cooled at 0° was passed excess ketene in a stream of dry nitrogen. The solution was then poured into ice water, and the precipitate was collected by filtration and dried, yield 98 mg (85%) of 1-acetoxy-4,5,6,7-tetrachlorobenzotriazole. Following recrystallization from benzene, the compound had mp 197.5-199.5° and was identical in all respects (ir, etc.) with the sample obtained by acetylation using the potassium salt and acetyl chloride, as described above.

Chlorination of *o*-Methoxyacetanilide (*o*-Acetanisidide).—Dry chlorine was passed through a solution of *o*-acetanisidide in glacial acetic acid, and upon completion of the reaction the solution was poured into ice water. The precipitated material was recrystallized from ethanol as colorless needles of 2-methoxy-3,4,5,6-tetrachloroaniline, mp 224-225° (lit.[19] mp 227.5°), with the correct elemental analysis for $C_9H_7Cl_4NO_2$, nmr ($CDCl_3$ τ 7.78 (s, CH_3CO), 6.13 (s, CH_3O).

Reaction of 2-Methoxy-3,4,5,6-tetrachloroaniline with Phosgene Followed by Methanol.—To a solution of 200 mg of 2-methoxy-3,4,5,6-tetrachloroaniline in 20 ml of anhydrous benzene and 0.5 ml of anhydrous triethylamine was added 4 ml of a 12.5% solution of phosgene in benzene, and the reaction mixture was maintained at ambient temperature for 1 hr. The solvent was evaporated *in vacuo*, the residue was treated with anhydrous ether, and triethylamine hydrochloride was removed by filtration. Ether was evaporated from the filtrate under reduced pressure, leaving a half-solid residue which showed very strong infrared absorption at 2220 cm^{-1}. The residue was treated with 10 ml of methanol, and from this solution pure methyl N-(2-methoxy-3,4,5,6-tetrachlorophenyl)carbamate crystallized, yield 170 mg (70%), mp 181-182°, undepressed on admixture with a sample of methyl N-(2-methoxy-3,4,5,6-tetrachlorophenyl)carbamate (**6a**). The infrared spectra of the samples from the two sources were identical.

Registry No.—**4a**, 18355-09-4; **4c**, 18425-98-4; **5a**, 18355-11-8; **6a**, 18355-12-9; **6c**, 18355-13-0; **7a**, 18355-14-1; **7c**, 18355-15-2; **10**, 18346-74-2; **12**, 18346-75-3; 2,3,5,6-tetrachlorophenylhydrazine, 18355-16-3; hydrazine salt of 1-hydroxy-4,6,7-trichlorobenzotriazole, 18355-17-4; 1-ethoxycarbonyloxy-4,5-6,7-tetrachlorobenzotriazole, 18355-18-5; 1-methoxy-4,5,-6,7-tetrachlorobenzotriazole, 18355-19-6; 1-ethoxy-4,5,6,7-tetrachlorobenzotriazole, 18355-20-9.

Acknowledgment.—The support of this work by Research Grant GP-2012, now GP-8407X, from the National Science Foundation is gratefully acknowledged.

The Structures of Two Diastereoisomeric Sulfoxides. 3,5-Dihydro-3-methyl-4,1-benzothiazepin-2(1H)-one 4-Oxides

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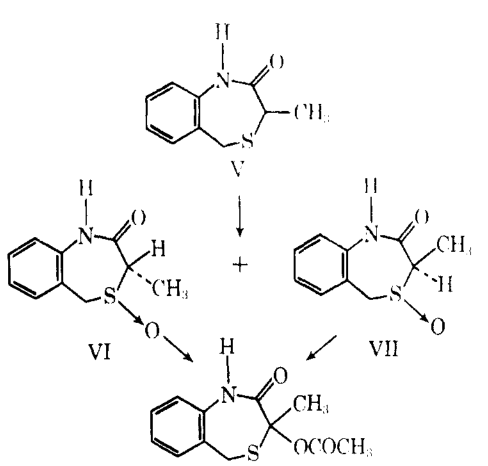
The sodium metaperiodate oxidation of 3,5-dihydro-3-methyl-4,1-benzothiazepin-2(1H)-one gave two diastereoisomeric sulfoxides with mp 220-223 and 246-248°, respectively. The crystal structure of the major product (mp 220-223°) has been determined and the 3-methyl group has been shown to be *trans* to the sulfoxide oxygen atom. The crystals are monoclinic, with $a = 13.20 \pm 0.02$ Å, $b = 4.71 \pm 0.01$ Å, $c = 17.16 \pm 0.03$ Å and $\beta = 113°15' \pm 15'$. There are four molecules of $C_{10}H_{11}NO_2S$ in the space group $P2_1/c$. The structure has been refined to an R factor of 0.09 on 1427 reflections, obtained photographically. The detailed geometry of the molecule in the crystal is described. In boiling acetic anhydride solution both sulfoxides interconvert and rearrange to 3-acetoxy-3,5-dihydro-3-methyl-4,1-benzothiazepin-2(1H)-one.

In the course of the study of 4,1-benzothiazepines, a new class of heterocyclic compounds[2] with interesting pharmacological properties, the Pummerer rearrangement[3] of sulfoxides was investigated as a method for the introduction of an acetoxy group on the carbon next to sulfur. In the 3-methyl series, we encountered the problem of separation and structure determination of two diastereoisomeric sulfoxides. This was resolved as follows.

The sodium metaperiodate oxidation[4] of racemic 3,5-dihydro-3-methyl-4,1-benzothiazepin-2(1H)-one (V), the synthesis[2] of which is fully described in the Experimental Section, gave two diastereoisomeric sulfoxides in a ratio of 3:1. They were separated by chromatography on a silica gel column. The major product was eluted first with 15% ethyl acetate-85% benzene mixture. The minor product was eluted subsequently with 75% ethyl acetate-25% benzene mixture and pure ethyl acetate. The structure of the major product was elucidated by X-ray analysis and determined as that of the *trans*-sulfoxide VI.



The X-Ray Analysis of the *trans*-Sulfoxide VI.—The crystals of VI are transparent needles belonging to the monoclinic system with $a = 13.20 \pm 0.02$ Å,

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[1] (a) University of Illinois. (b) Alfred P. Sloan Research Fellow. (c) Hoffmann-La Roche.

