

Matrix isolation and DFT calculations of the TMM radical cation generated via the single electron oxidation of a methylenecyclopropane

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Abstract—A γ -irradiation of 2,2-diphenyl-1-methylenecyclopropane (**3**) in a degassed *n*-butyl chloride glassy matrix at 77 K produced an intense UV/vis absorption band with λ_{ab} at 432 nm. This result and calculations based on density functional theory for its radical cation $\mathbf{3}^{+\cdot}$ and the corresponding trimethylenemethane radical cation ($\mathbf{2}^{+\cdot}$) strongly suggest that a single electron oxidation of **3** followed by ready ring opening affords $\mathbf{2}^{+\cdot}$, whose molecular geometry is largely twisted ($\theta = 44.0^\circ$), and the positive charge and spin are localized mainly in the diphenyl methyl and allyl moieties, respectively.

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A single electron reduction and oxidation of organic substrates induces considerable changes, not only in the electronic structure, but also in the molecular geometry and chemical reactivity of the substrates or intermediates. For example, lowering of the bond order, which is caused by injecting an electron into the lowest unoccupied molecular orbital (LUMO) with antibonding character and by ejecting an electron from the highest occupied molecular orbital (HOMO) with bonding character, makes it easy to cleave a C–C bond.

From this perspective, we recently reported¹ on the first matrix isolation of a trimethylenemethane (TMM, $\mathbf{1}^{\cdot-}$ in Chart 1)²-type radical anion derivative $\mathbf{2}^{\cdot-}$, generated via γ -irradiation of 2,2-diphenyl-1-methylenecyclopropane (**3**) at 77 K.³ UV/vis spectroscopic studies in a 2-methyltetrahydrofuran (MTHF)⁴ glassy matrix showed that $\mathbf{2}^{\cdot-}$ has an intense UV/vis absorption band with λ_{ab} at 496 nm. Theoretical calculations based on density functional theory (DFT) strongly suggested that $\mathbf{2}^{\cdot-}$ has a largely twisted ($\theta = 45.5^\circ$) molecular geometry and its negative charge and spin are considerably localized in the diphenylmethyl (subunit I) and allyl (subunit II) moieties (see $\mathbf{2}^{\cdot-}$ in Chart 1), respectively. Furthermore,

it has been suggested that some $\mathbf{3}^{\cdot-}$ still survived in the MTHF matrix at 77 K. A combination of matrix isolation followed by UV/vis absorption spectroscopy and DFT calculations provided valuable new insights into TMM chemistry and the methylenecyclopropane rearrangement.

Success in investigating $\mathbf{2}^{\cdot-}$ allowed us to study a variety of TMM-type intermediates using the same methods, including a radical cation counterpart⁵ $\mathbf{2}^{+\cdot}$, a diphenyl derivative of the parent TMM radical cation ($\mathbf{1}^{+\cdot}$).⁶ Regarding $\mathbf{2}^{+\cdot}$, Ikeda and Miyashi^{5c} previously proposed a largely twisted ($\theta = 44.0^\circ$) molecular geometry and the divided electronic structure of the dianisyl derivative of $\mathbf{2}^{+\cdot}$ using time-resolved absorption spectroscopy and electron paramagnetic resonance (EPR) spectroscopy on laser flash photolysis under photoinduced electron-transfer (PET) conditions, and theoretical calculations. This proposal, however, is still tentative from the perspective of the calculation because they used a semi-empirical method of AM1. Furthermore, they focused on a back electron-transfer (BET) process from the sensitizer radical anion to $\mathbf{2}^{+\cdot}$ in solution at 298 K, while we were interested in the ring-opening process from $\mathbf{3}^{+\cdot}$ to $\mathbf{2}^{+\cdot}$ in organic glassy matrix at 77 K. Accordingly, in this work, we studied UV/vis absorption spectroscopy on γ -irradiation of **3** in an *n*-butyl chloride (*n*-BuCl)⁴ glassy matrix at 77 K and DFT calculations of $\mathbf{2}^{+\cdot}$ at the UB3LYP/cc-pVDZ level of theory. Here,

