Transmission of Substituent Effects through 5-Membered Heteroaromatic Rings

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Ab initio calculations are carried out on protonation equilibria of 5-membered heteroaromatic aldehydes (5MHAs; heteroatom Y = NH, O, PH, and S and substituent Z = NH_2, OCH_3, SCH_3, CH_3, H, Cl, CHO, CN, NO_2) at the MP2/6-31G* level. Natural bond orbital (NBO) analyses show that the optimal localized natural Lewis structures of the protonated aldehydes, (**P**), are ortho (C^3) protonated (for Y = O, PH and S) and N-protonated (for Y = NH) forms in contrast to the standard structural Lewis formula for aldehydes, (**R**). The delocalizability of π lone-pair on the heteroatom ($n_\pi(Y)$) is in the order Y = NH > O > S > PH. The transmission efficiency of (Z) substituent effects to the carbonyl moiety run parallel to the delocalizability of $n_\pi(Y)$ for **R**, but is dominantly influenced by the cationic charge on C_α (C_α^+) for **P**, which is in the reverse order of the delocalizability of $n_\pi(Y)$. The Hammett ρ values for variation of Z in the protonation are determined by the difference in the transmission efficiencies between **P** and **R** states so that simple interpretation of their magnitude is not warranted. However, the magnitude of the gas-phase ρ_z^+ values decreases as the level of computation is raised from RHF/3-21G* to RHF/6-31G* and to MP2/6-31G* but increases again at the MP4SDQ/6-31G* level. Further decrease occurs when solvent effect (water) is accounted for by the SCRF method. Comparison of the SCRF ρ_z^+ values with those determined in the aqueous acid solution for Y = S and CHCH shows inadequacy of accounting for the solvent effects on the ρ values by a continuum model. It is noteworthy that semiempirical calculations, especially the AM1 method, give even lower magnitude of the gas-phase ρ values.

Introduction

Reactivities as well as physical properties of a heteroaromatic ring derivative depend strongly on the nature and conjugative ability of the heteroatom (Y). For the 5-membered heteroaromatics, **I** [pyrrole (Y = NH), furan (Y = O), phosphole (Y = PH) and thiophene (Y = S)], the transmission of 5-substituent effects to a probe or a reaction center at C^2 thus depends on the availability of lone-pair π electrons for 2,5-conjugation. The 2,5-positions are at para to each other and the
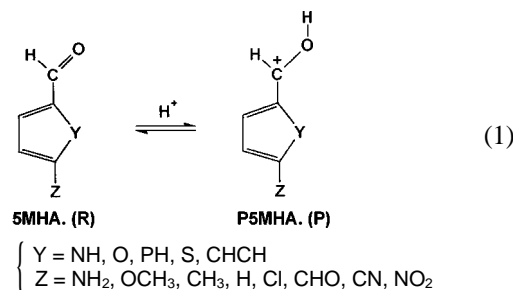

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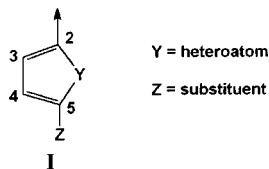
para substituent constants, σ_p (or σ_p^+), have been used.[1] Literature survey shows variety of orders for reactivity and physical properties between the 5-membered heteroaromatics. The electronegativity of heteroatoms increases as S < N < O and accordingly conjugation energy (kcal mol^{-1}) has been found to decrease in the order Y = S (28.7) > NH (21.2) > O (15.7).[2] Delocalization of the lone-pair electrons away from the heteroatom may be inferred from the dipole moment decrease ($\Delta D = D_{arom.} - D_{satd.}$) from their saturated counterparts; the net dipole moment of furan ($\Delta D = -1.03$) and thiophene ($\Delta D = -1.39$) is reduced whereas in pyrrole ($\Delta D = +0.23$) it is actually

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reversed from its nonaromatic counterparts as a results of delocalization of π lone-pair electrons.[3] On the other hand, electrophilic substitution at C^2 (or C^5) of **I** occurs much more readily compared to benzene, *e.g.* estimated bromination rates relative to benzene are Y = S (5×10^9) < O (6×10^{11}) < NH (3×10^{18}).[4a]

In the studies of the transmission of substituent effects, a knowledge of substituent (Z)-ring probe (at C^2) interactions is of great importance. The carbonyl moiety is one of the most commonly used and versatile probes for studying such interactions.[1c,5]

Carbocations are involved as intermediates in many types of organic reactions, *e.g.*, rearrangement, elimination and substitution reactions.[6] Carbocations are particularly susceptible to substituent effects because of their electron deficient nature.[7]

In this work, we investigated the transmission of substituent effects involved in the protonation equilibria of 5-membered heteroaromatic aldehydes (5MHAs) theoretically (eq 1). Our aims in this work are to clarify the origins for the various orders observed in reactivity and physical properties

$$\text{5MHA. (R)} \quad\rightleftharpoons\quad \text{P5MHA. (P)} \tag{1}$$

Y = NH, O, PH, S, CHCH
Z = NH_2, OCH_3, CH_3, H, Cl, CHO, CN, NO_2

of the 5-membered heteroaromatics, **I**, noted above, and to examine transmission efficiency of substituent effects

through the rings of the 5MHAs (**R**) and their protonated forms, P5MHAs (**P**), and also that involved in the protonation equilibria of 5MHAs by determining theoretical Hammett ρ values. The former two transmission efficiencies are the stationary state properties while the latter is a reaction (or activation) parameter. Various MO theoretical methods are used in evaluating the ρ values to examine basis set dependence of ρ, but all analysis involving MOs and structures were carried out using the *ab initio* results at the MP2/6-31G*//MP2/6-31G* level of theory.[8]

Computations

All structures were fully optimized at the RHF/3-21G*, RHF/6-31G*, and MP2/6-31G* levels[8] and vibrational frequency analyses were performed to confirm stationary states at the RHF/3-21G* and RHF/6-31G* levels for all Zs and MP2/6-31G* level for Z = H. The Hammett ρ values were also determined by the AM1[9] and PM3[10] semiempirical methods, by single point calculations at the MP4SDQ level[8] using the MP2 optimized geometries (MP4SDQ/6-31G*// MP2/6-31G*) and also by the density functional theory (DFT).[11] The DFT calculations used the Becke hybrid functional (at the B3LYP/6-31G*//B3LYP/6-31G* level) as implemented in the Gaussian 94 programs.[12] Natural bond orbital (NBO)[13] calculations were carried out using NBO 4.0 interfaced to Gaussian 94.[12] Since in this work we are dealing with the aromatic systems, the (π) lone-pair n, π and π^* orbitals are used in our NBO analyses.

