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DFT-PCM Studies of Solvent Effects on the Cross-Interaction Constants in Benzhydryl Cation and Anion Formation

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The Hammett ρ^+ and ρ^- values have been determined by varying substituent Y′ for a given Y in the benzhydryl cation and anion formation ($YH_4C_6{-}C^*H{-}C_6H_4Y'$ where C* is a cationic or an anionic center) at the RHF/3-21G*, RHF/6-31G*, RHF/6-31+G*, and B3LYP/6-31+G* levels. The failure of RHF theory in accounting for the stabilization by delocalization leads to the smaller magnitudes of ρ^+ and ρ^- with electron-donating and -withdrawing substituents, Y, respectively, than the corresponding DFT values. The effects of solvent (benzene, dichloroethane, and acetonitrile) on the ρ values were calculated by applying the conductor polarizable continuum model method to the DFT results. Finally, the cross-interaction constants ($\rho_{YY'}$) and their variation with solvent were determined. As the polarity (dielectric constant, ϵ) of the solvent is increased, the magnitude of ρ^+ and ρ^- decreased, whereas that of $\rho_{YY'}$ increased. Satisfactory correlations were obtained between ρ values (ρ^+, ρ^- and $\rho_{YY'}$) and the Kirkwood function f_k ($= \epsilon - 1/2\epsilon + 1$). The $\rho_{YY'}$ values are negative with a magnitude greater for the anionic ($\rho_{YY'}{}^-$) than the cationic ($\rho_{YY'}{}^+$) system.

Introduction

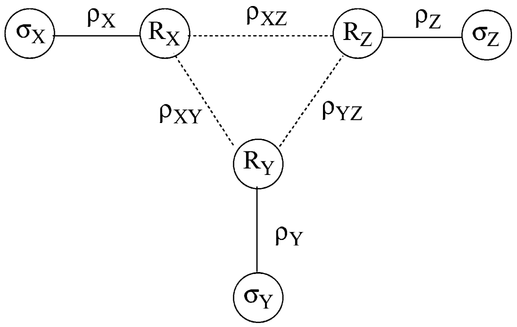
The Brønsted and Hammett relations have long served as useful tools for predictions of reactivity and mechanism of organic reactions. These linear free energy relationships have since been extended into more sophisticated forms, such as the one including cross-interaction constants (CICs),[1] and continue to contribute powerfully to reactivity theory and elucidation of reaction mechanism. The CICs, ρ_{ij}, are defined in eqs 1a and 1b where *i* and *j* denote substituent in the nucleophile (X), substrate (nonleaving group, Y), or leaving group (Z) in a nucleophilic substitution or an addition reaction, Scheme 1 (for S_N2 reactions). For equilibrium processes, k_{ij} and k_{HH} are replaced by equilibrium constants, K_{ij} and K_{HH}, respectively.

$$\log(k_{ij}/k_{HH}) = \rho_i\sigma_i + \rho_j\sigma_j + \rho_{ij}\sigma_i\sigma_j \tag{1a}$$

$$\rho_{ij} = \partial\rho_i/\partial\sigma_j = \partial\rho_j/\partial\sigma_i \tag{1b}$$

Abundant experimental data on applications of CICs to elucidation of mechanisms have been accumulated for various reaction types of nucleophilic substitution and addition reactions mostly in solution.[1,2] Some MO theoretical investigations have also been reported on the applications to the gas-phase reaction mechanisms.[3] However, no systematic theoretical works for the solvent effect on the CIC are available in the literature, although some experimental studies have been reported.[4] A number of DFT and ab initio works on the physical properties such as pK_a values involving Hammett correlations of the substituent effects have been reported.[5] However, theoretical investigations on the CICs are scarce. The main reason for the paucity of theoretical data on the CICs is the large reaction systems involved, since two rings with substituents are necessary for the CIC calculation. To derive reasonably reliable MO theoretical results, inclusion of polarization and diffuse functions with account of electron correlation effect is essential, and hence unduly large basis sets and computational expenses are required for reactions involving at least 15 heavy (non-hydrogen) atoms. However, the computational time and expenses can be drastically reduced with the use of the density functional theory (DFT) calculations[6] and theoretical studies on CICs are feasible.

SCHEME 1: S_N2 Type Transition State[a]



[a] R_i is a reaction center and σ_i is a substituent. Fragments are denoted as X, Y, and Z for the nucleophile, substrate and leaving group, respectively.

In this work, restricted HF and DFT calculations are performed on the benzhydryl cation and anion (Scheme 2,where C* is the cationic or the anionic center) formation processes. We determined the Hammett coefficients for cation ($\rho_Y{}^+$) and anion ($\rho_Y{}^-$) formation from the neutral benzhydryl molecule by varying substituents in both rings, Y and Y′. The CICs, $\rho_{YY'}$,

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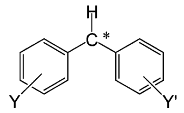
SCHEME 2



are then estimated using eq 1. Solvent effects on ρ_Y and $\rho_{YY'}$ are calculated by using the CPCM method[7] for three solvents, benzene, dichloroethane, and acetonitrile.

