Importance of Transition-state Steric Strain in the Nitrogen Inversion of Hydrazines

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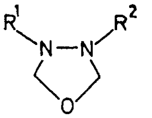
Summary Free energies of inversion for *NN′*-disubstituted 1,2,4-oxadiazolidines increase markedly with the bulk of the *N*-substituents.

In 1971, we postulated that the interconversion between stable conformers of cyclic and acyclic tetra-alkylhydrazines involved two types of *inversion* barriers, differentiated according to whether substituents passed each other in the transition state.[1] Strain between substituents which became eclipsed in the transition state was held to contribute significantly to the energy of such inversion barriers.[1] These concepts have been used to explain the conformational phenomena of *inter alia* hexahydropyridazines[2] and hexahydrotetrazines.[3]

We now report variable temperature n.m.r. data which directly demonstrate the dramatic effect on the energy barrier to inversion of increasing the steric strain between passing substituents and thus support the above explana-



(1) $R^1 = R^2 = Me$
(2) $R^1 = R^2 = Et$
(3) $R^1 = R^2 = CH_2Ph$
(4) $R^1 = R^2 = Pr^i$
(5) $R^1 = R^2 = Bu^t$
(6) $R^1 = Me, R^2 = Pr^i$

(7) (8)

TABLE

Coalescence temperatures and $\Delta G^{\ddagger}$ from n.m.r. measurements at 100 MHz for 3,4-disubstituted 1,3,4-oxadiazolidines.

Compound	*N*-Substituents	Temperature/K	$\Delta G^{\ddagger}$/kcal mol^{-1}
(**1**)	Me	212	10·6[a]
(**2**)	Et	242	12·0[b]
(**3**)	CH_2Ph	235	12·0[a]
(**4**)	Pr^i	384	19·4[a]
(**4**)	Pr^i	383	19·0[c]
(**5**)	Bu^t	>439	>21[c]
(**6**)	Me	283	14·6[a]
	Pr^i	265	13·6[a]

[a] Solvent: $CDCl_3$–$CFCl_3$. [b] Solvent: $CDCl_3$. [c] Solvent: $C_6H_2Cl_4$.

tions. Variable temperature n.m.r. data for the 1,3,4-oxadiazolidines (**1**)—(**6**) are consistent with slowing of the inversion process (**7**) → (**8**); the signal for the CH_2 groups of (**1**), for example, becomes an AB quartet as the temperature is lowered. The coalescence temperatures and $\Delta G^{\ddagger}$ values vary widely (Table). The largest values occur for the di-t-butyl derivative (**5**), and the smallest for the dimethyl compound (**1**) with the diethyl (**2**), dibenzyl (**3**), and the methylisopropyl compounds (**6**) occupying an intermediate place. This is good evidence that steric hindrance between eclipsed, or nearly eclipsed *N*-substituents in the transition state is a crucial factor in determining the size of energy barriers for the *N*-inversion of substituted hydrazines.

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