Studies on the Chemistry and Structure of the 1,4-Dithioniabicyclo[2.2.2]octane Cation

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The synthesis and characterization of several salts of the 1,4-dithioniabicyclo[2.2.2]octane cation ($C_6H_{12}S_2^{+2}$) are described. The tetrachlorozincate salt, $C_6H_{12}S_2ZnCl_4$, crystallizes in space group *Pnma* of the orthorhombic system with four molecules in a cell. The $C_6H_{12}S_2^{+2}$ cage forms a tightly packed oblate spheroid of approximate D_{3h} symmetry in which the S–S distance (3.130 ± 0.004 Å) is significantly less than the van der Waals S–S separation. With nucleophiles the 1,4-dithioniabicyclo[2.2.2]octane cation gives compounds of general formula Nuc-$CH_2CH_2SCH_2CH_2SCH_2CH_2$Nuc; the vinyl-1,4-dithianesulfonium ion is an important intermediate.

The 1,4-dithioniabicyclo[2.2.2]octane cation ($C_6H_{12}S_2^{+2}$, which will be referred to in this paper as the disulfonium cation) was first synthesized by Stahmann, Fruton, and Bergman[1] during their exhaustive work on mustard gas during World War II. The cage structure of this ion is common to the related molecules triethylenediamine, quinuclidine, and the parent hydrocarbon bicyclo[2.2.2]octane, all of which have been extensively studied either because their crystal structures undergo thermal transitions to plastic crystals[2] or because of controversy concerning the symmetry of the hydrocarbon cage.[3] The disulfonium cation is also one member of a class of compounds, sulfonium derivatives of mustard gas, that has provided valuable cytostatic agents for cancer chemotherapy.[4] Our particular interest in the disulfonium ion stems from its strained structure and its potential use as a bifunctional substrate in nucleophilic substitution reactions. To characterize this substrate we have undertaken studies designed to establish the physical and chemical properties of its salts.

Experimental Section

Preparation and Reaction of Disulfonium Compounds.—All melting points were determined in open end capillaries and are uncorrected. Analyses were performed by the Schwarzkopf Microanalytical Laboratory and by PCR Inc. No attempt was made to maximize yields. Pmr spectra were recorded on a Varian A-60 at 37°; all integrations were within ±5% of theoretical for the proposed structures.

Disulfonium Tetrachlorozincate.—This compound was prepared as originally described[1] and other disulfonium salts were derived from it or prepared *via* a similar procedure. Steam distillation of the filtrate from this preparation yielded *p*-dithiane: mp (methanol) 110°; pmr ($CDCl_3$) τ 7.09 (s, CH_2). *Anal.* Calcd for $C_4H_8S_2$: C, 39.96; H, 6.71; S, 53.34. Found: C, 39.99; H, 6.77; S, 52.72. The crude disulfonium tetrachlorozincate was crystallized from dilute hydrochloric acid to yield clear, thick tubular to short prismatic, polyhedral crystals: mp 276–278° dec; pmr (D_2O) τ 5.91 (s, CH_2). *Anal.* Calcd for $C_6H_{12}S_2ZnCl_4$: C, 20.27; H, 3.40; S, 18.04; Zn, 18.39; Cl, 39.89. Found: C, 20.40; H, 3.35; S, 17.94; Zn, 18.11; Cl, 40.06.

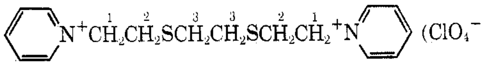
Disulfonium Perchlorate.—Disulfonium tetrachorozincate was dissolved in warm water, excess 72% perchloric acid added, and the solution cooled to yield crystals of disulfonium perchlorate: mp (H_2O) 276–277° dec; pmr (D_2O) τ 5.91 (s, CH_2). *Anal.* Calcd for $C_6H_{12}S_2(ClO_4)_2$: C, 20.76; H, 3.48; S, 18.47. Found: C, 20.87; H, 3.30; S, 18.44.

Disulfonium Chloride.—Disulfonium chloride was prepared from disulfonium tetrachlorozincate by exchanging tetrachlorozincate anions for chloride ions on a Dowex AG1-X8 anion-exchange resin. The desired product was recrystallized twice from water–isobutyl alcohol, and the resulting hydrated crystals were washed with 50% methanol–water and air dried. On being heated in a melting point capillary they partially dissolved from 40 to 110° in the water of crystallization and finally melted from 196 to 200°: pmr (D_2O) τ 5.91 (s, CH_2). *Anal.* Calcd for $C_6H_{12}S_2Cl_2 \cdot H_2O$: C, 30.38; H, 5.95; S, 27.03; Cl, 29.89; H_2O, 7.60. Found: C, 29.91; H, 5.94; S, 26.83; Cl, 29.86; H_2O, 8.16. On being dried *in vacuo* over P_2O_5 the hydrate was converted to the anhydrous form: mp 195–198°; pmr (D_2O) τ 5.91 (s, CH_2). *Anal.* Calcd for $C_6H_{12}S_2Cl_2$: C, 32.89; H, 5.52; S, 29.26; Cl, 32.35. Found: C, 32.93; H, 5.80; S, 29.41; Cl, 32.42.

Disulfonium Tetraphenylborate.—When an aqueous solution of sodium tetraphenylborate was added slowly to an aqueous solution of disulfonium tetrachlorozincate, disulfonium tetraphenylborate was quantitatively precipitated. This precipitate was crystallized from acetonitrile–95% ethanol, washed with 95% ethanol, and dried *in vacuo* over P_2O_5: pmr (DMF) τ 5.93 (s, CH_2). *Anal.* Calcd for $C_6H_{12}S_2[B(C_6H_5)_4]_2$: C, 82.44; H, 6.66; S, 8.15. Found: C, 81.22; H, 6.85; S, 7.92.

