Effects of Ionization in Linear Alkenes: A Study of the Radical Cations of 1- and 2-Pentene

Leif A. Eriksson,[†] Lars Sjöqvist,[‡] Sten Lunell,[*,†] Masaru Shiotani,[§] Masaku Usui,[§] and Anders Lund[‡]

Contribution from the Department of Quantum Chemistry, Box 518, Uppsala University, S-751 20 Uppsala, Sweden, Chemical Physics Laboratory, Department of Physics, Linköping University, S-581 83 Linköping, Sweden, and Department of Applied Physics and Chemistry, Faculty of Engineering, Hiroshima University, Higashi-Hiroshima, 724 Japan

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Abstract: The electronic ground states of the 1- and 2-pentene radical cations have been studied by ab initio calculations at the UHF, MP2, and SDCI levels, as well as experimentally, using low-temperature matrix isolation electron spin resonance (ESR). The ESR spectra, recorded in halocarbon matrices at temperatures between 77 and 145 K, are reported together with calculated structural parameters, total energies, and isotropic hyperfine (hf) coupling constants. For the 1-pentene radical cation, the ESR spectrum is explained by a rigid, nonplanar structure where the two terminal aliphatic carbon atoms are rotated out of the plane of the allylic fragment by approximately 25°. The singly occupied molecular orbital (SOMO) is found to be partially delocalized over the whole allylic fragment. The radical cation of 2-pentene, on the other hand, shows experimentally as well as theoretically a hf structure typical for a localized π-bond ionization, as normally expected in alkene radical cations. Deprotonation reactions of the radical cations in CF₂ClCFCl₂ matrices at 120 K resulted in the appearance of alkyl radicals.

1. Introduction

The structure of alkene radical cations has attracted recent attention, and several theoretical and experimental studies have been reported.[1] Radical cations are primary oxidation products in the radiation chemistry of hydrocarbons. They are extremely short-lived intermediates which are thought to participate in chemical reactions. For example, the radical cations of linear and branched alkenes are believed to play an important role in initiating polymerization reactions.[2]

Utilizing the halocarbon matrix isolation technique in combination with electron spin resonance (ESR) spectroscopy, several cationic species of unsaturated hydrocarbons have been investigated. In the pioneering work by Shida and co-workers, hyperfine (hf) coupling constants of butene radical cations stabilized in a CFCl₃ matrix were reported.[3] The smaller propene radical cation has also been studied by several experimental groups.[4,5] Using selectively deuterated compounds, detailed information about the hf structure was revealed, and the existence of a twisted structure was discussed.[4] The radical cation of butene and its isomers have been investigated thoroughly, with the emphasis made on the reactions of the radical ions in halocarbon matrices.[6] For longer linear alkene radical cations, such as the trans- and cis-3-hexene cations, it has been shown that the alkyl group attached to the olefinic segment is flexible, i.e., that the rotation barrier about the carbon bond connecting the olefinic and alkyl groups is low.[7] This observation has also been confirmed

by theoretical ab initio studies.[8] Bimolecular reactions involving alkene radical cations, forming neutral allyl radicals in glass-like halocarbon matrices, have been observed at elevated temperatures (ca. 110–120 K).[6] Fujisawa et al. have shown that the symmetry of the carbon skeleton of the radical ion is preserved during these reactions, and possible reaction mechanisms have been discussed.[6,9]

By removing an electron from the double bond in the neutral linear alkene, a radical cation with a singly occupied molecular orbital (SOMO) of π-type is generally formed.[3,4,6,7] From a theoretical point of view, the structures of alkene radical cations are very interesting. They have been proposed to exhibit twisted structures with respect to the weakened double bond, due to competitive forces between conjugation and hyperconjugation.[10] The magnitudes of the α-proton hf coupling constants are very sensitive to twisting about the double bond, thus making it possible to determine the local geometric structure by comparing calculated hf couplings with experimental ESR data.[11]

Relatively few calculations concerning the structure and hf parameters of linear alkene radical cations have been reported. Clark and Nelsen utilized semiempirical MO theory in an investigation of linear alkene radical cations up to a chain length of four carbon atoms.[12] However, contradictory results concerning the effect of alkyl group substitution on the structure, using different semiempirical methods, have been reported.[12,13] The structure and hf parameters of the trans- and cis-3-hexene radical cations have been investigated in detail using unrestricted Hartree-Fock (UHF), second-order Møller-Plesset perturbation theory (MP2) and configuration interaction (CI) methods.[8] The calculated hf coupling constants were found to be in good agreement with the experimental ESR results.[7] We are presently

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[†] Uppsala University.

[‡] Linköping University.

[§] Hiroshima University.

