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Unusual π-Donating Effects of π-Accepting Substituents on the Stabilities of Benzylic Cations: A Theoretical Study

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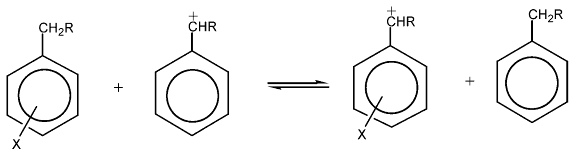
The π-donating effects of π-accepting X-substituents in substituted benzylic cations, $X-C_6H_5-CHR^+$ where $R = CF_3$, H and OCH_3, and X = *p*-NH_2, *p*-OCH_3, *p*-CH_3, H, *p*-F, *p*-Cl, *p*-CHO, *m*-CN, *p*-CN, *m*-NO_2 or *p*-NO_2, have been studied theoretically by using isodesmic hydride transfer reactions at various levels of theory. It might be difficult to determine the π-donating effects of π-acceptors using the simple Hammett-type linear equation, because it is not sensitive enough to include small π-donating effects. Therefore, this effect was estimated using the NBO deletion energy (ΔE_D) of the second-order charge-transfer interaction (ΔE_{ct}) between the π-orbitals (or lone pair orbitals) of the X-substituent and the π*-orbitals of phenyl ring. The extents of π-donating effects increased in the order X = *p*-NO_2 < *p*-CHO < *p*-CN ≪ *p*-Cl for both neutral and cationic species, and these effects were found to be more important for para- than for meta-substituents. Moreover, this could represent a general trend for π-donation by π-acceptors. On the other hand, the effects of R-substituents on this π-donating effect were found to be in the order R = OCH_3 < H ≅ CF_3, as predicted by natural resonance theory (NRT) analyses.

Introduction

Substituent effects on chemical equilibria or reaction rates have been extensively studied using linear free energy relationships (LFER) such as the Hammett[1] or Brönsted-type equation[2] to elucidate reaction mechanisms in physical organic chemistry. In particular, in the Hammett-type equation, substituent effects are managed using several different substituent constants, σ, σ^+ or σ^-, for reaction systems with different electronic demands.[3] However, it has been reported in theoretical[4] and experimental studies[5] that known π-electron acceptor substituents; e.g., nitro, cyano, or carbonyl groups destabilize carbocations less than is generally predicted by substituent constants. This indicates that carbocations might be stabilized to some extent by resonance between the π-orbital electrons on π-acceptors and an empty orbital in the cationic center. Therefore, these substituents could play important roles in many reactions proceeding via carbocationic intermediates, because reaction mechanisms and rates are affected by the stabilities of these intermediates.

In a previous study of conjugated cationic species,[6] $X-(CH{=}CH)_n-CH_2^+$, where $n = 1$ and 2, it was found that the stabilizing effects of cations decrease as the number of intervening vinyl groups, n, increases. This implies that π-electron demands are diminished in cations with $n = 2$, because the π-electron densities in these systems are more abundant than in those where $n = 1$. Therefore, the π-donating effects of π-acceptors are expected to decrease further in cationic species having relatively abundant π-electron densities. Indeed, this phenomenon has been reported by Reynolds et al. in para-substituted (X) benzyl cations, *p*-$X-C_6H_4-CH_2^+$, relative to allylic cations, $X-CH{=}CH-CH_2^+$, through analyses of π-electron densities.[4g]

As is well-known, the reactions of benzylic systems can proceed competitively via an S_N2 or S_N1 path when reaction conditions, such as reaction media, differ.[7] Therefore, the effects of π-acceptors are expected to play important roles in various reactions via an S_N1 path (which involves a benzylic cation intermediate) or via an S_N2 path (which involves a dissociative transition state (TS) with a partial positive charge at the reaction center). However, no detailed thermodynamically based quantitative analysis of the effects of π-acceptors has been reported. Therefore, in this work, the π-donating effects of π-acceptors in R-substituted benzylic cations, $R = CF_3$, H and OCH_3 were studied theoretically using isodesmic hydride transfer reactions, as shown in eq 1, at various levels of theory.



