

# Theoretical Study of Carbon–Halogen Bond Dissociation Enthalpies of Substituted Benzyl Halides. How Important Are Polar Effects?<sup>1</sup>

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**Abstract:** It has been suggested (Clark, K. B.; Wayner, D. D. M. *J. Am. Chem. Soc.* **1991**, *113*, 9363–9365) that C–Br bond dissociation enthalpies (BDEs) in 4-YC<sub>6</sub>H<sub>4</sub>CH<sub>2</sub>-Br decrease as Y becomes more electron-withdrawing because of increasing destabilization of the C<sup>δ+</sup>–Br<sup>δ-</sup> dipole and, furthermore, that the direction and magnitude of the effect of Y on 4-YC<sub>6</sub>H<sub>4</sub>Z-X BDEs could be correlated with the sign and magnitude, respectively, of the electronegativity difference between Z and X. The results of density functional theory (DFT) calculations using a locally dense basis set approach with the B3LYP functional and 6-311+G(2d,2p) as the primary basis set on 4-YC<sub>6</sub>H<sub>4</sub>CH<sub>2</sub>-X, for X = H, Br, Cl, and F with Y = NH<sub>2</sub>, HO, CH<sub>3</sub>O, CH<sub>3</sub>, H, CF<sub>3</sub>, CN, NO<sub>2</sub> and BH<sub>2</sub>, show that the effects of Y on CH<sub>2</sub>-X BDEs are small (≤2.0 kcal/mol) for all four classes of compounds and are roughly equal for each Y for the three halides. Furthermore, almost all Y's reduce CH<sub>2</sub>-X BDEs relative to Y = H. Clark and Wayner's intriguing hypothesis that the magnitude of the effects of Y on 4-YC<sub>6</sub>H<sub>4</sub>Z-X BDEs depends on the magnitude of the differences in the electronegativities of Z and X should be discarded.

For the past half-century, the influence, or lack of influence, of para-substituents, Y, on the Z–X bond dissociation enthalpies (BDEs) of compounds having the general formula 4-YC<sub>6</sub>H<sub>4</sub>Z-X has been a subject of intense experimental and theoretical interest. For phenols (Z = O, X = H),<sup>3</sup> anisoles (Z = O, X = CH<sub>3</sub>),<sup>4</sup> and anilines (Z = NH, X = H),<sup>5</sup> experiment and theory agree that electron-donating Y groups decrease the Z–X BDEs and that electron-withdrawing Y groups increase the Z–X BDEs. These substituent-induced changes in BDEs are most substantial for phenols. The 4-YC<sub>6</sub>H<sub>4</sub>O-H (and 3-YC<sub>6</sub>H<sub>4</sub>O-H) BDEs can be correlated with the  $\sigma^+$  substituent constant of Y,<sup>3a,c</sup> and the resulting straight line has a slope  $\rho^+ = 7.3$  kcal/mol.<sup>3a</sup> The values of  $\Delta$ BDE (4-YC<sub>6</sub>H<sub>4</sub>O-H – C<sub>6</sub>H<sub>5</sub>O-H) are, for example, –5.6 and 4.7 kcal/mol for Y = CH<sub>3</sub>O and CN, respectively.<sup>3c</sup> Similar correlations can be made for anisoles,  $\rho^+ = 2.9$  kcal/mol,<sup>4a</sup> and anilines,  $\rho^+ = 3$  kcal/mol.<sup>5a</sup> For toluenes, 4-YC<sub>6</sub>H<sub>4</sub>CH<sub>2</sub>-H<sup>6</sup> (and the related 10-substituted 9-methylanthracenes<sup>7</sup>), experiment and theory agree that the Y-

substituents have little or no effect on C–H BDEs, e.g.,  $\rho^+ = 0.5$  kcal/mol.<sup>6c</sup> The Y-substituents also have little or no effect on C–C BDEs in YC<sub>6</sub>H<sub>4</sub>CH<sub>2</sub>-CH<sub>3</sub><sup>8</sup> and 4-YC<sub>6</sub>H<sub>4</sub>C(CH<sub>3</sub>)<sub>2</sub>-CH<sub>3</sub>.<sup>9</sup>

In contrast to the foregoing, there is no agreement regarding the effect of substituents on benzyl bromide C–Br BDEs. Early studies on the unimolecular decomposition rates of benzyl bromides in the gas phase failed to reveal any substantial substituent effects on their C–Br BDEs.<sup>10</sup> Forty years later, in a ground-breaking study, Clark and Wayner<sup>11</sup> measured some 4-YC<sub>6</sub>H<sub>4</sub>CH<sub>2</sub>-Br BDEs in the liquid phase using the photoacoustic calorimetric (PAC) technique and found a rather large substituent effect. The most exciting part of their discovery was that electron-withdrawing Y-substituents decreased the C–Br BDEs. For example,  $\Delta$ BDE (4-YC<sub>6</sub>H<sub>5</sub>CH<sub>2</sub>-Br – C<sub>6</sub>H<sub>5</sub>CH<sub>2</sub>-Br) was 2.87 and 4.98 kcal/mol for Y = CF<sub>3</sub> and Y = CN, respectively. There may also have been a small strengthening of the C–Br bond for Y = CH<sub>3</sub> (~0.26 kcal/mol). A Hammett correlation of the C–Br BDEs (with  $\sigma$  rather than  $\sigma^+$ , vide supra) gave  $\rho = -5.5$  kcal/mol. Clark and Wayner were forthright in pointing out that, because there was little or no substituent effect on 4-YC<sub>6</sub>H<sub>5</sub>CH<sub>2</sub>-H BDEs, their C–Br BDE

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(2) (a) OCCI. (b) NRCC.

(3) Experimental methods: (a) Mulder, P.; Saastad, O. W.; Griller, D. *J. Am. Chem. Soc.* **1988**, *110*, 4090–4092. (b) Lucarini, M.; Pedullini, G. F.; Cipollone, M. *J. Org. Chem.* **1994**, *59*, 5063–5070. (c) Lind, J.; Shen, X.; Eriksen, T. E.; Merényi, G. *J. Am. Chem. Soc.* **1990**, *112*, 479–482. (d) Wayner, D. D. M.; Luszyk, E.; Ingold, K. U.; Mulder, P. *J. Org. Chem.* **1996**, *61*, 6430–6433. Theoretical calculations: (e) Jonsson, M.; Lind, J.; Merényi, G.; Eriksen, T. E. *J. Chem. Soc., Perkin Trans. 2* **1994**, 2149–2154. (f) Wright, J. S.; Carpenter, D. J.; McKay, D. J.; Ingold, K. U. *J. Am. Chem. Soc.* **1997**, *119*, 4245–4252. (g) Brinck, T.; Haeberlein, M.; Jonsson, M. *J. Am. Chem. Soc.* **1997**, *119*, 4239–4244.

