research Conference on Radiation Chemistry will be held at New Hampton School, New Hampton, New Hampshire, U.S.A. Enquiries should be addressed to Mr. W. George Parks, Director, Department of Chemistry, University of Rhode Island, Kingston, Rhode Island, U.S.A.

An International Symposium on Macromolecules, sponsored by the International Union of Pure and Applied Chemistry, will be held in Wiesbaden, Germany, on October 12—16th, 1959. Enquiries should be addressed to Dr. W. Mauss, Wiesbaden-Biebrich, Rheingaustrasse 25 (Kalle & Co. A.G.), Germany.

**Transfer of D.S.I.R. Stations.**—Three D.S.I.R. Stations—all concerned with the preservation, storage, handling, or protection of foodstuffs—will be transferred to the Agricultural Research Council on July 1st. They are the Ditton Laboratory at Larkfield, Kent, the Low Temperature Research Station at Cambridge, and the Pest Infestation Laboratory at Slough.

The agreement between the Council for Scientific and Industrial Research and the Agricultural Research Council—which has received the approval of the Lord President of the Council (Lord Hailsham)—was made because the two Councils believe that it is in the national interest to bring all Government research on food, other than fish, under one body. The aim is to make the research more effective.

**Translation of Papers on Iron and Steel.**—The British Iron and Steel Industry Translation Service, run on a co-operative basis by leading British iron and steel companies with the British Iron and Steel Research Association and The Iron and Steel Institute, will arrange a translation of any article connected with the manufacture of iron and steel.

Translations required urgently are put in hand straight away; before the invoice is sent, details are circulated to 150 steel companies, and others, to try to find others to share the cost. When cost is a factor, the enquiry is circulated first, and translation is not begun unless two or more other requests are received: the price, including illustrations, is less than half the net translating cost.

**Personal.**—*Professor S. J. Angyal* has been awarded the H. G. Smith Memorial Medal for 1958 for his work on sulphonamides, the Sommelet reaction, and the cyclitols. The Medal is awarded every year by the Royal Australian Chemical Institute to the member who, in the opinion of the Council of the Institute, has contributed most to the development of some branch of chemical science.

*Dr. H. J. Barber* has been awarded the degree of D.Sc. of London University for work in the field of chemotherapy.

*Professor D. H. R. Barton* has been selected as first recipient of the Roger Adams Award in Organic Chemistry. This Award is sponsored by the American Chemical Society, by Organic Reactions, Inc., and by Organic Synthesis, Inc., and consists of a medal and an honorarium of $5000. It is to be given biennially to a single individual, without regard to nationality, for outstanding contributions to research in organic chemistry.

*Dr. A. H. Beckett* has been awarded the D.Sc. degree of the University of London for his work in the field of medicinal and pharmaceutical chemistry.

The Society Medal of the Society of Chemical Industry, which is awarded not more than once every two years for conspicuous services to applied chemistry or to the Society, has been awarded for 1959 to *Dr. Francis H. Carr*, C.B.E.

*Sir Alexander Fleck*, who has been named the first Visiting Fellow of the American Section of the Society of Chemical Industry, has spent the first two weeks in April in the United States visiting the main chemical centres of the country.

*Sir Alexander Fleck* has accepted the Presidency of the Industrial Co-partnership Association.

The Honorary Degree of Sc.D. has been conferred by the University of Dublin upon *Professor E. L. Hirst*, Professor of Organic Chemistry in Edinburgh University.

The Senate of the University of London has conferred the title of Fellow of University College, London, upon *Professor R. S. Nyholm*.

*Dr. F. L. M. Pattison* has been appointed Professor and Head of the Department of Chemistry at the

University of Western Ontario, London, Ontario, Canada, effective from July 1st, 1959.

*Dr. D. Traill*, Research Director of the Nobel Division of Imperial Chemical Industries Limited, has been elected a Fellow of the Royal Society of Edinburgh.

*Dr. G. O. Aspinall* will be spending the months of September and October, 1959 visiting a number of centres in the United States and Canada to lecture.

*Professor D. M. Newitt*, Head of the Department and Courtauld Professor of Chemical Engineering at the Imperial College of Science and Technology, visited Spain in February to discuss the training of chemical engineers at the invitation of the Director of the Instituto Quimico de Sarria, Barcelona.

*Dr. F. G. T. O. Torto*, the Society's Local Representative for Ghana, will visit this country during the period June—September, 1959.

*Mr. K. L. Butcher*, Brotherton Lecturer in Chemical Engineering at the University of Leeds, has been promoted to the title and status of Senior Lecturer from October 1st.

*Mr. R. B. Fisher*, Demonstrator in Biochemistry at Oxford and Lecturer of Wadham College, Oxford, has been appointed to the Chair of Chemistry in relation to Medicine at Edinburgh University, in succession to *Professor G. F. Marrian*, who resigns on September 30th.

*Dr. T. W. Goodwin* has been appointed to the Chair of Agricultural Chemistry at Aberystwyth University in succession to *Professor R. O. Davies*, who retires at the end of the present session.

*Mr. N. H. Haddock*, of Imperial Chemical Industries Limited, has been transferred from photographic chemical research to undertake special researches in the field of dyestuffs chemistry.

*The Earl of Halsbury* has been invited to join the Board of Lancashire Dynamo Holdings in April as a Vice-Chairman.

*Dr. A. K. Kiang* has been appointed Senior Lecturer in Chemistry at the University of Malaya.

*Dr. A. C. Monkhouse*, who was recently Acting Director of Fuel Research of the Department of Scientific and Industrial Research, has been appointed Adviser to the Athlone Fellowships Scheme.

*Dr. E. N. Morgan* of Parke Davis & Co. Ltd. has been appointed to the newly created post of Research Manager at their Hounslow laboratories.

*Dr. K. T. Potts* has joined the staff of the Department of Organic Chemistry at the University of Adelaide.

*Dr. W. I. Pumphrey*, Manager of the Research Department of Murex Welding Processes Ltd., Waltham Cross, Herts., has been elected to the Court of Governors of the University of Birmingham as a representative of the Guild of Graduates.

*Dr. W. Rigby* has been appointed Lecturer in the Department of Organic Chemistry at the University of Leeds from October 1st.

*Mr. O. G. Weller*, who has held the position of Technical Manager of the Uganda Development Corporation Ltd. for some years, has succeeded the late Mr. Trefor Davies as technical executive officer of A.B.C.M., responsible for the work of the chemical engineering research and advisory service committee, the instrumentation advisory service committee, and the information exchange committee.

*Mr. J. Wood* has accepted a post at the Woodstock Agricultural Research Centre of Shell Research Ltd., near Sittingbourne.

## FORTHCOMING SCIENTIFIC MEETINGS

### London

Thursday, May 7th, at 7.30 p.m.

Meeting for the Reading of Original Papers. "Recent Developments in the Chemistry of the Ipecacuanha Alkaloids," by A. R. Battersby, R. Binks, G. C. Davidson, B. J. T. Harper, and S. Garratt. "Aldol, Pinacol, and Benzoin-type Reactions of $\Delta^1$-Pyrroline 1-Oxides," by R. F. C. Brown, V. M. Clark, M. Lamchen, B. Sklarz, and Sir Alexander Todd. "Perpendicular Conjugation in Some Octahedral Metallophthalocyanine Derivatives," by J. A. Elvidge and A. B. P. Lever. To be held in the Rooms of the Society, Burlington House, W.1. Coffee will be served in the Library from 7 p.m. (Abstracts of the Papers are available from the General Secretary.)

Thursday, June 4th, at 7.30 p.m.

Meeting for the Reading of Original Papers, "Kinetics and Orientation of Some Epoxide Ring-opening Reactions", by N. B. Chapman, N. S. Isaacs, and R. E. Parker. "Aromatic reactivity. Part III. Cleavage of Substituted Phenyltrimethylsilanes by Sulphuric Acid in Acetic Acid-Water," by F. B. Deans and C. Eaborn. "The Heats and Entropies of Ionisation of Some Aromatic and *N*-Heteroaromatic Amines," by J. J. Elliott and S. F. Mason. To be held in the Rooms of the Society, Burlington House, W.1. Coffee will be served in the Library from 7 p.m. (Abstracts of the Papers are available from the General Secretary.)

### Birmingham

Friday, May 1st, at 4.30 p.m.

Lecture, "The Structure and Reactivity of Reduced

Metallic Surfaces," by Professor K. W. Sykes, M.A., D.Phil. Joint Meeting with Birmingham University Chemical Society, to be held in the Chemistry Department, The University.

Friday, May 29th, at 7 p.m.
Lecture, "Polyethers," by Professor G. Gee, Ph.D., F.R.S. To be given at Courtaulds Ltd., Coventry.

**Durham**

Monday, May 4th, at 5 p.m.
Lecture, "Carbon-14 Compounds," by Dr. J. R. Catch. Joint Meeting with the Durham Colleges Chemical Society, to be held in the Science Laboratories, The University.

**Exeter**

Friday, May 22nd, at 5 p.m.
Lecture, "Optical Rotatory Dispersion in Structural Organic Chemistry," by Dr. W. Klyne. To be given in the Washington Singer Laboratories, Prince of Wales Road.

**Irish Republic**

April 29th, May 1st, and May 4th
Lecture, "A Generation of Chemotherapeutic Research," by Dr. F. L. Rose, O.B.E., F.R.I.C., F.R.S. Joint Meeting with the Institute of Chemistry of Ireland, the Royal Institute of Chemistry, and the Society of Chemical Industry.

To be held as follows:

April 29th, at 7.45 p.m. in the University Chemical Laboratory, Trinity College, Dublin.
May 1st, at 7.45 p.m., at University College, Cork.
May 4th, in the Chemistry Department, University College, Galway.

Friday, May 8th, at 7.45 p.m.
Lecture, "The Nature of the Active Centre of Chymotrypsin and Other Esterases," by Professor H. N. Rydon, D.Sc., D.Phil., F.R.I.C. Joint Meeting with the Werner Society, to be held in the University Chemical Laboratory, Trinity College, Dublin.

**Manchester**

Friday, May 1st, at 7.15 p.m.
Lecture, "Characterising the Useful Properties of Starch," by Dr. T. J. Schock. Joint Meeting with the Royal Institute of Chemistry and the Society of Chemical Industry, to be held in the Chemistry Lecture Theatre, The University.

**Northern Ireland**

Tuesday, May 5th, at 7.45 p.m.
Official Meeting and Tilden Lecture, "Nucleotides and Bacterial Cell-wall Components," by Professor J. Baddiley, D.Sc., Ph.D. To be given in the Chemistry Department, Queen's University, Belfast.

**Oxford**

(Joint Meetings with Oxford University Alembic Club to be held in the Inorganic Chemistry Lecture Theatre.)

Monday, May 4th, at 8.15 p.m.
Lecture, "Magnetic Properties of Molecules," by Dr. J. A. Pople.

Monday, May 18th, at 8.15 p.m.
Lecture, "Some Unnatural Products," by Professor E. R. H. Jones, D.Sc., F.R.S.

Monday, June 8th, at 8.15 p.m.
Lecture, "Graphite and its Crystal Compounds," by Professor A. R. Ubbelohde, D.Sc., F.R.S.

**St. Andrews and Dundee**

Friday, May 1st, at 5.15 p.m.
Lecture, "Chemical Effects due to Fission Fragments," by Dr. R. Spence, C.B., D.Sc., F.R.I.C. Joint Meeting with the University Chemical Society, to be held in the Chemistry Department, St. Salvator's College, St. Andrews.

---

# CENTENARY LECTURE*

## Spectra of Free Radicals

By G. Herzberg
(National Research Council, Ottawa, Canada)

In this lecture I propose to look at certain chemical problems from the point of view of the physicist and, more particularly, of the spectroscopist. Chemists have studied free radicals for many decades. A large variety of these radicals has been postulated in innumerable chemical reactions. Sometimes the arguments for the temporary existence of a free radical in a chemical reaction are somewhat ambiguous, or so they seem to a physicist. As a spectroscopist one would naturally want to observe the spectrum of a free radical before one would feel entirely convinced of its presence in a chemical reaction, a flame, an explosion, an electric discharge, etc. In addition, once a spectrum has been obtained it is possible to

---

* Delivered before the Chemical Society in London on October 16th, 1958; also in Dundee on October 15th, 1958; in Southampton on October 17th, 1958; in Sheffield on October 20th, 1958; and in Liverpool on October 21st, 1958.

derive from it useful information about the structure of the radical, its energy levels, and possibly its dissociation energies, all of which may be of importance for an understanding of its behaviour.

The spectra of many diatomic free radicals are well known. In emission, for example, the OH, NH, CH, $C_2$, and CN radicals are observed in all sorts of flames, in explosions, and in electric discharges. Most of them also occur in emission in the spectra of comets and some in the spectrum of the night glow. In absorption the same free diatomic radicals can be observed in suitable gases at high temperature. They have also been observed in the spectra of low-temperature stars, and a few even in interstellar absorption. The structure of these diatomic free radicals is well understood and I do not propose to discuss them in this lecture.

Until about ten years ago very little definite spectroscopic information was available about polyatomic free radicals. To be sure, several emission spectra observed in flames or discharges were ascribed to polyatomic free radicals (for example, the hydrocarbon flame bands to HCO, the α-bands of ammonia to $NH_2$), but there was no certainty of such an assignment since no detailed analysis of these spectra was available and they had not been observed in absorption under conditions under which the presence of these radicals could be considered as certain.

The first polyatomic free radical that was definitely identified by its spectrum was $CF_2$. This spectrum was first observed in emission in a discharge through $CF_4$ by Venkateswarlu[1] and later in absorption in a similar discharge by Barrow and his collaborators.[2] The structure of the spectrum and the conditions of observation led unambiguously to the result that it was due to $CF_2$.

Long before this identification of $CF_2$ by Venkateswarlu and Barrow, my own interest in the spectra of polyatomic free radicals had been stimulated by certain astrophysical problems. Indeed it is quite remarkable to what extent, in the field of free-radical spectroscopy, there is mutual stimulation between astrophysics and chemistry. In the present lecture I shall restrict myself mainly to a discussion of the work of my own laboratory, which means at the same time a restriction to very simple polyatomic free radicals.

## THE $C_3$ AND $SiC_2$ RADICALS

Ever since the spectra of comets have been observed, a group of bands near 4050 Å has been known. The emission of these bands is restricted mainly to the nucleus of the comet, but there it is very prominent. While most of the other features of cometary spectra were readily identified as due to the various diatomic free radicals already mentioned, the interpretation of the 4050 group remained in doubt for many years. In 1942 I succeeded in reproducing the 4050 group in the laboratory under conditions which were suggested by the assumption that this group is due to the $CH_2$ radical.[3] However, even though the production of these bands in a discharge tube seems to require the presence both of carbon and of hydrogen, it was shown in 1949 by Monfils and Rosen[4] that the substitution of deuterium for hydrogen produced a spectrum identical with the original one. The absence of any isotope shift in the spectrum (confirmed in our laboratory under much higher resolution by Douglas) of course ruled out any possibility that the spectrum was due to $CH_2$.

In order to ascertain whether carbon was present in the molecule responsible for the 4050 group, Douglas[5] investigated this spectrum using 50% and 100% $^{13}C$. In the experiments with 50% $^{13}C$ the principal band was found to be replaced by six bands, suggesting that the molecule responsible contains three carbon atoms. The simple fine structure of the principal band shows that the molecule is linear and the intensity alternation in this band in pure $^{13}C$ and the absence of alternate lines in $^{12}C$ give further proof that the molecule responsible is the free $C_3$ radical. The spacing in the rotational structure leads to a C–C distance of 1·28 Å. Unfortunately, the remainder of the 4050 group is so complex that, in spite of considerable work in various laboratories, it has not been analysed in detail. Therefore the vibrational frequencies of $C_3$ are not known.

