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Substituent Effects on the C−H Bond Dissociation Energy of Toluene. A Density Functional Study

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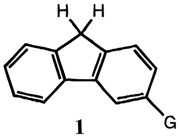
The bond dissociation energies of the benzylic C−H bond of a series of 16 para-substituted toluene compounds (p-X-$C_6H_4CH_3$) have been calculated with the density functional method (BLYP/6-31G*). The calculated substituent effects correlate well with experimental rates of dimerization of para-substituted α,β,β-trifluorostyrenes and rearrangement of methylenearylcyclopropanes. Both electron-donating and electron-withdrawing groups reduce the bond dissociation energy (BDE) of the benzylic C−H bond because both groups cause spin delocalization from the benzylic radical center. The calculated spin density variations at the benzylic radical centers correlate well with both the ESR hyperfine coupling constants determined by Arnold *et al.* and the calculated radical effects of the substituents. The relative radical stabilities are mainly determined by the spin delocalization effect of the substituents, and polar effect of the substituents are not important in the current situation. The ground state effect is also found to influence the C−H BDE.

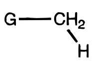
Introduction

While Hammett-type polar substituent parameters σ^X have significantly contributed to the understanding of structure−property relationships and reaction mechanisms,[1] they often fail in describing thermodynamic and kinetic properties of many carbon radical systems.[2] For example, it is well known that both electron-donating and electron-withdrawing substituents can reduce the C−H bond dissociation energies (BDEs) of systems such as **1** and **2** (the effects are in kcal/mol).[3,4]



1

G = H 0.0
G = OMe 7.0
G = CN 5.7



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G = H 0
G = OMe 12
G = CN 12

Table 1. Calculated Ground State Effect (GE), Radical Effect (RE), and Total Effect (TE) of Substituents in Para-Substituted Toluenes. Experimental Total Effect in Para-Substituted Benzyl Cyanide and the Activation Energies of Dimerization of Para-Substituted α,β,β-Trifluorostyrenes (140 °C) and Rearrangement of Methylenearylcyclopropanes (80 °C) Are Also Shown. All Tabulated Values are Energies in kcal/mol

	calculation			experiment		
G	GE	RE	TE	TE[a]	$\Delta\Delta G^{\ddagger b}$	$\Delta\Delta G^{\ddagger c}$
H	0.00	0.00	0.00	0	0	0
Me	−0.09	0.33	0.42	0.4	0.50	0.18
$SiMe_3$	0.25	0.67	0.42		0.48	0.29
F	−0.26	−0.10	0.16	0.1	0.04	−0.13
Cl	0.05	0.28	0.23	0.1	0.28	0.19
NMe_2	−0.37	1.82	2.19	4.0	2.30	1.45
OMe	−0.42	0.66	1.08	1.4	0.86	0.39
SMe	−0.14	1.26	1.40	0.7	1.20	0.69
COMe	0.42	1.64	1.22	−0.8	0.64	
COOH	0.45	1.34	0.89		0.48	0.57
$CONH_2$	0.34	1.04	0.70		0.64	
CN	0.58	1.44	0.86	−0.7	0.20	0.74
NO_2	0.66	1.70	1.04		0.12	0.92
SOMe	0.17	0.39	0.22		0.78	0.29
SO_2Me	0.44	0.44	0.00		0.33	0.28
CF_3	0.27	0.26	−0.01	−1.0	−0.39	

[a] Para-substituted benzyl cyanides, see refs 24a,c. [b] Dimerization of para-substituted α,α,β-trifluorostyrenes, see ref 5a. [c] Rearrangement of methylenearylcyclopropanes, see ref 7.

