

9, 4.727 mCi/mol. The yields were 4.25, 2.70, and 21.43%, respectively.

Amine 2 (as the nonradioactive hydrochloride), 18.04 mmol, was deaminated in 100 g of acetic acid containing 14 g of sodium acetate. The following radioactive materials were then added: 3, 0.2500 g, 0.3125 mCi/mol; 4, 0.1500 g, 0.3007 mCi/mol. When reisolated the diols gave carbon-14 assays as follows: 3, 0.1615 mCi/mol; 4, 0.1574 mCi/mol. The yields of 3 and 4 were 6.34 and 3.2%, respectively. Although 0.2500 g of radioactive 9 was added to the deamination mixture, it could not be reisolated because the yield of 9 is very low.

Appendix A, for Scheme V

Consider (Scheme IX) the two nonclassical ions ($B \leftrightarrow C$)_c formed from the amine 1a by the clockwise route (Scheme V), and ($B \leftrightarrow C$)_{cc} formed from the amine 1a by the counterclockwise route. Cations ($B \leftrightarrow C$)_c and ($B \leftrightarrow C$)_{cc} both should yield products 3a and 4a in the same ratio [3a:4a = x:(1-x)]. If the relative concentrations of ($B \leftrightarrow C$)_c and ($B \leftrightarrow C$)_{cc} are y and (1-y) respectively, then the fraction of D' in [3a]_c + [3a]_{cc} is

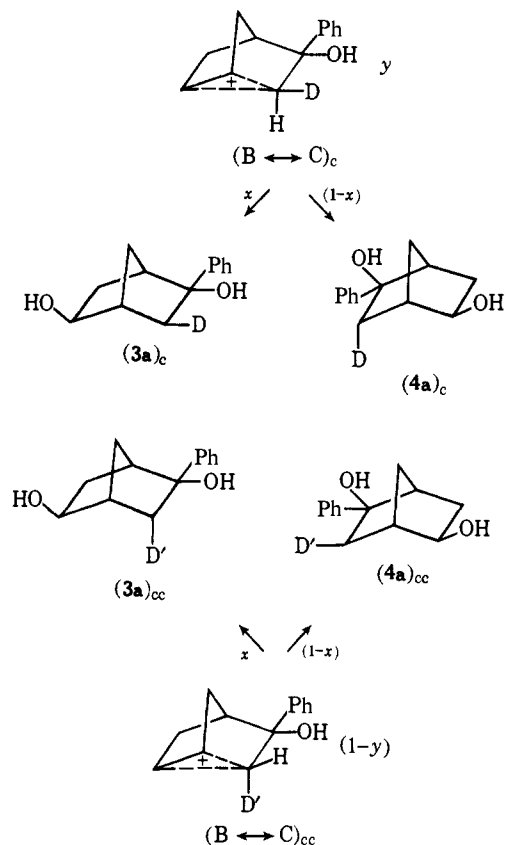
$$\left(\frac{D'}{D' + D}\right)_3 = \frac{x(1-y)}{xy + x(1-y)} = 1 - y$$

and the fraction of D' in (4)_c + (4)_{cc} is

$$\left(\frac{D'}{D' + D}\right)_4 = \frac{(1-y)(1-x)}{y(1-x) + (1-y)(1-x)} = 1 - y$$

Thus, nonclassical ions ($B \leftrightarrow C$)_c and ($B \leftrightarrow C$)_{cc} yield 3a and 4a with identical distributions of deuterium. If ($B \rightleftharpoons C$)_c and ($B \rightleftharpoons C$)_{cc}, however, are classical ions which have not yet reached their equilibrium concentrations, then the ratio of the two ions formed by the clockwise route ($B:C$)_c will be different than the ratio of the

Scheme IX



ions formed by the counterclockwise route ($B:C$)_{cc}, and the deuterium distributions in 3a and 4a should be different.

Molecular Geometry. III. The Structure of Racemic 7-Chloro-1,3,5-trimethyl-5H-pyrimido[5,4-b][1,4]benzothiazine-2,4(1H,3H)-dione, a Stable Sulfonium Ylide

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Contribution from the Department of Chemistry, University of Arizona, Tucson, Arizona 85721. Received February 22, 1971

Abstract: The crystal and molecular structure of racemic 7-chloro-1,3,5-trimethyl-5H-pyrimido[5,4-b][1,4]benzothiazine-2,4(1H,3H)-dione (I) has been determined using single-crystal X-ray diffraction techniques. The crystals are monoclinic in the space group $P2_1/n(C_{2h}^2)$ with four molecules in a unit cell of dimensions $a = 12.514$ (5), $b = 8.029$ (2), $c = 13.730$ (5) Å, and $\beta = 99.61$ (1)°. Least-squares refinement of the structure led to a final value of the conventional R factor of 0.059 for the 1699 data having $F_o^2 \geq 3\sigma(F_o^2)$. The charge delocalized representation (Ia) is estimated to contribute 85% to the overall bonding in this sulfonium ylide.

