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Dipole Moments and Resonance of Some Benzein Indicators and Related Compounds

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An apparatus for the measurement of dielectric constants of liquids by the heterodyne method and, in particular, for the determination of dipole moments is described. Dipole moments ($\times 10^{18}$ electrostatic unit (esu)) are reported for, 4-hydroxybenzophenone (3.96), 4,4′-dihydroxybenzophenone (4.49), 4-hydroxy-2-methyl-5-isopropylbenzophenone (3.59), fuchsone (5.83), benzaurin (6.85), aurin (7.96), *o*-cresolbenzein (6.70), thymolbenzein (6.67) and α-naphtholbenzein (6.07) using dioxane as solvent. The last six compounds contain the quinoidal structure and have unusually large moments. The values are nearly double those found for the derivatives of benzophenone that have corresponding polar groups. The influence of resonance involving highly dipolar excited structures in determining the actual state of these molecules is discussed.

I. Introduction

Development in recent years of the concept of quantum-mechanical resonance has been of value in interpreting the physical and chemical behavior of many types of organic molecules [1, 2].[1] The correlation between spectral absorption in the visible region by organic dyes and indicators and resonance has been emphasized by Bury [3]. A number of investigators, but particularly Brooker and coworkers [4], have had notable success in interpreting in terms of resonance certain characteristics of absorption in colored organic compounds.

Dipole moments of dyes and indicators are of interest in connection with the type of resonance which includes highly dipolar structures, as illustrated in figure 2 by structures II and III. The actual structure and charge distribution depend upon the relative contributions from the various structures involved in the resonance. When highly dipolar structures contribute significantly, the observed dipole moment differs from and is generally greater than that to be expected from a consideration of the classical structure alone, and the magnitude of this difference indicates the importance of these dipolar structures in the resonance.

The dipole moments of α-naphtholbenzein and thymolbenzein previously reported [5] were considerably larger than one would expect from a consideration of the classical structures alone. In the work now reported the measurements include other indicators of the benzein series and also some related hydroxybenzophenones that have corresponding polar groups. Structurally, the benzeins, or hydroxyfuchsones, differ from the familiar phenolphthalein and phenolsulfonphthalein series of indicators only in not having the carboxyl or sulfonic acid group. The compounds measured include 4-hydroxybenzophenone, 4,4′-dihydroxybenzophenone, 4-hydroxy-2-methyl-5-isopropylbenzophenone (thymolphenylketone), diphenylquinomethane (fuchsone), 4′-hydroxyfuchsone (benzaurin), 4′,4″-dihydroxyfuchsone (aurin) 4′-hydroxy-3,3′-dimethylfuchsone (*o*-cresolbenzein), 4′-hydroxy-3,3′-diisopropyl-6, 6′dimethylfuchsone (thymolbenzein), and α-naphtholbenzein. For brevity the names in parentheses will be used hereafter. The measurements were made with dioxane and, in several cases where solubility permitted, benzene as solvents. The moments found for fuchsone and the various hydroxyfuchsones are much larger than those of benzophenone and the corresponding hydroxy derivatives and indicate that dipolar resonance structures make a significant contribution to the actual state of these molecules.

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[1] Figures in brackets indicate the literature references at the end of this paper.

II. Materials

Thiophene-free benzene was refluxed and distilled over sodium just before use. Technical dioxane was purified by the method recommended by Weissberger [6] and then distilled over sodium immediately before use. 4-Hydroxybenzophenone and 4,4′-dihydroxybenzophenone were supplied by the Dow Chemical Co. The 4-hydroxybenzophenone was recrystallized from benzene, then from an ethanol-water mixture, and again from benzene. The melting point, 131° to 132° C did not change after the first recrystallization from benzene. The 4,4′-dihydroxybenzophenone was first washed with boiling benzene to extract the more soluble impurities and then recrystallized three times from an ethanol-water mixture. The melting point was 213° to 214° C. Purified samples of fuchsone and aurin were furnished by W. C. Bainbridge of H. Kohnstamm & Co., Inc.[2] Purified samples of thymolbenzein and thymolphenylketone were obtained from Cornell University.[3] α-Naphtholbenzein from Eastman Kodak Co. was twice recrystallized from glacial acetic acid. Additional recrystallization gave no further change in the molar absorption index determined with a Coleman model 10S spectrophotometer. Benzaurin was prepared by condensation of phenol with benzotrichloride [7]. The crude material was purified by two recrystallizations from glacial acetic acid. The melting point was 238° to 240° C. All materials were dried to constant weight in a vacuum oven at about 110° C. Carbon and hydrogen microanalyses were made by K. D. Fleischer on the following compounds:

Name	Found		Calculated	
	C	H	C	H
Thymolphenylketone	80.4	7.1	80.28	7.14
Fuchsone	88.1	5.5	88.34	5.47
Aurin	78.4	4.8	78.59	4.86
Thymolbenzein	83.7	7.8	83.80	7.83
αNaphtholbenzein	86.1	4.9	86.61	4.86

III. Apparatus

Measurements of capacitance were made by a heterodyne beat method [8]. A photograph of the assembled equipment is shown in figure 1. An RCA-type 154 beat-frequency oscillator with the following modification was used as the radio frequency source. The 450-$\mu\mu$f mica condenser in the tuned circuit of the variable oscillator was replaced by an equivalent capacitance consisting of a General Radio Co. type 722–N direct-reading precision condenser in parallel with the cell used for measuring dielectric constants. The fixed oscillator, which had a fundamental frequency of approximately 350 kc, was left intact. The input voltage was stabilized by means of a voltage stabilizer. The output of the oscillators was coupled resistively with a 1,000-cycle tuning fork electrically excited. The resulting beat note was then audible in a set of earphones used as the indicating device.

The precision condenser was equipped with a micrometer worm-gear drive to supplement the regular worm drive in order to increase the precision of setting. The scale of the micrometer contained 50 divisions with each, corresponding to a capacitance of about 0.004 $\mu\mu$f. The condenser was calibrated by a step method using a capacitance of approximately 3 $\mu\mu$f. A plot of the calibration correction with respect to scale reading showed a very definite periodicity corresponding with each complete revolution of the main worm drive.

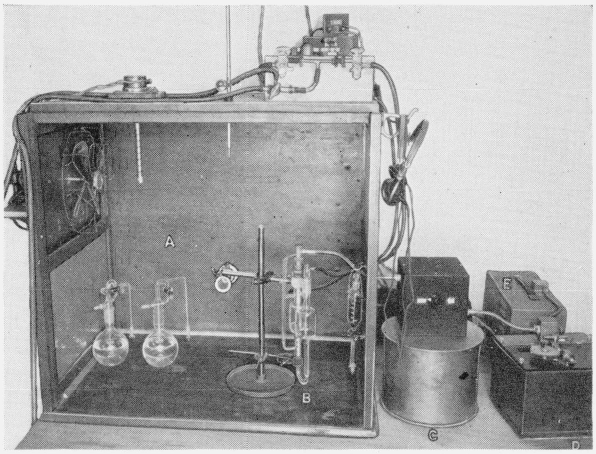

FIGURE 1.—*Assembly of apparatus showing air bath with front removed.*

A, Transfer flask, *B*, cell; *C*, reference condenser and switch box; *D*, precision condenser; *E*, beat frequency oscillator.

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[2] The authors express their appreciation to W. C. Bainbridge and coworkers for specially preparing and purifying these materials.

[3] These compounds were made available through the kindness of J. R. Johnson.

The cell was made of Pyrex glass, in which the two concentric electrodes were formed by deposition of a heavy silver mirror on the appropriate glass surfaces. Contacts between electrodes and leads were by thin platinum wires sealed through the glass walls. The cell was made in two sections which fitted together by means of a ground-glass joint. After deposition of the silver films, this joint was cemented rigidly in place. The inner section contained the ungrounded electrode with the lead, a rigidly mounted, small brass rod, passing up through the center. Contact between the platinum wire and rod was made with mercury held in place with cellulose nitrate cement. This lead was thoroughly shielded with a grounded brass tube. The outer section contained, in addition to the grounded electrode and lead, two enlarged bulbs of about 100-ml capacity each. These bulbs served as a reservoir to accommodate excess solution required in the procedure for making up solutions of varying concentrations to be described. The minimum volume of liquid needed to give constant capacitance was about 20 ml. The interelectrode air capacitance was approximately 40 $\mu\mu$f. Calibration of the cell was made with freshly purified benzene using the data of Hartshorn and Oliver [9] for the dielectric constant.