It has been suggested that in the absence of sizable steric interactions, both polar parameters and radical stabilization parameters are needed for the description of the substituent effect on carbon radical systems.[2] In this connection, there have been tremendous efforts in developing radical spin delocalization $\sigma^{\bullet}$ parameters for radical systems.[5−11] A nice summary can be found in Table 1 of ref 5a. The three most complete studies are by Arnold, Jiang and Ji, and Creary. In Arnold's approach,[6] the electron spin resonance (ESR) α-hydrogen

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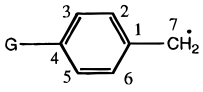
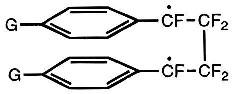
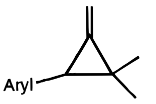
hyperfine coupling constants (α-hfc) of a series of para-substituted benzyl radicals **3** were measured. The $\sigma^{\bullet}_{\alpha}$ parameter directly reflects the spin density variation at the benzylic radical center.[12] Jiang and Ji derived $\sigma_{jj}^{\bullet}$ by careful studies on the kinetics of the thermal cycloaddition reaction of substituted α,*β*,*β*-trifluorostyrenes **4**.[5] It is assumed that the reaction transition state is close to the diradical intermediate. Creary studied the kinetics of the rearrangement of methylenearylcyclopropanes **5**, where the transition state is of a diradical character.[13,14]



3 Arnold, α-hfc



4 Jiang/Ji, kinetics



5 Creary, kinetics

Bond dissociation energies (BDE) and radical reactivities are affected by both the polar and spin-delocalization effects of the substituents in both ground state and radical, albeit to different degrees.[15−17] As mentioned, chemists have been trying hard to set up $\sigma^{\bullet}$ scales that are free from polar effects (σ^{X}) so that the nature of substituent effects can be better understood, e.g., by application of a dual-parameter equation involving both polar and spin delocalization parameters ($\rho^{X}\sigma^{X}$ and $\rho^{\bullet}\sigma^{\bullet}$). Several theoretical studies of the substituent effect on C−H BDE and Si−H BDE based on substituted methanes and substituted silanes have been reported.[4,18−23] Most of the studies do not attempt to separate the polar effect from radical spin delocalization effect. In a recent study of substituted silanes, we found that the calculated substituent effects on the Si−H BDE correlate well with the calculated changes in spin density and charge at the silyl radical center.[23] This gives at least a semiquantitative separation of the radical spin delocalization effect and polar effect.

In this paper we report a density functional study of the substituent effect on the benzylic C−H BDE for a series of para-substituted toluenes. Experimental studies of the substituent effect on benzylic C−H BDE are often on toluene derivatives where a functionalized benzylic group such as cyano or sulfonyl is present.[24,25] The current system is free from the possible complications caused by the polar benzylic group. We use isodesmic eqs 2 and 3 to evaluate the substituent effect on the stabilities of ground state (GE) and radical (RE). The total effect (TE) of substituent on the C−H BDE is the difference between RE and GE, as shown by eq 1. We

ground state effect (GE):

$$p\text{-G-C}_6\text{H}_4\text{CH}_3 + \text{C}_6\text{H}_6 \rightarrow \text{G-C}_6\text{H}_5 + \text{C}_6\text{H}_5\text{CH}_3 \quad (1)$$

radical effect (RE):

$$p\text{-G-C}_6\text{H}_4\text{CH}_2^{\bullet} + \text{C}_6\text{H}_6 \rightarrow \text{G-C}_6\text{H}_5 + \text{C}_6\text{H}_5\text{CH}_2^{\bullet} \quad (2)$$

total effect (TE = RE − GE)

$$p\text{-G-C}_6\text{H}_4\text{CH}_2^{\bullet} + \text{C}_6\text{H}_5\text{CH}_3 \rightarrow p\text{-G-C}_6\text{H}_4\text{CH}_3 + \text{C}_6\text{H}_5\text{CH}_2^{\bullet} \quad (3)$$

demonstrate that calculated spin density variation at the benzylic radical center correlate with Arnold's hfc measurements and with the calculated radical effect. We also analyze the contributions of the polar and radical spin delocalization effects to the total effect.

