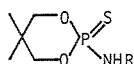


09.2-44 THE STEREOCHEMISTRY OF PHOSPHORUS HETEROCYCLES. STRUCTURES OF THREE NEW 2-AMINO-1,3,2-DIOXAPHOSPHORINANE 2-SULFIDES.

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 α). Structures were solved with direct methods and refined to $R=0.033$, 0.039 and 0.031 respectively.

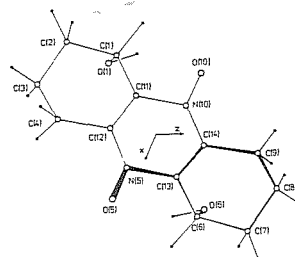
In all the cases dioxaphosphorinane rings adopt a flattened chair conformation. This might be explained by the anomeric effect which causes an increase of electron density around phosphorus (Van Nuffel et al. Cryst. Struct. Commun. (1980) 9, 733). The P=S double bond lengths are $1.925(1)$, $1.916(1)$ 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 π 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, C₁₂H₁₆N₂O₄. 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, $\beta=114.03(2)^\circ$, $V=569.9(1)$ Å³, $D_m=1.465$, $D_x=1.470$ Mg m⁻³, $\mu(\text{CuK}\alpha)=0.64$ mm⁻¹, $F(000)=488$. The intensities were collected on a Syntex P2₁ 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

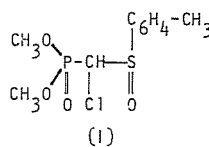
rings exist in half-chair conformations with asymmetry parameters: $\Delta C_2^{7,8}=0.7(6)$, $\Delta C_s^6=46.6(6)$ and $\bar{\psi}=32.7(3)^\circ$. The both symmetrically equivalent C-O bonds are in axial positions, in trans configuration. This research was supported by the project MR.I.9 from the Polish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

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

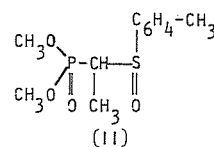
By A. Miller, M.W. Wieczorek and J. Karolak-Wojciechowska

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In the present work we describe the crystal structures of two α -phosphorylsulfoxide (I) and (II). This compounds are interesting models for the study on α -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.