(1)

$R = OCH_3$, H and CF_3

X = p-NH_2, p-OCH_3, p-CH_3, H, p-F, p-Cl, p-CHO, m-CN, p-CN, m-NO_2 and p-NO_2

Calculations

All the calculations were performed using the Gaussian 98 program.[8] Stationary species were fully optimized at RHF and MP2(FC) levels with 6-31G(d) basis set and characterized by frequency calculations at the RHF level. The calculated energies were further refined using the CBS-4M[9] and G3(MP2)[10] methods using optimized geometries at the MP2(FC) level. To examine the π-donating effects of π-acceptors, natural bond

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TABLE 1: Hydride Ion Affinities[a] for Species with X = H in kcal mol^{-1}

R	RHF	MP2	CBS-4	G3(MP2)
OCH_3	236.0	247.0	217.9	214.1
	(169.4)	(184.4)	(215.9)	(209.5)
H	265.1	281.4	248.5	245.9
	(198.4)	(218.8)	(246.5)	(241.3)
CF_3	281.6	295.9	269.2	260.7
	(214.9)	(233.3)	(267.2)	(256.2)

[a] Values in parentheses are corrected values obtained using the experimental enthalpy[17] of −0.52630 Hartree for the hydride ion instead of the calculated value.

orbital (NBO)[11] and natural resonance theory (NRT) analyses,[12] as developed by Weinhold and co-workers, were carried out using the NBO-5.0 program[13] interfaced with the Gaussian 98 program.

Results and Discussion

(A) R-Substituent Effects on Relative Stabilities. To compare R-substituent effects on the stabilities of benzylic cations, hydride ion affinities (HIA) (defined as the negative value of the reaction enthalpy of eq 2 (HIA = $-\Delta H°$)) were

$$C_6H_5CHR^+ + H^- \rightarrow C_6H_5CH_2R \tag{2}$$

calculated at various theoretical levels, as summarized in Table 1. In a previous study,[14] we found that the calculated HIA values for small hydrocarbons showed larger absolute errors even at highly accurate theoretical levels such as the G2 and G3 levels. Because these errors were caused by inadequate considerations of the energy of the hydride ion, calculated HIA values were improved when experimental enthalpy was employed for the hydride ion instead of theoretical values. Similarly, the calculated HIA values of the benzyl cation (R = H) (Table 1) were much larger than the experimental value of 237.8 kcal mol^{-1}.[15] For example, the calculated HIA value shows an error (8.1 kcal mol^{-1}) larger than the experimental value even at the G3(MP2) level, although calculated values at the RHF and MP2 levels are unreliable due to the lack of a diffuse function for the hydride ion in the 6-31G(d) basis set. However, the calculated value of HIA at the G3(MP2) level becomes 241.3 kcal mol^{-1} when the experimental enthalpy of the hydride ion is used,[16] and this corrected value is relatively consistent with the experimental value. Therefore, corrected HIA values at the G3(MP2) level were used in the following discussions.

To study the effect of the R-substituent in detail, stabilization energy (SE) (defined as the difference in HIA between two substituents), is shown in eq 3. The calculated SE(H → OCH_3)

$$SE(X \rightarrow Y) = HIA(Y) - HIA(X) \tag{3}$$

in the benzylic system is −31.8 kcal mol^{-1}. However, the experimental[17] and calculated SE(H → OCH_3) values for substituted-methyl cations, $R{-}CH_2^+$, are −69.0 and −74.8 kcal mol^{-1}, respectively. This indicates that the stabilizing effect of R = OCH_3 in benzylic cations is smaller than that in methyl cations. Similarly, the destabilizing effect of R = CF_3 relative to R = H might also be smaller in benzylic cations. However, direct comparisons are not feasible in this case, because the corresponding methyl analogue, $CF_3{-}CH_2^+$, does not exist as a stable structure at the MP2/6-31G(d) level.[18] This suggests that destabilization by the CF_3 substituent in the methyl cation is large compared to SE(H → CF_3) = 14.9 kcal mol^{-1} for the benzyl cation. Therefore, the R-substituent effects on the relative stabilities of benzylic cations, $C_6H_5{-}CHR^+$, are smaller than those of substituted-methyl cations, $R{-}CH_2^+$, in stabilizing the phenyl ring.

