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The Dipole Moment of *p*-Benzoquinone: Electro-optic Birefringence

BY ELLIOT CHARNEY

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The extraordinarily large difference between the polarization of *p*-benzoquinone calculated from measurements of the dielectric constant and the electronic polarization calculated from the index of refraction in the visible region has been interpreted several times as indicating that the molecule has a permanent dipole moment. In addition, a recent theoretical treatment suggested that the polarization anomaly could result from an extraordinary induced moment arising from the perturbation of the orbital following of the lone pair electrons on the oxygen in the presence of the static field used to make the dielectric constant measurements. Several of the experimental consequences of this proposal have been examined including the examination of the Kerr birefringence in benzene solution. The results indicate that, as expected, this centro-symmetric molecule has no permanent dipole moment, nor does it have an induced moment in an electric field large enough to explain the polarization differences. The principal polarizabilities and the total electronic polarization of *p*-benzoquinone have also been calculated using the concept of bond polarizabilities. The calculated polarization is in good agreement with measured values.

The unusually large difference between the total polarization and electronic polarization of *p*-quinone and a number of its symmetrical analogs led early investigators to propose that these molecules had large static dipole moments (about 0.7 Debye). Almost no other examples of differences much more than 5% of the total polarization had been observed previously while this difference, which is of the order of 8.2 cc., is about 23% of the total. After the planar symmetric configuration of *p*-quinone was established by Robertson,¹ Coop and Sutton² measured the temperature dependence and the total polarization in the vapor and in solution. They found that the polarization was independent of temperature and of state and concluded that the polarization difference arose from a large contribution from atomic polarization which they associated with a low frequency bending mode of the carbonyl group. Despite Coop and Sutton's fairly definitive examination of the question, subsequent investigators have continued to pursue the admittedly perplexing behavior of these compounds. Meredith, Westland and Wright,³ in particular, suggested that their measurements of the dielectric constant of pelleted solid benzo-, naphtho- and anthraquinone show that the atomic polarizations are not particularly high. Their measurements indicated only a very small difference between the total polarization P_T and the electronic polarization P_E ; the large difference found in solutions could not, accordingly, be attributed to atom polarization which should be almost independent of state since the nuclear vibrations which give rise to this contribution are, of course, relatively insensitive to changes of state⁴; they also found a significant temperature dependence of moment. Recently, Paoloni⁵ made the very interesting suggestion that, under the influence of the external electric field used in making the dielectric constant measurements, the orbital moment of the lone pair electrons of the oxygen atoms may contribute to an asymmetric charge distribution, resulting in an extraordinary contribution to the electronic polarization. Paoloni's thesis does not require deformation

of the planar arrangement of the nuclei for times long enough to give rise to a permanent moment resulting from the combination of the two C=O bond moments but does require the establishment of an induced asymmetric charge distribution much larger than that associated with the normal electronic polarization,⁶ *i.e.*, a dipole moment which would give rise to substantial molecular orientation in an electric field.

Some of the experimental consequences of this explanation were suggested by Paoloni and include the predictions: (1) that the intensity pattern of the rotational spectrum would be modified as a consequence of applying an external electric field, both in the rotational structure of vibrational bands and in the microwave region and (2) the molecules should exhibit electrical birefringence (Kerr effect) greater than that expected of the optically anisotropic molecule with zero permanent moment. Since the planar D_{2h} symmetry of the molecule would remain undisturbed so far as the nuclear vibrations are concerned, it is not too clear whether in the external field the induced asymmetry of charge would break down the infrared and Raman selection rule for the gaseous molecule, but if it did then another consequence of this explanation could be the appearance of the normally infrared forbidden, Raman allowed transitions of the a_g and b_g classes in the infrared spectrum of the vapor.⁷ Using an applied static field of 300 volts/cm., we have examined the infrared spectrum of gaseous *p*-benzoquinone under high resolution at vapor pressures of ~ 100 mm. in the region from 2000 to 400 cm^{-1} for the appearance of Raman allowed transitions and modifications of the rotational structure of the infrared allowed transitions. No effect of the electric field was found. The Raman band at 243 cm^{-1} usually attributed to C=O bending mode could not be examined directly since our apparatus did not permit observations to be taken in this region, but combinations of this band with other fundamentals (983 cm^{-1} , 1116 cm^{-1} , ?)⁸ were not observed to strengthen or appear when the electric field was applied.

(1) J. M. Robertson, *Proc. Roy. Soc., (London)*, **A150**, 106 (1935).

(2) I. E. Coop and L. E. Sutton, *J. Chem. Soc.*, 1269 (1938).

