Table 6. *Intermolecular and interlayer distances of cluster*

Cluster	Intermolecular distance* (Å)	Cluster	Interlayer distance* (Å)
(Monolayer)		(Island on the monolayer)	
Dimer	5·4967		
Tetramer	5·4726	Monomer	5·2823
Nonamer	5·4668	Dimer	5·4694
Hexadecamer	5·4658	Tetramer	5·5396
36 molecules	5·4586	Hexamer	5·5261
		(triple layer)	
Exp.†	5·13	Heptadecamer	4·4629
		34 molecules	4·4949
		Exp.†	4·833

*Average value.

†Benzene crystal at 270 K (Cox *et al.*, 1958).

the crystal formation at the center of the three-dimensionally symmetrical cluster. A more realistic model for the unit cell of a benzene crystal would be obtained if one were to consider a cluster consisting of 168 molecules with a pentalayer structure: *i.e.* 16, 36, 64, 36 and 16 molecules for the top, second, third (middle), fourth and bottom layers, respectively, because this is the smallest cluster in which the unit cell of a benzene crystal is reproduced at the center with none of the members of the unit cell at the surface of the cluster. Unfortunately, such a huge calculation has not been performed because of the economical and computational limits, although quantitative information is expected if it could be done.

The authors are indebted to Professor S. Fraga for an early release of his program, *SOMAR* (Simulation of molecular associations and chemical reactions). The computations were carried out at the Computer Center, the University of Tokyo, and the Computer Center, Chiba University. The authors thank the Computer Center, Institute for Molecular Science, Okazaki, for the use of the Hitac M-200H computer for a small part of the calculation. This work is supported in part by Grant in Aid for Scientific Research No. 59103011 from the Ministry of Education, Science and Culture.

References

BACON, G. E., CURRY, N. A. & WILSON, S. A. (1964). *Proc. R. Soc. London Ser. A*, **279**, 98–110.

BINKLEY, J. S., POPLE, J. A. & HEHRE, W. J. (1980). *J. Am. Chem. Soc.* **102**, 939–947.

CLEMENTI, E. (1980). *Computational Aspects for Large Chemical Systems*. Berlin, Heidelberg: Springer Verlag.

CLEMENTI, E., CAVALLONE, F. & SCORDAMAGLIA, R. (1977). *J. Am. Chem. Soc.* **99**, 5531–5557.

COX, F. G., CRUICKSHANK, D. W. J. & SMITH, J. S. S. (1958). *Proc. R. Soc. London Ser. A*, **247**, 1.

DUNCAN, M. A., DIETZ, T. G., LIVERMAN, M. G. & SMALLEY, R. E. (1981). *J. Phys. Chem.* **85**, 7.

EVANS, R. C. (1964). *An Introduction to Crystal Chemistry*, 2nd ed., p. 385. Cambridge Univ. Press.

FRAGA, S. (1982). *J. Comput. Chem.* **3**, 329–334.

FRAGA, S. (1983). *Comput. Phys. Commun.* **29**, 351–359.

HEENAN, R. K., VALENTE, E. J. & BARTELL, L. S. (1982). *J. Chem. Phys.* **78**, 243–248.

HOPKINS, J. B., POWERS, D. E. & SMALLEY, R. E. (1981). *J. Phys. Chem.* **85**, 3739–3742.

JANDA, K. C., HEMMINGER, J. C., WINN, J. S., NOVICK, S. E., HARRIS, S. J. & KLEMPERER, W. (1975). *J. Chem. Phys.* **63**, 1419–1421.

JOHNSON, C. K. (1965). *ORTEP*. Report ORNL-3794. Oak Ridge National Laboratory, Tennessee.

LANGRIDGE-SMITH, P. R. R., BRUMBAUGH, D. V., HAYNAM, C. A. & LEVY, D. H. (1981). *J. Phys. Chem.* **85**, 3742–3746.

NARTEN, A. H. (1967). *J. Chem. Phys.* **48**, 1630.

WAAL, B. W. VAN DE (1981). *Acta Cryst.* A**37**, 762–764.

WILLIAMS, D. E. (1980). *Acta Cryst.* A**36**, 715–723.

Acta Cryst. (1985). B**41**, 445–452

A New Type of σ-Sulfurane with a Transannular S···N Bond: Structures of *S*-Substituted *N*-Methyl-6,7-dihydro-5*H*,12*H*$^+$-dibenzo[*b*,*g*][1,5]thiazocinium Salts and *N*-Methyl-6,7-dihydro-5*H*-dibenzo[*b*,*g*][1,5]thiazocine *S*-Oxide

BY FUJIKO IWASAKI*

Department of Materials Science, The University of Electro-Communications, Chofu-shi, Tokyo 182, *Japan*

AND KIN-YA AKIBA

Department of Chemistry, Faculty of Science, Hiroshima University, Hiroshima 730, *Japan*

(*Received* 1 *February* 1985; *accepted* 22 *April* 1985)

Abstract

5*H*,12*H*$^+$-Dibenzo[*b*,*g*][1,5]thiazocinium hexafluorophosphate (I), 12-methoxy-6-methyl-6,7-dihydro-5*H*,12*H*$^+$-dibenzo[*b*,*g*][1,5]thiazocinium hexachloroantimonate (II), 6,12-dimethyl-6,7-dihydro-5*H*,12*H*$^+$-dibenzo[*b*,*g*][1,5]thiazocinium hexafluorophosphate (III) and 6-methyl-6,7-dihydro-5*H*-dibenzo[*b*,*g*][1,5]thiazocine *S*-oxide (IV) were determined by the X-ray method. Crystal data: (I) $C_{15}H_{15}ClNS^+.PF_6^-$, $M_r = 421{\cdot}77$, orthorhombic, *Pbca*,

---

* To whom all correspondence should be addressed.