TABLE 2: Gibbs Free Energy Changes ($\Delta G°$, kcal mol^{-1}) for Isodesmic Reactions, Eq 1, with R = H at 298 K

X	$\sigma^{+\,a}$	HF/6-31G*	MP2/6-31G*	CBS-4	G3(MP2)
p-NH_2	−1.30	−25.4	−25.3	−26.8	−26.7
p-OCH_3	−0.78	−17.0	−17.0	−16.2	−18.9
p-CH_3	−0.31	−7.0	−6.5	−5.6	−7.4
H	0.00	0.0	0.0	0.0	0.0
p-F	−0.07	0.3	0.3	−3.2	−0.6
p-Cl	0.11	3.8	1.4	1.6	−0.5
p-CHO	0.42	9.7	7.1	6.8	7.5
m-CN	0.56	14.3	14.5	11.3	13.3
p-CN	0.66	16.1	12.4	11.3	12.7
m-NO_2	0.71	16.2	16.0	11.5	14.1
p-NO_2	0.78	21.4	14.3	13.0	15.0
$\rho_X^{+\,b}$		−16.3	−14.8	−14.1	−15.3

[a] Values are taken from ref 19a. [b] Regression coefficients are better than 0.99 in all cases.

TABLE 3: Gibbs Free Energy Changes ($\Delta G°$, kcal mol^{-1}) for Isodesmic Reactions, Eq 1, with R = OCH_3 at 298 K

X	$\sigma^{+\,a}$	HF/6-31G*	MP2/6-31G*	CBS-4	G3(MP2)
p-NH_2	−1.30	−16.8	−15.3	−15.3	−16.1
p-OCH_3	−0.78	−10.2	−9.1	−9.2	−10.3
p-CH_3	−0.31	−4.5	−3.9	−4.1	−4.5
H	0.00	0.0	0.0	0.0	0.0
p-F	−0.07	1.3	1.4	1.4	1.0
p-Cl	0.11	5.6	4.0	3.0	3.0
p-CHO	0.42	9.0	6.7	6.6	7.4
m-CN	0.56	12.7	12.4	11.9	11.5
p-CN	0.66	13.2	10.2	10.2	10.8
m-NO_2	0.71	13.7	13.0	11.9	11.9
p-NO_2	0.78	16.6	11.1	11.7	12.2
$\rho_X^{+\,b}$		−11.9	−11.2	−10.1	−10.6

[a] Values are taken from ref 19a. [b] Regression coefficients are better than 0.99 in all cases.

TABLE 4: Gibbs Free Energy Changes ($\Delta G°$, kcal mol^{-1}) for Isodesmic Reactions, eq 1, with R = CF_3 at 298 K

X	$\sigma^{+\,a}$	HF/6-31G*	MP2/6-31G*	CBS-4	G3(MP2)
p-NH_2	−1.30	−28.2	−28.6	−33.1	−29.6
p-OCH_3	−0.78	−17.9	−18.2	−22.4	−19.7
p-CH_3	−0.31	−6.9	−6.4	−10.4	−7.2
H	0.00	0.0	0.0	0.0	0.0
p-F	−0.07	−0.3	−0.6	−4.8	−1.4
p-Cl	0.11	2.9	0.2	−5.0	−1.7
p-CHO	0.42	9.3	7.2	4.6	7.7
m-CN	0.56	14.1	14.3	10.9	13.5
p-CN	0.66	15.3	11.6	8.8	11.8
m-NO_2	0.71	15.8	15.3	11.2	13.6
p-NO_2	0.78	21.0	13.7	11.8	14.4
$\rho_X^{+\,b}$		−16.8	−15.6	−16.1	−15.9

[a] Values are taken from ref 19a. [b] Regression coefficients are better than 0.99 in all cases.

(B) π-Donating Effects of π-Accepting X-Substituents. Gibbs free energy changes ($\Delta G_g°$) for gas-phase isodesmic hydride transfer reactions (eq 1), calculated at various theoretical levels at 298 K, are summarized in Tables 2−4. The electronic energies of the neutral and cationic species have been collated in Supporting Information (Tables S1−S3). In general, the Gibbs free energy changes were well reproduced within 5 kcal mol^{-1}, when electron correlations were included in the computations at the MP2, CBS-4M and G3(MP2) levels. This indicates that our analyses of the π-donating effects of X-substituents are sufficiently reliable even at the MP2 theory level. However, the energy changes derived from the π-donating effects of

π-acceptors might be small in an absolute sense, because these are self-evidently secondary effects of π-accepting substituents. Therefore, in this work, π-donating effects were analyzed by using results from the highest theory level, i.e., G3(MP2).