Results and Discussion

All calculations were carried out with Pople's Guassian 92/DFT program.[26] We employed the nonlocal density functional[27] BLYP method, which uses Becke's 88 nonlocal exchange functional[28] and Lee−Yang−Parr nonlocal correlation functional.[29] These calculations were carried out with the standard 6-31G* basis set. The BLYP/6-31G* method has been shown to give quite satisfactory bond dissociation energies of many systems.[30] For geometry optimizations, substituents OMe, SMe, COMe, COOH, CONH_2, and NO_2[31] were constrained to be

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coplanar with the benzene ring.[32] Substituents NMe_2, SOMe, and SO_2Me were fully optimized. Harmonic vibration frequencies were calculated for toluene and benzyl radical from which zero-point energies and thermal energies were obtained.

The calculated total energies of substituted benzenes, para-substituted toluenes, and para-substituted benzyl radicals are collected in Table 1 of the supporting information. The calculated benzylic C−H BDE of toluene with thermal energy corrections (25 °C) is 84 2 kcal/mol. This value is about 5.7 kcal/mol lower than the experimental value of 89.9 kcal/mol.[33] It is generally acknowledged that the BLYP/6-31G* method gives slightly lower bond dissociation energy.[30]

The substituent effect is most commonly calculated by isodesmic reaction in which types of bonds are conserved.[34] We use three isodesmic reactions (eqs 1−3) to calculate the substituent effect on the stabilities of ground state (GE) and radical (RE) and on the C−H bond dissociation energy (TE). Since frequency calculations were not carried out for the para-substituted systems, the GE, RE and TE of substituents were calculated based on the energies in Table 1 of the supporting information.[35] The calculated TE, GE, and RE of para-substituents are given in Table 1, along with experimental relative C−H bond dissociation energies of seven para-substituted benzyl cyanides reported by Bordwell *et al.*,[24a] relative activation energies of dimerization of α,β,β-trifluorostyrenes,[5a] and thermal rearrangement of methylenearylcyclopropanes.[7]

In general, the calculated GE is negative for an electron-donating substituent and positive for an electron-withdrawing substituent. This clearly reflects the polar effect of these substituents: The methyl group of toluene is a weak donor, a para-donor causes a destabilization, and a para-acceptor results in a stabilization, although the effect is not large. Trimethyl silyl group gives a GE of 0.2 kcal/mol. This is not expected but is in accord with the polar σ_{mb} scaling.[5] On the other hand, except for the fluoro substituent, each substituent causes a stabilization to the benzyl radical (positive RE). The effect is the largest for NMe_2, NO_2, and COMe groups. As will be discussed in more detail, these groups cause the largest spin delocalizations.

Scheme 1 gives a more clear picture of the substituent effect. An electron-donating substituent destabilizes the ground state but stabilizes the benzyl radical. Thus, both the ground state effect and the radical effect reduce the benzylic C−H BDE. An electron-withdrawing substituent, on the other hand, stabilizes both the ground state and the benzyl radical. The benzylic C−H BDE is still reduced because the radical effect is larger than the ground state effect. It should be noted that this picture could change if there are polar benzylic groups or if the breaking bond is a polar bond.[16d]

