

Transmission of Substituent Effects through Five-Membered Heteroaromatic Rings, II. Deprotonation Equilibria of Phenol Analogues

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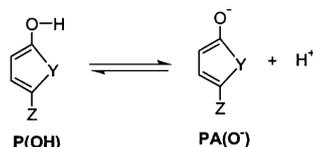
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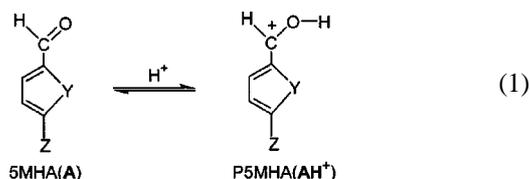
Transmission of substituent effects through 5-membered heteroaromatic rings is investigated theoretically at the RHF/6-31+G* and B3LYP/6-31+G* levels using the deprotonation equilibria of phenol analogues with heteroatoms Y = NH, O, PH and S. The increase in the resonance delocalization of the π lone-pair on the phe-



nolic oxygen atom, $n_{\pi}(\text{O})$, accompanied with the deprotonation depends on the heteroatom Y, in the order $\text{NH} < \text{O} < \text{PH} < \text{S}$. This represents the π electron accepting ability, or conversely reverse order of the π electron donating ability of the π lone-pair on Y, $n_{\pi}(\text{Y})$. The transmission efficiency of substituent effects is, however, in the reverse order $\text{NH} > \text{O} > \text{S}$, which represents the order of delocalizability of $n_{\pi}(\text{Y})$. A better correlation is obtained with σ_p^- than with σ_p for the Hammett type plots with the positive slope, $\rho^- > 0$, of the magnitude in the same order as that for the delocalizability of $n_{\pi}(\text{Y})$. The deprotonation energy, $\Delta G = [G(\text{PA}) + G(\text{H}^+) - G(\text{P})]$, decreases with the increase in the extent of resonance delocalization in the order $\text{NH} > \text{O} > \text{PH} > \text{S}$.

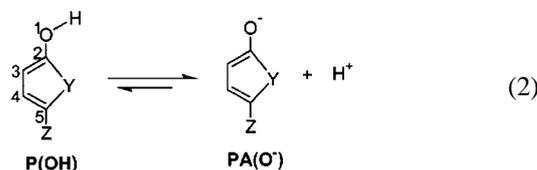
Introduction

In a previous work,¹ we investigated theoretically the transmission of substituent effects through 5-membered heteroaromatic rings involved in the protonation equilibria of aldehydes, eq. (1) where Y = NH, O, PH, S and CHCH with eight substituents Z. Both



the aldehyde (A) and its protonated form (AH⁺) are resonance stabilized by a π -donor para (C⁵) substituent, Z. The bond lengths (d_{12}) between the carbonyl (C¹) and ipso (C²) carbons were found to correctly represent the measure of resonance delocalization, and are better correlated with σ_p^+ than with σ_p as expected from the resonance delocalization of the π -donor substituents, Z.² The transmission of substituent effects in the aldehydes (A) was found to vary in parallel with the delocalizability of the π lone-pair on heteroatom ($n_{\pi}(\text{Y})$), Y = NH > O > S > PH. On the other hand, the trans-

mission of substituent effects in the protonated form (AH⁺) is dominantly influenced by the amount of cationic charge on C¹ and the para-delocalizability of the cationic charge on C¹ through the ring as a result of "competing resonance"³ between $n_{\pi}(\text{Y})$ and substituent Z. Since in this series, eq. (1), the transmission of substituent effects involves with a cationic functional center, C¹, it would be of much interest to explore theoretically the transmission behaviors involving with an anionic functional center. We therefore extend this series of work to the deprotonation equilibria of phenol analogues; Phenol \rightleftharpoons Phenolate anion + H⁺, eq. (2) where Y = NH, O, PH or S and Z = p-CH₃, H, p-H, p-Cl, p-NC, p-CN or p-NO₂. In this system, the π lone-pair on the oxygen atom is a strong donor and the para-substituent, Z, should become an acceptor, which is exactly an opposite role to the donor effect played by Z in eq. (1).⁴