Calculations

The equilibrium constants for benzhydryl cation (K^+) and anion (K^-) formation are estimated for eqs 2a and 2b, respectively

$$YC_6H_4CH_2C_6H_4Y' \xrightleftharpoons{K+} YC_6H_4C^+HC_6H_4Y' + H^- \quad (2a)$$

$$YC_6H_4CH_2C_6H_4Y' \xrightleftharpoons{K-} YC_6H_4C^-HC_6H_4Y' + H^+ \quad (2b)$$

The Hammett equation can be given as eq 3, where log K_i is defined as eq 4

$$\log(K_Y/K_H) = -\frac{\Delta G^\circ_Y - \Delta G^\circ_H}{2.303RT} = -\frac{\delta\Delta G^\circ}{1.364} = \rho\cdot\sigma_Y \quad (3)$$

$$\log K_i = \frac{\Delta G^\circ}{1.364}, \text{ where } \Delta G^\circ = G(\text{cation, or anion}) + G(H^-, \text{ or } H^+) - G(\text{neutral molecule}) \quad (4)$$

For cations and anions, the exalted σ values, σ^+ and σ^-, are used.[8] We need not be concerned with the absolute values of G(H^+) and G(H^-) since they cancel out in the Hammett equation. For a given Y, we varied the other substituent, Y′, and $\rho_{Y'}^+$ and $\rho_{Y'}^-$ values are obtained. The CICs, $\rho_{YY'}^+$ and $\rho_{YY'}^-$ are estimated from variation of ρ values against σ according to eq 1b.

The thermodynamic functions (ΔH, ΔS, and ΔG) were calculated within the ideal gas, rigid-rotor, and harmonic oscillator approximations, as implemented in Gaussian 98.[9] The calculation of ΔG_{gas} uses a reference state of 1 atm (298.15 K) and the calculation of ΔG in solution uses a reference state of 1 M so that conversion of ΔG_{gas}(1 atm) into ΔG_{gas}(1 M) is necessary by adding a factor of $RT\ln(24.46)$.[10] However in the calculations of Hammett ρ values, we are using relative ΔG values and therefore the correction term cancels out. The geometries and energies were fully optimized at the RHF/3-21G*, RHF/6-31G*, RHF/6-31+G* and B3LYP/6-31+G*[6c,d] levels. All stationary points were characterized by normal-mode analysis. Charges were calculated by using the natural population analysis (NPA) of Weinhold.[11] Solvent effects are estimated at the B3LYP level on the gas-phase geometries for benzene ($\epsilon = 2.27$), dichloroethane ($\epsilon = 10.0$) and acetonitrile ($\epsilon = 35.94$) by using the C−PCM (conductor PCM)[7c] method which is a modification of the PCM (polarizable continuum model) method of Miertus, Scrocco and Tomasi[7a,b] and allows efficient geometry optimization in solution. The Z matrices and energies are given in the Supporting Information.

Results and Discussion

1. Structures. The charges on C* and relevant geometries are collected in Table 1. The angles of rotation (ϕ) of the two rings around the bonds, d_1 and d_2 in Scheme 3, are mainly related to the relative delocalizabilities of substituents. When Y = Y′, the two aryl groups are twisted equally out of the plane of the central C*. The symmetry is destroyed by introducing an electron donor (e.g., Y = p-NH_2) in cation, or an electron acceptor (e.g., p-NO_2) in anion of one ring which causes an enhanced π-delocalization leading to a more coplanar Y-ring with sp^2 C*. This in turn will force the other (Y′) ring further out of the plane. Reference to Table 1 shows that in the ionic form the angle ϕ is reduced from the molecule ($\phi = 56.6°$ with Y = Y′ = H) with a larger decrease in the anionic form ($\phi = 7.7°$) than in the cationic form ($\phi = 17.7°$). This is related to a wider angle θ (133.0° vs 131.5°), a longer C*−ring bond length ($d_1 = d_2 = 1.424$Å vs 1.418Å), and of course a larger electronic charge on C* (−1.424 vs +0.056 electron unit) for the anionic than cationic form.

On the other hand, the solvent causes a greater twist, ϕ, by 6.2° compared to that in the gas phase for the *neutral* molecule, but ϕ is slightly reduced in the cation and anion upon solvation. The optimized geometries, bond lengths and bond angles, vary little upon solvation as can be seen in Table 1, and hence in the estimation of solvent effects on the ρ values application of the PCM model on the gas-phase geometries seems to be justified.

2. Effects of Substituent Y on $\rho_{Y'}$. *a. Cationic Systems.* The results of RHF and B3LYP calculations of $\rho_{Y'}^+$ values with variation of substituent Y are summarized in Table 2. In general, log $K_{Y'}^+$ is linearly correlated with $\sigma_{Y'}^+$ satisfactorily. The sign of $\rho_{Y'}^+$ is negative as expected for a process in which cationic charge develops on the functional center, C*. Electron donating substituent Y reduces the sensitivity of the cationic charge at C* to the substitution of Y′-ring: $\delta\sigma_{Y'}^+ < 0 \rightarrow \delta|\rho_{Y'}^+| < 0$. This decrease in $|\rho_{Y'}^+|$ is a result of the decrease in the cationic charge on C* due to electron donation from the Y-ring. Thus whenever the charge on C* is reduced by one ring, its sensitivity to the substituents on the other ring becomes weaker.[12] For example, a decrease in the cationic charge (Table 1) from +0.056 (Y = H) to +0.004 (Y= p-NH_2) with Y′ = H leads to a decrease in the magnitude of $\rho_{Y'}^+$ from −10.37 to −7.95.

