

relatively weak π -type three center bonds. This interpretation would explain the large overall accelerating effect of aryl, together with the relatively small difference between different aryl groups.

This discussion has been based on the assumption that the intermediate ions are better represented as π complexes (VIII) rather than as phenonium ions (XIV); for a discussion of the relationship between the two representations, see ref 26. It could be that the curvature of the plots in Figure 2 was merely an indication that the ions are better represented as XIV than as VIII. Since XIV is analogous to the intermediates in electrophilic substitution,²⁶ we would then expect a plot of the logarithms of solvolytic rate constants ($\log k$) vs. localization energies (E_{loc}) to be linear. In fact, however, a plot of $\log k$ vs. E_{loc} , the latter calculated by our SCF procedure,^{27, 29} shows the same curvature as the

(29) C. de Llano, Ph.D. Dissertation, The University of Texas at Austin, 1968.

plots of Figure 2. This of course is not surprising in view of the known²⁶ relationship between E_{loc} and ΔE .

Not only does this result not support the phenonium ion representation, but it even argues against it, for if the intermediates were phenonium ions, the curvature of the plots of $\log k$ vs. E_{loc} would be hard to explain, while the curvature of the plots in Figure 2 can be explained in a reasonable manner if the intermediates are best represented as π complexes.

The conclusions reached here are in agreement with those recently drawn by Schleyer and his collaborators³⁰ from studies of the rates of solvolysis of substituted 2-phenylethyl esters, using the Hammett relation. These showed in a very elegant way the transition from unassisted reaction with increasing nucleophilicity of the aryl group.

(30) C. J. Lancelot and P. von R. Schleyer, *J. Amer. Chem. Soc.*, **91**, 4291, 4296, 4297 (1969); C. J. Lancelot, J. J. Harper, and P. von R. Schleyer, *ibid.*, **91**, 4294 (1969).

The Structure of a Halosulfonium Salt. The 1:1 Adduct of Thiophane with Bromine

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Abstract: The structure of the 1:1 adduct of thiophane with bromine has been investigated by X-ray (space group Pnma, $a = 12.326$ (5), $b = 7.331$ (3), $c = 8.387$ (3) Å, $Z = 4$, $R = \Sigma||F_o| - |F_c||/\Sigma|F_o| = 0.085$ for 692 observed reflections) and nmr methods. In the solid state the tricoordinate sulfur atom is pyramidal and the S-Br-Br arrangement is linear with S-Br and Br-Br bond lengths of 2.32 and 2.72 Å, respectively. The ring appears planar, but highly anisotropic thermal coefficients were found for the β -carbon atoms. Minimum potential energy calculations suggest that the conformation of the thiophane ring has C_2 symmetry with a low energy barrier between the two enantiomers. Thus, the existence of a statistical distribution between both conformations, perhaps maintained through a dynamic process, provides the most satisfying interpretation of the X-ray results. The nmr data for solutions of the complex suggest rapid inversion of pyramidal coordination and a highly charged sulfur atom. Self-consistent charge extended Hückel calculations indicate a $+0.34$ charge on sulfur and a -0.8 charge on the terminal bromine, little involvement of sulfur d orbitals, and a very weak Br-Br interaction.

The molecular structure of the metastable adducts formed between organic sulfides and the reactive halogens bromine and chlorine has remained a persistent dilemma. Much of the mystery regarding their structure arises because of their instability with respect to thermal degradation, moisture, or disproportionation. By analogy to structures suggested for sulfur tetrafluoride^{3, 4} and its organic derivatives⁵ and halogenated derivatives of selenium,⁶ tellurium,⁷ and phos-

phorus,⁸ a trigonal-bipyramidal array of groups⁹ about sulfur has been considered a possibly stable one,¹⁰ and recently the complex of chlorine with bis(*p*-chlorophenyl) sulfide has been reported to have a trigonal-bipyramidal sulfur atom.¹¹ On the other hand the lability of protons on the carbons attached to sulfur,¹² the susceptibility of the carbon-sulfur bonds to cleavage forming carbonium ions,¹³ and the extreme ease with

11, 782 (1958); G. D. Christofferson and J. D. McCullough, *ibid.*, **11**, 249 (1958).

(8) E. L. Muetterties, W. Mahler, K. J. Packer, and R. Schmutzler, *Inorg. Chem.*, **3**, 1298 (1964); E. L. Muetterties, W. Mahler, and R. Schmutzler, *ibid.*, **2**, 613 (1963).

(9) A thorough review of pentacoordinate species is available: E. L. Muetterties and R. A. Schunn, *Quart. Rev. (London)*, **20**, 245 (1966).

