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Electronic Structure Calculations of Hydrocarbon Radical Cations: A Density Functional Study

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Abstract: The radical cations of methane, ethane, propane, *n*-butane, ethene, propene, and 1- and 2-butene are optimized at the first principles LCGTO-DFT level, using a DZP basis set and including nonlocal corrections to the exchange and correlation functionals. The optimized geometries are reported and compared with previously reported structures, obtained at the *ab initio* UHF or MP2 levels. The calculations show a general agreement between the DFT and MP2 optimized structures, although the DFT results tend to overestimate the C–H bond lengths by 0.02 Å. The structures of the carbon frameworks and all bond angles are, however, in very good agreement between the two methods. One notable exception is observed for the ethane cation, where the DFT calculations predict a much shorter bond length for the ionized C–C σ-bond (1.49 Å vs 1.58 Å (MP2/6-31G**)).

1. Introduction

The electronic structures of small hydrocarbon radical cations have previously been studied extensively using semiempirical[1] and *ab initio* UHF, MP2, and SDCI[2,3] techniques. Radical cations of the sizes studied in the present work (up to four carbon atoms) have often proven highly reactive, significantly reducing the number of experimental techniques available for the determination of their structures and properties. By calculation of the hyperfine (hf) structures at the optimized geometries and comparison of these with results from low-temperature matrix isolation ESR measurements, it has, however, been possible to answer a number of questions regarding, *e.g.*, Jahn–Teller distortions,[4,5] rotational barriers,[6] and reactions.[7] The previous *ab initio* studies clearly indicate that the inclusion of electron correlation in most cases is crucial for accurate determinations of the geometric and hyperfine structures of these species.[3] The spin contamination has previously been shown to be low for these compounds (see, *e.g.*, ref 3). At the UHF level, we generally observe values in the order $S(S+1) = 0.76$–0.77, to be compared with the ideal value of 0.75 for systems with one unpaired electron.

In the present work we have turned to density functional theory (DFT) to investigate the electronic ground-state structures of a set of linear (nonbranched) alkane and alkene radical cations with up to four carbon atoms. DFT has been shown to work very well in describing structures and properties of small closed shell molecules,[8] transition metal complexes,[9] and extended systems.[9,10] Little is known, however, about the ability of DFT to predict the properties of open shell compounds, which in *ab initio* approaches are known to be computationally much more demanding than the corresponding closed shell systems. Up to now, only a few studies of radical systems using DFT have been reported in the literature,[8,11,12] and none of these has dealt with charged species. Of particular interest is the fact that many of the hydrocarbon radical cations are Jahn–Teller active, and we will thus be able to investigate in detail the ability of DFT to describe the distortions from the highly symmetric neutral parent molecules to the often less symmetric radical cations. It would also be of great value to compute ESR parameters and compare these with experiments and *ab initio* results. This would determine in detail how accurate the presently generated structures are. Such a treatment lies, however, beyond the scope of the present paper, but will be addressed in future communications.

The rationale for choosing to investigate the present compounds using DFT is the advantage the method has over conventional *ab initio* methods in that we are able to treat much larger systems at a correlated level. It is furthermore known to require less computational effort than does, *e.g.*, UHF, MP2, or CI. By performing the analysis on the present set of computationally demanding compounds, where previous data from detailed investigations at the UHF and MP2 levels are available, a direct comparison between methods is furthermore possible. This will provide us with a valuable test of the credibility of the method, if we later wish to investigate larger, more complex systems that cannot be addressed using conventional *ab initio* techniques.

2. Methods

The radical cations of the four smallest linear alkanes (CH_4^+, $C_2H_6^+$, $C_3H_8^+$, n-$C_4H_{10}^+$) and alkenes ($C_2H_4^+$, $C_3H_6^+$, 1-$C_4H_8^+$, 2-$C_4H_8^+$) have been investigated using the linear combination of Gaussian-type orbitals, density functional theory (LCGTO-DFT) program deMon.[13] In the calculations, we use the local spin density approximation (LSD) due to Vosko, Wilk, and Nusair[14] and also include nonlocal density gradient corrections by Becke[15] for the exchange functional and by Perdew[16] for