The magnitude of $\rho_{Y'}^+$ is found to decrease as the level of calculation is raised, i.e., as the basis sets are increased from 3-21G* to 6-31+G* and also by accounting for electron correlation effect, RHF/6-31+G* → B3LYP/6-31+G*. There are two exceptions to the latter effect: For the strong delocalized systems with donors, p-NH_2 ($\sigma^+ = -1.30$) and p-OMe ($\sigma^+ = -0.78$), the magnitude of $\rho_{Y'}^+$ is actually greater (not smaller) for B3LYP than for RHF results. This can be attributed to the fact that electron correlation stabilizes delocalized electronic structure over localized ones, but RHF theory tends to be inaccurate in accounting for such effects.[13] Thus, for a more delocalized system with a stronger donor Y′, log $K_{Y'}$ value will be greater for B3LYP than for RHF leading to a steeper straight line Hammett plots for the former (Figure 1).

The smaller magnitude of $\rho_{Y'}^+$ ($\delta|\rho_{Y'}^+| < 0 \rightarrow \delta\rho_{Y'}^+ > 0$) for a stronger electron donor Y ($\delta\sigma_Y^+ < 0$) gives a negative CIC, $\rho_{YY'}^+$ ($= \partial\rho_{Y'}^+/\partial\sigma_Y^+ < 0$). This systematic decrease in $|\rho_{Y'}^+|$ with the increased electron donation from the Y-ring should result from a diminished polarization of the C*-C_6H_4Y system. The gas-phase CICs are much more negative with the RHF than with the DFT so that inclusion of electron correlation effect is essential for estimation of reasonably reliable CIC values.

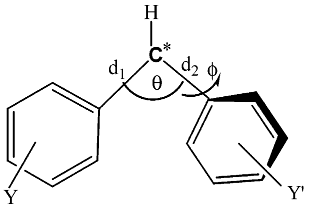
b. Anionic Systems. The RHF and B3LYP $\rho_{Y'}^-$ and $\rho_{Y'}^+$ values are summarized in Table 3. Linearities of the Hammett and CIC plots are satisfactory in all cases. The sign of $\rho_{Y'}^-$ is positive as the negative charge develops at C* in the deprotonation process. Since an electron withdrawing substituent in the

TABLE 1: Charges on C*[a] and Relevant Geometries[b] at B3LYP/6-31+G* Level

		neutral form					cationic form				
Y	Y′	charge	d_1	d_2	θ	ϕ	charge	d_1	d_2	θ	ϕ
p-NH$_2$	*p*-NH$_2$	−0.474	1.521	1.521	115.1	−56.70	−0.032	1.412	1.412	132.6	−14.76
	H	−0.478	1.519	1.520	115.0	−56.18	0.004	1.396	1.435	131.6	−22.73
	p-NO$_2$	−0.484	1.518	1.522	115.1	−46.16	0.007	1.390	1.444	130.9	−26.73
	H	−0.481	1.521	1.522	114.8	−56.61	0.056	1.418	1.418	131.5	−17.73
			(1.519)[c]	(1.522)	(114.5)	(−62.76)		(1.417)	(1.417)	(131.4)	(−17.61)
H			[1.520][d]	[1.521]	[114.3]	[−69.48]		[1.417]	[1.417]	[131.2]	[−18.21]
			{1.520}[e]	{1.521}	{114.5}	{−68.42}		{1.417}	{1.417}	{131.1}	{−18.15}
	p-NO$_2$	−0.487	1.520	1.521	114.6	−50.40	0.063	1.411	1.423	131.3	−20.63
p-NO$_2$	*p*-NO$_2$	−0.492	1.520	1.521	114.4	−56.51	0.074	1.420	1.420	131.2	−18.35
		neutral from					anionic form				
p-CH$_3$	p-CH$_3$	−0.480	1.521	1.521	114.8	−58.70	−0.403	1.424	1.424	132.7	−7.70
	H	−0.481	1.521	1.521	114.8	−57.98	−0.401	1.425	1.423	132.9	−7.04
	p-NO$_2$	−0.486	1.521	1.520	114.4	−55.65	−0.325	1.442	1.399	132.2	−7.50
	H	−0.481	1.521	1.522	114.8	−56.61	−0.416	1.424	1.424	133.0	−7.72
			(1.519)[c]	(1.522)	(114.5)	(−62.76)		(1.424)	(1.424)	(133.0)	(−5.82)
H			[1.520][d]	[1.521]	[114.3]	[−69.48]		[1.425]	[1.425]	[133.3]	[−2.98]
			{1.520}[e]	{1.521}	{114.5}	{−68.42}		{1.426}	{1.426}	{133.1}	{−4.43}
	p-NO$_2$	−0.487	1.520	1.521	114.6	−50.40	−0.341	1.441	1.400	132.4	−7.93
p-NO$_2$	p-NO$_2$	−0.498	1.520	1.521	114.4	−56.51	−0.302	1.417	1.417	132.7	−10.94

[a] NPA charges at the NBO−B3LYP/6-31+G* level. [b] Bond lengths and angles are in Å and degree, respectively. [c] Values in ( ) are in benzene at the CPCM-B3LYP/6-31+G* level. [d] Values in [ ] are in dichloroethan at the CPCM-B3LYP/6-31+G* level. [e] Values in { } are in acetonitrile at the CPCM-B3LYP/6-31+G* level.

