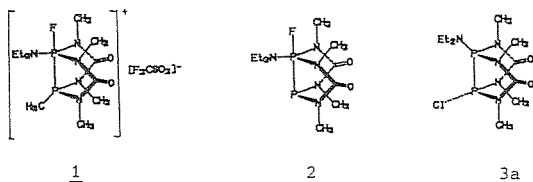


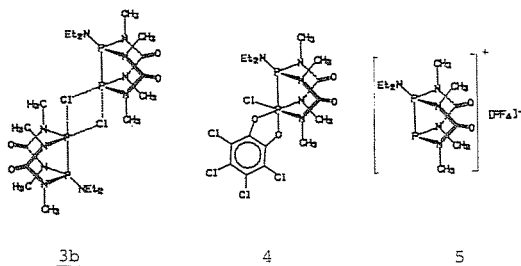
09. STRUCTURES OF ORGANIC, ORGANOMETALLIC AND COORDINATION COMPOUNDS

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-phosphorane. 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 phosphorane 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).



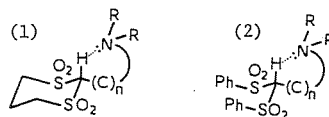
Similar to 3, the crystal structure analysis of 4 revealed that it cannot be formulated as a diphosphorane but rather as a phosphonium-phosphate. The donor-acceptor bond between P and Cl is much shorter than in the different forms of compound 3 (2.342 Å).



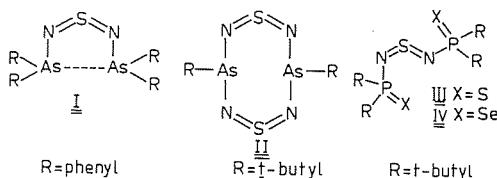
Whereas the overall butterfly shape of the bicyclus is not much affected by the changes in the environment of the phosphorus atoms some bonding parameters are subject to remarkable changes. The endocyclic P-N bond lengths fall into three distinct ranges, one around 1.71 Å which is found for P(III)-N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

¹H 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 SO₂-CHR-SO₂ 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) Å.



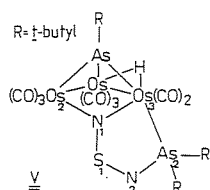
09.1-4 STRUCTURES OF SULPHUR DIIMIDES SUBSTITUTED BY Vb-GROUP ELEMENTS P AND As. By H. Betz, A. Gieren and T. Hübner, Max-Planck-Institut für Biochemie, Abteilung Strukturforschung I, 8033 Martinsried, FRG



	I	II	III	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 -As< unit in R₂As-N=S=N-AsR₂ compounds leads to the same stereochemistry as the isoelectronic -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

show, that a repulsion of the lone pairs on the As atoms is evident. If the coordination number of the Vb second row (P) or third row elements respectively increases to four and the valence state from three to five, also from sterical reasons there is no free coordination site available and therefore the usual *cis-trans* configuration is formed in the case of III and IV (A. Gieren et al., Z. Anorg. Allg. Chem. (1980) 467, 68). The S-N bond distances in I - IV (1.505-1.529 Å) show no significant π -interactions between SN_2 moieties and their substituents. A common feature of all known sulphur diimides, the coplanarity of SN_2 units with their bonding neighbours, is also fulfilled in I - IV.



V:	
Sp.Gr.	P2 ₁ /n
a (Å)	15.556(2)
b (Å)	23.885(4)
c (Å)	17.177(3)
β (°)	99.11(1)
Z	8
No. Ref.	9224
R	0.042

The reaction of I with $Os_3(CO)_9$ yields a cluster V in which the sulphur diimide subunit is still retained and co-planar with Os(3) and As(2). Os(2) deviates by only 0.68 Å from this plane. The S(1)-N(2) bond length of 1.53 Å is comparable to those in I - IV whereas the marginally lengthened S(1)-N(1) bond of 1.55 Å may be attributed to the three-fold coordination of the latter atom.

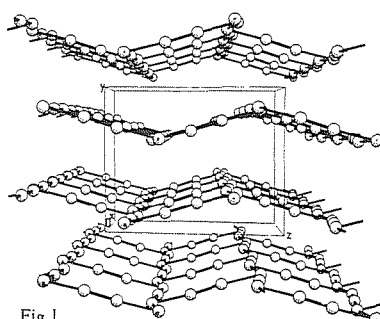


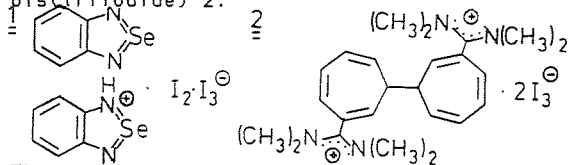
Fig. 1
(1980, 102, 5070). That can be described as an acid catalysed nucleophilic addition to the selenium of the SeN_2 unit and can be extrapolated to a model for hydrolysis of selenium diimides.

