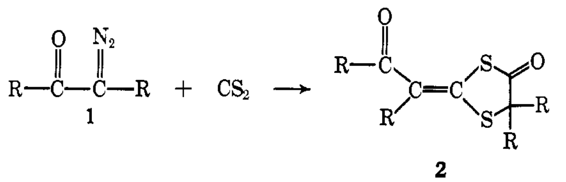
The Crystal and Molecular Structure of the Adduct from 3-Diazobutanone and Carbon Disulfide[1,2]

Jon A. Kapecki,[3] John E. Baldwin,[4] and Iain C. Paul[4]

Contribution from the Department of Chemistry and Chemical Engineering, University of Illinois, Urbana, Illinois 61801. *Received April 17, 1968*

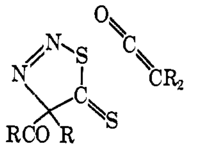
Abstract: An X-ray single-crystal structure analysis of the adduct $C_9H_{12}O_2S_2$ derived from the thermal decomposition of 3-diazobutanone in carbon disulfide has shown it to be a 2-methylene-1,3-dithiacyclobutane. The crystals are monoclinic, $a = 12.82$, $b = 13.48$, $c = 12.98$, $\beta = 104° 45'$, and the space group is C2/c with eight molecules in the unit cell. The structure was determined from photographic data, using a combination of Patterson, Fourier, and symbolic addition methods; the final R factor on 1517 nonzero independent structure amplitudes was 0.097. The geometry of the molecule is discussed, with special emphasis on the planar system formed by the substituted 2-methylene-1,3-dithiacyclobutane unit.

The reported conversions of carbon disulfide and azibenzil[5] (**1a**) or 3-diazobutanone[6] (**1b**) into the cycloadducts **2a** (or its geometrical isomer) and **2b** pose an intriguing challenge for mechanistic formulation and experimental exploration.



a, R = C_6H_5
b, R = CH_3

Among the several seemingly plausible pathways that may be written to rationalize the formation of these products is one positing a reversible formation of a 1,3-cycloadduct (**3a**) between the diazo ketone and carbon disulfide. Loss of nitrogen from the diazo ketone with concomitant Wolff rearrangement would afford a ketene (**3b**). The cycloadduct (**3a**) and the ketene could then react through a simultaneous 1,3-cycloaddition, 1,3-cycloelimination process—a reaction taking place *via* an eight-center bicyclic transition state—to give the heterocyclic product and nitrogen.



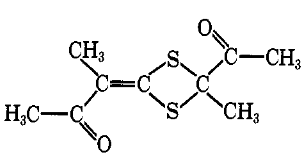
3a **3b**

In such a representation, the reacting centers themselves are disposed in a bicyclic[3.3.0] array; the reaction is not strictly analogous to those proceeding by "bicyclic mechanisms" wherein the reacting centers form one ring and are bridged by a second composed of atoms not involved in bond-making or -breaking processes during the conversion.[7]

This depiction of the events leading to the formation of cycloadduct **2** served as an enticing possibility to be pursued and a basis for preliminary conceptualization and planning of a thorough mechanistic study.

The simultaneous 1,3-cycloelimination, 1,3-cycloaddition formulation, it may be remarked, would be thermally allowed to be concerted according to the principles governing the conservation of orbital symmetry advanced by Hoffmann and Woodward.[8] Each of the two components of the reaction are thermally allowed 1,3-dipolar processes; hence, simultaneous occurrence of both is also allowed.

Recent experience[9,10] suggested the propriety of confirming structural assignments before embarking on detailed kinetic work. Although there appeared to be no obvious reason to question the structure of the cycloadduct **2a** derived from azibenzil, the nmr spectral characteristics reported[6] for **2b**—four methyl singlets of equal intensity at τ 7.57, 8.00, 8.14, and 8.36—did not seem to be consistent with the ascribed structure. Were the structure correct, the nmr data would indicate some subtle molecular idiosyncrasy such as hindered rotation preventing the molecule from having a plane of symmetry, two identical methyl groups, and a 1:1:2 ratio of absorption intensities in the nmr spectrum. In fact, the X-ray single-crystal structure analysis for the material reported[6] as the adduct **2b** establishes that it is the 2-methylene-1,3-dithiacyclobutane **4**.[11]



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Experimental Section

3-Diazobutanone was heated under reflux in carbon disulfide for 10 days. The excess carbon disulfide was removed, and the

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[1] Paper XX in a series on cycloadditions; paper XIX: S. Y. Hong and J. E. Baldwin, *Tetrahedron*, **24**, 3787 (1968).

[2] Partial support of this work by the National Institutes of Health (GM 12470 and GM 14381) is gratefully acknowledged.

[3] National Science Foundation Predoctoral Trainee, 1965–1968.

[4] Alfred P. Sloan Research Fellow.

[5] P. Yates and B. G. Christensen, *Chem. Ind.* (London), 1441 (1958).

[6] A. J. Kirby, *Tetrahedron*, **22**, 3001 (1966).