(1) See, e.g.: (a) Radical Ionic Systems. Properties in Condensed Phases; Lund, A., Shiotani, M.; Ed.; Kluwer: Dordrecht, 1991. (b) Shiotani, M. Magn. Reson. Rev. 1987, 12, 333.

(2) See, e.g.: (a) Tabata, M.; Lund, A.; Samskog, P.-O.; Lunell, S.; Huang, M.-B. J. Polym. Sci. 1988, A26, 2725, and references therein. (b) Tsuji, K.; Yoshida, H.; Hayashi, K. Polym. Lett. 1967, 5, 313.

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(13) Belville, D. J.; Bauld, N. L. J. Am. Chem. Soc. 1982, 104, 294.

100 G

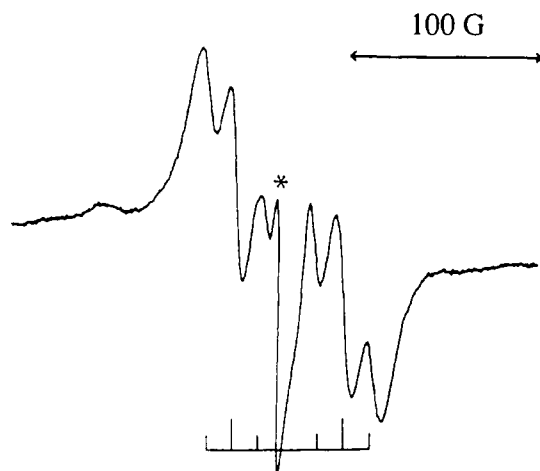studying the structure of linear alkene cations and their saturated analogues systematically, using the ab initio methods mentioned above.[14]

In this work we have studied the structures of 1- and 2-pentene radical cations by means of ab initio calculations and ESR measurements. Theoretical and experimental hf parameters for the pentene radical cations are presented, with emphasis on the theoretical analysis. The hyperfine and geometric structures of the 1-pentene cation are found to differ markedly from the corresponding structures of the *trans-* and *cis-*2-pentene isomers. The difference is explained as being due to a predicted nonplanarity of the carbon skeleton of the 1-pentene cation and related to the structure of the singly occupied molecular orbital (SOMO).

2. Experimental Section

The employed matrices, CFCl₃ (>99%), CF₃CCl₃ (>99%), and CF₂-ClCFCl₂ (>99%) were obtained commercially from Tokyo Kasei and Fluka. The solutes, 1-pentene (Fluka) and *trans-* and *cis-*2-pentene (Tokyo Kagaku Seiki), were used as received, without further purification. All matrices were degassed before usage. The samples were prepared on a vacuum line by mixing a small amount of the solute (less than 1.0 mol %) with the matrix. After preparation, the samples were cooled down to 77 K and thereafter exposed to radiolysis using X- or γ-rays. The ESR measurements were performed on Bruker ER 200 D and JEOL JAS-FX spectrometers.

3. Experimental Results

1-Pentene. The radical cation of 1-pentene was stabilized in CFCl₃ at 77 K. An ESR spectrum assigned to the 1-pentene cation, recorded under these conditions, is shown in Figure 1. This spectrum was analyzed using the following isotropic hf coupling constants: $a_1(1H) = 57.0$ G and $a_2(2H) = 16.0$ G (Table I). The spectrum did not change when the temperature was increased to 145 K. The large hf coupling (57.0 G) is attributed to one of the methylenic β-protons at C3, while the smaller (2 × 16.0 G) is attributed to the two terminal α-protons at C1 (see Theoretical Results). We also tried to observe the 1-pentene cation in other halocarbon matrices, but no ESR spectra which could be assigned to the radical cation were obtained. For example, in CF₂ClCFCl₂ a broad singlet was recorded at 77 K, indicating a possible formation of molecular aggregates. Increasing the temperature in this matrix above 77 K caused an irreversible change of the spectrum. At 110 K, a six-line spectrum with binomial distribution, having the splitting $a(5H) = 24.5$ G,

was observed. A further increase of the temperature to 120 K caused the appearance of an overlapping species which was assigned to the *trans-*1-ethylallyl radical (structure **1**).

