1-Naphthyltropylium Ions Having Condensed Aromatic Rings at the 8-Position: Dependence of the Intramolecular Charge-Transfer Interaction upon Geometry of the Donor

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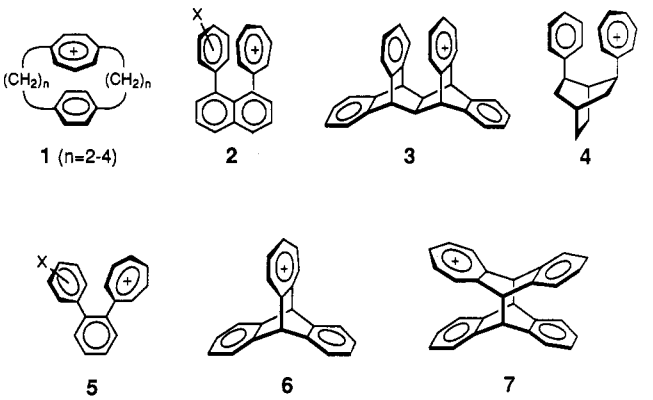
A series of 1-aryl-8-tropylionaphthalene cations (aryl = 1-naphthyl (**8a**), 2-naphthyl (**8b**), 1-pyrenyl (**8c**), and 2-pyrenyl (**8d**)) have been synthesized, in which the condensed aromatic system and a tropylium ring are placed at a face-to-face arrangement. The ^{1}H NMR spectra of these cations exhibit remarkable upfield shift for the tropylium ring protons in accord with such molecular geometry: this geometry is further supported by theoretical calculations both by MMP2 and by AM1. The cations **8a–d** show the intramolecular charge-transfer (CT) band at 510 (sh) (**8a**), 525 (sh) (**8b**), 585 (**8c**), and 600 (sh) nm (**8d**) in dichloromethane, indicating a correlation of the CT transition energy with the donor's ionization potential regardless of the relative geometry with the acceptor. In contrast, the indices of cation's thermodynamic stability, pK_{R^+} (6.27 for **8a**, 5.45 for **8b**, 6.28 for **8c**, and 5.75 for **8d**), and reduction potential (−0.649 V vs Ag/Ag^+ for **8a**, −0.601 for **8b**, −0.665 for **8c**, and −0.625 V for **8d**) are highly dependent on the mutual geometry of donor and acceptor, reflecting the effectiveness in overlap of donor's HOMO and acceptor's LUMO.

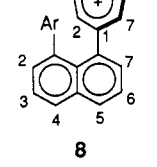
It is known that the tropylium ion as a typical hydrocarbon π-acceptor exhibits the intermolecular charge-transfer (CT) interaction with various aromatic hydrocarbons as π-donors.[1] Thus, incorporation of the tropylium ion and a π-donor in one molecule in a close proximity is expected to give an undissociable CT complex. It is then of considerable interest to clarify how this intramolecular CT interaction can affect the cation's intrinsic properties reflecting its thermodynamic stability. In a sense, such interaction can be recognized as a mode of electronic stabilization of carbocations in addition to the commonly known inductive and conjugative effects.

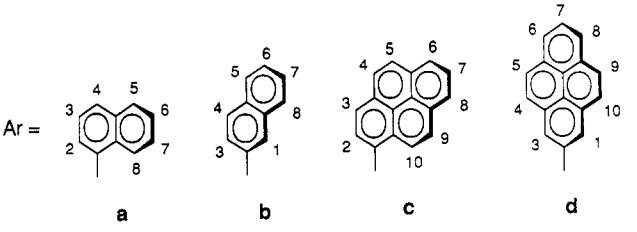
As the examples of such intramolecular CT complexes having the tropylium ring and a donor ring (benzene) in an essentially face-to-face arrangement, cations **1**,[2] **2**,[3] **3**,[4] and **4**[5] have so far been synthesized. As to the systems having the tropylium and benzene rings splayed and further separated from each other, the cations **5**,[6] **6**,[7] and **7**[8] have been reported.[9]

In our previous work, the electronic effects of the substituent (X) upon cationic properties were examined in detail for the 1,8-disubstituted naphthalene system **2**.[3] In this system, the donor and acceptor rings are supposed to take an essentially face-to-face conformation at close distance without any distortion resulting from molecular strain. Furthermore, this system has the synthetic advantage that various types of aromatic rings are readily



introduced as a donor system. In the present study, a series of condensed aromatics have been introduced as in the cations **8a–d**, and their spectral and physicochemical properties have been examined to clarify the effects of donor's π-basicity as well as the mutual geometry of the donor and acceptor systems.





Results and Discussion

Synthesis. 1-Aryl-8-tropylionaphthalenes **8a–d** were synthesized as shown in Scheme I by the method similar to the one used previously for the synthesis of **2**.[3] In the Grignard coupling of 1-bromo-8-cycloheptatrienylnaphthalene (**10**) with respective arylmagnesium bromides, the catalytic use of dichloro[1,3-bis(diphenylphosphino)-

(1) Feldman, M.; Winstein, S. *J. Am. Chem. Soc.* **1961**, *83*, 3338. Feldman, M.; Winstein, S. *Theor. Chim. Acta.* **1968**, *10*, 86. Dauben, H. J., Jr.; Wilson, J. D. *J. Chem. Soc., Chem. Commun.* **1968**, 1629. Beaumont, T. G.; Davis, K. M. C. *J. Chem. Soc. B* **1968**, 1010. Kampar, V. E. *Russ. Chem. Rev.* **1982**, *51*, 107.

(2) O'Connor, J. G.; Keehn, P. M. *J. Am. Chem. Soc.* **1976**, *98*, 8446. Horita, H.; Otsubo, T.; Sakata, Y.; Misumi, S. *Tetrahedron Lett.* **1976**, 3899. Horita, H.; Otsubo, T.; Misumi, S. *Chem. Lett.* **1978**, 807.

(3) Komatsu, K.; Abe, N.; Takahashi, K.; Okamoto, K. *J. Org. Chem.* **1979**, *44*, 2712.

