

were attempted, but no structure having a significantly lower energy and corresponding to a true minimum of the energy surface was found.

More work needs to be done on the interpretation of these experimental results. To model this system properly we would need to do lattice-dynamical calculations allowing for four (for the monoclinic phase) or eight (for the orthorhombic phase) linear combinations of the molecular motions within a unit cell and for integration over the Brillouin zone. This would present problems since available programs⁴⁴ do not seem adequate for the task.

Registry No. Ph_3PO , 791-28-6.

Supplementary Material Available: Table S1 gives positional and displacement parameters for the two structures at 150 K and Table S2 lists $|F_o|$ and F_c for both crystal modifications at 100 and 150 K (68 pages). Ordering information is given on any current masthead page.

(44) (a) Pawley, G. S. *Phys. Status Solidi* **1967**, 20, 347-360. (b) Filipini, G.; Gramaccioli, C. M.; Simonetta, M.; Suffritti, G. B. *J. Chem. Phys.* **1973**, 59, 5088-5101.

Carbon Acidity. 66. Equilibrium Ion Pair Acidities of Substituted Diphenylmethanes in Cyclohexylamine¹

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Abstract: The $\text{p}K_{\text{CsCHA}}$ values are reported for a number of symmetrically meta- and para-substituted diphenylmethanes. The $\text{p}K_{\text{CsCHA}}$ values for the meta series (Me, 33.8; OMe, 32.7; F, 29.9; CF_3 , 28.9; Ph, 32.3; H, 33.4) give a normal Hammett plot with $\rho = 9.69$. The para series (Me, 35.1; OMe, 37.6; Ph, 30.8; NMe_2 , 38.6; SPh, 28.8; CN, 23.0; SO_2Me , 22.4) do not fit attempted correlations with σ^- , the Yukawa-Tsuno modification, or dual substituent parameter approaches. Electron-donating groups are more anion destabilizing than in other reference systems. "Amphoteric" substituents, those that stabilize both anions and cations (phenyl, thio, etc.), cause special problems in generalized correlations.

Interest in substituent effects and in Hammett-type linear free energy relationship (LFER) continues undiminished as judged by recent reviews,²⁻⁹ undoubtedly because of the general success of such approximations in correlating a range of chemical phenomena and their utility in studies of reaction mechanism. Limitations of the original Hammett $\rho\sigma$ scheme in situations of high electron demand or supply have resulted in modification either by the use of "enhanced" σ values (e.g., σ^+ or σ^-)^{3,10,11} or by extensions to additional parameters such as σ_R , σ_R^+ , or σ_R^- .^{7,12,13} Substituent effects in situations of high electron demand, as in carbocation systems, have been amply documented by many studies in strong acidic media. The chemistry of high electron

supply, however, is not as well documented and is restricted mostly to substituted anilines and phenols. Few studies of substituent effects in carbanions are presently available.

Equilibrium acidities of substituted 9-phenylfluorenes are available in aqueous dimethyl sulfoxide (Me_2SO),¹⁴ but in these systems the phenyl group is twisted by steric effects with respect to the fluorenyl anion and the change of conjugative electron supply is limited. Similarly, equilibrium acidities are available for ring-substituted fluorenes,^{15,16} but substituent effects in these systems are complicated by the different modes of conjugation available in the fluorenyl system; e.g., the 3-position is conjugated directly (para) to the fluorenyl 9-position but the 2-position (meta) is also conjugated via the second benzene ring. More recently, Bordwell has summarized the results of a number of carbanion substituent effects in Me_2SO .¹⁷⁻¹⁹ These results will be discussed below.

In the present paper we report the equilibrium ion pair acidities on the cesium cyclohexanamide (CsCHA) scale, $\text{p}K_{\text{CsCHA}}$, for a series of symmetrically substituted diphenylmethanes. The examples include several compounds whose acidities are too low to measure in Me_2SO or related polar media, but the established correlation²⁰ between ionic $\text{p}K_{\text{Me}_2\text{SO}}$ and ion pair $\text{p}K_{\text{CsCHA}}$ for highly

(1) Paper 65 in this series: Streitwieser, A., Jr.; Bors, D. A.; Kaufman, M. J. *J. Chem. Soc., Chem. Commun.* **1983**, 1394. Paper 64: Streitwieser, A., Jr.; Swanson, J. T. *J. Am. Chem. Soc.* **1983**, 105, 2502.

(2) Hammett, L. P. "Physical Organic Chemistry"; McGraw-Hill: New York, 1940; Chapter 7.

(3) Jaffe, H. H. *Chem. Rev.* **1953**, 53, 191.

(4) Wells, P. R. "Linear Free Energy Relationships"; Academic Press, Inc.: New York, 1968.

(5) Johnson, C. D. "The Hammett Equation"; Cambridge University Press: London, Great Britain, 1973.

(6) Shorter, J. "Correlation Analysis in Organic Chemistry"; Oxford University Press: London, Great Britain, 1973.

(7) Ehrenson, S.; Brownlee, R. T. C.; Taft, R. W. *Prog. Phys. Org. Chem.* **1973**, 10, 1.

(8) Chapman, N. B.; Shorter, J. "Correlation Analysis in Chemistry"; Plenum Press: New York, 1978.

(9) Charton, M. *Prog. Phys. Org. Chem.* **1981**, 13, 119.

(10) Brown, H. C.; Okamoto, Y. *J. Am. Chem. Soc.* **1958**, 80, 4979.

(11) (a) Exner, O. "Advances in Linear Free Energy Relationships"; Plenum Press: London, 1972; Chapter 1. (b) Reference 8, Chapter 10, from ref 11a.

(12) Taft, R. W. "Steric Effects in Organic Chemistry"; Newman, M. S., Ed.; Wiley: New York, 1956; Chapter 13.

(13) Taft, R. W. *J. Phys. Chem.* **1960**, 64, 1805.

(14) Cockerill, A. F.; Lamper, J. E. *J. Chem. Soc. B* **1971**, 503.

(15) Bowden, K.; Cockerill, A. F. *J. Chem. Soc. B* **1970**, 173.

(16) Bowden, K.; Cockerill, A. F.; Gilbert, J. R. *J. Chem. Soc. B* **1970**, 179.

(17) Bordwell, F. G.; Algrim, D.; Vanier, N. R. *J. Org. Chem.* **1977**, 42, 1817-9.

(18) Algrim, D.; Bares, J. E.; Branca, J. C.; Bordwell, F. G. *J. Org. Chem.* **1978**, 43, 5024-6.

(19) Bordwell, F. G.; McCallum, R. J.; Olmstead, W. N. *J. Org. Chem.* **1984**, 49, 1424-7.

(20) Streitwieser, A., Jr.; Juaristi, E.; Nebenzahl, L. L. "Comprehensive Carbanion Chemistry"; Bunel, E., Durst, T., Eds.; Elsevier: New York, 1980; Chapter 7.

