Hindered Nitrogen Inversion in *N*-Halogenoaziridines and in *N*-Halogenoazetidines†

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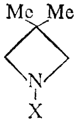
HINDERED nitrogen inversion has been studied by n.m.r. spectroscopy in various compounds containing hetero-atoms (O, N, S, P) adjacent to the nitrogen atom[1–5] and high barriers to inversion have been observed in many cases. Even though *N*-halogeno-amines have been included in some studies,[1,6] no barriers to inversion have yet been reported.

We give here a preliminary account of our study of nitrogen inversion in *N*-halogeno-amines. This also represents the first study of hindered nitrogen inversion in azetidines.[7] The *N*-halogeno-amines (II) and (III), (VI) and (VII), and (X) and (XI) have been prepared by treatment of the amines (I), (IV), and (VIII)[8] with a solution of the corresponding hypohalite.[9] The n.m.r. spectrum of (II) has been reported to be a single line at 20 MHz. operating frequency and rapid nitrogen inversion has been suggested.[6] However it seemed likely[4] that the single line was due to a small chemical-shift difference between the two types of protons of the slowly inverting system. Indeed at 60 MHz. and at 100 MHz. we observed an AA'BB' pattern (at *ca.* 2·2 p.p.m.) for the $CH_2{\cdot}CH_2$ protons of compound (II) at 30°. The 60 MHz. spectrum of compound (III) consisted, however, of a single line (at 2·06 p.p.m.) probably again because of very small chemical-shift differences. That this is the case follows from the spectra of (VI) and (VII) at 30°, which *both* contain two singlets for the CH_3 groups and an AB pattern for the CH_2 protons. On heating, these products decompose rapidly. However it was possible to establish that at 180° and 140° for compounds (VI) and (VII), respectively, the various signals were still present in the spectrum (together with decomposition products) and no coalescence had yet occurred.

(I) X = H
(II) X = Cl
(III) X = Br

(IV) X = H
(V) X = Me
(VI) X = Cl
(VII) X = Br



(VIII) X = H
(IX) X = Me
(X) X = Cl
(XI) X = Br

The 60 MHz. spectra of compounds (X) and (XI) at 30° consist of two singlets (due to the CH_3 and CH_2 protons).

On cooling, the CH_3 singlet in the spectrum of (X) splits into a doublet, while the CH_2 singlet changes into an AA'BB' pattern. In the case of compound (XI) one also observes a doublet for the

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† Previous paper in this series: J. E. Anderson and J. M. Lehn, *Tetrahedron*, in the press.
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TABLE

Spectral data and $\Delta G_c^\ddagger$ *values*[a]

Compound and solvent	Protons	Signals (temperature) at δ in p.p.m.	Δν (Hz.)	J (Hz.)	T_c	$\Delta G_c^\ddagger$ (kcal./mole)
(VI) HCB[b]	CH_3	two singlets (33°) at 1·15 (3H) and 1·47 p.p.m. (3H)	19·5	—	>180°	>23·5
	CH_2	AB pattern (33°) at 1·93 p.p.m. (2H)	16·5	2·6	—	—
(VII) HCB[b]	CH_3	two singlets (33°) at 1·17 (3H) and 1·47 p.p.m. (3H)	19·2	—	>140°	>21·3
	CH_2	AB pattern (33°) at 1·87 p.p.m. (2H)	18·1	3·1	—	—
(IX)	CH_3	singlet (33°) at 1·15 p.p.m. (6H)	—	—	—	—
$CFCl_3$		two singlets (−110°) at 1·03 (3H) and 1·28 p.p.m. (3H)	14·5	—	−98±3°	8·85
	CH_2	singlet (33°) at 2·75 p.p.m. (4H)	—	—	—	—
		AA′BB′ (−110°) at 2·75 p.p.m. (4H)[c]	31·7	5·8	−93±3°	8·5
(X)	CH_3	singlet (33°) at 1·20 p.p.m. (6H)	—	—	—	—
$CFCl_3$		two singlets (−77°) at 1·18 (3H) and 1·28 p.p.m. (3H)	5·9	—	−54±2°	11·5
	CH_2	singlet (33°) at 3·50 p.p.m. (4H)	—	—	—	—
		AA′BB′ (−77°) at 3·52 p.p.m. (4H)[c]	8·9	7·6	−46±3°	11·4
(X) CH_2Cl_2	CH_3	two singlets (−76°) at 1·17 (3H) and 1·27 p.p.m. (3H)	5·8	—	−47±2°	11·9
	CH_2	AA′BB′ (−76°)+ at 3·63 p.p.m. (4H)[c]	7·5	7·5	−43±2°	11·6
(XI)	CH_3	singlet (33°) at 1·23 p.p.m. (6H)	—	—	—	—
CH_2Cl_2		two singlets (−71°) at 1·19 (3H) and 1·26 p.p.m. (3H)	4·8	—	−56±2°	11·5
	CH_2	singlet (33°) at 3·68 p.p.m. (4H)	—	—	—	—
		singlet (−71°) at 3·68 p.p.m. (4H)	—	—	—	—

[a] Measurements done at 60 MHz.Varian A-60 spectrometer.

