

g. of neutral material and 0.188 g. of acidic material. From the combined acidic products there was obtained, by recrystallization from acetone-hexane, a total of 0.952 g. (42% from X) of II, m.p. 216–218°,  $\lambda_{\max}^{\text{EtOH}}$  3.0 and 5.95  $\mu$ .

*Anal.* Calcd. for  $C_{13}H_{22}O_3$ : C, 68.99; H, 9.80; neut. equiv., 226. Found: C, 69.06; H, 9.87; neut. equiv., 225.

Treatment of II with ethereal diazomethane afforded 4 $\beta$ ,9 $\beta$ -dimethyl-4 $\alpha$ -carbomethoxy-8 $\beta$ -hydroxy-*trans*-decalin, m.p. 95–96° (from hexane),  $\lambda_{\max}^{\text{CHCl}_3}$  2.8–2.9 and 5.80  $\mu$ .

*Anal.* Calcd. for  $C_{14}H_{24}O_3$ : C, 69.96; H, 10.06; Found: C, 70.08; H, 10.12.

The oily neutral material from the hydrolysis was subjected to a further 6 days of reflux with sodium hydroxide solution. The neutral material which remained after this hydrolysis was chromatographed on acid-washed alumina to afford an oil (ca. 10% from acetate X) which gave one broad peak on v.p.c. analysis (250°, column packing unrecorded) and exhibited  $\lambda_{\max}^{\text{EtOH}}$

2.8–2.9 and 5.79 (shoulder at 5.82)  $\mu$ ;  $\tau_{\max}^{\text{CCl}_4}$  9.32 (singlet,  $\text{CH}_2\text{-C<}$ ), 8.87 (singlet,  $\text{CH}_2\text{CCOOCH}_2\text{CH}_3$ ), 8.74 (center of triplet,  $\text{CH}_2\text{CH}_2\text{O}$ ), and 5.92 p.p.m. (center of quartet,  $\text{CH}_2\text{CH}_2\text{O}$ ), consistent with its being 4 $\alpha$ ,9 $\beta$ -dimethyl-4 $\beta$ -carboethoxy-8 $\beta$ -hydroxy-*trans*-decalin (XVII).

**Acknowledgment.**—This investigation was supported by Public Health Service Research Grant AM-05014 and a Frederick Gardner Cottrell Grant from the Research Corporation. Drs. W. S. Johnson, M. Brown, and V. J. Bauer contributed methylidihydroresorcinol. Professor K. L. Williamson generously ran the n.m.r. spectra.

## Electron-Transfer Polymers. XXVII. Solvent Effects on the Absorption Spectra of Partially Oxidized Oligomeric Hydroquinones

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The charge-transfer bands that appear when ethylhydroquinone, 1,3-bis(2,5-dihydroxyphenyl)propane (I), 1,5-bis(2,5-dihydroxyphenyl)pentane (II), and 1,3,5-tris(2,5-dihydroxyphenyl)pentane (III) are partially oxidized were investigated. Ethylquinhydrone shows two peaks at 360 and 450  $m\mu$ . Neither obeys the Beer-Lambert law, and both must be due to intermolecular quinhydrone. The three oligomers show absorption centering at about 440  $m\mu$ , due to intermolecular quinhydrone. In addition they show shorter wave length absorptions centering at about 370  $m\mu$  for I, 330  $m\mu$  for II, and 330 and 370  $m\mu$  for III. These obey the Beer-Lambert relation and are intramolecular. In the case of I, the position of the band also shifts from ca. 370 to ca. 350  $m\mu$  in going from 1 to 90% acetic acid. The intensities of these shorter wave length bands are sensitive to solvent composition. In highly aqueous solvent the intensity is markedly higher than in more highly organic mixtures. The increase in intensity, bespeaking an increase in complexation, increases proportionately with the value of the surface tension of the pure solvent. This is explained, following the hypothesis of Sinanoğlu and Abdunur for the analogous behavior of the double helix of DNA, as being due to the loss in solvent-cage surface area upon complex formation. A driving force of complex formation, in this view, then must be directly correlated with the change in free energy, which is proportional to the surface tension of the solvent multiplied by the change in solvent-cage surface area. Reasonable support for this hypothesis was found.