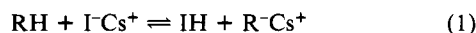
Table I. Spectral Data for Anions and pK_{CsCHA} Values

(XC_6H_4) ₂ CH ₂ X	anion λ_{max} (nm)	$10^{-3}\epsilon$	pK_{CsCHA} (per H) ^a
<i>m</i> -CH ₃	447	47.9 ± 1.4	33.80 ± 0.13 ^c
<i>m</i> -OCH ₃	441	39.2 ± 0.5	32.70 ± 0.13
<i>m</i> -F	436	41.5 ± 0.7	29.90 ± 0.17
<i>m</i> -CF ₃	441	47.1 ± 0.8	28.94 ± 0.13
<i>m</i> -C ₆ H ₅	457	43.2 ± 0.5	32.27 ± 0.11
H	441	50.2 ± 0.1	33.41 ± 0.11
<i>p</i> -CH ₃ ^b	446	44.0 ± 1.3	35.10 ± 0.15
<i>p</i> -OCH ₃	430	42.2 ± 1.6	37.6 ± 0.2
<i>p</i> -F	424	(unstable)	
<i>p</i> -Cl	452	(unstable)	
<i>p</i> -SO ₂ Me	515	103.1 ± 2.2	22.42 ± 0.04
<i>p</i> -CN	520	95.5 ± 0.1	22.98 ± 0.01
<i>p</i> -C ₆ H ₅ ^b	557	102 ± 0.4	30.83 ± 0.13
<i>p</i> -N(CH ₃) ₂	451	61.4 ± 5.9	38.6 ± 0.2
<i>p</i> -SC ₆ H ₅	500	101 ± 3	28.78 ± 0.12

^a Relative to pK_{CsCHA} of 9-phenylfluorene (18.49) with accumulated probable error. ^b Reference 45. ^c Correction of a previously reported value: Streitwieser, A., Jr.; Berke, C. M.; Robbers, K. *J. Am. Chem. Soc.* **1978**, *100*, 8271.

conjugated hydrocarbons strongly suggests that the present results would apply to these diarylmethanes as well.

Equilibria 1 were measured in cyclohexylamine with use of a dual-indicator approach; that is, both the test system, RH, and a reference, IH, serve as indicators whose conjugate bases are measured by visible spectrophotometry. Several approaches and the final correction for statistical effects to put the pK s on a per hydrogen basis have been summarized recently.^{20,21}



$$K_{rel} = [IH][R^-Cs^+]/[RH][I^-Cs^+] \quad (2)$$

$$pK_{CsCHA}(RH) = pK_{CsCHA}(IH) + pK_{rel} \quad (3)$$

The diarylmethane system was chosen because previous work had shown that the expected acidities would be in a measureable range in cyclohexylamine and that the system would be one of unusually high electron supply. Theoretical studies indicate that the diphenylmethyl anion involves only a modest twist of the phenyls from the mean molecular plane²² and that, therefore, substantial conjugation and charge delocalization are involved. Moreover, a recent X-ray structure of a diphenylmethyl anion salt shows the phenyls to be coplanar in the crystal.²³

Results and Discussion

The substituted diphenylmethanes were prepared generally by standard methods. Most were obtained by reduction of the appropriately substituted benzhydrol or benzophenone. The benzhydrols were prepared generally by allowing 2 equiv of an aryl Grignard reagent (or aryllithium) to react with 1 equiv of ethyl formate. Yields were generally good (41–95% based on ethyl formate as the limiting reagent) when the Grignard reagent was prepared in high dilution (<0.1 M). The benzhydrols were reduced by using either hydrogen over Pd/C in acidified methanol²⁴ or sodium borohydride in trifluoroacetic acid.²⁵ The benzophenones were reduced by using hydrazine hydrate and potassium hydroxide in di- or triethylene glycol.²⁶ Yields for all of these reactions were generally good (62–94%).

Bis(4-phenylthio)phenylmethane was prepared from diphenylmethane. Direct iodination with iodine and iodic acid in acetic acid²⁷ gave the intermediate bis(4-iodophenyl)methane,

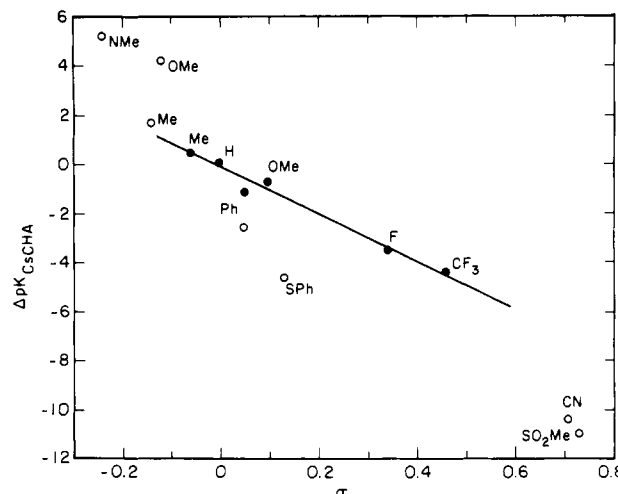


Figure 1. The pK_{CsCHA} values of di-meta-substituted diphenylmethanes (filled circles) give a normal Hammett correlation; the least-squares line shown is $\Delta pK_{CsCHA} = -9.693\sigma_m - 0.055$. The para substituents are shown as open circles.

which was combined with thiophenol in liquid ammonia to give the desired product upon radiation with light (350 nm).²⁸ Bis-(4-cyanophenyl)methane and bis(4-(methylsulfonyl)phenyl)methane were prepared from bis(4-bromophenyl)methane.^{29,30} Transmetalation of bis(4-bromophenyl)methane with *n*-butyllithium at -110°C in tetrahydrofuran followed by quenching with dimethyl disulfide produced bis(4-thioanisyl)methane, which was oxidized with 30% H_2O_2 in acetic acid to give bis(4-(methylsulfonyl)phenyl)methane in good yield.

Spectral data for the diarylmethylcesium ion pairs are given in Table I together with their equilibrium acidities on the CsCHA scale; e.g., pK_{CsCHA} (9-phenylfluorene) = 18.49.²⁰

Not all of the substituents formed stable anions in this system. Decomposition of the bis(4-chlorophenyl)methyl anion could be due to benzyne formation via elimination of HCl .³¹ This does not seem to be the cause for the instability of bis(4-fluorophenyl)methyl anion since the meta isomer is stable. This anion may decompose via elimination of fluoride and formation of a carbene which goes on to react with solvent. Unexpectedly, the bis(3-(trifluoromethyl)phenyl)methyl anion photodecomposes. All measurements with this compound had to be done in the dark. The bis(4-cyanophenyl)methyl anion decomposes with excess base and the amount of base used was carefully controlled.

The meta-substituted diphenylmethanes give a good linear Hammett correlation (Figure 1) with $\rho = 9.693$ (correlation coefficient = 0.993). The slope is in the normal range for doubly-substituted aryl systems with the charge one atom from the ring. For example, for single substituents, Bordwell reports ρ values of 5.3–5.7 for the acidities of ArOH , ArNH_2 , Ar_2CH_2 , and Ar_3CH in Me_2SO .^{18,19} A value of ρ in this range with meta substituents does not, by itself, indicate much about the delocalization of charge. However, the large deviation of para substituents from the meta correlation (Figure 1) does show the limitations of the simple Hammett procedure.

