Theoretical Reevaluation of the π-Donating Effect of Electron-Withdrawing Substituents in the Conjugated Cationic Systems

In Suk Han, Chang Kon Kim, Chan Kyung Kim, Hai Whang Lee, and Ikchoon Lee*

Department of Chemistry, Inha University, Inchon 402-751, Korea

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The π-donating effects of acceptor substituents are investigated theoretically using the high-level ab initio calculations for the isodesmic reactions, $X{-}(CH{=}CH)_n{-}CH_3 + (CH_2{=}CH)_n{-}CH_2^+ \rightarrow X{-}(CH{=}CH)_n{-}CH_2^+ + (CH_2{=}CH)_n{-}CH_3$ where $n = 1$ and 2 and X = NH_2, OCH_3, F, H, Cl, CHO, CF_3, CN, and NO_2. Electron delocalization is enhanced in the cationic systems and also by accounting for electron-correlation effect. The reaction energies ($\Delta H°$), bond-length changes (Δd), and electronic charge shifts (Δq_π) do not provide a reliable measure of the π-donating ability of the acceptor substituents. In contrast, the percentage contribution of resonance structures (wt %) by the natural resonance theory (NRT) analysis and the energy changes due to deletion of the relevant π orbitals (ΔE_D) are the better methods of evaluating the π-donating behaviors. Proper accounting of the stabilization energies due to π-donation by the electron acceptors in the conjugated cationic species is only possible with the high-level correlated methods. In contrast to the earlier reports that the two strong acceptors, X = CF_3 and NO_2, have some π-donating ability under strong π-electron demand conditions, the NRT and ΔE_D analyses do not support such an effect. We conclude that the π-donating effect of π-acceptors increases in the order X = CHO < CN < Cl. Stabilization of the correlated energies with X = CF_3 and NO_2 is almost entirely due to n−σ*-type charge-transfer delocalization.

Introduction

The substituent effects on the reaction mechanisms and reactivities have been extensively studied, and general characteristics of the substituent effects have been well-established long ago. However, the fact that substituents known as typical π-acceptors such as CN and CHO can act as π-donors in cationic species has been reported theoretically[1] as well as experimentally.[2] For example, Paddon-Row et al.[1a] have shown that formyl and cyano substituents operate as π-donors in unconjugated cationic species, $R^1(R^2)C^+{-}X$ (R^1 and R^2 = H or alkyl and X = CN, CHO, or CF_3) through ab initio calculations with the STO-3G and 4-31G basis sets. Similar results have also been reported by Reynolds et al.[1b] for conjugated and aromatic cationic species, $XCH{=}CHCH_2^+$ and $XC_6H_4CH_2^+$. These theoretical works on the π-donating behaviors of the acceptors in the cationic species have been experimentally supported by the ^{13}C NMR studies of the diaryl α-carbonyl cations, $(Ph)_2C^+$-COR.[2a]

Notwithstanding, one fundamental problem as to the precise nature of the π-donating behavior of acceptors still remains because most of the earlier theoretical works have been carried out at uncorrelated Hartree−Fock levels with relatively small basis sets. Thus, the results of the earlier theoretical works may be inaccurate qualitatively as well as quantitatively, for example, CHO- and CF_3-substituted methyl cations are not stable stationary species at the MP2 level,[3] although Paddon-Row et al. in their work have concluded that the two substituents have π-donating characters.[1a]

In this work, we have carried out high-level ab initio calculations using the complete basis set (CBS)[4] and Gaussian-3 (G3)[5] methods for the two hypothetical isodesmic hydride transfer reactions of conjugated cationic systems, eq 1, to

$$X{-}(CH{=}CH)_n{-}CH_3 + (CH_2{=}CH)_n{-}CH_2^+ \rightarrow X{-}(CH{=}CH)_n{-}CH_2^+ + (CH_2{=}CH)_n{-}CH_3 \quad \text{where}\quad X = NH_2, OCH_3, CH_3, H, F, Cl, CHO, CF_3, CN, NO_2 \quad \text{and} \quad n = 1{-}2 \qquad (1)$$

elucidate the π-donating effects of acceptors more precisely. However, the analyses of the pure π-donating behaviors of acceptors using the reaction energies only are probably not valid because the mutually compensating effects, that is, the favorable electron-donating and unfavorable accepting effects by the X-substituent, will be reflected in the reaction energies of eq 1. In other words, if the degree of π-accepting ability of the X-substituent is relatively larger than that of π-donating ability, the reaction energy will be highly unfavorable even though the absolute magnitude of the π-donating effect is substantial. The analyses using the π-charge densities can be also ambiguous because the calculated charge densities are largely dependent on the calculation methods as is well-known.[6] In this work, we have analyzed further the π-donating behaviors of π-acceptors using the natural resonance theory (NRT)[7] developed by Weinhold and co-workers together with the analyses using the energetics, charge densities, geometries, etc. The NRT method, which provides the relative weights of resonance structures, gives a reasonably quantitative description of the subtleties of electronic delocalization in a compact, chemically intuitive language.

Calculations

The Gaussian 98 program package[8] with standard Pople-type basis sets was used throughout. All stationary point species in

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* To whom correspondence should be addressed. E-mail: ilee@inha.ac.kr. Fax: +82-32-865-4855.