The Hammett equation,[1] eq 4a, is commonly used to correlate equilibrium or rate constants changes with substituent changes. The left-hand side of this equation can be substituted by the Gibbs free energy change of reaction (or the Gibbs free energy change of activation) as is shown in eq 4b. Note that σ^+ values

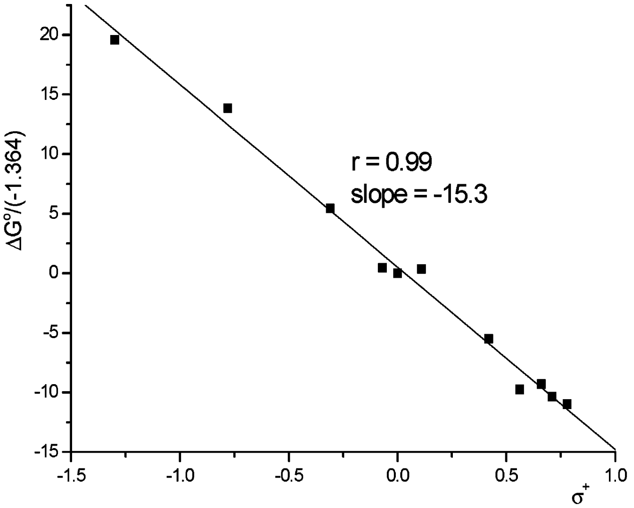
$$\log (K_X/K_H) = \rho_X^+\sigma^+ + \text{constant} \tag{4a}$$

$$-\frac{\Delta G°}{2.3RT} = \rho_X^+\sigma^+ + \text{constant} \tag{4b}$$

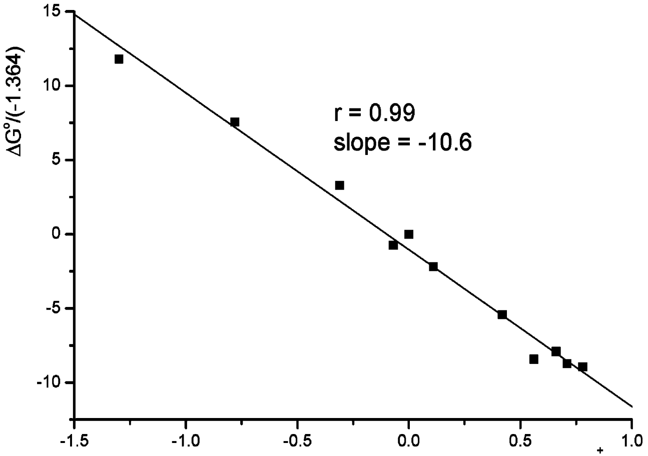
(and hence ρ^+) were used to consider positive charge development at the reaction center.[19] Plots of eq 4b are depicted in Figure 1 and the slopes (ρ_X^+) are also summarized in Tables 2−4. These figures show excellent linearity ($r > 0.99$) and the absolute magnitudes of slopes, $|\rho_X^+|$, increase in the order R = OCH_3 < H ≅ CF_3, although the $|\rho_X^+|$ for R = CF_3 is slightly larger than for R = H. This indicates that the X-substituent effects are larger for R = CF_3 and H than for R = OCH_3. These results well agree with the analyses of resonance structures; i.e., the effects of ring substituents (X) on the stabilities of cations are larger for R = CF_3 (and/or R = H) than R = OCH_3 due to the relatively large contribution to a resonance structure between the phenyl ring and the benzylic carbon center is the larger for R = CF_3 and H as compared to R = OCH_3 (vide infra).

