Barriers to Nitrogen Inversion in Acyclic Chloramines

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Summary The barriers to nitrogen inversion in some acyclic *N*-chlorodialkylamines have been measured by dynamic n.m.r. spectroscopy ($\Delta G^{\ddagger} = 9{\cdot}5$—$10{\cdot}5$ kcal mol^{-1}).

CONSIDERABLE information is available regarding the conformational stability of tervalent nitrogen in cyclic systems, particularly in aziridines where the nitrogen atom is constrained in a three-membered ring.[1] However, surprisingly little is known regarding the barriers to nitrogen inversion in acyclic compounds. We now report measurement of the barrier to inversion of the nitrogen pyramid in some acyclic *N*-chlorodialkylamines (**1**—**3**) using the dynamic n.m.r. method.[1c]

The inversion process (**4**a) $\rightleftharpoons$ (**4**b) was monitored by observing the n.m.r. signals of the geminal protons attached to the prochiral methylene carbon atoms. At $-90°$ the methylene protons of (**1**), (**2**), and (**3**) were anisochronous, indicating the absence of a molecular σ-plane (on the n.m.r. time-scale) containing the prochiral centres. This observation shows that the topomerisation[1b] process (**4**a) $\rightleftharpoons$ (**4**b) is slow on the n.m.r. time-scale. On raising the temperature the ABM_3 (in **1**), AB (in **2**), and ABM (in **3**) systems collapsed to A_2M_3, A_2, and A_2M systems, respectively, as rapid nitrogen inversion renders the diastereotopic methylene protons enantiotopic on the n.m.r. time-scale and hence isochronous.[2] The exchange rates at coalescence and the derived free energies of activation are presented in Table 1.

$(RCH_2)_2NCl$

(**1**; R = Me), (**2**; R = Ph), (**3**; R = Pr^i)

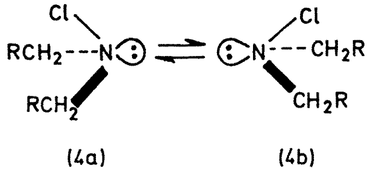

TABLE 1

N.m.r. data (at 100 *MHz) and free energy barriers* ($\Delta G^{\ddagger}$) *for nitrogen inversion in* N-*chlorodialkylamines*

Compound	Solvent	$\Delta\nu$[b] (Hz)	J_{AB} (Hz)	T_C (°)	k[c] (s^{-1})	$\Delta G^{\ddagger}$ at T_C (kcal mol^{-1})
(**1**)[a]	CS_2	13·0	13·0	-71	36	$10{\cdot}2 \pm 0{\cdot}2$
(**1**)[a]	CD_3OD	23·9	13·1	-61	65	$10{\cdot}5 \pm 0{\cdot}2$
(**2**)	$CHCl_2F$	27·0	13·4	$-71{\cdot}5$	71	$9{\cdot}9 \pm 0{\cdot}1$
(**2**)	CD_3OD	32·5	13·4	-74	78	$9{\cdot}8 \pm 0{\cdot}1$
(**3**)	$CHCl_2F$	22[d]	12·3	*ca.* -81	*ca.* 80[d]	$9{\cdot}5 \pm 0{\cdot}3$
(**3**)	CD_3OD	25[d]	12·3	*ca.* -80	*ca.* 80[d]	$9{\cdot}5 \pm 0{\cdot}3$

[a] Spectra obtained with decoupling of the methyl signal.

[b] Chemical shift nonequivalence of the methylene protons at the coalescence temperature (T_C) determined by adjusting the pre-exchange value to afford the optimum fit between experimental and calculated spectra.

[c] Exchange rates at coalescence of the AB system were computed using a programme which extracts the exchange rate directly from the digitised experimental spectrum; see J. Jonas, A. Allerhand, and H. S. Gutowsky, *J. Chem. Phys.*, 1965, **42**, 3396.

[d] Approximate analysis.

Inspection of Table 1 reveals a small decrease in $\Delta G^{\ddagger}$ with increasing bulk of the alkyl substituents (Et < $PhCH_2$ < Bu^i) in consonance with the general view that the planar transition state for nitrogen inversion is less hindered than the pyramidal ground state. The barriers determined in methanol are essentially unchanged from those obtained in less polar solvents. The literature is somewhat conflicting on the effect of solvent on the barrier to nitrogen inversion. Griffith and Roberts[3] have reported that the barrier to nitrogen inversion in *N*-benzyl-*NO*-dimethylhydroxylamine is considerably reduced in polar solvents (*e.g.* methanol).† However other workers[4,5] have suggested that the barrier to nitrogen inversion is enhanced in hydroxylic solvents such as methanol, owing to hydrogen bonding of the solvent to the nitrogen lone-pair electrons. The absence of the latter effect in (**1**), (**2**), and (**3**) may be attributed to the low basicity of the chloramines.

The barrier to nitrogen inversion in (**2**) may be compared with the recently reported barriers in dibenzylmethylamine, 1,1-dibenzylhydrazine, and *NN*-dibenzylhydroxylamine (Table 2).‡ The $\Delta G^{\ddagger}$ values in Table 2 roughly parallel the inductive order of the substituent (X) rather than the order of increasing number of lone-pair electrons. However this observation does not negate the view[8] that repulsive interactions between non-bonding electrons on adjacent heteroatoms are mainly responsible for the enhanced inversion barriers, since chlorine is a second-row element and may have considerably different electron repulsions than nitrogen or oxygen. Alternatively, $p\pi$–$d\pi$ bonding between the nitrogen lone pair and vacant chlorine orbitals may decrease the inversion barrier in the chloramines.

TABLE 2

Free energies of activation ($\Delta G^{\ddagger}$) *for nitrogen inversion in* $(PhCH_2)_2NX$

X	Solvent	$\Delta G^{\ddagger a}$ (kcal mol^{-1})	$(\Delta G_X{}^{\ddagger} - \Delta G_{Me}{}^{\ddagger})^d$
Me	$CH_2{=}CHCl$	6·7[b]	——
NH_2	$CHCl_2F$–CCl_2F_2	8·0[b]	1·3
Cl	$CHCl_2F$	9·9	3·2
OH	$CDCl_3$	12·8[c]	6·1

[a] The $\Delta G^{\ddagger}$ values were obtained at various temperatures, but a comparison is still valid as $\Delta S^{\ddagger}$ for nitrogen inversion is very small (see ref. 1a, c).
[b] Value taken from ref. 6.
[c] Value taken from ref. 7.
[d] Values (in kcal mol^{-1}) refer to the effect on the inversion barrier due to replacement of a methyl group with group (X).

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† Fletcher and Sutherland[7] have recently reported that methanol has only a very small effect on $\Delta G^{\ddagger}$ for nitrogen inversion in a series of related hydroxylamines. It therefore seems possible that the absence of signal splitting in *N*-benzyl-*NO*-dimethylhydroxylamine[3] down to −70° in methanol resulted from accidental chemical shift equivalence of the CH_2 protons rather than a very low nversion barrier.

‡ Cowley *et. al.* and Raban *et al.*[9] have pointed out that the barriers measured in hydroxylamines may refer to torsion around the N-O bond rather than nitrogen inversion; however Fletcher and Sutherland[7] have recently presented evidence that this is not the case.

[1] For recent reviews see: (a) A. Rauk, L. C. Allen, and K. Mislow, *Angew. Chem. Internat. Edn.*, 1970, **9**, 400; (b) H. Kessler, *ibid.*, p. 219; (c) G. Binsch, *Topics Stereochem.*, 1968, **3**, 97.
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