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TABLE 1: The Calculated Reaction Enthalpies ($\Delta H°$ in kcal mol^{-1}) at 298 K for the Isodesmic Reactions with $n = 1$ in Eq 1

X	RHF[a]	MP2[a]	B3LYP[a]	CBS-Q	G3	$\delta\Delta H°$ [b]
NH_2	−46.74	−52.36	−50.09	−51.36	−51.14	−4.40
OCH_3	−30.77	−34.59	−33.91	−34.76	−34.69	−3.92
CH_3	−13.35	−14.43	−16.37	−15.25	−15.27	−1.92
F	−2.71	−5.62	−6.56	−5.85	−5.18	−2.47
H	0.00	0.00	0.00	0.00	0.00	0.00
Cl	0.67	−5.70	−6.21	−7.93	−8.17	−8.84
CHO	13.41	9.38	9.90	10.44	10.43	−3.26
CF_3	16.57	14.81	11.96	15.80	14.94	−1.63
CN	19.74	14.77	12.28	12.17	14.21	−5.53
NO_2	31.74	20.72	19.34	19.45	19.86	−11.88

[a] 6-31G* basis set was used. [b] $\delta\Delta H° = \Delta H°_{G3} - \Delta H°_{RHF}$.

TABLE 2: The Electronic Energy Changes (ΔE in kcal mol^{-1}) for the Isodesmic reactions with $n = 1$ in Eq 1 Obtained at the RHF Level[a]

X	6-31G*	6-31+G*	6-31G(2df,p)	6-311+G(3d2f,2df,2p)	$\delta\Delta E$[b]
NH_2	−47.65	−47.03	−47.68	−47.17	0.66
OCH_3	−31.19	−31.02	−32.02	−31.73	−0.51
CH_3	−13.08	−13.53	−13.59	−14.21	−1.05
F	−2.95	−1.65	−4.51	−3.10	−0.14
H	0.00	0.00	0.00	0.00	0.00
Cl	0.54	−0.31	−0.95	−2.35	−2.99
CHO	13.89	14.95	13.58	15.04	2.03
CF_3	16.87	18.22	15.38	17.80	1.13
CN	20.39	20.50	20.26	20.59	0.54
NO_2	42.77	43.18	39.77	40.84	−1.93

[a] Single point calculations using MP2/6-31G* geometry. [b] $\delta\Delta E = \Delta E_{RHF/6-311+G(3d2f,2df,2p)} - \Delta E_{RHF/6-31G*}$.

the hypothetical isodemic hydride transfer reactions, eq 1, were fully optimized and were verified by the vibrational frequency calculations[9] at the RHF, B3LYP,[10] and MP2[11] levels with the 6-31G* basis set.[12] The calculated energies were further refined by the modified CBS-Q[4] and Gaussian-3 (G3)[5] methods for the reactions with $n = 1$ in eq 1 using the optimized geometries and thermochemical properties obtained at the MP2 level. For the reactions with $n = 2$ in eq 1, the calculations were limited up to the modified CBS-4 level[4] because CBS-Q and G3 calculations require enormous computational time and cost for the large reaction systems with more than five non-hydrogen atoms. The natural bond orbital (NBO)[13] and natural resonance theory (NRT)[7] analyses were also carried out using the NBO-4M program[14] interfaced to the Gaussian 98 program.

Results and Discussion

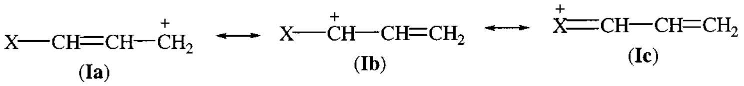
(A) Energetics. The reaction enthalpies, $\Delta H°$, for the hypothetical isodesmic reactions with $n = 1$ in eq 1 calculated at various theoretical levels are summarized in Table 1. The zero-point-corrected electronic energies (E_{ZPE})[15] of the neutral and cationic species are collected in Supporting Information (**S1**). It is generally known that the reaction energies of isodesmic reactions such as eq 1 are reproduced well even by simple computational methods[16] because the changes in the electron correlation energies are usually small because of the conservation of the number of bonds of equal types in reactants and products. However, examination of Table 1 shows that the $\Delta H°$ values obtained at the uncorrelated restricted Hatree−Fock (RHF) level are generally less exothermic or more endothermic than those at the correlated levels, that is, inclusion of electron correlation energies generally lowers the reaction enthalpies ($\delta\Delta H° = \Delta H°_{corr} - \Delta H°_{RHF} < 0$) as shown for $\delta\Delta H° = \Delta H°_{G3} - \Delta H°_{RHF}$ in Table 1.

Nevertheless, it is not certain whether the results of $\delta\Delta H° < 0$ were solely caused by the electron correlation effects, because, as is well-known, the results obtained by the CBS and G3 calculations include the mixed basis set effects. So, we have examined the basis set effects on the reaction energies (ΔE), and the results are collected in Table 2. However, as can be seen in Table 2, the variations of ΔE by basis set changes are, in general, small within 1.2 kcal mol^{-1} excepting for X = Cl, CHO, and NO_2 indicating that the basis set effects are relatively smaller than the electron correlation effects. For example, in the case of X = CN, $\delta\Delta E$ (= ΔE(RHF/6-311+G(3d2f,2df,2p) − ΔE(RHF/6-31G*)), which reflects the effect of the larger basis set, is only 0.54 kcal mol^{-1} (Table 2). Whereas $\delta\Delta H°$ (= $\Delta H°_{G3} - \Delta H°_{RHF}$), which includes both of the basis set and electron correlation effects, is −5.53 kcal mol^{-1} (Table 1). Even in the case X = Cl, $\delta\Delta H°$ is −8.84 kcal mol^{-1} but $\delta\Delta E$ is only −2.99 kcal mol^{-1}, albeit the $\delta\Delta E$ of X = Cl is the largest among those studied in this work. It appears, therefore, that the electron correlation effects are much more important than the basis set effects in the reactions of eq 1.

