protons on B^{10}. Admittedly this is not a completely satisfactory situation; however, it is the best place in the spectrum to check on progress of deuteration at the apex position.

The procedure chosen was to run somewhat compressed spectra, similar to those shown in Fig. 1. The heights of the two peaks were measured from the base line and the ratio of the second to the first was calculated. Pentaborane samples containing 0, 5 and 26.5% deuterium gave 0.660, 0.675 and 0.681, respectively, as peak ratios. At least five measurements were made for each deuterium content. If we make a rough calculation of the peak height ratio to be expected, taking into account the composite nature of peak y, the differences between the ratios listed above can be accounted for by a 10% difference in the extents of deuteration in the base terminal and apex hydrogen positions. We therefore conclude that as far as terminal hydrogens in pentaborane are concerned the rates of exchange in the base and apex positions are the same to within ±10%.

It should be pointed out that these studies do not permit us to eliminate mechanisms in which only base or apex terminal protons exchange with BD_3 followed by a more rapid intramolecular exchange between base and apex terminal protons. In view of the properties of pentaborane, however, we feel that this is an unlikely situation and a more probable mechanism is the exchange of deuterium between deuterated borane and each of the terminal hydrogen positions independently.

BALTIMORE, MD.
ARMY CHEMICAL CENTER, MD.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF TORONTO]

Interpretation of Abnormalities in Atom Polarization in Terms of Electric Moment

BY C. C. MEREDITH, L. WESTLAND AND GEORGE F WRIGHT

RECEIVED DECEMBER 14, 1956

Dielectric constant determinations of pelletted solid benzoquinone, naphthoquinone and anthraquinone show that the atom polarizations are not abnormally high. Assignment of the non-electronic polarization chiefly as orientation polarization has been confirmed by demonstration of temperature dependence. The distortion polarization of 4,4′-dinitrobiphenyl has also been shown to be normal, so this substance must have an electric moment of 1 *D*. All of these substances must have non-planar and non-linear structures. The so-called abnormal polarization (57 cc.) of ferric acetylacetonate seems to be partly (21 cc.) atomic and partly due to orientation polarization according to dielectric constant determinations of solids and solutions. Since some of these studies contradict earlier evidence the reliability of the measurements and the interpretation is discussed.

A discrepancy has been observed between the total electrostatic polarization and the electronic polarization in certain substances. This discrepancy has been assigned as atom polarization.[1] Typical compounds to which these molecular deformations are attributed are quinones, *p*-substituted biphenyls and metal acetylacetonates, none of which are presumed to contribute to orientation polarization. These types have been considered in the present study.

The Quinones

The difference, $P_T - P_E$ = 8–10 cc., for a series of 1,4-benzoquinones would indicate moments of 0.6–0.7 *D* but the orthodox expectation that quinones are planar, as well as the temperature-independent constancy of $P_T - P_E$ among these quinones, has brought forth the theory[2] of an atom polarization due to lateral deformation of "balanced carbonyl dipoles." The apparent dipole moment for 2,5-di-*t*-butylbenzoquinone (= 0.81 ± 0.03 *D* in benzene at 25°)[3] seems to be the only, and minor, exception to this generalization.

In view of this conclusion we sought by use of benzoquinone to test our method[4] for determination of atomic plus electronic polarization by use of solid organic compounds pelletted to maximum density. Already we had found reasonable agreement between our capacitance measurements of pelletted mercuric chloride (P_A = 5 cc.) and the value calculated from vapor phase dielectric constants (P_A = 6 cc.).[5] However our pelletted benzoquinone at 22 ± 2° showed a polarization of 30.1 cc.

This value is slightly lower than the 30.9 cc. determined for the electronic polarization at 5892.6 Å. in benzene solution but is slightly higher than the 28.4 cc. value accepted by many workers[1] and derived from group polarizations (26.8 cc.) plus 1.58 cc. of "exaltation."[6] In any event the derived value deviates from the observed pellet polarization only by the amount expected[7] for normal atom polarization. But this pellet polarization is 7–9 cc. less than the total polarization reported from benzoquinone in solution or in the gaseous state. Therefore the difference cannot be attributed to atom polarization.

In view of this discrepancy we have determined at several temperatures the dielectric constants and specific volumes of a series of solutions of benzoquinone. The precision of these determinations may be judged from Fig. 1 (solutions in benzene) and Fig. 2 (solutions in dioxane) from which the

---

[1] J. W. Smith, "Electric Dipole Moments," Butterworths, London, 1955, p. 271.

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

[3] H. Kofod, *Acta Chem. Scand.*, **7**, 928 (1953).