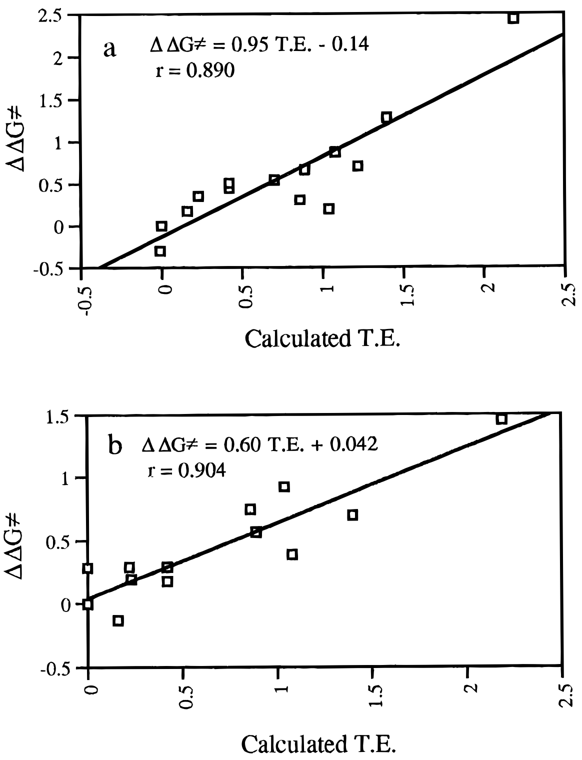
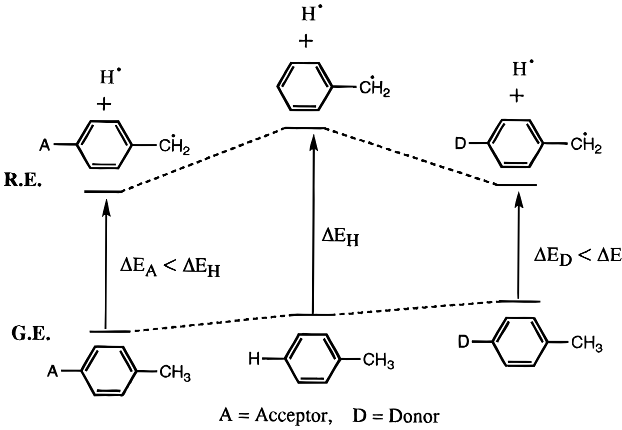


Figure 1. Correlation plots of calculated TE with observed activation energy: (a) dimerization of α,α,β-trifluorostyrenes by Jiang and Ji; (b) rearrangement of methylenearylcyclopropanes by Creary *et al.*

Scheme 1



Although all substituents except the CF_3 group reduce the benzylic C−H BDE (TE), the magnitudes of the substituent effects are not large. This is in general agreement with the small substituent effect observed by experiments.[24] The largest TE is for NMe_2 (2.1 kcal/mol). This is somewhat smaller than the 3.9 kcal/mol reported by Bordwell in substituted benzyl cyanide.[24a] Bordwell also reported a small increase in C−H BDE by COPh and CN groups. The descrepancy between experiment and calculation is likely caused by the presence of the benzylic cyano group in Bordwell's systems. The so-called captodative effect in radical chemistry has been widely disccussed.[36] The calculated TE are quite close to the measured activation energies of the dimerization of α,β,β-trifluorostyrenes[5] as shown in Figure 1a ($r = 0.89$).[37] The calculated TEs are systematically larger than the activation energies of rearrangement of methylenearylcyclopropanes reported by Creary *et al.*[7] However, the cor-

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[32] The $CONH_2$ should not be strictly planar because of pyramidalization for NH_2. For recent calculations, see: (a) Wong, M. W.; Wiberg, K. B. *J. Phys. Chem.* **1992**, *96*, 668 and references therein. (b) Wu, Y.-D.; Houk, K. N. *J. Org. Chem.* **1993**, *58*, 2043. We expect that the planar constraint does not affect our result very much.

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[35] We expect that thermal energy correction to GE, RE, and TE to be quite small because the para substituents cause only small geometrical changes in both toluene and benzyl radical. This is checked out for NO_2 and NMe_2 groups which cause the largest geometrical changes. The semiempirical PM3 frequency calculations indicate that the corrections to RE and TE are less than 0.2 kcal/mol.