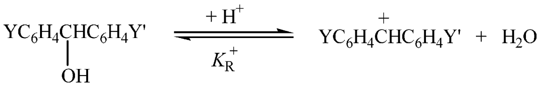
SCHEME 3



Y-ring ($\delta\sigma_{Y'}^{-} > 0$) reduces anionic charge on C*, the sensitivity of the charge on C* to the substitution of Y′-ring decreases, $\delta\sigma_{Y}^{-} > 0 \rightarrow \delta q_{C^*} < 0 \rightarrow \delta\rho_{Y'}^{-} < 0$. This is quite similar to the decrease in $|\rho_{Y'}^{+}|$ found with the decrease in the cationic charge by an electron donor Y in the cationic system noted above. Here again, the size of $\rho_{Y'}^{-}$ decreases as the basis sets are increased, whereas it increases as the electron correlation effect is included so that the size becomes greater for B3LYP than the corresponding RHF value. This is also attributed to the inaccurate estimation of energy stabilization by the RHF method for delocalized anionic systems with electron acceptor substituents. Since electron correlation (DFT) stabilizes the delocalized anions with electron acceptor Y′ substituents more than the localized ones,[13] log $K_{Y'}^{-}$ should be greater for electron acceptors and results in an increased slope of the Hammett plots relative to that with RHF theory (Figure 1).

The magnitude of $\rho_{Y'}^{-}$ decreases with an increase in the electron accepting power of the substituent Y, $\delta\sigma_{Y'}^{-} > 0 \rightarrow \delta\rho_{Y'}^{-} < 0$. This is of course due to the decrease in the anionic charge on C* by electron withdrawing of substituent Y. For example, a decrease in the anionic charge (Table 1) from −0.341 (Y = H) to −0.302 ($Y = p$-NO$_2$) with Y′ = *p*-NO$_2$ resulted in the decrease in $\rho_{Y'}^{-}$ from 12.74 to 8.95. The sign of $\rho_{YY'}^{-}$ becomes negative, $\rho_{YY'}^{-} = \partial\rho_{Y'}^{-}/\partial\sigma_{Y}^{-} < 0$.

3. Solvent Effects. The ρ_{Y}^{+} values of −4.22 in MeOH ($\epsilon = 32.66$), −4.15 in EtOH ($\epsilon = 24.55$) and −4.13 in 2-PrOH ($\epsilon = 19.92$) are reported for the solvolysis of monosubstituted benzhydryl chlorides at 25 °C.[14] Similarly, for the solvolysis of monosubstituted benzhydryl chlorides in 15(H$_2$O): 85(acetone)% (v/v) solution at 0 °C,[15] the estimated $\rho_{Y'}^{+}$ value is −4.10. The same value (−4.1) was also obtained for protonation equilibria (K_R^{+}) of the monosubstituted benzhydrols in aqueous sulfuric acid medium, eq 5.[16]


(5)

$$\underset{\text{OH}}{\underset{|}{\text{YC}_6\text{H}_4\text{CHC}_6\text{H}_4\text{Y}'}} \; \underset{K_R^{+}}{\overset{+\text{H}^{+}}{\rightleftharpoons}} \; \text{YC}_6\text{H}_4\overset{+}{\text{C}}\text{HC}_6\text{H}_4\text{Y}' + \text{H}_2\text{O} \qquad (5)$$

The DFT value of $\rho_{Y'}^{+} = -8.45$ in MeCN ($\epsilon = 35.94$) in Table 2 is ca. twice that of these values. The discrepancies may result from nonbulk (specific solvent) effects in the solvolysis, since we are assuming bulk effect only in our solvent effect studies. In the hydroxylic solvent the cationic charge on C* is dispersed or transferred to solvent by an n → p^{+} type charge-transfer interaction[17] from the lone pair electrons (2pπ type nonbonding orbital) on the oxygen atom to the cationic center C^{+} and as a result cationic charge is reduced leading to a reduced magnitude of $\rho_{Y'}^{+}$ values. There will also be a weak hydrogen bonding, in Scheme 4, in addition to the charge transfer by n → p^{+} interaction, which will also reduce the cationic charge on C*.

The magnitude of both $\rho_{Y'}^{+}$ and $\rho_{Y'}^{-}$ decreases with an increase in the dielectric constant ϵ of the solvent. This is due to the decrease in the energy of interaction (E) between two point charges (or dipoles) e_1 and e_2 at a distance r relative to the energy at infinite separation with an increase in ϵ, as given by the Coulomb's law,[18] eq 6

$$E = \frac{e_1 e_2}{\epsilon r} \qquad (6)$$

The $\rho_{Y'}$ values are linearly correlated with Kirkwood function,[19] f_K in eq 7. For Y = H the correlations are as given by eqs 8a and 8b

$$f_K = \frac{\epsilon - 1}{2\epsilon + 1} \qquad (7)$$

$$\rho_{Y'}^{+} = 4.02(\pm 0.17) f_K - 10.33(\pm 0.06);\ r = 0.998,\ n = 4 \qquad (8a)$$

$$\rho_{Y'}^{-} = -5.45(\pm 0.31) f_K + 12.68(\pm 0.11);\ r = 0.997,\ n = 4 \qquad (8b)$$

