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FURTHER EVIDENCE FOR THE INTRAMOLECULAR CHARGE-TRANSFER INTERACTION BETWEEN TROPYLIUM ION AND REMOTE BENZENE RINGS IN 9,10-DIHYDRO-9,10-(1,2-TROPYLIO)ANTHRACENE TETRAFLUOROBORATE AND ITS METHYL DERIVATIVES

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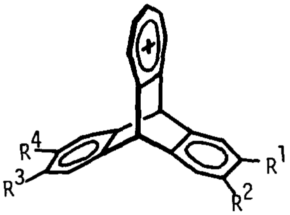
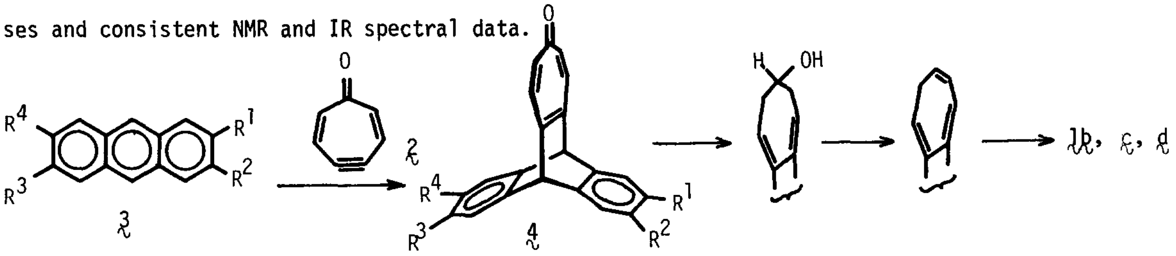
A series of 9,10-dihydro-9,10-(1,2-tropylio)anthracene tetrafluoroborates (1b-1d) has been prepared. The intramolecular charge-transfer interactions in 1b-1d were confirmed by their UV spectra and pK_{R^+} values. As a model compound 1,2,3,4-tetrahydro-1,4-(1,2-tropylio)naphthalene tetrafluoroborate (5) was also examined.

We recently reported[1)] a good case for the existence of an intramolecular charge-transfer (CT) interaction in the 9,10-dihydro-9,10-(1,2-tropylio)anthracene tetrafluoroborate (1a).[1,2)] An important aspect of the significance of this interaction seems not to have been mentioned and that is the fact that donor and acceptor are not in parallel planes. We now wish to report the synthesis and properties of a series of tropylium ions (1b-1d) having methyl group(s) in the benzene ring. The result of such study has led to significant advance in understanding of the unique intramolecular CT interaction.



1a : $R^1=R^2=R^3=R^4=H$ yellow needles, mp 110-135°(d)
1b : $R^1=CH_3$, $R^2=R^3=R^4=H$ yellow crystals, mp 137-145°(d)
1c : $R^1=R^2=CH_3$, $R^3=R^4=H$ yellow needles, mp 128-150°(d)
1d : $R^1=R^2=R^3=R^4=CH_3$ yellowish orange needles, mp 175-185°(d)

Reaction of 4,5-dehydrotropone (2)[3)] with anthracene (3a) is known to give the adduct (4a) which could be converted into 1a by reduction, dehydration, and hydride abstraction sequence.[1)] This synthetic method has been applied here to the preparation of 1b-1d. Cycloaddition reaction of 2 and 3 proceeded at room temperature in dichloromethane (cases of 3b and 3c) or at reflux in 1,2-dichloroethane (case of 3d) to give the corresponding tropone derivatives (4b-4d).[4)] The conversion of these tropones into the corresponding tropylium ions as tetrafluoroborate (1b-1d) was accomplished according to the following scheme exactly same as that used for the preparation of the parent ion 1a. Structures of 1b-1d were confirmed on the basis of their elemental analyses and consistent NMR and IR spectral data.



