Conformational Changes in Hydrazine and Hydroxylamine Derivatives Studied by Nuclear Magnetic Resonance Spectroscopy

By J. R. FLETCHER and I. O. SUTHERLAND*

(*Department of Chemistry, The University, Sheffield* S3 7HF)

Summary The temperature dependence of the n.m.r. spectra of *NN'*-diaryl-*NN'*-dialkylhydrazines is consistent with a substantial barrier to rotation about the N–N bond, but similar temperature dependence of the n.m.r. spectra of *NN*-dialkylhydroxylamines may be associated with a high barrier to nitrogen inversion.

THE observed temperature dependence of the n.m.r. spectra of a number of hydrazine[1] derivatives has been interpreted in terms of substantial barriers to rotation about the N–N bonds, and it has been shown[2] that nitrogen inversion barriers in hydrazines are of smaller magnitude than these rotational barriers. A study of the *NN'*-dibenzyl-*NN'*-diarylhydrazines (I) and (II) shows that the torsional barriers in these compounds are enhanced relative to those in the tetra-alkylhydrazines. Thus the n.m.r. spectra of compounds (I) and (II) each showed single AB systems for the methylene protons of the benzyl groups, when recorded at low temperatures, which coalesced to singlets at higher temperatures. This result is consistent[1] with non-planar conformations for (I) and (II) having considerable barriers to rotation about the N–N bond, together with the expected[3] rapid inversion (on the n.m.r. time scale) of the nitrogen configurations. The calculated free energy barriers to rotation (Table) show the expected relationships to the rotational barriers[1] for the N–N bond in tetra-alkylhydrazines (*ca.* 11 kcal mol^{-1}) and *NN'*-diacyl-*NN'*-dialkylhydrazines (*ca.* 23 kcal mol^{-1}) and are therefore entirely consistent with our views[1] concerning the barriers to conformational changes in hydrazine derivatives.

The temperature dependence of the n.m.r. spectrum of the trialkylhydroxylamine (III) was originally interpreted[4] in terms of a relatively high nitrogen inversion barrier. This view has been questioned[5] on the basis of observable small increases in the barrier with an increase in the steric requirements of the groups on either nitrogen or oxygen, and it has been suggested that the rate-determining step in the conformational change (IV) ⇋ (V) is rotation about the N–O bond rather than nitrogen inversion. A torsional barrier of this magnitude (12—13 kcal mol^{-1}) appeared to be rather improbable in view of the rather lower magnitude[6] of the analogous torsional barrier in *NO*-diacylhydroxylamines (*ca.* 10 kcal mol^{-1}). Examination of the temperature dependence of the n.m.r. spectra of the benzyl methylene groups of the hydroxylamine derivatives (VI)—(IX) indicates that all of these compounds show similar energy barriers for the conformational change (IV) ⇋ (V), resulting in the observation of AB systems at low temperatures which coalesce to singlets at higher temperatures (Table). In these cases a primarily torsional origin for the barrier appears unlikely in view of the lack of a steric effect associated with the replacement of an *O*-alkyl substituent, as in (III), by a much smaller hydrogen atom, as in (VI) and (VII). The same conclusion must also be drawn from the lowering of the barrier in the *O*-acetyl derivatives (VIII) and (IX), in which steric hindrance to rotation should be greater than in (VI) and (VII). We conclude that the energy barrier to the conformational change (IV) ⇋ (V) in

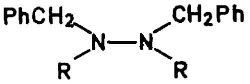
N.m.r. parameters (at 100 *MHz) and free-energy barriers to conformational changes in hydrazine and hydroxylamine derivatives*

Compound	Solvent	$\nu_A - \nu_B$(°K)[a] ±0·5Hz	J_{AB} ±0·5Hz	T_C(°K) ±2°	k_C[b] s^{-1}	$\Delta G^{\ddagger}$ at T_C[c] kcal mole^{-1}
(I)	$CDCl_3$	18·3(231)	17·0	286	77	14·2
(II)	$CDCl_3$	15·6(219	17·0	271	70	13·5
(VI)	$CDCl_3$	24·7(219)	12·5	257	62	12·8
	CD_3OD	20·4(219)	13·0	243	51	12·2
(VII)	$CDCl_3$	27·5(231)	12·5	260	77	12·9
	CD_3OD	27·4(219)	13·2	248	76	12·3
(VIII)	$CDCl_3$	17·3(207)	13·0	239	40	12·1
	CD_3OD	26·7(207)	13·0	246	60	12·3
(IX)	$CDCl_3$	28·1(213)	13·0	244	83	12·0
	CD_3OD	31·8(219)	13·0	250	87	12·3

[a] In a few cases ($\nu_A - \nu_B$) was temperature dependent and the value given refers to the temperature stated, ($\nu_A - \nu_B$) at T_C was obtained by extrapolation from low temperature measurements. The Table refers only to the benzyl methylene groups.