[7] M. S. Newman, S. Mladenovic, and L. K. Lala, *J. Amer. Chem. Soc.*, **90**, 747 (1968); *cf.* H. Behringer, J. Kilger, and R. Wiedenmann, *Tetrahedron Lett.*, 1185 (1968).

[8] R. Hoffmann and R. B. Woodward, *Accounts Chem. Res.*, **1**, 17 (1968), and references therein.

[9] M. G. Newton, J. A. Kapecki, J. E. Baldwin, and I. C. Paul, *J. Chem. Soc., B.*, 189 (1967).

[10] J. E. Baldwin, *J. Org. Chem.*, **32**, 2438 (1967).

[11] A preliminary communication on this work has appeared: J. A. Kapecki, J. E. Baldwin, and I. C. Paul, *Tetrahedron Lett.*, 5307 (1967).

Table I. Distribution of Normalized Structure Factors[a] Compared to Theoretical Values for Centric and Acentric Structures

	Centric	Acentric	Found
$\langle E \rangle$	0.798	0.886	0.746
$\langle E^2 \rangle$	1.000	1.000	1.000[b]
$\langle \lvert E^2 - 1 \rvert \rangle$	0.968	0.736	1.033
Percentage terms with $E > 1$	32.0	37.0	30.3
$E > 2$	5.0	1.8	5.6
$E > 3$	0.30	0.01	0.66

[a] For all data including accidental absences. [b] E's are scaled so that $\langle E^2 \rangle = 1.0$.

Table II. Symbol Equivalences[a] and Sign-Determining Symbol Assignments

Symbol[b,c]	h	k	l	E	No. of interactions[c]										
A	4	8	5	3.00	54	Positive to assign origin									
B	$\bar{3}$	5	4	3.54	72	+	−	+	+	−	+	−	+	−	−
C	$\bar{3}$	9	5	3.12	45	Positive to assign origin									
D	$\overline{10}$	2	4	3.11	53	+	+	+	+	−					
E	$\overline{12}$	8	3	2.86	40	−	−	+	+	+	−	+	−	+	+
F	9	1	2	3.48	57	−	−	+	−	+					
G	$\bar{5}$	9	3	2.67	47						−	+	−	+	−
H	1	3	2	2.90	87						−	−	+	+	−
Percentage of contradictions among symbol equivalences[d]						13	46	46	50	51	13	14	15	23	58

[a] Symbols D and F were replaced by G and H in the second set of sign-determining symbol assignments. [b] The starting symbols for the sign-determining assignments were chosen as the six symbols of appropriate parity[13,14] having the largest product of E times the number of interactions (see footnote c). [c] Interactions in the Σ_2 formula[13] among the 30 reflections (and their symmetry equivalents) with highest E value. [d] Number of contradictions in sign determination in the group of 339 reflections with $E > 1.35$, expressed as a percentage of the total number of symbol equivalences found among that group of reflections.

mixture cooled to yield small, lemon-yellow crystals. Recrystallization of the adduct from 95% ethanol gave fine, almost colorless needles (mp 125–126°; lit.[6] mp 126°) belonging to the monoclinic system. Cell parameters, $a = 12.82 \pm 0.02$, $b = 13.48 \pm 0.01$, $c = 12.98 \pm 0.01$ Å, and $\beta = 104° 45' \pm 6'$, were obtained from $h0l$ and $0kl$ precession photographs at 25° (Mo Kα, λ 0.7107 Å) using a 60-mm film-to-crystal distance and a Polaroid casette. The unit cell volume is 2168.7×10^{-24} cm^3; assuming eight molecules of $C_9H_{12}O_2S_2$ (mol wt 216.3) in the unit cell, the calculated density would be 1.34 g cm^{-3}. The value measured by flotation in an aqueous zinc chloride solution is 1.33 g cm^{-3}. $F(000)$ is 912, and the linear absorption coefficient μ (Cu Kα) = 40.3 cm^{-1}. Systematic absences occur for the hkl reflections when $h + k = 2n + 1$, and for the $h0l$ reflections when $l = 2n + 1$. The space group is accordingly either C2/c (No. 15, $C_{2h}{}^6$) or Cc (No. 9, $C_s{}^4$); the number of molecules per unit cell and the racemic nature of the adduct suggest the former.

A crystal mounted about the c axis (needle axis) provided data for levels $hk0$ and $hk11$ with Cu Kα radiation (λ 1.5418 Å) at 25°. The intensities were recorded photographically on an equiinclination Weissenberg camera; a total of 1517 nonzero independent intensities was obtained by visual estimations out of an estimated 2256 independent reflections excluding systematic absences within the Cu Kα sphere. The data were corrected for Lorentz, polarization, and spot-shape[12] effects, but not for absorption. The dimensions of the approximately rectangular cross section of the crystal were 0.015×0.010 cm, and the maximum and minimum transmission factors to be applied to intensities would be 0.65 and 0.47, respectively. Initially, the various levels were scaled on the basis of time of exposure.