When hydroquinone, ethylhydroquinone, and the three oligomeric hydroquinones described in a previous paper,<sup>1</sup> namely, 1,3-bis(2,5-dihydroxyphenyl)propane (I), 1,5-bis(2,5-dihydroxyphenyl)pentane (II), and 1,3,5-tris(2,5-dihydroxyphenyl)pentane (III) are oxidized in 90% acetic acid, the solutions, initially colorless, gradually become yellow as the fraction of solute converted to quinone increases. When, however, the compounds are oxidized in dilute solution in 1% aqueous acetic acid, the solutions of the 1,3-bis and of the 1,3,5-tris compounds take on a deep red coloration with the first addition of oxidizing agent. The color reaches maximum intensity near the midpoint of the oxidation, then gradually, as quinone accumulates, gives way to the final clear yellow quinone color. This color production is reminiscent of the behavior observed when polyvinylhydroquinone is oxidatively titrated,<sup>2–4</sup> and also of the weaker dark color observed in relatively concentrated solutions of quinhydrone.<sup>5</sup> Dilute hydroquinone solutions show no visible quinhydrone color at the midpoint of an oxidative titration.

It has been shown that the molar extinction coefficient of the quinhydrone charge-transfer complex does not vary appreciably from one solvent to another.<sup>6</sup> Thus, the conclusion must be that the 1,3-propylene-linked oligomers possess some property which promotes the donor-acceptor (charge-transfer) interaction that appears in a highly aqueous solvent.

This matter has been investigated. The absorption spectra of partially oxidized ethylhydroquinone and the three oligomeric hydroquinones have been examined in several solvents and mixtures. The spectrum of the ethylquinhydrone complex (not previously reported) was examined over the region 220 to 600  $m\mu$  in 50% aqueous tetrahydrofuran by volume. Solutions of ethylhydroquinone and ethyl-*p*-benzoquinone were mixed, the component absorptions were subtracted, and two new overlapping yet distinct maxima were found at 360 and 450  $m\mu$ . Both were of approximately the same intensity, though the longer wave length band was considerably broader. They were affected similarly by changes in the concentration of either component, and neither of them obeyed the Beer-Lambert law. An attempt was made to determine the association constant and the molar extinction coefficient from each peak, but without success.

(1) R. E. Moser and H. G. Cassidy, *J. Org. Chem.*, **30**, 2602 (1965).

(2) M. Ezrin, I. H. Updegraff, and H. G. Cassidy, *J. Am. Chem. Soc.*, **75**, 1610 (1953).

(3) H. Kamogawa, Y.-h. C. Giza, and H. G. Cassidy, *J. Polymer Sci.*, **A2**, 4647 (1964).

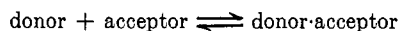
(4) H. G. Cassidy and K. A. Kun, "Oxidation-Reduction Polymers," Interscience Division, John Wiley and Sons, Inc., New York, N. Y., 1965.

(5) L. Michaelis and S. Granick, *J. Am. Chem. Soc.*, **66**, 1023 (1944).

(6) R. E. Moser and H. G. Cassidy, *ibid.*, **87**, 3463 (1965).

The Benesi-Hildebrand calculation,<sup>7</sup> with its usual modifications,<sup>8</sup> gave highly overestimated values of  $\epsilon_0$ , the extinction coefficient of the absorption of the complex, because of the overlapping of bands.<sup>9</sup>

A solution to this problem is found in the approach taken by Michaelis and Granick.<sup>5</sup> A measure of the intensity,  $\epsilon_{st}$ , the "absorption coefficient of the molecular compound under standard conditions," was determined for each absorption band. The equilibrium relation



is assumed, for which one may write an equilibrium constant  $K$  as shown by eq. 1 where (c), (D-c), and (A-c)

$$K = (c)/[(D-c)(A-c)] \quad (1)$$

are the equilibrium concentrations of complex, donor, and acceptor, respectively. The high dissociation of the complex allows the approximation to be made that

$$K' = (c)/(D)(A) \quad (2)$$

If eq. 2 is substituted into Beer's law, there is obtained the usual expression given by eq. 3.

$$\text{O.D.} = \epsilon_0(c) = \epsilon_0 K'(D)(A) \quad (3)$$

If  $\epsilon_0 K'$  is set equal to  $\epsilon_{st}$ , then

$$\epsilon_{st} = \text{O.D.}/(D)(A) \quad (4)$$

and the value  $\epsilon_{st}$ , essentially constant, encompasses the effects of association constant and extinction coefficient.

