Conformational Changes in Tetra-alkylhydrazines

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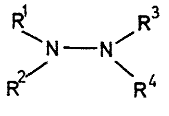
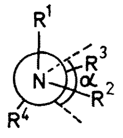
Summary The temperature dependence of the n.m.r. spectra of tetra-alkylhydrazines may be interpreted in terms of a substantial barrier to rotation about the N–N bond.

THE preferred conformation of hydrazine has been the subject of theoretical and experimental investigations,[1] but the conformations adopted by substituted hydrazines have not been established with certainty, and from the available experimental evidence they may depend upon the nature of the substituents.[2] We describe the temperature dependence of the n.m.r. spectra of some tetra-alkylhydrazines which provides evidence for a considerable barrier to rotation about the N–N bond.

The n.m.r. spectrum of the prochiral[3] benzyl methylene groups of the tetra-alkylhydrazines (I) and (II)† is observed as an AB system at low temperatures (below −60°) which coalesces to a singlet at higher temperatures, due to the increased rate of exchange between the A and B proton





(I) $R^1 = R^3 = CH_2Ph, R^2 = R^4 = Et$

(II) $R^1 = R^3 = CH_2Ph, R^2 = R^4 = CHMe_2$

(III)

(VI) $R^1 = R^2 = R^3 = CH_2Ph, R^4 = Et$

(VII) $R^1 = R^2 = CH_2Ph, R^2 = R^4 = COPh$

(VIII) $R^1 = R^3 = CHMe_2, R^2 = R^4 = COPh$

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† All new compounds were isolated as crystalline solids and have been fully characterised by analysis and spectral properties.

Nuclear magnetic resonance parameters and free-energy barriers to rotation about the N–N *bonds of hydrazine derivatives*

Compound	Solvent	$\nu_A - \nu_B$ $\pm 0\cdot2$ Hz.	J_{AB} $\pm 0\cdot2$ Hz.	T_c(°K) ±2°	$\Delta G^‡$ at T_c[a] kcal./mole
(I)	CS_2	51·6[b]	13·5[b]	222	10·7 ± 0·2[d]
(II)	CS_2	18·9[b]	15·8[b]	227	11·2 ± 0·2
	CS_2	7·0[c]	6·4[c]	212	11·2 ± 0·2
(VI)	CS_2	20·4[b]	12·5[b]	220	10·8 ± 0·2
(VII)	Pyridine	24·8[b]	15·0[b]	390	19·6 ± 0·5
(VIII)	$C_6H_5NO_2$	4·9[c]	6·6[c]	420	23·5 ± 0·5

[a] Calculated at the coalescence temperature T_c by comparison with computed spectra for compounds (I), (II), and (VI) and using appropriate expressions for the exchange rate at the coalescence temperature (ref. 5) for compounds (VII) and (VIII).

[b] Refers to methylene protons of $PhCH_AH_B$ group.

[c] Refers to methyl groups of $CHMe_AMe_B$ group.

[d] The same value of $\Delta G^‡$ was obtained for a solution of compound (I) in $CDCl_3$ and CD_3OD–$CDCl_3$ (1 : 1 and 2 : 1).

environments. The free-energy barriers to these exchange processes were calculated from the exchange rates at the coalescence temperatures, determined from a comparison of observed and calculated[4,5] spectral line shapes (see Table for results). The other prochiral substituents in (I) and (II) also gave temperature-dependent n.m.r. spectra and in particular the isopropyl methyl groups of (II) gave two equal-intensity overlapping doublet signals at low temperature which coalesced to a single doublet at higher temperatures.

