

sym-diphenyltriazene and mercury(II) nitrate in ethanol react to form (a) a yellow salt identical with that obtained using mercury(II) acetate, (b) a red isomer which may be isolated as such or

in the form of a di-solvate from pyridine, (c) an orange-colored compound which may be isomeric with the yellow and red salts.

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[JOINT CONTRIBUTION FROM THE JONES CHEMICAL LABORATORY, UNIVERSITY OF CHICAGO, AND THE FRICK CHEMICAL LABORATORY, PRINCETON UNIVERSITY]

The Reduction of Dipole Moment by Steric Hindrance in Di-*t*-butylhydroquinone and its Dimethyl Ether

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The dipole moments of di-*t*-butylhydroquinone and di-*t*-butylhydroquinone dimethyl ether have been measured, with the object of studying the steric effects of the bulky *t*-butyl groups upon the adjacent hydroxy or methoxy groups. The moments were obtained by means of the apparatus and methods previously described,^{1,2} the dielectric constants at a frequency of 520 kilocycles and the densities of solutions of the substances in benzene being determined. The benzene was purified by standard methods.

Experimental Results

The dielectric constants, ϵ , and the densities, d , at 25° of the benzene solutions containing the mole fraction, c_2 , of solute are given in Table I; the polarizations, P_2 , are listed in the last column. The polarization of the pure solvent is given as P_1 , and the values of P_2 are extrapolated to $c_2 = 0$ in order to obtain P_∞ . From P_∞ the moments μ are calculated by subtracting MR_D , the molar refraction for the D sodium line calculated from molar and atomic refractions given in Landolt-Börnstein. Any small error resulting from the use of these calculated molar refractions is negligible in comparison to the unusually large experimental errors in the moment values arising from the low solubilities and low dielectric constants of the solutes.

The Preparation of 2,5-Di-*t*-butylhydroquinone.—To a solution of hydroquinone (100 g.) in glacial acetic acid (1 liter) was added 200 cc. (160 g.) of *t*-butyl alcohol. The whole was cooled in an ice-bath and 200 cc. of oleum added slowly with good agitation and at a rate to maintain the temperature of the mixture below 20°. In about five to ten minutes after the last addition of the acid, crystallization began and was usually complete in about four hours. If no crystallization occurred at once, it usually could be brought about by keeping the reaction mixture overnight

in an ice box. The solid is collected on a fiber glass filter cloth, washed well with small quantities of cold acetic acid and dried *in vacuo* over sodium hydroxide. The yield is quantitative (98%). The substance melts without decomposition at 210–212° (uncor.)

The Preparation of 2,5-Di-*t*-butylhydroquinone Dimethyl Ether.—This substance could not be prepared conveniently by methylation of 2,5-di-*t*-butylhydroquinone with either dimethyl sulfate or diazomethane. It was therefore prepared by treating hydroquinone dimethyl ether with *t*-butyl alcohol in the presence of oleum.

A 70% yield of hydroquinone dimethyl ether was obtained by methylation of hydroquinone (110 g.) with dimethyl sulfate (200 cc.) in the presence of 80 g. (2 moles) of sodium hydroxide in 400 cc. of water.

To introduce the *t*-butyl groups into the dimethyl ether of hydroquinone much higher concentrations of sulfuric acid were necessary. After a few preliminary experiments the following procedure, which gave uniformly between 60 and 70% yields, was adopted.

To 30 g. of hydroquinone dimethyl ether dissolved in 100 cc. of glacial acetic acid, 50 cc. of *t*-butyl alcohol was added. The mixture was cooled and treated in small portions with 100 cc. of oleum. During this addition the reaction mixture was agitated and kept below 20°. The mixture turned very viscous and a solid separated. It was collected on a fiber glass filter cloth and washed well with small amounts of cold acetic acid, dried in a vacuum desiccator over sodium hydroxide, and finally crystallized from dilute alcohol. The material separated in long coarse

TABLE I
DIELECTRIC CONSTANTS, DENSITIES, POLARIZATIONS AT 25°, AND DIPOLE MOMENTS

c_2	ϵ	d	P_2
Benzene-Di- <i>t</i> -butylhydroquinone			
0.000000	2.2801	0.87200	(26.790 = P_1)
.001345	2.2848	.87253	116
.002070	2.2848	.87276	98
$MR_D = 67$, $P_\infty = 125 \pm 15$, $\mu = 1.68 \pm 0.20 \times 10^{-18}$			
Benzene-Di- <i>t</i> -butylhydroquinone Dimethyl Ether			
0.001909	2.2858	0.87235	124
.004330	2.2901	.87286	113
.01044	2.3011	.87406	110
$MR_D = 76$, $P_\infty = 120 \pm 7$, $\mu = 1.47 \pm 0.13 \times 10^{-18}$			

(1) Lewis and Smyth, *J. Chem. Phys.*, **7**, 1085 (1939).

