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# Dipole Moments of Some 2H-Cyclopenta[d]pyridazines

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The magnitudes of the dipole moments of 2-methyl-2H-cyclopenta[d]pyridazine, 2-phenyl-2H-cyclopenta[d]pyridazine, and of 5,7-dichloro-, 5,6,7-trichloro-, 5,7-dibromo-, 5,6,7-tribromo-, and 5,7-bis(trifluoroacetyl)-2-methyl-2H-cyclopenta[d]pyridazine have been measured in benzene at 20° and found to be 2.83 ± 0.04, 2.88 ± 0.04, 3.80 ± 0.06, 5.02 ± 0.08, 4.32 ± 0.07, 5.25 ± 0.08, and 6.71 ± 0.07, respectively. In all cases the ring heteroatoms are at the positive end of the dipole.

The dipole moment of azulene has been determined by solution methods (*4, 14, 16*) and more exactly (0.796 ± 0.014 D) from microwave spectral data (*15*). The orientation of the dipole along the long axis of the molecule with the positive end in the seven-membered ring was shown by the measurement of the dipole moments of appropriate azulene derivatives (*4, 9*).

The present study (*8*) was undertaken to determine the effect on the dipole moment of the modification of the azulene structure into a π-excessive heteroanalogue containing a π-equivalent nitrogen adjacent to the π-excessive one, and was made possible by the recent availability (*2, 3*) of sufficient quantities of molecules of this type (I and II). For the determination of the direction of the dipole moments, several derivatives (III–VII) having electron attracting substituents on the five-membered ring were used. The low solubility of the parent molecule (I, R = H) precluded its inclusion in the series.
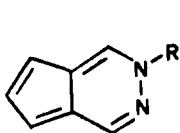
I, R = CH$_3$
II, R = C$_6$H$_5$
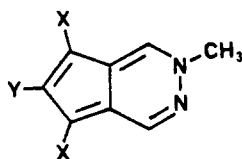
III, X = Cl; Y = H
IV, X = Y = Cl
V, X = Br; Y = H
VI, X = Y = Br
VII, X = COCF$_3$; Y = H

A combination of the methods of Hedestrand (*7*) and Guggenheim (*6, 11, 13*) was used to calculate the dipole moments from the solution data obtained. A discussion of this, including a direct consideration of the instrument (Dipolemeter Type DM 01) used in this study, may be found in the literature (*12*). The method has the important advantage of not requiring the determination of the densities of the solutions. With benzene as the solvent, the expression for the dipole moment simplifies to eq 1 which involves the accurate measurement of only the dielectric constant and the refractive index. The sodium D line was used for the latter since this has been shown to give good results and the compounds did not absorb in this region.

$$\mu^2 = (0.895 \times 10^{-38})(a_\epsilon - a_n)M_2 \text{ dyne cm}^4 \qquad (1)$$

where

$$a_\epsilon = \frac{\sum \epsilon_{12}\omega_2 - \sum \epsilon_1 \omega_2}{\sum \omega_2{}^2}$$

and

$$a_n = \frac{\sum n_{12}{}^2\omega_2 - \sum n_1{}^2\omega_2}{\sum \omega_2{}^2}$$

M is the molecular weight, ϵ is the dielectric constant, *n* is the refractive index, and ω is the weight fraction of the solvent (*1*), solute (*2*), or solution (*12*). The primary data are given in Table I and the molecular weights and calculated values in Table II.

The results with I and II show a dipole moment some three times larger than that of azulene. The increase in the size of the moment in III–VII reveals the orientation of the dipoles in these compounds and in I and II have the positive end in the six-membered ring. Thus the direction as in azulene is preserved, and the electron donation by the π excessive nitrogen more than compensates for the inductive effects of the two nitrogens and the presence of the unshared pair on the π equivalent one.

This interpretation is consistent with the analogous benzenoid heterocyclic compounds wherein the substitution of an adjacent π equivalent nitrogen for a ring carbon in pyrrole (μ = 1.8 D) results in a decrease in the moment for pyrazole (μ = 1.5 D). The latter has the same dipole orientation as pyrrole and I (*1*). The dipole moment for the corresponding compound, 2-methyl-2-pyrindine, related to I has not been measured, but Berson and

Table I. Dipole Moment Determination Data (Benzene, 20°)

