

# On the Direction and Magnitude of Radical Substituent Effects: The Role of Polar Interaction on Thermodynamic Stabilities of Benzylic C–H Bonds and Related Carbon Radicals

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The C–H bond dissociation enthalpies (BDEs) of *polarized* benzylic molecules, i.e., para-substituted phenylacetonitriles (PANs), and the spin variations of the radicals of the general type  $p\text{-GC}_6\text{H}_4\text{-CH}\cdot\text{Y}$  were investigated using density functional theory (DFT) calculations. In contrast to the commonly observed *S*-type substituent effect (see text), the present work shows that there should be *three* (rather than one) primary patterns (i.e., *S*, *O*, and counter-*O*) for remote G to affect spin and radical stability, depending upon the polarity of the  $\alpha\text{-Y}$  group. Correlation analyses reveal that both the direction and magnitude of spin/radical effects are quantitatively related to the intensity of polar interaction in radical system, as registered by either the calculated group charges of the phenyl ring ( $C_{\text{Ph}}$ ) or by the polar constant  $\sigma^+$ s (Figures 1–4). A unified platform (Scheme 1) to rationalize the apparent differences of radical substituent effect is proposed.

## Introduction

Substituent effects on the relative bond dissociation enthalpies ( $\Delta\text{BDEs}$ ),<sup>1–5</sup> or on radical stability/reactivity,<sup>6,7</sup> have for the past decades drawn substantial research attention from both experimental and theoretical aspects. It has been widely observed that carbon-centered radicals, e.g.,  $\text{G}\cdot\text{C}\cdot\text{RR}'$  and  $p\text{-GC}_6\text{H}_4\text{C}\cdot\text{RR}'$ , can be stabilized by both electron-donating groups ( $\text{G} = \text{EDG}$ ) and electron-withdrawing groups ( $\text{G} = \text{EWG}$ ).<sup>6,8</sup> In contrast, remote substituent effects on heteroatomic radicals (e.g.,  $\text{O}\cdot$ ,  $\text{N}\cdot$ ,

$\text{S}\cdot$ ) have been found to exhibit linear correlation with the polar Brown  $\sigma^+$  constants,<sup>9</sup> indicating that the stability of these radicals increases with EDG substitution but decreases with EWG substitution.<sup>1–3</sup> In fact, these findings are quite in accordance with the earlier so-called class *S/O* definition of Walter,<sup>10</sup> in which the terms “*S*” and “*O*” refer to radical stability being affected by EDG and EWG in the *same* and in the *opposite* directions, respectively. On the basis of this concept and previous experimental evidence,<sup>8</sup> carbon-centered radicals are obviously of the class *S* type, whereas heteroatom-centered radicals the class *O* type. The *O/S*-type variations of BDEs and the anticipated classification have also been demonstrated recently by a number of theoretical calculations.<sup>4,5</sup>

In our recent experimental work on the benzylic C–H BDEs of polarized toluenes (i.e.,  $p\text{-GC}_6\text{H}_4\text{CH}_2\text{-Y}$ ,  $\text{Y} = \text{EWG}$ ),<sup>11</sup> we found that the BDE variation induced by remote substitution showed, however, an *O*-pattern, viz., most of the strong *p*-EWGs *strengthen* the C–H bond rather than weaken the bond. This is inconsistent with the anticipation of a *S*-behavior from the previous  $\sigma^6$  and gas-phase BDE studies<sup>8</sup> for benzylic systems. The apparent discrepancy raised a simple but very fundamental question about the structural criteria that govern the patterns of carbon radical substituent effects. Yet despite the occasionally reported observations of the *O*-effect for

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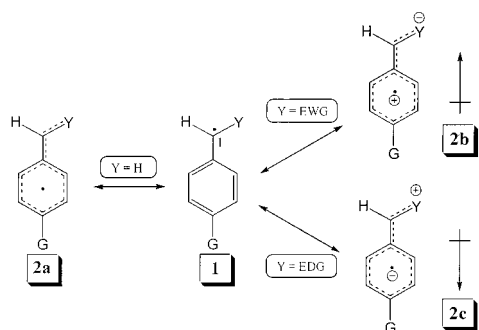
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Scheme 1



benzylic radicals,<sup>11b-d</sup> its generality as a new pattern of C-radical substituent effect has for a long time not been commonly realized and recognized.<sup>6b,11a</sup> The only substituent effect introduced in current textbooks for carbon radicals is still the *S*-type.<sup>12</sup> A complete spectrum of substituent effects for C-radicals has not been intensively described and its origins not yet analytically discussed. Indeed, as pointed out recently by Ingold et al.:<sup>4a</sup> “We must conclude that problems relating to the relative magnitudes and even the direction of the effect of substituents on benzyl radical stabilization/destabilization remain unsolved.”

As clearly demonstrated by our wide observations of the *O*-type *p*-GC<sub>6</sub>H<sub>4</sub>CH<sup>•</sup>-EWG radicals,<sup>11</sup> the direction of the substituent effect is actually controlled by apparent electronegativity of the benzylic carbon atom. So, the *direction* problem could now be better understood. However, due to the inherent limitation of the experimentally derived BDE data in quantitative differentiation of various contributors of radical stability (i.e., radical effect, polar effect, and ground-state effect), the *magnitude* of the problem has so far not been determined. Moreover, radicals of the *p*-GC<sub>6</sub>H<sub>4</sub>CH<sup>•</sup>-EDG type and the characteristics of their substituent effect have not been seriously considered yet. In this regard, theoretical analysis on the formerly observed experimental phenomena and quantitative differentiation of energetic components to further address the rules of the C-radical effect and the factor that governs the magnitude of the effects become necessary.