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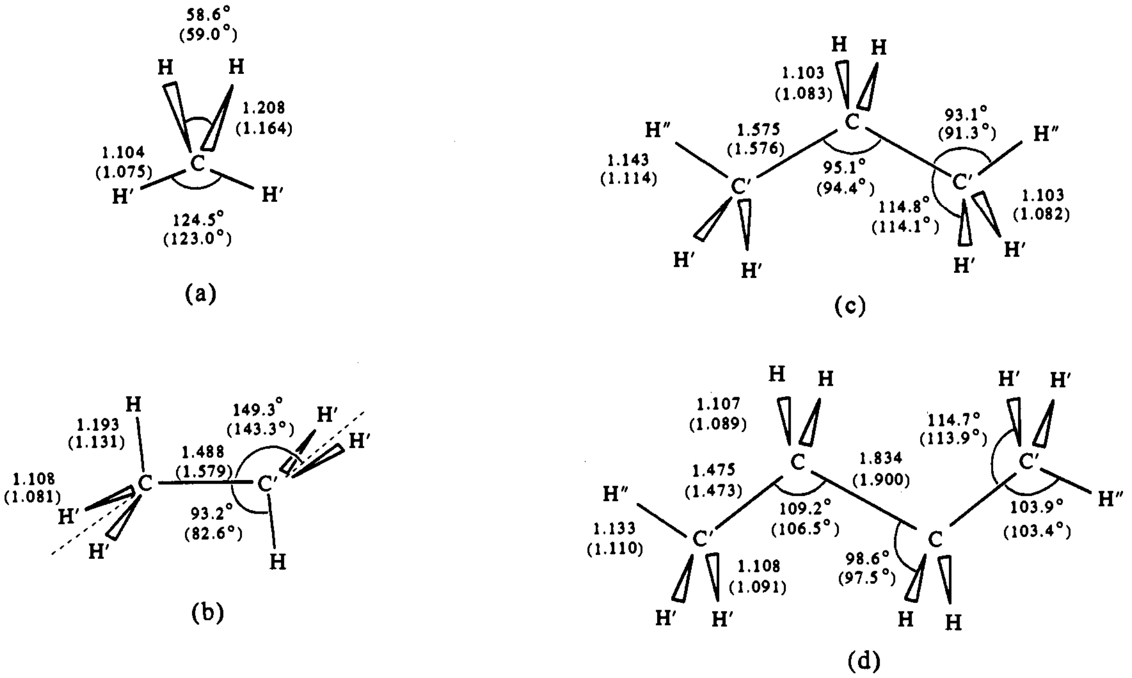

Figure 1. The BP/DZP optimized geometries of the (a) methane, (b) ethane, (c) propane, and (d) *n*-butane radical cations. The corresponding geometrical parameters obtained at the MP2/6-31G** level of theory[3,24] are indicated in parentheses (for *n*-butane: MP2/6-31G* [30]).

the correlation part (termed "BP" throughout the text), which have been previously shown to produce highly accurate geometries for a variety of systems.[8,17]

The geometry optimization calculations were performed using the Broyden–Fletcher–Goldfarb–Shanno (BFGS) algorithm,[18] with a convergence criterion of 0.0004 au for the norm of the gradient. In some cases, where convergence was found to be more difficult, a conjugate gradient method ($\alpha = 0.5$) was instead applied in the initial steps of the optimization procedures. For the particularly difficult case of the ethane radical cation (see below), the final optimizations were performed using the Davidon–Fletcher–Powell (DFP) algorithm.[19] No symmetry constraints were imposed in any of the optimizations. The net effect of using full optimization is that the convergence criterion may be fulfilled and the optimization stopped, while "equal" bond lengths and angles still differ slightly (up to 0.005 Å and 0.3°). In such cases, where it is obvious that the optimization eventually would yield structures of higher symmetry than C_1, we instead report the averaged values.

The basis set employed is of DZP quality and consists of an orbital part with contraction pattern (5211/411/1) for the carbon atoms and (41/1) for the hydrogens,[12] along with an auxiliary basis set for the fitting of the charge density and the exchange and correlation potential. As auxiliary basis, a (5,2;5,2) set was employed for the carbons, and for the hydrogens we used the (5,1;5,1) basis.[12] The fitting to the charge density is performed analytically, whereas the fitting of V_{xc} is performed numerically on a grid consisting of 32 radial shells and 26 points per randomly rotated grid. The energy convergence criterion within each SCF iteration was set to 1.0×10^{-6} au.

