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TAUTOMERISM IN 3-BROMOTROPOLONE

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SOME time ago, the highly mobile tautomerism in tropolone was postulated by Dewer (1) to rationalize its remarkable stability and symmetric character.

Ia

Ib

Although the tautomers, having the identical structures Ia and Ib (R=H), contribute equally to the equilibrium in tropolone itself, substituents situated asymmetrically on the ring may shift the equilibrium in favor of one tautomer. Such a shift in equilibrium should be detectable. Recently, the existence of these tautomers, Ia and Ib (R=X) in 3-isopropyltropolone, as well as of those in 4-isopropyltropolone, has been suggested Ikegami (2) on the basis of Raman spectroscopy.

In the course of a general study on the n.m.r. spectra of troponoids

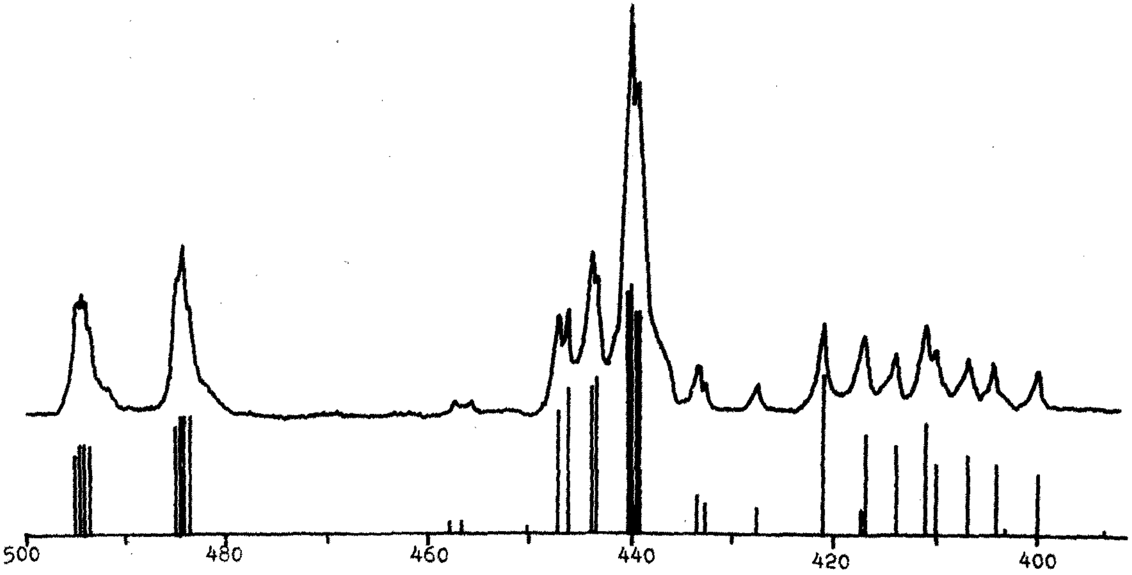

Fig. I Observed (top) and calculated (bottom) n.m.r. spectra of 3-bromotropolone.

(3), the spectrum of 3-bromotropolone was recorded (4) and was analysed as an ABCD system using Swalen's program (5) for an IBM 7090 electronic computor. The result is shown in Fig.I along with the spectrum. The chemical shifts and the coupling constants deduced are as follows: $\delta_{H4}=489.0_2$ cps, $\delta_{H5}=411.5_1$ cps, $\delta_{H6}=443.8_5$ cps, and $\delta_{H7}=439.9_7$ cps relative to internal tetramethylsilane, and $J_{45}=10.2_2$ cps, $J_{56}=9.6_5$ cps, $J_{67}=10.6_1$ cps, $J_{46}=0.9_5$, $J_{57}=1.2_0$ cps, and $J_{47}=0.2_1$ cps.

The spin-spin coupling constant (J) of the hydrogens attached to neighboring carbons can, according to McConnell (6), be expressed as the sum of the contribution (J^{π}) from the π-electrons and that (J^{σ}) transmitted through the σ-bonding electrons. The proportionality of J and the π-bond order (η) of the connecting carbons has also been derived theoretically (6) and has recently received experimental support (7), although these are disputable to some extent. Direct application of this principle to the coupling constants mentioned above, J_{45} and J_{67} being larger than J_{56}, suggests for the first time in troponoid compounds that the equilibrium in 3-bromotropolone (I, R=Br) is shifted towards Ib rather than to Ia, providing that the magnitude of J^{σ} stay constant in all carbon-carbon bonds concerned.

The results of our systematic study of the n.m.r. spectra of troponoid compounds will be published at a later date.

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