0108-7681/85/060445-08$01.50

$a = 17{\cdot}101\,(1)$, $b = 15{\cdot}327\,(1)$, $c = 13{\cdot}195\,(2)$ Å, $V = 3458{\cdot}7\,(6)$ Å^3, $Z = 8$, $D_x = 1{\cdot}620$ Mg m^{-3}, $\lambda(\mathrm{Cu}\ K\alpha) = 1{\cdot}5418$ Å, $\mu = 4{\cdot}499$ mm^{-1}, $F(000) = 1712$, room temperature; (II) $C_{16}H_{18}NOS^+.SbCl_6^-$, $M_r = 607{\cdot}39$, monoclinic, $P2_1/c$, $a = 11{\cdot}791\,(2)$, $b = 10{\cdot}593\,(2)$, $c = 18{\cdot}860\,(3)$ Å, $\beta = 98{\cdot}25\,(2)°$, $V = 2331{\cdot}3\,(6)$ Å^3, $Z = 4$, $D_x = 1{\cdot}730$ Mg m^{-3}, $\lambda(\mathrm{Mo}\ K\alpha) = 0{\cdot}7107$ Å, $\mu = 1{\cdot}926$ mm^{-1}, $F(000) = 1192$, room temperature; (III) $C_{16}H_{18}NS^+.PF_6^-$, $M_r = 401{\cdot}35$, orthorhombic, $Pbca$, $a = 16{\cdot}702\,(2)$, $b = 16{\cdot}352\,(2)$, $c = 12{\cdot}770\,(1)$ Å, $V = 3487{\cdot}7\,(5)$ Å^3, $Z = 8$, $D_x = 1{\cdot}530$ Mg m^{-3}, $\lambda(\mathrm{Cu}\ K\alpha) = 1{\cdot}5418$ Å, $\mu = 3{\cdot}055$ mm^{-1}, $F(000) = 1648$, room temperature; (IV) $C_{15}H_{15}NOS$, $M_r = 257{\cdot}35$, triclinic, $P\bar{1}$, $a = 8{\cdot}5145\,(7)$, $b = 9{\cdot}4444\,(7)$, $c = 16{\cdot}831\,(2)$ Å, $\alpha = 99{\cdot}23\,(1)$, $\beta = 99{\cdot}12\,(1)$, $\gamma = 91{\cdot}69\,(1)°$, $V = 1317{\cdot}0\,(2)$ Å^3, $Z = 4$, $D_x = 1{\cdot}298$ Mg m^{-3}, $\lambda(\mathrm{Cu}\ K\alpha) = 1{\cdot}5418$ Å, $\mu = 2{\cdot}004$ mm^{-1}, $F(000) = 544$, room temperature. The final R values are (I) 0·078, (II) 0·053, (III) 0·064 and (IV) 0·043 for 1973, 3221, 2272 and 4260 observed reflections, respectively. The conformation of the thiazocine (or thiazocinium) rings of these compounds is a distorted boat form without C_s or C_2 symmetry. Very strong transannular interactions are found between S and N atoms, which show the hypervalency of S. The S···N distances are 2·090, 2·207, 2·466, 2·593 and 2·624 Å for (I), (II), (III), (IV) *A* and (IV) *B*, respectively. The X_{ap}–S···N angles are 176·9, 175·0, 176·9, 179·5 and 179·1°, for (I), (II), (III), (IV)*A* and (IV)*B*, respectively, where the X_{ap}'s are Cl, OMe, Me and O for (I), (II), (III) and (IV), respectively. The configuration about the S atom is a distorted trigonal bipyramid with two apical S···N and S–X_{ap} bonds, two equatorial S–C bonds and the lone pair considered to occupy the third equatorial position. Therefore, these compounds are concluded to be a new type of σ-ammoniosulfurane.

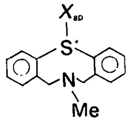
Introduction

The sulfuranes, which feature an unshared pair of electrons and a coordination number of four at the S atom, are examples of a broader category of species hypervalent molecules (Musher, 1969). A variety of organic σ-sulfuranes have been synthesized and the structures have been determined by X-ray analysis (Baenziger, Buckles, Maner & Simpson, 1969; Paul, Martin & Perozzi, 1972; Kálmán, Sasvári & Kapovits, 1973; Perozzi, Martin & Paul, 1974; Adzima, Chiang, Paul & Martin, 1978). Every compound bears electron-withdrawing apical groups due to the electron-rich and polarizable nature of the apical three-center four-electron bond.

A series of *S*-substituted *N*-methyl-6,7-dihydro-5*H*,12*H*$^+$-dibenzo[*b*,*g*][1,5]thiazocinium salts were synthesized and a transannular interaction between the S and N atoms was suggested from NMR study in solution (Akiba, Takee, Ohkata & Iwasaki, 1983). X-ray analysis for (I), (II), (III) and (IV) was carried out in order to investigate the conformations of the thiazocine rings, the transannular interaction in the crystalline state and also the effects due to the different substituents.

Table 1. *Experimental conditions*

	(I) $C_{15}H_{15}ClNS^+$ PF_6^-	(III) $C_{16}H_{18}NS^+$ PF_6^-	(II) $C_{16}H_{18}NOS^+$ $SbCl_6^-$	(IV) $C_{15}H_{15}NOS$
$-X_{ap}$	–Cl	–CH_3	–OCH_3	=O
Crystal size (mm)	0·30 × 0·40 × 0·10	0·09 × 0·30 × 0·35	0·12 × 0·30 × 0·35	0·34 × 0·30 × 0·25
$2\theta_{max}$ (°)	130	130	55	130
Scan width (°)	1·2 + 0·3 tan θ	1·1 + 0·4 tan θ	1·2 + 0·3 tan θ	1·0 + 0·5 tan θ
Max. *h*, *k*, *l*	20, 17, 15	19, 19, 14	15, 13, ±21	+9 − 10, ±10, 19
No. of reflections				
measured	2882	2966	5374	4560
observed	1973	2272	3221	4260
g	$6{\cdot}0 \times 10^{-7}$	$5{\cdot}3 \times 10^{-7}$		$1{\cdot}3 \times 10^{-6}$
R	0·078	0·064	0·053	0·043
wR	0·103	0·072	0·064	0·046
S	1·046	1·613	1·008	0·502



I X=Cl (PF_6^-)
II X=OMe ($SbCl_6^-$)
III X=Me (PF_6^-)
IV X=O

Experimental

Crystal data are listed in the *Abstract*. Colorless crystals of (I) and (IV) were obtained from dichloromethane solution. Those of (II) were recrystallized to give pale-yellow crystals from CH_2Cl_2 solution. Colorless crystals of (III) were grown from an Et_2O–CH_3CN solution. Crystals (I) and (II) were unstable in air and were sealed in thin glass capillaries during the intensity measurements. Intensities were collected on a Rigaku automatic diffractometer with graphite-monochromated radiation, using the ω–2θ scan technique with a scanning rate of 4° min^{-1} in 2θ. At both ends of the scan range 10 s [5 s for (I)] background counts were taken for each reflection. Reflections with $|F_o| \geq 3\sigma(F_o)$ were used for structure determination. Some experimental conditions are listed in Table 1. Absorption corrections were applied numerically.

Structures (I) and (III) were solved by the heavy-atom method after failure to solve them by *MULTAN*78 (Main, Hull, Lessinger, Germain, Declercq & Woolfson, 1978). The S atom for (III) and Cl and S atoms for (I) were located from three-dimensional Patterson maps. All the other non-H atoms were determined by means of successive Fourier syntheses and block-diagonal least squares. During the refinements it was revealed that PF_6^- ions were disordered for both compounds. Residual peaks around the P atoms in the difference maps were assigned as F atoms with the occupancy factors estimated from the peak heights. The positions of the H atoms were located from difference maps. All atoms were refined by block-diagonal least squares with anisotropic temperature factors for the F atoms with fixed occupancy factors 0·8 for (I) and 0·8 and 1·0 for (III) and for the other non-hydrogen atoms and with isotropic temperature factors for H and for the F atoms with occupancy factor 0·2.

For (II), the position of the Sb atom was deduced by the direct method with the program *MULTAN*78. The other non-hydrogen atoms were obtained from successive Fourier syntheses. Most H atoms were located from a difference map and the remaining two H belonging to methyl groups were deduced from the calculation and included in the refinement. For (IV) the structure was solved by means of *MULTAN*78. A difference map showed all the H atoms. The structures were refined by block-diagonal least squares with anisotropic temperature factors for non-hydrogen atoms and with isotropic ones for H.