[4] C. C. Meredith and G. F Wright, *Can. J. Technology*, **33**, 182 (1955).

[5] H. Braune and R. Linke, *Z. physik. Chem.*, **31B**, 12 (1935).

[6] G. G. Kikina, Ya. K. Syrkin and E. A. Shott-L'vova, *Izvest. Akad. Nauk. S.S.S.R. Otdel Khim. Nauk*, 563 (1954); *C. A.*, **48**, 13316 (1954).

[7] J. H. Van Vleck, "Theory of Electric and Magnetic Susceptibilities," Oxford Press, New York, N. Y., 1932, p. 46.

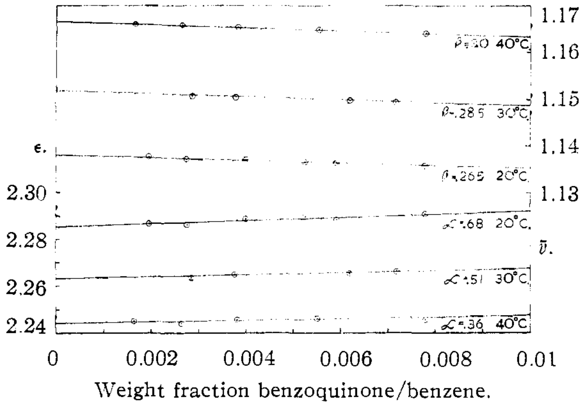


Fig. 1.—Dielectric constants and molar volumes.

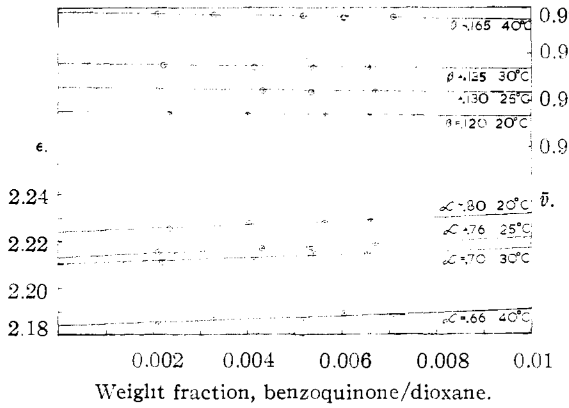


Fig. 2.—Dielectric constants and molar volumes.

derivatives of dielectric constant ϵ, and specific volume V, with respect to weight fraction (α and β, respectively) may be evaluated. Calculation by the method of Halverstadt and Kumler[8] for total polarization of the solute

$$P_{20} = \left[\frac{3\alpha V_1}{(\epsilon_1 + 2)^2} + \frac{\epsilon - 1}{\epsilon + 2}(V_1 + \beta)\right] M$$

leads to the polarization values in Table I. This method of calculation seems to be reliable since the dielectric constants for the pure solvents are in close numerical agreement (Table I) with ϵ obtained by extrapolation (Fig. 1 and 2) of $\delta\epsilon/\delta\omega$ to zero weight fraction ω. The maximum deviation shown in Table I (detd. − extrap./$\Delta\epsilon$) is 1%. This would lead to an error (largely from the slope of β) not exceeding 0.5 cc. in P_{20} for benzoquinone where M is 108. Thus there is no necessity for application of the corrections suggested by Smith[1] and the polarizations in Table I have been calculated by use of V, and ϵ of pure solvent. It is apparent that the polarization is not temperature independent, either in benzene or dioxane. Unfortunately a plot of these polarizations against reciprocal absolute temperature cannot be used to find, by extrapolation to $1/T = 0$, the intercept corresponding to distortion polarization because the Debye relationship is inadequate in this respect for solutions. Nevertheless an orientation polarization rather than an abnormal distortion (atom) polarization seems to be indicated by the temperature dependence.

TABLE I

POLARIZATIONS AND ELECTRIC MOMENTS OF BENZOQUINONE AT 500 KC.

Temp., °C.	ϵ, benzene Detd.	ϵ, benzene Extrap.	Polarization, cc., in Benzene	Polarization, cc., in Dioxane	ϵ, dioxane Detd.	ϵ, dioxane Extrap.	Moments, D, in Benzene	Moments, D, in Dioxane
20	2.284	2.285	41.9	40.6	2.224	2.224	0.75	0.70
25				39.7	2.216	2.213		.68
30	2.262	2.263	38.2	38.7	2.210	2.210	.63	.65
35	2.253	2.252	36.4				.56[a]	
40	2.245	2.244	35.1	37.3	2.189	2.184	.50	.60

[a] This value is reduced to 0.55 D when the polarization (36.1 cc.) is determined at 2600 kc.

