(40 mg) was obtained. Further elution with 5% ether–Skellysolve B yielded VI (100 mg). Product V was not recovered. VI had λ_{max}^{neat} 3.30–3.49 (s), 6.06 (s), and 6.22 μ (s); λ_{max}^{EtOH} 238 mμ. VII had $\lambda_{max}^{CCl_4}$ 3.39–3.52 (s), 5.86 (s), 6.03 (m), and 6.13 μ (m); λ_{max}^{EtOH} 253 (sh), 314 mμ.

Heating the dienone mixture (V, VI, and VII) with 5% hydrochloric acid at 60° for 30 min gave the following approximate product composition: 85% V and 15% VII. V had λ_{max}^{neat} 3.38–3.52 (m), 6.04 (s), 6.12 (s), and 6.30 μ (s); λ_{max}^{EtOH} 323 mμ.

6-Oxo-1,2,3,6-tetrahydroazulene (VIII).—A stream of dry carbon dioxide was bubbled through a stirred reaction mixture consisting of 75 ml of decalin, 0.262 g of dienone mixture (V, VI, and VII), 0.5 g of 10% palladium on charcoal, and 0.2 g of *p*-benzoquinone at 150 ± 5° for 18 hr. After cooling to room temperature, the palladium on charcoal was filtered off under vacuum and washed with ether. The ether was evaporated at reduced pressure, and the decalin was removed by chromatography on silica gel, eluting with Skellysolve B. Elution with 10% ether-benzene gave unreacted dienone (predominantly V) and unreacted *p*-benzoquinone. Further elution with chloroform gave VIII followed by hydroquinone. Extraction of VIII with boiling hexane and evaporation of the hexane at reduced pressure gave 0.046 g (17%) of a light yellow solid, mp 97–105°. Sublimation followed by two low-temperature recrystallizations from ether gave an analytical sample: mp 107–108° (white needles); λ_{max}^{EtOH} 231 mμ (log ε 4.29), 335 (4.12), and 336 (sh) (4.00); $\lambda_{max}^{CHCl_3}$ 3.42 (m), 6.16 (s), and 6.40 μ (s).

Anal. Calcd for $C_{10}H_{10}O$: C, 82.16; H, 6.90; mol wt, 146. Found: C, 81.84; H, 6.86; mol wt, 146 (mass spectrum).

Acknowledgment.—The authors are indebted to Dr. T. H. Kinstle for assistance with the mass spectrum and to Dr. G. F. Morris for assistance with the nmr calculations.

The Effect of Solvent on the Electronic Transitions of Benzophenone and Its *o*- and *p*-Hydroxy Derivatives

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The ultraviolet absorption spectra of benzophenone, *o*- and *p*-hydroxybenzophenones, and 2,4-dihydroxybenzophenone in the 215–400-mμ range were determined in 14 solvents of varying polarity. Both the $n \rightarrow \pi^*$ and $\pi \rightarrow \pi^*$ absorption maxima of benzophenone were correlated well by Kosower's solvent polarity parameter *Z*. The $\pi \rightarrow \pi^*$ absorptions of the hydroxy derivatives were separated into two groups, those in nonhydroxylic solvents and those in hydroxylic solvents, by the *Z* factor. Possible interpretations of these data are presented based on hydrogen bonding and electrostatic interactions.

Solvents often have a considerable effect on the ultraviolet absorption spectra of organic compounds.[1] These solvent effects are useful in determining the type of electronic transitions which are observed, *i.e.*, the blue shift of $n \rightarrow \pi^*$ transitions and the red shift of $\pi \rightarrow \pi^*$ transitions on changing to a more polar solvent from a less polar one.[1,2] Kosower[3] has developed a solvent polarity parameter, *Z*, which has been used successfully in correlating a number of solvent effects on $n \rightarrow \pi^*$ and $\pi \rightarrow \pi^*$ transitions.[4] In this paper are presented data on the solvent effects on the energy[5] of the $n \rightarrow \pi^*$ and $\pi \rightarrow \pi^*$ transitions of benzophenone and the various $\pi \rightarrow \pi^*$ transitions of *o*- and *p*-hydroxybenzophenone and 2,4-dihydroxybenzophenone.

Experimental Section

Materials.—The compounds used in this study were recrystallized to constant melting points (benzophenone, 48–48.5°; *p*-hydroxybenzophenone, 132–132.5°; *o*-hydroxybenzophenone, 38.5–39°; 2,4-dihydroxybenzophenone, 143.5–144°) and vacuum dried. No impurities were detected in these samples by infrared and mass spectral analyses. The solvents were either spectroquality reagent grade or center-cut redistilled materials. Reliable absorption maxima in dimethylformamide (DMF) and dimethyl sulfoxide (DMSO) could not be determined below *ca.* 270 mμ due to absorption by the solvent. All other solvents were usable down to *ca.* 215 mμ.

Spectra.—The ultraviolet spectra were obtained with Cary recording spectrophotometers, Models 11MS and 14, at 21 ± 2°. Maxima were reproducible to better than ±0.5 mμ. The true absorption maxima may be in error by as much as 5 or 10 mμ due to overlapping bands from different transitions and due to the fine structure (shoulders) of the bands themselves. These errors may account for some of the scatter observed in Figures 5–11. A twofold change in concentration or slight acidification of the alcoholic solvents with concentrated aqueous hydrochloric acid (2 drops/100 ml) failed to change the maxima. The wavelengths were calibrated with the mercury arc lines from 253.7 to 404.7 mμ.

The infrared spectra were obtained with a Beckman IR9 in 0.1-mm cells at room temperature. All $\nu_{C=O}$ are accurate to ±3 cm^{-1}.

