

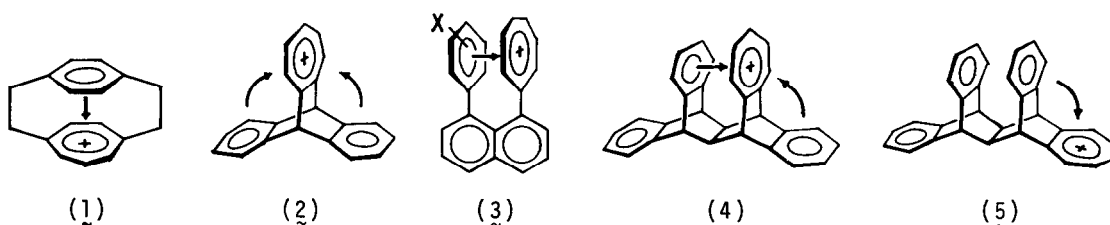
SYNTHESIS AND INTRAMOLECULAR CHARGE-TRANSFER INTERACTION OF
JANUENE CONTAINING THE TROPYLIUM RING (5,5a,6,11,11a,12-HEXAHYDRO-
5,12-(1,2-BENZENO)-6,11-(1,2-TROPYLIO)NAPHTHACENE CATIONS)

Koichi KOMATSU, Kenji TAKAHASHI, and Kunio OKAMOTO *

Department of Hydrocarbon Chemistry, Faculty of Engineering,
Kyoto University, Sakyo-ku, Kyoto 606, Japan

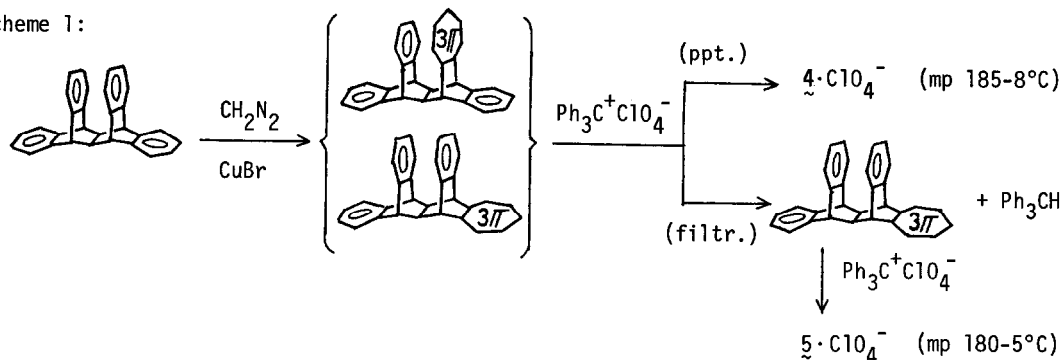
Summary: The tropylium analogues of janusene having the tropylium ring at the "Face" and "Lateral" positions have been synthesized, and their intramolecular charge-transfer interactions examined.

Recently, the intramolecular charge-transfer (CT) complex containing the tropylium ring as an acceptor gained much interest, as exemplified by the reported syntheses of [2.2](1,4)-tropylioparacyclophane (1),¹⁾ the tropylium analogue of triptycene (2),²⁾ and 1-aryl-8-tropyliophthalenes (3).³⁾ In the last example (3) reported from our laboratory, the two interacting aromatic rings are essentially in a face-to-face arrangement and are free of such ring deformation as observed in the paracyclophane system; however, there seems to be some molecular fluctuations of the facing rings such as rotation and in- and out-of-plane flippings with regard to the plane of the naphthalene ring. In this paper we wish to report the synthesis and properties of a new intramolecular CT system with the more rigid carbon framework, that is, janusene⁴⁾ having the tropylium ring either at the "Face" (4) or at the "Lateral" position (5).



The synthetic method is shown in Scheme 1. The CuBr-catalyzed reaction of janusene (0.600 g, 1.57 mmol) with diazomethane (4.81 mmol) in refluxing CH_2Cl_2 (7 ml) afforded the crude product, which exhibited, besides the signals for the unchanged janusene (ca. 60 %), complex multiplets at δ 6.5-4.7 in the ^1H NMR spectrum, indicating the formation of cycloheptatriene rings. Attempts for complete separation of this mixture were not successful at this stage. However, separation of the cations **4** and **5** was achieved successfully by controlling the amount of the hydride abstraction reagent as follows. Treatment of the CH_2Cl_2 solution of the crude product with $\text{Ph}_3\text{C}^+\text{ClO}_4^-$ in an amount 30-40 % equivalent to the whole

Scheme 1:



cycloheptatriene derivatives resulted in the formation of the perchlorate of the first cation as a yellow powder, after precipitation by the addition of ether. Similarly, the repeated hydride abstraction from the remaining hydrocarbon mixture afforded the second cation salt also as a yellow powder. From the spectral evidence shown below, the first cation was assigned to the isomer $\underline{4}$ with the "Face" tropylium ring, which is thermodynamically more stable, and the second to the isomer $\underline{5}$. Both cation salts were purified by repeated reprecipitation from $\text{MeCN-Et}_2\text{O}$. The yields in several repeated runs ranged from 19 to 28 % for $\underline{4}$ and from 19 to 36 % for $\underline{5}$, based on the consumed Janusene.