On the other hand, we note that all substituents irrespective of whether they are electron donors ($\delta\sigma < 0$) or acceptors ($\delta\sigma > 0$) stabilize ($\delta\Delta H° < 0$) the cationic form more than the neutral-substituted conjugated system, eq 1, when calculated at the correlated levels. The greater stabilization due to inclusion of electron correlation is seen to result not only from a stronger donor (X = NH_2, $\delta\Delta H° = -4.62$ kcal mol^{-1}) but also from a stronger acceptor (X = NO_2, $\delta\Delta H° = -12.29$ kcal mol^{-1}). We emphasize that electron correlation enhances all types of resonance delocalization, not only the π-type but also the σ-type, leading to energy stabilization. Conspicuous, unexpectedly large stabilizations are those for X = Cl ($\delta\Delta H° = -8.84$ kcal mol^{-1}) and X = CN ($\delta\Delta H° = -5.53$ kcal mol^{-1}). The smallest stabilization is found for X = CF_3 ($\delta\Delta H° = -1.63$ kcal mol^{-1}). These stabilizations ($\delta\Delta H° < 0$) upon hydride transfer forming the cationic conjugated system should include contributions such as (i) enhanced π-delocalization (structures **Ib** and **Ic**, Scheme 1) for π-donors and (ii) enhanced delocalization due to all other types of (e.g., proximate $\sigma-\sigma^*$ including $n-\sigma^*$, $\pi-\sigma^*$, $\sigma-\pi^*$, etc.)[17] orbital interactions (included in structure **Ia**, Scheme 1) for π-acceptors. Therefore, the $\delta\Delta H°$ values do not represent the π-donating effect (structure **Ic**) alone (but also include the σ delocalization effect) so that they are not a reliable measure for assessing the π-donating ability of the π-acceptors. Also, the relative orders of $\Delta H°$ by the RHF method are different from those of the correlated levels, for example, the $\Delta H°$ value for X = CF_3 is less endothermic by 3.17 kcal mol^{-1} at the RHF level but is more endothermic by 0.73 kcal mol^{-1} at the G3 level than that for R = CN. This indicates that the electron correlation effects are very important even for the typical isodesmic reactions, eq 1. Nevertheless, general trends of reaction enthalpies obtained at the RHF/6-31G* level are similar to those obtained at the correlated levels excepting a few cases as mentioned above. Therefore, unless higher accuracy is required, the results obtained at the RHF/6-31G* level will be sufficient.

On the other hand, the absolute $\Delta H°$ values obtained at the correlated levels, MP2, B3LYP, CBS-Q, and G3 levels, are very similar within about ±2.6 kcal mol^{-1}. Especially, the $\Delta H°$ values at the MP2 and G3 levels are very similar excepting only X = Cl. The relatively large difference in the X = Cl is mainly caused by the difference of basis sets between the MP2/6-31G* and G3 levels rather than the correlation effects. The

SCHEME 1



$\Delta E°$ values at the MP2 level are -5.79 and -8.10 kcal mol^{-1} with the 6-31G* and G3 large basis sets, respectively, and these $\Delta E°$ values at the MP2 level are nearly same as the $\Delta H°$ values. We note, however, that the $\Delta H°$ value for X = CN is more favorable by 3.63 and 0.73 kcal mol^{-1} at the CBS-Q and G3 levels, respectively, than that for X = CF_3. The difference in $\Delta H°$ between the two Xs at the MP2 level is only 0.04 kcal mol^{-1} with X = CN being still favored. However, this trend is reversed at the B3LYP level with X = CF_3 being more favored by 0.28 kcal mol^{-1} relative to X = CN. These comparisons show that the relatively lower levels of theory, for example, the MP2 and B3LYP levels with the relatively small basis set of 6-31G*, relative to the CBS and G3 levels may be inaccurate for calculating the energetics of the reactions, eq 1.

On the other hand, reference to Table 1 reveals that the reaction enthalpies, $\Delta H°$, are more favorable for the reactions with stronger electron-donating X-substituents ($\delta\Delta H° < 0$) as generally expected. However, the relative magnitude of $\Delta H°$ is reversed for some cases. For example, the reaction with X = Cl is more favorable by 2.08 and 2.99 kcal mol^{-1} than that with X = F at the CBS-Q and G3 levels, respectively. Similar reversal is also found for the reactions of X = CF_3 and CN, as has been shown above. The electron-accepting abilities are larger for X = Cl and CN than those for X = F and CF_3, respectively, under a weak to moderate π-electron demand condition because the Cl ($\sigma_p = 0.23$) and CN ($\sigma_p = 0.66$) substituents are, in general, regarded as stronger electron acceptors relative to F ($\sigma_p = 0.06$) and CF_3 ($\sigma_p = 0.54$), respectively, as the larger positive Hammett-type substituent constants (σ)[18] imply. Thus, the normal σ-values as an index for the electronic effect of a substituent are shown to be inadequate for the reactions involving a strong electron-deficient center with a strong π-electron demand such as in the conjugated cationic species studied in this work. Now in these cationic systems, the two substituents, X = Cl and CN, are proved to be weaker electron acceptors than X = F and CF_3, respectively, because the reaction enthalpies, $\Delta H°$, of the former two are less endothermic than those of the latter two despite the fact that they are commonly known as stronger π-acceptors. Thus, the enhanced stabilities of the two substituents, X = Cl and CN, are an indicative of the π-donating effect under extreme electron demand.

