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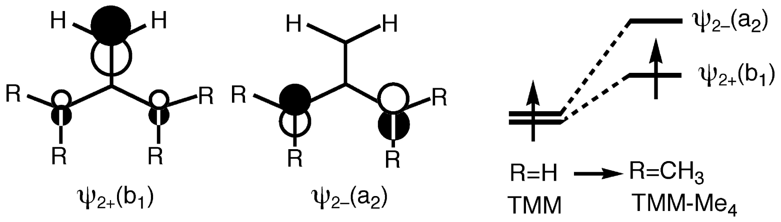

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Radical Cation of a Trimethylenemethane with a Nondegenerate Ground State

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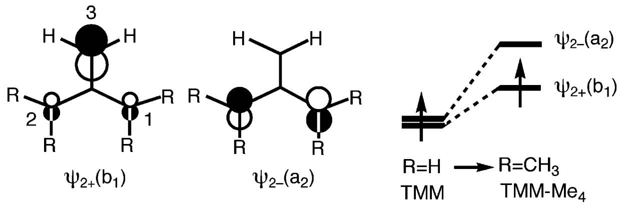
Abstract: Upon ionization by γ-irradiation in frozen $CFCl_3$, or by X-irradiation in an Ar matrix, 2,2,3,3-tetramethylmethylenecyclopropane (MCP-Me_4) readily undergoes ring opening to yield the radical cation of 1,1,2,2-tetramethyltrimethylenemethane (TMM-Me_4). The hyperfine-coupling constants for TMM-$Me_4{}^{\bullet+}$ are (mT) −1.99 (2H), +0.53 (6H), and +0.19 (6H), and the singly occupied orbital closely resembles one of the two degenerate nonbonding π-MOs (NBMOs) of trimethylenemethane (TMM). Due to the expected effect of the methyl substituents, this "symmetric" NBMO, ψ_{2+} (b_1), is energetically favored relative to its "antisymmetric" counterpart, ψ_{2-} (a_2), so that the ground state assumes a structure with $^2B_1$ symmetry in the C_{2v} point group. Calculations show that the ring opening in the primary radical cation MCP-$Me_4{}^{\bullet+}$ to yield TMM-$Me_4{}^{\bullet+}$ is spontaneous, whereas in the parent system (MCP$^{\bullet+}$ → TMM$^{\bullet+}$) a low barrier does exist. In contrast to the previously investigated case of the radical cation of tetramethyleneethane, the "electromer" of TMM-$Me_4{}^{\bullet+}$, in which the unpaired electron occupies ψ_{2-}, cannot be attained photochemically.

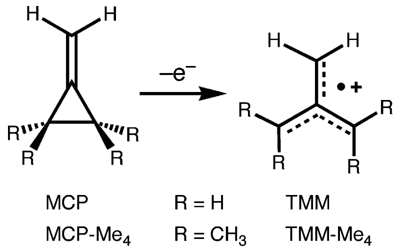
Introduction

Trimethylenemethane (TMM) is the simplest known 4π-electron system of D_{3h} symmetry, for which a Kekulé formula cannot be drawn without two unpaired electrons at least (non-Kekulé hydrocarbon).[1] A pair of electrons occupies a bonding π-MO ψ_1, and the remaining two electrons are accommodated by a pair of degenerate nonbonding π-MOs (NBMOs). Several ESR studies have shown that the ground state of TMM is a triplet (TMM$^{\bullet\bullet}$), with the two NBMOs singly occupied by the two unpaired π-electrons.[1,2] These NBMOs (b_1 and a_2, respectively, in the C_{2v} point group) can be formulated in the LCAO representation as

$$\psi_{2+}\,(b_1) = (1/\sqrt{6})(\phi_1 + \phi_2 - 2\phi_3) \quad \text{and}$$
$$\psi_{2-}\,(a_2) = (1/\sqrt{2})(\phi_1 - \phi_2)$$

where ϕ_1, ϕ_2, and ϕ_3 stand for the $2p_z$-AOs at the three peripheral C atoms of TMM. The pictorial diagram of the two NBMOs drawn below shows that ψ_{2+} is symmetric and ψ_{2-} is antisymmetric with respect to the vertical mirror plane that contains the bond connecting C-3 to the central atom.





