LETTERS TO THE EDITORS

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Structure of Dinitrogen Tetroxide

As the structure of the dinitrogen tetroxide molecule has recently been the subject of discussion[1], it may be of interest to record the following measurements, obtained from an X-ray study of single crystals of this compound. Previous diffraction work has been recorded by Vegard[2] and re-interpreted by Hendricks[3], but as this was confined to powder specimens the evidence is not conclusive.

In our present work, single crystals slowly crystallized from the gas were sealed into very thin-walled glass capillary tubes. These were maintained at a temperature of $-40°$ C. by means of a current of cold dry oxygen gas while being set and photographed on a Weissenberg type of X-ray spectrometer. Using copper $K\alpha$ radiation, complete rotation and oscillation photographs were obtained about the principal axes and diagonals of the unit cell.

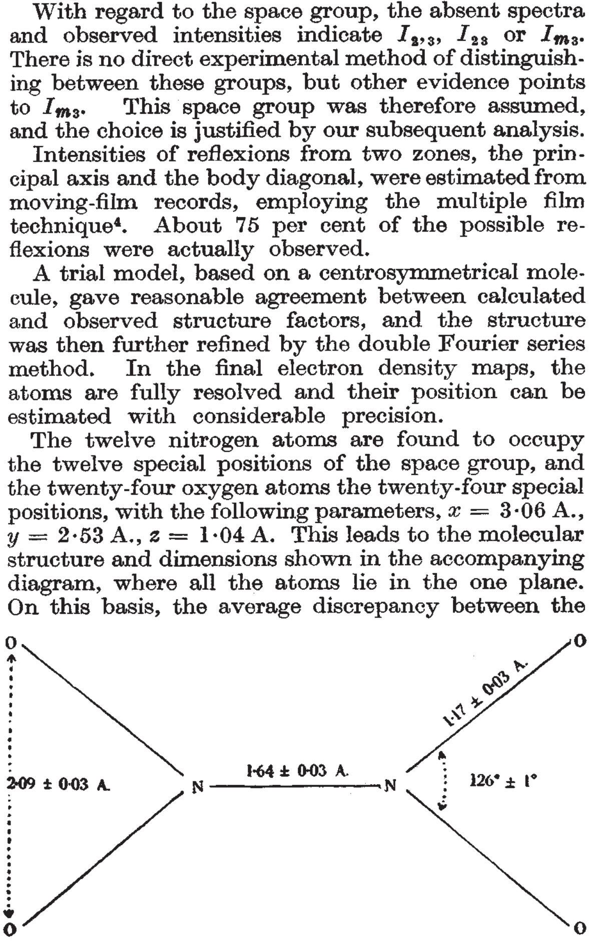
The system is apparently cubic, with $a = 7{\cdot}77 \pm 0{\cdot}01$ A., and the unit cell contains six molecules of N_2O_4 (density, measured, is 1·90–1·98, and calculated, 1·95 gm./c.c.). These results are in good agreement with previous work.

With regard to the space group, the absent spectra and observed intensities indicate $I_{2,3}$, I_{23} or I_{m3}. There is no direct experimental method of distinguishing between these groups, but other evidence points to I_{m3}. This space group was therefore assumed, and the choice is justified by our subsequent analysis.

Intensities of reflexions from two zones, the principal axis and the body diagonal, were estimated from moving-film records, employing the multiple film technique[4]. About 75 per cent of the possible reflexions were actually observed.

A trial model, based on a centrosymmetrical molecule, gave reasonable agreement between calculated and observed structure factors, and the structure was then further refined by the double Fourier series method. In the final electron density maps, the atoms are fully resolved and their position can be estimated with considerable precision.

The twelve nitrogen atoms are found to occupy the twelve special positions of the space group, and the twenty-four oxygen atoms the twenty-four special positions, with the following parameters, $x = 3{\cdot}06$ A., $y = 2{\cdot}53$ A., $z = 1{\cdot}04$ A. This leads to the molecular structure and dimensions shown in the accompanying diagram, where all the atoms lie in the one plane. On this basis, the average discrepancy between the calculated and observed F values is about 16 per cent for all the reflexions observed.



Dimensions of the dinitrogen tetroxide molecules

A point of special interest lies in the unusually long nitrogen – nitrogen bond of 1·64 A., the distance in hydrazine being about 1·47 A. The other bond-lengths and angles, being near the expected values, receive support from other investigations.