### Experimental Section

All spectra were measured under the conditions described in the preceding paper.<sup>1</sup> Spectroscopic solutions were prepared from freshly purified samples, under nitrogen, and were used immediately. Solvent mixtures were made by volume or by weight, as indicated.

Two questions were approached experimentally: one, the determination of  $\epsilon_{st}$  for the quinhydrone absorptions and equilibria using the equations described above, for monomers and oligomers in various solvents; and the other, the Beer-Lambert-law tests applied to the observed absorption bands. In all cases, mixtures were made by combining calculated amounts of solutions of the fully reduced and the fully oxidized forms. The mixtures, after several minutes, remained unchanged in spectral properties for at least 24 hr. (see Discussion). The charge-transfer (quinhydrone) spectrum was obtained by subtracting from the spectrum of the mixture the spectra of component hydroquinoid and quinoid forms, thus leaving the new bands in evidence. In one instance, however, the quinone absorption overlapped to such an extent, and was so intense, that measurement could not be made (Figure 1).

When reporting on the data for the oligomers (the bis and tris compounds),  $\epsilon_{st}$  was based upon the molar concentrations of the hydroquinonyl and quinonyl groups, rather than upon the concentrations of the oligomeric molecules themselves.

**Ethylquinhydrone.**<sup>1</sup>—The data for mixtures of ethylhydroquinone and ethyl-*p*-benzoquinone are given in Figure 1. Charge-transfer bands of essentially equal intensity were observed with maxima at about 360 and 450  $m\mu$ . The Beer-Lambert law was not obeyed by either of these absorption bands.

**1,3-Bis(2,5-dihydroxyphenyl)propane-Derived Quinhydrones.**<sup>1</sup>—In 1% aqueous acetic acid there was observed an intense peak at 370  $m\mu$  and a relatively weak shoulder at 440  $m\mu$ , with no other maxima in the range 220 to 600  $m\mu$ . Although these

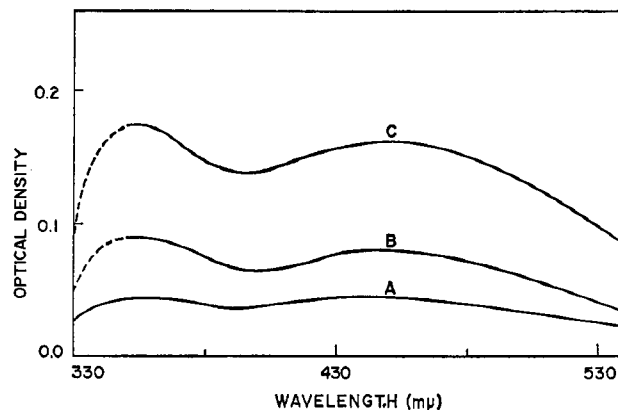


Figure 1.—Spectra of solutions of ethylquinhydrone in 50% aqueous tetrahydrofuran, 1:1 by volume: A,  $9.78 \times 10^{-2} M$  ethylhydroquinone,  $4.19 \times 10^{-3} M$  ethyl-*p*-benzoquinone; B,  $7.96 \times 10^{-2} M$  ethylhydroquinone,  $8.46 \times 10^{-3} M$  ethyl-*p*-benzoquinone; and C,  $1.99 \times 10^{-1} M$  ethylhydroquinone,  $8.46 \times 10^{-3} M$  ethyl-*p*-benzoquinone. At the higher quinone concentrations the quinone absorption was so intense that the 330- to 360- $m\mu$  portion of the spectrum could not be recorded.

two bands appeared in the same regions as the bands of ethylquinhydrone, they were distinguished by the marked difference in intensities and by the fact that the 370- $m\mu$  band obeyed the Beer-Lambert law (see below). When the fraction of water in solvent was decreased, there was observed a gradual shift of the intense maximum from 370  $m\mu$  in 1% acid to 350  $m\mu$  in 90% acetic acid. At the same time there was a gradual decrease in intensity of both bands. The data for the intense band are gathered in Table I. Since there was no practical way of determining the exact values of the factors of  $\epsilon_{st}$ , that is, the association constant and the extinction coefficient, there was no way to calculate  $\Delta F^\circ$  for formation of the complex represented by the band. Since, however, only relative values of a parameter of this dimensionality were needed for our purposes, we assumed that the extinction coefficient of the absorption of the complex remains constant through the series of solvents<sup>5,6</sup> and wrote  $\Delta F^\circ = -RT \ln K \approx -RT \ln (\epsilon_{st}/\epsilon_0) = -RT \ln \epsilon_{st} + K''$ , where  $K'' = RT \ln \epsilon_0$ . Thus, plots of  $\Delta F^\circ$  and of  $-RT \ln \epsilon_{st}$  against a function of solvent composition should show the same slope at any point. The values of  $-RT \ln \epsilon_{st}$ , needed in the Discussion, are included in the tables.

