Conformational Study of Twisted Ethylenes by Nuclear Magnetic Resonance Spectroscopy

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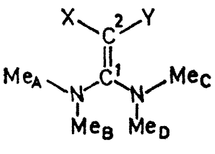
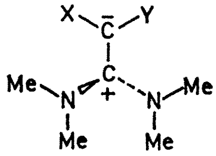
Summary The temperature-dependent n.m.r. spectra of 2-(diacylmethylene)-1,3-dialkylimidazolidines show that the molecules are twisted around the carbon–carbon double bonds and that the planar states represent energy maxima; in the 1,3-dibenzyl derivatives the benzylic protons are non-equivalent at ambient temperature and hindered rotation of the acyl groups is also observed.

IT is known[1,2] that 1,1-bis(dimethylamino)ethylenes with electron attracting groups on C(2) (I) have barriers to rotation around the carbon–carbon double bond ranging from *ca.* 20 to $<$ 7 kcal/mol. The low barriers are viewed as a consequence of a favourable polar transition state (II), in which the negative charge is stabilized in the carbanion X–$\bar{\text{C}}$–Y, and the positive charge in an amidinium ion. In (I), steric interaction between methyl groups B and D requires that the dimethylamino-groups be twisted out of the molecular plane, and consequently the amidinium ion in the transition state is destabilized. A planar arrangement of the amidinium system should give a lower barrier, which has been verified by a study of the temperature-dependent n.m.r. spectrum of (IIIa). Below -70 °C the *N*-methyl groups give rise to a symmetrical doublet, and the usual coalescence approximation[3] gives $\Delta G^{\ddagger} = 9{\cdot}8$ kcal/mol. At this temperature the analogous bis-dimethylamino-compound (I; X = Ph, Y = CN) has $\Delta G^{\ddagger} = 19{\cdot}3$ kcal/mol.[4]

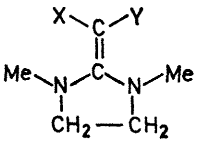
The 100 MHz spectrum of (IIIb) in methylene dichloride at room temperature consists of sharp singlets for the acetyl and *N*-methyl protons, and a broadened singlet for the methylene protons. When the temperature is increased the methylene signal is sharpened and at *ca.* $+70$ °C it has the same linewidth as the two other signals, but below ambient temperature it is broadened and resolves at *ca.* -15 °C into a multiplet of AA′BB′ type, the high-field half of which is noticeably broadened. At this temperature the *N*-methyl signal is still a sharp singlet, whereas the acetyl signal is broadened This is unexpected for a planar system where the *N*-methyl protons should feel the different anisotropy of the X and Y groups much more strongly than the methylene protons and consequently the *N*-methyl signals should give rise to a symmetrical doublet at a higher temperature than that at which the AA′BB′ spectrum of the methylene protons appears At still lower temperatures the acetyl and *N*-methyl signals split into unsymmetrical doublets indicative of slow rotation of one or both of the acetyl and benzoyl groups The n m r spectrum of the diacetyl compound (IIIc) shows a similar temperature dependence but the splitting of the methylene acetyl and *N* methyl signals occurs in the same temperature region This is reasonable, since the appearance of an AA′BB′ spectrum from the methylene protons requires that the acetyl groups are frozen in an *s-cis s trans* conformation with respect to the C(1)–C(2) bond, as shown by the bisdimethyl amino-analogue (I, X = Y = Ac) [1] The spectrum at low temperature shows about 20% of a second conformation, probably with both acetyl groups in the *s-cis* conformation, since a dipole–dipole repulsion should destabilize the *s-trans-s trans* conformation



(I)

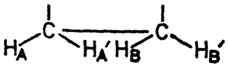


(II)



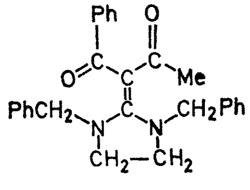
(III)†

	X	Y
a,	Ph	CN
b,	PhCO	CO_2Me
c,	Ac	Ac
d,	Ph	Ac
e,	PhCO	CO_2Et
f,	PhCO	CN



(IVa)