(4) Komatsu, K.; Takahashi, K.; Okamoto, K. *Tetrahedron Lett.* **1979**, 4747.

(5) Ikai, K.; Takeuchi, K.; Komatsu, K.; Tsuji, R.; Kinoshita, T.; Okamoto K. *Tetrahedron Lett.* **1989**, *30*, 99.

(6) Yamamura, K.; Nakatsu, K.; Nakao, K.; Nakazawa, T.; Murata, I. *Tetrahedron Lett.* **1979**, 4999.

(7) Nakazawa, T.; Murata, I. *J. Am. Chem. Soc.* **1977**, *99*, 1996.

(8) Komatsu, K.; Tsuji, R.; Takeuchi, K. *Tetrahedron Lett.* **1989**, *30*, 4689.

(9) See also: Komatsu, K.; Fujiura, R.; Okamoto, K. *J. Org. Chem.* **1988**, *53*, 3849.

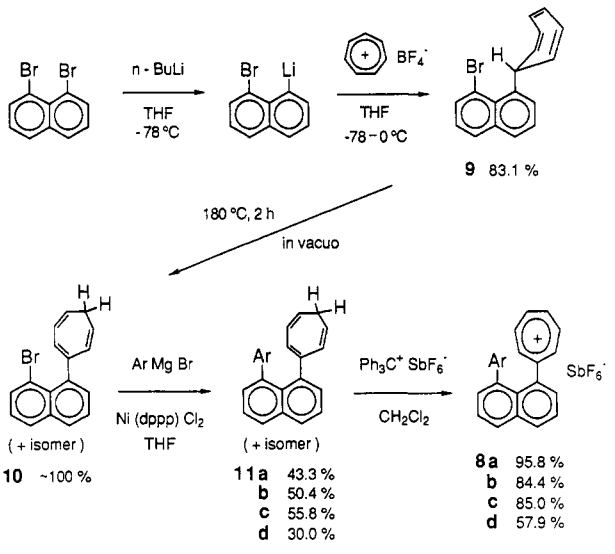
0022-3263/92/1957-0636$03.00/0

Table I. NMR Spectral Data of 1-Aryl-8-tropylionaphthalenes 8a–d

	^{1}H NMR (270 MHz, CD_3CN) δ, ppm				^{13}C NMR (67.8 MHz, CD_3CN) δ, ppm			
assignment	8a	8b	8c	8d	8a	8b	8c	8d
tropylium								
1					167.61	171.10	167.74	169.77
2	8.28	8.27	7.80	8.43	147.58	152.41	149.97	151.79
3	7.79	8.15	7.65	7.92	147.61	149.64	144.60	148.69
4	8.33	8.08	7.63	7.13	151.51	150.26	149.32	149.05
5	8.27	8.36	6.88	7.13	149.92	150.35	148.60	149.05
6	7.87	7.89	6.85	7.92	147.06	149.68	147.63	148.69
7	8.12	8.79	8.20	8.43	149.38	153.07	146.69	151.79
donor								
1		7.20		7.82	*a*	133.10	*c*	128.75
2	7.67		8.11		131.47	*b*	130.44	*d*
3	7.50	7.41	8.24	7.82	127.93	129.51	127.51	128.75
4	7.39	7.63	7.98	7.80	130.69	131.56	127.77	127.71
5	7.41	7.44	8.22	8.20	129.93	128.85	130.20	130.35
6	7.36	7.54	8.32	8.33	129.80	128.64	127.45	127.37
7	7.43	7.51	8.16	8.14	128.00	128.48	128.17	128.02
8	6.82	7.69	8.30	8.33	127.17	128.85	127.43	127.37
9			8.09	8.20			131.82	130.35
10			7.07	7.80			125.48	127.71
naphthalene								
2	7.70	7.79	7.92	7.95	132.64	131.69	132.54	131.83
3	7.81	7.83	7.91	7.88	128.04	128.03	128.12	128.02
4	8.25	8.22	8.31	8.26	131.43	130.62	131.26	130.62
5	8.31	8.30	8.35	8.33	133.89	133.76	133.92	133.62
6	7.72	7.76	7.72	7.75	126.46	126.62	126.48	126.69
7	7.41	7.61	7.34	7.52	133.70	135.42	134.06	135.43
others					*a*	*b*	*c*	*d*

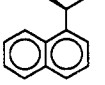
[a] Seven signals (singlet) corresponding to C-1, C-4a, and C-8a of the donor and the C-1, C-4a, C-8, and C-8a of naphthalene are observed: δ 141.92, 138.56, 136.97, 135.72, 133.96, 131.39, and 129.27. [b] Seven signals (singlet) corresponding to C-2, C-4a, and C-8a of the donor and C-1, C-4a, C-8, and C-8a of naphthalene are observed: δ 140.40, 139.22, 138.44, 136.49, 133.03, 132.61, and 130.88. [c] Eleven signals (singlet) corresponding to C-1, C-3a, C-5a, C-8a, C-10a, C-10b, and C-10c of pyrene and C-1, C-4a, C-8, and C-8a of naphthalene are observed: δ 138.50, 138.25, 137.30, 135.95, 132.45, 131.72, 131.04, 130.91, 129.72, 124.36, and 123.87. [d] Nine signals (singlet) corresponding to C-2, C-3a, C-5a, C-10b, and C-10c of pyrene and C-1, C-4a, C-8, and C-8a of naphthalene are observed: δ 140.12, 139.58, 138.56, 136.45, 132.87, 132.87, 131.99, 128.14, and 127.47.

Scheme I



propane]nickel(II)[10] ($Ni(dppp)Cl_2$) was found to be effective to give **11a–d** in 30–56% yields, whereas nickel(II) acetylacetonate[3] was not effective. The cations **8a–d** were isolated as air-stable powder with the color of orange for **8a**, reddish orange for **8b**, and reddish purple for **8c** and **8d**.