In order to test this observation further we have determined the dielectric constant of anthraquinone. Previously a moment of 0.6 D was reported without detail[9] but subsequently it was stated that the moment of this substance in the same solvent (benzene) was zero.[10] Actually the solubility in benzene is too low for precise measurement of dielectric constant. According to our study in dioxane at 30° the total solute polarization is 71.5 cc. There is some doubt about the electronic polarization. Fischer and Rogowski give the value 64 ± 2 cc. without stating their source or method. The refraction measured in a 0.3% solution in pyridine gives an electronic polarization for anthraquinone of 61.7 cc.[11] Our extrapolation of apparent dielectric constant *versus* pellet thickness gives a value of P_{E+A} of 61.1 cc. and from this value (and a density at 20° by flotation of 1.44) we calculate the electric moment to be 0.71 D.

We have found that 1,4-naphthoquinone behaves similarly with benzo- and anthraquinone. The combined electron and atom polarization deduced from pellet studies is close (45.9 cc.) to that expected (46.1 cc.) by group moment subtractive calculation from the observed P_E for anthraquinone. When this polarization of the solid is subtracted from the total solute polarization (77.0 cc.) of 1,4-naphthoquinone in benzene at 20° the corresponding moment is found to be 1.21 D. This value differs from that of benzoquinone by about the same amount (0.46 D) as was found in benzene at 25° for 1,2-benzoquinone (5.1 D) and 1,2-naphthaquinone (5.67 D).[12]

It is of interest to consider the source of the apparent moments of these quinones since temperature dependence seems to exclude an abnormal atom polarization. Orientation polarization has been considered previously in terms of molecular distortion due to thermal agitation.[13] Hampson, Hammick and Jenkins have observed that a deviation from planarity of 8° in benzoquinone due to thermal agitation would not be energetically absurd despite the resonance stabilization (13 kcal./mole) reported for benzoquinone.[14] However they aban-

---

(8) I. F. Halverstadt and W. D. Kumler, THIS JOURNAL, **64**, 2988 (1942).

(9) R. J. W. LeFevre, "Dipole Moments," Methuen, London, 1938, pp. 73 and 93.

(10) E. Fisher and F. Rogowski, *Physik. Z.*, **40**, 331 (1939).

(11) J. Schuyler, L. Blom and D. W. van Krevelen, *Trans. Faraday Soc.*, **49**, 1391 (1953).

(12) S. Nagakura and A. Kuboyama, THIS JOURNAL, **76**, 1003 (1954).

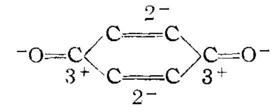
(13) D. L. Hammick, G. C. Hampson and G. I. Jenkins, *J. Chem. Soc.*, 1263 (1938).

(14) L. Pauling and J. Sherman, *J. Chem. Phys.*, **1**, 614 (1933).

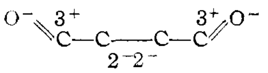
don this explanation because the period of carbonyl bending calculated from the infrared absorption at 120 cm.$^{-1}$ is too small (10^{-13} sec.) to contribute to the orientation polarization.

Of course there is implied in this reservation the common-sense expectation that benzoquinone will be planar in its unactivated, and especially in the orbitally degenerate, state expected for such substances. However, the present experimental evidence requires a factual rather than a common-sense attitude, and some explanation of a permanent moment must be devised. If the group moment for each carbonyl is taken as 2.5 *D* then the moment for benzoquinone in the vapor phase[2] (0.67 *D*) may be accounted for by a 6° deviation of these groups from planarity.

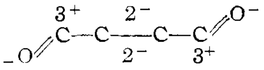
In this circumstance a "boat" type of structure may be postulated in which the atom cores may be disposed in an electronic field such as is described as structure I, in Fajans' sense.[15] The 3$^+$C atom cores may then be considered to be disposed symmetrically within the field, forming a constellation such as II (boat) rather than the chair form III, in which a lesser symmetry obtains, especially with respect to the 3$^+$C atoms.



I



II



III

Thus the non-planar structure II has been defined, like that of water or ammonia, as the lowest energy state of free benzoquinone. This structure might also be considered as a distortion caused by interaction with the solvent, and therefore might resemble iodine in polarizable solvents.[16,17] This latter relationship is doubtful. The excess of polarization over that accountable as electronic, which we have found for benzoquinone to be temperature dependent, has previously been observed in carbon tetrachloride, hexane and in the vapor state.[1,2] Under these conditions iodine does not exhibit orientation polarization. Furthermore the behavior of benzoquinone in solvents like benzene and dioxane (in which iodine has a moment) is unique with respect to the type of temperature dependence that has been observed.