Both the cations $\underline{4}$ and $\underline{5}$ are reduced with NaBH_4 in MeOH quantitatively to the corresponding cycloheptatriene derivatives, which show the molecular ion peak at m/e 396. Also both of these cation salts exhibit quite similar IR spectra with strong bands at 1470 and 1100 cm^{-1} , indicating the presence of the tropylium ring and ClO_4^- anion, respectively. However, the ^{13}C NMR data are notably different for $\underline{4}$ and $\underline{5}$ as shown in Table 1. The general upfield shift of the tropylium ring carbons of the cation $\underline{4}$ as compared with $\underline{5}$ seems to indicate the more positive charge delocalization to the facing phenyl ring in the cation $\underline{4}$.

The definitive structural assignment was made based on the 220 MHz ^1H NMR spectra⁵⁾

Table 1. ^{13}C NMR Data for Janusene and the cations $\underline{4}$ and $\underline{5}$

Compd	Chemical shift δ (CD_3CN), ppm from SiMe_4						
	Tropylium		Phenyl			Bridgehead	
	ipso	others	ipso	others		central	other(s)
Janusene (in CDCl_3)	—	—	140.5 145.9	123.1 125.7	125.5 125.8	45.2	49.2
Cation $\underline{4}$	172.8	149.1 151.0 151.1	141.8 141.9 145.1	124.6 127.0 128.5	126.2 128.1 128.8	46.6	48.1 56.1
Cation $\underline{5}$	174.7	150.0 150.6 153.6	135.9 141.0 146.3	124.1 126.7 128.4	126.6 126.7 128.4	42.4	48.4 55.8

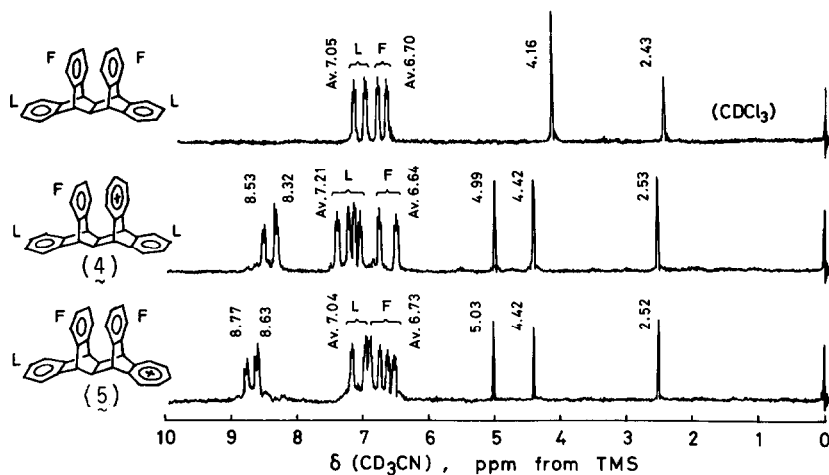


Fig. 1. 220 MHz ^1H NMR Spectra of janusene and the cations 4 and 5.

shown in Fig. 1. In the spectrum of janusene, out of four multiplets of phenyl protons, the two at the upper field are assigned to the protons of "Face" rings, which are shielded by 0.35 ppm compared with those of "Lateral" rings due to the presence of the opposite aromatic ring.⁴⁾ Accordingly, upon comparison of the spectra for the cations 4 and 5, the one with the tropylium protons which are ca. 0.3 ppm more shielded is assigned to the cation 4 with the tropylium ring at the "Face" position. The respective chemical shifts of the phenyl protons at the "Face" and "Lateral" positions are also in accordance with these assignments.