Structure Determination. The density of vectors on the $P(u, 0, w)$ section of the Patterson map supported the space group assignment as C2/c and indicated that both sulfur atoms in the molecule lay on or near the plane $y = 0$. Positional assignments were made for the two sulfur atoms, leading to an S–S distance of 2.9 Å. Unfortunately, all electron density maps based on these positions led to complete mirror pseudo-symmetry about the plane $y = 0$, and these maps provided little evidence for a structure resembling **2b**. A peak, presumably representing a carbon atom bonded to the two sulfur atoms, also lay on the plane $y = 0$. Several rounds of structure factor and Fourier map calculations aimed at destroying the pseudo-symmetry led to the probable identification of a five-atom grouping, attached to the carbon atom bonded to the two sulfur atoms. The region about the other bonding positions of the sulfur atoms in these maps was still greatly affected by pseudo-symmetry. As no structure with a five-membered ring could be recognized at this stage we decided to seek confirmation of the positions for the sulfur atoms by further examination of the Patterson map and by computing E maps on the basis of the symbolic addition method.[13,14]

Each peak above a certain height on the $P(u, 0, w)$ section of the Patterson map was considered to represent a vector between sulfur atoms related by symmetry, and Fourier maps, based on each single sulfur position, were calculated. Only two of these maps contained another peak which might represent a second sulfur atom at a position consistent with the Patterson map; the sulfur positions used to generate these two maps corresponded to the two positions in the initial assignment.

Various statistical tests incorporated in the FAME program indicated that the space group was centric (Table I). Six reflections, chosen on the basis of high E value and the large number of Σ_2-type[13] interactions among the 339 reflections with $E > 1.35$, were given letter symbols (Table II). Five E maps were computed on the basis of five different sign combinations assigned to these six reflections. The first three maps were rejected because each placed a sulfur atom on a twofold rotation axis. The fourth map contained the same S–S vector as before but the positions of the "sulfur" atoms were inconsistent with the Patterson map. The map from the fifth sign combination contained two large peaks at the same positions as the assignment by Patterson methods; however, it also contained many more peaks than there were atoms in the molecule. Two reflections, which had been given letter symbols and which were causing a large number of discrepancies in sign determination, were replaced (Table II), and a second group of five E maps was computed. The map corresponding to the second sign combination had two large peaks at the suspected sulfur positions and contained only a small number of other peaks.

Thus, reassured as to the correctness of the positions for the sulfur atoms, we reexamined both the most promising E map and the heavy atom map, and found strong evidence for structure **4**. Inclusion of all atoms other than hydrogen in a structure factor calculation followed by several cycles of full-matrix least-squares refinement,[15] varying positional and isotropic thermal parameters, reduced the R factor, $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$, to 0.16. The

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

(13) An authoritative description and review of this method is given by J. Karle and I. L. Karle, *ibid.*, 21, 849 (1966).

(14) We used a series of programs written by E. B. Fleischer, A. L. Stone, and R. B. K. Dewar of the University of Chicago. One of the programs, FAME, incorporates statistical tests and calculates normalized structure factors. Another program, MAGIC, determines signs by the Karle–Hauptman Σ_2 relationship[13] from a basic set of reflections which are given letter symbols.

(15) We used the program written by P. K. Gantzel, R. A. Sparks, and K. N. Trueblood, "International Union of Crystallography World List of Crystallographic Computer Programs," 1962, No. 384.

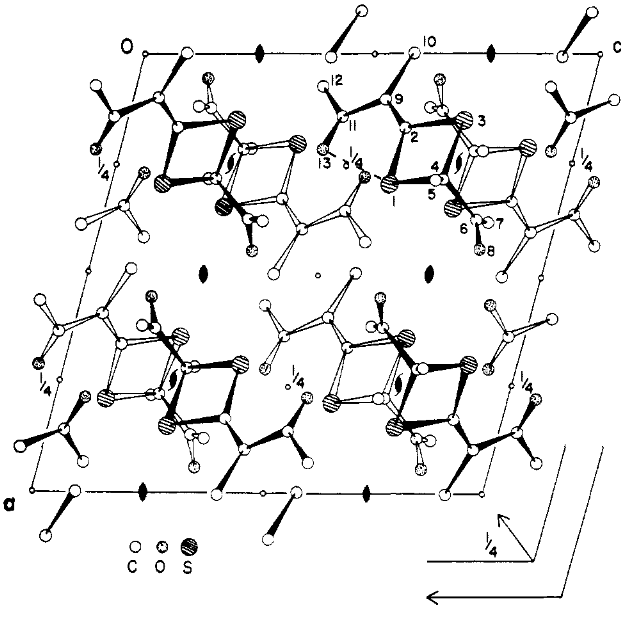

Figure 1. View of the molecular structure looking along the *b* axis. The atom numbering for the coordinates of the molecule given in Table III is shown.

weighting scheme was $w^{1/2} = 45.0/F_o$, when $F_o \geq 45.0$, and $w^{1/2} = F_o/45.0$, when $F_o \leq 45.0$, and the quantity minimized was $\Sigma w||F_o| - |F_c||^2$. Rescaling the levels of data and introduction of anisotropic thermal parameters, followed by four cycles of refinement, reduced R to 0.097 for all observed reflections.[16] Calculations of the structure factors for the unobserved reflections did not reveal any anomalies. A difference map did not show any significant residual electron density not included in the calculations.

