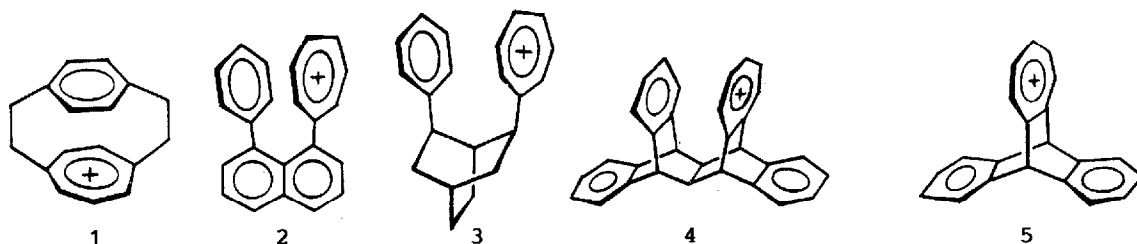


SYNTHESIS OF ANTHRACENE PHOTODIMER INCORPORATING  
A TROPYLIUM RING AND ITS FACILE RETRO[4+4] CLEAVAGE<sup>1</sup>

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**Abstract:** The title cation **6** has been prepared and exhibits an intramolecular charge-transfer band at  $\lambda_{\max}$  440 nm in  $\text{CH}_2\text{Cl}_2$ ; **6** undergoes a facile retro[4+4] cleavage owing to weakening of the central  $\sigma$  bonds due to  $\sigma$ - $\pi$  orbital mixing.

The tropylium ion has been successfully utilized as a probe for intramolecular electronic interaction between closely located  $\pi$ -systems. For example, clear intramolecular charge-transfer (CT) interaction has been observed in the cations **1** (CT band  $\lambda_{\max}$  ( $\text{CH}_2\text{Cl}_2$ ) 354 nm),<sup>2</sup> **2** (392 nm),<sup>3</sup> **3** (381 nm),<sup>4</sup> and **4** (334 nm with a shoulder at 365-450 nm).<sup>5</sup> In these cations, donor (benzene) and acceptor (tropylium) rings are placed in an essentially face-to-face arrangement.<sup>6</sup> The CT absorption is observed even in the cation **5**,<sup>7</sup> in which the  $\pi$ -systems are separated apart by a dihedral angle of 120°. In order to compare with these cations, we synthesized and examined the properties of the cation **6** (Scheme 1), which has the donor and acceptor rings separated by the dihedral angle<sup>8a</sup> inbetween those of the former cations and **5**.



The cation **6** was synthesized according to Scheme 1. Because of poor solubility and, therefore, low concentration of the starting material **7**,<sup>8b</sup> an excessive amount of diazomethane (9.8 mmol) had to be used for the ring-

Scheme 1.

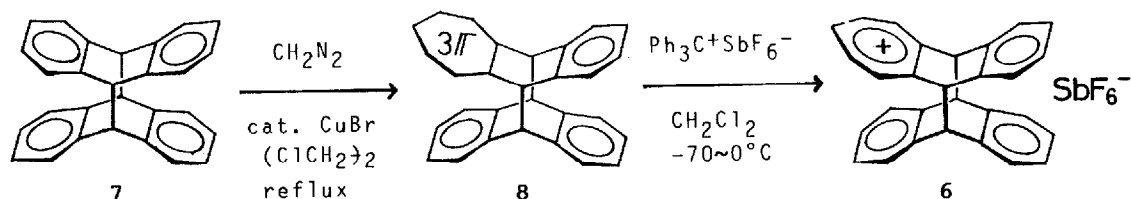
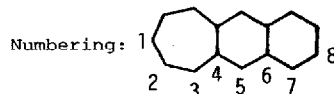


Table 1. Spectral Properties of the Cations 6 and 10

Cation	Vis(CH <sub>2</sub> Cl <sub>2</sub> ) λ/nm(log ε)	<sup>1</sup> H NMR (CD <sub>3</sub> CN;90MHz) δ / ppm	<sup>13</sup> C NMR (CD <sub>3</sub> CN;22.5MHz) δ / ppm
6	440 (3.21) (422 (3.34)) <sup>a</sup>	8.81-8.49(m, 5H, Trop <sup>+</sup> )	175.8(s), 153.2(d), 151.9(d), 150.6(d) : Trop <sup>+</sup>
		7.20-6.80(m, 12H, Benz)	142.6(s), 142.2(s), 140.0(s), 128.8(d), 128.4(d),
		5.39(d, 2H, J=11.0Hz, >CH-)	128.2(d), 128.1(d), 128.0(d), 127.3(d) : Benz
		4.92(d, 2H, J=11.0Hz, >CH-)	59.6(d), 53.4(d) : >CH-
10	610 (3.20) (593 (3.17)) <sup>a</sup>	9.86(d, 2H, J=10.1Hz, H-3)	164.2(d, C-3), 161.5(d, C-1),
		9.62(s, 2H, H-5)	141.2(d, C-2), <sup>b</sup> 139.4(s, C-4),
		9.22(t, 1H, J=9.5Hz, H-1)	137.7(s, C-6),
		8.64(dd, 2H, J=10.1, 9.5Hz, H-2)	137.3(d, C-5), <sup>b</sup>
		8.63(dd, 2H, J=6.7, 3.2Hz, H-7)	134.1(d, C-7),
		8.20(dd, 2H, J=6.7, 3.2Hz, H-8)	130.4(d, C-8)