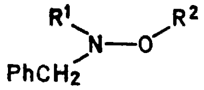
[b] Based upon the rate at which the computed line shape (ref. 10) shows coalescence.

[c] Errors are difficult to estimate: they are probably less than ±0·2 kcal mol^{-1}.



(I) R = Ph

(II) R = $C_6H_4 \cdot Me$-*p*



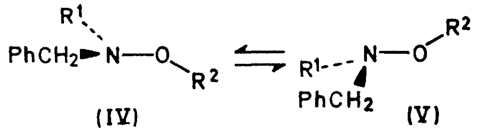
(III) $R^1 = R^2 = Me$

(VI) $R^1 = CH_2Ph, R^2 = H$

(VII) $R^1 = CHMe_2, R^2 = H$

(VIII) $R^1 = CH_2Ph, R^2 = Ac$

(IX) $R^1 = CHMe_2, R^2 = Ac$



(IV) (V)

NN-dialkylhydroxylamines and by analogy in trialkylhydroxylamines,[4,5] is primarily a barrier to nitrogen inversion and that the arguments used[5] concerning the effects of increased substituent size are misleading. The effects of deuteriomethanol upon these nitrogen inversion barriers (Table) indicate that such effects, at one time believed to be diagnostic for nitrogen inversion barriers,[7] must be interpreted with caution, particularly in cases where the amine molecule contains an hydroxyl substituent.

The rather greater effect of an oxygen substituent upon the nitrogen inversion barrier as compared with an adjacent nitrogen atom is consistent with the view that these effects may be thought of in terms[3] of increased lone-pair repulsion in the transition state for nitrogen inversion. The high nitrogen inversion barrier in hydroxylamines is also consistent with the lower barriers[6] associated with rotation about the N–CO bond in hydroxamic acid derivatives as compared with the analogous *NN*-dialkylamides. The contrast between the conformational situation in hydrazines and hydroxylamines as compared with that in sulphenamides[8] and aminophosphines[9] suggests that *d*-orbital participation may be important in N–X bonds where X is a second-row element.

(*Received, February 16th*, 1970; *Com.* 216.)

---

[1] J. R. Fletcher and I. O. Sutherland, *Chem. Comm.*, 1969, 706.

[2] M. J. S. Dewar and W. B. Jennings, *J. Amer. Chem. Soc.*, 1969, **91**, 3655; M. J. S. Dewar and W. B. Jennings, *Tetrahedron Letters*, 1970, 339.

[3] F. A. L. Anet and J. M. Osyany, *J. Amer. Chem. Soc.*, 1967, **89**, 352; F. A. L. Anet, R. D. Trepka, and D. J. Cram, *ibid.*, p. 357.

[4] D. L. Griffith and J. D. Roberts, *J. Amer. Chem. Soc.*, 1965, **87**, 4089.

[5] M. Raban and G. W. J. Kenney, jun., *Tetrahedron Letters*, 1969, 1295.

[6] B. J. Price and I. O. Sutherland, *Chem. Comm.*, 1967, 1070.

[7] J. E. Anderson and J. M. Lehn, *J. Amer. Chem. Soc.*, 1967, **89**, 81; F. G. Riddell, J. M. Lehn, and J. Wagner, *Chem. Comm.*, 1968, 1403.

[8] J. M. Lehn and J. Wagner, *Chem. Comm.*, 1968, 1298; M. Raban, G. W. J. Kenney, jun., and F. B. Jones, jun., *J. Amer. Chem. Soc.*, 1969, **91**, 6677.

[9] M. J. S. Dewar and W. R. Jackson, *J. Amer. Chem. Soc.*, 1968, **90**, 4185; H. Goldwhite and D. G. Rowsell, *Chem. Comm.*, 1969, 713 and references there cited.

[10] G. Binsch, *Topics Stereochem.*, 1968, **3**, 97.