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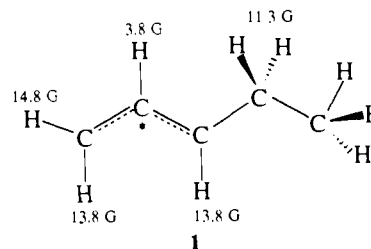
trans-2-Pentene. The radical cation of *trans-*2-pentene was stabilized in all three halocarbon matrices at 77 K. The best resolved spectrum was observed in CF₃CCl₃ and is depicted in Figure 2. This spectrum was simulated using the hf coupling constants $a_1(2H) = 11.9$ G, $a_2(1H) = 40.6$ G, $a_3(1H) = 45.1$ G, and $a_4(3H) = 28.4$ G. Assuming that the *trans-*2-pentene cation has a π-type SOMO and a planar double bond, the a_1 hf couplings are attributed to two α-protons attached to the double bond, and a_4 to the freely rotating methyl group protons of the C1 carbon. The two α-protons attached to the C2 and C3 positions are not magnetically equivalent by molecular symmetry. However, the experimental results show that the difference between the hf coupling constants is too small to be resolved, i.e., less than the experimental line width (ca. 3.0 G). The two hf couplings a_2 and a_3 are assigned to the β-protons on carbon C4. The hf coupling constants given above are very close to those attributed to the *trans-*3-hexene radical cation, which has a planar double bond.[7] This gives further support for the assignment made for the radical cation of *trans-*2-pentene.

The magnitude of the hf coupling constants was found to vary, depending on the employed matrix. The sum of the hf coupling constants at 77 K decreased from 170.9 G in CF₃CCl₃, to 160.5 G in CFCl₃ and CF₂ClCFCl₂. The methyl group protons are mainly responsible for this variation, whereas the changes in the β-proton hf coupling constants are small. The magnitudes of the α-proton hf couplings are essentially independent of the matrix used. The ESR spectra attributed to the *trans-*2-pentene radical cation in CF₃CCl₃ showed a temperature alteration in the region 77–180 K. Between 77 and 180 K, the magnitude of the β-proton hf coupling constants gradually decreased with increasing temperature. In CF₂ClCFCl₂, the ESR spectrum changed irreversibly at ca. 120 K. The spectrum observed above 120 K was analyzed with the following hf coupling constants: $a(1H) = 14.8$ G, $a(2H) = 13.8$ G, $a(2H) = 11.3$ G, and $a(1H) = 3.8$ G. These hf coupling constants can unambiguously be attributed to the *trans-*ethylallyl radical (**1**).

For the *trans-*2-pentene radical cation the following procedure was used to get an empirical estimate of the conformation of the alkyl group. Suppose that the β-proton hf coupling constants a_β are given by the cos² θ rule:[15] $a_\beta = B_0 + B_2 \cos^2 \theta$. If we neglect B_0, the dihedral angles $\theta_1 = 27°$ and $\theta_2 = \theta_1 + 120°$, with respect to the π-bond, are obtained. The derived $B_2 = 56.8$ G is close to the value obtained for the radical cation of *trans-*3-hexene ($B_2 = 56.6$ G).[7] The temperature-dependent line shape is mainly due to changes of the β-proton hf coupling constants. A similar effect has previously been observed in the study of the *trans-*3-hexene cation, and was explained by a torsional rotation about the carbon–carbon bond connecting the olefin and alkyl groups.[7,8] Although the hf coupling constant depends slightly on the employed matrix, it is suggested that these changes are not large enough to alter the electronic structure of the radical cation of *trans-*2-pentene.

cis-2-Pentene. The radical cation of *cis-*2-pentene could not be stabilized in any of the utilized matrices at 77 K with resolved

(14) Lunell, S.; Eriksson, L. A.; Huang, M.-B. *J. Mol. Struct.* (*THEOCHEM*) **1991**, *230*, 263.

(15) Carrington, A.; McLachlan, A. D. Introduction to Magnetic Resonance; Harper: New York, 1967.

Table I. Experimental Hyperfine Coupling Constants of Linear Alkene Radical Cations, Stabilized in Halocarbon Matrices

| cation	matrix	T (K)	isotropic proton hf coupling constant (G)[a]	ref
$CH_3CH{=}CH_2$	$CFCl_3$	77	$a(CH_3) = 24.0$, $a(CH) = 7.0$, $a(CH_2) = 23.0$, 12.0	4
	SF_6	77	$a(CH_3) = 27.0$, $a(CH) = 5.0$, $a(CH_2) = 16.0$, 14.0	4
$CH_2{=}CHCH_2CH_3$	$CFCl_3$	77	$a(CH) = 6.4$, $a(CH_2) = 9.8$, 16.6, $a(CH_2) = 39.0$	6
		130	$a(CH) = 3.5$, $a(CH_2) = 13.3$, $a(CH_2) = 37.1$	3
$CH_3CH{=}CHCH_3$	CF_3CCl_3	118	$a(CH_3) = 27.4$, $a(CH) = 9.9$	6
(trans)		130	$a(CH_3) = 23.9$, $a(CH) = 9.8$	6
$CH_2{=}CHCH_2CH_2CH_3$	$CFCl_3$	77	$a(1H) = 57.0$, $a(2H) = 16.0$	b
$CH_3CH{=}CHCH_2CH_3$	CF_3CCl_3	77	$a(2H) = 11.9$, $a(1H)$ 40.6, $a(1H) = 45.1$	
(trans)			$a(3H) = 28.4$	b
$CH_3CH_2CH{=}CHCH_2CH_3$	$CFCl_3$	77	$a(CH) = 12.5$, $a(CH_2) = 44.3$, 40.6	7
(trans)		130	$a(CH_2) = 12.5$, $a(CH_2) = 38.3$	7
$CH_3CH_2CH{=}CHCH_2CH_3$	$CFCl_3$	120	$a(CH) = 8.5$, $a(CH_2) = 51.1$, 17.4	7
(cis)				

