09.2-22 11-METHYLBENZ[*a*]ANTHRACENE: AN ALMOST PLANAR SUBSTITUTED BENZ[*a*]ANTHRACENE.

By C.E. Briant and D.W. Jones, School of Chemistry, University of Bradford, W. Yorkshire, BD7 1DP, England.

In continuation of an X-ray and neutron-diffraction investigation into the structures of parent and substituted polycyclic hydrocarbons relevant to carcinogenesis, we have determined the structure of 11-methylbenz[*a*]anthracene (11-MBA) from crystals kindly supplied by Professor M.S. Newman. 11-MBA, $C_{19}H_{14}$, almost inactive carcinogenically, crystallizes in an orthorhombic cell with dimensions 14.34 x 14.52 x 12.30 Å, Z = 8, space group *Pcab*, with one molecule in the asymmetric unit. From X-ray intensity data collected with MoK_α radiation on a Syntex *P*2_1 diffractometer with the help of Dr. W.S. McDonald (Leeds University), the structure was solved by the centrosymmetric direct-methods program in the SHELX 76 suite. Following Fourier difference syntheses for hydrogen location, anisotropic least-squares refinement ultimately reduced *R* to 0.05 over 955 independent reflections. Except at the substituent carbon, the C-C bond lengths (e.s.d. 0.006 Å) are much closer to those for the mean benz[*a*]anthracene structure derived from the structures of 1-MBA [Jones and Sowden, Cancer Biochem. Biophys., 4, 43 (1979)] and other methyl-substituted benz[*a*] anthracenes than to those of the BA parent in the complex of BA with pyromellitic anhydride [Foster, Iball, *et al.*, J.C.S. Perkin II, 682 (1976)]. The BA nucleus of 11-MBA is much more nearly planar than in the other methyl-substituted benz[*a*] anthracenes studied, with the benzo-ring inclined at 1.5° to the other rings; C(9) deviates most (0.04 Å) from the mean plane through all the ring-carbon atoms.

09.2-23 INDICATIONS OF ABSOLUTE CONFIGURATION FROM ANOMALOUS DISPERSION OF OXYGEN IN TWO NATURAL PRODUCTS:

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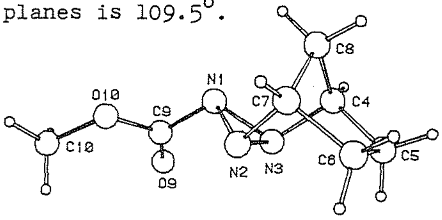
The crystal structure of cordifene epoxide ($C_{20}H_{24}O_8$) has been determined by direct methods and refined to R 3.62% over 1818 observed reflections. Similarly the crystal structure of epoxy rotenonic acid acetate ($C_{25}H_{26}O_8$) was determined and refined to R 4.41% over 1774 observed reflections. Both compounds are chiral (space group $P2_12_12_1$) and in view of the high oxygen content and reasonably good refinement, it was decided to investigate their absolute configuration with the anomalous dispersion of oxygen. The differences in R value for the two configurations were in each case statistically significant but unconvincing.

Both structures could be compared to similar compounds (of the same absolute configuration from chiroptical methods) whose absolute configuration had been determined crystallographically using the much larger anomalous dispersion of bromine (in one case measured subsequently to the above investigation). With the correct absolute configuration thus known by other methods, it was seen that for cordifene epoxide the wrong configuration was indicated by the statisically very significant differences in R value including anomalous oxygen whereas the correct configuration was indicated by the weighted R values although of dubious statistical significance. For epoxy rotenonic acid acetate there was no indication from the R values but the weighted R values gave the wrong configuration with statistical significance. Broadly similar results were obtained when the anomalous dispersion of carbon was also included in the calculations.

09.2-24 CRYSTAL STRUCTURE OF 1-METHOXYCARBONYL-2,3-(CYCLOPENTA-1,3-DIYL)-TRIAZIRIDINE.

By R.Prewo and J.H.Bieri, Organisch-Chemisches Institut der Universität Zürich, Switzerland.

