Non-equivalence in *NO*-Dialkyl-*N*-aralkylhydroxylamines: the N–O Rotation *versus* *N*-Inversion Controversy

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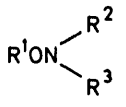
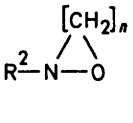
Variable temperature ^1H and ^{13}C n.m.r. spectra of *N*-benzyl-*NO*-dimethyl- and *NO*-dimethyl-*N*-(1-arylethyl)-hydroxylamines in deuteriotoluene are reported. The results are interpreted in terms of *N*-inversion rather than N–O rotation as the rate-limiting process governing the observation of non-equivalence.

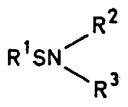
THE phenomenon of non-equivalence in acyclic (1) or cyclic (2) hydroxylamines and in the related sulphenamides (3) and (4) has attracted attention for many years.[1-3] In compounds of types (1), (3), and (4), both



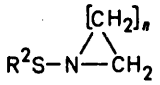
(1)



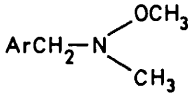
(2) $n = 1-4$



(3)

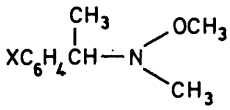


(4) $n = 1-4$



(5)

a; Ar = 2,6-$Cl_2C_6H_3$
b; Ar = *o*-ClC_6H_4
c; Ar = *o*-$CH_3C_6H_4$
d; Ar = *p*-$NO_2C_6H_4$
e; Ar = *p*-ClC_6H_4
f; Ar = β-$C_{10}H_7$
g; Ar = C_6H_5
h; Ar = *p*-$CH_3OC_6H_4$



(6)

a; X = *p*-CH_3O
b; X = H
c; X = *p*-NO_2

nitrogen inversion and N–O (or N–S) rotation † are necessary for diastereotopic protons (such as those of the methylene group when R^2 = benzyl) to become equivalent.[4] In consequence there has been much discussion as to whether nitrogen inversion or N–O or N–S rotation is the rate-limiting process from which non-equivalence originates.

Compounds of types (3) and (4) have been investigated by a number of workers and, except for the *N*-alkyl thioaziridines, the accumulated evidence points strongly towards rotation about the S–N bond as the high energy process.[5-10] For the majority of cyclic hydroxylamines (2) the general consensus indicates *N*-inversion as the origin of non-equivalence[3,11-13] and Roberts and Griffiths arrived at the same conclusions[14,15] for the acyclic hydroxylamines. Raban and Kenney however, preferred the opposite interpretation for (1),[4] a view which was subsequently contested by Sutherland,[16] but supported by Walter and Schaumann.[17] The object of the work described below was therefore to try to resolve this rotation–inversion dichotomy by introducing appropriate substituents into the phenyl rings of acyclic *N*-benzyl- (5a—h) and *N*-1-phenylethyl-hydroxylamines (6a—c).

RESULTS AND DISCUSSION

(i) *N-Aralkyl-NO-dimethylhydroxylamines* (5).—The ^1H n.m.r. spectra of (5) at room temperature in deuteriotoluene showed singlets for the *N*-methyl, *O*-methyl, and

TABLE 1

90 MHz ^1H N.m.r. spectra of (5a—h) in $C_6D_5CD_3$ at 30° and of the methylene protons of (5a—h) at −60°

Compound	δ					CH_2 at −60°	
	NCH_3	OCH_3	CH_2	Aryl	X	$\Delta\nu_{AB}$/Hz	J_{AB}/Hz
(5a)	2.68	3.38	4.05	7.2 (m)		42.5	12.6
(5b)	2.65	3.38	3.90	7.35 (m)		30.0	13.5
(5c)	2.55	3.25	3.75	7.15 (m)	2.40	42.9	12.3
(5d)	2.65	3.35	3.85	7.85 (q)		21.8	13.8
(5e)	2.60	3.38	3.70	7.30 (s)		26.6	12.3
(5f)	2.65	3.35	3.95	7.57 (m)		31.3	12.6
(5g)	2.60	3.35	3.75	7.30 (s)		29.1	12.8
(5h)	2.60	3.35	3.70	7.55 (q)	3.80	29.9	12.4

N-methylene protons at δ *ca.* 2.6, 3.3, and 3.8, respectively, together with signals for the aryl protons and any absorptions associated with the aryl substituents (see Table 1). As the temperature was lowered, the signal

† Equivalent to inversion at oxygen or sulphur.