The nature of the bonding in sulfonium ylides has been elucidated by chemical studies.²⁻⁵ Several reviews of the literature are available.⁶⁻⁸

(1) Part II in this series: John P. Schaefer and Karen Walthers, *Tetrahedron*, 27, 5289 (1971). This work represents a portion of the dissertation of L. L. Reed presented to the Graduate College of the University of Arizona in partial fulfillment of the requirements for the Ph.D. degree.

(2) K. W. Ratts, *Tetrahedron Lett.*, 4707 (1966).

(3) A. Hochrainer and W. Silhan, *Monatsh. Chem.*, 97, 1477 (1966).

The resolution of sulfonium salts into optically active components ruled out a planar bonding arrangement

(4) H. Nozaki, D. Tunemoto, Z. Morita, K. Nakamura, K. Watanabe, M. Takaku, and K. Kondo, *Tetrahedron*, 23, 4279 (1967).

(5) A. F. Cook and J. G. Moffatt, *J. Amer. Chem. Soc.*, 90, 740 (1968).

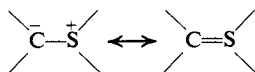
(6) A. W. Johnson, "Ylid Chemistry," Academic Press, New York, N. Y., 1966, Chapter 9.

(7) H. Nozaki, M. Takaku, D. Tunemoto, Y. Yamamoto, and K. Kondo, *Nippon Kagaku Zasshi*, 81, 1 (1967).

(8) H. König, *Fortschr. Chem. Forsch.*, 9, 487 (1968).

around the sulfur atom in ylides and a pyramidal configuration has been observed in 2-dimethylsulfuranylidene malonitrile⁹ and confirmed in the present investigation.

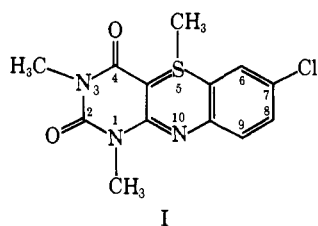
Theoretical and chemical studies have indicated that the ylide function



might stabilize the α carbanion by bond formation involving C(2p)–S(3d) orbitals. The limited crystallographic information available has been obtained from stabilized sulfonium ylides where extensive charge delocalization from the carbanion over dinitrile⁹ or ketoamide substituents (the present investigation) takes place.

Single crystals of sulfonium ylides are difficult to obtain due to the extreme reactivity of these compounds. Generally, the ylides that have been isolated are those that have substituents capable of stabilizing the carbanion function. Substituents such as β -diketo, keto ester, cyano ester, dinitrile, ketoamide, and others⁵ have been found to stabilize the ylide sufficiently to enable isolation and characterization of these compounds. However, the stabilization that allows the preparation of crystalline compounds suitable for crystallographic investigation complicates the confirmation of the interaction of the carbanion and the sulfonium ion, since charge delocalization onto O or N significantly decreases the carbanion character of the α carbon. Chemical evidence, revealed in abnormal infrared stretching frequencies in β -carbonyl sulfonium ylides,^{5,10} clearly shows that charge delocalization onto O is important and results in a lengthening of the carbon–oxygen bond. In addition, the trigonal planar bonding about the α carbon in I and II and in C(CN)₃⁻¹¹ contrasts with the expected nonplanar carbanion geometry.

The numbering scheme given in I corresponds to the IUPAC rules of nomenclature¹² and is *not* the scheme used in the crystallographic description.



Experimental Section

A sample of the compound C₁₃H₁₂N₃ClO₂S (I) was kindly provided by Dr. Irving Goldman of the Charles Pfizer Pharmaceutical Co. The molecular weight of I (calcd, 309.8 amu) was confirmed by mass spectroscopy and the observed fragmentation pattern was consistent with the postulated structure.

The material after recrystallization from chloroform afforded pale green, optically clear crystals that were stable toward air and moisture. Investigation of Weissenberg and precession photo-

graphs indicated monoclinic symmetry and revealed the following systematic absences: $h0l$ when $h + l \neq 2n$, $0k0$ when $k \neq 2n$. These conditions are consistent with the space group $P2_1/n$ (C_{2h}^5), an alternative setting of space group $P2_1/c$. Lattice parameters obtained from these photographs were: $a = 12.50$ (3), $b = 8.02$ (3), $c = 13.70$ (3) Å, $\beta = 99.5$ (3)°. With these cell constants the calculated crystal density corresponding to four molecules in the unit cell was 1.52 g cm^{-3} which was in good agreement with an observed density of 1.51 g cm^{-3} (21°) determined by flotation in bromobenzene–carbon tetrachloride mixtures.

A second, well-formed crystal, with dimensions $0.05 \times 0.19 \times 0.61$ mm, was selected and mounted with the long dimension collinear with the mounting fiber. Unit cell dimensions $a = 12.514$ (5), $b = 8.029$ (2), $c = 13.730$ (5) Å, $\beta = 99.61$ (1)° ($\rho_{\text{calcd}} = 1.51 \text{ g cm}^{-3}$) were determined by least-squares refinement of the angular parameters defining six reciprocal lattice points manually centered on a Picker FACS-I, computer-assisted, four-circle diffractometer.