(4) Experimental methods: (a) Suryan, M. M.; Kafafi, S. S.; Stein, S. E. *J. Am. Chem. Soc.* **1989**, *111*, 4594–4600. Theoretical calculations: (b) Reference 3e.

(5) Experimental methods: (a) Jonsson, M.; Lind, J.; Eriksen, T. E.; Merényi, G. *J. Am. Chem. Soc.* **1994**, *116*, 1423–1427. (b) Jonsson, M.; Lind, J.; Merényi, G.; Eriksen, T. E. *J. Chem. Soc., Perkin Trans. 2* **1995**, 61–65. (c) MacFaul, P. A.; Wayner, D. D. M.; Ingold, K. U. *J. Org. Chem.* **1997**, *62*, 3413–3414. Theoretical calculations: (d) Reference 3e.

(6) Experimental methods: (a) Zavitsas, A. A.; Pinto, J. A. *J. Am. Chem. Soc.* **1972**, *94*, 7390–7396. (b) Berkowitz, J.; Ellison, G. B.; Gutman, D. *J. Phys. Chem.* **1994**, *98*, 2744–2765. Theoretical calculations: (c) Reference 3e. (d) Fox, T.; Kollman, P. *J. Phys. Chem.* **1996**, *100*, 2950–2956. (e) Wayner, D. D.; Sim, B. A.; Dannenberg, J. J. *J. Org. Chem.* **1991**, *56*, 4853–4858. (f) Wu, Y.-D.; Wong, C.-L.; Chan, K. W. K.; Ji, G.-Z.; Jiang, X.-K. *J. Org. Chem.* **1996**, *61*, 746–750.

(7) Zhang, X.-M.; Bordwell, F. G.; Bares, J. E.; Cheng, J.-P.; Petrie, B. C. *J. Org. Chem.* **1993**, *58*, 3051–3059.

(8) Suryan, M. M.; Stein, S. E. *J. Phys. Chem.* **1989**, *93*, 7362–7365.

(9) Laarhoven, L. J. J.; Born, J. G. P.; Arends, I. W. C. E.; Mulder, P. *J. Chem. Soc., Perkin Trans. 2* **1997**, 2307–2312.

(10) Leigh, C. H.; Sehon, A. H.; Swarcz, M. *Proc. R. Soc. London* **1951**, *A209*, 97–110.

(11) Clark, K. B.; Wayner, D. D. M. *J. Am. Chem. Soc.* **1991**, *113*, 9363–9365.

results could not be attributed to the stabilizing effect of Y on the 4- $\text{YC}_6\text{H}_4\text{CH}_2^\bullet$  radicals. Instead, the substituent must exert its "important (i.e., greater) effect on the ground state of the parent" bromide. Thus, an electron-withdrawing group (ewg), Y, decreases the 4- $\text{YC}_6\text{H}_4\text{CH}_2\text{-Br}$  BDE because it destabilizes 4- $\text{YC}_6\text{H}_4\text{CH}_2\text{Br}$  relative to  $\text{C}_6\text{H}_5\text{CH}_2\text{Br}$ . It was suggested<sup>11</sup> that destabilization of 4- $\text{YC}_6\text{H}_4\text{CH}_2\text{Br}$  by ewg's might be due to hyperconjugation (provided the C–Br bond is perpendicular to the plane of the aromatic ring) or to substituent–dipole interactions. The latter explanation was preferred: "the C–Br bond is polarized so that the carbon has a partial positive charge (i.e.,  $\text{C}^{\delta+}\text{-Br}^{\delta-}$ ) . . . an electron-withdrawing substituent destabilizes the partial positive charge on the benzylic carbon and decreases the BDE". It was also pointed out that "the magnitude of this effect will depend on the electronegativity difference of the atoms or groups in the bond being broken". Clark and Wayner<sup>11</sup> further noted that the available  $\rho$  values (found from plots of 4- $\text{YC}_6\text{H}_4\text{Z-X}$  BDEs versus  $\sigma^+$  or  $\sigma$  for phenols, anisoles, toluenes, and benzyl bromides) gave a straight line when plotted against the differences in electronegativities of the bonding atoms in Z and X. Such a plot (expanded to include new results on anilines and phenylthioethers) was later made by Jonsson et al.<sup>5a</sup> (and is shown in their Figure 7).

The simple Y-substituent/Z–X dipole interaction model for explaining substituent effects on 4- $\text{YC}_6\text{H}_4\text{Z-X}$  BDEs is clearly of fundamental importance *if it is correct*. It was deduced by Clark and Wayner<sup>11</sup> on the basis of their 4- $\text{YC}_6\text{H}_4\text{CH}_2\text{-Br}$  BDE measurements, and its validity depends solely on the bond-weakening effect of ewg's on benzyl bromide BDEs. Support for a weakening of 4- $\text{YC}_6\text{H}_4\text{CH}_2\text{-Br}$  BDEs by electron-withdrawing groups was provided by some electrochemical measurements made by Andrieux et al.<sup>12</sup> which yield  $\Delta\text{BDE}$  (4- $\text{YC}_6\text{H}_4\text{CH}_2\text{-Br} - \text{C}_6\text{H}_5\text{CH}_2\text{-Br}$ ) = 4.34 and 3.38 kcal/mol for Y = C(O)OCH<sub>3</sub> and CN, respectively. However, more recently, Laarhoven et al.,<sup>9</sup> using the same PAC technique as that used by Clark and Wayner, could detect no substituent effect on  $\text{YC}_6\text{H}_4\text{CH}_2\text{-Br}$  BDEs for Y = 4-CN, 4-C(CH<sub>3</sub>)<sub>3</sub>, and 3-CF<sub>3</sub>. Furthermore, competitive thermolysis of benzyl bromides in the gas phase indicated that, for Y = H, 4-CN, 4-CF<sub>3</sub>, 4-C(CH<sub>3</sub>)<sub>3</sub>, 4-Br, 4-CH<sub>3</sub>O, and 3-CF<sub>3</sub>, any variation in  $\text{YC}_6\text{H}_4\text{CH}_2\text{-Br}$  BDEs was less than 1 kcal/mol.<sup>9</sup>