a) In CH<sub>3</sub>CN. b) Tentative assignments.

enlargement of 7 (0.432 g; 1.21 mmol) in refluxing 1,2-dichloroethane (200 ml). After evaporation of the solvent, the cycloheptatrienes 8 were separated from unchanged 7 (60 % recovery) by extraction with chloroform, and were treated with Ph<sub>3</sub>C<sup>+</sup>SbF<sub>6</sub><sup>-</sup> to give the salt 6 SbF<sub>6</sub><sup>-9</sup> as a brick-colored powder (51 % based on 8).

The spectral properties of the cation 6 are given in Table 1 together with those of the cation 10 which will be described below. In the <sup>1</sup>H NMR spectrum of 6, the tropylium protons are 0.37 ppm upfield shifted as compared with the reference cation 9<sup>10</sup> apparently due to the shielding by a benzene ring placed at the nearly facing arrangement. In the electronic spectrum (Fig. 1), the cation 6 shows a long-wavelength absorption in the visible range (λ<sub>max</sub> 440 nm in CH<sub>2</sub>Cl<sub>2</sub>), which exhibits a hypsochromic shift upon increasing the solvent polarity. This absorption is ascribed to the intramolecular CT interaction between the tropylium and the facing benzene rings.

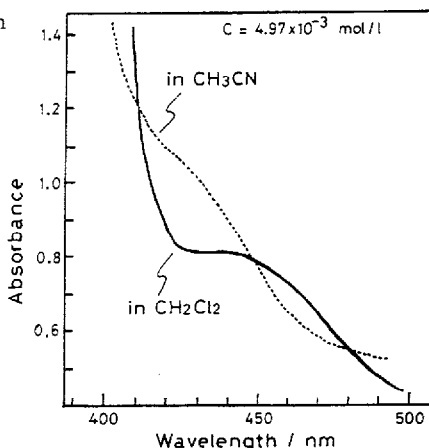
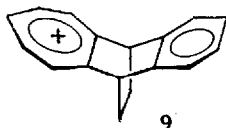


Figure 1. Visible spectra of the cation 6 taken at 0°C.

In sharp contrast with the precursor 7, which is thermally stable up to its mp,<sup>8c</sup> the cation 6 was found to be unstable even at room temperature in the dark, as is demonstrated by the <sup>1</sup>H NMR spectral change shown in Fig. 2. The species newly formed in place of consumed 6 were isolated and identified as anthracene and naphtho[b]tropylium ion 10.<sup>11</sup> Therefore, this facile cleavage is formally expressed as a retro[4+4] reaction (Scheme 2), which can proceed purely thermally without light irradiation. The cleavage was found to take place also in the solid phase (63 % cleavage after heating at 75°C for 1.5 min).

