

# Spectroscopic and DFT evidence for a nonclassical radical cation derived from 7-benzhydrylidenenorbornene

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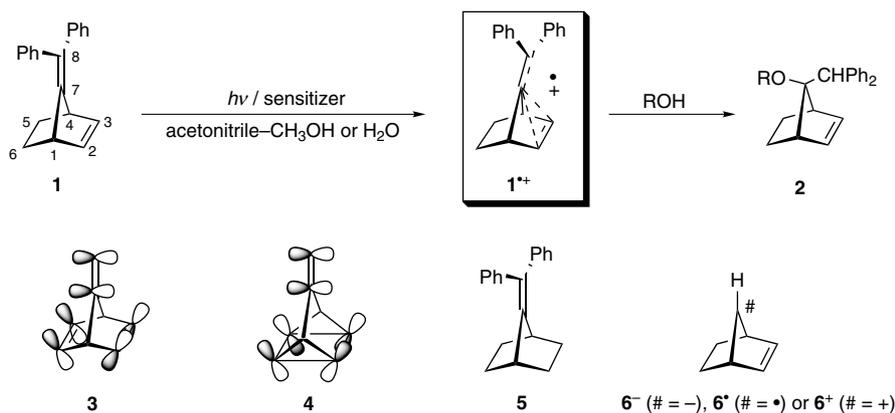
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**Abstract**—Nanosecond time-resolved UV/vis absorption spectroscopy on laser flash photolysis was conducted for photoinduced electron-transfer reactions of 7-benzhydrylidenenorbornene (**1**) and 7-benzhydrylidenenorbornane (**5**). The differences in the observed absorption bands and the structures of **1**<sup>•+</sup> and **5**<sup>•+</sup> were evaluated successfully using calculations based on (time dependent) density functional theory, confirming the nonclassical nature of **1**<sup>•+</sup>.

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Previously, Hirano, Ohashi and co-workers reported<sup>1,2</sup> the  $\pi$ -facial selective nucleophilic addition to the radical cation of 7-benzhydrylidenenorbornene (**1**, Scheme 1, anodic peak potential = +1.50 V vs SCE in acetonitrile), triggered by a photoinduced electron-transfer (PET) reaction using a sensitizer. The  $\pi$ -facial selectivity was explained by the possible generation of a nonclassical radical cation (**1**<sup>•+</sup>) involved with electronic coupling of exocyclic (C-7–C-8) and endocyclic (C-2–C-3) double

bonds. It was suspected that nucleophilic attack of a methanol or water molecule to **1**<sup>•+</sup> preferentially occurs from the *anti* side of the endocyclic double bond. Unfortunately, however, **1**<sup>•+</sup> was not observed directly. If **1**<sup>•+</sup> are observed using UV/vis absorption spectroscopy, it will be of value, because such electronic coupling was recognized as a homoconjugation and has been suggested to play a crucial role in electron-transfer reactions of 7-methylenenorbornadiene (**3**)<sup>3</sup> and 7-methylenequadricyclane (**4**)<sup>3</sup>



**Scheme 1.** Top: possible generation of a nonclassical radical cation (**1**<sup>•+</sup>) in the PET  $\pi$ -facial selective nucleophilic addition reaction of **1**. Bottom: a list of related compounds (**3–5** and **6**<sup>#</sup>).

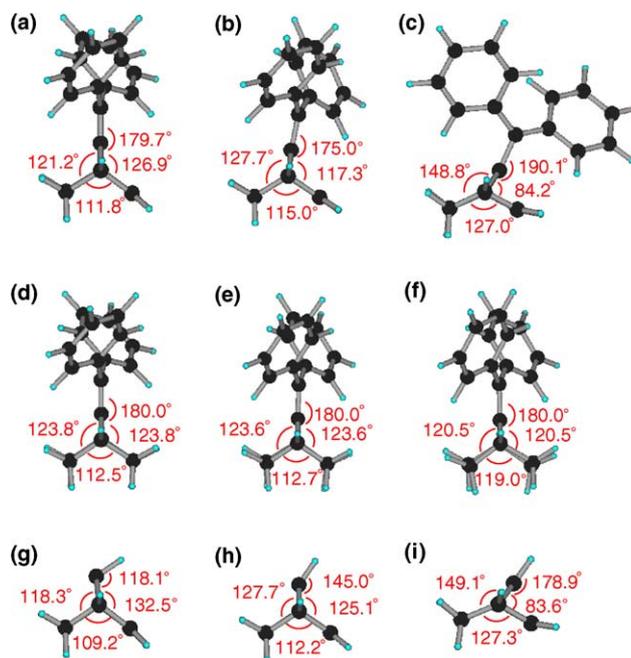
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and has only been detected by CIDNP.<sup>4</sup> Therefore, we studied nanosecond time-resolved UV/vis absorption spectroscopy on laser flash photolysis (LFP) of **1** and structurally related 7-benzhydrylidenebornane<sup>2</sup> (**5**, Scheme 1). Here, we report the direct observation of a nonclassical radical cation **1**<sup>+</sup> together with the results of density functional theory (DFT) and time-dependent (TD) DFT calculations.

