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THE S---O INTERACTION IN 2-(5-PHENYL-1,2-DITHIOLE-3-YLIO) PHENOLATE: AN X-RAY CRYSTALLOGRAPHIC AND INFRARED SPECTROSCOPIC STUDY.

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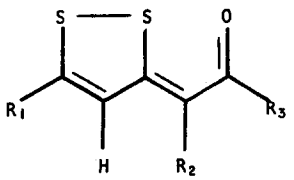
The S---O interaction in a number of α-(1,2-dithiole-3-ylidenic) ketones (I) has been studied by means of infrared spectroscopy and X-ray diffraction, leading to the proposal of a correlation between the length ($\underline{\delta}$) of the S---O contact and $\underline{\Delta\nu}$, the difference between the carbonyl vibration frequency in the methylene ketone and that in the corresponding dithiolylidene ketone.[1] Several contributors (eg IIa-d) to the structure of compounds of type (I) have been proposed.[2-6] The physico-chemical properties of the α-(1,2-dithiole-3-ylio) phenolate molecule (III) are very different from those of compounds of type (I).[4] The infrared spectrum of (III) does not show an absorption corresponding to the carbonyl group.[7] Comparison of the IR spectra in the range 1200-1700 cm^{-1} for the (5-phenyl-1,2-dithiole-3-ylio) phenolates ^{16}O, and enriched in ^{18}O, indicates that the only band that is noticeably shifted is that at 1284 cm^{-1} [1284 cm^{-1} in the ^{16}O compound (CS_2) to 1272 cm^{-1} in the ^{18}O compound (CS_2)].[7] This band is probably due to a vibration of the type "7a" of the phenolic ring [Wilson's notation][8] and is sensitive to substituents.[9] Thus structures of type (IIb-d) should be more important than those of (IIa) for the molecule of (III), leading one to anticipate a particularly short S---O distance in this molecule. An X-ray structure analysis was carried out on (III) to provide quantitative data on the S---O interaction.

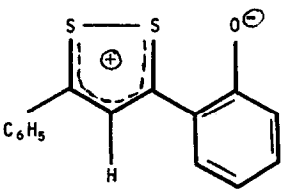
The crystals of (III) are thin, dark-red needles elongated along the $\underline{c}$-axis. Crystal data: $C_{15}H_{10}OS_2$, $\underline{M}$ = 270·1, orthorhombic, $\underline{a}$ = 24·920(5) Å, $\underline{b}$ = 13·089(3) Å, $\underline{c}$ = 7·622(2) Å, $\underline{Z}$ = 8, $\underline{D_c}$ = 1·44 g/cm^3, space group $\underline{Pbca}$, Cu K_α radiation ($\underline{\lambda}$ = 1·5418 Å). Intensity data were collected on a four circle Picker FACS-1 computer-controlled diffractometer. A total of 1256 independent non-zero reflections was obtained with $2\underline{\theta} \leq 130^0$. The structure was solved by the symbolic addition method[10] and has been refined by full-matrix least squares methods to an $\underline{R}$-factor of 0·058 on all non-zero data. The refinement involved anisotropic temperature factors for the non-hydrogen atoms and isotropic temperature factors for the hydrogen atoms. The molecular



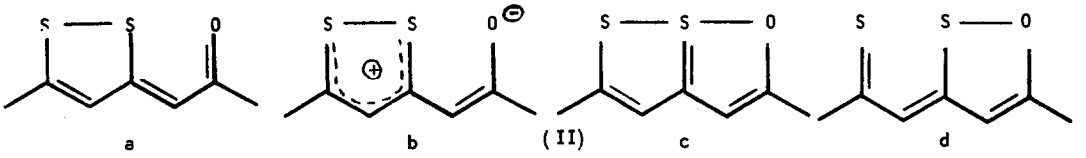
(I)

a) $R_1 = R_3 = CH_3$; $R_2 = H$

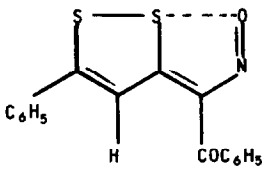
b) $R_1 = C_6H_5$; R_2, $R_3 = -(CH_2)_4-$



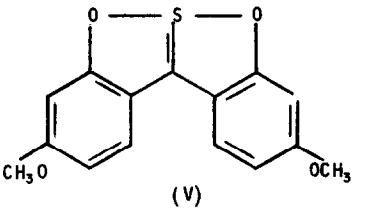
(III)