[2] M. Uskoković, G. Grethe, J. Iacobelli, and W. Wenner, *J. Org. Chem.*, **30**, 3111 (1965).

[3] R. Pummerer, *Ber.*, **43**, 1401 (1910).

[4] N. J. Leonard and C. R. Johnson, *J. Org. Chem.*, **27**, 282 (1962).

TABLE I

FRACTIONAL COORDINATES WITH ESTIMATED STANDARD DEVIATIONS IN PARENTHESES. ORIGIN AS IN "INTERNATIONAL TABLES FOR X-RAY CRYSTALLOGRAPHY." BEYOND C_{9a}, THE NUMBERING CONVENTION IS ARBITRARY

	x	*y*	*z*
N_1	0.3665 (4)	0.272 (1)	0.4621 (3)
C_2	0.3931 (5)	0.289 (1)	0.3932 (4)
C_3	0.3285 (4)	0.101 (1)	0.3195 (4)
S_4	0.1940 (1)	0.258 (1)	0.2511 (1)
C_5	0.1526 (5)	0.385 (1)	0.3352 (4)
C_{5a}	0.1692 (5)	0.175 (1)	0.4037 (4)
C_6	0.0803 (5)	0.027 (1)	0.4080 (4)
C_7	0.0945 (6)	−0.163 (1)	0.4728 (4)
C_8	0.1966 (6)	−0.202 (2)	0.5349 (4)
C_9	0.2875 (5)	−0.061 (2)	0.5326 (4)
C_{9a}	0.2747 (5)	0.126 (1)	0.4659 (4)
O_{10}	0.4681 (4)	0.442 (1)	0.3922 (3)
C_{11}	0.3906 (5)	0.029 (2)	0.2636 (5)
O_{12}	0.1233 (4)	0.006 (1)	0.2111 (3)
H_1	0.417	0.33	0.502
H_3	0.315	−0.11	0.343
$H_{5,1}$	0.075	0.42	0.306
$H_{5,2}$	0.190	0.56	0.353
H_6	0.016	0.02	0.357
H_7	0.033	−0.27	0.474
H_8	0.206	−0.33	0.581
H_9	0.360	−0.12	0.568
$H_{11,1}$	0.400	0.20	0.237
$H_{11,2}$	0.462	−0.04	0.297
$H_{11,3}$	0.347	−0.09	0.218

TABLE II

BOND DISTANCES (Å) WITH ESTIMATED STANDARD DEVIATIONS[a]

N_1–C_2	1.361 (8)
N_1–C_{9a}	1.419 (8)
C_2–C_3	1.505 (9)
C_2–O_{10}	1.229 (8)
C_3–S_4	1.853 (7)
C_3–C_{11}	1.525 (10)
S_4–C_5	1.833 (6)
S_4–O_{12}	1.498 (6)
C_5–C_{5a}	1.482 (9)
C_{5a}–C_6	1.393 (9)
C_{5a}–C_{9a}	1.400 (9)
C_6–C_7	1.382 (10)
C_7–C_8	1.361 (11)
C_8–C_9	1.387 (11)
C_9–C_{9a}	1.399 (10)

[a] The N–H and C–H distances all lie in the range 0.8–1.1 Å.

TABLE III

BOND ANGLES (DEGREES) WITH ESTIMATED STANDARD DEVIATIONS[a]

C_{9a}–N_1–C_2	125.9 (4)	C_5–C_{5a}–C_6	120.8 (5)
N_1–C_2–C_3	116.1 (6)	C_5–C_{5a}–C_{9a}	120.4 (4)
N_1–C_2–O_{10}	122.1 (7)	C_6–C_{5a}–C_{9a}	118.7 (4)
C_3–C_2–O_{10}	121.7 (6)	C_{5a}–C_6–C_7	121.3 (6)
C_2–C_3–S_4	112.3 (3)	C_6–C_7–C_8	119.6 (4)
C_2–C_3–C_{11}	113.0 (4)	C_7–C_8–C_9	121.0 (6)
S_4–C_3–C_{11}	107.9 (4)	C_8–C_9–C_{9a}	119.8 (4)
C_3–S_4–C_5	98.0 (3)	C_9–C_{9a}–N_1	120.9 (5)
C_3–S_4–O_{12}	104.0 (3)	C_9–C_{9a}–C_{5a}	119.5 (4)
C_5–S_4–O_{12}	107.1 (3)	C_{5a}–C_{9a}–N_1	119.6 (3)
S_4–C_5–C_{5a}	114.3 (3)		

[a] The bond angles involving hydrogen atoms bonded to atoms with sp^3 hybridization lie in the range 104–116°, and those involving hydrogen atoms bonded to sp^2-hybridized atoms lie in the range 108–124°.

$b = 4.71 \pm 0.01$ Å, $c = 17.16 \pm 0.03$ Å, and $\beta = 113° 15' \pm 15'$. There are four molecules of $C_{10}H_{11}NO_2S$ (mol wt 209.27) in the unit cell and the space group is $P2_1/c$. Least-squares refinement incorporating anisotropic temperature factors has given a final R factor of 0.09 on the 1427 independent structure amplitudes obtained by visual estimates of equiinclination Weissenberg photographs. The final values of the positional parameters are given in Table I. The bond distances and angles found in the molecule are listed in Tables II and III. Views of the molecule looking along the b and a axes are shown in Figures 1 and 2.

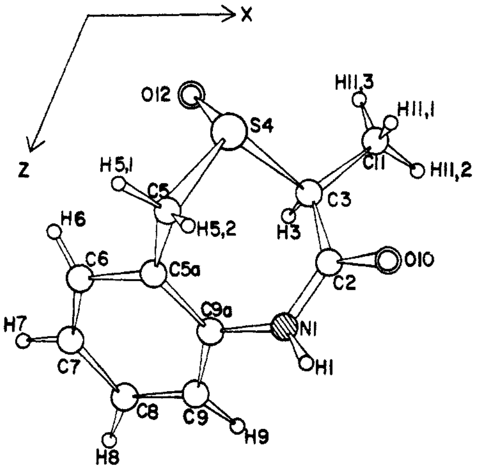

Figure 1.—View of the molecule along the b axis showing the atom numbering used in the analysis. The numbering after C-9a does not correspond to any established chemical convention.