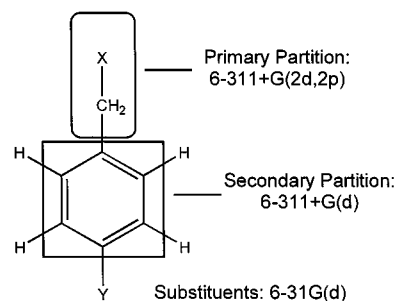
Since the experimental approach to 4- $\text{YC}_6\text{H}_4\text{CH}_2\text{-Br}$  BDEs yields inconsistent data, we decided to check Clark and Wayner's<sup>11</sup> suggestion that a 4- $\text{YC}_6\text{H}_4\text{Z}^{\delta+}\text{-X}^{\delta-}$  polarized bond would be weakened by electron-withdrawing Y using theoretical calculations.<sup>13</sup> That is, if the Clark and Wayner<sup>11</sup> concept is correct, the effect of electron-withdrawing Y groups on 4- $\text{YC}_6\text{H}_4\text{Z-X} - \text{C}_6\text{H}_5\text{Z-X}$   $\Delta\text{BDEs}$  should increase as the magnitudes of the Pauling electronegativity differences,  $\Delta\chi$ , between Z and X increase.<sup>14</sup> We have therefore used density functional theory to calculate C–H, C–Br, C–Cl, and C–F BDEs for Y = NH<sub>2</sub>, OH, OCH<sub>3</sub>, CH<sub>3</sub>, H, CF<sub>3</sub>, CN, NO<sub>2</sub>, and BH<sub>2</sub> in 4- $\text{YC}_6\text{H}_4\text{CH}_2\text{-H}$  ( $\Delta\chi = 0.4$ ), 4- $\text{YC}_6\text{H}_4\text{CH}_2\text{-Br}$  ( $\Delta\chi = -0.3$ ), 4- $\text{YC}_6\text{H}_4\text{CH}_2\text{-Cl}$  ( $\Delta\chi = -0.5$ ), and 4- $\text{YC}_6\text{H}_4\text{CH}_2\text{-F}$  ( $\Delta\chi = -1.5$ ).<sup>14</sup>

## Method of Calculation

The geometries of both the closed-shell (molecule) and open-shell (radical) structures were optimized and vibrational frequencies calcu-

(12) Andrieux, C. P.; Le Gorand, A.; Savéant, J.-M. *J. Am. Chem. Soc.* **1992**, *114*, 6892–6904.

(13) Jonsson et al.<sup>5c</sup> have previously reported the results of semiempirical calculations of 4- $\text{YC}_6\text{H}_4\text{CH}_2\text{-Br}$  BDEs and found a maximum variation of only ca. 1.5 kcal/mol (RHF/AM1) or ca. 1.25 kcal/mol (RHF/PM3) for Y = NH<sub>2</sub>, OH, CH<sub>3</sub>, H, CF<sub>3</sub>, and NO<sub>2</sub>, i.e., no significant changes in BDE.



**Figure 1.** Partitioning scheme for the use of locally dense basis sets (LDBS) in the determination of the 4- $\text{YC}_6\text{H}_4\text{CH}_2\text{-X}$  BDEs.

lated using the semiempirical AM1 method<sup>15</sup> as implemented in the program HyperChem Pro 5.1<sup>16</sup> for the personal computer. All other calculations presented in this paper used the Gaussian 94 suite of programs<sup>17</sup> compiled to run on a Silicon Graphics Challenge XL/8.

An AM1 vibrational frequency calculation was performed at each stationary point to determine the nature of the point (i.e., to distinguish a minimum from a transition state) and to obtain the zero-point energy (ZPE) at that point. Zero-point energies were scaled by a factor of 0.973 (ref 18) to correct for the anharmonicity in the vibrational potential surface.

Structures with the minimum AM1 heats of formation were used in the subsequent density functional theory (DFT) evaluation of the electronic energy,  $E_e$ . This was done using the B3LYP methodology,<sup>19</sup> which uses a hybrid exchange correlation functional combining the 1988 exchange functional of Becke<sup>20</sup> with the correlation functional of Lee, Yang, and Parr.<sup>21</sup> A restricted open-shell treatment was used to generate the Hartree–Fock starting point for the Kohn–Sham orbitals in the benzyl radicals.<sup>22</sup>

The (RO)B3LYP method was applied with locally dense basis sets (LDBS) as described by DiLabio and Wright.<sup>23</sup> The choice of primary basis set was 6-311+G(2d,2p) for the benzylic  $\text{CH}_2\text{X}$  group; secondary, 6-311+G(d) for the aromatic carbons; and tertiary, 6-31G(d) for all remaining atoms. This choice is illustrated in Figure 1. BDEs calculated using the LDBS approach have been shown to agree with results obtained using a uniform basis set, provided a reasonable partitioning scheme is chosen.<sup>24</sup>

To obtain the bond dissociation enthalpy,  $\Delta H^\circ_{298}$ , the zero-point-corrected (RO)B3LYP electronic energy was first corrected for translational and rotational contributions to the enthalpy and then  $RT$  was added so as to convert from energy to enthalpy ( $PV$  term). Vibrational enthalpy corrections have been omitted from these calculations.<sup>25</sup> Thus, the general expression for obtaining the enthalpy of the

(14) Pauling, L. *The Nature of the Chemical Bond*, 3rd ed.; Cornell University Press: Ithaca, NY, 1960; Chapter 3.

(15) Dewar, M. J. S.; Zoebisch, E. G.; Healy, E. F.; Stewart, J. J. P. *J. Am. Chem. Soc.* **1985**, *107*, 3902–3909.

(16) *Hyperchem Professional*, 5.1; Hypercube Inc.: Gainesville, FL, 1997.

(17) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Gill, P. M. W.; Johnson, B. G.; Robb, M. A.; Cheeseman, J. R.; Keith, T.; Petersson, G. A.; Montgomery, J. A.; Raghavachari, K.; Al-Laham, M. A.; Zakrzewski, V. G.; Ortiz, J. V.; Foresman, J. B.; Cioslowski, J.; Stefanov, B. B.; Nanayakkara, A.; Challacombe, M.; Peng, C. Y.; Ayala, P. Y.; Chen, W.; Wong, M. W.; Andres, J. L.; Replogle, E. S.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Binkley, J. S.; Defrees, D. J.; Baker, J.; Stewart, J. P.; Head-Gordon, M.; Gonzalez, C.; Pople, J. A. *Gaussian 94*, Revision D.4; Gaussian Inc.: Pittsburgh, PA, 1995.

(18) (a) Scott and Radom<sup>18b</sup> propose a scale factor of 0.9532 for scaling AM1 harmonic frequencies. However, since ZPEs typically have a greater scale factor by ca. 0.02, we used a scale factor of 0.973 for the AM1 ZPE. (b) Scott, A. P.; Radom, L. *J. Phys. Chem.* **1996**, *100*, 16502–16513.

(19) Becke, A. D. *J. Chem. Phys.* **1993**, *98*, 5648–5652.

(20) Becke, A. D. *Phys. Rev. A* **1988**, *38*, 3098–3100.

(21) Lee, C.; Yang, W.; Parr, R. G. *Phys. Rev. B* **1988**, *37*, 785–789.

(22) The unrestricted open-shell treatment (the default procedure in Gaussian 94) yields BDEs which are lower than the experimental values. The restricted open-shell treatment yields results in better agreement with experiment.