Although it is recognized that the extrapolation of total polarization *versus* reciprocal temperature to $1/T = 0$ is applicable only in vapor-phase studies we have plotted the polarizations of Table I against $1/T$ in Fig. 3. It may be seen that the benzoquinone polarizations in benzene (A, slope 31×10^3) intersect the line (*B*, slope 15×10^3) joining the polarizations determined in dioxane at a point corresponding to a polarization of 39.3 cc. By reference to Fig. 4 in which these data (after subtraction of P_{E+A} = 30.1 cc.) are expressed in terms of electric moments *versus* temperature, it may be seen that the deviations from the moment (0.67 *D*) calculated from vapor phase studies indicate both positive and negative solvent effect. It is of interest that the model, II, suggested for benzoquinone is of a type (where the axis normal to the dipolar axis is relatively long) for which such deviations are expected.[18]

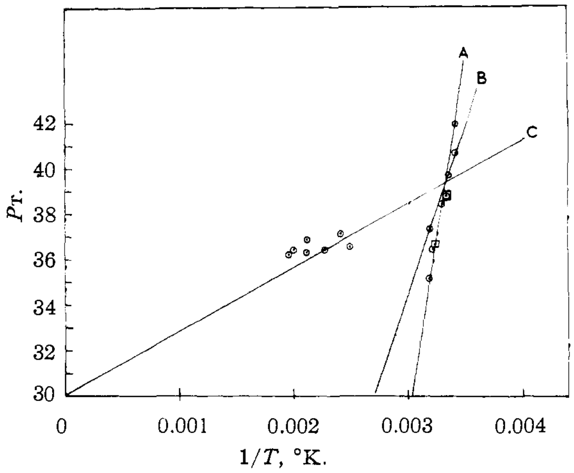


Fig. 3.—Total polarization *vs.* reciprocal temperature, benzoquinone.

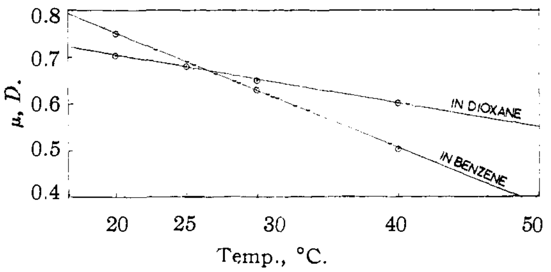


Fig. 4.—Dipole moments *vs.* temperature, benzoquinone.

One should not infer that benzoquinone is abnormal because of these moment variations with respect to temperature and solvent. Such variations are characteristic of most polarization studies but they seem insignificant except when the moment is the square root of a small number. Nevertheless efforts have been made to find theoretical justification for solvent effects (ref. 1, p. 127). However, no useful quantitative generalizations have been found because the electrostatic fields surrounding the molecules cannot be defined precisely.

In view of the difficulty of discovering molecular geometry which might rationalize the solvent effect (ref. 1, p. 145) we have utilized an empirical relationship shown in Fig. 3. We suggest that the intersection of the polarization lines A (benzene solutions) and B (dioxane solutions) may specify the point where solvent effects are minimal or absent. A line, C, has been drawn between the intersection and the point at $1/T = 0$ which represents the distortion polarization (30.1 cc.) determined from the dielectric constants of benzoquinone pellets. The points along this line, C, record the polarization data determined by Coop and Sutton for benzoquinone in the vapor phase. Although it is

---

(15) K. Fajans, *Chem. Eng. News*, **27**, 900 (1949).

(16) F. Fairbrother, *J. Chem. Soc.*, 1051 (1948).

(17) G. Kortum and H. Walz, *Z. Elektrochem.*, **57**, 73 (1953).

(18) F. C. Frank, *Proc. Roy. Soc.* (*London*), **A152**, 171 (1935).

apparent that these values are not sufficiently precise for a conclusive test it may be seen that the polarizations at the lower temperatures (which Coop and Sutton specified as most accurate) seem to be associated with the line C. If this formal association is valid the intersection of A, B and C would designate the dipole moment of benzoquinone as 0.67 *D*.

In order to test the significance of this intersection the polarization of benzoquinone in hexane at 35 and 27° has been determined and found to be 36.6 and 38.7 cc. Unfortunately for a good test these values (squares, Fig. 3) fall on line A, indicating that the solvent effect of hexane is not appreciably different from that of benzene. However the polarization at 27° corresponds to a moment of 0.65 *D*. The same value is observed for benzoquinone in carbon tetrachloride where P_T values of 41.0, 38.8 and 36.0 cc. are obtained at 20, 27 and 40°, respectively. Therefore our results designate the benzoquinone moment as 0.65–0.67 *D*.

