

## Theoretical Studies on the Protonation Equilibria of Benzoyl Derivatives

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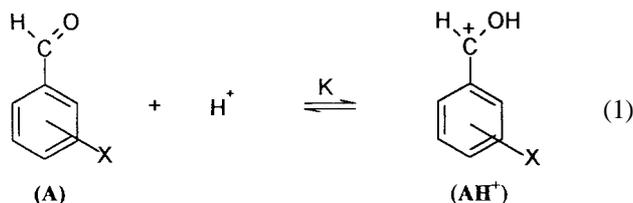
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The effects of ortho- ( $R = H$  and  $CH_3$ ) and Y-substituents ( $Y = OCH_3, CH_3, H$  and  $CN$ ), which are directly attached to the carbonyl carbon, on the protonation equilibria of the para-X-substituted benzoyl derivatives, 4-X-2,6-di-R-C<sub>6</sub>H<sub>2</sub>-C(=O)-Y, are investigated theoretically using the B3LYP method with 6-31+G\* basis set. Structurally, both of the (**B**) and (**BH**<sup>+</sup>) forms in the species with  $R = H$  are nearly coplanar regardless of the Y-substituents implying that the steric repulsion between Y-substituent and  $R = H$  is relatively small. In the species with  $R = CH_3$ , the torsional angle ( $\theta$ ) between the carbonyl moiety and aryl ring varies from zero to near right angle depending on the degree of steric repulsion between Y and  $R = CH_3$  and the resonance demand. However the reaction energies,  $\Delta G^\circ$ , for the protonation processes are more favorable for  $R = CH_3$  than for  $R = H$  due to stronger electron donating effect of  $R = CH_3$ , although the species with  $R = CH_3$  are unfavorable sterically. On the other hand, the Hammett type plots are progressively better correlated with  $\sigma^+$  than with  $\sigma$  values on going from  $Y = OCH_3$  to  $Y = CN$  for both species with  $R = H$  and  $CH_3$  indicating that the degree of resonance delocalization between carbonyl moiety and X-substituent is increased for a more electron accepting Y-substituent. Nevertheless the effects of  $R = CH_3$  on the magnitude of Hammett type reaction constants ( $\rho$  or  $\rho^+$ ) are not much different from those of  $R = H$ .

**Keywords:** Protonation equilibria, Benzoyl derivatives, Ortho-methyl substituent, B3LYP/6-31+G\*, NRT analysis.

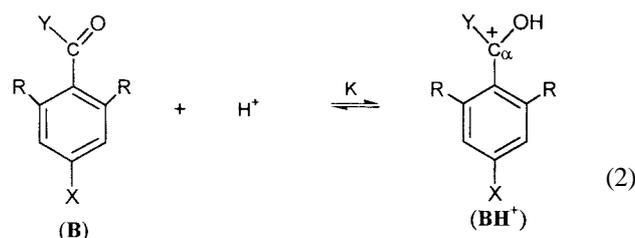
### Introduction

The protonation equilibria of the carbonyl compounds are one of the important chemical processes, since the numerous reactions of carbonyl compounds occur under the specific acid catalyzed condition. Thus the studies on the protonation equilibria of carbonyl compounds have been an interesting field in chemistry.<sup>1</sup> Recently, we have reported theoretical works on the protonation equilibria of the substituted benzaldehydes, eq. (1).<sup>2</sup> We have found that both the aldehyde (**A**) and its protonated form (**AH**<sup>+</sup>) are resonance-stabilized by a  $\pi$ -donor *para*-substituent, X, and hence the bond lengths ( $d_{cc}$ ) between the carbonyl ( $C_\alpha$ ) and ipso ( $C_{ip}$ ) carbon in both forms, (**A**) and (**AH**<sup>+</sup>), are better correlated with  $\sigma^+$  than with  $\sigma$  as expected from the resonance delocalization of the  $\pi$ -donor substituents.



However the extent of resonance-stabilization effect by a  $\pi$ -donor *para*-substituent is strongly dependent on the sub-

stituent directly attached to the carbonyl carbon. Moreover, it is expected that the resonance-stabilization effect of a  $\pi$ -donor *para*-substituent will be effective only for the species with a co-planar structure such as benzaldehyde, *i.e.*, the resonance-stabilization effect of a  $\pi$ -donor *para*-substituent will be less effective or diminished if the carbonyl compound had a non-planar structure due to steric reasons. Therefore, in this work, we have studied theoretically the effect of a Y-substituent, which is directly attached in the carbonyl carbon, for the protonation equilibria of the para-X-substituted benzoyl derivatives of eq. (2). Also, in order to investigate the effects of the X- and Y-substituents more thoroughly, the protonation equilibria for the system in which two *ortho*-positions of aryl ring are substituted by  $R = CH_3$  in eq. (2) have been studied. In the species with  $R = CH_3$  the extent of resonance delocalization will be decreased