(23) DiLabio, G. A.; Wright, J. S. *Chem. Phys. Lett.* **1998**, *297*, 181–186.

parent molecule and corresponding radical is

$$H^\circ_{298} = E_e + \text{ZPE} + \frac{3}{2}RT + \frac{3}{2}RT + RT = E_0 + 4RT \quad (1)$$

Since atoms have neither rotational contributions to the enthalpy nor zero-point energies, eq 1 becomes  $E_e + \frac{5}{2}RT$ . The electronic energy of the hydrogen atom was set to its exact value of  $-0.500\,00$  hartree.<sup>26</sup> We denote this methodology for calculating BDEs as BDE(B3LYP/LDBS//AM1/AM1), or BDE(AM1) for short.

The calculations on the benzyl bromides are necessarily accompanied by questions of spin–orbit coupling and the adequacy of the 6-311+G-(2d,2p) basis set to account for the polarizability of the bromine atom. Since we are mainly concerned with energy differences between benzyl bromide and substituted benzyl bromides, spin–orbit coupling effects should cancel out. The basis set would appear to be adequate because experiments with larger basis sets—including sets supplemented with additional polarization and diffuse functions—showed that substituent effects on C–Br BDEs did not vary between the 6-311++G(3df,3pd) and the 6-311+G(2d,2p) basis sets. We believe that whatever trends are obvious from fluorine through bromine should hold true for iodine as well.

To evaluate the relative accuracy of the semiempirical AM1 method in determining the geometries of the systems of interest in this study, geometry optimizations of toluene, the benzyl halides, and the benzyl radical were also performed at the (U)HF/6-31G\*, (U)MP2/6-31G\*, (U)SVWN5/6-31G\*, and (U)B3LYP/6-31G\* levels of theory.<sup>28</sup> The relevant structural information demonstrates that all five computational methods give very similar geometries for the  $C_6H_5CH_2-X$  structures (Table 1)<sup>29–31</sup> and for the benzyl radical (Table 2). Because of the speed of AM1 computations compared to DFT and ab initio methods (seconds versus hours), it seemed reasonable to conduct all the geometry optimizations at the AM1 level.

Since AM1 energy-minimized geometries are not identical to B3LYP energy-minimized geometries (see Table 1), BDE (AM1) values are likely to differ from BDEs based on B3LYP geometries. To examine this problem, we carried out a limited (for reasons of cost and time) survey of B3LYP-calculated BDEs for the 4-NH<sub>2</sub>- and 4-BH<sub>2</sub>-substituted and unsubstituted toluenes, benzyl fluorides, chlorides, and

(24) In the present case, the uniform basis set (6-311+G(2d,2p)) calculated C–Br BDEs for benzyl bromide and 4-NH<sub>2</sub>- and 4-BH<sub>2</sub>-substituted benzyl bromides were 55.6, 55.4, and 53.7 kcal/mol, respectively, values which are in excellent agreement with the corresponding LDBS-calculated values, viz., 55.8, 55.7, and 53.8 kcal/mol. It is also worth noting that O–H BDEs for 4-substituted phenols calculated using the LDBS method and the uniform basis set are in good agreement: Pratt, D. A.; Ingold, K. U. Unpublished results.

(25) In most of the substituted systems, the substituents are subject to low-frequency torsions, and these can make a significant contribution to the correction of the vibrational enthalpy. Since the description of these modes is problematic at any level of theory, it seemed appropriate to omit this enthalpy correction.

(26) This improves X–H BDEs in DFT calculations (where the hydrogen atom is not free of self-interaction) and is in the spirit of the high-level correction of Pople et al.,<sup>27</sup> which is essential in G2 X–H thermochemistry.

(27) Pople, J. A.; Head-Gordon, M.; Fox, D. J.; Raghavachari, K.; Curtiss, L. A. *J. Chem. Phys.* **1989**, *90*, 5622–5629.

(28) Restricted Hartree–Fock (RHF) geometry optimizations were performed on the closed-shell molecules, while an unrestricted starting point was used for the open-shell radicals. The same protocol was used for the Moller–Plesset perturbation calculations to second order (MP2) and the DFT methods (SVWN5, which uses the local spin density approximation, and the nonlocal B3LYP).

(29) It is worth noting that all four calculation methods predict that the preferred conformations of the benzyl halides have the C–F bond lying in the aromatic plane whereas the C–Cl and C–Br bonds are perpendicular to this plane. The benzyl fluoride conformation is presumably dictated by C–H hyperconjugation (calculation (B3LYP/LDBS//AM1/AM1) barrier to rotation of the CH<sub>2</sub>F group is only 0.33 kcal/mol). However, C–H hyperconjugation effects are overridden by steric factors in the cases of benzyl chloride and bromide.

(30) *CRC Handbook of Chemistry and Physics*, 76th ed.; Lide, D. R., Ed.; CRC Press: Boca Raton, FL, 1995.

(31) Sadova, N. L.; Vilkov, L. V.; Hargittai, I.; Brunvoll, J. *J. Mol. Struct.* **1976**, *31*, 131–142.

**Table 1.** Some Calculated Gas-Phase Equilibrium Geometries for Toluene and the Three Benzyl Halides

R, A, or D <sup>a</sup>	AM1	HF	MP2	B3LYP	exptl
R(C–H)	1.118	1.087	1.096	1.098	1.110 <sup>b</sup>
A(C–C–H)	109.9	111.0	111.2	111.3	
D(C–C–C–H)	89.7	89.4	89.0	89.4	
R(C–F)	1.382	1.368	1.397	1.389	1.399 <sup>c</sup>
A(C–C–F)	113.9	111.2	111.6	111.4	
D(C–C–C–F)	0	0	0	0	
R(C–Cl)	1.761	1.808	1.800	1.840	1.802 <sup>d</sup>
A(C–C–Cl)	111.7	112.5	111.9	112.6	109.4 ± 1.6 <sup>d</sup>
D(C–C–C–Cl)	90.2	90.2	89.7	90.1	90 <sup>d</sup>
R(C–Br)	1.933	1.977	1.980	2.008	1.978 <sup>d</sup>
A(C–C–Br)	112.8	112.1	111.0	112.0	110.0 ± 1 <sup>d</sup>
D(C–C–C–Br)	85.2	85.2	89.4	90.0	90 <sup>d</sup>

<sup>a</sup> Bond lengths (R) are in angstroms; angles (A) and dihedral angles (D) are in degrees. <sup>b</sup> Reference 30. <sup>c</sup> Reference 30; average crystalline value for C(sp<sup>2</sup>)–CH<sub>2</sub>–F. <sup>d</sup> Reference 31.

**Table 2.** Calculated Gas-Phase Bond Lengths<sup>a</sup> in the Benzyl Radical (Benzylic Carbon is C7)

bond	(U)AM1	(U)HF	(U)MP2	(U)SVWN5	(U)B3LYP
C1–C2	1.425	1.428	1.409	1.422	1.427
C2–C3	1.392	1.390	1.366	1.381	1.386
C3–C4	1.403	1.405	1.387	1.398	1.403
C1–C7	1.397	1.404	1.410	1.395	1.407

<sup>a</sup> All values are in angstroms.