TABLE I  
EFFECT OF AQUEOUS ACETIC ACID COMPOSITION ON THE INTENSITY OF THE 350-370- $m\mu$  COMPLEX BAND OF HALF-OXIDIZED 1,3-BIS(2,5-DIHYDROXYPHENYL)PROPANE AT 28°

Wt. % acid	Wave length, $m\mu$	$\epsilon_{st} \times 10^{-5}$	$(-RT \ln \epsilon_{st}) \times 10^{-11}$ , erg/mole
1.0	370	6.30	-3.342
10.0	370	4.09	-3.234
36.0	360	2.72	-3.132
63.0	360	2.20	-3.079
90.0	350	1.04	-2.891

**1,5-Bis(2,5-dihydroxyphenyl)pentane-Derived Quinhydrones.**<sup>1</sup>—In 1% aqueous acetic acid, maxima were observed at 330 and approximately 440  $m\mu$ , the former being of much higher intensity and being extremely sensitive to solvent composition, as shown in Table II.

**1,3,5-Tris(2,5-dihydroxyphenyl)pentane-Derived Quinhydrones.**<sup>1</sup>—The absorption maxima observed for this compound lay at 330, 370, and about 440  $m\mu$  in 1% aqueous acetic acid. The two shorter wave length bands were more intense than that at 440  $m\mu$ . Both were sensitive to the composition of the solvent, the 330- $m\mu$  band being more sensitive, and disappearing into a broad band as the concentration of water in the solvent decreased (Figure 2). The relevant data are gathered into Table III. The weak band at about 440  $m\mu$  did not obey the Beer-Lambert law.

(7) H. A. Benesi and J. H. Hildebrand, *J. Am. Chem. Soc.*, **71**, 2703 (1949).

(8) J. A. A. Ketelaar, C. Van de Stolpe, A. Goudsmit, and W. Dzeubas, *Rec. trav. chim.*, **71**, 1104 (1952); J. A. A. Ketelaar, C. Van de Stolpe, and H. R. Germann, *ibid.*, **70**, 499 (1951); R. S. Drago and N. J. Rose, *J. Am. Chem. Soc.*, **81**, 6138 (1959); K. Conrow, G. D. Johnson, and R. E. Bowen, *ibid.*, **86**, 1025 (1964).

(9) S. P. McGlynn, *Chem. Rev.*, **58**, 1113 (1958).

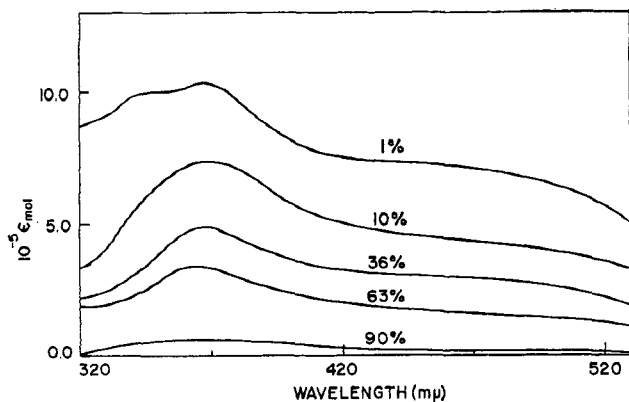


Figure 2.—Complex absorption spectra of quinhydrones from 1,3,5-tris(2,5-dihydroxyphenyl)pentane in aqueous acetic acid of different compositions by weight. See Table IV. The percentages are of acetic acid.