Calculations

In order to obtain the structures and energies for the stationary point species in the gas phase, all the geometrical

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parameters were fully optimized without any geometrical constraints using the density functional theory (DFT) method⁵ of Becke's 3-parameter hybrid method using the correlation functional of Lee, Yang and Parr (B3LYP)⁶ with 6-31+G* basis set,⁷ B3LYP/6-31+G*/B3LYP/6-31+G*. Frequency calculations were also performed to confirm the stationary point species.⁸

The calculated electronic energy change (ΔE_{el}) in the gas phase was converted to enthalpy change (ΔH) by correcting for the zero point vibrational energy (ΔE_{ZPVE}) with the application of a scaling factor 0.9845,⁹ thermal energy (ΔE_T) and $P\Delta V(= \Delta nRT)$ terms. The Gibbs free energy change (ΔG_0) was then obtained using the calculated entropy changes ($-T\Delta S$) as eq. (3).¹⁰

$$\begin{aligned} \Delta G &= \Delta E_{el} + \Delta E_{ZPVE} + \Delta E_T + \Delta nRT - T \Delta S \\ &= \Delta H - T \Delta S \end{aligned} \quad (3)$$

The solvation energies in aqueous solution with dielectric constant (ϵ) of 78.39 were calculated using the Polarizable Continuum Model (PCM)¹¹ at the B3LYP level using the gas-phase optimized geometries, PCM-B3LYP/6-31+G*/B3LYP/6-31+G*. The calculated solvation Gibbs free energy (ΔG_s) was then obtained by the energy difference between the gas phase energy and the energy of PCM calculation. The experimental aqueous ion solvation free energy of $\Delta G_s(H^+) = -260.9$ kcal mol⁻¹ was used for the solvation energy of H⁺ ion.¹² Thus the Gibbs free energy change (ΔG_{aq}) in aqueous solution is defined as eq. (4b).

$$\Delta G_{sol} = [\Delta G_s(\mathbf{PA}) + \Delta G_s(H^+)] - \Delta G_s(\mathbf{P}) \quad (4a)$$

$$\Delta G_{aq} = \Delta G_{gas} + \Delta G_{sol} \quad (4b)$$

Natural bond orbital (NBO) and population (NPA) analyses¹³ were carried out using NBO 3.1 interfaced to Gaussian-98 program. The analyses of the NBO levels were carried out with RHF results using the optimized geometries at B3LYP level, RHF/6-31+G*/B3LYP/6-31+G*, since the calculated MO levels at the RHF level are in better agreement with the experimental data than those by the DFT method.¹⁴ Gaussian-94 and 98 program packages¹⁵ were used throughout this work.

Results and Discussion

(A) Delocalizability of the π -lone pair on Heteroatoms(Y). The bond length of d_{12} is a measure of the reso-

Table 1. Calculated bond lengths (d in Å) for Z = H

Y	NH	O	PH	S
$d_{12}(\mathbf{P})$	1.3663	1.3481	1.3618	1.3617
$d_{12}(\mathbf{PA})$	1.2731	1.2482	1.2512	1.2447
Δd_{12}	-0.0932	-0.0999	-0.1106	-0.1170
$d_{34}(\mathbf{P})$	1.4347	1.4413	1.4584	1.4344
$d_{34}(\mathbf{PA})$	1.4293	1.4312	1.4291	1.4256
Δd_{34}	-0.0054	-0.0101	-0.0293	-0.0088