(10) See, for example (a) K. Mislow, T. Simmons, J. T. Melillo, and A. L. Ternay, Jr., *J. Amer. Chem. Soc.*, **86**, 1452 (1964); (b) K. Mislow, *Rec. Chem. Progr.*, **28**, 217 (1967); (c) J. I. Musher, *Angew. Chem. Intern. Ed. Engl.*, **8**, 54 (1969).

(11) N. C. Baenzliger, R. E. Buckles, Jr., R. J. Maner, and T. D. Simpson, *J. Amer. Chem. Soc.*, **91**, 5749 (1969).

(12) See, for example: F. G. Bordwell and B. M. Pitt, *ibid.*, **77**, 572 (1955); D. L. Tuleen and T. B. Stephens, *J. Org. Chem.*, **34**, 31 (1969); H. Bohme and H. Gran, *Ann.*, **581**, 133 (1953).

(1) On sabbatical leave from the Institute di Chimica Industriale del Politecnico di Milano, 20133 Milan, Italy.

(2) National Aeronautics and Space Administration Trainee, 1967-1969.

(3) L. Muetterties and W. D. Phillips, *J. Amer. Chem. Soc.*, **81**, 1084 (1959).

(4) F. A. Cotton, J. W. George, and J. S. Waugh, *J. Chem. Phys.*, **28**, 994 (1958); R. E. Dodd, L. A. Woodward, and H. L. Roberts, *Trans. Faraday Soc.*, **52**, 1052 (1955).

(5) W. A. Sheppard, *J. Amer. Chem. Soc.*, **84**, 3058 (1962).

(6) J. D. McCullough and G. Hamburger, *ibid.*, **63**, 803 (1941); **64**, 508 (1942); J. D. McCullough and R. E. Marsh, *Acta Crystallogr.*, **3**, 41 (1950).

(7) G. D. Christofferson, R. A. Sparks, and J. D. McCullough, *ibid.*,

which some of these materials form sulfoxides upon treatment with water¹⁴ all suggest the formation of an ionic intermediate in solution. Completely ignored as a possibility, so far as we can ascertain, has been the linear charge-transfer type structure formed between halogens and electron donors¹⁵ in spite of the report of a charge-transfer structure for the stable adduct of dibenzyl sulfide with iodine.¹⁵

In order to gain definitive structural information regarding halosulfonium salts, a single-crystal X-ray analysis of the 1:1 adduct (I) obtained by combination of thiophane with bromine has been carried out. This information was supplemented by nmr analyses, minimum potential energy calculations to support conformational arguments about the thiophane ring, and self-consistent charge extended Hückel calculations. The exceptional stability of our halosulfonium salt accounts for our choice of it as the object of this investigation, and the obvious implications of the X-ray structure with respect to the mechanisms both of hydrogen halide catalyzed racemization of sulfoxides and of the Pummerer reaction prompted our continued efforts.

Experimental Section

Preparation. 1-Bromothiophanium bromide, first described by Runge, Profft, and Drux,¹⁶ was obtained as yellow-orange single crystals (mp 80–81° dec) from cold methylene chloride solution; $\nu_{\text{max}}^{\text{CH}_2\text{Cl}_2}$ 285 cm^{-1} (ϵ 1800); $\nu_{\text{max}}^{\text{CH}_3\text{CN}}$ 280 cm^{-1} (ϵ 1800). Nmr absorption occurred at δ (CH_2Cl_2) 3.53 (4 H, m) and 2.41 ppm (4 H, m) and at δ (CD_3CN) 3.87 (4 H, m) and 2.42 ppm (4 H, m). Thermal degradation of this material provides 2,3-dibromothiophane and thiophane.¹⁷ One of the crystals was selected and, together with dehydrated mineral oil, was sealed in a thin capillary to prevent decomposition.

X-Ray Data. Determination of the orthorhombic unit cell dimensions (Table I) was accomplished in a preliminary investiga-

Table I. Unit Cell Parameters

1-Bromothiophanium bromide, $\text{C}_4\text{H}_6\text{SBr}_2$, mol wt = 247.98	
Orthorhombic, space group: Pnma, $Z = 4$, $F(000) = 472$	
a	$12.326 \pm 0.005 \text{ \AA}$
b	$7.331 \pm 0.003 \text{ \AA}$
c	$8.387 \pm 0.003 \text{ \AA}$
d_{exptl}	2.15 g/cm^3 (floatation method)
$d_{\text{X-ray}}$	2.17 g/cm^3
μR	1.65 (λ 1.5418 \AA)

tion using Weissenberg methods. On the basis of systematic absences, the possible space groups were Pnma and Pn2₁a. Intensity collection was performed with a Picker four-circle automated diffractometer coupled with a PDP-8 digital computer. The θ - 2θ scan mode (1.67° in 100 sec) with Ni-filtered $\text{Cu K}\alpha$ radiation (λ 1.5418 \AA) and pulse-height analysis was used, a total of 692 independent reflections being collected in the range of 2θ explored (0 – 130°). Two stationary-crystal-stationary-counter background counts of 10 sec were taken at the end of each scan. Because of the

