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

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WE describe an attempt to determine the steric requirements of the nitrogen lone pairs[1] in piperidine derivatives on the basis of the Bohlmann bands.[2]

We examined the i.r. bands (CCl_4) in the region 3020—2500 cm.$^{-1}$ of the following piperidines; piperidine (I), *trans*- and *cis*-perhydroquinolines (II and III), *trans,syn,trans*-, *trans,anti,cis*-, and *trans,syn,cis*-perhydroacridines (IV, V, and VI), *trans,anti,trans*-, *cis,syn,cis*-, and *trans,syn,cis*-perhydrophenanthridines (VII, VIII, and IX), *trans*- and *cis*-2,6-dimethylpiperidines (X and XI), *N*-methyl derivatives (Ia—XIa) of (I—XI), and quinolizidine (XII). It was considered that the

Bohlmann bands must be included in the bands in the region below 2820 cm.$^{-1}$ (Figure), since a sharp absorption minimum was observed at 2820 ± 3 cm.$^{-1}$ in each spectrum.† We also examined the spectra of *N*-benzoyl derivatives (Ib—XIb) of (I, II, IV, VII, and XI) in order to estimate the amount of background in the region below 2820 cm^{-1}, because in the amides the overlap of the lone pair with the antibonding σ^* C–H$_{ax}$ orbital on the adjacent carbon[3] would be forbidden due to the overlap with the benzoyl group. Then we have defined the difference between the integrated intensity (I_A) of the band in the 2820—2500 cm.$^{-1}$ range and that (I_B) of its background as that (A) of the Bohlmann band (Table).[4]

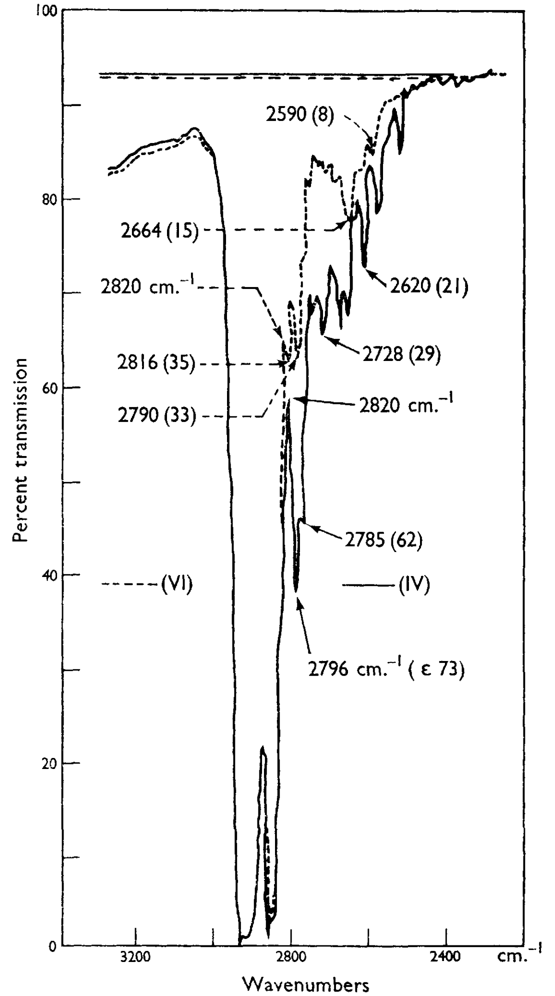

FIGURE. *Infrared spectra of perhydroacridines* (IV) *a nd*(VI); (IV): 5·82 *mg./*0·1 *ml.* CCl$_4$; (VI): 4·93 *mg./*0·1 *ml.* CCl$_4$; *both in* 0·2 *mm, cell.*

In view of the fact that the intensity A is concerned with the orientation of the lone pair, the number and kind of the relevant hydrogens (oriented *anti*-coplanar to the lone pair), the extent of the overlap in question,[3] and the ring distortions,[5] we have attempted to analyze the intensities assuming that the following formula holds for the compounds examined:‡

$$A = \Sigma N.n.I.S.R$$

where N is N_H or N_{Me}, n is n_p, n_s or n_t, I is I_p, I_s, or I_t, S is $S_{2\beta}$ or $S_{1\beta}$, and R is R_1, R_2, or R_3.

The "N_H and N_{Me}" refer to the mole fractions of conformers with an axially oriented lone pair on the nitrogen. The "n_p, n_s, and n_t" are the number of relevant hydrogens in CH$_3$, CH$_2$, and CH groups, respectively, and are given directly from the structure of the compound. The "I_p, I_s, and I_t" represent the intensities for the C–H vibrations in question (whose hydrogen is present *solely* in a compound involving no distortions and located in CH$_3$, CH$_2$, and CH groups, respectively) and are called the "unit intensity." The "$S_{2\beta}$ and $S_{1\beta}$" are the ratios of the intensity produced by each vibration in question to the corresponding unit intensity, when an axial CH$_2$ or CH$_3$ substituent is present at the β-position to *two* α-carbons and *one* α-carbon bearing the relevant hydrogen(s), respectively.[5] The "R_1 (=1), R$_2$, and R_3" are the ratios of the intensity of each vibration to the corresponding unit intensity, when there are one, two, and three relevant hydrogens in a compound, respectively.[3]

The values of these parameters have been estimated on the basis of the equations for the piperidines, having rigid or essentially fixed conformations, other than (III, IIIa, VIII, and VIIIa), and the following assumptions: (i) The mole fractions N_H and N_{Me} are approximately constant for all the *N*-unsubstituted- and *N*-methyl-piperidines having no CH$_2$ (or CH$_3$) group *syn*-axial to the lone pair or the hydrogen on nitrogen, respectively; namely, $N_H = N_H^*$ (N_H

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† The examination of each spectrum suggests that the tailing intensity in the region above 2820 cm.$^{-1}$ of the Bohlmann band would be negligibly small as compared with that in the region below 2820 cm.$^{-1}$ of the band produced by usual C–H stretching vibrations.