Tetra(disulfonium)cobalt(II) Decachloride Hydrate.—Cobaltous chloride hexahydrate, thiodiglycol, and concentrated HCl were refluxed according to the procedure given for the preparation of disulfonium tetrachlorozincate. The initial yield of blue crystals was dissolved in water and the resulting pink solution was washed with benzene. The addition of absolute ethanol and HCl yielded light orange crystals which were then crystallized from water–isopropyl alcohol. On being dried *in vacuo* over P_2O_5, or on being washed with absolute ethanol, this compound turned blue implying the conversion of octahedral cobalt(II) to tetrahedral cobalt(II) *via* dehydration. The pink derivative analyzes as $(C_6H_{12}S_2)_4CoCl_{10} \cdot 15H_2O$ and the blue derivative as $(C_6H_{12}S_2)_4CoCl_{10} \cdot 2H_2O$. DTA-TGA curves indicate that the pink compound is losing water even at room temperature. Addition of sodium tetraphenylborate to a water solution of either compound yielded disulfonium tetraphenylborate. *Anal.* Calcd for $(C_6H_{12}S_2)_4CoCl_{10} \cdot 15H_2O$: C, 22.58; H, 6.16; S, 20.09; Co, 4.62; Cl, 27.76. Found: C, 23.17; H, 6.29; S, 20.62; Co, 4.01; Cl, 27.58. Calcd for $(C_6H_{12}S_2)_4CoCl_{10} \cdot 2H_2O$: C, 27.65; H, 5.03; S, 24.60; Co, 5.65; Cl, 34.00. Found: C, 28.06; H, 5.28; S, 24.81; Co, 5.56; Cl, 34.03.

Dipyridinium 1,1′-[Ethylenebis(thioethylene)]diperchlorate.—



$$C_5H_5N^+CH_2CH_2SCH_2CH_2SCH_2CH_2{}^+NC_5H_5\ (ClO_4^-)_2$$

Disulfonium perchlorate (0.01 mol) and pyridine (0.1 mol) were added to 15 ml of dimethylformamide and the mixture refluxed for 2 hr. *p*-Dioxane was added to the warm solution which was then cooled to yield 3.6 g (71%) of white crystals. This product was crystallized from ethanol–water and then from warm water to yield 2.0 g of white plates: mp 175–177° dec; pmr (DMSO-d_6) τ 5.18 (t, H_1), 6.80 (t, H_2, J_{12} = 6.5 Hz), 7.18 (s, H_3), 0.78–1.95 (m, H_{py}). *Anal.* Calcd for $(C_5H_5NCH_2CH_2SCH_2)_2(ClO_4)_2$: C, 38.03; H, 4.39; N, 5.54; S, 12.69. Found (two separate

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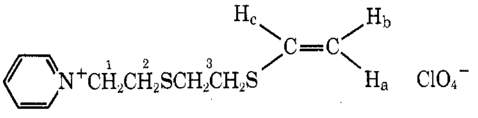
[1] M. A. Stahmann, J. S. Fruton, and M. Bergman, *J. Org. Chem.*, **11**, 704 (1946).

[2] (a) S. Change and E. F. Westrum, Jr., *J. Phys. Chem.*, **64**, 1551 (1960); (b) J. C. Trowbridge and E. F. Westrum, Jr., *ibid.*, **67**, 2381 (1963); (c) G. W. Smith, *J. Chem. Phys.*, **43**, 4325 (1965).

[3] (a) J. D. Dunitz and O. Ermer, Paper XIII-1, *Collect. Abstr., Int. Union Crystallogr., Eighth Gen. Assem. Int. Congr.*, 126 (1969); (b) O. Ermer and J. D. Dunitz, *Helv. Chim. Acta*, **52**, 1861 (1969); (c) A. F. Cameron, G. Ferguson, and D. G. Morris, *J. Chem. Soc.*, 1249 (1968).

[4] A. Luttringhaus and H. Machatzke, *Justus Liebigs Ann. Chem.*, **671**, 165 (1964), and references therein.

determinations of independently prepared samples): C, 38.45, 38.30; H, 4.71, 4.43; N, 5.50, 5.40; S, 12.74, 12.84. Work-up of the original filtrate yielded a small amount of *N*-[3,6-bis(thia)-7-octenyl]pyridinium perchlorate: pmr (DMSO-d_6) τ 5.16 (t, H_1), 6.76 (t, H_2, $J_{12} = 6.5$ Hz), 7.09 (m, H_3); the vinyl protons



yielded four doublets which can be accounted for by the reasonable[5a] parameters $H_a = 4.85$, $H_b = 4.74$, and $H_c = \tau$ 3.46 and $J_{ab} = 0$, $J_{bc} = 10$, and $J_{ac} = 17$ Hz.

Dipyridinium 1,1′-Ethylenediperchlorate.—Dipyridinium 1,1′-ethylenedibromide was prepared from 1,2-dibromoethane and pyridine according to published procedures.[5b] This was dissolved in water and excess 72% perchloric acid added to precipitate the perchlorate salt which was then recrystallized twice from water to yield white crystals: mp 307.5–308° dec: pmr (DMSO-d_6) τ 4.72 (s, CH_2), 0.87–1.93 (m, H_{py}). *Anal.* Calcd for $(C_5H_5NCH_2)_2(ClO_4)_2$: C, 37.42; H, 3.66; N, 7.27. Found: C, 37.49; H, 3.47; N, 7.37.

X-Ray Structure Determination. Unit Cell and Space Group.—Preliminary precession photographs (*hk*0, 0*kl*, *hk*1, 1*kl*) were taken at room temperature on a crystal of disulfonium tetrachlorozincate of approximate dimensions 0.25 × 0.20 × 0.30 mm using Cu K_α radiation. The observed systematic absences ($k + l$ odd for 0*kl*, *h* odd for *hk*0) are characteristic of the orthorhombic space groups *Pnma* and *Pn*2$_1$*a*. Final refinement was carried out in the centric space group *Pnma*, the reasons for this choice being discussed later. The cell dimensions, determined[6] from powder diffraction measurements (Table I),[7] were found to be $a = 13.18 \pm 0.015$, $b = 8.38 \pm 0.01$, and $c = 11.55 \pm 0.015$ Å in good agreement with those determined from the precession photographs. An observed density of 1.83 ± 0.01 g/cm^3, obtained by flotation in $CHBr_3$–CCl_4 solutions, agrees with that of 1.837 g/cm^3 calculated for four formula units in the cell. These observations require that in *Pnma* both the $ZnCl_4^{-2}$ and $C_6H_{12}S_2^{+2}$ ions lie on the planes of symmetry.

