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### The Electric Moments of Some Aromatic Compounds

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The electric moments of several benzene derivatives in which an electron-donating group is *para* to an electron-receiving group have been determined in solution at 25°. The observed moments of p.p'-bis-(dimethylamino)-benzophenone, p.p'-bis-(dimethylamino)-thiobenzophenone, p-nitrophenyl isocyanate, p-methoxyphenyl isocyanate, anisic acid and ethyl anisate are larger than calculated from vector addition of group moments; the increments provide evidence for an appreciable contribution of resonance structures involving group interaction to the normal states of these molecules. The moments of o-nitrophenyl isocyanate and o-*i*-butylnitrobenzene are lower than calculated presumably as a result of steric factors. The electric moments of several other compounds have been investigated to provide data for calculation of group moments and directions.

#### Introduction

When an electron-donating group and an electron-receiving group are *para* to one another in the benzene ring enhancement of resonance may occur<sup>1</sup> as the result of an additional contribution from structures involving group interaction. Since these have a large separation the dipole moment of the molecule may be larger than calculated from group moments provided the latter are computed from measurements on molecules in which this effect is small; many examples of such behavior are known.<sup>1</sup> Thus we might expect that structures such as I in anisic acid and II in ethyl anisate would be important and that the electric moments



of these compounds would be larger than the vector sums of the group moments. The electric moments of these compounds and of several other substances which might show this effect, including p,p'-bis-(dimethylamino)-benzophenone, p,p'-bis-(dimethylamino)-thiobenzophenone, 2,4,7-trinitrofluorenone and p-t-butylnitrobenzene, have been investigated.

(1) See, for example, L. Pauling, "Nature of the Chemical Bond," Cornell University Press, Ithaca, N. Y., 1940; G. W. Wheland, "The Theory of Resonance," John Wiley and Sons, Inc., New York, N. Y., 1944. The thiocyano and selenocyano groups show enhancement of resonance when *para* to an electron acceptor group but the effect is small (or absent) when they are *para* to an electron donor group.<sup>2</sup> Compounds in which the isocyano group is *para* to electron-donor and electron-acceptor groups have been studied to determine whether group interaction occurs in either type compound.

The electric moments of anisole (in dioxane), tbutylbenzene, p-t-butylbromobenzene, m-nitrophenyl isocyanate, m-nitrobenzoic acid and resorcinol diacetate have been determined to provide data for the calculation of group moments; these are substances in which enhancement of resonance should be unimportant.

Steric inhibition of resonance is responsible for lowering the electric moments of many ortho substituted aromatic nitro compounds.<sup>1</sup> The electric moments of *o*-nitrophenyl isocyanate and *o*-*t*butylbenzene might be expected to show this effect and they have, therefore, been measured.

#### Experimental

#### Apparatus and Method

Electric moments were determined in benzene or dioxane solution at 25°. Dielectric constants were measured by a heterodyne-beat method using a crystal-controlled fixedfrequency oscillator, and a negative-transconductance variable-frequency oscillator, similar to those described by Chien.<sup>3</sup> The beat frequency was amplified and connected to a loudspeaker for rough location of the null point; it was located precisely by use of a magic-eye electronic tube. The

(2) T. W. Campbell and M. T. Rogers, This Journal, 70, 1029 (1948).

(3) J. Chien, J. Chem. Educ., 24, 494 (1947).