The compound was synthesized by H.Hilpert in the group of Prof.Dreiding following a method previously published (C.Leuenberger, L.Hoesch, A.S.Dreiding, J.C.S.Chem.Comm., 1980, 1197-1198). To our knowledge this is the first crystal structure of a molecule containing a triaziridine ring.
The structure was determined from diffractometer data, space group $P2_1/c$, a=6.52, b=10.99, c=11.12Å, β=97.0°, 2752 independent reflections above 2.5σ(I), T~-140°C, R=0.037. As the refinement has not yet been completely finished, very small changes in the values may still occur.
All N-atoms have tetrahedral configuration. The N-N-C angles are 107±3.5°. The angle between the triaziridine and the C7-N2-N3-C4 plane is 104.5°. Selected bond lengths are N1-N2=1.479, N1-N3=1.458, N2-N3=1.490, N1-C9=1.438, N2-C7=1.503, N3-C4=1.504Å with standard deviations of 0.002Å as calculated from least-squares. The ester group is not vertical to the triaziridine ring but the angle between the two planes is 109.5°.



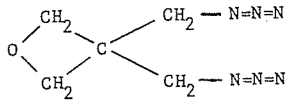
09.2-25 MOLECULAR STRUCTURE STUDIES ON ENERGETIC AZIDO COMPOUNDS.

By R. Gilardi and C. F. George, Laboratory for the Structure of Matter, Naval Research Laboratory, Washington, D. C. 20375, U.S.A.

Elastomeric polymers are used as stabilizing binders to make safer solid fuel propellant mixtures. If energetic substituents, such as nitro or azido groups, can be added to the polymer without loss of stabilizing properties, an increase in energy yield is obtained.

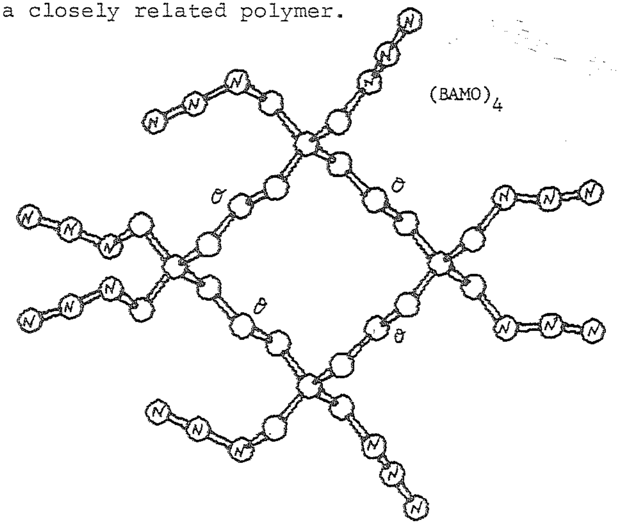
An elastic polymer with azido substitution can be made from 3,3-bis-azidomethyloxetane (BAMO). This monomer is a liquid at room temperature. Its vapor, at 120°C., was studied using gas electron diffraction techniques and the results will be presented.

(BAMO)



A cyclic tetramer of BAMO is usually formed as a side product during polymerization. The tetramer was leached from a polymer sample by soaking in chloroform and was crystallized. It crystallizes in the space group Pbcn with a = 12.07, b = 15.22, c = 18.18Å., and has one half molecule per asymmetric unit. The molecule contains 4 independent (8 total) methyl-azido groups, and difference map peaks indicate torsional disorder in the vicinity of at least 2 of these side-chains.

Finally, a study of the *X*-ray diffraction of the linear (as opposed to cross-linked) polymer of BAMO is in progress. Low angle ($2\theta \leq 40^{\circ}$) powder patterns can be obtained from untreated samples, indicating a tendency towards crystallization. Partially aligned fibrous samples have been obtained by drawing out films which were heated to the melting (softening) point. The fiber patterns, which are limited to a few strong reflections, appear to be monoclinic (or possibly triclinic) with a fiber repeat of c = 4.6 Å. This short repeat is consistent with a non-helical planar zigzag backbone, as is found in some forms of fibrous polyoxetane, a closely related polymer.



09.2-26 THE CONFORMATION OF HETEROCYCLIC SPIRO COMPOUNDS. X. THE STRUCTURE OF N-(γ-HYDROXYPROPYL)-GRANATANINE-3-SPIRO-5'-HYDANTOIN MONOHYDRATE ($C_{13}H_{23}N_3O_4$).