Results and Discussion

We have applied the *Z* parameter in our correlation study, and have determined approximate *Z* values for cyclohexane and diethyl ether based on the $n \rightarrow \pi^*$ and $\pi \rightarrow \pi^*$ transitions of benzophenone which were

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[1] (a) H. H. Jaffé and M. Orchin, "Theory and Applications of Ultraviolet Spectroscopy," John Wiley and Sons, Inc., New York, N. Y., 1962, pp 186, 206; (b) J. N. Murrell, "The Theory of the Electronic Spectra of Organic Molecules," Methuen and Co., Ltd., London, 1963, pp 163, 272; (c) A. E. Gillam and E. S. Stern, "An Introduction to Electronic Absorption Spectroscopy in Organic Chemistry," Edward Arnold Ltd., London, 1957, p 301.

[2] (a) N. S. Bayliss and E. G. McRae, *J. Phys. Chem.*, **58**, 1002, 1006 (1954); (b) M. Kasha, *Discussions Faraday Soc.*, **9**, 14 (1950); (c) K. B. Wiberg, "Physical Organic Chemistry," John Wiley and Sons, Inc., New York, N. Y., 1964, p 187; (d) G. C. Pimentel and A. L. McClellan, "The Hydrogen Bond," W. H. Freeman and Co., San Francisco, Calif., 1960, p 158; (e) C. Reichardt, *Angew. Chem. Intern. Ed. Engl.*, **4**, 29 (1965); (f) P. A. Leermakers and H. T. Thomas, *J. Am. Chem. Soc.*, **87**, 1620 (1965).

[3] (a) E. M. Kosower, *ibid.*, **80**, 3253 (1958); (b) J. E. Leffler and E. Grunwald, "Rates and Equilibria of Organic Reactions," John Wiley and Sons, Inc., New York, N. Y., 1963, p 309.

[4] (a) E. M. Kosower, *J. Am. Chem. Soc.*, **80**, 3261 (1958); (b) W. D. Closson and P. Haug, *ibid.*, **86**, 2384 (1964); (c) H. W. Davies and M. Schwarz, *J. Org. Chem.*, **30**, 1242 (1965); (d) ref 2e.

[5] The absorption maximum was used to calculate the energy of the excited state since the wavelength of the O—O band is unknown.[2a,6] This energy in kcal/mole was calculated from the wavelength of the absorption maximum by the usual procedure; *cf.* ref 1a, p 7.

[6] See (a) W. M. Schubert, J. Robins, and J. L. Haun, *J. Am. Chem. Soc.*, **79**, 910 (1957); (b) H. H. Jaffé and H. L. Jones, *J. Org. Chem.*, **30**, 964 (1965).

TABLE I

ULTRAVIOLET ABSORPTION MAXIMA (Mμ) OF BENZOPHENONE AND DERIVATIVES

		Benzophenone		p-Hydroxy-benzophenone	o-Hydroxy-benzophenone		2,4-Dihydroxybenzophenone		
Solvent	Z[a]	n → π^*[b]	$\pi \to \pi^*$[c]	ct[d]	ct[e]	$\pi \to \pi^*$[f]	o-ct[g]	p-ct[h]	$\pi \to \pi^*$[i]
Hexane	60.1[j]	346.5 f[k]	247.5	268.5 f	337.5	260	323.5	280	241
Cyclohexane	62.5[l]	346.5 f	248.5	270 f	338	260.5	324	281	241.5
Et_2O	65.2[l]	344 f	249	285 f	336.5	261	324	287	242.5
$(CH_2Cl)_2$[m]		340.5	252.5	282 f	338	263.5	324.5	284	242
DMF[n]	68.5	341		292.5	332.5		325	291.5	
DMSO[o]	71.1	340.5		295.5	321		325	292.5	
MeCN	71.3	338.5	250.5	284.5	335.5	262	323	286	241.5
n-BuOH	77.7	333.5	252.5	296	337.5	262	323.5	292	244
n-PrOH	78.3	333.5	252.5	296	337	261.5	327.5	291.5	244
EtOH	79.6	332.5	252	294.5	336.5	261	324.5	290.5	243.5
MeOH	83.6	331.5	252.5	293.5	335.5	260.5	324.5	290	243
MeOH–H_2O[p]		~322 sh[q]	257	294.5	334.5	261.5	325	291	242.5
H_2O	94.6	~322 sh	257.5	293.5	331.5	261.5	324.5	289.5	241
HCl–H_2O[r]		~321 sh	257.5	294	332	262	~320 sh	289.5	241

[a] Z values are those reported by Kosower[3a] unless otherwise noted. [b] ε 111–151. [c] ε 16,600–21,800. [d] Charge transfer; ε 15,300–18,800. [e] ε 2700–5600. [f] ε 13,500–16,100. [g] *ortho* charge transfer; ε 7700–12,200. [h] *para* charge transfer; ε 13,000–16,100. [i] ε 9300–12,200. [j] Value of 60.1 for isooctane used for hexane.[3a] The same solvent polarity factor (χ_R, based on a different system) was found for isooctane and n-hexane; *cf.* L. G. S. Brooker, A. C. Craig, D. W. Heseltine, P. W. Jenkins, and L. L. Lincoln, *J. Am. Chem. Soc.*, **87**, 2443 (1965). The same relative order of polarity for n-hexane, cyclohexane, and diethyl ether was found by these authors as found here. [k] Fine structure is apparent. [l] Z taken as the average of those values calculated for n → π^* and $\pi \to \pi^*$ energies of benzophenone (see Figures 5 and 6) by fitting remaining solvents for which Z values are known by least-squares method. [m] Z values calculated from n → π^* and $\pi \to \pi^*$ energies of benzophenone gave widely different values, 68.9 and 79.3, respectively. Kosower's[4a] data on mesityl oxide give values of 65.0 and 74.3. [n] N,N-Dimethylformamide. [o] Dimethyl sulfoxide. [p] 50:50 by volume. [q] Shoulder. [r] 0.100 N HCl.