An initial set of intensity data was collected using standard multiple-film data collecting techniques.

A second data set was collected on a Picker FACS-I four-circle computer-controlled diffractometer. The crystal was mounted such that the crystallographic a axis was approximately collinear with the ϕ axis of the diffractometer. A check of the crystal mosaicity was obtained using ω scans on two reflections. At a take-off angle of 0.9°, both scans showed half-height peak widths of 0.15° or less.

In a continuous run, 1997 unique data were collected employing a θ – 2θ scanning technique. All data in a spherical shell bound by 2θ in the range $4^\circ < 2\theta < 123^\circ$ were collected. Graphite monochromatized Cu K α radiation (λ 1.5418 Å) was used. The θ – 2θ scanning technique was characterized by a scan rate of 2.0°/min covering an interval of 2.0°. This interval was automatically modified to correct for radiation dispersion. Ten-second background determinations were made at each end of the scan interval. Aluminum foil attenuators were automatically inserted whenever the counting rate exceeded approximately 10^4 Hz. Three standard reflections were monitored every 1.5 hr. Except for random fluctuations, the intensities of these standards remained constant during the data collection.

The intensity data were reduced to F^2 and $\sigma(F^2)$ values using the computer program UCFACS.¹³ The reduction algorithm used was that of Corfield, Doedens, and Ibers.¹⁴ The polarization correction used was $P = 0.5(\cos^2 2\theta_m + \cos^2 2\theta_{hkl})$, where θ_m is the Bragg angle of the monochromator crystal and θ is the Bragg angle of a reflection hkl . The p factor used for more accurate weighing of intense reflections was assigned a value of 0.03. The Lorentz correction is $L = 1/\sin 2\theta$ where θ is the Bragg angle. No absorption correction (μ Cu K α = 35.1 cm⁻¹) was applied.

Structure Solution. This structure was solved using the normalized structure factors derived from the visually estimated intensity data. Phasing of these structure factors was accomplished by centrosymmetric direct method techniques.¹⁵ The necessary computations were performed using the computer program REL.¹³ An E map computed from 200 phased structure factors revealed 18 of the 20 nonhydrogen atoms of the molecule. The two atoms that were not found on this map were on the periphery of the molecule, and were readily located by a difference Fourier calculation using the entire set of observed structure factors. This Fourier synthesis also provided a check of the proposed model; it showed no significant electron density other than the two missing atoms.

Structure Refinement. The conventional R factor ($R = \sum |F_o| - |F_c| / \sum |F_o|$) based on the 20-atom model prior to full-matrix least-squares refinement was 0.39. This calculation was based on the observed reflections (1290 film data) and an overall temperature factor of 4.0 Å². Refinement of the structure using isotropic thermal parameters and unit weights reduced R_1 (defined as R above) to 0.20 and $R_2 = (\sum w(F_o - F_c)^2 / \sum w F_o^2)^{1/2}$ to 0.27 for all data. Refinement using the visually estimated data was terminated at this stage, and all subsequent refinement cycles were computed using the diffractometer data set. In these calculations, each observation was weighted using a statistically obtained weight, $w = 4F_o^2 / \sigma^2(F_o^2)$. Initially, the coordinates and isotropic thermal parameters obtained

(9) A. T. Christensen and W. G. Witmore, *Acta Crystallogr., Sect. B*, **25**, 73 (1969).

(10) H. Nozaki, K. Kondo, and M. Takaku, *Tetrahedron Lett.*, 251 (1965).

(11) P. Andersen, B. Klewe, and E. Thom, *Acta Chem. Scand.*, **21**, 1530 (1967).

(12) Private communication from Dr. Kurt L. Loening, Director of Nomenclature, Chemical Abstracts Service, The Ohio State University, Columbus, Ohio 43210.

(13) Computer programs used in the solution, refinement, and analysis of this structure include: Hamilton's UCFACS, Dewar's FAME, Long's REL, Zalkin's FORDAP, Busing and Levy's ORFLS, ORFFE, and Johnson's ORTEP.

(14) P. W. R. Corfield, R. J. Doedens, and J. A. Ibers, *Inorg. Chem.*, **6**, 197 (1967).

(15) M. M. Woolfson, "Direct Methods in Crystallography," Oxford University Press, London, 1961.

