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SYNTHESIS AND INTRAMOLECULAR CHARGE-TRANSFER INTERACTION OF *o*-TROPYLIOBIPHENYL TETRAFLUOROBORATES

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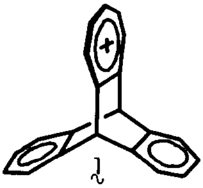
A series of *o*-tropyliobiphenyl tetrafluoroborates 4a-d has been synthesized. Evidences are presented to show that 4a-d exhibit strong intramolecular charge-transfer interaction between tropylium ion and remote aryl ring. The structure of 4a was determined by single crystal X-ray diffraction study.

We recently reported the synthesis and the intramolecular charge-transfer interaction in 9,10-dihydro-9,10(1,2-tropylio)anthracene tetrafluoroborate (1)[1] and some of its derivatives.[2] An important aspect of the significance of the charge-transfer interaction in 1 is the fact that donor and acceptor are not in parallel planes. It was noted that in these molecules the interaction is strong despite the minimized overlap of both donor and acceptor orbitals. In view of the fact that the tropylium ion is shown to be an effective electron acceptor as was found in [m.n](1,4)tropylioparacyclophane (2)[3] and 1-aryl-8-tropylionaphthalene (3),[4] study on the *o*-tropyliobiphenyl derivatives (4) as the model compound for the intramolecular charge-transfer interaction between nonparallel donor and acceptor would be of interest.



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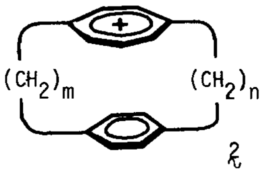

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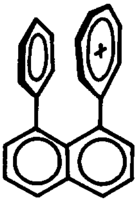

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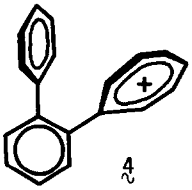

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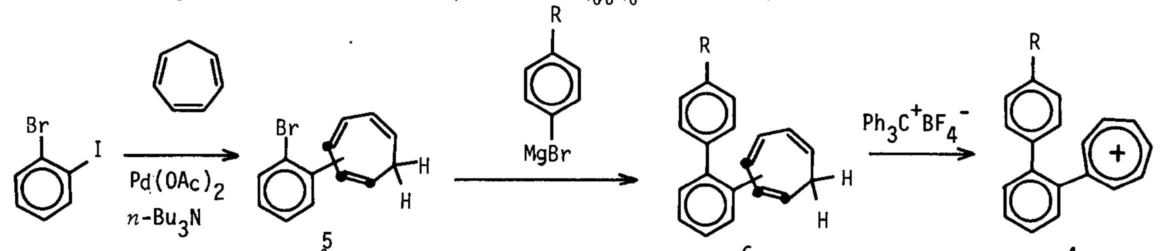
Synthesis of a series of *o*-tropyliobiphenyl tetrafluoroborates 4a-d used in this study was outlined in Scheme I. An isomeric mixture of *o*-bromophenyltropilidene (5) was prepared in 45% yield utilizing a general approach previously developed by Heck[5] that involve the palladium(II) acetate catalyzed arylation of tropilidene with *o*-bromoiodobenzene. Reaction of the mixture 5 with the corresponding arylmagnesium bromide in the presence of nickel(II) acetylacetonate[6] resulted in the formation of the biphenyl derivatives, **6a**-**d**, in 40-50% yield, which when treated with trityl tetrafluoroborate in dry dichloromethane followed by recrystallization from dichloromethane and ethyl acetate lead to the pure salts **4a**-**d** in 50-60% yield.



a: R=H, **5** b: R=CH$_3$, c: R=t-C$_4$H$_9$, **6** d: R=OCH$_3$ **4**

These tropylium salts are stable yellow orange crystals and their structure were evident by the synthetic sequences, elemental analyses, and spectral data. As shown in Table 1 and Fig. 1, the electronic spectrum of **4a** exhibits besides ultraviolet absorptions at 236 and 270 nm, two absorption maxima at 365 and 420 nm in its visible region. According to the previous study on the simple aryltropylium ions$^{7)}$ two bands observed in the UV region can be assigned to transitions within the tropylium ring whereas the band at 365 nm is assigned to a directly bonded aryl-to-tropylium charge-transfer excitation. The longest wavelength band at 420 nm, not found in the spectrum of the phenyltropylium tetrafluoroborate, was considered to be a charge-transfer band between the tropylium ion and remote (not directly bonded) aryl ring on the basis of the following evidences.