Structure. The structures of these cations were confirmed based on the NMR data shown in Table I. All signals were assigned unambiguously by means of two-dimensional NMR techniques (COSY and H/C COSY) and analyses of coupling patterns. To be noted are remarkable upfield shifts generally observed for the signals of tropylium-ring protons in the cations **8a–d** as compared with those in 1-naphthyltropylium ion (**12**)[3] (δ 9.19) as a reference. These upfield shifts are apparently due to



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shielding by the condensed aromatic rings placed at the facing position. In particular, H-5 and H-6 protons of the tropylium ring of **8c** resonate at such high field as δ 6.88 and 6.85, respectively.

The nonequivalence of all signals of the tropylium ring protons as well as carbons in **8a–c** also indicate that the rotations of the tropylium ring and the aromatic substituent at the naphthalene's 1,8-positions are restricted at room temperature within the NMR time scale. Further-

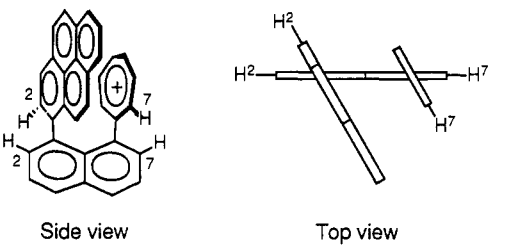

Figure 1. The structure of the cation **8c** in solution supposed from the results of NOESY experiment.

(10) Van Hecke, G. R.; Horrocks, W. D., Jr. *Inorg. Chem.* **1966**, *5*, 1968. Tamao, K.; Sumitani, K.; Kiso, Y.; Zembayashi, M.; Fujioka, A.; Kodama, S.; Nakajima, I.; Minato, A.; Kumada, M. *Bull. Chem. Soc. Jpn.* **1976**, *49*, 1958.

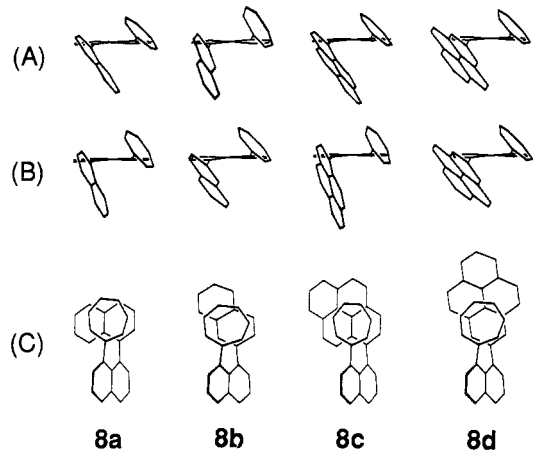

Figure 2. The energy-minimized structures for 1-aryl-8-tropylionaphthalenes **8a–d** calculated by MMP2 and AM1: (a) top view calculated by MMP2; (b) top view calculated by AM1; (c) head-on view calculated by AM1. The hydrogen atoms are omitted for clarity.

more, for the cation **8c** as a representative case, the nuclear Overhauser effect was observed between the signals of H-2 of pyrene and H-2 of naphthalene, and between the signals of H-7 of the tropylium ring and H-7 of naphthalene, when examined by the NOESY experiment. Consequently, it is supposed that the most stable conformation for this cation in solution is the one shown in Figure 1. In this conformation, the H-5 and H-6 protons of the tropylium ring are placed over the face of the pyrenyl group and are thus subjected to the maximal shielding effect as have been observed.

In good agreement with this supposition, theoretical calculations by semiempirical molecular orbital method (AM1)[11] indicated the optimized geometries of the cations **8a–d** to be as shown in Figure 2. Molecular mechanics (MMP2)[12] calculations were also conducted and indicated the energy-minimized structures to be similar to those obtained by AM1 calculations. In all cations, the two aromatic rings tend to be placed in a position facing with each other with the maximum overlap, in a nearly parallel arrangement. In spite of the possible operation of attractive CT interaction, both calculations indicated that the cations **8a–d** are somewhat deformed to relieve the nonbonding repulsive interaction between the π-clouds of two facing aromatic rings.[5] For all the cations, it is seen in Figure 2 that the repulsive interaction of π-clouds is relieved by slight deformation of the 1,8-disubstituted naphthalene moiety and splaying out of the donor and acceptor rings.[13]

The Charge-Transfer Interaction. The electronic absorption spectra of the cations **2** (X = H) and **8a–d** in dichloromethane are shown in Figure 3. The absorption at the region of 450–500 nm, which is observed in all cations irrespective of the donor structure, is assigned to the transition from the 1,8-disubstituted naphthalene moiety to the tropylium ring.[3] On the other hand, the absorptions at the longest wavelength region in the cations **8a-d** showed hypsochromic shifts upon changing the solvent to more polar acetonitrile (**8a**, λ_{max} /nm 510 (sh) in CH_2Cl_2 to 430 (sh) in CH_3CN; **8b**, 525 to 490 (sh); **8c**, 585 to 530; **8d**, 600 (sh) to 535 (sh)). This fact, together with the constancy of the absorption coefficients regardless of the change in concentrations, suggests that these absorptions arise from the intramolecular CT transition from the facing π-donor to the tropylium ion. As shown in Figure 4, a linear correlation is obtained when the values of CT transition energy ($h\nu_{CT}$ in eV) are plotted against ionization potentials (IP) of the donors. Although the slope (0.70) is smaller than unity, this correlation indicates that the value of $h\nu_{CT}$ depends solely on the π-basicity of the donor molecule irrespective of its geometry.