**Table 3.** Gas-Phase Bond Dissociation Enthalpies ( $\Delta H^\circ_{298}$ ) in Para-Substituted Toluenes, Benzyl Fluorides, Chlorides, and Bromides, 4- $YC_6H_4CH_2-X$ , with BDE(AM1) Values in Normal Font and BDE(B3LYP) Values in Italics<sup>a</sup>

Y <sup>b</sup>	YC <sub>6</sub> H <sub>4</sub> CH <sub>2</sub> -H	YC <sub>6</sub> H <sub>4</sub> CH <sub>2</sub> -F	YC <sub>6</sub> H <sub>4</sub> CH <sub>2</sub> -Cl	YC <sub>6</sub> H <sub>4</sub> CH <sub>2</sub> -Br
NH <sub>2</sub>	87.5 (–1.7)	95.7 (–0.5)	66.4 (–0.2)	55.4 (–0.2)
	88.5 (–1.9)	97.0 (–0.2)	68.5 (–0.1)	57.1 (0.0)
OH	88.3 (–0.9)	95.8 (–0.4)	66.6 (0.0)	55.7 (0.1)
OCH <sub>3</sub>	88.3 (–0.9)	95.8 (–0.4)	66.6 (0.0)	55.7 (0.1)
CH <sub>3</sub>	88.8 (–0.4)	95.8 (–0.4)	66.6 (0.0)	55.7 (0.1)
	89.2 (0.0)	96.2 (0.0)	66.6 (0.0)	55.6 (0.0)
H	90.4 (0.0)	97.2 (0.0)	68.6 (0.0)	57.1 (0.0)
	89.7 (0.5)	96.0 (–0.2)	66.1 (–0.5)	54.8 (–0.8)
CF <sub>3</sub>	88.7 (–0.5)	94.9 (–1.3)	65.0 (–1.6)	54.0 (–1.6)
NO	89.1 (–0.1)	95.2 (–1.0)	65.0 (–1.6)	54.1 (–1.5)
NO <sub>2</sub>	88.1 (–1.1)	94.5 (–1.7)	64.6 (–2.0)	53.7 (–1.9)
	89.0 (–1.4)	95.4 (–1.8)	66.3 (–2.3)	55.0 (–2.1)

<sup>a</sup> Differences from unsubstituted species  $\Delta BDE = BDE(4-YC_6H_4CH_2-X - C_6H_5CH_2-X)$  are given in parentheses. All values are in kcal/mol. <sup>b</sup> Values of the substituent constants for Y ( $\sigma_p$  and  $\sigma_p^+$ ) increase monotonically from NH<sub>2</sub> through to NO<sub>2</sub>. There are no  $\sigma$  values for BH<sub>2</sub>.

bromides at their B3LYP minimum geometries. We denote this method for calculating BDEs as BDE(B3LYP/LDBS//B3LYP/6-31G(d)), or BDE(B3LYP) for short. The errors in both the AM1- and B3LYP-calculated BDEs will generally be systematic so that, for each series of 4- $YC_6H_4CH_2-X$  compounds, the relative C–X BDEs (and hence C–X BDE differences) should probably be reliable to better than ca. ±0.2 kcal/mol, an uncertainty which arises because of small irreproducibilities in the geometry optimization and convergence of the SCF procedure. Since the calculated effects of substituents on C–X BDEs were found to be quite small ( $\leq$  ca. 2 kcal/mol), care should be taken in their interpretation.

## Results

The BDE(AM1) 4- $YC_6H_4CH_2-X$  bond dissociation enthalpies,  $\Delta H^\circ_{298}$ , are given in normal font for nine toluenes and the same number of benzyl fluorides, chlorides, and bromides in Table 3. The 12 BDE(B3LYP) calculations are given in italics in the same table.



## Discussion

**Toluenes.** The calculated values of the  $C_6H_5CH_2$ -H BDE, viz., 89.2 (AM1) and 90.4 (B3LYP) kcal/mol, are in excellent agreement with an experimental value of 88.6 (ref 6b) and the reviewed (best) value of 89.6 (ref 32) kcal/mol. Earlier B3LYP-based calculations of this quantity have been less successful, with values of 94.5 (ref 6d) and 87.9 (ref 33) kcal/mol. A mixed B3LYP calculation also gave 87.9 kcal/mol,<sup>34</sup> while a BLYP calculation gave 84.2 kcal/mol.<sup>6f</sup>

Electron-donating para-substituents ( $NH_2$ , OH,  $OCH_3$ , and  $CH_3$ ) and most electron-withdrawing para-substituents (CN,  $NO_2$ , and  $BH_2$ ) have weaker benzylic C–H bonds than toluene. Only the  $CF_3$  group induces an increase in the benzylic C–H BDE above that in toluene. Our present results agree well with two earlier DFT studies,<sup>6d,f</sup> which also found that the benzylic C–H bond was very slightly weakened ( $\leq 2$  kcal/mol) for all substituents examined (except *p*- $CF_3$ ).<sup>6f</sup>

Because both electron-donating and electron-withdrawing substituents cause C–H bond weakening, Hammett-type correlations with  $\sigma$  or  $\sigma^+$  are extremely unsatisfactory, and substituent effects on benzylic C–H BDEs cannot be attributed to polar effects. This is expected on the basis of earlier work<sup>3a,6a,e</sup> and, possibly, also because the (Pauling<sup>14</sup>) electronegativities of carbon (2.5) and hydrogen (2.1) are similar. *The effect of Y substituents on 4- $YC_6H_4CH_2$ -H BDEs must, therefore, be attributed mainly (or entirely) to the greater ability of Y to delocalize the unpaired electron relative to a hydrogen atom.* Since 4- $YC_6H_4CH_2$ -H BDEs show no clear dependence on the polar effect of Y, our calculated C–H BDEs would be expected to correlate with the ability of Y to delocalize the unpaired electron in 4- $YC_6H_5CH_2^*$  radicals.