TABLE I EMPIRICAL CONSTANTS, MOLAR REFRACTIONS, MOLAR POLARIZATIONS AND DIPOLE MOMENTS

Compd.	€1	а	$v_1$	ь	$P_2$	MRD	Obsd.	Calcd.
p,p'-Bis-(dimethylamino)-benzophenone (Michler								
ketone)	2.2725	39.13	1.14480	-1.000	643.3	84.01	5.23	4.43
p, p'-Bis-(dimethylamino)-thiobenzophenone (Thio-								
Michler ketone)	2.2726	50.50	1.14476	-1.167	811.9	92.44	5.93	4.87
2,4,7-Trinitrofluorenone	2.2721	4.075	1.14488	-2.347	112.8	69.27	1.46	1.68
<i>p</i> -Nitrophenyl isocyanate	2.2722	16.75	1.14472	-1.025	278.3	39.51	3.42	1.85
<i>m</i> -Nitrophenyl isocyanate	2.2727	16.45	1.14463	-0.778	279.6	39.51	3.42	3.51
o-Nitrophenyl isocyanate	2.2720	38.13	1.14475	834	597.0	39.51	5.22	5.48
<i>p</i> -Methoxyphenyl isocyanate	2.2730	12.50	1.14476	530	222.2	40.89	2.98	2.74
<i>p-t</i> -Butylbromobenzene	2.2760	5.04	1.14400	793	128.2	52.87	1.92	1.92
o-t-Butylnitrobenzene	2.2720	17.40	1.14550	475	305.9	50.69	3.53	3.81
<i>t</i> -Butylbenzene	2.2725	0.158	1.14473	+ .034	48.91	45.40	0.41	
Anisole (dioxane)	2.2215	2.357	0.97279	+ .043	65.54	32.96	1.26	
Anisic acid (dioxane)	2.3315	8.375	0.97035	288	152.1	37.17	2.37	2.09
<i>m</i> -Nitrobenzoic acid (dioxane)	2.2380	23.50	0.97277	520	370.5	88.10	4.03	4.19
Ethyl anisate	2.2730	8.617	1.14466	564	174.9	50.11	2.48	2.31
Resorcinol diacetate	2.2727	6.117	1.14478	729	139.1	48.48	2.10	2.14

cell consisted of three concentric rhodium-plated brass cylinders insulated from one another by glass spacers; the inner and outer cylinders were grounded. The cylinders were enclosed by a glass envelope which was provided with inlet and outlet tubes and with a connection to air pressure or, through a network of stopcocks, vacuum. Solutions were introduced and removed by pressure of dry air, and contacted only glass (and the metal cylinders). A calibrated precision condenser (General Radio Type 722-D) was used in parallel with the cell. The cell was calibrated with purified benzene and the average of a large number of measurements used. Temperature was controlled to  $\pm 0.01^{\circ}$  by a mercury regulator in conjunction with a thyratron control on the heater. Densities were measured by a modified Ostwald pycnometer.4

Measurements of density and dielectric constant were made on a series of five or six solutions ranging in mole fraction solute from 0.0005 to 0.0020. The molar polarization of the solute at infinite dilution  $P_2$  was calculated by the method of Halverstadt and Kumler.<sup>b</sup> The measured values of the dielectric constants  $\epsilon_{12}$ , and specific volumes  $v_{12}$ , of the solutions were plotted graphically against mole fraction solute. Within experimental error the points were found to fall on straight lines with slopes a and b, respectively; the intercepts at zero mole fraction of solute are  $\epsilon_1$  and  $v_1$ , respectively. The latter were used in place of the directly measured properties of the solvent in the calculations. The molar polarization of solute at infinite dilution  $P_2$ , and the dipole moment  $\mu$ , are calculated from the relations<sup>6</sup>

and

$$\mu = 0.0128 \sqrt{P_2 - MR_D}$$

 $P_{2} = \frac{3av_{1}M_{1}}{(\epsilon_{1}+2)^{2}} + (M_{2}v_{1}+M_{1}b) \frac{\epsilon_{1}-1}{\epsilon_{1}+2}$ 

The constants of this equation are shown in Table I for each compound along with the calculated molar polarizations. The molar refractions, computed from empirical constants in the case of solids and from measured densities and refractive indices in the case of liquids, are also shown in Table I. The distortion polarization is taken equal to the molar refraction MRD in most cases since the atomic polarization term tends to be cancelled by the error introduced in not extrapolating the electronic polarization to infinite wave length.

The probable error in the molar polarizations is  $\pm 0.03 P$ and the probable error in the dipole moments is  $\pm 0.10$ Debye where the moment is larger than 0.5. All electric moment values are in Debye units but the unit is usually not shown.

#### Materials

Benzene.-Thiophene-free benzene was twice partially frozen; the crystals from the second stage were melted and distilled over sodium; d<sup>26</sup>4 0.87356, n<sup>25</sup>D 1.4980.

**Dioxane**.—Dioxane was purified by the method of Fieser<sup>6</sup> and stored over sodium;  $d^{25}$ , 1.0287.

Michler Ketone, m-Nitrobenzoic Acid, Anisic Acid and o-, m- and p-Nitrophenyl Isocyanate.-Materials from Eastman Kodak Co. were recrystallized several times from solvents recommended in the literature.

