

## Twisting in Alkyl-Substituted Olefin Cation Radicals

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**Abstract:** UHF/AM1 semiempirical molecular orbital calculations have been used to investigate the effect of twisting on the ESR spectra of olefin cation radicals. It is concluded, in contrast to earlier results using MNDO calculations, that increasing alkyl substitution results in less twist around the central double bond and that the barrier to rotation through 90° increases with increasing alkyl substitution. These results are in accord with experimental observations.

The question of the structures of olefin cation radicals is one which has found much recent interest but one in which neither experiment nor theory can provide a definitive answer in many cases. The ethylene cation radical is found experimentally to be twisted about 25° in the gas phase with a planarization barrier of 0.7–0.8 kcal mol<sup>-1</sup>.<sup>1,2</sup> Shiotani and co-workers<sup>3a</sup> assigned the ESR spectrum obtained on irradiation of a dilute ethylene solution in a frozen halocarbon matrix to the ethylene cation radical. They assigned this spectrum to the ethylene cation radical, deducing a twisting angle of 40–50° from the large hydrogen splitting and the direction cosines of the <sup>13</sup>C *a*<sub>||</sub> features. However, Fujisawa et al.<sup>3b</sup> showed that ion–molecule reactions had occurred in the matrix and assigned the spectrum to the CH<sub>2</sub> end groups of a polymeric cation radical.

Handy et al.<sup>4</sup> have pointed out that very large basis set ab initio calculations with a high degree of correlation are necessary even to describe the torsional potential of H<sub>2</sub>C=CH<sub>2</sub><sup>•+</sup> qualitatively. In contrast, Bellville and Bauld<sup>5</sup> have pointed out that MNDO correctly predicts the twisted structure and have discussed the effect of alkyl substitution in olefin cation radicals on the basis of their MNDO results. They argue that the 40° twist and the 5.1 kcal mol<sup>-1</sup> planarization barrier calculated by MNDO for Me<sub>2</sub>C=CMe<sub>2</sub> are both quite reasonable on the basis of a simple steric effect and predict even more twist for more highly substituted tetraalkyl olefin cation radicals. However, MNDO is known<sup>6</sup> to underestimate rotation barriers in planar π-systems and not to treat hyperconjugation properly, so that it would be surprising if it gave a correct picture of olefin cation radical rotation profiles. If highly substituted olefin cation radicals were more twisted than Me<sub>2</sub>C=CMe<sub>2</sub><sup>•+</sup>, we would expect the barrier to rotation through 90° to be lowered significantly. However, Nelsen and Kapp<sup>7</sup> have published evidence that the barrier to rotation in 8,8'-bicyclo-[3.2.1]octylidene cation radicals is greater than 15 kcal mol<sup>-1</sup> and Berndt's group<sup>8</sup> has observed different ESR spectra for the even more sterically hindered *Z* and *E* forms of the 1,2-di-*tert*-butyl-1,2-dimethylethylene cation radicals at 188 K. Extreme steric hindrance can cause twisting about the double bond of olefin cation radicals, as for the very hindered tetra-*α*-tertiary olefin bi-2,2,5,5-tetramethylcyclopentylidene cation radical,<sup>9</sup> but the electronic effect of increasing substitution nevertheless seems to be to reduce the twist angle in olefin cation radicals.

ESR spectra for several simple alkylated olefin cation radicals in halocarbon matrices are now available,<sup>10–13</sup> as shown in Table I. Because the ESR spectra ought to be rather sensitive to twisting, these data should indicate whether twisting increases with increasing alkyl substitution or not. Although the original assignment of Shida et al. of the 2-butene cations being essentially planar<sup>10</sup> is generally accepted, the ESR spectra of the unsymmetrically substituted compounds have usually been interpreted as indicating substantial twisting.<sup>11,12</sup> We consider here the question of olefin cation radical geometry with the ESR data of

Table I in conjunction with Dewar's latest semiempirical MO method, AM1.<sup>13</sup> AM1 treats π-rotation barriers and hyperconjugation better than its predecessors and does not suffer as badly from the too large nonbonded interactions that plagued MNDO/3 and MNDO.<sup>14</sup> It also has the unexpected ability to predict both CH<sub>α</sub> and CH<sub>β</sub> ESR splittings accurately for Me<sub>*n*</sub>X species, where X = C•, N<sup>•+</sup>, O•, O<sup>•+</sup>, and S<sup>•+</sup> when quartet-annihilated<sup>15</sup> AM1-UHF spin densities are multiplied by 1177 G.<sup>16</sup> The success of the calculations at reproducing measured splitting constants suggests that AM1 should be useful for calculating the ESR spectra of olefin radical cations, which generally give ⟨*S*<sup>2</sup>⟩ values under 0.7501 after quartet annihilation. Although calculations of the ESR spectrum should be reasonable for the geometry calculated, the subtle question of the shape of the potential energy surface may not be handled well by AM1 calculations. Our approach has therefore been to calculate both the fully optimized geometries (which may be twisted) and those in which the central bond has not allowed to twist for each of the cation radicals considered. The agreement between the experimental ESR couplings and the calculated ones for both forms of the cation radical should give a reliable indication of the degree of twisting.