As the oscillator frequency drifts with time, some method is needed to eliminate the effect of this shift in frequency on the measured cell capacitance. Consequently, a reference air condenser of approximately the same capacitance as that of the cell when filled with solvent was arranged so that it could be substituted for the cell by means of a low-capacitance switch. The time required for settings was only a fraction of a minute, so the difference in capacitance between the cell and reference air condenser could be determined independently of any gradual drift in frequency of the oscillator.

An air bath was used to control the temperature of the cell at 32°±0.04° C. The temperature and relative humidity of the room containing the complete assembly were controlled at 25°±1° C and 45±3 percent, respectively. The sensitivity and stability of the apparatus were such that a change of 0.0001 in dielectric constant could be detected.

IV. Experimental Procedure

One of the chief sources of error in the determination of dipole moments from measurements on highly dilute solutions arises from contamination of the solvent and solutions, particularly by moisture from the air, during handling. Consequently, the design of the cell and the procedure for making up the solutions of varying concentrations were such as to minimize handling and exposure to the air. The solvent was distilled directly into a specially designed transfer flask. Then, by means of dried compressed air, part of this solvent was transferred to the cell and part used in making up a stock solution of solute. Solutions of varying concentrations were made up directly in the cell by successive additions of this stock solution from a weight burette. After each addition, mixing was accomplished by forcing, with dried compressed air, the solution into one of the bulbs and then into the other. When measurements of capacitance were completed on the final solution, a portion of this solution was transferred to a picnometer for determination of density. The density of the same batch of pure solvent was also determined.

V. Calculations and Data

Calculation of the molar polarization at infinite dilution, $P_{2\infty}$ was made by using the following equation given by Hedestrand [10], in which the subscripts 1, 2, and 12 refer respectively to solvent, solute, and solution.

$$P_{2\infty}=\frac{3P_1}{(\epsilon_1-1)(\epsilon_1+2)}\frac{\Delta\epsilon}{f_2}-\frac{P_1}{d_1}\frac{\Delta d}{f_2}+P_1\frac{M_2}{M_1}, \qquad (1)$$

where

ϵ=dielectric constant

$\Delta\epsilon=\epsilon_{12}-\epsilon_1$

f=mole fraction

d=density

$\Delta d=d_{12}-d_1$

M=molecular weight

$P_1=\frac{\epsilon_1-1}{\epsilon_1+2}\frac{M_1}{d_1}$=molar polarization of solvent.

The dipole moment, μ, was calculated from

$$\mu=0.1281[(P_{2\infty}-P_E)T]^{1/2}\times10^{-18}\ esu, \qquad (2)$$

where T is the temperature in degrees Kelvin, and P_E is the electronic polarization obtained by summation of the atomic refractivities listed in Landolt-Börnstein Tabellen, fifth edition.

The experimental and calculated data are given in table 1. A plot of $\Delta\epsilon$ vs f_2 was linear in each case. The slope of this line given in the third column opposite zero concentration was used in the evaluation of $P_{2\infty}$[4]. The separate values of $\Delta\epsilon/f_2$ for each concentration are also given for comparison. The average of these separate values agrees closely with the slope of the linear plot in all cases and shows that the lines pass through the origin, as should be the case. The three values of $\Delta d/f_2$ in parenthesis are based upon the estimated partial molar volumes of these compounds and the assumption of ideal mixing. In these cases the concentrations were rather low for the experimental determinations to be conveniently made. Because of the relatively small magnitude of the term in eq 1 containing $\Delta d/f_2$, the uncertainty in these estimates will have a practically negligible effect upon the dipole moments calculated. As an example, a 20-percent error in this estimate would alter the moment calculated for aurin by only 0.1 percent. The dielectric constant of dioxane by comparison with that of benzene was found to be 2.210. The value for benzene at 32° C was taken as 2.260 [9].