Like the band at 365 nm, the longest wavelength band at 420 nm shows a substantial blue shift accompanying the change from less polar dichloromethane to more polar acetonitrile as solvent (see Fig. 1) consisting with the solvent sensitivity of the charge-transfer band.$^{8)}$ Furthermore, in the visible spectra of a series of cations **4a**-**d**, there is a progressive red shift of the longest wavelength maximum with increasing donor ability whereas the band at 365 nm remains almost unchanged (Fig. 2 and Table 1). For these cations, the variation of the energy of the longest wavelength band with ionization potentials$^{9)}$ of the donor aryl ring is shown graphically in Fig. 3. The fairly good linear relationship of the plot confirms that the bands are of donor-acceptor type. Further evidence in support of the intramolecular charge-transfer interaction is obtained by electrochemical reduction potential data measured in dichloromethane by polarography using tetra-n-butylammonium perchlorate as supporting electrolyte (Table 1).$^{10)}$ The reduction potential shifts in the negative direction with increasing donor ability of the remote aryl ring. A plot of the reduction potentials against the ionization potentials for the donor moieties leads also to a fair straight line (Fig. 3).

Table 1. Physical Properties of 4a - 4d

	R	mp (°C)	UV-Vis nm (log ε)	^{1}H-NMR (CD_2Cl_2) δ	$E_{1/2}$ V *vs* SCE
4a	H	168-175	365 (3.90) 420 (3.64)$^{a)}$	8.86-9.08 (m,6H, $-C_7H_6^+$), 7.54-7.84 (m,4H,$-C_6H_4-$), 7.04-7.38 (m,5H,$-C_6H_5$)	-0.031_7
4b	CH_3	161-169	370 (3.89) 442 (3.60)$^{a)}$	2.29 (s,3H,$-CH_3$), 8.85-9.06 (m,6H,$-C_7H_6^+$), 7.52-7.80 (m,4H,$-C_6H_5$), 7.10, 6.96 (AB,4H,$-C_6H_4-$)	-0.042_9
4c	t-C_4H_9	160-164	369 (3.91) 446 (3.61)$^{a)}$	1.28 (s,9H,t-C_4H_9), 8.84-9.18 (m,6H,$-C_7H_6^+$) 7.54-7.83 (m,4H,$-C_6H_5$), 7.32, 7.02 (AB,4H,$-C_6H_4-$)	-0.035_6
4d	OCH_3	78-85	373 (3.93) 476 (3.50)$^{a)}$	3.75 (s,3H,$-OCH_3$), 8.86-9.04 (m,6H,$-C_7H_6^+$), 7.52-7.80 (m,4H,$-C_6H_5$), 7.02, 6.88 (AB,4H,$-C_6H_4-$)	-0.068_2

a) The CT bands are obtained by using a Du Pont 310 Curve Resolver.

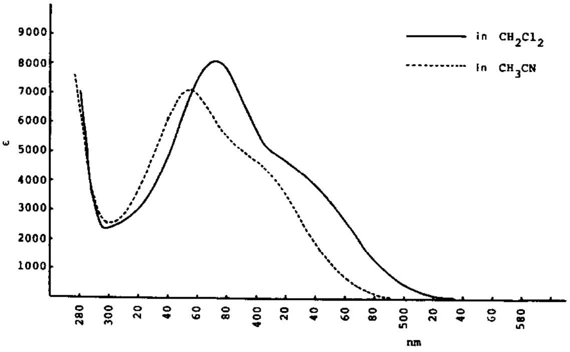


Fig. 1. Uv-Vis spectra of 4a in CH_2Cl_2 and CH_3CN.

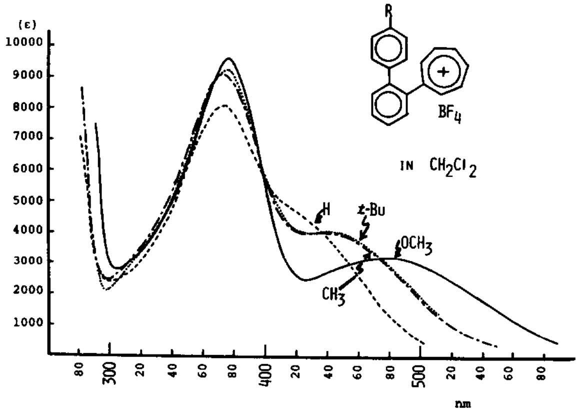


Fig. 2. Uv-Vis spectra of 4a-4d in CH_2Cl_2.

