TABLE VII

CHARACTERISTIC FREQUENCIES OF BORANES

Motion	B_2H_6[11]	$B_2H_2(CH_3)_4$[12]	B_5H_9
BH_2 stretch	2610	..	..
	2520	..	2610
BH stretch	..	..	2598
	2102	2137	1844
BH* stretch	1982	1987	1802
	1847		
	1180		
	1173		
BH_2 bend	1010	..	..
	970		
			1621
BH bend	..	..	1449
			1413
B–B stretch	..	..	1126
BH^*_2B stretch	799	844	799
BH* bend	370	365	605
			568

stretching frequency near 800 cm.$^{-1}$ which exhibits considerable boron isotopic structure and for B_5H_9 shifts on deuteration by a factor around 1.25.

The low frequency bands of B_5H_9 at 568 and 605 cm.$^{-1}$ show unexpectedly large isotopic shifts on deuteration. It is interesting that there is a corresponding mode of B_2H_6 at 370 cm.$^{-1}$ which shifts by a factor close to $\sqrt{2}$ on deuteration. These bands must correspond to bridge hydrogen motions and they provide the basis for the estimate of the frequency of one of the A_2 vibrational modes of B_5H_9 at 500 cm.$^{-1}$.

Thermodynamic Properties of Pentaborane.—Since several fundamental vibrations were selected only by consideration of expected vibrational type, it does not seem appropriate to include detailed calculations of thermodynamic functions. However, the entropy of gaseous B_5H_9 at 296°K., measured by Johnston, Kerr, Clarke and Hallett[6] together with the accurate values of the moments of inertia from the microwave studies[3,14] provide one check upon the present assignment. The calculated entropy of B_5H_9 at 296°K., 65.73 cal./deg. mole, may be compared to the experimental value, 65.75 cal./deg. mole.[6] This agreement is fortuitous since the uncertainty in each of the numbers is of the order of a few tenths of an entropy unit (the experimental entropy includes a -2.68 cal/deg. mole ideal gas correction based upon Berthelot's equation) but it probably does substantiate the conclusion that there is one unobserved, low frequency fundamental (assigned here as an A_2 mode at about 500 cm.$^{-1}$).

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[14] A report by H. J. Hrostowski and R. Myers on the microwave study of B_5H_9 and B_5D_9 is in press (*J. Chem. Phys.*). They give the product of the principal moments of inertia for $B_5{}^{11}H_9$, 2.460×10^{-114} g.^{6}cm.^{6}.

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[CONTRIBUTION FROM THE INSTITUTE OF SCIENCE AND TECHNOLOGY, UNIVERSITY OF TOKYO]

Dipole Moments and Absorption Spectra of *o*-Benzoquinone and its Related Substances

BY SABURO NAGAKURA AND AKIRA KUBOYAMA

RECEIVED APRIL 3, 1953

Dipole moments of *o*-benzoquinone and 1,2-naphthoquinone were determined in benzene solutions as 5.1 and 5.67 *D*, respectively. These high moments can be explained on the basis of the π-electron distribution calculated by the molecular orbital method. The solvent effects on the electronic absorptions were measured with *o*-, *p*-benzoquinone, 1,2- and 1,4-naphthoquinone. As a result of the measurement, it was found that the absorptions of these quinones appearing in the visible region shift to the side of shorter wave lengths with the increasing dielectric constant of the solvent. This probably shows that these absorptions are due to the n-π^*-transition.

It is known that quinones have many interesting properties. They absorb visible light; they form a group of molecular compounds[1]; their oxidation–reduction potentials are generally high and positive[2]; further, a certain quinone has an abnormally high dipole moment.[3] Of these properties oxidation–reduction potential appears to be an unique example of being fully studied; *viz.*, Evans, *et al.*,[2] have discussed this property in detail with reference to π-electrons.