The equilibrium constants expressed by the calculated reaction enthalpies ($-\Delta G°/(2.3RT)$) are correlated with the Hammett σ_p^+ constants, eq 2,[19] for reactions (eq 1) with $n = 1$. The

$$-\frac{\Delta G^o}{2.3RT} = \rho^+\sigma_p^+ + \text{constant} \qquad (2)$$

correlations for the ten Xs are generally satisfactory with the regression coefficients ranging from $r = 0.988$ (CBS-Q) to $r = 0.995$ (RHF). The slopes are approximately $\rho^+ = -25$ with the correlated level energies but the slope is $\rho^+ = -26$ for RHF. One noteworthy trend is that the linearity of the correlation deteriorates as the level of accounting for the electron correlation is raised: $r = 0.995$ (RHF) $\rightarrow$ 0.993 (MP2) $\rightarrow$ 0.991 (DFT) $\rightarrow$ 0.989 (G3) $\rightarrow$ 0.988 (CBS-Q). This reflects the fact that, as the calculated electron correlation energies become more accurate, the anomalous (π-donating) effect of acceptor substituents is more enhanced and leads further off from the otherwise linear plots. The slopes, ρ^+, for the $n = 2$ series are smaller, $\rho^+ \cong -19$, than those for the $n = 1$ series, but the linearities are similar (e.g., $r = 0.997$ (RHF), 0.997 (MP2), etc.). These trends manifest the effect of an increased π-electron density in the cationic species with $n = 2$ (vide infra).

SCHEME 2

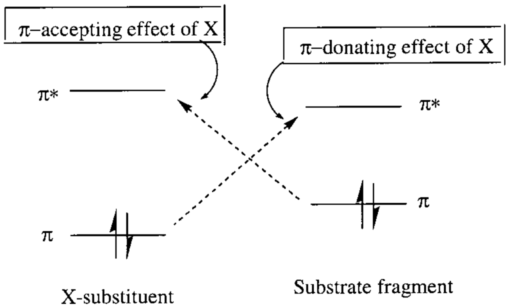


TABLE 3: Deletion Energies (ΔE_D in kcal mol^{-1}) Expressed as Destabilization Caused by Deletion of the Second-Order Charge Transfer Energies ($\Delta E^{(2)}_{\pi-\pi^*}$)[a] between π(X) and π^*(sub) Orbitals Calculated at NBO-RHF/6-31G*//MP2/6-31G* Levels[b]

n	X	species	$\Delta\epsilon$[c]	$F_{\pi\pi^*}$[d]	$\Delta E^{(2)}_{\pi-\pi^*}$	ΔE_D	$\delta\Delta E_D$[e]
1	Cl	neutral	0.66	0.100	19.01	13.2	25.7
		cation	0.35	0.185	100.06	38.9	
	CHO	neutral	0.72	0.063	6.73	5.1	3.4
		cation	0.67	0.081	12.14	8.5	
	CN	neutral	0.66	0.071	9.53	7.0	14.3
		cation	0.58	0.122	31.34	21.3	
2	Cl	neutral	0.65	0.101	19.17	13.1	15.1
		cation	0.58	0.146	44.93	28.2	
	CHO	neutral	0.71	0.063	6.78	5.1	1.5
		cation	0.68	0.071	9.37	6.6	
	CN	neutral	0.65	0.072	9.53	6.9	8.5
		cation	0.60	0.104	22.45	15.4	

[a] $\Delta E^{(2)}_{\pi-\pi^*} \cong -\langle\pi/|\hat{F}|\pi^*\rangle^2/(\epsilon_{\pi^*} - \epsilon_\pi)$ in kcal mol^{-1}. [b] The positive ΔE_D values represent destabilized energies. [c] The energy gaps between two interacting orbitals are given in au. [d] Fock-matric element is given in au. [e] $\delta\Delta E_D = \Delta E_D$(cation) $-$ ΔE_D(neutral).

We have attempted to estimate the magnitude of the π-donating effect of the π-acceptors using the deletion energy (ΔE_D),[14,17,20] which represents energy change destabilization caused by deletion of the second-order charge-transfer stabilization energy (ΔE_{ct})[21] between the π-orbital of the X-substituent and the π^*-orbital of the substrate fragment. Because the π-donating effect of the π-acceptors will mainly originate from the proximate $\pi-\pi^*$ interaction between the π-orbital of the X-substituent and the π^*-orbital of the substrate fragment as shown in Scheme 2, the magnitude of the π-donating effect of the π-acceptors can be estimated from the ΔE_D value. The ΔE_D is calculated using the NBO-4M program developed by Weinhold and co-workers, and the results are collected in Table 3.