Collection and Reduction of Intensity Data.—Three-dimensional X-ray intensity data were collected at room temperature on a disulfonium tetrachlorozincate crystal of approximate dimensions 0.25 × 0.35 × 0.35 mm using a Philips automated linear diffractometer, PAILRED; monochromatized Mo K_α radiation was obtained *via* a silicon crystal reflecting from the 111 plane. The crystal was mounted with the *b* axis colinear with the ω axis and data were collected by the ω-scan method (rate = 1.5°/min) for layers *hk*0 through *hk*16, the range of scan varying from ±1.5 to ±3.0° from the calculated peak. For layers *hk*0 through *hk*3 background was counted for 20 sec on each end of the scan, while for layers *hk*4 through *hk*16 this time was doubled. A total of 4448 reflections was examined within 2θ (Mo K_α) $\leq 60°$, which, after rejection of observations with unacceptably high background counts and averaging of symmetry related peaks, yielded 908 nonzero reflections the intensities of which were corrected for Lorentz and polarization effects in the usual manner. Refinement was initiated using only these nonzero reflections and then completed with a total of 1915 nonzero and zero observations. A 360° ω scan of the 040 reflection gave a variation in intensity of less than ±10% and therefore no corrections for absorption effects were made (the linear absorption coefficient for disulfonium tetrachlorozincate using Mo Kα radiation is 23.3 cm^{-1}). The intensities of two standard reflections monitored during the data collection showed only random fluctuations, although the crystal itself exhibited slight yellowing by the end of data collection.

Solution of Structure.—The structure was solved by a standard application of Patterson–Fourier and least-squares techniques.[8] In the least-squares calculations the sum of $w(|F_o| - |F_c|)^2$ was minimized, where $|F_o|$ and $|F_c|$ are the observed and calculated structure amplitudes, respectively. In the final refinement weights were defined as $1/\sqrt{w} = 6.0 - 0.2\,|F_o|$ for $|F_o| < 25$, $1/\sqrt{w} = 1.0 + 0.02(|F_o| - 130)$ for $|F_o| < 130$, and $1/\sqrt{w} = 1.0$ otherwise. Atomic scattering factors for Zn^{+2}, Cl^-, S, C, and H, and values for the anomalous scattering terms for Zn, Cl, and S were taken from Ibers[2] tabulation.[9a]

Refinement of the structure was carried out using two different models, the first of which required anisotropic carbon atoms C(1) and C(2) to lie on the mirror plane. However, this model led to large thermal motions perpendicular to the mirror plane for these atoms, as well as to chemically unreasonable C–C bond lengths (*vide infra*). Therefore a second model, assuming a disordered $C_6H_{12}S_2^{+2}$ unit (two ions with respective left- and right-handed twists about the S–S vector superposed at every cationic site, each C atom being given half weight), was introduced. Refinement of this model with isotropic carbon atoms yielded values of R_1 and R_2 of 0.110 and 0.0409, respectively, where

$$R_1 = \frac{\Sigma(|F_o| - |F_c|)}{\Sigma|F_o|} \text{ and } R_2 = \left[\frac{\Sigma w(|F_o| - |F_c|)^2}{\Sigma w|F_o|}\right]^{1/2}$$

Hamilton's *R*-factor test[10] showed that this second model with disordered, isotropic C atoms better describes the data than the first model with ordered, anisotropic C atoms at the 99.5% significance level.

Final difference Fourier syntheses for both models were quite similar, showing peaks around the Zn atom of 1.4–1.6 e/Å^3 and a continuum of peaks ranging downward from 1.0 e/Å^3 (corresponding to ~20% of the height of a C atom in this structure) throughout the rest of the lattice. Lists of the observed and calculated structure factors for both models are given in Tables II[7] and III.[7] Both models gave average refined C–H bond distances of 1.0 Å.

Results and Discussion

Preparation and Properties of Disulfonium Salts.—The disulfonium cation is easily prepared from thiodiglycol, the original preparation of Stahmann, Fruton, and Bergman[1] being advantageous in that the halogenating mixture contains tetrachlorozincate which selectively precipitates the disulfonium cation. The HCl–$CoCl_2$ preparation probably is successful for the same reason, although it is not obvious why a salt of the unusual stoichiometry $(C_6H_{12}S_2)_4CoCl_4 \cdot nH_2O$ should be formed. Combined DTA–TGA curves of this salt and of disulfonium chloride show that the cobalt salt is not a simple mixture of the disulfonium chloride and tetrachlorocobaltate, although in later stages of decomposition there is formed a compound of stoichiometry $C_6H_{12}S_2CoCl_4$ which powder diffraction measurements show to be isomorphous with disulfonium tetrachloro-

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[5] (a) R. M. Silverstein and G. C. Bassler, "Spectrophotometric Identification of Organic Compounds," 2nd ed, Wiley, New York, N. Y., 1967, pp 138, 144–145; (b) J. L. Hartwell and M. A. Pogorelskin, *J. Amer. Chem. Soc.*, **72**, 2040 (1950).

[6] We are grateful for the loan of equipment and expertise by Professor Paul Moore (Department of Geophysical Sciences, University of Chicago) towards this determination.

