

THE CRYSTAL AND MOLECULAR STRUCTURE OF 2-DESYLIDENE-1,3-DITHIOLANE

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Deoxybenzoin and carbon disulfide give rise to a dithioacid which upon treatment with dibromoethane yields 2-desylidene-1,3-dithiolane(1)(see Fig. 1)(hereinafter referred to as DD). DD is unusual in that it shows unusually weak carbonyl absorption in the infra-red and as a result it has been employed as a model compound to support the assignment of abnormally weak carbonyl absorptions observed for certain desaurins(2). The results of the X-ray structure determination of DD suggest the reason for the weak carbonyl absorption which, from all indications, appears to be of more general applicability than had originally been anticipated.

Crystals of DD grown from ethanol proved to be monoclinic, $a=9.54$, $b=17.40$, $c=9.83A.$, $\beta=116.83^\circ$, space group $P2_1/c$, with 4 molecules per unit cell. The intensities of the reflections (CuK α) were measured with a GE XRD-5 equipped with a single-crystal orienter and scintillation counter assembly using the stationary crystal-stationary counter technique with balanced Ni-Co filters. Of the 1,491 reflections possible to $\lambda A.$ resolution ($2\theta_{mx}=100^\circ$), 1,456 proved to be observable.

The positions of the sulfur atoms were determined from a sharpened three dimensional Patterson function and an electron density based on the phases of the sulfur atoms revealed the other 18 atoms of DD. The structure was refined through successive Fourier syntheses and then by the method of least squares employing anisotropic thermal parameters in structure factor computations. The positions of the hydrogen atoms were obtained from a final difference density and the final value of R was 0.105, including hydrogen atoms.

The bond distances and the bond angles of DD are shown in Fig. 1 (estimated standard deviations of about $\pm 0.015A.$ for distances and $\pm 1.5^\circ$ for angles). The out-of-plane distances from

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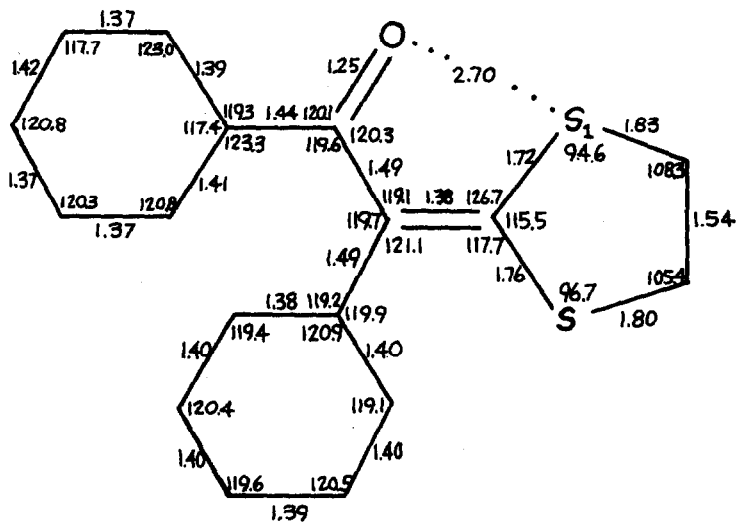


FIG. 1
Bond distances and bond angles

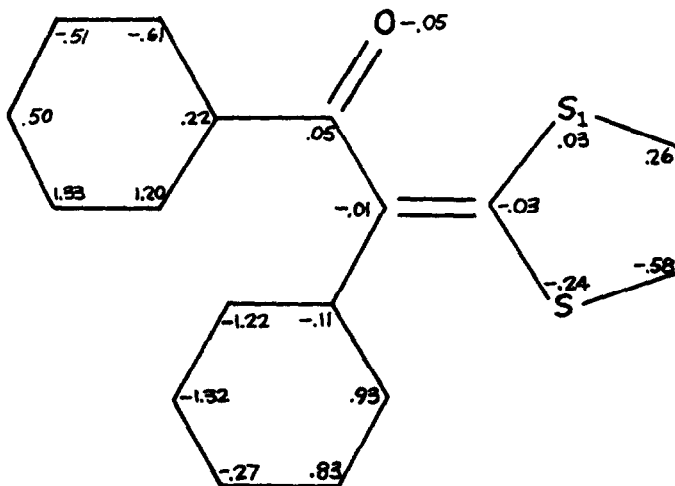


FIG. 2

Out-of-plane distances from L. S. plane of α,β unsaturated carbonyl and S_1

the plane of the α,β -unsaturated carbonyl system and S_1 are shown in Fig. 2. The phenyl groups are rotated out of the plane of the α,β -unsaturated carbonyl approximately $+29^\circ$ and $+41^\circ$, respectively, with the former being bent out of the plane by about -3° and the latter by about $+6^\circ$. One phenyl group is coplanar within $\pm 0.01\text{\AA}$, the other within $\pm 0.02\text{\AA}$, the 1,3 dithiolane ring is markedly non-planar and the α,β unsaturated carbonyl system with S_1 forms an approximately planar array. The latter array gives rise to an abnormally short sulfur-oxygen contact of 2.70\AA. Comparable observations have been made with other similar compounds (3) and also, the methyl ester of o-nitrobenzenesulfenic acid(4). Thus, an appreciable interaction exists between the sulfur and oxygen atoms which in turn must drastically alter the normal carbonyl absorption frequency. Finally, although the α,β unsaturated carbonyl system and S_1 are nearly planar, the ring system formed by the sulfur-oxygen interaction is distorted as is evidenced by the bond angles of C_2 of the 1,3 dithiolane.

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