

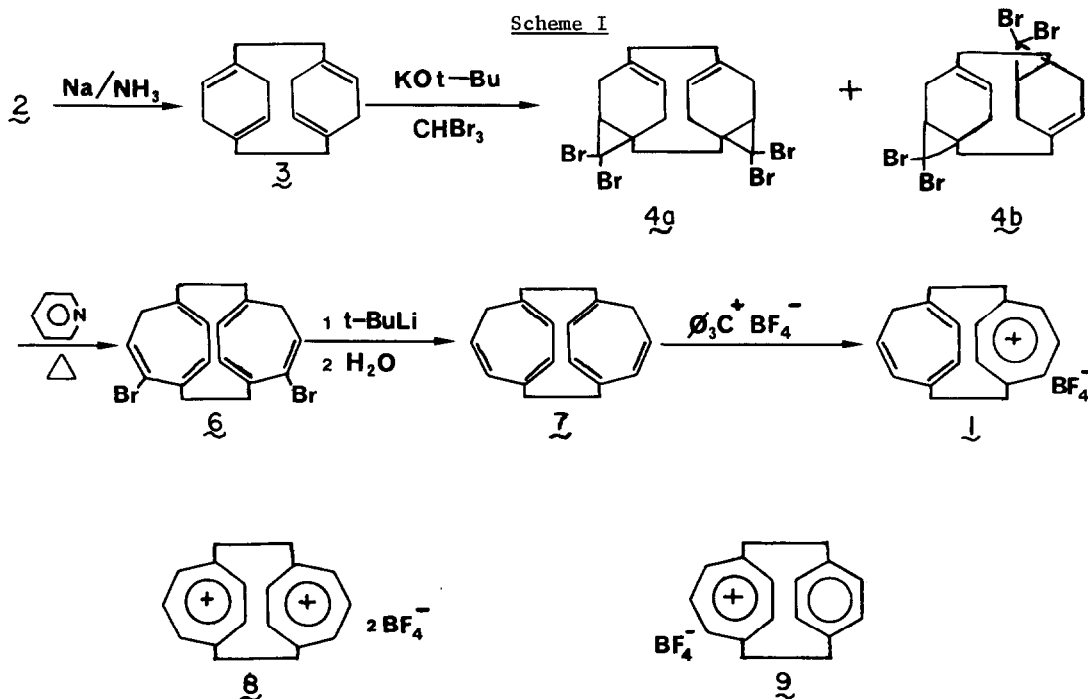
CYCLOPHANES. 12.¹ [2.2] (1,4)TROPYLIO(1,4)CYCLOHEPTATRIENOPHANE TETRAFLUOROBORATE.
SYNTHESIS AND CHARGE-TRANSFER INTERACTION²

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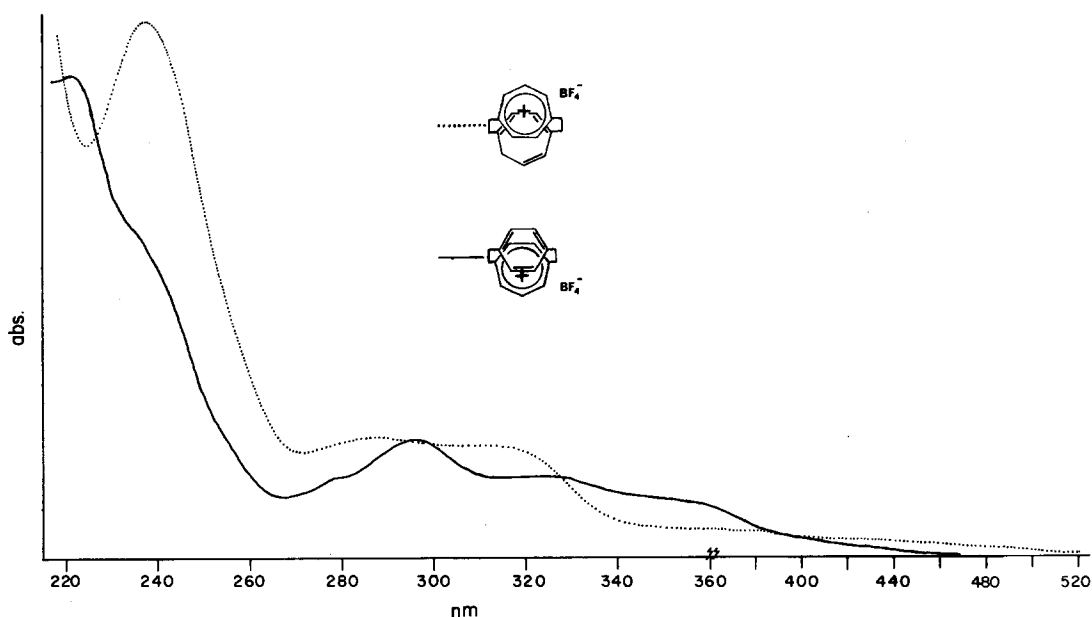
Intermolecular charge-transfer complexes are of great interest both theoretically and practically.³ Recently however strong emphasis is being placed on studies involving intramolecular charge-transfer complexes.⁴ These systems are of interest because of the potential they have as novel materials for organic semiconductors and because they are excellent models for the study of charge-transfer processes.^{3b,d} Unlike their intermolecular counterparts, intramolecular charge transfer complexes with a fixed orientation of donor and acceptor, are non-dissociable. The forced proximity not only prevents dissociation of donor-acceptor pairs that are necessarily in equilibrium in their intermolecular counterpart, but also allows an opportunity for forming charge-transfer complexes between molecular moieties which do not normally exhibit donor or acceptor capacity. We describe herein the synthesis of the intramolecular charge-transfer compound 1. To our knowledge, 1 represents the first example of the donor capacity of the cycloheptatriene moiety⁵ induced by the proximate tropylium acceptor.