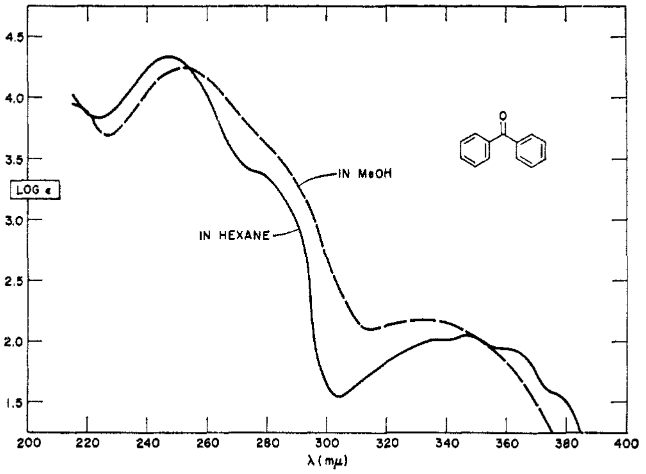


Figure 1.—Electronic absorption spectra of benzophenone.

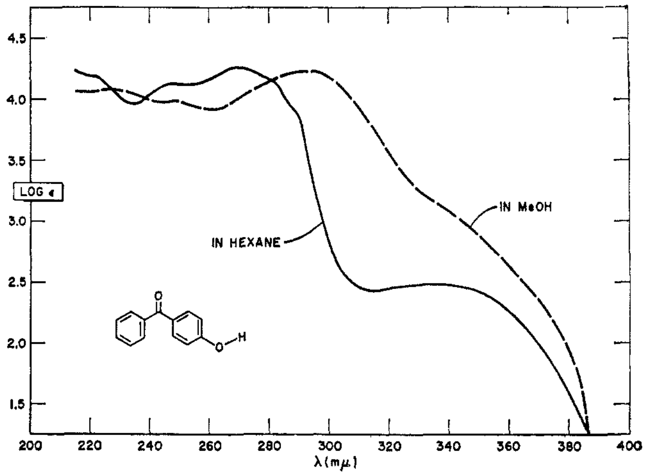


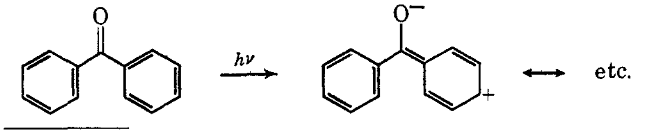
Figure 2.—Electronic absorption spectra of p-hydroxybenzophenone.

suitable for our purposes. The data are presented in Table I, and typical curves are given in Figures 1–4.

The n → π^* (Figure 5) and $\pi \to \pi^*$ (Figure 6) transitions of benzophenone are correlated reasonably well by the Z parameter. The origins of these shifts (electrostatic and hydrogen bonding) have been discussed elsewhere,[7] and will not be developed further here.

The only electronic transitions of the hydroxybenzophenones which we have attempted to correlate with solvent polarity were those whose absorption bands were sufficiently well resolved from other more intense absorption bands to allow a reasonable analysis. The n → π^* band of the p-hydroxy derivative is separated sufficiently from the more intense bands in hexane to show a maximum at 334 mμ (Figure 2). However, in the more polar solvents this transition is only a shoulder. The n → π^* bands of the o-hydroxy and 2,4-dihydroxy derivatives are not discernible. No attempt was made to correlate the $\pi \to \pi^*$ band (defined below) of the p-hydroxy compound (250 mμ in hexane, Figure 2) or the *ortho* charge-transfer band of the 2,4-dihydroxy derivative (323.5 mμ in hexane, Figure 4) due to the proximity of other bands.

The $\pi \to \pi^*$ bands of the hydroxy derivatives can be considered as arising from two different chromophoric groups, one involving the phenylcarbonyl group, and the other the hydroxyphenylcarbonyl group, HOC_6H_4CO.[8] The transitions which do not involve the hydroxy group are termed $\pi \to \pi^*$ transi-



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(7) (a) H. McConnell, *J. Chem. Phys.*, **20**, 700 (1952); (b) G. J. Brealey and M. Kasha, *J. Am. Chem. Soc.*, **77**, 4462 (1955); (c) R. S. Becker, *J. Mol. Spectry.*, **3**, 1 (1959); (d) M. Ito, K. Inuzuka, and S. Imanishi, *J. Chem. Phys.*, **31**, 1694 (1959); *J. Am. Chem. Soc.*, **82**, 1317 (1960).

(8) E. J. Moriconi, W. F. O'Connor, and W. F. Forbes, *ibid.*, **82**, 5454 (1960).