[7] The following tables and figures will appear in the microfilm edition of this volume of the journal: Table I, "Powder Diffraction Data for Disulfonium Tetrachlorozincate;" Combined Tables II and III, "Observed and Calculated Structure Factors for both Ordered and Disordered Models;" Table IV, "Positional and Thermal Parameters for Ordered Model;" Table V, "Selected Interatomic Distances and Angles for Ordered Model;" Table VII, "Positional and Thermal Parameters for Disordered Model;" Table IX, "Root-Mean-Square Displacements in Disordered Model;" Figure 1, "A Perspective Drawing of Disulfonium Tetrachlorozincate in the Ordered Model"; Figure 3, "A Perspective Drawing of one Disordered SCH_2CH_2S Linkage." Also included are statistical arguments in favor of the centric space group *Pnma*. Single copies may be obtained from the Business Operations Office, Books and Journals Division, American Chemical Society, 1155 Sixteenth Street, N.W., Washington, D. C. 20036, by referring to code number JOC-72-3481. Remit check or money order for $9.00 for photocopy or $2.00 for microfiche.

[8] In addition to the Sly–Shoemaker–Vanden Hende ERFR2 Patterson and Fourier synthesis program, the main programs used in this work were Dewar's SORFLS least-squares program and SORFEE function and error program (substantially modified versions of ORFLS and ORFEE by Busing, Martin and Levy) and C. K. Johnson's ORTEP thermal ellipsoid plotting program. All calculations were performed on the University of Chicago IBM 7094 computer.

[9] J. A. Ibers, "International Tables for X-ray Crystallography," Vol. 3, The Kynoch Press, Birmingham, England, 1965: (a) Tables 3.3.1A and 3.3.2C. (b) Table 4.1.10.

[10] W. C. Hamilton, *Acta Crystallogr.*, **18**, 502 (1965).

zincate.[11] Sulfuric acid (50%)also converts thiodiglycol into the disulfonium cation, as evidenced by the appearance of its characteristic pmr peak in the reaction mixture. No solid product could be isolated from this mixture, but steam distillation affords good yields of *p*-dithiane. All efforts to synthesize the disulfonium cage by combining *p*-dithiane and 1,2-dibromoethane failed, despite the use of a variety of solvents and metal ion catalysts. These observations indicate that *p*-dithiane is the thermodynamically stable end of the thiodiglycol–disulfonium–dithiane chain.

In general, the solubilities of disulfonium and trimethylsulfonium salts are similar. Thus, disulfonium chloride is very soluble in water, but insoluble in common organic solvents, while the tetraphenylborate salt is completely insoluble in water but soluble in polar organic solvents. The tetrachlorozincate and perchlorate salts are only slightly soluble in water: the solublility of the $ZnCl_4^{-2}$ salt is 33.3 mg/g of 0.01 *F* HCl solution and 26.4 mg/g of 0.1 *F* HCl solution at 25.0° (at 10.0° these values are 28.3 and 23.0); the solubility of the ClO_4^- salt is 12.8 mg/g of solution at 25.0° and 6.0 mg/g of solution at 10.0°. The tetrachlorozincate salt is generally insoluble in organic solvents, but the perchlorate salt will dissolve in polar solvents such as DMF.

Aqueous solutions of the $C_6H_{12}S_2^{+2}$ ion show no discernible light absorption in the ultraviolet, visible, or near-infrared regions of the spectrum. However, the solid disulfonium salts give characteristically simple infrared absorption spectra, exemplified by the following data for $C_6H_{12}S_2ZnCl_4$ in a KBr pellet at room temperature: 2930 (s), 2925 (s), 1400 (s), 1310 (m), 1205 (sh), 1200 (m), 1160 (vw), 1105 (w), 1000 (w), 810 (sh), 800 (s), 720 (m) cm^{-1}. By comparison with the infrared absorption spectra of triethylenediamine[12] and bicyclo[2.2.2]octane[13] it is reasonable to assign the bands at 2980 and 2925 cm^{-1} to CH_2 stretching, the band at 1400 cm^{-1} to CH_2 bending, and the band at 800 cm^{-1} to CH_2 rocking. With considerably less certainty the band at 1310 cm^{-1} may be assigned to CH_2 twisting, and the band at 720 cm^{-1} to C–S–C bending.

Description of Crystal Structure of $C_6H_{12}S_2ZnCl_4$.—The crystal structure of $C_6H_{12}S_2ZnCl_4$ consists of discrete $C_6H_{12}S_2^{+2}$ cations and $ZnCl_4^{-2}$ anions, each of which have site symmetry *m*. The $ZnCl_4^{-2}$ ion is a distorted tetrahedron, the Zn–Cl distances ranging from 2.259 ± 0.003 to 2.282 ± 0.003 Å and the Cl–Zn–Cl angles ranging from 107.16 ± 0.06 to 112.11 ± 0.07°. As pointed out by Meek and Ibers,[14] this situation is not unusual even in structures where hydrogen bonding to Cl cannot be invoked. The $C_6H_{12}S_2^{+2}$ ion is a tightly packed oblate spheroid with a S–S distance of 3.130 ± 0.004 Å. This is significantly less than the shortest van der Waals S–S separation observed to date, while it is almost exactly the same S–S distance as is observed within the layers of molybdenite[15] [sulfur atoms on opposite faces of a layer are connected by three molybdenum(IV) bridges analogous to the three ethylene bridges of the disulfonium cage] and as the transannular S–S distance in 1-acetonyl-1-thionium-5-thiacyclooctane perchlorate.[16] (See Table VI.[9b,17–26]) It is likewise noteworthy that the disulfonium S–S distance also falls within the range of inter- and intraligand S–S

TABLE VI

S–S DISTANCES (Å)