Table I. Atomic Coordinates^a

Atom	x	y	z
Cl	0.6808 (1) ^b	0.3979 (2)	0.4448 (1)
S	0.2849 (1)	0.1221 (1)	0.3698 (1)
O ₁	0.0257 (3)	-0.2571 (5)	0.5915 (3)
O ₂	0.1206 (3)	-0.1167 (5)	0.2960 (2)
N ₁	0.3119 (3)	0.0946 (5)	0.6010 (2)
N ₂	0.1610 (3)	-0.0728 (5)	0.5923 (3)
N ₃	0.0730 (3)	-0.1910 (5)	0.4434 (3)
C ₁	0.5720 (3)	0.3058 (5)	0.4884 (3)
C ₂	0.5724 (4)	0.2961 (6)	0.5899 (3)
C ₃	0.4862 (4)	0.2245 (6)	0.6234 (3)
C ₄	0.3945 (3)	0.1642 (5)	0.5586 (3)
C ₅	0.3986 (3)	0.1786 (6)	0.4577 (3)
C ₆	0.4862 (3)	0.2472 (5)	0.4219 (3)
C ₇	0.2350 (3)	0.0146 (5)	0.5440 (3)
C ₈	0.0829 (4)	-0.1781 (6)	0.5456 (4)
C ₉	0.1365 (4)	-0.1042 (6)	0.3879 (3)
C ₁₀	0.2170 (3)	-0.0030 (6)	0.4409 (3)
C ₁₁	0.1765 (5)	-0.0674 (9)	0.7026 (3)
C ₁₂	-0.0109 (5)	-0.3085 (8)	0.3936 (4)
C ₁₃	0.2072 (4)	0.3122 (7)	0.3564 (4)
H ₂ ^c	0.643 (3)	0.343 (5)	0.648 (3)
H ₃	0.489 (3)	0.219 (5)	0.693 (3)
H ₆	0.480 (3)	0.266 (5)	0.346 (3)

^a x, y, and z are expressed as fractional monoclinic coordinates.

^b The estimated standard deviations, given in parentheses, were obtained from the variance-covariance matrix from the final cycle of least-squares refinement. ^c Hydrogen atoms are given the number of the carbon atoms to which they are bonded.

Table II. Anisotropic Thermal Parameters^a

Atom	10 ⁴ β ₁₁	10 ⁴ β ₂₂	10 ⁴ β ₃₃	10 ⁴ β ₁₂	10 ⁴ β ₁₃	10 ⁴ β ₂₃
Cl	57 (1)	183 (2)	67 (1)	-11 (1)	11 (1)	10 (1)
S	54 (1)	183 (2)	30 (1)	-17 (1)	7 (1)	-6 (1)
O ₁	88 (3)	285 (9)	52 (2)	-52 (4)	7 (2)	-27 (3)
O ₂	96 (3)	259 (8)	82 (3)	-38 (4)	41 (2)	13 (4)
N ₁	63 (3)	199 (8)	38 (2)	-11 (4)	11 (2)	-9 (3)
N ₂	73 (3)	193 (7)	46 (2)	4 (4)	24 (2)	3 (3)
N ₃	61 (3)	166 (7)	58 (2)	-8 (4)	11 (2)	-1 (3)
C ₁	57 (3)	135 (8)	54 (3)	12 (4)	9 (2)	5 (4)
C ₂	58 (3)	209 (10)	50 (3)	4 (5)	3 (2)	-6 (4)
C ₃	62 (3)	202 (10)	39 (2)	-3 (4)	3 (2)	-9 (4)
C ₄	62 (3)	156 (8)	36 (2)	14 (4)	5 (2)	-4 (3)
C ₅	57 (3)	154 (8)	38 (2)	-1 (4)	3 (2)	-5 (3)
C ₆	52 (3)	162 (8)	40 (2)	2 (4)	7 (2)	4 (3)
C ₇	65 (3)	152 (8)	42 (2)	13 (4)	17 (2)	-2 (4)
C ₈	59 (3)	176 (8)	38 (2)	-2 (4)	13 (2)	-7 (4)
C ₉	63 (4)	167 (9)	64 (3)	1 (5)	-18 (3)	-3 (4)
C ₁₀	61 (3)	181 (9)	46 (3)	-4 (4)	10 (2)	-8 (4)
C ₁₁	129 (6)	338 (14)	36 (3)	-29 (7)	33 (3)	10 (5)
C ₁₂	88 (4)	230 (11)	84 (4)	-54 (6)	11 (3)	-15 (5)
C ₁₃	60 (3)	203 (10)	71 (3)	4 (5)	-2 (3)	25 (5)
H ^b						

^a The general anisotropic temperature factor has the form: $T = \exp[-(h^2\beta_{11} + k^2\beta_{22} + l^2\beta_{33} + 2hk\beta_{12} + 2hl\beta_{13} + 2kl\beta_{23})]$. ^b Hydrogen atoms were assigned a fixed isotropic temperature factor of 4.0 Å².

from refinement using the visually estimated data were employed. Convergence was rapid and afforded $R_1 = 0.12$ and $R_2 = 0.17$ after two cycles.

A second difference Fourier was then computed. The three phenyl hydrogen atoms (H₂, H₃, H₆) were the largest peaks on the electron density map with densities of approximately 0.5 e/Å³. The remaining nine methyl protons were not located. Ill-defined regions of electron density appeared around the methyl carbons (C₁₁, C₁₂, C₁₃) with a maximum electron density roughly one-third that of the phenyl protons. This lack of resolution of methyl hydrogens is most likely due to disorder and/or thermal motion.

