

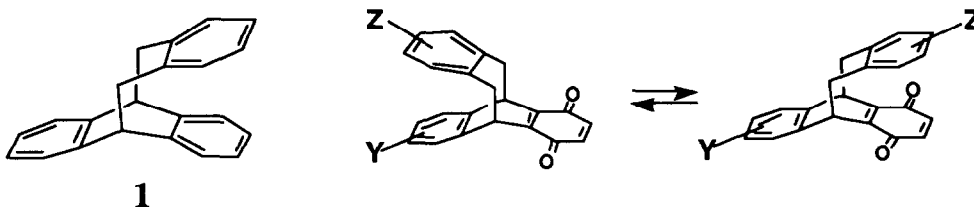
Synthesis, Structure, and Physical Properties of 1,11-*o*-Benzeno[2]orthocyclo[2](1,2)tropyliophane

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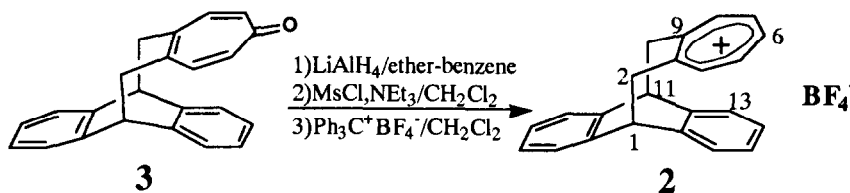
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Abstract: The title compound (**2**) has been synthesized, the structure and the physical properties of which are investigated by X-ray, spectroscopic analyses, and MO calculations. There exists charge transfer (CT) interaction between the tropylium ion and the facing phenyl ring. From the pK_R^+ value of **2**, it can be clear that the cation **2** is stabilized by the CT interaction. In spite of the presence of bond weakening $\sigma-\pi$ orbital mixing, the cation **2** withstands retro[4+4]type bond cleavage, which is quite interesting when compared to a facile cleavage for the congener with anthracene photodimer type structure.

As part of a program directed toward expanding the scope of an intramolecular charge transfer (CT) interaction between a donor and an acceptor with well-defined arrangement, we have recently demonstrated that 1,10-*o*-benzeno[2.2]orthocyclophane (**1**) and its derivatives could be an excellent system to evaluate through space $\pi-\pi$ interactions.¹⁾ Benzoquinones were incorporated in this system as electron accepting moieties and the energetics of the CT interaction between the acceptors and substituted benzenes were estimated by the analysis of the conformational equilibrium caused by the flipping of the upper π -deck.²⁾ Tropylium ion has been known as an effective π -acceptor as exemplified by the synthesis of many intramolecular CT complexes.³⁾



Incorporation of tropylium ion into the [2.2]orthocyclophane system would give an interesting information about intramolecular CT interaction. We have hence synthesized 1,11-*o*-benzeno[2]orthocyclo[2]tropyliophane (**2**). In this communication we report on the structure of **2** obtained by an X-ray crystallographic analysis and its physical properties.



Tropylium ion (**2**) was synthesized from [2.2]orthocyclopropenophane (**3**)⁴ in three steps.⁵ Final hydride abstraction from cycloheptatriene derivative was successful by using triphenylcarbenium tetrafluoroborate.^{3c,6}