The atomic scattering curves for neutral C, S, and O were taken from the compilation by Ibers.[17] No correction was made for anomalous dispersion. The final atomic coordinates with estimated standard deviations are listed in Table III while Table IV contains the final thermal parameters. The standard deviations are calculated from the standard formulas and may be slightly low due to neglect of systematic effects such as absorption. The atom numbering used in the analysis is shown in Figure 1 which is a view of the contents of the unit cell looking down the *b* axis.

Table III. Final Values of Atomic Coordinates in Fractions of the Unit Cell Edge with Standard Deviations (× 10^4) in Parentheses. Origin as in "International Tables for X-ray Crystallography"

	x	*y*	*z*
S(1)	0.2956 (1)	−0.0110 (1)	0.6044 (1)
C(2)	0.1694 (4)	0.0357 (4)	0.6180 (4)
S(3)	0.1554 (1)	−0.0286 (1)	0.7281 (1)
C(4)	0.2914 (5)	−0.0842 (3)	0.7238 (5)
C(5)	0.2895 (5)	−0.1950 (4)	0.7103 (5)
C(6)	0.3860 (5)	−0.0509 (5)	0.8197 (5)
C(7)	0.3923 (6)	0.0555 (5)	0.8533 (6)
O(8)	0.4556 (3)	−0.1090 (4)	0.8602 (4)
C(9)	0.1032 (4)	0.1064 (4)	0.5581 (4)
C(10)	−0.0046 (4)	0.1356 (5)	0.5853 (5)
C(11)	0.1409 (5)	0.1485 (4)	0.4721 (5)
C(12)	0.0718 (5)	0.2314 (4)	0.4069 (5)
O(13)	0.2256 (3)	0.1171 (3)	0.4487 (3)

Table IV. Final Anisotropic Thermal Parameters[a] Expressed as $\exp[-(b_{11}h^2 + b_{22}k^2 + b_{33}l^2 + b_{12}hk + b_{13}hl + b_{23}kl)]$, with Standard Deviations in Parentheses

	b_{11}	b_{22}	b_{33}	b_{12}	b_{13}	b_{23}
S(1)	63 (1)	68 (1)	70 (1)	23 (1)	54 (2)	14 (1)
C(2)	60 (3)	56 (3)	66 (4)	12 (5)	36 (6)	−13 (5)
S(3)	66 (1)	65 (1)	80 (1)	15 (1)	64 (2)	27 (1)
C(4)	80 (4)	41 (3)	89 (5)	1 (5)	55 (7)	14 (5)
C(5)	97 (5)	47 (3)	105 (5)	0 (6)	45 (8)	−24 (6)
C(6)	71 (4)	66 (3)	72 (5)	25 (6)	30 (6)	8 (6)
C(7)	102 (5)	72 (4)	99 (6)	−27 (8)	25 (9)	−32 (7)
O(8)	79 (3)	88 (3)	122 (4)	9 (5)	10 (6)	19 (6)
C(9)	59 (3)	57 (3)	59 (4)	0 (5)	40 (5)	−9 (5)
C(10)	66 (3)	78 (4)	75 (5)	29 (6)	41 (6)	1 (6)
C(11)	75 (4)	61 (3)	69 (4)	−8 (6)	14 (6)	−9 (5)
C(12)	97 (5)	65 (3)	89 (5)	37 (7)	36 (7)	36 (7)
O(13)	98 (3)	78 (3)	69 (3)	26 (5)	81 (5)	19 (4)

[a] Values given are × 10^4.

Results and Discussion

The results of the analysis establish structure **4** for the adduct. Bond distances and angles are given in Table V. Table VI contains important intramolecular distances which define the over-all geometry of the molecule; Table VII contains intermolecular contacts less than 3.80 Å. Details of various best plane calculations are given in Table VIII. The principal axes of the thermal ellipsoids are described in Table IX. A stereo picture of the contents of the unit cell viewed down the *b* axis and containing information on the atom vibrations is given in Figure 2. Some data on related molecules are collected in Table X.

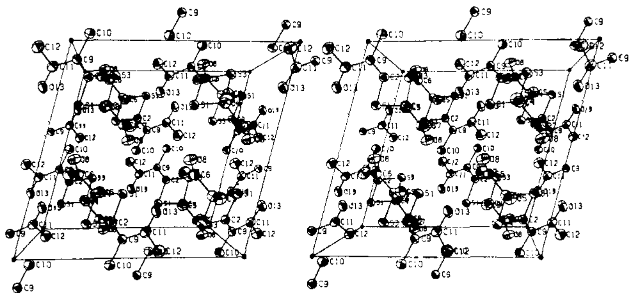

Figure 2. Stereoscopic pair of the contents of a unit cell viewed along the *b* axis. This figure was drawn with the aid of the ORTEP program and is best viewed with a hand stereoviewer.

