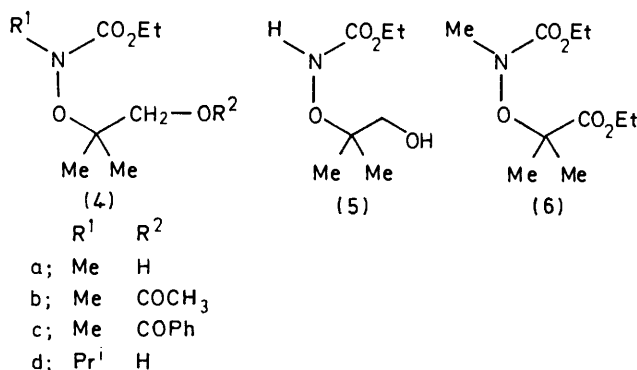
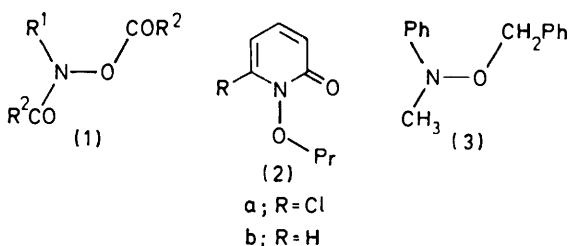


The Barrier to Rotation about the N–O Bond

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Barriers to rotation about the N–O bond in the hydroxylamine derivatives (4) have been found to be *ca.* 15 kcal mol⁻¹. There is a sizeable contribution to these barriers from non-bonded interactions in the transition states.

MOLECULAR orbital calculations on hydroxylamine^{1,2} suggest that the preferred conformation has the *trans*-arrangement of electron densities on oxygen and nitrogen, and that there is an appreciable (*ca.* 12 kcal mol⁻¹) barrier to rotation about the N–O bond.² Whilst the former result has been confirmed experimentally³⁻⁵ there has until now been no unambiguous measurement of the barrier to rotation about an N–O single bond in alkyl derivatives of hydroxylamine, although measurements that could arise from bond rotation or nitrogen inversion have been reported.⁶⁻⁸ Two reports of slow rotation about N–O bonds in acyl derivatives of hydroxylamine have appeared^{9,10} although in these cases it proved difficult to separate the intrinsic barrier to N–O bond rotation from additional steric contributions to the barrier. Price and Sutherland⁹ found barriers of *ca.* 10 kcal mol⁻¹ for compounds (1), whilst Raban and Kost¹⁰ found a barrier of 10 kcal mol⁻¹ for (2a) and estimated barriers of 8–9 kcal mol⁻¹ for (2b) and (3).



Neither group was able to separate the intrinsic N–O bond rotation barrier from additional strain in the transition state due to the N and O substituents. We

¹ L. Pedersen and K. Morukama, *J. Chem. Phys.*, 1967, **46**, 3941.

² W. H. Fink, D. C. Pan, and L. C. Allen, *J. Chem. Phys.*, 1967, **47**, 895.

³ F. G. Riddell, P. Murray-Rust, and J. Murray-Rust, *Tetrahedron*, 1974, **30**, 1087.

⁴ R. A. Y. Jones, A. R. Katritzky, S. Saba, and A. J. Sparrow, *J.C.S. Perkin II*, 1974, 1554.

now report results on the series of compounds (4), which show that steric factors contribute substantially to raising the barriers.

RESULTS

At +64° the ¹H n.m.r. spectrum of (4a) in chloroform consists of the expected resonances for the ethyl and *N*-methyl groups, a relatively sharp singlet for the *gem*-dimethyl group, and an A₂X system for the CH₂OH resonance. As the temperature is lowered the resonances due to the CH₂ and *gem*-dimethyl groups broaden and split with coalescences at *ca.* +30°. At –20° the *gem*-dimethyl group appears as a doublet and the CH₂OH group as an ABX system. The quartet of the ethyl group has also broadened slightly. These changes are compatible with the presence at the higher temperatures, when rotation about the N–O bond is rapid, of a time averaged plane of symmetry, which

TABLE 1

N.m.r. spectral data at fast exchange limit for CDCl₃ solutions (*ca.* 10%)

Compound	<i>T</i> /°C	<i>N</i> -Alkyl	Ethyl	<i>gem</i> -Dimethyl	Methylene	Other
(4a)	+64	3.14	1.29, 4.18	1.22	3.34	
(4b)	+35	3.14	1.30, 4.18	1.28	4.05	2.09
(4c)	+35	3.17	1.25, 4.16	1.37	4.30	
(4d)	+50	3.81, 1.26	1.30, 4.23	1.22	3.36	<i>ca.</i> 7.46 <i>ca.</i> 8.10
(6)	+35	3.17	1.29, 4.16, 1.30, 4.19	1.49		

