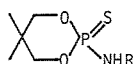


09.2-44 THE STEREOCHEMISTRY OF PHOSPHORUS HETEROCYCLES. STRUCTURES OF THREE NEW 2-AMINO-1,3,2-DIOXAPHOSPHORINANE 2-SULFIDES.

By W.M. Wolf, Technical University of Łódź, Łódź, Poland.

In attempt to study the electronic and steric interactions making an influence on the conformation of heterocycles containing phosphorus, the structures of three 2-amino-5,5-dimethyl-1,3,2-dioxaphosphorinane-2-sulfides were determined by x-ray analysis.



R=ethyl (A)  
3,5-dichlorophenyl (B)  
o-nitrophenyl (C)

All these compounds were synthesised by the conventional reaction of 2-chloro-5,5-dimethyl-1,3,2-dioxaphosphorinane with ethylamine, 3,5-dichloroaniline and o-nitroaniline respectively and subsequent addition of elemental sulfur.

**Crystal data:** (A)  $a=15.554(1)$ ,  $b=7.616(1)$ ,  $c=19.792(2)$  Å,  $\beta=104.802(7)^\circ$ ,  $I2/c, z=8$ ; (B)  $a=9.733(1)$ ,  $b=6.992(2)$ ,  $c=22.112(2)$  Å,  $\beta=102.56(1)^\circ$ ,  $P2_1/n, z=4$ ; (C)  $a=10.143(3)$ ,  $b=19.710(4)$ ,  $c=6.789(1)$  Å,  $\beta=94.75(2)^\circ$ ,  $P2_1/c, z=4$ .

Data were collected on a CAD4 diffractometer (MoK $\alpha$ ). Structures were solved with direct methods and refined to  $R=0.033$ ,  $0.039$  and  $0.031$  respectively.

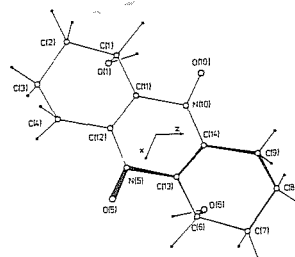
In all the cases dioxaphosphorinane rings adopt a flattened chair conformation. This might be explained by the anomeric effect which causes an increase of electron density around phosphorus (Van Nuffel et al. Cryst. Struct. Commun. (1980) 9, 733). The P=S double bond lengths are  $1.925(1)$ ,  $1.916(1)$  and  $1.915(1)$  Å respectively and correspond well with values found in similar compounds. The configurations around nitrogen atoms are almost planar (details will be discussed) with P-N bond lengths equal  $1.605(2)$ ,  $1.662(2)$  and  $1.667(1)$  Å respectively. The striking differences between P-N bond lengths lying in the equatorial (A) and axial (B), (C), positions are presumably caused by the  $p_\pi-d_\pi$  conjugation. The overlapping of the phosphorus  $d$  with the nitrogen  $\pi$  orbitals seems to be better in equatorial rather than in axial position. This effect is not strongly pronounced in the P=S bond because of the partially dipole character of this bond.

**Acknowledgments:** The University of Oxford Crystallographic Fund, Oriel College Oxford and British Council are gratefully acknowledged for the scholarship in the University of Oxford Chemical Crystallography Laboratory during which the data collection and the computations were performed.

09.2-45 THE STRUCTURE OF trans-1,6-DIHYDROXY-1,2,3,4,6,7,8,9-OCTAHYDROPHENAZINE 5,10-DIOXIDE, C<sub>12</sub>H<sub>16</sub>N<sub>2</sub>O<sub>4</sub>. By Z. Gaidecki\*, P. Grochulski and Z. Wawrzak, Institute of General Chemistry and Institute of Physics, Technical University of Łódź, Żwirki 36, 90-924 Łódź, Poland.

This work is a part of X-ray studies of octahydrophenazine derivatives (Gaidecki Z., Grochulski P. and Wawrzak Z. (1984). Acta Cryst. C40, in the press). The title compound crystallized in the space group  $P2_1/a$  with  $Z=2$ ,

$a=10.720(3)$ ,  $b=5.524(1)$ ,  $c=10.537(3)$  Å,  
 $\beta=114.03(2)^\circ$ ,  $V=569.9(1)$  Å<sup>3</sup>,  $D_m=1.465$ ,  $D_x=1.470$  Mg m<sup>-3</sup>,  $\mu(\text{CuK}\alpha)=0.64$  mm<sup>-1</sup>,  $F(000)=488$ . The intensities were collected on a Syntex P2<sub>1</sub> diffractometer.



