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.

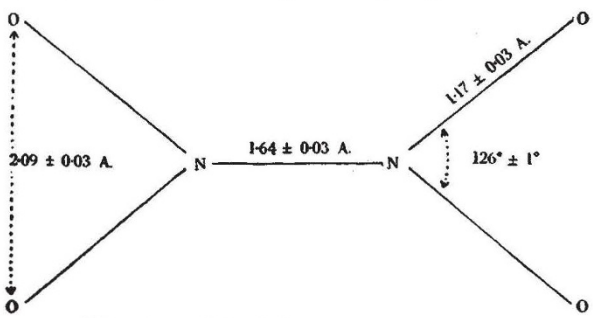
The system is apparently cubic, with $a = 7{\cdot}77 \pm 0{\cdot}01$ A., and the unit cell contains six molecules of N_2O_4 (density, measured, is 1·90–1·98, and calculated, 1·95 gm./c.c.). These results are in good agreement with previous work.

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.

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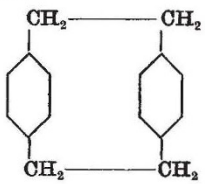
July 13.

[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 tri*cyclo* [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,