$R = H$  and  $CH_3$ ,

$Y = OCH_3, CH_3, H$  and  $CN$

$X = NH_2, OCH_3, CH_3, H, Cl, CN$  and  $NO_2$

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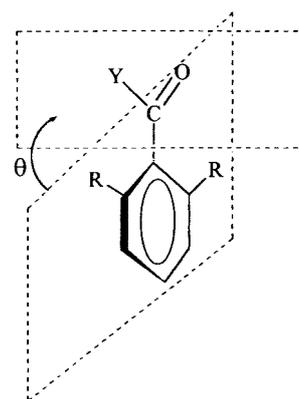
compared to R = H, because the molecular planarities in both the (**B**) and (**BH**<sup>+</sup>) forms can be obstructed by the repulsive steric effects between the two ortho methyl substituents and carbonyl moiety.

### Calculation

The Gaussian-98 program<sup>3</sup> was used in this work. The geometries were fully optimized at RHF/6-31G\* and B3LYP/6-31+G\* levels. The vibrational frequencies were calculated at the RHF/6-31G\* level to confirm the stationary point species.<sup>4</sup> The zero-point energy-corrected electronic energies were converted to enthalpy (H) by correcting for translational, rotational and vibrational contributions and adding RT (PV term) using the thermodynamic properties calculated at RHF/6-31G\* level. The Gibbs free energy changes,  $\Delta G$ , were then obtained using the calculated entropy changes,  $\Delta G = \Delta H - T\Delta S$ , at 298 K.<sup>5</sup> The natural resonance theory (NRT) analyses developed by Weinhold and co-workers<sup>6</sup> were carried out using NBO-4M program<sup>7</sup> interfaced to the Gaussian-98 program.

### Results and Discussion

**Structures.** To investigate the structural effects of the two ortho-methyl substituents (R = CH<sub>3</sub>) in eq. (2), torsional angles ( $\theta$ ) between carbonyl moiety and aryl ring as represented in Scheme 1 for the species with R = CH<sub>3</sub> are examined in Table 1. In the R = H systems, both the (**B**) and (**BH**<sup>+</sup>) forms are nearly coplanar ( $\theta \cong 0.0^\circ$ ) regardless of the substituents, X and Y. This might imply that the steric repulsion between Y-substituent and R = H is not so large. Whereas, as collected in Table 1, the angles,  $\theta$ , in the R = CH<sub>3</sub> systems vary from zero to near right angle. However, although the variations of the torsional angles in the R = CH<sub>3</sub> systems appear complex, these results are easily understandable by two factors which have opposite effects: (i) the degree of resonance delocalization between X-substituent and carbonyl carbon, C<sub>α</sub>, and (ii) the degree of steric repulsion between Y and R = CH<sub>3</sub>. In other words, if the degree of resonance delocalization between X-substituent and carbonyl carbon increases, the molecular planarity will be enforced and hence the magnitude of  $\theta$  will decrease. In con-



Scheme 1

trast, if the degree of steric repulsion between Y and R = CH<sub>3</sub> increases, the molecular planarity will be destroyed and  $\theta$  will increase.

Examination of Table 1 shows that both the (**B**) and (**BH**<sup>+</sup>) forms are non-planar by *ca.*  $\theta = 15\text{--}90^\circ$  for the species with R = CH<sub>3</sub> and Y = OCH<sub>3</sub> and CH<sub>3</sub>. This indicates that the steric repulsions between R and Y substituents are relatively large. However, as predicted above, the magnitude of  $\theta$  in the protonated forms, (**BH**<sup>+</sup>), is much smaller compared to that in the corresponding neutral forms, (**B**), by 21–29° and 23–57° for R = OCH<sub>3</sub> and CH<sub>3</sub>, respectively, since the resonance demand is enhanced in the (**BH**<sup>+</sup>) form so as to stabilize the cationic center, C<sub>α</sub>. In contrast, the magnitude of  $\theta$  in the species with Y = H and R = CH<sub>3</sub> is nearly zero indicating the coplanar structures for both the (**B**) and (**BH**<sup>+</sup>) forms. Therefore it is expected that the steric repulsion between Y = H and R = CH<sub>3</sub> is relatively weak compared to that between Y = OCH<sub>3</sub> or CH<sub>3</sub> and R = CH<sub>3</sub>, because the van der Waals radius of Y = H is much smaller than that of Y = OCH<sub>3</sub> or CH<sub>3</sub>. On the other hand, for the species with R = CH<sub>3</sub> and Y = CN, the (**B**) forms are non-planar by  $\theta \cong 26$  (X = NH<sub>2</sub>) ~ 44° (X = NO<sub>2</sub>), but the (**BH**<sup>+</sup>) forms are nearly coplanar ( $\theta \cong 0^\circ$ ). These  $\theta$  values for the species with Y = CN are much smaller compared to those for Y = OCH<sub>3</sub> or CH<sub>3</sub>. However these results are due to the differences in electronic effects rather than the steric effects between Y = OCH<sub>3</sub> or CH<sub>3</sub> and CN, *i.e.*, the demand of stabilization by the resonance delocalization in the species with Y = CN will be much larger than that those with Y = OCH<sub>3</sub> or CH<sub>3</sub> due to stronger  $\pi$ -accepting ability of Y = CN, even if the degrees of steric repulsion between two substituents, R and Y, are similar or larger for Y = CN compared to Y = OCH<sub>3</sub> or CH<sub>3</sub>.