Two final cycles of refinement using anisotropic thermal parameters for all nonhydrogen atoms were computed. Hydrogen atoms were given fixed isotropic thermal coefficients of 4.0 Å². The final values for R_1 and R_2 , calculated over the 1699 data with

Table III. Bond Distances

Bond	Bond distances, Å
C ₁ -Cl	1.741 (4)
C ₁ -C ₂	1.395 (6)
C ₁ -C ₆	1.371 (6)
C ₂ -C ₃	1.369 (7)
C ₃ -C ₄	1.414 (6)
C ₄ -N ₁	1.386 (5)
C ₄ -C ₅	1.399 (6)
C ₅ -S	1.765 (4)
C ₅ -C ₆	1.389 (6)
C ₇ -N ₁	1.303 (5)
C ₇ -N ₂	1.412 (5)
C ₇ -C ₁₀	1.403 (6)
C ₈ -O ₁	1.210 (5)
C ₈ -N ₂	1.368 (6)
C ₈ -N ₃	1.391 (6)
C ₉ -O ₂	1.248 (5)
C ₉ -N ₃	1.379 (6)
C ₉ -C ₁₀	1.400 (6)
C ₁₀ -S	1.721 (4)
C ₁₁ -N ₂	1.496 (6)
C ₁₂ -N ₃	1.490 (6)
C ₁₃ -S	1.803 (5)
C ₂ -H ₂	1.15 (4)
C ₃ -H ₃	0.96 (5)
C ₆ -H ₆	1.05 (4)

Table IV. Bond Angles

Atoms	Bond angle, deg	Atoms	Bond angle, deg
C ₁ -C ₂ -C ₃	119.2 (4)	C ₈ -N ₃ -C ₉	123.9 (4)
C ₁ -C ₆ -C ₅	118.5 (4)	C ₈ -N ₃ -C ₁₂	116.6 (4)
C ₂ -C ₁ -Cl	119.6 (3)	C ₉ -N ₃ -C ₁₂	119.5 (4)
C ₂ -C ₁ -C ₆	121.2 (4)	C ₉ -C ₁₀ -S	145.1 (3)
C ₂ -C ₃ -C ₄	122.3 (4)	C ₁₀ -C ₉ -O ₂	104.1 (2)
C ₃ -C ₄ -N ₁	117.2 (4)	C ₁₀ -C ₇ -N ₁	129.3 (4)
C ₃ -C ₄ -C ₅	115.7 (4)	C ₁₀ -C ₇ -N ₂	114.6 (4)
C ₄ -N ₁ -C ₇	118.3 (3)	C ₁₀ -C ₇ -N ₃	115.9 (4)
C ₄ -C ₅ -S	119.8 (3)	N ₂ -C ₈ -O ₁	121.2 (4)
C ₄ -C ₅ -C ₆	123.1 (4)	N ₂ -C ₈ -N ₃	117.1 (4)
C ₅ -S-C ₁₀	100.4 (2)	N ₁ -C ₇ -N ₂	116.1 (4)
C ₅ -S-C ₁₃	102.2 (2)	N ₁ -C ₇ -N ₃	121.7 (4)
C ₅ -C ₄ -N ₁	127.0 (4)	N ₃ -C ₉ -O ₂	120.7 (4)
C ₆ -C ₁ -Cl	119.2 (3)	C ₁ -C ₆ -H ₆	123 (2)
C ₆ -C ₁ -C ₆	117.0 (3)	C ₁ -C ₂ -H ₂	123 (2)
C ₇ -N ₂ -C ₈	124.1 (4)	C ₂ -C ₃ -H ₃	117 (3)
C ₇ -N ₂ -C ₁₁	118.4 (4)	C ₃ -C ₂ -H ₃	118 (2)
C ₇ -C ₁₀ -S	120.2 (3)	C ₄ -C ₃ -H ₃	120 (3)
C ₇ -C ₁₀ -C ₉	124.3 (4)	C ₅ -C ₆ -H ₆	119 (2)
C ₈ -N ₂ -C ₁₁	117.0 (4)		

$F_o > 3\sigma(F_o)$, were 0.058 and 0.088, respectively. Atomic scattering factors used for C, O, N, S, and Cl were those tabulated by Hanson, *et al.*,¹⁶ and those for H were obtained from Stewart, *et al.*¹⁷ A final structure factor calculation over the entire 1997 data gave $R_1 = 0.065$ and $R_2 = 0.089$.

Results and Discussion


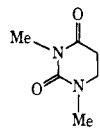
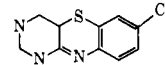
Table I lists the final atomic coordinates and Table II the anisotropic thermal parameters for the refined structure.¹⁸ The numbering scheme and stereoscopic view of the molecule are shown in Figure 1. Figure 2

(16) H. P. Hanson, F. Herman, J. D. Lea, and S. Skillman, *Acta Crystallogr.*, **17**, 1040 (1964).

(17) R. F. Stewart, E. R. Davidson, and W. T. Simpson, *J. Chem. Phys.*, **42**, 3175 (1965).