TABLE II  
EFFECT OF AQUEOUS ACETIC ACID COMPOSITION ON THE INTENSITY OF THE 330- $m\mu$  COMPLEX BAND OF HALF-OXIDIZED 1,5-BIS(2,5-DIHYDROXYPHENYL)PENTANE AT 28°

Wt. % acid	Wave length, $m\mu$	$\epsilon_{st} \times 10^{-5}$	$(-RT \ln \epsilon_{st}) \times 10^{-11}$ , erg/mole
1.0	330	15.10	-3.561
10.0	330	2.61	-3.122
36.0	330	0.56	-2.736
63.0	330	0.00	...
90.0	330	0.00	...

TABLE III  
EFFECT OF AQUEOUS ACETIC ACID COMPOSITION ON THE INTENSITIES OF THE 330- AND 360-370- $m\mu$  COMPLEX BANDS OF HALF-OXIDIZED 1,3,5-TRIS(2,5-DIHYDROXYPHENYL)PENTANE AT 28°

Wt. % acid	Wave length, $m\mu$	$\epsilon_{st} \times 10^{-5}$	$(-RT \ln \epsilon_{st}) \times 10^{-11}$ , erg/mole
1.0	370	10.30	-3.465
10.0	370	7.48	-3.385
36.0	370	4.83	-3.276
63.0	370	3.23	-3.175
90.0	360	0.55	-2.732
1.0	330	8.95	-3.430
10.0	330	3.90	-3.222
36.0	330	2.42	-3.103
63.0	330	1.99	-3.054
90.0	330	0.13	-2.371

**Beer-Lambert-Law Tests.**—Tests on the shorter wave length bands in the spectra of the partially oxidized oligomeric hydroquinones were carried out as follows. Stock solutions of nearly equal concentrations of corresponding oxidized and reduced forms of each oligomer were prepared in 36 wt. % aqueous acetic acid. The spectra were recorded and corrected for component absorptions. Five-milliliter portions of each stock solution were then removed and diluted with an equal volume of solvent and the complex spectra were measured. Three-milliliter portions of the stock solution were then removed and diluted to 10 ml. and the spectra were recorded. In all cases linear relationships between solute concentrations and absorption intensities were found.

### Discussion

The following conclusions need clarification. (1) New absorption bands are found when equimolar amounts of reduced and oxidized forms of given bis (I, II) or tris (III) oligomers are mixed, *i.e.*, I with its

oxidized form, II with its oxidized form, III with its oxidized form. Each of the three mixtures absorb in the 440-450- $m\mu$  region. In addition, I absorbs in the 350-370- $m\mu$  region, II absorbs at 330  $m\mu$ , and III absorbs at 360-370 and 330  $m\mu$ . These bands are present in addition to the bands due to hydroquinoid and quinoid groups.

When oxidized and reduced forms of an oligomer such as I are mixed, it must be expected on statistical reasoning that some redistribution occurs. In this redistribution some molecules, originally completely reduced (symbolized as H-R-H, where H represents the hydroquinoid group and -R- is the polymethylene moiety), react with completely oxidized molecules, Q-R-Q (Q represents quinoid), to yield two half-oxidized molecules, H-R-Q. It would therefore be expected, *a priori*, that two types of quinhydrone are present in such mixtures: intermolecular and intramolecular. These are conceived to be the explanation for the observed new (charge-transfer) absorption bands.

(2) Unlike quinhydrone itself, which shows one new band, ethylquinhydrone shows two new bands. Little data are available on the spectral properties of quinhydrones in solution. Tsubomura<sup>10</sup> has treated the charge-transfer spectrum of simple quinhydrone by a molecular orbital calculation, involving the lowest unfilled orbital of quinone and the highest filled orbital of hydroquinone. Conjugation of the lone-pair electrons of oxygen in hydroquinone with the  $\pi$  system of quinone presumably gives rise to a considerable stabilization. This was assumed to maintain the hydroquinonyl oxygens adjacent to the quinonyl oxygens, giving only one preferred rotational isomer.

Quinhydrone systems may become considerably more complicated when the components have substituents on each ring, for example, ethylquinhydrone. In solution, four possible preferred orientational isomers are conceivable, if Tsubomura's assumption about the relative positions of oxygen is correct. These are shown as a-d in Figure 3.  $\pi$  overlap between regions of like sign of the perturbed symmetric  $E_1$  orbital of hydroquinone<sup>11</sup> and the lowest unfilled orbital of quinone<sup>12</sup> makes these conformations favorable.