TABLE 2: Hammett $\rho_{Y'}{}^{+}$ Values and Cross-Interaction Constants, $\rho_{YY'}{}^{+}$, for Cation Formation[a]

		HF			DFT	CPCM		
Y	σ^+	3-21G*	6-31G*	6-31+G*	6-31+G*	benzene	$C_2H_4Cl_2$	MeCN
p-NH_2	−1.30	−7.67	−7.52	−7.38	−7.95	−6.47	−5.22	−4.99
p-OCH_3	−0.78	−8.95	−8.61	−8.41	−8.53	−7.45	−6.52	−6.42
p-CH_3	−0.31	−10.56	−10.23	−9.94	−9.25	−8.29	7.53	−7.38
H	0.00	−11.45	−11.00	−10.87	−10.37	−9.34	−8.58	−8.45
p-Cl	0.11	−11.42	−10.92	−10.72	−9.84	−9.01	−8.41	−8.03
m-Cl	0.37	−12.01	−11.56	−11.42	−10.36	−9.55	−8.89	−8.80
p-CN	0.66	−12.43	−12.08	−11.92	−10.53	−10.02	−9.65	−9.59
p-NO_2	0.79	−13.24	−12.64	−12.50	−10.93	−10.40	−9.99	−9.93
$\rho_{YY'}{}^{+}$		−2.56	−2.41	−2.43	−1.43	−1.85	−2.24	−2.29

[a] Correlation coefficients, $r > 0.98$

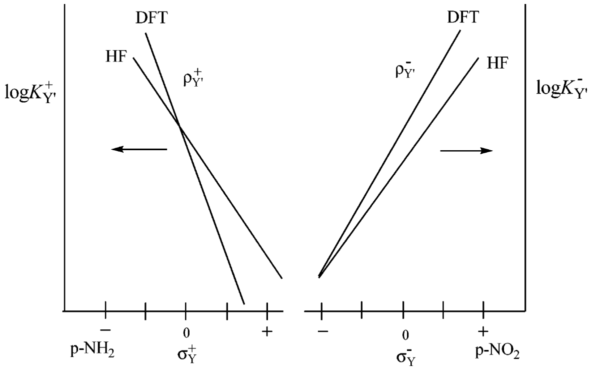


Figure 1. Schematic plots for the effect of stabilization (increase in $K_{Y'}$ values) by electron correlation (DFT). The $K_{Y'}{}^{+}$ for $\sigma_Y{}^{+} < 0$ and $K_{Y'}{}^{-}$ for $\sigma_Y{}^{-} > 0$ are lower for HF than for DFT due to inaccurate estimation of the stabilization by delocalization.

In contrast to the decrease in the magnitude of $\rho_{Y'}$ ($|\rho_{Y'}|$) with f_K, the magnitude of CICs increases with f_K, as given by eqs 9a and 9b

$$\rho_{YY'}{}^{+} = -1.82(\pm 0.05)f_K - 1.43(\pm 0.02);\ r = 0.999,\ n = 4 \tag{9a}$$

$$\rho_{YY'}{}^{-} = -2.22(\pm 0.17)f_{K\,-}\,2.55(\pm 0.06);\ r = 0.994,\ n = 4 \tag{9b}$$

The dependence of $\rho_{Y'}$ values on f_K is larger by more than two times than the corresponding dependence of $\rho_{YY'}$. This is as expected since the CICs are the second derivative and ρ_Y values are the first derivative parameters. We found no significant correlation between $\rho_{Y'}$ (or $\rho_{YY'}$) and the dielectric constant ϵ. Since the f_K values converge to 0.5 rapidly as ϵ is increased beyond ca. $\epsilon = 20$, both the $\rho_{Y'}$ and $\rho_{YY'}$ values stay practically constant within experimental error for solvents with ϵ greater than ca. 20 ($f_K = 0.463$). This means that the magnitude of ρ values will vary little with solvent provided only the bulk solvent effect is important for the reaction series. For example, the nearly constant $\rho_{Y'}{}^{+}$ values (−4.2) found for the solvolysis of benzhydryl chlorides in aqueous acetone[15] and the three alcohol solvents cited above[14] suggests that the bulk solvent effects are indeed small in the variation of ϵ (f_K) with nearly constant specific solvent effects for the solvolysis in the three alcohols. Similarly, the reaction constant ρ^* for polar effects of alkyl groups on bromination rates of alkenes calculated by Taft's equation, $\log(k/k_o) = \rho^*\Sigma\sigma^*$, is −3.1 in MeOH ($\epsilon$ = 32.66) which varies little with solvent changes to −3.1, −2.9, and −3.3 in acetic acid (ϵ = 6.17), 70% MeOH−H_2O and in H_2O (ϵ = 78.30), respectively.[20] This almost insignificant solvent sensitivity of ρ^* in bromination reflects the importance of bulk solvent effect in bromination, in contrast to the solvent dependence of ρ^* in solvolysis due to specific solvent effect.[21]