Besides the effect of Y-substituent, the magnitude of  $\theta$  in both the (**B**) and (**BH**<sup>+</sup>) forms is also influenced by X-substituents, since the magnitude of  $\theta$  progressively decreases on going from a stronger  $\pi$ -accepting ( $\Delta\sigma > 0$ ) to a stronger  $\pi$ -donating X-substituent ( $\Delta\sigma < 0$ ) for the species with non-planar structures. For example, in the species with Y = CH<sub>3</sub> and R = CH<sub>3</sub>, the magnitude of  $\theta$  progressively increases from 42° (X = NH<sub>2</sub>) to 89° (X = NO<sub>2</sub>) for the (**B**) forms and from 23° (X = NH<sub>2</sub>) to 32° (X = NO<sub>2</sub>) for the (**BH**<sup>+</sup>) forms, respectively. These results are undoubtedly caused by the

**Table 1.** Torsional angles ( $\theta$  in degree) between carbonyl moiety and aryl ring for the species with R = CH<sub>3</sub>

X	Y = OCH <sub>3</sub>		Y = CH <sub>3</sub>		Y = H		Y = CN	
	( <b>B</b> )	( <b>BH</b> <sup>+</sup> )	( <b>B</b> )	( <b>BH</b> <sup>+</sup> )	( <b>B</b> )	( <b>BH</b> <sup>+</sup> )	( <b>B</b> )	( <b>BH</b> <sup>+</sup> )
NH <sub>2</sub>	35.7	14.9	42.4	22.6	0.2	0.0	26.1	0.0
OCH <sub>3</sub>	39.4	18.9	58.9	24.2	0.3	0.0	30.2	0.0
CH <sub>3</sub>	45.3	19.6	68.1	26.2	0.2	0.0	34.3	0.0
H	49.4	22.9	75.0	28.4	0.0	0.0	37.5	0.0
Cl	46.9	21.7	70.7	27.3	0.2	0.0	36.1	0.0
CN	54.3	25.2	81.7	30.1	0.1	0.0	41.7	0.0
NO <sub>2</sub>	57.3	28.5	89.1	31.9	0.3	0.0	44.3	0.0

**Table 2.** The calculated bond lengths ( $d_{cc}$  in Å) between the carbonyl ( $C_\alpha$ ) and ipso ( $C_{ip}$ ) carbons

R	X \ Y	OCH <sub>3</sub>		CH <sub>3</sub>		H		CN	
		(B)	(BH <sup>+</sup> )	(B)	(BH <sup>+</sup> )	(B)	(BH <sup>+</sup> )	(B)	(BH <sup>+</sup> )
H	NH <sub>2</sub>	1.480	1.420	1.488	1.400	1.469	1.383	1.464	1.390
	OCH <sub>3</sub>	1.484	1.428	1.493	1.406	1.473	1.387	1.469	1.395
	CH <sub>3</sub>	1.488	1.438	1.498	1.417	1.478	1.395	1.475	1.402
	H	1.491	1.445	1.501	1.424	1.481	1.401	1.479	1.408
	Cl	1.490	1.440	1.501	1.420	1.480	1.397	1.478	1.404
	CN	1.495	1.449	1.506	1.428	1.485	1.404	1.485	1.411
	NO <sub>2</sub>	1.497	1.453	1.508	1.433	1.487	1.407	1.487	1.415
Susceptibility <sup>a</sup>		0.77	1.54	0.93	1.54	0.87	1.15	1.07	1.19
R	X \ Y	OCH <sub>3</sub>		CH <sub>3</sub>		H		CN	
		(B)	(BH <sup>+</sup> )	(B)	(BH <sup>+</sup> )	(B)	(BH <sup>+</sup> )	(B)	(BH <sup>+</sup> )
CH <sub>3</sub>	NH <sub>2</sub>	1.489	1.425	1.499	1.416	1.468	1.380	1.470	1.391
	OCH <sub>3</sub>	1.492	1.433	1.508	1.422	1.472	1.384	1.476	1.395
	CH <sub>3</sub>	1.496	1.442	1.512	1.431	1.477	1.390	1.482	1.400
	H	1.499	1.448	1.515	1.437	1.480	1.394	1.486	1.405
	Cl	1.498	1.444	1.515	1.433	1.479	1.392	1.485	1.402
	CN	1.503	1.452	1.518	1.441	1.485	1.398	1.492	1.408
	NO <sub>2</sub>	1.504	1.456	1.518	1.445	1.487	1.403	1.495	1.411
Susceptibility <sup>a</sup>		0.73	1.42	0.85	1.38	0.87	0.95	1.12	0.95

