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Ab Initio MO and Density Functional Theory Study of Substituent Effects on Electron Attachment to Benzyl Chlorides

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Reductive cleavage of para-substituted benzyl chlorides 4-Y−$C_6H_4CH_2Cl$ (Y = NH_2, MeO, Me, H, F, Cl, CF_3, NO_2) (**1**) and of $C_6F_5CH_2Cl$ (**2**) has been studied by MP2 and DFT methods. In contrast to the MP2 calculations, DFT calculations reveal the formation of radical anions from benzyl chlorides including those bearing donor substituents. The calculations also show the possibility of the formation of complexes of benzyl radicals with the chloride anion along the path of the reductive cleavage.

I. Introduction

The magnitude of reduction potentials,[1−3] and consequently, the possibility of an alternative single electron transfer (SET) pathway in nucleophilic substitution,[4] are strongly dependent on the substituents Y, R^1, and R^2 in benzyl halides Y−C_6H_4-CR^1R^2X (X = halogen). These substituents also determine the mechanism of benzyl halide cleavage induced by electron transfer (ET) either from cathode or a nucleophile. The results of electrochemical studies agree well with the hypothesis that the cleavage of the C−Cl or C−Br bond in the reduction of benzyl chlorides or bromides occurs simultaneously with ET, which is often described as dissociative electron attachment leading to benzyl radical and halide anion.[2,3,4b,d] An alternative stepwise mechanism has been established for the reduction of nitrobenzyl halides, which first accept an electron to form a transient radical anion (RA) that subsequently undergoes dissociation.[2,3,4b,d,5] Recent ab initio calculations[6] support the mechanism of dissociative electron attachment for benzyl chlorides and the analogous 4-pyridine derivatives. However, some other estimates[2b] and experimental data[5,7] have demonstrated that even benzyl halides lacking strong electron-withdrawing groups might also form relatively stable RAs, at least at low temperatures. These data suggest that the level of theoretical calculations applied hitherto to these models[6] was insufficient for reliable conclusions about the occurrence of RAs minima at the potential energy surfaces (PESs), even in the gas phase.

In the present work, the electron attachment to the benzyl chlorides **1** and **2** (see Figure 1) has been theoretically studied. First, the density functional theory (DFT)[8] calculations have been perfofrmed. Despite some shortcomings inherent in DFT calculations,[9] such calculations include electron correlation and are much faster than the traditional Hartree−Fock (HF) and post-HF techniques.[8,9a,b] DFT methods often give results, the quality of which is close to experimental data and comparable to or better than the second-order Møller−Plesset (MP2) perturbation theory results for neutral molecules,[9a,b,10−16] radicals[10−18] (including benzyl radicals[13a,19,20]), anions,[13d,17d] and even radical anions.[13d,21,22] DFT has proven to be efficient in calculations of bond energies,[9a,18,19,23,24] ionization potentials,[9a,11,13,23,25,26] and electron affinities.[9a,11,13,21,25−27] In this work, electron attachment to **1** and **2** has also been studied at the MP2 level of theory. DFT calculations has been found to demonstrate substantial advantages over the MP2 method in the study of radical anions of benzyl chlorides.

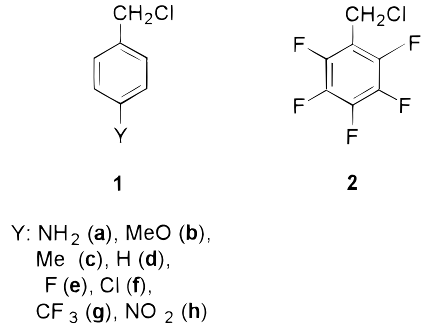

Figure 1. Benzyl chlorides **1** and **2**.

II. Computational Details

All calculations were performed with the Gaussian 94 (G94) suite of programs.[28] MP2 calculations with frozen core electrons (MP2(FC)) of all species under study (including full optimization of molecular geometries) were carried out using the 6-31G(d) basis set. The energies of optimized structures were further refined by single-point MP2 calculations with the 6-31+G(d,p) basis set and corrected by zero-point vibrational energies (ZPVE) scaled by 0.8929.[29] For DFT geometry optimization and energy calculations, one of the most widely employed functionals, BLYP,[30] was used in conjunction with the 6-31G(d) basis set. The final BLYP/6-31G(d) energies were corrected by ZPVE without scaling, as the scale factor for BLYP ZPVE values is known to be close to unity (1.02).[31] For closed shell molecules, the restricted MP2 and BLYP methods were applied, while for open shell systems, the respective spin

