Restricted Rotation around Several Bonds in 1-Acyl-2,2-bisdimethylaminoethylenes and Similar Compounds

By JAN SANDSTRÖM* and INGEGERD WENNERBECK

(*Department of Organic Chemistry, University of Lund, Lund, Sweden*)

WE have reported low barriers to rotation around carbon–carbon double bonds in ethylenes which on one carbon atom carry electron-attracting and on the other electron-donating substituents.[1] We have now studied two 1-acyl-2,2-bisdimethylaminoethylenes (I) and (II), which show hindered rotation around several bonds in the delocalised system. The temperature-dependent n.m.r. spectrum of the dimethylamino-groups of (I) is shown in the Figure. At higher temperatures it is a sharp singlet, indicating that all rotations are fast on the n.m.r. time scale. The broadening at lower temperature and the splitting at +20° are interpreted as the result of slow rotation around the carbon–carbon double bond. When the temperature is further lowered, the doublet sharpens in an unsymmetrical way, and between 0° and −10° two new and smaller signals emerge. Their appearance must be due to a slow rotation of the benzoyl group, giving rise to two conformations, (Ia) and (Ib), with unequal populations. The two weaker signals soon split into doublets with widely different separations, $\Delta\nu_0$ (Table), indicating slow rotation of the two dimethylamino-groups in the minor conformer. The narrow doublet changes into a singlet at still lower temperatures, most likely owing to a temperature-dependent chemical shift difference.

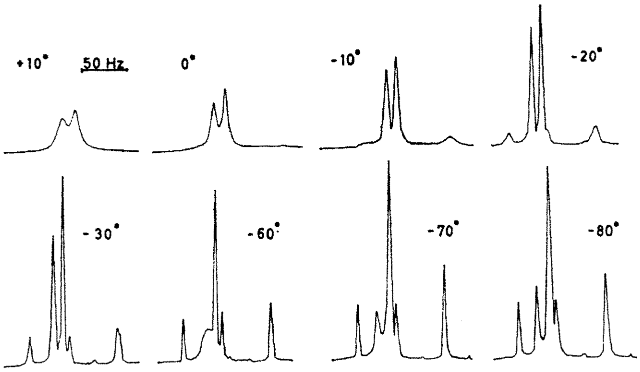


FIGURE. ^{1}H *N.m.r. spectrum of the dimethylamino-groups of* (I) *at* 100 MHz.

The low-field component of the doublet due to the major conformer broadens at lower temperatures and splits at −63°, whereas the high-field signal remains a singlet down to −120°. This may be due to a very low barrier to rotation for one dimethylamino-group, or to a small chemical shift difference. However, the barriers to rotation around the C(1)–C(2) double bond, the C(1)–benzoyl bond, both C(2)–N bonds in the minor conformer, and one C(2)–N bond in the major conformer manifest themselves in the temperature-dependent n.m.r. spectrum. Estimation of $\Delta G^{\ddagger}$ values from $\Delta\nu_0$ and coalescence temperatures[2] is uncertain when several rate processes affect the spectrum simultaneously, but approximate values have been calculated (Table). An alternative interpretation, which ascribes the coalescence at +20° to a slow rotation of the two dimethylamino-groups, is inconsistent with the changes in the spectrum at lower temperatures.

In a similar compound, 1,1-diacetyl-2,2-bisdimethylaminoethylene (II), a slow rotation of the dimethylamino-groups is, however, first observed. At room temperature, the acetyl protons give a sharp singlet and the dimethylamino-protons a broad one, which splits at +6° into a symmetrical doublet. This splitting cannot be caused by a slow rotation around the C(1)–C(2) bond, since the two dimethylamino-groups are magnetically equivalent as long as the rotation around the C(1)–acetyl bonds is rapid. Instead, the two methyl groups in each dimethylamino-group must become non-equivalent owing to slow rotation around the C(2)–N bonds. At lower temperatures the acetyl signal broadens, and splits at −65° into a symmetrical doublet. This can only be explained by slow rotation around both C(1)–acetyl bonds, which freezes the acetyl groups in a *cis–trans* arrangement with respect to the double bond. The symmetry of the doublet and the absence of other signals seems to rule out the possibility of notable concentrations of other conformers.