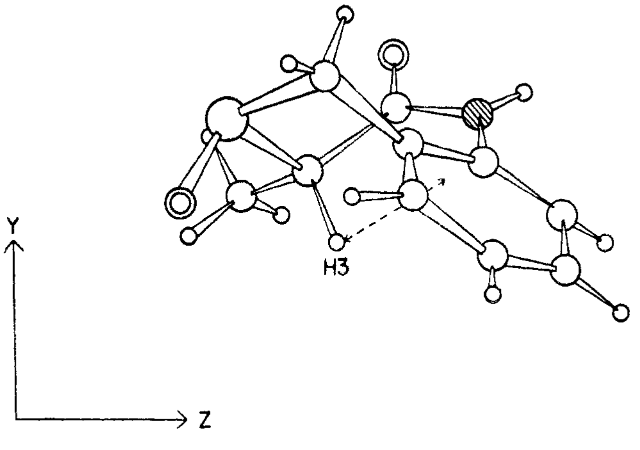

Figure 2.—View of the molecule along the a axis.

The relative configuration of the C—CH_3 and S→O groups is seen to be *trans*, with the methyl group adopting an equatorial position, while the sulfoxide oxygen is pseudoequatorial. The conformation of the seven-membered ring can be described as a distorted "boat"[5] relative to either the approximate plane through atoms C_3, S_4, C_{5a}, and C_{9a} with C_5, N_1, and C_2 lying 0.63, 1.15, and 1.08 Å, respectively, from this plane, or the very approximate plane through atoms N_1, C_2, S_4, and C_5 with C_3, C_{9a} and C_{5a} lying 0.18, 1.56 and 1.45 Å out of the plane. In the saturated carbocyclic series, seven-

(5) E L. Eliel, N. L. Allinger, S. J. Angyal, and G A. Morrison, "Conformational Analysis," Interscience, New York, N. Y., 1965, pp 206–209.

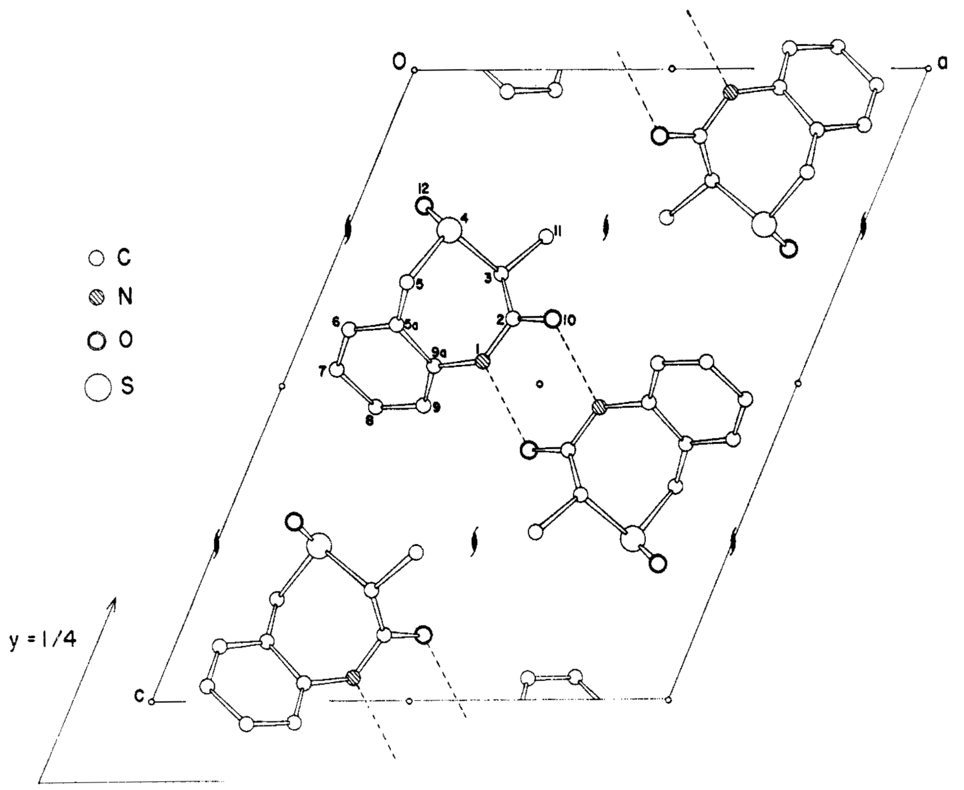

Figure 3.—Packing diagram viewed down *b*. The hydrogen bonds are marked by discontinuous lines.

membered rings can exist in a number of flexible conformations with the twist chair being considered the most stable.[6] The six atoms of the benzene ring, N_1, and C_5 are approximately planar (mean deviation 0.02 Å), as is the group of atoms C_{9a}, N_1, C_2, O_{10}, and C_3 (mean deviation 0.037 Å). These two rigid groups of atoms will impose considerable constraints on the conformation of the ring. These adjacent groups of four planar atoms (each containing C_{9a}) and the presence of the sulfur atom which forms much longer bonds to carbon make it unlikely that results valid in the flexible carbocyclic system will necessarily pertain in the thiazepine ring of VI. Furthermore, a survey[7] of carbocyclic seven-membered rings in sesquiterpenes indicates that the ring conformation is greatly dependent on the molecular environment.

The conformation of the seven-membered ring can also be described in terms of the dihedral angles involving the atoms in the ring (Table IV). The principal difference in detailed geometry of the ring from that implied by a Dreiding model can be described as an "unfolding" about the N_1–C_5 axis. This effect increases the C_2–N_1–C_{9a} and C_{5a}–C_5–S_4 angles to values of 125.9 and 114.3°, respectively, and is probably responsible for the unexpectedly large deviation from planarity in the group of atoms C_{9a}, N_1, C_2, O_{10}, and C_3. The groups of four atoms, C_{9a}, C_2, C_3, and O_{10} and N_1, C_2, C_3, and O_{10} are accurately planar with N_1 lying −0.11 Å from the plane through the first group, and C_{9a} lying 0.15 Å from that through the second group. This deviation is also shown by the dihedral angle of −9.4° made by atoms C_{9a} and C_3 when viewed along the N_1–C_2 bond. The most probable cause of this unfolding when compared with a wire model would be a repulsion between the C_3 proton and the π cloud of the aromatic ring. This hydrogen atom is reasonably well defined (although positioned to relatively low accuracy) and the small value of 104° for the H_3–C_3–H_{11} angle may be significant.