[a] Absolute values. [b] This work.
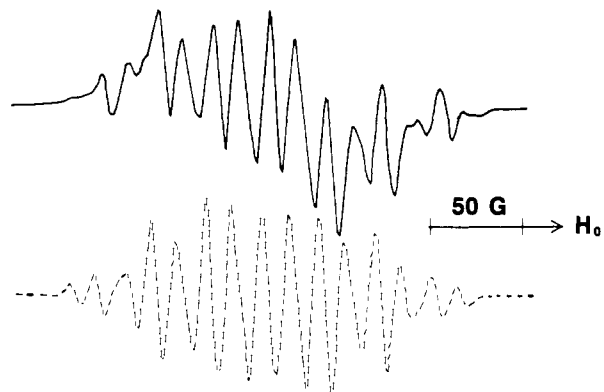
Figure 2. Experimental ESR spectrum attributed to the *trans*-2-pentene radical cation in CF_3CCl_3 at 77 K, together with the simulated one (dotted lines). The hf coupling constants employed in the simulation are given in the text and in Table I.

ESR spectra. In $CF_2ClCFCl_2$ a broad singlet was recorded. However, in analogy with the results observed for the trans isomer and the 1-pentene radical cation, the singlet decayed at approximately 120 K, and a new spectrum appeared. This spectrum was interpreted by the hf coupling constants $a(1H) = 15.8$ G, $a(2H) = 13.2$ G, $a(2H) = 14.2$ G, and $a(1H) = 3.8$ G, and is assigned to the *cis*-1-ethylallyl radical (structure **2**).

2
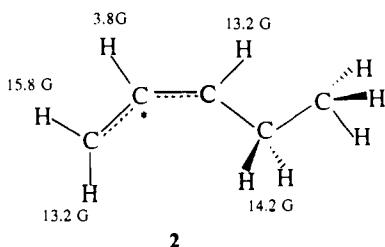
4. Theoretical Method

The electronic ground states of 1- and 2-pentene radical cations were studied theoretically using unrestricted Hartree–Fock (UHF),[16] second-order Møller–Plesset perturbation theory (MP2),[17] and configuration interaction (CI) calculations. To find and optimize stable geometries of the various conformations of the cations, UHF/6-31G**, MP2/3-21G**, and MP2/6-31G** calculations (including hydrogen p- and carbon d-functions in the basis sets[18]) were performed, using the program Gaussian

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(17) Møller, C.; Plesset, M. S. *Phys. Rev.* **1934**, *46*, 618.

(18) See, e.g.: Hehre, W. J.; Radom, L.; Schleyer, P. v. R.; Pople, J. A. *Ab Initio Molecular Orbital Theory*; Wiley-Interscience: New York, 1986.

$90.$[19] In the geometry optimizations, the spin contamination was acceptably small in all cases; $\langle S^2 \rangle_{UHF} \leq 0.77$.

To obtain a good description of the spin properties of the cations, configuration interaction calculations including all single and the most important double excitations (SDCI) from a restricted Hartree–Fock (RHF) reference determinant, as selected with MP2 theory,[20] were performed on the UHF and MP2 optimized geometries. These calculations, in which the van Duijneveldt (13s8p/10s)/[5s3p/4s] basis set[21] was used, were performed using the CI program package MELDF.[22] The energy threshold in the selection of the doubly excited configurations was 2×10^{-5} au, corresponding to 25–30 000 spin-adapted configurations. The square of the coefficient of the reference determinant was in all SDCI calculations above 0.87, justifying the use of a single determinant as reference function. All computations were performed on a Cray X-MP/416 computer.

