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QUINONE METHIDE - CRYSTAL STRUCTURE AND NMR STUDY OF 2.6-DIMETHYL-5' -p-METHOXYPHENYL-1', 2'-DITHIOL-3' : 4-YLIDENE-2,5- CYCLOHEXADIENONE.

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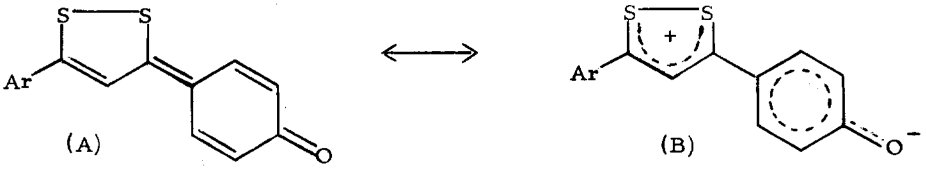
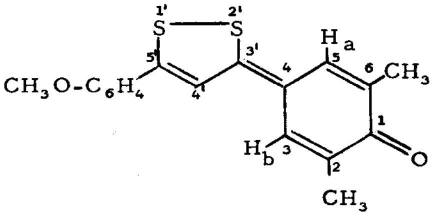
The synthesis of compounds that we may designate as 1',2'-dithiol-3' : 4-ylidene-2,5-cyclohexadienones (A) or 1',2'-dithiol-3' : 4-ylio-phenolates (B) has been the subject of several studies (1 to 5); these compounds have been described in these studies by mesomeric formulae (A) and (B) (1,3,4) or by a (B) formula (5). Nevertheless, the structural studies already carried out (1,3,4) show the importance of the (A) quinonoid formula. We have undertaken the examination of this problem by means of a structural analysis of the compound 1 (Ar = $p\text{-}CH_3O\text{-}C_6H_4$) by X-ray diffraction and by NMR spectroscopy.





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The thin, purple crystals of 1, which grew as a benzene solvate, had the following crystal data : $C_{18}H_{16}O_2S_2.1/2C_6H_6$, $\underline{M}$ = 367.5, orthorhombic, $\underline{a}$ = 19.19 (1), $\underline{b}$ = 20.32 (2), $\underline{c}$ = 9.525 (7) Å, $\underline{V}$ = 3714 Å^3, $\underline{Z}$ = 8, space group $\underline{P}\ \underline{b}\ \underline{c}\ \underline{a}$. The structure was solved by direct methods (6) and has been refined to an R-factor of 0.090 on 1877 reflections collected on a Picker FACS-1 diffractometer (CuK_α). A stereoscopic view of the molecule of 1 is shown in Figure 1. These crystallographic results show that the 1',2'-dithiol-3' : 4-ylidene cyclohexadienone system excluding the methoxyphenyl group is almost planar (max deviation of non-hydrogen atoms is 0.08Å); the methoxy phenyl ring makes an angle of 9.4° with the dithiole ring. On the other hand the distance C(3') - C(4) is relatively long [1.402 (10) Å] for a pseudo double bond and is nearer to the value of 1.42 (1)Å observed for the C(3') - C(2) bond in 5'-phenyl-1',2'-dithiol-3' : 2-ylio-phenolate [2-(5-phenyl-1,2-dithiol-3-ylio)phenolate (7)]. The double bond index calculated for the C(3') - C(4) bond from the interatomic distance according to the JULG or the ALLINGER method (8) is 0.65. We note that the carbonyl double bond index ($P_{c=o}$) calculated by the same method is 0.79, in good agreement with the one obtained from the ν_{co} wave number according to BERTHIER's relation for quinones (9) [ν_{co} = 1597cm^{-1} (4) $P_{c=o}$ = 0.809].