(13) G. E. Wilson, Jr., *J. Amer. Chem. Soc.*, **87**, 3785 (1965), and references therein; N. J. Leonard and G. E. Wilson, Jr., *ibid.*, **86**, 5307 (1964); W. D. Crow and N. J. Leonard, *Tetrahedron Lett.*, 1477 (1964); H. Kwart and L. J. Miller, *J. Amer. Chem. Soc.*, **80**, 884 (1958); L. A. Paquette and R. W. Houser, *ibid.*, **91**, 3870 (1969).

(14) H. H. Szmant in "Organic Sulfur Compounds," Vol. 1, N. Kharasch, Ed., Pergamon Press, Inc., New York, N. Y., 1961, Chapter 16; W. Tagaki, K. Kilukawa, K. Ando, and S. Oae, *Chem. Ind. (London)*, 1624 (1964).

(15) (a) O. Hassel and C. Rømming, *Quart. Rev. (London)*, **16**, 1 (1962); (b) C. Rømming, *Acta Chem. Scand.*, **14**, 2145 (1960).






(16) F. Runge, E. Profft, and R. Drux, *J. Prakt. Chem.*, **2**, 279 (1955).

(17) The products of this reaction were previously considered to be 3-bromobut-3-enesulfonyl bromide and thiophane: G. E. Wilson, Jr., and R. Albert, *Tetrahedron Lett.*, 6271 (1968).

approximately cylindrical shape of the crystal, absorption corrections for a diffracting cylinder were applied ($\mu R = 1.65$).

Nmr spectral data were obtained at -30° on saturated solutions of I in methylene chloride and acetonitrile and at ambient temperature on 20–25% solutions of all other compounds shown in Table II.

Table II. Chemical Shifts of α and β Protons of Thiophane Derivatives in CDCl_3 Relative to TMS

Compd	δ_α (Hz)	δ_β (Hz)
	165	115
	170	135
	183	133
	205	135
	212	135

^a In $\text{DMSO}-d_6$. ^b In CH_2Cl_2 .

Results

Structure Determination and Refinement. From analysis of the three-dimensional Patterson function, the array of the heavy atoms appeared to be in agreement with the centrosymmetrical Pnma space group. In fact, all the outstanding peaks were located on the planes with $y = 0$ and $y = 0.5$, and they were clearly attributable to interatomic vectors connecting Br and S atoms lying on parallel planes with constant y , separated by $b/2$. This is in agreement with the molecule lying on a crystallographic mirror plane, which contains the SBr_2 group. Accordingly, the x and z coordinates of the heavy atoms were derived from the Patterson peaks and a structure factor calculation was performed assuming the Pnma space group. A subsequent Fourier map allowed detection of the carbon atoms, after which the entire structure was refined by least-squares methods. Four full-matrix cycles were sufficient to reduce the R factor to 0.085 ($R = \Sigma |F_o| - |F_c| / \Sigma |F_o|$); the weighting scheme adopted corresponds to that suggested by Cruickshank ($w(hkl) = 1/(aF_o^2(hkl) + bF_o(hkl) + c)$; $a = 1/6$, $b = 1/18 \times F_o(\text{max})$, $c = 2bF_o(\text{min})$);¹⁸ Table III contains the final values of the fractional coordinates and thermal factors.¹⁹ The resulting molecular geometry is presented in Figure 1.

In view of the unusually large and strongly anisotropic thermal factors of S and C_β (see Table II and Figure 1)

(18) D. W. J. Cruickshank and D. E. Pilling, "Computing Methods and the Phase Problem in X-ray Crystal Analysis," R. Pepinsky and J. C. Speakman, Ed., Pergamon Press, New York, N. Y., 1961, p 32.

(19) A list of the observed and calculated structure factors will be deposited with the ASIS National Auxiliary Publication Service, c/o CCM Information Corp., 909 3rd Ave., New York, N. Y., 10022.