[1] M. van Gorkham and G. E. Hall, *Quart. Rev.*, 1968, **22**, 14.
[2] A. Rauk, L. C. Allen, and K. Mislow, *Angew. Chem. Internat. Edn.*, 1970, **9**, 400.
[3] (*a*) I. O. Sutherland, *Ann. Reports NMR Spectroscopy*, 1971, **4**, 71; (*b*) J. B. Lambert, *Topics Stereochem.*, 1971, **6**, 19; (*c*) J. M. Lehn, *Fortschritte Chem. Forsche*, 1970, **15**, 111.
[4] M. Raban and G. W. J. Kenney, jun., *Tetrahedron Letters*, 1969, 1295.
[5] J. M. Lehn and J. Wagner, *Chem. Comm.*, 1968, 1298.
[6] M. Raban, F. B. Jones, jun., and G. W. J. Kenney, jun., *Tetrahedron Letters*, 1968, 5055.
[7] M. Raban and F. B. Jones, jun., *J. Amer. Chem. Soc.*, 1969, **91**, 2180.
[8] M. Raban, G. W. J. Kenney, jun., and F. B. Jones, jun., *J. Amer. Chem. Soc.*, 1969, **91**, 6677.
[9] M. Raban and F. B. Jones, jun., *J. Amer. Chem. Soc.*, 1971, **93**, 2692.
[10] M. Raban, E. H. Carlson, S. K. Lauderback, J. M. Moldowan, and F. B. Jones, jun., *J. Amer. Chem. Soc.*, 1972, **94**, 2738.
[11] (*a*) W. D. Emmons, *J. Amer. Chem. Soc.*, 1957, **79**, 5739; (*b*) F. Montanari, I. Moretti, and G. Torre, *Chem. Comm.*, 1968, 1694.
[12] J. Lee and K. G. Orrell, *Trans. Faraday Soc.*, 1965, **61**, 2342.
[13] (*a*) F. G. Riddell, J. M. Lehn, and J. Wagner, *Chem. Comm.*, 1968, 1403; (*b*) D. L. Griffiths and B. L. Olson, *ibid.*, p. 1682; (*c*) M. Raban, F. B. Jones, jun., E. H. Carlson, E. Banucci, and N. A. Le Bel, *J. Org. Chem.*, 1970, **35**, 1496.
[14] D. L. Griffiths and J. D. Roberts, *J. Amer. Chem. Soc.*, 1965, **87**, 4089.
[15] D. L. Griffiths, B. L. Olson, and J. D. Roberts, *J. Amer. Chem. Soc.*, 1971, **13**, 1648.
[16] J. R. Fletcher and I. O. Sutherland, *Chem. Comm.*, 1970, 687.
[17] W. Walter and E. Schaumann, *Annalen*, 1971, **747**, 191.

due to the methylene protons broadened and finally became an AB quartet. Since no further changes were observed below −60°, the spectra at this temperature were taken as representing the limit of exchange and were therefore used for the calculation of $\Delta\nu_{AB}$ and J_{AB}.* The rate constants at coalescence k_c were then calculated according to equation (1).[3,18] By assuming

$$k_c = \pi(\Delta\nu_{AB}^2 + 6J_{AB}^2)^{\frac{1}{2}}/\sqrt{2} \qquad (1)$$

that the entropy of activation for the exchange was zero (see ref. 3*c*, p. 322) E_a was derived from $\Delta G^\ddagger$ and this enabled calculation of rate constants for each compound at an arbitrary temperature of −20°, in the middle of the range of coalescence temperatures (T_c). Values of T_c, k_c, k_{-20}, $\Delta G^\ddagger$ at T_c, and E_a are recorded in Table 2.