TABLE IV

DIHEDRAL ANGLES (DEGREES) IN THE SEVEN-MEMBERED-RING PORTION OF THE MOLECULE. THE DIHEDRAL ANGLE A–B–C–D IS CONSIDERED POSITIVE IF ATOM A HAS TO BE ROTATED CLOCKWISE TO ECLIPSE ATOM D

A	B	C	D	τ	A	B	C	D	τ
C_{9a}	N_1	C_2	C_3	−9.4	C_3	S_4	C_5	C_{5a}	−45.7
C_{9a}	N_1	C_2	O_{10}	173.0	O_{12}	S_4	C_5	C_{5a}	−81.3
N_1	C_2	C_3	S_4	82.7	S_4	C_5	C_{5a}	C_6	−103.7
N_1	C_2	C_3	C_{11}	−154.8	S_4	C_5	C_{5a}	C_{9a}	76.9
O_{10}	C_2	C_3	S_4	−99.7	C_5	C_{5a}	C_{9a}	N_1	−1.4
O_{10}	C_2	C_3	C_{11}	22.8	C_5	C_{5a}	C_{9a}	C_9	−145.5
C_2	C_3	S_4	C_5	−43.8	C_6	C_{5a}	C_{9a}	N_1	179.2
C_2	C_3	S_4	O_{12}	28.2	C_6	C_{5a}	C_{9a}	C_9	−3.0
C_{11}	C_3	S_4	C_5	−169.1	C_{5a}	C_{9a}	N_1	C_2	−51.2
C_{11}	C_3	S_4	O_{12}	−97.1	C_9	C_{9a}	N_1	C_2	131.1

A packing diagram of the structure viewed down the *b* axis is shown in Figure 3. Intermolecular hydrogen bonding involving the amide groups in adjacent molecules to form centrosymmetric dimers in the crystal is an important facet of the molecular packing. The N···O distance is 2.92 Å and the C_2–O_{10}···N_1, C_{9a}–N_1···O_{10}, and C_2–N_1···O_{10} angles are 126, 123, and 111°, respectively. These dimensions are fully consistent with N–H···O hydrogen bonding.[8] All other

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[6] J. B. Hendrickson, *J. Amer. Chem. Soc.*, **83**, 4537 (1961); **89**, 7036 (1967).

[7] A. M. Mathieson in "Perspectives in Structural Chemistry," Vol. I, John Wiley & Sons, Inc., New York, N. Y., 1967, p 70.

[8] G. C. Pimentel and A. L. McClellan, "The Hydrogen Bond," W. H. Freeman and Co., San Francisco, Calif., 1960, p 287.

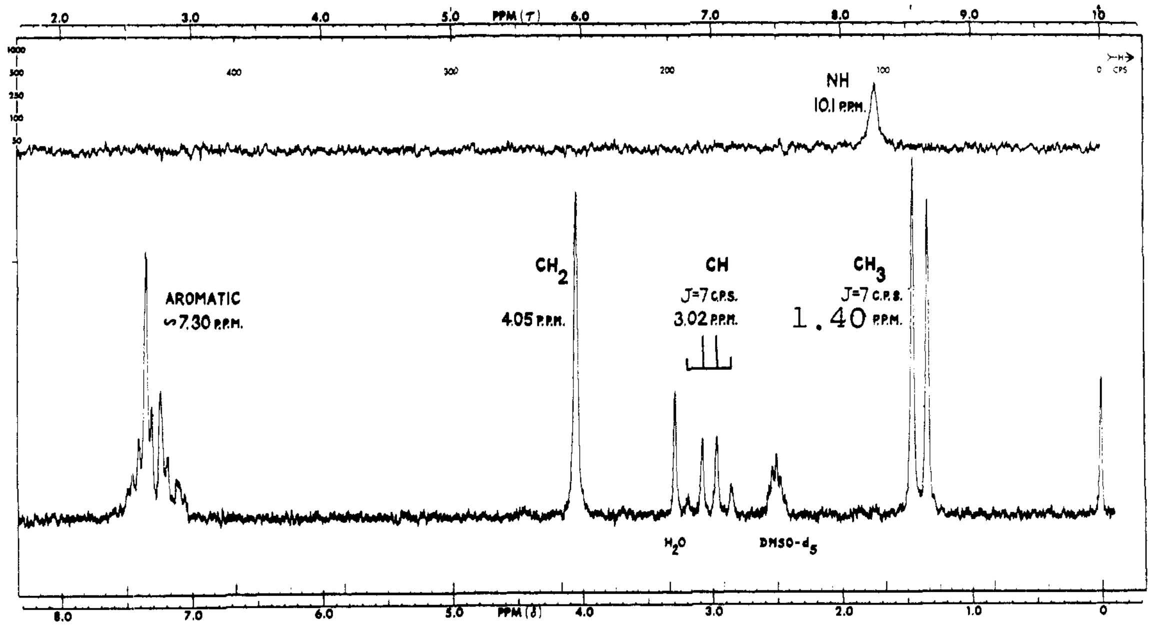

Figure 4.—Nmr spectrum of *trans*-sulfoxide VI.