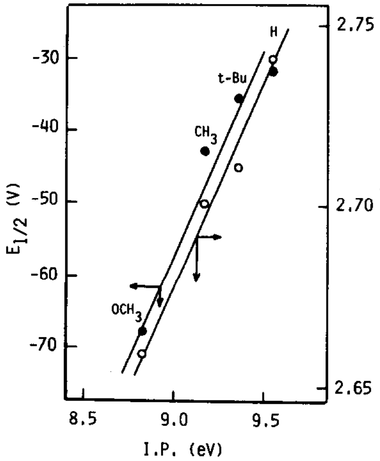


Fig. 3.
Plots of the IPs of the donor moieties of 4a-4d *vs*. the CT transition energies and reduction potentials.

The molecular structure of the cation in 4a determined by X-ray crystallographic analysis is illustrated in Fig. 4.$^{11)}$ The terminal phenyl (B) and tropylium rings (C) are twisted with respect to the central benzene ring (A) by 54° and 53°, respectively. Although the intramolecular nonbonded distances between two terminal rings (B and C) are found to be C(8)···C(13)=3.168(8)Å and C(8)···C(19)=3.290(8)Å, which are somewhat shorter than the sum of their van der Waals radii, the overall σ-type overlap of the interacting p-orbitals in 4a is presumed to be smaller than that of the two parallel oriented aromatic rings such as in 2 (m=n=2) and 3. Above mentioned results indicate that the intramolecular charge-transfer interaction can be existed even in a disadvantageous arrangement of the orbital systems of donor and acceptor such as 4.

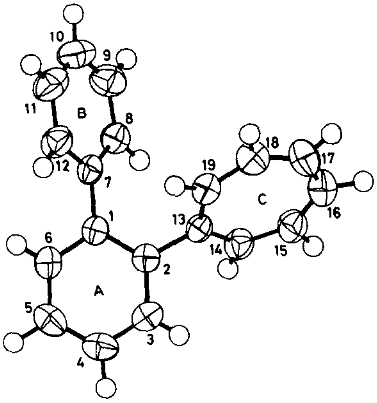


Fig.4. Molecular structure of o-tropyliobiphenyl cation in 4a, viewed perpendicular to the ring A.

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

2) T. Nakazawa, N. Abe, K. Kubo, and I. Murata, preceding paper of this issue.

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

4) K. Komatsu, N. Abe, K. Takahashi, and K. Okamoto, *J. Org. Chem.*, in press. We thank Professor Kunio Okamoto for informing us of his results prior to publication.

5) R. F. Heck and J. P. Nolley, Jr., *J. Org. Chem.*, 37, 2320 (1972).

6) R. L. Clough, P. Mison, and J. D. Roberts, *J. Org. Chem.*, 41, 2252 (1976).

7) G. Hohlneicher, R. Kiessling, H. C. Jutz, and P. A. Straub, *Ber. Bunsenges. Phys. Chem.*, 70, 60 (1966); P. Schuster, D. Vedrilla, and O. E. Polansky, *Monatsch. Chem.*, 100, 1 (1969).

8) E. Kosower, *J. Am. Chem. Soc.*, 80, 3253 (1958); K. Dimroth, C. Reichardt, T. Siepmann, and F. Bohlmann, *Justus Liebigs Ann.*, 661, 1 (1963); C. Reichardt and K. Dimroth, *Fortsch. Chem. Forsch.*, 11, 1 (1968).

9) G. F. Crable and G. L. Kearns, *J. Phys. Chem.*, 66, 436 (1962); J. D. Morrison and A. J. C. Nicholson, *J. Chem. Phys.*, 20, 1021 (1952).

10) We thank Dr. S. Himeno, Department of Chemistry, College of General Education, Kobe University, for the measurements of the reduction potentials.

11) Crystals of 4a are triclinic, space group $P\bar{1}$, with a=10.043(1), b=10.399(1), c=9.235(1) Å, α=92.43(1), β=100.19(1), γ=118.08(1)°, Z=2. The structure was solved by MULTAN procedure,[12] and refined by the block-diagonal least-squares method to a conventional R value of 0.081 for 2184 observed reflections collected on an automatic diffractometer. The orientation of the BF_4^- anion is somewhat disordered.

12) G. Germain, P. Main, and M. M. Woolfson, *Acta Crystallogr.*, A27, 368 (1971).

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