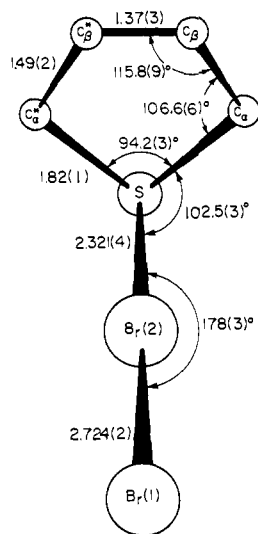


Figure 1. Molecular dimensions of 1-bromothiophanium bromide resulting from the X-ray refinement. The standard deviations, in parentheses, are given in units of the last significant digit.

we have investigated the possibility that the actual space group is the acentric $Pn2_1a$, assumed to contain a pseudomirror-symmetry plane crossing the molecule; investigation of this hypothesis was stimulated by the unexpected quasiplanar conformation of the thiophane ring resulting from the assumption of the $Pnma$ space group. Different least-squares refinements were tried, starting from molecular models deviating slightly from the mirror symmetry, but the results were always unsatisfactory, since either the symmetrical structure was obtained again, or completely unacceptable conformations resulted. We conclude, therefore, that either $Pnma$ is the actual space group, or the crystal symmetry is so slightly different from it as to be virtually indistinguishable within experimental errors.

Table III. Final Atomic Parameters (esd)^a

Atom	A. Positional Parameters		
	x/a	y/a	z/a
Br (1)	0.7100 (1)	0.2500	0.1139 (1)
Br (2)	0.6871 (1)	0.2500	0.4369 (1)
S	0.6729 (2)	0.2500	0.7128 (2)
C_α	0.5757 (6)	0.4315 (10)	0.7491 (9)
C_β	0.4674 (6)	0.3432 (10)	0.7629 (8)

Atom	B. Thermal Parameters					
	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Br (1)	7.0 (1)	6.1 (1)	2.0 (1)	0	0.0 (1)	0
Br (2)	4.8 (1)	6.0 (1)	2.4 (1)	0	0.1 (1)	0
S	3.8 (2)	9.4 (3)	1.6 (1)	0	0.1 (1)	0
C_α	6.7 (7)	5.4 (6)	3.6 (5)	-0.8 (7)	0.7 (12)	-0.7 (15)
C_β	5.3 (6)	6.5 (9)	19.6 (21)	0.1 (6)	3.0 (6)	0.4 (6)

^a Esd stands for estimated standard deviation, in units of the last significant digit.

Nmr Data. Two broad triplet-like envelopes occur at 2.41 and 3.53 ppm for I at -30° at which temperature the compound is stable in methylene chloride solution. The envelopes bear a striking similarity to those of thiophane itself and suggest that the time-averaged symmetry for both must be nearly identical. That this is

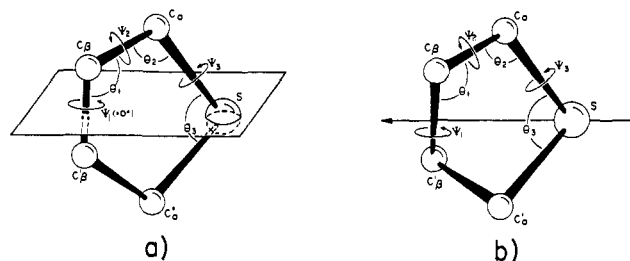


Figure 2. Mirror (C_s , a) and twofold symmetry (C_2 , b) models of the thiophane ring.

probably the result of exchange equilibria involving ionic species is suggested by the downfield shift of the α protons to 3.87 ppm when the solvent is changed to acetonitrile. The ionic nature of the bromosulfonium salt in solution is further indicated by the chemical shift of the α protons of I in relation to those of thiophane, its sulfoxide, sulfone, and S-methylsulfonium salt as shown in Table II.

Conformational Calculations. In 1959, Pitzer and Donath²⁰ determined the energy difference between the C_2 and the C_s conformations of a series of saturated five-membered rings with general formula $X(CH_2)_4$ ($X = CH_2, NH, O, S$). They assumed that the C_2 and the C_s conformations of each ring could be derived by employing the ring dihedral angles calculated for the corresponding conformations of cyclopentane and evaluating the resulting energies in terms of the torsional potentials around the bonds; the heteroatom was assumed to lie on either the twofold axis or the mirror plane. Because our interest was focused mainly on the geometry of the most stable conformer of I rather than on its energy content, we have undertaken a conformational analysis of the thiophane ring using the most reliable geometrical and physical parameters available.