The results of some AM1 calculations as a function of twist angle are shown in Table II. AM1-UHF predicts almost twice as large a *θ* value for H<sub>2</sub>C=CH<sub>2</sub><sup>•+</sup> as does MNDO-UHF,<sup>6</sup> and all terminal olefin radical cations are calculated to have substantial twists, although the planarization barrier is calculated to go down as alkyl substitution increases. In contrast to MNDO, all of the 1,2-dialkylated species are calculated to prefer planar geometries, and the twisting barrier is found to increase as more alkyl groups are added. We have used the calculated ESR splitting values as a function of the twist angle to test the reliability of these predictions.

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**Table I.** Experimental and Calculated<sup>a</sup> Proton Splittings (Gauss) for Olefin Cation Radicals

cation form	H (type)	exptl $a(H)$	ref	calcd opt twist angle, deg	calcd $a(H)$ at opt	calcd $a(H)$ at 0° twist
MeHC=CH <sub>2</sub>	CH <sub>3</sub> ( $\beta$ )	27	12 <sup>b</sup>	40	+18.7	+27.4
	=CH <sub>2</sub> ( $\alpha$ )	16, 14			+1.0, 0.0	-13.3, -13.4
	=CH ( $\alpha$ )	5			+11.6	-7.1
EtHC=CH <sub>2</sub>	CH <sub>2</sub> ( $\beta$ )	36.3-37	10, 13	40	+37.0	+49.1
	=CH <sub>2</sub> ( $\alpha$ )	13.0-13.3			-2.6, -2.8	-13.5, -13.6
	=CH ( $\alpha$ )	3.2-4.2			+8.5	-6.3
Me <sub>2</sub> C=CH <sub>2</sub>	CH <sub>3</sub> ( $\beta$ )	16.4-16.9	10, 12, 13	36	+13.9	+16.5
	=CH <sub>2</sub> ( $\alpha$ )	13.5-14.0			-9.8	-14.9
MeHC=CHMe (cis)	CH <sub>3</sub> ( $\beta$ )	23.6-24.1	10, 13	24	+24.8	+28.7
	=CH ( $\alpha$ )	9.3-9.5			-4.0	-9.6
MeHC=CHMe (trans)	CH <sub>3</sub> ( $\beta$ )	23.9-27.4	10, 13	5	+27.4	+27.5
	=CH ( $\alpha$ )	9.8-9.9			-9.2	-9.4
Me <sub>2</sub> C=CHMe	CH <sub>3</sub> ( $\beta$ )	16.8	11 <sup>c</sup>	0	16.9, 18.1	same
	CH <sub>3</sub> ( $\beta$ )	21.8			+25.7	
	=CH ( $\alpha$ )	26.0			-11.7	
c-C <sub>5</sub> H <sub>8</sub>	CH <sub>2</sub> ( $\beta$ )	53.0, 48.5	10 <sup>d</sup>		+43.9	same
	CH <sub>2</sub> ( $\gamma$ )	12.5, 5.5			(+5.1)	
	=CH ( $\alpha$ )	8.6			-9.1	
c-C <sub>6</sub> H <sub>10</sub>	CH <sub>2</sub> ( $\beta$ )	54.0, 22.5	10		55.7, 26.3	same
	=CH ( $\alpha$ )	8.8			-9.4	
[2.2.2]octene	=CH ( $\alpha$ )	0.4 (2 H, 4.2 K)	18		-10.5	same
		9.0 (4 H, 77 K)				

