Quantum Chemical Calculations on α-Substituted Ethyl Cations: A Comparison between B3LYP and Post-HF Methods

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Alkyl cations of the form $CH_3C(+)HR$ have been investigated using high-level quantum chemical methods to study the influence of α-substituents R (R = H, CH_3, $CH{=}CH_2$, $C{\equiv}CH$, F, and Cl) on cation geometries and relative energies with respect to the neutral precursors CH_3CH_2R. The results of density-functional B3LYP computations with a variety of basis sets were compared with MP2, MP4, QCISD(T), and CBS-Q model chemistry results and benchmarked against experimental data. The results show that geometrical features are already accurately described using B3LYP/6-311G(d,p) or MP2/6-311G(d,p). For a systematic study of the energetics of α-substitution on alkyl cations, B3LYP/6-311+G(d,p) and MP2/6-311+G(d,p) computations form a useful compromise between accuracy (average deviation within 1 kcal/mol of the experimental error) and computational efficiency. The electronic structures of these species and their precursors CH_3CH_2R were studied using both natural bond orbital (NBO) and Atoms-in-molecules (AIM) analyses. These analyses clearly show that the electron-donating power of α-substituents at (partially) positively charged carbon atoms does not correlate well with the thermochemical stabilization of cations provided by such substituents.

Introduction

The effects of substituents on the stability of reactive carbocations have been a classical topic in the field of physical organic chemistry,[1] leading to the definition of, e.g., the Hammett σ scales and derivatives thereof.[2] In light of this it is remarkable that systematic studies of these effects have largely been concentrated at the study of remote substituent effects and that less experimental studies have been performed on the effects of substituents bonded directly to the formally positively charged carbon atom. Some efforts have been made to define an α-substituent parameter for carbocations (γ^+) with limited success.[3] Given the ubiquity of intermediates with the general structure HC(+)R′R″, we became interested in these effects, especially since the formation of highly destabilized carbocations has recently become a field of significant interest. Both thermally[4] and photochemically[5] it has been shown to be feasible to produce carbocations with (highly) electronegative α-substituents, such as R = Cl, CN, CO_2CH_3, CHO, and even F and CF_3,[6] and such intermediates have found application in a wide variety of syntheses in the fields of organic and medicinal chemistry.[7] Quantitatively accurate estimates of the stability of these intermediates are therefore of importance for the further development of this field. There have been a number of theoretical studies performed on selected α-substituted carbocations,[8] but thus far there has not been a systematic study that provides such accurate estimates.

The effect of various α-substituents R on the stability of cations 1 (relative to X^- transfer) is given by the isodesmic reaction[9] in eq 1. In a preliminary theoretical study,[8d] the

$$H_3CCHRX + H_3CC(+)H_2 \xrightarrow{\Delta H} \underset{\mathbf{1}}{H_3CC(+)HR} + H_3CCH_2X \tag{1}$$

energetics of eq 1 have been investigated for eight substituents R, ranging from highly electron-donating to strongly electron-withdrawing substituents. A more extensive study did, however, reveal a dependence on the theoretical method used that was larger than required to get close to the experimental error (e.g., differences between MP2/6-31G(d)//HF/6-31G(d) and MP3/6-31G(d)//HF/6-31G(d), up to 6 kcal/mol for R = CH_3, X = H).[8e] Furthermore, the reaction enthalpy is influenced by the nature of X (by geminal stabilization or destabilization of the neutral species with X = F, Cl with respect to the species with X = H) up to 6 kcal/mol (MP3/6-31G(d)//HF/6-31G(d) for R = CH_3, X = F). Such effects play an important role in the solvolysis of α-silyl-substituted[10] and α-methoxy-substituted[11] compounds with various leaving groups, but the modeling of these effects suffered from basis-set truncation at the 6-31G(d) level.[8e] This can be improved by the use of larger basis sets, specifically including diffuse functions. A second improvement that has become available recently via the large increase in computational force is the feasibility of methods with significantly better accounts of electron correlation, such as MP4(SDQ) and QCISD(T). Third, over the past few years, density-functional theory (DFT) has provided theoretical methods which give a very good account of electron correlation at a computational cost that is even lower than MP2. For the case of

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isodesmic reactions such as eq 1, it has been reported that B3LYP computations with 6-31G(d) and 6-311+G(d) basis sets yield satisfactory results for the heats of reaction for a selection of alkyl cations.[12] Finally, the recently developed model chemistries using complete basis set extrapolations have provided composite computational methods which yield root-mean-square (rms) errors for a wide range of compounds on the order of 1 kcal/mol. Specifically, the CBS-Q method[13] yielded energetics with rms deviations from experiment of 1.1 kcal/mol for a set containing 166 molecules, radicals, anions, and cations.[14]

$$H_3CCH_2R + H_3CC(+)H_2 \xrightarrow{\Delta H} \underset{\mathbf{1}}{H_3CC(+)HR} + H_3CCH_3 \quad (2)$$

$$R = CH_3, CH{=}CH_2, C{\equiv}CH, F, \text{and } Cl$$

In this study we evaluate the possibility of studying the influence of α-substituents on the stability of alkyl cations using the isodesmic reaction of eq 2 by density-functional B3LYP, post-HF [MP2, MP4, and QCISD(T)], and CBS-Q computations. Since we are interested in both the energetic and electronic effects of a wide range of substituents on both alkylic and vinylic cations,[15] accurate benchmarking against the available experimental data is essential. Therefore, in the current paper, a start is made by investigation of various theoretical levels to determine whether accuracy and efficiency can be combined. To this aim, calculations for all ethyl cations $CH_3C(+)HR$ for which experimental data are currently available ($R = H$, CH_3, $CH{=}CH_2$, $C{\equiv}CH$, F, and Cl) were performed. All these compounds have been the subject of prior quantum chemical studies at various levels of theory.[8,14,16] There has been, however, no systematic analysis of the effect of basis-set size and specific electronic structure methods including DFT on the stability and electronic structures of a range of α-substituted cations. In this study, B3LYP computations with a variety of basis sets have been performed (ranging from 6-31G(d) to 6-311++G(3df,3pd)), which are compared with MP2, MP4, and QCISD(T) computations (with 6-31G(d), 6-311G(d,p), and 6-311+G(d,p) basis sets) and CBS-Q model chemistry results. The energies obtained using all these methods are subsequently benchmarked against experimental data. To monitor the electronic structure of the species under study, specifically any resonance effects that the α-substituents display, the electron distribution in the neutral and cationic species was computed using natural bond orbital (NBO) analysis[17] at all methods used in this study, except for the QCISD(T) method. Also, Atoms-in-molecules (AIM) analysis[18] was performed for all those substituents and methods for which this was feasible.[19]