In the present work, a detailed theoretical analysis of remote substituent effect on benzylic C–H BDEs and on related radical stability is presented, using density functional theory (DFT) calculations of para-substituted PANs, toluenes, and  $\alpha$ -methoxycarbonylphenylacetonitriles (MPAN)<sup>13</sup> Special attention has been paid to quantitate the polar interactions of para substituents on the stabilization of spin and of the entire system, as adjusted by varying the geminal substitution at the benzylic position. *Three* (instead of one or two as previously reported) primary patterns (i.e., *O*, *S*, and counter-*O* types, vide infra) of substituent effect for describing the behaviors of carbon radicals are disclosed and rationalized. A unified analytical platform (Scheme 1) that describes the mechanisms of spin/polar interactions and bridges the apparent gaps between the distinct types of

radical substituent effect is proposed. This provides a generalized understanding of the spin vs polar factors that control both the direction and magnitude of the substituent effect. On the basis of quantitative characterization of the electronic properties of the relevant radical species, the central role of polar interactions as reflected by the ring charge ( $C_{Ph}$ ) in dominating the behaviors of prepolarized radical species (the majority) is established.

### Method of Calculation

All calculations in this paper were performed using the GAUSSIAN 98W<sup>14</sup> program package. Both ab initio restricted open-shell Møller–Plesset perturbation theory truncated at the second order (ROMP2)<sup>15</sup> and the density functional hybrid method B3LYP<sup>16</sup> were used. Since the primary purpose of this study was to analyze the effects of substituents on the stabilities of radicals that are conventionally represented by  $\Delta$ BDE rather than the absolute values, the expensive ROMP2 method with basis sets larger than 6-31G(d) was applied only in the calculations of certain typical PAN derivatives in order to justify the use of cost-effective methods. The geometries and energies of the PAN and BEN series were calculated using B3LYP/6-31G(d). In addition, Dewar's semiempirical method AM1<sup>17</sup> was used to optimize the geometries of the bulky MPAN\* radicals. On this basis, the spin populations were calculated using UB3LYP/6-31G(d).<sup>18</sup> The obtained spin populations were found to be essentially the same as those calculated using the UB3LYP/6-31G(d)-optimized geometries (vide infra and see also the Supporting Information). In the following text, the single-point calculations using B3LYP/6-31G(d) on AM1 geometries are referred to as the B3LYP//AM1 method, whereas those on the B3LYP/6-31G(d) geometries are denoted as the B3LYP method.

The vibrational analysis was performed on the B3LYP/6-31G(d) geometries to verify the structures of minimum energy and to provide zero-point vibrational energies (ZPVEs, scaled by the recommended factor of 0.9806<sup>19</sup>). Calculated BDEs of PAN derivatives were corrected for ZPVEs and thermal effects due to transitional, rotational, and vibrational motions of the related nonlinear molecules/radicals. There are no rotational and vibrational degrees of freedom for the hydrogen atom, so the contribution from the last two corrections was ignored. The *PV* term was also included to convert energy change to enthalpy change. There were no imaginary vibrational frequencies in these calculations, indicating the molecules and related radicals under study correspond to the lowest potential minima.

Since the effect of para substitution on zero-point correction to BDEs in the PAN series was found to be smaller than 0.1

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(13) The use of MPAN\* to model EPAN\* was for a consideration of simplicity and computer time. The replacement of ethyl with methyl was believed not to induce a variation in either BDE or spin delocalization, especially in a relative sense.

**Table 1. Calculated  $\Delta$ BDEs (RSEs), Ground-State Effects (GE), and Radical Effects (RE) of Para-Substituted PANs,  $\Delta$ BDEs (RSEs) of Para-Substituted BENs, and Experimental  $\Delta$ BDEs (RSEs) of Para-Substituted EPANs<sup>a</sup>**

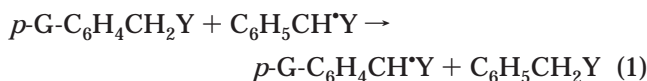
<i>p</i> -G	PAN <sup>a</sup>		EPAN <sup>a</sup>		BEN <sup>a</sup>
	$\Delta$ BDE (RSE)	GE <sup>b</sup>	RE <sup>c</sup>	$\Delta$ BDE (RSE) <sup>d</sup>	$\Delta$ BDE (RSE)
Me <sub>2</sub> N	-3.2 (3.2)	1.5	4.7		-1.8 (1.8)
MeO	-1.5 (1.5)	0.6	2.1	-2.0 (2.0)	-0.8 (0.8)
Me	-0.5 (0.5)	0.3	0.8	-0.3 (0.3)	-0.3 (0.3)
H	(0)	(0)	(0)	(0)	(0)
F	-0.2 (0.2)	-0.2	0.0	0 (0)	0.0 (0.0)
Cl	0.0 (0.0)	-0.6	-0.6	0.5 (-0.5)	-0.2 (0.2)
CO <sub>2</sub> Me	0.1 (-0.1)	-0.7	-0.8	1.7 (-1.7)	-0.6 (0.6)
CF <sub>3</sub>	0.7 (-0.7)	-1.0	-1.7	1.9 (-1.9)	0.1 (-0.1)
CN	0.3 (-0.3)	-1.5	-1.8	2.9 (-2.9)	-0.6 (0.6)
NO <sub>2</sub>	0.7 (-0.7)	-1.8	-2.5		-0.6 (0.6)

<sup>a</sup> Calculated by the B3LYP method. Energies are in kcal/mol.  $\Delta$ BDEs are derived from eq 1. RSE =  $-\Delta$ BDE. <sup>b</sup> Derived from eq 2. <sup>c</sup> Derived from eq 3. <sup>d</sup> Reference 11c.

kcal/mol (see the Supporting Information), this correction for  $\Delta$ BDEs was ignored. The charge and spin populations were calculated using the natural population analysis (NPA) scheme.<sup>20</sup>

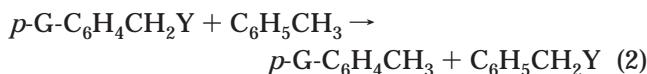
## Results

Relative bond dissociation enthalpies of the *p*-GC<sub>6</sub>H<sub>4</sub>-CH<sub>2</sub>Y systems were calculated according to the following isodesmic reaction.