Of course some rational alternative to the Debye relationship must eventually be found to equate $\delta P/\delta T$ (11.146) for benzoquinone in benzene and $\delta P/\delta T$ (5.409) in dioxane with the slope of line C in Fig. 3. Meanwhile it seems worthwhile in future to examine the polarizations of candidate substances in several solvents at different temperatures in order to ascertain whether the intersections of lines relating P_T to $1/T$ indicate vapor phase moments. Such a method, if reliable, would be convenient when vapor phase determinations are impractical.

In any circumstance it seems reasonable to assume that the observed effects of these non-polar solvents used with benzoquinone could not exist if the solute did not contain a permanent electric moment. This moment seems to us to be most reasonably explained by the bent molecule, structure II.

The evidence from dielectric constant evaluation of pelletted benzoquinone, which has led us eventually to an assignment of electric moment in this compound, was not entirely unexpected. Previously a small discrepancy between total and electronic polarization of diphenylmercury[19] was shown by measurement of pellets not to be due to abnormal atom polarization.[20] The $P_T - P_E$ difference was interpreted as an electric moment due to angularity in the C–Hg–C bond. Although this condition might seem to be unusual it may reasonably be attributed to the distortion of the "O" shell of the bulky mercury atom.

4,4′-Dinitrobiphenyl

The foregoing examples seem to show that planarity and linearity are not always necessary for electronic orbital degeneracy. It has seemed worthwhile to re-investigate other substances to which abnormal atom polarization has been assigned largely on the reasonable belief that they were geometrically planar or linear. We have chosen 4,4′-dinitrobiphenyl for which the difference between the total polarization and that part attributable to electron polarization (87.5 cc. minus 66 cc.) was designated as a high atom polarization of 21.5 cc. The alternative dipole moment (1.0 *D*) was considered only as an apparent one, because of the expectation that the substance would have axial symmetry.[21]

We have prepared pellets from 4,4′-dinitrobiphenyl and have extrapolated the ratios of apparent dielectric constant with respect to thickness to obtain the dielectric constant, free from edge-effect error. This extrapolation (A), together with those of benzoquinone (B), naphthoquinone (C), anthraquinone (E), mercuric chloride (F) and ferric acetylacetonate (G), are shown in Fig. 5. Calculation gives P_{E+A} for 4,4′-dinitrobiphenyl as 66.8 cc., or only 0.8 cc. higher than that ascribed to electronic polarization. Therefore the atom polarization is not abnormal.

In order to confirm that the polarization in excess of P_{E+A} is due to an electric dipole in 4,4′-dinitrobiphenyl we have determined the dielectric constants of benzene and dioxane solutions at 40°. The total polarizations at this temperature are 77.7 and 80.3 cc., the former being about 10 cc. lower than was observed by LeFèvre and Vine at 25° in benzene.[21] The dependence of polarization upon temperature thus indicates the existence of a real moment of *ca* 0.7 to 1.0 debye.

Although such a moment seems to be appreciable one must realize that a relatively small deviation from linearity can cause it. A polarization of 21 cc. (1 debye) is expected if two nitro groups (each *ca.* 4 *D*) at 7° were fixed in *cis* relationship at the *para* positions of coplanar biphenyl. Even if the rings were normal to each other the orientation polarization could be accounted for by nitro groups at an angle of 14.5° from the planes of the rings.

Actually this non-linearity is predicted in a sense by X-ray crystallographic studies. The space group assigned to crystalline 4,4′-dinitrobiphenyl[22] is the non-centrosymmetric "Pc." As Bunn has pointed out[23] centrosymmetrical molecules do not in fact assume non-centrosymmetrical space group arrangements. Furthermore the nitro groups in *meta*-dinitrobenzene are thought to be inclined from the plane of the benzene ring.[24]

Metal Acetonylacetates

Perhaps the most important examples of high atom polarization have been those of the metal acetylacetonates. A difference between total and electronic polarization at one temperature was first observed by Smith and Angus[25] for beryllium acetylacetonate. Later a careful study in a series of solvents at one temperature showed the total polarization to be reasonably constant,[26] thus excluding solvent effect as a cause of the difference between total and electronic polarization. Furthermore the same authors found that in decalin over a temperature range of 298–415° only a small down-

---

[19] G. C. Hampson, *Trans. Faraday Soc.*, **30**, 877 (1934).

[20] J. C. Sipos, H. Sawatzky and G. F. Wright, THIS JOURNAL, **77**, 2759 (1955).