The corresponding radical cation (TMM$^{\bullet+}$) is a 3π-electron system, in which the bonding MO ψ_1 is doubly occupied and the unpaired electron is shared by the NBMOs ψ_{2+} and ψ_{2-}; i.e., TMM$^{\bullet+}$ has a degenerate ground state subject to Jahn−Teller (JT) distortion.[3,4] The first attempts to observe the ESR spectrum of TMM$^{\bullet+}$ after γ-irradiation of methylenecyclopropane (MCP) in $CFCl_3$, CF_3CCl_3, and $CF_2ClCFCl_2$ matrices at 77 K had failed, and only the spectra of the triplet TMM$^{\bullet\bullet}$ [5,6a] and a few other, not fully identified species were detected.[3,5] Eventually, use of CF_2ClCF_2Cl or perfluorinated methylcyclohexane (CF_3-c-C_6F_{11}) as matrix led to an ESR spectrum

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‡ University of Basel.
§ University of Göttingen.

(1) Borden, W. T.; Iwamura, H.; Berson, J. A. *Acc. Chem. Res.* **1994**, *27*, 109.
(2) Dowd, P. *Acc. Chem. Res.* **1972**, *5*, 242.
(3) Komaguchi, K.; Shiotani, M.; Lund, A. *Chem. Phys. Lett.* **1997**, *265*, 217.
(4) Shiotani, M.; Komaguchi, K. In *EPR of Free Radicals in Solids*; Lund, A., Shiotani, M., Eds.; Kluwer Academic Publishers: Dordrecht, The Netherlands, 2003; p 175.
(5) Schmidlin, R., Ph.D. Dissertation, University of Basel, Switzerland, 1995.
(6) Gerson, F.; Huber, W. *Electron Spin Resonance Spectroscopy of Organic Radicals*; Wiley-VCH: Weinheim, Germany, 2003; (a) Figure 4.9, (b) p 216, (c) Table 8.2.

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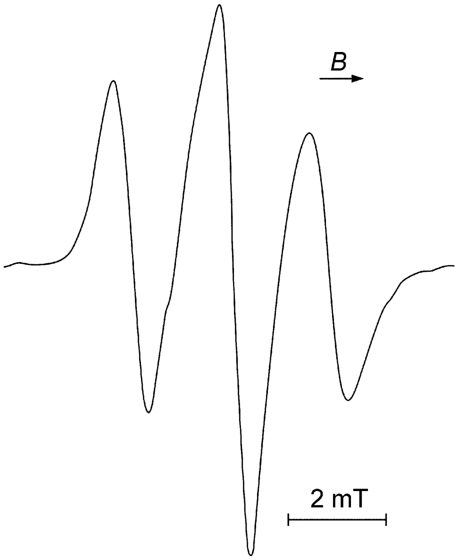

Figure 1. ESR spectrum of ionized MCP-Me$_4$ in frozen CFCl$_3$ at 150 K.

consistent with that expected for TMM$^{\bullet+}$.[3] This spectrum exhibits seven lines spaced by 0.93 mT with a binomial distribution of intensities, which indicates an effective D_{3h} symmetry. Single occupancy of either ψ_{2+} or ψ_{2-}, which would point to a static JT distortion, was not observed down to 4 K.[3] It is interesting to note that, even when ionization of MCP was effected at 4 K, no trace of MCP$^{\bullet+}$ was observed. This radical cation thus appears to undergo spontaneous ring opening to TMM$^{\bullet+}$, nonwithstanding the fact that calculations predicted a barrier of about 2 kcal/mol for the process.[7]

The degeneracy of the NBMOs ψ_{2+} and ψ_{2-} can be removed by perturbing the π-system of TMM. If the perturbation is due to electron-releasing substituents at π-centers 1 and 2, the MO ψ_{2-} with the larger squared LCAO coefficients ($^1/_2$) at these centers should be more strongly destabilized than ψ_{2+} for which the corresponding squared coefficients are only $^1/_6$. In the relevant radical cation, the degeneracy of the ground state would thus be removed in such a way that the unpaired electron occupies the lower lying MO ψ_{2+}[6b] (cf. the above MO scheme). This expectation should be met, e.g., in the radical cation of 1,1,2,2-tetramethyltrimethylenemethane (TMM-Me$_4$).