X-ray analysis In order to obtain the precise molecular structure an X-ray crystallographic analysis of **2** was carried out. The molecular geometry is presented in Figure 1.⁷ As is shown in this figure, **2** has a folded structure and three aromatic rings are almost planar, indicating that cation **2** has less strained π -electron system than [2.2]para- or -metacyclopolyliophanes.^{3b} The tropylium ring is close to regular heptagon. Average value of the seven C-C bond lengths is 1.385 Å. The three bonds around ring juncture (C3-C4; 1.396 Å, C3-C9; 1.411 Å, C8-C9; 1.392 Å) are all longer than the others (1.374 Å, average of the four bonds) suggesting an effect of the vicinal two alkyl substituents on bond elongation of the 7-membered ring. Two σ -bonds connecting the upper tropylium ring and the lower 9,10-dihydroanthracene moiety are conspicuously longer (C1-C2, 1.576 Å; C10-C11, 1.576 Å) than the normal C-C single bond (1.54 Å). The shortest non-bonded distance between the upper and the lower π decks is 2.775 Å (C9 -- C12). It is far shorter than normal π - π stacking distance and very close to that in [2.2]paracyclophane ensuring transannular π - π electronic interaction. At the same time it suggests that the two π decks are repulsive with each other. The steric repulsion causes the elongation of the C-C σ -bonds in the bridging chains to some extent and small out of plane deformation of the aromatic rings. The root mean square deviation of the seven membered ring from the planar structure is slightly larger (0.012 Å)⁸ than those of the other aromatic rings (0.04 Å for syn, 0.02 Å for anti benzene), suggesting smaller aromatic stability of the tropylium ion than that of the benzenes.

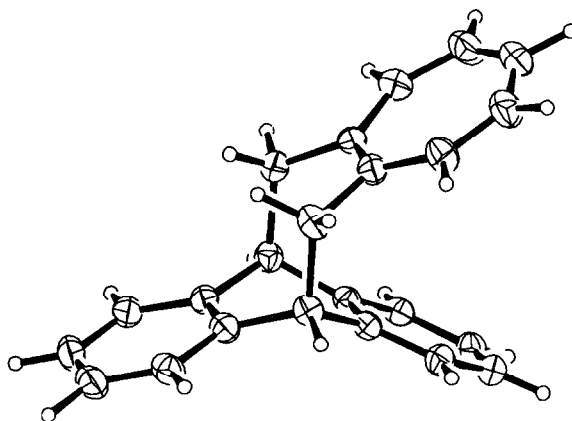


Figure 1. ORTEP Drawing of cation **2**.

Physical Properties Charge transfer type π - π interaction between the two facing aromatic rings was confirmed in UV spectra. The cation **2** shows an absorption ($\lambda_{\text{max}}=341$ nm in CH_2Cl_2), which exhibits a hypsochromic shift (5 nm) upon increasing the solvent polarity (acetonitrile). This hypsochromic shift supported that the absorption is due to the intramolecular charge transfer (CT) transition from the lower benzene ring to the upper tropylium ring. The assignment was further supported by CNDO/S-MO calculations.⁹ The calculations show that the HOMO for this molecule essentially consists of the highest occupied π orbital of the phenyl ring which is facing with tropylium ring. On the other hand, LUMO is almost identical with a π molecular orbital for the

tropylium ring. The calculated λ_{max} of the HOMO-LUMO transition is 360 nm, which is in good agreement with the experimental result.

The electronic interaction between the facing donor and acceptor moieties might be reflected in the pK_{R}^+ data of the cation. The pK_{R}^+ value of **2** (4.7^{10}) is slightly larger than those of 1,2-dimethyltropylium ion (**6**)¹¹ and cyclopentene or cyclohexene-fused tropylium ion.¹² Hence, the thermodynamic stability of cation **2** can be explained with through space π -electron supply from the facing phenyl ring to electron deficient tropylium ring. Since the magnitude of the through space stabilization is not so large, no prominent movement of ^{13}C chemical shifts of the tropylium ion was detected.

Worthy to note in connection with the thermodynamic stability is the high kinetic (thermal) stability of this tropyrium ion. Recently Komatsu and co-workers have reported a facile thermal cleavage of the two central C-C single bonds in a tropyliocyclophane (**4**) with anthracene photodimer type structure.¹³ Efficient π - σ^* orbital mixing¹⁴ between two facing π -system and σ^* -orbitals of the bonds connecting them has been claimed for the principal reason of the facile cleavage. Although similar π - σ^* orbital mixing can be operative in **2** as is evident from the elongated bridging bonds (*vide supra*), **2** is thermally stable up to its melting point. Extra reasoning to explain the high thermal stability of the ion should be addressed. We think that the calculated difference of the heat of formation for this thermal reaction should be a good probe for judging the thermal stability.