Table 2. Calculated C_1-C_7 Bond Length (Å), Natural Population Charge (C7) and Spin Density at Atoms C_1-C_7 Along with the ESR Hyperfine Coupling Constants at C_2/C_6, C_3/C_5, and C_7 of Para-Substituted Benzylic Radicals Reported by Arnold *et al*[6]

G	$r_{C1\text{-}C7}$	C7	S1	S2/S6	S3/S5	S4	S7	a2/a6	a3/a5	a7
H	1.412	0.066	−0.061	0.186	−0.065	0.215	0.640	5.10	−1.70	16.25
Me	1.411	0.057	−0.096	0.182	−0.064	0.218	0.630	5.05	−1.60	16.00
$SiMe_3$	1.410	0.068	−0.096	0.181	−0.063	0.220	0.627	5.03	−1.71	15.97
F	1.412	0.060	−0.096	0.182	−0.061	0.195	0.636	5.30	−1.75	16.42
Cl	1.410	0.072	−0.097	0.182	−0.064	0.207	0.626	5.24	−1.75	16.07
NMe_2	1.407	0.013	−0.086	0.162	−0.046	0.157	0.589			
OMe	1.410	0.037	−0.092	0.175	−0.055	0.178	0.617	5.02	−1.60	15.95
SMe	1.407	0.046	−0.094	0.174	−0.060	0.196	0.598	5.08	−1.73	15.23
COMe	1.405	0.098	−0.095	0.172	−0.059	0.203	0.588	5.00	−1.75	15.28
COOH	1.407	0.098	−0.095	0.174	−0.059	0.202	0.600	5.05	−1.75	15.55
$CONH_2$	1.407	0.087	−0.096	0.177	−0.062	0.210	0.608			
CN	1.406	0.102	−0.096	0.174	−0.059	0.206	0.595	5.00	−1.78	15.60
NO_2	1.405	0.122	−0.093	0.169	−0.055	0.190	0.584			
SOMe	1.410	0.079	−0.096	0.182	−0.062	0.208	0.624	5.03	−1.75	15.95
SO_2Me	1.410	0.101	−0.096	0.181	−0.060	0.211	0.629	5.03	−1.60	16.04
CF_3	1.410	0.091	−0.097	0.182	−0.062	0.209	0.631	5.19	−1.76	16.39

relation between the two values is reasonably well (0.904) as shown in Figure 1b. The mechanism of rearrangement of methylenecyclopropane has been studied both by experiment and calculation.[13,14] Both stepwise[14a,b] and concerted mechanisms[14c] have been proposed. The coefficient of about 0.6 in Figure 1b indicates that the transition state is of about 60% diradical character.

Table 2 gives the calculated C_1-C_7 bond length, atomic charge at C_7 according to natural population analysis (for numbering, see **3**),[38] spin density distributions,[39] and ESR α-hfc of benzyl radicals as reported by Arnold *et al.*[6] The calculated spin density at the benzylic center is 0.64. This indicates that there is considerable spin delocalization to the benzene ring. As expected, spin densities are mainly at the C_7, C_2, C_4, and C_6 (see S2/S6, S4, S7) positions. The C_1, C_3, and C_5 positions have small but negative spin densities. This is in accord with the expectation of spin alternation. The calculated ratios of spin densities of the parent benzyl radical are S3:S2:S4:S7 = 1:2.9:3.3:9.8. These are very close to the experimental ratios of 1:3:3.6:9.6 determined by Arnold *et al.*[6] We also note that the summation of spin density at positions C_2, C_3, C_5, and C_6 is nearly a constant for most of the substituents, in agreement with experimental observations with phenoxyl radicals.[40]

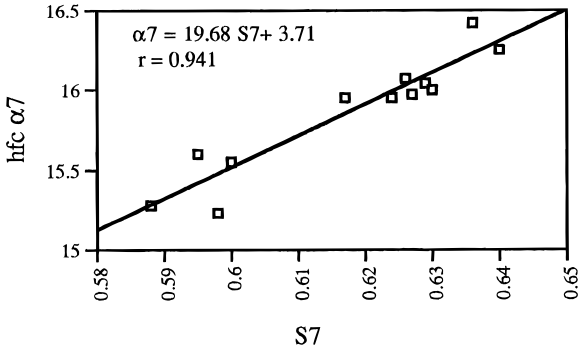
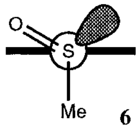


Figure 2. Correlation plot of ESR hfc of the benzylic radical center (α7) by Arnold against calculated spin density (S7).