These temperature-dependent changes in the n.m.r. spectra of the hydrazines (I) and (II) show that they exist in two enantiomeric sets of time-averaged conformations which are separated by a substantial energy barrier. This barrier may be associated either with inversion of configuration of the hydrazine nitrogen atoms or with hindered rotation about the N–N bond, all other possible conformational changes being unlikely to involve energy barriers of the observed magnitude. Hindered nitrogen inversion would be expected to result in the observation of two AB systems for the benzyl methylene groups at low temperatures, since (I) and (II) would exist as the pairs of diastereoisomers shown in the Scheme [for a symmetrically substituted hydrazine such as (I) and (II) the *RS* and *SR* conformations are identical but would nevertheless be associated with diastereotopic benzyl methylene protons]. Such effects have been reported for the n.m.r. spectra of tetrasubstituted diarsines[6] and diphosphines[7] but are not observable for the hydrazines (I) and (II). The consequences of hindered rotation about the N–N bond are difficult to consider in detail since the preferred torsion angle [defined as α, the dihedral angle between the two RNR angle bisectors, in the Newman projection (III) in which $\alpha > 0$] is not known, and even if the discussion is restricted to staggered conformations ($\alpha = \pm 60°, 180°$) nine different conformations of (I) and (II) must be considered. The discussion here is simplified by the assumption that the rapidly inverting nitrogen atoms may be represented as in the projection formulae (IV) and (V), which are related as mirror images. Projections (IV) and (V) may be considered as the average of all the conformations that are interconverted by rapid nitrogen inversion without rotation about the N–N bond, thus (IV) represents the conformations in which α lies between $-120°$ and $+120°$ and (V) would represent the enantiomers of these conformations. Slow rotation about the N–N bond and rapid nitrogen inversion would therefore result in the observation of a single AB system for the benzyl methylene groups in the symmetrical tetra-alkylhydrazines (I) and (II), but for tribenzylethylhydrazine (VI) one type of benzyl group [R^1 and R^2 in (VI)] would give rise to an AB system at low temperatures whereas the other benzyl group [R^3 in (VI)] would give a singlet A_2 system at all temperatures. The observed n.m.r. spectrum of the benzyl methylene groups of (VI) shows at low temperatures, exactly these features (Figure) and at higher temperatures, as expected for fast rotation about the N–N bond, both types of benzyl methylene groups give singlet signals (Figure).

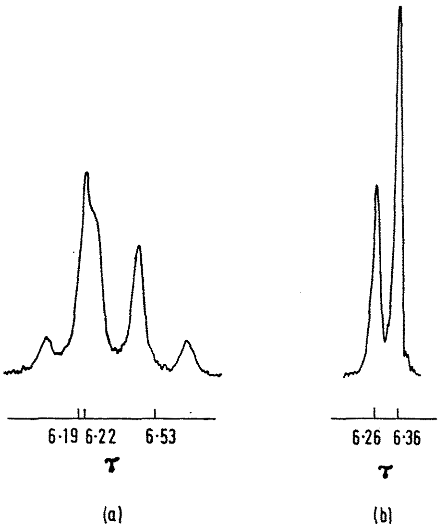
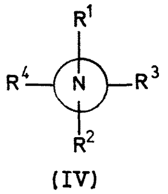
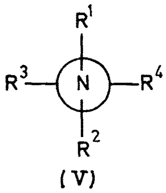


FIGURE. *The* 60 *MHz. n.m.r. spectrum of the benzyl methylene protons of tribenzylethylhydrazine* (VI) *in carbon disulphide at* (a) $-73°$ *and* (b) $+35°$.

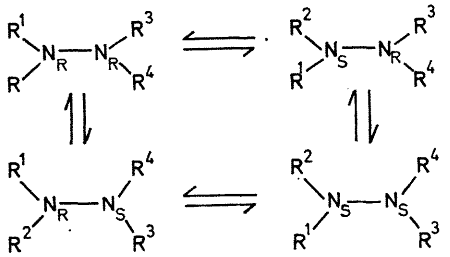


(IV)



(V)