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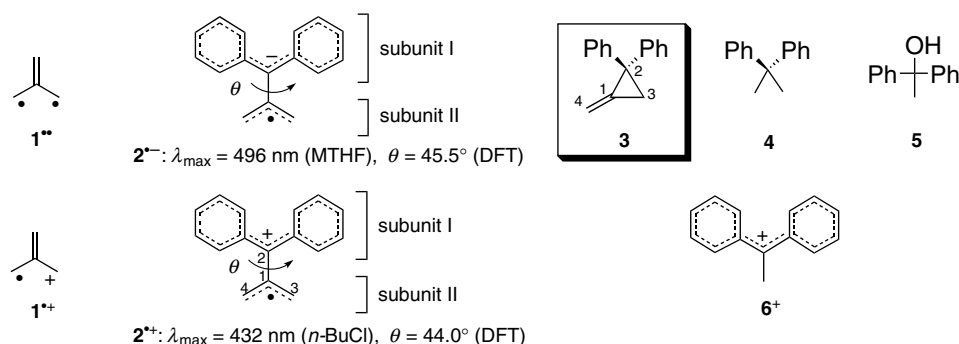


Chart 1. A list of TMM derivatives and structurally related compounds.

we report on the molecular geometry, electronic structure and generation process of $2^{\bullet+}$ in an *n*-BuCl matrix at 77 K.

A degassed *n*-BuCl glassy matrix of **3** (5 mM) was γ -irradiated with a ^{60}Co source at 77 K.^{7,8} As shown in Figure 1, intense absorption bands appeared with λ_{ab} at 344 and 432 nm. Two assignments for these bands are possible: the precursor radical cation $3^{\bullet+}$ and the TMM radical cation $2^{\bullet+}$ generated via $3^{\bullet+}$ (Scheme 1). For comparison, 2,2-diphenylpropane (**4**, 5 mM) was similarly γ -irradiated in degassed *n*-BuCl glassy matrix at 77 K.⁷ As a result, $4^{\bullet+}$ did not have major absorption bands in the 300–600 nm region. Conversely, the 1,1-diphenylethyl cation ($6^{\bullet+}$) generated from 1,1-diphenylethanol (**5**) possessed absorption bands with λ_{ab} at 314 and 424 nm in fluorosulfonic acid (FSO_3H) at 196 K (Fig. 2).⁹ These findings strongly suggest that the observed absorption bands ($\lambda_{\text{ab}} = 344$ and 432 nm, Fig. 1) are assigned to the TMM radical cation $2^{\bullet+}$, rather than $3^{\bullet+}$, and that its positive charge and spin are considerably localized in the diphenylmethyl (subunit I) and allyl (subunit II) moieties (see $2^{\bullet+}$ in Chart 1), respectively (vide infra). This assignment is in line with a previous findings.^{5c} However, we cannot always conclude that the lack of an absorption band for $3^{\bullet+}$ in the 300–600 nm region indicates the absence of $3^{\bullet+}$, because $3^{\bullet+}$ is not expected to have an absorption band

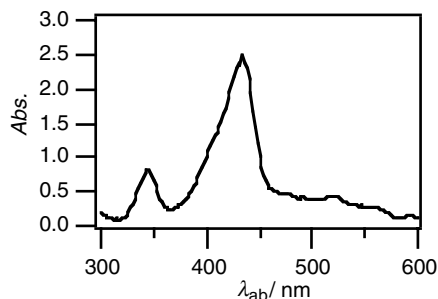
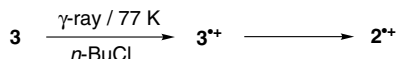


Figure 1. UV/vis absorption spectrum observed after γ -irradiation of **3** (5 mM) in an *n*-BuCl glassy matrix at 77 K.



Scheme 1. Possible generation of the TMM radical cation $2^{\bullet+}$ via a γ -irradiation of **3** in an *n*-BuCl glassy matrix at 77 K.