Figure 2 is the plot of calculated spin density at C_7 against measured α-hfc at the same position. A quite good correlation is realized with $r = 0.94$. This indicates that the calculations give quite reliable spin densities. The spin density variation at the C_2, C_3, C_5, and C_6 are smaller, and the correlations between calculations and experiment are not as good.

In accord with the largest radical effects by NMe_2, NO_2, and COMe, these groups also cause the largest spin delocalizations. The NMe_2 is the strongest π-donor, and NO_2 and COMe are powerful π-acceptors. These groups effectively accept spin density from the benzyl radical center through π-resonance. The spin delocalization is negligible for F and CF_3 groups, in agreement with the slightly negative σ• values derived from experiments. We also note that the spin delocalization is qualitatively coupled with the shortening of the C_1-C_7 bond length, although the magnitude of bond length change is not large.



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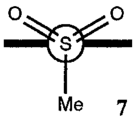

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The SOMe and SO_2Me groups need special comment. The best conformations for the two groups are shown by the Newman projections **6** and **7**. However, the calculated potential energy surfaces for the rotation of the C_4-S bonds are quite flat. Inclusion of thermal energy and entropy corrections is needed to determine the real global minimum conformations. It is likely that many conformations have similar stabilities. This may change the spin delocalization property because different conformations have quite different spin delocalization abilities.

Figure 3 gives correlation plots of calculated radical effect with spin density and charge variations at the benzylic radical center which are used to represent the spin delocalization effect and polar effect, respectively.[23] Figure 3a is the plot of calculated RE against ΔS7 and shows excellent correlation ($r = 0.98$). On the other hand, a similar plot of RE against ΔC7 gives scattered points with no correlation (not shown). When both ΔS7 and

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(36) For geminal effect in radicals, see: (a) Viehe, H. G.; Janousek, Z.; Mereny, R. in *Free Radicals in Synthesis and Biology*; Minisci, F., Ed.; Kluwer: Dordrecht, 1989; pp 1−26. (b) Biekhofer, H.; Hädrich, J.; Pakusch, J.; Beckhaus, H.-D.; Peters, K.; Schnering H.-G. v. *Ibid.* pp 27−36. (c) Korth, H.-G.; Lommes, P.; Sustmann, R.; Sylvander, L.; Stella, L. In ref 2, pp 167−170. (d) Pasto, D. J. *J. Am. Chem. Soc.* **1988**, *110*, 8164. (e) Leroy, G.; Sara, M.; Wilante, C. *J. Mol. Struct. (Theochem)* **1991**, *80*, 303.

(37) Substituents SOMe and SO_2Me are excluded.

(38) NBO Version 3.1: Glendening, E. D.; Reed, A. E.; Carpenter, J. E.; Weihold, F. University of Wisconsin, Madison.

(39) The S2/S6 is the average spin density at the C_2 and C_6 positions. The same for S3/S5.

(40) Dixon, W. T.; Moghim, M.; Murphy, D. *J. Chem. Soc.* **1974**, 1913.