<sup>a</sup>Susceptibility = (slope) × 100. Regression coefficients (r) are better than 0.98.

enhanced resonance-delocalization ability of a stronger  $\pi$ -donating X-substituent, *i.e.*, the degree of resonance delocalization between carbonyl moiety and X-substituent should be larger for a stronger  $\pi$ -donating X-substituent than for a stronger  $\pi$ -accepting X-substituent since the carbonyl moiety (Y-(C=O)-) itself acts as a  $\pi$ -accepting group.

To compare steric effects with resonance delocalization more thoroughly, the calculated bond lengths,  $d_{cc}$ , between the carbonyl ( $C_\alpha$ ) and ipso ( $C_{ip}$ ) carbons in the (B) and (BH<sup>+</sup>) forms are collected in Table 2. In general, the bond length  $d_{cc}$  reflects the degrees of steric repulsion and resonance delocalization between carbonyl moiety and aryl ring. As is well known, the larger the degree of steric repulsion the longer the  $d_{cc}$  becomes in order to release the unfavorable steric repulsion. The bond length  $d_{cc}$  becomes shorter as the degree of resonance delocalization is larger, since the double bond character in the  $d_{cc}$  is increased.

Examination of Table 2 shows that the  $d_{cc}(B)$  in the species with R = H and X = H decreases in the order Y = CH<sub>3</sub> > OCH<sub>3</sub> > H > CN. This order is mainly the results of the differences in the degree of resonance delocalization due to Y-substituents, since the degree of steric repulsion for the species with R = H and X = H is relatively small as discussed above. The degree of resonance delocalization due to Y-substituent will be larger for the Y-substituent with a more electron accepting power. Therefore this order indicates that Y = OCH<sub>3</sub> is acting as a stronger electron withdrawing substituent than Y = CH<sub>3</sub> in the neutral form (B), since the  $\sigma$ -accepting power of Y = OCH<sub>3</sub> is larger compared to Y = CH<sub>3</sub> even if Y = OCH<sub>3</sub> is generally known as a stronger  $\pi$ -donating

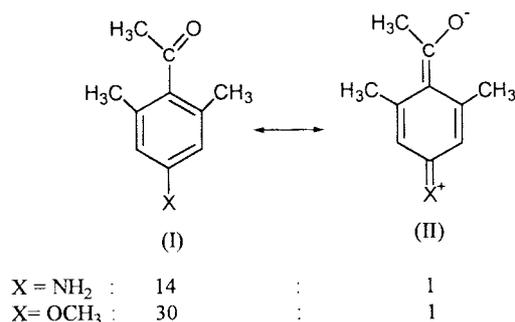
substituent. In contrast, the bond length  $d_{cc}(B)$  in the species with R = CH<sub>3</sub> decreases in the order Y = CH<sub>3</sub> > OCH<sub>3</sub> > CN > H. The order of  $d_{cc}(B)$  in the species with R = CH<sub>3</sub> is similar but reversed for Y = H and CN compared to that with R = H. This can be rationalized with the larger degree of steric repulsion between R = CH<sub>3</sub> and Y for Y = CN than for Y = H as discussed above in the torsional angle (Table 1). Thus the bond length  $d_{cc}$  is stretched for Y = CN so as to release the unfavorable steric repulsion, albeit the delocalizing ability, which makes  $d_{cc}(B)$  shorter, is larger for Y = CN than for Y = H.