Anisole, Ethyl Anisate, Resorcinol Diacetate and p-Methoxyphenyl Isocyanate.-Materials from Eastman Kodak Co. were dried and distilled through an efficient packed column; anisole, b.p. 152° (736 mm.);  $n^{25}$ D 1.5147,  $d^{25}_{4}$  0.9887; ethyl anisate, b.p. 156° (26 mm.),  $n^{25}$ D 1.5230,  $d^{25}_{4}$  1.0985; resorcinol diacetate,  $n^{25}$ D 1.5002,  $d^{25}_{4}$  1.1784; *p*-methoxyphenyl isocyanate, b.p. 120° (28 mm.),  $n^{25}$ D 1.5442,  $d^{25}_{4}$  1.1528.

*t*-Butylbenzene.—Material prepared by the Friedel–Crafts reaction was fractionated; b.p. 166–167° (746 mm.),  $n^{25}$ D 1.4902, d25, 0.8550.

Thio-Michler Ketone and 2,4,7-Trinitrofluorenone.— These compounds were obtained from Monomer-Polymer Corp., and were recrystallized twice before use.

p-t-Butylbromobenzene and o-t-Butylnitrobenzene.-These materials were synthesized and purified by Mr. M. L. Patapoff at the University of California, Los Angeles.

#### Results and Discussion

The group moment, and, in the case of nonaxial groups assumed to be freely rotating, the angle between the group moment and axis of rotation, has been obtained for each group from a previous compilation<sup>7</sup> or calculated from electric moments reported here and in the literature.8 The group moment for the *t*-butyl group, derived from the moments of *t*-butylbenzene and *p*-*t*-butyl-

bromobenzene, is 0.82 (C-H = 0.4, assumed). Previous values reported for the electric moment of t-butylbenzene have been slightly higher.<sup>8,9</sup> The group moment of the isocyanate group (1.89), and the angle between it and the axis of rotation  $(15^{\circ}50')$ , were computed from data in the literature.<sup>8</sup> Since the moment of anisole in dioxane (1.26) is close to that in benzene<sup>8</sup> (1.23), the same group moment has been used.<sup>3</sup>

Electric moments may be calculated for the aromatic ketones studied by use of the observed

(6) L. F. Fieser, "Experiments in Organic Chemistry," Second Edition, D. C. Heath & Co., New York, N. Y., 1941.

- (7) M. T. Rogers, unpublished results.
  (8) L. G. Wesson, "Tables of Electric Dipole Moments," Technology Press, Cambridge, Mass., 1948.
  - (9) H. Lumbroso, Bull. soc. chim. (France), 283 (1950).

<sup>(4)</sup> G. R. Robertson, Ind. Eng. Chem., Anal. Ed., 11, 464 (1936).

<sup>(5) 1.</sup> F. Halverstadt and W. D. Kumler, THIS JOURNAL, 64, 2988 (1942).

moment of benzophenone,<sup>8</sup> group moments, and assumed bond angles (120°-planar arrangement of bonds on the central carbon atom). The observed values are much larger than the calculated ones and the increments,  $\Delta = 0.80$  in p,p'-bis-(dimethylamino)-benzophenone and  $\Delta = 1.06$  in p,p'-bis-(dimethylamino)-thiobenzophenone, may be attributed to a small contribution from structures such as III to the ground state of the molecule.



Similar increments may be computed from electric moments reported in the literature<sup>10</sup> for p,p'-di-hydroxybenzophenone ( $\Delta = 0.64$ ), p,p'-dimethoxybenzophenone ( $\Delta = 0.32$ ) and p,p'-dimethoxy-thiobenzophenone ( $\Delta = 0.54$ ); structures analogous to III may be written in each case.

The electric moment calculated for 2,4,7-trinitrofluorenone (1.68) was obtained assuming exact cancellation of the nitro group moments in the 2and 7-positions. Some alteration of bond angles caused by the five-membered ring might account for the slightly lower value observed; no enhancement of resonance would be expected since all the substituents are electron acceptors.