For (I), (III) and (IV) strong reflections showed the secondary-extinction effect. After correction for the extinction the final refinement was performed. The quantity minimized was $\sum w(|F_o| - k^{-1}|F_c|)^2$. The weighting schemes used were: (I) $w = 1/(2{\cdot}899 + 0{\cdot}197|F_o| + 0{\cdot}0004|F_o|^2)$; (II) $w = 1/(8{\cdot}201 - 0{\cdot}1014|F_o| + 0{\cdot}0014|F_o|^2)$; (III) $w = 0{\cdot}7$ if $|F_o| < 10{\cdot}0$, $w = 1{\cdot}0$ if $10{\cdot}0 \leq |F_o| \leq 40{\cdot}0$ and $w = (40{\cdot}0/|F_o|)^2$ if $|F_o| > 40{\cdot}0$; (IV) $w = 0{\cdot}3$ if $|F_o| < 5{\cdot}0$, $w = 1{\cdot}0$ if $5{\cdot}0 \leq |F_o| \leq 20{\cdot}0$ and $w = (20{\cdot}0/|F_o|)^2$ if $|F_o| > 20{\cdot}0$. Atomic scattering factors were taken from *International Tables for X-ray Crystallography* (1974). All computations were performed on a HITAC M180 Computer of the Data Processing Center of the University of Electro-Communications with the programs *UNICS*III (Sakurai & Kobayashi, 1979), *MULTAN*78 and *ORTEP*II (Johnson, 1971). The final atomic parameters are given in Table 2.*

Results and discussion

Fig. 1 shows the structures of thiazociniums (I), (II) and (III) and thiazocine (IV) with the atom numbering. (IV) has two independent molecules, *A* and *B*, in the unit cell. Bond lengths and angles are listed in Table 3.

The conformations of the thiazocine rings of these compounds are essentially the same, a distorted boat without C_s or C_2 symmetry. The torsion angles in the thiazocine rings are listed in Table 4. The torsion angles S–C(1)–C(6)–C(7) and S–C(14)–C(9)–C(8), which should be zero for no strain in the ring, are 1·6 ~ 8·8°. The deviations from the mean planes defined by the four atoms C(1), C(6), C(9) and C(14) are also listed in Table 4. For these thiazocine rings, the deviations of these four atoms are within 0·18 Å, those of C(8) are within 0·40 Å, and S, N and C(7) are displaced markedly from the mean planes in the same direction. If the conformation were an idealized boat the torsion angle C(15)–N···S–lone pair would be zero. In this distorted boat conformation the value is about 30°. The lone pair of the N atom points towards the S atom. The same ring conformation has been reported for *N-tert*-butyl-5,6-dihydro-7*H*,12*H*-dibenz[*c,f*]azocine (Hardy & Ahmed, 1974). The conformational behavior of heterocyclic analogues of 5,6,7,12-tetrahydrodibenzo[*a,d*]cyclooctane in solution has been investigated by Gellatly, Ollis & Sutherland (1976). These compounds show two types of conformation: a more stable rigid chair–boat form (C_s symmetry) and a flexible boat–boat (C_s) or twist-boat (C_2) form. But the model for the twist-boat discussed in that paper has C_2 symmetry and there is no interaction between the two hetero-atoms at the 6- and 12-positions. Thus the ring conformation of the twist-boat in that paper is quite different from that of the distorted boat in the present study. The dihedral angles between the benzene rings are 78·4, 111·1, 75·3, 105·5 and 103·4° for (I), (II), (III), (IV)*A* and (IV)*B*, respectively.

The S···N distances are 2·090, 2·207, 2·466, 2·593 and 2·624 Å for (I), (II), (III), (IV)*A* and (IV)*B*, respectively. These values are shorter than the sum of the van der Waals radii (3·35 Å) (Pauling, 1960), indicating a transannular interaction between S and N. The transannular S···N interaction has been reported for 2-(2,4,6-trichlorophenylimino)perhydro-1,3,2,6-dioxathiazocine (Picard, Cazaux & Jaud, 1981), in which the ring has a boat–chair conformation and the S···N distance is 2·94 Å. As shown in Fig. 2, X_{ap}, S and N are approximately collinear, the X_{ap}–S···N angles being 176·9, 175·0, 176·9, 179·5 and 179·1° for (I), (II), (III), (IV)*A* and (IV)*B*, respectively. Dimensions about S···N bonds are listed in Table 5. The angles between the C(1)SC(14) plane and the S···N bond are 80·4, 75·4, 72·9, 68·0 and 66·8° for (I), (II), (III), (IV)*A* and (IV)*B*, respectively. The linear X_{ap}–S···N group is approximately normal to the plane of C(1)SC(14), especially in (I). The configuration about the S atom is a distorted trigonal bipyramid with two apical S···N and S–X_{ap} bonds, two equatorial S–C bonds and the lone pair considered to occupy the third equatorial position. Therefore, these structures are concluded to be of a new type of σ-ammoniosulfurane. For a typical spiro-sulfurane with two apical N ligands the S–N bond lengths are 1·899 and 1·897 Å and the C–S–C angle is 104·8° (Adzima *et al.*, 1978). (III) is the first example of a σ-alkylsulfurane with an apical alkyl group, although σ-sulfurane with an equatorial methyl group was reported by Lau & Martin (1977).

---

* Lists of structure factors, anisotropic temperature factors for non-hydrogen atoms, atomic parameters of F atoms with occupancy factor of 0·2 and H atoms, and bond lengths and angles for PF_6^- and $SbCl_6^-$ have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 42193 (63 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

The transannular S···N distances in these thiazocines are distributed widely, depending on the electronegativity of the X_{ap} atoms. The S···N length of 2·090 Å for (I) is the shortest transannular S···N length and corresponds to a Pauling's bond order of 0·34. The S–Cl length (2·192 Å) is longer than the sum of the covalent radii (2·03 Å). The apical S–Cl distances in dichlorobis(*p*-chlorophenyl)sulfurane have been reported to be 2·259 and 2·323 Å (Baenziger *et al.*, 1969). The S···N length (2·207 Å) in (II) corresponds to a bond order of 0·18. The S–O length of 1·657 Å is close to the value of 1·662 Å of S–O(alkoxy) in the asymmetric σ-sulfurane 2,2-dimethyl-6-oxo-8-phenyl-2*H*,6*H*-[1,2]thioxolo[4,5,1-*hi*]benzothioxole, in which the longer apical S–O length is 2·248 Å (Lam, Duesler & Martin, 1981). In methyl *o*-nitrobenzenesulfenate the S–O length is 1·65 Å (Hamilton & LaPlaca, 1964) and in 2-(2,4,6-trichlorophenylimino)perhydro-1,3,2,6-dioxathiazocine the S–O lengths are 1·624 and 1·634 Å (Picard *et al.*, 1981). S–O single-bond lengths are 1·53 ~ 1·62 Å for organic sulfates or 1·59 ~ 1·63 Å for sulfonates. For symmetric dialkoxysulfuranes two apical S–O lengths are within the range 1·83 ~ 1·92 Å (Paul *et al.*, 1972; Perozzi *et al.*, 1974). For (III) and

Table 2. *Positional parameters* [$\times 10^4$ *for* (I), (II) (*except* Sb $\times 10^5$), (III) and $\times 10^5$ *for* (IV)] *and equivalent isotropic temperature factors* (Å^2) *for non*-H *atoms*

$$B_{eq} = \tfrac{4}{3}\textstyle\sum_i \sum_j \beta_{ij} \mathbf{a}_i . \mathbf{a}_j .$$

