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The first observation in an organic medium and DFT calculation of the TMM radical anion generated via a single electron reduction of a methylenecyclopropane

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Abstract—γ-Irradiation of 2,2-diphenyl-1-methylenecyclopropane (**3**) in a degassed 2-methyltetrahydrofuran glassy matrix at 77 K gave an intense UV/vis absorption band with λ_{ab} at 496 nm. This result and calculations based on density functional theory for its radical anion $\mathbf{3}^{\cdot-}$ and the corresponding trimethylenemethane radical anion ($\mathbf{2}^{\cdot-}$) strongly suggest that single electron reduction of **3** followed by ready ring opening affords $\mathbf{2}^{\cdot-}$, whose molecular geometry is largely twisted ($\theta = 45.5°$), and the negative charge and spin are localized mainly in the diphenyl methyl and allyl moieties, respectively.

Since Dowd first generated the parent trimethylenemethane (TMM, $\mathbf{1}^{\cdot\cdot}$ in Chart 1),[1] various neutral TMM derivatives have been generated and studied from a variety of different perspectives.[2] Miyashi and Roth[3] were the first to generate a TMM radical cation derivative, ($\mathbf{2}^{\cdot+}$), via a photoinduced electron-transfer reaction using 2,2-diphenyl-1-methylenecyclopropane (**3**), and Ikeda and Miyashi[4] confirmed its reaction mechanism, molecular geometry (largely twisted, $\theta \approx 44°$, vide infra), and electronic structure (considerably divided) in spectroscopic, calorimetric, and semi-empirical calculation studies using its bis(4-methoxyphenyl) derivative.[5]

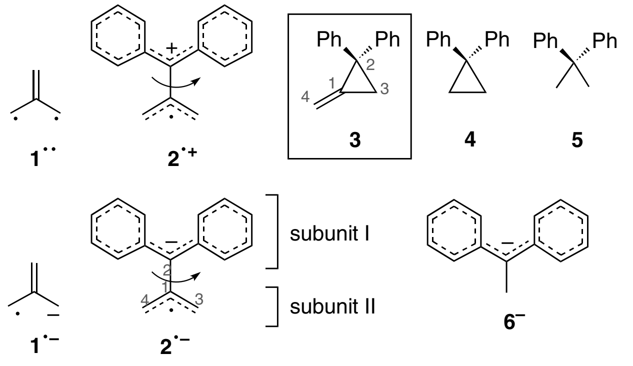

Chart 1. A list of TMM derivatives and structurally related compounds.

The generation of $\mathbf{2}^{\cdot+}$ from **3** is responsible for the C-2–C-3 bond (Chart 1) cleavage of $\mathbf{3}^{\cdot+}$ induced by ejection of an electron from the highest occupied molecular orbital (HOMO) of **3** with bonding character. In other words, lowering the bond order of $\mathbf{3}^{\cdot+}$ holds the key to produce $\mathbf{2}^{\cdot+}$. An alternative method of lowering the bond order is to inject an electron into the lowest unoccupied molecular orbital (LUMO) with antibonding character. Namely, **3** should have the potential to generate the corresponding TMM radical anion ($\mathbf{2}^{\cdot-}$) via a single electron reduction.

This concept is of interest because there are few studies of the parent TMM radical anion ($\mathbf{1}^{\cdot-}$) or its derivatives. As far as we know, the sole example is the nonreductive generation of $\mathbf{1}^{\cdot-}$ using the reaction of 3-(trimethylsilyl)-2-(trimethylsilylmethyl)propene with fluoride ion and molecular fluorine in the gas phase by Squires, Lineberger, and co-workers,[6] and there is no example of their generation or observation in an organic medium. Therefore, to test this concept, we conducted γ-irradiation of **3** in a 2-methyltetrahydrofuran (MTHF) glassy matrix at 77 K, which is a general method for generating radical anions. Here, we report the first isolation of TMM radical anion derivatives, that is $\mathbf{2}^{\cdot-}$, in an MTHF matrix,

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Keywords: Electron transfer; Absorption spectra; γ-Irradiation; Reaction mechanism.

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together with its molecular geometry and electronic structure evaluated using density functional theory (DFT) calculations at the UB3LYP/cc-pVDZ level of theory.

