# Torsional Barriers in *NN'*-Diacylhydrazines

By G. J. BISHOP, B. J. PRICE, and I. O. SUTHERLAND*

(*Department of Chemistry, The University, Sheffield*, 10)

THE large energy barrier to ring inversion of tetrahydropyridazine derivatives [*e.g.*, (I)] has been attributed[1-3] largely to the nonbonded interactions between the acyl substituents on the nitrogen atoms in the transition state for ring inversion. Similar observations have been made[3] of substantial barriers to rotation about the N–N bond of tetra-acylhydrazines [*e.g.*, (II)] and this results, which is in accord with the crystal structure of *NN'*-disuccinimide,[4] was rationalized in terms of nonbonded repulsions between the acyl substituents in a planar transition state. We now report evidence for hindered rotation about the N–N bond of certain acyclic *NN'*-diacylhydrazine derivatives.
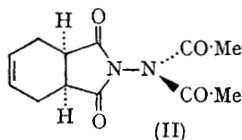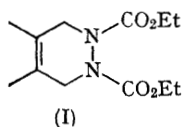
The 100 Mc./sec. nuclear magnetic resonance (n.m.r.) spectrum of *NN'*-dibenzyl-*NN'*-dimethoxycarbonylhydrazine (III) in deuteriochloroform at −40° (Figure) shows, in addition to a broad multiplet for the aromatic protons, four different methoxy-signals [τ 6·19 (0·88H), 6·22 (0·52H), 6·49 (3·72H), 6·53 (0·88H)] and four AB systems for the methylene protons [τ 5·02, 5·80, J_{AB} 14·9 c./sec. (0·59H); τ 5·23, 5·80, J_{AB} 15·0 c./sec. (0·35H); τ 5·58 (2·47H)†; τ5·60, 5·85, J_{AB} 14·9 c./sec.
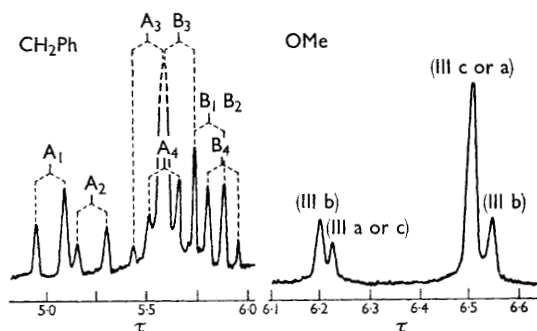

FIGURE. *The 100 Mc./sec. n.m.r. spectrum of the methylene and methoxy-protons of NN'-dibenzyl-NN'-dimethoxycarbonylhydrazine in deuteriochloroform at −40°. The AB systems are indicated by A_1B_1, etc.; the assignments of the methyl signals to conformations (IIIa, b, or c) are indicated. By inspection of relative intensities A_1B_1 and A_4B_4 correspond to conformation (IIIb) and A_2B_2 and A_3B_3 to conformations (IIIa and c).*

(I)

(II)

† The centre lines of this AB system are not resolved and it is not possible to estimate J_{AB} or $\nu_A - \nu_B$; the chemical-shift value refers to the mid-point.

TABLE

Nuclear magnetic resonance parameters and free-energy barriers to rotation about the N–N bond for compounds (III) *to* (VI)

Compound	Solvent	$(\nu_A - \nu_B)$ (c./sec. $\pm$ 0·5)	J_{AB} (c./sec.)	T_c (°c)	$\Delta G\dagger$ at $T^c{}_a$ (kcal./mole $\pm$ 0·3)
(III)	Nitrobenzene	10·5	14·6 ± 0·2	192 ± 2	23·5
(IV)	Nitrobenzene	5·1 [b]	14·2 ± 0·2	188 ± 2	23·4
(V)	Nitrobenzene	7·2	15·6 ± 0·4	190 ± 2	23·3
(VI)	Deuteriochloroform	84·7	14·8 ± 0·5	4 ± 5	13·2

[a] Calculated using the formula: $k_c = \pi[(\nu_A - \nu_B)^2 + 6J_{AB}{}^2]^{\frac{1}{2}}/\sqrt{2}$ (ref. 8).

[b] In this case $(\nu_A - \nu_B)$ is temperature dependent and the value refers to that estimated for T_c by extrapolation.