[21] R. J. W. LeFèvre and H. Vine, *J. Chem. Soc.*, 1878 (1938).

[22] J. N. von Niekerk, *Proc. Roy. Soc.* (*London*), **A181**, 314 (1943).

[23] C. W. Bunn, "Chemical Crystallography," Oxford Press, New York, N. Y., 1946, p. 251.

[24] E. M. Archer, *Proc. Roy. Soc.* (*London*), **A188**, 51 (1946).

[25] J. W. Smith and W. R. Angus, *ibid.*, **137A**, 372 (1932).

[26] A. E. Finn, G. C. Hampson and L. E. Sutton, *J. Chem. Soc.*, 1254 (1938).

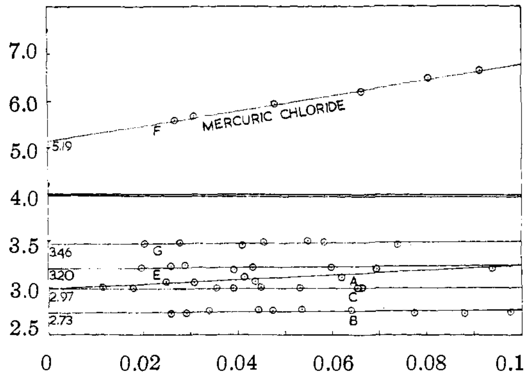


Fig. 5.—Dielectric constant *vs.* thickness of pellets.

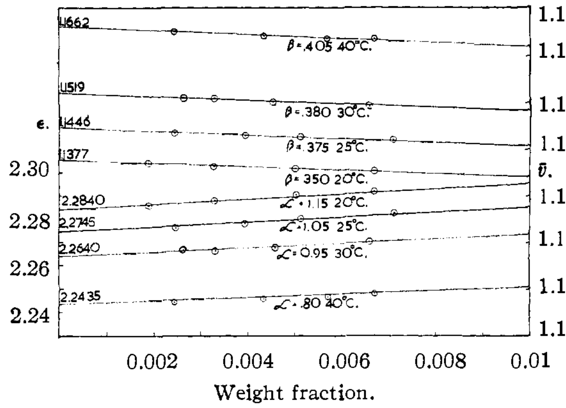


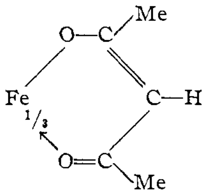
Fig. 6.—Dielectric constants and molar volumes *vs.* weight fraction, ferric acetylacetonate.

ward drift (86.91 to 85.10 cc.) in total polarization occurred. This temperature independence was confirmed[2] by vapor phase measurements from which the drift in total polarization was found to be even less (86.6 to 86.0 cc. from 185 to 255°) than was found for the solution measurements. Upon this evidence the difference between total and electric polarization (25–28 cc.) was designated as atom polarization.

By implication the other eight acetylacetonates examined by these workers were presumed to display high atom polarization even though no temperature coefficient studies were made. Therefore we expected to confirm the assigned atom polarization of 57 cc. for ferric acetylacetonate by extrapolation of our dielectric constant-pellet thickness ratios to zero pellet thickness. However, Fig. 5G shows a dielectric constant of 3.46. Since the density of ferric acetylacetonate is found to be 1.41 the P_{E+A} value by this measurement is only 112.7 cc. If the electronic polarization value (91.5 cc.) of Finn, Hampson and Sutton is subtracted from this number an atom polarization value of 21.2 cc. remains, by contrast to 57 cc.

In view of this large discrepancy we have determined the total polarization of benzene solutions of ferric acetylacetonate at 20, 25, 30 and 40° and have indeed found a temperature dependence corresponding to total polarization (calculated from α and β of Fig. 6) of 158.8, 150.6, 144.5 and 133.6 cc., respectively. These polarizations correspond to permanent moments of 1.48, 1.35, 1.25 and 1.05 *D*. With reference to the vapor phase study[2] these moments include solvent effects, both positive and negative, depending on the temperature. Therefore according to these experiments ferric acetylacetonate contributes both atomic and orientation polarization in the electric field. Perhaps it is fortuitous that the atomic polarization 21.2 cc. is approximate to that of beryllium acetylacetonate which has been shown not to have (and on the basis of the tetrahedral symmetry of beryllium would not be expected to have) a permanent moment.

The structural feature of ferric acetylacetonate which gives rise to an electric moment cannot be specified with assurance. In absence of orientation polarization one is tempted to attribute complete bonding degeneracy to the system, as was proposed by Finn, Hampson and Sutton. In the face of an observed orientation polarization one can in resonance theory easily rescind this attitude. Furthermore as Smith (p. 279) has pointed out[1] the constellar oscillation of the non-planar six-membered rings in this coördinate structure may give rise to either atom or orientation polarization depending on the relationship of this frequency to that of the applied field. Finally there is no compelling reason to assume that the electronic and nuclear fields are centrosymmetrically coincident in this substance.