Spectra

ESR and ENDOR. Ionization of of 2,2,3,3-tetramethylmethylenecyclopropane (MCP-Me$_4$) is easier than that of the parent MCP, as the four methyl groups lower the required energy from 9.6 eV[8,9] to 9.2 eV[10] in the gas phase (maximum of the first bands in the photoelectron spectra). When MCP-Me$_4$[11] was ionized in a CFCl$_3$ matrix by γ-irradiation at 77 K, an unresolved ESR signal extending over ca. 9 mT appeared. Upon raising the temperature to 150 K, the signal split into three broad components spaced by 1.99 ± 0.02 mT and diagnostic of two equivalent protons, undoubtedly those of the methylene group (Figure 1, peak-to-peak-distance 0.7 mT, $g = 2.00250 \pm 0.00005$). Because of the high hyperfine anisotropy usually encountered with large coupling constants of protons directly attached to π-centers (α-protons in ESR nomenclature), the ^{1}H ENDOR signals associated with the $|a_H|$ value of 1.99 mT and expected at $|a_H/2| \pm \nu_H = 42.5$ and 13.3 MHz escaped observation ($\nu_H = 14.56$ MHz). However, the ^{1}H ENDOR spectrum (Figure 2) exhibited signals of isotropic shape arising from two sets of equivalent protons, each set obviously consisting of six protons in two freely rotating methyl substituents.[12] The pair of signals at $\nu_H \pm |a_H/2| = 17.23$ and 11.89 MHz yields the coupling constant $|a_H|$ of 5.34 ± 0.08 MHz or 0.190 ± 0.003 mT, while the signal at $\nu_H + |a_H/2| = 22.0$ MHz indicates another $|a_H|$ value of 14.9 ± 0.3 MHz or 0.53 ± 0.01 mT (its low-frequency partner at $\nu_H - |a_H/2| = 7.1$ MHz is hardly above the noise level). The ESR spectrum is well reproduced by simulation with a line width of 0.3 mT, using the coupling constants $|a_H|$ of 1.99 mT for two protons and 0.53 and 0.19 mT, each for six protons. As will be justified below, the observed ESR and ENDOR spectra are attributed to TMM-Me$_4$$^{\bullet+}$, which is formed by opening the distal bond of the three-membered ring in ionized MCP-Me$_4$.

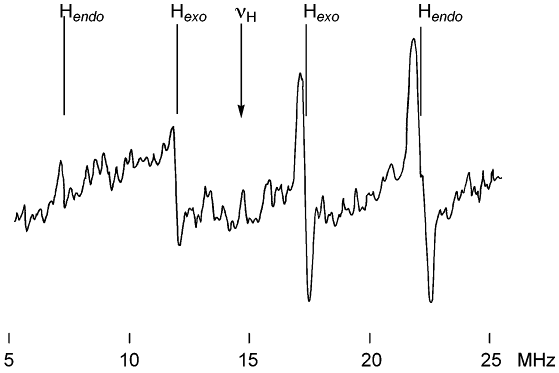

Figure 2. ^{1}H ENDOR spectrum of ionized MCP-Me$_4$ in frozen CFCl$_3$ at 150 K.

UV/Vis. Ionization of MCP-Me$_4$ in Ar at 10 K led to no perceptible coloration of the matrix. The reason becomes evident on inspection of Figure 3, which shows that the species formed in this process is practically transparent in the visible region of the spectrum (ignoring very weak absorptions which appeared only upon strong expansion). However, a weak, broad transition in the near-IR ($\lambda_{max} = 1700$ nm) was observed, next to bands of increasing intensity that peak at 390, 295, and 232 nm, respectively.

On subsequent irradiation of the sample through an 850 nm cutoff filter, all absorptions that were newly formed on X-irradiation are bleached (see red difference spectrum), which demonstrates that the above-mentioned bands all belong to the same species, and that only this species is produced by ionization (and is bleached on near-IR irradiation).

Unfortunately, the changes in the IR spectra recorded on the matrix-isolated samples, the electronic absorption spectra of which are shown in Figure 3, were too weak to be of any diagnostic value.

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(7) Du, P.; Borden, W. T. *J. Am. Chem. Soc.* **1987**, *109*, 5330.

(8) Wiberg, K. B.; Ellison, G. B.; Wendoloski, J. J.; Brundle, C. R.; Kuebler, N. A. *J. Am. Chem. Soc.* **1976**, *98*, 7179.

(9) Bieri, G.; Burger, F.; Heilbronner, E.; Maier, J. P. *Helv. Chim. Acta* **1977**, *60*, 2213.

(10) Kindermann, M. K.; Poppek, R.; Rademacher, P.; Fuss, A.; Quast, H. *Chem. Ber.* **1990**, *123*, 1161.

(11) Arora, S.; Binger, P. *Synthesis* **1974**, 801.

(12) Methyl substituents usually rotate freely in Freon matrices above 77 K on the hyperfine time scale. Accordingly, the three protons of each methyl group appear to be equivalent in the ENDOR spectrum of TMM-Me$_4$$^{\bullet+}$ at 150 K, although full rotation may be somewhat hindered due to the steric congestion by the *endo* groups (see the Calculations and Discussion).