The  $d_{cc}(BH^+)$  in the species with X = H decreases in the order Y = OCH<sub>3</sub> > CH<sub>3</sub> > CN > H for both R = H and CH<sub>3</sub>. This order is consistent with the electron-donating ability of Y, *i.e.*, the degree of resonance delocalization between carbonyl moiety and aryl ring is reduced as the electron-donating ability of Y-substituent is increased, and hence  $d_{cc}$  is stretched. Nevertheless, if so, this order seems to be inconsistent with the electron-donating ability of Y for Y = H and CN, since Y = CN is a much stronger electron acceptor than Y = H. However, in a cationic system, it has been shown experimentally<sup>8</sup> as well as theoretically<sup>9</sup> that  $\pi$ -acceptor substituents such as CHO and CN etc. can act as  $\pi$ -donors. We have also confirmed the  $\pi$ -donating ability of Y = CN in 1-substituted-allyl cations by the high level *ab initio* calculations using the Gaussian-3 and CBS-Q methods.<sup>10</sup> Therefore the order of  $d_{cc}(BH^+)$  agrees well with the  $\pi$ -donating abilities of Y. However, the distance,  $d_{cc}$ , in the species with R = CH<sub>3</sub> for both the (B) and (BH<sup>+</sup>) forms are, in general, slightly longer than those with R = H except for Y = H, reflecting the increasing steric repulsion for the species with R = CH<sub>3</sub>. The  $d_{cc}$  in the species with Y = H is similar for both R = H and CH<sub>3</sub>. Once again, these results indicate that the degrees of steric repulsion for both species with R = H and CH<sub>3</sub> are similar as predicted above (Table 1).

On the other hand, the  $d_{cc}$  bonds are shortened in the protonated forms, (BH<sup>+</sup>), compared to the neutral forms, (B). This bond contraction,  $\Delta d_{cc} (=d_{cc}(BH^+) - d_{cc}(B)) < 0$ , indicates stronger delocalization in the (BH<sup>+</sup>) form once again. Nevertheless we have analyzed the effects of the Y- and X-substituents in the individual states, (B) and (BH<sup>+</sup>) forms on the variations of the  $d_{cc}$  using the eq. (3) and the slopes of the plots of eq. (3)<sup>11</sup> are summarized in Table 2. In both the (B) and (BH<sup>+</sup>) forms, the plots of eq. (3) are better correlated with  $\sigma^+$  than  $\sigma$  constants<sup>12</sup> indicating the direct conjugation between  $C_\alpha$  and X. However, the fact that all the plots are better correlated with  $\sigma^+$  than with  $\sigma$  seems to be somewhat

$$d_{cc} = \text{slope} \times \sigma^+ \quad (3)$$

surprising, especially for the cases of Y = CH<sub>3</sub> with R = CH<sub>3</sub>; it could be predicted that the resonance delocalization by direct conjugation is difficult structurally, since the  $\theta$  in the (B) forms are significantly distorted by 42 and 59° even for X = NH<sub>2</sub> and OCH<sub>3</sub>, respectively, which are regarded as strong  $\pi$ -donor substituents. Nevertheless, the fact that the plot is better correlated with  $\sigma^+$  implies that the effect of



Scheme 2

resonance delocalization contributes dominantly to the substituent effects for a stronger  $\pi$ -donor substituent. This expectation are confirmed by the relative ratio of resonance structures obtained using the Natural Resonance Theory (NRT) developed by Weinhold and co-workers. The relative ratios between two resonance structures, unconjugated (I) and conjugated resonance structures (II), for the species with X = NH<sub>2</sub> and OCH<sub>3</sub> are represented in Scheme 2. As represented in Scheme 2, conjugated structure (II) contributes to the resonance structure by less than 10% as compared to structure (I). The ratio of the resonance structure (II) to (I) is negligibly small for the species with a relatively stronger electron acceptor X-substituent such as X = CN or NO<sub>2</sub> etc. The Hammett type plot such as eq. (3) reflects the changes of substituent effects and the contribution of the delocalized resonance structure of (II) becomes much larger for a stronger  $\pi$ -donor compared to a  $\pi$ -acceptor X-substituent. Therefore, although the relative contributions of the resonance structures of (II) are smaller than those of (I), the plots of eq. (3) could be better correlated with  $\sigma^+$  than with  $\sigma$ .