Compound	$10^3\omega_2$	$n^{20}D$	S^a	ϵ_{12}
I	5.202	1.5015	2537.8	2.307
I	5.307	1.5016	2558.2	2.317
I	9.83	1.5023	2622.2	2.351
I	10.39	1.5024	2648.8	2.364
I	15.92	1.5032	2721.1	2.403
I	16.43	1.5033	2719.5	2.402
I	21.40	1.5039	2994.3	2.441
I	21.84	1.5040	2780.1	2.434
II	5.139	1.5017	2567.6	2.322
II	10.51	1.5028	2598.0	2.338
II	15.94	1.5037	2652.8	2.367
II	21.46	1.5050	2708.4	2.396
III	5.177	1.5014	2590.4	2.334
III	5.156	1.5013	2595.9	2.337
III	10.17	1.5019	2684.3	2.384
III	10.70	1.5021	2683.4	2.383
III	16.30	1.5027	2782.6	2.435
III	15.08	1.5026	2759.3	2.423
III	23.51	1.5032	2846.4	2.469
III	16.85	1.5028	2792.3	2.440
IV	5.146	1.5012	2667.5	2.375
IV	10.07	1.5018	2786.9	2.437
IV	14.84	1.5022	2833.1	2.462
IV	21.99	1.5028	2965.0	2.531
V	5.067	1.5011	2596.9	2.338
V	10.27	1.5016	2667.1	2.374
V	16.69	1.5025	2740.6	2.413
V	20.23	1.5030	2769.4	2.418
VI	5.138	1.5010	2593.2	2.336
VI	11.98	1.5017	2686.0	2.384
VI	15.51	1.5023	2760.6	2.424
VI	20.22	1.5030	2824.4	2.457
VII	5.376	1.5009	2682.5	2.383
VII	10.24	1.5010	2821.6	2.456
VII	15.60	1.5011	2962.2	2.530
VII	20.82	1.5012	3083.3	2.593

^{a} Scale reading (corr) on dipolemeter.

Table II. Calculated Dipole Moment Results

Compound	M^a	a_ϵ	a_n	$\mu(D)$
I	132.16	7.233	0.463	2.83 ± 0.04
II	194.23	5.374	0.591	2.88 ± 0.04
III	201.07	8.929	0.890	3.80 ± 0.06
IV	235.52	12.217	0.304	5.02 ± 0.08
V	289.98	7.516	0.340	4.32 ± 0.07
VI	368.89	8.675	0.328	5.25 ± 0.08
VII	324.19	15.594	0.076	6.71 ± 0.07

^{a} Molecular weight.

co-workers have calculated a value of 5.6 D (5). The value found for I is less than this, as expected.

The relative solution dipole moments of chloro-, bromo-, and iodobenzene are apparently in the same order as the electronegativities of the halogens (10). When the moments for 1,3-dichloro-, 1,3-dibromo-, and 1,3-diiodoazulene were measured, it was noticed that the relative order was dibromo > dichloro ≃ diiodo (1). The difference between the dibromo and dichloro values was small (ca. 0.07 D) and therefore of doubtful significance, so the one that appeared to be unusual was that of the diiodo compound. In the present study the order is clearly dibromo (V) > dichloro (III), well beyond the limits of the experimental error of the method. Curiously, however, the relative

increase in the moment caused by the substitution of the third halogen onto the 6-position is in the opposite order: 1.22 D for chlorine (IV compared to III) and 0.93 D for bromine (VI compared to V). The thermal instability of the corresponding iodo compounds prevented their inclusion in the series.

The red shift in the long wavelength absorption caused by the substitution of halogen in the 1-position of azulene was explained on the basis of a reversal of the direction of the dipole accompanying the transition from the ground to the excited state and the concomitant stabilization of the excited state through an electronic release of electrons by the substituent (4). The observed red shift in the long wavelength maximum for III (25 mμ), V (25 mμ) and also for the corresponding diiodo compound (21 mμ) (3) point to an analogous behavior on the part of these compounds. The change in dipole direction on excitation is also in agreement with the spectral shift caused by changes in solvent polarity observed earlier for I (2).

Experimental Section

Solvents. The reagent grade calibration solvents (n-hexane, cyclohexane, di-n-butyl ether, and benzene) for the dielectric constant measurements and the benzene used in the solution studies were distilled through a glass-helices packed column and dried (molecular sieves) immediately prior to use.

Apparatus. Refractive indices were measured at the sodium D line wavelength on a Bausch and Lomb Abbe 3 L refractometer thermostated at 20.0°.

Dielectric constant measurements were taken with a Type DM 01 dipolemeter. A Type DFL 2 cell, modified such that it contained an inlet at the bottom of the cell, was used.

Dielectric Constant Determinations. The cell was calibrated with four solvents (vide supra) of known dielectric constant. The cell was filled through the inlet at the bottom, and the cell and sample were equilibrated at 20 ± 0.05° prior to each reading. Each series of measurements was preceded by a measurement on dry air to a clean cell standard. Between solutions the cell was' rinsed thoroughly with acetone, then with dry ether, and dried with dry air.

The average $\Delta\epsilon/\Delta S$ was determined from corrected scale readings (S) and the dielectric constant, ϵ_{12}, for each solution calculated from this and the scale reading (2492.0) for benzene.

Compounds. The preparations of compounds I–VII are described elsewhere (6, 7).

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