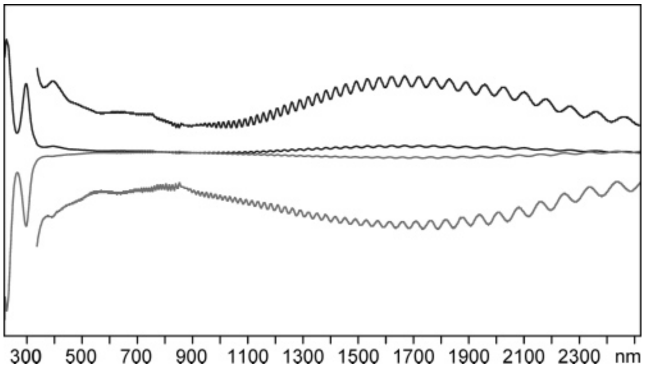

Figure 3. Difference spectra observed after ionization of MCP-Me$_4$ by X-irradiation in an Ar matrix at 20 K and after subsequent bleaching of the resulting radical cation by >850 nm irradiation (difference spectrum, the spectrum taken after irradiation or bleaching minus the spectrum taken before that event).

Calculations and Discussion

In first order, JT distortion reduces the symmetry of TMM$^{•+}$ from D_{3h} to C_{2v}. In this point group, the ground state has $^2B_1$ or $^2A_2$ symmetry, depending on which of the NBMOs, ψ_{2+} (b$_1$) or ψ_{2-} (a$_2$), respectively, is singly occupied. In the absence of distortions due to second-order effects, the JT potential energy surface on which these two states are located should show three equivalent minima and three equivalent transition states interconnecting them, all of C_{2v} symmetry.[13] UHF/6-31G** geometry optimizations in C_{2v} predicted the $^2A_2$ state to be slightly more stable than its $^2B_1$ counterpart,[3,4] which led the authors of this study to suggest that the effective D_{3h} symmetry and the coupling to six equivalent protons observed in the ESR spectrum at 4 K are brought about by averaging of three equivalent $^2A_2$ structures. For these structures, INDO calculations yielded ^{1}H hyperfine-coupling constants a_H of +0.20 mT for the two methylene α-protons at C-3 and −1.37 mT (*endo*)/−1.44 mT (*exo*) for the two pairs of such protons at C-1 and C-2.[3,4] Conversely, the corresponding a_H values for the $^2B_1$ structure were predicted as −1.99 mT for the two protons at C-3 and −0.35 mT (*endo*)/−0.29 mT (*exo*) for those at C-1 and C-2.

Remarkably, the ESR spectrum in Figure 2 exhibits the hyperfine splitting by the two methylene α-protons with $|a_H|$ of (exactly) 1.99 mT, while the ^{1}H ENDOR signals in Figure 3 are associated with coupling constants $|a_H|$ of 0.53 and 0.19 mT arising from the two sets, each of six protons in two methyl substituents (β-protons in ESR nomenclature). The hyperfine data derived from the observed ESR and ENDOR spectra are thus fully consistent with those expected for the radical cation of TMM-Me$_4^{•+}$, in which the shape of the singly occupied MO closely resembles that of ψ_{2+} (b$_1$), and the ground state should therefore have $^2B_1$ symmetry in the C_{2v} point group.

This assignment was corroborated by B3LYP/6-31G* calculations, which yield $a_H = -2.05$ mT for the two methylene α-protons and a_H(average) = +0.47 (*endo*)/+0.25 mT (*exo*) for the two sets of six methyl β-protons. These values hold for TMM-Me$_4^{•+}$ at a computed equilibrium geometry of C_2 symmetry (the C_{2v} symmetry is lowered due to steric congestion by the two *endo*-methyl groups). TMM-Me$_4^{•+}$ can also adopt an equilibrium geometry of C_s symmetry, but this conformation is 1.7 kcal·mol^{-1} less stable than that with C_2 symmetry, and the agreement between calculated and experimental $|a_H|$ values is also slightly inferior for the latter than for the former. It is noteworthy that all theoretical calculations for TMM-Me$_4^{•+}$ (and those for the $^2B_1$ structure of TMM$^{•+}$) predict the $|a_H|$ values at C-1 and C-2 to be larger for the *endo* than for the *exo* positions, in contrast to the analogous results for the $^2A_2$ structure of TMM$^{•+}$ and various allyl radicals.[6c] However, in the $^2B_1$ state (where the NBMO ψ_{2+} is singly occupied), the spin populations at C-1 and C-2 are low, whereas in the $^2A_2$ state (singly occupied NBMO ψ_{2-}), the spin is almost entirely located on these two atoms.[14]

According to B3LYP/6-31G* calculations, there is no stationary point on the potential energy surface that represents a minimum for the primary radical cation MCP-Me$_4^{•+}$. The results of these calculations, displayed in Figure 4, are relevant to understanding the mechanism of ring opening in MCP$^{•+}$ and in its tetramethyl derivative and to clarifying the structure of TMM$^{•+}$ and its derivative thus obtained.