Abrahams[18] has correlated C–S bond length with bond order assuming values of 1.82 Å for a C–S single bond and 1.61 Å for a double bond. There must be some doubt[19] as to the correct value for a C=S double bond, while a number of structures have been reported with C–S bonds in the 1.84–1.87-Å range.[20] The present length of 1.91 Å for the S(3)–C(4) bond is substantially longer than any reported previously, although there have been no other reports of C(sp^3)–S distances in four-membered rings. Furthermore, the

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(16) The list of *h*, *k*, *l*, F_o, and F_c is available from the American Documention Institute, Auxiliary Publications Project, Library of Congress, Washington, D. C. 20542, Document No. 10028. A copy may be secured by citing the document number and by remitting $1.25 for photoprints, or $1.25 for 35-mm microfilm. Advance payment is required. Make checks payable to Chief, Photoduplication Service, Library of Congress.

(17) J. A. Ibers, "International Tables for X-ray Crystallography," Vol. III, The Kynoch Press, Birmingham, England, 1962, pp 201–207.

(18) S. C. Abrahams, *Quart. Rev.* (London), 10, 407 (1956).

(19) See, *e.g.*, G. A. Jeffrey and R. Shiono, *Acta Cryst.*, 12, 447 (1959); O. Kennard in "International Tables for X-ray Crystallography," Vol. III, The Kynoch Press, Birmingham, England, 1962, pp 275–276; N. Trinajstić, *Tetrahedron Lett.*, 1529 (1968).

(20) H. L. Yakel, Jr., and E. W. Hughes, *Acta Cryst.*, 7, 291 (1954); L. K. Steinrauf, J. Peterson, and L. H. Jensen, *J. Amer. Chem. Soc.*, **80**, 3835 (1958); J. Peterson, L. K. Steinrauf, and L. H. Jensen, *Acta Cryst.*, **13**, 104 (1960); I. L. Karle and J. Karle, *ibid.*, **19**, 92 (1965).

Table V. Bond Distances (Å) and Angles (degrees)[a] in the Molecule with Estimated Standard Deviations

S(1)–C(2)	1.786 ± 0.005	C(6)–C(7)	1.495 ± 0.010
S(1)–C(4)	1.849 ± 0.006	C(6)–O(8)	1.202 ± 0.008
C(2)–S(3)	1.718 ± 0.006	C(9)–C(10)	1.561 ± 0.008
C(2)–C(9)	1.377 ± 0.007	C(9)–C(11)	1.441 ± 0.008
S(3)–C(4)	1.911 ± 0.006	C(11)–C(12)	1.539 ± 0.009
C(4)–C(5)	1.504 ± 0.007	C(11)–O(13)	1.271 ± 0.007
C(4)–C(6)	1.567 ± 0.009		
C(2)–S(1)–C(4)	83.4 ± 0.3	C(5)–C(4)–C(6)	111.3 ± 0.5
S(1)–C(2)–S(3)	101.2 ± 0.1	C(4)–C(6)–C(7)	118.7 ± 0.4
S(1)–C(2)–C(9)	129.1 ± 0.4	C(4)–C(6)–O(8)	119.9 ± 0.3
S(3)–C(2)–C(9)	129.7 ± 0.4	C(7)–C(6)–O(8)	121.2 ± 0.6
C(2)–S(3)–C(4)	83.4 ± 0.3	C(2)–C(9)–C(10)	120.0 ± 0.3
S(1)–C(4)–S(3)	92.1 ± 0.3	C(2)–C(9)–C(11)	115.5 ± 0.5
S(1)–C(4)–C(5)	115.8 ± 0.4	C(10)–C(9)–C(11)	124.5 ± 0.4
S(1)–C(4)–C(6)	109.4 ± 0.4	C(9)–C(11)–C(12)	116.9 ± 0.5
S(3)–C(4)–C(5)	113.9 ± 0.3	C(9)–C(11)–O(13)	121.9 ± 0.6
S(3)–C(4)–C(6)	113.1 ± 0.2	C(12)–C(11)–O(13)	121.2 ± 0.5

[a] In the preliminary communication,[11] the value of the S(1)–C(2)–S(3) angle was given incorrectly.

Table VI. Important Intramolecular Contacts (Å)

S(1)–S(3)	2.707 ± 0.002
S(1)–C(5)	2.846 ± 0.006
S(1)–C(6)	2.792 ± 0.007
S(1)–C(7)	3.277 ± 0.008
S(1)–O(8)	3.675 ± 0.006
S(1)–O(13)	2.636 ± 0.004
C(2)–C(4)	2.418 ± 0.008
S(3)–C(5)	2.871 ± 0.006
S(3)–C(6)	2.908 ± 0.007
S(3)–C(7)	3.261 ± 0.008
S(3)–O(8)	3.945 ± 0.005
S(3)–C(10)	3.256 ± 0.006
C(5)–O(8)	2.749 ± 0.008