TABLE

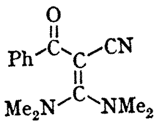
Compound	Bond	$\Delta\nu_0$ Hz	T_c°K	$\Delta G^{\ddagger}$ kcal./mole	Solvent
(I) (100 MHz)	C(1)–C(2)	10·5 ± 0·1	294 ± 1	15·3 ± 0·1	$CHCl_2F–CHClF$
	C(1)–COPh	72 ± 1	268 ± 2	13[a]	(1 : 1)
	C(2)–N	41 ± 1[b]	265 ± 2		
	(minor conf.)	2 ± 0·1[c]	248 ± 2	13·7 ± 0·1	
	C(2)–N (major conf.)	12 ± 1	210 ± 1	10·8 ± 0·1	
(II) (60 MHz)	C(1)–Ac	32 ± 0·5	208 ± 1	10·2 ± 0·1	$CS_2 + NH_2Cl_2$ (1 : 1)
	C(2)–N	5·1 ± 0·1	279 ± 1	15·0 ± 0·1	
(III) (60 MHz)	C(1)–$C_6H_4NO_2$	49 ± 0·5	228 ± 10	11·6 ± 0·4	$CS_2 + CDCl_3$ (1 : 2)
	C(2)–N	30 ± 0·5	263 ± 1	13·1 ± 0·1	
	C(1)–C(2)	19 ± 0·5	293 ± 1	15·0 ± 0·1	

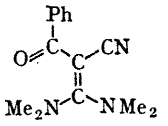
[a] As these two rotations are observed at nearly the same temperature, equation (6) in ref. 2 gives only very approximate $\Delta G^{\ddagger}$ values; [b] low-field doublet; [c] high-field doublet.

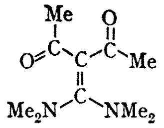
spectrum to an ABCD spectrum. The apparent simplicity of the spectrum is probably due to the similarity of the chemical shifts of the two protons *ortho* to the nitro-group, to the chemical shift differences, and to the dominance of the *ortho*- over the *meta*- and *para*-couplings. If the spectrum at low temperature can be approximated as a superposition of an AB and an AB′ spectrum, where $|\nu_B - \nu_B'|$ = 49 Hz, then the temperature-dependent spectrum can be analysed as two exchanging doublets, in which the splitting is due to coupling with non-exchanging nuclei, and it is permissible to use equation (6) in ref. 2 with $\delta\omega_0 = 0$ to obtain a rough estimate of $\Delta G^{\ddagger}$ (Table). The spectrum of the two dimethylamino-groups consists of a broad singlet at ambient probe temperature, and at +20° it splits into a symmetrical doublet, probably owing to slow rotation around the C(1)–C(2) bond. At about −10° the high-field component also splits (slow rotation of one dimethylamino-group), but the low-field component is not split down to −90°. The appearance of this part of the spectrum at low temperature, with three signals in the intensity ratio 1 : 2 : 1, could also be ascribed to two overlapping doublets. However, since the spectrum has the same appearance in *o*-dichlorobenzene down to −30°, a low barrier or a small chemical shift difference is a more acceptable explanation. It is hoped that this ambiguity will be removed by a complete line-shape analysis.

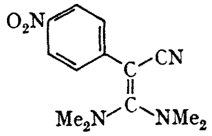
Slow rotation around the C(1)–C(2) bond should cause a further splitting of the dimethylamino-signal into a quartet, but this is not observed down to −120°. A small chemical shift difference is a very unlikely explanation in this case, since the strongly anisotropic acetyl groups are differently directed with respect to the dimethylamino-groups. Thus one concludes that in this compound the barriers to rotation around the C(1)–acetyl and the C(2)–N bonds are higher than that around the formal carbon–carbon double bond. The low C(1)–C(2) barrier can be rationalised if it is assumed that in the transition state one electron pair is transferred from the double bond to the acetylacetone portion. Then the transition state can be regarded as a combination of an amidinium ion and an acetylacetonate anion, which are excellently suited to stabilise a positive and a negative charge respectively and thus lower the energy of the transition state. In a similar compound with only one dimethylamino-group,[3] the carbon–carbon double-bond barrier is also very low (< 12 kcal./mole), though the positive charge in the transition state for rotation in this compound is stabilised only by an immonium ion structure.

In 1-cyano-2,2-bisdimethylamino-1-*p*-nitrophenylethylene (III) the aromatic protons show a normal AA′BB′ spectrum at ambient probe temperature. The high-field spectrum broadens at 0°, and collapses at −40° to −50°. At −80° the aromatic proton spectrum consists of the original low-field doublet at 485 Hz, now considerably broadened, and two equal, broad doublets at 439 and 390 Hz down-field from tetramethylsilane. The splitting of all three doublets is 9·5—10 Hz. The temperature-dependence of the spectrum is caused by restricted rotation of the *p*-nitrophenyl group, which should change the AA′BB′ spectrum to an ABCD spectrum.


(Ia)


(Ib)


(II)


(III)

This work was supported by the Swedish Natural Sciences Research Council.

(*Received, January 9th,* 1969; *Com.* 031.)

---

[1] G. Isaksson, J. Sandström, and I. Wennerbeck, *Tetrahedron Letters*, 1967, 2233.
[2] H. S. Gutowsky and C. H. Holm, *J. Chem. Phys.*, 1956, **25**, 1228.
[3] Y. Shvo, E. C. Taylor, and J. Bartulin, *Tetrahedron Letters*, 1967, 3259.