The work in the present paper was undertaken to study the problem somewhat in a wider scope. First, the dipole moments and visible and near ultraviolet absorption spectra measured for several quinones will be reported. Second, the experimental result on the dipole moment will be compared with the theoretical value obtained by the use of the molecular orbital method.

Experimental

Materials.—*o*-Benzoquinone[4] was prepared by oxidation of catechol and recrystallized from ether. The dark-red crystalline product melted at 60–70° with decomposition.

p-Benzoquinone was prepared by oxidation of commercial hydroquinone and purified by repeated sublimation, m.p. 116°.

1,4-Naphthoquinone[5] was obtained by oxidation of 1,4-

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[1] P. Pfeiffer, "Organische Molekülverbindungen," Ferdinand Enke, Stuttgart, 1927; G. Weiss, *J. Chem. Soc.*, 245 (1942), and 462 (1943); H. M. Powell, G. Huse and P. M. Cooke, *ibid.*, 153 (1943), and 435 (1943); L. Michaelis and S. Granick, THIS JOURNAL, **66**, 1023 (1944).

[2] G. E. K. Branch and M. Calvin, "The Theory of Organic Chemistry," Prentice-Hall, Inc., New York, N. Y., 1941, p. 303; E. Berliner, THIS JOURNAL, **68**, 49 (1946); M. G. Evans, *Trans. Faraday Soc.*, **42**, 113 (1946); M. G. Evans, J. Gergely and J. de Heer, *ibid.*, **45**, 312 (1949).

[3] C. C. Caldwell and R. J. W. Le Fèvre, *J. Chem. Soc.*, 1614 (1939). The dipole moment of phenanthrenequinone was determined by them as 5.6 *D*.

[4] R. Willstätter and A. Pfannenstiel, *Ber.*, **41**, 2580 (1908); S. Goldschmidt and F. Graef, *ibid.*, **61**, 1858 (1928); R. Kuhn and I. Hammer, *ibid.*, **83**, 413 (1950). *o*-Benzoquinone is unstable, so the measurement with this substance has been made within six hours after preparation.

[5] *Org. Syntheses*, **17**, 4, 24 (1937).

aminonaphthol which was prepared by reduction of Orange I. The product was crystallized from ether, m.p. 125°.

1,2-Naphthoquinone[5] was obtained according to the method of L. F. Fieser, m.p. 147–148°.

Benzene, petroleum benzine, methanol and chloroform used as the solvent were purified by the methods described in "Organic Solvents".[6]

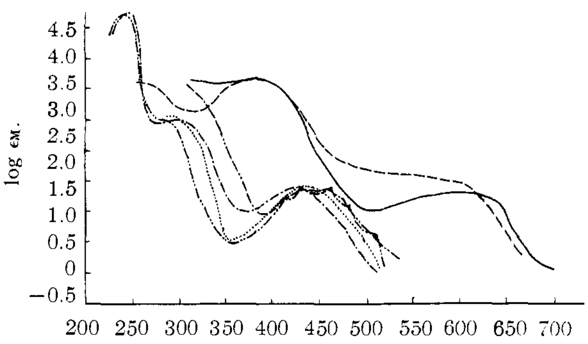

Fig. 1.—Absorption spectra of *o*- and *p*-benzoquinone in various solvents: —, *o*-benzoquinone in benzene; — — —, *o*-benzoquinone in chloroform; —·—, *p*-benzoquinone in petroleum benzine; ··— — —··, *p*-benzoquinone in benzene; ...., *p*-benzoquinone in chloroform; —·—, *p*-benzoquinone in water.