On the other hand, the slopes of eq. (3) reflect the susceptibilities of  $d_{cc}$  bond lengths to the variations of the X substituents in the individual (**B**) and (**BH**<sup>+</sup>) forms. Therefore, the magnitude of the slope is larger for (**BH**<sup>+</sup>) forms than for the corresponding (**B**) forms except for the species with Y = CN and R = CH<sub>3</sub> as summarized in Table 2, since the demand of the stabilization by resonance delocalization between carbonyl moiety and aryl ring will be larger for the (**BH**<sup>+</sup>) form than for the corresponding (**B**) form. The only exception for the species with Y = CN and R = CH<sub>3</sub> might be caused by the structural differences between (**B**) and (**BH**<sup>+</sup>) forms. As noted above, the (**B**) forms are non-planar but (**BH**<sup>+</sup>) forms are planar in the species with Y = CN and R = CH<sub>3</sub>. Therefore, the degrees of the steric repulsion as well as the resonance delocalization in (**B**) forms are much different from those of the (**BH**<sup>+</sup>) forms.

However, the susceptibilities of the functional centers to the variation of Y-substituent for the (**B**) forms are in reverse order to that of the (**BH**<sup>+</sup>) forms, *i.e.*, the magnitudes of the slopes are larger for the (**B**) forms but smaller for the (**BH**<sup>+</sup>) forms as the electron accepting power of Y increases. These trends reflect the competitive effects between the carbonyl moiety and X-substituent. In other words, in the neutral forms (**B**) the electron densities in the carbonyl moiety are

relatively rich compared with the protonated forms, (**BH**<sup>+</sup>). Thus the susceptibility (slope) becomes larger as the electron accepting power of the Y increases,<sup>11</sup> since the degree of the resonance delocalization will be enhanced between the carbonyl carbon, C<sub>α</sub>, and a stronger  $\pi$ -electron donating X-substituent. The electron densities in the carbonyl moiety are much poorer for the (**BH**<sup>+</sup>) forms, and hence the degree of the resonance delocalization is enhanced between the carbonyl carbon, C<sub>α</sub>, and a stronger  $\pi$ -accepting X-substituent as the electron donating power of the Y increases. So that the susceptibility becomes larger as the electron donating power of the Y increases for the (**BH**<sup>+</sup>) forms.

**Energetics.** The stabilization energies,  $\Delta G^\circ = G(\mathbf{AH}^+) - [G(\mathbf{A}) + G(\mathbf{H}^+)]$ , involved in the protonation process of eq (2) are summarized in Table 3. The electronic effects of R = CH<sub>3</sub> as an electron donor substituent are expected to be important besides the steric effects discussed above. These electronic effects of R = CH<sub>3</sub> compared to R = H could be inferred from the differences of  $\Delta G^\circ$  ( $\delta\Delta G^\circ$ ) in the species with Y = H, since the torsional angles (Table 1) for both of (**B**) and (**BH**<sup>+</sup>) forms for the species with Y = H and R = CH<sub>3</sub> are nearly zero indicating the coplanar structures. This implies that the degree of steric repulsion between R = CH<sub>3</sub> and Y = H is also relatively small and comparable to the case with R = H (*vide supra*). Therefore the  $\delta\Delta G^\circ$  between R = H and CH<sub>3</sub> for the species with Y = H may be considered as the differences of pure electronic effects. As expected, reference to Table 3 shows that the  $\delta\Delta G^\circ$  are more favorable by 5.1-6.5 kcal mol<sup>-1</sup> for R = CH<sub>3</sub> than for R = H, and hence these differences are caused by relatively stronger electron donating effect of R = CH<sub>3</sub> than R = H. However, unfortunately, for the species except for Y = H the magnitude of electronic effects by R = CH<sub>3</sub> cannot be estimated, since the favorable electronic and unfavorable steric effects by R = CH<sub>3</sub> are mutually cancel out each other, *i.e.*, it could be expected that the degrees of steric effect by R = CH<sub>3</sub> are different for the (**B**) and (**BH**<sup>+</sup>) forms, because the torsional angles (Table 1)

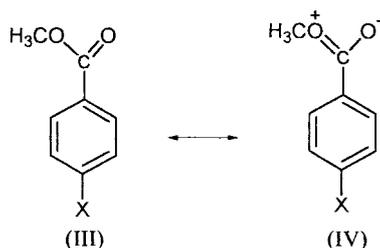
Table 3. The stabilization energies ( $\Delta G^\circ$  in kcal mol<sup>-1</sup>) at 298 K for the protonation process of eq. (2)