(2) Lewis and Smyth, *THIS JOURNAL*, **61**, 3063 (1939).

thin plates. The substance melted without decomposition at 103–104° (uncor.).

To prove that the *t*-butyl groups entered the same positions in hydroquinone and hydroquinone dimethyl ether, the compound obtained from the latter substance (m. p. 103–104°) was demethylated by heating with hydrobromic acid in glacial acetic acid. The substance isolated melted at 205–208° and did not depress the melting point of the compound prepared by introducing the *t*-butyl groups into hydroquinone.

Discussion of Results

The moments of the two compounds in Table I are to be compared with those of hydroquinone and hydroquinone dimethyl ether. Unfortunately, the solubility of hydroquinone in non-polar solvents is so low that its moment has been measured only by the molecular beam method, which gives merely the order of magnitude,³ and by the ordinary method with ether as a solvent.⁴ In this latter instance, compound formation with the solvent probably makes the observed value, 2.47, too high. The observed moments of catechol and of hydroquinone dimethyl ether are in good agreement with the moments calculated by Fuchs and Wolf⁵ on the assumption of complete freedom of rotation around the O to C bonds connecting the polar groups to the ring. This agreement in the case of catechol is surprising in view of the hydrogen bonding between its two hydroxyls indicated by its infra-red spectrum.^{5a} The two nearly equal peaks in its absorption curve have been accounted for^{5a} by a *cis* planar structure in which one of the two hydroxyl hydrogens forms a bond between the two oxygens. If the bond moments and valence angles remained unchanged, this planar structure should have a moment about 20% higher than the average value 2.2 calculated on the basis of free rotation. The existence of a considerable fraction of the molecules in a *trans* planar structure, which would have a moment about 30% lower than the calculated value 2.2, could account for the agreement between the observed value and that calculated on the assumption of free rotation around the C–O bonds. The agreement of this calculated value with the observed, evidently, cannot be taken as justification of the method of calculation.

(3) Estermann and Wohlwill, *Z. physik. Chem.*, **B20**, 195 (1933).

(4) Hassel and Naeshagen, *ibid.*, **B6**, 441 (1930).

(5) Fuchs and Wolf, "Hand- und Jahrbuch der Chemischen Physik," Vol. 6, I, Akademische Verlagsgesellschaft m. b. H., Leipzig, 1935, p. 398.

(5a) Wulf and Liddel, *THIS JOURNAL*, **57**, 1464 (1935); Pauling, "The Nature of the Chemical Bond," 2nd ed., Cornell University Press, Ithaca, New York, 1940, p. 325.

tion. However, the excellent agreement between the observed and calculated values for hydroquinone dimethyl ether seems to warrant the assumption that the value 2.2 calculated by the same method for hydroquinone is approximately correct. If the *t*-butyl groups in the compounds here measured did not restrict the rotations of the hydroxy or methoxy groups ortho to them, 2.2 and 1.7 should be, respectively, the moments of the substituted hydroquinone and of the substituted hydroquinone dimethyl ether, as shown by the calculated and observed values⁵ summarized in Table II.

TABLE II
OBSERVED AND CALCULATED MOMENTS ($\times 10^{18}$) OF
DIHYDROXY- AND DIMETHOXYBENZENES

	Calcd.	Obsd.
1,2-Dihydroxybenzene	2.21	2.16
1,4-Dihydroxybenzene	2.21	
1,4-Di- <i>t</i> -butyl-2,5-dihydroxybenzene	2.2	1.68
1,2-Dimethoxybenzene	1.77	1.31
1,3-Dimethoxybenzene	1.71	1.59
1,4-Dimethoxybenzene	1.69	1.73
1,4-Di- <i>t</i> -butyl-2,5-dimethoxybenzene	1.7	1.47

