[CONTRIBUTION FROM THE KEDZIE CHEMICAL LABORATORY, MICHIGAN STATE COLLEGE, AND THE DEPARTMENT OF CHEMISTRY OF THE UNIVERSITY OF CALIFORNIA AT LOS ANGELES]

The Electric Moments of Some Derivatives of Cinnoline, Pyridine and Quinoline

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The electric moments of cinnoline, three 4-substituted cinnolines and six methyl and chloro substituted pyridines and quinolines, have been measured in benzene solution at 25°. The observed values have been compared with those calculated by use of the group moments found empirically in benzene derivatives, and the observed moment of the parent heterocycle. The observed and calculated values agree within experimental error for the various methyl and chloro substituted heterocyclic compounds; however, the observed moments of 4-cinnoyl methyl ketone and 4-carbethoxycinnoline are considerably lower than calculated, showing that these strongly electron-attracting groups have larger group moments in the cinnoline series.

Electric moments have been widely used to study the effects of resonance in substituted benzenes,[1] but relatively few studies have been made on heterocyclic compounds. Since no measurements have been reported on cinnoline derivatives, we have investigated the dipole moments of cinnoline, 4-methylcinnoline, 4-cinnoyl methyl ketone and 4-carbethoxycinnoline in order to compare the resonance interactions in these with those in the analogous benzene derivatives.

Several studies have been made on substituted quinolines and pyridines[2–4] as well as on the parent heterocycles and the observed moments have been compared with moments calculated using the standard group moments derived from substituted benzenes. It is difficult to draw any conclusions from the reported values even when the substituent is a simple one such as the methyl group; thus there is reasonable agreement between the observed and calculated values with γ-picoline (2.57 D reported,[4] 2.61 calcd.), but not with α-picoline (1.72 reported,[2] 2.04 calcd.), 2.6-lutidine (1.65 reported,[3] 1.81 calcd.) or 2-methylquinoline (1.86 reported,[2] 1.99 calcd.). There is some indication that the halogens show a larger resonance effect in the chloro- and bromopyridines than in the chloro- and bromobenzenes, but the magnitude of the observed effects is not much larger than experimental error in 4-chloropyridine (0.84 reported,[4] 0.65 calcd.) or in 2-bromopyridine (2.98 reported,[3] 3.26 calcd.). We have determined the electric moments of 2-chloropyridine, 2-chloroquinoline and 4-methylquinoline, and have also reinvestigated the moments of 2-methylpyridine, 2,6-dimethylpyridine and 4-methylquinoline, so a comparison could be made of the methyl and chloro group moments in substituted pyridines, quinolines and benzenes.

Experimental

Materials. Cinnoline, 4-Methylcinnoline, 4-Carbethoxycinnoline and 4-Cinnoyl Methyl Ketone.—The samples of these compounds which we used were prepared by Miss Elise R. Elisberg under the direction of Dr. T. L. Jacobs and were kindly donated by them. The preparation and physical constants of these compounds have been reported by Jacobs, *et al.*[5]

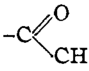
Lepidine, Quinaldine, α-Picoline, 2-Chloropyridine and 2,6-Lutidine.—Eastman Kodak Company materials were dried and fractionated through an efficient packed column; lepidine, b.p. 149–151° (40 mm.), $n^{25}\text{D}$ 1.6149, d^{25}_4 1.0806; quinaldine, b.p. 135.5–137° (39 mm.), $n^{25}\text{D}$ 1.6095, d^{25}_4 1.0592; α-picoline, b.p. 127.8° (745 mm.), $n^{25}\text{D}$ 1.4986, d^{25}_4 0.9405; 2,6-lutidine, b.p. 143° (740 mm.); 2-chloropyridine, b.p. 168° (739 mm.), $n^{25}\text{D}$ 1.5304, d^{25}_4 1.2029.

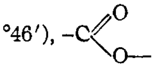
2-Chloroquinoline.—Eastman Kodak Company white label material was recrystallized twice from ethanol, m.p. 34°.

Apparatus and Method.—The electric moments were determined in benzene solution at 25° by use of apparatus and technique described previously[6]; dielectric constants and densities of from four to six solutions, ranging in mole fraction solute from 0.001 to 0.05, were measured for each compound. The molar polarization and dipole moments were calculated by the method of Halverstadt and Kumler.[7] The constants of their equation are shown in Table I, along with the calculated molar polarizations, molar refractions and dipole moments. The probable error in molar polarization is $\pm 0.03P$, in most cases, and the probable error in the dipole moments is about $\pm 0.10D$.

Discussion

The electric moment of cinnoline in benzene solution (4.14 D) is close to the values 3.94[8] and 4.20[9] (dioxane solution) and 4.32[9] (benzene solution) reported in the literature for pyridazine. The benzo group affects the dipole moment only slightly so we have assumed in all calculations that the cinnoline moment is directed along the perpendicular to the N–N bond, as in pyridazine. Electric moments of the other cinnoline derivatives were then calculated by use of the appropriate group moments and angles derived from an analysis of the data in literature[10] for benzene derivatives. The group moments and angles used are

–C–H (m = 0.40), –CH_3 (m = 0.80),

$-C(=O)CH_3$

(m = 2.71, θ = 56°46′),

$-C(=O)O{-}C_2H_5$

(m = 1.81, θ = 83°20′), –Cl (m = 1.15)

the angle is taken as 0° when the group vector is directed away from the ring and standard free rotation formulas were used for calculations involving the acetyl and carbethoxy groups.