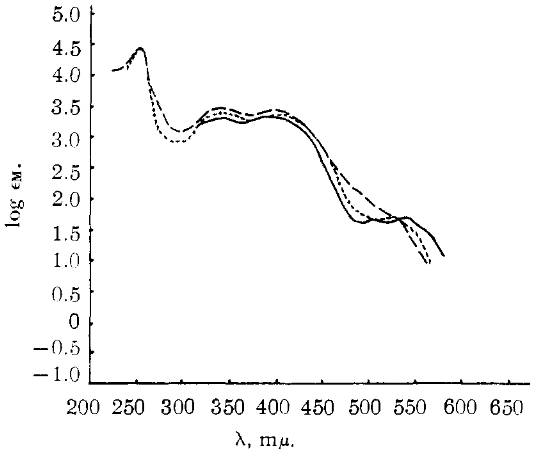

Fig. 2.—Absorption spectra of 1,2-naphthoquinone in various solvents: —, in benzene; -----, in chloroform; — — —, in methanol.

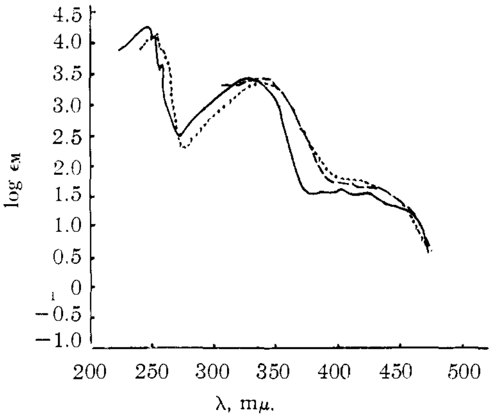

Fig. 3.—Absorption spectra of 1,4-naphthoquinone in various solvents: —, in petroleum benzine; — — —, in benzene; ------, in chloroform.

Methods and Results.—The absorption spectra were measured with a Beckman quartz spectrophotometer model DU. The results obtained in the present experiment are shown in Figs. 1–3. In these figures, the logarithm of the molar extinction coefficient (ϵ_M) is plotted against the wave length in millimicrons. The absorptions of *o*-benzoquinone[7] in hexane, ether and chloroform, *p*-benzoquinone[8] in *n*-hexane and chloroform, 1,2-naphthoquinone in ether, chloroform and alcohol, and 1,4-naphthoquinone[9] in alcohol have already been measured by several investigators. In the present experiment, absorption spectra were measured with *o*-benzoquinone in benzene and chloroform; *p*-benzoquinone in petroleum benzine, benzene, chloroform and water; 1,2-naphthoquinone in benzene, chloroform and methanol; 1,4-naphthoquinone in petroleum benzine, benzene and chloroform. Comparing present experimental results with those obtained by other investigators in the same solvent, it is seen that there is good accordance between them.

The dielectric constant was measured with the apparatus described previously.[10] All the measurements of the dielectric constant ϵ and the specific volume v were made in benzene solutions at 25°. The measured values of these two quantities are given in Table I, where ω is the weight fraction of the solute. Using these experimental results, the molecular polarization at infinite dilution, $P_{2\infty}$ was calculated by the Halverstadt and Kumler method.[11] From the value of $P_{2\infty}$,

$$P_{2\infty} = M\{3\alpha v_1/(\epsilon_1 + 2)^2 + (v_1 + \beta)(\epsilon_1 - 1)/(\epsilon_1 + 2)\}$$

the dipole moment μ was obtained by the usual equation

$$\mu = 0.01273\sqrt{(P_{2\infty} - MR_D)T}$$

In the above equation, the molecular refraction for the sodium D-line, MR_D was evaluated as the sum of the atomic refractions.

TABLE I

DIELECTRIC CONSTANTS AND SPECIFIC VOLUMES IN BENZENE SOLUTIONS OF *o*-BENZOQUINONE AND 1,2-NAPTHOQUINONE

(A) *o*-Benzoquinone; temp., 25.0°

ω	ϵ	v
0	2.274	1.14728
.000567	2.288	1.14676
.000877	2.298	1.14671
.001559	2.314	1.14686

$\alpha = 26.0$, $\beta = -0.29$, $\epsilon_1 = 2.274$, $v_1 = 1.147$, $P_{2\infty} = 561$ cc., $MR_D = 27.2$ cc., $\mu = 5.1$ *D*.

