[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT, UNIVERSITY OF MARYLAND]

# The Dipole Moments of Catechol, Resorcinol and Hydroquinone[1]

BY JOHN J. LANDER AND W. J. SVIRBELY

Assuming free rotation of groups, equations recently have been developed[2] which permit the calculation of the dipole moments of ortho, meta and para disubstituted benzene compounds. The dipole moments of catechol, resorcinol and hydroquinone have been measured in benzene with the object of comparing the measured values with the calculated values assuming free rotation and also with the calculated values assuming planar structures in an attempt to come to a more definite conclusion concerning the structures of those compounds.

## Materials and Experimental Procedure

**Benzene.**—Thiophene-free benzene was stirred with renewed quantities of concentrated sulfuric acid until coloration of the sulfuric acid no longer occurred. It was then washed with water, dried over calcium chloride and fractionally distilled over sodium, collecting the middle fraction. The benzene was stored in a glass bottle and used as required. Subsequent distillations of benzene solutions were made to recover the benzene for reuse. The recovered benzene was always added to the stock benzene stored over the calcium chloride.

**Catechol.**—Eastman Kodak Co. material was used (m. p. 103–104° uncor.); it had a definite purplish cast which could not be removed on ordinary recrystallization from benzene. After several attempts, the recrystallized product was dissolved in benzene at about 35°, and then filtered to remove the black residue. The filtrate was concentrated and the catechol was recovered and dried. The crystals were no longer colored (m. p. 104.5–105.5° uncor.).

**Resorcinol.**—Eastman Kodak Co. best grade was recrystallized from benzene and dried in a vacuum desiccator over anhydrous magnesium perchlorate (m. p. 110–111° uncor.).

**Hydroquinone.**—This slightly pink material was obtained from the New York Quinine and Chemical Works, Inc., and was dissolved in a hot mixture of absolute alcohol and benzene. The solution was filtered and cooled, yielding a white product, which was dried, recrystallized twice from benzene and finally dried in a vacuum desiccator (m. p. 173–174° uncor.). After use the hydroquinone was reclaimed from the benzene solutions and its melting point checked to observe whether any change had occurred in it during the course of the measurements, but none was noted.

**Procedure.**—The measurements were made by means of the heterodyne beat apparatus and methods previously described.[3]

## Experimental Results

Part of our experimental results are given in Table I, which lists the mole fractions of the solute, $N_2$, the densities of the solutions, $d$, the dielectric constants of the solutions, $\epsilon$, the molar polarizations, $P_2$, and the extrapolated value of $P_\infty$ obtained from the extrapolation of the polarization data given. For the check runs, the $P_\infty$ values only are given in Table I.

TABLE I

SUMMARY OF DATA IN BENZENE

| $N_2 \times 10^3$ | $d$ | $\epsilon$ | $P_2$ |
|---|---|---|---|
| Catechol (1,2-dihydroxybenzene) at 27° | | | |
| 0.0000 | 0.86943 | 2.2674 | $P_\infty$ = 175 |
| 3.0710 | (.87058) | 2.3000 | 182 |
| 4.8658 | .87122 | 2.3166 | 175 |
| 6.4915 | (.87182) | 2.3339 | 176 |
| 8.0997 | (.87243) | 2.3505 | 175 |
| 9.6948 | .87300 | 2.3669 | 175 |
| Run 2, $P_\infty$ = 169 | | | |
| Resorcinol (1,3-dihydroxybenzene) at 44° | | | |
| 0.0000 | 0.85149 | 2.2350 | $P_\infty$ = 112 |
| 1.5507 | .85202 | 2.2436 | 112 |
| 2.1431 | (.85224) | 2.2467 | 111 |
| 2.7825 | .85248 | 2.2503 | 111 |
| 3.2691 | (.85265) | 2.2530 | 111 |
| Run 2, $P_\infty$ = 116 | | | |
| Hydroquinone (1,4-dihydroxybenzene) at 44° | | | |
| 0.0000 | 0.85198 | 2.2291 | $P_\infty$ = 66 |
| .16751 | (.85226) | 2.2300 | 63 |
| .25934 | (.85241) | 2.2306 | 72 |
| .35285 | .85257 | 2.2309 | 62 |
| .44787 | (.85273) | 2.2314 | 62 |
| .52015 | (.85285) | 2.2320 | 69 |
| Run 2, $P_\infty$ = 75 | | | |

Densities in parentheses have been picked from a density–mole fraction plot.