(3) C. C. Meredith, L. Westland and G. F. Wright, *THIS JOURNAL*, **79**, 2385 (1957).

(4) Relative to electronic transitions.

(5) L. Paoloni, *THIS JOURNAL*, **80**, 3879 (1958).

(6) Usually order of the 0.01 debye.

(7) An effect of this type, but not specifically related to orbital following was predicted by E. U. Condon, *Phys. Rev.*, **41**, 759 (1932), and first reported by M. F. Crawford and J. R. Dagg, *ibid.*, **91**, 1569 (1953).

(8) T. Anno and A. Sadô, *Bull. Chem. Soc., Japan*, **31**, 734 (1958).

More definitive are the results of an examination of the electro-optic birefringence of *p*-benzoquinone in benzene solution.

Experimental

The electro-optic birefringence of acetone, benzene and a solution of *p*-quinone in benzene were measured at several discrete wave lengths from 480 to 600 $m\mu$ using a Cary Model 14 Spectrophotometer and a cylindrical glass cell containing nickel electrodes 48 mm. long and 10 mm. wide, with a 9 mm. separation. No special attempt was made to insure uniformity of the field other than to make the electrodes long compared to their separation and to provide them with smooth rounded edges. Instead the birefringences of the benzene and *p*-quinone solutions were calculated on the basis of calibration with acetone using the value of LeFèvre quoted by Narayana Rao⁹ for the Kerr constant of acetone ($B = 16.3 \times 10^{-7}$ at 589 $m\mu$). As a check on the validity of this calibration, the data also were used to calculate the transmission characteristics of the polarizers (Polaroid Type HN-22 in glass) and gave excellent agreement with the measured (and manufacturer's) values. The field strengths used ranged from 1.0 to 5.1 kv./cm. for the measurements with acetone and from 6.0 to 11.0 kv./cm. for the benzene and *p*-quinone solutions. The benzene was commercial thiophene-free benzene and was carefully distilled from sodium into a vessel containing sodium freshly washed with a previous fraction of the distilled benzene. The distillation was done in an atmosphere of dry nitrogen. The acetone was C.P. commercial acetone carefully distilled and kept over molecular sieve until ready for use. The *p*-quinone was twice-sublimed in vacuum and kept refrigerated in a sealed (evacuated) glass vessel in the dark until use. The solutions were prepared and transferred to the Kerr cell in a dry box under nitrogen using Pyrex vessels previously oven dried, washed with sodium dried benzene and then allowed to dry in the box under a steady flow of dry nitrogen. The benzene solution of *p*-quinone contained 0.109 mole fraction of *p*-quinone.

Results

The measurements of relative optical density (O.D.) of the sample between crossed polarizers to that of a blank cell containing the same liquid or solution made with and without the static field applied can be shown to be related to the Kerr constant B and the field strength E (in e.s.u./cm.) through

$$\frac{1-D}{D} = K \sin^2(\pi B l E^2) \quad (1)$$

where $D = \text{antilog} [\text{O.D.}_E - \text{O.D.}_C]$ and l is the optical path length through the sample and K is a proportionality constant dependent mainly on the transmission characteristics of the polarizers; the subscripts E and C refer respectively to measurements made with and without the field applied to the cell. The Kerr constant B is proportional to the measured birefringence and is defined by $\delta = 2\pi B l E^2$ where δ is the phase difference between the components of the radiation parallel and perpendicular to the applied field and is proportional to the difference of refractive indices of the liquid for plane polarized light parallel and perpendicular to the field, [$\delta = 2\pi l(\eta_{\parallel} - \eta_{\perp})/\lambda$]. For the small birefringence established in these experiments the $\sin^2(\pi B l E^2) \approx (\pi B l E^2)^2$ so that $(1-D)/D$ should be proportional to the second power of the Kerr constant and to the fourth power of the field strength. The data for acetone at 546 $m\mu$ (Table I) demonstrate the fourth power dependence of $(1-D)/D$ on field strength and provides calibration data for the cell. The birefringence of pure benzene and the solution of *p*-quinone

in benzene were measured at 580 $m\mu$ and at field strengths of 9.0 and 11.1 kv./cm. The average value of $(1-D)/DE^4$ for the pure liquid benzene and the *p*-quinone solutions are, respectively, $0.130 \pm 0.02 \times 10^{-8}$ and $0.134 \pm 0.02 \times 10^{-8}$. Thus, within the limits of precision of the measurements, the birefringence of *p*-quinone solution is the same as that of the benzene alone.