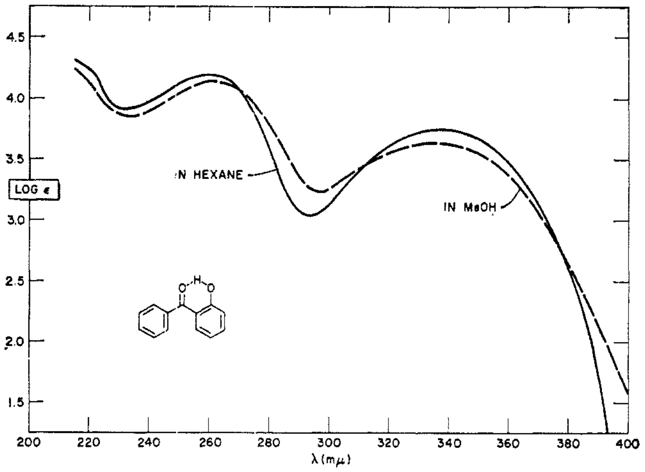


Figure 3.—Electronic absorption spectra of *o*-hydroxybenzophenone.

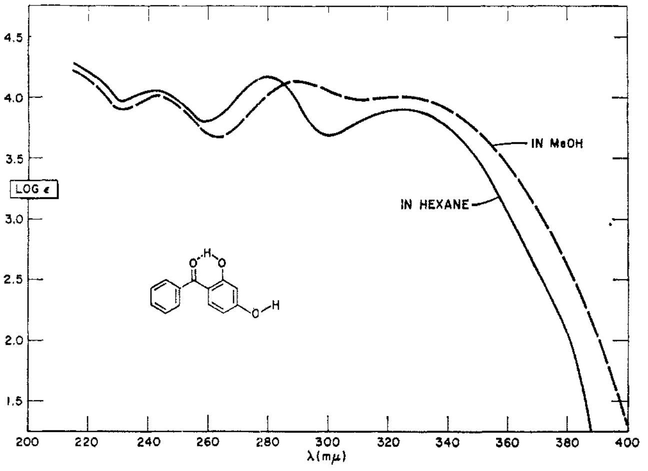


Figure 4.—Electronic absorption spectra of 2,4-dihydroxybenzophenone.

tions in this paper by analogy to the intense band in benzophenone itself. Transitions involving the hydroxyphenylcarbonyl group are designated intramolecular charge transfer (ct) transitions in this paper following the terminology of Porter and Suppan.[9–11] Although this distinction may be somewhat arbitrary since all of the π → π* transitions discussed here involve transfer of electron density, it does serve to emphasize the greater degree of charge separation in the excited states involving the hydroxy groups.

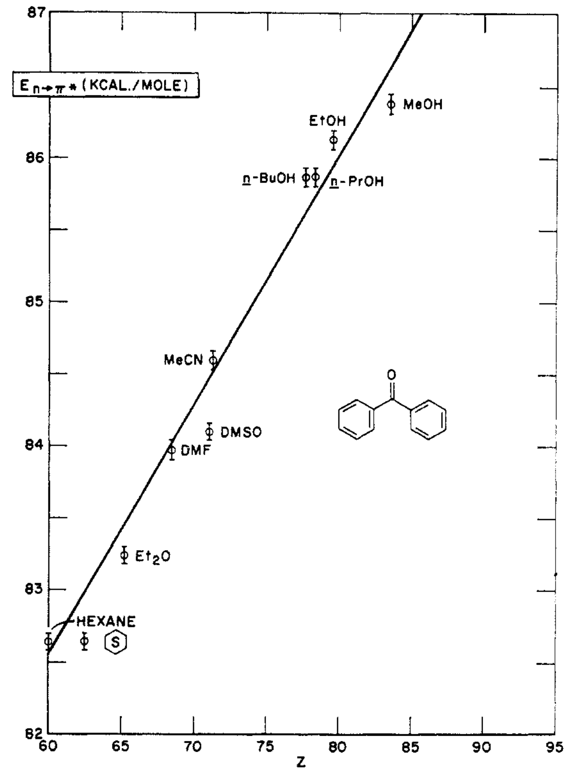


Figure 5.—Energy of n → π* transition of benzophenone as a function of solvent polarity parameter, *Z*.

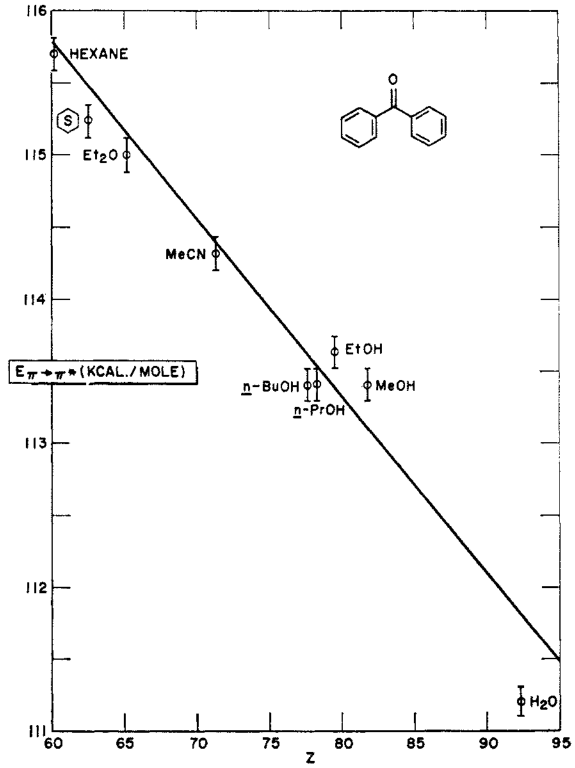
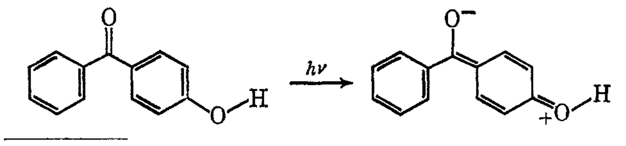


Figure 6.—Energy of π → π* transition of benzophenone as a function of solvent polarity parameter, *Z*.