Models of these molecules have been constructed with a set of atomic models designed by H. A. Stuart.⁶ In the 1,2-dihydroxybenzene model, the two hydroxyl hydrogen atoms interfere so little with one another that steric effects should not appreciably alter the moment. In the 1,2-dimethoxybenzene model, on the other hand, each methoxy group can turn less than 180° around its ring C to O bond without touching the other methoxy group. Synchronized rotation of the two groups would extend the angle of rotation to nearly 300°, but this angle is definitely restricted. In all these molecules variation of the moments with rotation of the groups depends upon the relative positions of the two group moment components perpendicular to the two axes of rotation. If these two components are perpendicular to the plane of the ring, the moment is a maximum when they point in the same direction, and a minimum when they point in opposite directions. Among other possible minima, there is one which occurs when the two components are in the plane of the ring and on opposite sides of their respective rotation axes. In the 1,2-dimethoxybenzene the two groups should tend to oscillate around the planar position corresponding to this minimum moment. The oscillations should extend approximately to the

(6) Stuart, *Z. physik. Chem.*, **B27**, 350 (1934).

two positions in which the rotating moment components are perpendicular to the plane of the ring. In the position with the two groups on the same side of the ring, the moment should be a maximum, whereas in the position with the two groups on opposite sides, the moment should be a minimum. The probability of a position with minimum moment is thus greater than it would be if the rotation were unrestricted; hence, the observed moment is considerably lower than the value calculated on the assumption of unrestricted rotation. In the 1,3- and 1,4-dimethoxybenzenes, since the two methoxy groups are too far apart to influence one another sterically the observed moments are not far from the calculated. The discrepancy between the observed and calculated values for 1,3-dimethoxybenzene (Table II) is somewhat greater than would be anticipated and may be the result of maximum errors in the two values.

When the bulky *t*-butyl group is next to a hydroxyl group on the ring, it restricts the rotation of the hydroxyl, possibly limiting it to an angle of little more than 180° . In 1,4-di-*t*-butyl-2,5-dihydroxybenzene positions of maximum and of zero moment lie at the extremes of an hydroxyl oscillation of 180° . At the mid-point of this oscillation, in the plane of the ring, there is another position of zero moment. The position favorable for maximum moment is the one with the two hydroxyl moments in the same plane on the same side of the ring. But the two *t*-butyl groups prevent the attainment of this relative position of the two hydroxyls for angles much greater than 90° ; consequently, the mean square moment is lower than it would be if these positions were equally probable, as they are in the unsubstituted hydroquinone. The considerable reduction of the moments below the values estimated in Table II is thus accounted for.

In 1,2-dimethoxybenzene the observed dipole moment is considerably lower than the calculated, whereas no such discrepancy occurs in the corresponding hydroxy compound. This difference in behavior is accounted for by the greater bulk of the methoxy groups. By analogy, the relative lowering of the moment of 1,4-di-*t*-butyl-2,5-dimethoxybenzene might be expected to be greater than that of the corresponding hydroxy compound. However, the model shows that the methoxy groups can rotate through angles but little less than 180° , whereas the hydroxy groups can rotate

through angles, probably, little greater than 180° . Consequently, the relative lowering of moment by steric repulsion should be little greater in the methoxy than in the hydroxy compound. Actually, the apparent lowering of the moment of 1,4-di-*t*-butyl-2,5-dimethoxybenzene below the calculated value (Table II) is only 14%, whereas the apparent lowering in the moment of the corresponding hydroxy compound, instead of being less, is 24%. However, the large experimental errors for the moment values given in Table I easily account for the apparent discrepancy. It may be concluded that the dimensions and valence angles of the atomic groups show that, in 1,4-di-*t*-butyl-2,5-dihydroxybenzene and in 1,4-di-*t*-butyl-2,5-dimethoxybenzene, the *t*-butyl groups limit the rotation of the hydroxy and methoxy groups in such a way as to effect a moderate reduction in the moments of the molecules; the relative reduction is probably a little greater in the methoxy compound. The moderate reductions in moment are evident in the experimental values, but the anticipated difference between the reduction is obscured by experimental error, and, perhaps, by a certain amount of molecular association in the hydroxy compound.

In the foregoing considerations, no account has been taken of possible resonance effects. In addition to the normal structures of the phenol molecule, there are three contributing structures in which a positively charged oxygen is connected by a double bond to the ring and an unshared pair of electrons is on another ortho or para carbon atom.⁷ The contributions of these structures apparently lower the dipole moment of phenol about 0.1×10^{-18} below the average moment of the aliphatic alcohols. This lowering is much smaller than that found in the analogous case of chlorobenzene, which may indicate that there is less double bond character in the C-O bond of phenol than in the C-Cl bond of chlorobenzene. Comparison of the observed and calculated moment values for the dihydroxy- and dimethoxybenzenes (Table II) indicates no demonstrable influence of the resonance of one hydroxy or methoxy group upon the resonance of the other. In view of previous failure⁸ to detect with certainty analogous resonance effects where methyl and methyl, methyl and chlorine, or chlorine and chlorine groups were involved, and in

(7) Pauling, "The Nature of the Chemical Bond," 2nd ed., Cornell University Press, Ithaca, N. Y., 1940, p. 204.