As can be seen in Table 3, the π-donating effect of π-acceptors is present *even in neutral species*, in which there is no strong electron-deficient center, although the ΔE_D values in the neutral species are much smaller than those in the cationic species. This indicates that *the π-donating effect of π-acceptors is general in nature*, even though the absolute magnitude of

TABLE 4: Percentage Weights (wt %) of the Resonance Structures in the Cationic Species with $n = 1$ Obtained by the NRT Analyses

	RHF			MP2		
X	**Ia**	**Ib**	**Ic**	**Ia**	**Ib**	**Ic**
NH_2	16.7	54.9	16.9	15.7	41.6	17.8
OCH_3	20.7	56.2	11.7	18.2	40.6	12.5
CH_3	38.3	54.0	2.4	33.1	44.2	3.7
F	36.1	52.2	4.6	31.8	44.2	5.6
H	48.5	48.5	0.0	45.2	45.2	0.0
Cl	37.0	46.3	6.5	29.9	38.3	8.7
CHO	45.5	43.6	1.2	35.6	33.9	2.8
CF_3	44.2	37.2	0.0	32.5	29.9	0.0
CN	46.3	43.0	2.6	34.4	32.9	4.7

the π-donating effect in the neutral molecule is actually much smaller compared to that of the π-accepting effect. On the other hand, the magnitude of ΔE_D increases in the order X = CHO < X = CN < X = Cl for both the cationic and neutral species. This means that the π-donating effect of X = Cl is the largest among the π-acceptors studied in this work. The largest π-donating effect of X = Cl can be rationalized by the fact that the π-electrons involved in X = Cl are 3p lone-pair electrons, whereas those in X = CHO and CN are the 2p π-bonding orbital electrons. Therefore, the flow of electron densities from X to the π^*-orbital of the substrate will be much larger for X = Cl than for X = CHO or CN because (i) lone-pair electrons are, in general, loosely bound compared to bonding electrons and (ii) the energy level of the 3p lone-pair orbital on X = Cl is higher compared to that of the 2p bonding π-orbitals in X = CHO or CN so that the charge-transfer stabilization energies, $\Delta E_{ct} \approx -F_{\pi\pi^*}{}^2/\Delta\epsilon$ where $\Delta\epsilon = \epsilon_{\pi^*} - \epsilon_\pi$ and $F_{\pi\pi^*}$ is the Fock matrix element, are larger. This is confirmed by $\Delta\epsilon$ and $F_{\pi\pi^*}$ values collected in Table 4; the energy level gaps, $\Delta\epsilon$, between two interacting orbitals in the cationic species increase in the order X = Cl < X = CN < X = CHO, but $F_{\pi\pi^*}$ increases in the reverse order at the NBO-RHF/6-31G*//MP2/6-31G* level.

The order of the π-donating effects by electron-withdrawing substituents estimated from the ΔE_D is consistent with the results of the NRT analyses. The percentage weights (wt %) of three important resonance structures representing the delocalization of cationic charge densities in the cationic species as shown in Scheme 1 are calculated by the NRT analysis[7] at RHF and MP2 levels as summarized in Table 4. The resonance structure of **Ic** reflects the π-donating effect of the X-substituent, and hence, the weight percent of the structure **Ic** is a measure of the π-donating effect. Therefore, in these NRT analyses, the resonance structures of **Ia** and **Ib**, which correspond to the sigma-inductive resonance structures, were chosen as the reference structures to compare with the weight percent of the resonance structure **Ic** and show the π-donating effects by X-substituents.

Reference to this table reveals that weight percents of the relatively short-range delocalized forms, **Ia** and **Ib**, are higher in the RHF than in the MP2 level results while that of the longer chain form (**Ib**) with a greater delocalized structure is higher in the MP2 than in the RHF results. This is again in keeping with the general trends of enhanced delocalized structures due to inclusion of electron correlation effect. In the NRT analyses, both the absolute magnitude of wt %(**Ic**) and relative ratios, wt %(**Ic**)/wt %(**Ia**) and wt %(**Ib**)/wt %(**Ia**), increase in the order CHO < CN < Cl.

However, in the calculations of the ΔE_D, we have excluded the species with $X = NO_2$ because the $X = NO_2$ and the substrate fragment in the cationic species are nearly perpendicular each other as represented in Scheme 3. Indeed, the planar structure is not a stable stationary species with one imaginary frequency at the uncorrelated RHF/6-31G* as well as the correlated MP2/6-31G* and B3LYP/6-31G* levels. According to the normal-mode analysis, the one imaginary frequency of the planar structure corresponds to a rotational mode leading to the perpendicular structure. Therefore, the $X = NO_2$ in the reaction systems with $n = 1$ cannot act structurally as a π-donor, although Reynolds et al.[1b] in their work have classified $X = NO_2$ as a π-donor comparable to $X = CH_3$. The perpendicular structure in the cationic species with $X = NO_2$ is formed for the sake of minimizing the unfavorable electron-accepting effect by stronger π-acceptor, $X = NO_2$, from the electron-deficient cationic center. This shows that the π-donating effect of $X = NO_2$ is actually a minor effect (or nonexistent), which is overwhelmed by a strong electron-withdrawing power, because if the π-donating effect of $X = NO_2$ is larger than the accepting effect, the structure of the cationic species with $X = NO_2$ will be planar so as to acquire the maximum stabilization energies by the π-donating effects.

SCHEME 3

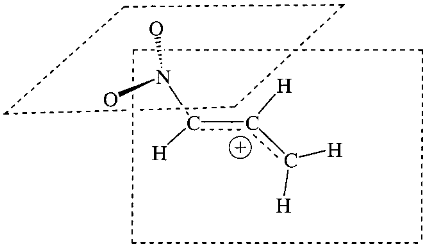


TABLE 5: The Calculated Reaction Enthalpies ($\Delta H°$ in kcal mol^{-1}) at 298 K for the Isodesmic Reactions with $n = 2$ in Eq 1

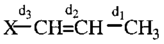
X	RHF[a]	MP2[a]	B3LYP[a]	CBS-4	$\delta\Delta H°$ [b]
NH_2	−33.20	−36.65	−34.72	−36.22	−3.02
OCH_3	−20.33	−22.32	−22.08	−21.84	−1.51
CH_3	−8.57	−8.94	−10.18	−9.60	−1.03
F	−0.54	−2.22	−3.20	−3.37	−2.83
H	0.00	0.00	0.00	0.00	0.00
Cl	3.02	−1.16	−1.65	−3.87	−6.89
CHO	12.11	8.98	10.32	8.97	−3.14
CF_3	13.29	11.84	10.44	11.85	−1.44
CN	17.35	13.13	12.76	10.80	−6.55
NO_2	25.07	17.59	20.03	19.88	−5.19

[a] 6-31G* basis set was used. [b] $\delta\Delta H° = \Delta H°_{CBS4} - \Delta H°_{RHF}$.

