in (3.00 mmol) in THF at 0 °C with stirring. The resulting mixture was stirred for 15 min and then cooled to −78 °C and treated with 1-bromooctane (0.193 g, 1.00 mmol).

2,2-Dimethyldecane (Preparative-Scale Procedure). Into a flame-dried, three-necked 500-mL flask equipped with a Teflon-coated stirring bar and a 50-mL addition funnel and capped with rubber septums was placed copper(I) iodide (6.66 g, 35.0 mmol) and THF (250 mL). This mixture was cooled to −5 °C and a solution of *tert*-butyllithium (41.3 mL, 60.0 mmol) was added dropwise over a period of 5 min. The dark solution was stirred between 0 °C and −5 °C for 15 min and then cooled to −78 °C and 1-bromooctane (1.88 g, 9.77 mmol) was added dropwise by syringe. This mixture was stirred at −78 °C for 2 h and then at room temperature for an additional 12 h. The resulting mixture was treated with 80 mL of 3 N HCl and filtered through a Kieselguhr mat, and the layers were separated. The organic phase was washed with two 50-mL portions of 3 N HCl and then with two 50-mL portions of saturated brine. The aqueous phase and washings were extracted with two 50-mL portions of petroleum ether, and the combined organic phases were dried ($MgSO_4$), concentrated, and distilled (bulb-to-bulb, 2.3 torr) yielding 1.60 g of a colorless liquid which GLPC analysis indicated to be ~80% 2,2-dimethyldecane.

Oxidation Procedures. Similar procedures were employed in all oxidation reactions. The following examples are typical.

The reaction mixture produced by the addition of a solution of *sec*-butyllithium (4.92 mL, 6.00 mmol) to a suspension of copper(I) iodide (6.57 g, 3.00 mmol) in THF prepared as described above was cooled to −78 °C. A stream of dry dioxygen was bubbled rapidly, with efficient stirring, through the solution for 5 min. The resulting mixture was allowed to warm to room temperature and treated as previously described prior to analysis of GLPC.

Oxidation with nitrobenzene (1.85 g) at −78 °C gave a mixture which was mixed thoroughly, then allowed to warm to ambient temperature, and treated as previously described prior to analysis by GLPC.

Reaction of 8 (R = *sec*-C_4H_9) with Methyl Ethyl Ketone. The reagent 8 (3.00 mmol, R = *sec*-butyl) prepared at 0 °C in THF (25 mL) and a weighed amount of internal standard were cooled to −78 °C and methyl ethyl ketone (63.0 mg, 0.886 mmol) was added by syringe. The resulting mixture was stirred at −78 °C for 1 h and then at ambient temperature for an additional 1.5 h. An aliquot of the mixture was removed and treated with 0.2 mL of water; the resulting solids were compacted by centrifugation and the supernatant solution was analyzed by GLPC.

Acknowledgments. This work was supported by the National Science Foundation (Grant 77-08331).

Registry No. 8 (R = *tert*-C_4H_9), 23402-75-7; 8 (R = *sec*-C_4H_9), 23402-73-5; 8 (R = C_4H_9), 24406-16-4; $C_8H_{17}Cl$, 111-85-3; $C_8H_{17}Br$, 111-83-1; $C_8H_{17}I$, 629-27-6; 2-chlorooctane, 628-61-5; 2-bromooctane, 557-35-7; 2-iodooctane, 557-36-8; 2-octyl tosylate, 1028-12-2; octyl tosylate, 3386-35-4; nonane, 111-84-2; 2-methyloctane, 3221-61-2; dodecane, 112-40-3; 5-methylundecane, 1632-70-8; 3-methylundecane, 1002-43-3; 2,2-dimethyldecane, 17302-37-3; 1-phenyloctane, 2189-60-8; 2-cyclohexen-1-one, 930-68-7; methyl vinyl ketone, 78-94-4; 3-methylcyclohexanone, 591-24-2; 3-butyl-2-cyclohexenone, 6301-49-1; 3-*tert*-butylcyclohexanone, 936-99-2; 2-octanone, 111-13-7; 2,2,3-trimethylnonane, 55499-04-2; 3,4-dimethyldecane, 17312-45-7; CuI, 7681-65-4; tetrakis[iodo(tributylphosphine)copper(I)], 28132-72-1; 5-methyl-5-undecanol, 21078-80-8; 3-*tert*-butylphenol, 585-34-2; 3-*tert*-butylcyclohexanol, 4534-70-7; iodo[bis(dibutyl sulfide)copper(I)], 35907-81-4; methyl ethyl ketone, 78-93-3; 3,4-dimethyl-3-hexanol, 19550-08-4; octane, 111-65-9; 3,4-dimethylhexane, 583-48-2.