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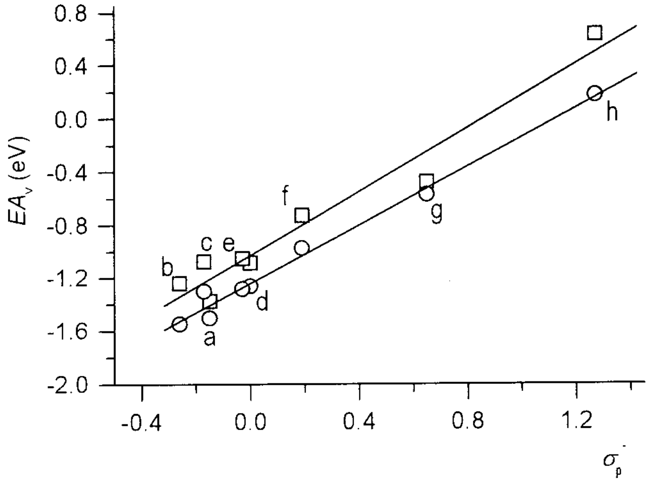


Figure 2. EA$_v$ values ((○) MP2, $r = 0.993$, $\rho = 1.10$; (□) BLYP, $r = 0.975$, $\rho = 1.20$) of the para-Y-substituted benzyl chlorides **1a**−**h**.

unrestricted (UMP2 and UBLYP) methods and the annihilation of the first spin contaminant by spin projection (PUMP2 and PUBLYP)[32] were used. Both the restricted (RHF/6-31G(d) and BLYP/6-31G(d)) and unrestricted (PUHF/6-31G(d) and PUBLYP/6-31G(d)) calculations of vibrational frequencies were performed to characterize the nature of the stationary points and to calculate the contribution of ZPVE for neutral molecules and open shell systems.

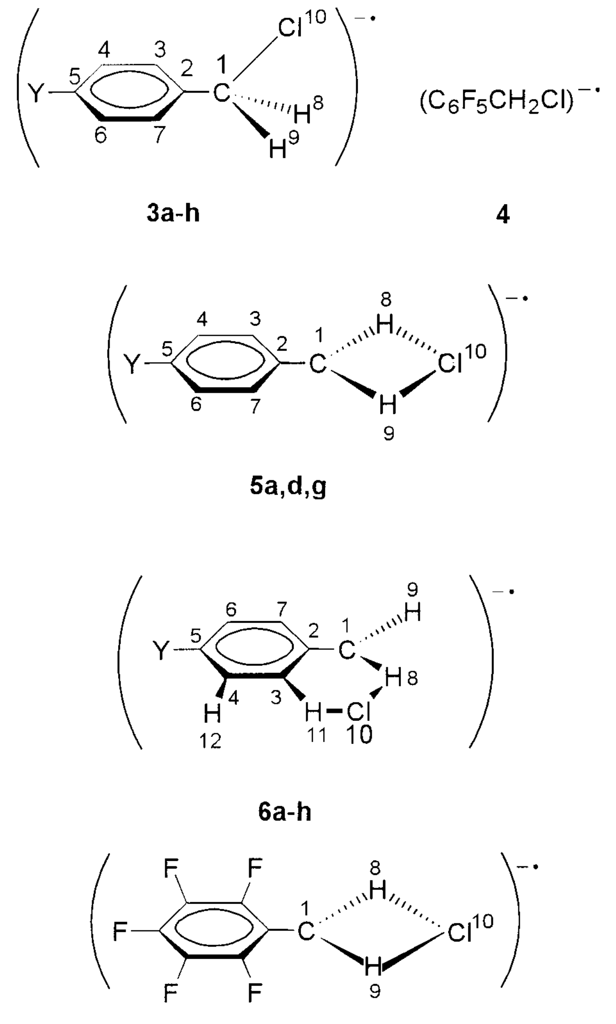
The values of vertical (EA$_v$) and adiabatic electron affinities (EA$_a$) of benzyl chlorides **1** and **2**, homolytic bond dissociation energies (BDEs) E_{BD} for C−Cl bonds in both neutral molecules **1** and **2**, their RAs, and the cleavage energies E_{cl} of other negatively charged systems with unpaired electrons giving rise to chloride anion and benzyl radicals, were determined by a standard approach through the calculation of energies of all involved species.

