The Electric Dipole Moments of some Methyl Substituted Pyrones and Pyranopyrandiones

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Monocyclic 2- and 4-pyrones, being resonance hybrids of covalent and dipolar structures (I, Ia, II, IIa), are known to have large dipole moments (1,2). The dipole moments of pyranopyrandiones formed by fusion of two 2- and/or 4-pyrone rings, may therefore be expected to vary according to the relative orientations of the component rings. Thus measurement of electric dipole moments should afford information not only about the gross structures of the pyranopyrandiones but also the extent of interaction between the π-electron systems of the two rings.

The moments of 4,6-dimethyl-2H-pyran-2-one (III) and 2,6-dimethyl-4H-pyran-4-one (IV) and of five methyl derivatives (V-IX) of three pyranopyrandiones, with distinctly different orientations, have now been determined in dioxan solution.

EXPERIMENTAL

The preparations of the compounds have been described (3,4, 5,6). Dielectric constants, densities and refractive indices were determined by standard procedures (7,8). The detailed results are summarised in Table I, using standard notation (8). Dioxan was refluxed in excess sodium until the sodium remained bright. Its density, refractive index and dielectric constant were determined afresh for each set of measurements.

Discussion

The dipole moments expected for the localised covalent structures (I-IX) can be computed by vector summation of bond and group moments (9) (C=O, 2.72; C-O, 1.66; C-Me, 0.40; C-H, 0.30 D). π Moments can be calculated from values of π charge densities obtained by the simple Hückel molecular orbital (HMO) approximation. These can be further improved by application of the ω technique to the HMO method. Semi-empirical molecular orbital theory may also be applied in the form of the CNDO/2 approximation to compute overall moments arising from the distribution of σ as well as π charge densities in the molecule. In making these calculations, each pyrone ring is assumed to have the shape of a regular hexagon with all bond lengths equal to 1.40 Å; other bond lengths required are: C=O, 1.18; C-C, 1.53 and C-H, 1.09 Å, assuming

tetrahedral valencies for extra-nuclear carbon atoms. Table II summarizes the results of all these calculations.

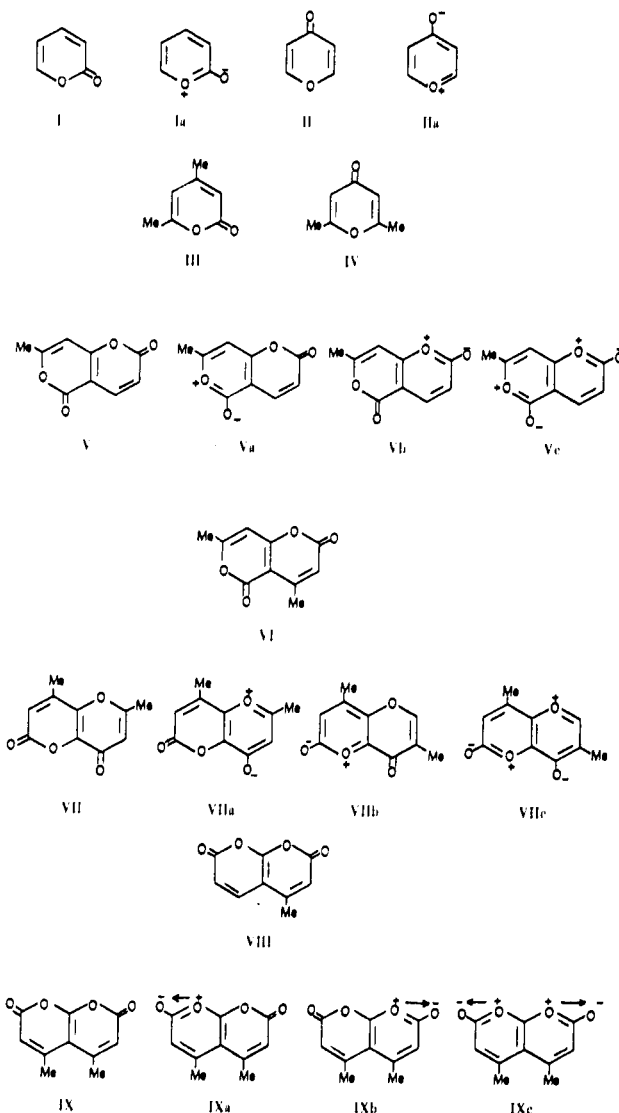If mesomeric effects were absent, the observed dipole moments of the compounds listed in Table II would