(*a*) (I) (X_{ap} = Cl, PF_6^-); occupancy factors of F atoms: 0·8

	x	*y*	*z*	B_{eq}
Cl	1311 (1)	2937 (1)	1117 (2)	4·8
S	1720 (1)	1616 (1)	1469 (1)	3·5
N	2124 (3)	380 (4)	1884 (5)	3·9
C(1)	1037 (4)	1437 (4)	2501 (5)	3·6
C(2)	328 (4)	1858 (5)	2584 (6)	3·8
C(3)	−116 (5)	1697 (6)	3435 (7)	5·0
C(4)	141 (5)	1120 (6)	4167 (7)	5·3
C(5)	846 (5)	676 (6)	4069 (6)	5·1
C(6)	1309 (4)	843 (5)	3214 (6)	4·1
C(7)	2070 (5)	412 (5)	2997 (6)	4·5
C(8)	1582 (5)	−270 (5)	1407 (6)	4·8
C(9)	1276 (5)	151 (5)	465 (6)	4·2
C(10)	995 (5)	−314 (5)	−361 (7)	5·0
C(11)	708 (5)	115 (6)	−1203 (6)	5·0
C(12)	716 (6)	1009 (6)	−1247 (6)	5·3
C(13)	1011 (5)	1484 (5)	−449 (6)	4·7
C(14)	1281 (4)	1063 (4)	387 (5)	3·5
C(15)	2919 (5)	287 (6)	1496 (7)	5·5
P	3325 (1)	2184 (1)	−1197 (2)	4·5
F(1)	3470 (4)	2998 (4)	−1906 (5)	6·2
F(2)	3204 (5)	1393 (5)	−462 (6)	8·7
F(3)	3926 (4)	1625 (5)	−1844 (6)	8·0
F(4)	4065 (4)	2506 (5)	−558 (6)	7·0
F(5)	2744 (5)	2764 (5)	−560 (7)	9·7
F(6)	2648 (4)	1818 (6)	−1878 (6)	8·5

(*b*) (III) (X_{ap} = CH_3, PF_6^-); occupancy factors of F atoms: (*a*) 1·0, (*b*) 0·8

	x	*y*	*z*	B_{eq}
C(16)	1320 (3)	2649 (3)	1055 (4)	5·1
S	1651 (1)	1625 (1)	1352 (1)	3·6
N	2164 (2)	257 (2)	1815 (3)	4·3
C(1)	1039 (2)	1391 (2)	2484 (3)	3·5
C(2)	328 (3)	1792 (2)	2667 (3)	4·0
C(3)	−107 (3)	1627 (3)	3565 (4)	4·9
C(4)	170 (3)	1039 (3)	4253 (4)	5·3
C(5)	862 (3)	627 (3)	4041 (4)	5·1
C(6)	1325 (2)	789 (2)	3164 (3)	3·9
C(7)	2088 (3)	347 (3)	2942 (4)	4·7
C(8)	1571 (3)	−262 (2)	1304 (4)	4·7
C(9)	1256 (2)	181 (3)	352 (3)	4·0
C(10)	958 (3)	−266 (3)	−504 (4)	4·9
C(11)	628 (3)	135 (3)	−1352 (4)	5·3
C(12)	594 (3)	957 (3)	−1380 (4)	5·2
C(13)	892 (3)	1426 (3)	−565 (4)	4·6
C(14)	1217 (2)	1027 (2)	301 (3)	3·5
C(15)	2979 (3)	155 (4)	1430 (5)	6·4
P	3303 (1)	2226 (1)	−1271 (1)	4·8
F(1)$^{(a)}$	3446 (3)	2972 (2)	−2028 (3)	10·0
F(2)$^{(a)}$	3161 (3)	1549 (3)	−458 (4)	11·4
F(3)$^{(b)}$	3929 (3)	1678 (3)	−1866 (4)	9·9
F(4)$^{(b)}$	4050 (3)	2593 (3)	−655 (4)	8·1
F(5)$^{(b)}$	2713 (3)	2816 (3)	−684 (5)	11·8
F(6)$^{(b)}$	2627 (3)	1815 (3)	−1931 (4)	10·1

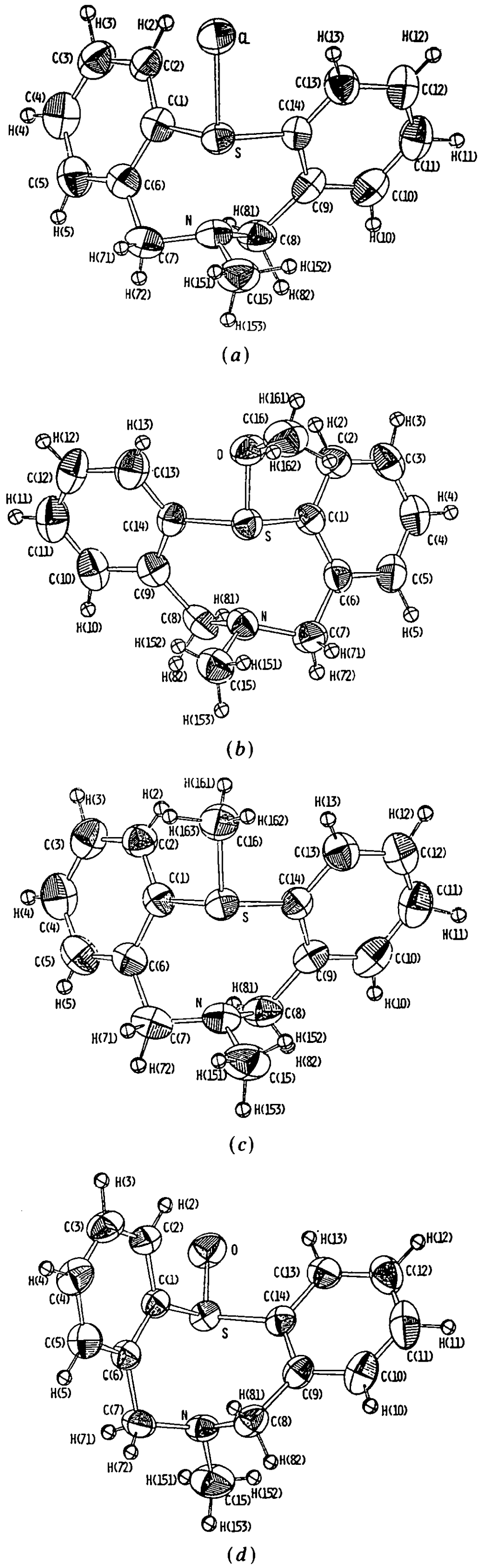
Table 2 (*cont.*)