	A. S–S Bonds
1.89[9b]	S_2 (gas phase)
1.99[17a]	$S_2O_3^{-3}$
2.00–2.15[18]	Polysulfides and disulfides
2.39[17b]	$S_2O_4^{-2}$
	B. Not Bonded, Weak Interaction
2.15–2.55[19]	Thiathiophthenes
2.58[20]	Intramolecular S–S distance in S_4N_4
	C. Not Bonded, Unknown Interaction
2.80[21]	Average intraligand S–S distance in several 1,1-dithiolato metal chelates
2.89[22]	Interligand S–S distance in bis(dithiobiureto)nickel(II)
2.99, 3.06[21]	Average inter- and intraligand S–S distances for six square planar 1,2-dithiolato metal chelates
3.06, 3.07[21]	Average intra- and interligand S–S distances for three trigonal prismatic 1,2-dithiolato chelates
3.12[16]	Transannular S–S distance in 1-acetonyl-1-thionia-5-thiacyclooctane perchlorate
3.13[a]	S–S distance in disulfonium cation
3.15[15]	Across layer S–S distance in molybdenite
3.17[15]	Along layer S–S distance in molybdenite
	D. Van der Waals Distances
3.37[23]	Shortest intermolecular distance in S_8
3.45–3.48[24]	Intramolecular S–S distance in *p*-dithiane and *p*-dithiane derivatives
3.49[25]	S^+–S^+ distance in tri-*n*-butylsulfonium fluoride hydrate
3.50[15]	Interlayer distance in molybdenite
3.50[23]	Shortest intermolecular distance in S_6
3.64[20]	Shortest intermolecular S–S distance in S_4N_4
3.70[26]	Pauling's value

[a] This work.

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[11] We are grateful for the loan of equipment, time, and expertise by Dr. Henry Hoekstra (Argonne National Laboratory) toward all the DTA-TGA measurements.

[12] G. S. Weiss, A. S. Parkes, E. R. Nixon, and R. E. Hughes, *J. Chem. Phys.*, **41**, 3759 (1965).

[13] J. J. Macfarlane and I. G. Ross, *J. Chem. Soc.*, 4169 (1960).

[14] D. W. Meek and J. A. Ibers, *Inorg. Chem.*, **9**, 465 (1970), and references therein.

[15] (a) Y. Takeuchi and W. Nowacki, *Schweiz. Mineral. Petrog. Mitt.*, **44**, 105 (1964); (b) R. G. Dickinson and L. Pauling, *J. Amer. Chem. Soc.*, **45**, 1466 (1923).

[16] S. M. Johnson, C. A. Maier, and I. C. Paul, *J. Chem. Soc. B*, 1603 (1970), and references therein.

[17] (a) M. Nordelli and G. Fava, *Acta Crystallogr.*, **15**, 477 (1962); (b) J. D. Dunitz, *ibid.*, **9**, 579 (1956).

[18] (a) F. A. Cotton and G. Wilkinson, "Advanced Inorganic Chemistry," 2nd ed, Interscience, New York, N. Y., 1966, p 551; (b) S. C. Abrahams, *Quart. Rev. (London)*, **10**, 407 (1956).

[19] (a) D. H. Reid, "Specialist Periodical Reports of Chemical Society, Organic Compounds of Sulphur, Selenium and Tellurium," Vol. I, 1970, pp 321–335; (b) S. M. Johnson, M. G. Newton, and I. C. Paul, *J. Chem. Soc. B*, 986 (1969).

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[23] J. Donohue, A. Caron, and E. Goldish, *J. Amer. Chem. Soc.*, **83**, 3748 (1961).

[24] (a) R. E. Marsh, *Acta Crystallogr.*, **8**, 91 (1955); (b) G. Y. Chao and J. D. McCullough, *ibid.*, **13**, 727 (1960); (c) H. T. Kalff and C. Romers, *ibid.*, **18**, 164 (1965).

[25] P. T. Beurskens and G. A. Jeffrey, *J. Chem. Phys.*, **40**, 2800 (1964).

[26] L. Pauling, "Nature of the Chemical Bond," 2nd ed, Cornell University Press, Ithaca, N. Y., 1944, p 189.

distances observed[21,27a] in many square planar and trigonal prismatic 1,2-dithiolato metal chelates. This short, relatively constant S–S distance has been used to infer residual S–S bonding in 1,2-dithiolato complexes,[21,27] and this bonding has in turn been invoked to explain the unusual coordination geometries of these complexes. However, since the geometry of the disulfonium cation restricts the nonbonding sulfur electrons to orbitals which are directed away from the S–S axis, it is clear that there can be no direct S–S interaction in this ion (although "through-bond coupling," as described by Hoffmann[28] for triethylenediamine, is possible) and the short S–S distance must merely be caused by the strained carbon framework. This result implies that factors other than S–S electronic interaction could cause the short S–S distances observed in 1,2-dithiolato metal chelates. The wide range of S–S distances listed in Table VI indicates that it is relatively easy to force sulfur atoms to significantly less than van der Waals distances, and it may be purely geometrical and packing considerations that determine the resulting S–S separation.

As mentioned previously, this structure was solved using two different models. The first model, involving ordered anisotropic C atoms, was discarded because it statistically did not fit the data as well as the second model and because it led to two sets of parameters that were chemically unreasonable. First, the average C–C bond distance (1.450 ± 0.007 Å) was much too short for sp^3-hybridized carbon atoms; 1.526 Å is the accepted "normal" value for this type of bond,[29] and values of 1.54,[12] 1.53,[3b] and 1.54[3c] Å have been measured for the comparable C–C distance in other 1,4-bicyclo[2.2.2]octane derivatives showing that the bicyclic cage system does not in itself lead to unusual C–C bond lengths. Second, abnormally large thermal parameters for C(1) and C(2) perpendicular to the mirror plane [and the corresponding combined parameters for C(3) and C(4)] were observed. These two anomalous parameters of the first model can most reasonably be accounted for by a model in which the disulfonium cage is distorted *via* right- and left-handed twists about the S–S vector. This can occur by the symmetric cage undergoing a torsional mode of vibration in the crystal lattice, or by a true disordered crystal structure involving equal amounts of randomly packed right-handed and left-handed twisted ions (in terms of the resultant diffraction data, this is equivalent to a crystal containing both twisted forms, each at half weight, superposed at each cationic site). These two mechanism for achieving disorder are crystallographically equivalent, the only difference between them being the magnitude of the energy barrier separating the right- and left-handed conformations, a small barrier corresponding to rapid torsional vibration and dynamic disorder and a large barrier corresponding to a static disorder with equal numbers of the two twisted forms distributed throughout the lattice. Refinement of the first ordered model in the presence of this disorder accounts for the observed elongated C atoms, since each ordered carbon ellipsoid would tend to stretch out to encompass the two disordered atoms, and for the observed short C–C distances, since these numbers would really represent the distance between midpoints of vectors joining two related disordered C atoms and not true C–C bond lengths.