nance delocalization of the π lone-pair on the oxygen atom, $n_{\pi}(O)$; the greater the delocalization of $n_{\pi}(O)$ into the ring, the shorter is the d_{12} . The bond lengths in Table 1 reveal that the d_{12} is the longest with Y = NH for both $\mathbf{P}(\mathbf{OH})$ and $\mathbf{PA}(\mathbf{O}^-)$ (Table 1) and the shortest with Y = O for $\mathbf{P}(\mathbf{OH})$ and with Y = S for $\mathbf{PA}(\mathbf{O}^-)$. This means that $n_{\pi}(N)$ is the strongest π -donor so that resonance delocalization of π lone pair on the oxygen, $n_{\pi}(O)$, into the ring is the weakest. The order of increasing bond length of d_{12} in the $\mathbf{PA}(\mathbf{O}^-)$ forms, S < O < PH < NH, matches with that of the $n_{\pi}(O)$ levels for different Y (Table 2), which indicates that the stronger the electron donor property of $n_{\pi}(Y)$, the higher is the $n_{\pi}(O)$ level, and the weaker is the resonance delocalization of $n_{\pi}(O)$ into the ring. This is at variance with the order of increasing bond length of d_{12} for the protonation equilibria of aldehydes (eq. (1)), NH < O < S < PH. This latter sequence of d_{12} demonstrates that the $n_{\pi}(N)$ is the strongest π donor toward the cationic center, the carbonyl carbon. Excepting the anomalous $n_{\pi}(P)$ ¹⁶ the two sequences of d_{12} for eqs. (1) (NH < O < S) and (2) (S < O < NH) are opposite, and indicates that the π -donor ability increases in the order, S < O < NH. The sequences of bond length changes in d_{12} accompanied in the protonation ($\mathbf{A} \rightarrow \mathbf{AH}^+$) and deprotonation ($\mathbf{P} \rightarrow \mathbf{PA}$) equilibria, $-\Delta d_{12} = d_{12}(\mathbf{AH}^+, \text{ or } \mathbf{PA}) - d_{12}(\mathbf{A}, \text{ or } \mathbf{P})$, are, however, the same, S > (PH >) O > NH. Likewise, the orders of changes in d_{34} , ($-\Delta d_{34}$ provides another measure of the resonance delocalization) are also the same in the two equilibria, eqs. (1) and (2), (PH >) O > S > NH. The reversal of the sequence from S > O ($-\Delta d_{12}$) to O > S ($-\Delta d_{34}$) may be related to the different π level gap changes involved in the equilibria.

We conclude that the π -donor ability increases in the order Y = S < O < NH but the resonance delocalization of the π -lone pair on the heteroatom, $n_{\pi}(Y)$, toward the functional center is the weakest for Y = NH increasing in the order NH < O < S for the deprotonation equilibria, eq. (2), which is

Table 2. The selected NBO lone pair ($n_{\pi}(O)$ and $n_{\pi}(Y)$) and π -bonds levels in hartree

	NH		O		PH		S	
	P	PA	P	PA	P	PA	P	PA
σ_{C-O}^*	0.6278	1.0481	0.6435	1.0790	0.6230	1.0471	0.6107	1.0509
π_{23}^*	0.1870	0.3363	0.1848	0.3444	0.1958	0.3366	0.1708	0.3282
π_{45}^*	0.1796	0.3605	0.1820	0.3523	0.1889	0.3359	0.1608	0.3356
O _{LP}	-0.5171	-0.1446	-0.5230	-0.1530	-0.5121	-0.1509	-0.5210	-0.1658
Y _{LP}	-0.3548	-0.1725	-0.4954	-0.2828	-0.5414	-0.3735	-0.3339	-0.1635
π_{23}	-0.3427	-0.1759	-0.3761	-0.1966	-0.3709	-0.1991	-0.3749	-0.2056
π_{45}	-0.3473	-0.1092	-0.3716	-0.1349	-0.3782	-0.1351	-0.3804	-0.1485

exactly the opposite to that for the protonation equilibria, eq. (1).¹

The increasing π -donor ability of $n_\pi(Y)$, $\text{PH} < \text{S} < \text{O} < \text{NH}$, leads to increasing negative charge (and electron population) on the phenolate oxygen atom, $q(\text{O}^-)$, in the same order, but in the reverse order within the ring (NBO charges in Table S1, Supplementary Materials).