Both p-nitrophenyl isocyanate ( $\Delta = 1.57$ ) and pmethoxyphenyl isocyanate ( $\Delta = 0.24$ ) have observed moments larger than expected, but the effect is much larger in the former. In p-nitrophenyl isocyanate resonance with two additional structures V and VI, with the same number of bonds as IV, can occur and the large increment observed presumably reflects the importance of these. Only one additional structure, VII, with one less bond than the principal structures, can be written for p-methoxyphenyl isocyanate, hence the relatively low observed increment for this compound is reasonable. The isocyanate group apparently behaves as an electron acceptor through the inductive effect and as an electron donor through the resonance effect.



The electric moment of anisic acid is larger than calculated ( $\Delta = 0.28$ ) and the increase indicates that structures such as I are important. The larger increments for *p*-hydroxybenzoic acid ( $\Delta =$ 

(10) A. A. Maryott and S. F. Acree, J. Research Natl. Bur. Standards, 38, 505 (1947).

0.27) and p-aminobenzoic acid ( $\Delta = 0.95$ ), obtained by comparing the moments calculated from the above group moments with observed values in the literature,<sup>8</sup> are evidence for an even greater importance of structures of type I in these compounds. Although the increment observed here for ethyl anisate ( $\Delta = 0.19$ ) is scarcely larger than experimental error, the somewhat larger increments shown by p-aminoethylbenzoate ( $\Delta = 0.55$ ) and phydroxyethylbenzoate<sup>4</sup> ( $\Delta = 0.35$ ) lend support to the hypothesis that structures of type II are of some importance in these compounds.

There is some question whether hyperconjugation of the type postulated to account for the electric moment of toluene becomes more, or less, important when the hydrogens of the methyl group are replaced by methyl groups. It is, therefore, interesting to compare the observed moments<sup>4</sup> of p-nitrotoluene and p-t-butylnitrobenzene with the calculated values; an increment of 0.19 is obtained for the latter compound compared with essentially zero increment in p-nitrotoluene. Although the increment is of the order of the errors involved, this suggests that structures of type VIII contribute to the ground state of the molecule



and, therefore, that the *t*-butyl group donates electrons, at least in part, by such a resonance The electric moment of o-t-butylmechanism. nitrobenzene (3.53) is lower than calculated (3.76); this is probably a result of steric inhibition of resonance since the bulky t-butyl group tends to prevent the nitro group from becoming coplanar with the ring. A decrease of about the same order  $(\Delta = -0.26)$  is found for *o*-nitrophenyl isocyanate, assuming free rotation of the isocyanate group. Any tendency for the isocyanate group to avoid the nitro group would lower the calculated moment below the free rotation value and improve the agreement with experiment; it is possible that both this and some twisting of the nitro group occur.

Although the carboxylic acids might be expected to show anomalies, the average deviation of the observed moments of twelve substituted benzoic acids from values calculated by group moments was found to be only 0.10 D (molecules in which enhancement of resonance is relatively unimportant were used). A value much lower than observed, as in p-methylsulfonylbenzoic acid,<sup>3</sup> therefore seemed to be significant and suggested that the hydroxyl hydrogen tends to point toward a strongly electronegative *meta* group. If this were true the electric moment of *m*-nitrobenzoic acid should also be lower than calculated and this is found to be true. It is also true for m-fluoro- and mchlorobenzoic acids where the observed values are 0.2 lower than calculated: since the moment of the molecule is low when the hydrogen atom is nearest the nitro group, a rather small tendency to favor this position would account for the observed decrements.

A group moment, and a value for the angle between this and the bond joining the group to the ring, have been calculated in a formal manner for the more complex carbethoxy and acetate groups. Since the assumption of free rotation about all single bonds is not justified in these cases, a more detailed analysis has not been attempted. From the moment of resorcinol diacetate reported here, and the literature values<sup>4</sup> for hydroquinone diacetate and *p*-cresyl acetate, the group moment (1.65) and angle (115°) may be found. Similarly a group moment (1.81) and angle (83°20') were obtained for the carbethoxy group. Group moments

used here are those considered appropriate for describing results obtained in benzene solution with the exception of the carboxylate group moment which is derived from data obtained in dioxane solutions.

