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CHEMICAL SHIFT NON-EQUIVALENCE OF DIASTEREOTOPIC GROUPS IN ALKYLSULPHINYL CHLORIDES

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In a recent communication[1], King and Beatson reported that 1-chloroethylsulphinyl chloride, at room temperature, shows an NMR spectrum typical of a mixture of two diastereoisomers due to the presence of two asymmetric centers, namely carbon and sulphur atoms. This seems to be the first reported evidence of optical stability for the SOCl group. This prompted us to communicate our unpublished results[2] for a series of simple alkylsulphinyl chlorides* in which the two X groups ought to be diastereotopic if the stability of SOCl group is comparable with that of the other sulphinyl derivatives[4] studied.

$R{-}CX_2{-}SOCl$

I) $X = CH_3$, $R = H$
II) $X = H$, $R = CH_3$
III) $X = H$, $R = C_6H_5$

We have observed non-equivalence of the CH_3/H groups in isopropyl- I and ethyl- II -sulphinyl chlorides. Non-equivalence is higher for the CH_3 groups than for the H atoms α with respect to the asymmetric center. The entity of non-equivalence is solvent and temperature dependent (see Tables 1 and 2) showing that conformational equilibria are also involved[5]. At present only the isopropyl derivative has been studied in detail, since the ethyl derivative has a more complicated pattern [the benzylsulphinyl chloride III is seen to have a singlet for the methylene protons in each solvent examined and, when dissolved in CS_2, also in the range of temperature 30°- -120°C. The same behaviour is also observed in trifluoroacetic acid ($\delta = 4.79$)].

At this stage it can be pointed out that the observed chemical shift non-equivalence indicates optical stability for the SOCl group[1].

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*) Prepared according to ref. (3).

TABLE 1 - Chemical shifts and coupling constants of isopropylsulphinyl chloride (I) in different solvents*

Solvent	δ_{CH_3} (A)	δ_{CH_3} (B)	Δ_{AB} (ppm)	δ_{CH}	J_{CH-CH_3}
$CDCl_3$	1.462	1.482	0.020	3.382	6.81
C_6D_6	0.951	0.983	0.032	2.623	6.98
CS_2	1.430	1.430	0.000	3.205	6.90
$(CD_3)_2CO$	1.450	1.450	0.000	3.540	6.98

*) NMR measurements were performed at 60 MHz on a Jeol instrument

TABLE 2 - Chemical shifts and coupling constants of isopropylsulphinyl chloride (I) in carbon disulphide solution at different temperatures

T°C	δ_{CH_3} (A)	δ_{CH_3} (B)	Δ_{AB} (ppm)	δ_{CH}	J_{CH-CH_3}
30	1.430	1.430	0.000	3.205	6.90
-10	1.348	1.362	0.014	3.223	6.89
-20	1.348	1.362	0.014	3.225	6.92
-40	1.344	1.362	0.018	3.236	6.85
-60	1.335	1.359	0.024	3.245	6.89
-80	1.329	1.359	0.030	3.248	6.83

This conclusion cannot be extended at present to the whole series of sulphinyl chlorides since the behaviour of the benzyl derivative might indicate that a general interpretation in this sense should not be given. However, we believe that conformational equilibria and a low intrinsic asymmetry must be at the origin of the unobserved non-equivalence in the methylene protons of benzylsulphinyl chloride, also in view of the fact that benzyl hydrogens are a less sensitive probe for the observation of magnetic non-equivalence than isopropyl methyls[6]. - "Consiglio Nazionale delle Ricerche" is thanked for financial support.

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