These limitations were recognized by Hammett in his original treatment and he proposed the use of "enhanced" values, σ^- , for systems of conjugating electron supply as in anilines and phenolate ions.² However, in the present case, an attempted correlation of the para substituents with σ^- parameters is not successful. The least-squares ρ value, 11.18, is higher than the correlation of the meta substituents. Moreover, there is a great deal of scatter. A simple criterion of the success of a correlation is given by the

(21) Vorpapel, E. R., thesis, Department of Chemistry, University of California, Berkeley, CA, 1981, p 59.

(22) Adams, S. M.; Banks, S. J. *Compt. Chem.* **1983**, *4*, 470–81.

(23) Olmstead, M. M.; Power, P. P. *J. Am. Chem. Soc.* **1985**, *107*, 2174.

(24) Hartung, W. H.; Siminoff, R. "Organic Reactions"; John Wiley and Sons, Inc.: New York, 1953; Vol. 7, p 263.

(25) Gribble, G. W.; Kelly, W. J.; Emery, S. E. *Synthesis* **1978**, 763.

(26) Minlow, H. J. *Am. Chem. Soc.* **1946**, *68*, 2487.

(27) Wirth, H. O.; Konigstein, O.; Kern, W. *Justus Liebig Ann. Chem.* **1960**, *634*, 84.

(28) Bunnett, J. F.; Creary, X. J. *Org. Chem.* **1974**, *39*, 3173.

(29) Friedman, L.; Shechter, H. J. *Org. Chem.* **1961**, *26*, 2522.

(30) Young, J. D.; Stevenson, G. R.; Bauld, N. L. J. *Am. Chem. Soc.* **1972**, *94*, 8790.

(31) Streitwieser, A., Jr.; Koch, H. F. J. *Am. Chem. Soc.* **1984**, *86*, 404.

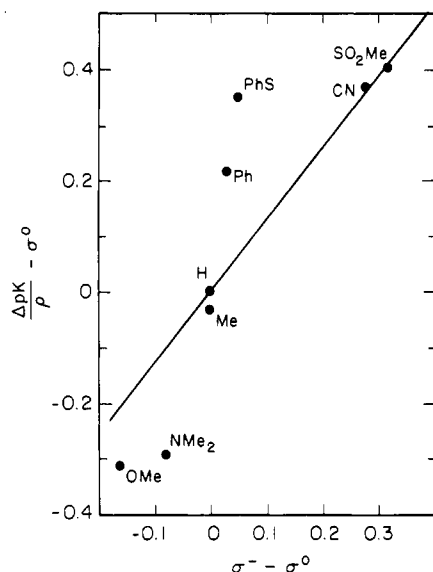


Figure 2. Yoshioka plot (ref 34) for para substituents. The least-squares line is defined by the points for H, CN, and SO_2CH_3 and is equal to $1.279 \Delta\sigma + 0.001$.

Table II. Substituent Parameters

substituent	δ_m^a	δ_p^a	δ_p^c
Me	-0.06	-0.14	-0.14
OMe	0.10	-0.12	-0.28
Ph	0.05	0.05	0.08
SPh		0.13	0.18
NMe ₂		-0.24	-0.32
SO ₂ Me		0.73	1.05
CN		0.71	0.99
F	0.34		
CF ₃	0.46		

^a Reference 9. ^b Reference 11b. The δ values of ref 35 are almost identical. ^c References 9 and 11b are essentially identical.

average deviation (AD) of calculated and experimental pK values. For the ordinary Hammett meta correlation (Figure 1), AD = 0.17, a reasonable value for a total experimental range of almost 5 pK units. For the σ^- correlation, however, AD = 1.07 for a range of 16 pK units. The points for *p*-phenyl and *p*-(thiophenyl) are especially far from the correlation line, 1.7 and 2.6 pK units, respectively.

In order to assess separately the roles of field effects and conjugation, the use of dual substituent effects has been advocated.³² One of the first such procedures is that of Yukawa and Tsuno,³³ which, for the present system, takes the form³⁴

$$pK^\circ - pK = \rho[\sigma^\circ + r(\sigma^- - \sigma^\circ)] \quad (4)$$

For meta substituents, the $\Delta\sigma$ term vanishes and the simple Hammett relation remains; that is, both meta and para substituents are treated in the same correlation. The application to the present pK_{CSCHA} values is given in Figure 2 in which the rearrangement suggested by Yoshioka et al.³⁴ is used; that is, the function $(\Delta pK/\rho) - \sigma^\circ$ is plotted against $\Delta\sigma$. The σ° values used are those derived by Exner^{11b} and by Hoefnagel and Wepster^{35,36} and are summarized in Table II. The correlation is not very good; phenyl, thiophenyl, and dimethylamino seem to be particularly divergent from the remaining points.

(32) Shorter, J., in ref 8, p 119.

(33) Yukawa, Y.; Tsuno, Y. *Bull. Chem. Soc. Jpn.* **1959**, *32*, 971. Yukawa, Y.; Tsuno, Y.; Sawada, M. *Bull. Chem. Soc. Jpn.* **1966**, *39*, 2274.

(34) Yoshioka, M.; Hamamoto, K.; T. *Bull. Chem. Soc. Jpn.* **1962**, *35*, 1723.

(35) Hoefnagel, A. J.; Wepster, B. M. *J. Am. Chem. Soc.* **1973**, *95*, 5357-66.

(36) Cf. the theoretical comparison of Vorpapel et al.: Vorpapel, E. R.; Streitwieser, A., Jr.; Alexandratos, S. D. *J. Am. Chem. Soc.* **1981**, *103*, 3777.

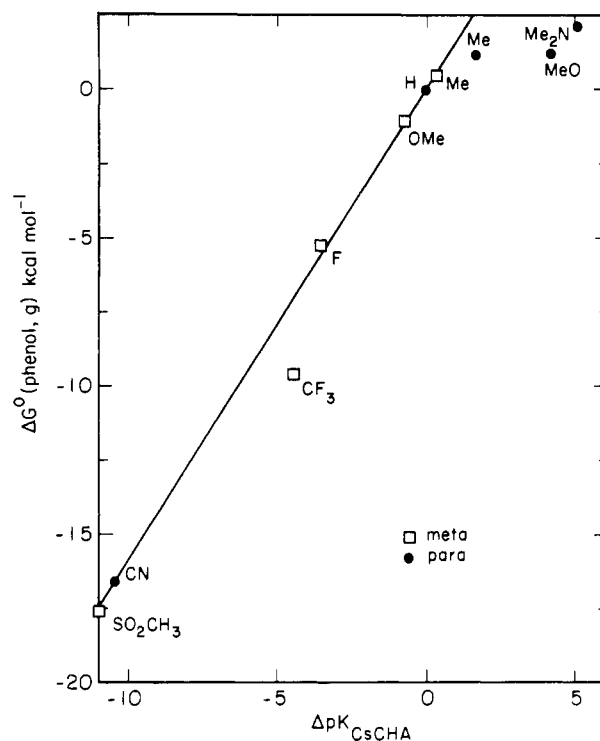


Figure 3. Comparison of pK_{CSCHA} of diarylmethanes with ΔG° for the gas-phase (ICR) acidities of phenols from ref 44.