We have confined our attention to the models containing a mirror plane and a twofold axis, a and b, respectively, in Figure 2; in both cases we have kept the bond lengths fixed so that, accounting for the loss of 2 degrees of freedom due to the assumption of symmetry, the resulting internal degrees of freedom are: $(3 \times 5) - 6$ (rigid body) $- 5$ (fixed bond lengths) $- 2$ (symmetry) = 2. We have neglected all interactions between nonbonded atoms, which must play a very small role, in view of the limited deformation attainable by the ring. The internal potential energy function connected with the rotation angles ψ around the single bonds has been assumed, $E(\psi) = \frac{1}{2}U_0(1 + \cos 3\psi)$, where $\psi = 0^\circ$ for the *cis* conformation and $U_0 = 2.8$ kcal/mol²⁰ for both the $C_\beta-C_\beta^*$ and the $C_\alpha-C_\beta$ bonds because of the small angular range actually permitted. An analogous energy function around the $C_\alpha-S$ bonds has been taken with $U_0 = 0.71$ kcal/mol.²¹ For the C-C-C and C-C-S bond angle deformations, we have assumed an elastic potential function

$$E(\theta) = \frac{1}{2}k(\theta - \theta_0)^2$$

where θ_0 , the zero-strain angles, have been taken equal to 112° ²² and 110° ,²³ respectively, and where the elastic

(20) K. S. Pitzer and W. E. Donath, *J. Amer. Chem. Soc.*, **81**, 3213 (1959).

(21) R. W. Kilb, *J. Chem. Phys.*, **23**, 1736 (1955).

constant has been taken equal to 136 kcal/mol radian² in both cases.²⁴ The zero-strain C-S-C angle has been set at 100°.²⁵ For the elastic constant, for which we could find no reliable experimental data, we tentatively chose three different values: 180, 136, and 90 kcal/mol radian². The energy minima showed only very small displacements (ca. 0.2° in the ψ and θ angles). Figure 3 shows the conformational energy plot for the twofold axis model as a function of $\theta_1 = \theta(\text{C-C-C})$ and $\psi_1 = \psi(\text{C}_\beta\text{-C}_\beta^*)$. A fairly well-resolved minimum is observable at $\theta = 107.5^\circ$ and $\psi = 46^\circ$; the energy of the best conformation for the mirror symmetry model is about 4.8 kcal/mol higher.

Extended Hückel Calculations. Calculations on I using the X-ray-determined coordinates of all atoms were performed using the extended Hückel method²⁶ adapted for the ω technique.²⁷ Off-diagonal elements of the Hamiltonian matrix were calculated using the Wolfberg-Helmholtz approximation with $K = 2.0$. The initial values for the valence-state ionization potentials for carbon, hydrogen, and the sulfur 3s and 3p orbitals were those given by Jaffe.²⁸ A value of -3.0 eV was used for the Coulomb integral of the 3d orbitals of sulfur in the absence of a formal charge.²⁹ The VSIP's for bromine were those suggested by Gray and Ballhausen.³⁰ Slater exponents are from Clementi.³¹ Correction of the VSIP's for carbon, hydrogen, and sulfur was performed using the Cusachs parameters³² and a damping factor of 0.25. A charge correction factor for bromine is not available, but values between 6.5 and 10.0 eV/unit charge were shown to have little effect on the final calculated charge distribution. Similarly, assuming the minimum potential energy conformation for the ring led to no substantial change in the calculated charge distribution among the sulfur and bromine atoms (Tables IV and V);

Table IV. Overlap Populations in the Thiophane-Bromine Adduct and the 1-Bromothiophanium Ion

Bond	Adduct ^a	Adduct ^b	Ion ^b
Br-Br	0.008	0.011	
Br-S	0.462	0.446	0.533
C α -S	0.699	0.700	0.716
C α -C β	0.727	0.749	0.749
C α -C β	0.735	0.384	0.386

^a Geometry from minimum potential energy calculation. ^b Geometry from X-ray data.

but it is interesting to note that the overlap between the two β -carbon atoms improves in this geometry and the

(22) A. I. Kitaigorodskii, "Organic Chemical Crystallography," Consultants Bureau, New York, N. Y., 1961, Chapter 5.

(23) A. McL. Mathieson, *Acta Crystallogr.*, **5**, 332 (1952).

(24) R. G. Snyder and J. H. Schachtschneider, *Spectrochim. Acta*, **21**, 169 (1965).

(25) N. Kharasch, "Organic Sulfur Compounds," Vol. 1, Pergamon Press, New York, N. Y., 1961, p 542.

(26) R. Hoffmann, *J. Chem. Phys.*, **39**, 1397 (1963); **40**, 2480 (1964).

(27) A. Streitwieser, "Molecular Orbital Theory for Organic Chemists," John Wiley & Sons, Inc., New York, N. Y., 1961, p 115.

(28) J. Hinze and H. H. Jaffe, *J. Amer. Chem. Soc.*, **84**, 540 (1962).

(29) T. Jordan, H. W. Smith, L. L. Lohr, Jr., and W. N. Lipscomb, *ibid.*, **85**, 846 (1963).