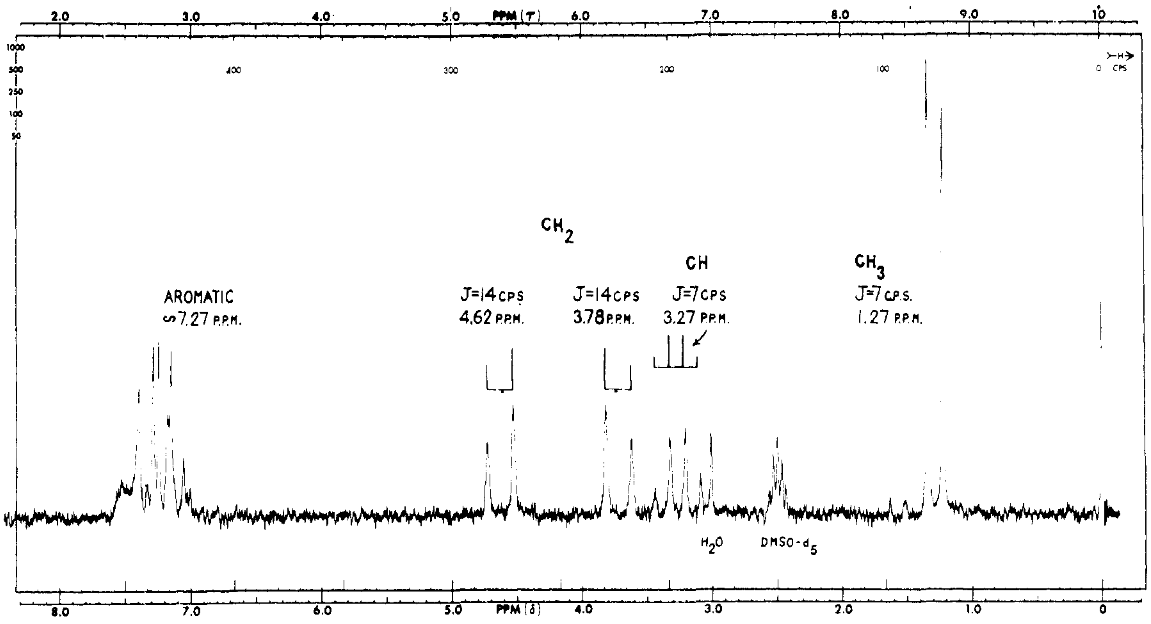

Figure 5.—Nmr spectrum of *cis*-sulfoxide VII.

intermolecular contacts are greater than the sums of the corresponding van der Waals radii (Table V).

The Nmr Data of the *trans*-Sulfoxide VI and *cis*-Sulfoxide VII.—The two diastereoisomeric sulfoxides VI and VII exhibit significant differences in the nmr spectra taken in dimethyl sulfoxide-d_6. The methyl protons appear as a doublet in the *trans* compound VI at δ 1.40 (J = 7 cps) (Figure 4) and in the *cis* compound VII at 1.27 (J = 7 cps) (Figure 5). The C_3-methine proton is shown as a quartet at δ 3.02 (J = 7 cps) in VI and at 3.27 (J = 7 cps) in VII. In the *trans*-sulfoxide VI the C_5-methylene protons appear as a singlet at δ 4.05 and in the *cis*-sulfoxide VII as an AB pattern at 3.78 (J = 14 cps) and 4.62 (J = 14 cps). When the nmr spectra were taken in dimethylformamide-d_7 at −30 and +150°, no significant changes were found. The last observation indicates that both sulfoxides exist in fairly rigid conformations.

Two sulfoxides, VI and VII, differ significantly in the rate of exchange of the C_3-methine proton with deuterium.[9,10] Both compounds were separately treated with 0.5 N NaOD in D_2O-dimethyl sulfoxide solution for 10 min and then acidified with CD_3COOD. In the recovered *cis*-sulfoxide VII, more than 75% of the C_3 proton was replaced with deuterium, as shown (Figure 6) by the disappearance of the signal for this proton (a quartet at δ 3.27, Figure 5) and by the collapse of the C_3-methyl doublet [δ 1.27 (J = 7 cps), Figure 5] to a singlet (Figure 6). In the same time, little or none of the C_3 proton in *trans*-sulfoxide VI was exchanged for deuterium (compare Figures 4 and 7). The inspection of Dreiding molecular models suggests that one should consider rigid distorted "boat" conformations for both

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(9) S. Wolfe and A. Rauk, *Chem. Commun.*, 778 (1966).

(10) A Rauk, E. Buncel, R. Y. Moir, and S. Wolfe, *J. Amer. Chem. Soc.*, **87**, 5498 (1965).

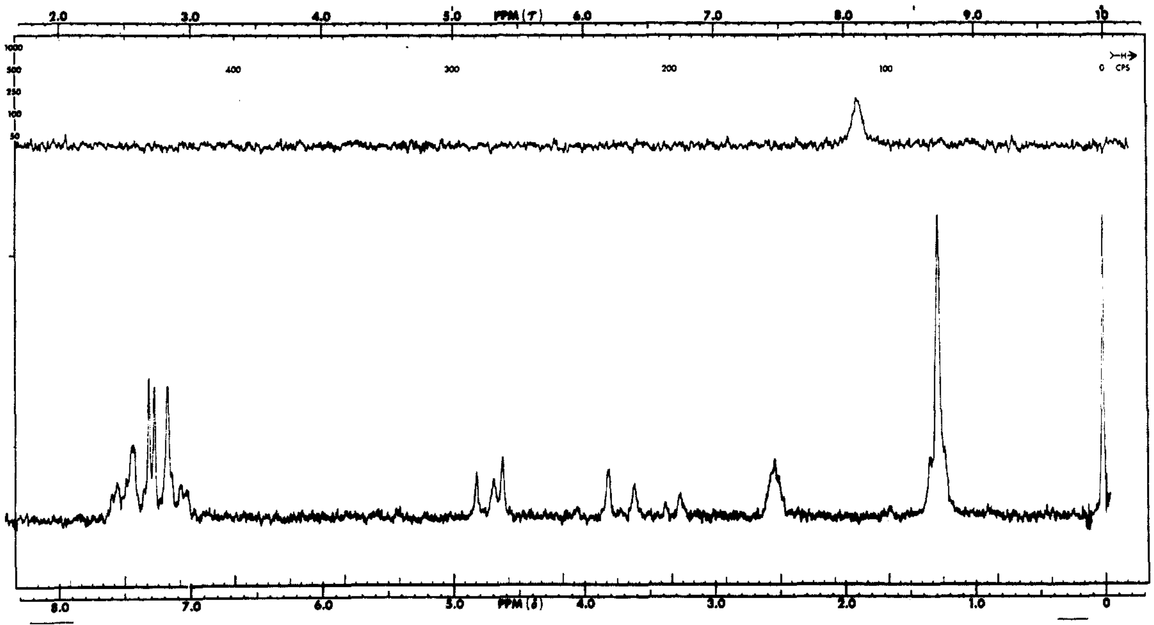

Figure 6.—Nmr spectrum of *cis*-sulfoxide VII after treatment with 0.5 *N* NaOD in D_2O-DMSO for 10 min.