(18) A listing of structure factors (Table VIII) will appear following these pages in the microfilm edition of this volume of the journal. Single copies may be obtained from the Reprint Department, ACS Publications, 1155 Sixteenth St., N.W., Washington, D. C. 20036, by referring to author, title of article, volume, and page number. Remit check or money order for \$3.00 for photocopy or \$2.00 for microfiche.

Table V. Least-Squares Planes^{a,b}

Atom	Plane 1, C ₆ H ₆	Plane 2, C ₉ C ₁₀ S C ₇	Plane 3, 	Plane 4, 	Plane 5, 
Cl	0.036	-1.754	-1.199	-1.321	-0.225
S	0.148	0.012	0.232	0.179	0.422
O ₁	-0.998	0.318	-0.037	0.015	-0.333
O ₂	-0.738	-0.020	0.057	0.033	-0.188
N ₁	-0.014	-0.128	-0.136	-0.151	0.212
N ₂	-0.406	0.207	0.026	0.045	0.045
N ₃	-0.897	0.126	- 0.014	0.000	- 0.288
C ₁	0.000	-0.293	-0.902	-0.992	- 0.116
C ₂	0.009	-1.241	-0.959	-1.031	- 0.118
C ₃	- 0.011	-0.869	-0.715	-0.763	- 0.022
C ₄	0.004	-0.490	-0.364	-0.405	0.121
C ₅	0.005	-0.554	-0.314	-0.374	0.125
C ₆	- 0.007	-0.958	-0.588	-0.672	0.001
C ₇	-0.217	0.016	- 0.024	- 0.032	0.128
C ₈	-0.777	0.226	- 0.007	0.023	- 0.197
C ₉	-0.661	0.015	0.014	0.003	- 0.145
C ₁₀	-0.327	- 0.042	0.004	- 0.017	0.057
C ₁₁	-0.364	0.224	-0.056	- 0.021	0.054
C ₁₂	-1.326	0.123	-0.077	- 0.049	- 0.577
C ₁₃	1.935	1.770	2.019	1.962	2.222
H ₂	0.007	-1.523	-1.228	-1.304	- 0.221
H ₃	-0.006	-0.843	-0.762	-0.798	- 0.028
H ₆	0.104	-0.873	-0.425	-0.523	0.120
l	- 0.437	- 0.694	- 0.633	- 0.645	- 0.522
m	0.900	0.719	0.768	0.759	0.852
n	- 0.012	- 0.032	- 0.099	- 0.088	- 0.036
d	- 0.529	- 1.377	- 0.714	- 1.648	- 1.201
Rms deviation	0.007	0.024	0.017	0.028	0.182

^a The equations of the planes are of the form $lX + mY + nZ = d$, where l , m , and n are the direction cosines of the plane normal and d (Å) is the distance of the plane from the origin. Figures in bold type are deviations of atoms comprising the plane. ^b The dihedral angle between planes 1 and 4 is 14.5°.

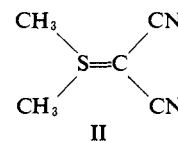
Table VI. Intermolecular Contacts (<3.60 Å) in the Crystal of I

Contact	Distance, Å
Cl-N ₂ ^a	3.37
Cl-C ₇	3.47
Cl-C ₈	3.43
O ₁ -C ₉	3.58
O ₁ -C ₁₂	3.50
O ₁ -C ₁₃	3.15
N ₂ -N ₃	3.58
N ₃ -C ₈	3.57
S-O ₂ ^b	3.45
O ₂ -C ₆	3.26
O ₂ -C ₁₃ ^c	3.29
Cl-C ₁₁	3.59

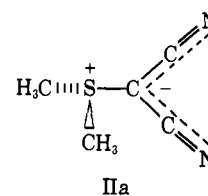
^a Refers to $-x, -y, -z$. ^b Refers to $1/2 - x, 1/2 + y, 1/2 - z$. ^c Refers to $1/2 + x, 1/2 - y, 1/2 + z$.

is a stereoscopic view depicting the molecular packing. Bond distances and angles computed from the parameters of Table I are presented in Tables III and IV, respectively. The estimated standard deviations of the distances and angles were derived from the variance-covariance matrix from the final cycle of refinement and appear in the tables in parentheses. Various least-squares planes are presented in Table V and Table VI lists the intermolecular contacts <3.60 Å.

The only ylide structure previously determined using X-ray diffraction techniques⁹ is that of 2-dimethylsulfuranylidene malononitrile (II).



Results of the study indicated that II, which is extremely polar in nature with a measured dipole moment of 8.08 D,⁹ has a planar SC(CN)₂ grouping and the expected pyramidal configuration about the sulfur atom. The best representation of II is the extensively charged delocalized structure, IIa.



The present investigation confirms the pyramidal bonding about the sulfur and indicates that charge delocalization is an important factor in the stabilization of I.