The intense absorptions of *p*-hydroxybenzophenone and 2,4-dihydroxybenzophenone in the 260–300-mμ region have been attributed to the intramolecular ct transition involving the *p*-hydroxy group.[9,10] In the nonhydroxylic solvents these compounds exhibited appreciable red shifts (Figures 7 and 8) which were expected on the basis of a greater lowering of the energy of the excited state with respect to the ground state by a more polar solvent. The transition energy in acetonitrile appears to be anomalous in both compounds.[13] In contrast to the nonhydroxylic solvents,



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[9] (a) G. Porter and P. Suppan, *Proc. Chem. Soc.*, 191 (1964); *Trans. Faraday Soc.*, **61**, 1664 (1965); (b) N. J. Turro, "Molecular Photochemistry," W. A. Benjamin, Inc., New York, N. Y., 1965, p 150.

[10] See also (a) J. VanAllan and J. F. Tinker, *J. Org. Chem.*, **19**, 1243 (1954); (b) V. Baliah and P. Subbarayan, *ibid.*, **25**, 1833 (1960).

[11] Scott[12] refers to this type of transition as an electron-transfer process.

[12] A. I. Scott, "Interpretation of the Ultraviolet Spectra of Natural Products," The MacMillan Co., Ltd., New York, N. Y., 1964, p 103.

[13] A possible explanation for the higher energy in acetonitrile compared with DMF and DMSO is that acetonitrile forms hydrogen bonds with the phenolic hydroxyl group less effectively than either DMF or DMSO. The stronger this hydrogen bond becomes the lower the transition energy should be.

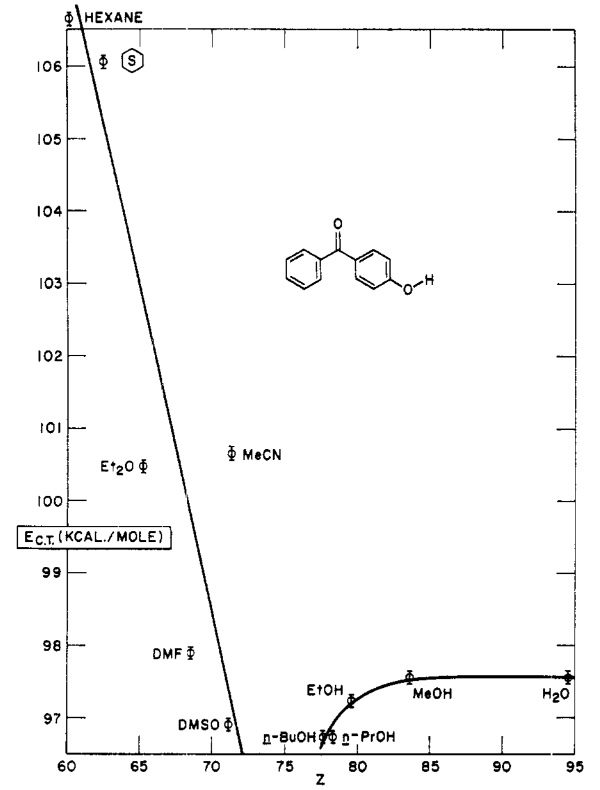


Figure 7.—Energy of charge-transfer transition of *p*-hydroxybenzophenone as a function of solvent polarity parameter, *Z*.

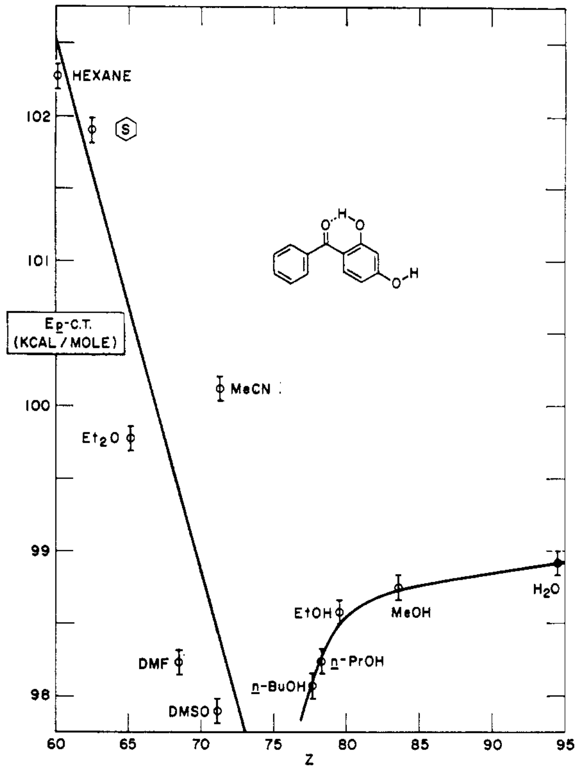
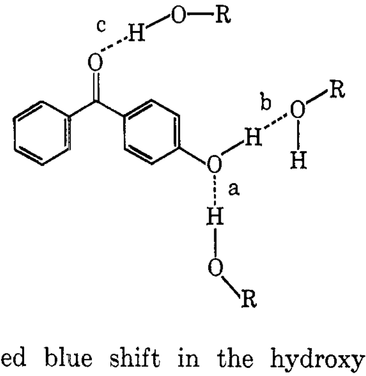


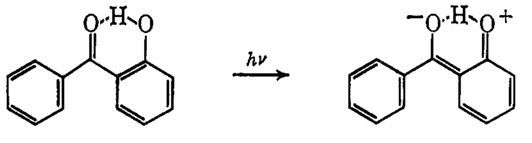
Figure 8.—Energy of *para* charge-transfer transition of 2,4-dihydroxybenzophenone as a function of solvent polarity parameter, *Z*.

these *p*-hydroxy compounds showed relatively little change in the hydroxylic solvents although a definite blue shift was observed in both cases on increasing the solvent polarity from butanol to water. A possible explanation for this reversal in trend is that other effects are superimposed on the solvent polarity effect. Various types of hydrogen bonding shown (a–c) probably have an effect on this electronic transition.