Alternatively, the lowest unfilled  $\pi$  orbital of quinone can overlap with regions of like sign of the perturbed antisymmetric  $E_1$  orbital of hydroquinone. This would give four additional favorable complex conformations, as shown in Figure 4. It should not be inferred from Figures 3 and 4 that only these eight conformations are allowed or can contribute to the charge-transfer spectrum. Rotations, displacements, and tilting of one component relative to the other all may contribute substantial effects.<sup>13</sup> Thus, the charge-transfer spectrum of ethylquinhydrone may result from a very large number of potential complex conformations. By analogy with simple quinhydrone which gives only one charge-transfer peak although possessing a donor with nondegenerate  $E_1$  levels, the conformations in

(10) H. Tsubomura, *Bull. Chem. Soc. Japan*, **26**, 304 (1953).

(11) L. E. Orgel, *J. Chem. Phys.*, **23**, 1352 (1955); E. M. Voigt, *J. Am. Chem. Soc.*, **86**, 3611 (1964); E. M. Voigt and C. Reid, *ibid.*, **86**, 3932 (1964).

(12) J. W. Sidman, *J. Chem. Phys.*, **27**, 429 (1957).

(13) L. E. Orgel and R. S. Mulliken, *J. Am. Chem. Soc.*, **79**, 4839 (1957).

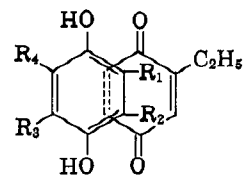
Figure 4 may not be important. The structures in Figure 3, on the other hand, resemble the known component conformation of crystalline quinhydrone.<sup>14</sup>

Steric repulsion between the adjacent ethyl groups in conformation a would decrease  $\pi$ -orbital overlap between donor and acceptor. This would produce a blue shift<sup>15</sup> in the charge-transfer absorption, relative to the peaks arising from complexes with conformations resembling b, c, and d. Wepster and his co-workers<sup>16</sup> have considered several analogous systems and their results are in agreement with this conclusion. Other investigators<sup>17</sup> have shown that, in general, increasing stability of a complex is associated with visible absorption at increasingly longer wave lengths. The 360-m $\mu$  peak of ethylquinhydrone may originate from complexes which resemble conformation a. The second peak, at 450 m $\mu$ , likely is due to one or more of the alternate conformations.

(3) The above discussion is designed to show how the 360-m $\mu$  peak of ethylquinhydrone might originate, so as to support our argument with respect to the oligomers (see 4 below). In any event, the two bands of ethylquinhydrone and the 440-m $\mu$  band of the oligomers, which fail to obey the Beer-Lambert relation, must arise from quinhydrone formed between two molecules—*intermolecular* quinhydrone. No other possibility exists for ethylquinhydrone, and this conclusion is most reasonable also for the 440-m $\mu$  band of the oligomeric quinhydrone.

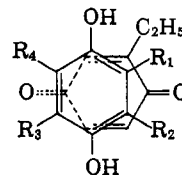
(4) That the shorter wave length bands of the oligomeric quinhydrone obey the Beer-Lambert law unequivocally characterizes them as arising from interaction within the molecule—*intramolecular* quinhydrone.<sup>18</sup> Such an interaction could result from folding of the half-oxidized molecule, as is indicated for the bis-1,3-quinhydrone in Figure 5. Assuming that the rings are parallel and symmetrically oriented and that the bond lengths and angles are normal, the distance between the rings would be approximately 2.5 Å. This is somewhat closer than the 3.1-Å separation in crystalline quinhydrone.<sup>10</sup> Compression of the solid complex has been shown to result in a red shift of the characteristic absorption,<sup>19</sup> which probably was due to a slight decrease in the internuclear distance with little change in relative ring conformation. In contrast, greatly increased overlap between donor and acceptor orbitals also increases no-bond-dative-bond mixing and can produce a blue shift.<sup>20</sup> Higher energy transitions are expected also if donor and acceptor rings are distorted from coplanarity.

Molecular models show that the distance separating the coplanar aromatic rings of half-oxidized 1,5-bis-(2,5-dihydroxyphenyl)pentane can vary from 2.5 to



- a,  $R_1 = C_2H_5$ ;  $R_2 = R_3 = R_4 = H$   
 b,  $R_2 = C_2H_5$ ;  $R_1 = R_3 = R_4 = H$   
 c,  $R_3 = C_2H_5$ ;  $R_1 = R_2 = R_4 = H$   
 d,  $R_4 = C_2H_5$ ;  $R_1 = R_2 = R_3 = H$

Figure 3.



