

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF NOTRE DAME]

Electric Moments of Ortho-substituted Phenols and Anisoles. II. The O—H---O Bridge¹

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Electric moments of the *o*-haloanisoles² reveal that steric effects and the strong double bond character of the oxygen-to-ring bond cause these molecules to be locked in a *trans* configuration. The moments of the *o*-halophenols indicate, in accord with the interpretation of infrared absorption spectra,³ that between 85 and 90% of these molecules have a *cis* configuration in carbon tetrachloride due to intramolecular hydrogen bonding. When these compounds are dissolved in dioxane, electric moment data reveal that this solvent forms hydrogen bonds with the *trans* molecules, thus causing a shift in the *cis-trans* equilibrium. The order of bond strengths is revealed by this shift to be OH---F > OH---Cl > OH---Br, the reverse of that assumed from the shift in the infrared absorption peaks.⁴ This order suggests that the important factor in the attraction of a positive hydrogen atom is the charge density on the negative atom.

These interpretations were based on moments calculated for these molecules in various configurations. The calculations were made with the aid of assumptions of oxygen valence angles of 120° in anisole and 115° in phenol, and a H—C bond moment of 0.3 Debye unit. Analysis of the moments of phenol, anisole and *p*-bromoanisole indicated a moment of 1.7 for the H—O bond in phenol, 1.0 for the methyl carbon-to-oxygen bond in anisole, and zero for the resultant of the ring carbon-to-carbon dipoles and the ring-to-oxygen bond moment in anisole (assumed to hold also for phenol).

The present investigation deals with substituted phenols and anisoles containing intramolecular OH---O bonds. The moments of catechol and guaiacol were determined to study hydrogen bonding in five-membered rings, and salicylaldehyde, *o*-hydroxyacetophenone and saligenin were selected for a study of six-membered rings. Measurements on veratrole and *o*-methoxybenzaldehyde were made to determine steric effects. In analyzing these moments the above bond angles and bond moments were assumed, along with those indicated in the discussion.

Experimental

Purification of Compounds.—All compounds except veratrole were best grade materials obtained from the Eastman Kodak Company. Saligenin and catechol were used without further purification. The remaining compounds were distilled through an efficient fractionating

column in an all-glass still, and fractions having a constant index of refraction were used in sample preparation. Veratrole was prepared by treating catechol with sodium hydroxide and methyl sulfate; the organic layer was washed with successive portions of a sodium hydroxide solution to remove the guaiacol before drying and distilling. The ethers supercool readily and physical constants of the liquids could be measured at temperatures well below the melting points. Physical constants: veratrole, b. p. 80–80.5° (10 mm.), m. p. 22.7°, n_D^{25} 1.53202, d_4^{25} 1.0801; guaiacol, b. p. 79.5–80° (10 mm.), m. p. 28.1°, n_D^{25} 1.54114, d_4^{25} 1.1288; *o*-hydroxyacetophenone, b. p. 79–80° (6 mm.), n_D^{25} 1.55700, d_4^{25} 1.1275; salicylaldehyde, b. p. 83–83.5° (19 mm.), n_D^{20} 1.5718; *o*-methoxybenzaldehyde, b. p. 94–95° (5 mm.), n_D^{20} 1.5616. Solvents were purified as in previous work.²

As the dielectric constants recently reported⁵ for benzene solutions of catechol at 27° reveal a $\Delta\epsilon/\Delta c_2$ ratio higher than my value, the dielectric constant of another solution at 25° was measured. A sample of catechol was re-

TABLE I
DIELECTRIC CONSTANTS AND DENSITIES OF BENZENE SOLUTIONS AT 25°

c_2	ϵ	d
	Catechol	
0.00000	2.277	0.8730
.00763	2.350	.8761
.00870	2.361	.8762
.00914	2.365
	Guaiacol	
0.00000	2.276	0.8726
.01179	2.374	.8760
.01908	2.434	.8785
.02997	2.526	.8818
	Salicylaldehyde	
0.00000	2.271	0.8714
.01701	2.475	.8773
.02377	2.557	.8799
.03920	2.744	.8850
	<i>o</i> -Hydroxyacetophenone	
0.00000	2.277	0.8730
.01269	2.458	.8773
.01784	2.529	.8795
.02315	2.608	.8810
	<i>o</i> -Hydroxybenzyl alcohol	
0.00000	2.276	0.8726
.00574	2.332	.8745
.00638	2.339	.8748
.00708	2.347	.8750
	<i>o</i> -Methoxybenzaldehyde	
0.00000	2.271	0.8714
.01122	2.557
.01687	2.700	.8772
.02449	2.903	.8797

(1) Presented before the Physical and Inorganic Division at the St. Louis meeting of the American Chemical Society, April, 1941.

(2) Anzilotti and Curran, THIS JOURNAL, **65**, 607 (1943).

(3) Pauling, *ibid.*, **55**, 94 (1936).

(4) Wulf, Liddel and Hendricks, *ibid.*, **55**, 2287 (1936).

(5) Lander and Svirbely, *ibid.*, **67**, 322 (1945).