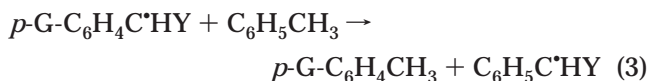


The results were used in the comparisons with the reported experimental  $\Delta$ BDE (vide infra).

A better description of the substituent effects on radical stability should include the contribution of the effect of substituent on parent molecule, which is also known as the ground-state effect (GE).<sup>21</sup> On the basis of the concept of the geminal effect,<sup>22,23</sup> in this paper, GE was defined via the following isodesmic reaction of eq 2.



Similarly, the "net" radical effect (RE) of substituent can be defined by the relevant isodesmic reaction (eq 3).



The results described above are given in the following tables: Table 1 compiles the results of  $\Delta$ BDEs of the PAN, BEN, and MPAN series and GEs and REs of the PAN series; Table 2 tabulates the calculated relative spin

**Table 2. Calculated Relative Spin Populations ( $\Delta S_1$ )<sup>a</sup> of Para-Substituted PAN's, Benzyl Radicals (BEN's), and  $\alpha$ -Cyano- $\alpha$ -methoxycarbonylbenzyl Radicals (MPAN's)**

<i>p</i> -G	PAN <sup>a</sup>	BEN <sup>a</sup>	MPAN <sup>a,b</sup>
Me <sub>2</sub> N	-0.063	-0.041	
MeO	-0.027	-0.016	-0.047 (-0.046)
Me	-0.011	-0.008	-0.018
H	(0)	(0)	(0)
F	-0.007	-0.002	-0.016 (-0.010)
Cl	-0.007	-0.010	-0.012
CO <sub>2</sub> Me	-0.010	-0.031	0.004
CF <sub>3</sub>	0.005	-0.006	0.015
CN	-0.009	-0.035	0.004 (0.004)
NO <sub>2</sub>	-0.007	-0.042	

<sup>a</sup> Calculated by the B3LYP method except as noted.  $\Delta S_1 = S_{(C)} - S_{(H)}$ . The  $S_{(H)}$  values of PAN<sup>a</sup>, BEN<sup>a</sup>, and MPAN<sup>a</sup> are 0.591, 0.726, and 0.504, respectively. <sup>b</sup> Data in italics were calculated by the B3LYP//AM1 method ( $S_{(H)}$  value for MPAN<sup>a</sup> calculated by the B3LYP//AM1 method is 0.482).

**Table 3. Deviations of the Calculated C-H BDEs from the Experimentally Determined Values for PAN Using B3LYP and ROMP2 on Several Basis Sets<sup>a</sup>**

substituents	<i>p</i> -Me <sub>2</sub> N	H	<i>p</i> -CN
(U)B3LYP/6-31G(d)	-4.2	-5.2	-5.2
(U)B3LYP/6-311+G(2d,2p)	-4.1	-4.7	-4.5
R(O)MP2/6-311+G(2d,2p)	-0.7	-1.9	-1.5
experimental BDE <sup>b</sup>	78.1 <sup>c</sup>	82.1	82.6

<sup>a</sup> In kcal/mol. <sup>b</sup> From ref 11c except noted. <sup>c</sup> From ref 11d.

**Table 4. Substituent Effects on C-H BDE of PAN Using B3LYP and ROMP2<sup>a</sup>**

substituents	<i>p</i> -Me <sub>2</sub> N	H	<i>p</i> -CN
(U)B3LYP/6-31G(d)	-3.0	(0)	+0.5
(U)B3LYP/6-311+G(2d,2p)	-3.4	(0)	+0.7
R(O)MP2/6-311+G(2d,2p)	-2.8	(0)	+0.9
experimental $\Delta$ BDE <sup>b</sup>	-4.0 <sup>c</sup>	(0)	+0.5

<sup>a</sup>  $\Delta$ BDEs are in kcal/mol. <sup>b</sup> From ref 11c except noted. <sup>c</sup> Reference 11d.

populations of the para-substituted PAN<sup>a</sup>, BEN<sup>a</sup>, and MPAN<sup>a</sup> radicals.

## Discussion

**Test of Theoretical Methodology of Computing BDEs and  $\Delta$ BDEs for Prepolarized Systems.** To test the adequacy of the B3LYP/6-31G(d) method for this work, the geometries of selected para-substituted PAN molecules and radicals (*p*-G = H, Me<sub>2</sub>N, CN) were optimized using (U)B3LYP/6-31G(d). Single-point energies were calculated using both the UB3LYP and ROMP2 methods with the 6-311+G(2d,2p) basis set on these geometries. Deviations of the calculated BDEs from the corresponding experimental values are presented in Table 3. The effects of substituents on radical stability ( $\Delta$ BDE) are given in Table 4.