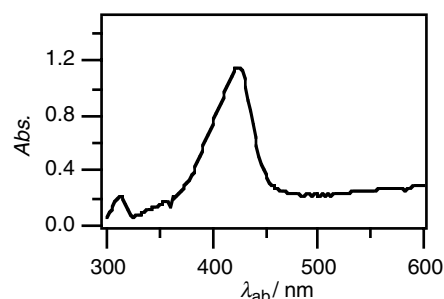


Figure 2. UV/vis absorption spectrum of $6^{\bullet+}$ generated from **5** in FSO_3H at 196 K.

in this region. Remember that the structurally related radical cation $4^{\bullet+}$ lacks clear absorption bands in this region.

To elucidate the ring opening process from $3^{\bullet+}$ to $2^{\bullet+}$, and the molecular geometry and electronic structure, we performed DFT calculations at the UB3LYP/cc-pVDZ level.^{10,11} Figure 3 shows the C-2–C-3 bond length ($d_{\text{C-2-C-3}}$, **3** in Chart 1)-dependent change in the relative potential energy (ΔE) for ring opening. The leftmost and rightmost points with $d_{\text{C-2-C-3}} = 1.63$ and 2.48 Å are for the optimized $3^{\bullet+}$ and $2^{\bullet+}$, respectively. The ΔE increased to a maximum at $d_{\text{C-2-C-3}} \approx 1.9$ Å, and then decreased monotonically, as $d_{\text{C-2-C-3}}$ increased from 1.63 to 2.48 Å. Estimating from ΔE , the ring opening of $3^{\bullet+}$ to give $2^{\bullet+}$ proceeded readily with a very small elongation barrier (ca. 0.4 kcal mol⁻¹) and the release of a large amount of energy (ca. 20 kcal mol⁻¹). These values are somewhat smaller than those of the ring opening process from $3^{\bullet-}$ to $2^{\bullet-}$ (ca. 2 and 28 kcal mol⁻¹, respec-

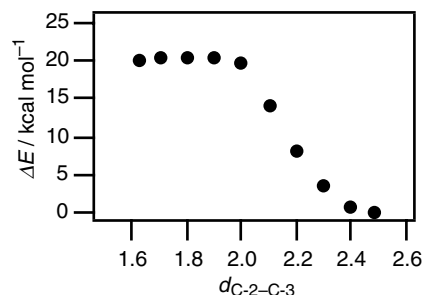


Figure 3. Bond length ($d_{\text{C-2-C-3}}$)-dependent changes in the relative potential energy (ΔE) in the course of ring opening from $3^{\bullet+}$ to $2^{\bullet+}$ calculated using UB3LYP/cc-pVDZ.

tively).¹ Anyway, this finding for the radical cation corroborates our assignment of the spectrum observed in the γ -irradiated *n*-BuCl glassy matrix of **3** (Fig. 1; vide supra). Again, note that some **3**⁺ might still survive the calculated low elongation barrier at 77 K.

Figure 4 shows the optimized molecular geometry of **2**⁺. The dihedral angles, θ and θ' , of C-3–C-1–C-2–C-5 and C-3–C-1–C-2–C-7 (Fig. 4d) were optimized to be +44.0° (Fig. 4) and –136.0°, respectively, while similar angles, ω and ω' , of C-1–C-2–C-5–C-6 and C-1–C-2–C-7–C-8 were both calculated to be +30.3°. These values correspond to those of **2**^{•–} optimized using UB3LYP/cc-pVDZ ($\theta = +45.5^\circ$, $\theta' = -134.5^\circ$, $\omega = \omega' = +25.3^\circ$). These findings, especially θ and θ' , suggest that the ground state of **2**⁺ is largely twisted. The optimized C-1–C-2 bond length ($d_{C-1-C-2}$), 1.48 Å, was slightly longer than the C–C bond length ($d_{C-C} = 1.47$ Å) of the orthogonal ethylene.¹² Therefore, the C-1–C-2 bond of **2**⁺ possesses a normal C–C single bond character. Furthermore, judging from the ΔE of **2**⁺ along the θ coordinate (Fig. 5), the rotation barrier around the