TABLE 1.—*Experimental and calculated data from which dipole moment, μ, is obtained*

$f_2\times10^3$	$\Delta\epsilon$	$\Delta\epsilon/f_2$	$\Delta d/f_2$	$P_{2\infty}$	P_E	μ
4-HYDROXYBENZOPHENONE IN DIOXANE						
						esu
0.000	------	22.2	0.389	371	57	3.96×10^{18}
4.442	0.0992	22.3	------	-----	---	
5.202	.1157	22.2	------	-----	---	
7.420	.1647	22.2	------	-----	---	
8.960	.1990	22.2	------	-----	---	
4,4′-DIHYDROXYBENZOPHENONE IN DIOXANE						
0.000	------	28.5	0.597	461	58	4.49
2.404	0.0714	29.7	------	-----	---	
3.554	.1001	28.2	------	-----	---	
6.526	.1877	28.8	------	-----	---	
9.522	.2718	28.5	------	-----	---	
THYMOLPHENYLKETONE IN DIOXANE						
0.000	------	18.3	0.22	333	75	3.59
1.066	0.0193	18.1	------	-----	---	
2.184	.0397	18.2	------	-----	---	
2.915	.0533	18.2	------	-----	---	
3.593	.0656	18.3	------	-----	---	
THYMOLPHENYLKETONE IN BENZENE						
0.0000	------	15.5	0.66	298	75	3.34
.3834	0.0059	15.4	------	-----	---	
.8123	.0125	15.4	------	-----	---	
1.037	.0163	15.7	------	-----	---	
FUCHSONE IN DIOXANE						
0.0000	------	47.5	0.36	758	79	5.83
.3105	0.0153	49.2	------	-----	---	
.7112	.0344	48.3	------	-----	---	
1.015	.0489	48.2	------	-----	---	
1.282	.0611	47.6	------	-----	---	
FUCHSONE IN BENZENE						
0.0000	------	46.1	0.75	752	79	5.80
.6203	0.0288	46.4	------	-----	---	
1.264	.0582	46.0	------	-----	---	
1.790	.0824	46.1	------	-----	---	
2.255	.1037	46.0	------	-----	---	
BENZAURIN IN DIOXANE						
0.0000	------	65.6	0.56	1,022	81	6.85
.1696	0.0111	65.4	------	-----	---	
.3515	.0231	65.7	------	-----	---	
.5423	.0357	65.8	------	-----	---	
.6878	.0450	65.5	------	-----	---	

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[4] The method of obtaining $P_{2\infty}$ and μ by using the Hedestrand equation, which is the limiting form of the Debye equation as the concentration approaches zero, has certain advantages particularly for measurements on highly dilute solutions. The amount of calculation is minimized and frequently more reliable values are obtained than with the procedure usually employed, which involves a separate calculation of P_2 at each concentration and then extrapolation to infinite dilution. As has been pointed out by Kumler [11], this latter method unduly weights one experimental point, namely, the dielectric constant of the solvent itself, so that a small error in its value may produce a relatively larger error in $P_{2\infty}$ and μ. A linear variation of $\Delta\epsilon$ with f_2 is characteristic of dilute solutions provided, of course, the solute is not appreciably associated. A straight line not passing through the origin suggests an error in the dielectric constant of the pure solvent. Errors attributable to this source have rather frequently led to incorrect values of the dipole moments when the usual method of calculation has been employed [11].

Similar considerations apply equally well to determinations of density, except that errors in density are often much less critical. As densities vary practically linearly with concentration for dilute solutions, it is generally unnecessary to determine densities of more than one or two of the more concentrated solutions.