(B) Transmission of Substituent Effects. The bond length changes indicate that the effects of Y and substituent Z at para position (C^5) are transmitted directly to the functional center, phenolate oxygen, and are manifested in a form of bond length contraction or stretching of d_{12} . The slope of the plot of d_{12} against σ_p^- (better correlates than σ_p) of substituent Z, eq. (5), gave susceptibility parameter, S , as

$$\delta d_{12} = S \sigma_p^- \quad (5)$$

a measure of the transmission efficiency of the substituent effect in the individual states of $\mathbf{P}(\text{OH})$ and $\mathbf{PA}(\text{O}^-)$ respectively. Similar analyses were also performed using Swain-Lupton dual substituent parameters (DSP, eq. (6),¹⁷ where F and R represent field and resonance substituent constants and f_d and r_d are the susceptibility to F and R, respectively. The results of S and r_d thus determined are summarized in

$$\delta d_{12} = f_d F + r_d R \quad (6)$$

Table 3. Reference to Table 3 reveals that although the magnitude of S is considerably greater than that of r_d the two are seen to vary in parallel (excepting again the anomalous behaviors of $Y = \text{PH}$) implying that the total susceptibility constant S is mainly influenced by the resonance effect, r_d . For both \mathbf{P} and \mathbf{PA} states, the magnitude of S (and ΔS) decreases in the order $\text{NH} > \text{O} > \text{PH} > \text{S}$, which is exactly the π -donor ability of $n_\pi(Y)$ (*vide supra*). Thus this order represents not only the π -donor ability but also the delocalizability of $n_\pi(Y)$ in response to the substituent changes (σ_p^-). Since the signs of S and r_d are negative, a stronger electron acceptor Z ($\delta\sigma_p^- > 0$) leads to a shorter d_{12} , *i.e.*, a greater degree of resonance delocalization of $n_\pi(\text{O})$ toward Z. The magnitude of S and r_d indicates that the susceptibility of phenoxide functional center to the change in Z runs parallel to the total delocalizability of $n_\pi(Y)$, *i.e.*, the greater the delocalizability of $n_\pi(Y)$ the stronger is the transmission effi-

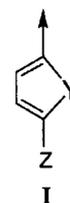
Table 3. Susceptibility Constants, S^a

$$\delta d_{12} = S \sigma_p^-, \text{ where } \delta d_{12} = d_{12}(\text{Z}) - d_{12}(\text{H})$$

Y	$S_{\mathbf{P}}$	$S_{\mathbf{PA}}$	DS^b	\mathbf{PA}^d	
				$f_d \times 10^2$	$r_d \times 10^2$
NH	-1.22	-1.71	-0.49	-0.83	-1.08
O	-1.22	-1.25	-0.03	-1.16	-0.45
PH	-1.13	-1.01	0.12	-0.64	-0.54
S	-1.01	-0.72	0.29 ^c	-0.90	-0.09

^aValues are $S \times 100$ and regression coefficients, $r > 0.93$. ^b $\Delta S = S_{\mathbf{PA}} - S_{\mathbf{P}}$. ^cZ = p-F was excluded. ^dField and resonance susceptibility constant, f_d and r_d , using Swain-Lupton relationship at B3LYP/6-31+G* level. $\delta d_{12} = f_d F + r_d R$.