When the bands in the photoelectron spectrum of MCP were assigned,[8,9] it was found that the lowest three electronic states of MCP$^{•+}$ are attained by ionization from the π-MO (b$_1$) and the two σ-Walsh-MOs (b$_2$ and a$_1$) of the cyclopropane ring. These MOs and the relative B3LYP/6-31G* energies of the corresponding ionic states at the optimized geometry of neutral MCP are shown on the left-hand side of Figure 4.[15] Optimization of the three states within C_{2v} symmetry leads to a very strong stabilization of the two σ-states (28.5 kcal/mol for $^2A_1$, 18.4 kcal/mol for $^2B_2$) and less so of the π-state ($^2B_1$, 5.4 kcal/mol), but none of the resulting structures represent minima on the potential energy surface ($^2A_1$ is a transition state, while $^2B_1$ and $^2B_2$ are second-order saddle points). When the exocyclic methylene group is twisted (lowering of the symmetry to C_2), the close-lying $^2B_1$ and $^2B_2$ states undergo vibronic coupling to yield an equilibrium structure of ^2B symmetry, in which the singly occupied MO corresponds to a mixture of the b$_1$ (π) and the b$_2$ (σ) MOs (cf. the third column in Figure 4).

As pointed out previously by Du and Borden,[7] this structure connects adiabatically to the $^2B_1$ state of TMM$^{•+}$ along a pathway involving disrotation of the cyclopropylidene CH$_2$ groups. The activation energy for the ring opening is predicted to be 2.31 kcal/mol, which explains why MCP$^{•+}$ was never observed.[3,5,16] In contrast to the MP2 and SDCI calculations of Du and Borden, but in accordance with the UHF/6-31G** calculations by Komaguchi et al.,[3] we found that the $^2A_2$ state of TMM$^{•+}$ is slightly more stable than the $^2B_1$ state (1.76 kcal/

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(13) Herzberg, G. *Molecular Spectra and Molecular Structure, Vol III: Electronic Spectra and Electronic Structure of Polyatomic Molecules*; Van Nostrand Reinhold: New York, 1966; p 48.

(14) As expected, the sum of the a_H values predicted by INDO[3,4] for the *endo*-protons at C-1 and C-2 in the $^2A_2$ and $^2B_1$ structures of TMM$^{•+}$ is equal to that for the *exo*-protons: −1.37 mT − 0.35 mT = −1.72 mT vs −1.44 mT − 0.29 mT = −1.73 mT. An increase (decrease) in the $|a_H|$ values for protons in one structure thus goes along with a decrease (increase) in the values for the corresponding protons in the other structure.

(15) B3LYP reproduces well the ionization energies and the ordering and the relative energies of the lowest three ionic states at the neutral geometry. The energy difference between the maxima of the first two peaks in the photoelectron spectrum of TMM was measured to be 0.90 eV, and the calculated difference between the corresponding ionic states is 0.87 eV. The difference between the first and the third peak is 1.78 eV experimentally vs 1.39 eV calculated. Thus, the B3LYP/6-31G* method appears to slightly overstabilize the $^2A_1$ relative to the other two ionic states of TMM.

(16) Including the zero-point energy difference, the activation energy drops to 2.05 kcal/mol. At 4 K, this energy is 250 times larger than *RT*, so even such a small barrier would be sufficient to effectively prevent *thermalized* MCP$^{•+}$ in its ^{2}B state from decaying to TMM$^{•+}$ at 4 K. However, the excess energy with which this state is initially endowed apparently suffices to surmount this barrier.