III. Results and Discussion

The values of EA$_v$ of benzyl chlorides were shown by MP2(FC)/6-31+G(d,p)//MP2(FC)/6-31G(d) and BLYP/6-31G(d) calculations to increase linearly with the electron-withdrawing character of the substituents (Figure 2).

As expected for negatively charged particles, the best linear correlations were observed for σ_p^- Hammett constants.[33] At the MP2(FC)/6-31+G(d,p)//MP2(FC)/6-31G(d) level, only **1h** (Y= NO$_2$) possesses a positive EA$_v$ value. For **2**, both MP2 and DFT gave negative EA$_v$ (−0.664 eV and −0.512 eV, respectively). On the other hand, at the MP2(FC)/6-31G(d) level, negative EA$_v$ values were obtained for **2** and all **1,** including **1h** (EA$_v$ = −0.507 eV) which is well-known to be easily reduced to the RA at the cathode,[2a] by γ-ray radiolysis[5] or in reactions with “carbanions”.[4,34] Thus, not unexpectedly, the agreement between theory and experiment for **1h** (Y=NO$_2$) is only achieved by inclusion of diffuse functions for heavy atoms and polarization functions for hydrogens.

Adiabatic electron affinities of benzyl chlorides **1** and **2** to give **3** and **4** (Figure 3) were found in DFT calculations to be positive for all **1** (Figure 4) and **2** (EA_a = 0.769 eV, without ZPVE correction). The PUMP2(FC)/6-31G(d) calculations failed to locate stable RAs **3a**−**3g**, which is likely to be accounted for by a serious distortion of the PESs for these systems due to the contamination of wave functions with higher spin states, especially if electron correlation is accounted for with perturbative methods.[35] Thus, even in PUMP2(FC)/6-31+G(d,p)// PUMP2(FC)/6-31G(d) calculations the values of $\langle S^2 \rangle$ for **3h** (Y = NO$_2$) are equal to 1.16 and 0.89 without and with annihilation, respectively.



3a-h **4**

5a,d,g

6a-h

7

Figure 3. Anion radiclas **3** and **4** of benzyl chlorides and complexes **5**−**7** of the benzyl radicals with chloride anion.

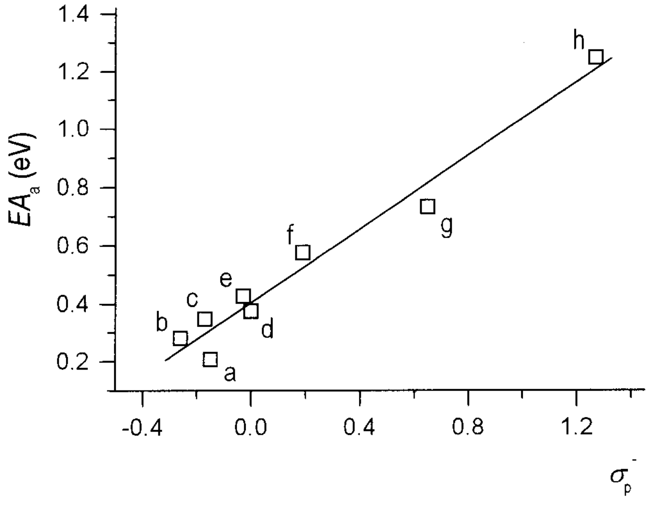


Figure 4. BLYP calculated EA$_a$ values of the para-Y-substituted benzyl chlorides **1a**−**h**; $r = 0.982$, $\rho = 0.63$.

On the other hand, the values of $\langle S^2 \rangle$ obtained for the radical anions **3** and **4** by the unprojected DFT calculations never exceeded 0.7611 (**3b**, Y = OMe), while after annihilation **4**

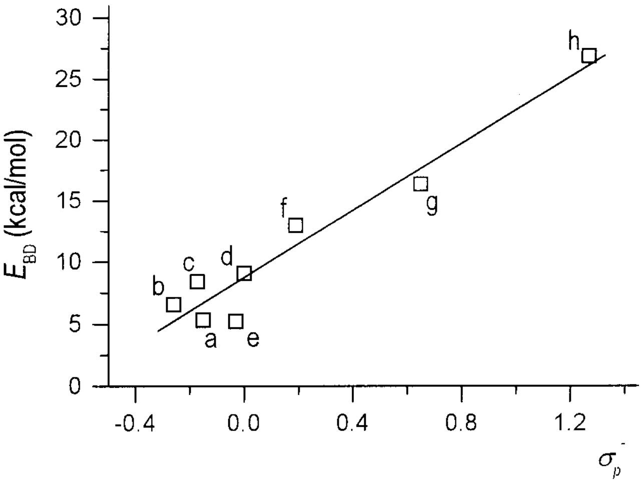


Figure 5. Correlation of the BLYP/6-31G(d) homolitic Cl10−C1 bond dissociation energies (E_{BD}) of the radical anions **3a**−**h** with the σ_p^- Hammett constants of Y; $r = 0.970$, $\rho = 13.6$.