(*c*) (II) (X_{ap} = OCH_3, $SbCl_6^-$)

	x	*y*	*z*	B_{eq}
S	2213 (2)	6652 (2)	7387 (1)	3·4
O	1555 (5)	7732 (5)	7816 (3)	4·3
N	3194 (5)	5345 (6)	6795 (3)	3·6
C(1)	3568 (7)	6703 (7)	7963 (4)	3·4
C(2)	3820 (7)	7662 (8)	8469 (5)	4·2
C(3)	4844 (8)	7577 (9)	8939 (5)	4·6
C(4)	5569 (8)	6598 (10)	8896 (5)	4·7
C(5)	5331 (7)	5656 (9)	8397 (5)	4·3
C(6)	4307 (7)	5701 (8)	7919 (4)	3·5
C(7)	3978 (7)	4718 (8)	7368 (5)	4·1
C(8)	3782 (7)	6146 (9)	6330 (4)	4·4
C(9)	3039 (6)	7285 (8)	6150 (4)	3·7
C(10)	3076 (8)	7995 (10)	5527 (5)	4·9
C(11)	2392 (9)	9042 (11)	5400 (5)	5·7
C(12)	1709 (8)	9395 (10)	5887 (6)	5·5
C(13)	1658 (8)	8731 (9)	6515 (5)	4·8
C(14)	2325 (6)	7651 (7)	6629 (4)	3·4
C(15)	2371 (8)	4485 (9)	6378 (5)	4·8
C(16)	898 (10)	7203 (10)	8309 (6)	6·3
Sb	21557 (5)	19826 (5)	88359 (3)	3·6
Cl(1)	3790 (2)	3259 (3)	9170 (1)	5·9
Cl(2)	540 (2)	724 (3)	8474 (2)	6·6
Cl(3)	2945 (2)	1306 (3)	7817 (1)	5·5
Cl(4)	1368 (3)	2645 (3)	9836 (2)	7·1
Cl(5)	3095 (3)	295 (3)	9502 (1)	6·7
Cl(6)	1284 (2)	3705 (3)	8172 (2)	5·8

(*d*) (IV) (X_{ap} = O)

	x	*y*	*z*	B_{eq}
S(*A*)	69202 (6)	19314 (6)	46602 (3)	3·2
O(*A*)	70907 (20)	32582 (18)	52980 (10)	4·7
N(*A*)	66304 (20)	−3493 (18)	35498 (11)	3·4
C(1*A*)	88846 (23)	17674 (21)	43766 (12)	2·9
C(2*A*)	99182 (26)	29763 (23)	46033 (14)	3·6
C(3*A*)	114600 (28)	29101 (27)	44412 (16)	4·5
C(4*A*)	119630 (28)	16377 (30)	40803 (16)	4·8
C(5*A*)	109366 (27)	4175 (26)	38628 (15)	4·1
C(6*A*)	93717 (24)	4775 (22)	39998 (13)	3·1
C(7*A*)	82235 (27)	−8201 (23)	37524 (15)	3·8
C(8*A*)	63353 (28)	2737 (26)	28107 (14)	4·1
C(9*A*)	56084 (24)	16983 (25)	29766 (13)	3·5
C(10*A*)	46633 (31)	22589 (32)	23598 (15)	5·1
C(11*A*)	40385 (33)	35948 (33)	25096 (19)	5·8
C(12*A*)	43581 (30)	44176 (28)	32703 (18)	5·0
C(13*A*)	52915 (25)	38890 (24)	38923 (15)	3·9
C(14*A*)	58999 (23)	25365 (22)	37535 (13)	3·1
C(15*A*)	53660 (32)	−13738 (29)	36209 (20)	5·8
S(*B*)	107860 (8)	77820 (7)	10929 (4)	4·5
O(*B*)	124299 (22)	81968 (25)	15613 (13)	6·6
N(*B*)	78931 (27)	70676 (23)	2958 (12)	4·9
C(1*B*)	97566 (31)	94347 (26)	11661 (14)	4.3
C(2*B*)	104459 (36)	105656 (29)	17695 (16)	5·4
C(3*B*)	97712 (47)	118782 (32)	18262 (21)	7·1
C(4*B*)	84651 (49)	120804 (32)	12748 (23)	7·7
C(5*B*)	77901 (41)	109648 (35)	6640 (21)	6·7
C(6*B*)	84223 (34)	96235 (28)	6038 (15)	4·8
C(7*B*)	76980 (37)	83824 (33)	−417 (16)	5·7
C(8*B*)	70681 (31)	69543 (31)	9754 (16)	5·0
C(9*B*)	81801 (29)	65099 (24)	16613 (14)	3·9
C(10*B*)	76173 (31)	57558 (26)	22145 (16)	4·6
C(11*B*)	86167 (35)	54067 (27)	28705 (16)	5·0
C(12*B*)	102154 (34)	58037 (28)	29954 (16)	4·9
C(13*B*)	108094 (30)	65457 (26)	24525 (15)	4·4
C(14*B*)	98126 (28)	68916 (23)	17865 (14)	3·7
C(15*B*)	77730 (50)	57472 (37)	−2938 (19)	7·7



(a)

(b)

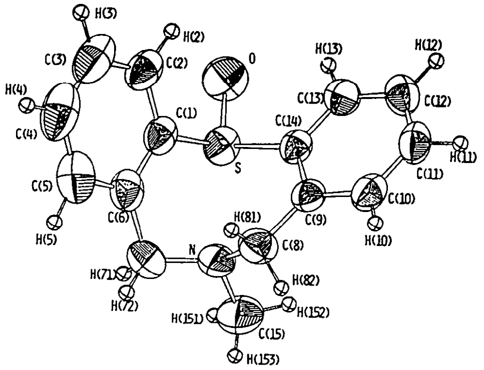
(c)

(d)

Fig. 1. *ORTEP*II (Johnson, 1971) drawings with atomic numbering. (*a*) (I), (*b*) (II), (*c*) (III), (*d*) (IV)*A* and (*e*) (IV)*B*. The thermal ellipsoids for non-H atoms are drawn at 50% probability.

Table 3. *Bond lengths* (Å) *and angles* (°) *of non-hydrogen atoms with their estimated standard deviations*

