Quadrupole Coupling Constants and Dipole Moments of Oxazole and Isoxazole

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RECENTLY the microwave spectra, quadrupole coupling constants, and dipole moments of oxazole and isoxazole have been reported.[1] A noteworthy feature is that the quadrupole splitting for isoxazole is much smaller than for oxazole. An explanation for this is provided by the molecular orbital calculations reported here, which also yield reasonable values for the dipole moments.

The π-electron systems were treated by a Pariser–Parr–Pople technique,[2] programmed for the KDF9 computer, and the π-moment calculated on the basis of a point-charge model. In the σ-moment calculations it was found necessary to include the 'lone pair' moments of oxygen and nitrogen; these were estimated on the basis of Burnelle and Coulson's[3] calculations on water, and of a method first suggested by Lucken.[4] π-Electron calculations on 1,2,5-oxadiazole, together with the experimentally determined quadrupole coupling constants[5] allowed the 'occupation numbers' of the σ-valency orbitals of the nitrogen atom to be deduced, and these were subsequently used in the oxazole and isoxazole calculations. The 'lone pair' moments obtained for oxygen and nitrogen were 1·33 D and 1·67 D, respectively. They are assumed to be transferable from one molecule to another of approximately the same valency angles. The total σ-moment was obtained by the vector addition of the 'lone pair' moments to the bond moments, the values $\mu_{CO} = 0\cdot8$ D., $\mu_{CN} = 0\cdot28$ D., $\mu_{NO} = 0\cdot30$ D. being used. The observed and calculated moments are given in Table 1.

TABLE 1. *Dipole moments*

	μ_σ	μ_π	μ (total)	μ (exp)
Oxazole	1·36 D	2·09 D	1·80 D	1·50 D
Isoxazole	3·44	1·24	3·11	2·90

In the quadrupole calculations the 'occupation numbers' are assumed to be transferable from one chemically similar molecule to another, and for e^2Qq_p, the quadrupole coupling constant for a

TABLE 2. *Inertial constants*

		A (Mc./sec.)	B (Mc./sec.)	C (Mc./sec.)
Oxazole	calc.	10,125·6	9592·6	4925·9
	exp.	10,050·94	9645·07	4919·42
Isoxazole	calc.	9831·5	9580·2	4836·6
	exp.	9786·24	9575·07	4836·95

TABLE 3. *Quadrupole coupling constants*

		χ_{aa} (Mc./sec.)	χ_{bb} (Mc./sec.)	χ_{cc} (Mc./sec.)
Oxazole	calc.	$-3·79$	$+0·88$	$+2·91$
	exp.	$-3·99$	$+1·58$	$+2·41$
Isoxazole	calc.	$-0·94$	$+0·72$	$+0·22$
	exp.	<1	<1	<1

single *p*-electron, a value of -10 Mc./sec. was used. The exact orientation of the inertial axes within the molecular frame is not known for oxazole, or isoxazole, but calculations based on a number of slightly different orientations (not reported here) indicate that the orientations of the models used are accurate to within a few degrees. The corresponding values for the inertial constants are given in Table 2, (together with the observed values).

The observed and calculated values for the quadrupole coupling constants χ_{ii} are given in Table 3. These are defined by the relations, $\chi_{aa} = e^2Qq_{aa}$, *etc.*

The calculations show that the lower values of the quadrupole coupling constants obtained for isoxazole are due to the influence of the neighbouring hetero-atom on the nitrogen.

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