The structure was solved by direct methods (MULTAN) and refined to a final  $R=0.043$  for 911 unique reflections. The view of the centrosymmetric molecule along [010] is shown in the picture. The six-membered saturated

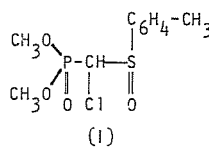
rings exist in half-chair conformations with asymmetry parameters:  $\Delta C_2^{7,8}=0.7(6)$ ,  $\Delta C_s^6=46.6(6)$  and  $\bar{\varphi}=32.7(3)^\circ$ . The both symmetrically equivalent C-O bonds are in axial positions, in trans configuration. This research was supported by the project MR.I.9 from the Polish Academy of Sciences.

09.2-46 THE CRYSTAL STRUCTURES OF THE  $\alpha$ -METHYL-(II) AND  $\alpha$ -CHLORO-(I)-(DIMETHYLPHOSPHORYL)-METHYL-p-TOLYLSULPHOXIDE

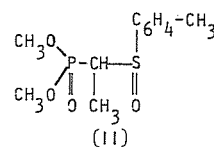
By A. Miller, M.W. Wieczorek and J. Karolak-Wojciechowska

Technical University of Łódź, 36 Żwirki, 90-924 Łódź, Poland

In the present work we describe the crystal structures of two  $\alpha$ -phosphorylsulfoxide (I) and (II). This compounds are interesting models for the study on  $\alpha$ -halogenation of chiral dimethylphosphorylmethyl-p-tolylsulfoxide. Especially it seems to be interesting in view of the significant role of conformational and electronic factors in the mechanism of these reaction.



$P2_12_12_1$ ;  $a=7.254(1)$   
 $b=7.718(1)$ ,  $c=23.893(4)$  Å;  
 $z=4$ ,  $R=0.0804$

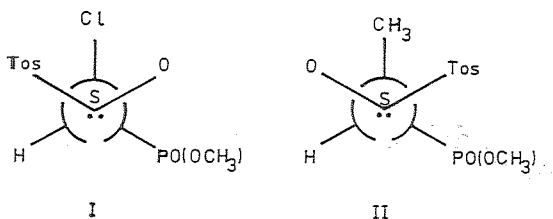


$P2_12_12_1$ ;  $a=24.030(3)$   
 $b=7.239(1)$ ,  $c=7.754(1)$  Å;  
 $z=4$ ,  $R=0.085$

The structures has been solved on the bases of diffractometer data by direct methods and refined by full-matrix least-squares.

## 09. STRUCTURES OF ORGANIC, ORGANOMETALLIC AND COORDINATION COMPOUNDS

On the basis of presented structure data (see the projection below), it is known that chlorination of  $\alpha$ -phosphorylsulfoxides occurs with prevailing retention of the configuration at the carbon atom.

09.2-48 CRYSTAL AND MOLECULAR STRUCTURE OF 3-(*o*-HYDROXYPHENYL)-1-PHENYLTRIAZENE 1-OXIDE,  $C_{12}H_{11}N_3O_2$ .

By S.K. Talapatra, S.B. Sarkar, S.C. Saha, P.K. De and Chitra Samanta, Department of Physics, Jadavpur University, Calcutta-700032, India.

In order to confirm the N-oxide form as revealed from IR studies and to establish the nature of hydrogen bonds, if any, it was considered necessary to investigate the structure of triazenes having ortho-substituents. From Weissenberg photographs and single crystal diffractometry at room temperature (300°K), the deep brown crystals of the title compound were shown to be

monoclinic,  $P2_1/n$ ,  $M_r = 229.0$ ,  $a = 6.569(2)$ ,  
 $b = 11.870(4)$ ,  $c = 13.889(4)\text{\AA}$ ,  $\beta = 94.95(2)^\circ$ ,  
 $V = 1079(1)\text{\AA}^3$ ,  $Z = 4$ ,  $D_x = 1.38\text{ g cm}^{-3}$  (aq. KI),  
 $D_c = 1.41\text{ g cm}^{-3}$ ,  $\lambda(\text{MoK}\alpha) = 0.71073\text{\AA}$ ,  $\mu = 1.06\text{ mm}^{-1}$ .