Computational Methods

All computations were performed with the Gaussian 94 (revisions D and E) suite of programs.[20] NBO computations were performed with the NBO 3.1 program[21] implemented in Gaussian 94. AIM[18] calculations were performed as implemented in Gaussian 94. Also, Mulliken charges[22] were calculated, but since their basis set dependence was shown to be substantially larger than the substituent effects of interest, these data are not discussed and are only given in the Supporting Information. Calculations on the compounds under study were performed using the B3LYP (Becke's three parameter nonlocal exchange hybrid functional[23] with the nonlocal correlation functional of Lee et al.[24]) method, Møller–Plesset second, and fourth-order perturbation theory, QCISD(T), and the CBS-Q model chemistry method.[13] All MPn ($n = 2, 4$) calculations take the correlation effects of all electrons into account, while for the QCISD(T) calculations, a frozen core was used. To obtain electronic data for the MP4 calculations, only single, double, and quadruple substitutions (MP4(SDQ)) were considered.

The geometries of all compounds under study were fully optimized. Optimizations of ethyl cation were started from a bridged (nonclassical) structure. All optimized structures were shown to be minima on the potential-energy surface via vibrational frequency computations. For the CBS-Q calculation of ethyl cation, the optimization and zero-point energy correction were performed at the MP2(FC)/6-31G(d′,p′) level instead of at the default levels of optimization at the MP2(FC)/6-31G(d′) level and zero-point energy correction[25] at the HF/6-31G(d′) level. This was necessary because inclusion of polarization functions and electron correlation are required for a proper description of the bridged ethyl cation.[26] Selected geometrical features of the species under study are discussed in the text, while all optimized geometries at all computational levels used are available as Supporting Information. All single-point computations were performed using the SCF = tight option in Gaussian 94.

Results and Discussion

Geometries. Full optimizations were performed for five cations of the form $CH_3C(+)HR$ with $R = H$, CH_3, $CH{=}CH_2$, $C{\equiv}CH$, F, and Cl and their corresponding neutral precursors (CH_3CH_2R) with B3LYP and MP2 computations using the 6-31G(d), 6-311G(d,p) and 6-311+G(d,p) basis sets. Typical geometrical features for these compounds are given in Figure 1, which depicts the results of B3LYP/6-311G(d,p) and MP2/6-311G(d,p) optimizations. These data display the characteristic differences between the two methods, while the basis-set dependence will be discussed later (vide infra).

The hybridization of the carbocationic center is sp^2 for all cations, except for ethyl cation (Figure 1). Consequently, the C–C bond length is shorter in the cations than in the corresponding neutral species (C_{sp^3}–C_{sp^3} bonds are generally longer than C_{sp^3}–C_{sp^2} bonds).[27] This effect ranges from 0.075 to 0.102 Å for B3LYP/6-311G(d,p) and from 0.068 to 0.099 Å for MP2/6-311G(d,p), while the C_α^+–H bond lengths are close to the C_α–H bond lengths in the corresponding neutrals. An increase in the C–H bond lengths at the C_β atom is found for hydrogen atoms that have orbital overlap with the carbocationic center, due to hyperconjugative effects (vide infra). This elongation of the C_β–H bond lengths is most pronounced for $R = CH_3$ (0.023 and 0.027 Å for B3LYP and MP2, respectively); for the other cations, elongations of 0.010 Å (±0.003 Å with variation of basis set or method) were observed for both B3LYP and MP2. For all substituents other than R = H, a decrease of the C–R bond length is found with both methods, which follows the order $Cl > F > CH{=}CH_2 \approx C{\equiv}CH \approx CH_3$ (r[C–Cl] is reduced most). In the case of ethyl cation, a symmetrically bridged structure is found to be the minimum on the potential-energy surface, in accordance with previous studies.[16] The corresponding decrease of the C–C bond length is 0.150 and 0.141 Å for the B3LYP and MP2 method, respectively, while the C–H bond length for the bridging hydrogen is substantially increased.

Comparison of the geometries optimized with B3LYP and MP2 using the 6-311G(d,p) basis set displays a strong similarity between the results of these two methods. This is shown most clearly in an indirect way via computation of B3LYP energies at MP2 optimized geometries. For instance, the calculated reaction enthalpy for $R = CH_3$ using B3LYP/6-311G(d,p)//MP2/6-311G(d,p) differs only 0.11 kcal/mol from the B3LYP/6-

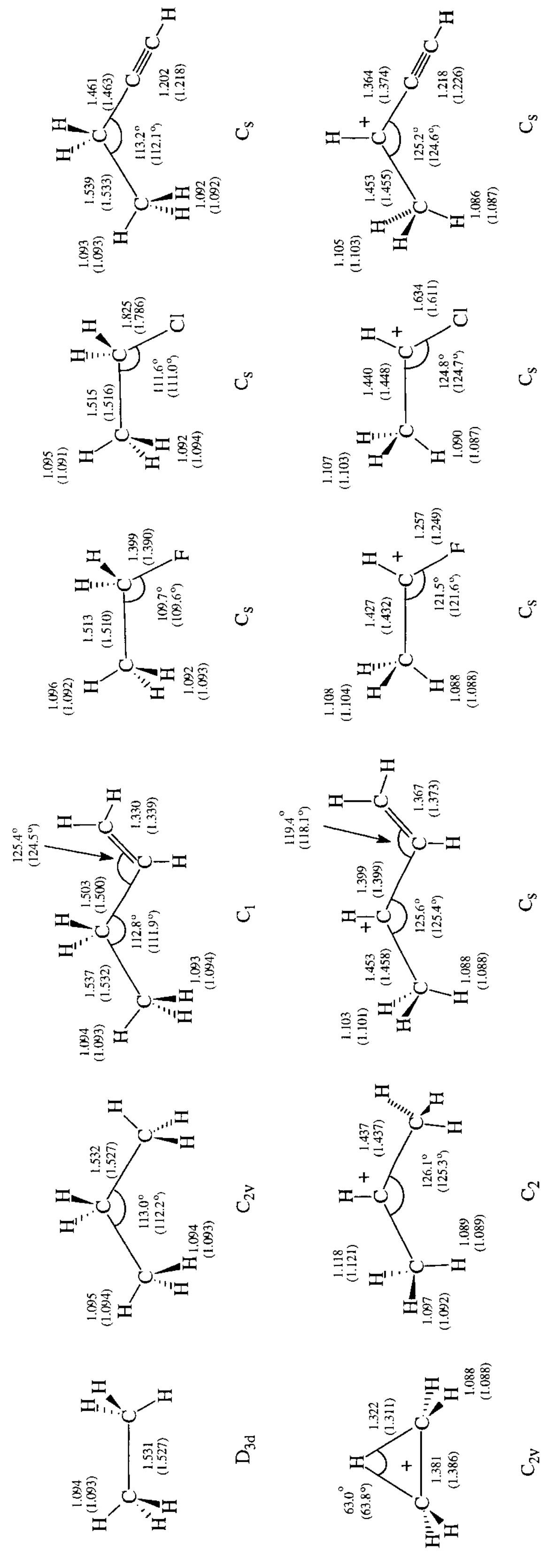

Figure 1. Selected geometrical features of the neutral species and cations under study calculated at the B3LYP and MP2/6-311G(d,p) (in parentheses) level.

