The Microwave Spectrum and Conformation of Piperidine

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THE microwave spectrum of piperidine has been investigated in detail between 8 and 35 GHz. We report here some results which relate to the conformation of the imino-hydrogen atom.[1]

The spectrum is dominated by the many Q-branch series of an oblate symmetric rotor obeying type-A selection rules, together with a few R-branch lines. No type-C lines, expected from considerations of the molecular geometry, have yet been identified. The Figure shows a typical Q-branch under the most favourable conditions of Stark modulation and signal-to-noise ratio. The degradation and splitting of high-J members of the Q-branch are due mainly to the deviations from oblate symmetry. The details of the assignment will be given elsewhere.

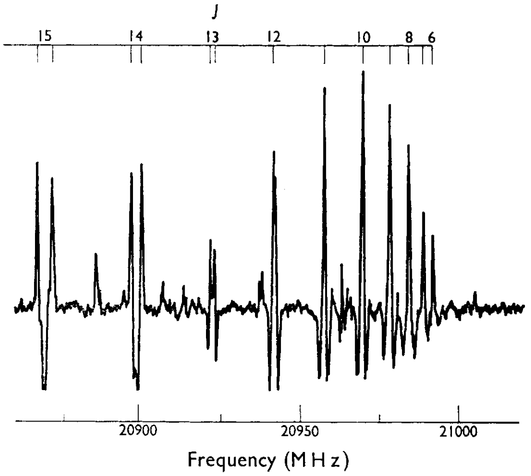

FIGURE. *Q-Branch ($K = 5 \leftarrow 6$) for piperidine in its axial conformation. Absorption intensity is upwards, Stark displacements (E = 60 v/cm.) downwards.*

The strongest Q-branch series and its associated R-branch lines for the normal (h_{11}) and N-deuteriated (d_1) species give the rotational constants in the first two columns of the Table. Planar moments are defined by:

$$P_\alpha = \sum_i m_i\,(r_{i\beta}^2 + r_{i\gamma}^2) = 0{\cdot}5(I_\beta + I_\gamma - I_\alpha)$$

where α, β, and γ are permutations of the principal axes a, b, c; $r_{i\alpha}$, $r_{i\beta}$, $r_{i\gamma}$ are Cartesian co-ordinates of the i'th atom in the molecule; and I_α, I_β, I_γ are the principal moments of inertia. From Kraitchman's equations[2] the substitution co-ordinates in Å of the imino hydrogen are (1·56, 0·0, 1·17), indicating the axial position.

A weaker series of Q-branches for both isotopic species and the associated R-branch lines for the h_{11} species have been analysed, giving the constants

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TABLE

Planar Moments (amu.A^2)	Axial hydrogen			Equatorial hydrogen		
	h_{11}	d_1	Δ	h_{11}	d_1	Δ
P_a	100·921	103·356	+2·435	100·88	105·62	+4·74
P_b	98·387	98·369	−0·018	97·85	97·85	(0·0)
P_c	14·060	15·440	+1·380	13·40	13·59	+0·19

in the second half of the Table. Since only two independent rotational constants are available experimentally for the d species, the third has been obtained assuming that the planar moment P_b does not change on deuteration. The substitution co-ordinates then are (2·18, 0·0, 0·43) indicating the equatorial position for this species.

The bulk of the rest of the spectrum has been analysed in terms of vibrational satellites of both conformers, the lowest vibration of which has been shown by Crowder and Scott[3] to be at 246 cm.$^{-1}$, a value consistent with our intensity measurements on the more prominent satellite series.

The relative intensities of the type-A lines of the two conformers I_{eq}/I_{ax}, corrected for the frequency factor in the intensity expression, are 0·161 ± 0·005 with the sample at −34° and 0·146 ± 0·005 with the sample at +20°. Assuming this difference to be due solely to the Boltzmann factor and the ratio of the dipole moment components along the a-axis, we have

$$I_{ax}/I_{eq} = (\mu_a^{ax}/\mu_a^{eq})^2\, e^{-\Delta E/kT}$$

whence $\Delta E = E_{ax} - E_{eq} =$

$$245 \pm 150 \text{ cal.mole}^{-1} \text{ and } \mu_a^{ax}/\mu_a^{eq} = 3{\cdot}2.$$

The μ_c components of the dipole moment have been measured directly from the linear Stark effect of the observed transitions, giving $\mu_c^{ax} = 0{\cdot}503$ and $\mu_c^{eq} = 0{\cdot}781$ D. With the assumption that the total dipole moment is the same in the two conformers, we have then $\mu_a^{ax} = 0{\cdot}63$, $\mu_a^{eq} = 0{\cdot}195$ D and the resultant total dipole moment is 0·80 D. This is considerably smaller than the value 1·19 D, measured in benzene solution by Aroney and Le Fèvre,[4] and we hope to obtain a direct measurement of μ_a to confirm our result.

The energy difference indicates that the equatorial conformer is the more abundant comprising 60% at 25°.

(*Received, March 11th*, 1968; *Com.* 293.)

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[3] G. A. Crowder and D. W. Scott, U.S. Department of the Interior (Bureau of Mines) Technical Report, 1965, 6630.

[4] M. J. Aroney and R. J. W. Le Fèvre, *J. Chem. Soc.*, 1958, 3002; M. A. G. Rau and B. N. Narayanaswany, *Z. phys. Chem.*, 1934, **26** *B*, 23, gave a value of 1·17 ± 0·2 D.