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THE STRUCTURE OF THE ADDUCT FROM 3-DIAZOBUTANONE AND CARBON DISULFIDE

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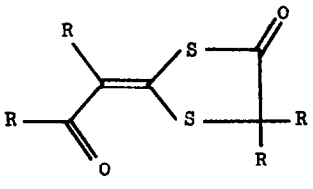
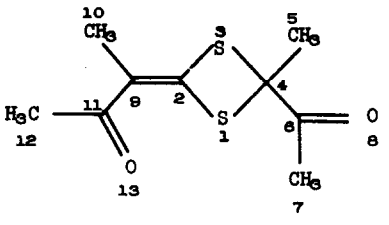
3-Diazobutanone in refluxing carbon disulfide affords an adduct $C_6H_{12}O_2S_2$ which has been assigned structure Ia (or its geometric isomer) (2), a formulation analogous to Ib (or its isomer) advanced for the cycloadduct from azibenzil and carbon disulfide (3). The three-dimensional X-ray single crystal structure determination now reported, however, establishes that the adduct is the 2-methylene-1,3-dithiacyclobutane derivative II.



I



II

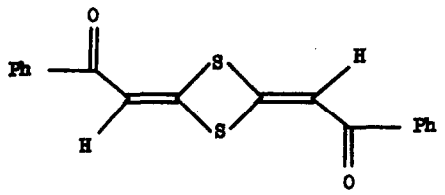
a: R = CH_3

b: R = Ph

Recrystallization of the adduct from 95% ethanol gave fine, almost colorless needles of mp 125-126° (lit. (2) mp 126°) belonging to one of the two monoclinic space groups, either C2/c or Cc. The former assignment, suggested by statistical tests and the number of molecules in the unit cell, was confirmed by the results of the analysis. The cell parameters were obtained on a precession camera using Mo-K_α radiation (λ = 0.7107 Å):

$\underline{a}$ = 12.82, $\underline{b}$ = 13.48, $\underline{c}$ = 12.98 Å, $\underline{\beta}$ = 104°45', $\underline{Z}$ = 8, $\rho_{calc.}$ = 1.34 g cm^{-3}, $\rho_{meas.}$ = 1.33 g cm^{-3} (flotation in aqueous zinc chloride). A total of 1517 non-zero structure amplitudes was obtained by visual estimation of equi-inclination Weissenberg photographs (Cu-K_α, $\underline{\lambda}$ = 1.5418 Å). The structure was solved by a combination of vector, Fourier, and symbolic addition methods; the major difficulty delaying the solution stemmed from the two sulfur atoms lying in the plane at $\underline{y}$ = 0 and causing complete pseudosymmetry in electron density maps based on the contributions of these two atoms alone. Subsequent full-matrix least-squares refinement incorporating anisotropic temperature factors has reduced the crystallographic $\underline{R}$-factor to a present value of 0.10 on all observed reflexions. A drawing of the molecule is shown in Figure 1.

The present values of the bond distances and angles are given in Table I. The four-membered sulfur-containing ring and the five atoms of the α,β-unsaturated carbonyl system are co-planar (mean deviation 0.04 Å), as was found for the ten central atoms of the recently reported desaurin III (4). As in III, the α,β-unsaturated carbonyl system adopts



III

the s-cis conformation with a correspondingly short sulfur-oxygen distance (Figure 1). The observed value, 2.63 Å, is considerably less than the combined van der Waals radii of sulfur and oxygen (3.25 Å) (5).

The mechanistic aspects of the reaction leading to adduct II are under continuing investigation; full details of the crystallographic work will be published in due course.