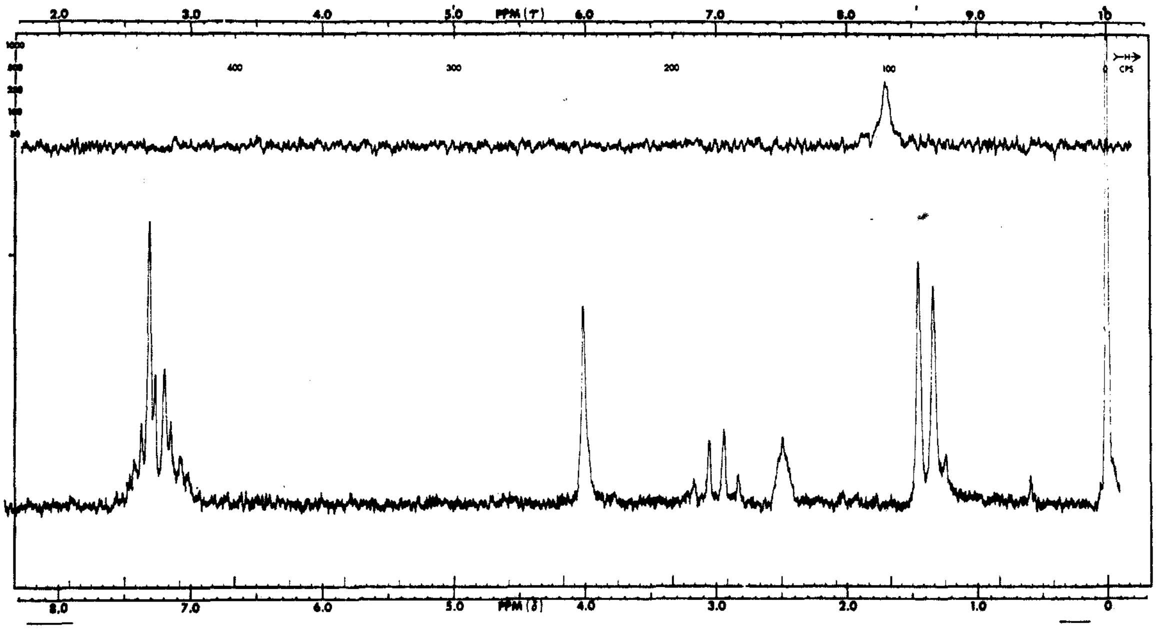

Figure 7.—Nmr spectrum of *trans*-sulfoxide VI after treatment with 0.5 *N* NaOD in D_2O-DMSO for 10 min.

TABLE V

INTERMOLECULAR DISTANCES (Å) LESS THAN 3.70 Å

$N_1 \cdots O_{10}$ (I)[a]	2.92
$C_2 \cdots O_{10}$ (I)	3.63
$C_9 \cdots O_{10}$ (II)[b]	3.47
$C_7 \cdots O_{12}$ (III)[c]	3.67
$C_6 \cdots O_{12}$ (III)	3.62
$O_{12} \cdots C_5$ (III)	3.46
$O_{12} \cdots C_6$ (III)	3.49
$C_7 \cdots C_7$ (IV)[d]	3.36
$C_7 \cdots C_6$ (IV)	3.69

[a] I refers to atom related to that in Table I by $1 - x$, $1 - y$, $1 - z$. [b] II refers to atom related to that in Table I by $1 - x$, $-y$, $1 - z$. [c] III refers to atom related to that in Table I by $-x$, $-{}^1/_2 + y$, ${}^1/_2 - z$. [d] IV refers to atom related to that in Table I by $-x$, $-y$, $1 - z$.

sulfoxides VI and VII. The X-ray analysis demonstrates such a conformation for the *trans* compound VI in the crystalline state. For the *cis* compound VII two distorted "boat" conformations may be considered, one with the oxygen of the sulfoxide group in pseudoequatorial position, the other with a pseudoaxial arrangement. The analysis of the nmr, ir, and uv data did not allow us to make any definite choice regarding one of these conformations. However, on the basis of the findings by Wolfe and Rauk,[9] the C_3-methine proton of VII, which exchanges rapidly with deuterium, should be positioned on a bisector of the angle between oxygen and lone electron pair of sulfur. From this viewpoint the conformation with the oxygen of the sulfoxide group in pseudoequatorial position would be favored.

At room temperature, the *trans*-sulfoxide VI is the thermodynamically more stable isomer. Individual treatment of both sulfoxides VI and VII for 3 days with 0.5 *N* sodium hydroxide in aqueous dimethyl sulfoxide solution gave the same equilibrium mixture which consisted of the *trans*-sulfoxide VI and *cis*-sulfoxide VII in a ratio of approximately 2:1, as indicated