Other dual substituent approaches have been proposed. In these approaches, meta and para substituents are treated as separate correlations. Swain and Lupton³⁷ attribute to each substituent just two basic electronic characteristics: a field constant, F , and a resonance constant, R . Their values for a number of substituents have recently been revised.³⁸ Their approach has been vigorously criticized³⁹ and defended.⁴⁰ Correlation between F , R , and the ΔpK_{CSCHA} of meta substituents gives the following weighting factors: $f = 5.42$, $r = 1.30$ with AD = 0.13. The fit is expected to be better since we have incorporated the increased flexibility of an additional parameter but the improvement is minimal. The para substituents give the values $f = 8.78$, $r = 3.34$, with AD = 0.94. The fit is still poor, despite the additional parameter, and individual points deviate widely.

Ehrenson, Brownlee, and Taft⁷ have proposed a related dual substituent approach based on different substituent parameters, σ_1 and σ_R . Their method was revised recently by Charton.⁹ This approach gives for the meta group $\rho_1 = 9.56$, $\rho_R = 3.96$, with AD = 0.11. For the para substituents, $\rho_1 = 10.52$, $\rho_R = 15.76$, AD = 1.09, and there is again substantial scatter. The three-parameter approach of Weeks and Horak⁴¹ fares no better; the addition of a term for σ_R^+ to the σ_1 and σ_R^- terms still gives a poor correlation with wide deviations.

None of the present LFERs works satisfactorily with the present data. We see several reasons for this situation. Our substituent set includes some that are *amphoteric*; that is, they stabilize adjacent cations and anions, but not necessarily to the same extent. Phenyl, for example, delocalizes charge regardless of its sign. Sulfide stabilizes positive and negative charges effectively but apparently by different mechanisms; electron donation to cations is important to give sulfonium ion character, but negative charge is apparently stabilized only by polarization. Other groups, such as methoxy and dimethylamino, stabilize cations and destabilize

(37) Swain, C. G.; Lupton, E. C., Jr. *J. Am. Chem. Soc.* **1968**, *90*, 4328.

(38) Swain, C. G.; Unger, S. H.; Rosenquist, N. R.; Swain, M. S. *J. Am. Chem. Soc.* **1983**, *105*, 492.

(39) Reynolds, W. F.; Topsom, R. D. *J. Org. Chem.* **1984**, *49*, 1989-92. Hoefnagel, A. J.; Oosterbeck, W.; Wepster, B. M. *Ibid.* **1984**, *49*, 1993-7. Charton, M. *Ibid.* **1984**, *49*, 1997-2001.

(40) Swain, C. G. *J. Org. Chem.* **1984**, *49*, 2005-10.

(41) Weeks, G.; Horak, V. *J. Org. Chem.* **1980**, *45*, 2068-71.

anions. Consequently, one cannot expect to handle these different types of substituents with single sets of substituent parameters. Moreover, the substituent properties have been characterized much more thoroughly in electron-deficient systems. The electron-rich systems that have been used have been almost entirely derived from the acidities of phenols and anilinium ions. In these cases, the charge delocalization to substituents is much less than that in carbanions. Moreover, it has been shown that the effects of some substituents are perturbed in aqueous solution by hydrogen bonding.⁴²⁻⁴⁴ Such hydrogen-bonding effects are not expected to be significant in cyclohexylamine solution.

These limitations apparently hold even in the gas phase. Extensive data are now available for substituted phenols in the gas phase.⁴⁴ The ion cyclotron resonance results are compared with the present diarylmethane acidities in Figure 3. For most substituents, the correlation is excellent. Electron-donating groups, however, are generally less effective in destabilizing phenolate ion in the gas than with diphenylmethyl anion in CHA. This result suggests that charge delocalization is much less important for phenolate ions than for benzylic anions. Unfortunately, the phenol study does not yet include a phenyl or sulfide substituent. We would predict that these groups would stabilize phenolate ion substantially less than would be suggested by Figure 3.

From our results it is clear that the original conclusions two and a half decades ago of Bekkum, Verkade, and Wepster⁴⁵ are still relevant, namely, that in those cases in which a substituent enters into conjugating para interactions with the reaction center, a multiplicity of (exalted) σ values is observed.

Experimental Section

Acidity Measurements. Spectral measurements were determined on a Cary 118 spectrometer using a thermostated cell block held at 25 °C. The path length of the reactor cell was calibrated with a solution of potassium permanganate. All hydrocarbons were recrystallized and sublimed before use. Cyclohexylamine (CHA, Aldrich) was fractionally distilled on a 5 ft, vacuum-jacked, sieve-tray column. The purified CHA was degassed on a vacuum line and transferred (bulb-to-bulb) to a second flask containing lithium cyclohexanamide (LiCHA). The CHA was stirred over LiCHA for at least 18 h to remove any acidic contaminants. Finally, the CHA was vacuum transferred to a glass ampule and brought into the glovebox.

To determine the extinction coefficients of a deprotonated hydrocarbon, the general procedure involved accurately weighing about 0.2–0.4 mg (on a Mettler Model ME 30 microbalance, ± 0.002 mg) of hydrocarbon and adding it to a calibrated reactor cell. About 3 mL of CHA was added, the exact amount being determined from the weight (on a Mettler Model PC440 open pan balance). A base line scan was taken at this point for anions that would not air quench to a colorless solution. A small amount of cesium cyclohexanamide (CsCHA, 2–4 μ L of a 0.19 M solution in CHA) was added to clean the glass surfaces of the cell and give a stable color. Then enough CsCHA was added to deprotonate the hydrocarbon and a spectrum (350–800 nm) was taken after a slight excess of base was added to ensure complete deprotonation of hydrocarbon. Replicate runs showed an error of less than 3%.

The procedure is more complex for those systems whose acidity approaches that of the solvent (*p*-methoxy and *p*-(dimethylamino) substituents). For these systems, the method used earlier with alkylbiphenyls⁴⁶ was used with an additional correction for the absorbance of CsCHA. An experimental extinction coefficient, ϵ_{exptl} , is defined as

$$\epsilon_{\text{exptl}} = A/[\text{RH}]_0L \quad (5)$$

in which A is the absorbance, $[\text{RH}]_0$ is the concentration of carbon acid, and L is the cell path length. For sufficiently acidic carbon acids and excess CsCHA, $\epsilon_{\text{exp}} = \epsilon$. For the less acidic compounds, eq 6 can be derived. $[\text{CsCHA}]_e$, the value at equilibrium, is calculated from eq 7

$$\epsilon_{\text{exptl}} = \epsilon - (1/K)(\epsilon_{\text{exptl}}/[\text{CsCHA}]_e) \quad (6)$$

in which B_T is the total base concentration, $[\text{CsCHA}]_e + [\text{RCs}]_e$, and ϵ_i is the extinction coefficient at the i th iteration. The experimental ϵ is

$$[\text{CsCHA}]_e = B_T - A/L\epsilon_i \quad (7)$$

used as the initial guess. A plot of ϵ_{exptl} vs. $\epsilon_{\text{exptl}}/[\text{CsCHA}]_e$ for several runs gives an extrapolated value of ϵ for use in eq 6. This value is used for a new guess for $[\text{CsCHA}]_e$ with use of eq 7, and the process is repeated to self-consistency. The absorbance of CsCHA at the λ_{max} of the hydrocarbon anion will cause the experimental absorbance A to be too large and is corrected at each iteration.