The molar refraction $MR_D$ is the same for all three compounds and was calculated from the atomic and molar refractions given in Landolt–Börnstein. The value of 30.83 for $P_E + P_A$ was taken equal to 1.05 $MR_D$. The dipole moments calculated in the usual manner along with their probable errors are given in the last column of Table II. The probable errors were estimated through consideration of the data for a particular experiment and also on the reproducibility of the data.

TABLE II

| | Moments ($\times 10^{18}$) Calcd.[a] | Obsd. |
|---|---|---|
| 1,2-Dihydroxybenzene | 2.21 | 2.62 ± 0.03 |
| 1,3-Dihydroxybenzene | 2.21 | 2.07 ± .02 |
| 1,4-Dihydroxybenzene | 2.21 | 1.4 ± .10 |

[a] Calculated by Fuchs and Wolf's method[2] assuming free rotation.

## Discussion of Results

The dipole moment of catechol is erroneously

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(1) Original manuscript received March 29, 1944.

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

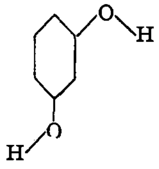
(3) (a) Davis, Bridge and Svirbely, THIS JOURNAL, **65**, 857 (1943); (b) Lander and Svirbely, *ibid.*, **66**, 235 (1944).

reported in the literature as equal to 2.16 *D*.[2,4] Based on that value, good agreement has been claimed[2,5] with the moment of 2.21 *D* calculated by Fuchs and Wolf on the assumption of complete freedom of rotation around the O to C bond connecting the polar groups to the ring. However, the infra-red spectrum[6] of catechol indicated that weak hydrogen bonding occurs in the molecule and that a *cis* planar structure in which one of the hydroxyl hydrogens forms a weak hydrogen bond with the other oxygen accounts satisfactorily for the observed spectrum. The observed value of the moment, namely, 2.62 *D* reported in this paper is not in agreement with the calculated value of 2.21 *D* indicating that the method of Fuchs and Wolf is not applicable to catechol. Using the following link moments[7] H–O = 1.6, H–C = 0.4, C–O = 0.7, and assuming the C—O—H valency angle to be 112° the resultant moment of the *cis* planar structure calculated by means of equations obtained in the usual method of vector summation, but without taking into account any link moment due to hydrogen bonding, is 2.71 *D*. The agreement between calculation and experiment assuming a *cis* planar structure is thus quite good. It appears therefore that both dipole moment and infra-red absorption studies support the *cis* planar structure for catechol.

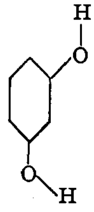
A comparison of the observed and calculated moments assuming free rotation for resorcinol and hydroquinone (Table II) shows reasonably good agreement in the case of resorcinol but a discrepancy in the case of hydroquinone. This discrepancy might be explained qualitatively by assuming greatly restricted rotation of the hydroxyl groups, thus leading to a lower experimental value than that which should have been the case if free rotation had occurred. It is hard to conceive however that resorcinol (1,3-dihydroxybenzene) should have almost free rotation of the hydroxy groups as the agreement between calculation and experiment would seem to indicate while hydroquinone (1,4-dihydroxybenzene) should have greatly restricted rotation. One concludes, therefore, that the agreement between experiment and calculation in the case of resorcinol is fortuitous and that the observed moments of both dihydroxy benzenes are not compatible with the theory of either free or partially restricted rotation.

On the assumption that the double bond character[8] of the C–O bond will be large enough to cause both resorcinol and hydroquinone to be essentially planar and also assuming that due to the orientation of the hydroxyl groups a number of planar configurations can occur[9] we have calculated moments for these compounds in the following fashion.

