NMR Spectra of Methylene Protons in Benzyl Sulfites and Benzenesulfinate

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Abnormal splitting of the methylene proton signal in diethyl sulfite found by Finegold[1] could be due either to i) the non-equivalence of the two methylene groups, because of a) a different bond character of S–O linkages contributed differently with $\pi_{p,d}$- bonding orbital[1], b) geometrical asymmetry, or c) internal C–H ···O–S hydrogen bonding of one side of the ethyl groups with the other left intact, or to ii) the long-range spin-spin coupling effect. Waugh and Cotton[2] rejected all the above possibilities by finding the same phenomenon also in ethyl benzenesulfinate, and attributed it to the magnetic non-equivalence of two protons on a methylene group caused by neighbors of asymmetric center (S atom)[3]. Lately Kaplan and Roberts[4] have shown that the analysis of the spectra of diethyl sulfite as ABC_3 spin system leads to a good agreement with those observed. Thus, it seems to be a timely contribution to offer a conclusive experimental support for the computation results.

The syntheses and the physical properties of the samples will be reported later. Spectral measurement was carried out with a Varian model DP 60 NMR spectrometer at 60 Mc./sec. The samples were dissolved in carbon tetrachloride to give 10% solution, except the nitro-derivative for which the saturated solution in chloroform was employed. Cyclohexane (1%) added to the solvent served as an internal standard, the side band technique[5] being employed throughout the reading of the signals.

The methylene protons in these benzyl esters give a typical quartet signal of AB spin system[6] which can rigorously be solved to afford the $\nu_A - \nu_B$ and J_{AB} values in Table I. The skewness of the spectra of alkyl sulfites may be interpreted similarly.

Since $\nu_A - \nu_B$ is independent of the ring substituents in spite of the dependence of $(\delta_A + \delta_B)/2$ on them, it must be the S=O bond anisotropy that shifts a hydrogen signal to the lower applied magnetic field by the amount observed. Moreover, as $\nu_A - \nu_B$ is about 7 c.p.s. and is comparable with that in rather rigid ethylene sulfite[7], the most populating conformation of benzyl sulfites can be regarded as I and its residence time should be relatively long as suggested by the scarce temperature dependence of the signal. In benzyl benzenesulfinate, $\nu_A - \nu_B$ rises up to 31.38 c.p.s. In this case (II), H_B is suffering from the S=O bond anisotropy, while H_A is situated in the diamagnetic second field produced by the ring current of the benzene ring in the magnetic field[8], resulting in a large $\nu_A - \nu_B$ value.

TABLE I. METHYLENE PROTON RESONANCE OF BENZYL SULFITES AND BENZENESULFINATE MEASURED AT 60 Mc./sec.

$(X\cdot C_6H_4CH_2O)_2SO$ X	$(\delta_A+\delta_B)/2$ τ Value	$\nu_A-\nu_B$ c.p.s.	J_{AB} c.p.s.
p-NO_2	4.85	7.77	12.81
p-Cl	5.17	6.43	12.03
H	5.19	7.44	11.87
p-Me	5.22	7.23	11.78
p-MeO	5.24	6.90	11.57
PhS(=O)OCH_2Ph	5.34	31.38	11.37

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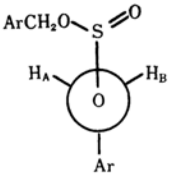

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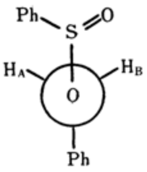

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