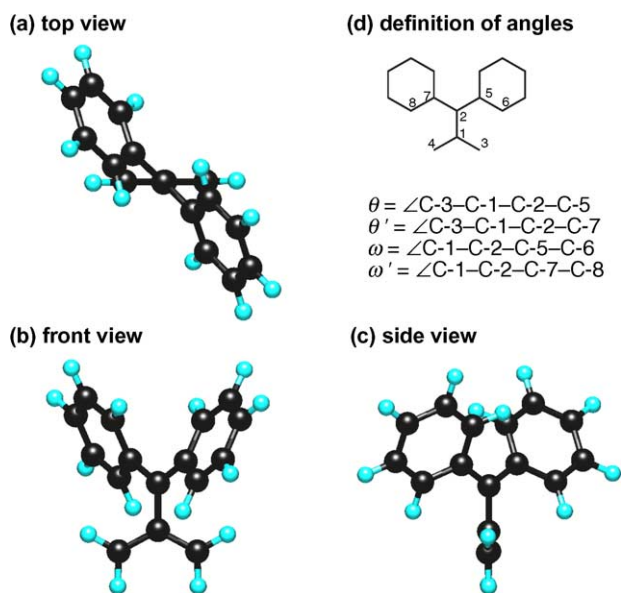


Figure 4. Molecular geometry of **2**⁺ optimized using UB3LYP/cc-pVDZ: (a) top, (b) front and (c) side views. (d) Atom notation and definition of the dihedral angles (θ , θ' , ω and ω') of **2**⁺.

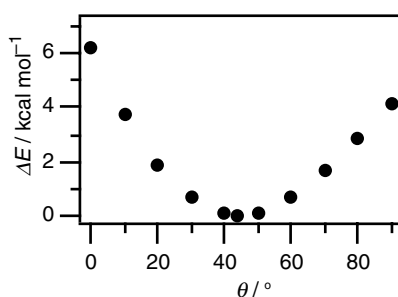


Figure 5. Potential energy (ΔE) curve of **2**⁺ along the dihedral angle (θ) calculated using UB3LYP/cc-pVDZ.

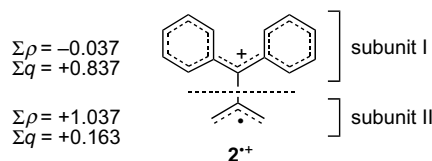


Figure 6. The sum of the partial spin (ρ) and charge (q) density of subunits I and II in **2**⁺, respectively.

C-1–C-2 bond was ca. 6 kcal mol^{–1} at $\theta \approx 0^\circ$, which corresponds to that of a normal C–C single bond (3–6 kcal mol^{–1}), indicating that the C-1–C-2 bond of **2**⁺ lacks the typical nature of a double bond.

Finally, we examined the electronic structure using the sum of the partial spin (ρ) and charge (q) density, $\Sigma\rho$ and Σq , respectively, computed with DFT calculations, as shown in Figure 6.¹³ The values, $\Sigma\rho = -0.037$ and $\Sigma q = +0.837$ for subunit I, and $\Sigma\rho = +1.037$ and $\Sigma q = +0.163$ for subunit II suggest that the positive charge and spin are mainly localized in subunits I and II, respectively. These calculation results are in accord with the conclusion based on UV/vis absorption spectroscopy.