1997 independent reflections with  $2\theta < 50^\circ$  were recorded. The structure was solved by direct methods using the MULTAN programs. The H-atoms were located by Fourier methods and also from the known geometry around C-atoms. The non-hydrogen atoms were refined anisotropically and H-atoms isotropically. The final discrepancy indices for 1449 observed reflections were  $R = 0.040$  and  $R_w = 0.062$ .

The molecules are nearly planar and have intramolecular N-H...O hydrogen bonds. The crystal structure is stabilized by a network of intermolecular O-H...O hydrogen bonds. The structure establishes the N-oxide form of triazene as in the case of 3-(*o*-carboxyphenyl)-1-phenyltriazene 1-oxide previously reported (*Acta Cryst.*, 1983, C39, 1075).

09.2-47 CONFORMATIONAL ANALYSES OF TWO 8 $\beta$ -*t*-BUTYL-*CIS*-DECAHYDROQUINOLINE SALTS: TWO DIFFERENT RING CONFORMATIONS

By Kay D. Onan and Martha Estes, Department of Chemistry, Northeastern University, Boston, MA 02115 and Friedrich W. Vierhapper, Institut für Organische Chemie, Universität Wien, A-1090 Wien, Austria

As a part of our investigation of the conformations of saturated six-membered rings bearing axial *t*-butyl groups, we have prepared the picrate (I) and chloride (II) salts of 8 $\beta$ -*t*-butyl-*cis*-decahydroquinoline and have determined their crystal structures. Both I and II crystallize in monoclinic space groups,  $I_0$  in  $P2_1/c$  with  $a = 13.335(2)$ ,  $b = 8.584(1)$ ,  $c = 22.419(3)\text{\AA}$ ,  $\beta = 126.29(1)^\circ$ ,  $Z = 4$ . Salt II crystallizes in space group  $C2$  with  $a = 17.035(1)$ ,  $b = 7.2880(5)$ ,  $c = 25.048(2)\text{\AA}$ ,  $\beta = 109.90(1)^\circ$ ;  $Z = 8$ . The structures were solved by direct methods and refined by full-matrix, anisotropic (Cl, O, N, C) least-squares to a present  $R$  of 9.3% over 2284 reflections for I and to  $R = 3.9\%$  over 2296 reflections for II. The rather high  $R$  value for I is due to disorder in the picrate anion. Surprisingly, the two molecules which compose the asymmetric unit of II are a racemic pair which displays essentially no difference in magnitudes of torsion angles between the molecules.

Chair conformations have been adopted by the heterocyclic rings in both salts. In II the saturated cyclohexane ring, which bears an axial *t*-butyl group, adopts a chair conformation flattened near this group. In I, however, the conformation adopted is a distorted twist-boat form, with the *t*-butyl group in an isoclinal orientation. This result corroborates earlier evidence given for a small energy barrier between a flattened chair form and a distorted twist-boat form in such a strained, flexible system (Onan and Vierhapper, *Tet. Lett.* (1984) 00).

09.2-49 STRUCTURE OF DI-SYNEPHRINE ETHER DI-HYDROBROMIDE ( $\alpha, \alpha'$ -*N*-METHYLAMINO METHYL-4,4'-DIHYDROXY DIBENZYL ETHER DIHYDROBROMIDE)

By R.P. Mukhopadhyay and J.K. Dattagupta, C. e. M.B. Division, Saha Institute of Nuclear Physics, Sector-I, Block-'AF', Bidhan Nagar, Calcutta-700 064, India.

Synephrine is a well known sympathomimetic amine. Structure of the phosphate complex salt of it has already been studied by us (*Acta Cryst.* (1982) B38, 2830-2834) where two molecules in the asymmetric unit exhibited different conformations. Structure analysis of the hydrobromide salt of this compound was undertaken by us. Synephrine has been treated with 30% aqueous HBr in 1.5:2 mole ratio in presence of ethyl alcohol at 27°C. The single crystals of the compound thus formed belong to monoclinic space group  $C2/c$  with unit cell dimensions  $a = 7.645$ ,  $b = 19.777$ ,  $c = 13.704\text{\AA}$ ,  $\beta = 98.32^\circ$ . Intensity data has been collected on a CAD-4 diffractometer and the structure has been solved by heavy atom method. The structural parameters have been refined by full-matrix least squares method upto an  $R$  value of 8.5% with isotropic temperature factors and without hydrogen atoms. The chemical formula of this compound is found to be  $(C_{19}ONH_{12}.HBr)_2O$ . Mass spectra of the compound has also been taken which supports this chemical structure. Details will be presented.