To perform the dual equilibrium acidity measurement, a suitable indicator must be found first. The ideal indicator has a pK_{CsCHA} which is within 2 pK units of the hydrocarbon of interest and a maximum absorbance at a wavelength which is at least 20 nm different from that of the hydrocarbon. The concentrations for the indicator and hydrocarbon must be adjusted so that absorbances from both of the anions are detectable in the spectrum. The actual procedure involves accurate weighing of both the hydrocarbon and indicator. Both hydrocarbons were added to a clean reactor cell followed by about 2–3 mL of CHA. The exact amount of solvent was determined by weight. A base line was taken at this point for compounds whose anions did not quench to colorless solutions. A small amount of CsCHA was added (2–4 μ L) to clean the reactor and establish a stable color. Additional base was added to obtain a maximum absorbance of about 0.8 unit. A spectrum (350–800 nm) was taken at a 1 nm/s scan rate after the contents were allowed to equilibrate for at least 15 min. Additional base was then added and a second spectrum was taken. This was sometimes repeated to obtain several absorbance values per reactor run. This technique is useful since the maximum error in these determinations comes from the absorbance values. Replicate runs showed errors of less than 0.05 pK unit when the above criteria were met.

Preparation of Diarylmethanes. The syntheses of bis(4-tolyl)methane and bis(4-biphenyl)methane have been described in an earlier paper.⁴⁷ Bis(4-cyanophenyl)methane was prepared by the method of Bauld et al.³⁰

The diethyl ether and tetrahydrofuran used as solvents were freshly distilled from sodium and transferred under nitrogen. Hexane used as eluent was distilled from calcium hydride before use. Magnesium metal turnings were used as supplied by Mallinckrodt, Inc. after being heated in a 150 °C oven for at least 4 h. Melting points were taken on Buchi apparatus and are uncorrected. NMR spectra were taken on a Varian T-60 Analytical NMR spectrometer or on a Varian EM-390 NMR spectrometer with tetramethylsilane as internal reference. Infrared spectra were taken between salt plates, unless otherwise stated, on a Perkin-Elmer Model 337 grating infrared spectrometer. Elemental analyses were performed by the Analytical Services Laboratory of the University of California, Berkeley. Mass spectra were obtained at 70 eV on a CEC-103 spectrometer. A Varian Serograph Model 920 gas-liquid chromatograph was used to purify the products. One of two columns was used. The 12 ft \times 0.25 in. column was packed with 20% carbowax 20 M on Chromosorb W. The 4 ft \times 0.25 in. column was packed with 5% SE 30 on Chromosorb W.

3,3'-Dimethylbenzhydrol. To a 1000-mL, three-neck, round-bottom flask equipped with a magnetic stirring bar, reflux condenser (recirculating ethylene glycol at –5 °C as heat transfer fluid), and a pressure equalizing dropping funnel, 2.92 g (0.120 mol) of magnesium metal turnings was added. This was followed by 50 mL of diethyl ether and 1.9 g (0.01 mol) of 1,2-dibromoethane. Within 5 min reaction had begun. An additional 700 mL of diethyl ether was added and the mixture was heated to reflux. Next, 19.7 g (0.115 mol) of 3-bromotoluene in 80 mL of diethyl ether was added over a period of 1 h. After the mixture was refluxed for 18 h, 3.70 g (0.05 mol) of ethyl formate (dried over 3A molecular sieves) in 30 mL of diethyl ether was added to the cooled Grignard reagent over a period of 30 min. A white precipitate formed near completion of the addition. After the mixture was refluxed for 18 h, the cooled suspension was added to a mixture of 200 g of ice and 100 mL of 10% sulfuric acid. The aqueous layer was separated and extracted twice with fresh diethyl ether. The combined extracts were washed successively with two 50-mL portions of 10% sulfuric acid, 50 mL of water, 50 mL of 3% sodium carbonate solution, and 50 mL of saturated sodium chloride solution and then dried over anhydrous magnesium sulfate. After the solution was filtered, the solvent was removed under vacuum to give 11.8 g of a yellow oil, which was purified on a 5 \times 54 cm silicate gel column with 5% by volume ethyl acetate in hexane as eluent. The first fraction contained unreacted starting material and some 3,3'-dimethylbiphenyl, net weight 2.0 g. The final fraction was the desired yellow liquid weighing 8.3 g (78% yield). NMR (T-60, CCl_4)

(42) Grob, C. A.; Schlageter, M. G. *Helv. Chim. Acta* **1976**, *59*, 264–276.

(43) Mashimi, M.; McIver, R. R., Jr.; Taft, R. W.; Bordwell, F. G.; Olmstead, W. N. *J. Am. Chem. Soc.* **1984**, *106*, 2717–8.

(44) Fujio, M.; McIver, R. T., Jr.; Taft, R. W. *J. Am. Chem. Soc.* **1981**, *103*, 4017–29.

(45) van Bekkum, H.; Verkade, P. E.; Wepster, B. M. *Recl. Trav. Chim. Pays-Bas* **1959**, *78*, 815.

(46) Streitwieser, A., Jr.; Guibé, F. *J. Am. Chem. Soc.* **1978**, *100*, 4532.

(47) Streitwieser, A., Jr.; Murdock, J. R.; Hafelinger, G.; Chang, C. J. *J. Am. Chem. Soc.* **1973**, *95*, 4248.

δ 2.26 (s, 6 H), 2.96 (d, 1 H), 5.42 (d, 1 H), 7.00 (m, 8 H); IR 3340 cm^{-1} (OH). Mass spectrum: 212, 119. High resolution mass spectrum: calcd 212.1201; found 212.1199.

The following substituted benzhydrols were prepared by the same procedure:

3,3'-Dimethoxybenzhydrol: 83%; mp 45–46 °C; NMR (CCl_4) δ 3.00 (s, 1 H), 3.62 (s, 6 H), 5.41 (s, 1 H), 6.80 (m, 8 H); IR 3400 cm^{-1} (OH). Anal. C, H.

3,3'-Difluorobenzhydrol: 95%; oil; NMR (CCl_4) δ 3.68 (s, 1 H), 5.49 (s, 1 H), 7.00 (m, 8 H); IR 3320 cm^{-1} (OH); mass spectrum 220, 123; high resolution mass spectrum, calcd for $\text{C}_{13}\text{H}_{10}\text{F}_2\text{O}$ 220.0700, found 220.0696.

3,3'-Bis(trifluoromethyl)benzhydrol (CAUTION: The Grignard reaction of 3-bromo(trifluoromethyl)benzene has been known to detonate;⁴⁸ high dilution (<0.1 M) should be maintained during this reaction): 61%; white solid; mp 47–48 °C; NMR (CCl_4) δ 2.63 (d, 1 H), 5.72 (d, 1 H), 7.42 (m, 8 H); IR 3340 cm^{-1} (OH); Anal. C, H.

3,3'-Diphenylbenzhydrol: 41%; glassy solid; NMR δ 3.40 (s, 1 H), 5.58 (s, 1 H), 7.20 (m, 18 H); IR 3350 cm^{-1} (OH).