Scheme I describes the synthesis leading to 1 and begins with the known Birch reduction (96%) of [2.2]paracyclophane (2).⁶ Treatment of 3 with dibromocarbene⁷ afforded a mixture of dicarbene adducts 4a and 4b (47%)⁸ along with monocarbene adduct 5.⁷ Dehydrohalogenation of 4 in pyridine afforded a mixture of isomeric dibromides 6 (39%).⁹ (The scheme is written for the major isomer of the anti-series derived from 4a. A similar minor syn-series is derived from 4b.) Reduction of C-Br bond with t-BuLi afforded [2.2](1,4)cycloheptatrienophane (7) (90%).¹⁰ Finally treatment of 7 with one equivalent of tritylfluoroborate afforded [2.2](1,4)tropylio(1,4)cycloheptatrienophane tetrafluoroborate (1).^{11,12}

Structural assignments were made by spectral analysis.^{13,14} Of particular interest is the electronic spectrum of 1 (see figure 1). Along with an absorption at 238 nm which is

Figure 1



indicative of transannular π - π interaction in [2.2]cyclophanes^{15a,b} and the absorption at 288 nm for both the cycloheptatriene and the tropylium chromophores⁷ there is observed a strong charge-transfer band at 313 nm which extends out to about 500 nm. This band is comparable to that observed in 9 (323 nm).⁷ Since donor capacity, relative to the same acceptor, can be correlated with the wavelength of the charge-transfer band,¹⁶ the similarity of the position of the two bands in 1 and 9 argues for the similar donor capacities of cycloheptatriene and benzene in these systems. The donor capacity of cycloheptatriene manifests itself due to its proximity to the tropylium acceptor and the existence of the complex demonstrates the effect that distance has on the complexing capacity of donor and acceptor. Attempts to prepare an intermolecular charge-transfer complex between cycloheptatriene and tropylium tetrafluoroborate were unsuccessful and no charge transfer bands were observed for the mixture of these compounds even at concentrations where tropylium ion

has been shown to form intermolecular complexes with weak π -donors.¹⁷ We thus see that the range of donors and acceptors in charge transfer complexes can be extended to include weakly interacting groups and the study of these systems should enhance our knowledge of the forces involved in charge-transfer processes. Our observations fulfill in part Mulliken's prediction¹⁸ of the possibility of forcing complex formation between apparently non-interactive moieties under extraordinary conditions.

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- Work supported by NSF. We gratefully acknowledge this assistance.
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- For the mixture of 4a and 4b: mp (168^o-179^oC); nmr (CDCl₃) δ 1.20-2.78 (m,18H), 5.40 (m,2H).
- There were two isomers in a ratio of 2:1; nmr (CDCl₃) δ 1.50-3.28 (m,12H); vinyl region, major isomer 4.55 (t,2H, J=7Hz), 6.40 (q,4H, J=11Hz), minor isomer 5.20-5.5 (m,2H), 5.9-6.5 (m,4H); uv(EtOH) λ_{nm} (ϵ) 220sh(18,500), 276(5330).
- mp, 126-30^oC; nmr (CDCl₃) δ 1.25-1.58 (m,2H), 1.9-2.9 (m,10H), 4.15-6.80 (m,8H); ms 236, 118; uv(EtOH) λ_{nm} (ϵ) 220sh(11,000), 259(4720).
- Nmr (CD₃NO₂) δ 1.0-1.3 (m,1H), 1.95-2.95 (m,4H), 3.15-3.80 (m,5H), 6.25-6.8 (m,4H), 8.0-8.26⁻(m,2H), 8.55-8.86 (m,3H); ir 1070 cm⁻¹, BF₄⁻; ms 236, 235, 145, 118, 91; uv(CH₃CN) λ_{nm} (ϵ) 238(37,300), 288(8510), 313(7970), 360sh(2570), 423sh(1750).
- Nmr spectral evidence [(CD₃NO₂) δ 9.09 (m), 7.74 (m), 4.05 (m) in ratio of 3:2:2] indicates that [2.2](1,4)tropylioparacyclophane ditetrafluoroborate (8) was formed on treatment of 7 with two equivalents of tritylfluoroborate. Rapid decomposition however precluded isolation.
- Satisfactory analyses were obtained for compounds 4, 6, 7. Numerous attempts to crystallize an analytical sample of 7 failed due to its instability, but a satisfactory mass spectrum was obtained (see reference 11).
- Spectral analysis indicates that the anti-isomer series predominates. Distinction

between 4a and 4b by nmr was not possible. However, the eleven degree melting point range for the analytical sample supports the presence of the two isomers. On the other hand the nmr spectrum of the mixture of the dibromides 6 had a principle isomer (anti) with a quartet centered at δ 6.40 ($J=11\text{Hz}$) and a triplet centered at δ 4.55 ($J=7\text{Hz}$). The nmr spectrum for 7 was clearly a mixture of isomers, but again the spectrum was too complicated for definitive analysis. It can be stated with some certainty however, that the conditions for conversion of 4 \rightarrow 6, 6 \rightarrow 7 and 7 \rightarrow 1 were not suitable for anti \rightleftharpoons syn interconversion. At worse compound 1 is a mixture of syn and anti isomers. This does not however detract from the important points regarding the donor properties of the cycloheptatriene ring and the charge transfer band in 1.

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