The $C_3$ molecule is a radical which, up to the time of its identification by spectroscopic means, had not even been postulated in any chemical reaction. However since that time its occurrence in the explosion of acetylene–oxygen mixtures has been demonstrated by means of its absorption spectrum by Norrish, Porter, and Thrush[6] and confirmed by Ramsay. It has also been found in the photolysis of diacetylene.[7] Furthermore, it has been observed by Garton[8] in a carbon tube furnace at a temperature of 2800° C and has been shown, by mass-spectrometric techniques, to be one of the principal molecules evaporating from

[1] Venkateswarlu, *Phys. Rev.*, 1950, **77**, 676.
[2] Laird, Andrews, and Barrow, *Trans. Faraday Soc.*, 1950, **46**, 803.
[3] Herzberg. *Astrophys. J.*, 1942, **96**, 314.
[4] Monfils and Rosen, *Nature*, 1949, **164**, 713.
[5] Douglas, *Astrophys. J.*, 1951, **114**, 466; Clusius and Douglas, *Canad. J. Phys.*, 1954, **32**, 319.
[6] Norrish, Porter, and Thrush, *Proc. Roy. Soc.*, 1953, *A*, **216**, 165.
[7] Callomon and Ramsay, *Canad. J. Phys.*, 1957, **35**, 129.
[8] Garton, *Proc. Phys. Soc.*, 1953, **66**, *A*, 848.

graphite at high temperatures.[9] By means of its emission spectrum, $C_3$ has been observed to be present in various flames.[10] Finally there is fairly strong evidence that $C_3$ occurs in the atmospheres of low-temperature carbon stars.[11]

More recently a radical similar to $C_3$ has been found in the spectra of stars as well as in the laboratory, namely, the radical $SiC_2$. For many years a series of very strong absorption bands was known in the spectra of a few carbon stars.[12] These bands were reproduced a few years ago at Ottawa by Kleman[13] in a carbon tube furnace charged with pure silicon at a temperature of 2200° C. The conditions of production of this spectrum make it certain that the molecule responsible contains both carbon and silicon. The vibrational structure of the spectrum together with the very narrow rotational structure make it extremely likely that the carrier of this spectrum is the free $SiC_2$ molecule in its unsymmetrical form: Si–C–C. Again this molecule has later been observed by mass-spectrometric means[14] in the evaporation of silicon carbide at high temperatures, although the mass spectrum can of course not distinguish between symmetrical and unsymmetrical $SiC_2$.

### FLASH PHOTOLYSIS: $NH_2$

It is natural to attempt to observe the absorption spectra of free radicals during the photodecomposition of an appropriate parent compound. Thus early attempts were made in 1942—43 to observe the spectrum of $CH_2$ (at that time believed to be the 4050 group) in absorption in photo-decomposed keten ($CH_2{=}CO$). The failure of these early experiments could be accounted for by either of two reasons: the stationary concentration of the $CH_2$ radicals was insufficient to produce an absorption spectrum, or the spectrum was not in the region investigated. As it turned out in this specific case, both reasons applied.

In order to overcome the first difficulty, that is in order to obtain much higher concentrations of free radicals than are obtainable in ordinary continuous photolyses, a flash-photolysis technique was developed first by Norrish and Porter[15] in Cambridge, and independently in Ottawa[16] and Pasadena.[17] As shown by Fig. 1 [facing p. 123], in this technique an absorption tube T containing the parent substance is irradiated by a discharge tube P through which a condenser of high capacity (up to 600 $\mu$F at a voltage of up to 10,000 v) is discharged. The extremely bright flash of short duration (20—1000 $\mu$sec.) produces momentarily a high concentration of photodecomposition products, that is, free radicals, in the absorption tube. During this time the light from a second flash tube is sent through the absorption tube to the slit of a spectrograph. The second flash tube is a fairly narrow tube which gives the continuous spectrum necessary for obtaining an absorption spectrum.

A considerable increase in the sensitivity of detection, or in other words in the intensity of the resulting absorption spectra, can be obtained by the use of the technique of multiple traversals through the absorption tube first described by White[18] and further developed in our laboratory.[19] This technique makes it possible to have an absorbing path in the photodecomposed gas of 40 or even 100 metres when the absorption tube is only one metre long. Two other important assets in our experiments were the availability of high spectroscopic resolution and the possibility of extending the observable region into the vacuum-ultraviolet. High resolution is necessary if one wants to detect very narrow absorption lines. Such narrow absorption lines can often not be observed at all with inferior resolution.

The use of high resolution proved decisive in the first example of a polyatomic free-radical spectrum that we found. In the past the so-called $\alpha$-bands of ammonia occurring in oxy-ammonia flames, in electric discharges through ammonia, in cometary spectra, and in fluorescence produced by far-ultraviolet light in ammonia, had been ascribed to various molecules, NH, $NH_2$, $NH_3$, $N_2H_4$, and others, although $NH_2$ seemed the most likely of these. Since photochemical investigations indicate that ammonia photodecomposes by the reaction:

$$NH_3 + h\nu \rightarrow NH_2 + H$$

it seemed worthwhile to attempt a flash-photolysis experiment of the type described, using ammonia as parent compound. If the $\alpha$-bands are in fact due to $NH_2$ they should occur in absorption in such an experiment. This actually turned out to be the case, as shown by Fig. 2, which gives the spectrum of an

---

[9] Chupka and Inghram, *J. Phys. Chem.*, 1955, **59**, 100; Thorn and Winslow, *J. Chem. Phys.*, 1957, **26**, 186.

[10] Durie, *Proc. Roy. Soc.*, 1952, *A*, **211**, 110; Kiess and Bass, *J. Chem. Phys.*, 1954, **22**, 569.

[11] McKellar, Swings, and Rao, *Monthly Notices Roy. Astron. Soc.*, 1953, **113**, 571.

[12] McKellar, *J. Roy. Astron. Soc. Canada*, 1947, **61**, 147.

[13] Kleman, *Astrophys. J.*, 1956, **123**, 162.

[14] Drowart, De Marie, and Inghram, *J. Chem. Phys.*, 1958, **29**, 1015.

[15] Norrish and Porter, *Nature*, 1949, **164**, 658.

[16] Herzberg and Ramsay, *Discuss. Faraday Soc.*, 1950, **9**, 80; Ramsay, *J. Chem. Phys.*, 1952, **20**, 1920; Callomon and Ramsay, *Canad. J. Phys.*, 1957, **35**, 129; Ramsay, *Ann. New York Acad. Sci.*, 1957, **67**, 485.

[17] Davidson, Marshall, Larsh, jun., and Carrington, *J. Chem. Phys.*, 1951, **19**, 1311.

[18] White, *J. Opt. Soc. Amer.*, 1942, **32**, 285.

[19] Bernstein and Herzberg, *J. Chem. Phys.*, 1948, **16**, 30.

oxy–ammonia flame and of the flash photolysis of ammonia taken with the same 21-ft. grating spectrograph. Nearly every line of the absorption spectrum of photodecomposed ammonia is matched by a line of the emission spectrum of the flame.

In order to be absolutely certain about the carrier of the spectrum, experiments were carried out both with ammonia containing $^{15}N$ and with deutero-ammonia. The former gave lines that were shifted by small amounts from the lines obtained with ordinary ammonia, while the latter gave a completely different spectrum as would be expected because of the large change of mass. There is therefore no question but that both nitrogen and hydrogen are present in the molecule responsible for this spectrum.

The $NH_2$ spectrum is a many-line spectrum, that is, it consists of a large number of single lines whose arrangement in the form of bands is quite indistinct. Without the use of high resolution this spectrum would not have been observed in absorption at all. The measurement and analysis of the $NH_2$ spectrum was carried out by Ramsay[20] and that of $ND_2$ by Ramsay and Dressler.[21] It took several years before the clue to the analysis of this extremely complicated spectrum was found but this has now been accomplished and a fairly complete analysis is available. This analysis confirms in every way the assumption that the molecule responsible is the free $NH_2$ radical and in addition supplies information about the structure of $NH_2$ both in the ground state and in the excited electronic state. In the ground state the molecule is non-linear with an angle of 103·5°. In the upper state it is linear. Table 1 gives the geometrical data that have been obtained. In the lower state the molecule is somewhat similar in structure to $H_2O$, that is, it is an asymmetric top, and this asymmetry accounts for the complexity of the spectrum. Because of the large change of angle in going from the ground state to the excited state there is a long series of absorption bands corresponding to increasing excitation of the bending vibration in the upper state. This accounts for the large extent of the spectrum. Unfortunately it has not yet been possible to determine the vibrational frequencies of the molecule in the ground state.

TABLE 1. *Structure of the* $NH_2$ *radical*

| | $r_0$(NH) | $\angle$HNH |
|---|---|---|
| Ground state | 1·024 | 103° 23′ |
| Excited state | 0·976 | 180° |

A band system similar to that of $NH_2$ was found by Ramsay[22] in the flash photolysis of $PH_3$. Large isotope shifts occur when $PH_3$ is replaced by $PD_3$ and therefore there is little question that the spectrum is due to the $PH_2$ (or $PD_2$) radical, even though a fine-structure analysis has not yet been accomplished.

### THE RADICALS HCO AND HNO

As mentioned before, the hydrocarbon flame bands which occur in almost all hydrocarbon flames in the region 2600—4100 Å have been ascribed for many years to the HCO molecule (Vaidya). It was thought that by an investigation of the flash photolysis of suitable parent compounds it would be possible to obtain these bands in absorption and thereby establish with more certainty whether or not they are due to HCO. However, in the region of these hydrocarbon flame bands no absorption was found in the flash photolysis of $H_2CO$, $CH_3{\cdot}CHO$, and $(HCO)_2$. On the other hand, a series of extremely weak bands were observed in the red and the green part of the spectrum.[23] In this case the use of multiple traversals in the absorption tube proved invaluable in increasing the intensity of the bands and making it possible to obtain a complete analysis.[24]

In Fig. 3 one of the bands observed in the flash photolysis of $CH_3{\cdot}CHO$ and the corresponding band found in that of $CD_3{\cdot}CDO$ are shown. The bands have an extremely simple structure consisting of a single *P*, *Q*, and *R* branch. There is a long progression of these bands for both isotopic molecules, as shown schematically in Fig. 4. The existence of a large isotope shift in going from the normal to the deuterated parent compound shows that the molecule involved does contain hydrogen. The narrowness of the fine structure immediately shows that there must be two heavier atoms present in addition to hydrogen, and the various parent compounds studied leave no doubt that these two other atoms are C and O, even though this has not been checked by isotopic substitutions. That the radical really is HCO is in agreement with a good deal of photochemical work on $H_2CO$, $CH_3{\cdot}CHO$, and $(HCO)_2$.

The very simple fine structure of the HCO absorption bands might lead one to believe that the molecule is linear in both the upper and the lower state. However, the observation of a long progression of bands corresponding to the bending vibration and of a very large combination defect between the *Q* branches on the one hand and the *P* and *R* branches on the other proves conclusively that the molecule is non-linear in the ground state and linear in the excited state. The geometrical parameters obtained in both states are given in Table 2.

---

[20] Ramsay, *J. Chem. Phys.*, 1956, **25**, 188; *Mem. Soc. Roy. Sci. Liége*, 1957, **18**, 471.
[21] Ramsay and Dressler, *J. Chem. Phys.*, 1957, **27**, 971; *Phil. Trans.*, in the press.
[22] Ramsay, *Nature*, 1956, **178**, 374.
[23] Ramsay, *J. Chem. Phys.*, 1953, **21**, 960.
[24] Herzberg and Ramsay, *Proc. Roy. Soc.*, 1955, **233**, 34.

TABLE 2. *Structure of the* HCO *radical*

| | $r_0$(CH) | $r_0$(CO) | ∠HCO |
|---|---|---|---|
| Ground state | (1·08 Å assumed) | 1·19$_8$ Å | 119° 30′ |
| Excited state | (1·07 Å assumed) | 1·183 Å | 180° |

One may ask how the spectrum can be so simple if the lower state is non-linear, since that implies that the molecule is an asymmetric top in the lower state. However, even in the bent configuration the molecule is still approximately a symmetric top. Only one or two $K$ values of the lower state can combine with a given $l$ value (vibrational angular momentum) in the upper state. Even with this simplification one would still expect a number of overlapping sub-bands where only one is observed. One has therefore to assume that energy levels with $l > 0$ in the upper state are strongly predissociated and thus not observed under high resolution. This explanation was confirmed by the observation under low resolution of diffuse absorption bands halfway between the sharp bands (see Fig. 4). These diffuse bands apparently correspond to $l = 1$ in the upper state which alternates with $l = 0$ as the lowest sub-level for each value of the vibrational quantum number of the bending vibration. The diffuseness of some of the bands means of course that the dissociation energy $D$(H–CO) of HCO must be less than the energy corresponding to these bands, that is, less than 37·7 kcal./mole.

The existence of diffuse bands at a comparatively long wavelength in a simple molecule like HCO may have an interesting astrophysical application. A number of diffuse interstellar lines are known which have so far defied all attempts at identification. While none of them agrees with the diffuse bands of HCO, it is at least possible that another triatomic molecule of the type HXY might also have a low dissociation energy and thus might be responsible for the diffuse interstellar lines. If so, and if this molecule could be found, it would clearly throw considerable light on the chemistry of the interstellar medium.

Until now no connection has been found between the HCO absorption bands and the hydrocarbon flame bands. The flash-photolysis investigations do not exclude the possibility that the hydrocarbon flame bands also belong to HCO and have the same lower state as the absorption bands, but the upper state must certainly be different. The upper state of the flame bands must be much higher and in it the molecule is in all probability bent, thus accounting for the great complexity of these bands.

When the DCO spectrum was first investigated an additional band was found at 7550 Å with a very different structure from the other DCO bands. The fact that it was impossible to find the analogue of this band for HCO led to the conclusion that it must have been due to an impurity introduced in the preparation of $CD_3$·CDO. It was shown by Dalby[25] at Ottawa that the 7550 Å band mentioned is actually due to DNO. He did find the corresponding band of HNO by studying the photodecomposition of nitroethane and of nitromethane, and also in the photoreaction between $NH_3$ and NO. It appears probable that the original band observed in the photolysis of $CD_3$·CDO was due to the presence of $C_2D_5$·$NO_2$ as an impurity.

In addition to the band at 7550 Å, two further much weaker bands were found at 7900 and 6850 Å corresponding to the excitation of the NH bending and NO stretching vibrations in the upper state. The isotope shift again proves that there is only one hydrogen atom present in the molecule. We have not carried out experiments with $^{15}$N or $^{18}$O but there can be little doubt that nitrogen and oxygen are the other two atoms involved in the molecule under consideration.

The fine structure of the two bands is fairly readily analysed. Fig. 5 shows the principal band of HNO. It consists of a number of sub-bands, each with simple $P$, $Q$, and $R$ branch structure. This difference from the HCO spectrum shows that the molecule is non-linear in both the upper and the lower state. The geometrical data derived for this molecule from the spectrum are given in Table 3.

TABLE 3. *Structure of the* HNO *radical*

| | $r_0$(NH) | $r_0$(NO) | ∠HNO |
|---|---|---|---|
| Ground state | 1·063 Å | 1·212 Å | 108° 35′ |
| Excited state | 1·036 Å | 1·241 Å | 116° 15′ |

The lifetime of HNO under the conditions of the photolysis experiments was found to be approximately 0·1 second, while HCO has a lifetime of only 50 microseconds. This difference is presumably connected with the fact that HCO has an odd electron while HNO has not.

### THE RADICALS NCO AND NCS

A few years ago Holland and Style[26] observed a group of bands near 4400 Å in the fluorescence of ethyl isocyanate excited by far-ultraviolet light. The same bands occurred also in a high-frequency discharge through the same compound. Similarly in methyl thiocyanate a number of bands were observed in the region 3750—4850 Å under similar conditions. More recently, Dixon and Ramsay[26] at Ottawa have obtained these bands in absorption in the flash photolysis of various compounds containing the NCO and the NCS group respectively. The observation of these bands in absorption in flash photolysis confirms the assumption by Holland and Style that

---

[25] Dalby, *Canad. J. Phys.*, 1958, **36**, 1336.

[26] Holland, Style, Dixon, and Ramsay, *Nature*, 1958, **182**, 336.

these bands are due to the free NCO and NCS radicals. For NCO in absorption, an additional band system was found in the region 2600—3200 Å. On the Ottawa plates taken under high resolution the fine structure of all the bands is very well resolved, as shown for one of the bands of the long-wavelength system of NCO in Fig. 6. These bands are shaded to the violet, while all the other bands are shaded to the red. The structure of these bands shows conclusively that both molecules are linear in all observed states.

The NCO radical is isoelectronic with the $CO_2^+$ molecule. It is therefore not surprising that the ground state of both NCO and NCS are found to be of the same type as that of $CO_2^+$, namely, $^2\Pi$. Also, the excited states are similar to those in $CO_2^+$. While a preliminary value for the moment of inertia of NCO has been obtained, it is not possible to derive from it the two internuclear distances; this would require the observation of the spectrum of an isotopic molecule.