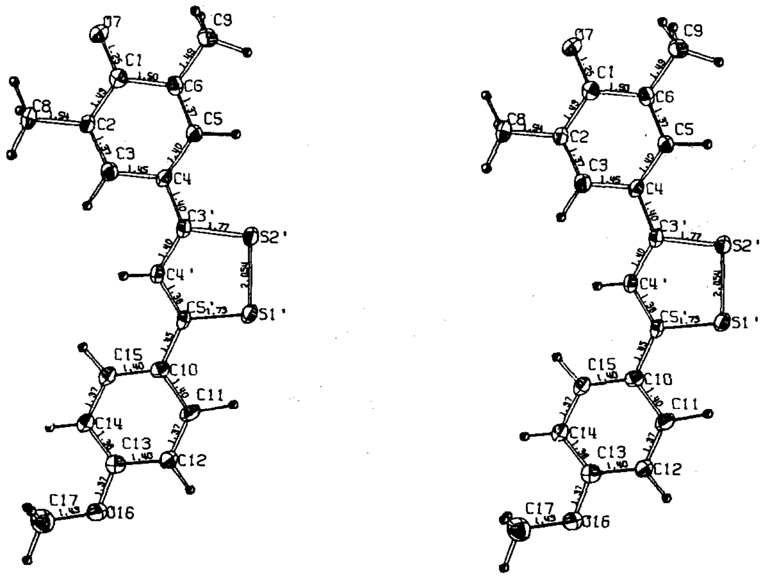

Figure 1 : Stereoscopic view of the molecule.

The S-S and C-S interatomic distances in the dithiole nucleus of 1 are much closer to the ones observed in 4-methyl-1,2-dithiol-3-thione (10) than to those of the 3-phenyl-1,2-dithiolylium ion (11). Similarly, a comparison of the distances in the cyclohexadienone ring in 1 with those of 2,6-dimethylbenzoquinone (12) anf of 2,6-dimethylphenol (13) shows that the structure is closer to a quinone than to a phenol. Thus the crystallographic results for 1 indicate the importance of the (A) form in the description of the structure of these compounds.

The NMR spectrum of 1 determined at 60 MHz in $CDCl_3$ shows that the H_a and H_b protons (7.25 p.p.m.) only give a broadened singlet (2.4 Hz at half-height); the shape of this signal is not modified over the temperature range of -80°C (solvent : acetone-d_6) to +100°C (solvent : pyridine-d_5). This result indicates that the line broadening is not due to restricted rotation. Furthermore the NMR spectrum of 1 determined at 270 MHz shows that the broadened singlet due to H_a and H_b is not modified (same width at half-height), thus excluding a quasi magnetic equivalence.

However, as irradiation of the methyl group resonance induces a narrowing of the signal of the H_a and H_b protons (at half-height : 0.7 Hz), we conclude that the line broadening of the H_a and H_b signals is essentially due to the coupling between these protons and those of the methyl groups.

Previously, we have demonstrated (4) that under the action of strong acids, compounds related to 1 are protonated on oxygen. The NMR spectrum of 1 determined in CF_3COOD is very similar to that of 1 determined in $CDCl_3$, with the exception of a shift of all the protons towards low fields due to the positive charge of the ion; this shift is particularly important for the hydrogen on C (4') in the dithiole ring (8.57 p.p.m. instead of 7.41 p.p.m.), since the positive charge is mainly localized on this ring. Furthermore, the H_a and H_b protons (7.72 p.p.m.) appear, as previously, as a broadened singlet (width at half-height : 2Hz).

Our results show that the exchange rate of the H_a and H_b protons is important with regard to the time scale for the NMR. Thus, according to the NMR data, there is free rotation about the C(3') - C(4) bond, whose double bond value according to the X-ray information is 0.65. The barrier to rotation depends on the difference in energy between the ground state where the 4-(1,2-dithiol-3-ylidene) cyclohexadienone system is coplanar, and the transition state which is formed during the rotation and which will have dipolar character. The energy of the transition state will depend particularly on the ability of the groups attached to C(3') and C(4) to carry a positive charge and a negative charge (14). The 1,2-dithiolylium ion is a typical aromatic ion (15) stabilized by resonance, while the phenolate anion will be stabilized by some of the same features that cause the neutral phenol structure to be ~ 31 Kcal./mole more stable than cyclohexadienone. Thus, because of the small difference in energy between the ground state and the transition state, the barrier to rotation is weak and is not significant under our experimental conditions.

We therefore deduce that the structure of compounds of type 1 is described well by the two resonance hydrids (A) and (B). The formula (A) predominates in the ground state on the basis of the X-ray and infrared results (4), whereas the ready polarization of these compounds, in particular of the C(3') - C(4) bond, account well for the weak barrier to rotation about these bonds as observed from the NMR spectra.

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