gave the highest $\langle S^2 \rangle$ value (0.7512). DFT optimization of **3b**−**h** and **4** revealed true minima on PESs. Only for **3a** (Y = NH_2) the calculations led to a low imaginary frequency (28.1i). Therefore, in contrast to MP2 calculations, DFT predicts the possibility of the formation of RAs at least in the gas phase for all benzyl chlorides under study except for **3a** (Y = NH_2) which bears the strongest donor substituent of the series. In other words, electron attachment to molecules **1** and **2** according to DFT calculations is not necessarily dissociative, which is in good agreement with the reported lifetimes of RAs of $C_6H_5CH_2X$ (X = F, Cl, Br) and 4-C_6H_5−$C_6H_4CH_2Cl$ measured in 2-Me-THF matrix at 85 K and below.[7]

Analysis of the vibrations of **3a** shows that the imaginary frequency 28.1i corresponds to the vibration of the Cl10 atom between the hydrogen atoms H8 and H9. Although **3a** is not a stable species, but rather a transition state, the structural data of **3a** will be used along with data of the other RAs in Hammett substituent constant correlations in order to achieve a comprehensive view over the whole series.

According to the DFT calculations, the chlorine atom in RAs **3** and **4** lies in a plane which is nearly orthogonal to the benzene ring as the dihedral angle Cl10−C1−C2−C3 varies from 86° to 90°. The angle Cl10−C1−C2 in **4** amounts to 117°, and in **3** this angle increases from 118° in **3h** to 141° in **3a**, showing a good linear correlation with the decreasing σ_p^- constants ($r = 0.916$). The distance C1−Cl10 increases also linearly from 2.521 Å in **3h** to 3.328 Å in **3a** with the decreasing σ_p^- values ($r = 0.914$).

The dissociation energy E_{BD} of the C1−Cl10 bond in **3** is positive for all species and increases linearly with increasing σ_p^- values (Figure 5). There is also a good correlation of these energies with the published E_{BD} for the C−Br bonds in RAs of the respective benzyl bromides.[2b] In **4**, the E_{BD} value is as large as 16.5 kcal/mol. For **3** bearing strong donor substituents (NH_2, MeO), E_{BD} is only 4.1−6.5 kcal/mol, which can be easily outweighed by the solvation of the chloride anion in polar solvents. Therefore, in polar media, the RAs of the benzyl chlorides **1a** and **1b** should not be formed, and indeed neither one has ever been observed.[2a,3] Still, in less polar media and particularly in hydrocarbon solvents at low temperatures, even such RAs might possess finite lifetimes. This assumption is even more valid for **3** with electron-withdrawing substituents as well as for **4**, for all of which E_{BD} exceeds 9 kcal/mol. In contrast to the RAs **3** and **4**, the E_{BD} values for the benzyl chlorides **1** are only weakly dependent on the substituent varying from 63.4 (**1e**) to 68.5 (**1a**) kcal/mol, which correspond to the E_{BD} values of the C−Br bonds in benzyl bromides.[36,37] Small effects (≤2 kcal/mol) of Y on CH_2−X BDEs in 4-Y−$C_6H_4CH_2$−X (X = H, Br, Cl, and F; Y = NH_2, HO, MeO, Me, H, CF_3, CN, NO_2, and BH_2) have been published recently by Ingold et al.[38] The calculated E_{BD} values for **1d** and **1h** amount to 68.5 and 64.9 kcal/mol and differ only by a few kcal/mol from the experimental E_{BD} values for the C1−Cl10 bond cleavages in **1d** and **1h**[2b,c] and for the C−Br bond dissociation energies in benzyl bromides.[36,37]