Results and Discussion

A. Stationary State Properties.   The carbonyl oxygen and heteroatom Y have syn arrangement with one exception of Y = O for which anti conformers are preferred for both 5MHA (**R**) and P5MHA (**P**) due to relatively strong electrostatic repulsion between the two oxygen atoms.[14] Moreover heavy atom framework in all the 5MHAs (**R**) and P5MHAs (**P**) have planar structures excepting for Y = PH which has a considerable degree of pyramidal structure (H atom on PH is out of plane by 72.4^o). Since the lone-pair, π and π^* orbitals are all orthogonal to the core σ-framework, by symmetry $\sigma \rightarrow \pi^*$ or $\pi \rightarrow \sigma^*$ interactions are strictly zero, and $\pi \rightarrow \pi^*$ type interactions only are considered to significantly contribute to the π delocalization in the NBO analysis.

A-1. Natural Bond Orbital Analysis.[13]   An SCF canonical MO (CMO) is expressed as linear combinations of atomic orbitals (LCAO), whereas a natural localized MO (NLMO) is formed by linear combinations of bond orbitals (LCBO). In natural bond orbital analysis the input basis set is transformed into various localized basis sets, natural atomic orbitals (NAOs), natural hybrid orbitals (NHOs), natural bond orbital (NBOs) and NLMOs. With the density matrix transformed to the NAO basis, the NBO program searches for an *optimal natural Lewis structure* which has the total occupancy of its occupied NBOs exceeding 99% of the total electron density for ordinary molecules, and in gen-

eral agrees with the pattern of bonds and lone pairs of the chemists standard structural Lewis formula. The diagonal elements of the Fock matrix in an NBO representation represent the energies of localized bonds (σ, π), antibonds (σ^*, π^*) and lone-pairs (n). Off-diagonal elements connecting the two blocks ($\Gamma_{\sigma\sigma^*}$) represent the bond-antibond, lone-pair-antibond and normally negligibly small antibond-antibond interactions. These types of bond-antibond ($\sigma \rightarrow \sigma^*$, n $\rightarrow \sigma^*$, $\pi \rightarrow \pi^*$ or n $\rightarrow \pi^*$) mixing of filled and unfilled bond orbitals lead to partial breakdown of the strictly localized Lewis structure picture. The corrections to the Lewis-type structure are usually small enough to be well approximated by simple second-order perturbative expressions, eq 2, where $\hat{F}$ is the Fork operator and ε_σ and ε_{σ^*} are NBO orbital energies. It has been shown that the second-order delocalization (or charge transfer, eq. 2) is dominated by first-neighbor vicinal interactions.[15] The second-(and third-) neighbor as well as inner-shell delocalizations are small.

$$\Delta E_{\sigma\sigma^*}^{(2)} = -2\frac{<\sigma|\hat{F}|\sigma^*>^2}{\varepsilon_{\sigma^*} - \varepsilon_\sigma} \qquad (2)$$

The NBO analysis is especially useful for predicting bonding changes involved in a first-neighbor vicinal $\pi \rightarrow \pi^*$ (e.g. $\pi_{12} \rightarrow \pi_{34}^*$) interaction; such an interaction leads to removal of electron density from a bonding π MO to an antibonding π^* MO, which will tend to break the two π bonds involved (π_{12} and π_{34}) and form a new central π bond in between the two vicinal π bonds (π_{23}) provided the interaction is strong.[15] It has been found that there is roughly a proportionality of one between the quantity of charge transferred into an orbital and the energy stabilization (in atomic unit) associated with the transfer.[13b] Therefore, a charge transfer of 0.10 e will have an associated charge transfer energy of ca. 60 kcal mol^{-1}, which should approximately correspond to or somewhat greater than a π bond energy (40-60 kcal mol^{-1}).[4b]

The NBO analyses applied to our 5MHAs (**R**) gave in all cases the optimal localized natural Lewis structures in Figure 1 which agree with the standard structural Lewis formula. The NBO Lewis structures for the protonated 5MHAs (P5MHAs) were, however, of rather unexpected forms (Figure 1). They are ortho polarized (positive charge on C^3) forms; for Y = NH the positive charge is on the nitrogen atom (occupancy of n_N is zero).

The energy and occupancies of the lone-pair (n), π and π^* NBOs are summarized in Table S1 (Supplementary Materials) together with the first-neighbor vicinal delocalization energies by the form of eq. 2. The overall frontier NBO level diagram is shown in Figure 2. We note that the lone-pair (n) level is the highest for Y = S (S > N > O > P), but the π - π^* energy gaps are the smallest for Y = NH. These two, the higher n level and narrower $\Delta\varepsilon_\pi$ ($= \varepsilon_{\pi^*} - \varepsilon_\pi$), are important for stronger first-neighbor vicinal charge transfer stabilization of the type given by eq. 2.

The delocalization effects due to n - π^* and/or π - π^* interactions in the 5MHAs (**R**) play a highly important role representing the departures from the strictly localized natural Lewis structure (Figure 1) to the secondary structures[13]
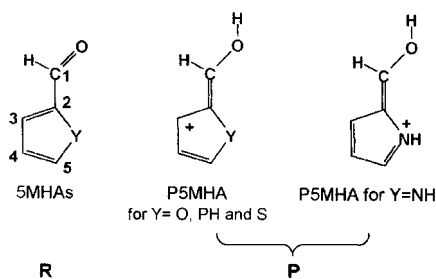
Figure 1. Optimal localized natural Lewis structures for 5MHAs (**R**) and P5MHAs (**P**).
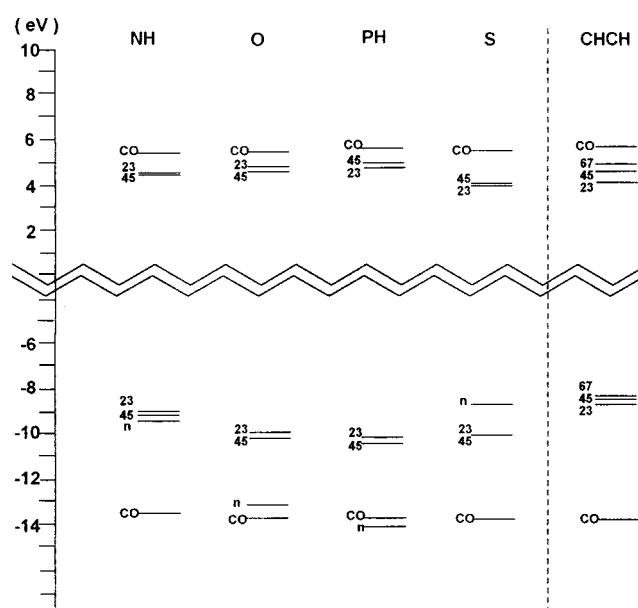

Figure 2. Frontier NBO levels (MP2/6-31G*). The lower half represents bonding orbitals, n, π_{CO}, π_{23}, π_{45} and π_{67}, and the upper half represents antibonding orbitals, π^*_{CO}, π^*_{23}, π^*_{45} and π^*_{67}. The n level is the highest for Y = S, whereas the energy gaps, $\Delta\varepsilon = \varepsilon_{\pi^*} - \varepsilon_{\pi}$, are the narrowest with Y = NH among the 5MHAs.