- e,  $R_1 = C_2H_5$ ;  $R_2 = R_3 = R_4 = H$   
 f,  $R_2 = C_2H_5$ ;  $R_1 = R_3 = R_4 = H$   
 g,  $R_3 = C_2H_5$ ;  $R_1 = R_2 = R_4 = H$   
 h,  $R_4 = C_2H_5$ ;  $R_1 = R_2 = R_3 = H$

Figure 4.

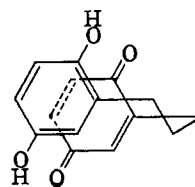


Figure 5.

5.0 Å., again assuming normal bond lengths and angles. This allows freedom of separation in both directions from the 3.1-Å internuclear distance of crystalline quinhydrone. As the distance between the coplanar rings of the pentylene-bridged oligomer decreases, steric hindrance between chain protons and aromatic protons increases. For this reason, the component groups may be held farther apart than the distance they would preferentially assume in an intermolecular complex. Consequently, the intervening chain apparently increases the observed (intramolecular) association constant, but favors conformations with relatively high charge-transfer transition energies.

The charge-transfer spectrum of partially oxidized 1,3,5-tris(2,5-dihydroxyphenyl)pentane in highly aqueous solvent showed peaks which are characteristic of both 1,3- and 1,5-quinonyl-hydroquinonyl intramolecular interactions, as well as normal intermolecular quinhydrone formation.

It would be desirable to show by actual isolation of derivatives that when fully reduced and fully oxidized oligomers are mixed the redistribution inferred from the spectral properties occurs, and to determine rate constants. The reaction is clearly a fast one, as would be expected.<sup>21</sup> In spite of many methods tested, we have not been able to find a quantitative method for rapidly "freezing" or "fixing" the composition of the mixture.<sup>22</sup>

(5) Solvent sensitivity of the charge-transfer bands of hydroquinone has been reported in some detail.<sup>6</sup>

(14) K. Nakamoto, *J. Am. Chem. Soc.*, **74**, 1739 (1952); B. Anex and L. Parkhurst, *ibid.* **85**, 3301 (1963).

(15) J. N. Murrell, *Quart. Rev.* (London), **15**, 191 (1961).

(16) J. Burgers, M. A. Hoefnagel, P. E. Verkade, H. Visser, and B. M. Wepster, *Rec. trav. chim.*, **77**, 491 (1958).

(17) R. Kuhn and A. Winterstein, *Helv. Chim. Acta.* **11**, 144 (1928); O. L. Baril and E. S. Hauber, *J. Am. Chem. Soc.*, **53**, 1087 (1931); W. Dilthey and R. Wizinger, *J. prakt. Chem.*, [2] **118**, 321 (1928).

(18) I. M. Kolthoff and E. B. Sandell, "Textbook of Quantitative Inorganic Analysis," 3rd Ed., The Macmillan Co., New York, N. Y., 1952, p. 616.

(19) D. R. Stephens and H. G. Drickamer, *J. Chem. Phys.*, **30**, 1518 (1959).

(20) S. H. Hastings, J. L. Franklin, J. C. Schiller, and F. A. Matsen, *J. Am. Chem. Soc.*, **75**, 2900 (1953).

(21) I. P. Gragerov and G. P. Miklughin, *Dokl. Akad. Nauk SSSR*, **62**, 79 (1948); L. A. Bothner-By, *J. Am. Chem. Soc.*, **73**, 4228 (1951).

(22) R. E. Moser, Ph.D. Dissertation, Yale University, 1965.

