The Detection of "*syn*" and "*anti*" Isomerism in Aromatic Sulphines

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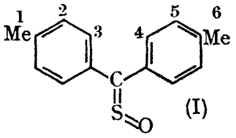
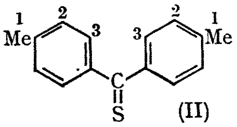
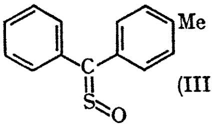
BY analysing the ^{1}H n.m.r. spectrum of (I)† it has been possible to show unambiguously that the C=S=O system in sulphines is a rigid nonlinear group which can thus allow the existence of "*syn*" and "*anti*" isomerism, as already observed for thioacyl chloride *S*-oxides[2] and for the thion-oxides of dithiocarboxylic esters.[3]



(I)



(II)



(III)

The 100 MHz. spectrum of a CCl$_4$ solution of (I) shows (Figure 1a) two different signals for the methyl groups with an intensity ratio 1 : 1. Measurements were carried out between room temperature and 80°. The two peaks not only differ in chemical shifts but also have different fine-structure patterns; the latter circumstance helped us in assigning the two bands to the corresponding "*syn*" and "*anti*" situations with respect to the C=S=O group.

The downfield signal ($\nu = 239{\cdot}8_5 \pm 0{\cdot}0_5$ relative to Me$_4$Si is a system with three bands within a range of $0{\cdot}3_0$ Hz. (Figure 1a). The upfield signal ($\nu = 237{\cdot}9_5 \pm 0{\cdot}0_5$) is a septet because of the coupling with the two pairs of protons

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† Prepared according to ref. (1), m.p. 90—91°.

in position 2 and 3 ($J_{1,2}$ $0{\cdot}6_5$, $J_{1,3}$ $0{\cdot}3_5$). The ratio of the two J values being approximately 2 : 1, the relative intensity of the multiplet is approximately 1 : 2 : 3 : 4 : 3 : 2 : 1.

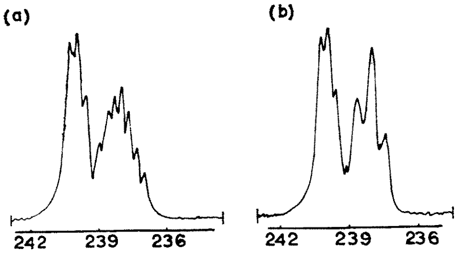

FIGURE 1

The assignment of these coupling constants has been tested by irradiating with a strong radiofrequency (Figure 1b) the region of the C-3 protons; the downfield triplet remains unchanged but the upfield septet becomes a triplet with J $0{\cdot}6_5$, the smaller coupling disappearing. The aromatic groups show different chemical-shift values depending on the situation with respect to the C=S=O group, and this explains the different patterns observed for the methyl groups, the latter being coupled with two different aromatic rings. Though a preliminary survey of the phenyl region of the spectrum leads to conclusions in agreement with those reached from the study of the aliphatic bands, its complicated spectral patterns require more sophisticated analysis to determine the exact chemical shifts and J values.

In order to assign the two bands of the methyl groups to a "*syn*" or to an "*anti*" situation with respect to the C=S=O of (I) the spectrum of the corresponding thioketone (II) has been recorded.

In the aliphatic region (Figure 2a) only one signal is observed, a septet with $\nu = 238{\cdot}0_5 \pm 0{\cdot}0_5$ and $J_{1,2}$ $0{\cdot}6_5$, $J_{1,3}$ $0{\cdot}3_5$. Again, by irradiating in the region of H-2 and H-3, respectively, the multiplet becomes either a septet with J $0{\cdot}6_5$ (Figure 2b), or a triplet with J $0{\cdot}3_5$ (Figure 2c).

It thus seems that the septet in the spectrum of compound (I) is due to a methyl group situated very similarly to the methyl group in (II), *i.e.*, "*anti*" with respect to the C=S=O group. The downfield triplet is therefore the signal of the *syn*-methyl.

These results suggest that in molecules like phenyl *p*-tolyl sulphine two isomers can, in principle, be obtained.

In fact the crude mixture from the peroxy-acid oxidation of the corresponding thioketone gave an n.m.r. spectrum whose aliphatic region is like that of Figure 1a; this means that both isomers are present in nearly 1 to 1 ratio. An attempt was therefore made to isolate one of them.

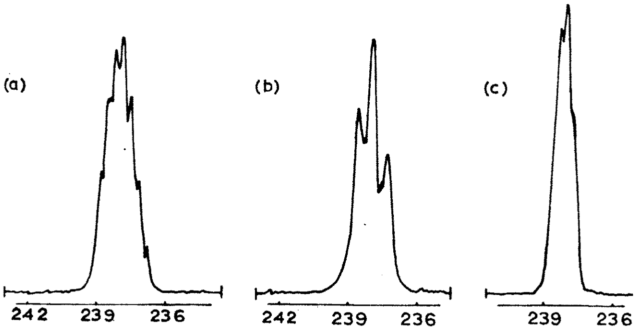

FIGURE 2

In Figure 3 the spectrum of the aliphatic region for the compound‡ m.p. 58—60° is reported; only one signal is observed for the methyl group, *i.e.* only one of the two isomers is present; since the spectrum is a triplet with $\nu = 240{\cdot}3_5 \pm 0{\cdot}0_5$ and the separation between the bands is $0{\cdot}3_0$ Hz., there seems little doubt that the *syn-p*-tolyl isomer (III) has been isolated.

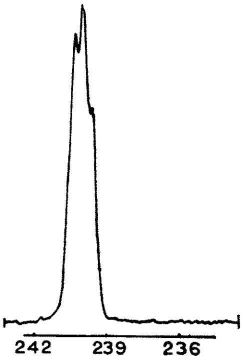

FIGURE 3

Further work is in progress to isolate also the "*anti*" isomer and to analyse completely the aromatic bands of the spectra.

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‡ This compound was purified by column chromatography on SiO_2 (eluent $C_6H_6 : Et_2O$ 1 : 1) and crystallized three times from petroleum. Correct elemental analysis and the expected i.r. spectrum were observed.

[1] B. Zwanenburg, L. Thijs, and J. Strating, *Rec. Trav. chim.*, 1967, **86**, 577.
[2] J. F. King and T. Durst, *Canad. J. Chem.*, 1966, **44**, 819.
[3] B. Zwanenburg, L. Thijs, and J. Strating, *Tetrahedron Letters*, 1967, 3453.