5. Theoretical Results

1-Pentene. In Figure 3 we show two conformers of the 1-pentene radical cation, both of which were found as local minima on the MP2/6-31G** potential hypersurface, and hence are predicted to be two possible stable conformers. These structures are the planar all-trans form of C_s symmetry, **a**, and the optimized nonplanar geometry **b** of C_1 symmetry, involving a torsional motion about the C2–C3 single bond. The electronic ground state of conformer **a** is ^2A (C_s symmetry), and ^2A for conformer **b** (C_1 symmetry). In Table II, the MP2/6-31G** optimized parameters of these are listed, along with the UHF, MP2, and SDCI energies, and the Davidson extrapolations to the full CI limit (SDCI(Q)).[23]

As seen in Table II, the bond lengths and angles for the two conformers are rather similar. For the carbon skeleton, the main differences are due to the local cis/trans arrangement in the saturated part, and the fact that in structure **b** a torsional angle of 23.7° is introduced about the C2–C3 bond, turning the C1 carbon out of the plane of the rest of the molecule (cf. Figure 3b). Thereby the protons H4 and H5 become inequivalent, which strongly affects the hf coupling constants of these atoms. For conformer **a**, both H4 and H5 show significantly elongated C–H bond lengths, whereas in conformer **b**, owing to the above-

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(20) Davidson, E. R.; Bender, C. F. *Chem. Phys. Lett.* **1978**, *59*, 369.

(21) van Duijneveldt, F. B. IBM Technical Report RJ945, 1971.

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(27) Lindgren, M.; Lund, A. *J. Chem. Soc., Faraday Trans.* **1987**, *83*, 1815.

Radical Cations of 1- and 2-Pentene

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(a)

(b)

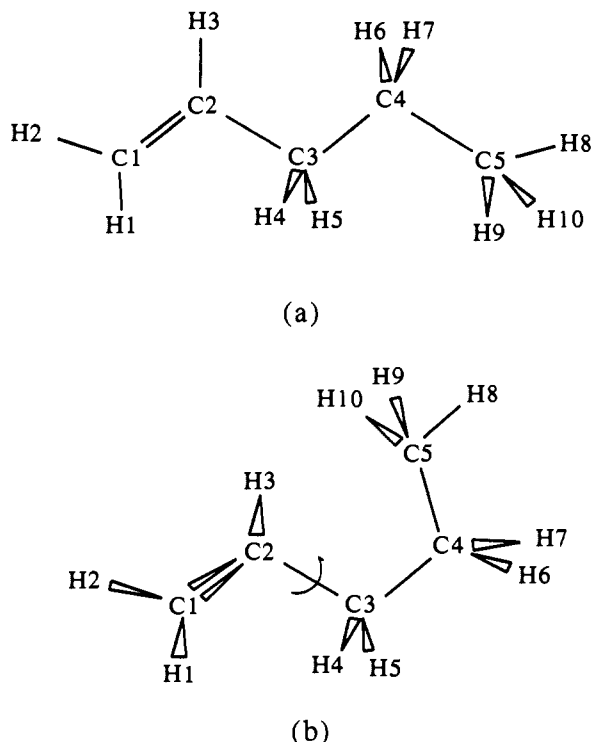**Figure 3.** The two conformations of the 1-pentene radical cation studied at the MP2/6-31G** level. The dihedral angle γ(H4–C3–C2–C1) in (b) is approximately 90°.

mentioned rotation, only the C3–H4 bond is elongated. Also the H4–C3–C2 angle in **b** differs markedly from the others.

It should be commented that the SOMO of conformer **b**, which strongly affects both the geometric and hyperfine features of the cation, is composed mainly of the p_π-orbitals of carbon atoms C1, C2, and C3, i.e., the p-orbitals perpendicular to the C1–C2–C3 plane. It is C1=C2 bonding and C2–C3 antibonding, which explains both the elongated C1–C2 double bond and the relatively short (1.44 Å) C2–C3 bond.

The hf structures of the two species, shown in Table III, give strong support for the nonplanar form **b** being responsible for the observed ESR spectra. The couplings of the two protons H4 and H5 at C3 are in the planar conformer **a** equivalent and only about half of the observed single coupling of 57 G. In structure **b**, however, most of the spin density is shifted from H5 to H4, giving the couplings 1 × 46 G and 1 × 5 G for these protons. This is consistent with the value of the dihedral angle γ(H4–C3–C2–C1) in structure **b**, which is 89.8°, giving a maximal overlap between the 1s orbital of H4 and the π-type SOMO on C1–C2–C3. The H5–C3–C2–C1 dihedral angle, in contrast, is only (–)17.5°, which places H5 almost in the nodal plane of the SOMO, explaining the small spin density on this hydrogen. Secondary consequences of the rotation around the C2–C3 bond are a slight decrease of the hf coupling on H3 as well as slight increases of the couplings on H1 and H2, in both cases improving agreement with experiment.

Energetically, the conformers **a** and **b** are on the UHF and MP2 levels predicted to have appromixately the same stability, with conformer **a** actually somewhat below **b** (11 kJ/mol at the MP2/6-31G** level). As discussed elsewhere,[11,14,28,29] the SDCI energies are not appropriate for total energy comparisons. This is because the selection of configurations in the present calculations is such as to give as accurate hfs parameters as possible, which not necessarily means the best possible total energies. The extrapolated SDCI(Q) energies, in contrast, although estimated

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(29) Feller, D.; Davidson, E. R. *Theor. Chim. Acta* **1985**, *68*, 57.
(30) Iwasaki, M.; Toriyama, K. *J. Am. Chem. Soc.* **1986**, *108*, 6441.