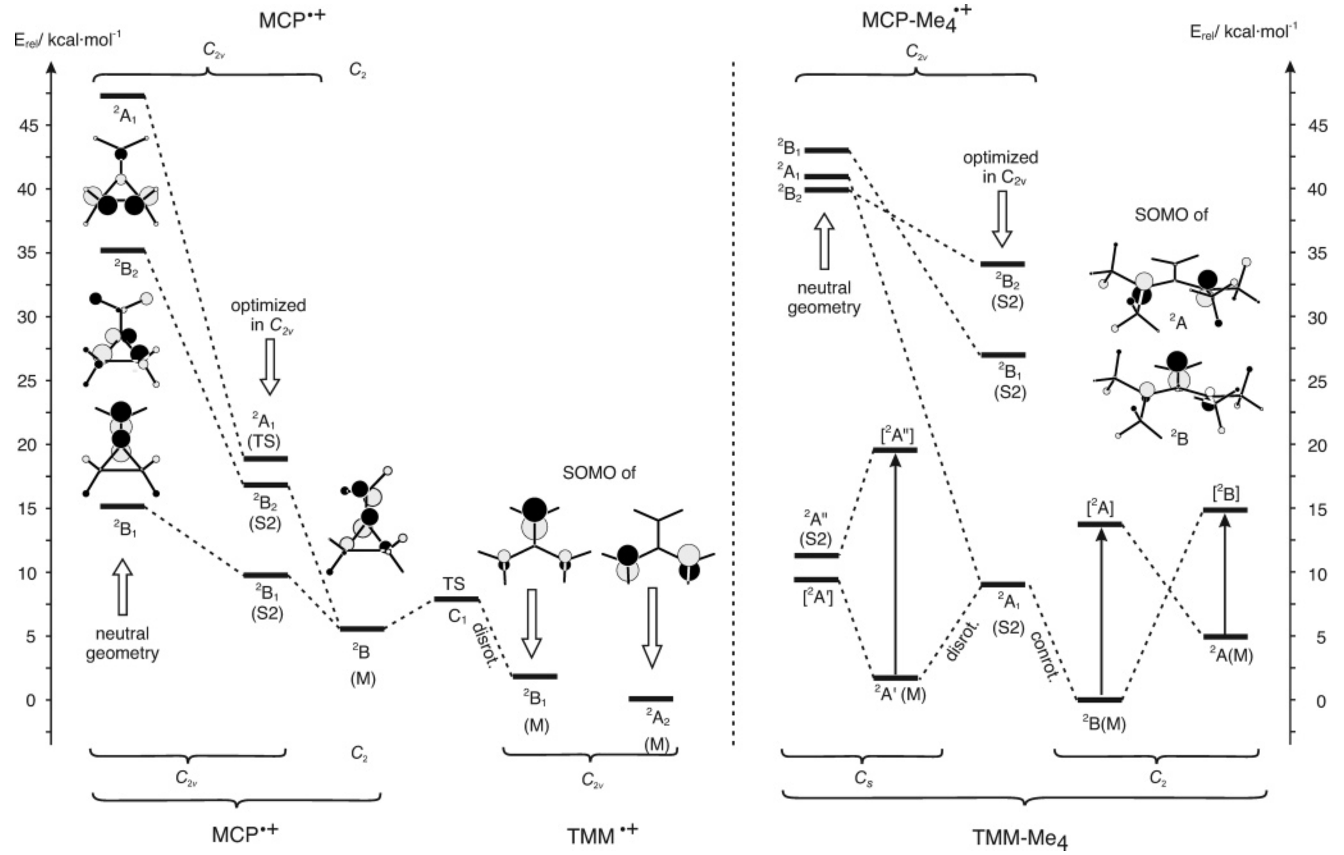

Figure 4. Potential energy surfaces for the decay of MCP$^{\bullet+}$ and MCP-Me$_4$$^{\bullet+}$ from B3LYP/6-31G* calculations (TS = transition state, S2 = second-order saddle point, M = minimum). For a discussion, see the text.

mol by B3LYP/6-31G*), but surprisingly both states turn out to be minima, which raises the question of the nature of this potential surface.[17] As the ESR spectrum of TMM$^{\bullet+}$ indicates effective D_{3h} symmetry, i.e., a dynamic JT distortion, even at 4 K, there is no experimental basis on which this question could be discussed. Therefore, we refrained from further exploration of this point.

Instead, we turned to the tetramethyl derivative (MCP-Me$_4$, right-hand side, top of Figure 4) for which, according to our calculations, the three above-mentioned states are much more closely spaced than in MCP. This result is in line with the photoelectron spectrum of MCP-Me$_4$, which shows a peak at 9.20 eV followed by a second peak at 9.42 and a shoulder at ca. 9.95 eV.[18] Although a quantitative comparison indicates that the $^2A_1$ state is probably again overstabilized by ca. 0.4 eV (and may in fact lie above the $^2B_1$ state at the neutral geometry), it clearly becomes the ground state on optimization of the three ionic states in C_{2v} symmetry. However, all stationary points found in this way turn out to be second-order saddle points subject to further spontaneous distortion. Both the disrotatory and the conrotatory ring openings of the $^2A_1$ state occur activationless and lead to $^2A'$ (C_s) and ^2B (C_2) equilibrium structures of TMM-Me$_4$$^{\bullet+}$, respectively, with the latter structure being 1.7 kcal/mol more stable (bottom of Figure 4).[19]