In conclusion, we would like to express our thanks to Dr. R. I. Reed for his interest in the work, and to Mr. R. McCulloch for help in building the complicated apparatus required.

J. S. Broadley
J. Monteath Robertson

Chemistry Department,
University, Glasgow, W.2.
July 13.

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[1] Ingold, C. K., and Ingold, E. H., *Nature*, **159**, 743 (1947).

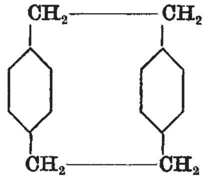
[2] Vegard, L., *Z. Phys.*, **68**, 184 (1931).

[3] Hendricks, S. B., *Z. Phys.*, **70**, 699 (1931).

[4] Robertson, J. M., *J. Sci. Instr.*, **20**, 175 (1943).

Preparation and Structure of Di-*p*-Xylylene

Polymerization products from *p*-xylene have been shown to contain, *inter alia*, a hitherto undescribed hydrocarbon, the novel structure of which has been determined solely by X-ray diffraction to be *tricyclo* [8 : 2 : 2 : $2^{4:7}$] hexadeca-4 : 6 : 10 : 12-(1) : 13 : 15-hexaene. We propose as a suitable trivial name 'di-*p*-xylylene'.



We have examined polymers made in these Laboratories by Messrs. Gill and Lord by the low-pressure pyrolysis of *p*-xylene using the technique described by Szwarc[1]. Extraction of the polymer with chloroform in a Soxhlet apparatus yielded a mixture of low molecular-weight compounds. This extract contained traces of an acetone-insoluble fraction, having m.p. 285° after re-crystallization from pyridine or glacial acetic acid. (The acetone-soluble fraction is being examined further.)

The crystals were found to be tetragonal, with $[a] = 7{\cdot}82$ A., $[c] = 9{\cdot}33$ A., space group $P4/mnm$-D_{4h}^{14}, and with two molecules to the unit cell. Further analysis, employing X-ray intensities from about 300 planes in appropriate Patterson and three-dimensional Fourier syntheses, showed the structure to be that of di-*p*-xylylene, as represented by the accompanying electron density diagram. The dimensions of the molecule are interesting. The three C—C aliphatic bond lengths are 1·54, 1·55 and 1·54 A., and the C—C bond lengths in the benzene rings are all 1·40 A., but the benzene rings are not quite flat. The two substituted carbon atoms in each benzene ring are each displaced from the plane of the other four by 0·13 A., presumably to relieve the strain in the system. The distance between the pairs of four unsubstituted carbon atoms is 3·09 A., and that between the substituted carbon atoms is 2·83 A. The angle between the bonds at the aliphatic carbon atom is 114½°.

This new hydrocarbon is analogous to *s*-dibenz*cyclo*octadiene (di-*o*-xylylene) described by Baker,

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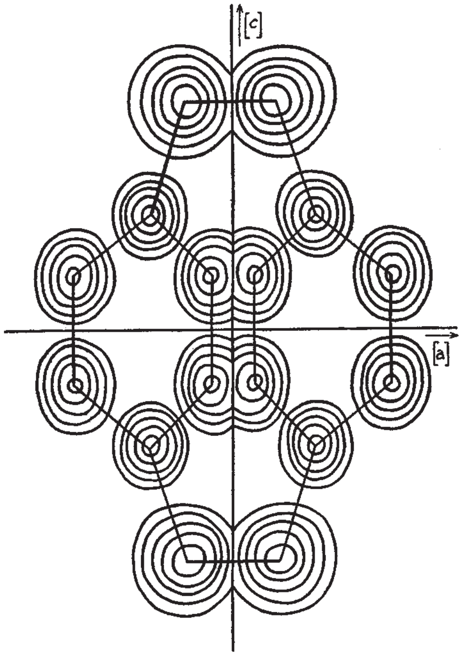

Composite three-dimensional electron density map of di-*p*-xylylene

Mann *et al.*[2]. Attempts to prepare di-*p*-xylylene by standard organic chemical methods have not been successful, and it is possible that the strained system may only be formed under drastic pyrolysis conditions and low pressures.