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#### [CONTRIBUTION FROM THE KEDZIE CHEMICAL LABORATORY, MICHIGAN STATE COLLEGE]

# The Electric Moments of Some Acetylenic Halides, Alcohols, Ethers and Amines

## BY MAX T. ROGERS AND MORTON B. PANISH

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The electric moments of propargyl bromide and iodide, and of several alkyl substituted derivatives of these, have been determined in benzene solution at  $25^{\circ}$ . The observed moments are in general lower than anticipated even when hyperconjugation is taken into account. If it is assumed that the acetylenic group is electron attracting, and leads to a reduction of 0.3 to 0.6 D in the carbon-halogen bond moment, reasonable calculated values are obtained. The electric moments of several acetylenic alcohols, ethers and amines are also reported and the values discussed.

#### Introduction

An electron diffraction investigation of a series of propargyl halides<sup>1</sup> showed that the carbon-halogen internuclear distances were longer than in the corresponding alkyl halides. To account for this observation it was postulated<sup>1</sup> that resonance structures of types I and II made a significant contribution to the ground state of the molecule. If this hypothesis were correct, the dipole

$$H - C \equiv C - C H_2 \overline{Br} \qquad H - C = C + 2 \overline{Br}$$

moments of the propargyl halides should be about as large as, or larger than, those of the corresponding alkyl halides even when hyperconjugation is taken into account. We have, therefore, investigated the electric moments in benzene solution of a series of acetylenic halides; to extend the study the electric moments of some other acetylenic derivatives have been measured. No values have been reported previously for any of these substances, but the moments of propargyl bromide and propargyl alcohol had been determined by Rogers and Patapoff.<sup>2</sup>

#### Results

The electric moment of propargyl bromide (1.49 D) may be compared with that of *n*-propyl bromide in benzene solution (1.95). If the moment of ethyl acetylene<sup>3</sup> (0.80) is used as a measure of the moment due to both hyperconjugation (structures of type III) and the difference in electronegativity between an acetylenic and normal carbon atom,<sup>4</sup> then the electric moments calculated

(1) L. Pauling, W. Gordy and J. H. Saylor, This Journal, 64, 1753 (1942).

(2) M. T. Rogers and M. L. Patapoff, unpublished results.

(3) L. G. Wesson, "Table of Electric Dipole Moments," The Technology Press, Cambridge, Mass., 1948; "Tables of Electric Moments of Substances in the Gaseous State," National Bureau of Standards Circular 537, Washington, D. C., 1953.

(4) See, for example, C. A. Coulson, "Valence," Oxford University Press, 1952.

for propargyl bromide and iodide are 1.85 and 1.80 D, respectively. The observed moments are lower by 0.35 and 0.60 D, respectively, and to account for the decrease it seems necessary to postulate that the carbon-halogen moments are lower in the propargyl halides. This could be attributed to an inductive effect, the acetylenic carbon atom being more electronegative than a normal carbon atom. We prefer to attribute it in a formal way to a resonance effect and consider that the contribution of structures such as IV and V to the ground state of the molecules is important.

$$\begin{array}{ccc} H^{+} & H^{+} & H^{-}C \equiv C - \overset{-}{C} H_{2} \overset{+}{B} r \\ H^{-} & H^{-}C \equiv C - \overset{-}{C} H_{2} \overset{+}{B} r \\ H^{-} & \overset{-}{C} \equiv C = C H_{2} \overset{+}{B} r \\ V \end{array}$$

A contribution of such structures equivalent to a decrease of 0.3 in the C–Br moment, or 0.6 in the C–I moment, reproduces the observed values when the hyperconjugation moment is also included. Since iodine has a lower ionization potential than bromine, the greater importance of structures IV and V in propargyl iodide is reasonable.

The effect becomes successively smaller as methyl groups are substituted for hydrogens on the carbon atom to which bromine is attached. Thus the moments of 2-bromo-3-butyne and 2methyl-2-bromo-3-butyne are lower than calculated from the moments of the analogous alkyl halides (2-bromobutane and 2-bromo-2-methylbutane) and the hyperconjugation moment (0.8), but the differences, 0.16 and 0.13, are smaller than for the propargyl compound and indicate either a decreased contribution from structures analogous to IV and V or a decreased importance of hyperconjugation. If the reduction in the C-Br moment is taken to be 0.15, representing a