TABLE 1.—*Experimental and calculated data from which dipole moment, μ, is obtained*—Continued

$f_2\times 10^3$	$\Delta\epsilon$	$\Delta\epsilon/f_2$	$\Delta d/f_2$	$P_{2\infty}$	P_E	μ
AURIN IN DIOXANE						
0.0000	------	88.0	[a] (0.7)	1,352	82	7.96
.0623	0.0054	86.8	------	-----	---	
.0706	.0063	89.2	------	-----	---	
.1059	.0092	86.9	------	-----	---	
.1174	.0103	87.7	------	-----	---	
.1340	.0120	89.5	------	-----	---	
.1567	.0136	86.8	------	-----	---	
o-CRESOLBENZEIN IN DIOXANE						
0.0000	------	62.5	(0.5)	985	90	6.70
.0935	0.0058	62.0	------	-----	---	
.1028	.0065	63.2	------	-----	---	
.1594	.0098	61.5	------	-----	---	
.2043	.0130	63.5	------	-----	---	
.2139	.0132	61.7	------	-----	---	
.2714	.0171	63.0	------	-----	---	
THYMOLBENZEIN IN DIOXANE						
0.0000	------	62.2	0.32	1,010	118	6.67
.2038	0.0123	60.4	------	-----	---	
.3468	.0212	61.2	------	-----	---	
.4606	.0283	61.4	------	-----	---	
.5513	.0339	61.5	------	-----	---	
α-NAPHTHOLBENZEIN IN DIOXANE						
0.0000	------	52.2	0.81	849	111	6.07
.1226	0.0063	51.4	------	-----	---	
.2599	.0137	52.7	------	-----	---	
.4127	.0216	52.4	------	-----	---	
.5605	.0292	52.1	------	-----	---	
α-NAPHTHOLBENZEIN IN BENZENE						
0.0000	------	46.1	(1.3)	775	111	5.76
.0751	0.0034	45.3	------	-----	---	
.1359	.0064	47.1	------	-----	---	
.1840	.0085	46.2	------	-----	---	

[a] Figures in parentheses are based upon the estimated partial molar volumes of these compounds and the assumption of ideal mixing.

VI. Discussion

The dipole moments obtained in dioxane are listed in table 2. The conventional formulas for these compounds are also shown. It is evident that the moments of fuchsone and the various hydroxyfuchsones, or benzeins, are unusually large. They range from 5.87 for fuchsone to 7.96 for aurin, and are generally nearly double the values predicted from the component group moments. Resonance involving the normal or conventional structure and highly dipolar structures evidently plays an important part in determining the actual state of these molecules. Of the numerous resonance structures possible, only three representative structures will be illustrated. These are shown for benzaurin in figure 2. Structure I is the normal, or conventional, formula. It should be born in mind that, in addition to structures II and III, a number of other dipolar structures where the positive charge resides on an ortho or para carbon atom of either of the two benzene rings may contribute to the resonance. Important contributions from structures like II might be anticipated because of the gain in Kekulé resonance energy through conversion of a quinoidal ring to a benzene ring.

To determine the effect of resonance on the dipole moments, it is necessary to know approximately the moment of the normal structure alone. Probably the most satisfactory comparison can be made using the moments of the corresponding derivatives of benzophenone. Structurally, the fuchsone differs from the benzophenone having corresponding substituent groups in that the double bond of the keto group is replaced by the