On the other hand, such excellent linearities ($r > 0.99$) seem to imply that the π-donating effects of π-acceptors are absent in the benzylic cations studied in this work, because these linearities would be expected to deteriorate if anomalous effects exist. However, close examination of Tables 2−4 reveals some interesting features about electron-withdrawing X-substituents; i.e., calculated ΔG_g° values are more stabilized for some X-substituents than might be expected from their σ^+ values. For example, the destabilizing effects of *p*-CN should be larger than those of *m*-CN, because the σ^+ value is larger for *p*-CN than for *m*-CN. However, the ΔG_g° values of *p*-CN are more favorable by 0.7 (R = OCH_3), 0.6 (R = H) and 1.7 kcal mol^{-1} (R = CF_3) than the corresponding values of *m*-CN at the G3(MP2) level. Moreover, the ΔG_g° values of *p*-Cl ($\sigma_p^+ = 0.11$) are negative for R = H and CF_3, indicating that the stabilizing effects of X = *p*-Cl are larger than those of X = H. This means that additional stabilizing effects are operative in the cases of *p*-Cl and *p*-CN and these additional stabilizing effects could be caused by the π-donating effects of these substituents. Based on the above analyses, it is probably difficult to quantify the π-donating effects of π-acceptors using a simple Hammett-type equation, eqs 4; i.e., the linear equation is not sensitive enough to identify such a small π-donating effects. However, we find that these additional stabilizing effects, π-donating effects, cannot be reproduced correctly at relatively low levels theory such as RHF and MP2 levels (see Table 2−4).

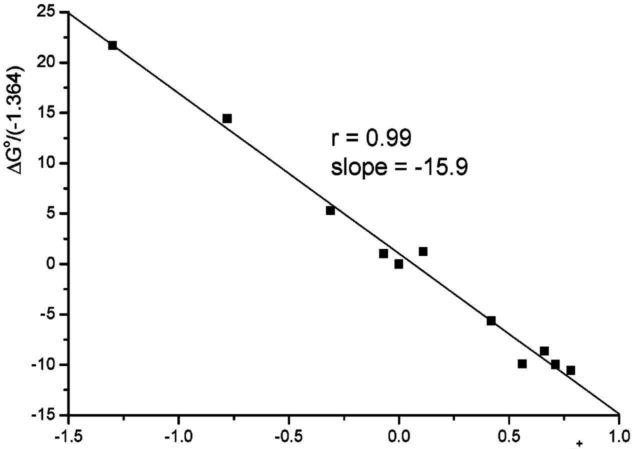
If ΔG_g° values reflect the total effect of substituents, it would be interesting to determine the pure π-donating effect of a given π-accepting X-substituent. The magnitude of a π-donating effect that contributes to ΔG_g° could be estimated from the second-order charge-transfer energy (ΔE_{ct})[20] between the π-orbitals (or lone pair orbitals) of the X-substituent and the π*-orbitals of the phenyl ring, because the π-donating effect (of π-acceptors) will clearly originate from the proximate $\pi-\pi$* interaction between these two orbitals. One way of estimating such an effect is to calculate the deletion energy (ΔE_D),[13,21] which represents the energy change caused by deletion of ΔE_{ct} between two interacting orbitals. Calculated ΔE_D values at the NBO-RHF/6-31G*//MP2/6-31G* level for X-substituents with $\sigma^+ > 0$ are summarized in Table 5. An examination of Table 5 shows that the magnitudes of ΔE_D for cationic species are larger than those of neutral species, which have no electron deficient center, as was reported in a previous paper for cationic species, X−(CH=



(a)R=H



(b) R=OCH_3



R=CF_3

Figure 1. Plots of $\Delta G°/1.364$ versus σ^+ values at the G3(MP2) level.

TABLE 5: Deletion Energies (ΔE_D) and Differences in Deletion Energies ($\delta\Delta E_D$)[a] Calculated at the NBO−RHF/6-31G*//MP2/6-31G* Levels (kcal mol^{-1})

		R = OCH_3		R = H		R = CF_3	
		ΔE_D	$\delta\Delta E_D$	ΔE_D	$\delta\Delta E_D$	ΔE_D	$\delta\Delta E_D$
p-Cl	neutral	9.7	4.1	9.5	10.4	10.0	11.7
	cation	13.8		19.9		21.7	
p-CHO	neutral	3.7	0.8	3.8	2.4	3.9	2.6
	cation	4.5		6.1		6.5	
m-CN	neutral	5.6	1.1	5.7	1.3	5.6	1.5
	cation	6.6		6.9		7.2	
p-CN	neutral	5.4	3.3	5.4	6.1	5.7	6.8
	cation	8.8		11.5		12.4	
m-NO_2	neutral	2.1	−0.1	2.2	1.3	2.1	1.4
	cation	2.0		3.4		3.5	
p-NO_2	neutral	2.1	1.8	2.9	0.5	2.1	2.4
	cation	3.9		3.4		4.5	

[a] $\delta\Delta E_D = \Delta E_D(\text{cation}) - \Delta E_D(\text{neutral})$.