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TABLE I

Bond Distances (in Å)
(Average estimated standard deviations = 0.013 Å)

S(1)-C(2).....1.80	C(6)-C(7).....1.48
S(1)-C(4).....1.85	C(6)-O(8).....1.21
C(2)-S(3).....1.72	C(9)-C(10).....1.59
C(2)-C(9).....1.36	C(9)-C(11).....1.42
S(3)-C(4).....1.90	C(11)-C(12).....1.55
C(4)-C(5).....1.53	C(11)-O(13).....1.27
C(4)-C(6).....1.61	

Bond Angles (in degrees)
(Average estimated standard deviations = 0.7°)

C(2)-S(1)-C(4)..... 83.3	C(5)-C(4)-C(6).....112.7
S(1)-C(2)-S(3).....106.6	C(4)-C(6)-C(7).....118.1
S(1)-C(2)-C(9).....128.5	C(4)-C(6)-O(8).....115.6
S(3)-C(2)-C(9).....130.8	C(7)-C(6)-O(8).....125.6
C(2)-S(3)-C(4)..... 83.7	C(2)-C(9)-C(10).....119.6
S(1)-C(4)-S(3)..... 92.3	C(2)-C(9)-C(11).....116.8
S(1)-C(4)-C(5).....115.8	C(10)-C(9)-C(11).....123.5
S(1)-C(4)-C(6).....108.4	C(9)-C(11)-C(12).....118.0
S(3)-C(4)-C(5).....114.8	C(9)-C(11)-O(13).....121.6
S(3)-C(4)-C(6).....111.1	C(12)-C(11)-O(13).....120.4

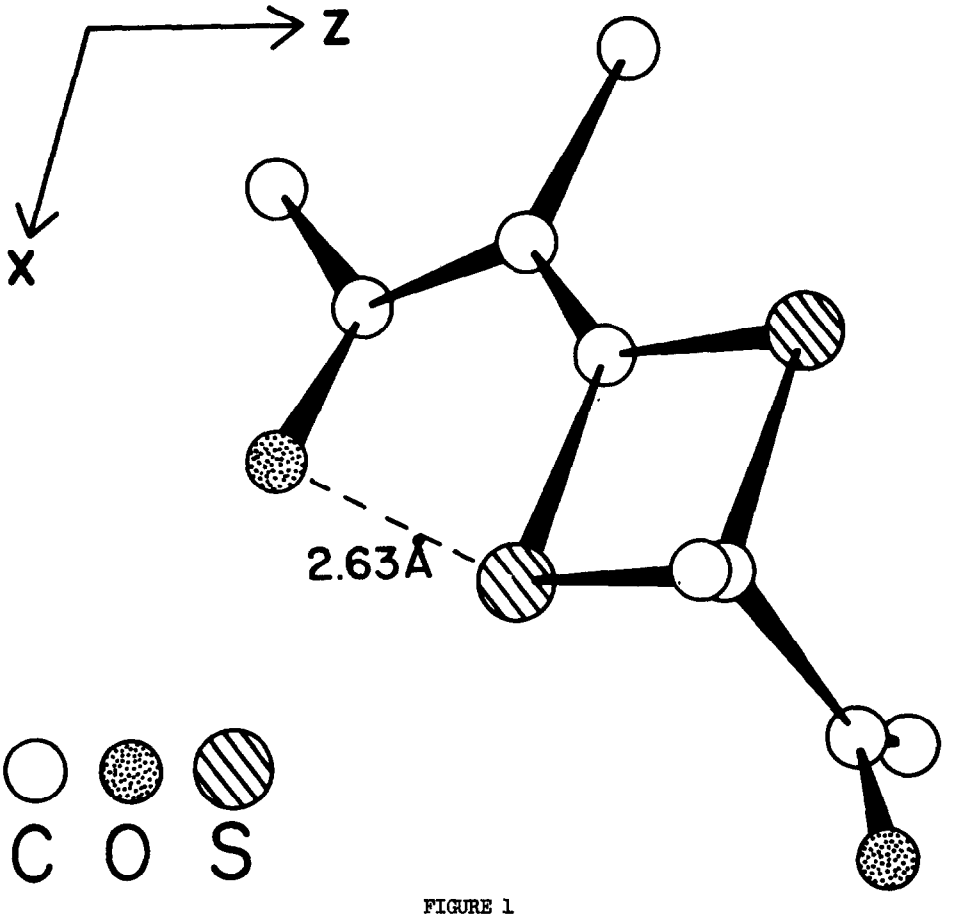

FIGURE 1

Perspective drawing of the molecule viewed along the b-axis.

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