ciency of the substituent effect through the ring toward the phenolate anionic center. This is rather surprising since the order of the substituent effect transmission efficiency is similar (except the anomalous $Y = \text{PH}$) to that found for the protonation equilibria of benzaldehydes, eq. (1). Thus, although actual amount of delocalization of $n_\pi(Y)$ is in the reverse order (*vide supra*) between the two (eqs. (1) and (2)), the delocalizability of $n_\pi(Y)$ and transmission efficiency of the substituent effect through the Y-ring are the same for the two equilibria. This order of delocalizability of $n_\pi(Y)$ is closely related to the experimentally found electrophilic substitution reactivity at C^2 (or C^5) of the heteroaromatic 5-membered ring, **I**. The estimated bromination rates relating to benzene



are $Y = \text{S} (5 \times 10^9) < \text{O} (6 \times 10^{11}) < \text{NH} (3 \times 10^{18})$.¹⁸

The susceptibility S represents the transmission efficiency of substituent effects for individual states, \mathbf{P} and \mathbf{PA} . However the difference in the two, $\Delta S = S_{\mathbf{PA}} - S_{\mathbf{P}}$, should represent changes in the transmission efficiency involved in the deprotonation equilibria, eq. (2). A similar substituent effect transmission measured by the energy changes involved in the deprotonation equilibria, eq. (2), is the Hammett coefficient, ρ_z^- in eq. (7)¹⁹ where ΔG is the reaction energy for eq. (2). Strong through-conjugation of negative charge on the

$$-\Delta G/2.3RT = \rho_z^- \sigma^- \quad (7)$$

phenoxide oxygen toward Z in the ring requires σ_p^- instead of σ_p .²⁰ The ρ_z^- values determined at different levels of energy computation are presented in Table 4. Reference to Table 4 shows that the ρ_z^- values calculated are all large positive indicating that strong negative charge development upon deprotonation. The magnitude is in the increasing order of $Y = \text{S} < \text{O} < \text{NH} (< \text{PH})$, which is the same order that for S and ΔS , (except for the anomalous behaviors of $Y = \text{PH}$ ¹⁶ as discussed above in the DSP analysis) and hence we arrived at the same conclusion that the greater the delocalizability of $n_\pi(Y)$, the greater is the transmission efficiency of substituent effects through the Y-ring. The magnitude of ρ_z^- (15.1-17.7 at the B3LYP/6-31+G* level)

Table 4. Calculated Hammett Type Reaction Constants, ρ_z^-

Y	RHF/6-31+G* ^a	B3LYP/6-31+G* ^b	PCM ^c
NH	17.46	17.0	9.2 ^d
O	16.72	16.5	8.5
PH	17.01	17.7	11.3
S	15.89	15.1	8.3

^aRegression coefficients, $r > 0.98$. ^bRegression coefficients, $r > 0.96$. ^cRegression coefficients, $r > 0.95$. ^dZ = p-CH₃ is excluded.

Table 5. Calculated deprotonation energies, ΔG ,^a in kcal mol⁻¹ for Z = H

Y	ΔG_g (B3LYP)	ΔG_{aq} ^b
NH	335.15	18.69
O	327.27	10.15
PH	324.98	15.22
S	322.65	11.74

^a $\Delta G = G(\mathbf{PA}) + G(\text{H}^+) - G(\mathbf{P})$ where $G(\text{H}^+) (= -6.28 \text{ kcal mol}^{-1})$ is calculated using a statistical thermodynamic relationship. ^b $\Delta G_{aq} = \Delta G_g(\text{B3LYP}) + \Delta G_{\text{sol}}(\text{PCM})$.

for the deprotonation equilibria (eq. (2)) is somewhat greater than that of ρ_z^+ (-11.1 ~ -12.3) at the B3LYP/6-31G* level) for the protonation equilibria (eq. (1)) at similar level of computation. Although the functional centers in the two equilibria are directly linked to the ring (C_α^+ in eq. (1) and O^- in eq. (2)), in the protonated aldehydes in eq. (1) an electron donor, OH, is attached to the C_α atom so that the resonance electron demand of the cationic center, C_α^+ , must be partially reduced, which in turn reduces the size of ρ_z^+ .

