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CONFORMATIONAL STUDIES BY DYNAMIC NUCLEAR MAGNETIC RESONANCE PART XI¹. THE DETECTION OF RESTRICTED ROTATION IN 2-NN-DIMETHYLAMINOTHIAZOLES.

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Only in a few cases has restricted rotation of amino groups bonded to aromatic rings been observed²⁻⁷. We report here the detection of such an effect when the aromatic group is thiazole. The NMR signal (singlet), corresponding to the pairs of methyls in 2-NN-dimethylaminothiazole (I) that are isochronous at room temperature, is reversibly split into two equivalent lines at -130°C.

The same phenomenon has been also observed in the 5-bromo-(II) and 5-nitro-2-NN-dimethylaminothiazole (III).

This effect depends upon the restricted rotation around the Ar-N bond owing to the relatively large contribution to the double bond character arising from resonance contributors, such as (B) and (C) to structure (A)



Computer simulation⁸ of the line shape of (III) at five different temperatures afforded the activation parameters for the rotation of the dimethylamino group (see Table). As observed in many analogous cases⁹ the activation entropy (ΔS^{\ddagger}) is negligible within the experimental errors; therefore ΔG^{\ddagger} can be identified with ΔH^{\ddagger} . As a consequence the free enrgies of activation (ΔG^{\ddagger}) measured at the coalescence temperature¹⁰ for the thiazoles (I)-(III) can be safely used as a measure of the rotational barrier (Table).

The much larger ΔG^{\neq} value observed for the 5-nitro derivative (III) with respect to (I), indicates that the electron withdrawing capabilities of a substituent in the para-like position-5, greatly enhance the Ar-N double bond character (more than 50% in the case of the nitro group).

This outlines the importance of the resonance structure (C) in describing the electronic distribution of these derivatives.

Table

Chemical shift differences (δv), coalescence temperatures (t_C) and free energies of activation (ΔG^{\neq}) for the Ar-N rotation of I - III in CHF₂Cl at 60 MHz. In the case of III the following thermodynamic parameters of activation were also measured by total line shape analysis: $\Delta H^{\neq} = 11.80\pm0.9 \text{ kcal mol}^{-1}$, $E_a = 12.3\pm0.9 \text{ kcal mol}^{-1}$, $\Delta S^{\neq} = -3\pm4 \text{ cal mol}^{-1}K^{-1}$ and LogA = $= 12.5\pm0.9$

Compound	δ√(Hz.)	t _C (°C)	ΔG^{\neq} (kcal mol ⁻¹)
I	7.7 (at -131°)	-123.5	7.7±0.1
II	9.9 (at -131°)	-122	7.7±0.1
III	12.4 (at -80°)	-31.5	12.4±0.1

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