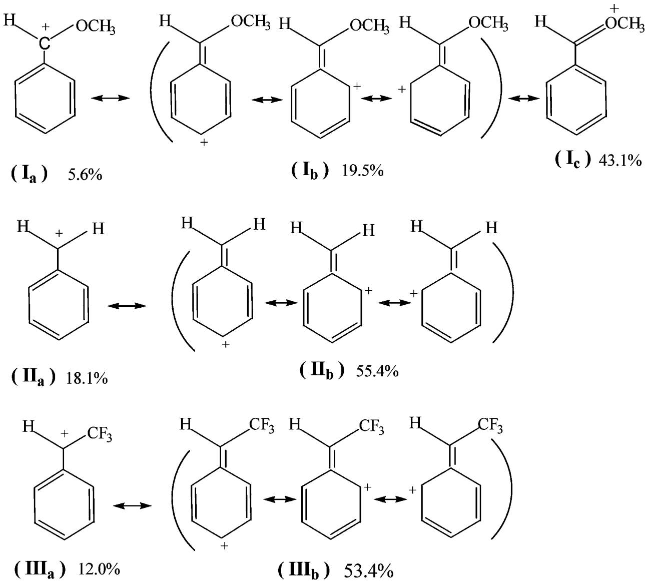
$CH)_n-CH_2^+$.[6] The ΔE_D's of cationic species increase in the order R = OCH_3 < H < CF_3 as would be expected from the electron donating/accepting abilities of these R-substituents. However, the ΔE_D values for some X-substituents in neutral species are nearly the same regardless of R-substituents, indicating that the π-donating effects of R-substituents are negligibly small. For example, the ΔE_D's of X = Cl in cationic species are 13.8, 19.9, and 21.7 kcal mol^{-1} for R = OCH_3, H and CF_3, respectively, but the corresponding ΔE_D's of neutral species are invariably ca. 10 kcal mol^{-1}. This indicates that the R-substituent plays a more important role in cationic species.

The magnitude of ΔE_D values increases in the order X = NO_2 < CHO < CN ≪ Cl for both neutral and cationic species as X-substituents vary, indicating that the π-donating effect is the largest for X = Cl. This order is wholly consistent with the previous results obtained for conjugated cationic species, $X-CH{=}CH-CH_2^+$ and $X-(CH{=}CH)_2-CH_2^+$, although the absolute magnitudes of ΔE_D values gradually decrease in the order $X-CH{=}CH-CH_2^+ > X-(CH{=}CH)_2-CH_2^+ > X-C_6H_4-CHR^+$. Therefore, the ordering, X = NO_2 < CHO < CN ≪ Cl, could represent a general trend for the π-donating abilities of π-acceptors.

(C) Resonance Structures. The relatively high stabilities of benzylic cations originate from resonance interactions between the phenyl ring and the cationic benzylic carbon center.[22] To examine the effects of R-substituent on the stabilities of benzylic cations, contributions of resonance structures with X = H were analyzed using the NRT method[12] at the NBO-RHF/6-31G(d)//MP2/6-31G(d) level. The calculated percentage weights (wt %) of some important resonance structures are presented in Scheme 1.