311G(d,p)// B3LYP/6-311G(d,p) calculated value (the reaction enthalpies of eq 2 are 23.26 and 23.37 kcal/mol, respectively). Also, for 2-propyl cation, a C_2-structure was found to be the lowest energy conformation with both B3LYP and MP2; the C_{2v} structure was calculated to be 0.11 and 0.73 kcal/mol higher in energy, respectively, in line with recent calculations by Koch et al.[8c] Some small systematic differences are nevertheless observable. For R = F and Cl, B3LYP computations systematically predict slightly larger C−halogen bond lengths than MP2 computations with the same basis set. This difference is larger for α-Cl (Δr = 0.039 and 0.023 Å for ethyl chloride and ethyl chloride cation, respectively) than for α-F (Δr = 0.009 and 0.008 Å for ethyl fluoride and ethyl fluoride cation, respectively). Bond lengths in the C−C≡CH moiety also show some slight variation with the method of calculation. B3LYP/6-311G(d,p) calculations predict the C−C bond to be 0.010 Å shorter for the cation and the C≡C bond length to be 0.016 and 0.008 Å longer for the neutral compound and the cation, respectively, than the corresponding bond lengths optimized with MP2/6-311G(d,p). All other bond lengths show only insignificant differences between B3LYP/6-311G(d,p) and MP2/6-311G(d,p) calculations (<0.002 Å). Small differences also occur for some of the C−C−R bond angles, which are generally calculated with B3LYP to be slightly larger than at the corresponding MP2 level. All these differences in geometry correspond, however, to only small energy differences between B3LYP and MP2, as seen from the comparison of MP2/6-311G(d,p)//B3LYP/6-311G(d,p) versus MP2/6-311G(d,p)//MP2/6-311G(d,p): computations of ethyl chloride, which displays the largest method dependence in its C−R bond length, yield a difference in total energy of only 0.33 kcal/mol between the two.

With the 6-311G(d,p) basis set, differences between B3LYP and MP2 optimized geometries are therefore generally small. However, both display quite significant basis-set variations in the C−C and C−halogen bond lengths themselves: B3LYP/6-31G(d) optimizations predict larger C−C and C−halogen bond lengths than the corresponding calculation using the 6-311G(d,p) basis set, while in contrast, basis-set truncation to 6-31G(d) in MP2 optimizations yields slightly smaller C−C and C−halogen bond lengths for all compounds including ethyl cation (see Supporting Information). The size of this effect is small for both methods (no deviations larger than 0.010 Å), but since the directions are opposite, the difference between B3LYP and MP2 increases. The C−H bond lengths and C−C−R bond angles in both neutral and charged species are not affected significantly by a decrease, to 6-31G(d), or increase, to 6-311+G(d,p), of the basis set used.

Geometry optimizations using the 6-311+G(d,p) basis set yield essentially the same geometries as the 6-311G(d,p) optimizations for both methods, except for ethyl fluoride (not for the α-F substituted cation). Deviations in geometry between the two basis sets are in all cases smaller than or equal to 0.001 Å or 0.1°, except for ethyl fluoride: inclusion of diffuse functions with B3LYP and MP2 yields an elongation of the C−F bond length of 0.007 Å for both methods.[28] Single-point B3LYP/6-311+G(d,p)//B3LYP/6-311G(d,p) computations, however, yield total energies for both ethyl fluoride and ethyl fluoride cation, which are within 0.04 kcal/mol of the total energies obtained by geometry optimization at the B3LYP/6-311+G(d,p) level.

In short: optimization with B3LYP/6-311G(d,p) yields geometries for the species under study that are very close to

TABLE 1. −Δ*H* (kcal/mol) for the Isodesmic Reaction in Eq 2 Using Different Basis Sets for Substituents CH_3, $CH{=}CH_2$, $C{\equiv}CH$, F, and Cl Compared to Experimental Data

		CH_3	$CH{=}CH_2$	$C{\equiv}CH$	F	Cl
(1)	experimental[a]	21.2 ± 2.7	30.5 ± 2.4	18.6[b]	7.1 ± 2.1	10.8 ± 1.3
(2)	B3LYP/6-31G(d)	24.53	40.54	26.56	13.42	11.43
(3)	B3LYP/6-311G(d,p)	23.37	37.62	23.31	9.98	9.63
(4)	B3LYP/6-311+G(d,p)	23.37	37.29	22.58	7.12	10.64
(5)	B3LYP/6-311++G(d,p)[c]	23.39	37.29	22.58	7.13	10.62
(6)	B3LYP/6-311++G(3df,3pd)[c]	23.24	36.67	22.32	8.18	11.69
(7)	MP2/6-31G(d)	19.12	35.34	18.02	9.83	9.71
(8)	MP2/6-311G(d,p)	17.03	31.63	15.05	9.24	9.09
(9)	MP2/6-311+G(d,p)	17.07	30.91	14.42	6.01	9.66
(10)	MP4(SDQ)/6-311+G(d,p)[d]	17.94	27.17	15.83	6.20	10.28
(11)	QCISD(T)/6-311+G(d,p)[d]	17.09	27.88	16.95	6.35	10.89
(12)	CBS-Q	18.63	31.98	16.94	7.02	10.14

[a] The experimental reaction enthalpies are average numbers based on experimentally determined heats of formation for the species under study,[33] with full account of the reported experimental uncertainties (reported standard deviations are σ_{n-1} values). [b] For the alkynyl-substituted cation, only one experimental heat of formation, without specified experimental error, has been reported. [c] Single-point calculation on the B3LYP/6-311+G(d,p) optimized geometry. [d] Single point calculation on the MP2/6-311+G(d,p) optimized geometry.

those obtained via MP2/6-311G(d,p) optimizations, while further expansion of the basis set has little effect on the optimized geometries.