3. Results and Discussion

Figures 1 and 2 show the optimized structures of the linear alkane and alkene radical cations obtained in the present work. The structures and properties of these two classes of compounds differ significantly. For the alkane cations, ionization generally occurs from an orbital mainly localized on one or more of the C–C σ-bonds. It is furthermore found, through extensive theoretical studies, that the terminal methyl groups after the ionization tilt inward and that the hyperfine structure (the "unpaired spin density") becomes largely confined to the in-plane, inward-tilted hydrogen atoms.[3] The C–H bonds of these two atoms also become significantly elongated, compared to the other C–H bonds in the molecules.

The alkenes, on the other hand, undergo ionization primarily from the C=C π-orbital, leading to completely different structural features and properties. Much effort has been devoted to resolve whether the weakened double bond becomes nonplanar as a result of the ionization. Only in exceptional cases[20-22] have standard *ab initio* optimization techniques predicted nonplanarity, whereas semiempirical methods generally produce torsional angles about the C=C bond that, after further optimization at, *e.g.*, the MP2 level, yield hyperfine structures in close agreement with experiment. The torsional angles giving the best fit with experiments range from 25° (ethene cation) to 0° (*i.e.*, a planar structure; *trans*-2-pentene cation) and are generally found to decrease with increasing size of the saturated part of the molecule.[3] The potential surface with respect to torsional motion about the weakened C=C double bond is found to be extremely flat in these systems.[3,21,22] The unpaired spin density is for the alkene cations generally confined to the α- and β-protons only.

3.1. Alkane Cations. Methane. Methane is in many respects the prototype of a Jahn–Teller active system and distorts in the cationic state from the symmetric T_d structure to a C_{2v} structure with two significantly elongated C–H bonds (HCH angle ≃ 60°) and two hydrogens that attain shortened bonds with an H'CH' bond angle around 125°. This structure was confirmed only a few years ago, as a result of extensive *ab initio* geometry optimizations and hf structure calculations, in comparison with ESR spectra for the doubly deuterated species.[4,23,24]

In Figure 1a, we show the optimized structure obtained at the BP/DZP level in the present work, together with the MP2/6-31G** optimized geometry.[24] The DFT structure clearly re-

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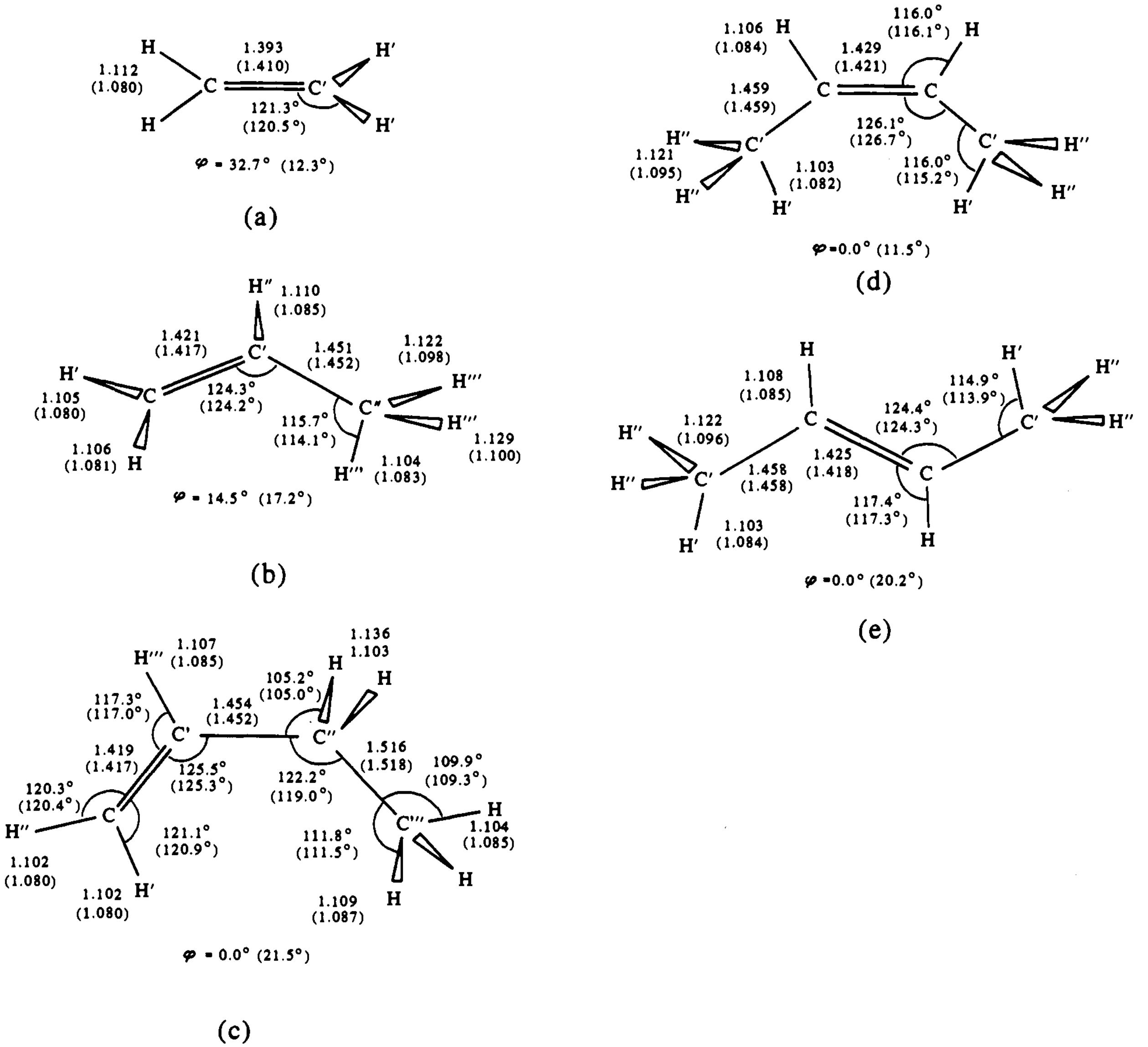