shown in Figure 3. The departure from the Lewis structure is in general very large: the n - π^* and/or π - π^* charge transfer interaction amounts over 0.20 e (Table S1, Supplementary Materials) which will lead to over *ca.* 120 kcal mol^{-1} [13b] in magnitude in many 5MHAs (decreasing in the order, Y = NH > S > O > PH). In this connection, it is to be noted that for benzene the amount of π - π^* charge transfer out of each π bond that is needed to convert from one resonance structure to the other is 0.33 e. [13b] This π^* occupancy for forming the alternative resonance structure is almost satisfied for benzaldehyde (Y = CHCH) with π_{23}* (0.37 e), π_{45}* (0.31 e) and π_{67}* (0.28 e). Of the two possible zwitterionic delocalized forms, ortho- and para-polarized, the latter form should be preferred because in this form opposite charges created are farther apart with a longer chain of dipolar resonance structure as represented schematically below each secondary structure using a hexatrienyl chain. *Thus the secondary Lewis structure due to the second-order charge transfer in **R** will lead mainly to para-polarized form.* Such para polarized zwitterion formation due to through-conjugation (or 2,5-
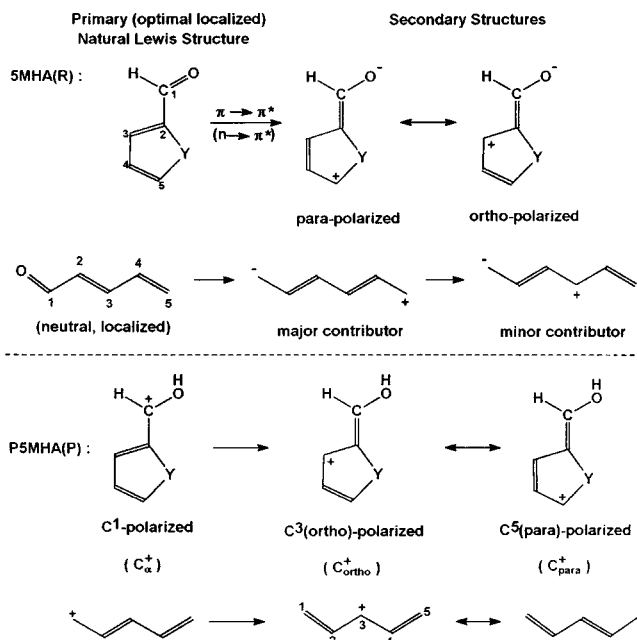

Figure 3. Primary and Secondary Natural Lewis Structures of 5MHAs (**R**) and their protonated forms, PMHAs (**P**).

conjugation in **I**) of an electron-donating substituent is indeed a well-recognized resonance effect within aromatic carbonyl compounds.[1c,5b,e]

Upon protonation of the 5MHAs, depending on the delocalizability of the π lone-pair, electrons on the heteroatom Y, n_π(Y), toward the cationic center, C$_\alpha$ (*vide infra*), two localized natural Lewis structures are formed: n_π(NH) has the strongest delocalizability and almost complete delocalization takes place (resulting in the N$^+$ form) leaving very weak charge on C$_\alpha$. The delocalization of n_π(Y) causes to form C$^+_{ortho}$ structures for Y = O, PH and S. This preference of the C$^+_{ortho}$ form is consistent with the elementary MO theory prediction of the central positive charge as illustrated in Figure 3 using a pentadienyl cation chain.[16] The optimal natural Lewis structures for the P5MHAs (**P**) are therefore of the two types (Figure 1). Here again, the π^* occupancies are in general large with over 0.20 e, associated stabilization energies of *ca.* 120 kcal mol^{-1}, [13b] in most cases (the order of decreasing π^* occupancy is the same as that for **R**). This means that for **P** also the departure from the localized natural Lewis structure (Figure 1) should be large.

A-2. Geometries and Charges.   The MP2/6-31G* results of relevant bond lengths are summarized in Table 1. In both **R** (weakly para polarized) and **P** (strongly ortho polarized) forms, d$_{CO}$ is stretched while d$_{12}$ is contracted. These geometry changes depend on facility of charge delocalization in the ring which in turn is dependent on the delocalizability of the π lone-pair on Y. As expected from the stronger delocalization effect due to the full positive charge in **P**, the geometrical changes in the **P** forms are much greater than those in the **R** forms; d$_{CO}$ is longer by *ca.* 0.02 Å whereas d$_{12}$ is shorter by *ca.* 0.07 Å in **P** than **R**. In all cases, d$_{CO}$ is the longest and d$_{12}$ is the shortest for Y = NH while exactly the

Table 1. Bond Lengths for 5 MHAs. (Z = H, in Å)
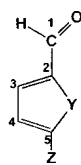
		NH	O	PH	S	CHCH
d_{CO}	**R**	1.2358	1.2292	1.2310	1.2298	1.2273
	P	1.3183	1.3048	1.3091	1.3076	1.2984
	Δd	0.0825	0.0756	0.0781	0.0778	0.0711
d_{12}	**R**	1.4469	1.4575	1.4591	1.4586	1.4797
	P	1.3731	1.3821	1.3833	1.3824	1.4028
	Δd	-0.0738	-0.0754	-0.0758	-0.0761	-0.0769
d_{34}	**R**	1.4079	1.4174	1.4427	1.4113	1.3952
	P	1.3806	1.3915	1.4111	1.3869	1.3874
	Δd	-0.0273	-0.0259	-0.0316	-0.0244	-0.0078

opposite holds for Y = CHCH, which should reflect the strongest and weakest delocalizations of Y = NH and CHCH, respectively.

For both **R** and **P**, the delocalized structures are either C_{para}^+ or C_{ortho}^+ in which d_{12} is a double bond. A satisfactory measure of the total delocalizability of π lone-pair electrons of the heteroatom Y ($n_\pi(Y)$) due to C_{para}^+ and C_{ortho}^+ forms may therefore be provided by the extent of d_{12} contraction for a fixed substituent Z (= H), *i.e.*, the shorter the d_{12}, the stronger is the total delocalizability of $n_\pi(Y)$ from the ring. The total resonance electron delocalization effect of Y according to the contraction of d_{12} (-d_{12}) decreases in the order NH > O > S > PH for both **R** and **P**. Despite the different site of polarization in the natural Lewis structures, the agreement in the two orders is good. This is reasonable since the only difference between **R** and **P** is that in the latter there is a strong positive charge on C_α so that resonance delocalization will be so much stronger proportionally for different Y. The electrophilic reactivity order (NH > O > S >> CHCH) of 5-membered heteroaromatic rings quoted[4] in the Introduction can be ascribed to the decreasing order of total resonance delocalization of $n_\pi(Y)$.

The double bond character (measured by the extent of contraction) of d_{34} (-d_{34}) in the **R** and **P** states have different origin, from that of d_{12}. The d_{34} double bond is obtained only in the para delocalized form, C_{para}^+, whereas the d_{12} double bond is in both C_{para}^+ and C_{ortho}^+. The double bond character of d_{34} is now in the order NH > S > O > PH, which is different from that of d_{12}.