There are several scales of “electron delocalization by Y-substituents”, of which the best are probably those derived from electron spin resonance (ESR) spectroscopic measurements rather than from measurements of the kinetics of some particular reaction. There would appear to be three ESR-based scales of electron delocalization in substituted benzylic radicals, the  $\sigma_\alpha^*$  scale of Arnold,<sup>35</sup> the  $\sigma^*$  scale of Jackson and Shariff,<sup>36</sup> and the D scale of Adam and Harrer.<sup>37</sup> Each of the  $\sigma^*$  scales contains values for only four (the same four) of the eight substituents considered in the present work. Both  $\sigma^*$  scales imply that the spin densities at the benzylic positions decrease along the series 4-H > 4- $CH_3$  > 4- $CH_3O$  > 4-CN, and they further agree that in 4- $CF_3C_6H_4CH_2^*$  the spin density on the benzylic group is greater than that in  $C_6H_5CH_2^*$ .<sup>35,36</sup> The D scale has *D* values for all substituents except  $BH_2$ .<sup>37</sup> However, the D scale is surprising in that it implies that two substituents, viz., 4- $CH_3O$  and 4-HO, which would be expected to decrease spin density on the benzylic carbon atoms, actually increase the spin density

(32) Afeefy, H. Y.; Liebman, J. F.; Stein, S. E. Neutral Thermochemical Data. In *NIST Chemistry WebBook*; Mallard, W. G., Linstrom, P. J., Eds.; NIST Standard Reference Database No. 69; National Institute of Standards and Technology: Gaithersburg, MD, March 1998; 20899 (<http://webbook.nist.gov>).

(33) van Scheppingen, W.; Dorrestijn, E.; Arends, I.; Mulder, P.; Korth, H.-G. *J. Phys. Chem.* **1997**, *101*, 5404–5411.

(34) Kafafi, S. A.; El-Gharkawy, E.-S. R. H. *J. Phys. Chem. A* **1998**, *102*, 3202–3208.

(35) Arnold, D. R. In *Substituent Effects in Radical Chemistry*; Viehe, H. G., Janousek, Z., Merényi, R., Eds.; NATO ASI Series C; Reidel Publ. Co.: Dordrecht, The Netherlands, 1986; Vol. 189, pp 171–188 and references cited therein.

(36) Jackson, R. A.; Shariff, M. *J. Chem. Soc., Perkin Trans. 2* **1996**, 775–778.

(37) Adam, W.; Harrer, H. M. *Anal. Chim. Acta* **1997**, *33*, 271–276. Adam, W.; Harrer, H. M.; Kita, F.; Nau, W. M. *Pure Appl. Chem.* **1997**, *69*, 91–96.

relative to the unsubstituted species, whereas the (electronically comparable) 4- $NH_2$  group does, indeed, induce a decrease in spin density at the benzylic positions. The *D* value for the 4- $CF_3$  group indicates that this group, as well as 4- $CH_3$ , 4-CN, and 4- $NO_2$ , decreases spin density at the benzylic carbon atoms. Our results, viz., C–H bond-weakening by 4- $CH_3O$  and bond-strengthening by 4- $CF_3$  (see Table 3), are clearly more consistent with either  $\sigma^*$  scale than with the D scale.<sup>38</sup> However, the correlation with  $\sigma^*$  is poor because both  $\sigma^*$  scales indicate that the 4-CN group is roughly twice as effective as the 4- $CH_3O$  group in delocalizing the unpaired electron, whereas our calculations indicate that 4-CN is roughly half as effective as 4- $CH_3O$  in weakening the corresponding benzylic C–H bonds (see Table 3). 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 unresolved.

**Benzyl Halides.** The calculated values of the  $C_6H_5CH_2$ -Br BDE are 55.6 (AM1) and 57.1 (B3LYP) kcal/mol, which may be compared with the following experimental values: 55.9 or 53.1 kcal/mol (electrochemical measurements),<sup>12</sup> 60.7 kcal/mol (PAC measurements),<sup>9,39</sup> 60.9 kcal/mol (thermolysis of benzyl bromide in the gas phase),<sup>9,40</sup> and the reviewed (best) value of 56.2 kcal/mol.<sup>32</sup> Earlier calculated values of this BDE ranged from 42.3 to 59.3 kcal/mol, depending on the level of theory.<sup>3c</sup> Our calculated values of the  $C_6H_5CH_2$ -Cl BDE are 66.6 (AM1) and 68.6 (B3LYP) kcal/mol, which may be compared with experimental values of 69.1 or 71.6 kcal/mol (electrochemical measurements)<sup>12</sup> and the reviewed value of 73.9 kcal/mol.<sup>32</sup> For benzyl fluoride, our calculated C–F BDEs are 96.2 (AM1) and 97.2 (B3LYP) kcal/mol. The uncoupled infrared C–F stretching frequency for  $C_6H_5CH_2F$  in the liquid phase ( $1018\text{ cm}^{-1}$ ) has been utilized to calculate a  $C_6H_5CH_2$ -F BDE of  $98.6 \pm 2$  kcal/mol.<sup>41</sup> The uncoupled IR stretching frequency method has been further refined,<sup>42</sup> and the current estimate of the  $C_6H_5CH_2$ -F BDE is  $95.9 \pm 2$  kcal/mol.<sup>43</sup>

The foregoing comparison of our calculated benzyl halide BDEs with literature values shows that there is excellent agreement for benzyl fluoride (as might be expected). The literature BDEs for benzyl bromide range so widely that it is not surprising that our calculated values fall within this range. More interestingly, our calculations give C–Br BDEs very close to the (NIST) reviewed (best) value. Since our calculated C–F and C–Br BDEs agree so well with literature values, we would also have expected good agreement for the C–Cl BDE. Obviously, this is not the case, presumably because the calculated C–Cl bond length is in poor agreement with experiment (see Table 1).

The calculated BDEs for 4- $YC_6H_4CH_2$ -Br show relatively little dependence on the nature of Y ( $\leq 2$  kcal/mol, see numbers in parentheses in the fifth column in Table 3). Thus, our results are more consistent with those of Leigh et al.<sup>10</sup> and Laarhoven et al.<sup>9</sup> (i.e., no significant substituent effects on C–Br BDEs) than with the results of Clark and Wayner<sup>11</sup> or Andrieux et al.<sup>12</sup> (i.e., substantial effects, see the introduction). We therefore

(38) However, it is important to note that calculated spin densities on the benzylic carbon atom in the 4- $YC_6H_4CH_2^*$  radicals indicate that all substituents, including the 4- $CF_3$  group, increase delocalization of the unpaired electron.<sup>6f</sup>

(39) Clark and Wayner<sup>11</sup> did not determine this BDE but assumed it was 59.4 kcal/mol from literature data.

(40) Leigh et al.<sup>10</sup> did not determine this BDE.

(41) Zavitsas, A. A. *J. Phys. Chem.* **1987**, *91*, 5573–5577.

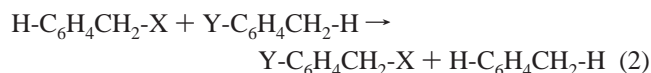
(42) Zavitsas, A. A.; Chatgililoglu, C. *J. Am. Chem. Soc.* **1995**, *117*, 10645–10654.