R	Y				
	X	OCH <sub>3</sub>	CH <sub>3</sub>	H	CN
H	NH <sub>2</sub>	-204.43	-212.04	-207.98	-198.33
	OCH <sub>3</sub>	-199.75	-206.51	-201.85	-192.22
	CH <sub>3</sub>	-196.57	-201.8	-196.92	-185.99
	H	-193.8	-197.56	-191.74	-180.85
	Cl	-191.93	-196.06	-190.69	-180.72
	CN	-184.3	-188.15	-182.55	-172.59
	NO <sub>2</sub>	-181.9	-185.62	-176.48	-169.29
CH <sub>3</sub>	NH <sub>2</sub>	-206.69	-208.85	-212.92	-202.61
	OCH <sub>3</sub>	-201.7	-204.01	-207.16	-196.33
	CH <sub>3</sub>	-198.56	-199.99	-201.74	-189.62
	H	-195.76	-196.01	-197.9	-185.45
	Cl	-193.33	-193.99	-196.58	-184.92
	CN	-186.61	-186.09	-188.64	-176.53
	NO <sub>2</sub>	-184.57	-183.45	-186.02	-173.92

are decreases in ( $\mathbf{BH}^+$ ) forms.

On the other hand, the  $-\Delta G^\circ$  for the species with R = H and X = H decreases in the order Y = CH<sub>3</sub> > OCH<sub>3</sub> > H > CN. This stabilization energy order may be mainly caused by the stabilizing abilities of cationic center, C<sub>α</sub>, by Y in the ( $\mathbf{BH}^+$ ) forms. Of course, if the stabilization energy order only results from the stabilizing abilities of Y in the ( $\mathbf{BH}^+$ ) forms, this order should be reversed for Y = OCH<sub>3</sub> and CH<sub>3</sub>, because the stabilizing ability of cationic center in the ( $\mathbf{BH}^+$ ) form is undoubtedly larger for Y = OCH<sub>3</sub> than for Y = CH<sub>3</sub>. However, the stabilization energies are actually originated by the difference of stabilizing effects between ( $\mathbf{B}$ ) and ( $\mathbf{BH}^+$ ) forms. Therefore, although the degree of stabilization by Y = OCH<sub>3</sub> is larger than that by CH<sub>3</sub> in ( $\mathbf{BH}^+$ ) form, if the same effect is also operates in ( $\mathbf{B}$ ) form, then the net stabilization energy,  $-\Delta G$ , will be larger for Y = CH<sub>3</sub> rather than for Y = OCH<sub>3</sub>. This stabilization effect by Y = OCH<sub>3</sub> in ( $\mathbf{B}$ ) form is indeed confirmed by the NRT analysis, *i.e.*, the ratio of the resonance structure (III) to (IV) with X = H is *ca.* 6 : 1 as represented in Scheme 3. The contribution of the resonance structure such as (IV) is negligible in ( $\mathbf{B}$ ) form with Y = CH<sub>3</sub>, since the resonance structure such as (IV) in ( $\mathbf{B}$ ) form with Y = CH<sub>3</sub> can only be achieved by the *pseudo-π* structure of Y = CH<sub>3</sub>.

The  $-\Delta G^\circ$  for the species with R = CH<sub>3</sub> and X = H decreases in the order Y = H > CH<sub>3</sub> > OCH<sub>3</sub> > CN. This order is similar to that with R = H except for Y = H, *i.e.*, the relative order of  $-\Delta G$  is the same for Y = OCH<sub>3</sub>, CH<sub>3</sub> and CN in both of R = H and CH<sub>3</sub>, but the  $-\Delta G$  of Y = H is the largest for the species with R = CH<sub>3</sub>. This result indicates that the stabilization by electronic effects of Y = OCH<sub>3</sub> or CH<sub>3</sub> in the ( $\mathbf{BH}^+$ ) form cancels out by the unfavorable steric repulsions between Y and R = CH<sub>3</sub> as discussed above. Indeed, these unfavorable steric repulsions are also revealed by the differences in  $-\Delta G$  between Y = OCH<sub>3</sub> and CH<sub>3</sub>, *i.e.*, although the values of  $\Delta G$  for both of R = H and CH<sub>3</sub> are larger for Y = CH<sub>3</sub> than for Y = OCH<sub>3</sub>, the difference of  $\Delta G$  between Y = OCH<sub>3</sub> and CH<sub>3</sub> for the species with R = CH<sub>3</sub> is much smaller compared to that with R = H as can be seen in Table 3. For example, the difference of  $\Delta G$  between Y = OCH<sub>3</sub> and CH<sub>3</sub> is 3.7 kcal mol<sup>-1</sup> for the species with R = H and X = H but is only 0.3 kcal mol<sup>-1</sup> for the species with R = CH<sub>3</sub> and X = H. These results show that the unfavorable steric repulsion in the ( $\mathbf{BH}^+$ ) form increases much more for the species with Y = CH<sub>3</sub> than with Y = OCH<sub>3</sub>, since the torsional angle in the ( $\mathbf{BH}^+$ ) decreases much more than in the ( $\mathbf{B}$ ) form for the species with Y = CH<sub>3</sub> relative to Y = OCH<sub>3</sub>.