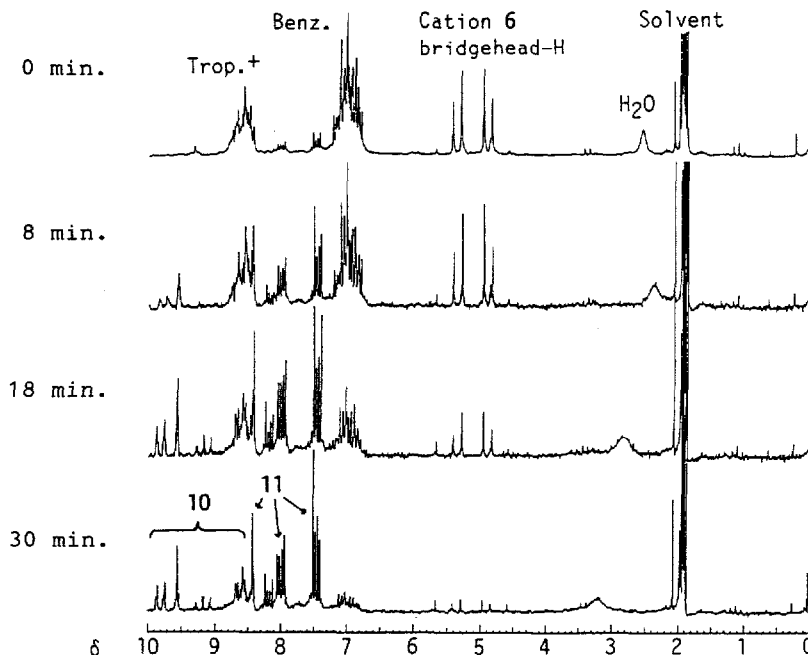


Figure 2.  $^1\text{H}$  NMR (90 MHz) spectral change of the cation 6 at  $35.1^\circ\text{C}$  in  $\text{CD}_3\text{CN}$ .

Scheme 2.



The first-order rate constants of this cleavage were determined in  $\text{CD}_3\text{CN}$  by  $^1\text{H}$  NMR at  $0\sim 35^\circ\text{C}$  to give the results shown in Table 2. Among the activation parameters, the value of  $\Delta S^\ddagger$  appears to be rather small for a bond cleavage yielding two species. This might be taken as the indication for a transition state structure which resembles the structure of the cation 6 itself. Thus, it is tempting to assume that the two  $\sigma$ -bonds are loosened and then cleaved simultaneously while retaining the positive charge mainly delocalized in the seven-membered ring, though the possibility for stepwise cleavage cannot be rigorously ruled out.

This weakening of the central  $\sigma$ -bonds is supposed to have originated from some intramolecular electronic effect caused by introduction of the tropylium ring. Previously, the appreciable elongation of the corresponding bonds in 7

Table 2. Kinetic Data and Activation Parameters ( $\text{CD}_3\text{CN}$ )

Temp. / $^\circ\text{C}$	$10^5 k_1$ / $\text{s}^{-1}$	Activation Parameters ( $25^\circ\text{C}$ )
35.1	100	$E_a = 23.5 \pm 0.3$ kcal/mol
25.0	32	$\Delta H^\ddagger = 23.0 \pm 0.3$ kcal/mol
19.8	16	$\Delta S^\ddagger = 2.4 \pm 0.5$ cal/mol $\cdot$ K
15.0	6.7	$\Delta G^\ddagger = 22.3 \pm 0.1$ kcal/mol
0.0	0.8	

(1.62 Å),<sup>8a</sup> relative to normal single bonds, has been interpreted by Mislow et al. as the results of both a transfer of  $\sigma$ -electron density into  $\pi^*$  orbitals and a donation from  $\pi$  to  $\sigma^*$  orbitals.<sup>12</sup> Since the LUMO of the tropylium ion is significantly lowered as compared with benzene, the  $\sigma$  to  $\pi^*$  donation would be considerably enhanced resulting in further weakening of the  $\sigma$ -bonds in the cation **6**, as is actually observed in facile cleavage at ambient temperatures.<sup>13</sup>

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- 8) a) The dihedral angle between the facing rings is determined as 46°: M. Ehrenberg, *Acta Cryst.*, 20, 177 (1966). b) D. O. Cowan and R. L. Drisko, "Elements of Organic Photochemistry", Plenum, New York, 1976, Chap. 2, p. 37. c) Above its mp ( $\sim 260^\circ\text{C}$ ), dissociation occurs to give anthracene.
- 9) mp  $\sim 143^\circ\text{C}$  (Completely cleaved to anthracene and the cation **10** at this temp.); IR  $\nu$  (KBr) 3010, 2920, 1620, 1590, 1475, 1450, 1145, 895, 815, 780, 765, 740, 655  $\text{cm}^{-1}$ ; Anal. Calcd for  $\text{C}_{29}\text{H}_{21}\text{SbF}_6$ : C, 57.55; H, 3.50 %. Found: C, 57.02; H, 3.42 %.
- 10)  $^1\text{H}$  NMR  $\delta$  ( $\text{CD}_3\text{CN}$ ) 9.02(m, 5H), 7.48(dd, 2H), 7.18(dd, 2H), 5.18(s, 2H), 1.93(s, 4H);  $^{13}\text{C}$  NMR  $\delta$  ( $\text{CD}_3\text{CN}$ ) 174.0(s), 153.1(d), 151.3(d), 150.8(d), 139.8(s), 128.5(d), 125.8(d), 51.1(d), 25.0(t): K. Komatsu, K. Takahashi, and K. Okamoto, unpublished; see also T. Nakazawa, N. Abe, K. Kubo, and I. Murata, *Tetrahedron Lett.*, 1979, 4995.
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