The observed blue shift in the hydroxylic solvents could be accounted for by hydrogen bonding from the hydroxylic solvent to the hydroxyl oxygen atom of the hydroxy ketone (a). The more strongly the solvent is hydrogen bonded to this oxygen atom, the more the ground state energy will be lowered with respect to the excited state; in the excited state the positive character of the phenolic oxygen atom will lessen the importance of the hydrogen bond.[14] Methanol appears to hydrogen bond with heteroatoms more strongly than does ethanol, which in turn hydrogen bonds more strongly than propanol and butanol.[16] The phenolic hydrogen bond (b) would also produce the observed shift if the order of increasing hydrogen bond strength were *n*-BuOH > *n*-PrOH > EtOH > MeOH > HOH. Hydrogen bonding at the carbonyl group c would be expected to produce a red shift since the carbonyl oxygen atom is more negative in the excited state than the ground state. This latter type of hydrogen bonding is probably one of the reasons for the lower transition energy in the hydroxylic solvents as compared with the nonpolar solvents such as hexane or cyclohexane.

The low-energy transitions (320–340 mμ) of *o*-hydroxybenzophenone and 2,4-dihydroxybenzophenone have been attributed to an intramolecular process involving the *o*-hydroxyl group.[10a,17] The higher



energy transitions (260–265 and 240–245 mμ, respectively) have been described as benzenoid bands.[10a,18] The change in energy of the transition of these two processes (except the *ortho* ct transition of 2,4-dihydroxybenzophenone, Table I) as a function of *Z* is shown in Figures 9–11. The most striking feature of these spectra is the relative insensitivity of the transi-

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[14] This effect is similar to the n → π* blue shift with carbonyl compounds in hydroxylic solvents.[7b] Similar reasoning has been applied to the dipolar excited state of aniline.[2c,15]

[15] W. M. Schubert and J. M. Craven, *J. Am. Chem. Soc.*, **82**, 1357 (1960).

[16] (a) A. Balasubramanian and C. N. R. Rao, *Spectrochim. Acta*, **18**, 1337 (1963); (b) ref 1a, p 187; (c) ref 2c, p 188.

[17] Reference 12, p 102.

[18] The corresponding band in *o*-hydroxyacetophenone has also been described as an electron-transfer band. It appears that these absorptions are best described as π → π* transitions similar to that in benzophenone.

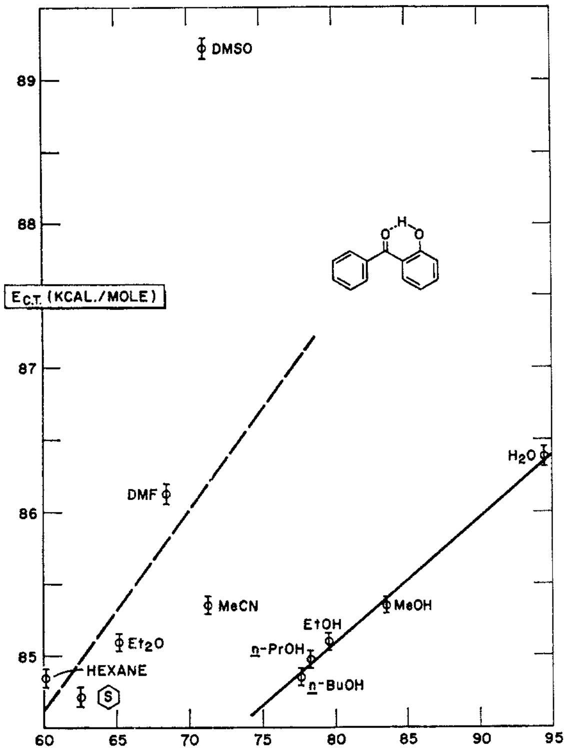

Figure 9.—Energy of charge-transfer transition of *o*-hydroxybenzophenone as a function of solvent polarity parameter, *Z*.

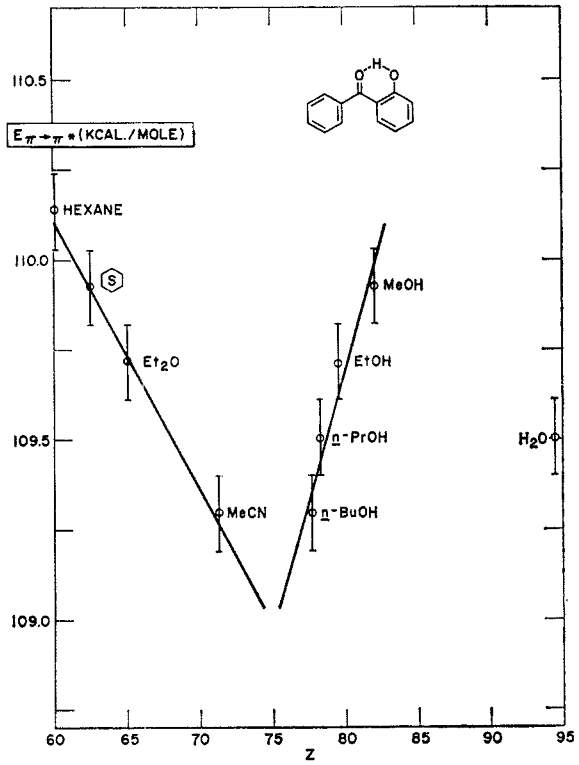

Figure 10.—Energy of $\pi \rightarrow \pi^*$ transition of *o*-hydroxybenzophenone as a function of solvent polarity parameter, *Z*.