Experimentally, the $\rho_{YY'}{}^{+}$ value of −1.64 was obtained by estimation from the solvolysis rate data of benzhydryl chloride in 85(v/v)% acetone−water solution at 0 °C[15] and also from the protonation equilibria of disubstituted benzhydrols,[16] eq 5. Our DFT-CPCM value of −2.29 in MeCN (ϵ = 35.94) for the benzhydryl cation formation process is again larger since only the bulk solvent effect is considered. The discrepancy is again smaller than the corresponding discrepancy in $\rho_{Y'}$ values since the CICs are the second derivative parameters. As stated above, we expect a very small difference in the CIC value with solvent changes which will be within experimental error, since there is only a small change in f_K, and hence in the $\rho_{Y'}$ as well as $\rho_{YY'}$ value, above $\epsilon \cong 20$. For the bromination of 1,1-diphenylethylene, $\rho_{YY'}{}^{+}$ was −1.55 in MeOH at 25°C,[20] which is slightly smaller than that for the benzhydryl system (−1.64)[15,16] due to weak delocalization of cationic charge into C_β moiety (CH_2Br) in the transition state, Scheme 5.

For the benzhydryl system with a strong cationic charge development in the TS, the magnitude of the experimental $\rho_{YY'}{}^{+}$ value is estimated to be by far greater; for the solvolysis of α-CF_3-benzhydryl tosylates ($YC_6H_4{\cdot}CCF_3{\cdot}C_6H_4Y'$-OTs) in 80% EtOH−$H_2O$ at 25 °C gave $\rho_{YY'}{}^{+} = -5.5$ (r = 0.924, n = 3).[15] Although this value is a rough estimate, the large negative value obtained can be interpreted to indicate a strong cationic charge development in the TS. Thus, the CIC between substituents in the two rings of benzhydryl system also depend on the strength of charge developed on the functional center, C*, in the TS or in the equilibrium, suggesting that the magnitude of CIC is a function of change in the polarization of the molecule as a whole in the reaction in contrast to $\rho_{Y'}{}^{+}$ values which are dependent on the change in the polarization involving a single ring.

When there is another carbon (C_β) between the two rings, as in stilbene, the magnitude of CIC will be attenuated approximately by a falloff factor of 3.8 (3.5 from bromination)[20] which was experimentally obtained by the ratio of $\rho_\alpha{}^{+}/\rho_\beta{}^{+}$ from the dehydration of 1,2-diphenylethane.[20] For example, for the bromination of stilbenes in methanol, an estimated value of $\rho_{YY'}{}^{+}$ was −0.51.[20] This is a quite reasonable value compared with −0.61 estimated from the value of −2.3 (−2.3/3.8 = −0.61) for MeCN in Table 2 considering the attenuation due to an extra carbon inserted by a factor of 3.8.

The dependence of $\rho_{Y'}{}^{-}$ and $\rho_{YY'}{}^{-}$ on f_K is slightly greater than the corresponding values of $\rho_{Y'}{}^{+}$ and $\rho_{YY'}{}^{+}$, respectively. This seems to result from the stronger negative charge (q^-) in the anionic than the positive charge (q^+) in the cationic system on C*.

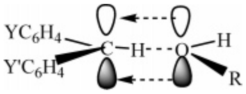
Experimental data on the anionic forms of benzhydryl system are very scarce, and comparison of our DFT results with experiments is limited. Since there will be strong hydrogen bonding of the anionic carbon center by hydroxylic (or protic) solvent molecules, the anionic charge will be reduced in the

TABLE 3: Hammett $\rho_{Y'}^{-}$ Values and Cross-Interaction Constants, $\rho_{YY'}^{-}$, for Anion Formation[a]

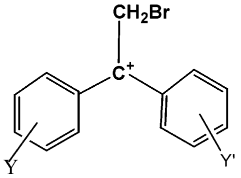
		HF			DFT	CPCM		
Y	σ^-	3-21G*	6-31G*	6-31+G*	6-31+G*	benzene	$C_2H_4Cl_2$	MeCN
p-CH_3	−0.17	14.29	13.27	12.83	12.94	11.71	11.01	10.75
H	0.00	14.02	13.08	12.64	12.74	11.33	10.28	10.16
p-Cl	0.19	12.82	12.08	11.89	12.32	11.02	9.93	9.88
m-Cl	0.37	12.80	11.95	11.56	12.15	10.75	9.84	9.63
m-CN	0.56	12.62	11.66	11.39	12.03	10.91	10.20	10.01
m-NO_2	0.71	12.28	11.48	11.18	11.19	9.89	8.67	8.58
p-CN	1.00	10.62	10.06	9.68	10.50	8.85	−7.59	7.36
p-NO_2	1.27	7.89	8.19	7.70	8.95	6.99	5.18	4.84
r$\rho_{YY'}^{-}$		−3.91	−3.22	−3.25	−2.59	−2.98	−3.54	−3.62

