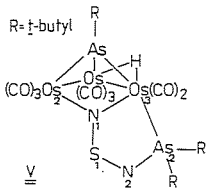
show, that a repulsion of the lone pairs on the As atoms is evident. If the coordination number of the Vb second row (P) or third row elements respectively increases to four and the valence state from three to five, also from sterical reasons there is no free coordination site available and therefore 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 (1.505-1.529Å) 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

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 $Os_3(CO)_{12}$ 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.

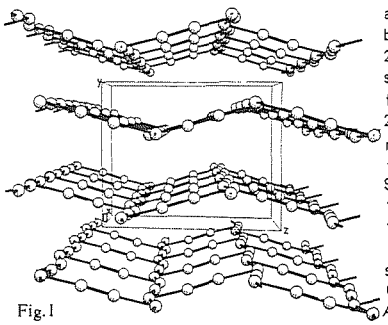


Fig.1

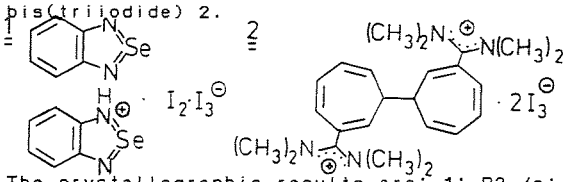
ternately associated by a hydrogen bond NH--N (N--N: 2.87Å) and two short Se--N-contacts (2.69, 2.97Å), yielding a ribbon-like structure. One of these Se--N-contacts is the shortest we found so far in investigations on selenium diimides (Gieren et al., J. Am. Chem. Soc., 1980, 102, 5070). That can be 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 4.25Å. 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 2.914Å). 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 1.321Å), 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. Strukturforschung I, 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: $P2_1/n$; a = 9.320(3), b = 13.812(2), c = 17.159(3)Å, β = 98.11(2)°, Z = 4; final R = 0.034 for 4111 unique reflexions with $I>2\sigma(I)$; 2: $P\bar{1}$; a = 8.394(3), b = 9.117(2), c = 13.848(3)Å, α = 67.93(2)°, β = 70.35(2)°, γ = 65.36(2)°, 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 arrangments (Fig. 1). The polyiodide layers contain several well known substructures of polyiodides. The bond distances are 2.865 and 2.984Å in the I_3^- unit, 2.749Å in the I_2 molecule and the 'secondary' I--I bond distances vary from 3.358 to 3.616Å. The benzoselenadiazole and the benzoselenadiazolium ion are al-

09.1–6 BONDING PARAMETERS AT S IN SULFIDES, SULFOXIDES AND SULFONES.

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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. S-C(ar)	Term. S-C(al)	Term. 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, 0.023Å, remains also with thermal corrected parameters from a refinement based on 86K data with $(\sin\theta)/\lambda>0.90Å^{-1}$. Charge density features sustain that these bonds are different.