

Dipole Moments and ^{14}N Quadrupole Coupling Constants in Some Heterocyclic Compounds: All Valency Electron Calculations

By D. W. DAVIES*

(Chemistry Department, University of Birmingham)

and W. C. MACKRODT

(Mathematical Institute, University of Oxford)

PREVIOUS calculations on the dipole moments and ^{14}N quadrupole coupling constants of oxazole and isoxazole, in which only the π -electrons were treated were reported.¹ Further calculations including all the valency electrons on these and eight other similar molecules have been made by the CNDO/2 method of Pople and Segal², a Fortran IV programme written by Segal³ being modified to run on the KDF9 computer. The parameters were those chosen by Pople and Segal^{2b} for small molecules. The calculations were all made for experimental or assumed internuclear distances, and required about three minutes computer time per molecule.

The dipole moments calculated with the atomic charge densities alone gave low values, but the inclusion of atomic polarization terms^{2a} led to calculated values that are all within ± 0.40 D of

the experimental values (Table 1). In addition, the dipole moment of the hitherto unstudied 1,2,3-oxadiazole is predicted to be 3.60 D. The calculated values are notably better than those obtained for the same compounds by the extended Hückel method.⁴ As in the dipole calculations, the matrix elements of the field-gradient tensor were calculated using the one-centre terms only. Slater orbitals were used as approximations to the atomic orbitals and for e^2Qq the value -14.0 Mc./sec. was found to be more appropriate than the value -10.0 Mc./sec. used previously.¹ The agreement with the available experimental results is good for most molecules (Table 2), particularly for the coupling constants perpendicular to the molecular frame. For these the two- and three-centre contributions to the field-gradient matrix elements are, in general, much smaller than for

TABLE 1. Dipole moments (D)

Molecule	Calculated			Experimental			Ref.
	μ_a	μ_b	μ_{Total}	μ_a	μ_b	μ_{Total}	
Furan	0.71	—	0.71	0.661 ± 0.006	—	0.661 ± 0.006	5
Pyrrrole	2.11	—	2.11	1.84 ± 0.03	—	1.84 ± 0.08	6
Oxazole	1.24	0.62	1.38	1.34 ± 0.1	0.66 ± 0.1	1.50 ± 0.1	7
Isoxazole	2.13	2.21	3.07	1.98 ± 0.1	2.12 ± 0.1	2.90 ± 0.1	7
1,2,5-Oxadiazole ..	—	3.50	3.50	—	3.38 ± 0.04	3.38 ± 0.04	8
1,3,4-Oxadiazole ..	3.15	—	3.15	3.04 ± 0.04	—	3.04 ± 0.04	9
1,2,3-Oxadiazole† ..	3.58	0.42	3.60	—	—	—	—
1,2,4-Oxadiazole ..	1.33	0.21	1.34	1.20 ± 0.2	0.20 ± 0.2	1.20 ± 0.2	10
Pyridine	2.16	—	2.16	2.15 ± 0.05	—	2.15 ± 0.05	11
Pyridazine	3.82	—	3.82	4.22 ± 0.06	—	4.22 ± 0.06	14

† Representation chosen so that the *b*-axis, in this case *not* the intermediate inertial axis, was parallel to the N(3)-C(4) band.

TABLE 2

¹⁴N Quadrupole coupling constants (Mc./sec.)

Molecule	Calculated			Experimental			Ref.
	χ_{aa}	χ_{bb}	χ_{cc}	χ_{aa}	χ_{bb}	χ_{cc}	
Pyrrrole	+4.91	+1.96	-6.87	+1.43 ± 0.05	+1.24 ± 0.05	-2.67 ± 0.02	12
Oxazole	-4.29	+1.95	+2.34	-3.99	+1.58	+2.41	7
Isoxazole	+0.97	-1.08	+0.11	<1	<1	<1	7
1,2,5-Oxadiazole ..	-1.19	+0.01	+1.18	-0.69 ± 0.09	-0.46 ± 0.13	+1.15 ± 0.04	8
1,3,4-Oxadiazole ^a ..	-3.12	+2.15	+0.97	-3.80 ± 0.01	+2.02 ± 0.02	+1.78 ± 0.02	12
1,2,3-Oxadiazole ^b ..	-0.78	+2.45	-1.67	—	—	—	—
1,2,3-Oxadiazole ^b ..	-1.97	-1.45	+3.42	—	—	—	—
1,2,4-Oxadiazole ..	-1.61	+2.53	-0.92	—	—	—	—
1,2,4-Oxadiazole ..	-0.64	-1.07	+1.71	—	—	—	—
Pyridine	-5.99	+2.59	+3.40	-4.88 ± 0.04	+1.43 ± 0.03	+3.45 ± 0.02	13
Pyridazine ^c	-4.11	+1.01	+3.10	-4.646 ± 0.01	+1.378 ± 0.02	+3.268 ± 0.01	14

^a χ_{ab} (calc) = +3.19 Mc./sec., χ_{ab} (exp) = +2.70 ± 0.05 (ref. 12).

^b Representation as in Table 1.

^c χ_{ab} (calc) = +3.54 Mc./sec., χ_{ab} (exp) = +2.66 ± 0.16 (ref. 14). (ϕ) angle to diagonalize quadrupole tensor. ϕ (calc) = 27.1°. ϕ (exp) = 20.7° ± 0.9° (ref. 14). ^ indicates particular nitrogen nucleus in the molecule.

the in-plane terms. There appears to be no obvious physical argument to explain the anomalously large calculated constants for pyrrole and for this molecule, contrary to the general rule, the *sum* of multi-centre terms might be appreciable. Despite the lack of agreement for pyrrole, the method may well provide a basis for analyses of complicated microwave spectra, when for example, there is appreciable coupling between two or more ¹⁴N nuclei. It is of special interest to note that in 1,2,3-oxadiazole and 1,2,4-oxadiazole the calculated values are negative for the 2-N perpendicular coupling constants.

Further calculations on asymmetric molecules (not reported here) have shown that although the dipole moment components often differ from the measured values, their ratio is remarkably close to

experiment.¹⁵ For most molecules, this result was used to fix the orientation of the inertial axes in the molecular frame. For oxazole, the orientation was also calculated from the quadrupole asymmetry parameter η

$$\text{where } \eta = (\chi_{aa} - \chi_{bb}/\chi_{cc}),$$

the difference between this and that calculated from $|\mu_a : \mu_b|$ being about 3°. The close agreement between dipole and quadrupole predictions is further confirmation of the usefulness of the CNDO/2 method in such calculations.

The values obtained are better than the previous π -electron only calculations, and the inclusion of the σ -electrons provides a more satisfactory theoretical basis.

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