TABLE 2

Values of T_c, k_c, $\Delta G^\ddagger$, E_a,* and k_{-20} for (5a—h) in $C_6D_5CD_3$

Compound	T_c/°C (±1)	k_c/s^{-1}	$\Delta G^\ddagger/T_c$ kcal mol^{-1}	E_a/ kcal mol^{-1}	k_{-20}/ s^{-1}
(5a)	−28.3	116.7	11.93	12.42	277
(5b)	−29.3	99.2	11.96	12.46	263
(5c)	−16.0	116.5	12.55	13.05	77.7
(5d)	−20.2	89.4	12.47	12.98	89.4
(5e)	−17.3	90.5	12.62	13.13	67.3
(5f)	−16.3	97.6	12.63	13.14	66.3
(5g)	−15.7	95.0	12.67	13.19	60.5
(5h)	−12.2	94.7	12.85	13.38	41.7

* Calculated from the relationship $E_a = \Delta H^\ddagger + RT$ assuming $\Delta H^\ddagger = \Delta G^\ddagger$ *i.e.* $\Delta S^\ddagger = 0$.

It was then only necessary to provide an experimental justification for the assumption that $\Delta S^\ddagger \approx 0$ for each exchange process. This was accomplished by a computer generated simulation of the methylene signal for (5h) between 0 and −30°. The experimental results are shown in Table 3 and a linear regression analysis of

TABLE 3

Rate constants for the exchange of the methylene protons of (5h) in $C_6D_5CD_3$ at 90 MHz [a]

T/K (±1)	273	268	263	261	259	257	255	253	243
k/s^{-1}	373	193	122	102	84.0	68.0	56.5	40.9 [b]	14.0 [c]

[a] Unless stated otherwise, $\Delta\nu_{AB}$ 30.0, J_{AB} 13.0, and $W_{\frac{1}{2}}$ 2.4 Hz. [b] $\Delta\nu_{AB}$ 29.0 Hz. [c] $\Delta\nu_{AB}$ = 29.2 Hz.

the data gave equation (2) (r 0.9983) from which a value of E_a 59.5 ± 1.3 kJ mol^{-1} was calculated. A plot of ln

$$\ln k = -7.12 \pm 0.16(1/T) + 32.6 \qquad (2)$$

k against $1/T$ with error limits of ±1 K in T gave a more realistic value of E_a of 59.5 ± 4.2 kJ mol^{-1}. This leads to a value of $\Delta H^\ddagger$ of 57.0 ± 4.2 kJ mol,$^{-1}$ which compares with $\Delta G^\ddagger$ (at T_c) 53.2 kJ mol^{-1}. Hence the assumption of $\Delta S^\ddagger$ *ca.* 0 appears to be valid.

(ii) N-(1-*Arylethyl*)-NO-*dimethylhydroxylamines* (6). A more rigorous test of this hypothesis was provided by a line shape analysis of the ^{1}H and ^{13}C n.m.r. data for the coalescence of the *N*-methyl group in (6b).[18] This enabled data to be collected over a temperature range of 40° and hence minimised the errors arising from the lack of precision in measuring the temperature.

At room temperature in deuteriotoluene the ^{1}H n.m.r. spectra of (6) consisted of a doublet for the *C*-methyl protons (at δ *ca.* 1.4), singlets for the N–CH_3 and O–CH_3 protons (at δ 2.4 and 3.4, respectively), and a quartet for the methine proton (δ *ca.* 3.6), together with signals for the aromatic ring and the *p*-methoxy-substituent in (6c). The ^{13}C spectra consisted of singlets for the *C*-, *N*-, and *O*-methyl carbons together with signals for the methine and aromatic carbons (see Table 4). On cooling, the

TABLE 4

^{1}H and ^{13}C n.m.r. spectra of (6a—c) in $C_6D_5CD_3$

(A) At 30 °C

	δ					
Compound	C-Me	N-Me	O-Me	CH	Ar	X
(i) ^{1}H N.m.r.						
(6a)	1.40 (d)	2.43	3.44	3.45	7.00 (q)	3.75
(6b)	1.33 (d)	2.41	3.40	3.60	7.25	
(6c)	1.38 (d)	2.50	3.37	3.70	7.85 (q)	
(ii) ^{13}C N.m.r.						
(6a)			Not recorded			
(6b)	20.6	42.7	60.2	69.0	*a*	
(6c)	20.0	42.3	60.0	68.0	*b*	

(B) At −60 °C

	Δν/Hz				T_c/K			
Compound	C-Me	N-Me	OMe	CH	CMe	NMe	OMe	CH
(i) ^{1}H N.m.r.								
(6a)	29.3	4.3	23.3		263	245	261	
(6b)	37.6	5.9	31.1		257	250	257	
(6c)	38.2	15.0	34.6		253	247	256	
(ii) ^{13}C N.m.r.								
(6b)	34.2	34.6	18.3	41.5	265	265	255	267
(6c)	*c*	29.3	17.9	28.5	*c*	250	245	250

[a] Four signals at *ca.* 127 p.p.m. [b] Four signals at 123, 128, 147, and 151 p.p.m. [c] Obscured by signal from methyl groups of solvent.