TABLE II
 DIELECTRIC CONSTANTS AND DENSITIES OF DIOXANE
 SOLUTIONS AT 25°

ϵ_2	ϵ	d
Catechol		
0.00000	2.215	1.0275
.00987	2.339
.01701	2.433	1.0302
.02215	2.494	1.0339
Guaiacol		
0.00000	2.215	1.0275
.01228	2.319	1.0298
.01673	2.359	1.0301
.03158	2.489	1.0330
Veratrole		
0.00000	2.215	1.0275
.01016	2.239
.01573	2.255	1.0287
.02745	2.282	1.0294
Salicylaldehyde		
0.00000	2.217	1.0271
.00961	2.345
.01140	2.367	1.0291
.01480	2.410	1.0292
<i>o</i> -Hydroxyacetophenone		
0.00000	2.215	1.0275
.01230	2.404
.01644	2.467	1.0301
.02020	2.523	1.0308
<i>o</i> -Hydroxybenzyl alcohol		
0.00000	2.215	1.0275
.01314	2.362
.01795	2.420	1.0316
.01942	2.438	1.0321

 TABLE III
 POLARIZATIONS AND ELECTRIC MOMENTS

	P_∞	MR_D	μ
Catechol (benzene)	167.8	29.7	2.58
Catechol (dioxane)	207.1	29.7	2.93
Guaiacol (benzene)	155.2	34.57	2.41
Guaiacol (dioxane)	155.0	34.57	2.41
Veratrole	72.7	39.64	1.23
Salicylaldehyde (benzene)	207.3	34.42	2.88
Salicylaldehyde (dioxane)	220.9	34.42	2.99
<i>o</i> -Hydroxyacetophenone (benzene)	246.6	38.88	3.16
<i>o</i> -Hydroxyacetophenone (dioxane)	256.5	38.88	3.23
<i>o</i> -Methoxybenzaldehyde	406.3	38.95	4.21
<i>o</i> -Hydroxybenzyl alcohol (benzene)	178.5	34.1	2.64
<i>o</i> -Hydroxybenzyl alcohol (dioxane)	193.7	34.1	2.78

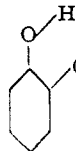
crystallized twice from benzene. The product melted sharply at 103.5°. The $\Delta\epsilon/\Delta c_2$ ratio agreed with the average value obtained four years before. As a check on the apparatus, the dielectric constants of three solutions of benzamide in dioxane were measured at 30.1°. The average $\Delta\epsilon/\Delta c_2$ ratio checked that obtained by Svirbely and co-workers.⁶

Measurements and Calculations.—The measurements of dielectric constants and densities, and the calculation of

solute polarizations at infinite dilution have been described previously.⁷ Indices of refraction at 25° were obtained with a Pulfrich and those at 20° with an Abbe refractometer. Literature values for the densities of salicylaldehyde⁸ and *o*-methoxybenzaldehyde⁹ at 20° were used in calculating molar refractions. Those molar refractions listed to but three significant figures in Table III were calculated from the values for benzene and the monosubstituted benzenes. The distortion polarizations of the aldehydes and ketone were taken as 1.1 MR_D in accord with the large atomic polarization found for the carbonyl group.¹⁰ All other distortion polarizations were calculated as 1.05 MR_D .

Discussion of Results

The absorption spectrum of guaiacol in carbon tetrachloride indicates that practically all of the solute molecules have a *cis-trans* configuration



due to hydrogen bonding. The mo-

ment calculated for guaiacol in this configuration is 2.45. The value calculated for the *trans-trans* form is 0.8 in benzene and 0.9 in dioxane, assuming that the intermolecular hydrogen bonding produces a moment of 0.2 in the direction of the H—O vector. The observed moment is 2.41 in both benzene and dioxane. The rupture by dioxane of some of the intramolecular bonds with the subsequent formation of hydrogen bonds with the *trans-trans* molecules should result in a decrease in moment. The moment of guaiacol in dioxane indicates that very few, if any, of the intramolecular bonds are broken, and that the anisole oxygen forms stronger hydrogen bonds than do the halogen atoms in the *o*-halophenols. The charge densities on the methoxy oxygen in guaiacol and the fluorine in *o*-fluorophenol appear from analysis to be very nearly equal, and the distance factors are practically identical. The greater strength of the O—H...O bond indicates that oxygen has a specific attraction for a positive hydrogen beyond that predicted on the basis of charge density alone.

The equal heights of the two absorption peaks in the 7,000 cm^{-1} region of the spectrum of catechol in carbon tetrachloride indicate a *cis-trans* configuration for the solute molecules.³ The moment calculated for this structure, the resultant of two phenol vectors, 1.6, at an angle of 60°, is 2.8. The calculated moment for the *trans-trans* form is 0.8. The observed moment in dioxane, 2.93, indicates that this solvent forms a hydrogen bond with the *trans* hydrogen without breaking the five-membered ring. The moment in benzene, 2.58, suggests that a few of the catechol molecules are associated, although this interpretation is not supported by the measurements of Lander and Svirbely,⁴ which reveal that the di-

(7) McCusker and Curran, *ibid.*, **64**, 614 (1942).