(IVb)



(V)

The spectra of (IIId—f) also show temperature dependence indicating two different rate processes the acyl rotation and the rotation around the double bond The former affects both the *N*-methyl and the methylene spectrum, whereas the latter affects only the methylene spectrum. These spectra are best explained by assuming a potential curve for compounds (I) and (IIIa) such as the lower one in the Figure, whereas compounds (IIIb—f) are represented by the upper curve The change from the lower to the upper curve is brought about by an increased stabilization of the conformation with the dihedral angle $\theta = 90°$, *i e* a decreased difference in π-electron energy between the planar and orthogonal conformations, combined with an increased steric effect in the planar conformation In the planar conformation the non-equivalence of the methylene protons is represented by (IVa), and in the twisted conformation by (IVb) This hypothesis can be tested by substituting suitable prochiral groups such as benzyl groups for the *N*-methyls, since the benzylic methylene protons are non-equivalent in the non-planar conformations and exchange sites when θ passes 0 or 180° In agreement with this, the benzylic protons of (V) show an AB spectrum, and the coalescence temperature (T_c = 61 °C) and the spectral parameters ($\Delta\nu_{AB}$ = 37 1 Hz J_{AB} 15 0 Hz in fluorobenzene at 100 MHz) give $\Delta G^{\ddagger}$ = 16 4 kcal/mol [6] At lower temperatures the AB spectrum broadens in an unsymmetrical fashion owing to slow rotation of the acyl group(s)

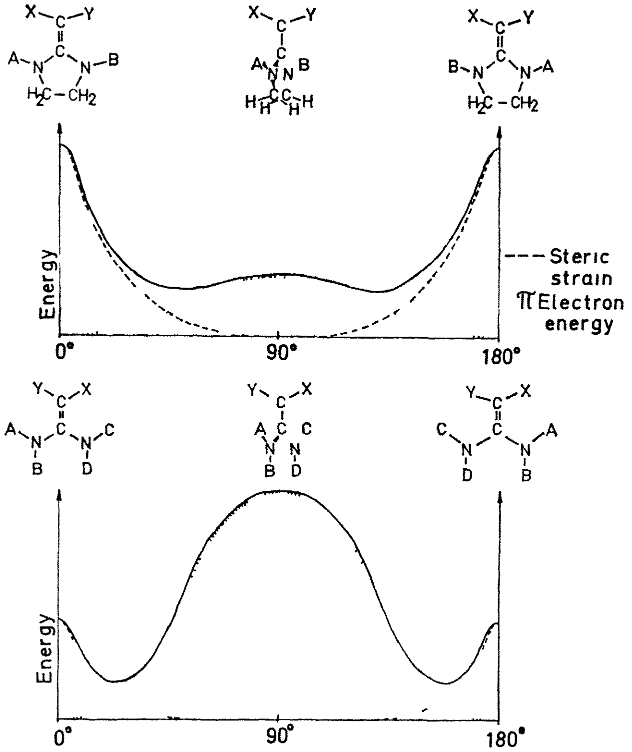


FIGURE *Assumed potential curves for compounds* (I) *and* (II)

If the potential barrier at $\theta = 90°$ were sufficiently high, a slow passage from one minimum to the other across this barrier should cause a doubling of the *N*-methyl or *N*-benzyl signal in the accessible temperature region, and an estimation of the barrier should be possible No such doubling has been observed in the systems (IIIb—f), but it is possible that a system could be constructed with a substantial barrier at $\theta = 90°$ by choosing a combination of substituents X and Y with a low capacity for stabilizing a negative charge and with a sufficient steric effect for θ = 0 or 180°

Overcrowded ethylenes are known in the bifluorenylidene[7,8] and bianthronylidene[9] series, where the steric strain is relieved by folding instead of twisting the molecules In bifluorenylidenes with prochiral groups in the 1,1′-positions,

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† The preparation of these compounds is described in ref 5

Ollis *et al*[10] have observed two rate processes, identified as a configurational inversion and a *cis–trans*-isomerization, which correspond to the processes discussed above

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