The C₁₃-S distance, 1.803 (5) Å, agrees well with the carbon-sulfur distance (1.809 Å) found in dimethyl sulfide determined by microwave spectroscopy,¹⁹ and the average methyl carbon-sulfur distance of 1.825 (10) Å in II. The C₅-S bond distance (1.765 (4) Å

(19) W. Maier, *Angew. Chem.*, 73, 120 (1961).

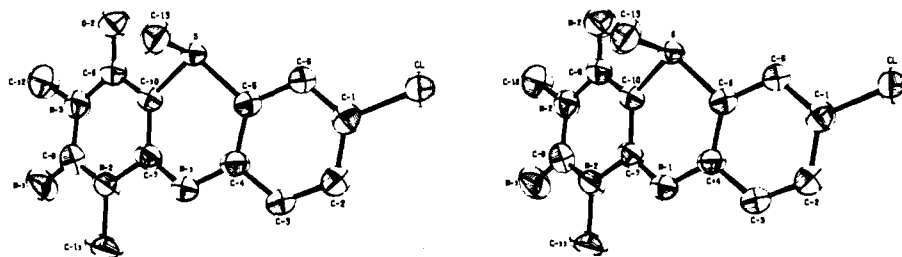
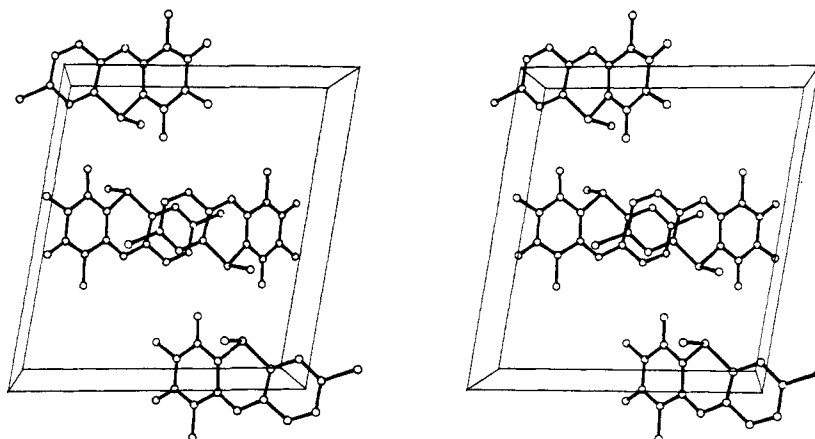


Figure 1. Stereoscopic view of sulfonium ylide.

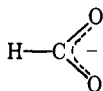
Figure 2. Stereoscopic view of the contents of a unit cell. The view along b has a horizontal and c vertical.

compares favorably with an average value 1.763 Å found for the $C(sp^2)$ -S bond.²⁰⁻²⁴ The carbon-sulfur bond in chloropromazine (1.75 (1) Å) was considered to contain 13% double bond character.²³

The remaining carbon-sulfur bond, C_{10} -S, 1.721 (4) Å, is significantly shorter than C_5 -S and compares well to the analogous carbon-sulfur bond in ethylene-thiourea (1.708 Å) which was postulated to contain approximately 20% double bond character.²⁵

In contrast, the length of the carbon-sulfur double bond in 4-methyl-1,2-dithia-4-cyclopentene-3-thione and tetraethylthiuram disulfide was found to be 1.66 Å.^{26,27}

The carbonyl distance, C_8 -O, 1.210 (5) Å, agrees well with the predicted value of 1.210 Å²⁸ and the longer carbonyl distance, C_9 -O₂, 1.248 (5) Å, is comparable to the average carbon-oxygen distance of 1.25 (1) Å found for the



group in various salts of formic acid.²⁹

(20) J. P. Schaefer, *Chem. Commun.*, 743 (1967).

(21) S. Hosoya, *Acta Crystallogr.*, **20**, 429 (1966).

(22) J. D. Bell, J. F. Blount, O. V. Briscoe, and H. C. Freeman, *Chem. Commun.*, 1656 (1968).

(23) J. J. H. McDowell, *Acta Crystallogr., Sect. B*, **25**, 2175 (1969).

(24) J. J. H. McDowell, *ibid.*, *Sect. B*, **26**, 954 (1970).

(25) P. J. Wheatley, *ibid.*, **6**, 369 (1953).

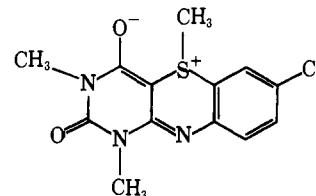
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(27) I. L. Karle, J. A. Estlin, and K. Britts, *ibid.*, **22**, 273 (1967).

(28) L. Pauling, "The Nature of the Chemical Bond," 3rd ed, Cornell University Press, Ithaca, N. Y., 1960.

