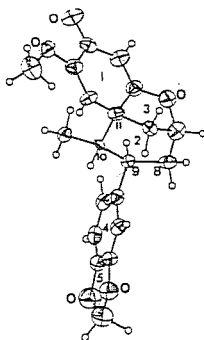


09. STRUCTURES OF ORGANIC, ORGANOMETALLIC AND COORDINATION COMPOUNDS

09.2-14 THE CONFORMATIONAL ANALYSIS OF FUTOENONE - A NOVEL SPIRO-CYCLO HEXADIENONE DERIVATIVE. By Sandhya Roychowdhury and M. Ghosh, X-ray Laboratory, Presidency College, Calcutta, and P. Roychowdhury, Department of Physics, University College of Science, Calcutta.

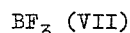
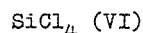
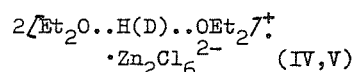
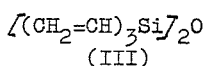
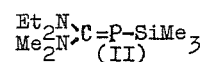
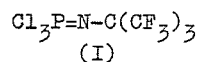
To study the unusual conformation of the title compound ($C_{20}H_{20}O_3$) and consequently find an answer to some of its chemical activity, the structure analysis was undertaken. The compound crystallizes in the orthorhombic space group $P2_12_12_1$, with 4 molecules in the unit cell of dimensions $a=6.1269$, $b=14.256$, $c=18.436$ Å. The X-ray data were collected on a Nonius CAD-4 diffractometer with graphite monochromated $MoK\alpha$ radiation. The structure was determined by direct methods and refined anisotropically by block diagonal least squares to a final R of 0.073 for 1190 reflections for $F > 3\sigma(F)$.

All atoms of the semiquinone moiety (ring 1) except C(11) lie on a plane since the torsion angles associated with this group were within 6° of zero. The cyclohexane group which assume a distorted chair configuration is severely strained. Unusual lengthening of C(10)-C(11) bond (1.589) was observed which may be attributed to the hinging of the 2-methoxy semiquinone group around C(11). The semiquinone ring has a tendency to acquire a planar form which therefore tends to bring the off-plane C(11) to its plane thereby distorting the tetrahedral configuration and pulling the associated C(10)-C(11) bond. C(9)-C(10) bond (1.565) and C(9)-C(8) bond (1.577) are strained by the bulky group methylene dioxy phenyl (ring 4 and 5) being linked to C(9). The semiquinone and the cyclohexane moieties are twisted with respect to each other about C(11) to form the 5,5,0 spiro undecan. The opening of this spiro with acetic acid is attributed to the strained configuration. The five-membered tetrahydrofuran (ring 3) is a half chair and the ring containing the methylene dioxy group (ring 5) acquires an envelope type conformation. Intermolecular distances indicate that the van der Waals forces are the predominant type of interaction that stabilises the structure.



09.2-15 LOW TEMPERATURE X-RAY STUDIES OF COMPOUNDS, LIQUID AND GASEOUS AT ORDINARY CONDITIONS. By M.Yu. Antipin and Yu.T. Struchkov, Nesmeyanov Institute of Organoelement Compounds of the USSR Academy of Sciences Moscow USSR

Low temperature X-ray experiments essentially expand possibilities of the X-ray analysis in investigation of organic and organoelement compounds which are liquid or even gaseous at ordinary conditions. We have developed and successfully used for more than 20 structures a simple technique for growing monocrystals of substances with melting points in the range from 0 to $-130^\circ C$ directly on an autodiffractometer equipped with low temperature device. Monocrystals of a quite good quality, suitable for an X-ray study, are obtained either by a "zone" melting method or simply by a very slow cooling of the samples of well-crystallizing liquids, sealed in thin-walled capillaries (the cooling speed near m.p. is 0.1-0.3 degr/hr.). Here are some interesting examples of the structures studied



The P=N bond length in I is shortened to 1.505 Å, while the bond angle at N atom is increased to 142.9° . These values are the more prominent for acyclic phosphazo compounds.

On the contrary, in the derivative II of two-coordinated phosphorus the P=C bond length is increased to 1.761 Å. These unexpected values of geometrical parameters in I and II are due to electronic factors and steric effects. The quantum-chemical calculations of electronic structure II are in a full agreement with the X-ray data. In disiloxane III a rather rare linearity of the SiOSi moiety is found with bond length Si-O 1.614 Å. In the novel cations IV and V the length of the very strong hydrogen bond O..H(D)..O is equal to 2.396 Å regardless of the nature of the central (H or D) atom. This fact is an evidence of the single-minimum potential of this hydrogen bond. The specific character of this bond is manifested in IR spectra. The molecular packing in crystal VI is similar to that of CCl_4 before studied. In crystal of VII, which is gaseous substance at room temperature, BF_3 molecules are planar, while B atoms are extra-coordinated by F atoms of surrounding molecules (B...F 2.6-2.7 Å). All diffraction experiments were performed on "Syntex P2" diffractometer at $-120^\circ C$ ($-150^\circ C$ for BF_3). "Zone" melting method for crystal growing was described earlier (Kravets, Antipin, Kulishov, Struchkov, Kristallographia (1977) 22, 1118).