Because the two MOs that are degenerate in TMM remain close in energy in TMM-Me$_4$, one expects a low-energy electronic transition associated with an electron promotion from ψ_{2+} to ψ_{2-}. Indeed, this transition was observed in the near-IR (Figure 3). The fact that the two involved states are of different symmetry, both in the C_s and C_2 conformations, allows their vertical energy difference to be obtained by separate SCF calculations. Thus, the ^2A state lies 14.8 kcal/mol above ^2B in C_2, while the $^2A''$ state lies 17.8 kcal/mol above $^2A'$ in C_s. These energy differences translate into $\lambda_{max} = 1926$ nm (C_2) and 1606 nm (C_s) for the expected electronic absorption bands. Similar predictions, $\lambda_{max} = 2098$ nm (C_2) and 1705 nm (C_s), were obtained by the TD-DFT method (thus accounting for the possibility that excited states are described by more than one singly excited configuration). In addition, these calculations give a weak band at ca. 350 nm but no transitions of comparable or higher intensity than the near-IR band down to ca. 280 nm, in accordance with experiment (Figure 3). However, as all predic-

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(17) A reviewer has pointed out that UB3LYP calculations do not afford the same energy for the $^2B_1$ and $^2A_2$ states at D_{3h} geometries of TMM$^{\bullet+}$, and that this artifactual symmetry breaking could have an effect on the relative energies of the two states in C_{2v} symmetry. Indeed, at the JT conical intersection of TMM$^{\bullet+}$ located by CASSCF(3,4)/6-31G* calculations, the $^2A_2$ state is 1.84 kcal/mol more stable than the $^2B_1$ state by B3LYP/6-31G*. This artifact may be expected to impart stability also to the relaxed $^2A_2$ state. Optimization of the two geometries by CASSCF(3,4) leads to a $^2A_2$ transition state 0.46 kcal/mol above a $^2B_1$ minimum; i.e., the JT surface shows the expected topology at this level. However, single-point CASPT2 calculations at these geometries (which do not differ significantly from those found by the B3LYP method) revert the stability again in favor of the $^2A_2$ state (by 0.27 kcal/mol). In all probability the JT surface of TMM$^{\bullet+}$ is so flat that the system undergoes almost unhindered pseudorotation along the bottom of a "Mexican hat"-type JT potential.

(18) P. Rademacher, University of Essen, personal communication (the photoelectron spectrum is shown in the Supporting Information).

(19) Actually, we located another, unsymmetrical minimum of MCP-Me$_4$$^{\bullet+}$ similar to that found recently by van der Hart for the parent MCP$^{\bullet+}$ (Van der Hart, W. J. *Int. J. Mass Spectrom.* **2001**, *208*, 119; cf. Figure 2, structure 13B). However, because this structure lies 12.4 kcal/mol above the (twisted) $^2A_1$ state of MCP-Me$_4$$^{\bullet+}$, which decays spontaneously to TMM-Me$_4$$^{\bullet+}$, it was not considered further.

tions for the near-IR band are within ±0.15 eV of the observed excitation energy (ca. 1700 nm, corresponding to 0.73 eV), they cannot serve to distinguish the C_2 from the C_s structure.

The states attained in the course of the excitation of TMM-Me$_4^{\bullet+}$ can relax to form "electromers",[20] which might be reached photochemically from the initially formed states, analogous to the case of the tetramethyleneethane radical cation.[21] For the C_2 species, relaxation of the excited ^{2}A state leads to a new minimum (rightmost side of Figure 4), ca. 5 kcal/mol above the equilibrium geometry of the ^{2}B state, which in turn lies now vertically 8.8 kcal/mol above the relaxed ^{2}A state. This energy gap translates into an absorption maximum at 3260 nm, i.e., at much longer wavelength than the observed near-IR band, which excludes the relaxed ^{2}A state as a carrier of this spectrum. As no new absorptions were found to arise in this range on bleaching TMM-Me$_4^{\bullet+}$ either, we conclude that this bleaching is due to photoinduced charge recombination in the Ar matrix. On the side of the C_s conformer, relaxation of the excited $^2A''$ state leads to a second-order saddle point which decays back to the $^2A'$ ground state on loss of symmetry.

It should be noted here that passing from CFCl$_3$ to Ar as a matrix host at 4 K may cause a change in the structure of radical cations subject to JT distortion. A notable example is the benzene radical cation for which the JT-distorted structures are separated by a very small energy gap,[22] and the ground state assumes a structure with $^2B_{2g}$ symmetry in Freons,[23,24] whereas a $^2B_{1g}$ state was found in Ar.[25] However, such a change is improbable to occur in tetramethyl-substituted radical cations[26] such as TMM-Me$_4^{\bullet+}$, in which the analogous gap is several orders of magnitude larger. Thus, it is very unlikely that the change from CFCl$_3$ to Ar will revert the ordering of states in TMM-Me$_4^{\bullet+}$.