(B) 1,2-Naphthoquinone; temp., 25.0°

0	2.270	1.14715
0.001494	2.301	1.14662
.002002	2.311	1.14634
.002266	2.320	1.14639
.002512	2.325	1.14605
.003880	2.355	1.14581

$\alpha = 22.2$, $\beta = -0.32$, $\epsilon_1 = 2.270$, $v_1 = 1.147$, $P_{2\infty} = 701$ cc., $MR_D = 36.0$ cc., $\mu = 5.67$ *D*.

Theoretical

The calculation of the π-electron density has been carried out with *o*- and *p*-benzoquinone by use of the same molecular orbital method as we pre-

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(6) A. Weissberger and E. Proskauer, "Organic Solvents," Oxford Univ. Press, New York, N. Y., **1935**, p. 103, 105, 114, 118 and 153.

(7) S. Goldschmidt and F. Graef, *Ber.*, **61**, 1858 (1928).

(8) E. A. Braude, *J. Chem. Soc.*, 490 (1945).

(9) J. R. Price, A. R. Winzor and A. K. Macbeth, *ibid.*, 327 (1935).

(10) S. Nagakura and A. Kuboyama, *Repts. Inst. Sci. Techn., Univ. Tokyo*, **4**, 242 (1950).

(11) I. F. Halverstadt and W. D. Kumler, THIS JOURNAL, **64**, 2988 (1942). According to their method, $P_{2\infty}$ is obtained by the equation where M is the molecular weight of the solute. The values of α, β, ϵ and v, necessary for the calculation are given in Table I.

viously applied to some heterocyclic molecules[12] and the amide group.[13] In the present investigation,[14] calculations were repeated six and four times for *o*- and *p*-benzoquinone, respectively, until the evaluated values of the π-electron densities become self-consistent.[12-16] The final results for them are given in Fig. 4.[17]

Discussion

π-Electron Densities and Dipole Moments.—The theoretical π-electron densities given in Fig. 4 show that oxygen atoms in *o*- and *p*-benzoquinone have excesses of π-electrons by 0.475e and 0.503e, respectively. These results seem to be reasonable in comparison with those obtained by several workers for the ionic character of the carbonyl bond in acetone.[13,18,19] By the use of these theoretical values of π-electron densities, the dipole moment of *o*-benzoquinone can be calculated as 7.5 *D*.[20] This value will become lower probably by about 1.5 *D*, if the inductive effect between two large dipoles belonging to adjacent carbonyl bonds is taken into consideration.[21] Therefore the moment predicted by the theory is not in conflict with the experimental value of 5.1 *D*.

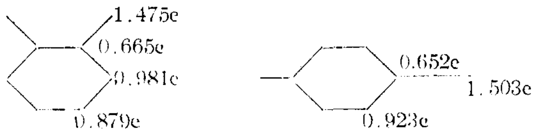

Fig. 4.—π-Electron densities of *o*- and *p*-benzoquinone.

The dipole moment of 1,2-naphthoquinone obtained in the present measurement is almost equal to that of phenanthrenequinone determined by Caldwell and Le Fèvre.[3] It will be noticed that the dipole moments of these two substances are somewhat larger than that of *o*-benzoquinone. Indeed, this fact appears to reveal that the π-electron migration from carbon atoms in the ring to oxygen atoms increases with the addition of the benzene ring.