In contrast to d_{12} contraction due to both the C_{para}^+ and C_{ortho}^+ forms, Y = S exhibits a greater para delocalizability due only to the C_{para}^+ form *within the ring* than Y = O. This should be a manifestation of the effect of higher lone-pair level of S (-8.8 eV) than O (-13.3 eV) (Figure 2) leading to a greater charge-transfer-energy lowering due to a smaller energy gap, $\Delta\varepsilon = \varepsilon_{\pi^*} - \varepsilon_n$, in the strong first-neighbor vicinal $n_\pi(Y) \rightarrow p_Z(C^5)$ delocalization in the para polarized form, where such charge transfer stabilizations have a greater

effect than those involving π^* located outside of the ring (*e.g.* π_{12}^* in the C_{ortho}^+ form). Since charge transfer of n is also dependent on the matrix element, $<n \mid \hat{F} \mid \pi^*>$, the d_{34} bond is the shortest, *i.e.*, the delocalization of n is the greatest with Y = NH albeit the energy level of nitrogen lone-pair (-9.4 eV) is lower than that for sulfur; S being a second row element, the $2p\pi$ - $3p\pi$ overlap will be smaller and hence the matrix element will be smaller for Y = S.[17] The extent of d_{34} contraction therefore depends strongly on the para-delocalizability of $n_\pi(Y)$ and should be the origin of dipole moment decrease evidenced on going from nonaromatic to aromatic 5-membered heterocycles[3] noted in the Introduction. Thus the contraction, *i.e.*, double bond character, of d_{12} depends on the total, ortho and para, delocalizability whereas the contraction of d_{34} depends only on the para delocalizability as the optimal localized natural Lewis structures reveal (Figure 3).

It has been shown that natural population analysis (NPA) provides a more realistic and stable measure for comparing electron distributions in different systems and should be preferred to the traditional Mulliken population analysis (MPA) for this purpose.[13,18] We have shown in Table 2 NBO charges of relevant atoms and the ring. We note that charges in the **P** states are greater in all cases than those corresponding charges in the **R** states by *ca.* 0.1 e on O (more negative), C^3 and C^5 (less negative), and *ca.* 0.4 e (more positive) on the ring. A greater delocalization of $n_\pi(Y)$ should lead to a weaker positive charge on C^1 (C_α) and greater positive charges on C^3, C^5 and ring. In fact the order of decreasing positive charge on C^1 (C_α) PH > S > O > NH agrees with that of the increasing total delocalizability of $n_\pi(Y)$ PH < S < O < NH. We note that positive charge on the para position, C^5, is the strongest in both **R** and **P** forms for Y = O indicating that Y = O has the strongest para-delocalizibilicity of the C_α^+ charge *through the ring*.

A-3 Transmission of Substitution Effects.   The above NBO analysis indicates that the effects of Y and substituent

Table 2. NBO Charges for 5MHAs (Z = H, in electron unit)

		NH	O	PH	S	CHCH
C^1	**R**	0.339	0.328	0.352	0.351	0.376
	P	0.337	0.352	0.378	0.372	0.437
	Δq	-0.002	0.024	0.026	0.021	0.061
O	**R**	-0.532	-0.494	-0.497	-0.499	-0.495
	P	-0.631	-0.592	-0.598	-0.598	-0.577
	Δq	-0.099	-0.098	-0.101	-0.099	-0.082
C^3	**R**	-0.273	-0.273	-0.206	-0.244	-0.213
	P	-0.186	-0.175	-0.098	-0.162	-0.146
	Δq	0.087	0.098	0.108	0.082	0.067
C^5	**R**	-0.050	0.107	-0.534	-0.445	-0.223
	P	0.088	0.240	-0.446	-0.362	-0.131
	Δq	0.138	0.133	0.088	0.083	0.092
Ring	**R**	0.034	0.006	-0.007	-0.001	-0.026
	P	0.495	0.432	0.430	0.354	0.349
	Δq	0.461	0.426	0.437	0.355	0.375

Z at para position (C^5) will be transmitted directly to the carbonyl carbon and are manifested in a form of bond length contraction of d_{12}. We have therefore plotted d_{12} against σ_p^+ of substituent Z[19] at C^5 and susceptibility parameter, S, was derived from the slope (eq. 3) as a measure of the transmission efficiency of para substituents in the **R** as well as in the **P** states.

$$\delta d_{12} = S\sigma_p^+ \qquad (3)$$

We have also carried out similar analyses using dual substituent parameters (DSP),[19] eq. 4, where F and R represent field and resonance substituent constants and f_d and r_d the susceptibility constants for F and R, respectively.[20] The results of S and r_d for **R** and **P** are collected in Table 3. The magnitude of S and r_d should provide a measure of transmission efficiency of substituent effects. Although the magnitude of S is considerably greater than that of r_d, the magnitude of S and r_d is seen to vary in parallel implying that the total susceptibility constant S is predominantly influenced by the resonance constant, r_d.

$$\delta d_{12} = f_d F + r_d R \qquad (4)$$

For the 5MHAs (**R**), both S and r_d decrease in the order NH > O > S > PH. This order is the same as that of the order of delocalizability of $n_\pi(Y)$ determined for **R** using the extent of d_{12} bond contraction; thus susceptibility (S or r_d) of the carbonyl moiety to the effect of substituent Z at the para position in R run parallel to the total delocalizability of $n_\pi(Y)$, *i.e.*, the greater the delocalizability of $n_\pi(Y)$, the stronger is the transmission efficiency of substituent effect from the para position (C^5) toward C_α. The transmission of the para substituent effect should, however, be strongly dependent on the para delocalizability through the ring since the polarization places positive charge on the para position. In the **R** form the para-polarized form is predominant so that the total delocalizability is in fact dependent on the para delocalizability. In general the transmission of substituent effects is less efficient for the 5MHAs with Y = second-row element than those with Y = first-row element, and is the lowest with benzaldehyde (Y = CHCH). This trend is a consequence of the lower degree of $2p\pi$ - $3p\pi$ overlap for the second-row element and the longer chain involved with Y = CHCH.

In the protonated forms, **P**, the cationic charge on C_α can be delocalized by resonance electron donation either from

$n_\pi(Y)$ or from the Z-substituted ring; the former should be the preferred electron source being nearer to C_α. The amount of cationic charge on C_α will therefore vary in inversely parallel to the delocalizability of $n_\pi(Y)$; the stronger the delocalizability of $n_\pi(Y)$, (*e.g.*, Y = NH) the lower is the cationic charge on C_α, and conversely the weaker the delocalizability of $n_\pi(Y)$, (Y = PH) the stronger is the positive charge on C_α.