It appears probable that the NCO and NCS free radicals observed in the flash photolysis are primary products in the photolyses, that is, arise from reactions such as:

$$CH_3{\cdot}NCO + h\nu \rightarrow CH_3 + NCO$$

## THE RADICAL $CH_3$

The discovery of a spectrum of the free $CH_3$ radical was one of the principal aims in our programme of investigations of free-radical spectra. It took many years before a $CH_3$ spectrum was in fact observed. Many unsuccessful attempts were made in the region from 9000 to 2300 Å by studying the photolysis of numerous compounds which were thought to be suitable, using different pressures, long absorbing paths, and high resolution. Since $CH_3$ is isoelectronic with $NH_2$ one might have expected a transition in the visible region. However, if the nature of this predicted electronic transition is considered, following Walsh,[27] it is found that it would be a forbidden transition if the molecule were planar. This may account for the failure to find any absorption in the visible and the near-ultraviolet region. Therefore experiments were started in the vacuum-ultraviolet where one finds strong Rydberg transitions, at least near the ionisation limit, for almost all molecules that have stable excited states near this limit. However, the difficulties of working with flash photolysis in the vacuum-ultraviolet are considerable. Because of the strong absorption of the parent molecules only extremely low pressures (of the order of 0·01 mm.) can be used, and at these low pressures the absorption of the radical that is wanted may be too weak. Another difficulty is, for example, scattered light from the visible and the near-ultraviolet region which may obscure the very much weaker continuum in the vacuum-ultraviolet.

In spite of these difficulties a Rydberg series was eventually observed[28] in the flash photolysis of dimethylmercury. This Rydberg series starts at 1500 Å and consists of five members, some of which may be seen in Fig. 7. Later the same Rydberg series was found in the flash photolysis of a number of other parent compounds such as $CH_3{\cdot}CHO$, $(CH_3)_2CO$, $(CH_3)_2N_2$, $CH_3I$, and $CH_3Br$. Since there is strong photochemical evidence that $CH_3$ radicals are produced in the photodecomposition of all these molecules, it appeared extremely likely that the observed Rydberg series is in fact due to free $CH_3$. A corresponding slightly shifted series was found in deuterated dimethylmercury (see Fig. 7). Finally, under the conditions under which this Rydberg series appeared most prominently, an additional diffuse band was observed at 2160 Å which makes the observation of $CH_3$ much simpler since it does not require the use of a vacuum-spectrograph. The corresponding band of the fully deuterated compound is at 2144 Å and shows some fine structure. Spectra were also taken with intermediate concentrations of deuterium and show clearly (see Fig. 8) that four isotopic species are present, as would be expected if the molecule responsible is $CH_3$ (that is $CH_3$, $CH_2D$, $CHD_2$, and $CD_3$).

From the limit of the Rydberg series one obtains a precise value for the ionisation potential of the $CH_3$ radical. One finds 9·840 ev for $CH_3$ and 9·832 ev for $CD_3$, results that agree most satisfactorily with the (less accurate) mass-spectrometric value of 9·90 ± 0·1 ev.

The fine structure of the $CD_3$ band (see Fig. 8) was further investigated. It shows clear evidence of a slight intensity alternation. According to theory, such an intensity alternation in what appears to be a so-called parallel band can occur only if the molecule is planar in at least one of the two states involved. Since there is only a single prominent band accompanied by two or three very much weaker bands, it follows from an application of the Franck–Condon principle that if the molecule is non-planar in one of the two states it cannot deviate from planarity very much in the other. However, the weaker bands are difficult to interpret on the assumption that both states are planar. We therefore come to the provisional conclusion that the $CH_3$ molecule deviates slightly from a planar configuration in the ground state, while it is planar in all the observed excited

---

[27] Walsh, *J.*, 1953, 2260.

[28] Herzberg and Shoosmith, *Canad. J. Phys.*, 1956, **34**, 523.

states. This would be in agreement with the theoretical prediction that the $CH_3^+$ molecule is planar.

Further analysis of the rotational structure of the $CD_3$ band at 2144 Å yields an approximate value for the moment of inertia of $CD_3$ in the ground state about an axis at right angles to the symmetry axis. This value is 5·769 × $10^{-40}$ g. cm.$^2$. It is of course not sufficient to determine completely the structure of the $CD_3$ molecule, and the lack of a fine structure in $CH_3$ makes it impossible to obtain a second moment of inertia that would allow a complete structure determination. However, the following are two values for the CD distance corresponding to two different assumptions for the angle $\beta$ of the CD bond with the symmetry axis:

$$\beta = 90^\circ : r_0(\mathrm{CD}) = 1{\cdot}072 \text{ Å}$$
$$\beta = 75^\circ : r_0(\mathrm{CD}) = 1{\cdot}061 \text{ Å}$$

For smaller values of $\beta$, $r_0$ would be still smaller. In view of the known C–D distances in other molecules, it seems extremely unlikely that $r_0$ for $CH_3$ could be less than 1·060 and therefore one will have to conclude that the angle $\beta$ is larger than 75° in agreement with the tentative conclusions already mentioned. Even for a planar configuration ($\beta = 90^\circ$) the C–D distance comes out distinctly smaller than in methane, where it is 1·093 Å. The smallness of the C–D distance may be related to the high C–H bond dissociation energy in $CH_3$ compared with that in $CH_4$.

Extensive experiments have been carried out in order to find at longer wavelengths the predicted forbidden transition in $CH_3$, but without success. If this transition could be found it would enable one to obtain much more definite information about the geometrical structure of $CH_3$, in particular about the question of the exact height of the pyramid in the ground state. The only hope, at present, of obtaining this information lies either in the study of the infrared spectrum of $CH_3$ or in the study of the analogue of the 2160 Å band in $CT_3$. Both investigations are being attempted at Ottawa.

## THE RADICALS $CH_2$ AND $C_2H$

As mentioned earlier, when the 4050 group was still believed to be due to $CH_2$, various attempts were made to obtain it in absorption under conditions under which a high concentration of $CH_2$ could be expected. When it became clear that the 4050 group is not due to $CH_2$, attempts were made to study carefully the whole accessible region of the spectrum down to 1200 Å in order to see whether or not the true $CH_2$ spectrum could not be found. For most of these experiments the photolysis of keten ($CH_2{=}CO$) was used for the production of the $CH_2$ radicals. Since the ionisation potential of $CH_2$ according to mass spectrometric data is approximately 11·9 ev,[29] that is, appreciably higher than that of $CH_3$, it was expected that any Rydberg series of $CH_2$ would be at correspondingly shorter wavelengths. Unfortunately, at these short wavelengths the parent absorption is very strong and very low pressures (less than 10 $\mu$) had to be used. No absorption that may be due to $CH_2$ was found in this region. This failure may be due to the fact that the partial pressure of the $CH_2$ radicals was too low or to the fact that there is no simple Rydberg series in $CH_2$.

At somewhat longer wavelengths fairly strong absorption bands of CO were found in absorption in consequence of the photolysis, showing that photodecomposition actually does occur. Some of the CO bands arise from vibrationally excited CO molecules (up to $v'' = 3$), indicating either that the CO molecules formed in the photolysis are vibrationally excited or that the temperature resulting from the flash photolysis is so high that a high vibrational temperature results. Fig. 9 shows a small section of the spectra obtained. One of the hot bands is visible in the photolysis spectrum, but not in the spectrum of the residue. Also a high rotational temperature is clearly indicated by the much greater length of the branches during photolysis than afterwards.

In order to reduce the temperature during photolysis the keten was mixed with helium, argon, or hydrogen in the ratio 100:1. The photolysis spectra under these conditions showed much shorter branches in the CO bands, corresponding roughly to room temperature, but the "hot" bands with $v'' = 1$ and 2 were still present; that is, CO like other molecules loses its vibrational energy only very slowly. Since the converse also appears to hold, that is, CO acquires vibrational energy very slowly, it follows that the first alternative mentioned previously applies, namely, that the CO molecule is formed with vibrational energy in the photolysis of keten.

In the visible and the near-ultraviolet region much longer paths could be used for the study of the $CH_2$ absorption because of the much lower or absent absorption of the parent molecule. However, in spite of considerable time and effort no discrete absorption was found except the CH band at 3143 Å which occurred both in pure $CH_2{=}CO$ and in the 100:1 helium–keten mixture as shown in Fig. 10. The presence of CH may be ascribed to the photodecomposition of $CH_2$ in a weak continuous-absorption region.

The failure to find a discrete absorption of $CH_2$ says, of course, nothing about the existence and stability of the free $CH_2$ radical. It is entirely possible that $CH_2$ has only continuous absorptions in the

[29] Langer, Hipple, and Stevenson, *J. Chem. Phys.*, 1954, **22**, 1836.

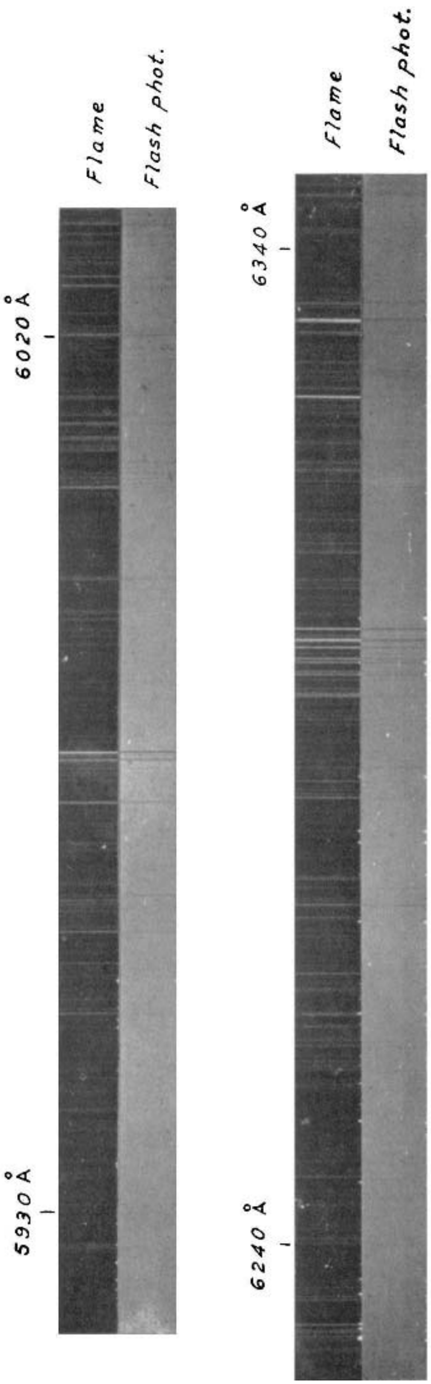


FIG. 2. *Emission spectrum of an oxy–ammonia flame compared with the absorption spectrum of photodecomposed ammonia obtained by flash photolysis.* (*Both spectra were taken with the same 21-ft. grating. Only two small sections of the very extensive spectrum are shown. Some detail has been lost in reproduction.*)

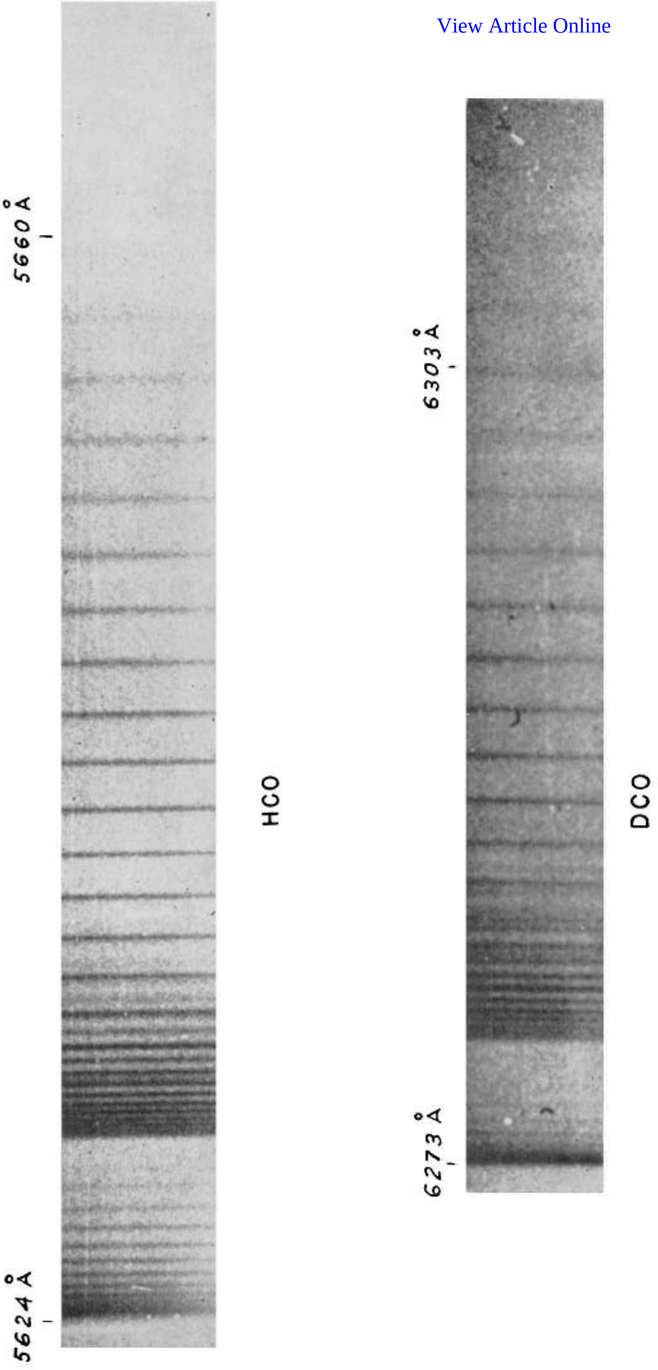


FIG. 3. *Absorption bands of* HCO *and* DCO *obtained in the flash photolysis of acetaldehyde and deuteroacetaldehyde.*

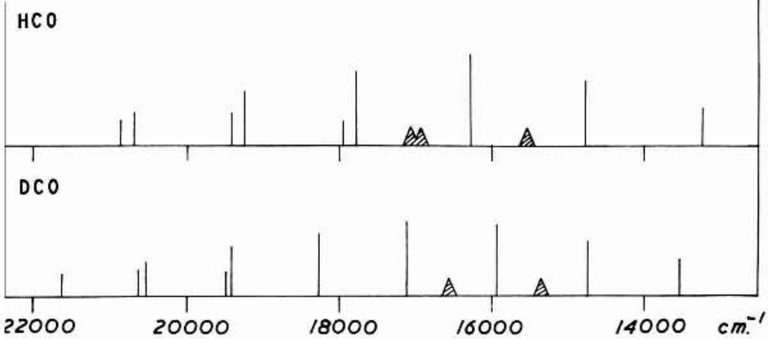


FIG. 4. *Schematic representations of the absorption spectrum of* HCO *and* DCO. (*The shaded triangles denote diffuse bands.*)

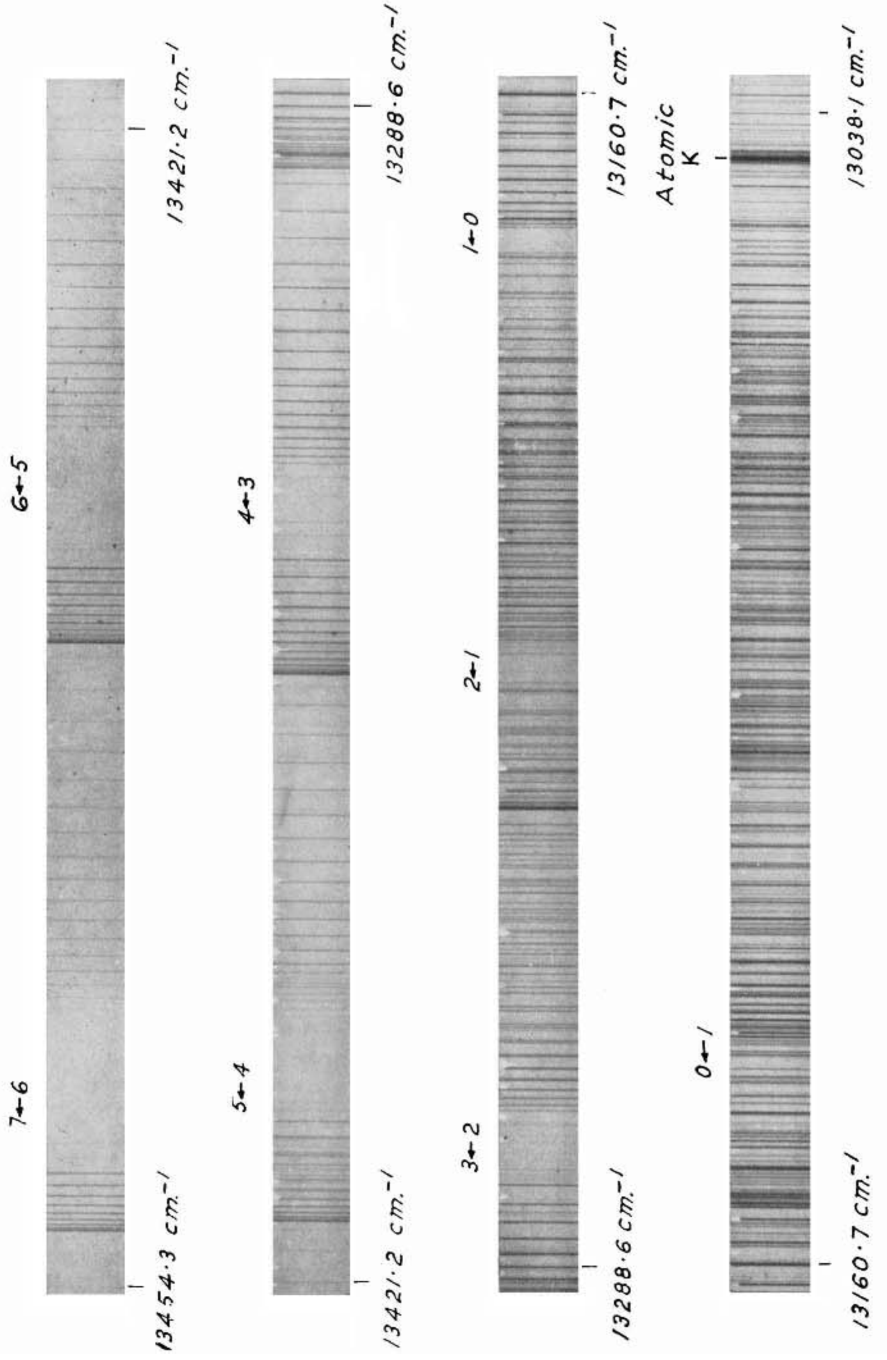


FIG. 5. *Principal absorption band of* HNO *obtained in the flash photolysis of nitromethane.* (*The numbers at the top of each strip indicate the K′–K″ values of the sub-bands. The spectrum was obtained in the first order of a* 35-*ft. grating spectrograph.*)