TABLE 2

Free energies of activation and coalescence data

Compound	<i>T</i> _c /°C	$\Delta\nu$ /Hz	ΔG_c^\ddagger /kcal mol ⁻¹
(4a) ^a	+30 ± 2	43, <i>J</i> _{AB} 12.5 Hz	14.8 ± 0.2
(4b) ^b	+10 ± 3	<i>ca.</i> 2.5	15.5 ± 1.0
(4c) ^b	+10 ± 3	<i>ca.</i> 2	15.5 ± 1.0
(4d) ^a	+33 ± 3	36, <i>J</i> _{AB} 12.5 Hz	15.1 ± 0.3
(6) ^b	<i>ca.</i> –60	<i>ca.</i> 3	11.5 ± 1.0

^a Using the AB quartet approximation for coalescence of AB part of the ABX spectrum. ^b Based on splitting of the quartet of the ethyl group.

is lost at low temperatures as rotation becomes slow on the n.m.r. time scale. Slow rotation is effectively making the N–O bond a chiral centre in the molecule, rendering the appropriate groups diastereotopic. The N–O bond rotation interconverts two enantiomers. Similar changes attribut-

⁵ F. G. Riddell and D. Rankin, in preparation.

⁶ D. L. Griffith and J. D. Roberts, *J. Amer. Chem. Soc.*, 1965, **87**, 4089.

⁷ M. Raban and G. W. J. Kenney, *Tetrahedron Letters*, 1969, 1295.

⁸ W. Walter and E. Schaumann, *Annalen*, 1971, **747**, 191.

⁹ B. J. Price and I. O. Sutherland, *Chem. Comm.*, 1967, 1070.

¹⁰ M. Raban and D. Kost, *J. Org. Chem.*, 1972, **37**, 499.

able to slowing of N-O bond rotation are observed in compounds (4b-d) and (5) (Tables 1 and 2).

DISCUSSION

Normally bond rotation about sp^3-sp^2 bonds is associated with a low barrier and a six-fold potential function;¹¹ however in this case the barrier is large and the predominant component is two-fold. Although it seems certain that the intrinsic barrier to rotation about the N-O bond must play some role in these results it is clear from other measurements that steric hindrance is also important. Compound (5), lacking an *N*-alkyl group, shows no changes due to slow rotation at temperatures down to -60° (*i.e.* $\Delta G^\ddagger < ca. 10$ kcal mol⁻¹). The presence of an alkyl group on nitrogen is thus important in slowing down the rate of rotation and raising the barrier height. Compound (6) with a planar ethoxycarbonyl group attached to the *gem*-dimethyl has a significantly lower barrier than (4a). Possibly the ethoxycarbonyl group slips past the hindering nitrogen substituents more readily than does a methyl due to its half thickness (*ca.* 170 pm) being less than the radius of a methyl group (*ca.* 200 pm).

Hydrogen bonding between the hydroxy groups in (4a and d), and the nitrogen atom does not seem to

¹¹ See for example studies on toluene and nitromethane, H. Rudolf, H. Dreizler, A. Jaeschke, and P. Windling, *Z. Naturforsch.*, 1967, **22a**, 940; E. Tannenbaum, R. J. Myers, and W. D. Wynn, *J. Chem. Phys.*, 1968, **48**, 1220.

contribute to raising the barrier since the *O*-acyl derivatives (4b and c) show almost identical barriers.

The fact that the nature and size of the substituents alter the barrier to N-O bond rotation in the acyl derivatives reported here, and the substantially higher barriers in this series (4) compared with compounds (1)-(3) studied earlier suggest that the barriers in the earlier series may contain similar additional steric contributions. Thus the intrinsic barrier to N-O bond rotation in *N*-acylhydroxylamines, shorn of steric factors, is < 9 kcal mol⁻¹. Although the *N*-acyl groups could be exerting a modifying influence, these results suggest a lower barrier in alkyl derivatives than that proposed by Raban and Kenney⁷ (ΔG^\ddagger 12.3-12.9 kcal mol⁻¹), whose results probably need reinterpreting as due to slowing of nitrogen inversion (see however ref. 10).

EXPERIMENTAL

The preparation of the compounds (4) is described elsewhere.¹² Acetylation and benzylation were carried out by standard methods. The compounds were characterised by microanalysis either of the compounds or of derivatives, and by their ¹H n.m.r. spectra (Table 1).

Variable temperature spectra were obtained on a Perkin-Elmer R32 (90 MHz) instrument on *ca.* 10% w/v solutions in CDCl₃.

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¹² F. G. Riddell, M. H. Berry, and E. S. Turner, *Tetrahedron*, in the press.