In contrast to the CT transition, which is the vertical excitation, the presence of the CT interaction is supposed to affect the thermodynamic properties of the tropylium ion at its ground state.[14] Then we measured the pK_{R^+} and

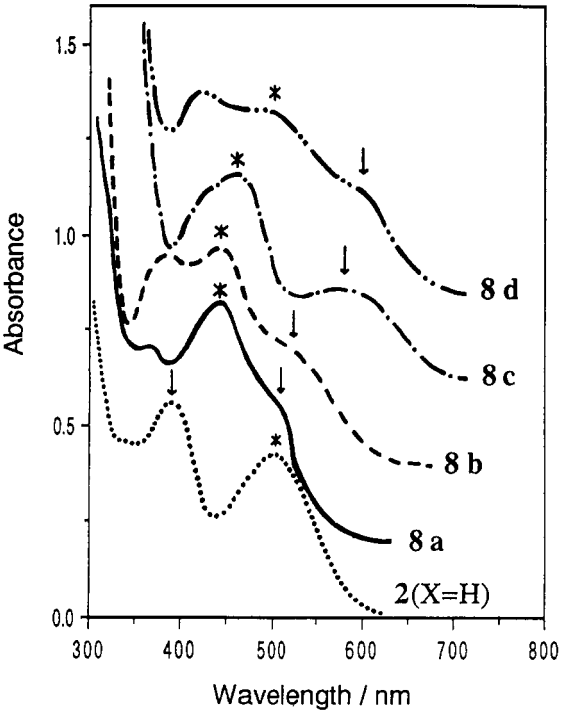

Figure 3. The electronic absorption spectra for the 1-aryl-8-tropylionaphthalenes **2** (X = H) and **8a–d** in CH_2Cl_2; concentration, 1.00×10^{-4} M; cell path, 1 cm. The absorbance for each spectrum is shifted upward by 0.2 with respect to the spectrum of **2** (X = H). The absorptions due to the intramolecular CT transition between the facing aromatic rings are denoted by ↓ and those due to the transition from the 1,8-disubstituted naphthalene moiety to the tropylium ring denoted by asterisks.

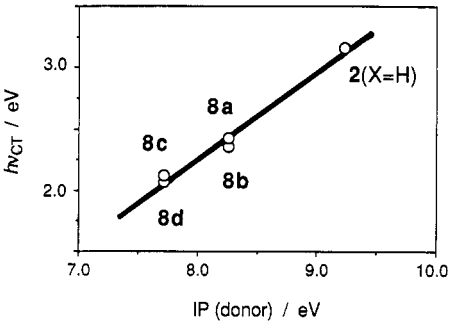

Figure 4. Plot of CT transition energy ($h\nu_{CT}$) for the 1-aryl-8-tropylionaphthalenes **2** (X = H) and **8a–d** against the ionization potential (IP) of donor moiety; slope, 0.70.

(11) Dewar, M. J. S.; Zoebisch, E. G.; Healy, E. F.; Stewart, J. J. P. *J. Am. Chem. Soc.* **1985**, *107*, 3902. Calculated using the AMPAC system: QCPE 527.

(12) The MMP2(82) program was obtained from QCPE. The calculations were conducted by regarding the tropylium ring as composed of neutral sp^2-hybridized carbons.

(13) The splayed-out angles between the donor and acceptor rings in **8a**, **8b**, **8c**, and **8d** were calculated as 20°, 26°, 20°, and 23° by MMP2 and 23°, 23°, 22°, and 23° by AM1, respectively.

(14) Foster, R. *Organic Charge-Transfer Complexes*; Academic Press: London, 1969; Chapter 2, p 19.

Table II. Ionization Potentials (IP) of Donors, CT Transition Energies ($h\nu_{CT}$), pK_{R^+}, and Reduction Peak Potentials (E_p) for the Cations 12, 2 (X = H), and 8a–d

compd	IP (donor), eV	$h\nu_{CT}$,[a] eV	pK_{R^+}[b]	E_p[c] V vs Ag/Ag^+
12			3.1_2	-0.47_0
2 (X = H)	9.23[d]	3.16	5.0_3	-0.59_7
8a	8.26[e]	2.43	6.2_7	-0.64_9
8b	8.26[e]	2.36	5.4_5	-0.60_1
8c	7.72[f]	2.12	6.2_8	-0.66_5
8d	7.72[f]	2.07	5.7_5	-0.62_5

[a] Calculated from λ_{CT} in CH_2Cl_2. [b] Measured spectrophotometrically in CH_3CN–H_2O (1:1 by vol) at 25 °C. Uncertainty limit, ±0.05. [c] Reduction peak potential determined by cyclic voltammetry in CH_3CN with tetrabutylammonium perchlorate as a supporting electrolyte; scan rate, 0.1 V/s. Uncertainty limit, ±0.005 V. [d] Howell, J. O.; Goncalves, J. M.; Amatore, C.; Klasinc, L.; Wightman, R. M.; Kochi, J. K. *J. Am. Chem. Soc.* **1984**, *106*, 3968. [e] Wacks, M. E.; Dibeler, V. H. *J. Chem. Phys.* **1959**, *31*, 1557. [f] Wacks, M. E. *J. Chem. Phys.* **1964**, *41*, 1661.

Table III. Energy Levels of Frontier Orbitals for 2 (X = H) and 8a–d Calculated by AM1

	eigenvalue, eV				
orbital	**2** (X = H)	**8a**	**8b**	**8c**	**8d**
2nd LUMO	−5.49	−5.44	−5.43	−5.37	−5.35
LUMO	−5.69	−5.61	−5.62	−5.53	−5.54
HOMO	−11.53	−11.29	−11.24	−10.56	−10.57
2nd HOMO	−12.35	−11.64	−11.62	−11.44	−11.22

reduction peak potentials (see Experimental Section) of the cations **8a–d**, which are the measures of thermodynamic stabilities of the cations relative to the corresponding covalent and radical species, respectively. The results are shown in Table II together with the ionization potential of the donor moiety and the observed CT transition energy. Apparently, the pK_{R^+} value of the tropylium ion does not simply correlate with the π-donor ability of the facing aromatic system as expressed by its ionization potential, but is rather affected by the geometry between the donor and acceptor rings. Thus, the introduction of the 1-naphthyl group as in the cation **8a** increases the pK_{R^+} by 1.24 unit as compared with the phenyl derivative **2** (X = H), whereas introduction of the 2-naphthyl group as in **8b** brings about a much smaller increase in pK_{R^+} (0.42 unit). Even when a wide π-electronic system such as pyrene is introduced, the increase in stability is not so profound, and, again, the 2-substituted derivative **8d** exhibits only modest effect compared with that in the 1-substituted derivative **8c**. A quite similar tendency is observed also for the data of reduction peak potential.