Figure 2. The radical cations of (a) ethene, (b) propene, (c) 1-butene, and (d) *cis*- and (e) *trans*-2-butene, obtained at the BP/DZP level. In the figures we also show the structures obtained at the MP2/6-31G** level.[3,5] For the ethene cation (a), the comparison is made with MP2/6-311++G(2d,2p) results.[3] The torsional angles shown in parentheses for b–e were obtained using the MNDO method, whereas the MP2/6-31G** calculations predict planar geometries.[3]

produces all the features of the C_{2v} structure obtained at the MP2 level, although the C–H bonds are predicted to be more elongated. This is in better accordance with the experimentally determined structure,[25] obtained through Coulomb-explosion experiments, using extremely thin targets and a low-excitation ion source. The experimental HCH and H'CH' bond angles are 67° and 122°, respectively, giving support for the interpretation of a C_{2v} type of structure for the cation. The experimental bond lengths are all around 1.20 Å, but are associated with an uncertainty of up to 0.04 Å. The uncertainty in bond angles is approximately 3°.[25]

Ethane. Through extensive ESR and *ab initio* SDCI//MP2 studies, the ethane radical cation has been found to distort from the highly symmetric D_{3d} structure of the neutral parent molecule, with all six hydrogens in equal positions, to a structure of C_{2h} symmetry with two of the hydrogen atoms (in "*trans*" positions) tilted inward.[5,26,27] The hyperfine structure in this semibridged diborane-like structure is confined to the two bridging hydrogens (a_{iso}(SDCI//MP2) = 2 × 133 G, in agreement with the experimental values a_{iso}(exp) = 2 × 152.5 G[26]). At any lower level of theory or smaller basis set than MP2/6-31G**, the orbital ordering between the ionized $1e_g$ orbitals and the close-lying doubly occupied $3a_{1g}$ orbital (at the neutral D_{3d} structure) is rearranged, leading to an erroneous D_{3d}-type structure with a significantly elongated C–C bond (R(C–C) ≃ 2.0 Å) and all six hydrogens equal. This conformation can, however, be ruled out on the basis of the observed hf pattern.

Using density functional theory, in which electron correlation is included explicitly through the exchange and correlation potential, V_{xc}, we find the structure to be highly dependent on the choice of geometry optimization algorithm. The default BFGS algorithm will in this case, and with the present convergence criteria, yield the erroneous elongated D_{3d} geometry, whereas most other algorithms (conjugate gradient, steepest descent, DFP, etc.) produce the correct semibridged C_{2h}-type structure. Similar problems were also encountered during the optimization of the methane cation, where the structure reported in the figure was obtained using the conjugate gradient method.