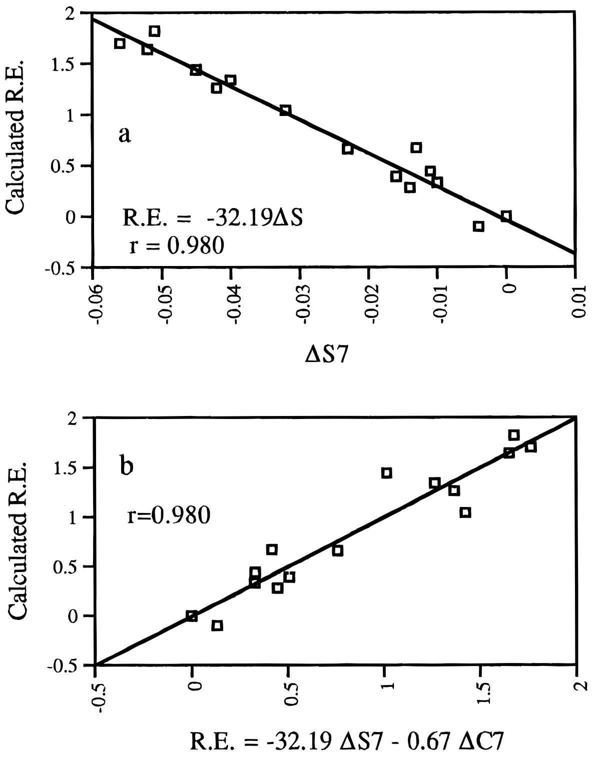

Figure 3. Correlation plots of calculated radical effect (RE) against (a) calculated spin density variation at the benzylic radical center (ΔS7), and (b) calculated spin density and charge variations.

ΔC7 are used as variables (Figure 3b), the correlation is essentially the same as in Figure 3a. The small coefficient (−0.67) for ΔC7 indicates that the contribution of polar effect to RE is very small, and the radical is mainly stabilized by the spin delocalization effect of the substituents. The small polar effect is understandable because of the poor polar characteristic of the $CH_2^{\bullet}$ moiety. In a separate paper we will discuss the substituent effect on the phenoxy O−H bond dissociation energy, where the radical effect is much larger and largely contributed from the polar effect of a para-substituent.[41]

Since the ground state effect, which is primarily caused by the polar effect of the substituent, also contributes to the C−H BDE, it is necesary to use both the spin delocalization effect and the polar effect to describe the substituent effect on the C−H BDE. Figure 4 is the correlation plot of the calculated total effect (TE) against the calculated ΔS7 and ΔC7. Excellent correlation is found. Therefore, it is conceptually misleading to evaluate radical-stabilizing abilities of substituents directly

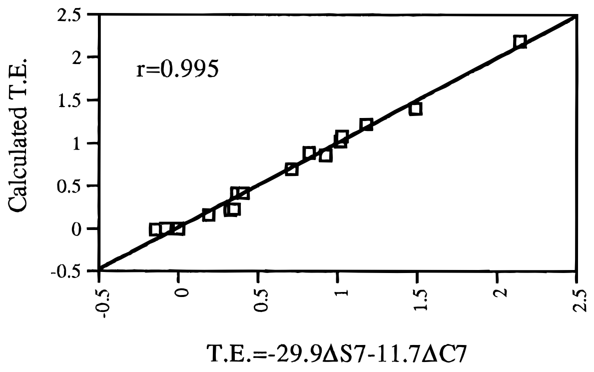

Figure 4. Correlation plot of calculated total effect (TE) against calculated ΔS7 and ΔC7.

from BDE data without considering the polar effects on BDE. Since ΔS7 and ΔC7 are of similar magnitudes, it is evident that the spin delocalization effect is more important than the polar effect in the benzyl radical systems. Our calculations show that this is also true when the substituent is geminal to the breaking C−H bond as in **2**.[42]

In summary, the nonlocal BLYP/6-31G* density functional method calculates the benzylic C−H BDE and the substituent effect on the C−H BDE quite satisfactorily. Both the ground state effect and radical effect influence the C−H BDE. A para electron-donating substituent destabilizes the ground state but stabilizes the radical, resulting in reduced C−H BDE. An electron-withdrawing substituent stabilizes the ground state but stabilizes the benzyl radical even more, also resulting in reduced C−H BDE. The calculated spin density variation correlates well with measured ESR α-hfc of benzyl radicals. The radical effect is largely caused by the spin delocalization effect of a para-substituent.

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Supporting Information Available: A table of calculated total energies of monosubstituted benzenes, para-substituted toluenes, and para-substituted benzyl radicals (1 page). This material is contained in libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

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(41) Wu, Y.-D.; Lai, D. K. W. *J. Org. Chem.*, submitted.

(42) Wu, Y.-D.; Wong, C.-L.; Li, B.-R.; Ji, G.-Z.; Jiang, X.-K. Manuscript in preparation.