Scheme 3

**Table 4.** The Hammett type reaction constants,  $\rho$  and  $\rho^+$ , and the ratio of  $f/r$  obtained by DSP analyses

R	Y	$\rho$	$\rho^+$	$f/r^a$
H	OCH <sub>3</sub>	-11.2 (r = 0.995)	-7.6 (r = 0.981)	1.3
	CH <sub>3</sub>	-13.4 (r = 0.991)	-9.2 (r = 0.995)	0.9
	H	-14.3 (r = 0.988)	-9.9 (r = 0.996)	0.8
	CN	-14.4 (r = 0.980)	-10.1 (r = 0.997)	0.6
CH <sub>3</sub>	OCH <sub>3</sub>	-11.2 (r = 0.997)	-7.7 (r = 0.989)	1.2
	CH <sub>3</sub>	-13.0 (r = 0.994)	-8.9 (r = 0.989)	1.1
	H	-13.5 (r = 0.988)	-9.4 (r = 0.997)	0.8
	CN	-14.3 (r = 0.980)	-10.0 (r = 0.998)	0.6

<sup>a</sup>Regression coefficients (r) are better than 0.995.

**Reaction Parameters.** The reaction constants ( $\rho$  and  $\rho^+$ ) in the Hammett type relationship<sup>13</sup> of eq. (4) are collected in Table 4. Interestingly, the plots of the  $\Delta G^\circ$  are progressively better correlated with  $\sigma^+$  than with  $\sigma$  values on going from Y = OCH<sub>3</sub> to Y = CN for both species with R = H and CH<sub>3</sub>. For example, the plots of eq. (4) are better correlated with the  $\sigma$  (regression coefficient, r = 0.995 and 0.997 for R = H and CH<sub>3</sub>, respectively) than  $\sigma^+$  (r = 0.981 and 0.989 for R = H and CH<sub>3</sub>, respectively) for the species with Y = OCH<sub>3</sub>. On the contrary, the plots of eq. (4) are better correlated the  $\sigma^+$  (r = 0.997 and 0.998 for R = H and CH<sub>3</sub>, respectively) rather than  $\sigma$  (r = 0.980 for both of R = H and CH<sub>3</sub>) for the species with Y = CN. This indicates that the degree of resonance delocalization between carbonyl moiety and X-substituent increases for more electron-accepting Y-substituent. Consequently the magnitude of the reaction constants ( $\rho$  or  $\rho^+$ ) becomes large as the electron-accepting power of Y-substi-

$$-\frac{\Delta G^\circ}{2.303RT} = \rho\sigma(\text{or } \rho^+\sigma^+) \quad (4)$$

tuent increases due to the enhanced interaction between the carbonyl moiety and X-substituents. However the magnitudes of the  $\rho$  and/or  $\rho^+$  values are very similar for both of the species with R = H and CH<sub>3</sub>. Therefore it is expected that the effects of R = CH<sub>3</sub> on the reaction constants do not differ from those of R = H, although the structural effects by R = H and CH<sub>3</sub> are very different (Table 1).

These expectations are confirmed by using the Swain-Lupton dual substituent parameters (DSP) analyses<sup>14</sup> of eq. (5) where F and R represent field and resonance substituent constants and  $f$  and  $r$  are the susceptibility to F and R, respectively. The ratio of two susceptibility parameters,  $f/r$ , are also summarized in Table 4. As can be seen in Table 4,

$$-\frac{\Delta G^\circ}{2.303RT} = fF + rR \quad (5)$$

the magnitude of the ratio,  $f/r$ , progressively decreases on going from Y = OCH<sub>3</sub> to CN for both of the species with R = H and CH<sub>3</sub> and these results imply strongly the enhanced contributions of resonance delocalization for Y = CN compared with Y = OCH<sub>3</sub>. These trends are consistent with those

of reaction constants discussed above, *i.e.*, the plots of eq. (4) are progressively better correlated with  $\sigma^+$  than with  $\sigma$  values indicating the enhanced effects of resonance delocalization on going from Y = OCH<sub>3</sub> to Y = CN. However the relative magnitudes of the  $f/r$  are very similar for both R = H and CH<sub>3</sub> in the species with a same Y-substituent. These results indicate that the relative contributions between the resonance and inductive effects are very similar for both the species with R = H and CH<sub>3</sub>. Once again, this is in good agreement with the expectations from the magnitudes of the reaction constants above, *i.e.*, the magnitudes of the  $\rho$  and/or  $\rho^+$  values are very similar for both of the species with R = H and CH<sub>3</sub>.

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