The DFT optimized structure of the ethane radical cation is shown in Figure 1b, along with the MP2/6-31G** optimized geometry.[5] All main features of this ^2A_g state are clearly

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reproduced at the LCGTO-DFT-BP level, although the C–C bond is shorter and the C–H bonds are longer than what was obtained at the MP2 level. Most likely, the presently optimized C–C bond is somewhat too short, which will lead to an overestimation of the rotational barrier in the ethane cation.

Fixing the C–C bond length at 1.6 Å and reoptimizing the structure gave the angles HCC′ = 84.8° and XCC′ = 149.0°, respectively (X denoting the bisector of the two C–H′ bonds, *cf.* Figure 1b). Furthermore, the carbon–hydrogen bonds thereby become shortened to 1.165 (*R*(C–H)) and 1.103 Å (*R*(C–H′)), respectively. The energy difference between this conformer and the completely optimized structure (with *R*(C–C′) = 1.485) is found to be only 3.6 kJ/mol at the BP/DZP level. These findings indicate that the potential energy curve for C–C stretching is extremely flat in this region, resulting in a highly nonrigid structure.

Propane. The propane cation is, unlike the two previous cases, not Jahn–Teller active, in that the orbital subject to ionization in the neutral parent molecule is the nondegenerate $4b_2$ orbital.[24,28] Similar to the ethane molecule there are, however, other doubly occupied orbitals present within a small energy spacing, leading to a relatively large structural reorganization upon ionization of the propane molecule. The propane cation maintains the C_{2v} symmetry of the parent molecule, but with elongated C–C bonds, a "flipping" of the terminal methyl groups (analogous to the situation encountered in the ethane cation, described above), and a decrease in the CCC bond angle to a value close to 95°. Furthermore, the in-plane C′–H″ bonds (*cf.* Figure 1c) become elongated, and these two hydrogens will carry most of the unpaired spin density. Once again it is found, using standard *ab initio* techniques, that electron correlation must be included at the MP2 level in conjunction with polarized basis sets, in order to predict a structure of correct symmetry.[3,28] Uncorrelated treatments and/or basis sets without polarization functions instead predict an "asymmetric" structure, where the two C–C bonds are no longer equal. Again, this conformation has been ruled out on the basis of producing an incorrect hyperfine structure.

The structure of the propane radical cation, obtained in the present study, is reported in Figure 1c. Except for the more elongated carbon–hydrogen bonds, the geometry agrees very well with that obtained at the MP2/6-31G** level.[3] In particular we note the excellent agreement for the geometric parameters of the carbon framework and that the correct trend is reproduced in terms of the lengths of the C–H, C′–H′, and C′–H″ bonds.

***n*-Butane.** The *n*-butane cation has been the subject of extensive theoretical studies, with respect to its electronic and hyperfine structures,[29,30] as well as showing interesting effects of vibrational stabilization in the partially deuterated species.[30] Optimizations at the HF/6-31G** and MP2/6-31G* levels have shown the *trans* conformer to be slightly more stable than its *gauche* counterpart, by a few kilojoules/mole. The geometric parameters are, however, very similar for the two forms, and the computed hydrogen hf coupling constants agree equally well with experimental data.[30] In the present study we have investigated the *trans* structure only.

In *n*-butane, the ionization occurs from a MO with large σ-bond character, confined mainly to the central C–C bond. This bond will thus become significantly elongated as a result of the ionization (*R*(C–C) ≃ 2.0 Å). Furthermore, the two inplane hydrogens of the terminal methyl groups obtain significantly decreased bond angles and elongated C′–H″ bonds,[30] in analogy with the structures found for the ethane and propane radical cations. The small energy difference between the *trans* and *gauche* conformers mentioned above can most likely be related to the elongated central C–C bond, leading to a very low barrier toward pseudorotation within the molecule.