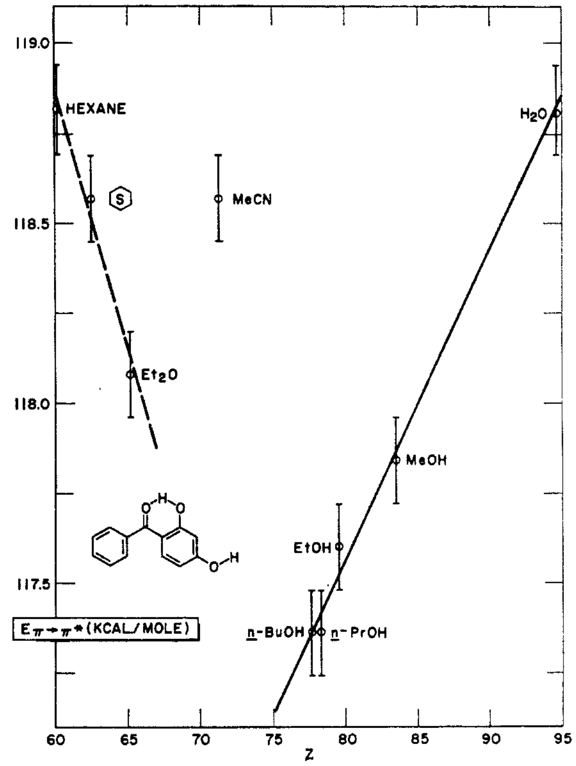

Figure 11.—Energy of $\pi \rightarrow \pi^*$ transition of 2,4-dihydroxybenzophenone as a function of solvent polarity parameter, *Z*.

tion energies to the solvent,[19] except for DMSO (Figure 9). The shifts observed in the hydroxylic solvents for the ct transition of *o*-hydroxybenzophenone are qualitatively the same as those shown for the *p*-hydroxy derivative. The same explanation could account for the shifts in this case [hydrogen-bonding type (a)]. The nonhydroxylic solvents show erratic shifts, but a general blue shift is apparent with increasing polarity (Figure 9). This result is rather unexpected since one would predict the nonhydroxylic solvents to show a red shift similar to that observed with *p*-hydroxybenzophenone. A possible explanation for this result is that the more polar solvents, *i.e.*, DMSO and possibly DMF, can compete with the carbonyl oxygen for the hydrogen bond with the hydroxyl proton. Since the carbonyl oxygen is more negative in the excited state than the ground state, any factor lessening the amount of intramolecular hydrogen bonding will tend to increase the energy of the excited state more than the ground state. This would have the over-all effect of a blue shift.[23] Evidence in support of this proposal was obtained from infrared absorption data in DMSO and carbon tetrachloride solutions (Table II). The 1659-cm^{-1} absorption of the *o*-hydroxy derivative in DMSO is prob-

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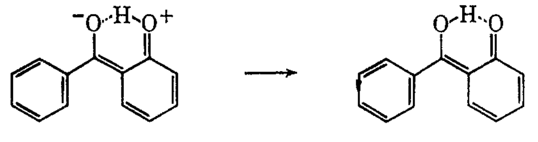
[19] Dearden and Forbes[20] and Morton and Stubbs[21] have noted the solvent insensitivity of the transition energies of *o*-hydroxybenzaldehyde and *o*-hydroxyacetophenone. *o*-Hydroxybenzophenone has been shown to be intramolecularly hydrogen bonded.[22] Infrared measurements on 2,4-dihydroxybenzophenone in dilute carbon tetrachloride solution show both free and intramolecularly hydrogen-bonded hydroxyl groups.

[20] J. C. Dearden and W. F. Forbes, *Can. J. Chem.*, **38**, 1837 (1960).

[21] R. A. Morton and A. L. Stubbs, *J. Chem. Soc.*, **143**, 1347 (1940).

[22] (a) N. M. Cullinane, R. A. Woolhouse, and V. V. Bailey-Wood, *Rec. Trav. Chim.*, **80**, 116 (1961); (b) J. R. Merrill, *J. Phys. Chem.* **65**, 2023 (1961).

[23] It has been proposed that the photochemistry of *o*-hydroxybenzophenone can be explained by the conversion of the excited ct state to the enolic form.[24]



[24] (a) J. N. Pitts, Jr., H. W. Johnson, Jr., and T. Kuwana, *J. Phys. Chem.*, **66**, 2456 (1962); (b) C. Walling in "Molecular Rearrangements," Vol. 1, Part 1, P. de Mayo, Ed., Interscience Publishers, Inc., New York, N. Y., 1963, p 455; (c) A. Beckett and G. Porter, *Trans. Faraday Soc.*, **59**, 2051 (1963).