Such geometry effects seem to have resulted from the difference in overlap of the frontier molecular orbitals of the donor and acceptor, and we next looked into the electronic structures of the cations calculated by AM1. The calculated energy levels of the frontier orbitals are shown in Table III. For all cations the LUMO's and the second LUMO's[15] are localized at the tropylium ring and the HOMO's are localized at the facing donor moiety. One exception is the cation **2** (X = H): here, the HOMO is localized at the conjunctive naphthalene moiety and the second HOMO at the facing benzene ring, which is in agreement with the previous assignment of the second absorption from the longest wavelength absorption to the intramolecular CT band between the facing donor and acceptor rings.[3]

(15) The LUMO's and the second LUMO's have originated from two degenerate LUMO's of the unsubstituted tropylium ion, and their energy differences are quite small (0.14–0.19 eV).

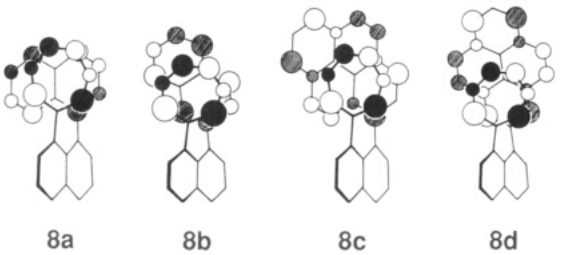

Figure 5. The overlap between HOMO and the second LUMO for 1-aryl-8-tropylionaphthalenes **8a–d** superimposed on the energy-minimized structures calculated by AM1.

On the other hand, the difference in the cationic stability can be explained qualitatively by means of Figure 5, which illustrates the frontier orbitals of the mutually interacting donor and acceptor rings[16] superimposed on the energy-minimized structures calculated by AM1. Among four intramolecular CT cations **8a–d**, the 1-naphthyl homologue **8a** has the most favorable geometry for overlap of the HOMO and the second LUMO, just as has been reported by Kochi and co-workers for the intermolecular complex between naphthalene and tropylium ion.[17] The optimum overlap between the HOMO and the second LUMO makes the intramolecular CT interaction most effective and results in pronounced stabilization of the tropylium ion **8a**. In the cation **8b** having the 2-naphthyl group as a donor, the HOMO–second LUMO overlap is out of phase. Similarly, between the cations **8c** and **8d**, the cation **8c** having the pyrene ring substituted at the 1-position exhibits the much better overlap, again in good agreement with the experimental results on the cationic stability.

In conclusion, in the present system, the CT transition reflects the π-basicity of the donor moiety itself regardless of its geometry, whereas the thermodynamic stability of the acceptor cation is greatly affected by mutual geometry of the donor and acceptor, which critically controls the HOMO–LUMO overlap of the donor and acceptor ring systems.

Experimental Section

Melting points are uncorrected. Elemental analyses were performed by the Microanalytical Center, Kyoto University, Kyoto. Infrared spectra were recorded with a Hitachi Model 215 or a Perkin-Elmer Model 1600 spectrophotometer. UV–vis spectra were determined with a Hitachi Model 200-10 spectrophotometer. NMR spectra were taken on a JEOL GX400 (400 MHz for ^1H NMR), a JEOL GSX270 (270 MHz for ^1H and 67.8 MHz for ^{13}C NMR), a JEOL FX90 (90 MHz for ^1H and 22.5 MHz for ^{13}C NMR), or a Hitachi Model R-24 (60 MHz for ^1H NMR) spectrometer using tetramethylsilane as an internal standard. Two-dimensional NMR spectra were taken on a JEOL GSX270 spectrometer. A high-resolution mass (HRMS) spectrum was recorded on a Hitachi Model M-80 double-focusing mass spectrometer with a Hitachi Model M-003 data processing system.

THF and ether were freshly distilled from sodium benzophenone ketyl before use. CH_2Cl_2 and CH_3CN were distilled from P_2O_5. 1,2-Dibromoethane was distilled from $CaCl_2$. Tropylium tetrafluoroborate,[18] triphenylmethyl (trityl) hexafluoroantimonate,[19] 1,8-dibromonaphthalene,[20] 1-bromopyrene,[21] 2-

(16) For the acceptor moiety, the coefficients of the second LUMO's are shown, since they, rather than the LUMO's, exhibit more effective overlap with HOMO's of the facing donor rings throughout the cations **8a–d**.

(17) Takahashi, Y.; Sankararaman, S.; Kochi, J. K. *J. Am. Chem. Soc.* **1989**, *111*, 2954.

(18) Conrow, K. *Org. Synth.* **1963**, *43*, 101.

(19) Thummel, R. P.; Chyangkoon, P. *J. Org. Chem.* **1983**, *48*, 596.

(20) Hodgson, H. H.; Whitehurst, J. S. *J. Chem. Soc.* **1947**, 80.

(21) Gumprecht, W. H. *Organic Syntheses*; Wiley: New York, 1973; Collect. Vol. 5, p 147.

bromopyrene,[22] 1-tropylionaphthalene tetrafluoroborate (12·BF_4^-),[3] and 1-phenyl-8-tropylionaphthalene perchlorate (2 (X = H)·ClO_4^-)[3] were prepared according to the literature. All reactions which require anhydrous conditions were conducted under an atmosphere of argon or nitrogen. Medium-pressure liquid chromatography (MPLC) was carried out using silica gel 60 (E. Merck, particle size 0.040–0.063 mm, 230–400 mesh ASTM). Theoretical calculations were performed on FACOM M-780/30 and FACOM VP-400E computers of Kyoto University Data Processing Center.