The significant question, of course, is what would the magnitude of the dipole moment of *p*-quinone have to be for the observed birefringence of the quinone solution to be significantly different from that of pure benzene. To provide an answer, it is necessary to calculate the effect that a polar *p*-quinone would have on the Kerr constant of the solution and compare this with the sensitivity of the measurement.

Since the molar volumes of *p*-quinone and benzene are not significantly different for the purpose of this calculation, the Kerr constant of the solution, B_{12} , can be expressed in terms of Kerr constants of the constituents and their concentrations

$$B_{12} = B_1 C_1 + B_2 C_2 \quad (2)$$

TABLE I
BIREFRINGENCE OF LIQUID ACETONE, EXPERIMENTAL (546 $m\mu$)

Field strength, E (e.s.u./cm.)	$(1-D)/D$	$(1-D)/DE^4$
7.40	0.0403	1.3×10^{-6}
9.25	.0926	1.3×10^{-6}
10.9	.172	1.2×10^{-6}

If the subscript 2 is used to designate the solute then, in terms of the molar Kerr constant K_2 of the solute, the measured Kerr constant¹⁰ is

$$B_2 = \frac{\eta_2}{\lambda} \left[\frac{\rho_2}{M_2} (\epsilon_2 + 2)^2 K_2 / \left(\frac{\eta_2}{\eta_2^2 + 2} \right)^2 \right] \quad (3)$$

whence

$$B_{12} = B_1 C_1 + \frac{K_2 C_2}{\lambda A_2} \quad (4)$$

where

$$A_2 = \frac{\rho_2}{M_2} \eta_2 (\epsilon_2 + 2)^2 / \left(\frac{\eta_2}{\eta_2^2 + 2} \right)^2$$

and ρ_2 , M_2 , η_2 and ϵ_2 are, respectively, the density, molecular weight, index of refraction (optical) and dielectric constant of the solute, and λ is the wave length in cm. at which the measurement is made. For given values of C_2 , λ , let

$$C_2/\lambda A_2 = L_2$$

and we can rewrite eq. 4 as

$$B_{12} = B_1 C_1 + L_2 K_2 \quad (5)$$

Using Otterbein's¹¹ definition, the molar Kerr constant may be expressed in terms of the principal polarizabilities α_1 , α_2 and α_3 and dipole moments μ_1 , μ_2 and μ_3 of the solute

$$K_2 = J \left\{ (\alpha_1 - \alpha_2)^2 + (\alpha_2 - \alpha_3)^2 + (\alpha_3 - \alpha_1)^2 + \frac{1}{kT} \left[(\mu_1^2 - \mu_2^2)(\alpha_1 - \alpha_2) + (\mu_2^2 - \mu_3^2)(\alpha_2 - \alpha_3) + (\mu_3^2 - \mu_1^2)(\alpha_3 - \alpha_1) \right] \right\} \quad (6)$$

(10) H. A. Stuart, "Die Struktur des Freien Moleküls," Springer-Verlag, Berlin, 1952.

(11) G. Otterbein, *Physik. Z.*, **25**, 240 (1934).

(9) D. A. S. Narayana Rao, *Trans. Faraday Soc.*, **54**, 954 (1958).

where $J = (2\pi N_0/9) (1/45 kT)$, N_0 is Avogadro's number, k is the Boltzmann constant and T the absolute temperature. With reference to *p*-quinone, define the directions 1, 2 and 3, respectively, as in the molecular plane perpendicular to the oxygen-oxygen axis, perpendicular to the molecular plane, and in the molecular plane parallel to the O-O axis. Then, according to Paoloni's proposal (as well as to the hypothesis of slow deformation of the planar configuration), a moment μ is developed perpendicular to the molecular plane, *i.e.*, $\mu_1 = \mu_3 = 0$; $\mu_2 > 0$. For this case, equation 6 reduces to

$$K_2 = J\{P + P'\mu_2^2/kT\}$$

where $P = (\alpha_1 - \alpha_2)^2 + (\alpha_2 - \alpha_3)^2 + (\alpha_3 - \alpha_1)^2$

$$P' = 2\alpha_2 - \alpha_1 - \alpha_3$$

Substituting in eq. 5

$$B_{12} = B_1C_1 + \frac{L_2JP'}{kT}\mu_2^2 + L_2JP \quad (7)$$

If, however, μ_2 as well as μ_1 and μ_3 is identically zero, then

$$B_{12}^0 = B_1C_1 + L_2JP \quad (8)$$

where the superscript zero is used to designate the non-polar case. Thus, the difference in the Kerr constant of the solution between the case where the molecule has a dipole moment perpendicular to the plane in which the axes of maximum polarizability lie is given by