(30) C. J. Ballhausen and H. B. Gray, "Molecular Orbital Theory," Benjamin, New York, N. Y., 1964.

(31) E. Clementi and D. L. Raimondi, *J. Chem. Phys.*, **38**, 2686 (1963).

(32) L. C. Cusachs and J. W. Reynolds, *ibid.*, **43**, S160 (1965); L. C. Cusachs, J. W. Reynolds, and D. Barnard, *ibid.*, **44**, 835 (1966).

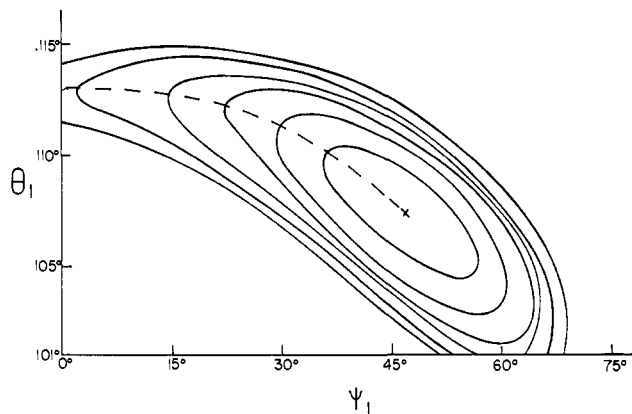


Figure 3. Plot of the conformational energy as a function of ψ_1 and θ_1 (see Figure 2b) for the C_2 model of the thiophane ring. Contours are drawn at intervals of 1 kcal/mol, starting from the energy of the most stable conformation, indicated by a cross. The dashed line represents a possible path for the interconversion of enantiomers.

atoms bear a smaller negative charge. A value of 8.0 eV/unit charge was used in the final calculations.

Table V. Atomic Charges in the Thiophane-Bromine Adduct and the 1-Bromothiophanium Ion

Atom	Adduct ^a	Adduct ^b	Ion ^b
Br (1)	-0.81	-0.81	
Br ₂ (2)	0.13	0.12	0.11
S	0.35	0.34	0.49
C α	-0.07	-0.10	-0.09
C β	-0.15	-0.28	-0.27

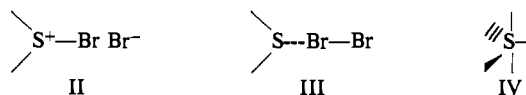
^a Geometry from minimum potential energy calculation. ^b Geometry from X-ray data.

The derived overlap populations are shown in Table IV and the calculated atomic charges are displayed in Table V. Occupations of the d orbitals on sulfur are calculated to be only 1% of that for the s and p orbitals, thus indicating they contribute relatively little to the bonding.

Self-consistent charge-extended Hückel calculations were also performed on a hypothetical halosulfonium salt obtained by removing a bromide ion from the complex without disturbing any other coordinates, and the results are summarized in Tables IV and V.

Discussion

The structure of the crystalline 1:1 complex of thiophane with bromine is interesting for a number of reasons. On the basis of the linear arrangement of S-Br-Br, only the two extreme electronic structures II and III, ionic and charge transfer, are appropriate, the tetracoordinate alternatives (IV) being eliminated. It is likewise unrealistic to consider even weak interaction



of the sulfur atom with bromine atoms of neighboring molecules as the nearest terminal and internal bromine atoms are 3.39 and 4.02 Å distant, respectively (Figure 4).

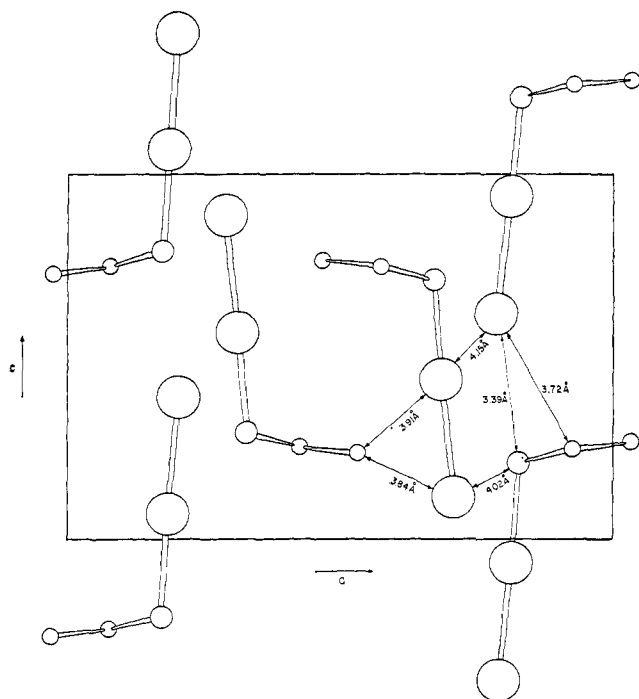


Figure 4. Molecular packing of 1-bromothiophanium bromide. Hydrogen atoms are omitted, the shortest intermolecular distances are indicated.