Table VII. Intermolecular Contacts Less Than 3.8 Å

C(10)–O(8)$_{\mathrm{II}}$	3.54	O(8)–O(13)$_{\mathrm{IV}}$	3.43
C(11)–O(13)$_{\mathrm{III}}$	3.62	S(1)–O(8)$_{\mathrm{V}}$	3.37
C(12)–O(13)$_{\mathrm{III}}$	3.46	C(4)–O(8)$_{\mathrm{V}}$	3.69
S(3)–C(11)$_{\mathrm{IV}}$	3.60	C(5)–O(8)$_{\mathrm{V}}$	3.79
S(3)–O(13)$_{\mathrm{IV}}$	3.02	C(6)–O(8)$_{\mathrm{V}}$	3.55
C(4)–O(13)$_{\mathrm{IV}}$	3.27	O(8)–O(8)$_{\mathrm{V}}$	3.34
C(6)–O(13)$_{\mathrm{IV}}$	3.10	C(7)–C(12)$_{\mathrm{VI}}$	3.63
C(7)–O(13)$_{\mathrm{IV}}$	3.59	O(8)–C(10)$_{\mathrm{VII}}$	3.54
II, $^1/_2 - x$, $^1/_2 + y$, $^3/_2 - z$		V, $1 - x$, y, $^3/_2 - z$	
III, $^1/_2 - x$, $^1/_2 - y$, $1 - z$		VI, $^1/_2 + x$, $^1/_2 - y$, $^1/_2 + z$	
IV, x, $\bar{y}$, $^1/_2 + z$		VII, $^1/_2 - x$, $-^1/_2 + y$, $^3/_2 - z$	

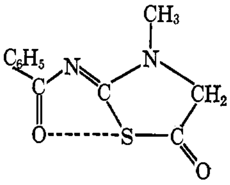
differences in the S(1)–C(4) and S(3)–C(4) distances and the differences in the S(1)–C(2) and S(3)–C(2) distances are significant, but are not readily explainable at the present moment.

A preliminary report[21] on the structure of the desaurin (**5**), which has a crystallographic center of symmetry, indicates that the two crystallographically nonequivalent C–S bonds have effectively the same length, 1.764 and 1.766 Å. The greatest difference between the dithiacyclobutane rings in the two compounds is the expected contraction of the SCS bond angle at C(4) in **4** to 92° compared to 101° at C(2) and to similar values for both angles in **5**.[22]

With the exception of C(5), O(8), C(6), and C(7), the molecule is planar to a first approximation (average deviation 0.04 Å, Table VIII, plane F); the dithiacyclobutane ring is accurately planar within the limits of the analysis (±0.01 Å). Closer examination of the question of planarity of the nine atoms, however, reveals significant "bending" of the group of atoms C(2), C(9), C(11), O(13), and C(12) from the best plane through the four atoms of the ring. There is also a rotation of 4° about the C(9)–C(11) bond, as witnessed by C(2) and C(10) lying +0.07 and −0.09 Å out of the best plane through C(9), C(11), O(13), and C(12). The result of these two combined effects is to place O(13) within 0.01 Å of the plane defined by S(1) and its two bonded atoms.

A particularly noteworthy feature of the structure concerns the intramolecular S(1)--O(13) interaction (Figure 1) leading to an S--O distance of 2.64 Å, compared to the accepted value for the sum of the van der Waals radii of 3.25 Å.[23] There is also an intermolecular S(3)--O(13) contact of 3.02 Å.

There are several parallels in the literature for the type of S--O intramolecular interaction occurring in **4** (see Table X). Distances ranging from 2.38 to 2.70 Å have been found in two dithiofurophthenes[24,25] (*e.g.*, **6**), in the methyl ester of *o*-nitrobenzenesulfenic acid (**7**),[26] in the desaurin (**5**),[21] in 2-benzoylimino-3-methylthiazolid-5-one (**8**),[27] in 2-desylidene-1,3-dithiolane (**9**),[28] in the symmetrical 3,5-diacetamido-1,2-dithiolium bromide (**10**),[29] and in the corresponding 3,5-diacetylimino-1,2-dithiole anion.[30] Furthermore, it appears likely that there are similar contacts in thioindigo,[31,32] and in a bisalkylidene-1,2,4,5-tetrathiin



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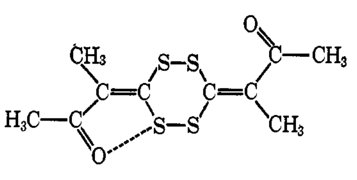

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(21) See Table X, footnote *d*.

(22) The actual value for this angle in **5** is not given in ref 21, but the assumption that the relevant moiety is planar leads to a value of 98.1°.

(23) L. Pauling, in "The Nature of the Chemical Bond," 3rd ed, Cornell University Press, Ithaca, N. Y., 1960, p 260.

(24) M. Mammi, R. Bardi, G. Traverso, and S. Bezzi, *Nature*, **192**, 1282 (1961).

(25) See Table X, footnote *e*.

(26) See Table X, footnote *f*.

(27) H. Steeple, *Acta Cryst.*, **14**, 847 (1961).

(28) See Table X, footnote *g*.

(29) See Table X, footnote *h*.