The second model takes into account the distortion about the S–S axis by approximating electron density at a C atom position as two overlapping spheres rather than as an elongated ellipsoid. Tables VII,[7] VIII, and IX[7] give, respectively, the positional and thermal parameters, the principal interatomic distances and angles, and the pertinent root-mean-square thermal displacement values for this second model with disordered C atoms. Figure 2 shows two different views of the left-handed form of the disordered cage, the distortion from D_{3h} symmetry being quite obvious (average angle of twist is ±7.8°). In this model tbe average observed C–C bond distance, S–C bond distance, C–S–C angle, and S–C–C angle [1.52 (2) Å, 1.80 (2) Å, 100.6° (7) and 114.6° (11), respectively) are in very good agreement with the normal values for these parameters observed in simple sulfonium ions and *p*-dithiane derivatives (1.53 Å for a C–C bond,[3b,c,16,24] 1.82 Å for a sulfonium S–C bond,[16,30] 100° for a C–S–C angle,[16,24] and 112–

TABLE VIII

SELECTED INTERATOMIC DISTANCES AND ANGLES (C$_6$H$_{12}$S$_2$ZnCl$_4$, DISORDERED MODEL)

Bond distances, Å	Bond angles, deg
Zn–Cl(1), 2.283 (3)	Cl(1)–Zn–Cl(2), 109.40 (9)
Zn–Cl(2), 2.260 (3)	Cl(1)–Zn–Cl(3), 107.16 (6)
Zn–Cl(3), 2.267 (2)	Cl(2)–Zn–Cl(3), 112.15 (7)
Average, 2.270	Cl(3)–Zn–Cl′(3), 108.62 (6)
	Average, 109.33
S(1)–S(2), 3.130 (4)	
	C(1D)–S(1)–C(3DA), 98.2 (7)
S(1)–C(1D), 1.808 (10)	C′(1D)–S(1)–C(3DB),[a] 102.1 (7)
S(2)–C(2D), 1.794 (9)	C(2D)–S(2)–C(4DA), 101.5 (7)
S(1)–C(3DA), 1.807 (16)	C′(2D)–S(2)–C(4DB), 100.5 (7)
S(1)–C(3DB), 1.753 (16)	Average, 100.6
S(2)–C(4DA), 1.794 (17)	
S(2)–C(4DB), 1.834 (15)	C(2D)–C′(1D)–S(1),[a] 113.5 (7)
Average, 1.798	C(4DA)–C(3DB)–S(1), 115.2 (12)
	C(4DB)–C(3DA)–S(1), 116.1 (12)
C(1D)–C′(2D),[a] 1.523 (12)	C(1D)–C′(2D)–S(2), 114.4 (7)
C(3DA)–C(4DB), 1.450 (21)	C(3DA)–C(4DB)–S(2), 115.5 (10)
C(3DB)–C(4DA), 1.582 (24)	C(3DB)–C(4DA)–S(2), 112.4 (13)
Average, 1.518	Average, 114.6

Nonbonded distances, Å	Dihedral angles,[b] deg	
C(1D)–C′(1D), 0.521 (22)	C(1D)–C(2D)–S(1) C′(1D)–C′(2D)–S(1)[a]	21.9 (18)
C(2D)–C′(2D), 0.393 (27)	C(1D)–C(2D)–S(2) C′(1D)–C′(2D)–S(2)	12.6 (10)
C(3DA)–C(3DB), 0.389 (23)	C(3DA)–C(4DA)–S(1) C(3DB)–C(4DB)–S(1)	13.8 (14)
C(4DA)–C(4DB), 0.401 (24)	C(3DA)–C(4DA)–S(2) C(3DB)–C(4DB)–S(2)	14.2 (15)
Average, 0.426	Average, 15.6	
	C′(1D)–C′(2D)–S(1) C(3DB)–C(4DB)–S(1)	122.7 (15)
	C′(1D)–C′(2D)–S(2) C(3DB)–C(4DB)–S(2)	120.7 (14)
	C(1D)–C(2D)–S(1) C(3DA)–C(4DA)–S(1)	115.4 (14)
	C(1D)–C(2D)–S(2) C(3DA)–C(4DA)–S(2)	123.5 (14)
	Average, 120.6	

[a] Primed atoms are generated from unprimed ones by operation of mirror plane at $y = 1/4$. Each cage consists of three primed and three unprimed carbon atoms. [b] Between planes each defined by three atoms.

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(27) (a) E. I. Steifel, Z. Dori, and H. B. Gray, *J. Amer. Chem. Soc.*, **89**, 3353 (1967); (b) R. J. Gillespie, Paper No. 16 in "Werner Centennial," *Advan. Chem. Ser.*, **62**, 221 (1967); (c) H. B. Gray, R. Eisenberg, and E. I. Steifel, *ibid.*, Paper No. 42, **62**, 641 (1967).

(28) R. Hoffmann, *Accounts Chem. Res.*, **4**, 1 (1971).

(29) D. R. Lide, Jr., *Tetrahedron*, **17**, 125 (1962).

(30) A. Lopez-Castro and M. R. Truter, *Acta Crystallogr.*, **17**, 465 (1964).

116° for a S–C–C angle[16,24]). These comparisons show first that the strain induced in the bicyclic cage (by forcing the S–S distance to be less than the van der Waals separation) is not large enough to distort seriously its geometry from that which would be predicted from simple models, and second that the disordered model leads to more chemically reasonable bond parameters than does the ordered model.