(43) Zavitsas, A. A. Private communication.

considered the possibility that the different experimental results which have been reported were a consequence of the dielectric constants of the media in which the measurements were made. That is, a medium with a high dielectric constant would be expected to solvate benzyl bromide (dipole moment = 2.03 D)<sup>44</sup> better than the benzyl radical (dipole moment = 0.09 D),<sup>44</sup> thus stabilizing the molecule relative to the radical and possibly leading to the substituent effects on C–Br BDEs which have been reported.<sup>11,12</sup> This idea is consistent with the fact that substituent effects were small (<1 kcal/mol) for measurements in the gas phase<sup>9,10</sup> but were substantial for electrochemical measurements in acetonitrile (dielectric constant 37) and dimethyl formamide (dielectric constant 38).<sup>12</sup> However, the idea is not consistent with the fact that PAC measurements in triethylsilane/benzene (3:1, v/v),<sup>11</sup> a low dielectric constant medium, gave even larger substituent effects on C–Br BDEs than the electrochemical measurements (see the introduction), nor with the fact that PAC experiments in ethyl acetate (dielectric constant 6) showed no significant substituent effects.<sup>9</sup>

To explore the possibility of a medium effect on C–Br BDEs, the calculations on benzyl bromide and 4-cyanobenzyl bromide (4.10 D, radical 5.11 D)<sup>44</sup> were repeated in a self-consistent induced polarized continuum model (SCI PCM) reaction field with the dielectric constant set to 37 D.<sup>45</sup> There were no significant changes in the two C–Br BDEs, which suggests that the properties of the reaction medium are unlikely to be responsible for the reported effect of substituents on 4-YC<sub>6</sub>H<sub>4</sub>-CH<sub>2</sub>-Br BDEs.

**The “Purely Polar” Effect.** Returning to Table 3, a comparison of the numbers in parentheses in columns 3, 4, and 5 of Table 3 reveals that the small effects substituents have on C–Br BDEs are quite closely matched by the effects of the same substituents on C–Cl and C–F BDEs. Our calculations therefore imply that the intriguing hypothesis<sup>11</sup> that the direction and magnitude of the effects of Y-substituents on 4-YC<sub>6</sub>H<sub>4</sub>Z-X BDEs depends on the differences in the electronegativities of the bonding atoms in Z and X *should be discarded*. However, this does not mean that Y has no “purely polar” effect on carbon–halogen BDEs in the benzyl halides. To “see” this purely polar effect, it is, of course, necessary to correct for the major (though still very small, i.e., <2 kcal/mol even for the 4-NH<sub>2</sub> group) effect of Y on 4-YC<sub>6</sub>H<sub>4</sub>Z-X BDEs arising from electron delocalization into the Y substituent, i.e., to correct for the stabilizing effect of each Y on the 4-YC<sub>6</sub>H<sub>4</sub>CH<sub>2</sub><sup>•</sup> radicals. This can be done by comparing the carbon–halogen BDEs with the carbon–hydrogen BDEs in the correspondingly substituted toluenes via the calculated enthalpy change,  $\Delta\Delta\text{BDE}$ , for the isodesmic reaction:

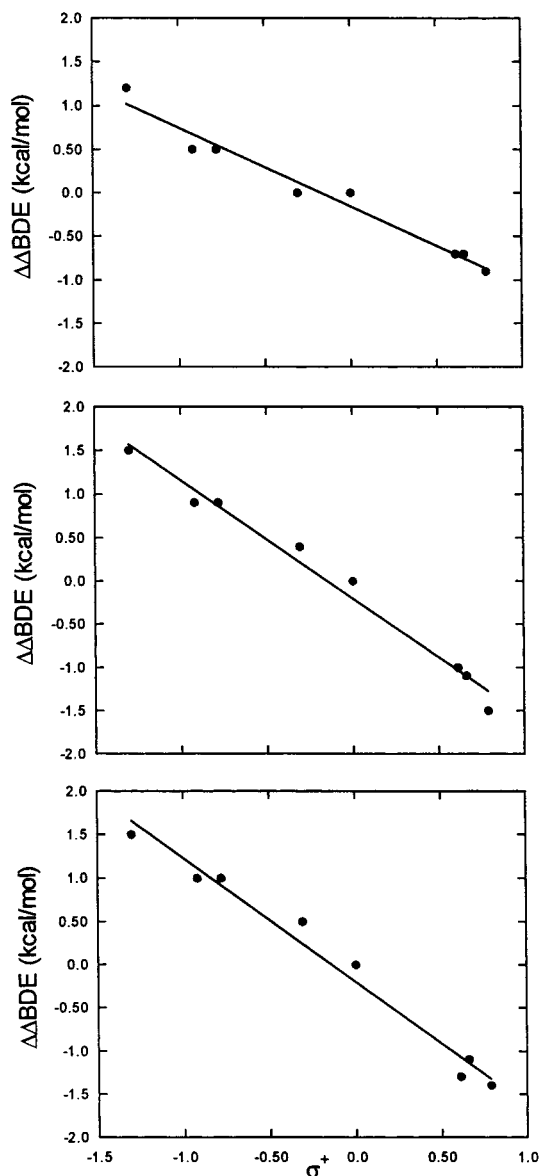


From the data given in parentheses in Table 3, this enthalpic change is most readily obtained via the following quantity (for the same Y):

$$\Delta\Delta\text{BDE}(\text{X} - \text{H}) = [\Delta\text{BDE}(4\text{-YC}_6\text{H}_4\text{CH}_2\text{-X} - \text{C}_6\text{H}_5\text{CH}_2\text{-X})] - [\Delta\text{BDE}(4\text{-YC}_6\text{H}_4\text{CH}_2\text{-H} - \text{C}_6\text{H}_5\text{CH}_2\text{-H})] \quad (3)$$

(44) DFT dipole moments were calculated with the uniform basis set 6-311+G(2d,2p).

(45) Previous calculations on O–H BDEs in aminophenols using this model have been shown to reproduce predicted trends. Wright, J. S.; Pratt, D. A.; McKay, D. J. Unpublished results.



**Figure 2.** Plots against  $\sigma_p^+$  (Y) of  $\Delta\Delta\text{BDE}(\text{X} - \text{H}) = [\Delta\text{BDE}(4\text{-YC}_6\text{H}_4\text{CH}_2\text{-X} - \text{C}_6\text{H}_5\text{CH}_2\text{-X})] - [\Delta\text{BDE}(4\text{-YC}_6\text{H}_4\text{CH}_2\text{-H} - \text{C}_6\text{H}_5\text{CH}_2\text{-H})]$  for the same Y and X = F (top), Cl (middle), and Br (bottom) based on BDE(AM1) calculations.