A degassed MTHF glassy matrix of **3** (5 mM) was γ-irradiated with a ^{60}Co source at 77 K.[7] As shown in Figure 1, an intense absorption band appeared with λ_{ab} at 496 nm. Two assignments for the 496-nm band are possible: the precursor radical anion $\mathbf{3}^{\cdot-}$ and the TMM radical anion $\mathbf{2}^{\cdot-}$ generated via $\mathbf{3}^{\cdot-}$ (Scheme 1). For comparison, 1,1-diphenylcyclopropane (**4**, 5 mM) and 2,2-diphenylpropane (**5**, 5 mM) were similarly γ-irradiated in degassed MTHF glassy matrices at 77 K. As a result, neither $\mathbf{4}^{\cdot-}$ nor $\mathbf{5}^{\cdot-}$ had any significant absorption bands in the 300–600 nm region.[7,8] Conversely, the 1,1-diphenylethyl anion ($\mathbf{6}^{-}$) has an absorption band with $\lambda_{ab} = 477$ nm in cyclohexylamine,[9] which is the sole study on the absorption band of $\mathbf{6}^{-}$. These findings strongly suggest that the observed absorption band ($\lambda_{ab} = 496$ nm, Fig. 1) is assigned to the TMM radical anion $\mathbf{2}^{\cdot-}$ rather than $\mathbf{3}^{\cdot-}$ and that 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 (vide infra). However, some $\mathbf{3}^{\cdot-}$ may still remain in the matrix though there is no spectroscopic evidence for $\mathbf{3}^{\cdot-}$, unfortunately. Remember that $\mathbf{3}^{\cdot-}$ is not expected to have an absorption band in the 300–600 nm region, similar to $\mathbf{4}^{\cdot-}$ and $\mathbf{5}^{\cdot-}$.

To gain insight into the ring opening process from $\mathbf{3}^{\cdot-}$ to $\mathbf{2}^{\cdot-}$, the molecular geometry and electronic structure, we performed DFT calculations at the UB3LYP/cc-pVDZ level.[10,13] Figure 2 shows the C-2–C-3 bond length ($d_{\text{C-2–C-3}}$, see Chart 1)-dependent change in the relative potential energy (ΔE) for ring opening. In Figure 2, the leftmost and rightmost points with $d_{\text{C-2–C-3}} =$ 1.58 and 2.52 Å are for the optimized $\mathbf{3}^{\cdot-}$ and $\mathbf{2}^{\cdot-}$, respectively. The ΔE value increased to reach a maximum at $d_{\text{C-2–C-3}} \approx 1.8$ Å, and then decreased monotonically, as $d_{\text{C-2–C-3}}$ increased from 1.58 to 2.52 Å. Estimating from ΔE, the ring opening of $\mathbf{3}^{\cdot-}$ to give $\mathbf{2}^{\cdot-}$ proceeds readily with a relatively small elongation barrier (ca. 2 kcal mol^{-1}) and the release of a large amount of energy (ca. 28 kcal mol^{-1}). This finding rationalizes our assignment of the spectrum observed in the γ-irradiated MTHF glassy matrix of **3** (Fig. 1, vide supra). Again, note that some $\mathbf{3}^{\cdot-}$ may still survive the calculated low elongation barrier at 77 K.

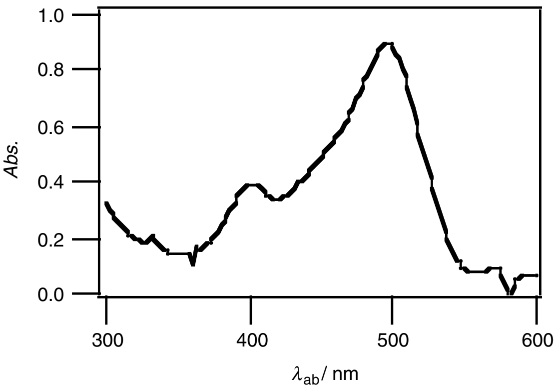


Figure 1. UV/vis absorption spectrum observed after γ-irradiation of **3** (5 mM) in an MTHF glassy matrix at 77 K.

$$\mathbf{3} \xrightarrow[\text{MTHF}]{\gamma\text{-ray / 77 K}} \mathbf{3}^{\cdot-} \longrightarrow \mathbf{2}^{\cdot-}$$

Scheme 1. Possible generation of the TMM radical anion $\mathbf{2}^{\cdot-}$ by γ-irradiation of **3** in an MTHF glassy matrix at 77 K.