The electronic absorption spectra of these ions are illustrated in Fig. 1. From these spectra it has become apparent that for a series of methyl derivatives there is a progressive red shift of the absorption maximum in the long wavelength region compared with that of the parent ion 1a which we have previously assigned to CT band.1) Furthermore, the substantial blue shift accompanying the change from methylene chloride to acetonitrile as solvent was also observed.5) As shown in Fig. 2, the observed CT absorption of 1a could be resolved by using a Du Pont 310 curve resolver into three bands. Same analysis was also performed for 1b and 1c, and the results are summarized in Table 1. The plots of the transition energies of the 1st and 2nd CT bands against the 1st ionization potentials of the corresponding aromatic hydrocarbon moieties, i.e., o-xylene,6) 1,2,4-trimethylbenzene,6) and durene6) for 1a, 1b, and 1c, respectively, [see Fig. 3] give two parallel straight lines with the slope of 0.38 whose value is significantly smaller than unity indicating that the intramolecular CT interaction between tropylium ion and remote benzene rings is strong despite unfavorable orbital overlap of donor and acceptor.7)

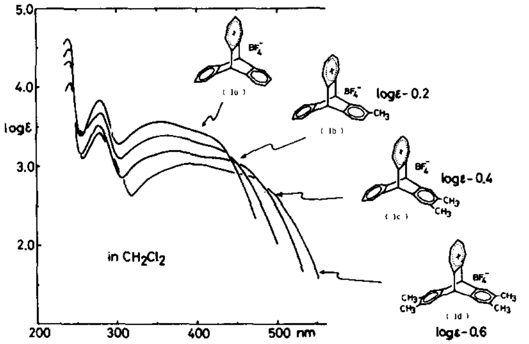


Fig. 1. Electronic spectra of 1a-1d.

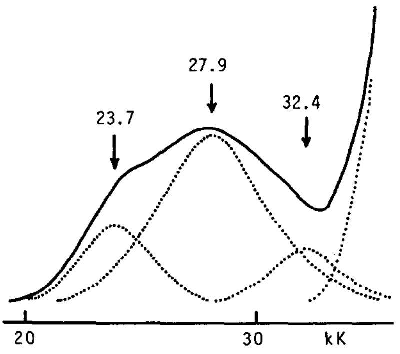


Fig. 2. Observed (——) and resolved (······) CT-bands of 1a.

For the interpretation of the CT absorptions of 1a-1d, some complications arise from the fact that two donor moieties contribute to the CT absorptions and also the interaction between two benzene rings could not stricktly be neglected. As more simplified model, 1,2,3,4-tetrahydro-

1,4-(1,2-tropylio)naphthalene tetrafluoroborate (**5**), yellow prisms, mp 133-135°C (d), was synthesized from 9,10-dihydro-9,10-ethanoanthracene through ring expansion by diazomethane followed by hydride abstraction. The cation **5** exhibits only two CT-bands at 25.8, 29.0 kk in CH_2Cl_2 and 27.3 30.3 kk in CH_3CN (see Fig. 4). From this finding, we would quite tentatively explain three CT-bands observed in **1a**-**1d** as a result of the interaction of two pairs of CT-states concerning each donor. The above mentioned plots (Fig. 3) could lead to the conclusion that the LUMO and the second LUMO play an important role in the 1st and 2nd CT-bands, respectively. However, the energy difference between 1st and 2nd CT-bands of **1a** (0.52 eV), **5** (0.40 eV), and **1c** (0.50 eV) are of similar values to those between 1st and 2nd ionization potentials of donor moieties (o-xylene, 0.45 eV; durene, 0.50 eV)$^{8)}$ suggesting that these two CT-bands can be assigned to the electronic transitions excited from the HOMO and the second HOMO to the LUMO, respectively. Although the alternative judgment of these two possibilities is obscure at present, the latter seems to be consistent with the results obtained by a modified version of the CNDO/2 calculations on **5**.$^{9)}$

Table 1. Resolved Charge-Transfer Maxima of **1a**, **1b**, and **1c** in CH_2Cl_2.