[a] Correlation coefficients, $r > 0.95$

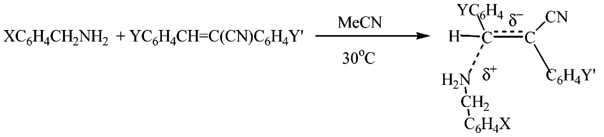
SCHEME 4



SCHEME 5



hydroxylic solvents by the specific solvation and hence the ρ values should be substantially smaller than our estimated values based on purely bulk solvent effects. We think therefore that our results of the ρ^- and the CICs will be substantially larger than the corresponding experimental values if available; this is exactly the same situation as we found with the cationic forms. In the nucleophilic additions of benzylamines to β-cyanostilbenes in acetonitrile at 30 °C,[22] eq 10, the $\rho_{YY'}^{-}$ value of −0.72 was obtained. The value compares satisfactorily with our theoretical value for the benzhydryl anion formation in acetonitrile, $\rho_{YY'}^{-} = -3.62$, considering that there is attenuation by a factor of ca. 3.8[20] by an extra carbon and that the value is for the activation process in which the charge development is ca. one-half of the full charge on the functional centers C_α and C_β since the reaction has progressed to approximately halfway through to completion.



$$XC_6H_4CH_2NH_2 + YC_6H_4CH{=}C(CN)C_6H_4Y' \xrightarrow[30^\circ C]{MeCN} H{-}\underset{\underset{\underset{C_6H_4X}{|}}{\underset{CH_2}{|}}}{\underset{H_2N\ \delta^+}{\vdots}}{\overset{YC_6H_4}{C}}\overset{\delta^-}{\cdots}C(CN)C_6H_4Y' \quad (10)$$

Conclusions

1. The Hammett coefficients, ρ^+ and ρ^-, are dependent on the charge developed on the functional center, C*. Thus, whenever the charge on C* is reduced by one ring (Y), its sensitivity to the substitution on the other ring, $\rho_{Y'}^{+}$ and $\rho_{Y'}^{-}$, becomes weaker.

2. The RHF theory cannot account for the stability induced by electron delocalization due to the electron-donor and -acceptor substituents in the cationic and anionic systems, respectively. As a result, the magnitude of the RHF $\rho_{Y'}^{+}$ and $\rho_{Y'}^{+}$ values for such systems becomes smaller than the corresponding DFT values.

3. The ρ (ρ^+, ρ^- and $\rho_{YY'}$) values are linearly correlated with the Kirkwood function, $f_K = \epsilon - 1/2\epsilon + 1$, but not with dielectric constant, ϵ, of the solvent.

4. The magnitude of ρ^+ and ρ^- values decreases, but that of the cross-interaction constant, $\rho_{YY'}$, increases, with the polarity (f_K) of the solvent.

5. Since the Kirkwood function, f_K, converges rapidly to 0.5 for ϵ greater than ca. 20, the ρ values stay practically constant beyond $\epsilon \cong 20$ as the solvent is changed ($\rho \cong$ constant for $\epsilon > 20$) within experimental errors.

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Supporting Information Available: Z matrices and energies. This material is available free of charge via the Internet at http://pubs.acs.org.

References and Notes

(1) (a) Lee, I. *Chem. Soc. Rev.* **1990**, *19*, 317. (b) Lee, I. *Adv. Phys. Org. Chem.* **1992**, *27*, 57. (c) Isaacs, N. S. *Physical Organic Chemistry*, 2nd ed.; Harlow: Essex, U.K., 1987; Chapter 4. (d) Miller, S. I. *J. Am. Chem. Soc.* **1959**, *81*, 101. (e) Cordes, E. H.; Jencks, W. P. *J. Am. Chem. Soc.* **1962**, *84*, 4319. (f) Dubois, J.-E.; Ruasse, M.-F.; Argile, A. *J. Am. Chem. Soc.* **1984**, *106*, 4840.

(2) (a) Lee, I. *J. Phys. Org. Chem.* **1996**, *9*, 661. (b) Lee, I.; Lee, H. W. *Collect. Czech. Chem. Commun.* **1999**, *64*, 1529. (c) Lee, I. *Chem. Soc. Rev.* **1995**, *24*, 223. (d) Lee, I.; Sung, D. D. *Curr. Org. Chem.* **2004**, *8*, 557.

(3) (a) Kim, C. K.; Lee, I. *Bull. Korean Chem. Soc.* **1997**, *18*, 395. (b) Lee, I.; Lee, D.; Lee, J. K.; Kim, C. K.; Lee, B.-S. *J. Chem. Soc., Perkin Trans. 2* **1996**, 2519. (c) Lee, D.; Kim, C. K.; Lee, B.-S.; Lee, I. *Bull. Korean Chem. Soc.* **1995**, *16*, 1203. (d) Lee, I.; Kim, C. K.; Chung, D. S.; Lee, B.-S. *J. Org. Chem.* **1994**, *59*, 4490.

(4) (a) Lee, I.; Kang, H. K.; Lee, H. W. *J. Am. Chem. Soc.* **1987**, *109*, 7472. (b) Lee, I.; Kim, H. Y.; Kang, H. K.; Lee, H. W. *J. Org. Chem.* **1988**,*53*, 2678. (c) Lee, I.; Shim, C. S.; Chung, S. Y.; Lee, H. W. *J. Chem. Soc., Perkin Trans. 2*, **1988**, 975. (d) Lee, I.; Choi, Y. H.; Rhyu, K. W.; Shim, C. S. *J. Chem. Soc., Perkin Trans. 2* **1989**, 1881.