Table II. Structural Parameters[a] from the MP2/6-31G** Optimization Calculations and UHF, MP2, SDCI, and SDCI(Q) Energies for the Two Conformations of the 1-Pentene Radical Cation Shown in Figure 3[b]

	a	b
R(C1–C2)	1.415	1.413
R(C2–C3)	1.455	1.441
R(C3–C4)	1.523	1.546
R(C4–C5)	1.522	1.523
R(H1–C1)	1.082	1.081
R(H2–C1)	1.080	1.080
R(H3–C2)	1.086	1.084
R(H4–C3)	1.105	1.124
R(H5–C3)	1.105	1.090
R(H6–C4)	1.090	1.088
R(H7–C4)	1.090	1.088
R(H8–C5)	1.086	1.086
R(H9–C5)	1.088	1.089
R(H10–C5)	1.088	1.089
$\angle$(C1–C2–C3)	123.0	123.3
$\angle$(C2–C3–C4)	116.6	119.6
$\angle$(C3–C4–C5)	111.5	115.3
$\angle$(H1–C1–C2)	120.6	120.7
$\angle$(H2–C1–C2)	120.9	120.7
$\angle$(H3–C2–C1)	119.7	119.0
$\angle$(H4–C3–C2)	106.7	95.6
$\angle$(H5–C3–C2)	106.7	112.4
$\angle$(H6–C4–C3)	108.9	106.7
$\angle$(H7–C4–C3)	108.9	109.3
$\angle$(H8–C5–C4)	110.3	108.5
$\angle$(H9–C5–C4)	111.1	111.8
$\angle$(H10–C5–C4)	111.1	112.3
γ(C1–C2–C3–C4)	180.0	156.3
E_{UHF}	–194.862 75	–194.856 14
E_{MP2}	–195.551 14	–195.547 21
E_{SDCI}	–195.239 56	–195.198 70
$E_{SDCI(Q)}$	–195.425 8	–195.446 5

[a] Bond lengths are in ångströms, bond angles in degrees, and energies in atomic units (1 au = 2627.3 kJ/mol). [b] The angle γ(C1–C2–C3–C4) is the torsional angle formed between the planes C1=C2–C3 and C2–C3–C4. The labeling of the individual atoms refers to Figure 3a.

Table III. Calculated Isotropic Proton Hyperfine Coupling Constants (G) of the 1-Pentene Radical Cation[a]

	a	b
H1	–14.82	–15.91
H2	–14.95	–15.82
H3	–7.58	–6.63
H4	27.30	46.38
H5	27.30	4.94
H6	0.65	2.78
H7	0.65	0.82
H8	–0.08	0.02
H9	0.10	0.49
H10	0.10	0.21

[a] The values are obtained from SDCI calculations on the MP2/6-31G** optimized geometries. For the labeling of individual atoms, see Figure 3a. The experimentally obtained hf couplings are reported in Table I.

rather than explicitly calculated, are useful for such comparisons, since they eliminate the truncation effects which are coupled to the selection of a limited number of determinants in the CI.[23] We have, in fact, previously found the SDCI(Q) total energy to predict a more accurate equilibrium geometry than the MP2 calculations.[11] At the extrapolated SDCI(Q) level, conformer **b** is found to be the more stable one, by some 52 kJ/mol (cf. Table II), which supports the interpretation based above on the hf structure.

Apart from these conformers, obtained at the MP2/6-31G** level, a set of planar structures was also investigated using the smaller 3-21G** basis. These conformers differ mainly in the relative orientation of the saturated part of the system. SDCI calculations of all these additional structures show hf structures

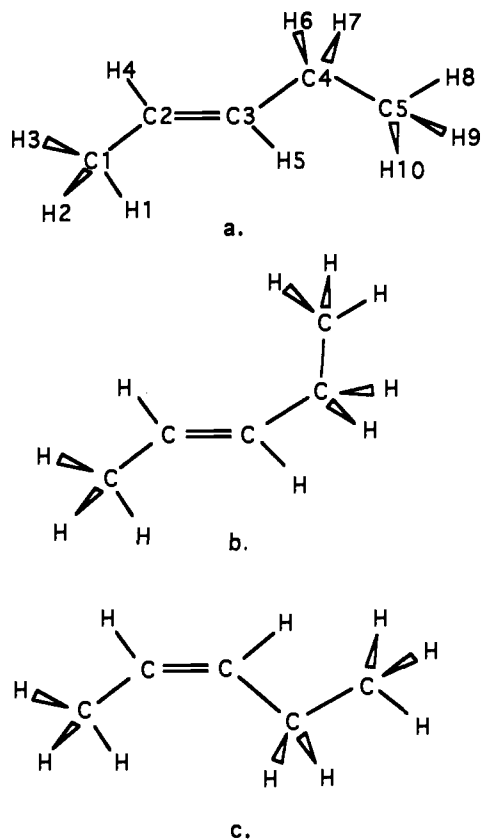3248 *J. Am. Chem. Soc., Vol. 115, No. 8, 1993*