To compare the strength of π-donating effect by π-acceptors in the reactions with varying π-electron chain length, the hypothetical isodesmic reactions with $n = 2$ in eq 1 are also investigated and the reaction enthalpies, $\Delta H°$, are summarized in Table 4. Although the levels of calculation for the reaction systems with $n = 2$ are limited up to the CBS-4 level because of the size of the reaction systems, energetics at the CBS-4 level should provide more accurate and more reliable results than those obtained at the MP2 and B3LYP levels as discussed above. The relative orders of $\Delta H°$ predicted at the CBS-4 level for $X = CF_3$ and CN and for X = F and Cl are consistent with those at the CBS-Q and G-3 levels for $n = 1$ (Table 1). However, for those at the lower levels, RHF, MP2, and B3LYP, the relative orders are reversed so that the predictions at the lower-level correlated methods are unreliable.

Examination of Table 5 shows that the trends of the reaction enthalpies obtained at the CBS-4 level for the reactions with $n = 2$ are very similar to those for the reactions with $n = 1$. However, the absolute magnitudes of the reaction enthalpies,

TABLE 6: Calculated Bond Lengths (*d* in Å) of the Reactions with *n* = 1 at the MP2/6-31G* Level

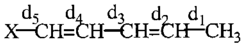


$X\overset{d_3}{-}CH\overset{d_2}{=}CH\overset{d_1}{-}CH_3$

X	neutral d_1	neutral d_2	neutral d_3	cation d_1	cation d_2	cation d_3	Δd^a Δd_1	Δd^a Δd_2	Δd^a Δd_3
NH_2	1.4991	1.3426	1.3512	1.4302	1.3006	1.4062	−0.1479	+0.0876	−0.1056
OCH_3	1.5005	1.3425	1.3563	1.4239	1.2274	1.3662	−0.1442	+0.0814	−0.1388
CH_3	1.4997	1.3396	1.3731	1.3982	1.4598	1.4998	−0.1266	+0.0586	−0.0400
F	1.4982	1.3308	1.3682	1.3944	1.2820	1.3581	−0.1300	+0.0636	−0.0761
H	1.4996	1.3378	1.3836	1.3836	1.0876	1.0851	−0.1160	+0.0458	+0.0025
Cl	1.4985	1.3353	1.3691	1.4023	1.6398	1.7344	−0.1294	+0.0670	−0.0946
CHO	1.4945	1.3448	1.3838	1.3872	1.5060	1.4684	−0.1107	+0.0425	+0.0376
CF_3	1.4958	1.3372	1.3857	1.3814	1.5172	1.4866	−0.1101	+0.0442	+0.0031
CN	1.4945	1.3448	1.3832	1.3929	1.4130	1.4319	−0.1113	+0.0481	−0.0189
NO_2	1.4938	1.3337	1.3626	1.4079	1.4234	1.4571	−0.1312	+0.0742	−0.0337

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

TABLE 7: Calculated Bond Lengths (*d* in Å) of the Reactions with *n* = 2 at the MP2/6-31G* Level



$X\overset{d_5}{-}CH\overset{d_4}{=}CH\overset{d_3}{-}CH\overset{d_2}{=}CH\overset{d_1}{-}CH_3$

X	neutral d_1	neutral d_2	neutral d_3	neutral d_4	neutral d_5	cation d_1	cation d_2	cation d_3	cation d_4	cation d_5
NH_2	1.4978	1.3476	1.4501	1.3506	1.3974	1.3525	1.4337	1.3694	1.4112	1.3103
OCH_3	1.4978	1.3469	1.4530	1.3498	1.3609	1.3557	1.4276	1.3777	1.4019	1.2882
CH_3	1.4972	1.3467	1.4544	1.3467	1.4972	1.3623	1.4159	1.3982	1.3773	1.4743
F	1.4970	1.3460	1.4535	1.3377	1.3552	1.3629	1.4154	1.3941	1.3729	1.3005
H	1.4971	1.3462	1.4559	1.3445	1.0847	1.3662	1.4098	1.4098	1.3662	1.0861
Cl	1.4964	1.3469	1.4527	1.3426	1.7299	1.3631	1.4158	1.3949	1.3797	1.6641
CHO	1.4951	1.3485	1.4481	1.3525	1.4637	1.3683	1.4085	1.4100	1.3709	1.4882
CF_3	1.4956	1.3469	1.4521	1.3440	1.4849	1.3691	1.4069	1.4133	1.3634	1.5088
CN	1.4951	1.3481	1.4485	1.3526	1.4280	1.3691	1.4082	1.4089	1.3758	1.4179
NO_2	1.4945	1.3480	1.4480	1.3413	1.4509	1.3697	1.4072	1.4116	1.3625	1.4583