(30) A. Hordvik and E. Sletten, *Acta Chem. Scand*, 20, 2043 (1966).

(31) E. A. Gribova, G. S. Zhdanov, and G. A. Gol'der, *Kristallografiya*, 1, 53 (1956); *Soviet Phys. Cryst.*, **1**, 39 (1956).

Table VIII. Distances (Å) from Various Best Planes in the Molecule[a]

	A	*B*	*C*	*D*	*E*	*F*	*G*	*H*
S(1)	*0.00*	*−0.01*	*−0.01*	0.19	0.00	*0.00*	*0.00*	*0.00*
C(2)	*0.00*	*−0.01*	*−0.01*	0.07	*0.00*	*−0.02*	*0.00*	*0.00*
S(3)	*0.00*	*−0.01*	*0.02*	0.13	0.05	*0.01*		
C(4)	*0.00*	*0.01*	0.04	0.28	0.07	*0.05*		*0.00*
C(5)						−1.12		
C(6)						1.41		
C(7)						2.68		
O(8)						1.41		
C(9)	0.04	*0.01*	*0.00*	*0.00*	*0.00*	*−0.01*	*0.00*	
C(10)	0.04	0.00	*−0.01*	−0.10	*0.00*	*−0.03*		
C(11)	0.08	0.04	*0.01*	*0.01*	*0.00*	*0.00*	*0.00*	
C(12)	0.20	0.14	0.10	*0.00*	0.07	*0.08*		
O(13)	−0.01	−0.04	−0.08	*0.00*	−0.09	*−0.08*	−0.09	0.00
Average ESD of atoms in best plane	0.00	0.01	0.01	0.01	0.00	0.04	0.00	0.00

[a] The deviations of the atoms included in the best plane calculation are italicized.

Table IX. Root Mean Square Vibrations along the Principal Axes of the Thermal Ellipsoids (Å^2) and the Direction Cosines of the Three Principal Axes Referred to *a*, *b*, and *c**

		Maximum			Intermediate			Minimum	
S(1)		0.27			0.23			0.20	
	−0.392	−0.771	−0.501	0.118	−0.583	0.804	0.913	−0.256	−0.319
C(2)		0.24			0.23			0.20	
	0.336	0.733	−0.592	0.579	0.335	0.743	0.743	−0.592	−0.312
S(3)		0.28			0.23			0.20	
	0.294	0.587	0.754	−0.323	0.804	−0.500	0.900	0.097	−0.426
C(4)		0.27			0.24			0.19	
	0.254	0.154	0.955	0.964	−0.119	−0.237	0.077	0.981	−0.179
C(5)		0.30			0.27			0.20	
	0.362	0.230	−0.903	−0.931	0.038	−0.363	0.049	−0.972	−0.228
C(6)		0.26			0.24			0.22	
	0.618	0.783	0.077	−0.342	0.179	0.922	0.708	−0.596	0.379
C(7)		0.31			0.29			0.23	
	−0.743	−0.109	0.660	−0.559	0.644	−0.523	0.367	0.758	0.539
O(8)		0.33			0.28			0.24	
	0.454	−0.210	−0.866	−0.305	−0.950	0.071	−0.837	0.232	−0.495
C(9)		0.23			0.22			0.20	
	0.099	−0.863	0.496	−0.639	−0.437	−0.633	0.763	−0.255	−0.594
C(10)		0.28			0.24			0.21	
	0.419	0.907	0.044	0.022	−0.059	0.998	0.908	−0.417	−0.044
C(11)		0.26			0.24			0.22	
	−0.843	0.002	0.537	0.242	−0.891	0.383	−0.480	−0.453	−0.751
C(12)		0.29			0.28			0.21	
	0.697	0.580	0.421	−0.627	0.210	0.750	−0.347	0.787	−0.510
O(13)		0.30			0.25			0.20	
	0.663	0.567	0.489	−0.491	0.822	−0.288	−0.565	−0.050	0.823

(**11**).[33] A comparison of the typical dimensions in some of these compounds is given in Table X. All of these molecules contain a five-atom conjugated system linking sulfur to oxygen. There are molecules which *geometrically* could have a short S--O distance, but which do not satisfy the criterion of a five-atom conjugated system. Such an example is thiophene-2-carboxylic acid[34] where the hydroxyl rather than the carbonyl oxygen is closer to sulfur (2.95 Å); in a similar vein, one can visualize several conformations of **4** which could bring O(8) close to one of the sulfur atoms, yet a conformation with O(8) and C(5) virtually eclipsed is preferred.