The PUMP2(FC)/6-31G(d) optimizations of **1a** and **1g** with one extra electron lead to nearly planar complexes **5a**, **5g** and **6a**, **6g** (only the H atoms of the NH_2 group and the F atoms of the CF_3 group are out of plane) (Figure 3). Complexes **5d** and **6d** have been located as saddle points by PUMP2(Full)/6-31G(d) and PUMP2(FC)/6-31G(d) calculations, respectively, while earlier data[6a] revealed an imaginary frequency only for **5d**. For **2**, PUMP2(FC)/6-31G(d) calculation led to complex **7** (Figure 3) with a large imaginary frequency (151.8i) corresponding to a transition state. PUMP2(FC)/6-31G(d) optimization of other **1** with one extra electron gave directly the complexes **6**. Such types of complexes were most recently considered in ab initio studies of the dissociative electron attachment to benzyl chloride,[6] benzotrichloride, and to the analogous 4-pyridine derivatives.[6b]

The PUMP2 energies of **5a** and **5d** are higher than the energies of **6a** and **6d** by 5.2 and 5.9 kcal/mol, respectively. The analysis of the vibrational frequencies showed that the stationary points are true minima only for **6c** and **6h**. The theoretical prediction of the formation of a stable species **6c** is in agreement with the experimental observation of complexes of mono- and dimethyl-substituted benzyl radicals with the chloride anion, although the structures of these complexes were not determined.[40] For **6a**,**b**,**d**−**g**, one imaginary frequency is present (from 35.6i (**6b**) to 47.9i (**6f**)), while two imaginary frequencies are found for **5** in the range of 47i−76i. Thus, PUHF/6-31G(d) frequency calculations, performed with MP2 located extrema, are in a poor agreement with the experimental data which show that benzyl radicals may actually bind halide ions to form detectable species.[7,41] This discrepancy is most likely accounted for by a significant contamination of the UHF wave functions both in uncorrelated and in MP2 correlated calculations, which may have a significant impact on vibrational frequencies.[42] Indeed, PUMP2/6-31+G(d,p)//PUMP2/6-31G(d) calculated $\langle S^2 \rangle$ values for **6a**−**6h** are as high as 1.25−1.27, and even after annihylation, $\langle S^2 \rangle$ is still not lower than 0.97−0.98.

On the other hand, unrestricted Kohn−Sham wave functions are known to be much less contaminated by higher spin states, which leads to more accurate estimations of vibrational frequencies in DFT calculations.[42] Complexes **6** are therefore easily localized as true minima on the PESs in PUBLYP/6-31G(d) calculations, for which $\langle S^2 \rangle$ values never exceeded 0.7501. DFT calculations result in an imaginary frequency only for **6c** (30.98i). Although we have failed to discover a rationale for this abnormal result, data for **6c** will be included in the analysis of the substituent effects on the structure and properties of complexes **6**. For electron attachment to **2**, neither DFT nor MP2 calculations revealed complexes analogous to **6**, possibly due to the lack of ortho-hydrogen atoms in the phenyl ring.

Although most of **6** have been assigned to transition states by MP2 calculations, their geometries are very close to their DFT counterparts that correspond to true minima. Indeed, as shown in Figure 6 (the correlation coefficients r of the

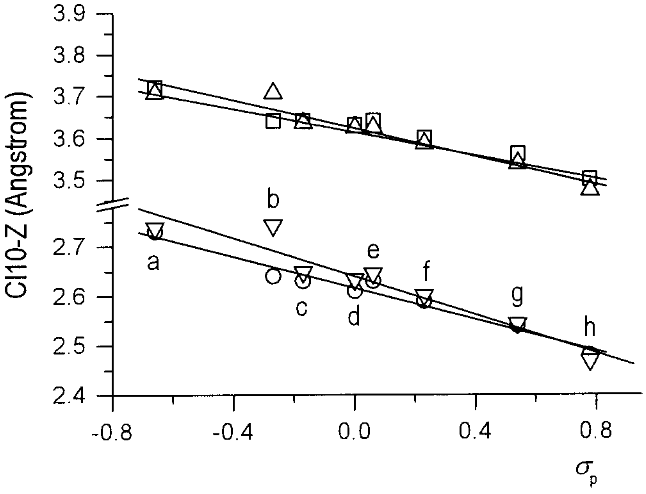


Figure 6. Correlations of the Cl10-Z distances (Z = C1: (□) BLYP, $r = 0.973$, $\rho = -0.14$; (△) MP2, $r = 0.966$, $\rho = -0.17$. Z = H8: (○) BLYP, $r = 0.979$, $\rho = -0.16$; (▽) MP2, $r = 0.954$, $\rho = -0.19$) in the complexes **6a**−**h** with the σ_p Hammett constants of Y.

corresponding linear regressions to the σ_p^- constants are lower and equal to 0.883−0.936), the trends of variation the Cl10−C1 and Cl10−H8 distances, decreasing with growing acceptor strength of the substituent both in MP2 and DFT calculations, are essentially the same. Simultaneously, the Cl10−H11 distances steadily increase from 2.561 Å in **6a** to 2.836 Å in **6h** (DFT), while the MP2 calculations show that these distances vary in a narrow range from 2.469 Å (**6b**) to 2.525 Å (**6c**) without any definite trends.