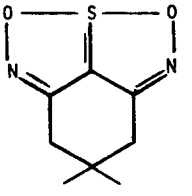
a b (II) c d



(IV)



(V)



(VI)

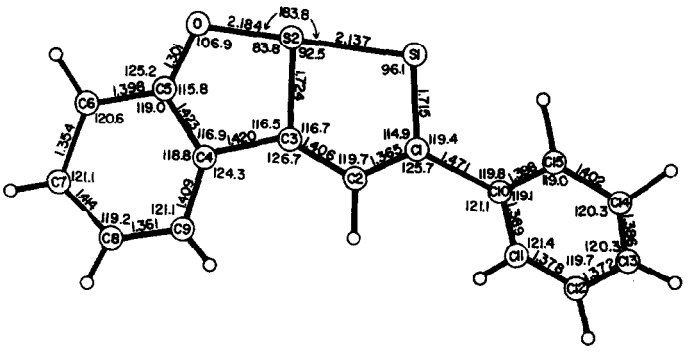


Figure 1: Bond lengths and angles in (III). The typical esd of the S-S, S-O, S-C, and C-C bonds are 0·003, 0·007, 0·008, and 0·012 Å.

dimensions found in the study are shown in Figure 1.

The S---O length of 2·184(7) Å in (III) is shorter than any of the lengths found in compounds of type (I). The S---O (nitroso) length of 2·034(5) Å found in (IV)[11] and the lengths of 1·875-1·879 Å found in the symmetrical molecules (V)[12] and (VI)[13] are the only examples of shorter S---O lengths. Furthermore, the C-O length of 1·301(9) Å is longer than those found in compounds of type (I) and approaches the length (1·316-1·319(4) Å) found in (V). It is closer to the value expected for a phenol (1·36Å)[14] than to that for a quinone (1·22Å).[15] The S-S length of 2·137(3) Å is longer than any of the values reported for compounds of type (I). The large external C-C-O angle at C(5) is a further indication of a strong S---O attractive interaction.

The X-ray results thus indicate that compounds of type (III) must be described mainly by structures such as (IIb), (IIc), and (IId). They are in very good agreement with the observations made by IR spectroscopy and further justify the hypothesis of a correlation between the IR frequencies observed and the S---O·distance in the compounds of type (I).

REFERENCES

(1) R. Pinel, Y. Mollier, E. C. Llaguno, and I. C. Paul, Chem. Commun., 1352 (1971).

(2) D. Festal, O. Coulibaly, R. Pinel, C. Andrieu, and Y. Mollier, Bull. Soc. Chim. France, 2943 (1970).

(3) Y. Mollier, F. Terrier, and N. Lozac'h, ibid., 1778 (1964).

(4) R. Pinel, Y. Mollier, and N. Lozac'h, ibid., 856 (1967).

(5) B. J. Lindberg, S. Hogberg, G. Malmsten, J.-E. Bergmark, O. Nilsson, S.-E. Karlsson, A. Fahlman, U. Gelius, R. Pinel, M. Stavaux, Y. Mollier, and N. Lozac'h, Chemica Scripta, 1, 183 (1971).

(6) R. Gleiter, D. Schmidt, and H. Behringer, Chem. Commun., 525 (1971).

(7) R. Pinel and Y. Mollier, Bull. Soc. Chim. France, 1385 (1972).

(8) E. B. Wilson, Phys. Rev., 45, 706 (1934).

(9) S. Pinchas, D. Sadeh, and D. Samuel, J. Phys. Chem., 69, 2259 (1965).

(10) J. Karle and I. L. Karle, Acta Crystallogr., 21, 849 (1966).

(11) P. L. Johnson, K. I. G. Reid, and I. C. Paul, J. Chem. Soc., Sect. B, 946 (1971).

(12) R. D. Gilardi and I. L. Karle, Acta Crystallogr., B27, 1073 (1971).

(13) E. C. Llaguno and I. C. Paul, to be published (1972).

(14) S. R. Byrn, D. Y. Curtin, and I. C. Paul, J. Amer. Chem. Soc., 94, 890 (1972).

(15) D. Rabinovich and G. M. J. Schmidt, J. Chem. Soc., Sect. B, 127 (1967).