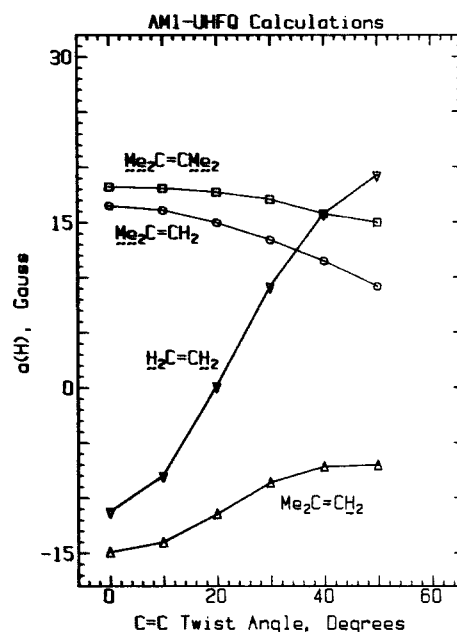
<sup>a</sup> Calculated from AM1-UHF calculations with quartet-annihilated H spin density  $\times 1177$  as  $a(H)$  (G). <sup>b</sup> Reported for SF<sub>6</sub> matrix at 130 K. CFCl<sub>3</sub> matrix, 130 K gave the following: CH<sub>3</sub>, 14; =CH<sub>2</sub>, 16 and 19; =CH, 9. At 77 K, larger differences between the =CH<sub>2</sub> splittings are observed; 12 and 23 for a CHCl<sub>3</sub> matrix; ref 12 reports 11.0 and 23.5. <sup>c</sup> The authors suggested the following as an alternate assignment to the same spectrum: =CH, 620; 2 CH<sub>3</sub>, 16.7; CH<sub>3</sub>, 21.0. <sup>d</sup> For "frozen" spectrum at 77 K. At 130 K, ring reversal equilibrates the hydrogens and the following were observed: CH<sub>2</sub> ( $\beta$ ), 49.3 (4 H); CH<sub>2</sub> ( $\gamma$ ), 7.0 (4 H); =CH, 9.8.

**Table II.** AM1-UHF Calculations<sup>a</sup> on Alkene Cation Radicals

species (neutral)	$\Delta H_f(\text{opt})$ , kcal/mol	twist $\angle$ , $\theta$ , deg	$\Delta\Delta DH_f$ , ( $\theta = 0^\circ$ )	$\Delta\Delta H_f$ , ( $\theta = 90^\circ$ ) <sup>b</sup>
H <sub>2</sub> C=CH <sub>2</sub>	242.6	44.6	4.7	11.3
MeHC=CH <sub>2</sub>	222.0	40	1.1	7.3
EtHC=CH <sub>2</sub>	213.9 <sup>c</sup>	40	1.1	7.2
Me <sub>2</sub> C=CH <sub>2</sub>	205.4	36	0.8	5.8
cis-MeHC=CHMe	202.4	24	0.3	10.6
trans-MeHC=CHMe	201.4	5	0.0	11.6
Me <sub>2</sub> C=CHMe	187.6	0	0.0	10.6
Me <sub>2</sub> C=CMe <sub>2</sub>	173.9	0	0.0	13.7
c-C <sub>5</sub> H <sub>8</sub>	206.1	0		
c-C <sub>6</sub> H <sub>10</sub>	192.2	0		

<sup>a</sup> See ref 17. <sup>b</sup> Calculated with flat carbons, equivalent ends if symmetrical. For C<sub>2</sub>H<sub>4</sub><sup>++</sup>, only 0.1 kcal/mol stabilization occurs when this D<sub>2</sub> symmetry is allowed to relax to C<sub>2</sub>. <sup>c</sup> CH<sub>3</sub>CH<sub>2</sub>-CHC dihedral angle 0° is calculated to be 0.06 kcal/mol more stable than 180° at the energy optimum and 0.38 less stable for  $\theta = 0^\circ$ .

The general characteristics of the  $\alpha$  and  $\beta$  splittings calculated for olefin cation radicals are shown in the figures for the parent, mono-, di-, and tetramethyl compounds. Figure 1 shows the results obtained for H<sub>2</sub>C=CH<sub>2</sub><sup>++</sup>, Me<sub>2</sub>C=CH<sub>2</sub><sup>++</sup> and Me<sub>2</sub>C=CMe<sub>2</sub><sup>++</sup>. The  $\alpha$  splittings in the ethylene cation radical are far more sensitive to twisting than those in the isobutene cation radical, and the  $\beta$ -methyl splittings are relatively insensitive to the twist angle. Localization of the positive charge on the alkylated carbon (and hence the spin on the methylene) in the isobutene cation radical means that the spin density at the CH<sub>2</sub> carbon does not change strongly on twisting. In the ethylene cation radical, on the other hand, twisting allows direct spin delocalization from the vicinal carbon center to the CH<sub>2</sub> group and therefore increased the calculated splitting markedly. The *cis*- and *trans*-2-butene cation radicals show similar effects to the ethylene cation radical (because the charge is not localized on one carbon), but not to such a high degree (see Figure 2). The hyperconjugative stabilization provided by the methyl groups reduces the importance of hyperconjugation across the double bond on twisting, and so the  $\alpha$  coupling constants are less sensitive than in the parent system. Figure 3 shows the calculated data for the propene cation radical. As might be expected, the  $\alpha$  splittings are more sensitive to twisting than in the more highly substituted olefin cation radicals. The hydrogen *geminal* to the methyl group is the most sensitive because it interacts with the CH<sub>2</sub> group, where most of the spin is localized,