(8) Carswell and Pfeifer, *ibid.*, **50**, 1765 (1928).

(9) Auwers, *Ann.*, **408**, 239 (1915).

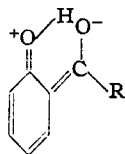
(10) Coop and Sutton, *J. Chem. Soc.*, 1269 (1938).

(6) Davis, Bridge and Svirbely, *This Journal*, **65**, 857 (1943).

electric constant is a linear function of concentration even at very low solute mole fractions.

By comparison with the *trans* configuration observed for the *o*-haloanisoles, a *trans-trans* structure is predicted for veratrole. The moment calculated for this configuration is 0.5, and for the *cis-trans* configuration, 2.1. The observed moment in dioxane, 1.23, compares with a moment of 1.31 in benzene.¹¹ These values indicate either that an appreciable number of these molecules have a *cis-trans* configuration, or that the interaction of each methoxy group with the ring is much weaker than in the haloanisoles.¹² A model of a *cis-trans* veratrole molecule, constructed with the aid of values for interatomic distances listed by Wheland,¹³ shows that this configuration is possible only if two hydrogen atoms of the *cis* methyl group are 55° above and below the plane of the benzene ring, at which positions they are 1.7 Å. from the adjacent oxygen atom, a distance observed for strong hydrogen bonds. Interaction of this type, at a greater distance and with a more highly negative oxygen, occurs in the esters of the carboxylic acids. The structure of veratrole may be clarified by determining the moments of 1,2-dimethoxy-4,5-dimethylbenzene and 1,2-dimethoxy-4,5-dichlorobenzene. The author hopes to carry out these measurements at a later date.

In calculating the moments of salicylaldehyde and *o*-hydroxyacetophenone for configurations involving planar chelate rings, the moment, 1.9, of benzaldehyde and acetophenone was assumed to be at angles of 50 and 55°, respectively, with the ring-to-carbon bond. The calculated moments, 2.65 and 2.8, compare with observed moments of 2.88 and 3.16 for these compounds in benzene. As the moment vector due to the contribution of the structure



is at an angle of approximately 100° with the calculated moments, the large observed moments indicate that this contribution is appreciable. This stabilization of the dipolar ion structure by hydrogen bonding is also evidenced by the exaltations, 0.6 and 0.8 cc., in the observed molar refractions of these compounds. By comparison, the ob-

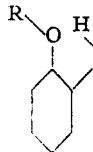
(11) Weissberger and Sängewald, *Physik. Z.*, **30**, 792 (1929).

(12) A decrease in the contribution of the $\text{RO}^+=\text{C}_6\text{H}_4\text{OR}^-$ structures would increase the ring-to-oxygen moment, change the direction of the anisole vector, and increase the moment of the *trans-trans* form.

(13) Wheland, "The Theory of Resonance," John Wiley and Sons, Inc., New York, N. Y., 1944, p. 286.

served molar refraction of *o*-methoxybenzaldehyde is only 0.1 cc. higher than the value calculated from the refractions of anisole, benzaldehyde and benzene. More striking evidence of the strong interaction between the hydroxyl and carbonyl groups in salicylaldehyde and *o*-hydroxyacetophenone is presented by the ultraviolet absorption spectra of these compounds.¹⁴

The large moment observed for *o*-methoxybenzaldehyde, 4.21, indicates a configuration



stabilized by resonance and a weak

CH---O bond. This configuration has the maximum calculated moment, 4.1.

The absorption spectrum of saligenin, *o*-hydroxybenzyl alcohol, in carbon tetrachloride has two peaks of nearly equal heights with a peak separation of 157 cm^{-1} as compared to a separation of 64 cm^{-1} (fundamental) in the spectrum of catechol, indicating stronger intramolecular O—H---O bonds in the alcohol.¹⁵ Electrostatic factors favor the phenol hydrogen as the bridge former. In calculating moments for various configurations, alcohol C—O and H—O bond moments of 0.8 and 1.6 were assumed. The calculated moment for a configuration having a planar ring is 3.1, much higher than the observed moments in benzene and dioxane, 2.64 and 2.78. A likely configuration involving a six-membered chelate ring is one having the alcohol oxygen 30° above the plane of the benzene ring (required for an O---H distance of 1.7 Å.) and the alcohol O—H bond turned downward at such an angle as to allow the phenol hydrogen to interact with a specific pair of unshared oxygen electrons. The moment calculated for this structure is 2.85, in fair agreement with the observed values.

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Summary

Electric moments have been determined for catechol, guaiacol, veratrole, salicylaldehyde, *o*-methoxybenzaldehyde, *o*-hydroxyacetophenone and saligenin in benzene and dioxane. The values obtained indicate that the intramolecular OH---O bond is stronger than the OH---F bond.

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(14) Morton and Stubbs, *J. Chem. Soc.*, 1347 (1940).

(15) Davies, *Trans. Faraday Soc.*, **36**, 1114 (1940); **34**, 1427 (1938).