A fuller description of the properties and structure determination of this new hydrocarbon will be submitted for publication in the *Journal of the Chemical Society*. We are indebted to Dr. R. S. Cahn, of the Chemical Society, for consultation about nomenclature.

C. J. Brown
A. C. Farthing

Research Laboratories,
Imperial Chemical Industries, Ltd.,
Hexagon House,
Manchester 9.
June 29.

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[1] Szwarc, M., *J. Chem. Phys.*, **16**, 128 (1948).

[2] Baker, W., Banks, R., Lyon, D. R., and Mann, F. G., *J. Chem. Soc.*, 27 (1945).

Spectrographic Examination of Chromatographic Columns

In the determination of metallic traces, insufficient attention has been paid either to the advantages of direct spectrography of chromatographic columns, or to the chromatographic behaviour of organic metal complexes, although in the latter sphere the use of oxine[1] and of violuric acid[2] has been reported.

Working with alumina as adsorbent and using dithizone complexes, we have established the position of a number of metals in the undeveloped column by cutting it into a series of short sections and examining these sections spectrographically. We have concentrated initially on the estimation of very small traces of cadmium, and the procedure outlined below for this element illustrates the general technique.

The sample solution (normally acid) is made ammoniacal in the presence of ammonium citrate, and is then completely extracted with a solution of dithizone in carbon tetrachloride. A column of activated alumina (Spences 'H' 100–200 mesh) 5 cm. long and 4 mm. in diameter is prepared, and the extract after washing and filtration is poured through, using suction. The first centimetre, which normally weighs between 100 and 130 mgm., is cut out and retained for the estimation of cadmium.

Spectrographic examination is carried out using a carrier-distillation technique similar to that described by Scribner and Mullin[3], but employing silver chloride[4] as carrier and arsenic as internal standard. The anode cup-charge of 40 mgm. is subjected to a direct-current arc of 10 amp., and duplicated spectra are photographed on a Kodak *B*10 plate, using a Hilger large quartz spectrograph. The ratio of strengths of cadmium 2288·0 A. and arsenic 2288·1 A. is determined and compared with that of standard samples photographed on the same plate. Quantities of cadmium between 0·1 and 0·5 μgm. can conveniently be determined by the method with a standard deviation of 10 per cent. This represents concentrations of between 0·02 and 0·1 parts per million on a 5-gm. sample; this sample weight can, of course, be varied to enable a wider range of concentrations to be covered. With special care, a quantity of cadmium as small as one-fiftieth of a microgram can be detected qualitatively.

It is planned to extend the procedure to include other elements amenable to chromatographic treatment, using dithizone or other reagents.

The permission of the Chief Scientist, Ministry of Supply, to make this communication is acknowledged.

J. E. Dunabin
H. Mason
A. P. Seyfang
F. J. Woodman

Chemical Inspectorate,
Ministry of Supply,
Springfields, Lancs.
July 8.

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[1] Erlenmeyer and Dahn, *Helv. Chim. Acta*, **22**, 1369 (1939).

[2] Erlenmeyer and Schoenauer, *Helv. Chim. Acta*, **24**, 878 (1941).

[3] Scribner and Mullin, *J. Res. Nat. Bur. Stand.*, **37** (December 1946).

[4] Harrison and Kent, U.S. Atomic Energy Research Report *MDDC* 1581 (declassified).

Diffusion in Ion-Exchange Media

During an investigation into the behaviour of solutions of direct cotton dyes of the aromatic azo sodium sulphonate type on ion-exchange materials, it was found that selective penetration of the resin structure occurs.

Solutions containing the derived sulphonic acids of a number of dyes of relatively high molecular weight were obtained (together with the inorganic acids derived from the salts present in the commercial products) by treatment with the cation-exchange 'Zeokarb 215' operating on the hydrogen cycle. These solutions, when passed through the acid-absorbing, anion-exchange resin 'De-Acidite B', gave an effluent containing the pure dye acid with, apparently, little absorption of the dye on the basic resin. This was unexpected as the dye acids were thought to be highly dissociated in solution, and this was afterwards confirmed by electrometric titration.

Cernescu[1] has shown that the effective capacity of the natural zeolite, chabazite, for the substituted ammonium ion decreases with increasing ionic radii. Kunin and Winters[2] have also shown a similar de-

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