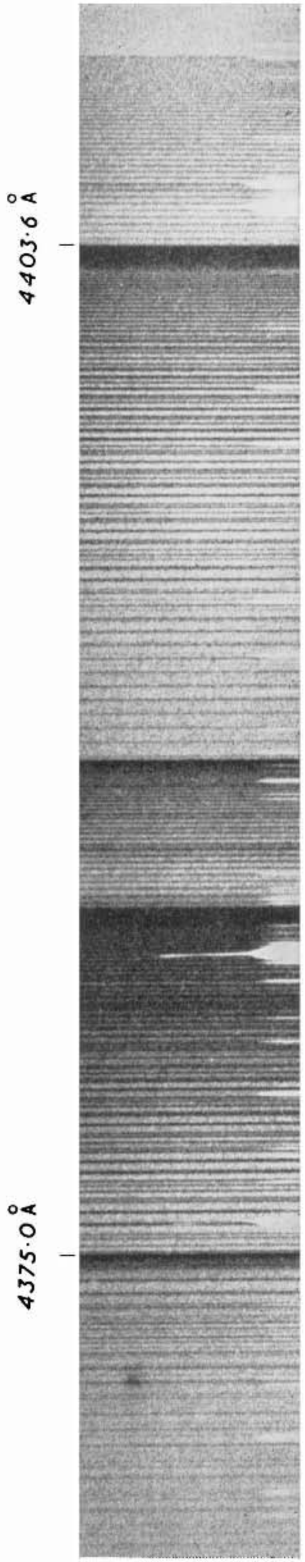


FIG. 6. *Strongest absorption band of* NCO *obtained in the flash photolysis of* HNCO.

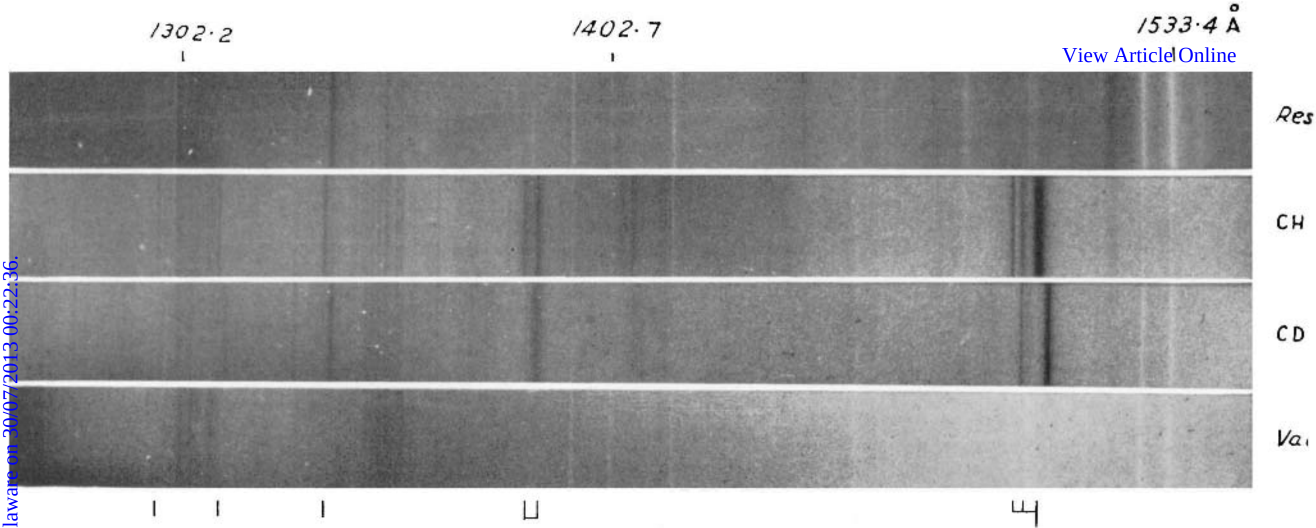


FIG. 7. *Rydberg series of bands of* $CH_3$ *and* $CD_3$ *obtained in the flash photolysis of dimethylmercury and deuterodimethylmercury.*

(*For comparison the spectrum of the source in vacuum and the absorption spectrum of the residue are shown. The Rydberg series of* $CH_3$ *is marked at the bottom.*)

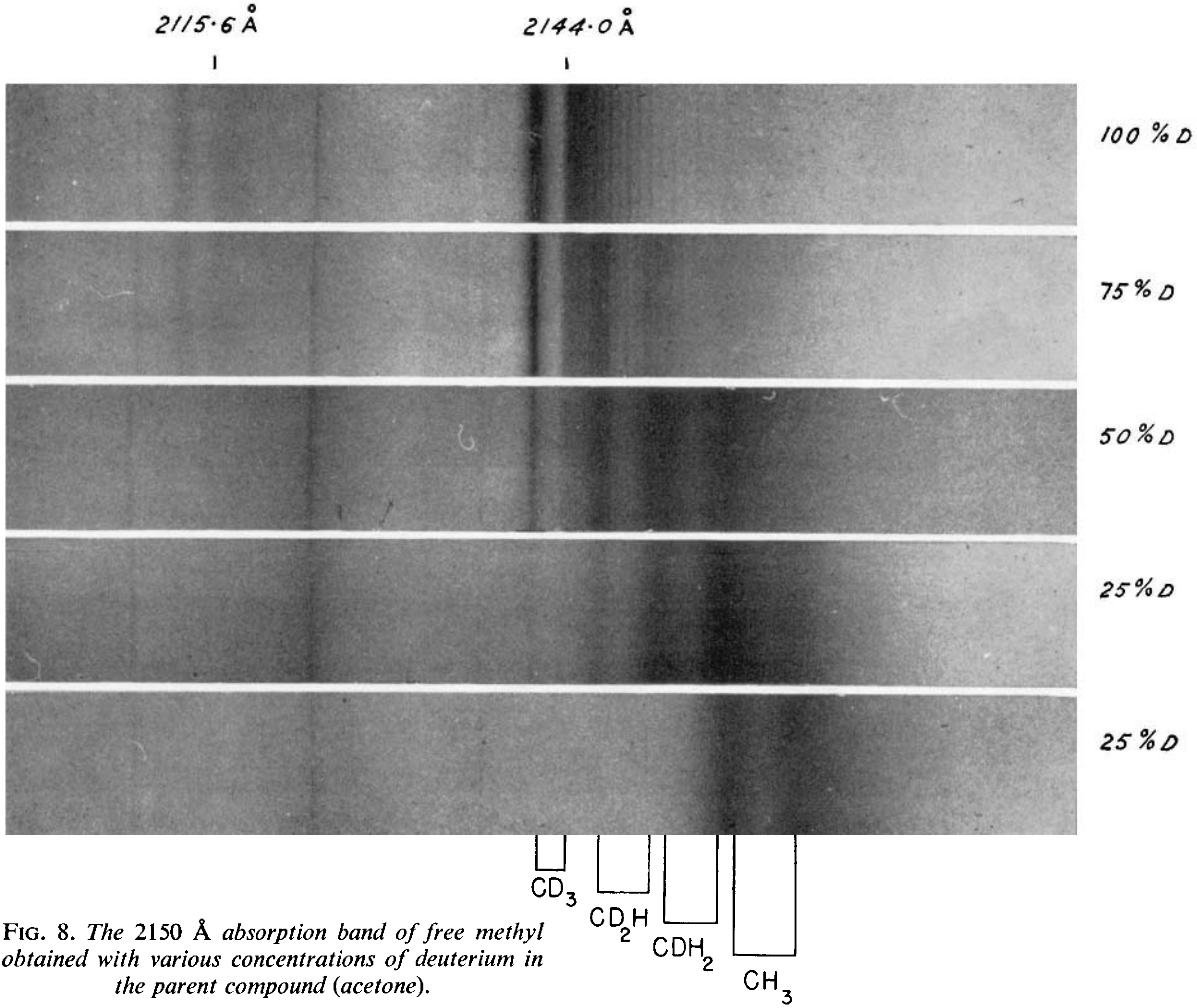


FIG. 8. *The* 2150 Å *absorption band of free methyl obtained with various concentrations of deuterium in the parent compound* (*acetone*).

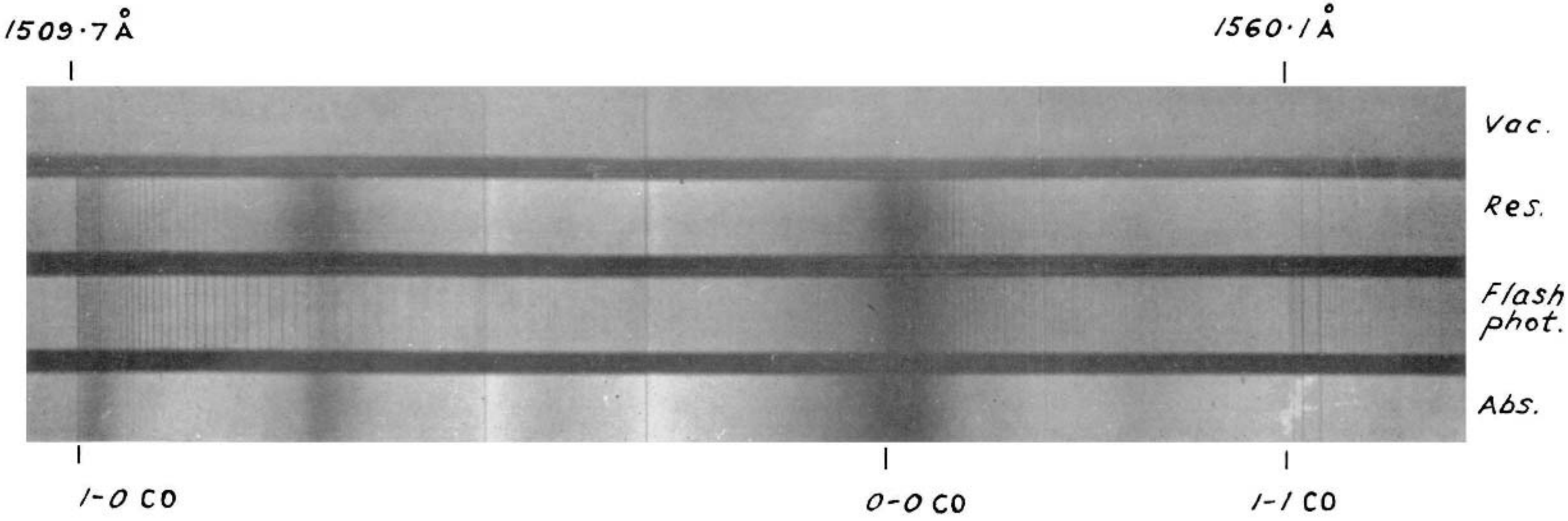


FIG. 9. *CO bands in the flash photolysis of keten. (CO is weakly present in the absorption spectrum of the parent compound because of photolysis produced by the light source. The* 1–1 *band of* CO *is present only during photolysis, not in the spectrum of the residue.)*

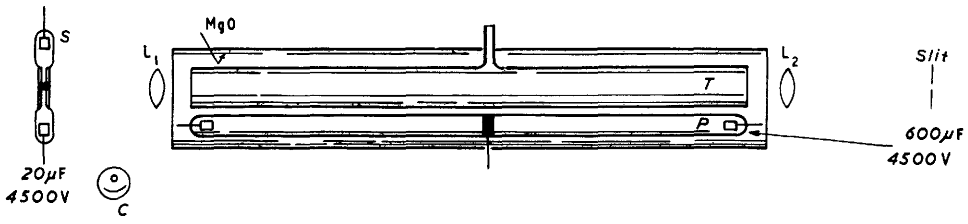


FIG. 1. *Flash-photolysis apparatus.*

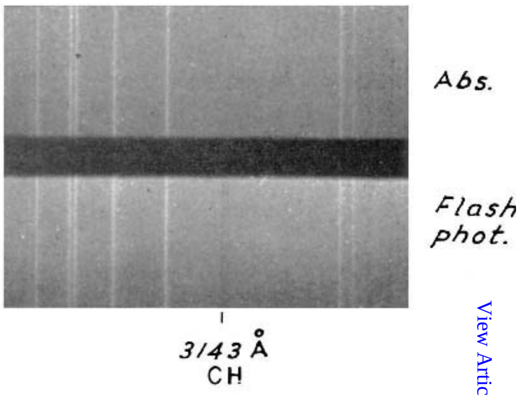


FIG. 10. CH *band in the flash photolysis of a* 100 : 1 *helium–keten mixture.*
*(The white spectral lines are emission lines in the source.)*

accessible region and these are far more difficult to establish and identify with certitude than discrete absorptions. It may be recalled that the $CH_4$ molecule has continuous absorptions only, in the whole region so far investigated (other than the infrared). Thus, if $CH_4$ were a free radical it would be extremely difficult to detect spectroscopically.

Another molecule in which we have been interested for some time and whose spectrum we have not yet found is the $C_2H$ radical. A promising parent compound for obtaining free $C_2H$ appeared to be propiolaldehyde ($HC_2{\cdot}CHO$), since the aldehyde group gives rise to a fairly strong absorption in the near ultraviolet which will in all probability lead to photodecomposition, and since it is easy to establish the occurrence of photodecomposition by an observation of the known HCO bands. The HCO bands were indeed observed in the photolysis of propiolaldehyde, but in spite of much effort no discrete absorption that might be ascribed to $C_2H$ was found. That $C_2H$ actually was present under the conditions of the experiment follows indirectly from the observation of acetylene ($C_2H_2$) and, particularly, diacetylene ($C_4H_2$) absorption bands in the spectrum of the residue. It appears that the only way in which diacetylene can be formed on photolysis of propiolaldehyde is by the recombination of two $C_2H$ radicals formed in this photolysis.

Experiments were also carried out with a 100 : 1 mixture of helium and propiolaldehyde. In this mixture the spectra of $C_2H_2$ and $C_4H_2$ occur even during the photolysis, and not only in the residue as in the case of the undiluted gas. Moreover, a few "hot" bands of $C_2H_2$ have been found under these conditions.

### CONCLUSION

A large amount of work on free polyatomic radicals has been carried out in other laboratories. It is not possible to give here an adequate summary of it, but reference may be made to Norrish's Liversidge lecture[30] and to a forthcoming review article by Ramsay.[31]

Further work in this field will be of importance, both from the point of view of the chemist interested in establishing the presence of free radicals in various chemical reactions and from the point of view of the physicist interested in the structure of simple molecules.

[30] Norrish, *Proc. Chem. Soc.*, 1958, 247.

[31] Ramsay, *Adv. Spectroscopy*, in the press.