The authors wish to thank the National Research Council of Canada for generous financial support and Mr. Henry Sawatzky for experimental aid.

Experimental

Reagents.—Mercuric chloride was Mallinckrodt reagent, used as received. Benzoquinone was purified by repeated crystallization from 95% ethanol, m.p. 113.5°, d^{20}_4 1.313. Naphthoquinone, obtained as a by-product in naphthalene oxidation to phthalic acid, was five times crystallized from 95% ethanol using Darco decolorization, m.p. 148.4°, d^{20}_4 1.385. Anthraquinone (Kahlbaum) was twice crystallized from chloroform (38 ml. per g.), m.p. 281°, d^{20}_4 1.440. The 4,4′-dinitrobiphenyl was crystallized from ethanol (with Darco) and benzene, m.p. 240.9–241.8°, d^{20}_4 1.445. The ferric acetylacetonate was prepared by Claisen's method[27] in 82% yield, m.p. 179–180°, and was thrice purified by solution in benzene (3.5 ml. per g.) and then addition of petroleum ether (b.p. 60–70°, 4 ml. per g.), m.p. 181.5°, d^{20}_4. All melting points are corrected against reliable standards. The melting points were found to be identical when these substances were recovered after determinations of dielectric constant except for benzoquinone where the melting point was decreased to 112.5°. All recoveries from solution were effected by vacuum evaporation at room temperature.

Solvents.—Benzene and dioxane were purified as described previously but were maintained and delivered under positive pressure of nitrogen freed from oxygen, water and carbon dioxide. No metallic sodium was used in the storage containers. The initial dielectric constant (2.284, 20°; 2.262, 30°; 2.245, 40°) and densities (0.8788, 20°; 0.8681, 30°; 0.8628, 35°; 0.8575, 40°) of the benzene were unchanged after six months of such storage. However the

---

[27] A. Hantzsch and C. H. Desch, *Ann.*, **323**, 13 (1902).

initial dielectric constants (2.224, 20°; 2.216, 25°; 2.210, 30°; 2.189, 40°), though not the densities (1.0336, 20°; 1.0278, 25°; 1.0225, 30°; 1.0109, 40°), of the dioxane slowly changed during this period. The change could be detected by vacuum evaporation of a 50-ml. aliquot which left a few colorless crystals, m.p. about 45°; also dioxane containing this impurity (probably peroxide) badly discolored benzoquinone and rendered such determinations unreliable. The source of this impurity has not been located. Possibly it involves the oxygen introduced by a pipet into the nitrogen-filled bottle.

Refractive Indices.—An Abbé refractometer of ±0.00002 precision was used for measurements of solutions of various concentrations. For benzoquinone in benzene $\delta n/\delta\omega$ was 0.042 and in dioxane was 0.120.

Dielectric Constants of Solutions.—The apparatus described previously[4] was altered by temperature regulation of the test cell with water circulated by a $^3/_4$ hp. centrifugal pump from a thermostated bath heated or cooled by regulation prescribed by a thermistor embedded in the metal wall of the test cell. This thermistor was balanced in a Wheatstone bridge against a second, matched, thermistor immersed in the master bath (±0.01°) in which the density determinations were made. The stray inductance errors in the measuring system were evaluated by the substitution method and were found to cause a positive capacitance error at the standard condenser of 16–22% (non-linear) at 5 mc., 3.6–5% (non-linear) at 2.6 mc., but only 0.1% at 500 kc. and 0.002% at 220 kc. All measurements but one have been carried out at 500 kc. The field strength is about 1 e.s.u.

The Pellet Press.—The success of the solid dielectric constant determination is largely due to the quality of this device. This die is fabricated from Crucible Steel Co. "Ketos" bar 2 inches in diameter and 1 inch long axially drilled centrally for accommodation of the finely powdered substance and also drilled with three holes spaced equally at a distance of 0.75 inch from the center. These holes match threaded holes in a "Ketos" disc 2 inches in diameter and 0.75 inch thick which forms the base of the die. The two pieces are held tightly together by means of three 0.125 × 1.7 inch cap screws. Both pieces are hardened to Rockwell C of 60 and the flat surfaces are finely surface-ground. The axially central hole also is ground to size after hardening.