‡ The integrated intensities of the bands near 2900 cm.$^{-1}$, produced by usual C–H stretching vibrations, of a series of aliphatic hydrocarbons have been interpreted well on the basis that the hydrocarbon molecule behaves like a non-interacting mixture of CH$_3$, CH$_2$, and CH structural groups (S. A. Francis, *J. Chem. Phys.*, 1950, **18**, 861).

TABLE

Integrated intensities of the Bohlmann bands of piperidine derivatives[a]

Compounds	Intensities[b] I_A	I_B	A	Compounds	Intensities[b] I_A	I_B	A_B
(Ia)	11·4	0·8[c]	10·6	(I)	5·6	0·6[h]	5·0
(IIa)	11·2	1·2[d]	10·0	(II)	5·6	1·0[i]	4·6
(IIIa)	11·6	1·2[d]	10·4	(III)	6·7	1·0[i]	5·7
(IVa	11·8	1·8[e]	10·0	(IV)	6·0	1·6[j]	4·4
(Va))	12·5	1·8[e]	10·7	(V)	7·0	1·6[j]	5·4
(VIa)	6·5	1·8[e]	4·7	(VI)	3·6	1·6[j]	2·0
(VIIa)	12·2	1·7[f]	10·5	(VII)	6·1	1·5[k]	4·6
(VIIIa)	12·6	1·7[f]	10·9	(VIII)	7·3	1·5[k]	5·8
(IXa)	10·3	1·7[f]	8·6	(IX)	4·7	1·5[k]	3·2
(Xa)	5·7	1·0[g]	4·7	(X)	2·8	0·8[l]	2·0
(XIa)	10·5	1·0[g]	9·5	(XI)	5·4	0·8[l]	4·6
(XII)	11·5	1·0[i]	10·5				

[a] The spectra were recorded at 23° in CCl_4 solutions *ca.* 0·03M in the appropriate solute. [b] The unit: (l./cm.^{2} mole) × 10^{-3}. [c–g] These figures denote the intensities (I_B) in the 2820—2500 cm.$^{-1}$ range of (Ib, IIb, IVb, VIIb, and XIb), respectively. [h–l] These figures were obtained by multiplication of I_B of (Ib, IIb, IVb, VIIb, and XIb) and the following fractions, 8/10, 14/16, 20/22, 20/22, and 12/14, respectively.

of piperidine) and $N_{Me} = 0{\cdot}95$.[6] (ii) For the compound (V) having the aforementioned axial group, the mole fraction N_H is expressed by $N_H\beta_S$, where β_S is a parameter showing the effect of the group. In the compound (Va) the *N*-methyl group is essentially fixed at the equatorial position, namely, $N_{Me} = 1$. From a series of equations for [Ia, IIa (and VIIa), IVa (and Va and XIa), I, II (and VII), and IV (and XI)], the following relations can be obtained:

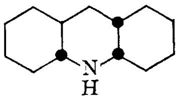
$$I_S = 0{\cdot}94{\cdot}I_p \text{ and } I_t = 0{\cdot}84{\cdot}I_p \qquad (1)$$

$$N_H{}^*{\cdot}I_p{\cdot}R_2 = 2{\cdot}64 \times 10^3 \text{ l./cm.}^2 \text{ mole and}$$
$$I_p{\cdot}R_3 = 3{\cdot}88 \times 10^3 \text{ l./cm.}^2 \text{ mole} \qquad (2)$$

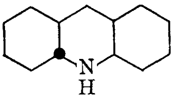
Inserting eq. (2) into the equations for (IX) and (IXa) yields $S_{2\beta} = 0{\cdot}71$. From these values and the equations for (VIa) and (Xa) and also that for (V), we can obtain the following values:

$$N_H{}^* = 0{\cdot}70 \quad \text{and} \quad \beta_S = 1{\cdot}22$$

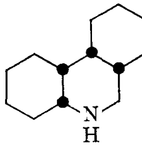
The present result $N_H{}^* = 0{\cdot}70$ indicates that a hydrogen atom is more space-demanding than the nitrogen lone pair, and is consistent with that obtained by Allinger ($N_H{}^* = 0{\cdot}68$),[6] Katritzky,[1b] Booth[1c] and their co-workers, but not with those of other authors.[7] The disagreement might be attributable to the difference in the experimental conditions or methods, or to the assumptions involved tacitly in the analysis of the results.



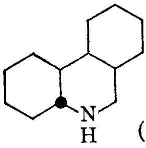
(V)



(VI)



(VIII)



(IX)

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