(8) Smyth and Lewis, THIS JOURNAL, **62**, 721 (1940).

view of the smallness of the lowering of the phenol moment, no interaction of resonance effects should be detectable in these moments. This conclusion is in harmony with the absence of any considerable difference between the acid constants of phenol and hydroquinone, although these constants are much more easily influenced by small differences in charge than are the dipole moments. Furthermore, the calculated moments⁹ for *p*-methyl, *p*-chloro-, and *p*-bromophenol and for *p*-methyl, *p*-fluoro, *p*-chloro, *p*-bromo and *p*-iodoanisole agree fairly well with the observed values, giving no evidence of an interaction of resonance effects. On the other hand, the moments calculated for *p*-nitro and *p*-nitrosophenol are considerably lower than the observed values and the calculated moment for *p*-nitroanisole is somewhat lower than that observed. There a marked interaction of the resonance effects is shown.

Birtles and Hampson¹⁰ have shown that the moments of nitrodurene and aminodurene are lower than those of the corresponding benzene derivatives and close to those of the corresponding alkyl compounds. Presumably, steric repulsion of the adjacent methyl groups in the durennes tends to keep the atoms attached to the nitrogen from lying in the plane of the ring and, thereby, reduces the contributions from highly polar doubly-bonded structures in which these atoms must lie in that plane. Other nitro compounds have also been discussed⁸ from this standpoint. Among the contributing structures of hydroquinone and hydroquinone dimethyl ether, those

with a double bond between the oxygen and the ring should have the hydroxyl hydrogen or the methoxy methyl in the plane of the ring. *cis* structures with maximum moment and *trans* structures with zero moment should be equally probable so that any rigidity of the oxygen-to-ring bonds caused by contributions from these structures should not alter the resultant moment. However, in the di-*t*-butylhydroquinone and its dimethyl ether, the *cis* form would be impossible because of the repulsion of the *t*-butyl groups; hence, the contribution of the doubly-bonded structures to the observed moment would be zero. The rather small moment lowering produced by the two *t*-butyl groups is thus additional evidence for the smallness of the amount of double bond character in the oxygen-to-ring bonds in these molecules.

Summary

Di-*t*-butylhydroquinone and di-*t*-butylhydroquinone dimethyl ether have been prepared. The dielectric constants and densities of their solutions in benzene have been measured and used to calculate the dipole moments of the compounds.

The steric repulsion of the *t*-butyl groups restricts the rotational freedom of the hydroxy and methoxy groups in such a way as to cause a moderate reduction in the moments of the molecules. The moments of these and other hydroxy- and methoxybenzenes suggest that the bond between the oxygen and the ring has only a small amount of double bond character.

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(9) Ref., 5, pp. 390, 398.

(10) Birtles and Hampson, *J. Chem. Soc.*, 10 (1937).

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The Exchange Reaction between Simple Alkyl Iodides and Iodide Ion¹

BY HERMAN SEELIG AND D. E. HULL

The work of several investigators who have used radio-iodine as an indicator has shown that an exchange of iodine can be effected between the simple aliphatic iodides and the iodide ion.^{1a} In 1937 Hull, Schiflet, and Lind² discovered a marked temperature effect in the exchange between sodium iodide and ethyl iodide in alcohol

solution. The reaction was fast at 80°, but did not proceed appreciably in five minutes at room temperature. McKay³ reported a similar result in this exchange, and also in the case of several other aliphatic iodides. These experiments were only qualitative in nature, and no calculation of the energy of activation could be made from them.

Quantitative experiments have been done in similar exchanges with bromide ion in aqueous

(1) This paper is based on a thesis submitted by Herman Seelig to the Graduate School of the University of Minnesota in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

(1a) Juliusberger, Topley and Weiss, *J. Chem. Phys.*, **3**, 437 (1935).

(2) Hull, Schiflet and Lind, *THIS JOURNAL*, **58**, 1822 (1936).

(3) McKay, *Nature*, **139**, 283 (1937).