It has been shown that an electron donor α-substituent, *e.g.*, OCH$_3$, causes a decrease in, or attenuation of, resonance electron donation from the Z-substituted benzene ring. For example, the value of $\rho_Z^\pm = -9.3$ for the equilibrium formation of 1-phenylethyl cation , **II**, decreases to $\rho_Z^\pm = -2.2$ for the corresponding reaction with a methoxy group on the
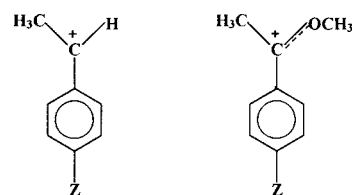
α-carbon, **III**.[7c,21]

This reflects that delocalization of positive charge onto the oxygen atom of OCH$_3$ in **III** causes a large decrease in the charge density on C_α.[7c,d] As a result of the competing resonance,[22] there is a large concomitant decrease in the electron demand from the Z-substituted ring leading to the greatly reduced transmission efficiency (much lower - $\rho_Z^\pm$) of Z-substituent effects.

A similar competition for the resonance electron supply to the cationic center occurs in the protonated form, **P**, between $n_\pi(Y)$ and the Z substituted ring. As noted above $n_\pi(NH)$ is the strongest electron donor so that very weak positive charge is left on C_α (the NBO charge is 0.337), whereas $n_\pi(PH)$ is the poorest resonance electron donor with the highest positive charge on C_α (the NBO charge is 0.378, Table 2). The order of decreasing transmission efficiency represented by r_d and S is O > PH > S > NH, which does not agree with that of the cationic charge, C_α^+, (PH > S > O > NH) with one exception of the strongest efficiency for O. One can rationalize, therefore, the order of transmission efficiency as essentially in the order of cationic charge C_α (C_α^+) but is also influenced by the para-delocalizability with the strongest transmission efficiency for Y = O for which the para-delocalizability through the ring is the strongest. The weaker the total delocalizability of $n_\pi(Y)$, the higher is the positive charge left on C_α, and consequently the greater will be the electron demand from the Z-substituted ring. But since the substituents are at para position, para-delocalizability *through* the ring becomes important also in determining the transmission efficiency.

We therefore conclude that the transmission efficiency of para substituent effects to C_α for **P** is strongly dependent on the cationic charge on C_α (C_α^+) mixed with the effect of para-delocalizability through the ring (O > PH > S > NH), in contrast to that of **R** where the total (ortho and para) delocaliz-

Table 3. Susceptibility constants, S, and r_d in protonation equilbria.[a] $\delta d_{12} = S\sigma_p^+$: $\delta d_{12} = d_{12}(Z) - d_{12}(H)$ $\delta d_{12} = f_d F + r_d R$

		NH	O	PH	S	CHCH
	R	0.92	0.79	0.58	0.76	0.57
$S \times 10^2$	**P**	0.92	1.32	1.23	1.07	1.15
	ΔS	0.00	0.53	0.65	0.31	0.58
	R	0.48	0.46	0.35	0.45	0.34
$r_d \times 10^2$	**P**	0.53	0.85	0.79	0.65	0.75
	Δr_d	0.05	0.39	0.44	0.20	0.41

[a]Z = SCH$_3$ is excluded in the regression.

ability prevails, NH > O > S > PH.

Thus for Y = NH the transmission efficiency of substituent effects from C^5 is the greatest in **R** but is the lowest in **P**, both of which are originated from the most facile delocalization of the lone-pair on N among the heteroatoms studied in this work leading to the greatest π^* occupancy in the optimal natural Lewis structures of **R** and **P**.

Quite interestingly, the orders of para-delocalizability *within* the ring, NH > S > O > PH, can be reproduced by focussing on only the roles of the key bond orbitals involved in the transformations of **P** (C^+_{ortho}) into C^+_{para}; the C^+_{para} structures are formed from C^+_{ortho} by $p_Z(C^3) \leftrightarrow \pi_{45}$ within the ring (π_{34} is formed at the expense of $p_Z(C^3)$ and π_{45}) interaction and second-order charge-transfer energies (in kcal mol^{-1}) calculated for the interaction can be arranged in the order of NH(C^+_{para}) > S(-209.9) > O(-197.9) > PH(-148.7). The satisfactory reproduction of the order NH > S > O > PH by considering only the charge-transfer interaction energies of $p_Z(C^3)$ with π_{45} within the ring indicates that the departure from the localized Lewis structure is large (*vide supra*) and the interactions between $p_Z(C^3)$ and π_{45} constitute major changes involved in such structural transformations.

B. Activation and Reaction Parameters. In this part we deal with paramerters representing changes of a quantity (Q) on going from the initial, 5MHAs (**R**), to transition states ($\Delta Q^{\neq} = Q^{\neq} - Q_R$) or to the final stationary states, P5MHAs (**P**), ($\Delta Q^o = Q_P - Q_R$).

B-1. Stabilization Energies. The stabilization energies involved in the protonation, $\Delta E^o = E_P - E_R$, are summarized in Table 4. The stabilization energies, $-\Delta E^o$, decrease in the order NH > PH > S > O. Examination of changes in the optimal natural Lewis structure on protonation, **R** → **P** eq. 5, reveals that π_{12} is formed while π_{CO} and π_{23} are destroyed in the process. Accordingly, the ΔE^o values are related to the charge transfer stabilization energies, eq. 2, involved in such first-neighbor vicinal interactions, eq. 6. The order of $\sum \Delta E_{ct}$ calculated from Table S1 is indeed in agreement with that of ΔE^o. Moreover, the relative stabilization energies of $\delta \sum \Delta E_{ct}$ are approximately of the right order of magnitude of the corresponding $\delta \Delta E^o$ values. Satisfactory agreement between $\delta \Delta E^o$ and $\delta \sum \Delta E_{ct}$ including Y = NH is again a result of the large π^* occupancies (*vide supra*) and suggests that first-
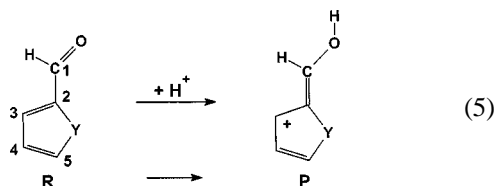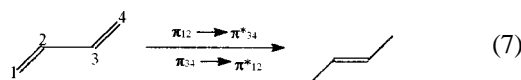
neighbor vicinal charge transfer interactions between π_{CO} and π_{23} constitute the major contribution to the stabilization energies. Therefore a rule that an intervening π bond (π_{23}) is formed at the expanse of the two interacting first-neighbor vicinal π bonds ($\pi_{12} \leftrightarrow \pi_{34}$), eq. 7, can be safely applied in the NBO analyses of a π conjugation system.

$$\delta \Delta E^o \approx \delta \sum \Delta E_{ct} = \Delta E_{ct}(\pi_{23} \to \pi^*_{CO}) + \Delta E_{ct}(\pi_{CO} \to \pi^*_{23}) \quad (6)$$

$$(7)$$

B-2. Rotational Barriers ($\Delta E^{\neq}$) and Energy Differences between Rotamers (ΔE). The rotational barriers ($\Delta E^{\neq}$) around d_{12} and energy differences (ΔE) between the two rotamers are shown in Table 5. As expected from their double bond character of d_{12}, the barrier heights, $\Delta E^{\neq}$, for the P states are much higher (by *ca.* 3 times) than those for the R states.; the π bond over d_{12} is a second order effect arising from the first-neighbor vicinal $\pi \to \pi^*$ delocalization in R, whereas it is a first order effect constituting the formal Lewis structure of P. For both R and P, the barrier to rotation increases (PH < S < O < NH) in the order of the decrease in the d_{12} bond length, (PH > S > O > NH). This suggests that the largest contribution to the barrier height arises from the double bond character of d_{12}, which has to be broken in order to allow free rotation. The top of the barrier in all cases corresponds to a 90° rotated form from the stable R states. The energy difference, ΔE, between the two stationary states, anti and syn, are small.