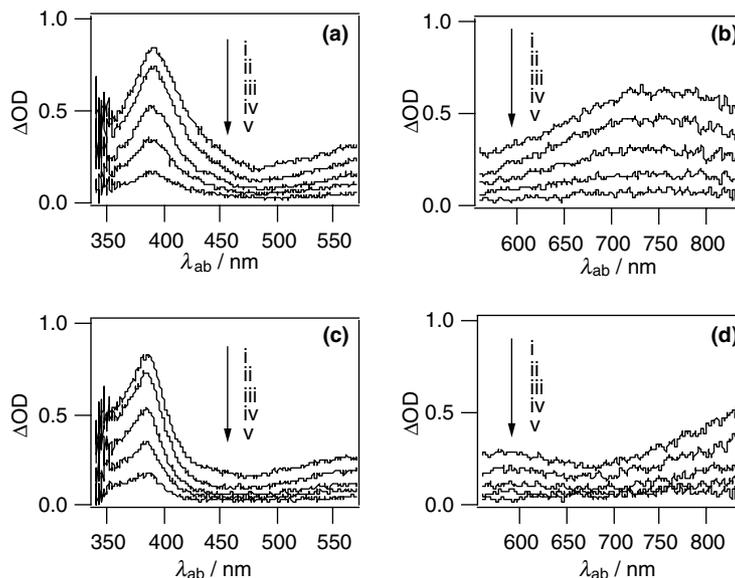
Nanosecond time-resolved UV/vis absorption spectroscopy on LFP<sup>5</sup> was performed with *N*-methylquinolinium tetrafluoroborate (NMQ<sup>+</sup>BF<sub>4</sub><sup>-</sup>) and toluene as a sensitizer and a cosensitizer,<sup>6</sup> respectively, in aerated acetonitrile at 298 K. As shown in Figure 1a and b, laser excitation (355 nm) of NMQ<sup>+</sup>BF<sub>4</sub><sup>-</sup> with **1** in aerated acetonitrile gave an intense sharp absorption band with  $\lambda_{ab}$  at 391 nm (band A), a broad weak absorption band at 480–580 nm (band B), and a broad intense absorption band at 600–850 nm (band C).<sup>7</sup> The differential optical densities ( $\Delta OD$ ) observed at 391, 560, and 750 nm decreased synchronously with almost the same rate constant,  $k_d \sim 7 \times 10^5 \text{ s}^{-1}$ , indicating that these bands originate in the same species, **1**<sup>+</sup>. Similarly, **5**<sup>+</sup> had three bands: a sharp intense absorption band with  $\lambda_{ab}$  at 386 nm (band A'), a broad weak absorption band at 500–650 nm (band B'), and a broad intense absorption band at >700 nm (band C') (Fig. 1c and d).<sup>7</sup> Interestingly, the  $\lambda_{ab}$  (391 nm) of band A of **1**<sup>+</sup> was redshifted slightly, compared with that (386 nm) of band A' of **5**<sup>+</sup>, while a large blueshift was observed for the  $\lambda_{ab}$  (600–850 nm) of band C of **1**<sup>+</sup> as compared to that (>700 nm) of band C' of **5**<sup>+</sup>.

To gain insight into the electronic structure of **1**<sup>+</sup>, we performed DFT calculations<sup>8</sup> for **1**, **1**<sup>+</sup>, **5**, and **5**<sup>+</sup>. As shown in Figure 2a, the subunit of the exocyclic double bond in the neutral **1** bends slightly toward the C-5–



**Figure 2.** Side views of **1** (a), **1**<sup>+</sup> (b), **1**<sup>2+</sup> (c), **5** (d), **5**<sup>+</sup> (e), **5**<sup>2+</sup> (f), **6**<sup>-</sup> (g), **6**<sup>-</sup> (h), and **6**<sup>+</sup> (i) optimized using the (U)B3LYP/(aug-)cc-pVDZ calculations.

C-6 methylene side at the B3LYP/cc-pVDZ level. Conversely, **1**<sup>+</sup> is calculated to bend in the opposite manner, as shown in Figure 2b. The C-1–C-7–C-4 skeleton and the exocyclic double bond of **1**<sup>+</sup> bend to the side of the endocyclic double bond by 5.2° [= (360.0° – 115.0°) / 2 – 117.3°] and 5.0° (= 180.0° – 175.0°), respectively, at the UB3LYP/cc-pVDZ level. Note that the calculation suggests a symmetrical structure for **5** and **5**<sup>+</sup>, the structurally related species without an endocyclic double bond (Fig. 2d and e).



**Figure 1.** Nanosecond time-resolved UV/vis absorption spectra observed in the LFP of **1** (a and b, 1 mM) and **5** (c and d, 1 mM) under NMQ<sup>+</sup>BF<sub>4</sub><sup>-</sup> (10 mM)–toluene (1 M)–sensitized conditions in aerated acetonitrile. Spectra (i) 100 ns, (ii) 400 ns, (iii) 1  $\mu$ s, (iv) 2  $\mu$ s, and (v) 5  $\mu$ s.

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