It must be noted at this point that, in the first model, the elongation of C(1) and C(2) perpendicular to the mirror plane could possibly be due to an incorrect assignment of the space group to *Pnma* instead of to $Pn2_1a$. There has been much discussion recently[31] concerning the difficulty in deciding between such related space groups and unfortunately there does not seem to be a direct least-squares solution to the problem.[32] However, we believe *Pnma* to be the correct space group since the other five atoms on the mirror plane do *not* exhibit large thermal parameters perpendicular to the mirror as they would if $Pn2_1a$ were the correct space group, refinement being carried out in *Pnma*. This implies that the anomaly is peculiar to the carbon atoms, and indeed the thermal parameters for C(3) and C(4) (in the first model) are abnormally large in those directions corresponding to vibration about the S–S axis. In addition, the usual statistical tests[7] indicate that the data are better described by a centric space group.

While X-ray data cannot differentiate between the dynamic and static mechanisms of disorder, three indirect arguments can be made which favor, but do not establish, the dynamic mechanism. (1) In studying the pmr of solid triethylenediamine, Smith[2c] observed a line narrowing at −85° which is ascribed to restricted reorientation about the N–N axis. While it is difficult to assess quantitatively the effect of increasing the size and charge of the heteeroatoms in this cage system, qualitatively both effects would tend to favor the symmetrical D_{3h} transition state (in which the heteroatoms are furthest apart) at the expense of the enantiomers of D_3 symmetry and therefore lower the activation energy of torsional rotation in the disulfonium system relative to that observed for triethylenediamine. Thus it is very reasonable to describe the disulfonium cage as undergoing rapid torsional vibration at room temperature, which is 100° higher than the temperature at which triethylenediamine begins to show this vibration. (2) Combined DTA–TGA curves from 30 to 600° for the solids $C_6H_{12}S_2ZnCl_4$, $C_6H_{12}S_2Cl_2$ (anhydrous and monohydrate), $C_6H_{12}S_2(ClO_4)_2$, and $(C_6H_{12}S_2)$-$CoCl_{10}\cdot nH_2O$ show no consistent phase transformation that can be ascribed to the onset of torsional vibration.[11] Although this is negative evidence, it is consistent with the proposition that rapid torsional vibration is already occurring at room temperature. (3) The root-mean-square component of thermal displacement[7] for a disordered C atom along the vector defined by itself and its related disordered atom varies from 37 to 53% of the distance between these two atoms. To explain this result within the static mechanism would require invoking a large energy barrier (obtained *via* a crystal lattice locking effect) between two geometrically very similar ions. This seems to be less reasonable than a simple torsional vibration which carries one form into the other.

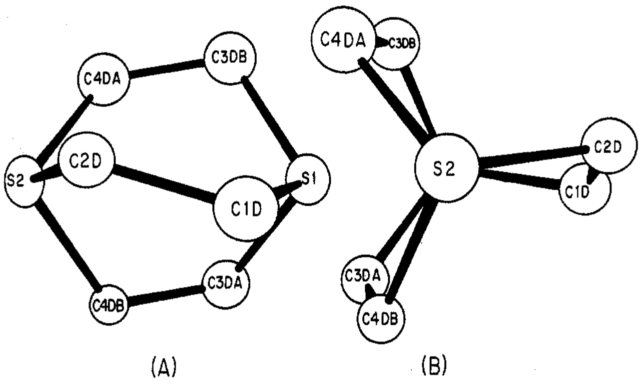
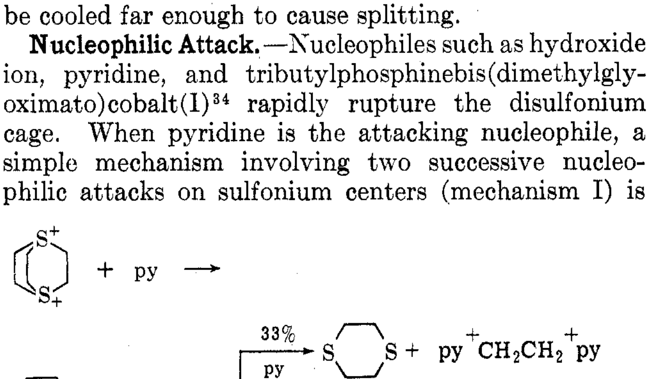


Figure 2.

Pmr Solution Spectra.—The pmr spectra of the $C_6H_{12}S_2^{+2}$ ion at room temperature in a variety of solvents consists of a single sharp peak (width at half height about 1 Hz, depending on concentration, etc.) at τ 5.91. The position of this peak indicates that the net dipositive charge of the disulfonium cation deshields the CH_2 protons relative to those in the ethyldimethylsulfonium ion (τ 6.52, center of quartet in D_2O), but that deshielding is not so effective as in the methylenebis(dimethylsulfonium) ion (τ 4.80 in trifluoroacetic acid).[33] The narrowness of the $C_6H_{12}S_2^{+2}$ signal indicates that both protons of the CH_2 group experience the same average environment and thus in solution the disulfonium ion has effective D_{3h} symmetry. If this situation arises because of rapid torsional vibration about the S–S axis, cooling a sample solution should lead to line broadening and eventually to splitting of the signal as the disulfonium ion approaches D_3 symmetry. This experiment does lead to significant line broadening, but the results are equivocal since the sample could not be cooled far enough to cause splitting.

Nucleophilic Attack.—Nucleophiles such as hydroxide ion, pyridine, and tributylphosphinebis(dimethylglyoximato)cobalt(I)[34] rapidly rupture the disulfonium cage. When pyridine is the attacking nucleophile, a simple mechanism involving two successive nucleophilic attacks on sulfonium centers (mechanism I) is



shown not to be effective since III is not observed as a reaction product. In addition, III does not accumulate as an intermediate since its characteristic CH_2 pmr signal cannot be detected in the reaction mixture even though independent experiments show that this ion is stable under the reaction conditions. Several additional observations indicate that these reactions proceed

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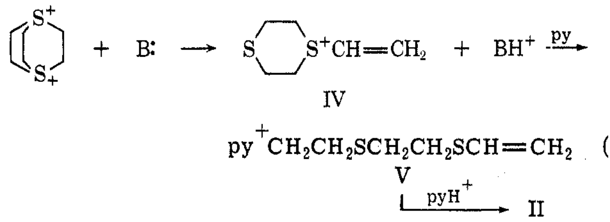
(31) (a) B. van Dijk and G. J. Visser, *Acta Crystallogr., Sect. B*, **27**, 846 (1971); (b) H. Einspahr and J. Donohue, *ibid.*, **27**, 846 (1971); (c) J. D. Lef, *ibid.*, **27**, 847 (1971); (d) J. Donohue, *ibid.*, **27**, 1071 (1971).