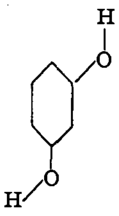
The resorcinol molecule was assumed to have any of four planar configurations of which the first and second are alike, namely



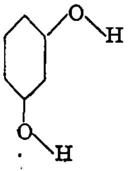
1.57 *D*



1.57 *D*

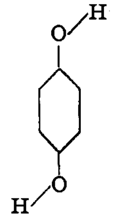


3.08 *D*

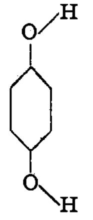


2.07 *D*

Using the same link moments as before, the resultant moment of each configuration was calculated by means of equations obtained in the usual method of vector summation. The results are given under their respective structures. The hydroquinone molecule was assumed to have any of four planar configurations which however due to duplication can be represented by only two planar configurations, namely



0.00 *D*



2.97 *D*

Using the same procedure as before, one obtains the calculated moments given under each structure. If one now calculates the average moments of resorcinol and hydroquinone by means of the relation obtained from theory, namely, that the average moment will be equal to the square root of the arithmetical mean of the squares of the moments of the various configurations (assuming all structures to be equally probable) one obtains the values of 2.16 *D* and 2.09 *D* for resorcinol and hydroquinone, respectively. Again agreement is good in the case of resorcinol but poor for hydroquinone. If one assumes different weighting fractions for the various structures, it is possible to make calculation agree with experiment.[10] Such a procedure would involve giving

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[4] (a) Smyth, "Dielectric Constant and Molecular Structure," A. C. S. Monograph 55, Reinhold Publ. Corp., New York, N. Y., 1931; (b) Dipole Moments—Transactions of the Faraday Society, Sept., 1934; (c) References 2, 4a, and 4b quote Weissberger and Sängewald, *Physik. Z.*, **30**, 792 (1929), as their reference. The original paper does not contain any data on catechol. A further survey of the literature indicates that the dipole moment of catechol apparently has not been measured.

[5] Oesper, Smyth and Kharasch, THIS JOURNAL, **64**, 937 (1942).

[6] (a) Wulf and Liddel, *ibid.*, **57**, 1464 (1935); (b) Pauling, "Nature of the Chemical Bond," 1st ed., Cornell University Press, Ithaca, N. Y., 1939, p. 305.

[7] LeFèvre, "Dipole Moments," Methuen & Co., Ltd., p. 59, 1938.

[8] Ref. 6b, p. 302.

[9] The single absorption peaks of resorcinol and hydroquinone show that there is very little interaction between the two hydroxy groups (Ref. 6).

[10] It is interesting to note that if one takes the arithmetical mean of the moments of the various configurations assuming all structures to be equally probable, one obtains values of 2.07 *D* and 1.48 *D* for resorcinol and hydroquinone, respectively. The agreement is very good in both cases. However, there seems to be no theoretical basis for taking the arithmetical mean of the moments.

less weight to the high moment structures in both cases, a step which is quite reasonable. It is concluded therefore that the planar configurations appear to be more acceptable in the cases of resorcinol and hydroquinone than is the concept of free or partially restricted rotation.

### Summary

1. The dipole moments of catechol, resorcinol and hydroquinone have been determined in benzene and are equal to 2.62, 2.07 and 1.4 *D*, respectively.

2. The agreement between the experimental moment of catechol and the calculated value obtained by using vector addition of link moments and by assuming a *cis* planar structure involving a weak hydrogen bond is excellent.

3. Planar configurations for resorcinol and hydroquinone are more acceptable on comparison of experiment and calculation than are the structures assuming either free or partially restricted rotation of the hydroxyl groups.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF CALIFORNIA]

# *trans*-2-Butene. The Heat Capacity, Heats of Fusion and Vaporization, and Vapor Pressure. The Entropy and Barrier to Internal Rotation

BY LESTER GUTTMAN AND KENNETH S. PITZER

## Introduction and Discussion

The potential barrier to the rotation of a methyl group attached to an olefinic structure has been the subject of several investigations[1-6] principally concerned with the propylene molecule. In 1940 one of the present authors[5] pointed out that while an entropy value for propylene obtained on the basis of the Third Law of Thermodynamics was uncertain because of the possibility of end for end random orientation of the molecules in the crystal, the corresponding value for *trans*-2-butene would not be uncertain because both ends of the molecule are the same. The study described below was undertaken to establish definitely the potential barrier, which would be expected to be the same for propylene and *trans*-2-butene.