B-3 Basis Set Dependence of ρ_Z^+. The Hammett correlation, eq. 8, for variation of substituent Z at C^5 using the σ_p^+

$$-\frac{\Delta E_o}{2.3RT} = \rho^+ \sigma^+ \quad (8)$$

constant[1] yielded various gas-phase $\rho_Z^{\pm}$ values depending on the level of computation used as shown in Table 6. For comparison with experimental values, we have included benzaldehyde (Y = CHCH). The magnitude of $\rho_Z^{\pm}$ is within the range of ρ^+ (-10 to -14) reported for generation of benzylic

$$(5)$$

Table 4. Relative Stabilization Energies. (Z = H, in kcal mol^{-1})
$\Delta E^o = E(\mathbf{P})-E(\mathbf{R})$ and $\sum \Delta E_{ct} = \Delta E_{ct}(\pi_{CO} \to \pi^*_{23}) + \Delta E_{ct}(\pi_{23} \to \pi^*_{CO})$

	NH	O	PH	S	CHCH
$\delta \Delta E^o$	-8.9	-0.8	-4.7	-2.5	0.0 (-203.2)
$\delta \sum \Delta E_{ct}$	-10.5	-4.3	-5.9	-5.4	0.0 (-32.3)

Table 5. Rotational Barrier ($\Delta E^{\neq}$) and Energy Difference (ΔE) in kcal mol^{-1}
$\Delta E_R^{\neq} = \Delta E^{\neq}_R - \Delta E_R : \Delta E_P^{\neq} = \Delta E^{\neq}_P - \Delta E_P$
$\Delta E = | E_{anti} - E_{syn} |$

		NH	O	PH	S	CHCH
$\Delta E^{\neq}$	$\Delta E_R^{\neq}$	15.2	11.2	9.9	10.6	8.5[a]
	$\Delta E_P^{\neq}$	40.4	33.3	29.3	30.3	21.8
	$\delta \Delta E^{\neq}$	25.2	22.2	19.4	19.7	13.3
ΔE	ΔE_R	4.1	1.1	2.2	1.6	0.0
	ΔE_P	2.8	0.2	2.2	1.5	0.0
	$\delta \Delta E$	-1.3	-0.9	0.0	-0.1	0.0

[a]Experimental values ranging from 7.6 to 7.9 kcal mol^{-1} are reported in various organic solvents : F. A. L. Anet and M. Ahmad, *J. Am. Chem. Soc.*, **86** 119 (1964) : T. Drakenberg, R. Jost and J. Sommer, *J. Chem. Soc. Chem. Commun.*, 1011 (1974) : L. Lunazzi, *Tetrahedron Lett.*, 1205 (1975).

Table 6. Basis set dependence of $\rho_Z^{\ddagger}$

	NH	O	PH	S	CHCH
AM1	-9.59	-10.51	-11.14	-8.64	-8.58
PM3	-7.98	-9.65	$-^a$	-8.60	-7.84
RHF/3-21G*	-13.53	-14.22	-13.63	-12.61	-11.00
RHF/6-31G*	-12.99	-13.81	-12.71	-12.20	-10.76
MP2/6-31G*	-11.01	-11.96	-11.32	-10.52	-10.00
B3LYP/6-31G*	-11.54	-12.32	-11.51	-11.10	-10.39
MP4/6-31G*	-12.04	-13.02	-12.23	-11.44	-10.61
				$(-12.5)^c$	$(-9.2)^c$
SCRF//MP2 /6-31G*^{d}	-8.72	-9.07	-10.30	-7.62	-6.63
				$(-2.12)^e$	$(-2.0)^e$

^{a}Unreliable geometries. ^{b}Z = SCH$_3$ is excluded. ^{c}The gas-phase values estimated by $\rho_Z^{\ddagger}$ (soln) = 0.17 $\rho_Z^{\ddagger}$ (gas)[5e] for **IV** and **V**. ^{d}Electron withdrawing groups are excluded. ^{e}Experimental values in aqueous acid solution at 298 K for **IV** and **V**.[1c]

cations in the gas phase and solution.[23a,b] In contrast, it is much greater than the $\rho_Z^{\ddagger}$ values of -2.12 and -2.17 for the protonantion (pK$_a$ values) of 5-substituted 2-acetylthiophenes (**IV**)[1c] and 4-substituted acetophenones (**V**)[24a] respectively in aqueous sulfuric acid solution at 298K. However, the former corresponds to $\rho_Z^{\ddagger}$ = -12.5 in the gas phase when the correlation between the ΔpK$_a$ values in solution and in the gas phase is applied (ΔpK$_a$(soln) = 0.17 · ΔpK$_a$(gas)),[5e] whereas the experimental gas phase value for the latter is $\rho_Z^{\ddagger}$ = -7.51 based on $\Delta G^0/2.303RT$ vs σ^+ plot at 300 K.[24b]

Noto et al. found that substitution of C$_6$H$_5$ (resonance substituent constant,[19b] R = -0.08) for CH$_3$ (R = -0.13) in **IV** to **VI** causes practically no change in $\rho_Z^{\ddagger}$ (= -2.15) in aqueous solution.[1c] However the systems studied in this work have a weak electron donor (H; R = 0.0)[19b] compared to CH$_3$ so that the magnitude of ρ_Z values are expected to be decreased somewhat due to the "competing resonance" effect discussed above. Therefore we expect that the magnitude of $\rho_Z^{\ddagger}$ values for Y = S and CHCH to be slightly smaller than the corresponding gas phase values for **IV** ($\rho_Z^{\ddagger} \cong$ -12.5) and ($\rho_Z^{\ddagger} \cong$ -7.5). We note in Table 6 that the $\rho_Z^{\ddagger}$ values derived from correlated energies (MP2, MP4SDQ and B3LYP levels) for Y = S ($\rho_Z^{\ddagger}$ = -10.5 - -11.4) are smaller than the gas phase values for **IV**. In contrast, the magnitude of the corresponding values for Y = CHCH ($\rho_Z^{\ddagger} \cong$ -10.0 ~ -10.1) is larger and inconsistent with this expectation, but is in good agreement with the experimental gas phase value of $\rho_Z^{\ddagger}$ = -9.2 based on $\Delta G^0/2.303RT$ vs σ^+ plot at 300 K.[24b]

The magnitude of $\rho_Z^{\ddagger}$ is seen to decrease as the level of computation is raised from RHF/3-21G* to RHF/6-31G*, and to MP2/6-31G*. However, at the MP4SDQ/6-31G* level, the magnitude of $\rho_Z^{\ddagger}$ becomes greater again. This fluctuation of the magnitude of $\rho_Z^{\ddagger}$ suggests that further raising of the level of accounting for the electron correlation effect should lower the magnitude somewhat from that at the MP4SDQ/6-31G* level. This leads us to the DFT (at the B3LYP/6-31G* level) $\rho_Z^{\ddagger}$ values as the reasonably acceptable gas-phase values.