Thermodynamics. Geometry optimizations were performed using the B3LYP and MP2 methods with the 6-31G(d), 6-311G(d,p), and 6-311+G(d,p) basis sets. B3LYP single-point calculations with 6-311++G(d,p) and 6-311++G(3df,3pd) basis sets were performed using the B3LYP/6-311+G(d,p) optimized geometries, and MP4(SDQ)/6-311+G(d,p) and QCISD(T)/6-311+G(d,p) single-point calculations were performed using the MP2/6-311+G(d,p) optimized geometries. Besides the B3LYP and post-HF calculations, CBS-Q model chemistry calculations were also performed. The total energies, corrected with a scaled zero-point energy calculated at the level of geometry optimization,[29] were used to calculate the reaction enthalpies of eq 2 (Table 1). Comparison of the calculated reaction enthalpies with the experimental ones displays, in general, a good to very good agreement between them, including the order of stabilization: $CH{=}CH_2 > CH_3 > C{\equiv}CH > Cl > F$. Except for the B3LYP data with the smallest basis set used [6-31G(d)], all deviations from the experimental data are within 5 kcal/mol for $R = CH_3$, $C{\equiv}CH$, F, and Cl, while for $R = CH{=}CH_2$ the errors are up to 7 kcal/mol; many of the errors are, however, substantially smaller than these maxima. This is a significant improvement over previously studied methods[8d,e] and suggests that currently available computational methods can yield the accuracy needed to describe the thermodynamics of the isodesmic reaction of eq 2. The strengths and weaknesses of the various methods appear in more detail in the separate discussion of the results for the five substituents.

The α-methyl group is with all methods computed to be a strongly stabilizing substituent at carbocationic centers and stabilizes the cation 17−25 kcal/mol more than an α-hydrogen atom. The B3LYP calculations do, all but one, predict this stabilizing effect within experimental error: the computed reaction enthalpies are 2.0−3.3 kcal/mol higher than the experimentally determined reaction enthalpy, depending on the basis set used. The largest deviation from the experimental value is found for the 6-31G(d) basis set, but this deviation decreases to within the experimental uncertainty upon going to 6-311G (d,p). Further expansion of this triple-ξ basis set with more d polarization functions, f polarization functions, or diffuse functions barely affects the reaction enthalpy. The post-HF methods, on the other hand, underestimate the stabilization by 2.1−4.1 kcal/mol. With MP2 computations, an increase of the basis set from 6-31G(d) to 6-311G(d,p) yields an *increase* of the deviation to 4.2 kcal/mol, which is just outside the experimental error. This does not systematically improve on inclusion of diffuse functions in the basis set, inclusion of Møller−Plessett corrections to the fourth order, or taking the correlation effects into account with the QCISD(T) method. It requires the CBS-Q model chemistry to get back within experimental error. As the data for all methods in Table 1 do already account for differences in zero-point energies, this shows the importance of basis-set saturation and the empirical corrections in the CBS-Q method.

For α-$CH{=}CH_2$, the stabilization is overestimated (and outside the experimental uncertainty) with B3LYP by 6.2−10.0 kcal/mol. The largest deviation is again found for the 6-31G(d) basis set, and enlargement to a 6-311G basis with added polarization and diffuse functions yields a systematic drop in the deviation. With this substituent, the deviation for B3LYP is larger than that found for the post-HF methods, especially for the MP2/6-311G(d,p) and MP2/6-311+G(d,p) entries, which agree with the experimentally derived data (see Table 1, entries 8 and 9). As in the case of $R = CH_3$, the 6-31G(d) basis appears to be too small for quantitative agreement with experiment. The error is 4.8 kcal/mol for MP2/6-31G(d), which improves to 1.1 kcal/mol, and within experimental uncertainty, for MP2/6-311G (d,p). The effect of a larger basis set (6-311G(d,p) compared to 6-31G(d)) changes the reaction enthalpy with 2.9 kcal/mol for B3LYP and 3.7 kcal/mol for MP2 calculations. The computed reaction enthalpy suggests a smaller stabilization in both cases, which is closer to the experimental value. Further expansion of the basis set by inclusion of extra polarization or diffuse functions yields a small improvement for both methods (up to 0.9 kcal/mol) but still does not bring the B3LYP data within the limits of experimental uncertainty. This contrasts with the data of MP2 computations with at least a triple-ζ quality basis set and with the CBS-Q data, all of which agree with the experimental data within experimental error.

Calculations on the α-$C{\equiv}CH$ substituent show that the computed stabilization varies between 14 and 27 kcal/mol depending on the method and basis set used. The B3LYP calculations, like for $R = CH_3$ and $CH{=}CH_2$, predict reaction enthalpies that are higher than the experimental one by 3.7−8.0 kcal/mol. The largest deviation is found for the smallest basis set, and the difference between the calculated and experimentally found value decreases with increasing basis set. Increasing the size of the basis set from double to triple ξ decreases the stabilization energy by 3.3 kcal/mol. Inclusion of a set of diffuse functions yields another 0.7 kcal/mol. Further expansion of the basis set has only a minor effect. The post-HF calculations differ less from the experimentally derived reaction enthalpy than the B3LYP calculations (from 0.6 to 4.2 kcal/mol). The largest difference is with MP2, in this case found for the 6-311+G(d,p) basis set, while both the 6-31G(d) and the 6-311G(d,p) basis sets predict values closer to the experimental value (deviations of 0.6 and 3.7 kcal/mol, respectively). In fact, by an apparent cancellation of errors, the best data are obtained with the smallest basis set used: MP2/6-31G(d). Our MP4 and QCISD(T) calculations also predict values that are closer to the experimental reaction enthalpy (deviations of 2.8 and 1.6 kcal/mol, respectively) than MP2/6-311+G(d,p). The QCISD(T) and CBS-Q calculations are in excellent agreement with the experimental value, the deviation being 1.6 and 1.7 kcal/mol, respectively. It is not possible to obtain an experimental uncertainty in the case of R = C≡CH, since to the best of our knowledge no experimental error for the heat of formation of this cation has been reported. Assuming that the experimental uncertainty will be of the same order as for the other substituents under study (2−3 kcal/mol), the results of the MP2/6-31G(d), QCISD(T)/6-311+G(d,p)//MP2/6-311+G(d,p), and CBS-Q computations will be within the margins of experimental error.