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These findings indicate that the charge delocalized structure, Ia, is the major canonical structure to be considered in the bonding scheme for I. The average



Ia

phenyl carbon-carbon distance, 1.389 (5) Å, is in good agreement with the generally accepted value (1.394 Å).²⁹

The C-Cl bond length (1.741 (4) Å) agrees favorably with the average value of 1.737 (16) Å tabulated by Palenik, *et al.*³⁰

Table VII lists selected bond distances in II and the average values for analogous bonds in the structures of caffeine and theophylline.^{31,32} The largest difference

Table VII

Bond	Present study, Å	Caffeine, ^a theophylline, Å
C_7-N_2	1.412 (5)	1.40
N_2-C_{11}	1.496 (6)	1.48
C_8-N_2	1.368 (6)	1.35
C_8-N_3	1.391 (6)	1.41
N_3-C_{12}	1.490 (6)	1.48
C_9-N_3	1.379 (6)	1.37
C_9-C_{10}	1.400 (6)	1.43

^a References 31 and 32.

(30) G. J. Palenik, J. Donohue, and K. N. Trueblood, *Acta Crystallogr., Sect. B*, **24**, 1139 (1968).

(31) D. J. Sutor, *ibid.*, **11**, 453 (1958).

(32) D. J. Sutor, *ibid.*, **11**, 83 (1958).

(C₉-C₁₀, 0.03 Å) is in agreement with the description of the charge-delocalized nature of I which predicts that C₉-C₁₀ should have considerable double bond character.

Selected least-squares planes are presented in Table V. The molecular plane (plane 5, Table V) composed of ring atoms reveals the approximate planarity of the ring system. Table VI lists the intermolecular contacts, <3.60 Å. The shortest contact observed (3.15 Å) in-

volves C₁₃ and O₁. This contact compares to the calculated value of 3.40 Å which results from the sum of the van der Waals radii of the oxygen atom and the methyl group.²⁸

Table VIII lists h , k , l $10|F_o|$ and $10|F_c|$ for the 1997 data collected.¹⁸

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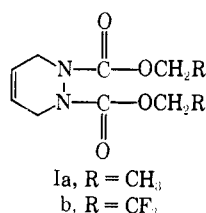
Nuclear Magnetic Resonance Studies of the Conformations of 1,2-Dicarboxy-1,2,3,6-tetrahydropyridazines

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Contribution from the Department of Chemistry, University of California, Santa Barbara, Santa Barbara, California 93106. Received May 27, 1971

Abstract: Variable-temperature proton and fluorine-19 nmr experiments suggest that 1,2-dicarbomethoxy-1,2,3,6-tetrahydropyridazine and 1,2-dicarbotrifluoroethoxy-1,2,3,6-tetrahydropyridazine exist as at least four distinct conformational isomers. At low temperatures, the rate of equilibration between these isomers becomes slow, and as the sample temperature is raised to about 30°, the changes in the proton or fluorine spectra can be accounted for in terms of processes that have activation free energies of 14–16 kcal/mol. Consideration of the pmr signals from the ring protons indicates that the heterocyclic six-membered ring is conformationally immobile during these changes and that only at much higher temperatures does ring inversion occur at an appreciable rate ($\Delta G^\ddagger \sim 20$ –22 kcal/mol). The nature of the low-temperature rate processes is discussed.

The stereochemical capabilities of nitrogen have been widely studied by magnetic resonance and recent reviews have admirably summarized the information that has been obtained about the kinetics of stereomutation at nitrogen in both the pyramidal amine state^{2,3} and in the planar amide configuration^{4,5} by these techniques. Tetrahydropyridazines with carbomethoxy (Ia)



or carbomethoxy substituents at the nitrogen atoms have been of particular interest in this regard since pmr studies of these and related molecules have indicated that at least two distinct conformational equilibrations can take place in these systems.^{4,5} By proper choice of assumptions, either of these processes can be assigned to any one of three types of conformational interchange: (a) inversion of the cyclohexene-like tetrahydropyridazine ring,⁶ (b) inversion of trihedral amide nitrogen atoms in analogy to the process found in ammonia,⁷

or (c) restricted rotation about the carbamate N—C=O bond system similar to that found in simpler carbamates.⁸ These assignments have, therefore, been the source of some controversy.

The first published observations of the unusual conformational properties of tetrahydropyridazines were reported by Breliere and Lehn.⁹ These authors interpreted changes in the pmr spectrum of II in terms of a high-temperature interconversion process ($\Delta G^\ddagger = 18.9$ kcal/mol), assigned to inversion of the heterocyclic ring, and a low-temperature process ($\Delta G^\ddagger = 14.8$ kcal/mol) ascribed to rotation about the carbon-nitrogen bond of the carbamate system. A challenge to this interpretation was effectively answered.^{10–12} In contrast, Daniels and Roseman offered a rationalization based on inversion of nitrogen for the complex pattern of methoxyl pmr signals that arise from III when the sample temperature is lowered.¹³

Allred, *et al.*, have examined the variable-temperature pmr spectra of bridged tetrahydropyridazines (IV, V) in order to assess the nature of conformational processes that occur in the absence of any possible ring inversion.¹⁴ In the hydrazine (V), the pmr spectral changes

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(3) A. Rauk, L. C. Allen, and K. Mislow, *Angew. Chem., Int. Ed., Engl.*, **9**, 400 (1970).
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