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THE CRYSTAL STRUCTURE OF 6-BENZOYL-3-HYDROXY-1-METHYL-5-PHENYL THIABENZENE-1-OXIDE

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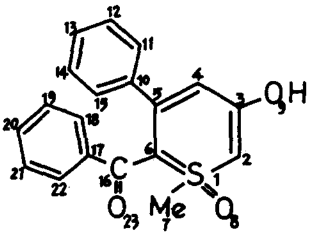
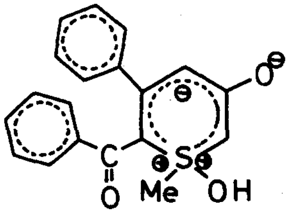
Several thiabenzene derivatives have been synthesized and discussed in relation to ylide-ylene structure and the aromaticity of the heterocyclic ring system (1). It had been impossible to prepare the crystals of these compounds suitable for X-ray analysis. Recently we succeeded in obtaining a beautiful yellow crystal of 6-benzoyl-3-hydroxy-1-methyl-5-phenyl-thiabenzene-1-oxide, (I), synthesized from dimethyloxosulfonium 1-benzoyl-2-phenyl-3-ethoxycarbonylallylide (2). Thus, this compound has enabled us to successfully determine the structure by X-ray crystallographic analysis.



(I)



(II)

The C-S bond lengths of 1.706 and 1.696 Å with the standard deviation of within 0.01 Å, found in (I) agree well with those of the conjugated ones (1.70 Å), and are shorter than a normal C-S single bond (ca. 1.80 ± 0.05 Å), but longer than a double bond (1.65 ± 0.05 Å) (3). The deviations of the five carbon atoms from the least-squares plane through the atoms C(2), C(3), C(4), C(5) and C(6) are found to be quite small (maximum 0.06 Å). The lengths of C(3)-C(4), C(4)-C(5), C(5)-C(6) and C(2)-C(3) are 1.41, 1.40, 1.42 and 1.33 Å respectively, and they do not differ significantly except the double bond character of C(2)-C(3). The values of the three bond lengths are close to that of the benzenoid double bond. Concerning the conjugation system, although the bond lengths of C-S, and most of the C-C in the thiabenzene ring are shown to agree well with the length of conjugated ones, the sulfur atom deviated about

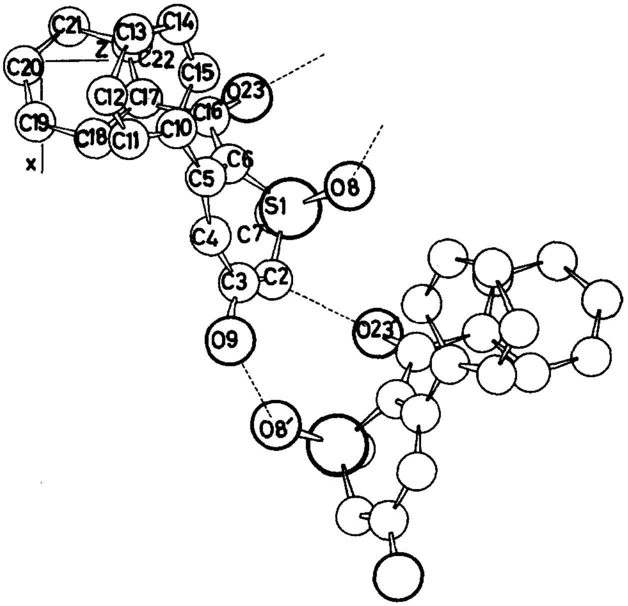
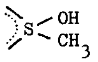
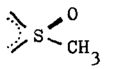
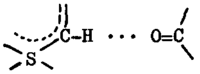


FIG. 1

0.6 Å from the least-squares plane which consists of the remaining five carbon atoms of the thiabenzene ring. Also, in the n.m.r. spectrum, the chemical shifts of 6.12 and 5.62 ppm for the thiabenzene hydrogens are more like those of usual double bond hydrogens than those of benzenoid hydrogens. Thus, conclusions deduced from the nature of conjugation systems, such as thiuret ion (3), could not be extended to the present molecule.

The least-squares planes of the benzene and the thiabenzene ring are in a twisted arrangement at about 35° to one another. The carbonyl carbon C(16) is connected at C(6) with a deviation 0.48 Å from the thiabenzene plane, on the opposite side with respect to the sulfur atom. Spatially, the benzoyl group partially overlies the benzene and thiabenzene rings in quite close proximity to make intramolecular non-bonded interaction. They are 3.15 Å for C(5)···C(17), 3.22 Å for C(10)···C(17), and 3.26 Å for C(10)···C(18).

The positions of hydrogen atoms could be found by the D-synthesis. From this, the main contribution of sulfur to the chemical structure is concluded to be the sulfoxonium structure  $>S<^{OH}_{CH_3}$ rather than the sulfoxide  $>S<^{O}_{CH_3}$: the hydrogen atom is transferred from phenolic proton attached to the O(9) through the intermolecular hydrogen bond. The distance of 2.74 Å between O(9) and O(8') (Fig. 1) is usual for a OH···O hydrogen bond. Thus, the structure can be referred to as the mesoionic structure (II), (4). Another intermolecular interaction should be thought since the distance between C(2) and O(23') is 3.12 Å. This suggests there is a hydrogen bond of the form  , which may be resulted from an increase of the bond polarity of sulfur atom and/or reinforcement by the double bond character in C(2)-C(3) as mentioned (5).

The yellow crystal is orthorhombic with the unit cell dimensions; a = 10.41 Å, b = 13.50 Å, and c = 23.51 Å. There are eight molecules per unit cell and the space group is Pbca from the extinction rule. The intensities were estimated visually from equi-inclination Weissenberg photographs of the 0kl-9kl layers; the multiple-film technique was employed. After several hundred hours of X-ray exposure, the crystal turned brown. The 7kl to 9kl reflections were taken from another crystal.

The analysis was done by heavy atom technique, using sulfur atom. Sharpened Patterson function and Sim's weighting scheme were used, because the sulfur atom did not seem to be heavy enough in relation to the other lighter atoms. The first Fourier map showed the whole layout of the molecular structure, except the two carbon peaks attached to the benzoyl ring. Since the positions of some light atoms were perturbed by the effect of the sulfur which was located in the near quarter to a and b directions (fractional coordinations are 0.23 and 0.23), the second Fourier synthesis was calculated, the phases being based on additional four atoms around the sulfur. In the next round, the R-factor was 46.5% with isotropic temperature factor. Five cycles of the full matrix least-squares refinements gave the R-factor 14.5% with all isotropic temperature factors. Almost all of the hydrogen atoms have been found on the D-synthesis and the R-factor decreased to 13.5% by including hydrogen atoms.

The fluctuation of the magnitude of the temperature factor was observed, their mean value being 5.12 $Å^2$ for phenyl group from C(17) to C(22), 3.07 $Å^2$ for the carbons in the thiabenzene ring C(2) to C(6). This may be interpreted as a large thermal vibration or disorder of the benzoyl and phenyl group in the periphery of the molecule.

Further experiments at low temperature are in progress.

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