Absorption Spectra.—According to the experimental results given in Figs. 1–3, it is apparent that the absorption of *o*-, *p*-benzoquinone, 1,2- and 1,4-naphthoquinone appearing in the visible region are all due to a weak electronic transition (ϵ, 10–100) and their maxima surely shift to the shorter wave length with the increasing dielectric constant of the solvent. On the other hand, the absorption maxima appearing in the near ultraviolet region, whose molar extinction coefficients are 300–30,000 exhibit the reverse tendency in their solvent effects. That is to say, the former absorption is the "blue-shift"[22] band, while the latter is the "red-shift" band. In the present investigation, we are concerned chiefly with the "blue-shift" band, because it is undoubtedly the cause of the color of quinones. The "blue-shift" band, which is observed with many other compounds containing heteroatoms, has been intensively investigated by several workers,[13,22,23] and it has been generally inferred that this noticeable phenomenon arises from the singlet–singlet n–π^* transition. So it seems reasonable to consider that the weak visible absorption bands of the quinones referred to above should be due to this transition. Furthermore the fact that the molar extinction coefficients of these bands are smaller than 100 also supports this view, because a low intensity is found to be the marked characteristic of the n–π^*-transition.[22] The same conclusion has already been obtained by McConnell[22] and other investigators[23a,b] for the visible absorption of *p*-benzoquinone. By the present investigation it was found that the colors of three other quinones may also be attributable to the n–π^*-transition.

Acknowledgment.—The authors wish to thank Prof. S. Mizushima and Prof. K. Higasi for their advice and encouragement throughout this investigation.

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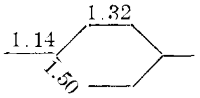
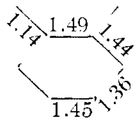
[12] S. Nagakura and T. Hosoya, *Bull. Chem. Soc. Japan*, **25**, 179 (1952).

[13] S. Nagakura, *ibid.*, **25**, 164 (1952).

[14] The bond distances necessary for the evaluation of the overlap integral have been determined by Robertson (J. M. Robertson, *Proc. Roy. Soc.* (*London*), **A150**, 106 (1935)) for *p*-benzoquinone.



For *o*-benzoquinone, however, bond distances have not been yet determined experimentally. So the values obtained from the bond orders were used for C–C bonds of this compound. The final values of them are given in the diagram



In these two diagrams the values are represented in units of Å.

[15] G. W. Wheland and D. E. Mann, *J. Chem. Phys.*, **17**, 264 (1949).

[16] Y. Kurita and M. Kubo, *Bull. Chem. Soc. Japan*, **24**, 13 (1951).

[17] The value of the π-electron density (q_i) is calculated by the following equation (G. W. Wheland and L. Pauling, THIS JOURNAL, **57**, 2086 (1935))

$$q_i = 2\sum_{j=1}^{4} C^2_{ij}$$

where C_{ij}'s are the coefficient of the atomic orbital in the j-th molecular orbital which is represented as a linear combination of the $2p\pi$ atomic orbitals.

[18] J. B. Bentley, K. B. Everard, R. J. B. Marsden and L. E. Sutton, *J. Chem. Soc.*, 2957 (1949).

[19] L. Pauling, "The Nature of the Chemical Bond," Cornell Univ. Press, Ithaca, N. Y., 1940, p. 75.

[20] The dipole moment due to the σ-electron distribution is expected to be very small for a C=O bond (L. Pauling, "The Nature of the Chemical Bond," Cornell Univ. Press, Ithaca, N. Y., 1940, p. 75). So this value was obtained on the assumption that the dipole moment of *o*-benzoquinone will be principally determined by the π-electron distribution alone.

[21] The contribution of the inductive effect was calculated by the same method as described in the following reference; H. M. Smallwood and K. F. Herzfeld, THIS JOURNAL, **52**, 1919 (1930).

[22] H. McConnell, *J. Chem. Phys.*, **20**, 700 (1952).

[23] (a) H. L. McMurry, *ibid.*, **9**, 241 (1941); (b) H. Baba, *J. Chem. Soc. Japan*, **72**, 341 (1951); (c) M. Kasha, *Disc. Faraday Soc.*, 14 (1950); (d) F. Halverson and R. C. Hirt, *J. Chem. Phys.*, **19**, 711 (1951).