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Figure 4. The three conformations of the 2-pentene radical cation studied in the theoretical part of this work.

very typical for π-type ionized alkenes,[14] i.e., approximately 2 × −15 G and 1 × −8 G for the three α-protons, and 2 × 23 G for the two protons at C3. The too large absolute value for the proton at C2 and the existence of two equivalent couplings from the protons at C3 rule out these structures as being responsible for the experimentally observed ESR spectrum.

As discussed in a previous paper,[14] ab initio UHF and MP2 geometry optimizations often fail to produce a twist angle about the ionized C=C bond in alkene radical cations. In those cases, semiempirical MNDO[24] calculations have proven to give estimates of the twist angles which are in good agreement with experimental data. For the 1-pentene radical cation, the various ab initio geometry optimizations also failed in predicting a twisted structure. In this case, MNDO calculations resulted in a structure with a 13° twist about the ionized C=C bond. A calculation was therfore attempted where the twist angle was fixed at this value, while the remaining parameters were reoptimized at the MP2/3-21G** level. The hf structure of this compound did, however, show the same erroneous pattern as the various planar conformers described above. It is only through a torsional motion about the C2–C3 bond, as obtained in conformer **b**, that H4 and H5 become chemically inequivalent, thereby producing a hf structure in satisfactory agreement with the experimental one.

2-Pentene. Two trans and one cis isomer of the 2-pentene radical cation, shown in Figures 4,**a**, **b** (trans), and **c** (cis), have been investigated using the MP2/3-21G** and SDCI techniques as outlined above. For the labeling of the individual atoms, we refer to Figure 4a. The electronic ground states are, for all three conformations of the 2-pentene radical cation, ^{2}A (C_s symmetry). No out-of-plane or twisted structures were considered in the theoretical studies.

In Table IV, the structural parameters obtained from the geometry optimization calculations are presented, along with the UHF, MP2, SDCI, and SDCI(Q) energies. We can see that the bond lengths are essentialy identical for the three conformations

Table IV. Structural Parameters for the Three Conformers a, b, and c of the 2-Pentene Radical Cation (Figure 4), Obtained from MP2/3-21G** Geometry Optimization Calculations[a]

	a	b	c
R(C1–C2)	1.484	1.485	1.485
R(C2–C3)	1.430	1.430	1.434
R(C3–C4)	1.487	1.484	1.487
R(C4–C5)	1.554	1.552	1.555
R(H1–C1)	1.079	1.079	1.078
R(H2–C1)	1.090	1.090	1.090
R(H4–C2)	1.078	1.076	1.077
R(H5–C3)	1.079	1.079	1.078
R(H6–C4)	1.093	1.093	1.092
R(H8–C5)	1.080	1.080	1.080
R(H9–C5)	1.081	1.082	1.081
$\angle$(C1–C2–C3)	123.8	123.5	125.1
$\angle$(C2–C3–C4)	122.8	125.0	124.1
$\angle$(C3–C4–C5)	114.3	117.2	113.8
$\angle$(H1–C1–C2)	113.0	113.2	113.8
$\angle$(H2–C1–C2)	108.8	108.8	108.5
$\angle$(H4–C2–C3)	117.9	118.1	117.3
$\angle$(H5–C3–C2)	117.5	117.2	116.9
$\angle$(H6–C4–C3)	107.6	106.3	107.9
$\angle$(H8–C5–C4)	109.3	108.8	109.3
$\angle$(H9–C5–C4)	110.5	111.1	110.5
E_{UHF}	−193.828 80	−193.829 39	−193.827 47
E_{MP2}	−194.335 77	−194.336 97	−194.334 95
E_{SDCI}	−195.218 83	−195.218 88	−195.215 98
$E_{SDCI(Q)}$	−195.476 4	−195.476 6	−195.477 0

[a] In the table we also report the UHF, MP2, SDCI, and extrapolated SDCI(Q) energies.