In conclusion, we reconfirmed the molecular geometry and electronic structure of the TMM radical cation derivative, that is, **2**⁺, in an *n*-BuCl glassy matrix at 77 K using UV/vis absorption spectroscopy and the DFT calculations at the UB3LYP/cc-pVDZ level. The C-2–C-3 bond cleavage of **3**⁺ resulted from lowering the bond order triggered by ejecting an electron from the HOMO with bonding character. The DFT calculations suggest that **2**⁺ has a largely twisted molecular geometry and a considerably localized electronic structure, similar to **2**^{•–}. Subunits I and II of **2**⁺ are twisted with each other around the C-1–C-2 bond. The positive charge and spin are mainly distributed to subunits I and II, respectively. These phenomena can be ascribed to the effects of steric interaction between the two phenyl moieties and the allyl radical moiety and those of aryl-induced charge delocalization.²ⁱ Although it is hard to separate them because they work in close operation, it is likely that the steric interaction is the primary factors. Another result was evaluation of the elongation barrier for the ring opening of **3**⁺. The DFT calculations suggest that **3**⁺ cleaves to **2**⁺ (ca. 0.4 kcal mol^{–1}) more readily than **3**^{•–} cleaves to **2**^{•–} (ca. 2 kcal mol^{–1}). This work also provided important insights for a similar γ -irradiation in methylcyclohexane, which is a typical method for generating radical cations and radical anions simultaneously.

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Supplementary data

The DFT calculation results for 2^+ . Supplementary data associated with this article can be found, in the online version, at [doi:10.1016/j.tetlet.2005.12.063](https://doi.org/10.1016/j.tetlet.2005.12.063).

