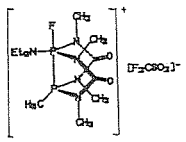
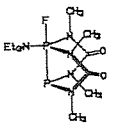
09.1–2 VERSATILE STEREOCHEMISTRY IN BICYCLIC DIPHOSPHORUS COMPOUNDS: By D. Schomburg, Gesellschaft für Biotechnologische Forschung, Mascheroder Weg 1, 3300 Braunschweig, Germany.

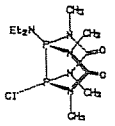
The structures of a series of mixed-valence 2,4,6,8 tetraaza-diphosphabicyclo(3.3.0)octane-3,7-dione derivatives have been determined. This class of compounds proved to exhibit a wide range of possible geometries and coordination numbers for the phosphorus atoms. The described compounds 1-5 include P(III) with coordination numbers 3, 4 and 5 and P(V) with coordination numbers 4, 5 and 6. Whereas the phosphorus atoms in compounds 1 and 2 have "normal" geometries with the fluorine atom and P(III) in the axial positions of the pentacoordinated trigonal-bipyramidal phosphorus, the analogue chlorine derivative 3 shows unexpected structural properties. It is not a phosphorane-phosphane like 2 but a phosphonium-phosphoranide. It crystallizes with three independent molecules in the unit cell and shows adduct formation between chlorine - which is no longer bound to P(V) - and the lower-valent phosphorus. In 3a P(III) has a distorted trigonal-bipyramidal geometry with a stereoactive lone pair. In the chlorine-bridged dimer the two phosphoranide phosphorus atoms and the two chlorine atoms form a planar ring with bond angles near 90° and P-Cl distances between 2.998 and 3.103 Å. In the monomeric form 3a the P-Cl distance is about 0.2 Å shorter (2.815 Å).



1

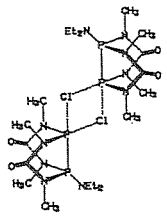


2

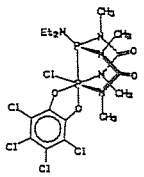


3a

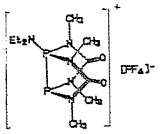
Similar to 3, the crystal structure analysis of 4 revealed that it cannot be formulated as a diphosphorane but rather as a phosphonium-phosphate. The donor-acceptor bond between P and Cl is much shorter than in the different forms of compound 3 (2.342 Å).



3b



4

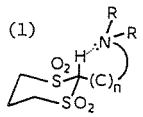


5

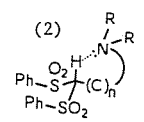
Whereas the overall butterfly shape of the bicyclus is not much affected by the changes in the environment of the phosphorus atoms some bonding parameters are subject to remarkable changes. The endocyclic P-N bond lengths fall into three distinct ranges, one around 1.71Å which is found for P(III)-N and equatorial P(V)-N in 1, 2, and 5, one around 1.64 A for phosphonium P(V)$^{+}$-N bonds in 1, 3a, 3b, 4 and 5 and one around 1.75 A for the P$^{(-)}$-N bonds in 3a, 3b and 4. P-P bonds are found in the range 2.165 Å (4) - 2.19 Å (3,5) - 2.25 Å (1,2).

09.1–3 HYDROGEN BONDS INVOLVING POLAR C-H GROUPS. By R. L. Harlow, Central Research and Development Dept., Experimental Station, E. I. du Pont de Nemours and Co., Wilmington, DE 19898, U.S.A., and Chuen Li and M. P. Sammes, Dept. of Chemistry, University of Hong Kong, Pokfulam Road, Hong Kong.

^{1}H n.m.r. spectroscopy has clearly indicated the presence of intramolecular C-H--N hydrogen bonds in both cyclic (1) and diphenyl (2) disulphones. Significant downfield shifts for the SO_2-CHR-SO_2 methine proton have been noted for select derivatives; the C-H--N interaction is found to be optimal when (a) it formed part of a six-membered ring, (b) the acceptor was a piperidino or dimethylamino nitrogen atom, and (c) there was one methyl substituent in the chain to reduce conformational mobility. Crystal structure determinations have been carried out on a number of these compounds with the following results: 2-(2,2-dimethyl-3-piperidino-1-yl)-1,3-dithian 1,1,3,3-tetraoxide has an extended-chain conformation with no C-H--N bond; 2-(3-dimethylamino-2-methylprop-1-yl)-1,3-dithian 1,1,3,3-tetraoxide has two molecules per asymmetric unit, one with an extended-chain conformation and one with a C-H--N bond; 1,1-bisphenyl-sulphonyl-4-dimethylbutane has a very short H--N bond of 2.34(3) A.

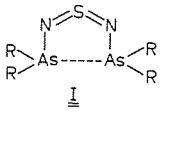


(1)

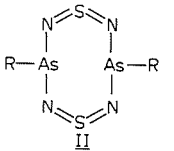


(2)

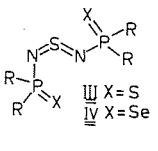
09.1–4 STRUCTURES OF SULPHUR DIIMIDES SUBSTITUTED BY Vb-GROUP ELEMENTS P AND As. By H. Betz, A. Gieren and T. Hübner, Max-Planck-Institut für Biochemie, Abteilung Strukturforschung I, 8033 Martinsried, FRG



I



II



III X=S
IV X=Se

R=phenyl R=t-butyl R=t-butyl

	I	II	III	IV
Sp.Gr.	I2/c	$P2_1/n$	$P2_1/c$	$P2_1/c$
a (Å)	21.205(3)	6.490(1)	11.821(2)	11.878(3)
b (Å)	5.904(4)	10.145(2)	11.342(3)	11.355(2)
c (Å)	23.802(4)	23.719(3)	17.170(4)	17.281(3)
β (°)	132.42(2)	95.09(1)	94.42(2)	94.44(2)
Z	4	4	4	4
No.Ref.	2327	2665	4074	3964
R	0.051	0.052	0.034	0.043

For the formally open chained sulphur diimide I unexpectedly a cis,cis-configuration of the N=S=N moiety was found, due to As---As binding interactions, compensating for the three-fold coordination of these atoms. The As---As distance (3.379(1)Å) in I is even shorter than that in II (3.683(1)Å). The $-\overline{As}<$ unit in R_2As-N=S=N-AsR_2 compounds leads to the same stereochemistry as the isoelectronic $-\overline{S}-$ unit in R-S=N=S=N=S-R type sulphur diimides (J. Leitch et al., J. Cryst. Mol. Struct. (1973) 3, 337; F.P. Olsen et al., Inorg. Chem. (1973) 12, 1353; E.M. Holt et al., J. Chem. Soc. Dalton (1974) 1357). In spite of the binding As---As interactions details of structure I and II