Table V. Data as in Table III, but for the 2-Pentene Radical Cation[a]

	a	b	c
H1	−0.06	−0.07	−0.13
H2, H3	24.66	25.18	22.27
(H1,H2,H3)$_{av}$	16.42	16.76	14.80
H4	−11.66	−11.83	−11.69
H5	−11.37	−11.06	−11.26
H6, H7	26.70	24.29	24.98
H8	−0.24	−0.30	−0.31
H9, H10	0.47	−0.04	0.39

[a] For the labeling of individual atoms, see Figure 4a. Experimental data are reported in Table I. Experimentally, a rotational average of the three methyl group proton hf couplings is observed, presented in the table as (H1,H2,H3)$_{av}$.

studied, the only exception being a slight elongated C=C bond in the cis conformer **c**. The steric effects of the different foldings of the ethyl tail in the two trans isomers **a** and **b**, and that of the local cis/trans orientation around the double bond affect, however, the bond angles slightly. From the absolute energies, listed in Table IV, it is found that conformation **b** is the energetically most favorable one. The difference compared to the other trans conformation **a** is, however, less than 3 kJ/mol at all levels of theory. The cis form **c** also lies very close in energy to the trans conformers.

The hyperfine structures of the 2-pentene radical cations are presented in Table V. For the α-protons there is an excellent agreement with the experimental ESR data reported above for any of the three considered structures. The hf couplings with positive sign ($a(H_\beta)$) are, as is usual at this level of approximation, only about 60% of the experimental ones (cf. refs 28 and 29), taking into account that the observed coupling of 28.4 G is assigned to a rotational average over H1, H2, and H3. As previously reported,[8,14] the fact that the unpaired electron mainly introduces a spin density at the α- and out-of-plane β-protons in small alkene radical cations is once again confirmed. We also note that the asymmetry of the molecule shifts the spin density distribution somewhat toward the longer side chain of the double bond, as has also been observed for, e.g., the 2-hexene radical cation.[14] The

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observed agreement between the experimental and theoretical hf structures of the 2-pentene radical cations thus indicates that we here have a typical π-bond ionization, in contrast to the findings of 1-pentene.

6. Discussion

The radical cations of 1- and 2-pentene have been investigated by means of low-temperature halocarbon matrix isolation ESR and computational ab initio techniques. The experimentally obtained isotropic proton hf coupling constants are compared with those obtained from accurate SDCI calculations, in order to determine the most probable geometric structures of the cations.

For the 1-pentene cation, the experimentally determined hyperfine coupling constants, recorded at 77 K in CFCl$_3$, have the absolute values $a_1(1H) = 57.0$ G and $a_2(2H) = 16.0$ G, and cannot be explained by assuming a planar structure with a typical π-bond SOMO or a structure where a torsional angle is introduced about the weakened C1=C2 double bond, the latter having been observed for a large number of smaller linear alkene cations.[14] A comparison with the hf couplings assigned to, e.g., the 1-butene radical cation in CFCl$_3$ at 77 K (Table I) indicates that the 1-pentene cation exhibits a different structure. In the 1-butene cation, the two methylene protons at C3 are equivalent with a coupling of 39 G,[6] indicating that all carbon atoms are (on the time average) situated in the same plane. In the 1-pentene radical cation, on the other hand, the large hf coupling constant (57.0 G) suggests that a rotation about the C2–C3 σ-bond is introduced. This conclusion is also supported by the theoretically determined hf coupling constants, generated from SDCI calculations on the various conformations. It is found that, at the extrapolated SDCI-(Q) level, a nonplanar structure where the C1 carbon is rotated out of the molecular plane is the most stable one. The calculated hf structure of this species satisfactorily reproduces the one observed experimentally.

The electronic structure obtained for the 1-pentene cation also provides an explanation to the observed differences in rigidity between 1-pentene$^+$, on one hand, and 2-pentene$^+$ or 3-hexene$^+$,[7,8] on the other. 2-Pentene$^+$ and 3-hexene$^+$, stabilized in halocarbon matrices, are typical π-type radical cations; i.e., the SOMO is essentially localized to the double bond, whereas, as mentioned above, the SOMO of 1-pentene$^+$ extends also over the adjacent carbon C3. In the π-type radical cations, there is essentially free rotation about the sp^2–sp^3 bond, whereas in 1-pentene$^+$, such rotation has not been observed (see Experimental Results). This is consistent with the calculated shortening of the sp^2–sp^3 bond from 1.51 to 1.44 Å on ionization, which as already mentioned depends on the antibonding character of the SOMO between C2 and C3.

The nature of the SOMO in 1-pentene$^+$ can to a large extent be attributed to the length of the saturated tail, making the ionization energies of the π-bond and the alkyl tail approach each other. In 2-pentene, the saturated part of the molecule is one carbon atom shorter and thus has a higher ionization energy. The mixing between the π orbital and the highest occupied orbital of the saturated part will therefore be smaller, and a typical ionization from a localized π-bond is observed.

For the 2-pentene radical cation, three planar conformers, shown in Figure 4, were optimized. The results from the SDCI calculations of the hyperfine parameters (Table V) are in very good agreement with the ESR measurements, and are interpreted as a pure π-bond ionization.