References and notes

- Ikeda, H.; Namai, H.; Kato, N.; Ikeda, T. *Tetrahedron Lett.*, **2006**, *47*, 1501–1504.
- For reports on TMM-type biradicals, see: (a) Dowd, P. *J. Am. Chem. Soc.* **1966**, *88*, 2587–2589; (b) Berson, J. A. In *Rearrangements in Ground and Excited States*; Mayo, P. d., Ed.; Academic: New York, 1980; Vol. 1, pp 311–390; (c) Borden, W. T. In *Diradicals*; Borden, W. T., Ed.; John Wiley & Sons: New York, 1982; pp 1–72; (d) Berson, J. A. In *Diradicals*; Berson, W. T., Ed.; John Wiley & Sons: New York, 1982; pp 151–194; (e) Berson, J. A. In *Reactive Intermediate Chemistry*; Moss, R. A., Platz, M. S., Jones, M., Jr., Eds.; John Wiley & Sons: Hoboken, 2004; pp 165–203; (f) Little, R. D. *Chem. Rev.* **1996**, *96*, 93–114; (g) Allan, A. K.; Carroll, G. L.; Little, R. D. *Eur. J. Org. Chem.* **1998**, 1–12; (h) Nakamura, E.; Yamago, S. *Acc. Chem. Res.* **2002**, *35*, 867–877; (i) Ikeda, H.; Namai, H.; Taki, H.; Miyashi, T. *J. Org. Chem.* **2005**, *70*, 3806–3813.
- For reports on the parent TMM radical anion (1^-), see: (a) Wenthold, P. G.; Hu, J.; Squires, R. R. *J. Am. Chem. Soc.* **1994**, *116*, 6961–6962; (b) Wenthold, P. G.; Hu, J.; Squires, R. R.; Lineberger, W. C. *J. Am. Chem. Soc.* **1996**, *118*, 475–476; (c) Wenthold, P. G.; Hu, J.; Squires, R. R.; Lineberger, W. C. *J. Am. Soc. Mass Spectrom.* **1999**, *10*, 800–809.
- MTHF and *n*-BuCl are typical matrix solvents used for generating radical anions and radical cations, respectively, on γ -irradiation.
- (a) Takahashi, Y.; Miyashi, T.; Mukai, T. *J. Am. Chem. Soc.* **1983**, *105*, 6511–6513; (b) Miyashi, T.; Kamata, M.; Mukai, T. *J. Am. Chem. Soc.* **1986**, *108*, 2755–2757; (c) Miyashi, T.; Takahashi, Y.; Mukai, T.; Roth, H. D.; Schilling, M. L. M. *J. Am. Chem. Soc.* **1985**, *107*, 1079–1080; (d) Ikeda, H.; Nakamura, T.; Miyashi, T.; Goodman, J. L.; Akiyama, K.; Tero-Kubota, S.; Houmam, A.; Wayner, D. D. M. *J. Am. Chem. Soc.* **1998**, *120*, 5832–5833; (e) Ikeda, H.; Akiyama, K.; Takahashi, Y.; Nakamura, T.; Ishizaki, S.; Shiratori, Y.; Ohaku, H.; Goodman, J. L.; Houmam, A.; Wayner, D. D. M.; Tero-Kubota, S.; Miyashi, T. *J. Am. Chem. Soc.* **2003**, *125*, 9147–9157.
- For reports on the parent TMM radical cation (1^+) and other TMM-type radical cations, see Refs. 6a and 6b–h, respectively: (a) Komaguchi, K.; Shiotani, M.; Lund, A. *Chem. Phys. Lett.* **1997**, *265*, 217–223; (b) Miyashi, T.; Takahashi, Y.; Ohaku, H.; Ikeda, H.; Morishima, S.-i. *Pure Appl. Chem.* **1991**, *63*, 223–230; (c) Painter, S. L.; Blackstock, S. C. *J. Am. Chem. Soc.* **1995**, *117*, 1441–1442; (d) Nakamura, M.; Toganoh, M.; Ohara, H.; Nakamura, E. *Org. Lett.* **1999**, *1*, 7–9; (e) Chou, P. K.; Gao, L.; Tichy, S. E.; Painter, S. L.; Blackstock, S. C.; Kenttämaa, H. I. *J. Phys. Chem. A* **2000**, *104*, 5530–5534; (f) Brown, E. C.; Borden, W. T. *J. Phys. Chem. A* **2002**, *106*, 2963–2969; (g) Bally, T.; Maltsev, A.; Gerson, F.; Frank, D.; de Meijere, A. *J. Am. Chem. Soc.* **2005**, *127*, 1983–1988; (h) Ikeda, H.; Nomura, T.; Akiyama, K.; Oshima, M.; Roth, H. D.; Tero-Kubota, S.; Miyashi, T. *J. Am. Chem. Soc.* **2005**, 14497–14504.
- An *n*-BuCl solution containing **3** (5 mM) was degassed by repeating five freeze (77 K)–pump (10^{-3} mmHg)–thaw (ambient temperature) cycles and sealed at 10^{-5} mmHg at 77 K. This matrix was irradiated at 77 K for 40 h with γ -rays from a 4.0 TBq ^{60}Co source at the Cobalt 60 γ Ray Irradiation Facility, Tohoku University.
- Product analyses of the γ -irradiated *n*-BuCl matrix containing **3** (46 mg, 5 mM, 200 h) after annealing resulted in a recovery of **3** in 56%. The low material balance may be ascribed to lack of efficient back electron transfer BET to 2^+ . For BET in the PET reaction of **3**, see Refs. 5d and 5e.
- Seku, T. J.; Kranenburg, P. *Spectrochim. Acta A* **1973**, *29A*, 803–805.
- DFT calculations were performed using the program Gaussian 98.^{10a} Figure 4a–c was drawn using the WinMOPAC 3.9 software.^{10b} (a) Frisch, M. J. et al. Gaussian 98, (Revision A.11.4), Gaussian Inc., Pittsburgh PA, 1998; (b) WinMOPAC 3.9, Fujitsu Ltd., Tokyo, Japan, 2004.
- Time-dependent (TD)-DFT calculations (UB3LYP/cc-pVDZ level) of 2^+ suggest the electronic transitions at $\lambda_{\text{et}} = 336$ (oscillator strength, $f = 0.093$) and 376 nm ($f = 0.438$). Although these values differed somewhat from the observed $\lambda_{\text{ab}} = 344$ and 432 nm for 2^+ , similar differences between calculated and the observed values ($\lambda_{\text{et}} = 298$ and 375 nm, $\lambda_{\text{ab}} = 314$ and 424 nm) were also found for 6^+ . Therefore, the TD-DFT calculations are in line with the assignment.
- Krylov, A. I.; Sherrill, C. D. *J. Chem. Phys.* **2002**, *116*, 3194–3203.
- The ρ and q values for each atom are summarized in the Supplementary data.