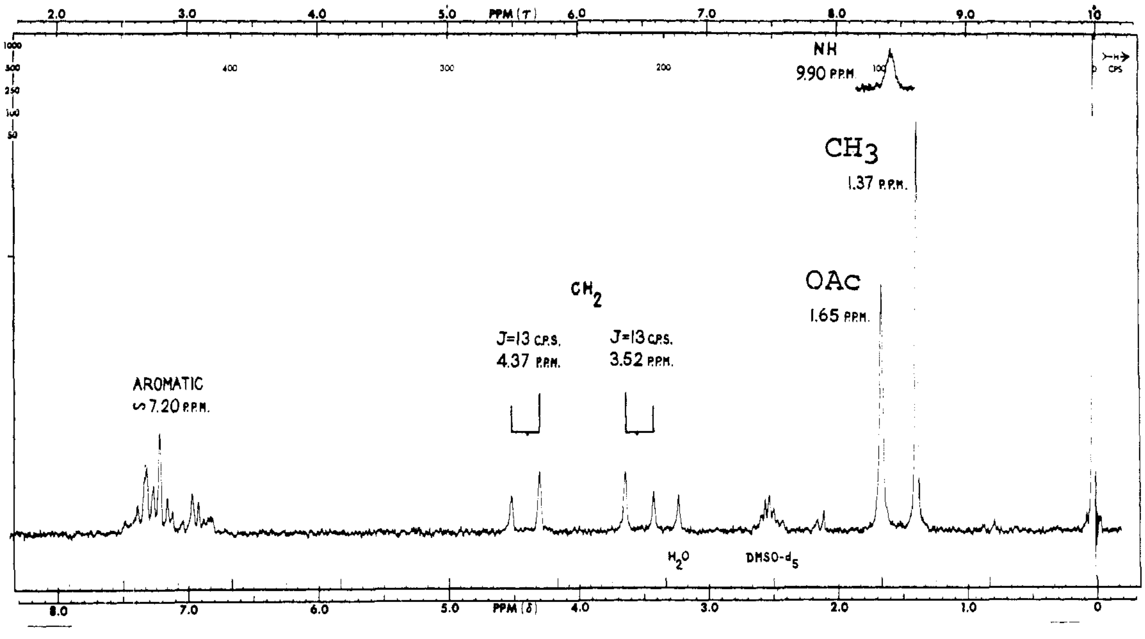

Figure 8.—Nmr spectrum of the rearranged product VIII.

by nmr. The isomerization occurred also under the conditions of Pummerer rearrangement, which was carried out with both sulfoxides VI and VII in boiling acetic anhydride for 5 hr. In each case, a 25:30:42 mixture of VI, VII, and rearranged product, 3-acetoxy-3,5-dihydro-3-methyl-4,1-benzothiazepin-2(1H)-one (VIII), was produced. The structure of VIII is supported by elemental analysis and by ir (the acetoxy group at 1730 and 1230 cm^{-1}) and nmr spectra [Figure 8, C$_3$-methyl singlet at δ 1.37, the acetoxymethyl singlet at 1.65, C$_5$-methylene protons' AB pattern at 3.58 and 4.48 (J = 13 cps), and aromatic protons' multiplet centered at 7.20].

Experimental Section[11]

(2-Nitrobenzylmercapto)lactic Acid (III).—To a solution of 69 g of *o*-nitrotoluene in 300 ml of carbon tetrachloride were added 90 g of bromosuccinimide and 2 g of benzoyl peroxide and the suspension was refluxed for 3 hr. After cooling, the succinimide was filtered, and the solution was evaporated to dryness. The crude *o*-nitrobenzylbromide (I) was dissolved in 200 ml of acetone and the solution was added dropwise to an ice-cold stirred solution of 53 g of thiolactic acid (II) and 40 g of sodium hydroxide in 300 ml water. The reaction mixture was stirred for 24 hr at room temperature, made strongly alkaline, extracted with methylene chloride, then acidified with acetic acid, and extracted again with methylene chloride. The last extract was washed with water, dried over anhydrous sodium sulfate, and evaporated. The crystalline residue was recrystallized from acetone. It gave 82 g of III: on heating, the crystals transformed at 127–128 and melted at 130–132°; ir ($CHCl_3$) 1712 (-COOH) and 1530 and 1336 cm^{-1} (-NO_2); uv (isopropyl alcohol), λ_{max} 250 mμ (ϵ 5200).

Anal. Calcd for $C_{10}H_{11}NO_4S$ (241.27): C, 49.78; H, 4.60; N, 5.81; S, 13.26. Found: C, 49.76; H, 4.43; N, 5.57; S, 13.21.

***dl*-3,5-Dihydro-3-methyl-4,1-benzothiazepin-2(1H)-one (V) from III.**—To a solution of 48.2 g of III in 1200 ml of methanol was added 5 g of 10% palladium-on-carbon catalyst, and the suspension was hydrogenated at room temperature at a pressure of 200–270 psi until the theoretical amount of hydrogen was absorbed. The catalyst was filtered and the solution was evaporated. The noncrystalline residue was dissolved in 2000 ml of xylene and the solution was refluxed for 2 hr with slow distillation of xylene, so that at the end the volume was reduced to 1000 ml. After cooling, the crystalline precipitate was filtered and recrystallized from acetone. It gave 28 g of V: mp 188–189°, after transformation at 183–187°; ir ($CHCl_3$) 3400 (>N—H) and 1680 cm^{-1} (>C=O); uv (isopropyl alcohol) λ_{max} 236 mμ (ϵ 6440).

Anal. Calcd for $C_{10}H_{11}NOS$ (193.27): C, 62.15; H, 5.74; N, 7.25; S, 16.59. Found: C, 61.97; H, 5.62; N, 7.26; S, 16.68.

***trans*- (VI) and *cis*-*dl*-3,5-Dihydro-3-methyl-4,1-benzothiazepin-2(1H)-one 4-oxide (VII) from V.**—To a suspension of 3.86 g of V in 250 ml of methanol at 0° was added 42 ml of 0.5 *N* sodium metaperiodate solution. The mixture was stirred for 1 hr in an ice bath, then for 3 hr at room temperature. The precipitated sodium iodate was filtered, and the solution was evaporated to dryness. To the residue was added 500 ml of acetone, the mixture was refluxed 30 min and filtered, and the filtrate was evaporated. The crystalline residue was recrystallized from acetone to give 3.4 g of a mixture of sulfoxides, mp 199–205°. Three grams of this mixture was chromatographed on a 100-g silica gel column. The fractions eluted with 15% ethyl acetate–85% benzene mixture were combined and recrystallized from acetone to give 2.25 g of VI: mp 220–223°; ir (Nujol) 1665, 1046, and 1065 cm^{-1}; uv (isopropyl alcohol) λ_{max} 264–266 mμ (ϵ 3050).

Anal. Calcd for $C_{10}H_{11}NO_2S$ (209.27): C, 57.40; H, 5.30; N, 6.69; S, 15.32. Found: C, 57.63; H, 5.52; N, 6.63; S, 15.12.

The fractions eluted with 75% ethyl acetate–25% benzene mixture and pure ethyl acetate were combined, and after recrystallization from acetone gave 0.75 g of VII: mp 246–248°; ir (Nujol) 1665 and 1045 cm^{-1}; uv (isopropyl alcohol) λ_{max} 225–226 mμ (ϵ 21,300) and 268–269 (2700).

Anal. Calcd for $C_{10}H_{11}NO_2S$ (209.27): C, 57.40; H, 5.30; N, 6.69; S, 15.32. Found: C, 57.14; H, 5.53; N, 6.67; S, 15.58.