In the electronic spectra shown in Fig. 2, the cations 4 and 5 exhibit the long-wavelength absorptions extending to the visible range. These absorptions, which are apparently absent in the spectra of janusene and of the reference cation with the only σ framework (6),⁶⁾

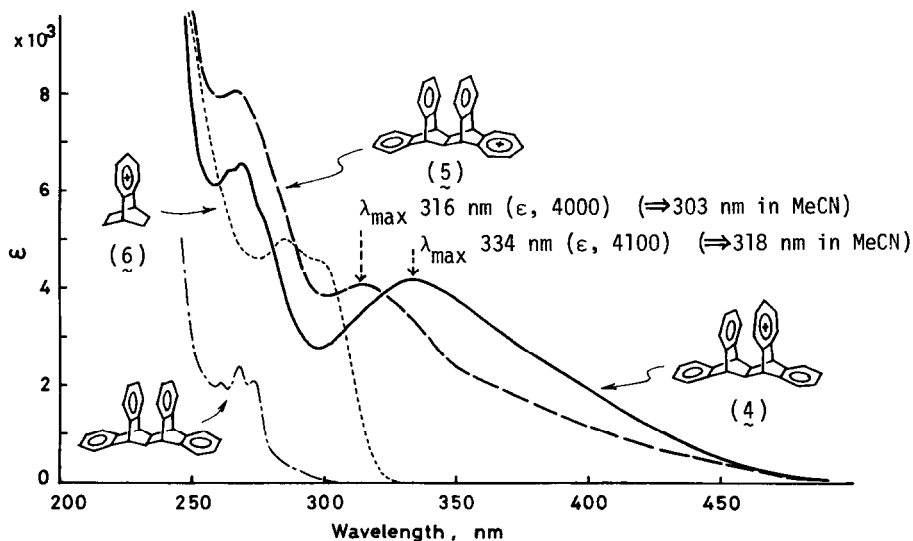


Fig. 2. Electronic spectra of janusene and the cations 4, 5, and 6 in CH_2Cl_2 .

Table 2. Reduction potential and pK_{R^+} data

Cation	Reduction potential ^{a)}		
	V vs SCE	pK_{R^+} ^{b)}	
		50% aq.MeCN	50% aq.EtOH
<u>4</u>	-0.405	8.67	7.93
<u>5</u>	-0.280	6.35	5.65
Tropylium	-0.120	4.01 ^{c)}	3.10

a) CV peak potential at a Pt electrode; scan rate, 0.1V/sec; cation, 1mM in CH_2Cl_2 ; supporting electrolyte, TBAP, 0.1M. b) Determined spectrophotometrically at 25°C; accuracy, ± 0.10 . c) C. Jutz and F. Voithenleitner, Chem. Ber., 97, 29 (1964).

exhibit the hypsochromic shift upon changing the solvent to more polar MeCN. From these facts, these absorptions are considered to arise from the intramolecular CT interaction between the tropylium and phenyl rings.

In the cation 4 the tropylium ring can interact with both the "Face" and "Lateral" donor rings, while in the cation 5 the donor ring is double-layered but separated from the tropylium ring with a dihedral angle of approximately 120° . This difference in electronic interaction is reflected in the reduction potential and pK_{R^+} data of the cations as shown in Table 2. Both the cations 4 and 5 are considerably stabilized as compared with the unsubstituted tropylium ion. However, noteworthy is the fact that the through-space π -electron supply from the donor ring, which is forced to face against the acceptor ring as in the cation 4, results in 0.13 V increase in reduction potential (i.e. decrease in electron affinity) and also the increase in pK_{R^+} value by about 2.3 pK units. The remarkably high pK_{R^+} value of 4 (8.67 in 50% aq.MeCN) ranks this cation as one of the most stable hydrocarbon cations having the tropylium unit known at present.⁷⁾

References:

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- 3) K. Komatsu, N. Abe, K. Takahashi, and K. Okamoto, J. Org. Chem., 44, 2712 (1979).
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- 5) Cation 4, δ (CD_3CN) 8.53 (2H), 8.32 (3H), 7.38 (2H), 7.22 (2H), 7.16 (2H), 7.06 (2H), 6.78 (2H), 6.49 (2H), 4.99 (2H), 4.42 (2H), 2.53 (2H). Cation 5, δ (CD_3CN) 8.77 (2H), 8.63 (3H), 7.14 (2H), 6.94 (2H), 6.89 (2H), 6.77 (2H), 6.68 (2H), 6.56 (2H), 5.03 (2H), 4.42 (2H), 2.52 (2H).
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- 7) The reported hydrocarbon cations with the tropylium unit, having the pK_{R^+} value higher than 8, are cyclohept[a]acenaphthylenium (pK_{R^+} 8.7; K. Yamamoto and I. Murata, Angew. Chem., 88, 262 (1976)) and cyclohepta[cd]phenalenium ions ($pK_{R^+} \geq 8.4$; I. Murata, K. Yamamoto, and Y. Kayane, *ibid.*, 86, 862 (1974)).

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