Table I

Polarizations, Refractions and Dipole Moments[a] in Dioxan[b] at 25°

Compound	$\alpha\epsilon_1$	β	γ	∞P_2 (CC)	R_D (exptl)	R_D (Calcd.)	μ (D)
III 4,6-Dimethyl-2H-pyran-2-one	26.4	0.042	0.211	466	35.7	33.17	5.6 ± 0.1
IV 2,6-Dimethyl-4H-pyran-4-one	20.2	0.043	0.201	649	35.3	33.17	4.9 ± 0.1
V 7-Methyl-2H,5H-pyrano[4,3-b]pyran-2,5-dione	5.9	0.219	0.150	213	43.9	41.53	2.9 ± 0.3
VI 4,7-Dimethyl-2H,5H-pyrano[4,3-b]pyran-2,5-dione	6.7	0.231	0.170	257	52.9	46.17	3.0 ± 0.1
VII 2,8-Dimethyl-4H,6H-pyrano[3,2-b]pyran-4,6-dione	41.4	0.175	0.164	1345	50.5	46.17	8.0 ± 0.1
VIII 4-Methyl-2H,7H-pyrano[2,3-b]pyran-2,7-dione	31.7	0.288	0.209	958	44.9	41.53	6.7 ± 0.1
IX 4,5-Dimethyl-2H,7H-pyrano[2,3-b]pyran-2,7-dione	33.0	0.171	—	1088	—	46.17	7.1 ± 0.5

(a) Dipole moments were calculated assuming that $_E$P (electronic polarization) = R_D (experimental). (b) Owing to difficulties with solubility, only solutions of low concentration could be made. This was especially true of compound IX.

Table II

Calculated and Experimental Moments

Compound	Localised Bond Moments (D)	HMO (D)	ω-technique (D)	CNDO/2 (D)	$\Delta\mu$(a) (D)	Experimental (D)
I 2H-Pyran-2-one	4.4	—	—	4.9		ca 5.0 (b)
II 4H-Pyran-4-one	1.8	—	—	3.6	1.9	3.7 (c)
III 4,6-Dimethyl-2H-pyran-2-one	4.4	—	—	—	1.2	5.6 ± 0.1
IV 2,6-Dimethyl-4H-pyran-4-one	1.8	—	—	—	3.1	4.9 ± 0.1
V 7-Methyl-2H,5H-pyrano[4,3-b]pyran-2,5-dione	1.2	11.2	7.5	5.9	1.7	2.9 ± 0.3
VI 4,7-Dimethyl-2H,5H-pyrano[4,3-b]pyran-2,5-dione	1.1	11.2	7.5	6.2	2.1	3.0 ± 0.1
VII 2,8-Dimethyl-4H,6H-pyrano[3,2-b]pyran-4,6-dione	5.4	16.1	10.2	8.4	2.6	8.0 ± 0.1
VIII 4-Methyl-2H,7H-pyrano[2,3-b]pyran-2,7-dione	7.0	6.9	3.6	6.9	-0.3	6.7 ± 0.1
IX 4,5-Dimethyl-2H,7H-pyrano[2,3-b]pyran-2,7-dione	7.2	7.5	4.5	7.5	-0.1	7.1 ± 0.5

(a) $\Delta\mu$ is defined as the difference between the experimental values and the corresponding values calculated from bond and group moments. (b) This is an estimated value, since the compound is difficult to obtain and its moment has apparently never been measured. Its value is judged to lie between 4.4 D (calculated from bond moments) and 5.5 D (observed for 4,6-dimethyl-2H-pyran-2-one). (c) From M. Rolla, M. Sanesi and G. Traverso, Ann. Chim. (Rome), 42, 673 (1952).

approximate closely to the corresponding values calculated from group and bond moments i.e. we would expect $\Delta\mu$ to be close to zero. However, we see from Table II that $\Delta\mu$ has unusually large values in the case of compounds II to VII. This strongly suggests that appreciable delocalisation of the π electrons occurs in these molecules, in agreement with other physical observations (10) and with the fact that these molecules can be formulated in terms of a large number of dipolar resonance structures. Among these, the ones with the positive charge on the ethereal oxygen such as those shown below, are of special importance as they would be stabilised by the presence of at least one ring having the benzenoid structure.

CNDO/2 calculations of dipole moment were also performed to see whether reasonable agreement with observed values could be obtained for these large molecules. From Table II, we find that with the exception of V and VI, the CNDO/2 dipole moments agree well with those found by direct measurement, including the case of the prototype molecule, 4-pyrone (II). The CNDO/2 moment for 2-pyrone (1, 4.9 D) is also close to the estimated experimental value of 5.0 D. In view of this moderately good agreement, it is surprising that large discrepancies should occur in the case of V and VI where the net atomic electronic charges appear to have been overestimated. It is possible that the errors which cancelled out in the neglect of all two-electron integrals which depend on the overlapping of charge densities of different atomic basis orbitals, have failed to do so in the case of V and VI.

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