(32) We are indebted to the referees for bringing this point to our attention.

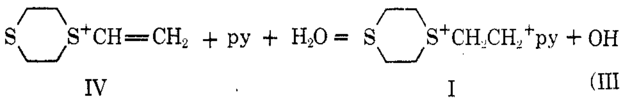
(33) C. P. Lillya and P. Miller, *J. Amer. Chem. Soc.*, **88**, 1559 (1966).

(34) G. N. Schrauzer and E. Deutsch, *ibid.*, **91**, 3341 (1969).



(II)

through intermediate IV (mechanism II). (1) The reaction of 1 equiv of sodium hydroxide with aqueous disulfonium perchlorate yields IV. (2) Both I and IV have been isolated[1] and shown to be interconvertible *via* the rapid equilibrium III. (3) When the pyridine–disulfonium reaction is run in dimethylformamide, the pmr spectra of the reaction solutions exhibit signals characteristic of vinyl protons and V is obtained as a by-product. Independent experiments show that II will not undergo elimination to give V under the reaction conditions and therefore V arises from nucleophilic attack by pyridine on IV (which is not expected to yield *p*-dithiane and *N*-vinylpyridinium ion in light of the inertness of vinyl halides to nucleophilic attack[35]). (4) Doering[36] has shown that the reaction of hydroxide ion with 2-bromoethyldimethylsulfonium ion rapidly yields the vinyldimethylsulfonium ion by elimination of HBr. (He has also observed that hydroxide rapidly attacks 1-thioniabicyclo[2.2.1]heptane.[37])



(III)

The magnitudes of the rates of OH^- attack on the two disulfonium centers, relative to H–D exchange, are indicated by the observation that, when molar deuterioxide is allowed to react with disulfonium chloride, mass spectral analysis of the resultant *p*-dithiane shows that it has undergone exactly 50% H–D exchange. This can be understood if deuterioxide rapidly attacks the disulfonium ion before H–D exchange can take place, giving either intermediate IV or the -OD analog of intermediate I. This intermediate is then subject to deuterioxide-catalyzed H–D exchange *via* the accepted mechanism for sulfonium ions.[38] Thus only those hydrogens on carbons bound to the sulfonium sulfur will exchange before the second, slower hydroxide attack occurs, leading to the observed 50% deuterium content of the *p*-dithiane product.

Registry No.—Disulfonium tetrachlorozincate, 35616-90-1; *p*-dithiane, 505-29-3; disulfonium perchlorate, 35624-14-7; disulfonium chloride, 5344-51-4; disulfonium tetraphenylborate, 35616-91-2; tetra(disulfonium)cobalt(II) decachloride hydrate, 35616-92-3; dipyridinium 1,1′-[ethylenebis(thioethylene)]diperchlorate, 35624-16-9; *N*-[3,6-bis(thia)-7-octenyl]pyridinium perchlorate, 35624-17-0; dipyridinium 1,1′-ethylenediperchlorate, 6601-41-8.

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[35] L. F. Fieser and M. Fieser, "Advanced Organic Chemistry," Reinhold, New York, N. Y., 1961, p 341.

[36] W. von E. Doering and K. Schreiber, *J. Amer. Chem. Soc.*, **77**, 514 (1955).

[37] W. von E. Doering and A. K. Hoffmann, *ibid.*, 521 (1955).

[38] C. C. Price and S. Oae, "Sulfur Bonding," Ronald Press, New York, N. Y., 1962, pp 153–155.

The Synthesis of 2,4-Diketo-5-phenyl-Δ^5-7-oxa-1,3-diazabicyclo[4.4.0]decane and 2,4-Diketo-3-phenyl-Δ^5-7-oxa-1,5-diazabicyclo[4.4.0]decane[1]

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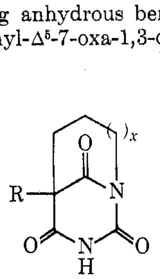
In an attempt to secure 5-phenyl bicyclo barbiturates, *N*-(haloalkyl)-5-phenylbarbituric acids were prepared and converted to their corresponding thallous salts. Nitrourea and alkanolamines were allowed to react to produce *N*-(hydroxyalkyl)ureas, which were converted to the corresponding *N*-(hydroxyalkyl)-5-phenylbarbituric acids and *via* these alcohols to the halides. When cyclization of the thallous salts of the *N*-(halopropyl)-5-phenylbarbituric acids was attempted in benzene–water, no intramolecular C-alkylation occurred and the only product isolated was 2,4-diketo-3-phenyl-Δ^5-7-oxa-1,5-diazabicyclo[4.4.0]decane. Utilizing anhydrous benzene as the solvent for the cyclization reaction, the product obtained was 2,4-diketo-5-phenyl-Δ^5-7-oxa-1,3-diazabicyclo[4.4.0]decane.

As part of a study on the steric aspects of selective central nervous system depression, attempts have been made to find general synthetic routes to bridged barbiturates, 1, to be investigated as antiepileptic agents.



1

R = alkyl, aryl

$x = 0, 1, 2$

One such barbituric acid, 5-phenyl-7-methoxy-2,4,9-triketo-1,3-diazabicyclo[3.3.1]nonane (2), was prepared by base-catalyzed intramolecular attack of an imide nitrogen on the primary bromo function of 5-phenyl-5-(2-methoxy-3-bromopropyl)barbituric acid

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[1] Taken in part from the dissertation presented by J. W. Ayres, August 1970, to the Graduate School of the University of Kansas in partial fulfillment of the requirements for the Doctor of Philosophy degree.