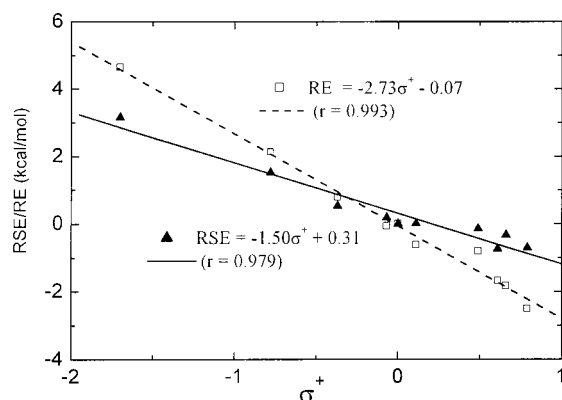
Inspection of Table 3 indicates that the basis set effects for the B3LYP are small. The largest difference between the results obtained using 6-31G(d) and 6-311+G(2d,2p) is only 0.7 kcal/mol. Table 3 also shows that B3LYP/6-31G(d) underestimates the BDEs by 4–5 kcal/mol, whereas the ROMP2/6-311+G(2d,2p) method gives BDEs very close to those of the experiments. Obviously, the B3LYP is not as good a method as ROMP2 in accurately reproducing experimental BDEs in an absolute sense for

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**Figure 1.** Calculated substituent effect on radical stabilization energy (RSE) and radical effects (RE) for PAN• versus  $\sigma^+$  constants.

polarized molecules. This is in line with the results of recent high-level ab initio studies.<sup>24,25</sup>

However, as shown in Table 4, substituent effects on the C–H BDE of PAN calculated by the methods listed are all in good agreement with those of experiments. This indicates that the noted underestimation of C–H BDEs by B3LYP/6-31G(d) for prepolarized systems is systematic and would not interfere with the investigation on substituent effects. Henceforth, a “pre-polarized system” means a molecule or, especially, a radical in which the charge density of its phenyl ring is perturbed by the benzylic  $\alpha$ -substitution (relative to the toluene or benzyl radical).

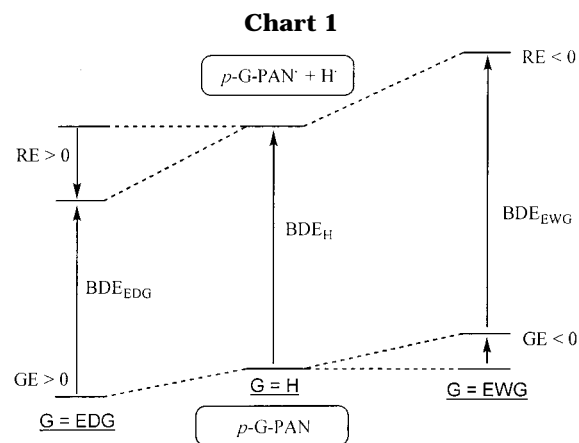
**Substituent Effect on RSEs ( $-\Delta$ BDEs), Ground-State Effects (GE), and Radical Effects (RE).** If the convention commonly used in the literature to equate relative BDE as the quantitative measure of radical stabilization energy (RSE)<sup>1–3,7,8</sup> is followed, the substituent effect on radical stability can be derived simply by computing the  $\Delta$ BDE values from an isodesmic reaction similar to eq 1.

However, as mentioned previously, the true RSE should include a contribution from the floating of the ground-state effect (GE) induced by the same substitution.<sup>21</sup> This can be readily assessed by the use of the isodesmic reaction similar to eq 2.

The derived RSEs of the PAN series are listed in Table 1. The experimental RSEs of *p*-GC<sub>6</sub>H<sub>4</sub>CH(CN)CO<sub>2</sub>Et (referred as EPAN, which is analogous to MPAN)<sup>11a</sup> are also listed for the purpose of comparison.

Table 1 shows that the PAN• radical is stabilized by all donor groups (positive RSE) but destabilized by all strong acceptor groups (negative RSEs), demonstrating an *O*-type BDE variation. Correlation of the derived RSEs versus Brown  $\sigma^+$  constants is basically linear (Figure 1, filled triangles); the negative slope ( $-1.5$  kcal/mol) reflects an electron-deficient state of the benzylic carbon (C<sub>1</sub>) and the dominant role of polar effect to the overall radical stability.

The GE data in Table 1 show that the EDGs stabilize the ground-state PAN molecule, whereas the EWGs do just the opposite. Because the influence of substituents on GEs follows essentially the same direction as it does



for the PAN• radical, the REs should be expected to be greater than RSEs. Correlation of RE versus Brown  $\sigma^+$  (Figure 1,  $r = 0.993$ , hollow squares) and GE versus Hammett  $\sigma_p$ <sup>9</sup> ( $r = 0.987$ , see the Supporting Information) are both linear, reflecting again the importance of polar effect on the pre-polarized PAN• radical and molecule. It is noted that the effect of substituents on the ground-state PAN molecule (GE) is quite sizable (ranging 3.3 kcal/mol), which is in contrast to the negligible effect on nonpolar toluenes of the *p*-GC<sub>6</sub>H<sub>4</sub>CH<sub>3</sub> type reported previously.<sup>4a,b</sup> Nevertheless, the basic principle commonly practiced in the literature to use  $\Delta$ BDE to approximate RSE should still hold valid in the present cases because the net substituent effect on the PAN radical (RE) is even greater (ranging 7.2 kcal/mol). In this sense, the observed *O*-type RSE variation can be understood by realizing that the PAN• radicals are more strongly stabilized/destabilized by polar substituents than the corresponding molecules. This relationship is schematically depicted in Chart 1.

The B3LYP calculations of relative C–H BDEs of some *p*-GC<sub>6</sub>H<sub>4</sub>CH<sub>2</sub>–H molecules were also carried out for the purpose of comparison (Table 1). The  $\Delta$ BDE(BEN•) values show that the “regular” benzyl radical is clearly of the *S*-type, which is in contrast to the *O*-type variation of the PAN• RSEs revealed presently by both theoretical and experimental studies (Table 1). This obvious inconsistency of substituent effects for carbon radicals of the same benzylic family implies an essential difference in their controlling factors of radical stability. Indeed, the above-demonstrated linear correlation of the radical parameters of PAN• with the polar substituent constant  $\sigma^+$  (see Figure 1) and the fairly good correspondence of RSE-(BEN•) with the radical constant  $\sigma_{jj}^{*6b}$  ( $r = 0.96$ ) indicate that the stability of these two radical series, PAN• and BEN•, is dominated, respectively, by polar effects and spin-delocalization effects.