***dl*-3-Acetoxy-3,5-dihydro-3-methyl-4,1-benzothiazepin-2(1H)-one (VIII) from VI or VII.**—A mixture of 2 g of VI and 40 ml of acetic anhydride was heated for 5 hr at 100°. After evaporation the residue was chromatographed on a 60-g silica gel column. The fractions eluted with a 2% ethyl acetate–98% benzene mixture were combined, and after recrystallization from acetone gave 1 g of VIII: mp 186–187°; ir (KBr) 3250 (>N—H), 1730, 1685, and 1250 cm^{-1}; uv (isopropyl alcohol) λ_{max} 207 mμ (ϵ 29,000) and 243 (5800).

Anal. Calcd for $C_{12}H_{13}NO_3S$ (251.31): C, 57.35; H, 5.19;

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[11] Melting points are corrected. The nmr spectra were recorded on a Varian A-60 spectrometer using tetramethylsilane as internal reference.

N, 5.57; S, 12.76. Found: C, 57.53; H, 5.18; N, 5.45; S, 12.48.

The fractions eluted with a 15% ethyl acetate–85% benzene mixture were combined, and after crystallization from acetone gave 0.5 g of VI, mp 213°. This product was identified by comparison of the spectra with those of the sample prepared in the preceeding experiment. The fractions eluted with a 75% ethyl acetate–25% benzene mixture were combined and crystallized from acetone to give 0.6 g of VII, mp 242.5–245°. This material was also identified by comparison with the sample prepared in the preceding experiment.

The same result was obtained when the reaction was carried out with VII instead of VI.

X-Ray Analysis of *trans-dl*-3,5-Dihydro-3-methyl-4,1-benzothiazepin-2(1H)-one 4-oxide VI. Crystal Data and Data Collection.—Transparent needlelike crystals of VI were obtained by recrystallization from acetone. Cell parameters, as determined on a 60-mm precession camera using Mo K_α radiation ($\lambda = 0.7107$ Å), are $a = 13.20 \pm 0.02$ Å, $b = 4.71 \pm 0.01$ Å, $c = 17.16 \pm 0.03$ Å, and $\beta = 113° 15' \pm 15'$. The volume of the unit cell is 980.2×10^{-24} cm^3, and, assuming four molecules of $C_{10}H_{11}NO_2S$ (mol wt 209.27) in the unit cell, the calculated density is 1.417 g cm^{-3}; the value measured by flotation in a mixture of methylene dichloride and methyl iodide is 1.40 g cm^{-3}. Systematic absences, $h0l$, when $l = 2n + 1$, and $0k0$, when $k = 2n + 1$, determine the space group as $P2_1/c$ (C^5_{2h}, no. 14). $F(000)$ is 440, and the absorption coefficient for Cu K_α is 22.9 cm^{-1}.

A needle with an approximate equidimensional cross-sectional area was mounted about the needle axis (*i.e.*, *b* axis) and the levels of data $h0l$ to $h4l$ were collected on multiple-film packs with an equiinclination Weissenberg camera (Cu K_α radiation). The intensities were measured visually by comparison with a calibrated strip. Corrections were applied for Lorentz, polarization, spot shape,[12] and the K_{α_1}–K_{α_2} splitting effects. The intensities from the various hnl levels were initially placed on the same relative scale by consideration of the X-ray exposure times. A total of 1427 independent, nonzero structure amplitudes was obtained.

Structure Determination.—A three-dimensional Patterson synthesis indicated two possible positions for the sulfur atom (the y coordinate was 0.25 in each case and the z coordinate of one of the positions differed by 0.25 from that of the other position). A Fourier synthesis, with calculated signs based on the sulfur atom occupying one of these positions, gave a relatively clear picture of the molecule, but also contained a pseudoimage reflected through a false mirror plane at $y = 1/4$. Only in the case of the sulfoxide oxygen atom, however, did a pseudoimage appear as a possible genuine position. A further round of structure factor and Fourier calculations clearly indicated the *trans* configuration for the sulfoxide oxygen atom relative to the C–CH$_3$ group.

Least-squares refinement[13] on positional and isotropic thermal parameters for all atoms other than hydrogen reduced the crystallographic R factor, $R = \Sigma||F_o| - |F_c||/\Sigma F_o|$, to 0.14. The weighting scheme used has $\sqrt{w} = |F_o|/12.8$, when $|F_o| \leq 12.8$, and $\sqrt{w} = 12.8/|F_o|$, when $|F_o| > 12.8$; the quantity minimized was $\Sigma w||F_o| - |F_c||^2$. At the conclusion of the isotropic refinement, the interlevel scale factors were adjusted to give the best fit to the $\Sigma|F_c|$. Three cycles of least-squares refinement on positional and anisotropic parameters for all atoms other than hydrogen further reduced R to 0.11.

A difference map was calculated and the largest positive peaks corresponded to reasonable positions for most of the hydrogen atoms in the molecule. In the few instances, where doubt existed regarding the location of the hydrogen atoms, these atoms were positioned using standard criteria. Two cycles of least-squares refinement, varying positional and anisotropic thermal parameters on all atoms other than hydrogen, and including all hydrogen atoms in the structure factor calculations ($B_\theta = 3.0$ Å^2) gave a final R factor of 0.094 on all observed reflections.[14] The principal change in molecular dimensions involved the C–CH$_3$ distance which decreased from 1.55 to 1.525 Å.

While unobserved reflections were not included in the refinement, structure factors for these reflections were calculated from the final parameters. In no case were any significant discrepancies found.[14]

Registry No.—III, 1141-22-6; V, 18520-97-3; VI, 18520-98-4; VII, 18520-99-5; VIII, 18521-00-1.

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[12] D. C. Phillips, *Acta Cryst.*, **7**, 746 (1954).

[13] Using a modified version of the program written by P. K. Gantzel, R. A. Sparks, and K. N. Trueblood, "I. U. C. World List of Crystallographic Computer Programs," International Union of Crystallography, 1962, no. 384.

[14] The final values of h, k, l, F_o, and F_c and the anisotropic thermal parameters are available (order document no. NAPS-00094) from ASIS National Auxiliary Publications Service, c/o CCM Information Sciences, Inc., 22 West 34th Street, New York, N. Y. 10001; remit $1.00 for microfilm or $3.00 for photocopies.