X_{ap}	(I) Cl	(II) O	(III) C(16)	(IV)*A* O	(IV)*B* O
X_{ap}–S	2·192 (3)	1·657 (6)	1·804 (5)	1·501 (2)	1·501 (2)
S–C(1)	1·815 (7)	1·798 (8)	1·811 (4)	1·815 (2)	1·809 (3)
S–C(14)	1·822 (7)	1·799 (8)	1·812 (4)	1·816 (2)	1·827 (2)
O–C(16)		1·409 (13)			
N–C(7)	1·472 (10)	1·476 (11)	1·451 (6)	1·446 (3)	1·449 (4)
N–C(8)	1·500 (11)	1·465 (12)	1·457 (6)	1·449 (3)	1·450 (4)
N–C(15)	1·459 (11)	1·473 (12)	1·458 (7)	1·458 (4)	1·454 (5)
C(1)–C(2)	1·377 (10)	1·397 (12)	1·377 (6)	1·385 (3)	1·394 (4)
C(1)–C(6)	1·389 (10)	1·383 (11)	1·397 (6)	1·387 (3)	1·394 (4)
C(2)–C(3)	1·377 (11)	1·395 (13)	1·384 (7)	1·384 (4)	1·377 (5)
C(3)–C(4)	1·381 (13)	1·354 (14)	1·383 (7)	1·369 (4)	1·370 (6)
C(4)–C(5)	1·389 (13)	1·373 (14)	1·363 (7)	1·389 (4)	1·388 (5)
C(5)–C(6)	1·402 (12)	1·399 (12)	1·387 (7)	1·389 (3)	1·386 (5)
C(6)–C(7)	1·488 (11)	1·483 (12)	1·493 (7)	1·506 (3)	1·507 (4)
C(8)–C(9)	1·494 (12)	1·502 (13)	1·510 (7)	1·501 (3)	1·496 (4)
C(9)–C(10)	1·389 (12)	1·401 (13)	1·407 (7)	1·394 (4)	1·392 (4)
C(9)–C(14)	1·402 (10)	1·376 (11)	1·386 (6)	1·397 (3)	1·400 (3)
C(10)–C(11)	1·381 (12)	1·372 (15)	1·381 (7)	1·385 (4)	1·374 (4)
C(11)–C(12)	1·371 (13)	1·359 (15)	1·345 (7)	1·369 (4)	1·375 (4)
C(12)–C(13)	1·377 (13)	1·386 (14)	1·355 (7)	1·380 (4)	1·383 (4)
C(13)–C(14)	1·359 (11)	1·388 (13)	1·395 (6)	1·391 (3)	1·384 (3)
X_{ap}–S–C(1)	95·3 (2)	97·0 (3)	101·0 (2)	104·4 (1)	104·8 (1)
X_{ap}–S–C(14)	97·6 (2)	94·3 (3)	102·8 (2)	103·3 (1)	103·7 (1)
C(1)–S–C(14)	104·6 (3)	107·6 (4)	104·6 (2)	98·7 (1)	99·1 (1)
S–O–C(16)		112·8 (6)			
C(7)–N–C(8)	113·7 (6)	113·5 (7)	116·3 (4)	115·2 (2)	115·7 (2)
C(7)–N–C(15)	114·3 (6)	114·1 (7)	115·3 (4)	114·4 (2)	115·9 (3)
C(8)–N–C(15)	111·4 (6)	111·8 (7)	114·6 (4)	113·7 (2)	113·4 (3)
S–C(1)–C(2)	123·8 (6)	121·2 (6)	121·5 (3)	116·5 (2)	116·7 (2)
S–C(1)–C(6)	113·1 (5)	117·0 (6)	116·9 (3)	122·1 (2)	122·1 (2)
C(2)–C(1)–C(6)	123·1 (7)	121·6 (8)	121·7 (4)	121·2 (2)	121·0 (3)
C(1)–C(2)–C(3)	117·8 (7)	117·9 (8)	120·0 (4)	119·7 (2)	119·5 (3)
C(2)–C(3)–C(4)	120·6 (8)	120·5 (9)	119·1 (5)	119·6 (5)	120·1 (4)
C(3)–C(4)–C(5)	121·6 (8)	121·9 (9)	120·1 (5)	120·8 (3)	120·7 (4)
C(4)–C(5)–C(6)	118·4 (8)	119·3 (9)	122·5 (5)	120·2 (2)	120·5 (3)
C(1)–C(6)–C(5)	118·4 (7)	118·8 (8)	116·5 (4)	118·3 (2)	118·2 (3)
C(1)–C(6)–C(7)	116·9 (7)	118·5 (7)	121·0 (4)	120·3 (2)	120·0 (3)
C(5)–C(6)–C(7)	124·6 (7)	122·8 (8)	122·5 (4)	121·3 (2)	121·8 (3)
N–C(7)–C(6)	105·2 (6)	105·7 (7)	108·1 (4)	109·0 (2)	108·5 (2)
N–C(8)–C(9)	106·2 (6)	106·8 (7)	108·5 (4)	110·2 (2)	110·2 (2)
C(8)–C(9)–C(10)	123·5 (7)	122·2 (8)	120·0 (4)	121·6 (2)	121·1 (2)
C(8)–C(9)–C(14)	119·3 (7)	118·0 (8)	122·2 (4)	121·0 (2)	120·9 (2)
C(10)–C(9)–C(14)	117·2 (7)	119·7 (8)	117·8 (4)	117·4 (2)	117·9 (2)
C(9)–C(10)–C(11)	120·6 (8)	119·5 (9)	120·3 (5)	121·4 (3)	121·6 (3)
C(10)–C(11)–C(12)	120·5 (8)	119·7 (10)	120·8 (5)	120·7 (3)	120·1 (3)
C(11)–C(12)–C(13)	120·0 (9)	122·7 (10)	121·2 (5)	119·1 (3)	119·5 (3)
C(12)–C(13)–C(14)	119·6 (8)	117·3 (9)	118·5 (4)	120·7 (2)	120·7 (2)
S–C(14)–C(9)	114·1 (5)	118·6 (6)	119·0 (3)	124·3 (2)	124·1 (2)
S–C(14)–C(13)	123·7 (6)	120·3 (7)	119·4 (3)	114·9 (2)	115·7 (2)
C(9)–C(14)–C(13)	122·1 (7)	121·1 (8)	121·5 (4)	120·7 (2)	120·2 (2)



(e)

Fig. 1 (*cont.*).

Table 4. *Torsion angles (°) in the thiazocine rings and the deviations from the mean planes defined by* C(1), C(6), C(9) *and* C(14)

E.s.d.'s are 0·3 ~ 0·9° for torsion angles and 0·008 ~ 0·03 Å for distances.

X_{ap}	(I) Cl	(II) O	(III) C(16)	(IV)*A* O	(IV)*B* O
C(14)–S–C(1)–C(6)	72·7	−79·9	83·2	−85·9	−84·7
S–C(1)–C(6)–C(7)	−3·9	4·8	−1·6	4·8	6·1
C(1)–C(6)–C(7)–N	−29·1	25·3	−34·0	30·8	33·3
C(6)–C(7)–N–C(8)	−72·1	77·3	−65·7	69·1	63·8
C(7)–N–C(8)–C(9)	140·7	−142·5	132·9	−129·2	−130·8
N–C(8)–C(9)–C(14)	−22·8	26·9	−29·6	27·4	30·2
C(8)–C(9)–C(14)–S	2·8	−6·6	6·4	−8·8	−6·5
C(9)–C(14)–S–C(1)	−69·3	68·0	−66·1	66·6	62·2
C(6)–C(7)–N–C(15)	158·4	−153·0	155·9	−156·4	−159·8
C(9)–C(8)–N–C(15)	−88·4	86·8	−88·4	96·0	91·7
C(1)	0·161	−0·163	0·130	−0·140	−0·178
C(6)	−0·128	0·116	−0·103	0·091	0·125
C(9)	0·133	−0·061	0·112	−0·032	−0·027
C(14)	−0·136	0·114	−0·117	0·093	0·093
X_{ap}	−0·725	0·489	−0·815	0·680	0·557
S	−1·035	0·931	−0·992	0·968	0·907
N	−1·362	1·340	−1·340	1·447	1·480
C(7)	−1·283	1·216	−1·205	1·226	1·316
C(8)	−0·263	0·304	−0·214	0·397	0·394

(IV), S–X_{ap} lengths are within the range of the normal S–C and S=O distances.

Besides the S–X_{ap} distances the difference in S···N interaction affects many parts of the structures. As can be seen from Tables 3 and 5, the dimensions about the S and N atoms change markedly with the S···N distance. As the S···N length decreases, the S–C length and the X_{ap}–S–C angle decrease and the C–S–C angle increases. For (I) and (II), the eight-membered ring flattens with endocyclic angles S–C(1)–C(6), S–C(14)–C(9), C(1)–C(6)–C(7) and C(14)–C(9)–C(8) which are smaller than those of (III) and (IV), while the exocyclic angles S–C(1)–C(2), S–C(14)–C(13), C(5)–C(6)–C(7) and C(8)–C(9)–C(10) of (I) and (II) are larger than those of (III) and (IV). The displacement of the S atom from the ideal equatorial plane of the trigonal bipyramid decreases as the S···N distance decreases. The S···N distance also correlates to the geometry of the ammonio group. The longer C–N distances and the smaller C–N–C angles are observed for (I) and (II). Thus, the geometry about N comes closer to a regular tetrahedron as the S···N length decreases. The displacements of N atoms from the planes of C(7)C(8)C(15) are 0·394, 0·394, 0·316, 0·349 and 0·330 Å for (I), (II), (III), (IV)*A* and (IV)*B*, respectively. These facts clearly show the contribution of the transannular electron transfer between S and N, such as

$$\geqq\mathrm{S}^{+}\cdots\mathrm{N}\leqq \;\rightleftharpoons\; \geqq\mathrm{S}\text{–}\mathrm{N}^{+}\leqq.$$

Slight deviations from the above relationships between the S···N distances and the geometries are found in (I). This is due to the high strain of the thiazocine ring for such a short transannular bond formation.

