Infrared-spectral Studies on the Orientation of the Lone Pairs in Piperidine Derivatives

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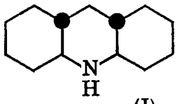
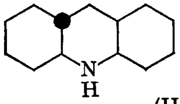
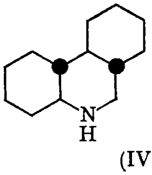
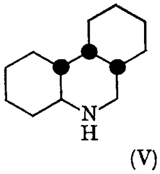
RECENTLY attention has been drawn to the steric requirement of a nitrogen lone-pair.[1] We present here evidence supporting arguments[2] that a hydrogen on nitrogen prefers the equatorial conformation.

We examined the i.r. spectra (CCl_4 containing 0·05 M of n-BuOH, cell length 0·5 mm., 20°) in the region 3700—3100 cm.$^{-1}$ of the following piperidines (0·2 M): *N*-methyl derivatives of *trans,syn,-trans-*, *trans,anti,cis-*, and *trans,syn,cis*-perhydroacridines (I, II and III), *trans,anti,trans-* and *trans,syn,cis*-perhydrophenanthridines (IV and V),


(I)


(II)


(IV)


(V)

and *trans*-perhydroquinoline (VI). Each solution of the compounds except (II) exhibited a broad absorption (transmission *ca.* 65%) centred near ᔭ320 cm^{-1} due to the OH groups bonded to the N atoms, as well as a sharp band (*ca.* 80%) at 3640 cm.$^{-1}$ due to the free OH groups, while that of compound (II) showed a weak broad absorption

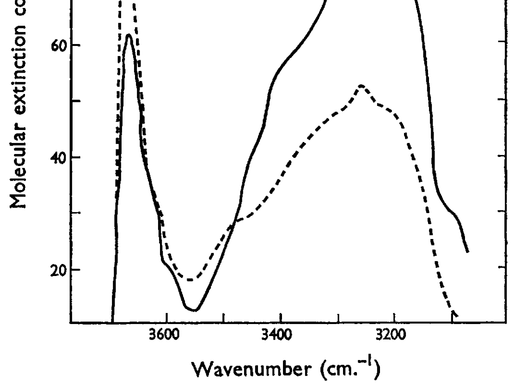


FIGURE. *Infrared spectra of perhydroacridines* (I) *and* (II) *in* CCl_4 *solutions containing* n-BuOH *at* 20°: (I) *and* (II) 0·15 M; n-BuOH 0·05 M; *cell length* 0·5 mm.

(*ca.* 80%) centred near 3420 cm.$^{-1}$ along with the sharp band (*ca.* 80%). All these compounds [(I)—(VI)] have rigid conformations concerning the rings and showed almost equal basicities (pK_a 9·63, 9·67, 9·65, 9·45, 9·54, and 9·37, respectively, in 60% aqueous EtOH, 20°). Accordingly, the observed difference of the frequency shifts between (II) (*ca.* 240 cm.$^{-1}$) and the other compounds (*ca.* 400 cm.$^{-1}$) apparently arises from that of the hydrogen bond-lengths,[3] which must be attributed to the presence of an axial methylene group located at the β-position to the N atom in (II). This result is consistent with the *N*-methyl group being almost exclusively equatorial.

We next measured the spectra (Figure)† of (I) and (II) (0·15 M), in each of which both the relevant, broad and sharp bands were observed near 3240 and at 3640 cm.$^{-1}$, respectively.‡ In the spectrum of (I) the former band was stronger than the latter. The situation became just the opposite in the case of (II), where the intensity of the broad band *decreased*. This spectral behaviour is interpreted on the basis of that the lone-pair assumes mainly an axial conformation in both the compounds and, when the alcohol is added, only compound (II) is partly inverted to a less stable conformer with the lone-pair equatorial and forms the hydrogen bond of almost the same length as (I).

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† The intensity ϵ in the Figure denotes the difference of the molecular extinction coefficients between each ternary solution and the corresponding one containing no *n*-BuOH.

‡ The absorption intensities due to the free and N- or O-bonded NH groups would be negligibly small, because (I) or (II) showed only weak absorptions (ϵ <5) near 3300 cm.$^{-1}$ at the concentration 0·02—1·25 *M* in the CCl_4 solution.

[1] F. G. Riddell, *Quart. Rev.*, 1967, **21**, 364.

[2] T. Masamune and M. Takasugi, *Chem. Comm.*, 1967, 626; K. Brown, A. R. Katritzky, and A. J. Waring, *J. Chem. Soc.* (*B*), 1967, 487; H. Booth and A. H. Bostock, *Chem. Comm.*, 1967, 177; N. L. Allinger, J. G. D. Carpenter, and F. M. Karkowski, *J. Amer. Chem. Soc.*, 1965, **87**, 1232 (*cf.* J. B. Lambert, R. G. Keske, R. E. Carhart, and A. P. Javanovich, *J. Amer. Chem. Soc.*, 1967, **89**, 3761).

[3] *Cf.* L. P. Kuhn, *J. Amer. Chem. Soc.*, 1952, **74**, 2492; K. Nakamoto, M. Margoshes, and R. E. Rundle, *J. Amer. Chem. Soc.*, 1955, **77**, 6480.