The surface-ground surfaces between which the powder is compressed to a pellet are presented by two pieces of hardened drill rod finely turned to the exact (+0.000–0.0001 inches internal) diameter of the centrally axial hole in the top member of the die assembly. The bottom piece of drill rod is 0.125–0.375 inch long depending on the life of the die, which gradually expands after long usage where the powder is compressed. This short piece of drill rod is expelled in front of the finished pellet after removal of the bottom plate. Pressure both for compression of the powder and extrusion of the pellet is provided by the other piece of drill rod which is 1.25 inch long; its upper surface obviously need not be surface ground since it receives the ram of the hydraulic press.

All metal parts should be washed with an efficient solvent (usually acetone) after each pellet extrusion, then liberally oiled. The oil is thoroughly wiped away before preparation of the next pellet.

Pellets.—The consolidation of pellets either 0.2500 inch or 0.2675 inch in diameter and of various thicknesses is accomplished as has been described previously[4] under a hydraulic pressure of 10,000 p.s.i. but not *in vacuo.* It is important that the finely powdered substance be distributed uniformly in the die, by twisting the pressing pin without appreciable load, before the hydraulic ram is applied. The dielectric constant of a finished pellet is determined by placing a lump of amalgam on the bottom electrode, smoothing it flat and placing upon this amalgam a pellet upon the top of which is another lump of amalgam. After the pellet is centered between the electrodes by means of a chamfered sleeve on the upper electrode the micrometer is screwed down in order uniformly to extrude laterally as much amalgam as possible without fracturing the pellet. Excess of amalgam is brushed away carefully in order to leave both amalgam layers as nearly as possible at the diameter of the pellet and electrodes.

Early measurements were carried out by use of a zinc amalgam (Zn:Hg, 1 g.:6 g.) which was sufficiently inert that all pellets except those of mercuric chloride could be cleaned and remeasured for evaluation of precision. The mercuric chloride reacted rapidly with the zinc amalgam, preventing oscillation (V.F.O.) within a few minutes because the resistance of the pellet rapidly decreased from 80–100,000 ohms to about 10,000 ohms. Eventually this amalgam would completely liquefy the pellet, but at the moment that the V.F.O. ceased to function because of conductivity the pellet face was apparently unaffected when the amalgam was completely brushed from it. However the cleaned pellet was still a conductor when an inert (tin) amalgam replaced that of zinc. This phenomenon has not been explained. Successful measurements of new mercuric chloride pellets can be made either directly with tin amalgam or with zinc amalgam if the surfaces of the pellets are first coated with an invisible layer of Vaseline.

Amalgams.—The zinc amalgams deteriorate after a few days in contact with air so amalgams with other metals have been examined. Indium and iron amalgams are gritty while silver amalgam is too resilient. Copper amalgam is satisfactory but best is a tin amalgam (1 g. Sn:3 g Hg) which is always briefly ground, before each application, in the mortar in which it has been prepared by grinding together the two metals. This amalgam is stable for weeks.

Dielectric Constants of Solids.—Determinations have been carried out with the apparatus described previously and also with a duplicate circuit in which the precision was increased fivefold by reducing the variable capacitance in the V.F.O. to 110 pf. The determinations were made in a room at 20 ± 1° with 45 R.H. In order to avoid stray capacitance–inductance errors the dielectric constant determination[4] was altered. The thickness of the pellet was first determined with the pellet test condenser. Then the pellet and amalgam were installed and the V.F.O. was balanced to zero beat with respect to the 500 kc. crystal-controlled oscillator. The pellet and amalgam were then removed quickly and thoroughly and the pellet condenser readjusted to zero beat. In a convenient variation of this technique both adjustments rapidly could be made 50 cycles off zero beat by inclusion of a Hewlett–Packard frequency meter into the circuit. In either circumstance the dielectric constant was evaluated as: thickness of pellet *versus* equivalent thickness of air.

Dipole Moments of 4,4′-Dinitrobiphenyl.—Dioxane solutions at 40° gave a value of $d\epsilon/d\omega = 1.00$ extrapolating smoothly to $\epsilon_1 = 2.1914$ and of $dV/d\omega = 0.425$ extrapolating to $V_1 = 0.9895$. Total polarization (80.3 cc.) thus may be expressed after deduction of $P_{E+A} = 66.9$ cc. as $\mu = 0.83$ *D*. Benzene solutions at 40° behaved erratically but a least squares evaluation of 12 analyses gave $d\epsilon/d\omega = 0.55$ extrapolating to $\epsilon_1 = 2.2419$ and $dV/d\omega = 0.445$ extrapolating to $V_1 = 1.1667$. The calculated total polarization (77.7 cc.) thus leads to a moment of 0.74 *D*.

TORONTO, CANADA