Values of  $\Delta\Delta\text{BDE}(\text{X} - \text{H})$  are given in Table 4. These values clearly demonstrate that Y substituents do have a purely polar effect on 4-YC<sub>6</sub>H<sub>4</sub>CH<sub>2</sub>-X (X = Br, Cl, F) BDEs. Furthermore, this purely polar effect is in the same direction as was first suggested by Clark and Wayner,<sup>11</sup> viz., electron-donating Y substituents strengthen the carbon–halogen bonds, and electron-withdrawing Y substituents weaken these bonds. These purely polar effects on BDE correlate remarkably well with the  $\sigma_p^+$  constants for Y (see Figure 2), viz.,

$$\text{X} = \text{Br}, \quad \rho^+ = -1.43 \text{ kcal/mol}, \quad \langle R \rangle = 0.989$$

$$\text{X} = \text{Cl}, \quad \rho^+ = -1.36 \text{ kcal/mol}, \quad \langle R \rangle = 0.991$$

$$\text{X} = \text{F}, \quad \rho^+ = -0.90 \text{ kcal/mol}, \quad \langle R \rangle = 0.985$$

Nau<sup>46</sup> has drawn rather similar conclusions regarding the “polar ground-state stabilization energy (PSE)” effect of Y substituents on 4-YC<sub>6</sub>H<sub>4</sub>CH<sub>2</sub>-Br BDEs using AM1 calculations

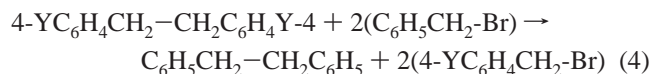
(46) Nau, W. M. *J. Org. Chem.* **1996**, *61*, 8312–8314.

**Table 4.** [ $\Delta\text{BDE}(4\text{-YC}_6\text{H}_4\text{CH}_2\text{-X} - \text{C}_6\text{H}_5\text{CH}_2\text{-X}) - [\Delta\text{BDE}(4\text{-YC}_6\text{H}_4\text{CH}_2\text{-H} - \text{C}_6\text{H}_5\text{CH}_2\text{-H})] = \Delta\Delta\text{BDE}(X - \text{H})$ ] for the Same Y:  $\Delta\Delta\text{BDE}(\text{AM1})$  in Normal Font,  $\Delta\Delta\text{BDE}(\text{B3LYP})$  in Italics<sup>a</sup>

Y <sup>b</sup>	$\sigma^+$ <sup>c</sup>	$\Delta\Delta\text{BDE}(\text{F-H})$	$\Delta\Delta\text{BDE}(\text{Cl-H})$	$\Delta\Delta\text{BDE}(\text{Br-H})$
NH <sub>2</sub>	-1.30	{ 1.2 <i>1.7</i>	{ 1.5 <i>1.8</i>	{ 1.5 <i>1.9</i>
OH	-0.92	0.5	0.9	1.0
OCH <sub>3</sub>	-0.78	0.5	0.9	1.0
CH <sub>3</sub>	-0.31	0.0	0.4	0.5
H	0	0.0	0.0	0.0
CF <sub>3</sub>	0.61	-0.7	-1.0	-1.3
CN	0.66	-0.7	-1.1	-1.1
NO <sub>2</sub>	0.79	-0.9	-1.5	-1.4
BH <sub>2</sub>	(0.48) <sup>d</sup>	{ -0.6 <i>0.4</i>	{ -0.9 <i>-0.9</i>	{ -0.8 <i>-0.7</i>

<sup>a</sup> All values are in kcal/mol. <sup>b</sup> Same as footnote *b* in Table 3. <sup>c</sup> Hansch, C.; Leo, A. *Substituent Constants for Correlation Analysis in Chemistry and Biology*; Wiley: New York, 1979. <sup>d</sup> Estimated from this work, see text.

and the following isodesmic reaction:



The trends in the calculated enthalpies for isodesmic reaction 4 ( $\Delta H_4$ ) should correspond to the trends in the calculated enthalpies for isodesmic reaction 2 (and 3), i.e., to  $\Delta\Delta\text{BDE}(X-\text{H})$ . The values for  $\Delta H_4$  do, indeed, show the same trend as  $\Delta\Delta\text{BDE}(X-\text{H})$  but are smaller in magnitude. For example, from a graph,<sup>46</sup>  $\Delta H_4$  is ca. 0.4 kcal/mol smaller for Y = 4-NH<sub>2</sub> than for Y = H, i.e., the C-Br bond in 4-NH<sub>2</sub>C<sub>6</sub>H<sub>4</sub>CH<sub>2</sub>Br was calculated to be stronger than that in C<sub>6</sub>H<sub>5</sub>CH<sub>2</sub>Br, while for Y = 4-NO<sub>2</sub>,  $\Delta H_4$  is ca. 0.6 kcal/mol larger than for Y = H, i.e., the C-Br bond in 4-NO<sub>2</sub>C<sub>6</sub>H<sub>4</sub>CH<sub>2</sub>Br is weaker than that in

C<sub>6</sub>H<sub>5</sub>CH<sub>2</sub>Br. Our own calculations give 4-NH<sub>2</sub>C<sub>6</sub>H<sub>4</sub>CH<sub>2</sub>-Br and 4-NO<sub>2</sub>C<sub>6</sub>H<sub>4</sub>CH<sub>2</sub>-Br BDEs stronger and weaker than C<sub>6</sub>H<sub>5</sub>CH<sub>2</sub>-Br by 1.5 and 1.4 kcal/mol, respectively (see Table 4). Nau<sup>46</sup> calculated  $\Delta H_4$  for benzyl bromide and nine 4-substituted benzyl bromides and found that the PSEs correlated very well with  $\sigma$  (rather than  $\sigma^+$ ). The qualitative agreement between Nau's calculations and our own is gratifying. The absence of quantitative agreement can probably be attributed to the different levels of theory and different isodesmic reactions employed in the two studies.

Our calculations (and Nau's<sup>46</sup>) imply that substituents do exert a *purely polar* effect on the BDEs of benzyl halides, but it is surprising that the magnitudes of these effects are so similar for bromine, chlorine, and fluorine. In fact, our  $\rho^+$  values correlate extremely well with the DFT-calculated dipole moments<sup>44</sup> of the benzyl halides, viz., C<sub>6</sub>H<sub>5</sub>CH<sub>2</sub>Br, 2.03 D ( $\rho^+ = -1.43$ ); C<sub>6</sub>H<sub>5</sub>CH<sub>2</sub>Cl, 1.94 D ( $\rho^+ = -1.36$ ); and C<sub>6</sub>H<sub>5</sub>CH<sub>2</sub>F, 1.66 D ( $\rho^+ = -0.90$ ), rather than with the carbon-halogen electronegativity differences, as might have been expected.

Finally, our calculations allow us to assign a substituent constant to the BH<sub>2</sub> group for the first time. From the three  $\Delta\Delta\text{BDE}(X - \text{H})$  vs  $\sigma^+$  plots and the data for the 4-BH<sub>2</sub> group in Table 4, we find  $\sigma_p^+(\text{BH}_2) = 0.42, 0.51,$  and  $0.50$  for X = Br, Cl, and F, respectively, giving what is probably a fairly reliable mean  $\sigma_p^+$  value of 0.48.

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