The results as presented below show definitely that the potential barriers in *trans*-2-butene and propylene are in the vicinity of 2000 cal. per mole and that propylene molecules are oriented regularly in their crystals. This conclusion is in agreement with the later papers of Kistiakowsky and his collaborators[4,7] and the work of Telfair.[6] Apparently the hydrogenation equilibrium data of Frey and Huppke[8] are in error by factors near two (in the equilibrium constant), which accounts for the lower potential barriers reported by one of the present authors in 1937.

While the conclusion stated above is quite definite, minor uncertainties remain in the assignment of vibration frequencies. Therefore it seems best to postpone final statistical mechanical calculations until a later date.

## Experimental

**Material.**—Through the kindness of Professor John G. Aston of Pennsylvania State College, there was made available to us a sample of *trans*-2-butene, whose purity, as estimated from premelting behavior, was about 99.3%. Visual examination of the just-melted compound revealed the presence of liquid-insoluble impurity which would not have appeared in the premelting. By a single distillation in a 25-plate column, the liquid-insoluble impurity was apparently removed almost completely from a middle fraction. This fraction was further purified by a single fractional crystallization *in vacuo*, with the result that the material used in the measurements contained 0.37% of impurity, assuming ideal liquid solutions and no solid solution. The weight of sample used was 52.79 g., or 0.9409 mole, the molecular weight being taken as 56.104.

**Apparatus.**—The calorimeter used in all the measurements was of conventional design, although a few modifications are worthy of note.

The calorimeter proper, of copper, was joined to the filling line by about 1 meter of thin-walled 1/8″ german silver tubing. The german silver tube was well soldered to the heavy radiation shield, and hence heat leak down it was kept at a low value. Pure (C. P.) platinum wire, 0.1 mm. in diameter, was threaded back and forth through a bundle of thin-walled glass capillaries to give a compact strain-free resistance thermometer, which was placed in a case so situated as to be completely surrounded by the sample. Copper foil between and around the tubes afforded thermal contact with the walls of the case. Electrical connections to the thermometer were made through heavy platinum leads sealed vacuum-tight through glass beads and projecting a short distance above the upper surface of the calorimeter. The case was filled with helium at one atmosphere.

It was originally intended that the thermometer should conform to international temperature scale requirements. Unfortunately, the inclusion of some short leads of less pure platinum prevented this. However, the thermometer was compared at numerous temperatures with another thermometer which had been calibrated in the desired manner.[9] Deviations from a linear relation between their resistances were computed and plotted on a large scale, and a temperature scale drawn up by interpolation and careful smoothing. Small changes which occurred sub-

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(1) K. S. Pitzer, *J. Chem. Phys.*, **5**, 473 (1937).

(2) G. B. Kistiakowsky, J. R. Lacher and W. W. Ransom, *ibid.*, **6**, 900 (1938).

(3) T. M. Powell and W. F. Giauque, THIS JOURNAL, **61**, 2366 (1939).

(4) B. L. Crawford, Jr., G. B. Kistiakowsky, W. W. Rice, A. J. Wells and E. B. Wilson, Jr., *ibid.*, **61**, 2980 (1939).

(5) K. S. Pitzer, *Chem. Rev.*, **27**, 39 (1940).

(6) D. Telfair, *J. Chem. Phys.*, **10**, 167 (1942).

(7) G. B. Kistiakowsky and A. G. Nickle, *ibid.*, **10**, 78, 146 (1942).

(8) F. E. Frey and W. F. Huppke, *Ind. Eng. Chem.*, **25**, 54 (1933).

(9) K. S. Pitzer and D. W. Scott, THIS JOURNAL, **65**, 803 (1943).