^{1}H and ^{13}C n.m.r. spectra broadened until at −60° (again taken as the limit of exchange) the ^{1}H n.m.r. spectrum showed a doublet of doublets for the *C*-methyl group, two doublets for the N–CH_3 and O–CH_3 protons (population ratio in each doublet *ca.* 1 : 2), and a doublet of quartets for the methine proton which was partially obscured by the O–CH_3 resonance. In the ^{13}C spectra each of the singlets for the *C*-, *N*-, and *O*-methyl carbons and the singlet for the methine carbon also split into unequally populated doublets (see Table 4). The *N*-methyl group was selected for simulation in both the ^{1}H and ^{13}C n.m.r. since in the ^{1}H spectra it provided a simple, two-site exchange problem with no coupling to be considered and the signal was entirely clear of any other peaks in the spectrum.

The results of the computer simulation are recorded in Table 5. A linear regression analysis of ln k against $1/T$ gave equation (3) (r 0.998 1) from which a value of

$$\ln k = -7.18 \pm 0.16(1/T) + 32.5 \qquad (3)$$

E_a of 59.5 ± 1.3 kJ mol^{-1} was derived. A plot of ln k against $1/T$ including the errors in T (± 1°) gives a

* $\Delta\nu_{AB}$ and J_{AB} did not vary significantly between −50 and −70° and $W_{\frac{1}{2}}$ for non-coalescing signals (*e.g.*, the NMe group) emained constant to −60°.

[18] R. J. Kurland, M. B. Rubin, and W. B. Wyse, *J. Chem. Phys.*, 1964, **40**, 2426.

more realistic figure of E_a of 59.5 ± 3.4 kJ mol^{-1}. This leads to a value of $\Delta H^{\ddagger}$ of 57.0 ± 3.4 kJ mol^{-1} which compares with a value for $\Delta G^{\ddagger}$ 54.6 kJ mol^{-1}.* Again $\Delta S^{\ddagger}$ is zero or at most +6 J K^{-1} mol^{-1} (see ref. 3*c*, p. 322). The values of k at −25° for (6) as calculated from an iterative fit of the line shape are also shown in Table 6.

TABLE 5

Rate constants for the coalescence of the N-CH_3 group of (6b) in $C_6D_5CD_3$

T/K (±1)	$\Delta\nu_{AB}$/Hz	Population ratio	$W_{\frac{1}{2}}$/Hz	k/s^{-1}
(A) ^{1}H N.m.r. at 90 MHz				
235	8.2	0.34 : 0.66	3.0	2.15
237	8.2	0.35 : 0.65	3.4	4.15
240	7.8	0.35 : 0.65	3.0	6.60
245	8.0	0.33 : 0.67	3.5	11.4
250	8.2	0.37 : 0.63	3.1	25.8
(B) ^{13}C N.m.r. at 22.63 MHz				
250	34.9	0.38 : 0.62	1.7	27.5
255	34.9	0.38 : 0.62	1.4	43.5
260	34.9	0.38 : 0.62	1.4	73.5
265	35.2	0.34 : 0.66	1.4	108
270	34.9	0.31 : 0.63	1.7	182

TABLE 6

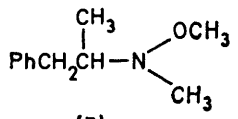
Values of k at −25 °C (k_{-25}) for (6a—c) computed from line shape analysis of ^{1}H and ^{13}C n.m.r. data

Compound	(6a)	(6b)	(6c)
k_{-25}/s^{-1}	13.6	18.5	48.3 *
k_{-25} (from Gutowsky)/s^{-1} †	13.7	18.6	47.4

* Average of three values for the NMe, OMe, and CH carbons (50.7, 46.8, and 47.4 p.p.m., respectively). † Calculated using $k_c = \pi\Delta\nu/\sqrt{2}$ which takes no account of population differences and assuming E_a 13.0 kcal mol^{-1} for each compound. For this calculation T_c is taken as the temperature at which an inflection in the coalescing signal can just be observed.