The reaction enthalpies for the isodesmic reaction for R = CH_3, CH═CH_2, and C≡CH show that these substituents are strongly electron-donating groups, as might have been expected for R = CH_3 and CH═CH_2 based on their negative σ values ($\sigma_p^+ = -0.31$ and -0.16, respectively).[2] In contrast, for R = C≡CH, an electron-withdrawing effect and hence destabilization of the cation would have been expected if the σ_p^+ value (+0.18 for C≡CH) had been a good indicator for stabilization by this α-substituent. Also, for R = Cl, a positive σ_p^+ value is reported (0.11), while for R = F, a small stabilizing effect would have been predicted ($\sigma_p^+ = -0.07$). Despite the differences in the sign of σ_p^+, the reaction enthalpies in Table 1 for α-F and α-Cl are also negative, irrespective of the theoretical method used. This means that both α-F and α-Cl are *stabilizing* substituents when directly attached to a carbocationic center. Therefore, σ_p^+ is apparently a poor stabilization indicator for α-substituents.

The computed degree of stabilization of the cation by the halogen substituents again depends on the basis set used. The 6-31G(d) and 6-311G(d,p) basis sets predict α-F to be more stabilizing than α-Cl, but upon further increase of the basis set, this order changes and the chloro substituent becomes the more stabilizing one. The effects of the addition of diffuse functions (comparison between 6-311G(d,p) and 6-311+G(d,p) basis sets) are rather small for R = Cl (0.6−1.0 kcal/mol, B3LYP and MP2 data), but for R = F, the stabilizing effect decreases by 3 kcal/mol both for the B3LYP and post-HF methods upon inclusion of diffuse functions and becomes more in line with the experimental value. The contrast between this effect for α-Cl and α-F shows the need for a detailed description of the lone pairs in these halogen atoms: electron−electron repulsion within the set of lone pairs is expected to be larger for F than for Cl, due to the smaller size of F atoms, and also larger for the neutral α-F species than for the α-F cation, due to the delocalization of the positive charge in the cation (vide infra under Charges). This is indeed observed (see Supporting Information): the decrease in total energy (B3LYP data) for ethyl fluoride in going from 6-311G(d,p) to 6-311+G(d,p) is significantly larger (7.43 mHartree) than for the α-F or α-Cl cations and for ethyl chloride (2.38, 2.13, and 1.18 mHartree, respectively). This explains the relatively large effect of diffuse functions on the reaction enthalpy of eq 2 for R = F (Table 1). The CBS-Q computed reaction enthalpies show very small deviations from the experimentally derived reaction enthalpies for both substituents (0.1 and 0.7 kcal/mol for R = F and Cl, respectively).

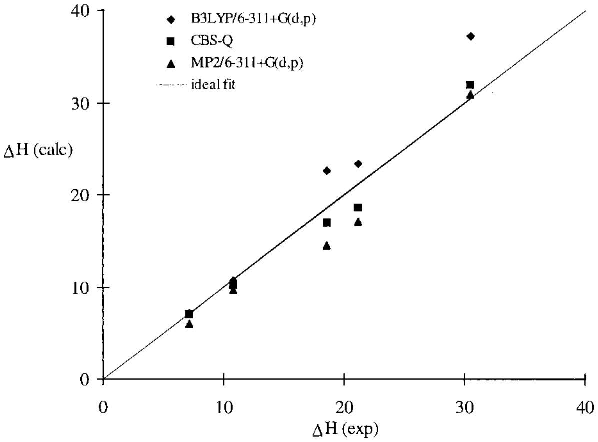

Figure 2. Reaction enthalpies calculated (kcal/mol) at the B3LYP, MP2/6-311+G(d,p), and CBS-Q levels compared to the experimental values.

From this analysis it follows that basis sets containing diffuse functions [6-311+G(d,p)] are necessary to reproduce the correct order of stabilization for the cations under study, regardless of the method used. A further increase of the basis set using B3LYP or methodological improvements by going from MP2 to MP4(SDQ) or QCISD(T) show no significant improvement.

An overall comparison of the reaction enthalpies computed using B3LYP/6-311+G(d,p), MP2/6-311+G(d,p) and CBS-Q with the experimental reaction enthalpies is shown in Figure 2. The deviations from the experimental reaction enthalpies are about equal for the B3LYP data (average deviation is 2.6 kcal/mol) and the MP2 data (average deviation is 2.2 kcal/mol). The CBS-Q derived reaction enthalpies show a somewhat smaller deviation of 1.3 kcal/mol. Given the general experimental uncertainty of 2−3 kcal/mol, agreement with experiment is on average very good. More significant differences are observable in the maximum deviations, which decrease going from B3LYP (6.8 kcal/mol) via MP2 (4.2 kcal/mol) to CBS-Q (2.6 kcal/mol). In fact, the CBS-Q calculated reaction enthalpies agree with the experimental data for all five α-substituents under study within experimental error. Given this high reliability, CBS-Q seems rather useful for calibration of lower level calculations for this type of systems in case no experimental results are available.

Charges. In Tables 2−4 the increases in the charges at the substituents R and at the substituted carbon atom C_α between neutral species and cation are reported. In Tables 2 and 3 the NBO-calculated charge increases are given for all methods and basis sets, except for the QCISD(T) and CBS-Q methods, with which is it not possible to calculate such electronic properties within Gaussian 94. In Table 4, the AIM-calculated charge increases are given both for the substituents R and the substituted carbon atoms C_α for a subset of methods and basis sets.[19]

Apart from NBO and AIM, Mulliken population analysis was also performed. These charges do, however, display a large basis-set dependence. For instance, the charge on α-CH═CH_2 varies between 0.526 (B3LYP/6-311+G(d,p) value) and 0.150 (B3LYP/6-311++G(3df,3pd) value) with variation between two basis sets that are energetically close to the level of basis-set saturation (Table 1, column 2, entries 4 and 6). As a second example, for α-CH_3, the inclusion of diffuse functions, in going from MP2/6-311G(d,p) to MP2/6-311+G(d,p) changes the Mulliken group charge for R from 0.303 to 0.622! This large dependence on the basis set makes Mulliken charges unsuitable

TABLE 2. Increase in NBO-Calculated Charge at the Substituent R between Neutral Species and Alkyl Cation

		H	CH_3	$CH{=}CH_2$	$C\equiv CH$	F	Cl
(1)	B3LYP/6-31G(d)	0.086	0.200	0.399	0.363	0.209	0.483
(2)	B3LYP/6-311G(d,p)	0.076	0.196	0.388	0.350	0.224	0.476
(3)	B3LYP/6-311+G(d,p)	0.078	0.192	0.385	0.347	0.229	0.474
(4)	B3LYP/6-311++G(d,p)[a]	0.077	0.186	0.385	0.347	0.230	0.474
(5)	B3LYP/6-311++G(3df,3pd)[a]	0.076	0.182	0.382	0.348	0.225	0.474
(6)	MP2/6-31G(d)	0.083	0.184	0.404	0.336	0.218	0.496
(7)	MP2/6-311G(d,p)	0.076	0.183	0.399	0.325	0.236	0.486
(8)	MP2/6-311+G(d,p)	0.078	0.176	0.394	0.322	0.235	0.483
(9)	MP4(SDQ)/6-311+G(d,p)[b]	0.081	0.162	0.368	0.324	0.230	0.474

a Single point calculation using the B3LYP/6-311+G(d,p) optimized geometry. *b* Single point calculation using the MP2/6-311+G(d,p) optimized geometry.