Fig. 3 shows molecular projections along the S···N bonds for (I) and (II). The S–Cl bond for (I) and S–C(16) for (III) bend toward the S lone pair. On the other hand, the apical S–O bond of (II) is bent away from the lone pair, toward the equatorial C atoms. For many sulfuranes the apical S–X_{ap} bonds were bent away from the S lone pair, especially in

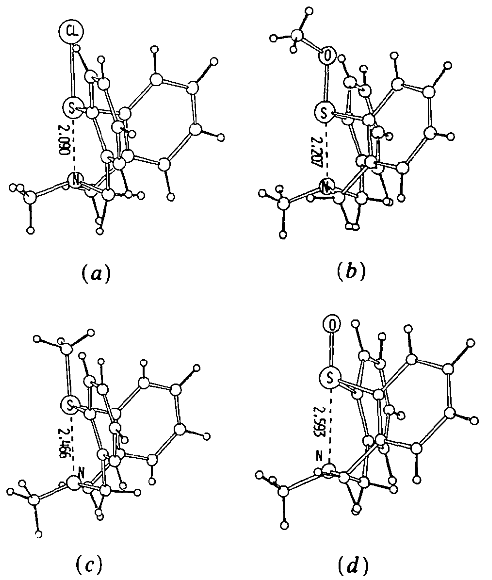


Fig. 2. Perspective views of the σ-ammoniosulfuranes. (*a*) (I), (*b*) (II), (*c*) (III), (*d*) (IV)*A*. (Distance in Å.)

Table 5. *Interatomic distances* (Å) *and angles* (°) *about* S···N *contacts*

X_{ap}	(I) Cl	(II) O	(III) C(16)	(IV)*A* O	(IV)*B* O
S···N	2·090 (3)	2·207 (7)	2·466 (4)	2·593 (2)	2·624 (2)
X_{ap}–S···N	176·9 (2)	175·0 (3)	176·9 (2)	179·5 (1)	179·1 (1)
C(1)–S···N	83·0 (3)	80·8 (3)	79·3 (2)	75·4 (1)	74·8 (1)
C(14)–S···N	85·4 (3)	82·1 (3)	80·1 (2)	76·3 (1)	75·6 (1)
C(7)–N···S	102·1 (5)	103·3 (5)	96·6 (3)	97·2 (1)	95·6 (2)
C(8)–N···S	106·7 (5)	105·5 (5)	100·7 (3)	101·2 (1)	99·8 (2)
C(15)–N···S	107·7 (5)	107·8 (5)	110·3 (3)	113·2 (2)	113·9 (2)

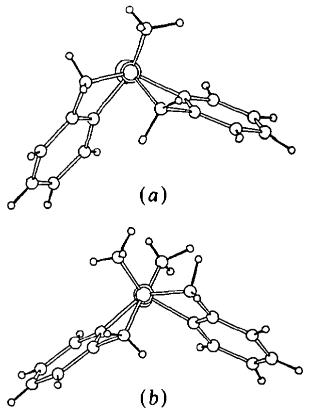


Fig. 3. Projection of the molecules along the N···S bonds for (*a*) (I) and (*b*) (II).

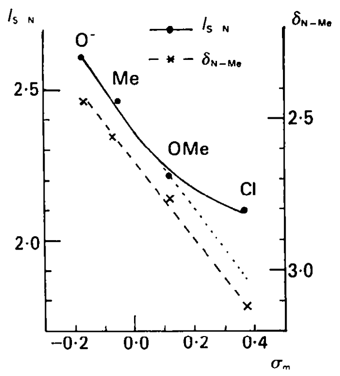


Fig. 4. Hammett plot of H NMR chemical shifts of N–Me groups in solution against σ_m and the relationships between the S···N distances (Å) in the crystalline state and σ_m.

the case of apical S–O bonds. This has been attributed to the repulsion effect between X_{ap} and the lone pair (Perozzi *et al.*, 1974). Some exceptions are observed for $(Me_2N)_2SF_2$ (Cowley, Riley, Szobota & Walker, 1979), dichlorobis(*p*-chlorophenyl)sulfurane (Baenziger *et al.*, 1969) and $C_2H_4SSeBr_2$ (Battelle, Knobler & McCullough, 1967), in which the apical S–F, S–Cl and Se–Br bonds are bent toward the lone pair of S or Se. For $(Me_2N)_2SF_2$ and $(p\text{-}Cl\text{-}Ph)_2SCl_2$ the distortions are attributed to short intermolecular contacts about F or Cl, while for $C_2H_4SSeBr_2$ the distortion has been ascribed mainly to intramolecular repulsions between Br and equatorial CH_2. For (I) and (III), one of the reasons may be the repulsion between the Cl or CH_3 group and H in the phenyl rings.

Fig. 4 shows a Hammett plot of H NMR chemical shifts of the NMe group in solution against σ_m (Akiba *et al.*, 1983). This shows very good linearity. The S···N distances in the crystalline state also fit the Hammett relationship except for (I). These facts indicate that the electron-withdrawing effect of the substituent at the S atom is transmitted to the NMe group through the S···N bond and also that these compounds retain the same conformation in solution.

The crystal structures are shown in Fig. 5. The crystal structure of (III) is isostructural to that of (I). There are channels constructed with thiazociniums along the *c* axis in which PF_6^- ions are sheathed. There are no contacts less than the sum of the van der Waals radii in these crystal structures.