**Figure 1.** Calculated (AM1-UHF with quartet annihilation (AM1-UHFQ)) ESR splittings for CH<sub>2</sub>=CH<sub>2</sub><sup>++</sup>, Me<sub>2</sub>C=CH<sub>2</sub><sup>++</sup>, and Me<sub>2</sub>C=CMe<sub>2</sub><sup>++</sup> as a function of the C=C twist angle. The protons causing the splitting are underlined.

on twisting. However, the two methylene protons also show a strong dependence on twisting because there is relatively little hyperconjugative stabilization available from the single methyl group. The monosubstituted compounds are particularly sensitive to matrix interactions, but their spectra at higher temperatures agree well with the calculations. The energy surface for twisting is calculated to be quite shallow, but this is not found to cause the large difference in the =CH<sub>2</sub> proton splittings observed at very low temperatures. A specific matrix interaction that caused bending at the CH<sub>2</sub> carbon of the monosubstituted olefin cation radicals (which have the highest ionization potentials<sup>17</sup>) would

(17) For a discussion of the effect of ionization potential on matrix interactions, see: Clark, T.; Hasegawa, A.; Symons, M. C. R. *Chem. Phys. Lett.* **1985**, *116*, 79.

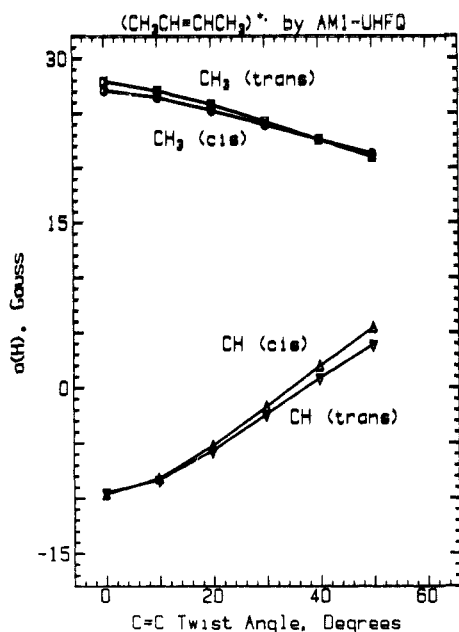


Figure 2. Calculated (AM1-UHFQ) ESR splittings for the propene cation radical as a function of the twist angle.  $H_2$  is the methine proton, and  $H_c$  and  $H_t$  are the methylene protons *cis* and *trans* to the methyl group, respectively.

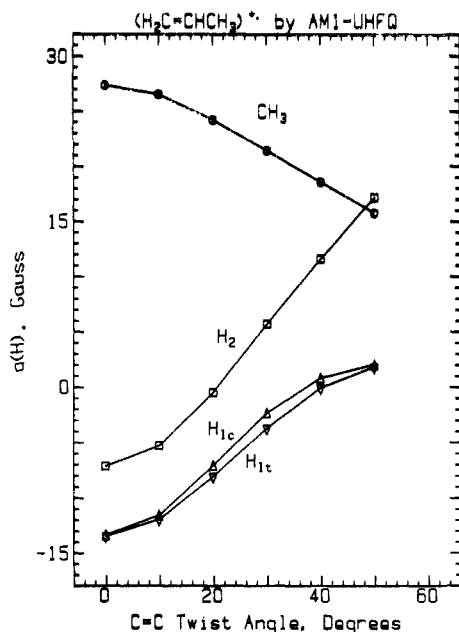


Figure 3. Calculated (AM1-UHFQ) ESR splittings as a function of the twist angle for *cis*- and *trans*-2-butene cation radicals.