TABLE 3. Increases in NBO-Calculated Charge at the Substituted Carbon Atom (C_α)

		H	CH_3	$CH{=}CH_2$	$C\equiv CH$	F	Cl
(1)	B3LYP/6-31G(d)	0.224	0.601	0.444	0.483	0582	0.330
(2)	B3LYP/6-311G(d,p)	0.245	0.608	0.452	0.482	0.567	0.339
(3)	B3LYP/6-311+G(d,p)	0.240	0.616	0.472	0.492	0.568	0.347
(4)	B3LYP/6-311++G(d,p)[a]	0.243	0.628	0.475	0.494	0.570	0.352
(5)	B3LYP/6-311++G(3df,3pd)[a]	0.243	0.634	0.486	0.495	0.578	0.352
(6)	MP2/6-31G(d)	0.212	0.630	0.465	0.521	0.600	0.339
(7)	MP2/6-311G(d,p)	0.248	0.633	0.479	0.532	0.590	0.354
(8)	MP2/6-311+G(d,p)	0.242	0.647	0.492	0.542	0.591	0.364
(9)	MP4(SDQ)/6-311+G(d,p)[b]	0.248	0.676	0.525	0.545	0.600	0.388

[a] Single-point calculation using the B3LYP/6-311+G(d,p) optimized geometry. [b] Single-point calculation using the MP2/6-311+G(d,p) optimized geometry.

TABLE 4. Increase in AIM-Calculated Charges at Substituent R and Carbon Atom C_α

		R				C_α			
		CH_3	$CH{=}CH_2$	$C\equiv CH$	Cl	CH_3	$CH{=}CH_2$	$C\equiv CH$	Cl
(1)	B3LYP/6-31G(d)	0.414	0.560	0.502	0.449	0.172	0.108	0.146	0.271
(2)	B3LYP/6-311G(d,p)	0.404	0.550	0.488	0.448	0.193	0.116	0.164	0.256
(3)	MP2/6-311G(d,p)	0.403	0.555	0.482	0.442	0.194	0.130	0.176	0.188

for studying substituent effects. On the other hand, NBO charges are only slightly affected by basis-set variations and are consequently better suited to analyze the electronic properties of the compounds under study.[30]

All entries in Tables 2−4 yield positive values, indicating that the positive charge is substantially delocalized onto the substituent R (Tables 2 and 4) and not only increases at the formally charged carbon atom (Tables 3 and 4). In ethyl cation (R = H), the charge development occurs largely at the bridging (β) hydrogen atom, which makes the increase at C_α and R relatively small, irrespective of the computational method and basis set size used: some difference is found between the 6-31G (d) and 6-311G(d,p) basis sets both for the B3LYP and MP2 methods: 0.021 and 0.036 electron at R, respectively. Further expansion of the basis set (B3LYP data; Tables 2 and 3, entries 3−5) or improved account of electron correlation (MP4(SDQ) data; Tables 2 and 3, entry 9) has little effect.

For the α-CH_3 substituent, most of the charge increase is found at C_α. With B3LYP, a small but distinct basis set effect is found, as expansion of the basis set systematically increases the charge on the cationic center (from 0.601 to 0.634; Table 3, entries 1−5) and decreases the charge on the methyl groups (from 0.200 to 0.182; Table 2, entries 1−5). This effect is also found for the post-HF methods with improvement of either basis set or theoretical method (from 0.630 to 0.676; Table 3, entries 6−9). The α-$CH{=}CH_2$ and α-$C\equiv CH$ substituents are also capable of stabilizing the cation by charge delocalization, as is indeed calculated via NBO calculations: the positive charge is almost entirely delocalized over the unsaturated moiety ($C^+{-}CH{=}CH_2$ and $C^+{-}C\equiv CH$) of the substituents. For α-$C\equiv CH$, this increase of positive charge on R is computed to be smaller than for α-$CH{=}CH_2$ by 0.036 (±0.003 with variation of basis set or method) and 0.065 (±0.021) as obtained from B3LYP and post-HF calculations, respectively. As in the case of the α-CH_3 substituent, the delocalization onto R diminishes with increasing basis-set size and yields a larger charge on the substituted carbon atom (Tables 2 and 3, columns 3 and 4). The increase on the substituted carbon is, however, larger than the decrease observed for the α-$CH{=}CH_2$ substituent, in contrast to the increases for α-$C\equiv CH$, where the increase on C_α is of the same magnitude as the decrease on R. This implies that basis-set expansion for α-$CH{=}CH_2$ not only decreases the charge delocalization onto the substituent but also decreases the charge delocalization onto the methyl group in this cation.

For R = F, the B3LYP-computed increases of charge at the substituent R and at C_α are of the same order as is found for R = CH_3. The delocalization of positive charge is thus practically the same for the α-fluorine and α-methyl substituent! This is also computed with all post-HF methods of a sufficient theoretical level and basis set size (higher than MP2/6-31G(d)). The absolute value of the NBO charge on F in the neutral species is −0.40 (±0.01), while it is −0.17 (±0.02) in 1-fluoroethyl cation. The charge increase is even larger in the case of the α-Cl substituent, which loses 0.48 (±0.02) electrons upon H^- transfer and obtains a charge of 0.40 (±0.02). This charge delocalization is accompanied by significant strengthening of the C−Cl bond, which is observable via significant increases in the bond orders (vide infra).