The S-Br distance (2.32 Å) of the complex is only 0.09 Å larger than the covalent bond length,³³ but the Br-Br distance of 2.72 Å is 0.43 Å greater than the single bond length in the bromine molecule.³⁴ By comparison the S-I distance in the benzyl sulfide-iodine complex is 1.22 Å larger than the sum of the covalent radii, and the I-I distance is only 0.15 Å larger than the single bond length in iodine.¹⁴ A very similar situation obtains for the complex of iodine with 1,4-dithiane.³⁵ To the best of our knowledge, no previous example of such a strong charge-transfer interaction between a donor atom and halogen acceptor, as evidenced by both elongation of the halogen-halogen bond and shortening of the donor-halogen bond to nearly the single bond length, has been reported. It appears then that the greatest contributor to the solid state electronic representation is the ionic one (II). This was supported by the self-consistent charge-extended Hückel calculations which indicated a low overlap population (Table IV) in the Br-Br bond and a charge of about -0.8 on the terminal bromine atom.

For an ionic complex, our initial intuitive guess would have positioned the gegenion close to the presumably sulfonium sulfur atom. On the basis of the observed structure it seemed possible then that the internal bromine might bear considerable positive charge, thus explaining the ability of this material to brominate double bonds. The extended Hückel calculations showed, however, that the internal bromine bears a charge of only about +0.1 compared to a charge of about +0.3 on the sulfur atom. A calculation on the free cation without the polarizing effect of the gegenion showed the charge on sulfur still to be

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(34) I. L. Karle, *J. Chem. Phys.*, **23**, 1739 (1955).

(35) G. Y. Chao and J. D. McCullough, *Acta Crystallogr.*, **13**, 727 (1960).

considerably greater (0.47) than that on the bromine (0.15). The pyramidal coordination about sulfur with a C-S-C angle of 94.2° and C-S-Br angles of 102.5° (Figure 1) is quite similar to that found in the dibenzyl sulfide-iodine adduct¹⁵ (C-S-C angle, 93°; C-S-I angles, 100°). By extrapolation these results seem to indicate that pyramidal coordination at sulfur could be general for sulfonium salts, quite compatible with earlier chemical data³⁶ which indicate further that bonding in sulfonium salts uses predominately p orbitals.

The nmr results are consistent with a representation of the structure in solution as being highly ionic, the chemical shift of the α -methylene protons being greater than those in 1-methylthiophanium iodide, but the symmetry of the multiplets for α and β protons and the similarity of the spectrum to that of thiophane seem to require a mechanism for symmetrization of the formally nonequivalent α protons. This could arise through pyramidal inversion or by bromide displacement at the sulfonium sulfur atom, but symmetrization through dissociation to thiophane and bromine appears more attractive based on the X-ray structure which demonstrates the presence of a significant interaction between the two bromine atoms.

The X-ray data indicate that the average conformation of the thiophane ring is nearly planar. However, from the thermal parameters reported in Table III a strongly anisotropic motion of the β -carbon atom is apparent; the major axis of their thermal ellipsoid is very closely orthogonal to the ring plane. The corresponding B component ($\sim 20 \text{ \AA}^2$), whose magnitude is four times as large as the average of the other B_{ii} factors, can hardly be explained in terms of thermal vibrations only, and is most likely to be related to some sort of structural disorder. In particular the image of the ring could derive from the superposition of two or more different conformational models. Our minimum potential energy calculations indicate that two enantiomers containing a twofold axis are the most stable conformers of the thiophane ring;^{19,37} therefore, it appeared natural to verify that our X-ray results could be explained by the simultaneous presence of two C_2 ring enantiomers, and to compare the geometry of the best fitting models with those predicted from energy calculations.

We have assigned two different positions to each of the C_β atoms, symmetrically displaced in either direction from the average ring plane (Figure 5). The amount of the displacement has been approximately evaluated assuming that the observed thermal parameter perpendicular to the average ring plane ($\approx B_{33}(C_\beta) \approx 20 \text{ \AA}^2$, see Table III) is equal to $8\pi^2(\delta^2 + t^2)$ ³⁸ where t^2 is the mean-square amplitude due to their thermal vibration; this amounts to assuming that the thermal effect and the effect of conformational disorder can be treated independently. The value of $8\pi^2 t^2$ has been equated to 5 \AA^2 , i.e., the approximate average value of the B_{ii}

(36) W. J. Pope and S. J. Peachey, *J. Chem. Soc.*, **77**, 1072 (1900); S. Smiles, *ibid.*, **77**, 1174 (1900).