References

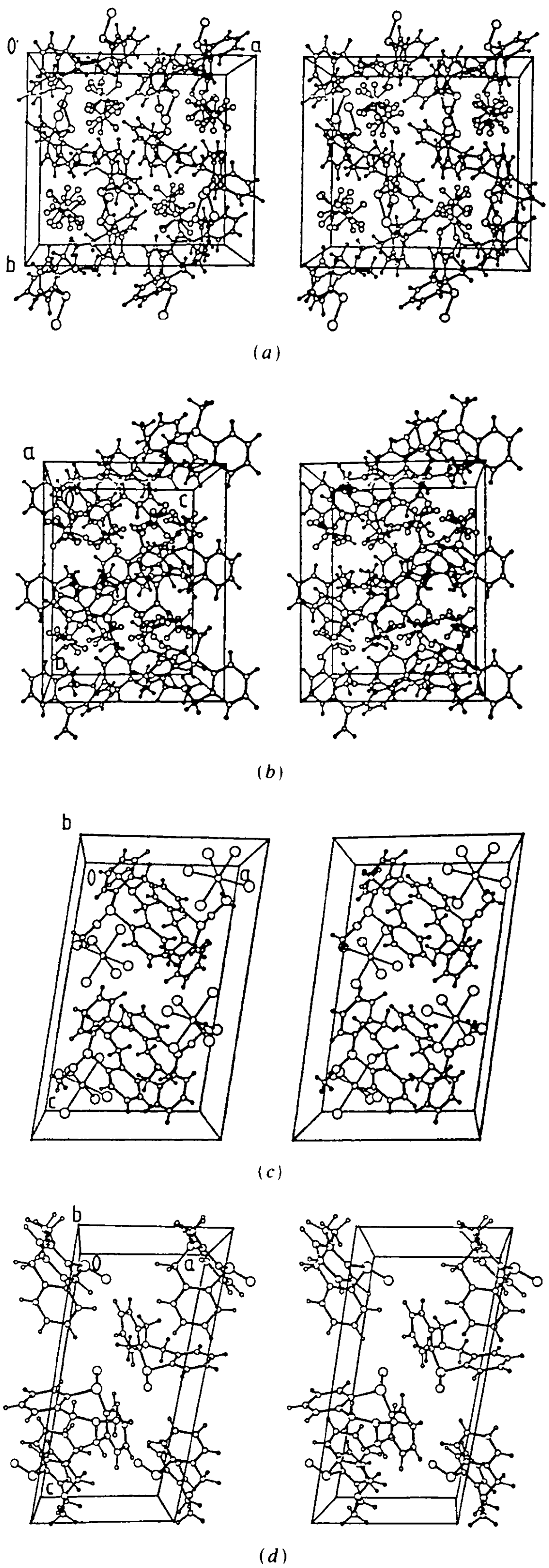
Adzima, L. J., Chiang, C. C., Paul, I. C. & Martin, J. C. (1978). *J. Am. Chem. Soc.* **100**, 953-962.

Akiba, K., Takee, K., Ohkata, K. & Iwasaki, F. (1983). *J. Am. Chem. Soc.* **105**, 6965-6966.

Baenziger. N. C., Buckles, R. E., Maner, R. J. & Simpson, T. D. (1969). *J. Am. Chem. Soc.* **91**, 5749-5755.

Battelle, L., Knobler, C. & McCullough, J. D. (1967). *Inorg. Chem.* **6**, 958-962.

Cowley, A. H., Riley, P. E., Szobota, J. S. & Walker, M. L. (1979). *J. Am. Chem. Soc.* **101**, 5620-5624.



(*a*)

(*b*)

(*c*)

(*d*)

Fig. 5. Stereoscopic views of the crystal structures. (*a*) (I), (*b*) (III), (*c*) (II) and (*d*) (IV).

GELLATLY, R. P., OLLIS, W. D. & SUTHERLAND, I. O. (1976). *J. Chem. Soc. Perkin Trans.* 1, pp. 913-925.
HAMILTON, W. C. & LAPLACA, S. J. (1964). *J. Am. Chem. Soc.* **86**, 2289-2290.
HARDY, A. D. & AHMED, F. R. (1974). *Acta Cryst.* B**30**, 1674-1677.
International Tables for X-ray Crystallography (1974). Vol. IV. Birmingham: Kynoch Press. (Present distributor D. Reidel, Dordrecht.)
JOHNSON, C. K. (1971). *ORTEP*II. Report ORNL-5138. Oak Ridge National Laboratory, Tennessee.
KÁLMÁN, A., SASVÁRI, K. & KAPOVITS, I. (1973). *Acta Cryst.* B**29**, 355-357.
LAM, W. Y., DUESLER, E. N. & MARTIN, J. C. (1981). *J. Am. Chem. Soc.* **103**, 127-135.
LAU, P. H. W. & MARTIN, J. C. (1977). *J. Am. Chem. Soc.* **99**, 5490-5491.
MAIN, P., HULL, S. E., LESSINGER, L., GERMAIN, G., DECLERCQ, J.-P. & WOOLFSON, M. M. (1978). *MULTAN*78. *A System of Computer Programs for the Automatic Solution of Crystal Structures from X-ray Diffraction Data.* Univs. of York, England, and Louvain-la-Neuve, Belgium.
MUSHER, J. I. (1969). *Angew. Chem. Int. Ed. Engl.* **8**, 54-68; *Angew. Chem.* **81**, 68-83.
PAUL, I. C., MARTIN, J. C. & PEROZZI, E. F. (1972). *J. Am. Chem. Soc.* **94**, 5010-5017.
PAULING, L. (1960). *The Nature of the Chemical Bond*, 3rd ed. Ithaca: Cornell Univ. Press.
PEROZZI, E. F., MARTIN, J. C. & PAUL, I. C. (1974). *J. Am. Chem. Soc.* **96**, 6735-6744.
PICARD, C., CAZAUX, L. & JAUD, J. (1981). *J. Chem. Soc. Perkin Trans.* 2, pp. 1554-1557.
SAKURAI, T. & KOBAYASHI, K. (1979). *Rikagaku Kenkyusho Hokoku*, **55**, 69-77.

International Union of Crystallography

Acta Cryst. (1985). B**41**, 452-453

Prices of *Acta Crystallographica* and *Journal of Applied Crystallography*

The Executive Committee of the International Union of Crystallography is pleased that it has not been necessary to increase the subscription rates and the prices of back numbers for *Acta Crystallographica* and *Journal of Applied Crystallography* as from 1 January 1986.

Acta Crystallographica

The following rates will apply for Volumes A42, B42 and C42 (1986). All subscription rates are fixed in Danish kroner. The US dollar equivalents are no longer given because of rapid fluctuations in exchange rates.

Complete volumes, regular price per volume

Sections A, B & C (combined subscription)	Dkr 5250
Section A only	Dkr 1275
Section B only	Dkr 1275
Section C only	Dkr 3000

Complete volumes, reduced price for individuals

Sections A, B & C (combined subscription)	Dkr 1450
Section A only	Dkr 350
Section B only	Dkr 350
Section C only	Dkr 850

All subscribers in the USA and Canada should add to the above subscription rates the additional charges for airfreighting as mentioned below.

The reduced-rate subscriptions are ordinarily only available to members of recognized scientific societies, and applications must be accompanied by a written undertaking that the journal is for the personal use of the subscriber and will not be made available to libraries, institutions, *etc.* These conditions also apply to persons wishing to order back numbers at the reduced rates.

Single parts

The price of single parts of any Section of Volume 42 (1986) is Dkr 320.

Journal of Applied Crystallography

The following rates will apply for Volume 19 (1986). All subscription rates are fixed in Danish kroner. The US dollar equivalents are no longer given because of rapid fluctuations in exchange rates.

Complete volumes, regular price per volume	Dkr 1275
Complete volumes, reduced price for individuals	Dkr 400

All subscribers in the USA and Canada should add to the above subscription rates the additional charge for airfreighting as mentioned below.

The same conditions apply to reduced-rate subscriptions as in the case of *Acta Crystallographica* (see above).

Single parts

The price for single parts of Volume 19 (1986) is Dkr 320.

Airfreighting of copies to the USA and Canada

Deliveries of *Acta Crystallographica* and *Journal of Applied Crystallography* to the USA and Canada in 1986 will continue to be by air freight to New York and thence by second class mail. The use of this service is obligatory for all subscribers in those countries. The charges in Danish kroner are as given below.

Acta Crystallographica	
Sections A, B & C (combined subscription)	Add Dkr 380
Section A only	Add Dkr 90
Section B only	Add Dkr 90
Section C only	Add Dkr 220
Journal of Applied Crystallography	Add Dkr 70