Single-bond–No-bond Resonance and Valency Tautomerism in 1,2-Dithiole Derivatives

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The unique characteristics[1] of 3-thioacylmethylene-1,2-dithioles (I) have been variously attributed to single-bond–no-bond resonance [(Ia $\longleftrightarrow$ (Ib)],[2] to valency tautomerism [(Ia) $\rightleftharpoons$ (Ib)],[3] or to the presence of tetravalent sulphur,[4] as in structure (Ic). The results of recent *X*-ray diffraction studies[5] suggest, however, that no single one of these hypotheses can provide an adequate account of the molecular structure of compounds (I). In searching for related examples of tautomeric or mesomeric structures among compounds of the 1,2-dithiole series, we have investigated the synthesis and properties of 4-thioacyl-1,2-dithiole-3-thiones (II) and 7-thioacylbenzo-1,2-dithiolylium salts (V).

The 5-phenyl-4-thiobenzoyl compound (IIa) had previously been obtained[6] by the action of phosphorus pentasulphide (in boiling xylene) on the corresponding 4-benzoyl compound (IIIa)[6,7] and this method was found to be applicable† to other compounds of the same type. The ^{1}H

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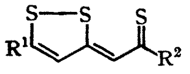
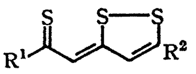
† In our hands, the method failed completely unless the phosphorus pentasulphide had been recrystallised twice (Soxhlet method) from carbon disulphide.

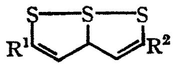
n.m.r. spectrum of the 4-thio-*p*-toluoyl-5-*p*-tolyl compound (IIb) contained two methyl singlets (τ 7·65 and 7·70 in CDCl$_3$) thus showing that the two aryl groups are not rendered equivalent by single-bond–no-bond resonance.



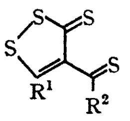
(Ia)



(Ib)

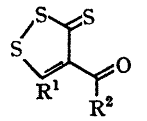


(Ic)



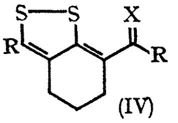
(II)

R^1	R^2
(a) Ph	Ph
(b) *p*-MeC$_6$H$_4$	*p*-MeC$_6$H$_4$
(c) Ph	*p*-MeC$_6$H$_4$

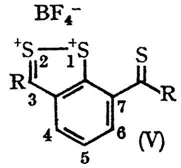


(III)

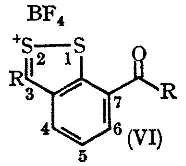
R^1	R^2
(d) *p*-MeC$_6$H$_4$	Ph
(e) Ph	*p*-MeOC$_6$H$_4$
(f) *p*-MeOC$_6$H$_4$	Ph



(IV)



(V)



(VI)

a: R=Ph
b: R=*p*-MeC$_6$H$_4$
c: R=*p*-MeO·C$_6$H$_4$
d: R=MeS

However, attempts to prepare the 4-thio-*p*-toluoyl-5-phenyl and 4-thiobenzoyl-5-*p*-tolyl compounds, (IIc) and (IId), gave identical products which, as shown by the presence of two methyl signals in their n.m.r. spectra, were mixtures of the two isomeric thioacyl compounds. Similar identical mixtures [of (IIe) and (IIf)] were obtained from the isomeric ketones, (IIIe) and (IIIf). We conclude that isomeric thioacyl compounds (II; $R^1 \neq R^2$) are interconvertible but that the tautomeric equilibrium is not rapidly established (on the n.m.r. time-scale) at room temperature.

Treatment of the thiones (IV; X = S)[8] and the ketones (IV; X = O) with triphenylmethyl fluoroborate gave, respectively, the thioacylbenzodithiolylium salts (V) and the corresponding acyl compounds (VI). The equivalence of the two groups (R) in the thioacyl cations (V) was shown by the coincidence of their ^{1}H n.m.r. signals in each of the compounds (Vb, c, and d). By way of contrast, the corresponding substituent groups in the acyl cations (VIb and c),‡ did not give coincident signals. The 4- and 6-protons, on the other hand, were magnetically equivalent in both types of cation, (V) and (VI), all of which gave spectra containing A$_2$B multiplets of the same general appearance ($\tau_A \sim 1·0$; $\tau_B \sim 1·7$; $J_{AB} \sim 8$Hz in CF$_3$·CO$_2$H).

The apparent symmetry of the cations (V) might be due either to resonance or to a rapidly-established tautomeric equilibrium between two equivalent structures of type (V). At the present time, however, we have insufficient evidence to enable a distinction to be made.

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‡ The salt (VId) has not been obtained.

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