Analysis of the MP2 calculated charge and spin density distributions showed that the interaction of the Cl10 atom with C1, H8, and H11 in **6** is mostly electrostatic. Thus, according to the MP2 results, **6** are electrostatic complexes of the respective benzyl radical with the chloride anion. In contrast, at the DFT level, the interaction of Cl10 with C1, H8, and H11 in **6** is also mostly electrostatic; however, it has an appreciable contribution of covalent bonding. At the DFT level, the complex **6h** is less stable by 2.6 kcal/mol than **3h**, while all other complexes **6a**−**6g** are more stable than the corresponding RAs **3** by 3.7, 3.1, 2.5, 2.4, 3.1, 2.4, and 0.8 kcal/mol, respectively. These data clearly show that the pathways of reductive cleavage of **1h** as compared to all other compounds **1** seem to be rather different.

DFT calculated E_{cl} energies of the cleavage of **6** to the corresponding free benzyl radicals and the chloride anion linearly increase with the electron-withdrawing ability of the substituents (Figure 7). They are of the same order of magnitude as the respective E_{BD} for the RAs (Figure 5). This means that the stabilities of both the RAs **3** and the complexes **6** (bearing the same substituents) toward the dissociation to benzyl radical and the chloride anion are comparable. Compared to DFT, the MP2 calculations show that the stabilities of **6** are less sensitive to the growth of the Hammett substituent constant. This is evidenced by a smaller slope $\rho = 5.6$ of the line corresponding to the MP2 calculated E_{cl} values for **6** (Figure 7, circles) than in the case of the DFT calculated E_{cl} values (Figure 7, squares, $\rho = 9.4$). The lower sensitivity of the MP2 calculated **6** to substituent properties is not surprising because MP2 calculations describe complexes **6** as purely electrostatic.

IV. Conclusions

Theoretical study of the reductive cleavage of para-substituted benzyl chlorides 4-Y−$C_6H_4CH_2Cl$ and of $C_6F_5CH_2Cl$ show that, in contrast to the MP2 calculations, DFT calculations reveal the formation of radical anions from benzyl chlorides including those bearing donor substituents. The calculations also demonstrate the possibility of the formation of complexes of benzyl radicals with the chloride anion along the path of the reductive cleavage.

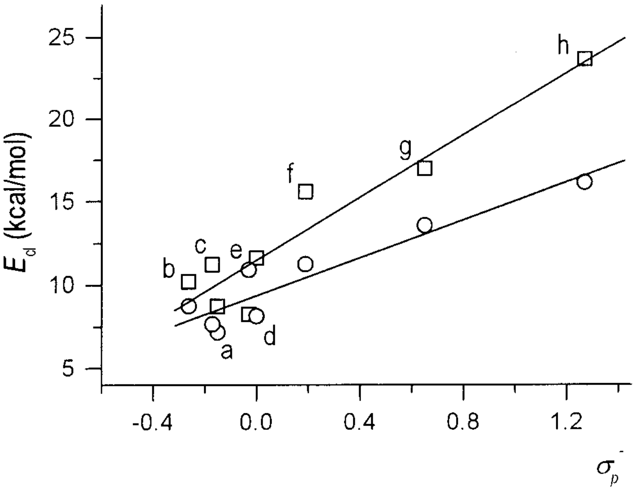


Figure 7. Correlations of the energies E_{cl} ((□) BLYP, $r = 0.947$, $\rho = 9.4$; (○) MP2, $r = 0.936$, $\rho = 5.6$) of the cleavage of the complexes **6a**−**h** into the corresponding benzyl radical and chloride anion with the σ_p^- Hammett constants of Y.

The results show that the actual picture of the reductive cleavage of benzyl and alkyl halides is likely to be more complex than that considered so far.[1−4,43] According to our calculations and the literature data, this process appears to include the formation of complexes of benzyl[6a,40,41] or alkyl[44] radicals with halide anions. The formation of such complexes can occur even along the pathway of the so-called dissociative ET. Our results show that the description of the dissociative ET must be revised to involve the formation of complexes of benzyl or alkyl radicals with halide anions, which may be more significant than the diffusion of radicals and anions from the solvent cage.[43]

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