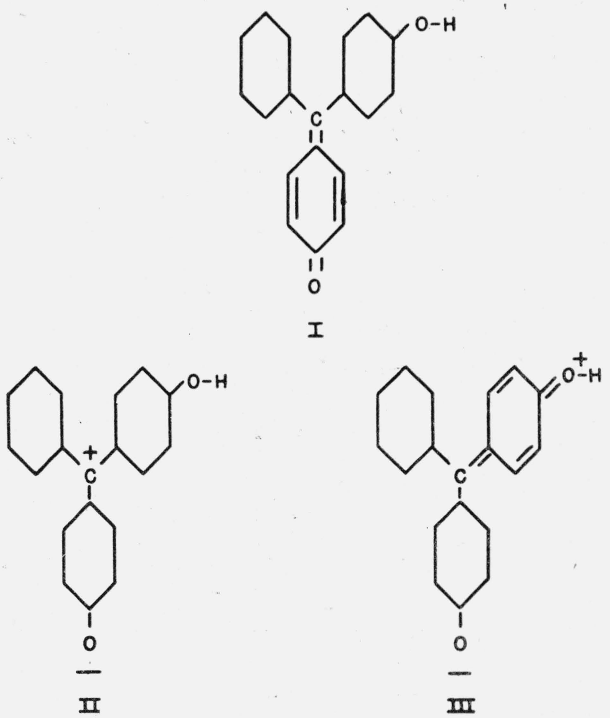
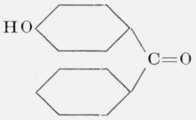
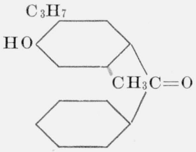
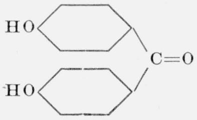
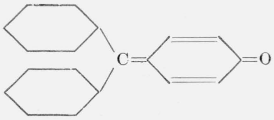
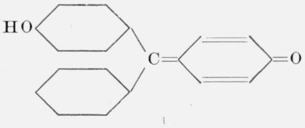
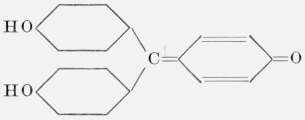
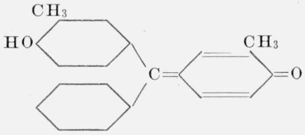
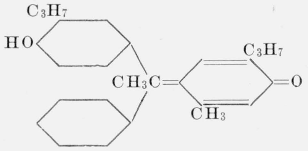
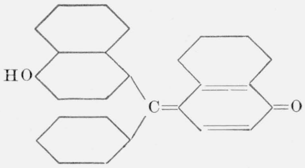


FIGURE 2.—*Most-probable resonant structures for benzaurin, with I, the conventional formula, II and III, the excited dipolar structures.*

quinoidal group. If resonance involving this quinoidal group does not occur, the moments of the corresponding fuchsone and benzophenone derivatives should be about the same. A small difference might be attributed to a change in inductive effects or to a slight shift in valence angles. The relatively large differences actually observed are listed in table 2 under the heading Δ μ for the four cases where a direct comparison can be made. Fuchsone was compared with benzo-

TABLE 2.—*Structural formulas, dipole moments in dioxane, μ, and the increments in dipole moments, $\Delta\mu$, attributable to resonance*

Compound	Structural formula	μ	$\Delta\mu$
4-Hydroxybenzophenone		*esu* 3.96×10^{18}	*esu*
Thymolphenylketone		3.59	
4,4′-Dihydroxybenzophenone		4.49	
Fuchsone		5.83	2.88×10^{18}
Benzaurin		6.85	2.89
Aurin		7.96	3.47
o-Cresolbenzein		6.70	
Thymolbenzein		6.67	3.08
p-Naphtholbenzein		6.07	

phenone, the moment of which was taken as 2.95 [12].

The dipole moment of fuchsone is 2.9 greater than that of benzophenone. The absence of a hydroxyl group precludes structure III. Because of the many possible dipolar structures that may be involved, a reliable quantitative estimate of the extent of resonance based upon this increment in dipole moment cannot be made at present. If the molecule had a fixed dipolar structure as represented by II, the moment estimated from the charge and its distance of separation would be about 27 as a maximum. Allowance for polarization induced in the molecule because of this high separation of charge would lower this estimate. It would appear that highly dipolar structures, such as II, make a contribution of at least 10 percent, and probably considerably more, to the actual state of fuchsone.

Benzaurin has a moment about 2.9 greater than that for 4-hydroxybenzophenone. This increment is practically the same as for fuchsone. The presence of one hydroxyl group does not appear to enhance the contribution of dipolar structures to the resonance.

In aurin there is a para hydroxy group in both phenyl rings, so that there are possible two equivalent structures corresponding to III. The increase in moment over that for 4,4′-dihydroxybenzophenone is about 3.5, or 0.6 larger than the increment for fuchsone or benzaurin. A small but significant contribution from structures like III is indicated.