The present deMon calculations predict a substantially shorter value for the central C–C σ-bond than does MP2/6-31G* (1.834 vs 1.900 Å) and, as a consequence, slightly larger CCC′ bond angles (109.2° vs 106.2°). The central C–C bond is still, however, also in the DFT calculations found to be significantly elongated compared to the situation in the neutral parent molecule. The HCC bond angles are in close agreement between the two methods, but the various C–H bond lengths are again overestimated by ≃0.02 Å in the DFT calculations. Thus, it appears that the DFT calculations underestimate the bond length modification of the carbon framework when the ionized MO is localized on one C–C σ-bond (*cf.* the ethane and butane cations), whereas when the SOMO is more delocalized, a very good agreement is predicted. Studies on more systems of similar type are, however, necessary before any definite conclusions can be drawn in this matter.

3.2. Alkene Cations. Ethene. Due to its smallness and importance as a precursor in, *e.g.*, the formation of polyethene, the ethene cation has previously been studied in great detail, utilizing highly sophisticated theoretical techniques and extended basis sets. At the CEPA/6-311G** (coupled electron pair approximation) level, a torsional angle (ϕ) of 16° is found;[20] using the MP2/6-311++G(2d,2p) method the value $\phi = 12°$ has been reported,[3] whereas at the UHF level, a planar structure is always predicted to be the most stable.[3,20] Experimentally, the torsional angle is known to be around 25°,[31,32] a value also obtained using semiempirical MNDO methods.[1] The other experimental parameters are *R*(C═C) = 1.405 Å, *R*(C–H) = 1.091 Å, and ∠HCC = 117.85°.[32]

The BP/DZP calculations performed in the present work predict a torsional angle of 33° (*cf.* Figure 2a). Using a smaller basis set, fewer grid points for the fitting of V_{xc}, or uncorrected LSD calculations all produce slightly larger values of the torsional angle. From Figure 2a we also note that the π-bond is somewhat shorter than the experimental and MP2/6-311++G(2d,2p) values (1.393 vs 1.405 and 1.410 Å, respectively). The C–H bonds are elongated by 0.03 Å relative to the MP2 results, and the HCC angle is slightly overestimated.

Decreasing the torsional angle to the experimental value of 25° raises the energy by 4.8 kJ/mol (1.1 kcal/mol) relative to the BP/DZP optimized structure. Adjusting also the remaining geometrical parameters (*R*(C═C), *R*(C–H), and ∠HCC) to their corresponding experimental values leads to a further increase in energy by approximately 10 kJ/mol.

Propene. Previous *ab initio* calculations up to the MP2/6-31++G** level all predict the propene radical cation to be planar. Semiempirical calculations do, however, predict the torsional angle about the double bond to be 17°.[3] From comparisons between computed (SDCI//MP2) and experimental hf structures, a twisted structure is found to give the best agreement. At the extrapolated full-CI level,[33] the 17° twisted, MP2 reoptimized geometry is, furthermore, found to be slightly more stable than the planar form.[3] The potential surfaces for all cations in this class of compounds are, however, very flat with respect to wagging motions about the weakened double bond. This is also illustrated by the energies obtained for the optimized planar geometries compared to those where the 17° torsional angle is imposed. At the HF/6-31G** and MP2/6-31G** levels, this difference is only 2.9 and 1.6 kJ/mol, respectively.[34]

The present DFT calculations yield a torsional angle about the C═C bond of 15°. With the exception of the C–H bonds that are around 0.02 Å longer than the corresponding MP2/6-31G**

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values (*cf.* Figure 2b), all other geometrical parameters are in very close agreement between the two methods. A single-point calculation with the torsional angle set equal to 0 yields an energy difference of less than 0.1 kJ/mol obtained at the BP/DZP level, in agreement with the flatness of the potential surface observed in previous studies.

1-Butene. In the 1-butene radical cation, the saturated part is now large enough to allow for structural features formed through pseudorotation about the central C–C σ-bond (*i.e.*, "*cis*", "*trans*", and "*gauche*" conformers), in addition to the local planarity/nonplanarity of the ionized C=C bond. The cation has previously been studied theoretically, with respect to its hyperfine structure,[3] as well as being one of the first steps in the radical-induced polymerization of ethene.[7] At the UHF and MP2 levels (using a 6-31G** basis), the carbon skeletons of the *cis* and *trans* forms are found to be planar, whereas the *gauche* structure has a $\angle$CC′C″C‴ torsional angle of $\simeq 100°$. The *cis* conformer at the MP2 and extrapolated full-CI levels is found to be slightly more stable than the *trans* isomer and also has a reported hyperfine structure that agrees well with experimental results.[3,35]