In contrast to 1, 2 exhibits isolated cations as well as anions. The shortest I-I contact distance is 4.25 Å. Both, the two anions and the cation are positioned on symmetry centres. Therefore, the slightly disordered I_3^- anions are symmetrical (I-I: 2.909 and 2.914 Å). The cycloheptatriene ring has the normal boat conformation and shows weak π -interaction between formal single and double bonds. The plane of the amidinium- π -system is tilted against the adjacent planes of the cycloheptatriene ring by 57° and 86°. Furthermore, due to steric reasons, the $N(CH_3)_2$ groups are slightly rotated by 19° and 25° outside the plane of the amidinium- π -system, respectively. The bond distances in the amidinium system are equal (1.325 and 1.321 Å), showing the delocalisation of the positive charge.

09.1-5 THE CRYSTAL STRUCTURES OF TWO POLYIODIDE SALTS OF ORGANIC CATIONS.

By T. Hübner and A. Gieren, Max-Planck-Institut für Biochemie, Abt. f. Strukturforchung 1, 8033 Martinsried, BRD.

We have performed the X-ray structure analyses of the polyiodides 2,1,3-benzoselenadiazole-2,1,3-benzoselenadiazolium pentaiodide 1 and *N,N,N',N',N'',N'',N''',N''''*-octamethyl[bi-2,4,6-cycloheptatriene-1-yl]-3,3'-dicarboxamidinium bis(triiodide) 2.



The crystallographic results are: 1: P2₁/n; $a = 9.320(3)$, $b = 13.812(2)$, $c = 17.159(3)$ Å, $\beta = 98.11(2)^\circ$, $Z = 4$; final $R = 0.034$ for 4111 unique reflexions with $I > 2\sigma(I)$; 2: P1; $a = 8.394(3)$, $b = 9.117(2)$, $c = 13.848(3)$ Å, $\alpha = 67.93(2)^\circ$, $\beta = 70.35(2)^\circ$, $\gamma = 65.36(2)^\circ$, $Z = 1$; final $R = 0.029$ for 3364 unique reflexions with $I > 2\sigma(I)$. Both structures were solved by direct methods combined with Patterson syntheses.

In 1 no isolated I_5^- units occur, but slightly puckered polyiodide layers formed by linear I_3^- anions and I_2 molecules. Almost linear triiodide chains are aggregated by I_2 forming layers, which realize a new variation of polyiodide arrangements (Fig. 1). The polyiodide layers contain several well known substructures of polyiodides. The bond distances are 2.865 and 2.984 Å in the I_3^- unit, 2.749 Å in the I_2 molecule and the 'secondary' I-I bond distances vary from 3.358 to 3.618 Å. The benzoselenadiazole and the benzoselenadiazolium ion are al-

09.1-6 BONDING PARAMETERS AT S IN SULFIDES, SULFOXIDES AND SULFONES. By B.C. Hauback and F. Mo, Institutt for røntgenteknikk, Universitetet i Trondheim-NTH, N-7034 Trondheim-NTH, Norway.

Charge densities and structure parameters have been determined by X-ray diffraction to examine bonding at S in the solid state. Mean values of bond lengths and angles of 5-7 well refined structures in each group of compounds, which are partly analyzed in our laboratory and partly reported structures, are given in the table. Weighted sample errors are in parentheses. Parameters involving aromatic (ar) and aliphatic (al) C atoms are listed separately.

	Non-term.		Term.		
	S-C(ar)	S-C(al)	S-C(al)	C-S-C(ar)	C-S-C(al)
Sulfides	1.776(2)	1.811(2)	1.797(2)	103.0(4)	99.9(2)
Sulfoxides	1.800(1)	1.807(3)	1.789(3)	98.4(2)	96.1(8)
Sulfones	1.765(3)	1.781(2)	1.758(1)	105.1(4)	104.5(3)

Bond angles in both aliphatic and aromatic groups of sulfides are larger than in the sulfoxides, the order being sulfone > sulfide > sulfoxide. The same trend, which is not predicted by simple models for bonding, was found also in diffraction studies of gaseous species (Hargittai et al., Acta Chim. Acad. Sci. Hung. (1977) 93, 279). A tentative explanation has been given. (Schmiedekamp et al., J. Am. Chem. Soc. (1979) 101, 2002).

We observe that in the aliphatic group the S-C bonds (non-term.) are very similar in the sulfides and sulfoxides, and longer than in the sulfones. In the aromatic series S-C distances in the sulfides and the sulfones are comparable and both shorter than in the sulfoxides.

The difference between terminal and non-terminal S-C(al) bonds in sulfones, 0.023 Å, remains also with thermal corrected parameters from a refinement based on 86K data with $(\sin\theta)/\lambda > 0.90 \text{ \AA}^{-1}$. Charge density features sustain that these bonds are different.