

arylazotriphenylmethanes,<sup>9</sup> and, under certain circumstances, diacyl peroxides.<sup>10</sup>

(9) D. H. Hey, *J. Chem. Soc.*, 1966 (1934).

(10) H. Gelissen and P. H. Hermans, *Ber.*, **58**, 285 (1925).

DEPARTMENT OF CHEMISTRY  
BRANDEIS UNIVERSITY  
WALTHAM, MASSACHUSETTS 02154

SAUL G. COHEN  
JESSE NICHOLSON

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### Solvent Effects on the C<sup>13</sup> Chemical Shift of the Substituted Carbon Atom of Phenol<sup>1</sup>

Sir:

A recent investigation of the effect of solvents on the C<sup>13</sup> chemical shift of the carbonyl group of acetone<sup>2</sup> and other carbonyl-containing compounds<sup>3</sup> indicates that the shift is quite sensitive to an environment consisting of proton donors, relatively insensitive to environment if proton donors are absent, and may provide a useful tool for the study of acidic and hydrogen-bonding properties of solvents. In the hope of developing an analogous means of studying the basic properties of solvents, we have undertaken a solvent-shift study of the C<sup>13</sup> magnetic resonance spectra of phenol.

The C<sup>13</sup> spectra of phenol were obtained in natural abundance in 1:4 mole fraction solutions of phenol in several reagent grade or Eastman White Label solvents. A measuring frequency of 15.1 Mc./sec. and the rapid passage dispersion mode technique described previously by Lauterbur<sup>4</sup> were employed. Shifts were measured in a concentric-sphere sample container,<sup>5</sup> to eliminate bulk susceptibility effects, with respect to an external reference of a saturated aqueous NaO<sub>2</sub>C<sup>13</sup>CH<sub>3</sub> solution in the center sphere, using the side-band technique.

The observed C<sup>13</sup> shifts of the substituted carbon atom, and the carbon atoms situated *ortho*, *meta*, and *para* to the substituted carbon atom, are presented in Table I. They may be considered reliable to about ±0.5 p.p.m. In those cases where the assignment of the resonance lines was not straightforward due to weak and/or overlapping signals, reliable data could not be obtained readily and are not presented. Inspection of the table reveals that the shifts of *meta* carbons vary only slightly with solvent, with no obvious trends apparent. The variations of the *ortho* and *para* shifts with solvent are relatively small and do not appear to follow a recognizable pattern, except that in the most basic media they become interchanged with respect to their values in less basic solvents. Probably the most interesting set of shifts in this work are those of the substituted carbon atom and our discussion will be limited primarily to those shifts. They span a total range of 12.7 p.p.m., the largest positive shift occurring in cyclohexane solution and the largest negative shift in a system consisting of phenol, sodium ethoxide, and ethanol in mole proportions of 1:1:4, in which the phenol exists in the form of solvated phenoxide ion.

Table I shows that the resonance line for the substituted carbon atom experiences a definite trend to lower field as the basicity of the solvent increases. In

(1) This investigation was supported by a PHS research grant (GM 11439-01) from the National Institute of General Medical Sciences, Public Health Service.

(2) G. E. Maciel and G. C. Ruben, *J. Am. Chem. Soc.*, **85**, 3903 (1963).

(3) G. E. Maciel and J. J. Natterstad, unpublished results.

(4) P. C. Lauterbur, *J. Am. Chem. Soc.*, **83**, 1838 (1961).

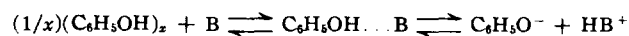
(5) H. Spiesecke and W. G. Schneider, *J. Chem. Phys.*, **35**, 722 (1961).

TABLE I  
C<sup>13</sup> CHEMICAL SHIFTS OF PHENOL IN 1:4 MOLE FRACTION SOLUTIONS IN SEVERAL SOLVENTS (P.P.M. WITH RESPECT TO BENZENE)

Solvent	Carbon-1	<i>ortho</i>	<i>meta</i>	<i>para</i>	Δν, cm. <sup>-1a</sup>
Cyclohexane	-26.9	12.6	-1.8	7.9	
Carbon tetrachloride	-27.0	11.9	-1.5	6.9	0
Benzotrifluoride	-27.1				
Nitromethane	-27.2				
Benzene	-27.9				24
Ethyl acetate	-28.4	13.5	-0.7	9.6	51
Acetonitrile	-28.6	12.9	-1.5	8.8	87
Diethyl ether	-29.1	12.9	-1.3	9.2	96
Dioxane	-28.9	13.1	-1.1	9.4	111
Tetrahydrofuran	-29.0	14.6	0.0	10.1	117 <sup>b</sup>
Acetone	-29.2	12.7	-1.8	8.2	121
Dimethyl sulfoxide	-29.8	13.2	-1.5	8.9	158 <sup>c</sup>
<i>t</i> -Butylamine	-30.1				
Tri- <i>n</i> -butylamine	-30.3	11.3	-0.3	11.3	243 <sup>d</sup>
Diethylamine	-30.6	11.1	-0.4	11.1	268 <sup>d</sup>
Ethanol-sodium ethoxide <sup>e</sup>	-39.6	8.2	-1.9	13.6	