TABLE II
INFRARED ABSORPTION MAXIMA OF
HYDROXYBENZOPHENONES (CM^{-1})

Compound	$\nu_{C=O}$ (CCl$_4$)	$\nu_{C=O}$ (DMSO)
Benzophenone	1664[a]	1657[a b]
p-Hydroxybenzophenone	1661[c]	1645[d]
o-Hydroxybenzophenone	1633[a]	1659[d]
		1626[e]
2,4-Dihydroxybenzophenone	1632[c]	1624[d]
		~1620–1600[e]

[a] Concentration 2% (w/v). [b] The difference in $\nu_{C=O}$ in CCl$_4$ and DMSO is comparable to those found with other carbonyl compounds; *cf.* C. D. Ritchie, B. A. Bierl, and R. J. Honour, *J. Am. Chem. Soc.*, **84,** 4687 (1962). [c] Concentration 0.1%. [d] Concentration 5%. [e] Weaker of two bands observed.

ably due to an intermolecularly hydrogen-bonded species involving the phenol and a solvent molecule.[25] The 2,4-dihydroxy derivative does not show a nonhydrogen-bonded carbonyl absorption. This observation is in agreement with the finding that the *ortho* ct transition of this compound in DMSO is not shifted to higher energy (Table I) as is the case for the *o*-hydroxy compound. The reason the 2,4-dihydroxy compound does not form an intermolecular hydrogen bond is probably due to the electron-donating effect of the *p*-hydroxy group. This electron donation would increase the electron density on the carbonyl oxygen atom compared with the *o*-hydroxy compound and therefore strengthen the intramolecular hydrogen bond.[27]

In the nonhydroxylic solvents the small red shifts expected for the $\pi \rightarrow \pi^*$ transitions of *o*-hydroxybenzophenone and the 2,4-dihydroxy derivative are observed. The hydroxylic solvents produce the opposite effect. Some other subtle factors must be in effect in this case.[28] Perhaps the phenolic hydroxyl groups are also involved more directly in these $\pi \rightarrow \pi^*$ transitions than is apparent from the simplified theory presented in this paper.

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[25] Other cases of effective hydrogen bonding between phenols and DMSO have recently been reported.[26]

[26] (a) G. J. Karabatsos and F. M. Vane, *J. Am. Chem. Soc.*, **85**, 3886 (1963); (b) R. J. Ouellette, *Can. J. Chem.*, **43**, 707 (1965).

[27] See Z. Yoshida and M. Haruta, *Tetrahedron Letters*, 3745 (1965). The author wishes to thank a referee for bringing this reference to his attention.

[28] Blue shifts are known for $\pi \rightarrow \pi^*$ transitions.[2a]

Dimeric Dihydroresorcinol.
6-(3-Ketocyclohexenyl)-5-ketohexanoic Acid[1]

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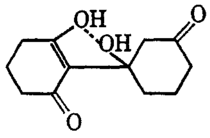
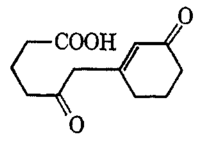
Evidence which requires the reformulation of the dimer of 1,3-cyclohexanedione as 6-(3-ketocyclohexenyl)-5-ketohexanoic acid includes λ_{max}^{EtOH} 238 mμ (log ϵ 4.14), indicative of a conjugated enone system, a solution in aqueous bicarbonate without change in absorption spectrum, a formation of the enolate (pK_a = 10.8) of the enedione system with $\lambda_{max}^{2N\,NaOH}$ 397 mμ (*ca.* 4.7), and the formation of a *p*-bromophenacyl ester. Dehydration of the dimer gives 2-(3-ketocyclohexenyl)cyclohexane-1,3-dione, predominately in the enol form, in which the two chromophoric systems are independent of one another due to the noncoplanarity of the ring systems. The difference in the acidity of the dehydrated dimer and the hydrogenated dehydrated dimer is an approximate measure of the difference in acid-strengthening effect of an sp^2 carbon as compared to an sp^3 carbon and amounts to 3.9 pK units.

We prepared a sample of Stetter's dimeric dihydroresorcinol[2] in the hope that it could be caused to condense further to a bridged polycyclic system in the manner that may account for the products arising from the acid hydrolysis of 2,2′,4,4′,6,6′-hexamethyl-4,4′-bi-4H-pyran.[3] In the course of working with this substance we were led to inquire into the accuracy of the original structural assignment. Stetter's formulation of the dimerization of cyclohexane-1,3-dione and the subsequent structure proof by dehydration, catalytic reduction, and retro-Claisen—Wolff–Kishner reduction to the known 6-cyclohexylhexanoic acid proceeded as in Scheme I.

Subsequently, Eskola[4] prepared the same dimer under different conditions and reported its ultraviolet spectrum to exhibit a maximum at 239 mμ in ethanol. While **2** might conceivably give an ultraviolet absorption if it existed in an enol form **6**, and the stability of the enolic form of the dimer due to internal hydrogen bonding might explain the unusually high conversion of a ketone to its aldol condensation product, we considered that the structure **7** might better accommodate the reported preparation in high yield and properties of the dimer. This structure would arise from **2** by dehydration *via* **3** and retro-Claisen cleavage of the cyclohexanedione ring.



6



7

More definite evidence for **7** as opposed to **6** was obtained as follows. A *p*-bromophenacyl ester was prepared which analyzed correctly for a monocarboxylic

[1] Presented at the Midwest Regional American Chemical Society Meeting, Nov 4, 1965.

[2] H. Stetter, E. Siehnhold, E. Klauke, and M. Coenen, *Chem. Ber.*, **86**, 1308 (1953).

[3] K. Conrow and P. C. Radlick, *J. Org. Chem.*, **26**, 2260 (1961).

[4] S. Eskola, A. Auvinen, A. Hirvimies, T. Rinne, and R. Waris, *Suomen Kemi*, **27B**, 88 (1954).