The observed temperature dependence of the n.m.r. spectra of the hydrazines (I), (II), and (VI) is thus more consistent with a high barrier to rotation about the N–N bond than with a high barrier to nitrogen inversion. No further temperature dependence, other than line broadening, is observable in the n.m.r. spectra down to $-100°$. Further evidence that rotation about the N–N bond rather than nitrogen inversion is the process associated with the n.m.r. changes comes from the increase in $\Delta G^{\ddagger}$ as the size of the alkyl substituents is increased. Similar effects have also been reported for the rotational barrier about the S–N bond in sulphenamides[8] and the N–O bond of hydroxylamines.[9] A decrease in $\Delta G^{\ddagger}$ for an increase in substituent size would be expected for a process involving nitrogen inversion.[10] Finally, nitrogen inversion rates have been shown[11] to be markedly decreased in solvents such as methanol, and the value of $\Delta G^{\ddagger}$ for the hydrazine (I) is unaffected by the addition of methanol to the solution. The effect of substituent size upon rotational barriers is more clearly observable for the diacylhydrazines (VII) and (VIII) [for N–N rotational barriers in (VII) and (VIII), measured by the observation of the temperature dependence of the n.m.r. spectra of the prochiral benzyl and isopropyl substituents, see Table], and may also be used in this case to verify that the conformational change involved is rotation about the N–N bond as previously postulated.[12]



SCHEME. *Conformational changes in tetra-alkylhydrazines associated with nitrogen inversion, the subscripts R and S on each nitrogen atom refer to its absolute configuration defined by the Cahn–Ingold–Prelog system. The arrows refer to inversion at a single nitrogen atom only.*

(*Received, May* 8*th*, 1969; *Com.* 637.)

[1] For recent references see A. Veillard, *Theoret. Chim. Acta*, 1966, **5**, 413; L. Pedersen and K. Morukama, *J. Chem. Phys.*, 1967, **46**, 3941; W. H. Fink, D. C. Pan, and L. C. Allen, *J. Chem. Phys.*, 1967, **47**, 895.

[2] W. H. Beamer, *J. Amer. Chem. Soc.*, 1948, **70**, 2979; D. R. Lide and D. E. Mann, *J. Chem. Phys.*, 1959, **31**, 1129; C. B. Coburn, F. A. Johnson and C. Haney, *ibid.*, 1965, **43**, 4526; L. S. Bartell and H. K. Higginbotham, *Inorg. Chem.*, 1965, **4**, 1346; S. J. Brois, *Tetrahedron Letters*, 1968, 5997.

[3] K. R. Hanson, *J. Amer. Chem. Soc.*, 1966, **88**, 2731.

[4] S. Alexander, *J. Chem. Phys.*, 1962, **37**, 967; J. Heidberg, J. A. Weil, G. A. Jarmson, and J. K. Anderson, *ibid.*, 1964, **41**, 1033.

[5] J. A. Pople, W. G. Schneider, and H. J. Bernstein, "High Resolution Nuclear Magnetic Resonance," McGraw-Hill, New York, 1959, ch. 10; M. Oki, H. Iwamura, and N. Hayakawa, *Bull. Chem. Soc. Japan*, 1963, **36**, 1542; R. J. Kurland, M. B. Rubin, and W. B. Wise, *J. Chem. Phys.*, 1964, **40**, 2426; F. B. Mallory, S. L. Manatt, and C. S. Wood, *J. Amer. Chem. Soc.*, 1965, **87**, 5433; F. G. Riddell and J. M. Lehn, *Chem. Comm.*, 1966, 375.

[6] J. B. Lambert, *J. Amer. Chem. Soc.*, 1968, **90**, 1350.

[7] J. B. Lambert and D. C. Mueller, *J. Amer. Chem. Soc.*, 1966, **88**, 3669.

[8] J. M. Lehn and J. Wagner, *Chem. Comm.*, 1968, 1298; M. Raban, F. Jones, jun., and G. W. J. Kenney, *Tetrahedron Letters*, 1968, 5055; M. Raban, *J. Amer. Chem. Soc.*, 1968, **90**, 2985.

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

[10] S. J. Brois, *J. Amer. Chem. Soc.*, 1967, **89**, 4242.

[11] 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.

[12] G. J. Bishop, B. J. Price, and I. O. Sutherland, *Chem. Comm.*, 1967, 672.