The NBO charge increases calculated with B3LYP and the post-HF methods show a good agreement with each other and generally display only a marginal basis-set dependence (no differences >0.03 were calculated). Regardless of which method

TABLE 5. Increase in NBO-Calculated Bond Order between the Neutral Compounds and the Corresponding Cations

		$C_\alpha-R$[a]						$C_\beta-C_\alpha$[a]					
		H	CH_3	$CH=CH_2$	$C\equiv CH$	F	Cl	H	CH_3	$CH=CH_2$	$C\equiv CH$	F	Cl
(1)	B3LYP/6-31G(d)	−0.05	0.20	0.37	0.36	0.37	0.60	0.50	0.20	0.15	0.17	0.20	0.17
(2)	B3LYP/6-311G(d,p)	−0.04	0.21	0.36	0.34	0.38	0.60	0.45	0.21	0.16	0.17	0.21	0.16
(3)	B3LYP/6-311+G(d,p)	−0.05	0.21	0.35	0.34	0.38	0.60	0.46	0.21	0.16	0.17	0.20	0.17
(4)	B3LYP/6-311++G(d,p)[b]	−0.04	0.21	0.36	0.34	0.38	0.60	0.46	0.21	0.16	0.17	0.20	0.17
(5)	B3LYP/6-311++G(3df,3pd)[b]	−0.04	0.21	0.35	0.34	0.37	0.59	0.46	0.21	0.16	0.17	0.19	0.17
(6)	MP2/6-31G(d)	−0.05	0.19	0.35	0.29	0.36	0.60	0.47	0.19	0.13	0.14	0.16	0.14
(7)	MP2/6-311G(d,p)	0.03	0.19	0.35	0.28	0.37	0.61	0.42	0.19	0.13	0.15	0.16	0.14
(8)	MP2/6-311+G(d,p)	−0.03	0.19	0.34	0.28	0.37	0.61	0.42	0.19	0.13	0.15	0.16	0.14
(9)	MP4(SDQ)/6-311+G(d,p)[c]	−0.03	0.16	0.33	0.29	0.34	0.57	0.41	0.16	0.13	0.13	0.14	0.12

[a] Negative values indicate that the $C_\alpha-R$ or $C_\beta-C_\alpha$ bond is weaker in the cation than in the corresponding neutral species. [b] Single-point calculation using the B3LYP/6-311+G(d,p) optimized geometry. [c] Single-point calculation using the MP2/6-311+G(d,p) optimized geometry.

TABLE 6. Increase in AIM-Calculated Bond Orders for the $C_\alpha-R$ and $C_\beta-C_\alpha$ Bonds

		$C_\alpha-R$				$C_\beta-C_\alpha$			
		CH_3	$CH=CH_2$	$C\equiv CH$	Cl	CH_3	$CH=CH_2$	$C\equiv CH$	Cl
(1)	B3LYP/6-31G(d)	0.20	0.36	0.37	0.58	0.20	0.14	0.15	0.18
(2)	B3LYP/6-311G(d,p)	0.21	0.35	0.36	0.58	0.21	0.16	0.16	0.18
(3)	MP2/6-311G(d,p)	0.21	0.34	0.29	0.58	0.21	0.13	0.14	0.16

or basis set is used, the order of charge increase on the α-substituent is Cl > $CH=CH_2$ > $C\equiv CH$ > F ≥ CH_3 while the absolute values of the charge on the α-substituents on the cation follows the order $CH=CH_2 \approx Cl > C\equiv CH > CH_3 \gg F$ (see Supporting Information).

Similar studies of the charge development were performed using Bader's topologically based Atoms in molecules (AIM) approach.[18] These AIM charge calculations (Table 4) predict large charge increases on the α-substituents and rather low increases on the substituted carbon atom upon H^- transfer. As for the NBO properties, the AIM charges display only minor effects of the differences in method and basis set used for the α-methyl, α-ethenyl, and α-ethynyl substituents. This is, however, not the case for α-Cl, for which the increase in charge calculated at the MP2/6-311G(d,p) level on the formally charged carbon atom is significantly smaller than for the corresponding B3LYP calculation: 0.188 compared to 0.256 (Table 4, entries 2 and 3).

The radically different approach to depict the charge distribution over the molecule of AIM in comparison with NBO affects conclusions about the effect of an α-substituent on the electronic structure of a cation. Comparison of the AIM charges (Table 4) with the NBO data (Tables 2 and 3) shows that not only the calculated increases differ in magnitude from the NBO-derived charge increases, but also that the order of the charge increase is changed. The calculated order for the AIM charge increases on the α-substituents is $CH=CH_2 > C\equiv CH > Cl > CH_3$ irrespective of theoretical method or basis set (cf. NBO: $Cl > CH=CH_2 > C\equiv CH > CH_3$).[19] Since AIM calculations cannot be performed for all substituents using basis sets with diffuse functions, it is currently not possible to explore the effects of larger basis sets on the AIM charges. Since inclusion of such diffuse functions proved to be necessary to obtain accurate reaction enthalpies, especially for the α-halogen substituents, a basis-set dependence of the AIM-calculated electronic structure cannot be excluded.

Regardless of the method used to calculate electronic properties, the charges on the α-substituent and the substituted carbon atom C_α do not show any quantitative correlation with the stabilizing effect of the substituents. The order of stabilization found for the high-level calculations is $CH=CH_2 > CH_3 > C\equiv CH > Cl > F$, while for all different levels of calculations the increases of the NBO charge on the substituents is $Cl > CH=CH_2 > C\equiv CH > F \geq CH_3$. The limited amount of AIM charges predict the following order: $CH=CH_2 > C\equiv CH > Cl > CH_3$, and this order is also different from the order of stabilization. This implies the necessity of a clear conceptual difference between the use of *stabilizing* and *electron-donating* when speaking about the substituent effects on cations or centers with partial positive charge. Specifically, the α-methyl group is much better in stabilizing a carbocation than an α-fluoro-substituent, but the charge increase at both these substituents is very similar. Analogously, α-Cl is a better electron-donating substituent than α-$CH=CH_2$, but the latter is a thermochemically better stabilizer of such cations.

Bond Orders. The effects of α-substituents on the electronic structure of the cations under study is also well displayed by the difference in bond orders between $C_\alpha-R$ and $C_\beta-C_\alpha$ in the neutral compound and cation. Such data are presented in Tables 5 (NBO bond orders) and 6 (AIM bond orders). The increase in the $C_\alpha-R$ bond order depends significantly on the nature of the substituent R, while the increase in the $C_\beta-C_\alpha$ bond order is almost constant (+0.12 to +0.21 over all substituents, methods, and basis sets; Table 5).[31]

From the data in Table 5, it follows that such increases in the NBO bond order are only marginally affected by the basis-set size within the group of basis sets used. A small but systematic method effect in the increase of the $C_\beta-C_\alpha$ bond order is noticeable: the increase is with all post-HF calculations computed to be about 0.03 smaller than with the B3LYP calculations. The only exception is formed by MP4(SDQ)/6-311+G(d,p) calculations, which predict systematically lower increases in the $C_\beta-C_\alpha$ and $C_\alpha-R$ bond orders than all other methods. Interestingly, this is not as much the case for the α-ethenyl and α-ethynyl substituents as for the other α-substituents, in contrast with the expectation that systems with smaller HOMO−LUMO gaps are affected more by improved accounts of the electron correlation.