---

## COMMUNICATIONS

### Perpendicular Conjugation in Some Octahedral Metallophthalocyanine Derivatives

By J. A. Elvidge and A. B. P. Lever
(Organic Chemistry Research Laboratories, Imperial College, London, S.W.7)

We have prepared true octahedral (6-co-ordinate) metal complexes in the phthalocyanine series for the first time. Only a few 6-co-ordinate solvates, such as the diamagnetic dipyridineferrous phthalocyanine,[1] have been obtained before. Of our new compounds, dihydroxymanganese$^{IV}$ phthalocyanine and aquohydroxychromium$^{III}$ phthalocyanine are unique in being dibasic acids. No examples are known in inorganic chemistry of the displacement of a proton from a hydroxy-group attached directly to a chelated metal atom. Evidently there is considerable stabilisation of the anions of the above phthalocyanine derivatives and this may be achieved through sharing of the negative charge with the aromatic $\pi$-electron system. For this to occur there must be conjugation between the mutually perpendicular phthalocyanine and oxy-groups. Perpendicular conjugation has not previously been considered but appears possible through $p_\pi$–$d_\pi$ orbital overlap.

Manganous phthalocyanine[2] ($\mu_{eff}$[3] 4·34 B.M., $\theta$ + 9) with methanolic potassium cyanide yields hydroxycyanomanganese$^{IV}$ phthalocyanine PcMn(CN)OH (where Pc = phthalocyanine residue) in which the manganese is in the 6-co-ordinate quadrivalent state ($\mu_{eff}$ 3·88 B.M., $\theta$ – 5). Similarly, methanolic sodium hydroxide yields dihydroxymanganese$^{IV}$ phthalocyanine $PcMn(OH)_2$, which, on dissolution in the saturated reagent, affords disodium dioxymanganese$^{IV}$ phthalocyanine $[PcMnO_2]^{2-}2Na^+$ ($\mu_{eff}$ 4·00 B.M., $\theta$ – 49). Electrophoresis demonstrated the anionic character.

Chromium phthalocyanines have now been authenticated for the first time.[4] Chromium phthalocyanine PcCr (unit cell 3·4 × 42·5 Å, by electron-diffraction) is readily oxidised, but is stabilised by co-ordination with pyridine, the magnetic moment ($\mu_{eff}$ 3·16 B.M., $\theta$ – 35) confirming the 6-co-ordinate structure for the solvate PcCr,2py (py = pyridine).

[1] Barrett, Frye, and Linstead, *J.*, 1938, 1157.

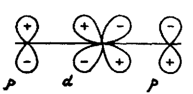
[2] Barrett, Dent, and Linstead, *J.*, 1936, 1719.

[3] See Figgis and Nyholm, *J.*, 1959, 331; the present complexes obey the Curie–Weiss law over the range studied, *i.e.*, 110—295°K.

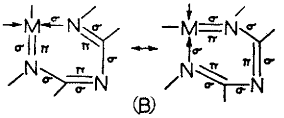
[4] Cf. ref. 2, and Anderson, Bradbrook, Cook, and Linstead, *J.*, 1938, 1151.

Chromium$^{\text{III}}$ phthalocyanine is obtained from chromic acetate and phthalonitrile as the 4-co-ordinate hydroxide $[\text{PcCr}]^+\text{OH}^-$ ($\mu_{\text{eff}}$ 4·03 B.M., $\theta$ — 15) (migration of the coloured ion to the cathode). This, with aqueous-ethanolic acid, gives aquohydroxychromic phthalocyanine $\text{PcCr(H}_2\text{O)OH}$ which is not a loose hydrate but a 6-co-ordinate tervalent chromium complex ($\mu_{\text{eff}}$ 3·52 B.M., $\theta$ — 10): its reconversion into $[\text{PcCr}]^+\text{OH}^-$ requires heating at 400°/$10^{-6}$ mm. Aquohydroxychromium$^{\text{III}}$ phthalocyanine with methanolic sodium hydroxide gives disodium oxyhydroxychromium$^{\text{III}}$ phthalocyanine $[\text{PcCr(OH)O}]^{2-}2\text{Na}^+$ ($\mu_{\text{eff}}$ 3·91 B.M., $\theta$ — 155)* (migration of the coloured ion to the anode). Pyridine likewise displaces two protons to yield the dipridinium salt $[\text{PcCr(OH)O}]^{2-}2\text{pyH}^+$ ($\mu_{\text{eff}}$ 4·06 B.M., $\theta$ — 15): an alternative structure $[\text{PcCr(OH)}_2]^-\text{pyH}^+,\text{py}$ is eliminated by the stability at 150°/20 mm. and the infrared absorption.

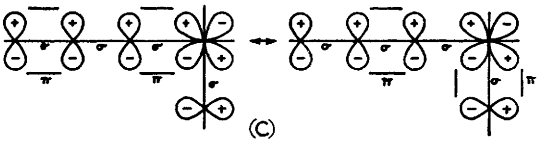
The feasibility of $\pi$-bond formation by overlap of $p$- with $d$-orbitals (cf. A) has been discussed by Craig and Paddock.[5] Because adjacent lobes of a $d_{xz}$- or $d_{yz}$-orbital have opposite signs, full $d_\pi p_\pi$ conjugation round a ring (*i.e.*, degeneracy) is possible only with even numbers of the two contributing types of atom. A suitable metal atom M bound by the phthalocyanine ligand could therefore be conjugated only to one or other of a pair of nitrogen atoms at a time by $d_\pi p_\pi$ overlap. A valence-bond partial representation is shown at (B). Only a small gain in resonance energy is likely from this conjugation because the four equivalent sets of canonical structures cannot be hybridised. Nevertheless this limited conjugation between metal and planar phthalocyanine ligand will allow of further conjugation with other groups attached perpendicularly to the metal. A $p$-orbital of such a group could overlap with one of the $d$-orbitals already considered and give rise to a $\pi$-bond to the metal along the $z$-axis. There would be perpendicular conjugation and attendant possibilities of resonance (cf. C).



(A)

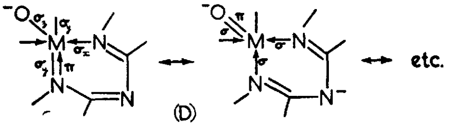


(B)



(C)

These ideas make it possible to account for the stability (*i.e.*, existence) of the anions $[\text{PcMnO}_2]^{2-}$ and $[\text{PcCr(OH)O}]^{2-}$ through a sharing of the negative charge on oxygen with the rest of the molecule as indicated by the partial formulæ (D).



(D)

This degeneracy through perpendicular conjugation is possible only if $d_{xz}$- and/or $d_{yz}$-orbitals of the metal are vacant, so it might be observed in octahedral complexes of titanium and vanadium, besides chromium (spin-free) and manganese$^{\text{IV}}$ (spin-free), but not in those of the next transition metals, iron, cobalt, nickel.

The ultraviolet- and the visible-light absorption of the analogues of vitamin $B_{12}$ ($B_{12a}$, etc.) are closely similar to one another,[6] but those of the octahedral phthalocyanines show variations which are too large to be ascribed to inductive effects and are presumably a manifestation of the perpendicular conjugation.

We thank Dr. I. S. Kerr for electron-diffraction measurements and the Department of Scientific and Industrial Research for a maintenance grant (to A.B.P.L.).

(*Received, February 23rd,* 1959.)

---

* The value of $\theta$ renders uncertain the interpretation of $\mu_{\text{eff}}$, but tervalency for the metal follows from other results.

[5] Craig and Paddock, *Nature*, 1958, **181**, 1052.

[6] Kaczka, Wolf, Kuehl, and Folkers, *J. Amer. Chem. Soc.*, 1951, **73**, 3569.

## Trimethyl-lead Hydride

By R. DUFFY and A. K. HOLLIDAY
(THE UNIVERSITY, LIVERPOOL)

ALTHOUGH lead forms a very unstable hydride $\text{PbH}_4$ and stable tetra-alkyl derivatives $\text{PbR}_4$, no intermediate alkyl-lead hydrides [*e.g.*, $\text{R}_3\text{PbH}$] have hitherto been prepared.

The reaction of tetramethyl-lead with aluminium borohydride was shown[1] to form the unstable trimethyl-lead borohydride $\text{Me}_3\text{PbBH}_4$; this decomposed to lead, hydrogen, and methyl diboranes. As an alternative means of preparing trimethyl-lead borohydride, the reaction of trimethyl-lead chloride and potassium borohydride in liquid ammonia has been investigated. The initial reaction expected here

---

[1] Holliday and Jeffers, *J. Inorg. Nuclear Chem.*, 1958, **6**, 134.

is $Me_3PbCl + KBH_4 \rightarrow Me_3PbBH_4 + KCl$, and when equimolar amounts of reactants were used at −33° potassium chloride was precipitated. The solvent ammonia was then removed slowly at −78°, without appreciable loss of volatile boron or lead compounds. When the residue was warmed to −5°, some volatile material rapidly distilled off (over a very short path) and was all immediately condensed at liquid-nitrogen temperature. This material contained all the lead and no boron. No hydrogen or methane was produced during its formation, and the remaining solid residue contained only potassium chloride and a substance of empirical formula $BH_3,NH_3$. The condensate melted at about −100°, without evolution of gas, to a homogeneous colourless liquid. The only known alkyl-lead compound of comparable volatility is tetramethyl-lead, m.p. −27°. All these facts point to the conclusion that the substance obtained is trimethyl-lead hydride, formed by the reaction $Me_3PbBH_4 \rightarrow Me_3PbH + BH_3,NH_3$. This was supported by the reaction (qualitatively and quantitatively controlled) with hydrogen chloride, which yielded hydrogen and trimethyl-lead chloride in accordance with the equation $Me_3PbH + HCl \rightarrow Me_3PbCl + H_2$.

The trimethyl-lead hydride was thermally very unstable, decomposing slowly above −100° to a red solid stable at −78° and methane ($CH_4:Me_3PbH$ = 1:2). This indicated that the red solid might be pentamethyl-dilead hydride: $2Me_3PbH \rightarrow Me_3Pb\cdot PbMe_2H + MeH$. Further decomposition of the latter gave lead, tetramethyl-lead, hydrogen, and methane in amounts corresponding to $Me_5Pb_2H$.

The use of liquid ammonia as a solvent for metathetical borohydride reactions may be a useful general method of preparing hydrides, since it is clear that the donor power of ammonia can effect fission of a $BH_3$ group from a borohydride, so leaving the hydride.

(*Received, February 10th*, 1959.)

## The Action of $^{60}$Co-$\gamma$-Radiation on Propene and Allyl Alcohol in Aqueous Solution

By P. G. CLAY, J. WEISS, and J. WHISTON
(KING'S COLLEGE, UNIVERSITY OF DURHAM, NEWCASTLE ON TYNE, 1)

*Propene*.—When aqueous solutions of propene–oxygen (1:1; total press. 1 atm.) are irradiated with $^{60}$Co-$\gamma$-rays, the main product is a hydroperoxide formed with the comparatively high yield of $G$ 2·6 ($G$ = molecules/100 ev). The yield of the oxidation products associated with a break of C–C bonds was relatively small, *viz.*, $G$(formaldehyde) $\sim$ 0·4; $G$(formic acid) $\sim$ 0·4; $G$(acetaldehyde) $\sim$ 0·4; and $G$(propionaldehyde) $\sim$ 0·2. Traces of acetone were also detected; in addition hydrogen peroxide is formed, with $G(H_2O_2)$ = 1·9.

The total yields of the organic radiation products (hydroperoxides + aldehydes + formic acid) were somewhat higher at pH 1·2 ($G$ = 4·0) than at pH 5·5 ($G$ = 2·9).

When the hydroperoxide in the irradiated solution was decomposed by ferrous sulphate, propylene glycol was produced: a good material balance was obtained between the hydroperoxide decomposed and the glycol and ferric salt produced. This and some related observations suggest that the hydroperoxide is a hydroxyhydroperoxide, $CH_3\cdot CH(O_2H)\cdot CH_2\cdot OH$.

When, however, aqueous solutions of propene–oxygen are irradiated in the presence of ferrous salt, the major product was propionaldehyde which was formed in the relatively high yield of $G \sim 20$, which must be due to some chain process.

*Allyl Alcohol*.—When allyl alcohol ($10^{-3}$M) was irradiated in aqueous solution, in the absence of oxygen, acraldehyde and propylene glycol were formed, both with a yield of $G$ = 1·2. In the presence of oxygen (1 atm.), irradiation of allyl alcohol solutions at pH 1·2 gave acraldehyde in a yield of $G$ = 1·2, glycollaldehyde $G$ = 1·7 and formaldehyde $G$ = 1·5, in addition to an organic hydroperoxide which was also formed with a yield of $G$ = 2. Further investigation has shown that here the glycollaldehyde and formaldehyde are secondary products from the decomposition of the organic hydroperoxide during the analytical procedure. From an investigation of the rate of liberation of iodine from iodide, by the irradiated solution, it appeared that two hydroperoxides were formed. The most obvious route to acraldehyde would be by initial hydrogen abstraction by the hydroxyl radicals (produced from the water), whereas formation of the hydroperoxide would presumably be initiated by addition of a hydroxyl radical to the double bond.

The relatively high yields of the organic hydroperoxides, particularly from allyl alcohol, suggest that, in addition to hydroxyl radicals, hydrogen atoms and/or $HO_2$ radicals may be capable of adding to the double bond, as in the reactions of ethylene previously studied.[1]

One of us (P.G.C.) is indebted to the British Oxygen Company for the award of a Research Fellowship and another (J. Whiston) thanks the D.S.I.R. for a maintenance grant.

---

[1] Clay, Johnson, and Weiss, *J.*, 1958, 2175.

# The Structure of Diaboline

By A. R. BATTERSBY and H. F. HODSON
(THE UNIVERSITY, BRISTOL)

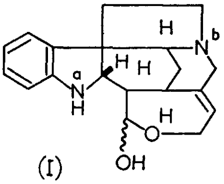
THE tertiary base diaboline was first isolated as its crystalline hydrochloride from the bark of *Strychnos diaboli* Sandwith by King[1] who assigned to it the molecular formula $C_{21}H_{26}O_3N_2$. Bader, Schlittler, and Schwarz[2] pointed out that the ultraviolet spectrum of diaboline is characteristic of an *N*-acylindoline; the alkaloid was proved to be an *N*-acetylindoline by acid-hydrolysis to deacetyldiaboline which showed an indoline absorption spectrum. The Swiss workers tentatively suggested a cryptophenolic[3,4] *N*-acetyl-7-hydroxyindoline structure for diaboline on the basis of their reported alkali-solubility of diaboline and deacetyldiaboline and the similarity of certain colour reactions of diaboline to those of vomicine. It was, however, emphasised that the evidence for a phenolic hydroxyl group was by no means conclusive.

Our re-examination of the tertiary bases from *S. diaboli* by partition chromatography[5] of the hydrochlorides on cellulose has so far given two crystalline alkaloids, both *N*-acylindolines. The major alkaloid, representing at least 0·1 % of the dry bark, has been shown to be diaboline by a rigorous comparison with the late Dr. H. King's material.[1]

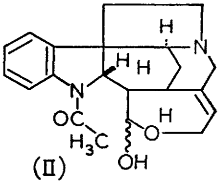
As noted by Witkop and Patrick,[3] the infrared carbonyl stretching frequencies of diaboline and its *O*-acetyl derivatives are at variance with an *N*-acetyl-7-hydroxyindoline structure for the base. It has now been shown that no phenolic hydroxyl group is present in diaboline, and that deacetyldiaboline is in fact the Wieland–Gumlich aldehyde[6] (I). The experimental evidence and reasoning which led us to make this direct comparison will be described in the full paper now in preparation. Considerable care was taken with the proof of identity because of the difficulties caused by dimorphism[2] in this series; the comparison involved m.p. and mixed m.p. of the base, m.p. 211—213° (Bader *et al.*[2] record m.p. 197—198°), the picrate, m.p. 235—237°, and the methopicrate,* m.p. 234—236°. Also the infrared spectra of the base and its hydrochloride and methochloride are superimposable upon those of the Wieland–Gumlich aldehyde and the corresponding derivatives; the corresponding salts in the two series have identical $R_F$ values in two solvent systems; the rotations of deacetyldiaboline and the Wieland–Gumlich aldehyde are identical.

Diaboline is thus $N_a$-acetyl Wieland–Gumlich aldehyde (II), $C_{21}H_{24}O_3N_2$, and a reassessment of the published[1,2] analytical data for diaboline and its salts shows that they are in moderate agreement with this formulation. However, the figures given for deacetyldiaboline by Bader *et al.*[2] lead directly to the correct molecular formula for this base.

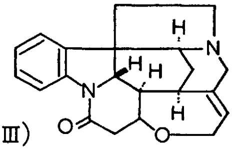
The Wieland–Gumlich aldehyde (I) has been isolated as the base[7] (caracurine-VII) and as the $N_b$-metho-derivative[8] (hemitoxiferine-I) from *Strychnos toxifera*. Diaboline (II) is thus intermediate in complexity between these alkaloids and strychnine (III) and its occurrence in *S. diaboli* has considerable interest in connection with the later stages of the proposed biogenetic scheme[9] for strychnine.