The reasons behind this apparent difference in their governing factors of radical stability are conceivably related to the difference in their polarity, which functions to tune the relative contributions of spin delocalization and polar interaction to the overall radical stability. In this connection, an inspection of the role of polar effect on spin delocalization should be desirable.

**Polar Effect on Spin Delocalization.** Although spin delocalization has been widely discussed in the radical literature, the role of polarity changes on spin stabilization/destabilization has, however, not been clearly addressed. From Brinck et al.’s<sup>5a</sup> recent B3LYP calculations

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(25) Parkinson, C. J.; Mayers, P. M.; Radom, L. *J. Chem. Soc., Perkin Trans. 2* **1999**, 2305.

**Table 5. Calculated Radical Parameters<sup>a</sup> of Para-Substituted PAN's ( $\sigma_{\text{PAN}}$ ), Benzyl Radicals ( $\sigma_{\text{BEN}}$ ), and  $\alpha$ -Cyano- $\alpha$ -methoxycarbonylbenzyl Radicals ( $\sigma_{\text{MPAN}}$ ) and Some Experimental  $\sigma$  Scales in the Literature**

<i>p</i> -G	$10\sigma_{\text{PAN}}$	$10\sigma_{\text{BEN}}$	$10\sigma_{\text{MPAN}}^b$	$10\sigma_{\alpha}^c$	$\sigma_{\text{H}}^d$	$\Delta D^e$
Me <sub>2</sub> N	1.07	0.56			1.00	0.32
MeO	0.46	0.22	0.94	0.18	0.23	-0.04
Me	0.19	0.11	0.50	0.15	0.15	0.15
H	(0)	(0)	(0)	(0)	(0)	(0)
F	0.12	0.03	0.28	-0.11	-0.02	-0.17
Cl	0.12	0.14	0.25	0.11	0.22	0.09
CO <sub>2</sub> Me	0.17	0.43	-0.16	0.43	0.33	0.52
CF <sub>3</sub>	-0.08	0.08	-0.27	-0.09	-0.01	0.11
CN	0.15	0.48	-0.16	0.40	0.42	0.54
NO <sub>2</sub>	0.12	0.58			0.36	0.90

<sup>a</sup> Derived from eq 4. The spin populations used are calculated by the B3LYP method except as noted. <sup>b</sup> From the spin populations calculated by the B3LYP//AM1 method. <sup>c</sup> Reference 6a. <sup>d</sup> Reference 6b. <sup>e</sup> Reference 6e.

of phenoxy series, one could sense that the effect of EDGs on spin delocalization is notably greater than that of EWGs, which is in contrast to the comparable effects of EDG/EWG found in the relatively nonpolar benzyl systems.<sup>6a</sup> Since this may imply a role of polarity difference in altering the extent of radical spin, we in this work have calculated spin populations for two prepolarized radical families (*p*-G-PAN<sup>•</sup> and *p*-G-MPAN<sup>•</sup>) (Table 2) and by using the method of Arnold (eq 4)<sup>6a</sup> derived the radical substituent constants  $\sigma_{\text{PAN}}$  and  $\sigma_{\text{MPAN}}$ . These values, together with a few representative  $\sigma^+$  scales of benzylic radicals in the literature, are compiled in Table 5. The hyperfine coupling constants (hfc's) of the PAN<sup>•</sup> radical calculated in this work using UB3LYP/6-31G(d) were found to agree very well with the experimental esr hfc's<sup>26</sup> ( $r = 0.9975$ ) and are provided as Supporting Information.

$$\sigma_{\text{PAN}}^+ = 1 - \frac{S_{(p-G)}}{S_{\text{H}}} = - \frac{\Delta S_1}{S_{\text{H}}} \quad (4)$$

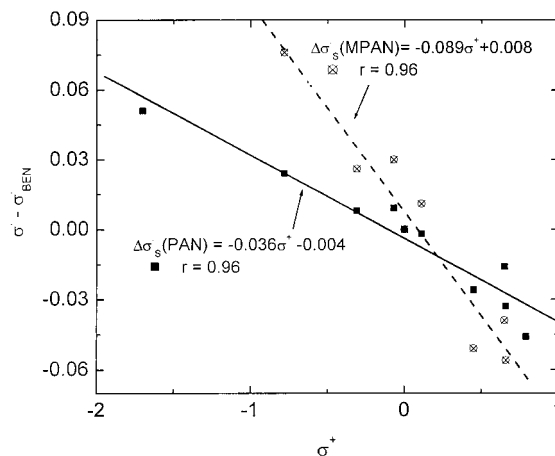
Inspection of the  $\sigma_{\text{PAN}}$  and  $\sigma_{\text{BEN}}$  data in Table 5 shows that all para substituents, except for *p*-CF<sub>3</sub>, are spin stabilizing ( $\sigma^+ > 0$ ), which is basically in agreement with the trends as exhibited by experimentally derived  $\sigma^+$  constants<sup>6</sup> (Table 5) of benzyl radicals. However, a comparison of the relative sizes of the substituent parameters between  $\sigma_{\text{PAN}}$ 's and those of the benzyl radicals reveals an interesting fact that, similar to the above-mentioned situation for phenoxy radicals, the prepolarized PAN<sup>•</sup> system again differs from the nonpolar benzyl radicals in that the  $\sigma_{\text{PAN}}$ (EDG)'s are all greater than  $\sigma_{\text{PAN}}$ (EWG)'s. A supportive evidence to this phenomenon is found from an esr study of the *p*-GC<sub>6</sub>H<sub>4</sub>C<sup>•</sup>(CH<sub>3</sub>)CN radicals, which showed that the *p*-EWG indeed delocalizes the spin less effectively than *p*-EDG.<sup>27</sup> It then follows that if the parent radical is further polarized, as in the case of MPAN<sup>•</sup>, by an additional CO<sub>2</sub>Me group at the benzylic carbon, the contrast between the effects of EDG vs EWG on spin should be expected to be even greater. In fact, this is exactly what is seen from the  $\sigma_{\text{MPAN}}$  data in Table 5. The negative  $\sigma_{\text{MPAN}}$  values of the  $\pi$ -acceptor

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**Figure 2.** Polar effect on spin delocalization for PAN<sup>•</sup> and MPAN<sup>•</sup> relative to BEN<sup>•</sup>:  $\Delta\sigma_s(\text{PAN})$  and  $\Delta\sigma_s(\text{MPAN})$  versus  $\sigma^+$ .

groups indicate that these EWGs even induce *localization* for the odd electron in the MPAN<sup>•</sup> system. Here again, the strong influence of polarity difference of various radical systems on spin delocalization is demonstrated.