The rate constants at −20° (Table 2) leave no doubt as to the origin of the low temperature non-equivalence. The *ortho*-substituents cause an increase in rate and by currently accepted criteria [3,4] such steric acceleration is consistent with *N*-inversion as the rate-limiting process.† The use of both chloro and methyl substituents demonstrates that the acceleration is unlikely to be electronic in origin. Furthermore, the β-naphthyl group also shows slight steric acceleration over the phenyl group. The electronic effects are also consistent with rate-determining *N*-inversion since electron-withdrawing groups (*p*-NO_2 and *p*-Cl) enhance the rate whereas electron-donating groups inhibit the rate. This is also true for the doubly asymmetric hydroxylamines (6) and although one would not wish to place too much faith in ρ values from such a small number of data points (5d, e, g, and h) give ρ +0.7 and (6a—c) give ρ 1.0, and a reasonable correlation with the σ substituent constants in both cases. Perhaps the planar transition state for *N*-inversion is stabilised slightly by a ' through-space ' conjugation with the aromatic ring or possibly by a σ-inductive effect along the C–C–N bond. In fairness however, it should be added that reduction of electron density at nitrogen would also be expected to reduce the barrier to N–O rotation by reducing lone-pair interactions. Thus, in isolation, the electronic effect is not a useful diagnostic for *N*-inversion *versus* N–O rotation in this system. In contrast, electronic effects were used successfully to diagnose rate-limiting N–S rotation in acyclic sulphenamides [7-10] but the difference between sulphenamides and hydroxylamines is probably due to the interaction of the nitrogen lone pair in sulphenamides with the vacant *d*-orbitals on sulphur which effectively increases the bond order between nitrogen and sulphur.

Finally it should be noted that *NO*-dimethyl-*N*-(1-methyl-2-phenylethyl)hydroxylamine (7) showed no



(7)

non-equivalence down to −94° (CH_2Cl_2 solvent). This suggests that either nitrogen inversion or N–O rotation is fast on the n.m.r. time scale in such compounds even at low temperature, or that the intrinsic non-equivalence of the system is only substantial (*i.e.* observable) when the phenyl group is in close proximity (α) to the nitrogen.

* Calculated as an average of several experiments by using the equation $k = \pi\Delta\nu/\sqrt{2}$ which, strictly, should only be applied to exchange between equally populated sites. We have found however, that this approximation is remarkably good (see for example, Table 6).

† *Note added in proof:* We are indebted to Professor F. G. Riddell (Stirling University) for a preview of submitted, but as yet unpublished, results which support this proposal.

EXPERIMENTAL

^{1}H and ^{13}C n.m.r. spectra were recorded at 90 and 22.63 MHz respectively using a Bruker HFX 90 instrument. Spectra were generally obtained using 20% w/v solutions of the hydroxylamines in deuteriotoluene in order to minimise concentration effects between compounds. The line shape analyses were performed on a Nicolet 1080 computer with an iterative least-squares analysis program written by D. A. C.

All the hydroxylamines were prepared from *NO*-dimethylhydroxylamine (8) and the appropriate aralkyl halide using the following general method as detailed for *NO*-dimethyl-*N*-1-phenylethylhydroxylamine (6b).

A mixture of *NO*-dimethylhydroxylamine hydrochloride (2.44 g, 0.025 mol), 1-phenylethyl bromide (4.6 g, 0.025 mol), and sodium carbonate (3.5 g, 0.03 mol) in acetonitrile (20 ml) was stirred at room temperature for 1 h until evolution of carbon dioxide had ceased. The mixture was then heated under reflux for 24 h, filtered to remove sodium chloride, and the solvent distilled off at atmospheric pressure. The residue was distilled under reduced pressure to give a liquid (2.5 g, 50%), b.p. 80° at 14 mmHg, n_D^{20} 1.499 0; ^{1}H and ^{13}C n.m.r. data in Table 4.