[b] HCB = hexachlorobutadiene.

[c] Data and results obtained by treating the AA′BB′ pattern as an AB system. These values are therefore less accurate.

CH_3 groups at −76° but the CH_2 signal remains a singlet.

The spectrum of the amine (IX) at 30° contains three singlets due to the CH_2, N-CH_3, and C-CH_3 protons. At *ca.* −110° one observes an ill-resolved AB pattern (in fact, presumably an AA′BB′ system) for the CH_2 protons, a singlet for the N-CH_3 protons and a doublet for the C-CH_3 groups.

The spectral parameters at various temperatures are described in the Table. Furthermore, using these data and the coalescence temperatures, T_c, for the various signals the free energies of activation $\Delta G_c^\ddagger$ at T_c have been calculated by means of the usual equations.[10] The values of T_c and $\Delta G_c^\ddagger$ are also given in the Table.

These results show that in the *N*-halogeno-amines (VI) and (VII) [and therefore also in (II) and in (III)] nitrogen inversion is very slow at 30° and that the inversion barrier (as measured by $\Delta G_c^\ddagger$) is very high (see Table). In comparison, a $\Delta G_c^\ddagger$ value of *ca.* 20·5 kcal./mole at +130° may be calculated for the *N*-methyl-amine (V) (in CCl_4) from literature results;[11] the *N*-methyl-azetidine derivative (IX) has a $\Delta G^\ddagger$ value of 8·8 kcal./mole at −98°. The *N*-halogeno-derivatives show appreciably higher $\Delta G^\ddagger$ values: 11·5 kcal./mole at −54° for (X) and 11·5 kcal./mole at −56° for (XI).

In these compounds the four-membered ring is very probably puckered, as in bromocyclobutane for instance;[12] however, the ring-puckering barrier is very small (*ca.* 0·3 kcal./mole for bromocyclobutane[12]), so that the hindered inversion at the nitrogen centre is accompanied by very fast ring inversion.

It thus appears§ that the nitrogen inversion barriers are appreciably ***higher*** for *N*-chloro- and for *N*-bromo-amines than for the corresponding *N*-methyl compounds. The effect of the halogens is to ***increase*** the barrier, as has also been observed for other hetero-atoms.[1–5]

If the physical origin of the nitrogen inversion barrier resides in a 2*s* → 2*p* electronic transfer as a thoeretical study of ammonia and of ethyleneimine

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§ Assuming that there is not a very large entropy of activation term which might cancel the variations in $\Delta G^\ddagger$ so as to give similar $\Delta H^\ddagger$ values for the various compounds.

(I) seems to indicate,[13] it follows that, in amines with N–X (X = hetero-atom) bonds¶ an even more important $2s \rightarrow 2p$ transfer of electron density is taking place on going from the pyramidal ground state to the transition state. This point is being studied. A complete line-shape analysis of the temperature-dependent spectra is also in progress.

Note added in proof: D. Felix and A. Eschenmoser (*Angew. Chem.*, in the press) have recently succeeded in isolating the two *N*-invertomers of 7-aza-7-chlorobicyclo[4,1,0]heptane.

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¶ It seems that fast nitrogen inversion is taking place in perfluoropiperidine (L. W. Reeves and E. J. Wells, *Discuss. Faraday Soc.*, 1962, **34**, 177). In this case other factors may play an important role.

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[7] Studies of nitrogen inversion in four-membered-ring compounds containing two hetero-atoms (diazetidinones, oxazetidines) have been reported recently (see refs. 2 and 5). Changes in the spectrum of *N*-ethylazetidine at very low temperatures have been noticed: A. T. Bottini and J. D. Roberts, *J. Amer. Chem. Soc.*, 1958, **80**, 5203.

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[9] A. F. Graefe and R. E. Meyer, *J. Amer. Chem. Soc.*, 1958, **80**, 3939.

[10] See, for instance, previous papers in this series and references therein.

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