<sup>a</sup> Frequency shift of O-D stretching band of CH<sub>3</sub>OD in these solvents, taken from ref. 7 unless otherwise noted. <sup>b</sup> Reference 8. <sup>c</sup> Reference 9. <sup>d</sup> Reference 10. <sup>e</sup> Sample consisted of phenol, sodium ethoxide, and ethanol in mole ratios of 1:1:4.

the case of highly basic solvents, this trend can be understood most simply in terms of changes in the position of the rapid multiple equilibrium



to favor the proton-transfer product, solvated phenoxide ion, as the strength of the base B increases. However, in moderately basic or weakly basic solvents, the equilibrium concentrations of phenoxide ion would be too small to influence the observed weighted-average chemical shifts significantly. In this case the most realistic interpretation of the trend to lower fields with increasing solvent basicity appears to be the increasing influence of hydrogen bonding of phenol to solvent. Thus, the position of the above equilibrium and its consequent effect on the observed chemical shift depends on the ability of solvent to form a hydrogen-bonded complex with phenol and thus compete with the phenol self-association state which is predominant in inert and weakly basic solvents at the concentrations employed in this study.<sup>6</sup>

For comparison, Table I includes solvent shifts, Δν, of the O-D stretching frequency of CH<sub>3</sub>OD, which Gordy<sup>7</sup> and Tamres and Searles<sup>8-10</sup> have used as indices of the basic strengths of solvents with respect to hydrogen bonding to methanol. Qualitative correlations can also be made with other reported measures of solvent basicities.<sup>11-13</sup> This apparent relationship of solvent shift in weakly and moderately basic solvents to the ability of the solvent to accept a proton in a hydrogen-bonded complex is consistent with the fact

(6) C. M. Huggins, G. C. Pimentel, and J. N. Shoolery, *J. Phys. Chem.*, **60**, 1311 (1956).

(7) G. C. Pimentel and A. L. McClellan, "The Hydrogen Bond," W. H. Freeman and Co., San Francisco, Calif., 1960, p. 91.

(8) S. Searles and M. Tamres, *J. Am. Chem. Soc.*, **73**, 3704 (1951).

(9) M. Tamres and S. Searles, Jr., *ibid.*, **81**, 2100 (1959).

(10) M. Tamres, S. Searles, E. M. Leighly, and D. W. Mohrman, *ibid.*, **76**, 3983 (1954).

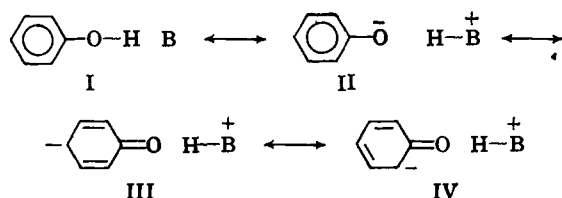
(11) B. B. Howard, C. F. Jumper, and M. T. Emerson, *J. Mol. Spectry.*, **10**, 117 (1963).

(12) B. Lemanceau, C. Lussan, and M. Souty, *J. chim. phys.*, **59**, 148 (1962).

(13) V. W. Strehmeyer and A. Echte, *Z. Elektrochem.*, **61**, 549 (1957).

that the  $C^{13}$  resonance signal of the hydroxyl-substituted carbon atom of salicylaldehyde and related hydroxyaromatic compounds with well-established intramolecular hydrogen bonds<sup>14</sup> occurs about 6 p.p.m. downfield from the value one would predict from simple additivity relations.<sup>15</sup>

At the present stage of our understanding of  $C^{13}$  shifts it is difficult to account with certainty for the postulated effect on the  $C^{13}$  spectrum of hydrogen bonding of phenol to solvent. However, a qualitative explanation can be formulated in terms of the following valence bond description of the complex in which phenol is hydrogen bonded to a base B (which may be either solvent or another phenol molecule in the case of self-association).



