The S···O Interaction in Some Sulphur-containing Ketones: *X*-Ray Crystallographic and Infrared Spectroscopic Study

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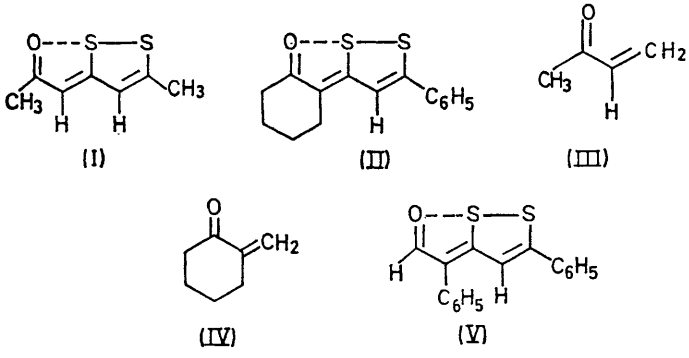
Summary The length of the S···O intramolecular contact [2·255(8) Å] in 2-(5-phenyl-1,2-dithiole-3-ylidene)cyclohexanone (II) as determined by *X*-ray diffraction supports a distance *vs.* infrared spectral correlation for compounds with S···O (ketone) intramolecular contacts.

WEAK intramolecular S···O contacts have been studied by spectroscopic[1] and *X*-ray diffraction[2] methods in our respective laboratories for some time. We now report the preliminary results of a possible correlation between these studies.



(I) (II) (III) (IV) (V)

The absorption band partly due to the carbonyl vibration in (I) occurs at 1595 cm^{-1} in C_2Cl_4 solution and at 1578 cm^{-1} in KBr discs.[3] This assignment was made by comparison of the spectrum of (I) with that of (I) 26% enriched in ^{18}O; $\nu(C^{18}O)$ 1583 cm^{-1} (C_2Cl_4). In the case of (II), the carbonyl vibration frequency occurs at 1568 cm^{-1} in C_2Cl_4 solution and at 1564 cm^{-1} in KBr discs.[4] Although these results might suggest a stronger S···O interaction in (II) than in (I), we consider that a more valid comparison would involve the differences, $\Delta\nu$, between the carbonyl frequencies in the ketones with and without the sulphur atoms. The carbonyl frequencies of (III) in C_2Cl_4,[5] and of (IV) in CCl_4[6] are 1706 and 1697 cm^{-1}, respectively. The $\Delta\nu$ values for (I) and (II) are therefore 111 and 129 cm^{-1}, and imply a stronger S···O contact in (II) than in (I).[3] This trend has now been confirmed by the comparison of the results of an *X*-ray crystal structure study of (II) with the previously-published results on (I).[7]

The crystals of (II) are reddish needles elongated along the *c*-axis. *Crystal data*: $C_{15}H_{14}OS_2$, $M = 274{\cdot}1$, monoclinic, $a = 12{\cdot}915(2)$, $b = 13{\cdot}143(2)$, $c = 7{\cdot}621(1)$ Å, $\beta = 95{\cdot}80(1)°$, $D_m = 1{\cdot}420$ g cm^{-3}, $Z = 4$, $D_c = 1{\cdot}428$ g cm^{-3}, space group $P2_1/c$. Intensity data were collected on a Picker FACS-1 computer-controlled diffractometer using Cu-K_α radiation. A total of 1371 independent, non-zero structure amplitudes was obtained. The structure, incorporating anisotropic thermal parameters for the non-hydrogen atoms, has been refined to an *R*-factor of 0·069 on all observed data. The molecular dimensions are shown in the Figure.

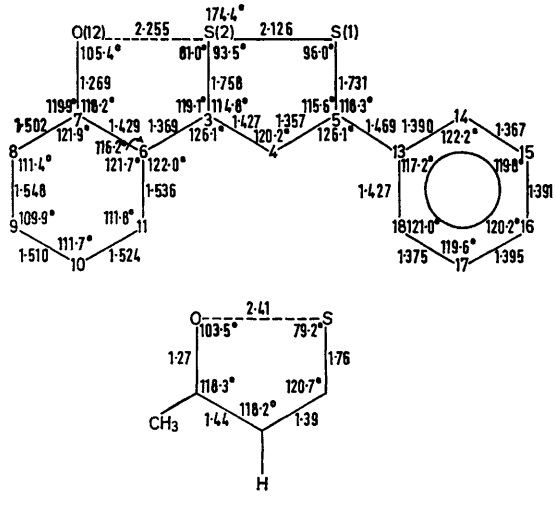


FIGURE. *Bond lengths and angles in* (II); *the e.s.d. of* S–S, S–C, S–O, C–C, *and* C–O *lengths are* 0·004, 0·009, 0·008, 0·014—0·018, *and* 0·013 Å, *respectively; the e.s.d. of the angles range from* 0·40 *to* 0·80°. *The dimensions in the five-membered ring in* (I) *are also shown.*

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The S–S and S · · · O lengths are 2·126(4) and 2·255(8) Å, respectively. The S–S bond is marginally longer than that (2·12 Å) found in (I)[7] or that [2·106(3) Å] found in the aldehyde (V),[8] and significantly longer than the range of lengths (2·03—2·10 Å) found in S–S bonds unperturbed by intramolecular contacts.[9] However, the S · · · O contact is the shortest so far reported involving a carbonyl group oxygen atom and is 0·15 Å shorter than the length of 2·41 Å reported in (I).[7] Only in cases involving oxygen atoms of nitroso-groups have shorter S · · · O contacts been reported;[10] in these cases also, the S–S bonds are much longer than the accepted S–S single bond lengths. Other than the S · · · O distance, the pattern of bond lengths in the dithiole-ylidene nucleus of (II) is very similar to those in (I)[7] and in (V).[8] The substantial difference in the S · · · O contacts in (I) and (II) is thus achieved by very slight differences in the other dimensions in the five-membered "ring" formed by the S · · · O contact in the two compounds (Figure). However, the similarity of the carbonyl stretching frequencies of (II) in KBr discs and in solution suggests that the S · · · O distance is an intrinsic molecular property rather than a consequence of crystal packing forces.

The best planes through the two "five-membered" rings of the central portion of the molecule of (II) are within 1°22′ of being coplanar and the best plane through the central eight atoms is slightly (maximum deviation 0·031 Å), but significantly non-planar. The conformation of the cyclohexanone ring can be described as a "half-chair"[11] with the two carbon atoms, C(9) and C(10), disposed 0·281 and 0·504 Å on opposite sides of the best plane through C(3), C(6), C(7), C(8), C(11), and O(12).

Our results on (II) suggest that there is a correlation between the $\Delta\nu$ values for ketones with the length of the S · · · O contact. Further *X*-ray structural studies are in progress to provide additional data to test the range of validity of this correlation.

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