(I)



(II)



(III)

Grateful acknowledgement is made to the Medical Research Council for financial support and to Dr. J. Walker who very generously provided the diaboline and *S. diaboli* bark for our work.

(*Received, February 25th,* 1959.)

---

* The m.p. of this salt was incorrectly reported[8] as 134—136°.

[1] King, *J.*, 1949, 955.

[2] Bader, Schlittler, and Schwarz, *Helv. Chim. Acta*, 1953, **36**, 1256.

[3] Witkop and Patrick, *J. Amer. Chem. Soc.*, 1954, **76**, 5603.

[4] Orazi, Corral, Holker, and Djerassi, *J. Org. Chem.*, 1956, **21**, 979; Snyder, Strohmayer, and Mooney, *J. Amer. Chem. Soc.*, 1958, **80**, 3708.

[5] Schmid, Kebrle, and Karrer, *Helv. Chim. Acta*, 1952, **35**, 1864.

[6] Wieland and Gumlich, *Annalen*, 1932, **494**, 191; Wieland and Kaziro, *ibid.*, 1933, **506**, 60; Anet and Robinson, *J.*, 1955, 2253.

[7] Bernauer, Pavanaran, von Philipsborn, Schmid, and Karrer, *Helv. Chim. Acta*, 1958, **41**, 1405.

[8] Battersby and Hodson, *Proc. Chem. Soc.*, 1958, 287.

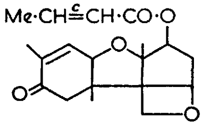
[9] Woodward, *Nature*, 1948, **162**, 155.

# The Structure and Biogenesis of Trichothecin

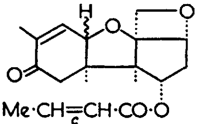
By J. Fishman, E. R. H. Jones, G. Lowe, and M. C. Whiting
(Dyson Perrins Laboratory, Oxford University)

Freeman, Gill, and Waring[1] have recently described an extensive investigation of the structure of trichothecin, an antifungal metabolic product of *Trichothecium roseum* Link. Their array of experimental evidence was originally explained in terms of structures (I) and (Ia). Through a generous gift of material and access to their unpublished results we have been able to continue the study and finally clinch structure (I).

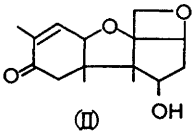
Mild hydrolysis of trichothecin yielded trichothecolone (II), oxidised with chromic acid to trichothecodione (III), which with 10% aqueous sodium hydroxide at 100° was found[1] to give a mixture of *p*-xyloquinone and the quinol. No fragment from the other carbocyclic ring could be isolated. An impure compound $C_8H_{12}O_2$ was obtained[1] analogously from the acid (IV) and it seemed that further investigation of this acid offered the best opportunity of obtaining and separating identifiable fission products. Under carefully controlled conditions treatment of the acid (IV) with alkali yielded the more stable stereoisomer[2] of 2,5-dimethylcyclohexane-1,4-dione (VI) and 2-methyl-3-oxocyclopent-1-enecarboxylic acid[3] (VII). The racemisation of five asymmetric centres is noteworthy. The process can be regarded as a reverse-Michael reaction (cf. IV), facilitated by the release of a considerable amount of compression energy associated with the stereochemistry indicated and followed by cleavage (cf. V) at the *β*-position to the carbonyl group. Under the anaerobic conditions chosen the intermediate hydroxycyclohexenone could not become aromatic and hence yielded the diketone (VI) but the only partially reduced acid (IX) gave *p*-xyloquinol (VIII) along with the product (VII).



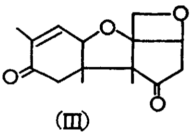
(Ia)



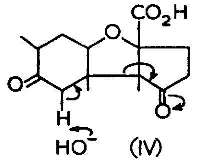
(I)



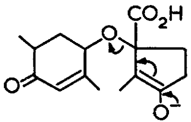
(II)



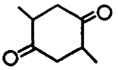
(III)



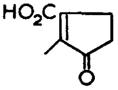
(IV)



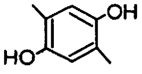
(V)



(VI)



(VII)



(VIII)

It had been hoped at the outset of our investigations that a further study of isotrichothecolone,[1] an alkali-isomerisation product of trichothecolone (II), would help to throw light on the trichothecin structure. However, complex rearrangements occur in this reaction and also in the formation of another product, allodihydrotrichothecolone, obtained when zinc dust is added to the alkaline reaction mixture. Nevertheless their respective structures (X) and (XI) had profound implications for trichothecin stereochemistry (cf. I) which is determined with the exception of the one centre.

The structure (I) for trichothecin does not obey the classical isoprene rule, but it can be derived from a tri-isoprenoid precursor by a 1,3- or a double 1,2-methyl group migration. The accompanying, but structurally unrelated metabolites, rosololactone and rosenonolactone, have been found[4] to conform to the biogenetic isoprene rule.[5]

[2-$^{14}$C]Mevalonic lactone (XII) was incorporated (*ca.* 0·5%) into trichothecin (I). Degradations, mainly employing the above fission reaction, indicate a distribution of radioactivity as in (XIV) and hence support a biogenesis of the carbon skeleton from three mevalonate units (XIII) involving two successive 1,2-methyl group shifts. [A 1,3-shift would demand a labelled atom either in the methylene group of the four-membered ring or in a methyl group of the diketone (VI); both possibilities were eliminated.]

---

[1] Freeman, Gill, and Waring, *J.*, 1959, 1105.

[2] Stephenson, unpublished work.

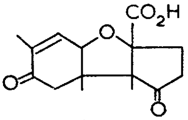
[3] Sutter and Schlittler, *Helv. Chim. Acta*, 1949, **32**, 1860. We are indebted to Dr. Schlittler for a sample of the acid obtained by degradation of picrotoxin.

[4] Birch, Rickards, and Smith, *Proc. Chem. Soc.*, 1958, 223; Britt and Arigoni, *ibid.*, 1958, 224.

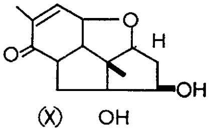
[5] Ruzicka, Eschenmoser, and Heusser, *Experientia*, 1953, **9**, 357; Cornforth, Cornforth, Popjak, and Youhotsky-Gore, *Biochem. J.*, 1958, **69**, 146.

None of the mevalonate radioactivity was found in the *cis*-crotonate group whereas, when the fungus was grown on a medium containing sodium [1-$^{14}$C] acetate (incorporation *ca.* 0·2%), 95% of the activity resided there. Acetate is clearly used up much faster for crotonate than for mevalonate synthesis, and our mevalonate experiment provides further support for the suggestion[6] that the acetate → mevalonate process is irreversible.

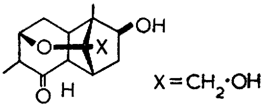
(*Received, February* 19*th*, 1959.)



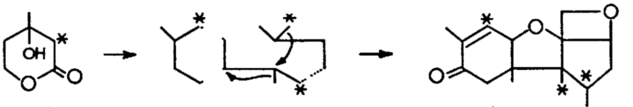
(IX)



(X)



(XI)



(XII) (XIII) (XIV)

---

[6] Birch, English, Massy-Westropp, and Smith, *J.*, 1958, 369.

## The Use of Spherical Samples in High-resolution Nuclear Resonance Spectroscopy

By P. Higham and R. E. Richards
(Physical Chemistry Laboratory, Oxford)

It is common practice to use cylindrical sample tubes in high-resolution nuclear resonance spectroscopy because these are easy both to fill and to use. There are, however, two disadvantages associated with this type of sample container: first, that a considerable volume of the sample is unused, because the radio frequency coil is usually much shorter than the liquid column; secondly, that if an external reference sample is used in a central or annular capillary the chemical shifts measured must be corrected for the difference of susceptibilities of the two liquids.

The first disadvantage can be overcome to some extent by using a plug in the glass cylinder made, *e.g.* of Nylon.[1] The second disadvantage can be overcome by using an internal reference compound, although this method can cause serious difficulties when aromatic solvents are being used.

Both of these difficulties are overcome by the use of spherical sample holders.[2] Glass ampoules with spherical cavities[3] are difficult to make and therefore expensive; they are also very difficult to fill and empty, especially if solutions of involatile solutes are used. Small glass bulbs can be blown and fitted inside a normal cylindrical sample tube,[4] but it is almost impossible to obtain perfectly spherical containers in this way and the filling factor produced is inevitably low.

A method of preparing spherical samples has been devised which both overcomes the difficulties described above and is relatively simple to carry out. A cylindrical sample tube is filled with a suitable gel. We have used a gel prepared from 10 g. of normal "laboratory gelatine" in 25 ml. of boiled-out water. A glass syringe is made by drawing a long spill on a piece of capillary tubing, and a stiff rubber teat is fixed to the end of the tubing. The syringe is calibrated by weight or with the aid of an "Agla" micrometer syringe. The sample tube of gelatine is warmed to 35—40° and held horizontally. A calculated volume (about 0·03 ml.) of the sample is injected into the gelatine at about the correct height from the bottom of the tube, and the sample forms a bubble in the gelatine matrix. The tube is then rotated slowly while the gel cools and the tube tilted so as to obtain a perfectly spherical bubble at just the correct position. If the sample and gel are of the same density, it is easy to adjust the position of the bubble in the tube by adding or removing gelatine from below the bubble by means of a second glass syringe. When the gel has cooled, the sample tube can be used in the ordinary way except that only low spinning speeds can be permitted to avoid distortion of the bubble.

This method has been used in the laboratory for studying samples when only small quantities are

[1] Varian Associates, Tech. Bull. Vol. II, No. 3, 1959.

[2] Andrew, "Nuclear Magnetic Resonance," Cambridge Univ. Press, 1955, p. 78.

[3] Primas and Gunthard, *Helv. Phys. Acta*, 1957, **30**, 315.

[4] Bothner-by and Glick, *J. Chem. Phys.*, 1957, **26**, 1647.

available, or when it was desirable to use an external standard without susceptibility correction. Its only limitations are that the sample must be immiscible and unreactive with water and that there is a strong resonance from the water in the gel which obscures a small region of the spectrum.

The usual volume of sample used is 0·03 ml. and in general a minimum amount of solute of $10^{-4}$ mole is required, although with a low signal:noise ratio smaller amounts can be studied. When this method is used the amount of material for a given signal:noise ratio is about one-third of that required in a cylindrical sample tube with a plug.

The resolving power obtained is at least as good as that observed with cylindrical samples. The Figure shows recordings of the hydrogen resonance of nitrobenzene run in a cylindrical tube and in a spherical bubble.

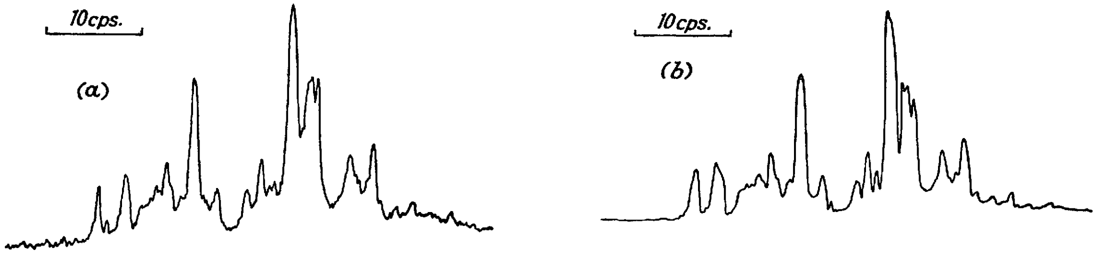


FIG. 1. *Nitrobenzene in* (*a*) *bubble and* (*b*) *cylindrical tube.*

*Chemical shifts* (*c./sec.*) *at* 40 *Mc./sec.*

| Compound | Uncorr. shifts from published data | Corr. values | Bubble values | Shifts with cyclohexane as internal reference |
|---|---|---|---|---|
| Chloroform | −33·9 | −25·0 | −23·4 | −20·3 |
| Benzene | 0 | 0 | 0 | −16·7* |
| Toluene ring | 3·1 | 3·7 | 3·2 | −11·6* |
| Toluene methyl | 199·4 | 200·0 | 200·0 | 183·8* |
| Cyclohexane | 212·2 | 212·5 | 212·2 | 212·5 |

* Note anomalous effect of aromatic solvents.

An additional advantage is concerned with the accurate location of peaks. The water in the gel provides a very convenient external standard and because of the spherical shape of the sample corrections for susceptibility differences are unnecessary. The accuracy obtainable is indicated by the measurements, in the Table, of the positions of the resonances of a number of organic liquids. The first column gives the chemical shifts, in cycles per second at 40 Mc./sec. which have been selected[5] as the best available values measured in cylindrical samples. From the magnetic susceptibilities of the samples[6] these shifts have been corrected for the effects of susceptibility by using the classical $2\pi\kappa/3$ bulk susceptibility effect for cylinders. The third column gives comparable values obtained by the gel-bubble method. These figures have been obtained by multiplying our measurements by 40/29·92, because our spectrometer operates at a frequency of 29·92 Mc./sec., but no correction for susceptibility was applied. The agreement with the corrected values is within the accuracy of the susceptibility measurements.

The same compounds were studied by using cyclohexane (5%) as an internal standard in cylindrical tubes, and the chemical shifts are recorded in column 5. The values confirm the view that in aromatic solvents significant errors can occur.[7]

A considerable number of materials has been tried for use with samples which are miscible with or reactive to water. We have not yet found a material which does not suffer from one of the disadvantages that (*a*) it does not wet glass, (*b*) it sets too sharply, (*c*) it has a complex spectrum of its own, or (*d*) it melts at too high a temperature.

(*Received, March 5th,* 1959.)

---

[5] Reilly, Mellon Newsletter No. 2, 1958, p. 5.

[6] Handbook of Chemistry and Physics, 37th edn., 1956.

[7] Bothner-by and Glick, *J. Chem. Phys.*, 1957, **26**, 1651.

## Electron Spin Resonance in Crystals of the Amminoperoxydicobalt Complexes

By E. E. SCHNEIDER and J. WEISS
[DEPARTMENT OF PHYSICS (E.E.S.) and DEPARTMENT OF CHEMISTRY (J.W.), KING'S COLLEGE, UNIVERSITY OF DURHAM, NEWCASTLE ON TYNE]

WITH reference to the recent Communication[1] on the electron spin resonance spectrum of the $[(NH_3)_5Co{\cdot}O_2{\cdot}Co(NH_3)_5]^{5+}$ ion in solution, we report our investigations with single crystals of the amminoperoxydicobalt sulphate. Our measurements were carried out at 9·5 and 32 kMc./sec. with assemblies of small (aligned) single crystals. The resonance spectrum is strongly orientation-dependent and consists, in general, of two peaks corresponding to two non-equivalent molecules in the unit cell. The principal components of the *g*-factor derived from a preliminary analysis were: $g_{\parallel} = 2{\cdot}12$ and $g_{\perp} = 1{\cdot}99$. These results and the large orientation-dependent width of the individual lines (200—500 gauss) are consistent with the sharing of the positive hole between the two cobalt ions. The large spin–orbit coupling of $Co^{4+}$ and the hyperfine interaction arising from the nuclear moment of $^{59}Co$ would account for the large *g*-shift, $(g_{\parallel}-g_0) = 0{\cdot}12$ and the large width of the resonance. The results of Bernal *et al.*[1] for solutions support these findings. Some of these results were presented at the Colloque Ampère in Paris, July, 1958. More detailed studies with individual single crystals are in progress.

(*Received, March* 19*th*, 1959.)

---

[1] Bernal, Ebsworth, and Weil, *Proc. Chem. Soc.*, 1959, 57.

## Substituted Manganese Carbonyl Derivatives

By R. S. NYHOLM and D. V. RAMANA RAO
(UNIVERSITY COLLEGE, GOWER STREET, LONDON, W.C.1)

VERY few compounds are known in which one or more of the CO groups of dimanganese decacarbonyl have been replaced by a neutral molecule, *e.g.*, $R_3P$. An example of these is the triphenylphosphine compound $[Mn(CO)_4Ph_3P]^0$ prepared by Hieber and Wagner.[1] This complex is monomeric in benzene, so the manganese atom is five-covalent. It is paramagnetic with the magnetic moment expected for one unpaired electron. We have been studying the behaviour of $Mn_2(CO)_{10}$ with *o*-phenylenebisdimethylarsine (D) and find that two CO groups per manganese atom may be replaced readily. Two derivatives have been isolated, both of which have the empirical formula $MnD(CO)_3$, one being monomeric and the other dimeric in freezing benzene. The two forms are prepared as follows with properties as shown.