The effect of polar interaction on spin delocalization may also be viewed, more quantitatively, by examining the relationship of relative radical constant  $\Delta\sigma_s$  versus the polar constant  $\sigma^+$  ( $\Delta\sigma_s = \sigma - \sigma_{\text{BEN}}$ , subscript s refers to spin). It is obvious that the term  $\Delta\sigma_s$  describes a gain or a loss of spin by remote substituent relative to that of the reference system benzyl. Here, the benzyl radical is taken as the reference because it is relatively nonpolar ( $\mu = 0.13$  D). Figure 2 shows that plots of  $\Delta\sigma_s(\text{PAN})$  and  $\Delta\sigma_s(\text{MPAN})$  vs  $\sigma^+$  are both linear, the larger slope of the latter clearly reflects a stronger polar influence on the spin of the MPAN<sup>•</sup> radical relative to that of the PAN<sup>•</sup> radical.

**The Direction of Radical Substituent Effect As Affected by Polar Interaction: A Unified Rationale for the Distinct S-, O-, and Counter-O-Patterns.** On the basis of the foregoing discussion, it is conceivable that if a radical is polarized to the direction opposite to that of the PAN<sup>•</sup> or MPAN<sup>•</sup> by substituting the  $\alpha$ -EWG with an  $\alpha$ -EDG, the opposite trend of spin variation as induced by remote substituent should be expected. Indeed, an earlier esr study of *p*-GC<sub>6</sub>H<sub>4</sub>C<sup>•</sup>(OMe)CH<sub>3</sub> radicals did show that *p*-EDGs generally *destabilize* the spin whereas *p*-EWGs stabilize the spin.<sup>27</sup> It is therefore conceivable that there may exist actually three basic patterns (instead of one, i.e., the S-type, as reported) of spin delocalization effect for benzylic-type carbon radicals alone. That is, the S-pattern (both EDG and EWG stabilize the spin), the O-pattern (spin is stabilized by EDG but destabilized by EWG), and the counter-O-pattern (spin is destabilized by EDG but stabilized by EWG). To rationalize these seemingly very distinct spin effects, a unified analytical platform on the basis of polar interactions is proposed (Scheme 1).

Scheme 1 shows three forms (**2a–c**) of polar interaction between para substituent G and the  $\alpha$ -Y group of varying polarity. When Y is an H atom, the spin is delocalized into the nonpolar ring system (i.e., **2a**) and could be further delocalized by either a *p*-EDG or a *p*-EWG. If Y is an EWG (**2b**), only the *p*-EDG is compatible to the radical polarity so as to allow the spin to be further

**Table 6.** esr Hyperfine Coupling Constants (hfc's, Gauss) for Para-Substituted Benzylic Carbon Radicals,<sup>a</sup> Derived Spin Delocalization Parameter  $\sigma\sigma^b$  of *p*-MeO and *p*-CN, and Relative Phenyl-Ring Charge ( $\Delta C_{Ph}$ )<sup>c</sup>

	ArC*(CN)CH <sub>3</sub> <sup>d</sup>		ArCH <sub>2</sub> <sup>e</sup>		ArC*(CH <sub>3</sub> ) <sub>2</sub> <sup>f</sup>		ArC*(OMe)CH <sub>3</sub> <sup>d</sup>	
	<i>a</i> H <sub>β</sub>	<i>σ</i> <sup>g</sup>	<i>a</i> H <sub>α</sub>	<i>σ</i> <sup>g</sup>	<i>a</i> H <sub>β</sub>	<i>σ</i> <sup>g</sup>	<i>a</i> H <sub>β</sub>	<i>σ</i> <sup>g</sup>
<i>p</i> -MeO	14.61	0.087	15.95	0.018	16.10	0.011	15.75	-0.016
<i>p</i> -H	16.00	(0)	16.25	(0)	16.28	(0)	15.50	(0)
<i>p</i> -CN	15.90	0.006	15.60	0.040	15.37	0.056	13.95	0.100
Δ <i>C</i> <sub>Ph</sub>	0.111		(0)		-0.019		-0.118 <sup>i</sup>	