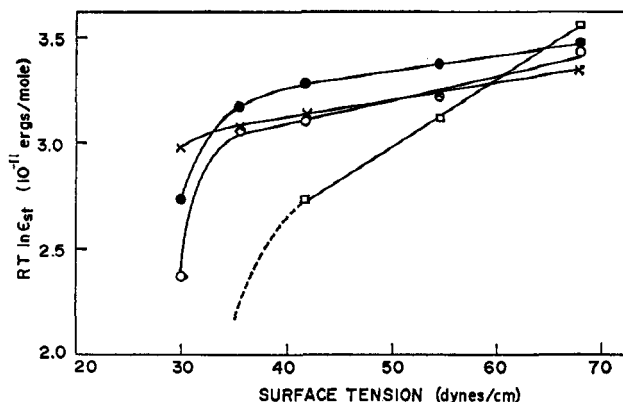


Figure 6.—Surface tensions of various concentrations of aqueous acetic acid are plotted against the values of  $RT \ln \epsilon_{st}$  for absorption maxima of intramolecular oligomeric quinhydrone in these solvents: X, 1,3-bis compound from I at 350–370  $m\mu$ ;  $\square$ , 1,5-bis compound from II at 330  $m\mu$ ; and O, 1,3,5-tris compound from III at 330  $m\mu$ ; and  $\bullet$ , at 360–370  $m\mu$ .

It was shown, in support of an hypothesis advanced by Sinanoğlu and Abdalnur<sup>23</sup> in relation to denaturation of DNA, that differences in quinhydrone association constants in various solvents may arise primarily from differences between the free energy (surface energy) required to create a solvent cavity around the complex relative to two cavities around the dissociated components. A nearly linear dependence between the complex formation reaction standard free energy ( $\Delta F^\circ$ ) and corresponding solvent surface tensions ( $\sigma$ ) was found as evidence for this relationship. The slope of the resulting straight line was taken as an empirical measure of  $\Delta A$ , the resultant loss in solvent-cage surface area upon complex formation. That is,  $\Delta F^\circ \propto \sigma \Delta A$ .

The relatively simple analysis of solvent effects on quinhydrone is also applicable to complexes arising from the partially oxidized oligomeric hydroquinones. In these cases, however, absolute values for the association constants and standard free energies are not available. As explained above, the energy function,  $-RT \ln \epsilon_{st}$ , was evaluated for each complex and was used in the calculations. In line with this reasoning, the functions contained in Tables I, II, and III were plotted against corresponding values of solvent surface tension. Resulting curves are shown in Figure 6.

(23) O. Sinanoğlu and S. Abdalnur, paper presented at the Symposium on Molecular Mechanisms in Photobiology, Wakulla Springs, Fla., Feb. 1964.

As in the case of simple quinhydrone, the intensities of the complex absorptions decrease with decreasing surface tension of the solvent. Thus, the calculated values of  $\Delta A$  are negative and correspond to a decrease in solvent surface areas. Slopes of the linear regions of the curves in Figure 6 have been determined and from these quantities, values of  $\Delta A$  per molecule were calculated. Table IV summarizes the results.

TABLE IV  
CALCULATED VALUES OF  $\Delta A$  FOR INTRAMOLECULAR COMPLEXING OF PARTIALLY OXIDIZED OLIGOMERIC HYDROQUINONE IN AQUEOUS ACETIC ACID AT 28°

Compound	Wave length, $m\mu$	$\Delta A$ , $\text{\AA}^2$
1,3-Bis(2,5-dihydroxyphenyl)propane	360–370	-13.4
1,5-Bis(2,5-dihydroxyphenyl)pentane	330	-52.3
1,3,5-Tris(2,5-dihydroxyphenyl)pentane	370	-14.9
1,3,5-Tris(2,5-dihydroxyphenyl)pentane	330 (highly aqueous)	-25.8
1,3,5-Tris(2,5-dihydroxyphenyl)pentane	330 (highly organic)	-14.7

The data in Table IV show that approximately 13–15  $\text{\AA}^2$  of solvent surface area/molecule is lost when hydroquinonyl and quinonyl groups which are linked by a propylene bridge interact to form a quinhydrone complex.  $\Delta A$  becomes about  $-52 \text{\AA}^2$  when a pentylene bridge connects the complex components. The intermediate value for the 330- $m\mu$  band of 1,3,5-tris(2,5-dihydroxyphenyl)pentane in highly aqueous solvents probably reflects overlapping of the two bands in the complex spectrum of this compound. It is conceivable that the difference in  $\Delta A$  for 1,3 and 1,5 interaction arises from solvation of the intervening hydrocarbon chain. Alternatively, the difference may result from a difference in the geometry of the complexed molecules. In the least, however, it provides an empirical explanation for the enhanced solvent sensitivity of the complex spectrum of 1,5-bis oligomers relative to that of 1,3-bis compounds. We believe that these conclusions and speculations bear directly on the interpretation of the behavior of oxidation-reduction polymers.<sup>3,4</sup>

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