Conclusion

Ionization of 2,2,3,3-tetramethylmethylenecyclopropane (MCP-Me$_4$) in a CFCl$_3$ or an Ar matrix and opening of the three-membered ring leads to a trimethylenemethane radical cation (TMM-Me$_4^{\bullet+}$) with a nondegenerate ground state. It is demonstrated by ESR and ENDOR spectroscopy that the unpaired electron resides in the ψ_{2+} (b$_1$) orbital of TMM-Me$_4^{\bullet+}$; i.e., the ground state should have $^2B_1$ symmetry in the C_{2v} point group, as it is expected on the basis of simple perturbation considerations. Substitution of the π-radical cation TMM$^{\bullet+}$ to yield TMM-Me$_4^{\bullet+}$ thus removes effectively the degeneracy of the ground state. An analogous removal of the degeneracy by lowering of the symmetry from D_{3d} to C_{2h} was observed for the σ-radical cation of cyclohexane upon 1,4-dimethyl substitution.[27] According to B3LYP/6-31G* calculations, steric interaction between the methyl groups in TMM-Me$_4^{\bullet+}$ forces this cation to distort to C_2 or C_s symmetry. However, the similarity of the spectra predicted for these two structures does not allow an unambiguous assignment to one of them. The state of TMM-Me$_4^{\bullet+}$ with the unpaired electron occupying the π-MO ψ_{2-} (a$_2$) can relax to an electromer which represents a second minimum on the potential energy surface. In contrast to the previously investigated case of the radical cation of tetramethyleneethane,[21] this state cannot be attained photochemically in the case of TMM-Me$_4^{\bullet+}$. Calculations show that MCP-Me$_4^{\bullet+}$ decays to TMM-Me$_4^{\bullet+}$ in an entirely barrierless processs,[28] whereas the parent MCP$^{\bullet+}$ is protected from such a spontaneous collapse to TMM$^{\bullet+}$ by a small barrier.

Experimental Part

MCP-Me$_4$ was prepared according to the procedure of Arora and Binger,[11] yet employing 1.5 equiv of 1,1-dichloroethane and 1.5 equiv of *n*-butyllithium per mole of 2,3-dimethyl-2-butene to give the intermediate 1-chloro-1,2,2,3,3-pentamethylcyclopropane in 67% yield (lit. yield 40%) as a colorless solid with mp 29 °C (lit. "oil"). It was dehydrochlorinated with 1.3 equiv of potassium *tert*-butoxide in dimethyl sulfoxide to furnish the title compound in 93% yield (lit. yield 78%). After distillation, MCP-Me$_4$ was ≥99% pure (according to GC), and was used without further purification.

For ESR spectroscopic studies, the radical cation was generated by γ-irradiation (^{60}Co source) of a diluted solution of MCP-Me$_4$ in frozen CFCl$_3$ at 77 K, and the temperature of the sample was gradually raised to 150 K. ESR and ENDOR spectra were recorded on a Varian-E9 spectrometer and a Bruker ESP-300 system, respectively, with external fields of 340 mT.

In the matrix isolation experiments, MCP-Me$_4$ had a sufficient vapor pressure to be premixed with an equimolar quantity of methylene chloride (which serves as an electron scavenger) and a 1000-fold excess of Ar prior to deposition of the mixture on a CsI plate kept at 20 K. After deposition, the sample was cooled to the lowest temperature attainable by the closed-cycle cryostat (ca. 10 K). Spectra were recorded on a Perkin-Elmer Lambda 900 UV/vis/near-IR spectrometer.

Quantum Chemical Calculations. The geometries of all species were optimized by the B3LYP density functional method[29,30] as implemented in the Gaussian 98 program package,[31,32] using the 6-31G* basis set. All stationary points (minima, transition states) were characterized by second-derivative calculations. Radical cations were calculated on the basis of densities modeled by spin-unrestricted wave functions.[33] Excited-state calculations were done with the TD-DFT method,[34,35] also at the B3LYP/6-31G* level.

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(20) By "electromers" we denote distinct isomers which have the same atom connectivities and very similar geometries but different electronic structures.

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Supporting Information Available: Cartesian coordinates and energies (including enthalpies and free energies) of all stationary points discussed in this study and photoelectron spectrum of TMM-Me_4 (PDF, TXT). This material is available free of charge via the Internet at http://pubs.acs.org.

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