(0·59)H]. These signals may be associated with three conformations (IIIa, b, and c), each of which exists in two chiral forms, which result from hindered rotation about the N–CO and N–N bonds. The reasons for rejecting an interpretation in terms of hindered rotation about the O–CO bonds[5,6] will be discussed in a later Paper. The chirality of the conformations (IIIa, b, and c) leads to the possibility of geminal proton non-equivalence within each benzylic methylene group.[7] At higher temperatures the four methoxy-signals coalesce to a singlet and the four AB
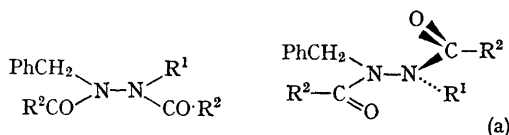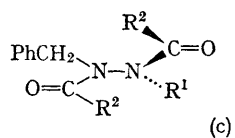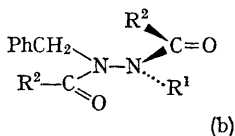

(III) R¹=CH₂Ph, R²=OMe
(IV) R¹=CH₂Ph, R²=Me
(V) R¹=R²=CH₂Ph
(VI) R¹=H, R²=CH₂Ph

systems coalesce to a single AB system. The temperature range in which these changes occur is consistent[2] with averaging of the signals which result from hindered rotation about the N–CO bonds, but the observation of an AB system from the methylene protons up to 80° indicates that rotation about the N–N bond is still slow on the n.m.r. time-scale at this temperature. The coalescence of the AB system was studied using 60 Mc./sec. spectra of a nitrobenzene solution, from the coalescence temperature and the spectral para-meters the free energy barrier to rotation about

the N–N bond was calculated[8] (see Table). The NN'-dibenzylhydrazine derivatives (IV) and (V) show similar evidence for a large barrier to rotation about the N–N bond (see Table). The postulated AB systems were verified at low temperature by the appropriate spin-tickling or spin-decoupling experiments; spectroscopic changes associated with hindered rotation about the N–CO bonds will be described in the full Paper. The temperature dependence of the n.m.r. spectrum of (III) has previously been reported[5] but the conclusions reached differ from those described here.

The 60 Mc./sec. spectrum of the methylene protons of the N-benzyl group of (VI) are observed as an AB system at −50° and the AB system coalesces to a singlet at higher temperatures. We associate these spectroscopic changes with hindered rotation about the N–N bond, but in this case (see Table) the calculated energy barrier for this rotational process is considerably lower than those for compounds (III), (IV), and (V).

From these results we conclude that the barrier to rotation about the N–N bond of the NN'-dialkyl-NN'-diacylhydrazines is high, and that the ground-state conformation is the twisted form (VII) in which (a) repulsions between the sub-stituents on the two nitrogen atoms are minimized and (b) repulsion between the π-electrons of the two urethane systems is also minimized. It seems unlikely that interatomic nonbonding interactions in an eclipsed transition-state (VIII) can account

(VII)   (VIII)
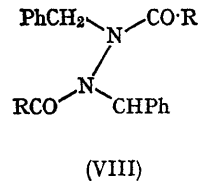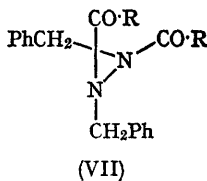
for more than a part of the observed energy barrier, and we conclude that in these diacyl-hydrazine systems interelectronic repulsions make

a significant contribution to the observed energy barrier to rotation about the N–N bond.

This conclusion, which is in accord with the observed barriers to ring inversion of tetrahydropyridazines, obviously has a close relationship to the observation[9] of dihedral angles of close to 90° for the N–N bond of hydrazine and its derivatives, and to the unusually large nitrogen inversion barriers that have been observed[10] for cyclic hydrazine derivatives. The extent to which interelectronic repulsions are responsible for the

torsional barrier in the NN-diacylhydrazines is being investigated further, as is the relationship between the results for the dialkylhydrazine derivatives (III), (IV), and (V), the monoalkylhydrazine derivative (VI) and the reported planarity of NN'-diformylhydrazine[11] and NN'-diacetylhydrazine[12] in the crystalline state. We thank Dr. J. Feeney of Varian Associates for the 100 Mc./sec. spectra of compound (III).

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