The NBO-computed increase in the $C_\alpha-R$ bond order (Table 5) depends strongly on the substituent R and follows the order: $Cl > F \approx CH=CH_2 \geq C\equiv CH > CH_3$. This order differs somewhat from the order found for the NBO-calculated charge increases at R ($Cl > CH=CH_2 > C\equiv CH > F \geq CH_3$), i.e., the charge increase on α-$CH=CH_2$ is significantly higher than at the α-fluorine substituent (Table 2). This shows the strong σ inductive electron-withdrawing and π electron-donating effect of fluorine.

For R = CH_3, the smallest increase in the C_α−R bond order is found, despite the fact that the stabilizing effect is strong (Table 1). The α-CH_3 substituent stabilizes mainly through hyperconjugation,[16h] and apparently a relatively small contribution of the [C═C H^+] resonance structure accounts for this. The two methyl groups in the optimized structure for 2-propyl cation are orientated in such way as to maximize the hyperconjugative stabilization (Figure 1). In line with this, hydrogen atoms with maximum overlap with the formally empty p-orbital at the carbocationic center display an increase in bond length (0.016 Å) and an accompanying decrease in bond order of 0.024 for the B3LYP/6-311+G(d,p) data. Especially for R = Cl, the delocalization of charge onto the α-substituent yields a significantly increased C_α−R bond order upon H^- transfer: from 0.96 (±0.04) in ethyl chloride to 1.55 (±0.05) in 1-chloroethyl cation. The C_α−R bond orders for the other substituents studied also increase (Table 5), which leads to the bond order values of 1.18 (±0.06), 1.35 (±0.05), 1.35 (±0.06), and 1.17 (±0.04) for α-CH_3, α-CH═CH_2, α-C≡CH, and α-F in the respective cations.

The remarkably larger increase in the C_α−R bond order for R = Cl than for R = CH═CH_2 or C≡CH is also observed with AIM-derived bond orders. AIM bond order increases (Table 6) are in excellent agreement with the NBO-derived bond order changes, differing at most 0.02 units. However, the AIM-derived increases in bond order do not correlate with the AIM charges (in contrast to such correlation between NBO charges and NBO bond orders). The pattern of increase in bond order resembles the NBO-derived order (Cl > CH═CH_2 ≈ C≡CH > CH_3), while the increases in AIM charge are CH═CH_2 > C≡CH > Cl > CH_3. This is understandable considering that the bond order is roughly related to the total number of electrons between two atoms while the charges on each of these, of course, depends on the way of splitting this electron density between the atoms. Since the latter is done radically different in the topological AIM method than in the orbital-based NBO method, differences between these methods are to be expected and are indeed found. Unfortunately, this fundamental difference limits the possibility of discussing which data set (Tables 2 and 3 vs 4) is better (although AIM is less arbitrary than NBO),[30a] thereby as yet hampering the presentation of definitive arguments in the case of differences, as found for the charge increase on α-Cl and α-CH═CH_2 or α-C≡CH.

Conclusions

B3LYP and post-HF computations have been performed on α-substituted carbocations $CH_3C(+)HR$ and their neutral precursors CH_3CH_2R. The stabilities of these substituted ethyl cations were compared to that of ethyl cation (R = H). The five substituents studied (R = CH_3, CH═CH_2, C≡CH, F, and Cl) are all stabilizing the cation compared to R = H in the order CH═CH_2 > CH_3 > C≡CH > Cl > F. Both qualitative ordering, and generally satisfactory quantitative agreement with experiment, was obtained with B3LYP/6-311+G(d,p) and MP2(Full)/6-311+G(d,p). Electronic structure data for all compounds were obtained using the NBO and AIM methods, which are in close agreement with each other. NBO analysis is presently somewhat preferable over AIM, because of the wider applicability and substantially lower computational costs.

The α-Cl substituent stabilizes the cation by electron donation, which is reflected in the increase in both positive charge on the substituent and in the significant increase of the C−Cl bond order. The amount of charge delocalization for R = Cl is even greater than for R = CH═CH_2. Despite this strong resonance effect, the enthalpic stabilization by an α-Cl substituent is moderate compared to that of α-CH_3, α-CH═CH_2, and α-C≡CH, due to the inductive effect of the chlorine atom. The smaller stabilization offered by R = F than by R = Cl is reflected in a lower increase in charge on the substituent and a lower increase in bond order C_α−F. This in line with the larger inductive effect of fluorine compared to chlorine. The resonance effect of the strongly stabilizing α-CH═CH_2 substituent is between the effects of α-F and α-Cl. The α-C≡CH group shows about the same resonance effect as α- CH═CH_2, but the stabilization by α-C≡CH is only about one-half of that of the alkenyl group. The charge delocalization onto the methyl group, mainly through hyperconjugation, is about equal to that offered by α-F, but α-CH_3 is a far stronger enthalpically stabilizing substituent. In general, no clear correlation exists between "electron-donating" and "enthalpically stabilizing" for these α-substituents.

Basis sets with diffuse functions are necessary for a proper description of the reaction enthalpy for the α-fluorine substituent. The accuracy of the calculated reaction enthalpies is about equal for B3LYP/6-311+G(d,p) and MP2/6-311+G(d,p) and on average within 1 kcal/mol of the experimental uncertainty. Further expansion of the basis set for B3LYP does not improve the calculated reaction enthalpies. Methodological improvements by single-point calculations using MP4/6-311+G(d,p) or QCISD(T)/6-311+G(d,p) at the MP2/6-311+G(d,p) optimized geometries are overall only marginally affecting the reaction enthalpies. The CBS-Q method is the best, but also computationally the most demanding, method used and calculates the reaction enthalpy for all substituents under study to within the experimental uncertainty. This method can, therefore, likely be used as a benchmark for reaction enthalpies calculated at a lower level of theory in cases where no experimental results are available.

The structural differences, both geometrical and electronic, for the compounds under study between B3LYP and post-Hartree−Fock methods as MP2, MP4, and QCISD(T) are minor. This suggests the possibility of optimizing geometries relatively fast with B3LYP/6-311G(d,p), given the potentially linear scaling of density-functional theory computations,[32] and the use of single-point calculations at higher levels of theory with basis sets including diffuse functions for agreement with experiment to within the experimental error.

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Supporting Information Available: Tables of the Gaussian 94 archives files, zero-point energies, and all relevant charges and bond orders for all compounds studied. Ordering information is given on any current masthead page.

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