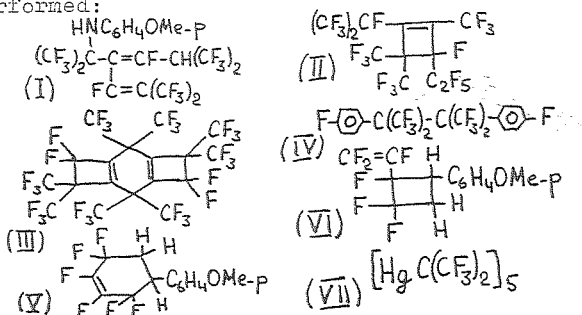


09.2-39 THE STRUCTURES OF POLYFLUOROORGANIC COMPOUNDS. By M. Yu. Antipin, Yu. T. Struchkov Nesmeyanov Institute of Organo-Element Compounds, Academy of Sciences, Moscow, USSR.

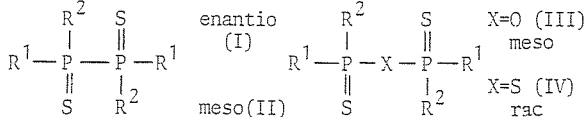
In order to establish peculiarities of molecular geometry of new polyfluoroorganic compounds caused by the presence of a considerable number of electron-accepting fluorine atoms and bulky CF₃-groups the X-ray study of following representatives of this series was performed:



Results of the present structural study of I, II, V-VII allowed to elucidate the mechanism of their formation. The comparison of molecular parameters I-VII shows that the introduction of electron-accepting bulky CF₃-groups causes the considerable lengthening of single C-C bonds (up to 1.671 Å in IV) and distortions of bond angles at sp²-hybridized carbon atoms. The fluorine substitution at ethylene carbons gives rise to the shortening of C=C double bonds (e.g. 1.300 Å in V and VI).

09.2-40 CONFIGURATIONS AND CRYSTAL STRUCTURES OF DIPHOSPHINEDISULFIDES AND DERIVATIVES. By D. Mootz, H. Wunderlich, H.-G. Wussow, Institut für Anorganische Chemie und Strukturchemie, Universität Düsseldorf, Germany

For NMR investigations and model calculations Hägele, Tossing et al. (J.C.S. Dalton, in prep.) synthesized a series of stereoisomeric organo-diphosphinedisulfides (I, II) and related oxanes (III) and sulfanes (IV). We report four crystal structures of these (R¹=bu^t, R²=me):



Crystallographic and experimental data are given in the Table. Structure determinations were carried out routinely. I and II were identified as a stereoisomeric pair of an enantiomeric and the meso form, resp., with an av. distance P-P of 2.267(1) Å. The torsion angle S-P-P-S in I is 78° (abs. conf. not det.) while it has to be 180° in II (point symmetry $\bar{1}$ of the molecule). III was identified as meso and reveals an angle P-O-P of 138.5(3)° and an av. distance P-O of 1.625(6) Å while IV is rac with P-S-P 104.8(1)° and a linking av. P-S of 2.124(1) Å.

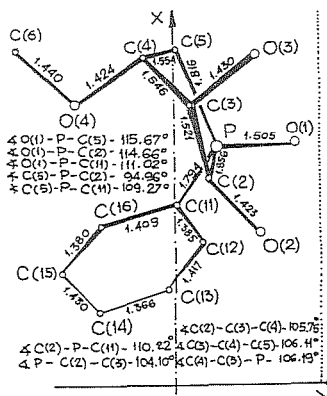
| Compd. | (I) | (II) | (III) | (IV) |
|-----------------------|-----------------|-------------|-----------|-----------|
| a [Å] | 6.582(4) | 6.765(1) | 18.186(3) | 12.297(1) |
| b | 14.663(5) | 7.788(3) | 8.250(3) | 13.432(1) |
| c | 3.463(5) | 8.060(3) | 11.318(3) | 20.069(2) |
| α [°] | | 73.39(3) | | |
| β | 110.27(4) | 64.94(2) | 108.26(2) | |
| γ | | 80.54(3) | | |
| sp. gr. | P2 ₁ | P $\bar{1}$ | Cc | Pbca |
| Z | 2 | 1 | 4 | 8 |
| R; R _w [%] | 6.9; 5.9 | 3.3; 4.1 | 4.4; 4.6 | 4.9; 6.1 |

09.2-41 THE STRUCTURE OF THE PRECURSOR OF PHOSPHATETRAFURANOS: 2,3-DIHYDROXY-4-METHOXY-1-PHENYLPHOSPHOLANE 1-OXIDE, C₁₁H₁₅O₄P.

By Z. Gałdecki, Institute of General Chemistry, Technical University of Łódź, 90-924 Łódź, Poland.

This study is a continuation of our X-ray investigations on the structures and conformations of phospholane and phospholene derivatives. The title compound (I) was first prepared by R. Bodalski and T. Janecki from 4-hydroxy-1-phenyl-2-phospholene-1-oxide by hydroxylation of the double bond with the protected hydroxyl group at C(4) (Private communication (1980)). The structure of the above mentioned intermediate compound has already been reported (Gałdecki and Głowska, Acta Cryst. (1980) B36, 1495-1497). The phosphafuranoses are very interesting not only from the point of view of their chemistry but also because of their potential biological activity (Takayanagi et al., Carbohydr. Res. (1978) 68, 105-113). The present study was started with two aims: to compare the conformations of P-containing five-membered rings in the absence of an unsaturated bond and to assign relative configurations at the P(1), C(2), and C(3) atoms to elucidate the mechanism of the stereospecific reaction in which the molecule was formed.

The compound crystallizes in the monoclinic space group Cc with a=14.417(1), b=11.588(1), c=8.0214(8) Å, $\beta=120.812(6)^\circ$ and Z=4. The intensities of 1260 independent reflexions were collected on a Syntex P2₁ diffractometer using copper radiation. The structure was solved by direct methods (MULTAN) and refined by full-matrix least-squares to a final R of 0.041 using the XRAY 76 system. The positions of all H atoms were found from ΔF syntheses and were refined isotropically. The remaining atoms were refined assuming anisotropic temperature factors. All the three oxygen atoms at



P(1), C(2) and C(3) are in cis configurations. The molecules are linked into chains parallel to [001] (through the glide c) by bifurcated (at O(1)) hydrogen bonds with O(1)···O(2) and O(1)···O(3) distances of 2.75(1) and 2.68(1) Å, respectively. Bond lengths and valency angles found in the structure are close to those reported earlier for 2-hydroxy-5-hydroxy-methyl-1-phenylphospholane-1-oxide (II), 2-hydroxy-2-methyl-1-phenylphospholane-1-oxide (III) and 2-hydroxy-1-phenylphospholane-1-oxide (IV) (Gałdecki and Głowska, Acta Cryst. (II) (1980) B36, 2809-2812. (III) *ibid.* (1980) B36, 2191-2193. (IV) *ibid.* (1981) in the press), if differences in chemical formulae are taken into account. However, surprisingly high differences in the phospholane ring conformation are visible. In (IV) the ring adopts a nearly ideal half-chair conformation with a twofold axis through the P atom, whereas in (I), (II) and (III) the phospholane rings have C(3) sofa conformations. The differences in asymmetry parameters result from the different position of the substituents, especially those participating in hydrogen bonding. The substituent at position 2 and 5 appears to affect the ring conformation most. In the structural formulae the best mirror plane or two-fold axis are shown.