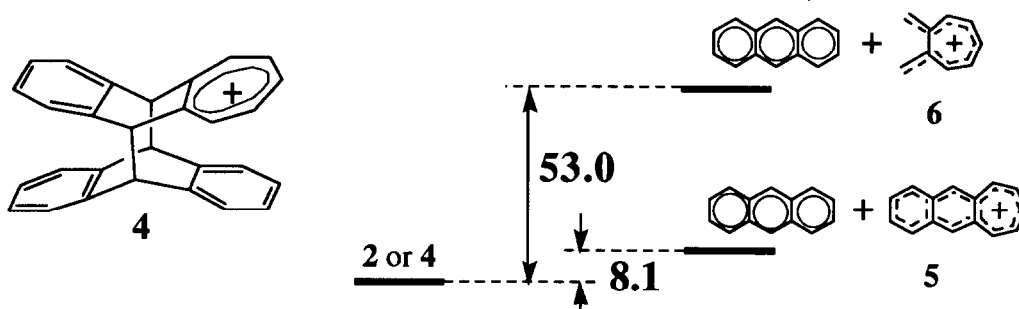


Figure 2. Schematic diagram of the heats of formation (kcal/mol) for the cleavage of C-C bridge bonds of cation **2** and **4**.

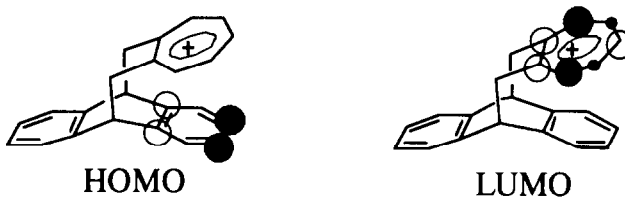
Relative differences of the heat of formation obtained by PM3 calculation are shown in Figure 2.¹⁵ The difference between cation **4** and its two reaction products, anthracene and cation **5**, indicates that this reaction is slightly endothermic. On the other hand, the corresponding difference for **2** is quite large (53.0 kcal/mol). The large energy difference between the two reactions should be due to the difference of the stability of two cationic products (**5** and **6**). According to Bell-Evans-Polanyi's principle,¹⁶ it is evident that the more endothermic the reaction the larger the activation energy. The large endothermic nature of this reaction should thus reflect the stabilities of the cationic **2**.

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- 5) **2**: yellow prisms; m.p. 176 °C; IR(ν_{KBr} , cm^{-1}) 3600-3200 (broad, OH), 1480, 1445, 1160-1020, 785; $^1\text{H-NMR}$ δ (CDCl_3 , 270MHz, ppm) 8.75-8.55 (m, 5H), 7.34-7.20 (m, 4H), 7.15-7.03 (m, 4H), 4.68 (t, 2H, $J=6.75\text{Hz}$), 3.89 (d, 4H, $J=6.75\text{Hz}$); $^{13}\text{C-NMR}$ δ (CDCl_3 , 400MHz, ppm) 174.2, 154.5, 150.8, 150.6 (Trop⁺); 141.6, 127.2, 126.7 (Benz); 49.9 (methylene), 45.4 (methine).
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- 7) The crystallographic data of **2** are as follows: Monoclinic, $P2_1/n$, M.F. $\text{C}_{23}\text{H}_{19}\text{BF}_4$, M.W. 381.21, $a=14.210$ (4), $b=10.013$ (2), $c=13.508$ (3) Å, $\beta=109.82$ (2)°, $V=1829.4$ (8) Å³, $Z=4$, Reflections 2220, $R=0.066$.
- 8) The value observed in **2** is much larger than those in dithieno[2,1-b;4,5-b']tropylium perchlorate (0.03 Å) [B. Aurivillius, *Acta Chem. Scand.*, **B28**, 681 (1974)] and in dithieno[1,2-b;5,4-b'] derivative (0.07 Å) [J.-E. Andersson, *Acta Cryst.*, **B35**, 1349 (1979)].
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