4,4'-Dimethoxybenzhydrol: white needles; mp 68–69 °C;⁴⁹ NMR (CCl_4) δ 2.54 (d, 1 H), 3.72 (s, 6 H), 5.48 (d, 1 H), 6.84 (m, 8 H); IR 3300 cm^{-1} (OH) (Nujol); Anal. C, H.

4,4'-Difluorobenzhydrol: 43%; white needles; mp 47–48 °C;⁵⁰ NMR (CCl_4) δ 3.91 (s, 1 H), 5.40 (s, 1 H), 6.96 (m, 8 H); IR 3350 cm^{-1} (OH); Anal. C, H.

Bis(3-tolyl)methane. A mixture of 7.09 g (33 mmol) of 3,3'-dimethylbenzhydrol, 0.5 g of 5% Pd/C, 3 drops of 70% perchloric acid, and 150 mL of methanol was purged with hydrogen and agitated under a low-pressure (2 atm) hydrogen atmosphere for 12–18 h at room temperature. Workup consisted of neutralization of the suspension with a 5% aqueous sodium carbonate solution followed by filtration with Celite filter aid. The solvent was removed at reduced pressure to give a semi-solid residue, which was digested with diethyl ether. The ether layer was dried over anhydrous magnesium sulfate and filtered, and the solvent was removed under vacuum to give 5.3 g (82% yield) of a yellow oil: NMR (CCl_4) δ 2.23 (s, 6 H), 3.77 (s, 2 H), 6.92 (m, 8 H). A sample was purified by GLC to give a colorless liquid. Anal. C, H.

The following diarylmethanes were prepared by the same procedure.

Bis(3-anisyl)methane: 80%; colorless liquid; NMR δ 3.68 (s, 6 H), 3.82 (s, 2 H), 6.60 (m, 6 H), 7.05 (m, 2 H); Anal. C, H.

Bis(3-fluorophenyl)methane: 78%; colorless liquid; NMR (CCl_4) δ 3.88 (s, 2 H), 7.00 (m, 8 H); Anal. C, H.

Bis(3-trifluoromethylphenyl)methane: 94%; colorless needles; mp 40–41 °C; NMR (CCl_4) δ 4.06 (s, 2 H), 7.34 (m, 8 H); Anal. C, H.

Bis(4-anisyl)methane: 87%; colorless needles; mp 50–51 °C; NMR (CCl_4) δ 3.70 (s, 6 H), 3.76 (s, 2 H), 6.76 (m, 8 H); Anal. C, H.

Bis(4-fluorophenyl)methane (hydrogenation time 90 h): 62%; colorless solids; mp 28–9 °C;⁵¹ NMR (CCl_4) δ 3.76 (s, 2 H), 6.90 (m, 8 H); Anal. C, H.

Bis(3-biphenyl)methane. In a 250-mL, three-neck, round-bottom flask equipped with a magnetic stirring bar, dropping funnel, thermometer, nitrogen purge, and an ice bath, 50 mL of trifluoroacetic acid and 5 mL of trifluoroacetic anhydride were chilled to 0–5 °C. Next, 2.0 g of sodium borohydride pellets was added and stirred for 30 min. Gas evolution was very slow and well controlled. A solution of 3.5 g of bis(3-biphenyl)benzhydrol in 25 mL of dichloromethane was added dropwise over a period of 20 min. The ice bath was removed and the two-phase system was stirred for 8 h at room temperature. Two more sodium borohydride pellets and 15 mL of trifluoroacetic acid were added and stirring was continued for 42 h. Workup consisted of neutralization with 50% aqueous sodium hydroxide keeping the temperature below 30 °C with the addition of ice followed by extraction with 3 \times 50 mL portions of diethyl ether. The combined ether layer was washed twice with 50-mL portions of water and once with 50 mL of saturated sodium chloride solution and dried over anhydrous sodium sulfate before the solvent was evaporated. The viscous oil was purified on a 4 \times 30 cm silica gel column with 5% ethyl acetate in hexane (v/v) as eluent to give 1.1 g (33% yield) of white crystalline flakes, melting range 83–86 °C. Two recrystallization from petroleum ether and sublimation at 130 °C gave the pure compound: mp 89–90 °C; NMR δ 4.04 (s, 2 H), 7.30 (m, 18 H); Anal. C, H.

Bis(4-iodophenyl)methane. To a 500-mL, three-neck, round-bottom flask equipped with a magnetic stirring bar, thermometer, reflux condenser, and an infrared heating lamp, 16.8 g (0.10 mol) diphenylmethane, 200 mL of glacial acetic acid, 20.3 g (0.16 g-atom) of iodine, 5 mL of

sulfuric acid, 10 mL of carbon tetrachloride, and 7.0 g (0.04 mol) of iodic acid in 20 mL of water were added. The dark mixture was heated to 80–85 °C for 3.5 h. Iodine sublimed onto the walls of the flask and up the condenser. Carbon tetrachloride was added to help rinse the iodine off the walls. Workup consisted of pouring the contents of the flask onto 2000 g of ice. The oil was collected in diethyl ether and washed with dilute sodium bisulfite solution followed by dilute sodium carbonate solution, 3 \times 100 mL portions of water, and 2 \times 50 mL portions of saturated sodium chloride solution, and then the mixture was dried over anhydrous sodium sulfate. TLC showed a mixture of mono- and diiodo products. Evaporation of the solvent followed by crystallization from hexane and recrystallization from methanol gave 5.7 g (14% yield) of product, mp 93–94 °C (lit.²⁷ mp 93–94 °C).

Bis(4-(phenylthio)phenyl)methane. To a tube equipped with a dry ice condenser and a magnetic stirring bar was added 5.0 g (11.9 mmol) of bis(4-iodophenyl)methane which had been ground to a fine powder. The tube was chilled to –78 °C and 3.65 mL (3.93 g, 35.7 mmol) of thiophenol was added. The reaction contents were warmed enough to melt the thiophenol and to allow stirring of the suspension. After the mixture was chilled back down to –78 °C, liquid ammonia was distilled onto the reactants (280 mL). This procedure avoided spattering problems which occurred when thiophenol was added to the liquid ammonia. This mixture was irradiated with 350-nm light for 4.5 h in a Rayonett photolysis reactor. After evaporation of the solvent, the solid residue was taken up in water and diethyl ether. The ether layer was washed with 3 \times 100 mL portions of a dilute sodium carbonate solution to remove excess thiophenol. After successively washing the ether layer with 4 \times 75 mL portions of water and 2 \times 50 mL portions of saturated sodium chloride solution, the solution was dried over anhydrous sodium sulfate and evaporated to dryness. All of the aqueous washings were added to bleach to oxidize the mercaptan to the less offensive disulfide. TLC of the crude product showed considerable starting material. Recrystallization of the crude product from hexane gave mostly starting material. Cooling the mother liquor gave 0.48 g of nearly pure product, which was recrystallized from methanol followed by recrystallization from petroleum ether to give 150 mg of pale yellow crystals, mp 100–103 °C. Sublimation at 140 °C gave a white powder: mp 104–105 °C; NMR (CCl_4) δ 3.92 (s, 2 H), 7.20 (m, 18 H); Anal. C, H.