	1a	**1b**	**1c**
1st CT	422 nm (23.7 kK)	431 nm (23.2 kK)	455 nm (22.0 kK)
2nd CT	358 nm (27.9 kK)	373 nm (26.8 kK)	385 nm (26.0 kK)
3rd CT	309 nm (32.4 kK)	318 nm (31.4 kK)	327 nm (30.6 kK)

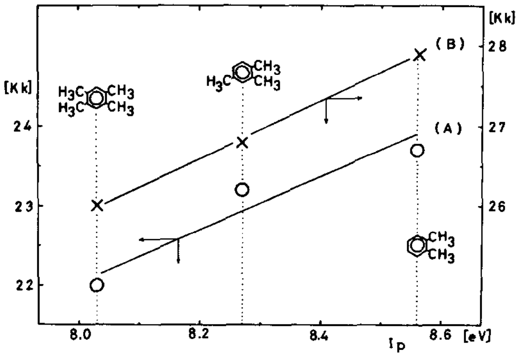


Fig. 3. Plots of 1st(A) and 2nd(B) CT energies *vs.* 1st IPs of the corresponding aromatic moieties.

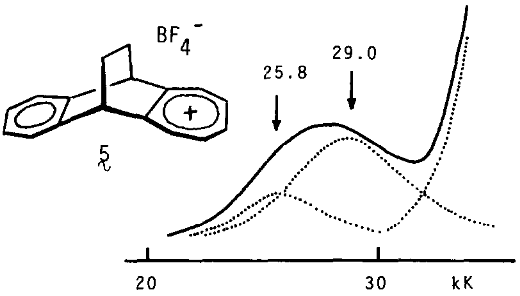


Fig. 4. Observed (——) and resolved (······) CT-bands of **5**.

Further evidence for the intramolecular remote π-π interaction between benzene and tropylium ion was provided by the pK_R+ values of **1a**-**1d** measured in 20% aqueous acetonitrile by the standard spectrophotometric method. Inspection of these values thus obtained (**1a** : 4.85; **1b** : 4.95; and

1c : 5.2; clearly indicates that the thermodynamic stability of the tropylium ion increases with increasing methyl substitution. This finding also support the idea of through-bond homoconjugative interaction[10)] because the donor and the acceptor are in an unfavorable spacial position for through space interaction.

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REFERENCES AND FOOTNOTES

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

2) D. N. Butler and I. Gupta, *Can. J. Chem.,* 56, 80 (1978).

3) T, Nakazawa and I. Murata, *Angew. Chem.,* 87, 742 (1975); *Angew. Chem. internat. Ed.,* 14, 711 (1975).

4) All new compounds described in this paper gave satisfactory elemental analyses and spectral data consistent with the proposed structures.

5) M. Feldman and S. Winstein, *J. Am. Chem. Soc.,* 83, 3338 (1961); idem., *Tetrahedron Lett.,* 853 (1962); idem., *Theor. Chim. Acta,* 10, 86 (1968); M. Feldman and B. G. Graves, *J. Phys. Chem.,* 70, 955 (1966); see also E. Kosower, *J. Am. Chem. Soc.,* 80, 3253 (1958); K. Dimroth, C. Reichardt, T. Siepmann, and F. Bohlmann, *Justus Liebigs Ann. Chem.,* 661, 1 (1963); C. Reichardt and K. Dimroth, *Fortsch. Chem. Forsch.,* 11, 1 (1968).

6) H. W. Gibson, *Can. J. Chem.,* 51, 3065 (1973).

7) R. S. Mulliken and W. B. Person, *"Molecular Complexes"* Wiley Interscience, 1969, New York.

8) J. P. Maier and E. Heilbronner, *"Electron Spectroscopy: Theory, Techniques and Applications,"* C. R. Brundle and A. D. Baker, Ed., Academic Press, London 1976.

9) Examining the coefficients of the molecular orbitals, the two CT bands of **5** could be assigned to the electronic transitions from the HOMO and the next HOMO of the benzene system to the acceptor tropylium system. The LUMO and the next LUMO of the acceptor equally contribute to both the 1st and 2nd CT-transitions. Details will be published by Professor Masahiro Hatano and Dr. Akio Tajiri. We thank them for informing us of their results prior to publication.

10) H. Iwamura and K. Makino, *J. C. S. Chem. Commun.,* 720 (1978)

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