$|\Delta H°|$, are smaller for the reactions with $n = 2$ than those with $n = 1$ (Tables 1 and 5), indicating that the effects of X-substituents are relatively weaker for the reactions with $n = 2$. These results reflect that the π-electron demand is weaker because the π-electron densities of the species with $n = 2$ are more abundant relative to the cationic species with $n = 1$. This is confirmed by the magnitude of ΔE_D collected in Table 3. As can be seen in Table 3, the magnitudes of ΔE_D in the two neutral species with $n = 1$ and 2 are nearly same indicating that the π-effect is independent of the chain length of the π-system. However, the magnitudes of ΔE_D are much larger in cationic species with $n = 1$ than $n = 2$. This is caused by weaker π-electron demand in cationic species with $n = 2$ than in those with $n = 1$. Consequently, the magnitude of $\delta\Delta E_D$ for the reactions with $n = 2$ is about half of those with $n = 1$, that is, the π-donating effect of π-acceptors has diminished in the reaction systems with $n = 2$, as expected. Nevertheless, the relative order of magnitude for the $\delta\Delta E_D$ is the same for both systems with $n = 1$ and 2. Thus, it can be concluded that the π-donating effect of π-acceptors increases in the order CHO < CN < Cl.

(B) Structures. The bond lengths (*d*) optimized at the MP2/6-31G* level are summarized in Tables 6 and 7. For the reactions with $n = 1$, the variations of bond lengths of d_2 with X-substituents in neutral species are much smaller than those in the cationic species. This indicates that the effects of X-substituents on the bond lengths are larger in cationic species. However, any simple relationships between the bond length, d_2, and a physical property of the X-substituent could not be found in both neutral and cationic species. Close examination of Table 6 reveals that for all substituents (X) the bond length of d_1 contracts, while that of d_2 stretches in the cationic species as expected from the resonance structure **Ib**. The contraction of d_1 is, however, greater than the stretching of d_2, reflecting the greater contribution of **Ib** than **Ia**. The NRT analysis in Table 4 confirms the greater contribution of **Ib** than **Ia** only for π-donors, X = NH_2, OCH_3, CH_3, F, and Cl, but not for π-acceptors, X = CHO, CF_3, and CN. Thus, the geometrical changes upon hydride transfer are not simply related to the π-donating ability alone. This is true with the bond length changes of d_3, which should reflect the contribution of structure **Ic**. If the structure **Ic** contributes substantially, d_3 should contract. This is evident with all of the normal π-donors, but there are anomalies with π-acceptors: for X = CHO and CF_3, d_3 stretches, while for X = Cl, CN, and NO_2, it contracts. The NRT (Table 4), as well as ΔE_D (Table 3), analysis shows that for electron-withdrawing substituents structure **Ic** contributes in the cationic species with X = Cl, CHO, and CN but not in those with X = CF_3 and NO_2. This again demonstrates the unreliability of the geometrical changes as a measure of the pure π-electronic effects. The bond-length changes in the $n = 2$ systems (Table 7) also show similar behavior to that exhibited in the $n = 1$ systems. These results are somewhat different from those reported by Reynolds et al.,[1b] in which X = CF_3 was shown to have some π-donating ability. Therefore, we have further analyzed the π-electron densities for X-substituents and substrate fragments, $q_\pi(X)$ and $q_\pi(\text{sub})$, in the neutral and cationic forms with $n = 1$, and the results are summarized in Table 8. The $q_\pi(X)$ value decreases ($\Delta q_\pi(X) < 0$) gradually, while the $q_\pi(\text{sub})$ value increases ($\Delta q_\pi(\text{sub}) > 0$) as the π-electron-donating power of the X-substituent becomes larger. Especially, for X = Cl, CN, and CHO moieties, the $q_\pi(X)$ values in the neutral species are larger indicating the π-electron accepting effects of the substituents, X. However, the $q_\pi(X)$ values for X = Cl, CHO, and CN in the cationic forms decrease reflecting that the π-electron densities flow out from the

TABLE 8: Calculated π-Electron Densities (q_π in Electron Unit)[a] Obtained by the Natural Population Analysis (NPA) at the MP2 Level

	neutral		cation			
X	q_π(X)	Q_π(sub)[b]	q_π(X)	Q_π(sub)[b]	Δq_π(X)	Δq_π(sub)
NH_2	1.719	2.090	1.458	2.503	−0.261	0.413
OCH_3	1.821	2.098	1.561	2.400	−0.260	0.302
CH_3		1.999		2.099		0.100
F	1.908	2.052	1.772	2.192	−0.136	0.140
H		1.993		1.992		−0.001
Cl	1.909	2.050	1.650	2.308	−0.261	0.258
CHO	2.059	1.926	1.938	2.039	−0.121	0.113
CF_3		1.972		2.019		0.047
CN	2.018	1.968	1.857	2.121	−0.161	0.153

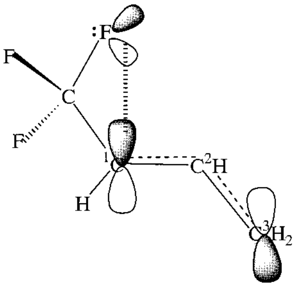
[a] The π-electron densities are obtained by the electron densities of $2p_z$ and $3p_z$ orbitals for 1st and 2nd row elements, respectively, in the NPA analysis. [b] Sum of the π-electron densities in the substrate fragment.