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[1] See, for example, G. W. Wheland, "The Theory of Resonance," John Wiley and Sons, Inc., New York, N. Y., 1944.

[2] M. G. Rau and B. N. Narayanaswamy, *Z. physik. Chem.*, **B26**, (1934).

[3] C. E. Goethals, *Rec. trav. chim.*, **54**, 299 (1935).

[4] D. G. Leis and B. C. Curran, THIS JOURNAL, **67**, 79 (1945).

[5] T. L. Jacobs, S. Winstein, R. E. Henderson and E. C. Spaeth, *ibid.*, **68**, 1310 (1946).

[6] M. T. Rogers and J. D. Roberts, *ibid.*, **68**, 843 (1946).

[7] I. F. Halverstadt and W. D. Kumler, *ibid.*, **64**, 2988 (1942).

[8] W. C. Schneider, *ibid.*, **70**, 627 (1948).

[9] Obtained by recalculation of the data of W. Hückel and W. Johnentz, *Ber.*, **75B**, 1438 (1942).

[10] L. G. Wesson, "Tables of Electric Dipole Moments," Technology Press, Cambridge, Mass., 1948.

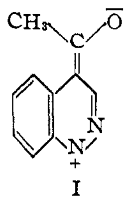
TABLE I

EMPIRICAL CONSTANTS,[a] MOLAR REFRACTIONS,[b] MOLAR POLARIZATIONS AND DIPOLE MOMENTS AT 25°

ϵ_{10}	α^1	V_{10}	β^1	P_2^∞	MR_D	$\mu_{obs.}$	$\mu_{calcd.}$
Cinnoline							
2.2730	24.30	1.14480	−0.55	388.6	37.83	4.14	..
4-Methylcinnoline							
2.2705	29.075	1.14500	−0.60	462.9	43.00	4.53	4.49
4-Cinnoyl methyl ketone							
2.2725	9.30	1.14484	−0.755	177.8	47.93	2.52	3.42
4-Carbethoxycinnoline							
2.2700	18.53	1.14493	−0.85	321.8	54.18	3.62	4.00
4-Methylquinoline (lepidine)							
2.2710	9.34	1.14470	−0.407	176.7	(46.24)	2.52	2.56
2-Methylquinoline (quinaldine)							
2.2700	5.74	1.14470	−0.368	124.6	(46.84)	1.95	1.99
2-Chloroquinoline							
2.2730	15.33	1.14495	−0.738	263.9	46.74	3.26	3.22
2-Methylpyridine (α-picoline)							
2.2725	5.325	1.14463	−0.0975	107.7	(29.05)	1.96	2.04
2-Chloropyridine							
2.2730	14.563	1.14462	−0.465	241.8	(29.18)	3.22	3.28
2,6-Dimethylpyridine (lutidine)							
2.2700	5.15	1.14475	−0.054	105.60	33.85	1.87	1.81

[a] The observed dielectric constants ϵ_{12}, and specific volumes, V_{12}, of the solutions were plotted graphically against mole fraction of solute. The points fall, within experimental error, on straight lines with slopes α^1 and β^1, respectively, and the intercepts at zero mole fraction are ϵ_{10} and V_{10}, respectively. The molar polarizations at infinite dilution P_2^∞, and the dipole moments μ, expressed in Debye units, were calculated from these constants. [b] Molar refractions were calculated from empirical constants, except those in parentheses which were found experimentally.

The observed moment of 4-methylcinnoline (4.53 *D*) agrees well with the calculated value (4.49 *D*), but the measured moments of 4-cinnoyl methyl ketone (4.52 *D*) and 4-carbethoxycinnoline (3.62 *D*) are considerably lower than the calculated values, 3.42 and 4.00, respectively. Thus strong electron attracting groups show a larger interaction with the cinnoline ring than with the benzene ring. The contribution of structures of types I and II to the ground states of 4-cinnoyl methyl ketone and 4-carbethoxycinnoline, respectively, must be larger than the contributions of the analogous structures in the benzene derivatives from which the group moments were derived. A small additional effect might also be anticipated through the contribution of structures of type III which place the positive charge in the second ring. The electric moments of 5-nitro-, 6-nitro- and 8-nitroquinoline reported in the literature[11] are all lower than values calculated using the nitro moment in nitrobenzene, indicating that quinoline, like cinnoline is a better electron donor than benzene. On the other hand, the calculated and observed values for the moment of 4-carbethoxypyridine[2] agree within experimental error.



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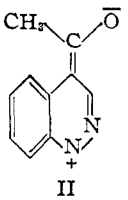

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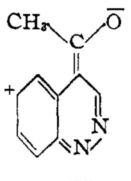

III

The observed and calculated moments of 2-methylpyridine, 2-chloropyridine, 2,6-dimethylpyridine, 2-methylquinoline, 4-methylquinoline and 2-chloropyridine, are compared in Table I. The agreement is, in all cases, within experimental error indicating that the methyl and chloro- group moments in pyridine and quinoline are close to those in benzene.

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[11] C. G. LeFèvre and R. J. W. LeFèvre, *J. Chem. Soc.*, 1470 (1935).