By F. Florencio, P. Smith-Verdier and S. García-Blanco. Departamento de Rayos X, Instituto Rocasolano, CSIC, Serrano 119, Madrid (6), Spain.

This structure has been determined to check the conclusions drawn by Avendaño and Bellanato (1980) from IR studies which showed that the N atom belonging to the two piperidine rings was a quaternary N. In all other compounds of this series this N atom is ternary. The structure was solved by use of the program MULTAN (Main, Woolfson, Lessinger, Germain, Baggio and Declercq, 1978). The refinement was carried out by several cycles of full-matrix least squares with isotropic and anisotropic thermal parameters. The H atoms were located in a difference map (except the water H atoms) and included in the refinement with isotropic temperature factors. The final R values were R=0.052 and R_w=0.066. The bicyclo nonane system adopts a boat-chair conformation.

The quaternary character of the piperidinic N deduced from IR studies has been confirmed. This quaternization is due to proton transfer from the hydantoin ring to the basic piperidine N. Consequently a "zwitterion" structure is present. This structure is stabilized by the water molecule.

An intricate three dimensional network holds the molecules together.

09.2-27 THE CRYSTAL STRUCTURE OF 7,11-DIPHENYLSPIRO [5,5] UNDECANE-1,9-DIONE.

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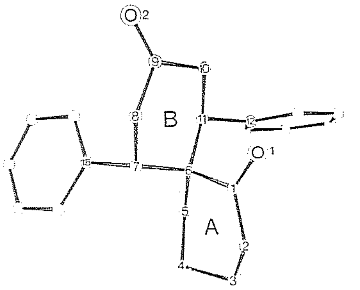
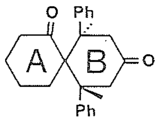
7,11-diphenylspiro[5,5] undecane-1,9-dione(I) reacts readily with bromine to yield a variety of products, four of whose crystal structures have been determined (Sommerville and Laing, Acta Cryst., B34, (1978) 670; 672; 674; 676). While one was a simple tribromo-substitution product, three were oxygen-bridged derivatives resulting from attack by the keto oxygen (1) of ring A on the carbon atoms (9) or (10) of ring B. The non-bonded separations between these atoms in the parent compound(I) were of interest, and the crystal structure was therefore determined.

The unit cell is monoclinic, C2, a = 18.52(1), b = 9.770(5), c = 20.24(1)Å, β = 101.68(5)°, V = 3586.2 Å^3. Z = 8, D_m = 1.23 g cm^{-3}, i.e. two molecules per asymmetric unit. Data were collected on a Philips four-circle diffractometer (C.S.I.R., Pretoria) with graphite-monochromated Mo Kα radiation for θ between 3 and 25°. Of 3275 reflexions measured, 1820 were classed as observed; $I > 1.65\sigma(I)$. The structure was solved after some difficulty by Direct Methods, and refined anisotropically by block-diagonal lease squares to a final R of 0.062 (H atoms included).

The two molecules in the asymmetric unit are a racemic pair. Other than the chirality, there are no major differences between the two molecules; even the torsion angles are of almost identical magnitude. The six-membered rings A and B are both slightly distorted chairs; the phenyl ring at C(7) is axial, while that at C(11) is equatorial. The non-bonded contacts between the keto oxygen on ring A and the pertinent carbon atoms on ring B are short; O(1)···C(8) = 3.31, 3.30; ···C(9) = 3.36, 3.40; ···C(10) 2.88, 2.90 Å. The analogous distances in the tribromo derivative are 3.03, 3.33 and 2.89 Å respectively. It is quite clear that it is these close contacts that allow the facile O-bridging to occur, and that substitution of hydrogen by bromine atoms alpha to the keto groups causes surprisingly little change to the conformation of the rings.





(I)

There are no close intermolecular contacts. However, in projection down either x or y, the molecules are related by a pseudo mirror, with the phenyl rings parallel to the plane of projection. This parellelism causes a regularity in the arrangement of the atoms and hence has a marked effect on the intensity statistics. This was a cause of difficulty in the solution of the structure. This case of a racemic pair of molecules per asymmetric unit in space group C2 is certainly unusual, if not unique.