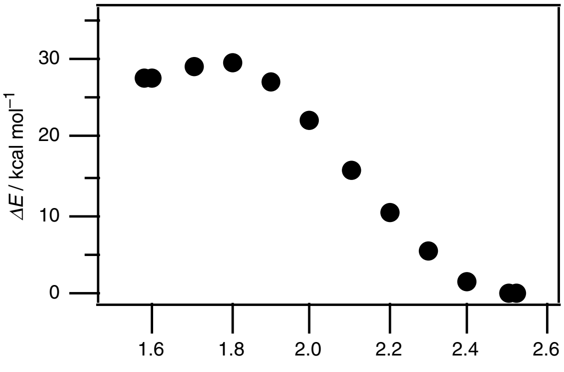


Figure 2. Bond length ($d_{\text{C-2–C-3}}$)-dependent changes in the relative potential energy (ΔE) in the course of ring opening from $\mathbf{3}^{\cdot-}$ to $\mathbf{2}^{\cdot-}$ calculated using UB3LYP/cc-pVDZ.

Figure 3 shows the optimized molecular geometry of $\mathbf{2}^{\cdot-}$. 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. 3d) were optimized to be +45.5° (Fig. 4) and −134.5°, 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 +25.3°. The

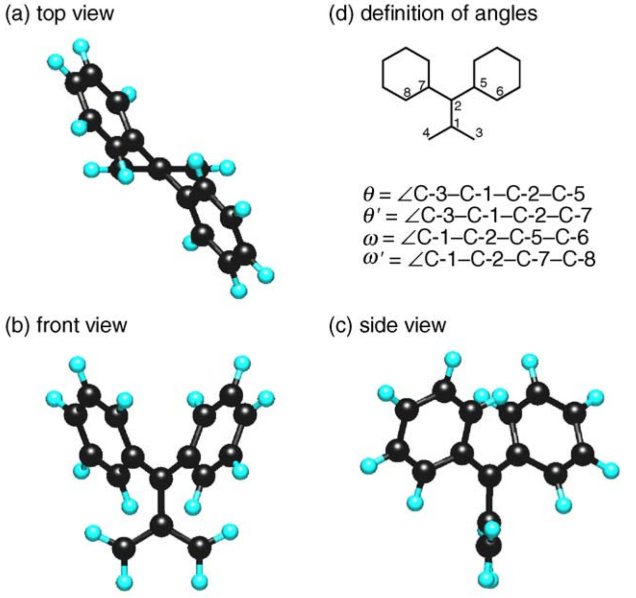


Figure 3. Molecular geometry of $\mathbf{2}^{\cdot-}$ optimized using UB3LYP/cc-pVDZ: (a) top, (b) front, and (c) side views. (d) Atom notation and definition of the dihedral angles (θ, θ', ω, and ω') of $\mathbf{2}^{\cdot-}$.

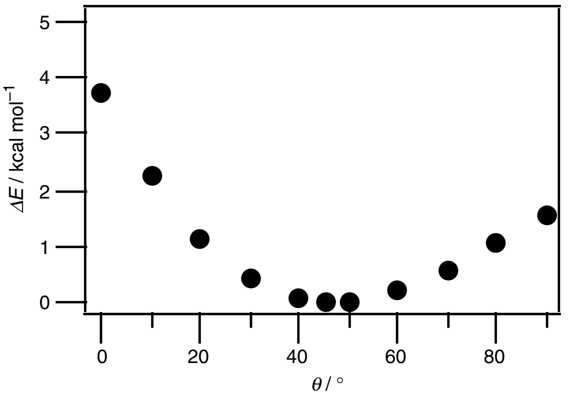
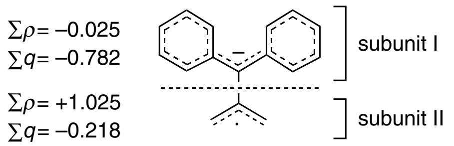


Figure 4. Potential energy (ΔE) curve of $\mathbf{2}^{\cdot-}$ along the dihedral angle (θ) calculated using UB3LYP/cc-pVDZ.