Typical analytical data are: *Dimer*: C, 36·9; H, 3·9; As, 34·0; Mn, 12·6. *Monomer*: C, 37·1; H, 3·9; As, 35·1; Mn, 12·75. $C_{13}H_{16}O_3As_2Mn$ requires C, 36·7; H, 3·8; As, 35·3; Mn, 12·9%.

In a Nujol mull and in chloroform solution, the infrared spectra of the two forms are identical, bands being observed at 1957 and 1860 cm.$^{-1}$ in Nujol and 1958 (s) and 1905 cm.$^{-1}$ (s) in chloroform. Both the compounds dissolve in chloroform, but only the monomer can be isolated subsequently. However, the spectra of the two forms do differ in carbon disulphide; the dimer shows bands at 1944 (s), 1927 (s), and 1885 (s) cm.$^{-1}$, whereas the monomer absorbs at 1965 (s) and 1918 (s) cm.$^{-1}$. Further, the melting points of the dimer and the monomer are unchanged on recovery of material from carbon disulphide solutions.

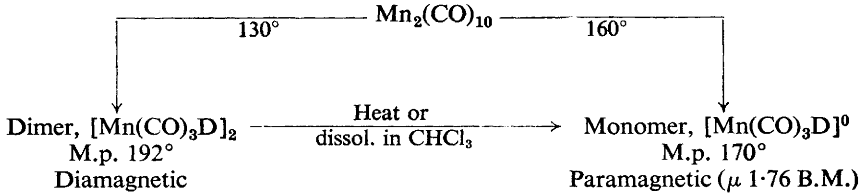
It seems reasonable to suggest that initially one diarsine molecule is attached to each Mn atom in the dimer and that on further heating the Mn–Mn bond is broken. One might have expected an equilibrium between the monomer and the dimer, depending upon the temperature. However, it is found that although the dimer is converted into the monomer on further heating or melting, reconversion into the dimer on cooling to room temperature does not take place. We therefore regard the dimer as a metastable intermediate in the formation of the (stable) monomer. In these two compounds we have an unusual example of polymeric isomerism. If either form is heated at a higher temperature for a long time, more CO is lost and a more strongly paramagnetic compound ($\mu \sim 3{\cdot}6$ B.M.), probably $Mn(CO)_2D$, is formed. This unstable derivative is being investigated.

When titrated spectrophotometrically with bromine in chloroform, both forms react with the loss of one mole of CO per Mn atom, a sharp end-point occurring after two equivalents of bromine have been added—a reaction which does not occur with $Mn_2(CO)_{10}$ under these conditions. A pale yellow bivalent manganese compound, $MnD(CO)_2Br_2$, can be isolated (Found, C, 25·3; H, 3·5; Br, 29·4; Mn, 10·1. $C_{12}H_{16}As_2O_2Br_2Mn$ requires C, 25·8; H, 2·9; Br, 28·7; Mn, 9·9%). The compound is paramagnetic ($\mu_{\text{eff}}$ 2·3 B.M.), indicating one unpaired electron, as expected for an octahedral spin-paired

---

[1] Hieber and Wagner, *Z. Naturforsch.*, 1957, **12b**, 478.

*Action of the diarsine* (D) *on* $Mn_2(CO)_{10}$ *when heated together* in vacuo *for* 6 *hr.*



Both the monomer and the dimer are pale yellow and are non-electrolytes in $MeNO_2$.

complex of Mn(II). This complex decomposes at 202° and is virtually a non-electrolyte in nitromethane. When iodine is used as oxidant, only one equivalent is absorbed and no carbon monoxide is evolved. The product is a non-electrolyte and is diamagnetic: it is clearly the octahedral Mn(I) derivative, $MnD(CO)_3I$, of interest since few Mn(I) compounds are known.

The authors are indebted to the Ethyl Corporation (U.S.A.) for a gift of manganese carbonyl and to the Indian Government for an award (to one, D.V.R.R.), also to Mr. C. Barraclough who is investigating the infrared spectra of these compounds.

(*Received, February* 30*th*, 1959.)

## The Nuclear Magnetic Resonance Spectrum of a New Plant Amino-acid; Evidence for a Pyrazole Ring

By L. Fowden, F. F. Noe, J. H. Ridd, and R. F. M. White
(University College, Gower Street, London, W.C.1)

The work on heterocyclic compounds carried out by two of us (J.H.R. and R.F.M.W.) suggests that proton magnetic resonance can be of use in distinguishing between glyoxaline and pyrazole rings and in identifying the position of substituents. The proton magnetic resonance spectrum of glyoxaline has already been discussed;[1] in deuterium oxide the spectrum consists of two lines of relative areas 1:2 assigned to the protons at the 2- and the 4(5)-position respectively (see Fig. *a*). A third line, not shown in the Figure, is caused by the protons moving between the nitrogen atom and the residual water in the solvent. In 1-methylglyoxaline the 4- and the 5-position are no longer equivalent but the spectrum of a solution of 1-methylglyoxaline in deuterium oxide shows two peaks in the low-field region of areas 1:2 (Fig. *b*), so that, under these conditions, the chemical shift between the 4- and the 5-proton must be negligible. The nuclear magnetic resonance spectra of solutions of pyrazole and 1-methylpyrazole in deuterium oxide indicate that there is little chemical shift between the 3- and the 5-proton and that these are spin-spin coupled with the 2-proton; the larger peak is split into a doublet and the smaller into a triplet, with separations of the multiplet components of about 2·5 c./sec. These spectra are illustrated diagramatically in the Figs. *c* and *d*, the length of the line indicating the relative peak areas; the fine structure is omitted.

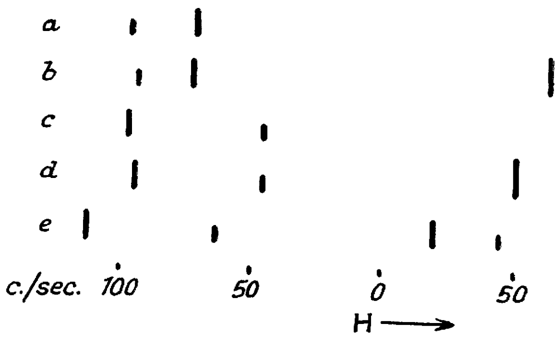
In the spectrum of glyoxaline and 1-methylglyoxaline, the peak arising from the unique hydrogen atom occurs at a lower field than that arising from the equivalent pair of hydrogen atoms, but in the spectrum of pyrazole and 1-methylpyrazole, the reverse is true and the separation of the peaks is much greater. These differences probably suffice to distinguish *N*-substituted glyoxalines from *N*-substituted pyrazoles.

Concurrently with the above work, two of us (L.F. and F.F.N.) have extracted a new amino-acid from water-melon seed (*Citrullus vulgaris* var. Tom Watson). The compound, $C_6H_9O_2N_3$, is isomeric with histidine. It is considerably less basic than histidine and with hydrogen iodide gives rise to alanine (detected chromatographically) amongst other products. If the molecule contains an alanine residue, then, from the empirical formula, this is probably attached to a glyoxaline or a pyrazole ring. The fission of the alanine residue from the ring by hydrogen iodide suggests that the linkage is to a ring-nitrogen atom.

The nuclear magnetic resonance spectrum of this amino-acid in 3N-sodium deuteroxide in deuterium oxide is shown in the Fig. *e*. In the low-field region, two peaks of relative areas 2:1 are obtained: as shown in the Figure, their relative positions and the separation between them are characteristic of a

---

[1] Gillespie, Grimison, Ridd, and White, *J.*, 1958, 3228.



*Proton magnetic resonance spectra with a water capillary as the reference zero.*

*a*, *Glyoxaline. b*, 1-*Methylglyoxaline. c*, *Pyrazole. d*, 1-*Methylpyrazole. e*, *New amino-acid. a—d*, *in* $D_2O$; *e*, *in* 3N-NaOD–$D_2O$.

pyrazole ring. The shift of the two peaks to lower field, relative to pyrazole and 1-methylpyrazole, is probably a solvent effect; the spectrum of 1-methylpyrazole is modified in a similar way in a similar medium. The two peaks showed indications of spin-spin interaction but this was not resolved, probably because the viscous medium caused viscosity broadening of the peaks. The peaks in the high-field region are assigned to the alanine residue; the peak at 20 c./sec. is a doublet and that at 50 c./sec. is a triplet, with components separated by 6 c./sec. This fine structure suggests that the pyrazole ring is attached to the β-carbon atom of alanine. Thus the spectrum of the amino-acid suggests that it is β-1-pyrazolylalanine.

This compound appears to be the first example of a naturally occurring pyrazole derivative.

Two of us (L.F. and F.F.N.) thank the Ferry-Morse Seed Co. (California) for the gift of the watermelon seed, and one of us (F.F.N.) is grateful for an American Cancer Society Fellowship.

(*Received, March 6th*, 1959.)

---

## Effect of Benzene as a Solvent on the Photochlorination of Butyryl, Valeryl and Hexanoyl Chloride

By H. J. DEN HERTOG and P. SMIT

(LABORATORY OF ORGANIC CHEMISTRY OF THE AGRICULTURAL UNIVERSITY, WAGENINGEN, THE NETHERLANDS)

RECENTLY G. A. Russell described a remarkable effect of some aromatic solvents and certain non-aromatic liquids on the photochlorination of several carbon compounds.[1] They accentuated the difference in reactivity of carbon–hydrogen bonds in these compounds. In his third paper Russell concluded that the relative reactivities determined mainly by the stability of the incipient free radicals are very sensitive to changes in solvents, but that there is little solvent effect on relative reactivities determined chiefly by polar effects. This conclusion seems to contradict results of an investigation on the photochlorination of fatty acid derivatives which is in progress in our laboratory.[2]

We treated a mixture of 1 mol. of fatty acid chloride and 4 mols. of benzene at 20° with 0·35 mol. of chlorine under irradiation with ultraviolet light. The composition of the mixture of monochloro-derivatives formed was established by fractional distillation *in vacuo* and countercurrent distribution of the lower fractions. The results are summarised in the Table, together with those previously obtained when chlorinating the acid chloride in absence of the solvent.[2]

| Substrate | Solvent | Relative reactivity towards chlorine* at position stated | | | |
|---|---|---|---|---|---|
| | | β | γ | δ | ε |
| Butyryl chloride | $C_6H_6$ | 1·0 | 0·35 | — | — |
| | None | 1·0 | 0·6 | — | — |
| Valeryl chloride | $C_6H_6$ | 1·0 | 4·3 | 0·75 | — |
| | None | 1·0 | 3·05 | 1·2 | — |
| Hexanoyl chloride | $C_6H_6$ | 1·0 | 4·5 | 15·8 | 1·05 |
| | None | 1·0 | 3·6 | 5·1 | 1·75 |

* The reactivities of the C–H bonds at α-positions are omitted as the amounts of α-isomers formed are very small. The divergent reactivities of the $C_\beta$–H bonds are assumed to be 1·0.

Hexanoyl chloride gives the most information about a possible solvent effect upon the deactivation of C–H bonds by an electron-withdrawing group; its molecule contains a series of $C_{sec}$–H bonds with strongly decreasing electron density from δ to α. The ratio of the reactivities towards free chlorine of the $C_\delta$–H and $C_\varepsilon$–H bonds in hexanoyl chloride amounts to 5·1/1·75 = 2·9. This value is but slightly lower than that given by Russell for the relative reactivities of $C_{sec}$–H and $C_{prim}$–H bonds in pentane

---

[1] Russell, *J. Amer. Chem. Soc.*, 1957, **79**, 2977; 1958, **80**, 4987, 4997, 5002.

[2] Cf. den Hertog, de Vries, and van Bragt, *Rec. Trav. chim.*, 1955, **74**, 1561; Smit and den Hertog, *ibid.*, 1958, **77**, 73.

(3·7) which only depend on the resonance stabilisation of the incipient free radicals. Thus, it appears again that the inductive effect of the carbonyl chloride group is scarcely felt at the $\delta$- and the $\epsilon$-position and that the enhancement of the relative reactivities of these bonds by addition of benzene as a solvent from 2·9 to 15·0 only must be ascribed to the resonance stabilisation of the incipient radicals in question. Whereas the ratio (react.$C_\delta$–H): (react.$C_\epsilon$–H) increases to five-fold, the relative reactivities of $C_\delta$–H and $C_\beta$–H bonds increase from 5·1 to 15·8 (*i.e.*, more than three-fold) by the solvent effect. The change in relative reactivities of $C_\delta$–H and the $C_\alpha$–H bonds would probably yield a still higher ratio. Thus, in hexanoyl chloride the polar effect is not less important than the resonance effect in determining the change in reactivity of carbon–hydrogen bonds by addition of a complex-forming solvent.

For comparison the relative reactivities of the C–H bonds in valeryl and butyryl chloride are given, all depending on both the resonance and polar effect. In propionyl chloride the relative reactivities at $\alpha$ and $\beta$ are about the same (2:5) whether benzene is used as a solvent or not; this fact again elucidates the importance of the polar effect.

(*Received, February 6th,* 1959.)

## The Mass Spectra of Phosphorus(V) Halides

By T. KENNEDY, D. S. PAYNE, R. I. REED, and W. SNEDDEN
(THE UNIVERSITY, GLASGOW, W.2)

MASS-SPECTROSCOPIC data for dichlorotrifluorophosphorane up to a mass of 160 have been given in a recent paper.[1] The range of masses accessible with the instrument then employed has been extended, enabling reliable results on masses up to at least 400 to be obtained. Samples of "phosphorus pentachloride" $[PCl_4^+][PCl_6^-]$ and of a new compound recently prepared by two of us (T.K. and D.S.P.) of empirical composition $P_2Cl_9F$ have now been examined.

The two substances were prepared for examination under strictly anhydrous conditions and were admitted through taps greased with KEL-F grease. The vapour pressures of the solids were both sufficiently high for the experiment to be conducted without the sample being heated. An ionisation energy of 50 ev was employed. The ion species were identified by counting from known background masses of residual hydrocarbon gases and confirmed by observation of the mass spread due to the isotopes of chlorine.

The cracking pattern of "phosphorus pentachloride" showed peaks which were assigned to the ion species $P_2Cl_9$, $P_2Cl_7$, $P_2Cl_5$, $P_2Cl_3$, $P_2Cl_2$, and $P_2Cl$ as well as a collection of peaks corresponding to species containing one phosphorus atom. For $P_2Cl_9F$, peaks were assigned to the ion species $P_2Cl_9F$, $P_2Cl_8F$, $P_2Cl_7F$, $P_2Cl_6F$, $P_2Cl_5F$, $P_2Cl_3F$, $P_2Cl_2F$, and $P_2ClF$ in addition to fragments containing one phosphorus atom.

Several recent investigations have indicated the existence of polymerised metallic halides in the vapour state. However, whilst it has been known for many years that the halides of phosphorus(V) are based largely on ionic lattices, the considerable amount of information on the vapour densities, particularly of "phosphorus pentachloride," has provided evidence only of dissociation, never of association. Attempts by one of us (D.S.P.) to measure the molecular weight of "phosphorus pentachloride" in the vapour phase at relatively low temperatures, under conditions in which the dissociation is known to be very small, gave no indication of association, within the limits of measurement. It is clear, however, from the mass spectra that association does occur.

The existence of $P_2X_{10}$ units (where X represents Cl or F) and associated fragments in the mass-spectrometer could be explained by a collision hypothesis, *e.g.*, $PX_5 + PX_5^+ \rightarrow P_2X_{10}^+$, etc., but in view of the absence of fragments containing two fluorine atoms in the experiment with $P_2Cl_9F$ and the relatively small amounts of $PX_5$ species likely to be present this seems unlikely. It is also possible that a parent of even higher molecular weight occurs and that this on ionisation breaks up to give $P_2X_{10}$, etc.. units. However, the most reasonable hypothesis is that there are $P_2X_{10}$ units in equilibrium with the solid at room temperature. The solid being of the type $[PX_4^+][PX_6^-]$, the units are formed essentially by evaporation of a cation–anion pair from the surface of the crystal.

In the $P_2X_{10}$ and other $P_2$ units a halogen bridge involving a four-membered ring could be possible. This would be in keeping with many other polymeric halides, and indeed might be likely in that the resulting complex would have octahedrally disposed halogens around the phosphorus atoms, rather than the trigonal bipyramid arrangement as found in the case of the "phosphorus pentachloride" molecule.[2] The exact composition of the vapour with respect to monomeric and dimeric units in equilibrium with the solid and the detailed structure of these units remains to be investigated.

(*Received, February 19th,* 1959.)