Thymolphenylketone has a moment 0.37 less than that of 4-hydroxybenzophenone. Only a part of this difference can be attributed to the somewhat lower moment reported for thymol (1.54) [13] than for phenol (1.70) [14]. Steric factors associated with the two alkyl groups would appear to exert an effect. Rotation of the hydroxyl group about the carbon-oxygen bond should be partially restricted by the adjacent isopropyl group. An effect of this sort has been reported by Smyth [15] from a measurement of the moment of 1,4-di-t-butyl-2, 5-dihydroxybenzene. Completely free rotation of the thymolic ring about the carbonyl carbon-aromatic carbon bond should also be prevented by steric interaction between its methyl group and the adjacent phenyl ring. The net result of these two factors would be to restrict the relative orientations of the hydroxyl group with respect to the carbonyl group in such a way as to lower the resultant moment of the molecule.[5] This effect can be best illustrated by employing scale models, such as the Fisher-Hirshfelder atomic models.

By comparison with the other hydroxyfuchsones, the moment of 6.07 for α-naphtholbenzein is rather low. Although the moment of the corresponding ketone was not measured, it should not differ greatly from 4-hydroxybenzophenone. The moment of α-naptholbenzein is about 0.8 lower than that of benzaurin, whereas a somewhat larger value might have been predicted for the following reason. Although structure II is less stable than I, this difference is less than it would otherwise be because of the Kekulé resonance energy gained through conversion of the quinoid ring into a benzene ring. Replacing the quinoid by a naphthoquinoid group should give additional stability to structure II by virtue of the increased Kekulé resonance energy of naphthalene over that of benzene. The lower moment might possibly be explained by steric factors that would interfere with the resonance. For convenience only, two of the many possible excited resonance structures were considered in figure 2. A number of additional dipolar structures, not explicitly involving the hydroxyl group, where the resonance extends through more than one ring, are possible. This resonance would tend to bring all rings involved into a coplanar configuration by giving the bond joining each ring to the central carbon atom a partial double-bonded character, and, conversely, this resonance would be inhibited if steric factors interfered with this coplanar alinement. Steric effects apparently prevent three phenyl rings, as in the ion of crystal violet [16], from becoming coplanar, and the effect would be much more pronounced for the larger naphthyl groups.

Thymolbenzein differs structurally from benzaurin only in having a methyl and an isopropyl group in each of the two chromophoric rings. These alkyl groups are para with respect to each other, so that their group moments virtually cancel. The moment is slightly lower than for benzaurin. The difference between the moments of thymolbenzein and thymolphenylketone is, how-

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[5] It is immaterial with regard to the resultant dipole moment whether one regards a hydroxyl group attached to an aromatic ring as freely rotating or as existing with equal probability in "*cis*" and "*trans*" positions because of resonance. On the latter basis the lower moment of thymolphenylketone would be interpreted as a steric effect favoring the "*cis*" structure with its lower resultant moment.

ever, about 3.1, or 0.2 larger than the corresponding increment for benzaurin. Assignment of this increment entirely to resonance is subject to some uncertainty. If steric factors preventing freedom of rotation, as discussed previously, are responsible for the lower moment of thymolphenylketone, the same sort of effect would be operative in thymolbenzein, but its influence on the moment would be different because the presence of the alkylated quinoidal group would limit further the possible relative orientations of the hydroxyl group. Consequently, comparison of the moment of thymolbenzein with that of thymolphenylketone is not quite as direct a measure of the influence of the polar resonance structures as in previous cases. As the increment for thymolbenzein is not very different from that for fuchsone or benzaurin, steric effects of the second type discussed in connection with the lower moment of α-naphtholbenzein and preventing coplanarity of the rings do not appear to be significant in this case. The moment of 6.70 for *o*-cresolbenzein is influenced to a slight extent by the small group moments associated with the methyl group in each of the chromophoric rings.

The dipole moments of fuchsone, thymolphenylketone, and α-naphtholbenzein in benzene listed in table 1 are 0.03, 0.25, and 0.31 unit lower, respectively, than in dioxane. The appreciable differences for the latter two compounds containing the hydroxyl group can be attributed to the formation of hydrogen bonds with the dioxane.

VII. References

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