One would expect that the increasing basicity of solvent would increase the strength of the hydrogen bond between phenol and solvent, that is, increase the relative importance of canonical structures II, III, and IV. While a consideration of the charge densities implied by this description or by the inductive effects one might anticipate for hydrogen bonding is not immediately useful in interpreting the observed  $C^{13}$ -O shifts, the assumed effect on C-O bond order embodied in the valence-bond description may be illuminating. If one considers the chemical shift of the carbonyl carbon atom in *p*-benzoquinone, -59.4 p.p.m., as an indication of a value to be expected for the hypothetical chemical shift of the substituted carbon atom of structure III or IV, then the decrease of shift with increasing solvent basicity with respect to hydrogen bonding becomes understandable in terms of the increasing contribution of these structures to the valence-bond description of phenol. Of course, when the solvent basicity is increased to the point where appreciable concentrations of solvated phenoxide ion exist, then the hydrogen-bonding effect blends into, or is overshadowed by, the influence of the ion on the equilibrium-average shift which is observed. It is interesting that the changes in chemical shift experienced by the *ortho* and *para* carbons as the hydroxyl proton is removed by proton transfer to a strong base (ethoxide) are in opposite senses. We hope that further experiments with substituted phenols, additional solvents, and higher dilutions will allow a precise distinction to be made between the different interactions considered here and will provide a system with a wider range of shifts more suitable for the quantitative characterization of pertinent solvent properties.

(14) G. E. Maciel and G. B. Savitsky, *J. Phys. Chem.*, **68**, 437 (1964).  
 (15) G. B. Savitsky, *ibid.*, **67**, 2723 (1963).

DEPARTMENT OF CHEMISTRY  
 UNIVERSITY OF CALIFORNIA  
 DAVIS, CALIFORNIA

GARY E. MACIEL  
 RONALD V. JAMES

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### Stable Trianion Radicals

Sir:

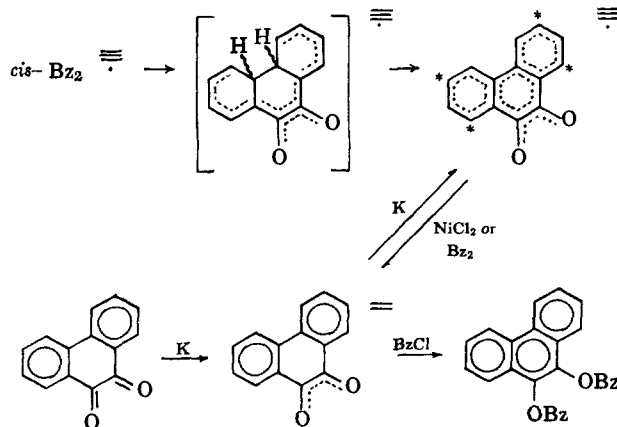
Benzil readily accepts one or two electrons in discrete steps to form an anion radical ( $Bz_2^{\cdot-}$ ) and dianion ( $Bz_2^{2-}$ ), respectively.<sup>1</sup> An HMO calculation<sup>2</sup> gives the eigenvalue  $E = \alpha$  (nonbonding) for the MO being filled in these reactions. More interesting is the fact that even at the dianion stage benzil has a vacant MO

TABLE I  
 HMO ENERGY LEVELS FOR PhCOCOPh

	$Bz_2$	$Bz_2^{\cdot-}$	$Bz_2^{2-}$	$Bz_2^{3-}$
Energy Level	Empty	Empty	Empty	Empty
Occupancy	0	1	2	3
Energy Value				$\alpha - 0.79\beta$
Occupancy	0	1	2	2
Energy Value				$\alpha$
Occupancy	0	1	2	2
Occupancy	0	1	2	2
Occupancy	0	1	2	2

of not too high energy ( $E = \alpha - 0.79\beta$ ) (see Table I). Recent work<sup>3</sup> led us to believe that coulombic repulsions in a trianion radical might not be extreme and accordingly it seemed possible that benzil might accept a third electron to form a novel trianion radical ( $Bz_2^{3\cdot-}$ ).

The red dianion of benzil ( $\lambda_{max}$  470 m $\mu$ ) is indeed converted to a purple trianion radical ( $\lambda_{max}$  555 and 410 m $\mu$ ) in 3 hr. by a 100% excess of potassium in refluxing THF. That the new species is a trianion radical is shown by its acid titer (triacidic base) and e.p.r. signal. A tetraanion could not be induced to form. Addition of 0.5 mole of benzil per mole of trianion radical, to convert the latter to the dianion stage, followed by treatment with excess benzoyl chloride, gave a 70% yield of 9,10-dibenzoyloxyphenanthrene. Anhydrous nickel chloride followed by benzoyl chloride gave the same ester in 60% yield. It appears that most of the trianion radicals have cyclized and lost hydrogen (molecular hydrogen is not evolved, however) forming the phenanthrenequinone trianion radical. The various oxidative treatments convert this to the dianion, which is dibenzoylated by added benzoyl chloride. This formulation is supported by the direct



(1) H. Staudinger and A. Binkert, *Helv. Chim. Acta*, **5**, 702 (1922).  
 (2) Using parameters  $\alpha_0 = \alpha + 2\beta$ ,  $\beta_{CO} = \beta\sqrt{2}$ , and, where applicable,  $\beta_{Ph-C}$  (cross conjugation) = 0.8 $\beta$ .  
 (3) N. L. Bauld, *J. Am. Chem. Soc.*, **86**, 2305 (1964).