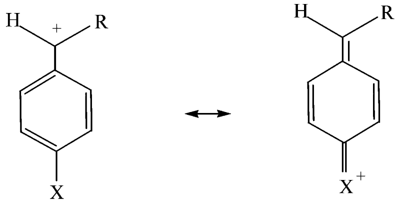
As expected, the wt % of the resonance structure $\mathbf{II_b}$ was found to be about three times that of resonance structure $\mathbf{II_a}$ in a simple benzyl cation (R = H). Similarly, $\mathbf{III_b}$ was found to be the most important resonance structure for R = CF_3, indicating that benzylic carbon stabilization is mainly achieved by the π-donating effect of the phenyl ring. Moreover, similar contributions in the wt %'s of $\mathbf{II_b}$ and $\mathbf{III_b}$ are quite well consistent with the $|\rho_X^+|$ values discussed above; i.e., the $|\rho_X^+|$ values are similar for R = CF_3 and H and their magnitudes would be expected to depend largely on the contributions of resonance structures $\mathbf{II_b}$ and $\mathbf{III_b}$. On the other hand, for the methoxy benzyl cation (R = OCH_3), the resonance structure $\mathbf{I_c}$ is the most important, and resonance structure $\mathbf{I_b}$ contributes only by about half of $\mathbf{I_c}$. This indicates that the stabilizing effect of R = OCH_3 is larger than that of the phenyl ring.

SCHEME 1



The contributions of the wt %'s of resonance structures could be confirmed by the bond length (d_{C-C}) between benzyl carbon and *ipso* carbon of phenyl ring. The d_{C-C} in neutral species with X = H are similar in all cases (R = OCH_3, 1.503 Å; R = H, 1.506 Å; R = CF_3, 1.507Å). However, in cationic species, the d_{C-C} is much longer for R = OCH_3 (1.422 Å) compared to that for R = H (1.374) or CF_3 (1.375 Å). Therefore, bond length changes are also agree well with the contributions of the wt %'s of resonance structures shown in Scheme 1.

(D) Structural Effects on π-Donation by π-Acceptors. Table 5 shows that ΔE_D values are nearly independent of the locations of X-substituents, i.e., meta or para, in neutral species. However, these values are much larger for the para-position than for the meta-position in cationic species. For example, the ΔE_D values for R = H are 5.7 and 5.4 kcal mol^{-1} for *m*-CN and *p*-CN, respectively, in neutral species, but the corresponding values are 6.9 and 11.5 kcal mol^{-1} in the respective cationic species. These results could be simply explained using resonance structures, i.e., in cationic species with *p*-X, the delocalized resonance structure, **IV**, which can stabilize the cationic benzylic carbon center directly, could be an important resonance structure as noted above. However, such a resonance structure is in principle not possible for cationic species with *m*-X. As a result, *the above* indicates that the π-donating effects of π-acceptors are more important for para than for meta substituents.



(IV)

Nevertheless, Table 5 shows some interesting features for X = NO_2; i.e., the ΔE_D values for cationic species with *m*-NO_2 and *p*-NO_2 are not very different. Moreover, the ΔE_D values of the cationic species with *p*-NO_2 is slightly larger for R = OCH_3 than for R = H. These results seem to be somewhat extraordinary. However, a close examination of the optimized structures reveals a clue. In many cationic species, the X-substituents are coplanar with the aromatic ring to maximize proximate $\pi-\pi^*$ interactions. However, this is not possible for *p*-NO_2 with R = H or CF_3; i.e., the NO_2 group deviates from the aromatic plane by ca. 7° and 10° for these respective R groups. These distortions are necessary to reduce unfavorable excess electron withdrawal from the electron deficient benzylic fragments by the *p*-NO_2 substituent. And as a result of this distortion, the ΔE_D values for *m*-NO_2 and *p*-NO_2 become almost the same, although the π-donating effect is nevertheless expected to be larger for *p*-X.

Conclusion

The π-donating effects of π-accepting X-substituents in substituted benzylic cations, $X-C_6H_5-CHR^+$, could not be determined by using the simple Hammett-type linear equation, because the Hammett-type equation is not so sensitive as to include small π-donating effects. Moreover, these effects might not be reproduced correctly at relatively lower level theory such as RHF and MP2 levels. Instead, an accurate level of theory such as the G3(MP2) employed in this work could be used to clarify such a small effect correctly. We found that the deletion energy and NRT analyses were very useful tools for studying the π-donating effects of π-accepting substituents.

Acknowledgment. This work was supported by Korea Research Foundation Grant (KRF-2002-070-C00061).

Supporting Information Available: Summary of the electronic energies for isodesmic reactions with R = H (Table S1), R = OCH_3 (Table S2), and R = CF_3 (Table S3). This material is available free of charge via the Internet at http://pubs.acs.org.

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