N-(1-p-*Methoxyphenylethyl*)-NO-*dimethylhydroxylamine* (6a) was a liquid obtained in 90% yield from 1-*p*-methoxyphenylethyl bromide (from *p*-methoxystyrene and HBr) and (8), b.p. 66° at 0.1 mmHg, n_D^{20} 1.508 2 (Found: C, 68.25; H, 8.7; N, 7.1. $C_{11}H_{17}NO_2$ requires C, 67.7; H, 8.7; N, 7.2%).

NO-*Dimethyl*-N-(1-p-*nitrophenylethyl*)*hydroxylamine* (6c) was a pale yellow liquid obtained in 80% yield from (8) and 1-*p*-nitrophenylethyl bromide,[19] b.p. 86—88° at 0.1

[19] P. M. Kochregin and K. S. Bushueva, *Zhur. obshchei Khim.*, 1962, **32**, 3033.

mmHg, n_D^{20} 1.535 1 (Found: C, 57.1; H, 6.6; N, 13.95. $C_{10}H_{14}N_2O_3$ requires C, 57.15; H, 6.65; N, 13.35%).

N-Benzyl-*NO*-dimethylhydroxylamine (5g) was as reported previously.[14,20]

N-(2,6-*Dichlorobenzyl*)-NO-*dimethylhydroxylamine* (5a) was a liquid obtained in 80% yield from α,2,6-trichlorotoluene (Aldrich) and (8), b.p. 66—67° at 0.2 mmHg, n_D^{20} 1.536 8 (Found: C, 48.75; H, 4.75; Cl, 31.95; N, 5.8. $C_9H_{11}Cl_2NO$ requires C, 49.1; H, 5.0; Cl, 32.25; N, 6.35%).

N-(o-*Chlorobenzyl*)-NO-*dimethylhydroxylamine* (5b) was a liquid obtained in 65% yield from α.2-dichlorotoluene (Fluka) and (8), b.p. 34—36° at 0.03 mmHg, n_D^{20} 1.515 4 (Found: C, 57.6; H, 6.4; Cl, 19.15; N, 7.2. $C_9H_{12}ClNO$ requires C, 58.2; H, 6.45; Cl, 19.35; N, 7.55%).

NO-*Dimethyl*-N-(o-*methylbenzyl*)*hydroxylamine* (5c) was a liquid obtained in 80% yield from *o*-methylbenzyl bromide (Aldrich) and (8), b.p. 36—38° at 0.25 mmHg, n_D^{20} 1.499 1 (Found: C, 72.45; H, 9.0; H, 8.55. $C_{10}H_{15}NO$ requires C, 72.7; H, 9.1; N, 8.5%).

NO-*Dimethyl*-N-(p-*nitrobenzyl*)*hydroxylamine* (5d) was a pale yellow liquid obtained in 52% yield from *p*-nitrobenzyl bromide (B.D.H.) and (8), b.p. 76—77° at 0.1 mmHg, n_D^{20} 1.534 7 (Found C, 55.2; H, 6.1; N, 14.5. $C_9H_{12}N_2O_3$ requires C, 55.1; H, 6.1, N. 14.3%).

N-(p-*Chlorobenzyl*)-NO-*dimethylhydroxylamine* (5e) was a liquid obtained in 87% yield from α,4-dichlorotoluene (Aldrich) and (8), b.p. 40—42° at 0.06 mmHg, n_D^{20} 1.515 0 (Found: C, 58.6; H, 6.55; Cl, 21.3; N, 7.5. $C_9H_{12}ClNO$ requires C, 58.2; H, 6.45; Cl, 19.35; N, 7.55%).

NO-Dimethyl-*N*-β-naphthylmethylhydroxylamine (5f) was a pale yellow liquid obtained in 52% yield from β-bromomethylnaphthalene [21] and (8), b.p. 115° at 0.65 mmHg, n_D^{20} 1.580 3.

N-(p-*Methoxybenzyl*)-NO-*dimethylhydroxylamine* (5h) was a liquid obtained in 90% yield from *p*-methoxybenzyl bromide [22] and (8), b.p. 42° at 0.1 mmHg, n_D^{20} 1.506 9 (Found: C, 66.05; H, 8.3; N, 7.85. $C_{10}H_{15}NO_2$ requires C, 66.3; H, 8.3; N, 7.75%).

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