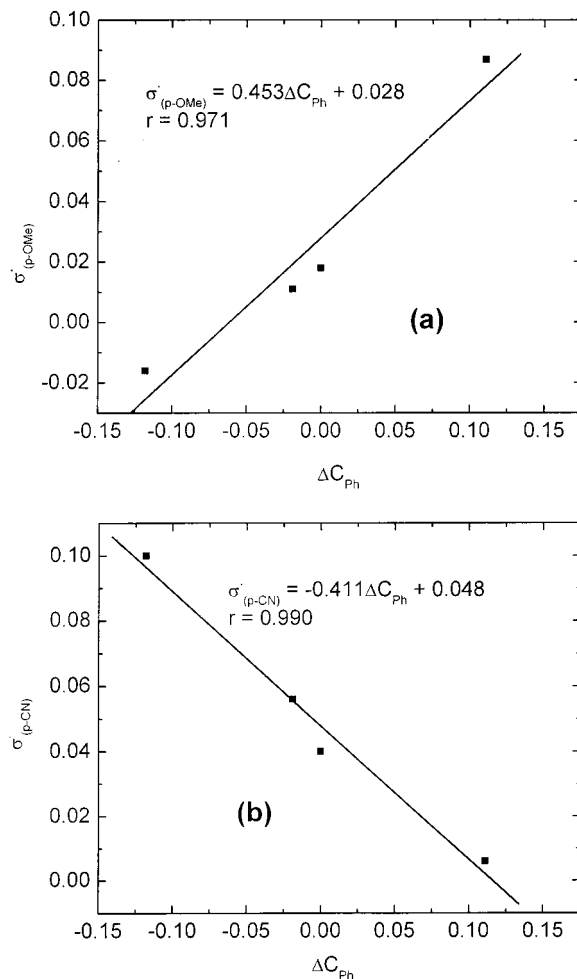
<sup>a</sup> *a*H<sub>α</sub> and *a*H<sub>β</sub> refer to the hfc values of benzylic α-H and α-CH<sub>3</sub>, respectively. <sup>b</sup> Derived from hfc values by the method of Arnold ( $\sigma^g_{(p-G)} = 1 - aH_{(p-G)}/aH_{(p-H)}$ ).<sup>6a</sup> <sup>c</sup> Calculated by the B3LYP method. Δ*C*<sub>Ph</sub> = *C*<sub>Ph</sub>(C\*XY) - *C*<sub>Ph</sub>(BEN\*). *C*<sub>Ph</sub>(BEN\*) = -0.070. <sup>d</sup> Reference 28. <sup>e</sup> Reference 6a. <sup>f</sup> Reference 28. <sup>i</sup> Value for analogous PhC\*(OH)CH<sub>3</sub> radical.

delocalized in an enlarged system, whereas a *p*-EWG would prohibit the formation of **2b** due to a conflicting polar interaction and, therefore, tends to localize the spin to the benzylic C<sub>1</sub> position (as in **1**). On the other hand, if Y is an EDG, as in the case of **2c**, the opposite trend of spin variation as a result of polar interaction should be expected. Obviously, the herein-mentioned three types of polar interaction within the benzylic radical systems **2a**, **2b**, and **2c** are bound to respectively lead to the distinct *S*-, *O*-, and counter-*O*-types of spin delocalization effect.

On this basis, it is conceivable that the proposed polar mechanism generates a unified "continuous spectrum" in which the para substituent could behave in various ways to stabilize the charge and spin because the polarity of the radical can in principle be tuned by the α-Y group of any degree of electron-donating/withdrawing capacity. In this sense, the well-documented spin delocalization by all *p*-EDGs and *p*-EWGs on benzylic carbon radicals studied in the literature<sup>6</sup> could then be viewed as one special case that is valid only to nonpolarized radicals.

**The Magnitude of Radical Stabilization As Affected by Polar Interaction: Toward a Quantitative Understanding of Radical Substituent Effect.** Scheme 1 suggests that the pattern and intensity of polar interaction as varied by remote substitution in a prepolarized system (**2b** or **2c**) be guided mainly by the electrostatic interaction between substituent G and the charged phenyl ring. It then follows that the group charge of the phenyl (referred as *C*<sub>Ph</sub>) can be taken to represent the strength of a phenyl to electronically react with a particular referencing G. On the basis of these tactics, the effect of polar interaction on the radical spin of some representative **2a**, **2b**, and **2c** systems was inspected. Table 6 presents the calculated *C*<sub>Ph</sub>'s [Δ*C*<sub>Ph</sub>'s, referenced to *C*<sub>Ph</sub>(BEN\*)] of PhC\*(CN)CH<sub>3</sub> (**2b**), PhCH<sub>2</sub>• (**2a**), PhC\*(CH<sub>3</sub>)<sub>2</sub> (**2c**), and PhC\*(OMe)CH<sub>3</sub> (**2c**), along with the experimental esr hfc's of the corresponding para-substituted species found in the literature. Only those of the *p*-OMe and *p*-CN derivatives were selected there to respectively exemplify the situations for EDGs and EWGs.

It is immediately noted from Table 6 that the derived parameters  $\sigma^g_{(p-OMe)}$  and  $\sigma^g_{(p-CN)}$  values decrease and increase, respectively, as the polarity of the benzyl radical is varied by α-Y groups of gradually increasing electron-donating intensity. Alternatively, such a trend of spin variation can be viewed, more quantitatively, on the basis of the changes in the internal polar interaction as registered by the Δ*C*<sub>Ph</sub> values (the ring charge relative to that of the parent benzyl). Correlations of  $\sigma^g_{(p-OMe)}$  and  $\sigma^g_{(p-CN)}$  versus Δ*C*<sub>Ph</sub> are satisfactorily linear (Figure 3); both plots indicate that, as the electronic attraction between the interacting *p*-G and phenyl ring increases,

**Figure 3.** Correlation plots of (a)  $\sigma^g_{(p-OMe)}$  and (b)  $\sigma^g_{(p-CN)}$  versus relative phenyl-ring charge ( $\Delta C_{Ph}$ ).

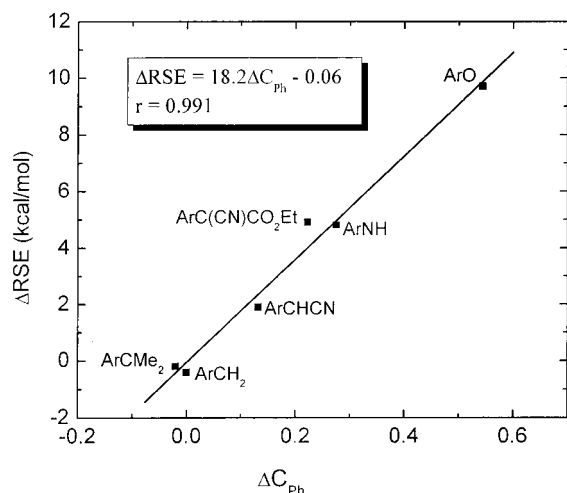
the spin delocalization increases, and vice versa. It is clear that plots of this sort, while certainly need further refinery, would nevertheless provide, for the first time, a practical clue for discussing the problem regarding the magnitude of radical substituent effect on a quantitative basis.