$$B_{12} - B_{12}^0 = \frac{L_2JP'}{kT}\mu_2^2 \quad (9)$$

and is therefore proportional to the square of the dipole moment. Since the birefringence as measured by $(1-D)/D$ is proportional to the second power of the Kerr constant, it is obvious and well-known that the birefringence is very strongly dependent on the existence or magnitude of the dipole moment. The calculation of $B_{12} - B_{12}^0$ requires a knowledge of the principal optical polarizabilities of *p*-quinone for which no known experimental data exist. The principal polarizabilities were therefore calculated using the hypothesis of bond polarizabilities¹² and the values of bond polarizabilities from Wang¹³ and bond angles for *p*-quinone from the X-ray investigation of Robertson.¹ The bond angles for C=C-H were based on the assumption that the hydrogen nuclei lie on a radius vector from the center of the six carbon plane through the carbon atoms to which they are bonded. Only a very small error is involved in this assumption since the CH bond polarizability makes only a relatively small contribution to the total polarizability. From these data, the principal polarizabilities of *p*-quinone are $\alpha_1 = 137 \times 10^{-26}$, $\alpha_2 = 60.2 \times 10^{-26}$ and $\alpha_3 = 176 \times 10^{-26}$ cc.¹⁴ Using these values, the dependence of $\Delta B_{12} = B_{12} - B_{12}^0$ on μ_2 for 0.109 mole fraction *p*-quinone in benzene was calculated. The results are shown in Fig. 1. A very conservative estimate of the precision of these measurements indicates that the minimum observable ΔB_{12} is of the order 2×10^{-8} and consequently the maximum possible value

(12) K. G. Denbigh, *Trans. Faraday Soc.*, **36**, 936 (1940).

(13) S. N. Wang, *J. Chem. Phys.*, **7**, 1012 (1939).

(14) The electronic polarization calculated from these derived values of α_1 is 31.5 cc. in rather good agreement with the 30.9 cc. measured by Meredith, *et al.*,² and only 10% from the 28.4 measured by Hammick, Hampson and Jenkins, *J. Chem. Soc.*, 1263 (1938).

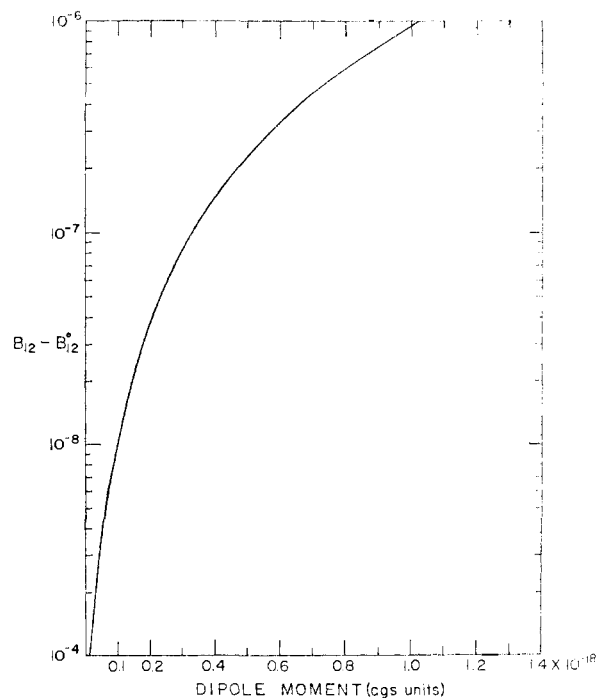


Fig. 1.—Calculated dependence of the difference between the birefringence of pure benzene and a solution in benzene of a polar molecule having the optical polarizability characteristics of *p*-quinone, on the dipole moment of the polar molecule along the axis of minimum polarizability.

for the static or electric field induced dipole moment is less than 0.15 Debye.¹⁵ Since the dipole moment required to explain the extraordinary polarization of *p*-quinone is about 0.7 Debye, it is apparent that no explanation of the polarization based on a static or induced dipole moment is valid.

These experiments are definitive with respect to the absence of a supposed large permanent or electric field induced dipole moment of *p*-quinone, but no new light is shed on the origin of the extraordinarily large difference between the electronic and total polarization of *p*-quinone and related molecules. Of the various explanations, the one based on a large atom polarization still seems most plausible and experimental verification awaits the measurement of the absolute intensities of all the fundamental vibrational modes or of the refractive index through the corresponding spectral region.

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(15) A preliminary search for microwave absorption by gaseous *p*-quinone also failed to reveal the existence of a dipole moment. The maximum undetectable μ in this experiment was also of the order of 0.2 Debye (V. A. Laurie, private communication).