(5) (a) Politzer, P.; Abu-Awwad, F.; Murray, J. S. *Int. J. Quant.Chem.* **1998**, *69*, 607. (b) Gross, K.; Seybold, P. G. *Int. J. Quantum Chem.* **2000**, *80*, 1107. (c) Gross, K.; Seybold, P. G. *Int.J. Quantum Chem.* **2001**, *85*, 569. (d) Gross, K.; Seybold, P. G.; Peralta-Inga, Z.; Murray, J. S.; Politzer, P. *J. Org. Chem.* **2001**, *66*, 6919. (e) Hollingworth, C. A.; Seybold, P. G..; Hadad, C. M. *Int. J. Quantum Chem.* **2002**, *90*, 1396.

(6) (a) Levine, I. N. *Quantum Chemistry*, 5th ed.; Prentice Hall: Upper Saddle River, NJ, 2000; Chapter 15. (b) Parr, R. G.; Yang, W. *Density Functional Theory of Atoms and Molecules*; Oxford University Press: Oxford, U.K., 1989. (c) Becke, A. D. *J. Chem. Phys.* **1993**, *98*, 5648. (d) Lee, C.; Yang, W.; Parr, R. G. *Phys. Rev. B* **1988**, *37*, 785.

(7) (a) Mennucci, B.; Tomasi, J. *J. Chem. Phys.* **1977**, *106*, 5151. (b) Miertus, S.; Scrocco, E.; Tomasi, J. *Chem. Phys.* **1981**, *55*, 117. (c). Tomasi, J.; Persico, M. *Chem. Rev.* **1994**, *94*, 2027. (d) Barone, V.; Cossi, M. *J. Phys. Chem. A* **1998**, *102*, 1995. (e) Eckert, F.; Klamt, A. *AIChE J.* **2002**, *48*, 369.

(8) Hansch, C.; Leo, A.; Taft, R. W. *Chem. Rev.* **1991**, *91*, 165.

(9) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Zakrzewski, V. G.; Mongomery, J. A.; Stratmann, R. E.; Burant, J. C.; Dapparich, S.; Millam, J. M.; Daniels, A. D.; Kudin, K. N.; Strain, M. C.; Farkas, O.; Tomasi, J.; Barone, V.; Cossi, M.; Cammi, R.; Mennuci, B.; Pomelli, C.; Adamo, C.; Clifford, S.; Ochterski, J.; Petersson, G. A.; Ayala, P. Y.; Cui, Q.; Morokuma, K.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Cioslowski, J.; Ortiz, J. V.; Stefanov, B. B.; Liu, G.; Lishenko, A.; Piskorz, P.; Komaromi, I.;

Gomperts, R.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Gonzalez, C.; Challacombe, M.; Gill, P. M. W.; Johnson, B. G.; Chem. W.; Wong, M. W.; Andres, J. L.; Head-gordon, M.; Replogle, E. S.; Pople, J. A. *Gaussian 98*, revision A.7; Gaussian, Inc.: Pittsburgh, PA, 1998.

(10) Liptak, M. D.; Shields, G. C. *J. Am. Chem. Soc*. **2001**, *123*, 7314.

(11) Reed, A. E.; Weinstock, R. B.; Weinhold, F. *J. Chem. Phys*. **1985**, *83*, 735.

(12) Neuvonen, H.; Neuvonen, K.; Pasanen, P. *J. Org. Chem*. **2004**, *69*, 3794.

(13) (a) Glendening, E. D.; Weinhold, F. *J. Comput. Chem*. **1998**, *19*, 610. (b) Glendening, E. D.; Badenhoop, J. K.; Weinhold, F. *J. Comput. Chem*. **1998**, *19*, 628. (c) Cramer, C. J. *Essentials of Computational Chemistry. Theories and Models*; Wiley: Chichester, U.K., 2002; Chapter 8.

(14) Nishida, S. *J. Org. Chem.* **1967**, *32*, 2692, 2695.

(15) Tsuno, Y.; Fujio, M. *Adv. Phys. Org. Chem*. **1999**, *32*, 267.

(16) Mindl, J.; Vecera, M. *Collect. Czech. Chem. Commun*. **1972**, *37*, 1143.

(17) (a) Kim, C. K.; Li, H. K.; Lee, B.-S.; Kim, C. K.; Lee, H. W.; Lee, I. *J. Org. Chem*. **2002**, *67*, 1953. (b) Lee, I.; Li, H. G.; Kim, C. K.; Lee, B.-S.; Kim, C. K.; Lee, H. W. *Bull. Korean Chem. Soc*. **2003**, *24*, 583. (c) Lee, I. *Int. Rev. Phys. Chem*. **2003**, *22*, 263.

(18) Hine, J. *Structural Effects on Equilibria in Organic Chemistry*; Wiley: New York, 1975; Chapter 2.

(19) Reichardt, C. *Solvents and Solvent Effects in Organic Chemistry*, 2nd ed.; VCH: Weinheim, Germany, 1988; Chapter 4.

(20) Ruasse, M. F. *Adv. Phys. Org. Chem*. **1993**, *28*, 207.

(21) Bentley, T. W.; Bowen, C. T.; Morten, D. H.; Schleyer, P. v. R. *J. Am. Chem. Soc*. **1981**, *103*, 5466.

(22) Oh, H. K.; Kim, I. K.; Sung, D. D.; Lee, I. Submitted to *Bull. Korean Chem. Soc*.