Similarly, the relationship between RSE (or  $-\Delta BDE$ ) values as one other index of radical stability and polar effect can also be examined. Table 7 lists the calculated ring charges (presented as Δ*C*<sub>Ph</sub>) of some typical radical systems (including both the nonpolar and prepolarized) whose R-H (or C-CH<sub>3</sub>) BDEs are currently available. Though the correspondence of RSEs with Δ*C*<sub>Ph</sub>'s for the *p*-OMe- and *p*-CN-substituted radicals is not as good (*r*: 0.93–0.94), due largely to the experimental errors of the BDEs collected from various sources, the relative RSEs were found to correlate quite nicely with the ring charges

**Table 7. Relative BDEs ( $\Delta$ BDEs, kcal/mol) for Para-Substituted Radicals,<sup>a</sup> Differences in RSE between *p*-MeO and *p*-CN ( $\Delta$ RSEs, kcal/mol),<sup>b</sup> and Relative Phenyl-Ring Charges ( $\Delta C_{Ph}$ )<sup>c</sup>**

	ArO <sup>d</sup>	ArNH <sup>e</sup>	EPAN <sup>f</sup>	PAN <sup>f</sup>	ArCH <sub>2</sub> <sup>g</sup>	ArCMe <sub>2</sub> <sup>h</sup>
$\Delta$ BDE( <i>p</i> -MeO)	-5.3	-1.9	-2.0	-1.5	-1.1 <sup>i</sup>	-1.0 <sup>i</sup>
$\Delta$ BDE( <i>p</i> -CN)	4.3	2.9	2.9	0.4	-1.5	-0.7
$\Delta$ RSE	9.6	4.8	4.9	1.9	-0.4	0.3
$\Delta C_{Ph}$	+0.544	+0.275	+0.222 <sup>j</sup>	+0.132	(0)	-0.019

<sup>a</sup>  $\Delta$ BDE<sub>(G)}</sub> = BDE<sub>(G)}</sub> - BDE<sub>(H)}</sub>. <sup>b</sup>  $\Delta$ RSE =  $\Delta$ BDE<sub>(*p*-CN)}</sub> -  $\Delta$ BDE<sub>(*p*-OMe)}</sub>. <sup>c</sup> See footnote c in Table 7. <sup>d</sup> Reference 1a. <sup>e</sup> Reference 2a. <sup>f</sup> Reference 11c. <sup>g</sup> Derived from ArCH<sub>2</sub>-CH<sub>3</sub> BDEs in ref 29. <sup>h</sup> Derived from ArCMe<sub>2</sub>-CH<sub>3</sub> BDEs in ref 8d. <sup>i</sup> For *p*-OH substitution. <sup>j</sup> For MPAN<sup>\*</sup>, see ref 13.



**Figure 4.** Correlation of difference in radical stabilization energy ( $\Delta$ RSE) versus relative phenyl-ring charge ( $\Delta C_{Ph}$ ).

( $r = 0.991$ , Figure 4). This again shows a definite role of polar interaction in a radical system in predicting radical stability.

### Conclusion

The present DFT calculations of the C–H BDEs of phenylacetonitriles confirmed the early experimental observations of the *O*-type variation of BDEs by remote EDG/EWG for pre-polarized benzyl radicals. In addition

to the confirmation of the two reported types of radical substituent effect (i.e., *S* and *O*) by BDE calculations, computational analysis on spin parameters further revealed that there actually exists one more distinct pattern of remote substituent effect (i.e., the counter-*O* type) for carbon radical. A unified analytical platform (Scheme 1) that links and rationalizes the apparently distinct patterns of substituent behavior in affecting radical stability is proposed on the basis of the directions of radical polarity as judged by varying the  $\alpha$ -Y substitution. Thus, a complete spectrum of C-radical effect consisting of all the three basic patterns is first outlined. This work first clearly demonstrated that it is the polar interaction in pre-polarized benzyl radical that plays the crucial role in altering both the direction and magnitude of substituent effect on spin and radical stability. The quantitative/semiquantitative correlations (Figures 1–4) drawn between radical parameters ( $\sigma^{\cdot}$  or RSE) and polar parameters (the calculated  $C_{Ph}$  or literature  $\sigma^+$ ) suggest a clue for assessing the magnitude of radical substituent effect with some predicting power.

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**Supporting Information Available:** Table of calculated spin populations for para-substituted benzylic carbon radicals (PAN<sup>\*</sup>, BEN<sup>\*</sup>, MPAN<sup>\*</sup>); table of substituent effects on ZPVEs to C–H BDEs in typical substituted PANs; correlation between the ground-state effect (GE) in para-substituted PAN molecules and polar constants ( $\sigma_p$ ); comparisons between calculated hyperfine coupling constants for PAN<sup>\*</sup>, BEN<sup>\*</sup>, and MPAN<sup>\*</sup> and corresponding experimental values; correlation plot between calculated radical stabilization energies for BEN<sup>\*</sup> radical and Jiang's radical constants  $\sigma_{ij}^{\cdot}$ ; plot comparing spin populations for the MPAN<sup>\*</sup> radical calculated by the B3LYP//AM1 method and by the B3LYP method; table of experimental C–H BDE studies of  $\alpha$ -electron-withdrawing substituted toluenes previously reported by this group; geometries of PANs, PAN<sup>\*</sup>s, and typical MPAN<sup>\*</sup>s, optimized at the (U)B3LYP/6-31G(d) level and in *Z*-matrix form. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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