Further lowering of the magnitude occurs when solvent

effect (water) is taken into account using the SCRF method.[25] It has been shown that electron acceptor substituents, Cl, CN, NO$_2$ and CHO groups, destabilize cations less than would be expected only on the basis of their inductive
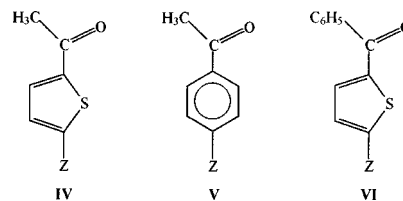
effects due to resonance delocalization of the π-orbital on the electron-acceptor substituents to the cation center.[7a,26] We found that, in the Hammett plots using the SCRF energies, electron acceptors show considerable positive deviations from linearity so that we excluded them from the Hammett plots. These positive deviations of electron-withdrawing substituents in water are consistent with the experimental observation of the increased π-contribution of such substituents in solution.[7a,27] Comparison of the SCRF $\rho_Z^{\ddagger}$ values for Y = S (-7.62) and Y = CHCH (-6.63) with those of **IV** (-2.12) and **V** (-2.17) in aqueous acid solution indicates that the SCRF method gives too large (negative) ρ_Z values. We therefore think that the continuum model of accounting for the solvent effects on the Hammett ρ values may not be adequate, and specific solvation effects such as hydrogen bonding may be important.

Quite surprisingly, semiempirical methods, AM1 and PM3, gave substantially lower values which are even lower than those at the MP2/6-31G* level. This could be due to the partial incorporation of electron correlation effects by using empirical parameters in the semiempirical methods. In this connection there is an interesting report of a satisfactory agreement between the experimental gas phase and AM1 ρ values for the chloride exchanges in the para substituted benzyl chlorides when electron-withdrawing groups only are considered; both gave the ρ value of *ca*. 6.

The trends of changes in $\rho^+{}_Z$ with the heteroatom Y are similar irrespective of the level of calculations: relatively large negative values are obtained for Y = O, and the lowest value for Y = CHCH. It should be noted that the $\rho^+{}_Z$ value does not represent the transmission efficiency of the substituent effects (which is a stationary state property, S and r_d in Table 3) but represents a change in the transmission efficiency (*i.e.*, ΔS and Δr_d) upon protonation (**R** → **P**). However, since the transmission efficiencies, S, are much greater in **P** than in **R** (Table 3), the magnitude of $\rho^+{}_Z$ follows roughly, but not exactly, that of S for the **P** state, (NH < S < PH < O).

Conclusions

The following can be concluded from this study.
(1) The natural bond orbital (NBO) analysis provides quantitative as well as qualitative interpretations of the effects of the heteroatom Y and substituent Z on various stationary state properties and reaction (and activation) parame-

ters by focussing on the role of the individual π (π^*) bonds. A rule can be established: An intervening π bond is formed (π_{23}) at the expense of the two interacting first-neighbor vicinal π bonds ($\pi_{12} \leftrightarrow \pi_{34}$).

(2) The transmission of substituent effects in **R** varies in parallel to the delocalizability of $n_\pi(Y)$ which is in the order Y = NH > O > S > PH.

(3) The transmission of substituent effects in **P** is dominantly influenced by the amount of cationic charge on C_α and the para-delocalizability of the cationic charge on C_α through the ring as a result of "competing resoance" between $n_\pi(Y)$ and substituent Z.

(4) The transmission efficiency is a stationary state property (*S*), while the Hammett constant ρ is a reaction (or activation) parameter.

(5) The Hammett $\rho_Z^\pm$ values decrease as the level of computation is raised with further lowering when solvent (water) effect is accounted for by the SCRF method. Comparison of the SCRF $\rho_Z^\pm$ values with the experimental results shows inadequacy of accounting for the solvent effects on ρ by a continuum model.

(6) The dominant contributor to the stabilization energies, $\Delta E^o = E_P - E_R$, is the vicinal π - π^* interactions between π_{CO} and π_{23}. The barriers to rotation around d_{12} are determined by the double bond character of d_{12}.

Supporting Material. Table S1 is available from the Research Section of http://dragon.inha.ac.kr/~kckyung.

References

1. (a) Hammett, L. P. *Physical Organic Chemistry*; McGrawhill: New York, 1940; p 189. (b) Charton, M. In *Correlation Analysis in Chemistry: Recent Advances*; Chapman, N. B., Shorter, J., Ed.; Plenum: New York, 1978; Chapter 5. (c) Noto, R.; Gruttadauria, M.; Rosselli, S.; Spinelli, D. *J. Chem. Soc., Perkin Trans 2* **1996**, 829.

2. Allinger, N. L.; Cava, M. P.; DeJongh, D. C.; Johnson, C. R.; Lebel, N. A.; Stevens, C. L. *Organic Chemistry*; Worth: New York, 1971; p 252.

3. Streitwieser, A.; Heathcock, C. H. *Introduction to Organic Chemistry*, 2nd ed.; Collier MacMillan: London, 1981; p 1069.

4. (a) Alder, R. W.; Baker, R.; Brown, J. M. *Mechanism in Organic Chemistry*; Wiley-Interscience: London, 1971; p 291. (b) *Ibid*. p 7.

5. (a) Craik, D. J.; Brownlee, R. T. C. *Prog. Phys. Org. Chem.* **1983**, *14*, 1. (b) Dell'Erba, C.; Sancassan, F.; Novi, M.; Petrillo, G.; Mugnoli, A.; Spinelli, D.; Consiglio, G.; Gatti, P. *J. Org. Chem.* **1988**, *53*, 3564. (c) DeMaria, P.; Fontana, A.; Spinelli, D. *J. Chem. Soc., Perkin Trans. 2* **1991**, 1067. (d) Murray, R. W.; Morgan, M. M. *J. Org. Chem.* **1991**, *56*, 684; (e) Chimichi, S.; DellErba, C.; Gruttadauria, M.; Noto, R.; Petrillo, G.; Sancassan, F.; Spinelli, D. *J. Chem. Soc., Perkin Trans 2* **1995**, 1021.

6. Lowry, T. H.; Richardson, K. S. *Mechanism and Theory in Organic Chemistry*, 3rd ed.; Harper and Row: New York, 1987; Chapters 4, 5 and 7.