Bis(4-chlorophenyl)methane. To a 1000-mL, three-neck, round-bottom flask equipped with reflux condenser, thermometer, magnetic stirring bar, and heating mantle was added 20.1 g (80.0 mmol) of 4,4'-dichlorobenzophenone, 22.5 g (0.288 mol) of 64% aqueous hydrazine, 16.5 g (0.256 mol) of potassium hydroxide, and 400 mL of diethylene glycol. The mixture was heated to 130–140 °C for 1.5 h. During this time the mixture became dark yellow-orange with much foaming. The reflux condenser was replaced by a distillation head, and the temperature was increased to 190 °C while water and excess hydrazine were removed. After being heated for 2 h at 190–200 °C, the yellow solution was cooled to 120 °C and added to 1000 mL of cool water. After the solution was chilled at 0 °C for 18 h, the solid was collected and recrystallized from 150 mL of methanol to give 13.3 g (65% yield) of product, which was further sublimed at 50 °C to give fine white crystals, mp 54–55 °C (lit.⁵⁰ mp 56–57 °C). Anal. C, H.

The same procedure was used for **bis-(4-dimethylamino)phenyl)-methane:** 96%; white crystals; mp 88–89 °C (lit.⁵² mp 89–90 °C); NMR (CCl_4) δ 2.82 (s, 12 H), 3.70 (s, 2 H), 6.48 (d, 4 H), 6.90 (d, 4 H); Anal. C, H, N.

Bis(4-(methylsulfonyl)phenyl)methane. To a 100-mL, round-bottom flask equipped with a magnetic stirring bar, 1.08 g (3.3 mmol) of bis-(4-bromophenyl)methane was dissolved in 20 mL of tetrahydrofuran under dry N_2 atmosphere. The stirred solution was then cooled down to –100 to –115 °C with a hexane–liquid nitrogen bath followed by slow addition of 4 mL of 2.3 M *n*-butyllithium (9.2 mmol).⁵³ After being stirred at –110 to –115 °C for 5 min, the red solution was quenched with 3 mL of dimethyl disulfide. The resulting solution was warmed to room temperature and treated with 30 mL of diethyl ether. Workup consisted of successive washings with 0.1 M HCl, 10% sodium bicarbonate solution, and saturated sodium chloride solution, and the solution was dried over anhydrous magnesium sulfate. After the solvent and excess dimethyl disulfide were removed under vacuum, 0.806 g (94% yield) of bis(4-thioanisyl)methane was obtained: NMR (CDCl_3) δ 2.42 (s, 6 H), 3.8 (s, 2 H), 7.16 (q_{AB} , 8 H, $J = 9$ Hz).

This product was dissolved in 10 mL of glacial acetic acid and treated with 9 mL (104 mmol) of 30% hydrogen peroxide⁵⁴ in a 100-mL,

(48) Calcinari, R. *Chem. Ind. (London)* **1971**, 120.

(49) Picard, J. P.; Kearns, C. W. *Can. J. Chem.* **1950**, *28B*, 56.

(50) Tsugo, O.; Tashiro, M. *Bull. Chem. Soc. Jpn.* **1967**, *40*, 115.

(51) Gunther, F. A.; Blinn, R. C. *J. Am. Chem. Soc.* **1950**, *72*, 4282.

(52) Sosnovsky, G.; Yang, N. C. *J. Org. Chem.* **1960**, *23*, 899. Horner, L.; Betzel, C. *Justus Liebig Ann. Chem.* **1953**, 579, 175.

(53) Fox, M. A.; Chen, C.-C.; Campbell, K. A. *J. Org. Chem.* **1983**, *48*, 321.

(54) Gilman, H.; Beaber, N. J. *J. Am. Chem. Soc.* **1925**, *47*, 1449.

round-bottom flask equipped with a magnetic stirring bar and a reflux condenser. The solution was stirred at 60–65 °C for 17 h and poured into 50 mL of ice water. The solid was collected by filtration to give 0.85 g (87% yield) of product: NMR (CDCl₃) δ 3.01 (s, 6 H), 4.12 (s, 2 H), 7.33 (d, 4 H, J = 8 Hz), 7.87 (d, 4 H, J = 8 Hz). Recrystallization from 95% ethanol and sublimation at 190 °C to give a colorless powder; mp 197–198 °C; IR (CHCl₃) 1600, 1410, 1320, 1150, 1090 cm⁻¹; mass spectrum 324, 165; Anal. C, H, S.

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Registry No. 3,3'-H₃CC₆H₄CH(OH)C₆H₄CH₃, 13389-72-5; 3-BrC₆H₄CH₃, 591-17-3; OHCOCH₂CH₃, 109-94-4; 3,3'-H₃CC₆H₄C₆H₄CH₃, 612-75-9; 3,3'-H₃COC₆H₄CH(OH)C₆H₄OCH₃, 55360-45-7; 3-CH₃OC₆H₄Br, 2398-37-0; 3,3'-FC₆H₄CH(OH)C₆H₄F, 98586-21-1; 3-FC₆H₄Br, 1073-06-9; 3,3'-F₃CC₆H₄CH(OH)C₆H₄CF₃, 1598-89-6; 3-F₃CC₆H₄Br, 401-78-5; 3-C₆H₅C₆H₄Br, 2113-57-7; 4,4'-CH₃OC₆H₄CH(OH)C₆H₄OCH₃, 728-87-0; 4-CH₃OC₆H₄Br, 104-92-7; 4,4'-FC₆H₄CH(OH)C₆H₄F, 365-24-2; 4-FC₆H₄Br, 460-00-4; 3,3'-H₃CC₆H₄CH₂C₆H₄CH₃, 21895-14-7; 3,3'-H₃COC₆H₄CH₂C₆H₄OCH₃,

