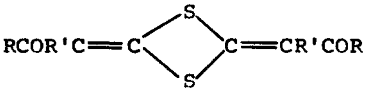
Tetrahedron Letters No.4, pp. 373-377, 1967. Pergamon Press Ltd. Printed in Great Britain.

THE STRUCTURE AND STEREOCHEMISTRY OF THE DESAURIN FROM ACETOPHENONE

T. R. Lynch, I. P. Mellor, S. C. Nyburg and P. Yates
Department of Chemistry, University of Toronto
Toronto 5, Ontario, Canada

(Received 17 November 1966)

The desaurins, a class of high melting heterocyclic sulfur compounds, have previously been shown to have the structural formula I (1), but no evidence on their stereochemistry has been presented.



I

A complete three-dimensional X-ray analysis has been performed on the desaurin from acetophenone (I, R=Ph,R^1=H), $C_{18}H_{12}O_2S_2$, prepared by the method of Kelber and Schwarz (2), to confirm the desaurin structure and to determine the stereochemistry and the dimensional details of the 1,3-dithiete ring.

The desaurin crystallizes from nitrobenzene as small plates, m.p. 270-272.5° (dec.), in the monoclinic system with space-group $P2_1/c$. The least squares refined cell parameters are $\underline{a} = 5.470 \pm 0.008$ Å, $\underline{b} = 4.848 \pm 0.012$ Å, $\underline{c} = 28.299 \pm 0.008$ Å, $\beta = 96.90 \pm 0.10°$; $\underline{Z} = 2$, $\underline{D}_{\underline{m}} = 1.44_4$, $\underline{D}_{\underline{x}} = 1.44_5$ g. cm^{-3}. The intensities of 1493 independent reflections (1020 observed) were measured visually. The independent sulfur atomic position was determined from the three-dimensional Patterson function, and the remaining oxygen and carbon atoms were located from successive three-dimensional electron-density syntheses. The positional and thermal parameters were refined by ten cycles of full matrix least squares (the final six cycles involving anisotropic temperature factors). The hydrogen atoms, located from a difference synthesis, were incorporated into the final structure factor calculation, for which the reliability index, $\underline{R}$, was 0.12 for the 1493 measured reflections. Sections of a final three-dimensional electron-density distribution taken through the atomic centres parallel to (010) are shown in Fig. 1, together with a drawing of the corresponding asymmetric unit.

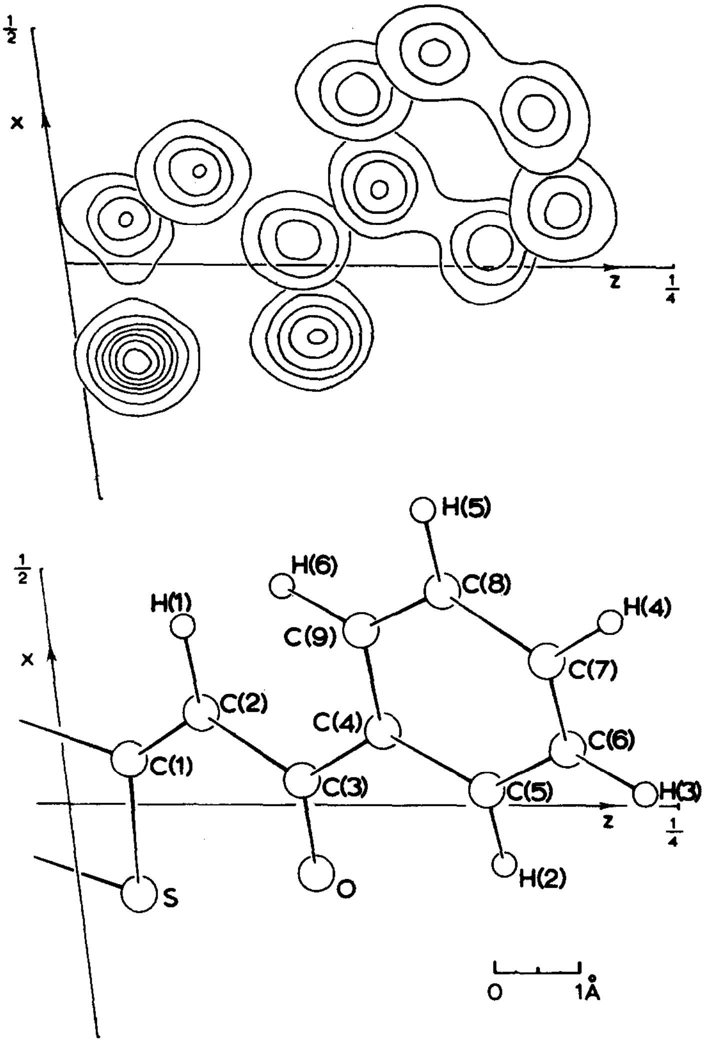


FIG. 1

Composite electron density normal to [010]. Contour intervals at C and O atoms $1.0 e\text{Å}^{-3}$, at S, $2.0 e\text{Å}^{-3}$, (the zero contour is omitted).

The space group and the presence of two molecules per unit cell require a centrosymmetric molecule. Thus the 1,3-dithiete ring must be planar and the desaurin must be the trans-isomer. The structure analysis reveals that the α,β-unsaturated carbonyl system is in an s-cis conformation, as illustrated in Fig. 1. Bond lengths and bond angles of interest are shown in Fig. 2.

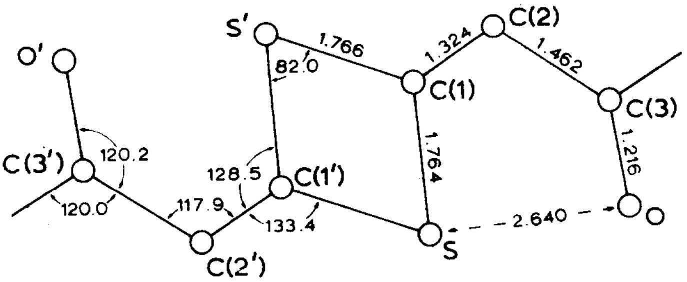
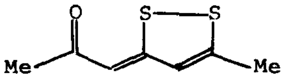


FIG. 2

Bond lengths and bond angles of the central 10 atoms of the molecule. The estimated standard deviations in the bond distances are 0.01 Å, except in those involving S where they are 0.006 Å. The estimated standard deviations in the bond angles are less than 0.6°.

The most striking feature of the molecular structure is the close planarity of the ten central atoms (the mean deviation from the least squares plane is 0.006 Å). Associated with this planarity is the short sulfur-oxygen distance of 2.640 ± 0.006 Å (the sum of the van der Waals radii of oxygen and sulfur is commonly accepted to lie within the range 3.05 - 3.25 Å (3,4)). The planarity and short sulfur-oxygen distance are similar to that found in the α,β-unsaturated keto sulfide II (5). In addition, the distortions of the exocyclic angles at C(1) and the angle



II

at C(2) suggest a sulfur-oxygen attraction.

The mean sulfur-carbon bond length of 1.765 ± 0.006 Å is in accord with other sp^2-carbon-sulfur bond distances reported (5,6), while the intramolecular sulfur-sulfur distance of 2.665 Å is substantially less than the sum of the van der Waals radii (3.3 - 3.7 Å), as also is the C(1) - C(1') distance of 2.315 Å.

Full details of the structure determination will be published elsewhere.

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