# CONFORMATIONAL STUDIES BY DYNAMIC NUCLEAR MAGNETIC RESONANCE PART XI․ THE DETECTION OF RESTRICTED ROTATION IN 2-NN-DIMETHYIAMINOTHIAZOLES. 

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Only in a few cases has restricted motation of amino groups bonded to aromatic rings been obser $\operatorname{ved}^{2-7}$. We report here the detection of such an effect when the aromatic group is Lhiazole. 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 $-130^{\circ} \mathrm{C}$.

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 simulation ${ }^{8}$ of the line shape of (III) at five different temperatures afforded the activation parameters for the rotation of the dimethylamino gnoup (see Table). As observed in many analogous cases ${ }^{9}$ the activation entropy ( $\Delta S^{\neq}$) is negligible within the experinental errors; therefore $\Delta G^{\neq}$can be identified with $\Delta H^{\neq}$. As a consequence the free enrgies of activation ( $\Delta G^{\neq}$) measured at the coalescence temperature ${ }^{10}$ for the thiazoles (I)-(III) can be safely used as a measure of the rotational barrier (Table).

The much larger $\Delta G^{\neq}$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 ( $\delta v$ ), coalescence temperatures ( $t_{C}$ ) and free energies of activation $\left(\Delta G^{\neq}\right.$) for the Ar-N rotation of I - III in $\mathrm{CHF}_{2} \mathrm{Cl}$ at 60 MHz . In the case of III the following thermodynamic parameters of activation were also measured by total line shape analysis: $\Delta \mathrm{H}^{\neq}=11.80 \pm 0.9 \mathrm{kcal} \mathrm{mol}{ }^{-1}, \mathrm{E}_{\mathrm{a}}=12.3 \pm 0.9 \mathrm{kcal} \mathrm{mol}^{-1}, \Delta \mathrm{~S}^{\neq}=-3 \pm 4 \mathrm{cal} \mathrm{mol}^{-1} \mathrm{~K}^{-1}$ and LogA $=$ $=12.5 \pm 0.9$

| Compound | $\delta V(\mathrm{~Hz})$. | $\mathrm{t}_{\mathrm{C}}\left({ }^{\circ} \mathrm{C}\right)$ | $\Delta G^{\neq}\left(\mathrm{kcal} \mathrm{mol}{ }^{-1}\right)$ |
| :--- | :---: | :---: | :---: |
| I | $7.7\left(\right.$ at $\left.-131^{\circ}\right)$ | -123.5 | $7.7 \pm 0.1$ |
| II | $9.9\left(\right.$ at $\left.-131^{\circ}\right)$ | -122 | $7.7 \pm 0.1$ |
| III | $12.4\left(\right.$ at $\left.-80^{\circ}\right)$ | -31.5 | $12.4 \pm 0.1$ |

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