1-Bromo-8-(2,4,6-cycloheptatrien-1-yl)naphthalene (9) and Its Thermal Isomerization. A previously reported procedure[3] was modified so as to use *n*-butyllithium (*n*-BuLi) instead of lithium metal. To a stirred solution of 1,8-dibromonaphthalene (0.876 g, 3.06 mmol) in THF (14 mL) cooled at −78 °C was added dropwise over 5 min a solution of 1.66 M *n*-BuLi in *n*-hexane (1.87 mL, 3.10 mmol). The solution was stirred at −78 °C for 12 min, and to this was added tropylium tetrafluoroborate (0.579 g, 3.25 mmol) in one portion to give a dark green suspension. This mixture was stirred at −78 °C for 1 h, at 0 °C for 40 min, and at room temperature for 1 h, and then treated with 10% HCl (70 mL). The aqueous solution was extracted with ether (50 mL × 3). The combined organic solution was washed with saturated $NaHCO_3$ (50 mL) and with 10% NaCl (50 mL × 3), dried over $MgSO_4$, and evaporated under reduced pressure to give 0.980 g of the crude product. The crude product was purified by MPLC eluted with *n*-hexane to give 1-bromo-8-(2,4,6-cycloheptatrien-1-yl)naphthalene (**9**) (0.756 g, 83.1%) as a pale yellow oil: the ^1H NMR spectrum agreed with the reported data.[3]

The cycloheptatriene derivative **9** was thermally isomerized by the literature method[3] to give a mixture of two isomers, the 1,3,6-cycloheptatrien-1-yl derivative **10** and the 1,3,5-cycloheptatrien-1-yl derivative **10′**, as shown by the ^1H NMR analysis.[3]

1-(1-Naphthyl)-8-tropylionaphthalene Hexafluoroantimonate (8a·SbF_6^-). A solution of 1-naphthylmagnesium bromide was prepared by adding dropwise a solution of 1-bromonaphthalene (0.632 g, 3.05 mmol) in ether (4 mL) to magnesium (0.0865 g, 3.56 mmol) and 1,2-dibromoethane (0.043 g, 0.23 mmol) in ether (1 mL) with magnetic stirring and heating to reflux and then stirring for 1 h at room temperature. This solution was added dropwise, using a syringe, to a stirred solution of an isomeric mixture of **10** and **10′** (0.335 g, 1.13 mmol) and Ni(dppp)Cl_2 (5 mg, 0.009 mmol) in ether (3 mL) over 10 min at room temperature. The mixture was stirred at 35 °C for 7 h and at room temperature for 60 h and then quenched with H_2O. The mixture was separated, and the aqueous layer was extracted with ether (50 mL). The ethereal solution was washed with 10% HCl, 5% $NaHCO_3$, and 10% NaCl, dried over $MgSO_4$, and evaporated under reduced pressure. The crude product (0.659 g) was purified by MPLC eluted with *n*-hexane to give 1-(1,3,6-cycloheptatrien-1-yl)-8-(1-naphthyl)naphthalene (**11a**) and its positional isomers (0.168 g, 43.3%) as an yellow oil: ^1H NMR ($CDCl_3$) δ 8.02–7.15 (m, 13 H, aromatic H), 7.00–4.34 (m, 5 H, olefinic H), 2.81–0.69 (m, ~2 H, CH_2).

A solution of trityl hexafluoroantimonate (0.168 g, 0.350 mmol) in CH_2Cl_2 (1.5 mL) was added to a stirred solution of **11a** and the isomers (0.168 g, 0.488 mmol) in CH_2Cl_2 (2 mL) at 0 °C, over 2 min, to give a deep red solution. The mixture was stirred at 0 °C for 15 min and at room temperature for 1 h. After addition of 44 mL of ether, the resulting precipitates were collected, washed with ether, and dried in vacuo to yield 1-(1-naphthyl)-8-tropylionaphthalene hexafluoroantimonate (**8a**·SbF_6^-) (0.194 g, 95.8%) as an orange powder: mp 220.2–222.9 °C dec; IR (KBr) ν 3100, 3050, 1595, 1510, 1485, 1440, 1365, 1250, 835, 810, 800, 780, 775, 745, and 650 cm^{-1}; UV–vis λ_{max} (CH_2Cl_2) 266 nm (log ε 4.20), 285 (sh) (4.06), 300 (4.05), 363 (3.72), 441 (3.79), 510 (sh) (3.45); λ_{max} (CH_3CN) 261 nm (log ε 4.19), 284 (sh) (4.08), 297 (4.10), 417 (3.75), 430 (sh) (3.73). Anal. Calcd for $C_{27}H_{19}F_6Sb$: C, 55.99; H, 3.31. Found: C, 56.00; H, 3.32. For NMR data, see Table I.

1-(2-Naphthyl)-8-tropylionaphthalene Hexafluoroantimonate (8b·SbF_6^-). A solution of 2-naphthylmagnesium bromide was prepared by the method similar to the one described above from 2-bromonaphthalene (0.556 g, 2.68 mmol), magnesium (0.0713 g, 2.93 mmol), and 1,2-dibromoethane (0.071 g, 0.38 mmol) in THF (4 mL). The solution of the Grignard reagent was added to a stirred solution of **10** and **10′** (0.192 g, 0.653 mmol) and Ni(dppp)Cl_2 (5 mg, 0.009 mmol) in THF (2 mL) over 3 min. The mixture was stirred at 60 °C for 23 h and then quenched with H_2O. The mixture was worked up in the same way as described above. From the crude product (0.447 g) was separated, by means of MPLC eluted with *n*-hexane, 1-(1,3,6-cycloheptatrien-1-yl)-8-(2-naphthyl)naphthalene (**11b**) and its positional isomers as an orange-yellow solid (0.114 g, 50.7%): ^1H NMR ($CDCl_3$) δ 8.15–7.29 (m, ~13 H, aromatic H), 7.20–4.73 (m, 5 H, olefinic H), 2.90–0.35 (br m, 2 H, CH_2).