explain the low-temperature results. Both the  $\beta$ -methyl splitting and the  $\alpha$ -proton splittings are consistent with a nearly planar structure as are those for  $Me_2C=CH_2^{*+}$ . Neither analysis reported<sup>11</sup> for the very complex  $Me_2C=CHMe^{*+}$  spectrum agrees well at all with the calculated splittings, but twisting does not appear to be the problem. The authors of the experimental work<sup>11</sup> note that the background signal overlaps the wings of the spectrum so that neither of the assignments reported is very certain. We note that the spectral width calculated by AM1 is 194 G, compared with an experimental value of either 192 or 225 G. The very high splitting assigned to the vinylic proton in this compound must be regarded as doubtful until further experimental work is available. The conclusion suggested by the calculations, however, is that  $Me_2C=CHMe^{*+}$  is planar, on the basis of both the results for this compound and the trends shown by other olefin cation

radicals. The  $\beta$ -hydrogen splitting obtained for cyclopentene is substantially smaller than that obtained experimentally, in contrast to the reverse situation for the  $\beta$  splitting of the butene cation radical. Although AM1 predicts a planar  $C_5$  ring to be the energy minimum, bending until the calculated ratio between the two  $\beta$  splitting constants is the observed 1.09 is found to be very easy ( $C=C$ ,  $CH_2CH_2$  dihedral angle about  $176^\circ$ ; energy under 0.2 kcal mol<sup>-1</sup> higher than the minimum).  $\gamma$  splittings are not handled well by these calculations,<sup>16</sup> and we place no significance on the good agreement of the observed and calculated splittings. The cyclohexene cation radical  $\beta$  splittings are calculated rather well, especially in comparison to the 1-butene cation radical and cyclopentene cation radical. Also shown in Table II are the splittings recently reported<sup>18</sup> for the radical generated from bicyclo-[2.2.2]octene. The 2 H splitting observed at 4.2 K is not consistent with that calculated for the cation of the starting olefin nor with that observed experimentally for the other *cis*-1,2-dialkyl olefin cation radicals.

The data shown in Table II allow a consistent picture of the structures of olefin cation radicals. Apart from the two experimentally uncertain olefins, the calculated AM1 ESR splittings are all consistent with essentially planar  $C=C^{*+}$  linkages for the alkylated olefin cation radicals, including propene cation radical. *cis*-2-Butene cation radical may show some twisting, but the results are not accurate enough to decide on the exact structure. Therefore, the only olefin radicals with a well-documented twisted structure are the ethylene cation radical itself and the trimethylsilyl olefin cation radicals reported by Sakurai et al.<sup>19</sup> These exceptions are easy to understand on the basis of a competition between hyperconjugation and one-electron  $\pi$ -bonding as stabilizing factors. The ethylene cation radical can only benefit from hyperconjugation by twisting about the central bond. The observed structure is a compromise that allows the singly occupied  $\pi$ -orbital, which is an extremely strong acceptor, to interact with the CH bonds without sacrificing the one-electron  $\pi$ -bond. As the olefin is substituted with alkyl groups, however, these take over the hyperconjugative stabilization of the SOMO, so that twisting is no longer necessary. The situation is different in the case of trimethylsilyl substituents. Hyperconjugation by an  $\alpha$ -trimethylsilyl group is very weak because of the electropositive nature of silicon.<sup>20</sup> Twisting the central bond, however, allows the positive charge to be stabilized by hyperconjugation with  $\beta$ -trimethylsilyl substituents across the double bond. Cation stabilization by  $\beta$ -trimethylsilyl is known<sup>20</sup> to be a very large effect that can compete with the one-electron  $\pi$ -bond.

In conclusion, comparison of the calculated splittings with the experimental splittings indicates that AM1 calculates the mono- and the 1,1-disubstituted compounds to be more twisted than they really are. The trend toward more difficult twisting as the number of substituents increases given by AM1 is consistent with experimental results, as indicated in the first paragraph, and we suggest that the opposite conclusion reached by Bellville and Bauld was caused principally by the too large nonbonded interactions given by MNDO.<sup>6,14</sup> Qualitatively, olefin cation radicals should twist when hyperconjugative stabilization can only be achieved by interaction with  $\beta$ -substituents, as in the parent ethylene cation radical and in the trimethylsilyl olefin cation radicals. When  $\alpha$ -substituents are available to stabilize the positive charge hyperconjugatively, the tendency to twist goes down sharply.

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(18) Calculations were carried out with the AMPAC 1.00 Package (*QCPE Bull.* 1986, 506, 24a) with Bischof's spin annihilation subroutine (*QCPE Bull.* 1979, 383).

(19) Numone, K.; Toriyama, K.; Iwasaki, M. *Tetrahedron* 1986, 42, 6315.

(20) See, for instance: Fleming, I. In *Comprehensive Organic Chemistry*; Pergamon: Oxford, 1979; Vol 3.