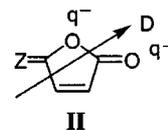
(C) Deprotonation Energies, ΔG . The deprotonation energies, ΔG in kcal mol⁻¹, are shown in Table 5. The ΔG value will be the greater, the higher is the level of phenoxide

$$\Delta G = [G(\mathbf{PA}) + G(\text{H}^+)] - G(\mathbf{P}) \quad (8)$$

anionic form, $G(\mathbf{PA})$, and the lower is the level of phenolic form, $G(\mathbf{P})$. The order of decreasing ΔG for Z = H is NH > O > PH > S which is the reverse order of bond length changes in d_{12} , $-\Delta d_{12}$, upon deprotonation. Since the amount of d_{12} contraction in the deprotonation, $-\Delta d_{12}$, should represent the increase in the extent of resonance delocalization of $n_\pi(\text{O})$ toward the Y-ring, the order of decreasing ΔG found correctly predict stabilization upon deprotonation. Thus, the π -acceptor ability of NH is the weakest, or conversely the π -donor ability of NH is the greatest, so that resonance delocalization of exocyclic $n_\pi(\text{O})$ into the Y-ring, and hence the resonance stabilization is the least for NH. Similarly, the order of decreasing deprotonation energy corresponds to the reverse order of the change in resonance delocalization in the deprotonation. This order found for eq. (2) is not related in anyway to the order obtained for eq. (1); in the latter an extra group, OH, is attached to the functional cationic center, C_α^+ , so that the resonance delocalization is also influenced by this extra group.

(D) Solvent Effects. The solvent effects on the deprotonation energies, ΔG , and the Hammett ρ_z^- value estimated by the PCM method are shown in Tables 5 and 4, respectively. The solvent effect appears to stabilize most the phenoxide anionic form (\mathbf{PA}) of Y = O. The deprotonation energy in the aqueous solution for Y = O is greatly reduced and predicted to be the lowest deprotonation energy for Y = O with other systems generally following the gas-phase order, Y = NH > PH > S (> O). The inspection of NBO charges reveals that the total negative charge on the two heteroatoms, $q(\text{O}^-) + q(\text{Y})$, is the largest for Y = O, which will

no doubt increase dipole moment of the phenoxide anion for Y = O so that the greatest solvation stabilization of the \mathbf{PA} form for Y = O is achieved, **II**.



On the other hand, the solvent effects on the transmission efficiency, ρ_z^- , seems rather uniform over different Y systems; the gas-phase order of ρ_z^- is maintained in solution. This is reasonable since in the change of substituent Z the relative change of the dipole moment between different Y systems in the gas-phase should remain the same in solution because of the gas-phase geometries used in the calculation of solvent effects.

Summary and Conclusion

The extent of resonance delocalization decreases with an increase in the π electron donating ability of the π -lone pair on heteroatom Y, $n_\pi(\text{Y})$, S > PH > O > NH. Since the stability of anionic form, $\mathbf{PA}(\text{O}^-)$, is strongly influenced by the extent of resonance delocalization, the deprotonation energy, $\Delta G = G(\mathbf{PA}) - G(\mathbf{P})$, is in the same order. The susceptibility of functional center, oxygen, to the substituent changes upon deprotonation depends strongly on the π -lone pair delocalizability of Y, $n_\pi(\text{Y})$, which increases in the order S < O < NH. Thus actual delocalization is the smallest with Y = NH, but the delocalizability of $n_\pi(\text{Y})$ is the greatest with Y = NH and accordingly the magnitude of positive Hammett coefficients increase in the order S < O < NH. The solvent exhibits a uniform effect on the transmission efficiency so that the gas-phase order is maintained in solution. Stability of phenolate anion for Y = O increases in solution due to the increase in dipole moment and the deprotonation energy becomes the smallest with Y = O, unlike in the gas phase.

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

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 16. The structures of the **P** and **PA** forms for Y = PH show that the molecules are not coplanar with pyramidal angle of ca. 95-98° at the P atom. This could be ascribed to the anomalous behaviors of this compound.
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