# Hindered Rotation in *NO*-Diacylhydroxylamines

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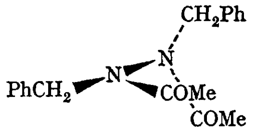
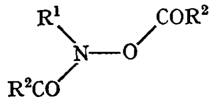
WE recently reported[1] evidence for a substantial barrier to rotation about the N–N bonds of certain *NN'*-diacylhydrazines, *e.g.*, (I), the ground state being the nonplanar conformation shown. These results suggested that the ground-state conformation of *ON*-diacylhydroxylamines, *e.g.*, (II), would be similarly nonplanar, and that the energy barrier to rotation about the N–O bond might be measurable by nuclear magnetic resonance (n.m.r.) spectroscopy. In view of the current interest in torsional barriers[2] we now present the preliminary results of this investigation.

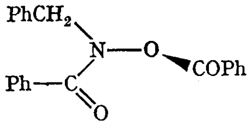
The low-temperature (−80°) n.m.r. spectrum of a solution of the hydroxylamine derivative (II) in deuteriochloroform–carbon disulphide (1 : 1) shows a broad AB system ($\tau_A$ 4·16, $\tau_B$ 5·55, $J_{AB}$ 15·5 c./sec., 1·3 H) and a broad singlet ($\tau$ 4·88, 0·7 H), both of which may be assigned to the methylene protons of the N–CH$_2$Ph residue. At higher temperatures these signals coalesce to a singlet ($\tau$ 5·00, 2H). We associate these spectroscopic changes with slow (on the n.m.r. time scale) interconversion of two pairs of enantiomeric nonplanar conformations, (VII) and (VIII), at low temperature, the benzylic methylene group of the more abundant conformation showing the geminal magnetic nonequivalence[3] which results from the chirality of these conformations. The temperature range and manner in which the spectroscopic changes occur indicate that the energy barriers to rotation about both the N–O and N–CO bonds of (II) are of approximately the same magnitude, but due to the complexity of the changes it is only possible to make a rough



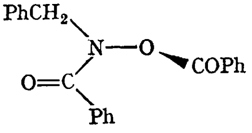
(I)



(II) R$^1$=CH$_2$Ph, R$^2$=Ph
(III) R$^1$=CH$_2$Ph, R$^2$=Me
(IV) R$^1$=R$^2$=CH$_2$Ph
(V) R$^1$=Me, R$^2$=Ph
(VI) R$^1$=R$^2$=Me



(VII)



(VIII)

TABLE

*Nuclear magnetic resonance parameters*[a] *and free-energy barriers to rotation about the* N–O *and* N–CO *bonds for compounds* (II) *to* (VI)

| Compound | Solvent | Bond | $\tau_A$ | $\tau_B$ | $P_A$ | $P_B$ | $J_{AB}$ (c./sec.) | $T_c$ (°C) | $\Delta G\ddagger$ at $T_c$[b] (kcal./mole) |
|---|---|---|---|---|---|---|---|---|---|
| (II) | CDCl$_3$–CS$_2$ (1:1) | N–O | 4·16 | 5·55 | | | 15·5 | *ca* −65[c] | *ca* 9·8[c] |
| (III) | CDCl$_3$–CS$_2$ (2:1) | N–O | 4·51 | 5·85 | | | 15 | −71 ± 3 | 9·6 ± 0·2 |
| (IV) | CDCl$_3$–CS$_2$ (2:1) | N–O | 4·50 | 5·68 | | | 16 | −69 ± 3 | 9·6 ± 0·2 |
| (V) | CDCl$_3$–C$_5$H$_5$N (1:5) | N–CO | 6·33 | 6·47 | 0·80 | 0·20 | | −75 ± 5 | 10·5 ± 0·3[d] |
| (VI) | CDCl$_3$ | N–CO | 6·52 | 6·67 | 0·17 | 0·83 | | −16 ± 2 | 13·3 ± 0·1[e]<br>14·2 ± 0·1[e] |

[a] For compounds (II), (III), and (IV) $\tau_A$, $\tau_B$, and $J_{AB}$ refer to the low-temperature AB system from the *N*-benzyl methylene group; for compounds (V) and (VI) $\tau_A$, $\tau_B$, $p_A$, and $p_B$ refer to the low-temperature *N*-methyl signals and their relative intensities.

[b] Calculated for AB systems using the formula: $kc = \pi\,[(\nu_A - \nu_B)^2 + 6\,J_{AB}^2]^{\frac{1}{2}}/\sqrt{2}$ (ref. 6); calculated at 0° for compound (VI) from the plot of $\log_{10} k$ against $1/T$, the two values for this compound refer to conformation A → conformation B and conformation B → conformation A.

[c] The coalescence is complex, $\Delta G\ddagger$ is estimated for the AB system only and is approximate.

[d] $\Delta G\ddagger$ is based upon $k' = p_A k_A + p_B k_B$.

[e] The associated Arrhenius parameters are $E_a = 14·7 \pm 0·9$ kcal./mole, $\log_{10} A = 13·8 \pm 0·9$ (A → B) and $E_a = 15·1 \pm 0·9$ kcal./mole, $\log_{10} A = 13·4 \pm 0·9$ (B → A).

estimate of the barrier heights (see Table) from the approximate coalescence temperature.

Hindered rotation about the N–CO bond of *NO*-dibenzoylhydroxylamines may be separately studied using the derivative (V); the low-temperature (−85°) N–Me signals ($\tau$ 6·33, 1·6 H; $\tau$ 6·47, 0·4 H) coalesce at −75° indicating that the energy barrier to N–CO rotation is low (see Table) as compared with simple benzamides[4] but in accord with the results obtained for (II). The lowering of the amide rotational barrier is possibly associated with the inductive effect of the *O*-acyl substituent on the nitrogen atom. A similar low rotational barrier is observed for the N–CO bond of the *NO*-diacetylhydroxylamine (VI) (see Table); in this case the Arrhenius parameters, obtained from a more complete study of the temperature dependence[5] of the N–Me n.m.r. signals, indicate that the observed energy barrier is largely due to the enthalpy of activation.

The low-temperature n.m.r. spectra of the diacylhydroxylamine (III) and (IV) indicate an energy barrier to N–O rotation of the same order as for compound (II), again the ground-state conformation is nonplanar. In these cases the coalescence of the low-temperature AB system from the *N*-benzyl methylene group is not complicated by n.m.r. temperature-dependence associated with hindered N–CO rotation, consequently reasonably accurate estimates of free-energy barriers at the coalescence temperatures can be made in the usual way[6] (see Table). The details of the n.m.r. spectra of these compounds will be reported in the full Paper.

As in the case of the diacylhydrazine derivatives[1] it is difficult to estimate the relative importance of steric and electronic influences upon the N–O rotational barrier; as far as we are aware there are no crystallographic data available for *NO*-diacylhydroxylamines. The nature of this torsional barrier is being further investigated.

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