Major factors influencing the S--O length are the values of the bc, cd, and de angles (Table X) within the "five-membered ring" closed by the S--O interaction. When one of these angles is forced to a large value, *e.g.*, as in **4** and **5** where it is an external angle to a four-membered ring, the distance tends to lie toward the upper limit of the range of contacts. The "five-membered rings" formed by the S--O contacts appear to be close to planar,[21,28,30] the maximum deviation of oxygen from the best plane through the other four atoms being 0.06 Å in one of the rings in **10**,[29] and 0.09 Å in the present structure. Hamilton and LaPlaca[26] have commented on the near-linearity of the O--S–W configuration and indicated that this is a favorable situation for sulfur p- and d-orbital participation. While exact values for this angle are rarely available from the preliminary communications, the angles of 171° in **10**[29] and 156° in the present work suggest that there

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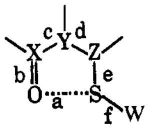
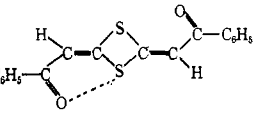
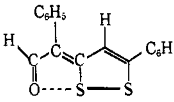
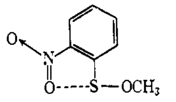
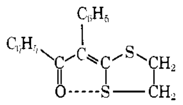
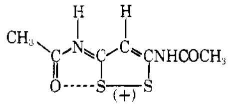
[32] H. von Eller, *Bull Soc. Chim. Fr.*, 1426 (1955); see also W. B. Pearson, Ed., "Structure Reports," NVA Oosthoek's Uitgevers Mij, Utrecht, 1954, p764.

[33] N. W. Alcock and A. J. Kirby, *Tetrahedron*, **22**, 3007 (1966).

[34] M. Nardelli, G. Fava, and G. Giraldi, *Acta Cryst.*, **15**, 737 (1962).

Table X. Comparison of Dimensions in Molecules with S–O Intramolecular Contacts



	Ref	a	b	c	d	e	ab	bc	cd	de	ae	af
Present work		2.64	1.27	1.44	1.38	1.79	100	122	116	129	73	156
 **5**	*b, d*	2.64	1.22	1.46	1.32	1.76	*a*	120	118	129	*a*	*a*
 **6**	*e*	2.38	1.26	1.43	1.39	1.76	101	122	116	120	80	*a*
 **7**	*f*	2.44	1.24	1.45	1.41	1.77	106	118	115	124	77	*a* (almost linear)
 **9**	*g*	2.70	1.25	1.49	1.38	1.72	*a*	120	119	127	*a*	*a*
 **10**	*c, h*	2.54 (3)	1.21 (2)	1.39 (2)	1.36 (2)	1.74 (1)	100 (1)	120 (1)	122 (1)	119 (1)	77 (1)	171

[a] This value not given in preliminary report. [b] The molecule has a crystallographic center of symmetry. [c] In **10** there is almost mirror symmetry relating the two halves of the molecule. The dimensions given above are the mean values with the maximum deviations indicated in parentheses. [d] T. R. Lynch, I. P. Mellor, S. C. Nyburg, and P. Yates, *Tetrahedron Lett.*, 373 (1967). [e] A. Hordvik, private communication (1968). [f] W. C. Hamilton and S. J. LaPlaca, *J. Amer. Chem. Soc.*, **86**, 2289 (1964). [g] W. H. Schmidt and A. Tulinsky, *Tetrahedron Lett.*, 5311 (1967). [h] A. Hordvik and H. M. Kjoge, *Acta Chem. Scand.*, **20**, 1923 (1966).

may be a definite correlation between length of the S--O bond and the degree of distortion from linearity of the af angle (Table X). There is also evidence that, in some of these compounds,[29,30] the sulfur atom can participate in an intermolecular S--O interaction longer than the intramolecular contact but still less than the sum of the van der Waals radii, such that the sulfur and its four "bonded" atoms are approximately coplanar. A proposal that the environment of the sulfur atom is really part of a trigonal bipyramid with electron lone pairs situated at the vacant positions has been used to rationalize mechanisms in the chlorination of arenesulfonyl chlorides.[35] In the present instance S(1) has a very long contact of 3.37 Å with O(8) of an adjacent molecule such that the O(8)$_v$ lies 0.33 Å out of the plane of S(1), C(2), C(4), and O(13).

Structure of Adduct from Azibenzil. Since the adduct assigned formula **2b** is in fact correctly represented by structure **4**, might the cycloadduct obtained from azibenzil have an analogous constitution and require similar reformulation? Chemical evidence obtained in these laboratories[36] and an independent synthesis[37] of the adduct **2a** rule out this possibility; an X-ray single-crystal analysis on a heavy atom derivative of **2a** now in progress[38] should clarify the remaining geometrical ambiguity in the structure.

Acknowledgment. We thank Mrs. Suzanne M. Johnson for helpful discussions concerning the application of the symbolic addition method and Miss Nancy Zwan for estimating the intensities. The stereo view was drawn by ORTEP, written by C. K. Johnson, Oak Ridge National Laboratory, and the Fourier maps were computed using ERFR-2, written by J. H. van den Hende. All computations were carried out on the IBM 7094 at the University of Illinois.

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(35) E. N. Givens and H. Kwart, *J. Amer. Chem. Soc.*, **90**, 378 (1968); **90**, 386 (1968), and references cited therein.

(36) J. A. Kapecki, unpublished results.

(37) P. Yates and L. L. Williams, *Tetrahedron Lett.*, 1205 (1968).

(38) In the laboratory of Professor S. C. Nyburg; P. Yates, private communication.