51095-48-8; 3,3'-FC₆H₄CH₂C₆H₄OCH₃, 98586-06-2; 3,3'-F₃CC₆H₄CH₂C₆H₄CF₃, 86845-35-4; 4,4'-H₃COC₆H₄CH₂C₆H₄OCH₃, 726-18-1; 4,4'-FC₆H₄CH₂C₆H₄F, 457-68-1; 3,3'-C₆H₅C₆H₄CH₂C₆H₄C₆H₅, 79128-89-5; 3,3'-C₆H₅C₆H₄CH(OH)C₆H₄C₆H₅, 98586-20-0; 4,4'-IC₆H₄CH₂C₆H₄I, 4611-15-6; C₆H₅C-H₂C₆H₅, 101-81-5; 4,4'-C₆H₅SC₆H₄CH₂C₆H₄SC₆H₅, 34745-83-0; C₆-H₅SH, 108-98-5; 4,4'-ClC₆H₄CH₂C₆H₄Cl, 101-76-8; 4,4'-ClC₆H₄CoC₆H₄Cl, 90-98-2; 4,4'-(H₃C)₂NC₆H₄CH₂C₆H₄N(CH₃)₂, 101-61-1; 4,4'-(H₃C)₂NC₆H₄COC₆H₄N(CH₃)₂, 90-94-8; 4,4'-MeSO₂C₆H₄CH₂C₆H₄SO₂Me, 22183-07-9; 4,4'-BrC₆H₄CH₂C₆H₄Br, 1941-86-2; 4,4'-H₃CSC₆H₄CH₂C₆H₄SCH₃, 22276-28-4; 4,4'-NCC₆H₄CH₂C₆H₄CN, 10466-37-2; 3,3'-H₃CC₆H₄CH-C₆H₄CH₃ Cs⁺, 98586-07-3; 3,3'-H₃COC₆H₄CH-C₆H₄OCH₃ Cs⁺, 98586-08-4; 3,3'-FC₆H₄CH-C₆H₄F Cs⁺, 98586-09-5; 3,3'-F₃CC₆H₄CH-C₆H₄CF₃ Cs⁺, 98586-10-8; 3,3'-C₆H₅C₆H₄CH-C₆H₄C₆H₅ Cs⁺, 98586-11-9; C₆H₅C-H-C₆H₅ Cs⁺, 18300-97-5; 4,4'-H₃CC₆H₄CH-C₆H₄CH₃ Cs⁺, 18300-96-4; 4,4'-H₃COC₆H₄CH-C₆H₄OCH₃ Cs⁺, 98586-12-0; 4,4'-FC₆H₄CH-C₆H₄F Cs⁺, 98586-13-1; 4,4'-ClC₆H₄CH-C₆H₄Cl Cs⁺, 98586-14-2; 4,4'-MeSO₂C₆H₄CH-C₆H₄SO₂Me Cs⁺, 98586-15-3; 4,4'-NCC₆H₄CH-C₆H₄CN Cs⁺, 98586-16-4; 4,4'-C₆H₅C₆H₄CH-C₆H₄C₆H₅ Cs⁺, 98586-17-5; 4,4'-(H₃C)₂NC₆H₄CH-C₆H₄N(CH₃)₂ Cs⁺, 98586-18-6; 4,4'-C₆H₅SC₆H₄CH-C₆H₄SC₆H₅ Cs⁺, 98586-19-7.

Carbon Acidity. 67. The Indicator Scale of Cesium Ion Pairs in Tetrahydrofuran

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Abstract: An equilibrium cesium ion-pair indicator scale relative to 9-phenylfluorene at $pK_a = 18.49$ has been established for 22 hydrocarbons in tetrahydrofuran. Comparison of this scale to those developed in Me₂SO and DME shows the scale to be independent of solvent. Visible absorbance spectral characteristics of the indicator anions are also reported and discussed in relation to other solvents. Thermodynamic studies of the equilibrium reactions were carried out over a temperature range of -20 to 25 °C and reveal the importance of internal rotation on the entropy of reactions. Thermodynamic constants found for reaction between fluorenes show a complex behavior and are generally not interpretable at this time.

Quantitative and semiquantitative equilibrium acidity data for a wide variety of carbon acids have been presented by several investigators. Since the pioneering work of Conant, Wheland, and McEwen in the 1930's,¹ acidity scales have been proposed for weak carbon acids in many solvents, including dimethyl sulfoxide (Me₂SO),² dimethoxyethane (DME),³ and *N*-methylpyrrolidin-2-one (NMP).⁴ For over two decades, research in our own laboratories has focused on the determination of the relative acidity of carbon acids in cyclohexylamine (CHA) solvent. Cyclohexylamine is a relatively nonpolar solvent, and the anions present in this solvent exist almost entirely as ion pairs. By assuming a pK_a value of 18.49 for 9-phenylfluorene, relative equilibrium ion-pair indicator scales have been developed for both lithium and cesium gegenions.⁵ Much additional data have been

made available by application of the H₂ technique to aqueous and alcoholic organic solvent mixtures.⁶ Collectively, this body of data has provided valuable insight into the various factors which determine the ease of ionization of a carbon acid.

Unfortunately, relatively few carbanion-forming reactions are performed in these solvents. Instead, metalation reactions conducted in ethereal solvents, especially tetrahydrofuran (THF), have increased enormously in both scope and usage in recent years.⁷ However, despite the widespread use of this solvent in synthetically useful transformations, relatively little quantitative ion-pair acidity data are currently available in THF.⁸ Therefore,

(1) (a) Conant, J. B.; Wheland, G. W. *J. Am. Chem. Soc.* **1932**, *54*, 1212. (b) McEwen, W. K. *J. Am. Chem. Soc.* **1936**, *58*, 1124.

(2) (a) Matthews, W. S.; Bares, J. E.; Bartmess, J. E.; Bordwell, F. G.; Cornforth, F. J.; Drucker, G. E.; Margolin, Z.; McCallum, R. J.; McCollum, G. J.; Vanier, N. R. *J. Am. Chem. Soc.* **1975**, *97*, 7006. (b) Bordwell, F. G.; Matthews, W. S. *J. Am. Chem. Soc.* **1974**, *96*, 1214, 1216. (c) Bordwell, F. G.; Bartmess, J. E.; Drucker, G. E.; Margolin, Z.; Matthews, W. S. *J. Am. Chem. Soc.* **1975**, *97*, 3226. (d) Bordwell, F. G.; Drucker, G. E. *J. Org. Chem.* **1980**, *45*, 3325.

(3) Petrov, E. S.; Terekhova, M. I.; Shatenshtein, A. I. *Zh. Obshch. Khim.* **1974**, *44*, 1118 (*Engl. Transl.* p 1075).

(4) Bordwell, F. G.; Branca, J. C.; Hughes, D. L.; Olmstead, W. N. *J. Org. Chem.* **1980**, *45*, 3305.

(5) Streitwieser, A., Jr.; Juaristi, E.; Nebenzahl, L. L. In "Comprehensive Carbanion Chemistry"; Buncl, E., Durst, T., Eds.; Elsevier: New York, 1980.

(6) (a) Steiner, E. C.; Gilbert, J. M. *J. Am. Chem. Soc.* **1965**, *87*, 382. (b) Bowden, K.; Stewart, R. *Tetrahedron* **1965**, *21*, 261. (c) Steiner, E. C.; Starkey, J. D. *J. Am. Chem. Soc.* **1967**, *89*, 2751. (d) Bowden, K.; Cockerill, A. F. *J. Chem. Soc. B* **1970**, 173. (e) Cox, R. A.; Stewart, R. *J. Am. Chem. Soc.* **1976**, *98*, 488. (f) Cockerill, A. F.; Lamper, J. E. *J. Chem. Soc. B* **1971**, 503.

(7) (a) Biellmann, J. F.; Ducep, J. B. *Org. React.* **1982**, *27*, 1. (b) Gschwend, H. W.; Rodriguez, H. R. *Org. React.* **1979**, *26*, 1. (c) Stowell, J. C. "Carbanions in Organic Synthesis"; Wiley: New York, 1979.

(8) The following work was done at approximately 0.1 M anion concentrations and was probably complicated by aggregation effects: (a) Fraser, R. R.; Bresse, M.; Mansour, T. *J. Chem. Soc., Chem. Commun.* **1983**, 620. (b) Denniston, A. D. "Acidities of Amines and 1,3-Dithianes in Tetrahydrofuran", Dissertation, University of Washington, 1979; *Diss. Abstr. Inter. B* **1979**, *40*, 749-b.