(37) The existence of twofold symmetry has been found in a similar system, ethylene sulfate, where the angle formed between the C-C bond and the O(2)-S-O(2) plane was $20.6 \pm 0.5^\circ$: F. P. Boer, J. J. Flynn, E. T. Kaiser, O. R. Zaborsky, D. A. Tomalia, A. E. Young, and Y. C. Tong, *J. Amer. Chem. Soc.*, **90**, 2970 (1968).

(38) M. J. Buerger, "Crystal Structure Analysis," John Wiley & Sons, Inc., New York, N. Y., 1967, p 231.

Table VI. Geometry of the Thiophane Ring^a

	Conformational analysis	X-Ray data
$d(\text{S}-\text{C}_\alpha)$	1.82 Å (assumed)	1.82 Å
$d(\text{C}_\alpha-\text{C}_\beta)$	1.54 Å (assumed)	1.55 Å
$d(\text{C}_\beta-\text{C}_\beta^*)$	1.54 Å (assumed)	1.62 Å
θ_1	107.5°	101.6°
θ_2	105.7°	106.2°
θ_3	95.6°	94.2°
ψ_1	46°	56°
ψ_2	35°	44°
ψ_3	13°	16°

^a See Figure 2 for the symbols, C_2 symmetry.

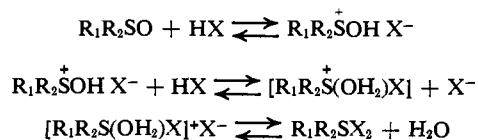
thermal factors over all the atoms (Table III); correspondingly the resulting value of δ is 0.43 Å.

Table VI reports all the parameters of the minimum energy conformation compared with those derived from the above procedure. In view of the approximations involved in both types of calculations, the agreement may be considered as satisfactory.

The maximum intramolecular barrier to the inversion between the two C_2 conformers is approximately 5 kcal/mol, according to the energy map reported in Figure 3. This value is low enough that, in the hypothesis of relatively low hindrance effects due to the packing, the possibility of a dynamic flipping between the two conformers in the crystal state cannot be excluded.

The structure of the thiophane-bromine adduct could have mechanistic implications in the racemization of optically active sulfoxides by hydrogen halides. In the currently favored scheme for hydrogen chloride catalyzed racemization of sulfoxides (Scheme I),^{10b} the

Scheme I



sulfodichloride, where symmetrization is thought to occur, has been considered to be in solution either a slightly distorted trigonal bipyramid with a plane of symmetry or a set of enantiomeric halosulfonium salts rapidly interconverting through backside displacements by halide ion. We consider that loss of chirality of sulfodihalides through the rapid dissociation equilibrium

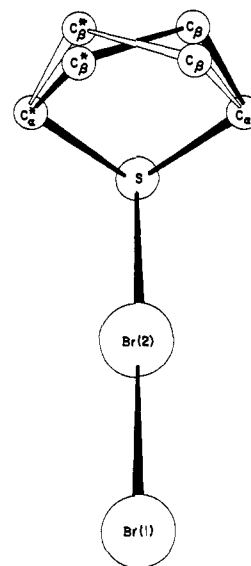
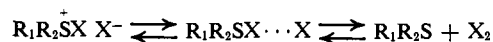


Figure 5. Superposition of the enantiomer conformers of 1-bromothiophanium bromide having C_2 ring symmetry.

could also be a favorable process in many cases and would explain the fact that reduction of the sulfoxide is often observed. The position of such an equilibrium would be determined by the oxidation potentials involved, but the rate of dissociation would depend on the ease with which bonding is established between the positive halogen and incoming halide ion. Thus a fluorosulfonium fluoride, if generated, should dissociate only slowly, leading to slow racemization and negligible reduction, but an iodosulfonium salt should dissociate quickly and, because iodine is a weak complexing agent, completely. Both the rates and positions of the dissociation equilibria for the chlorosulfonium and bromosulfonium salts might be expected to be sensitive to the electronic nature of the groups around the sulfur atom, and one would thus expect to find cases where dissociation to produce sulfide is highly favored. Although the importance of the proposed equilibrium is unverified, it is interesting that the predictions for interrelationships between the several halosulfonium salts based on it are in accord with normal experimental results.^{10, 39}

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(39) R. A. Strecker and K. K. Andersen, *J. Org. Chem.*, **33**, 2234 (1968); H. Gilman and J. Eisch, *J. Amer. Chem. Soc.*, **77**, 3862 (1955)