No torsional angles are, however, found about the ionized C=C bond at the same levels of theory, although semiempirical calculations predict $\phi_{cis} \simeq 21°$ and $\phi_{trans} \simeq 10°$.[3] A slight bending angle is also reported for the *cis* isomer; *i.e.*, the torsional angles formed by the H′C=C′C″ and H″C=C′H‴ atoms differ (*cf.* Figure 2c). Since the energetics and hyperfine results from the previous work all favor the *cis* conformer, we have here chosen to investigate this structure exclusively, using the BP/DZP method. In Figure 2c the optimized geometry is depicted together with the planar MP2/6-31G** geometry of ref 3. Also the present calculations predict a completely planar structure, in agreement with the UHF and MP2 findings. The carbon framework is in perfect agreement, as are the various HCC bond angles.

2-Butene. The geometries of the *cis*- and *trans*-2-butene radical cations, depicted in parts d and e, respectively, in Figure 2, are again very similar to those obtained at the MP2/6-31G** level.[3] They also resemble the optimized MP2 and UHF structures in that both species are found to be planar. Employing MNDO theory, the torsional angles 20.2° and 11.5° were found for the *cis*- and *trans*-isomers, respectively.[3] At the UHF and MP2 levels, the ^2A_u ground state of the *trans* form is reported to be between 5 and 8 kJ/mol more stable than the planar *cis* conformer ($^2B_1$ state). At the extrapolated full-CI level, the energy difference is instead in favor of the *cis* structure, by 1–3 kJ/mol[3]. The *cis* form is furthermore reported to be the primary reaction product in the photoinduced isomerization reaction of the 1-butene radical cation.[7,36] The DFT calculations performed in the present work predict the difference to be around 1 kJ/mol in favor of the *trans* form.

Although the potential surface is very flat with respect to moderate changes in the torsional angle about the equilibrium geometry, the *cis*/*trans* isomerization barrier is fairly large in the 2-butene cation, since we now have to break a π-bond in order to perform the pseudorotation. At the HF/6-31G** level, the isomerization barrier is reported to be ca. 170 kJ/mol (41 kcal/mol),[34] a value that presumably will decrease substantially when electron correlation is included. Still, the rotational barrier in the 2-butene radical cation can be assumed to be significantly larger than in the cation of *n*-butane and somewhat larger than in the 1-butene cation. These effects remain to be verified, however, and were not pursued further in the present study.

4. Conclusion

In the present work, first principles LCGTO-DFT calculations, including nonlocal corrections for the exchange and correlation potential, are for the first time conducted on a series of linear alkane and alkene radical cations. The basis set employed for the geometry optimization calculations is of "double-ζ + polarization" (DZP) quality, which has been found to work very well for closed shell compounds, neutral radicals, and hydrogen-bonded systems.[8,12,17]

The optimized carbon–carbon bond lengths and the various bond angles are all found to be close to the results from previous MP2/6-31G** optimization calculations. One exception is found in the Jahn–Teller distorted ethane cation, where the present calculations predict a 0.1 Å shorter C–C bond than does MP2. The C–H bonds, on the other hand, are generally found to be more elongated than the corresponding MP2 values, by approximately 0.02 Å.

The structural features of the alkane cations are all clearly reproduced with the present method, in that the ionization occurs from a MO with mainly C–C σ-bonding character and that the terminal methyl groups become "tilted" inward whereby the two in-plane hydrogen atoms (one on each methyl group) attain semibridged positions. For the smaller alkene cations, the DFT calculations, as opposed to the UHF and MP2 results, predict the local structure about the C=C bonds to be nonplanar. The introduced torsional angle is slightly overestimated for the ethene cation, compared to the experimental torsional angle.[31,32] The larger alkene radical cations (1- and 2-butene), are all found to be planar at the present level of theory, in agreement with the conclusions of previous *ab initio* optimization calculations.[3] The present calculations furthermore unambiguously support the previous observations, that the potential surfaces with respect to torsional motions about the weakened C=C bonds are very flat.

All calculations were performed on an Alliant FX2800 computer. The CPU time required for each geometry optimization is on the same order as the corresponding MP2 calculations, although the DFT calculations require far less external memory.

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