TABLE 9: Delocalization Energies (ΔE_{del} in kcal mol^{-1}) between the X-Substituent and the Substrate Fragment Calculated at the RHF/6-31G*//MP2/6-31G* Level

X	ΔE_{del}(T)[a]	ΔE_{del}(X)[b]	$\delta\Delta E_{del}$(X)[c]
Cl	81.1	77.5	77.5
CHO	38.0	22.3	13.8
CF_3	35.7	18.1	−2.9
CN	68.4	37.5	29.9

[a] Total delocalization energies between the X-substituent and the substrate fragment. [b] Partial delocalization energies due to charge transfer from the X-substituent to the substrate. [c] Delocalization energies excluding contributions of the n−σ* interactions between n(X) and σ*(C−X) orbitals.

SCHEME 4



X-substituent to the substrate moiety. The magnitudes of Δq_π(X) and Δq_π(sub) increase in the order X = CHO < X = CN < X = Cl. This is in line with the orders of π-donating ability predicted by the NRT and ΔE_D analyses. However, interestingly, the Δq_π(sub) for X = CF_3 is +0.047*e*. This suggests that the π-electron density in the substrate fragment increases by the π-electron donating effect of X = CF_3. The putative π-electron donating effect of X = CF_3 seems, however, somewhat strange because there are no π lone-pair electrons or other π-orbitals that can directly conjugate with the π*-orbital of the substrate fragment existing in the C-atom of X = CF_3. Although X = CF_3 could act as a hyperconjugative π-electron donor as evidenced with X = CH_3, the other possible way would be through-space interaction between lone-pairs of the F-atom and the π*-orbital of the substrate fragment as shown in Scheme 4. Nevertheless, such π-donating behavior is inconsistent with our NRT and ΔE_D analyses. The through-space interaction as shown in Scheme 4 should be very weak because the distance between the C^1-atom and the F-atom is relatively far (2.36 Å). The increase in the substrate π-electron density for X = CF_3 (Δq_π(sub) > 0) in the cationic form, therefore, comes most likely from other proximate σ−π*-type charge-transfer delocalizations. Therefore, it is expected that the π-electron-donating effect of X = CF_3 is not important, and the trend shown by the electron transfer, Δq_π, involved in the cationic species is also not a good measure of the π-donating ability.

This expectation is confirmed by the proximate bond−antibond (including all types of n−π*, n−σ*, σ−σ*, etc.) delocalization energies (ΔE_{del}) between X and the substrate fragments. The delocalization energies are obtained by zeroing all of the off-diagonal elements of the common block between X and the substrate in the Fock matrix using the NBO method,[13] and the results are summarized in Table 9. As can be seen in Table 9, total delocalization energies (ΔE_{del}(T)), as well as partial delocalization energies (ΔE_{del}(X)), which are caused by the delocalization of one direction from X to the substrate fragment, increase in the order X = CF_3 < X = CHO < X = CN < X = Cl. This order is consistent with the predicted π-donating abilities of X-substituents discussed above. Nevertheless, the relative magnitudes of the delocalization energies, ΔE_{del}(T) and ΔE_{del}(X), for X = CF_3 are very similar to those for X = CHO. Examination of Table 8 reveals that the charge transfer occurs almost entirely from the n_F−σ^*_{C-C}-type interaction[7,13,21b] for X = CF_3 whereas it comes from other types of proximate charge delocalizations, for example, π−π*, n−π*, σ−σ*, etc., rather than n_X−σ^*_{C-C} for X = Cl, CHO, and CN.[7,13,21b] Thus, if the contributions of the n−σ* interactions are deleted, the net delocalization ($\delta\Delta E_{del}$(X)) from X to the substrate fragment, and hence the net stabilization by the substituent X = CF_3, will be nearly zero. Once again, this result indicates that the π-donating ability of X = CF_3 is not real. A similar interpretation of the net energy stabilization by X = NO_2 ($\delta\Delta H°$ = −12.29 kcal mol^{-1} in Table 1) can be offered, that is, other (than π−π*) types of proximate charge-transfer interactions (generally expressed as σ−σ*-type) stabilize the correlated energies of the cationic species.

Summary and Conclusion

The π-donating effect of π-acceptor substituents increases in the order X = CHO < X = CN < X = Cl under a strong electron demand as in the conjugated correlated levels. Inclusion of electron correlation energies, in general, lowers the reaction enthalpies ($\delta\Delta H° = H°_{corr} - H°_{RHF} < 0$) as shown for $\delta\Delta H° = H°_{G3} - H°_{RHF}$ in Table 1. All substituents, irrespective of whether they are electron donors ($\delta\sigma < 0$) or acceptors ($\delta\sigma > 0$), stabilize ($\delta\Delta H° < 0$) the cationic form relative to the neutral-substituted conjugated system, eq 1, when calculated at the correlated levels. The greater stabilization due to inclusion of electron correlation is seen to result not only from a stronger donor (X = NH_2, $\delta\Delta H°$ = −4.6 kcal mol^{-1}) but from stabilization ($\delta\Delta H°$) by the π-acceptors in the conjugated cationic systems. In contrast to the earlier reports that two strong acceptors, X = CF_3 and NO_2, have some π-donating ability under strong π-electron demand, our NRT and ΔE_D analyses show no such π-donor effect by the two acceptor substituents; the stabilization of correlated energies with these two substituents is entirely caused by n−σ*-type charge-transfer interactions. In general, electron correlation enhances all types of delocalization (proximate σ−σ* charge-transfer interactions, which include π−π*, n−π*, n−σ*, σ−σ*, etc.) so that the studies involving electron delocalization are better suited to respectably high-level correlated rather than RHF level methods.

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Supporting Information Available: A table of electronic energies corrected for the zero-point vibrational energies. This material is available free of charge via the Internet at http://pubs.acs.org.

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