---

[1] Kennedy and Payne, *J.*, 1959, 1228.

[2] Brockway and Beach, *J. Amer. Chem. Soc.*, 1938, **60**, 1836.

# Echitamine

By T. R. GOVINDACHARI and S. RAJAPPA

(DEPARTMENT OF CHEMISTRY, PRESIDENCY COLLEGE, MADRAS, INDIA)

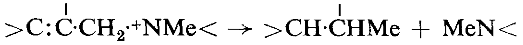
GOODSON and HENRY[1] isolated the alkaloid echitamine as its "hydrochloride," $C_{22}H_{28}O_4N_2,HCl$, from various *Alstonia* species. Besides clearing up disputed points in earlier investigations[2] of the alkaloids of *Alstonia scholaris*, they obtained the following information: The free base could not be obtained by basification of the hydrochloride. Mild alkaline hydrolysis leads to "demethylechitamine" and methanol, indicating the presence of a methoxycarbonyl group. Distillation of "echitamine hydrochloride" with alkali yields methylamine and a substance giving indole colour reactions.

We now find that the alkaloid contains one OMe, one NMe, and no CMe group. Potentiometric titration against N/100-sodium hydroxide indicates that the salt is, not a hydrochloride, but a quaternary chloride. The alkaloid shows absorption maxima in ethanol at 235 and 295 m$\mu$ (log $\epsilon$ 3·93, 3·55), unaffected by addition of acid. From this it is inferred that the alkaloid is a dihydroindole derivative with $N_a$ and $N_b$ separated by not more than two carbon atoms,[3] $N_b$ being the quaternary centre carrying the $\equiv$NMe$^+$ group. The chloride shows infrared bands at 3·04 (OH), 3·17 (NH), 5·79 (ester), and 13·2 $\mu$ (o-disubstituted benzene) and no band near 4·15 ($\equiv$ NH$^+$) or 7·2 $\mu$ (CMe).

The ultraviolet absorption of the acetyl derivative[1] ($\lambda_{max.}$ 235, 295 m$\mu$; log $\epsilon$ 3·94, 3·50) is very similar to that of echitamine chloride and the infrared spectrum exhibits bands at 2·92 (NH), 5·70 (ester), and 8·14 $\mu$ (OAc).

Mild alkaline hydrolysis of the alkaloid gave "demethylechitamine," which must be a betaine since potentiometric titration still indicated the presence of a quaternary centre.

Catalytic reduction of echitamine chloride at atmospheric pressure gave a tertiary base (a mixture of stereoisomers) showing absorption at 247 and 307 m$\mu$, indicating that it is a dihydroindole. In acid solution, there is a hypsochromic shift of both these bands, suggesting that the two nitrogen atoms are separated by only one carbon atom.[3] The base had infrared absorption bands at 3·57 (>NMe)[4] and 7·20 $\mu$ (CMe). The ready formation of this tertiary base with newly formed >NMe and CMe groups indicates the presence of an allylamine system:[5]



$$>C{:}\overset{|}{C}{\cdot}CH_2{\cdot}{}^{+}NMe< \;\rightarrow\; >CH{\cdot}\overset{|}{C}HMe + MeN<$$

Acetylation of the tertiary base gives an $N_aAc$ derivative as indicated by infrared (amide band at 6·0 $\mu$), and ultraviolet spectra ($\lambda_{max.}$ 252; $\lambda_{infl.}$ 282 m$\mu$) and a positive Otto reaction. Hence the alkaloid must have a free $N_aH$ group.

Dehydrogenation of the tertiary base by selenium gives, besides indoles, a basic product isolated as the picrate, m.p. 253° (decomp.). The base liberated from the picrate has $\lambda_{max.}$ in ethanol at 245 and 307 m$\mu$ and $\lambda_{max.}$ in ethanolic hydrochloric acid at 245, 327, and 355 m$\mu$. The spectrum of a neutral solution is strikingly similar to that of 1′-methylpyrrolo(2′:3′-3:4)quinoline.[6] The infrared spectrum contains no NH band but a well-defined band at 7·22 $\mu$ (CMe).

We thank the Council of Scientific and Industrial Research for the award of a Senior Research Fellowship (to S.R.).

(*Received, February* 24*th*, 1959.)

---

[1] Goodson and Henry, *J.*, 1925, **127**, 1640; Goodson, *J.*, 1932, 2626.

[2] Gorup-Besanez, *Annalen*, 1875, **176**, 88; Hesse, *ibid.*, p. 326; 1880, **203**, 144; *Ber.*, 1880, **13**, 1841; Harnack, *Arch. exp. Path. Pharm.*, 1877, **7**, 126; *Ber.*, 1878, **11**, 2004; 1880, **13**, 1648.

[3] Hodson and Smith, *J.*, 1957, 1877.

[4] Braunholtz, Ebsworth, Mann, and Sheppard, *J.*, 1958, 2780.

[5] Bickel, Schmid, and Karrer, *Helv. Chim. Acta*, 1955, **38**, 649.

[6] Eiter, *Monatsh.*, 1948, **79**, 17; Eiter and Nagy, *ibid.*, 1949, **80**, 607.

---

# OBITUARY NOTICE

## CECIL HENRY DESCH

1874—1958

CECIL HENRY DESCH, F.R.S., died in a London hospital on Thursday, June 19th, 1958. This distinguished metallurgical scientist, whose published work is known in all parts of the world, was 84 years of age and had lived in retirement for some years.

Born in 1874 in London, son of Henry Thomas Desch, he was educated at Birkbeck School, Kingsland, and Finsbury Technical College, London. From there he went to the University of Würzburg, where he obtained the degree of Ph.D., and subsequently he returned to University College, London, later receiving the degree of D.Sc. of the University of London.

He was trained as an organic chemist, but joined the metallurgical department of King's College, London in 1902 and became research assistant to the late Professor A. K. Huntington.

In 1909, the year of his marriage to Elison Ann, daughter of Professor W. Ivison Macadam of Edinburgh, he was appointed lecturer in Metallurgical Chemistry at the University of Glasgow, where he remained until the end of World War I. For the next two years he was Professor of Metallurgy at the Royal Technical College, Glasgow, until in 1920, on the death of Dr. J. O. Arnold, he became Professor of Metallurgy at Sheffield University, occupying the Chair for 11 years.

In 1931 Dr. Desch was appointed Superintendent of the Metallurgy Department of the National Physical Laboratory, Teddington, in succession to Dr. W. Rosenhain, but did not take up his duties there until the following year because of his visit, at the end of 1931, to the United States of America, where he delivered the George Fisher Baker course of lectures on the chemistry of solids at Cornell University, Ithaca, New York. In 1934 this course of lectures was printed in book form and entitled "The Chemistry of Solids."

After retiring from his position at the National Physical Laboratory in 1939, Dr. Desch was soon directly connected with industry. In 1943 he was appointed to the Board of Directors of Richard Thomas & Company Ltd. and was responsible for the direction of the research and development activities of the firm; upon the amalgamation with Baldwins Ltd., he resigned his directorship and was subsequently associated with the Whitehead Iron and Steel Company.

In the academic field, Dr. Desch has received wide recognition. He was elected a Fellow of the Royal Society in 1923, was President of the Faraday Society from 1926—1928, President of the Institute of Metals from 1938—1940, and President of the Iron and Steel Institute from 1946—1948, having been awarded the Bessemer Gold Medal in 1938 for his work in the advancement of metallurgy. He was also awarded, in 1941, the Platinum Medal of the Institute of Metals, was a corresponding member of the Académie des Sciences and held the honorary degrees of Glasgow and Leoben (South Austria) Universities.

In addition to his well known writings in the metallurgical and chemical fields he was interested in sociology and as a member of the Institute of Sociology he presented a number of papers on this subject.

His published work includes the popular "Metallography" (1910) which was translated into German in 1914 and has run to several editions, and the well known "Intermetallic Compounds " (1914).

During Dr. Desch's long career a major change took place in the outlook on metallurgical teaching and research. In his early years, studies in inorganic chemical analysis formed a large part of the metallurgist's training; subsequently the applications of physics, physical chemistry, and thermodynamics in the study of metals were all greatly extended. Desch himself did a great deal to foster these developments both by his teaching and in the post-graduate research laboratory which he set up and equipped in Sheffield in the early '20s. Here physicists, chemists, and engineers worked together with metallurgists on many problems in physical metallurgy.

His many degree students will remember the outstanding clarity of his lectures. His post-graduate students still remark on the phenomenal detail and scope of his knowledge of metallurgical literature and recall his quiet kindness and diligence in ensuring that they received the full credit for any original work which they accomplished.

C. SYKES.

## APPLICATIONS FOR FELLOWSHIP

(Fellows wishing to lodge objections to the election of these candidates should communicate with the Honorary Secretaries within ten days of the publication of this issue of *Proceedings*. Such objections will be treated as confidential. The forms of application are available in the Rooms of the Society for inspection by Fellows.)

Ahmad, Sanjid Shamin, M.Sc. 54 Noel Street, Hyson Green, Nottingham.
Arene, Eugene O. Tedder Hall, University College, Ibadan, Nigeria.
Bailey, Jennifer Vivien. Highfield Hall, Omdurman Road, Highfield, Southampton.
Barnett, Gerald Wilton. Flat 4, 60 Wymers Wood Road, Burnham, Bucks.
Bhatia, Iqbal Singh, M.Sc., Ph.D. Indian Tea Association, Tocklai Experimental Station, Cinnamara, P.O., Assam, India.
Bhatia, Yog Raj, M.Sc. 1 Petersfield Avenue, Slough, Bucks.
Bishop, Robert John. 29 Kingswood Avenue, Bromley, Kent.
Bourn, Patricia Margaret, B.Sc. Imperial Chemical Industries Limited, Akers Research Laboratories, The Frythe, Welwyn, Herts.
Bryan, Robert Finlay, Ph.D. Laboratorium für Organische Chemie, Eidg. Technische Hochschule, Zurich 6, Switzerland.
Bullock, Pete Bradley. Divisional Laboratory, 67 Wellington Road, Edgbaston, Birmingham.
Burrows, Brian Frederick, B.Sc. Department of Chemistry, The University, Bristol, 8.

Burton, Ronald Eliot, B.A. 392 Harold's Cross Road, Terenure, Dublin.
Cazes, Jack, B.S. 614 Junius Street, Brooklyn, 12, N.Y., U.S.A.
Corbin, James Lee, B.A. Kedzie Chemical Laboratory, Michigan State University, East Lansing, Michigan, U.S.A.
Cox, Alan. 32 Keswick Grove, Seedley, Salford, 6, Lancs.
Critchley, John Philip, Ph.D. Truro, Strawberry Lane, Wilmslow, Cheshire.
Dailey, William Sebastian. 53 Courtenay Gardens, Upminster, Essex.
Dale, Anthony Richard. 7 Waller Road, Beaconsfield, Bucks.
Davidson, James Alan. 19 Gilroy Way, Orpington, Kent.
Dikko, Muhammed. University College, Ibadan, Nigeria.
Domsky, Irving Isaac, Ph.D. Sterling Chemistry Laboratory, Yale University, New Haven, Conn., U.S.A.
Douraghizadeh, Khosrow. 60 Idmiston Road, West Norwood, London, S.E.27.
Duffy, John Alastair, Ph.D. 50 Leahurst Crescent, Harborne, Birmingham, 17.
Foot, John Rodney. 34 Carnock Road, Manadon, Plymouth, Devon.
German, Reginald James, B.Sc. Department of Chemistry, The University, Birmingham, 15.
Goh, Siew Kee. Central Medical Store, General Hospital, Kuching, Sarawak.
Golfier, Michel Jean Francois. Laboratoire de Chimie Organique, École Polytechnique, 17 Rue Descartés, Paris, 5, France.
Hardy, Frederick Edward, B.Sc. 47 Bolingbroke Street, Heaton, Newcastle on Tyne, 6.
Hayman, Nigel Ward. 29 Bartlemus Road, Oxford.
Helgen, Lon Endre, B.A. 2703 Yale Station, New Haven, Conn., U.S.A.
Hiscock, Alan Keith. 44 Lime Grove, New Malden, Surrey.
Hiskey, Richard Grant, A.B., M.S., Ph.D. Department of Chemistry, University of North Carolina, Chapel Hill, North Carolina, U.S.A.
Hopton, Frederick James, B.Sc. 49 Oak Road, Horfield, Bristol, 7.
Hutchinson, John. 14 Hirst Grove, Darlington, Co. Durham.
Israel, Mervyn, M.S., Ph.D. Department of Chemistry, University of Michigan, Ann Arbor, Michigan, U.S.A.
Jaffe, Fred, Ph.D. W. R. Grace & Co., Washington Research Center, Clarksville, Md., U.S.A.
Jones, Richard Arnold Yardley, B.A., M.S. University Chemical Laboratory, Lensfield Road, Cambridge.
Last, Walter Allan, B.A. 49 Queen Anne Street, London, W.1.
Marinier, Bernard, Ph.D. University Chemical Laboratory, Lensfield Road, Cambridge.
Mohrig, Jerry Robert, B.S. Department of Chemistry, University of Colorado, Boulder, Colorado, U.S.A.
Moore, Francis Hugh, B.Sc. Department of Chemistry, University of Auckland, Auckland, New Zealand.
Morcom, Ronald Edgar, B.Sc., A.R.I.C. 20 Oakwood Avenue, Borehamwood, Herts.
Mundye, Anthony Arnold John. 73 Verulam Road, Greenford, Middx.
Nash, Glynn Michael. 77 Tudor Drive, Watford, Herts.
Ndupu, Bismarck Livingstone Nwobi. University College, Ibadan, Nigeria.
Neve, Sidney George, B.Sc. 27 Gableson Avenue, Brighton, 5, Sussex.
Newton, Alan Branford. Needler Hall, Cottingham, Nr. Hull, Yorks.
Nutten, Albert John, Ph.D., F.R.I.C. Government Chemist's Laboratory, Hong Kong.
Nwaji, Martin Nwege. Hall Two, University College, Ibadan, Nigeria.
Oke, Olusegun Ladimeji. Mellamby Hall, University College, Ibadan, Nigeria.
Pincock, Richard E., B.S., A.M. Converse Chemical Laboratory, Harvard University, Oxford Street, Cambridge, 38, Mass., U.S.A.
Prout, Ernest George, M.Sc., Ph.D. Department of Chemistry, Rhodes University, Grahamstown, South Africa.
Poë, Anthony John, M.A., B.Sc. 87 Westgate, Chichester, Sussex.
Rafiq, Muhammad, B.Sc., B.Pharm. Department of Chemistry, School of Pharmacy, Brunswick Square, London, W.C.1.
Ransley, Derek Leonard, B.Sc. Sterling Chemistry Laboratory, Yale University, Prospect St., New Haven, Conn., U.S.A.
Ratcliffe, Neil Thomas. 33 White Hart Road, Chalvey, Slough, Bucks.
Redford, David George, B.Sc. 32 Welbeck Avenue, Bromley, Kent.
Ringold, Howard J., Ph.D. Research Laboratories, Syntex, S.A., Apdo. Postal 2679, Mexico, D.F., Mexico.
Roberts, John Angel. c/o Investigation & Research Div., Private Bag 28, Ministry of Animal Health, Kaduna, Northern Nigeria.
Roberts, Vivien Gabrielle. 74 Primrose Avenue, Chadwell Heath, Essex.
Rodwell, Kenneth, B.A. 68 Browning Road, Enfield, Middx.
Saracoğlu, Saim. Department of Chemistry, King's College, London, W.C.2.
Sheldrick, Peter, A.B. 2607 Piedmont Avenue, Berkeley, 4, California, U.S.A.
Sherman, Warren Vincent, B.Sc. 98 Herent Drive, Ilford, Essex.
Shipley, Dudley Keith, B.Sc., A.R.I.C. 25 Oakfield Avenue, Birstall, Leicester.
Speroni, Giovanni, D.Chem. Via Gino Capponi 9, Florence, Italy.
Steyermark, Paul R., Ph.D. W. R. Grace & Co., Research & Development Division, Clarksville, Maryland, U.S.A.
Taylor, David Robin, B.A. c/o Rectory, 1 Range Road, Whalley Range, Manchester, 16.
Teibo, Benjamin Olanrewaju. Kuti Hall, University College, Ibadan, Nigeria.
Wain, John Gordon. 248A Quarmby Road, Huddersfield, Yorks.
Wallace, Thomas Joseph, M.S. Department of Chemistry, University of Connecticut, Storrs, Conn., U.S.A.
Wessely, Friedrich, D.Phil. Wahringerstrasse 38, Vienna IX, Austria.
Willcocks, Doreen V. 39 Bay Street, Mosman, Sydney, N.S.W., Australia.