The hydride abstraction from **11b** and the isomers (0.114 g, 0.330 mmol) with trityl hexafluoroantimonate (0.0516 g, 0.108 mmol) by the same method as above afforded 1-(2-naphthyl)-8-tropylionaphthalene hexafluoroantimonate (**8b**·SbF_6^-) (0.0528 g, 84.4%) as a reddish orange powder: mp 220.5–221.5 °C dec; IR (KBr) ν 3060, 3020, 1600, 1510, 1485, 1440, 1365, 1265, 1185, 890, 840, 835, 820, 780, 750, and 655 cm^{-1}; UV–vis λ_{max} (CH_2Cl_2) 272 nm (log ε 4.22), 281 (sh) (4.20), 304 (sh) (4.12), 383 (3.74), 442 (3.75), 525 (3.47); λ_{max} (CH_3CN) 270 (sh) nm (log ε 4.18), 280 (sh) (4.17), 300 (sh) (4.13), 414 (3.59), 490 (sh) (3.28). Anal. Calcd for $C_{27}H_{19}F_6Sb$: C, 55.99; H, 3.31. Found: C, 55.85; H, 3.32. For NMR data, see Table I.

1-(1-Pyrenyl)-8-tropylionaphthalene Hexafluoroantimonate (8c·SbF_6^-). A solution of 1-pyrenylmagnesium bromide was similarly prepared from 1-bromopyrene (0.868 g, 3.09 mmol), magnesium (0.0944 g, 3.88 mmol), and 1,2-dibromoethane (0.100 g, 0.53 mmol) in THF (8.5 mL). The solution of the Grignard reagent was added to a stirred solution of **10** and the isomer (0.269 g, 0.906 mmol) and Ni(dppp)Cl_2 (3 mg, 0.006 mmol) in THF (4 mL) over 2 min. The mixture was stirred at 60 °C for 30 h, and then quenched with H_2O. Workup as described above afforded the crude product (0.564 g) as an oily soild, which was subjected to MPLC eluted with *n*-hexane to give 1-(1,3,6-cycloheptatrien-1-yl)-8-(1-pyrenyl)naphthalene (**11c**) and its positional isomers as an orange solid (0.212 g, 55.8%): ^1H NMR ($CDCl_3$) δ 8.00–6.90 (m, 15 H, aromatic H), 6.27–4.43 (br m, 5 H, olefinic H), 2.83–1.32 (br m, 2 H, CH_2).

The hydride abstraction from **11c** and the isomers (0.0731 g, 0.175 mmol) with trityl hexafluoroantimonate (0.0696 g, 0.145 mmol) afforded 1-(1-pyrenyl)-8-tropylionaphthalene (**8c**·SbF_6^-) (0.0805 g, 85.0%) as a red-purple powder: mp 267.7–268.5 °C dec; IR (KBr) ν 3050, 3000, 1600, 1505, 1485, 1440, 1260, 1250, 1245, 1185, 1085, 860, 855, 850, 840, 780, 775, 750, 730, 685, and 655 cm^{-1}; UV–vis λ_{max} (CH_2Cl_2) 240 (sh) nm (log ε 4.75), 270 (sh) (4.48), 277 (4.52), 343 (4.37), 355 (sh) (4.32), 420 (sh) (3.69), 461 (3.75), 585 (3.41); λ_{max} (CH_3CN) 268 (sh) nm (log ε 4.45), 275 (4.46), 334 (sh) (4.28), 346 (4.35), 405 (sh) (3.63), 436 (3.68), 530 (3.34). Anal. Calcd for $C_{33}H_{21}F_6Sb$: C, 60.67; H, 3.24. Found: C, 60.41; H, 3.11. For NMR data, see Table I.

1-(2-Pyrenyl)-8-tropylionaphthalene Hexafluoroantimonate (8d·SbF_6^-). A solution of 2-pyrenylmagnesium bromide was similarly prepared from 2-bromopyrene (0.219 g, 0.779 mmol), magnesium (0.0316 g, 1.30 mmol), and 1,2-dibromoethane (0.086 g, 0.46 mmol) in THF (4 mL). The solution of the Grignard reagent was added to a stirred solution of **10** and its isomer (0.300 g, 1.01 mmol) and Ni(dppp)Cl_2 (3 mg, 0.006 mmol) in THF (2 mL) over 2 min. The mixture was stirred at 60 °C for 21.5 h and worked up to give a brown oil (0.434 g), which was subjected to MPLC to give 1-(1,3,6-cycloheptatrien-1-yl)-8-(2-pyrenyl)naphthalene (**11d**) and its positional isomers (0.0977 g, 30.0%) as an orange solid: ^1H NMR ($CDCl_3$) δ 8.36–7.15 (m, ~15 H, aromatic H), 6.50–4.42 (br m, 5 H, olefinic H), 3.53–1.50 (br m, ~2 H, CH_2); HRMS *m/z* calcd for $C_{33}H_{22}$ 418.1719, found 418.1702.

The hydride abstraction from **11d** and the isomers (0.0947 g, 0.226 mmol) with trityl hexafluoroantimonate (0.0881 g, 0.184 mmol) afforded 1-(2-pyrenyl)-8-tropylionaphthalene hexafluoroantimonate (**8d**·SbF_6^-) (0.0696 g, 57.9%) as a reddish purple powder: mp 213.5–214.0 °C dec; IR (KBr) ν 3061, 2924, 2865, 2358, 2342, 1725, 1636, 1603, 1482, 1131, 853, 833, 763, 719, 709, 668, 659, and 648 cm^{-1}; UV–vis λ_{max} (CH_2Cl_2) 260 (sh) nm (log ε 4.48), 275 (4.46), 300 (4.36), 311 (4.37), 323 (4.35), 339 (4.30), 423 (3.76), 440 (3.72), 600 (sh) (3.45); λ_{max} (CH_3CN) 261 (sh) nm (log ε 4.47), 272 (4.43), 294 (4.35), 305 (4.34), 319 (4.33), 334 (4.33), 400 (3.74), 446 (3.73), 535 (sh) (3.49). Anal. Calcd for $C_{33}H_{21}F_6Sb$: C, 60.67;

(22) Harvey, R. G.; Schmolka, S.; Cortez, C.; Lee, H. *Synth. Commun.* **1988**, *18*, 2207.