7. (a) El-Nahas, A. M.; Clark, T. *J. Org. Chem.* **1995**, *60*, 8023. (b) Mishima, M.; Inoue, H.; Fujio, M; Tsuno, Y. *Tetrahedron Lett.* **1989**, *30*, 2101. (c) Richard, J. P.; Rothenberg, M. E.; Jencks, W. P. *J. Am. Chem. Soc.* **1984**, *106*, 1361. (d) Amyes, T. L.; Stevens, I. W.; Richard, J. P. *J. Org. Chem.* **1993**, *58*, 6057.

8. Hehre, W. J.; Radom, L.; Schleyer, P. v. R.; Pople, J. A. *Ab Initio Molecular Orbital Theory*; Wiley: New York, 1986; Chapter 4.

9. Dewar, M. J. S.; Zoebisch, E. G.; Healy, E. F.; Stewart, J. J. P. *J. Am. Chem. Soc.* **1985**, *107*, 3902.

10. Stewart, J. J. P. *J. Comput. Chem.* **1989**, *10*, 209.

11. (a) Becke, A. D. *J. Chem. Phys.* **1988**, *96*, 2155. (b) Lee, C.; Yang, W.; Parr, R. G. *Phys. Rev. B* **1988**, *33*, 3098.

12. Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Gill, P. M. W.; Johnson, B. G.; Robb, M. A.; Cheeseman, J. R.; Keith, T. A.; Petersson, G. A.; Montgomery, J. A.; Raghavachari, K.; Al-Laham, M. A.; Zakrzewski, V. G.; Ortiz, J. V.; Foresman, J. B.; Cioslowski, J.; Stefanov, B. B.; Nanayakkara, A.; Challacombe, M.; Peng, C. Y.; Ayala, P. Y.; Chen, W.; Wong, M. W.; Andres, J. L.; Replogle, E. S.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Binkley, J. S.; Defrees, D. J.; Baker, J.; Stewart, J. J. P.; Head-Gordon, M.; Gonzalez, C.; Pople, J. A. *Gaussian 94*; Gaussian, Inc.: Pittsburgh, PA, 1995.

13. (a) Brunck, T. K.; Weinhold, F. *J. Am. Chem. Soc.* **1979**, *101*, 1700. (b) Reed, A. E.; Curtiss, L. A.; Weinhold, F. *Chem. Rev.* **1988**, *88*, 899. (c) Glendening, E. D.; Weinhold, F. *J. Comput. Chem.* **1998**, *19*, 593, 610. (d) Glendening, E. D.; Badenhoop, J. K.; Weinhold, F. *J. Comput. Chem.* **1998**, *19*, 628.

14. Han, I. S.; Kim, C. K.; Jung, H. J.; Lee, I. *Theor. Chim. Acta* **1996**, *93*, 199.

15. (a) Musso, G. F.; Figari, G.; Magnasco, V. *J. Chem. Soc., Faraday Trans 2* **1985**, *81*, 1243. (b) Epiotis, N. D.; Cherry, W. R.; Shaik, S.; Yates, R.; Bernardi, F. *Structural Theory of Organic Chemistry*, Part II; Springer-Verlag: Berlin, 1977.

16. (a) Dewar, M. J. S. *MO Theory of Organic Chemistry*; McGraw-Hill: New York, 1969; p 184 (b) Smith, D. A.; Ulmer, C. W. II *J. Org. Chem.* **1997**, *62*, 5110.

17. (a) Olah, G. A.; Rasul, G.; Heiliger, L.; Prakash, G. K. S. *J. Am. Chem. Soc.* **1996**, *118*, 3580. (b) Epiotis, N. D.; Cherry, W. R.; Shaik, S.; Yates, R.; Bernardi, F. *Structural Theory of Organic Chemistry*, Part 1; Springer-Verlag: Berlin, 1977.

18. Reed, A. E.; Weinhold, F. *J. Am. Chem. Soc.* **1986**, *108*, 3586.

19. (a) Ehrenson, S.; Brownlee, R. T. C.; Taft, R. W. *Prog. Phys. Org. Chem.* **1973**, *10*, 1. (b) Ruff, F.; Csizmadia, I. G. *Organic Reactons, Equilibria, Kinetics and Mechanism*; Elsevier: Amsterdam, 1994; Chapter 7.

20. (a) Swain, C. G.; Lupton, E. C. *J. Am. Chem. Soc.* **1968**, *90*, 4328. (b) Swain, C. G.; Unger, S. H.; Rosenquist, N. R.; Swain, M. S. *J. Am. Chem. Soc.* **1983**, *105*, 492.

21. These values are actually resonance parameters, $\rho^r = \rho^n \cdot r^+$, in the Yukawa-Tsuno treatment, $\log(k/ko) = \rho^n [\sigma^n + r^+(\sigma^+ - \sigma^n)]$.[22a]

22. (a) Yukawa, Y.; Tsuno, Y.; Sawada, M. *Bull. Chem. Soc. Jpn* **1966**, *39*, 2274. (b) London, G. M.; Berke, C. *J. Am.*

Chem. Soc. **1974**, *96*, 4508.

23. (a) Allen, A. D.; Kanagasabapathy, V. M.; Tidwell, T. T. *J. Am. Chem. Soc*. **1986**, *108*, 3470. (b) Mishima, M.; Inoue, H.; Fujio, M.; Tsuno, Y. *Tetrahedron Lett.* **1990**, *31*, 685. (c) Lee, I. *J. Phys. Org. Chem.* **1996**, *9*, 661.

24. (a) Stewart, R.; Yates, K. *J. Am. Chem. Soc.* **1958**, *80*, 6355. (b) Mishima, M.; Mustanir; Fujio, M.; Tsuno, Y. *Bull. Chem. Soc. Jpn.* **1996**, *69*, 2009.

25. (a) Ventura, O. N.; Bartolucci, J. P. *Theor. Chim. Acta* **1984**, *64*, 229. (b) Tapia, O.; Goscinski, O. *Mol. Phys*. **1975**, *29*, 1653. (c) Karelson, M. W.; Tamm, T.; Katritzky, A. R.; Szefram, M.; Zerner, M. C. *Int. J. Quant. Chem*. **1990**, *37*, 1.

26. (a) Dixon, D. A.; Charlier, P. A.; Gassman, P. G. *J. Am. Chem. Soc.* **1980**, *102*, 3957. (b) Paddon-Row, M. N.; Santiago, C.; Houk, K. N. *J. Am. Chem. Soc.* **1980**, *102*, 6561.

27. (a) Olah, G. A.; Arvanaghi, M.; Prakash, G. K. S. *J. Am. Chem. Soc.* **1982**, *104*, 1628. (b) Gassman, P. G.; Talley, J. J.; *Tetrahedron Lett.* **1981**, *22*, 5253. (c) Amyes, T. L.; Richard, J. P.; Novak, M. *J. Am. Chem. Soc.* **1992**, *114*, 8032.