sum of calculated internal angles $\angle$C-1–C-2–C-5 = 118.6°, $\angle$C-5–C-2–C-7 = 122.8°, and $\angle$C-7–C-2–C-1 = 118.6°, was 360°, suggesting the sp^2-like hybridization of C-2 in $\mathbf{2}^{\cdot-}$. In fact, it was suggested that the two σ bonds of the C-2 carbon of $\mathbf{2}^{\cdot-}$ are hybridized with (s,p) = (34.20%, 65.74%) in the directions of C-5 and C-7, whereas in the direction of C-1, the residual σ bond of C-2 carbon takes an (s,p) = (31.52%, and 68.42%) hybridization.[14] Note that C-2 of $\mathbf{2}^{\cdot-}$ is sp^2-like in hybridization while the methyl anion, CH_3^-, has an sp^3 hybridized carbon. This phenomenon is due to both electronic and geometric factors. The former is a conjugation of the negative charge to the two phenyl groups of $\mathbf{2}^{\cdot-}$, while the latter is the easing of potential steric hindrance between the two phenyl groups on C-2 with a hypothetical sp^3 hybridization.

These findings, especially θ and θ', suggest that the ground state of $\mathbf{2}^{\cdot-}$ is largely twisted. The optimized C-1–C-2 bond length ($d_{\text{C-1–C-2}}$), 1.49 Å, is slightly longer than the C–C bond length ($d_{\text{C–C}} = 1.47$ Å) of the orthogonal ethylene.[15] Therefore, the C-1–C-2 bond of $\mathbf{2}^{\cdot-}$ possesses a normal C–C single bond character. Furthermore, judging from the ΔE of $\mathbf{2}^{\cdot-}$ along the θ coordinate (Fig. 4), the rotation barrier around the C-1–C-2 bond is lesser than 4 kcal mol^{-1} at $\theta \approx 0°$, which corresponds to that of the normal C–C single bond (3–6 kcal mol^{-1}), indicating that the C-1–C-2 bond of $\mathbf{2}^{\cdot-}$ does not have 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, $\sum\rho$ and $\sum q$, respectively, computed with DFT calculations, as shown in Figure 5.[16] The values, $\sum\rho = -0.025$ and $\sum q = -0.782$ for subunit I, and $\sum\rho = +1.025$ and $\sum q = -0.218$ for subunit II suggest that the negative charge and spin are mainly localized in subunits I and II, respectively. These calculation results are in accord with the conclusion based on absorption spectroscopy.



$\mathbf{2}^{\cdot-}$

Figure 5. The sum of the partial spin (ρ) and charge (q) density of subunits I and II in $\mathbf{2}^{\cdot-}$, respectively.

In conclusion, we first observed the TMM radical anion derivative, that is $\mathbf{2}^{\cdot-}$, generated in organic medium using γ-irradiation of **3** in an MTHF glassy matrix at 77 K. The C-2–C-3 bond cleavage of $\mathbf{3}^{\cdot-}$ results from lowering the bond order triggered by an electron injection to the LUMO with antibonding character. The DFT calculation at the UB3LYP/cc-pVDZ level suggests that $\mathbf{2}^{\cdot-}$ has a largely twisted molecular geometry and a considerably localized electronic structure. Subunits I and II are largely twisted with each other around the C-1–C-2 bond. The negative charge and spin are mainly distributed to subunits I and II, respectively. These phenomena are also similar to the case of $\mathbf{2}^{\cdot+}$: the corresponding subunits I and II are largely twisted with each other around the C-1–C-2 bond, and the positive charge and spin are mainly distributed to the corresponding subunits I and II, respectively.[17] This work is significant from the perspective of providing a new system of radical anion rearrangement, because such reaction systems are not documented very often,[18] as compared to those of radical cation rearrangements. Further studies (e.g., comparison with the parent $\mathbf{1}^{\cdot-}$) are now in progress, and will be published elsewhere.

Acknowledgments

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Supplementary data

The DFT calculation result for $\mathbf{2}^{\cdot-}$ and the absorption spectra of the MTHF matrices of $\mathbf{4}^{\cdot-}$ and $\mathbf{5}^{\cdot-}$ obtained after γ-irradiation at 77 K. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.tetlet.2006.01.024.

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