H, 3.24. Found: C, 59.10; H, 3.52. Satisfactory analytical data could not be obtained due to hygroscopicity. For NMR data, see Table I.

pK_{R^+} Measurement. The pK_{R^+} values were determined for the cations **2** (X = H), **8a–d**, and **12** in CH_3CN–H_2O (1:1 by vol) at 25 °C according to the spectrophotometric method previously reported.[23] All the cations and the corresponding neutralized compounds were stable in this solvent during the measurement. After each measurement, the reversibility was confirmed by regeneration of the cation's spectrum upon acidifying the neutralized solution. The UV–vis spectrum was recorded on each cation in 10–15 solutions of buffers spaced through a pH range of 2–3 units on each side of the pK_{R^+}. The pH values were read on a Horiba Model H pH meter calibrated with standard buffers before use.

Cyclic Voltammetry. Cyclic voltammograms were obtained at the scan rate of 0.1 V/s by the use of a Hokuto-Denko HA104 potentiostat, a HB107A function generator, a Hitachi 057 X-Y recorder, and a three-electrode cell composed of platinum wire working and counter electrodes and a Ag/0.01 M $AgNO_3$ (CH_3CN) reference electrode. All the sample solutions were 1 mM in cations and 0.1 M in tetra-*n*-butylammonium perchlorate as a supporting electrolyte in CH_3CN. Irreversible cathodic peaks were observed for all cations. The peak potentials were read and corrected with reference to ferrocene ($E_{1/2}$ +0.083 V) added as an internal standard after each measurement.

(23) Komatsu, K.; Masumoto, K.; Waki, Y.; Okamoto, K. *Bull. Chem. Soc. Jpn.* **1982**, *55*, 2470.

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Supplementary Material Available: Two-dimensional NMR spectra of 1-aryl-8-tropylionaphthalenes **8a–d** (12 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

Perchlorotriphenylene: A Compound with Severe Molecular Twisting?

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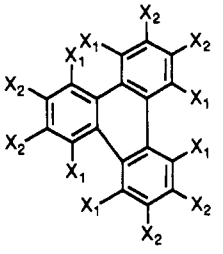
Perchlorotriphenylene has been reported several times in the literature. However, there is inconclusive evidence that this compound has actually been prepared. Severe molecular twisting to relieve steric interactions of "ortho" chlorines may preclude any stable existence. The compound is discussed in context with other severely twisted molecules, and methods are proposed for its synthesis.

Perchlorotriphenylene, $C_{18}Cl_{12}$, is a member of a family of compounds whose general structure is:



The parent triphenylene, $C_{18}H_{12}$, has more than 1300 mentions in the literature, and perfluorotriphenylene, $C_{18}F_{12}$, has received nine references.[1-9] The crystal structures of both triphenylene[10] and perfluorotriphenylene[4] show distortions from planarity in the solid state, due to steric interactions of the "ortho" hydrogens or fluorines (X_1 in the general structure).

This distortion from planarity caused by the twisting of a molecule to achieve a measure of stability is well documented (especially by Ballester[11] in his review on perchloro organic chemistry). A few examples are shown in the structures of hexadecafluoro-1-phenyltriphenylene,[9] decachlorophenanthrene,[12] octachloronaphthalene and tetrabenznaphthalene,[13] octafluorodibenzothiophene,[14] perchloro-1,1-diphenylethylene,[15] and perchlorobifluorenylidene,[16] which has a 67° twist around the ethylene bond. 9-18-Diphenyltetrabenz[*a*,*c*,*h*,*j*]anthracene[17] has been synthesized with the anthracene molecule twisted by 65.7° end to end, and the same paper postulates that helical complexes with twists of 90° or even 180° might be synthesized.

With this background of stable twisted molecules, it is

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(1) Bowen-Jones, J.; Brown, D. S.; Massey, A. G.; Slater, P. J. *J. Fluorine Chem.* **1986**, *31*, 75.
(2) Razuvaev, G. A.; Vyshinskaya, L. I.; Timoshenko, S. Y. *Zh. Obshch. Khim.* **1981**, *S1*, 2004.
(3) Pozdnyakovich, Y. V.; Shteingarts, V. D. *Zh. Org. Khim.* **1977**, *13*, 1911.
(4) Hursthouse, M. B.; Smith, V. B.; Massey, A. G. *J. Fluorine Chem.* **1976**, *10*, 145.
(5) Woodard, C. M.; Hughes, G.; Massey, A. G. *J. Organomet. Chem.* **1976**, *112*, 9.
(6) Pozdnykovich, Y. V.; Chuikova, T. V.; Bardin, V. V.; Shteingarts, V. D. *Zh. Org. Khim.* **1976**, *12*, 690.
(7) Smith, V. B.; Massey, A. G. *Tetrahedron* **1964**, *25*, 5495.
(8) Cohen, S. C.; Massey, A. G. *J. Organomet. Chem.* **1967**, *10*, 371.
(9) Beaumont, C. A.; Bowen-Jones, J.; Brown, D. S.; Massey, A. G.; Watkin, J. *J. Organomet. Chem.* **1988**, *344*, 1.
(10) Ahmed, R. R.; Trotter, J. *Acta Crystallogr.* **1963**, *16*, 503.
(11) Ballester, M. *Adv. Phys. Org. Chem.* **1989**, *25*, 267.
(12) Herbstein, F. H.; Kapon, M.; Merksamer, R. *Acta Crystallogr.* **1976**, *B22*, 2205.
(13) Herbstein, F. H. *Acta Crystallogr.* **1979**, *B35*, 1661.
(14) Bowen-Jones, J.; Brown, D. S.; Massey, A. G. *Phosphorus Sulfur Relat. Elem.* **1988**, *35*, 67.
(15) Ballester, M.; Riera, J.; Badia, C. *Tetrahedron Lett.* **1974**, 1199.
(16) Ballester, M.; Castaner, J.; Riera, J.; Dela Fuente, G.; Camps, J. *J. Org. Chem.* **1985**, *50*, 2287.
(17) Pascal, R. A., Jr.; McMillan, W. D.; Van Engen, D. *J. Am. Chem. Soc.* **1986**, *108*, 5652.

0022-3263/92/1957-0641$03.00/0