1-Aryl-8-tropylionaphthalene Perchlorates: Synthesis and Intramolecular Charge-Transfer Interaction

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A series of 1-aryl-8-tropylionaphthalene cations [aryl = phenyl (**4a**), *p*-methylphenyl (**4b**), *m,m*-dimethylphenyl (**4c**), *p*-methoxyphenyl (**4d**), *p*-(trifluoromethyl)phenyl (**4e**), and *m,m*-bis(trifluoromethyl)phenyl (**4f**)] have been synthesized by nickel(II)-catalyzed coupling of 1-bromo-8-cycloheptatrienylnaphthalene with the corresponding arylmagnesium halides followed by hydride abstraction. The ^1H NMR spectra of **4a–f** indicated that the two aromatic rings at the peri positions are in a face-to-face arrangement. The absorption band at 373 nm observed in the electronic spectrum of **4a** in acetonitrile was assigned to the intramolecular charge-transfer band between the phenyl and tropylium rings based on the solvent and substituent effects. This intramolecular electronic interaction results in stabilization of the cation **4a** by 2.1 pK_{R^+} units and the increase in its reduction potential by 0.182 V as compared with the reference cation, 1-tropylionaphthalene (**5**). A better linear correlation was obtained when the values of pK_{R^+} and reduction potential for **4a–f** were plotted against the substituent constant σ_m^+ rather than against σ_p^+. This result together with the substituent effect upon the ^1H NMR chemical shift of the tropylium ring protons suggests that the electronic effect of the substituents would be transmitted inductively through the σ overlap of p orbitals of the two aromatic rings facing each other.

There has been considerable interest in the *intra*molecular charge-transfer complex,[1-3] since it can be regarded as an undissociable donor–acceptor pair, and thus serves as the most fundamental model system for the study of *inter*molecular charge-transfer interaction. Recently, a strong π acceptor with a full positive charge, the tropylium ion, was shown to be an effective probe to detect the

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[1] (1) For example, see (a) D. J. Cram and A. C. Day, *J. Org. Chem.*, **31**, 1227 (1966); (b) D. J. Cram and J. M. Cram, *Acc. Chem. Res.*, **4**, 204 (1971); (c) W. Rebafka and H. A. Staab, *Angew. Chem.*, **85**, 831 (1973); **86**, 234 (1974); (d) H. A. Staab and U. Zapf, *ibid.*, **90**, 807 (1978), and the earlier publications cited therein; (e) H. Tatemitsu, B. Natsume, M. Yoshida, Y. Sakata, and S. Misumi, *Tetrahedron Lett.*, 3459 (1978), and the earlier publications cited therein; (f) R. Luhowy and P. M. Keehn, *J. Am. Chem. Soc.*, **99**, 3797 (1977), and the references cited therein; (g) Y. Fukazawa, M. Aoyagi, and S. Ito, *Tetrahedron Lett.*, 1067 (1978); (h) T. Nakazawa, Y. Niimoto, and I. Murata, *ibid.*, 569 (1978).

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

(3) (a) T. Nakazawa and I. Murata, *J. Am. Chem. Soc.*, **99**, 1996 (1977); (b) D. N. Butler and I. Gupta, *Can. J. Chem.*, **56**, 80 (1978).

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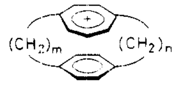
intramolecular π–π interaction when the tropylium ring was suitably incorporated in the system. For example, the intramolecular charge-transfer band was unambiguously observed in $[m.n](1,4)$-tropylioparacyclophanes (**1**)[2] and



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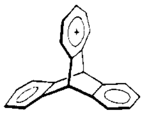

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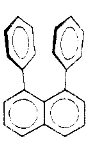

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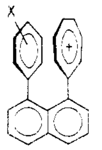

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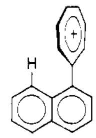
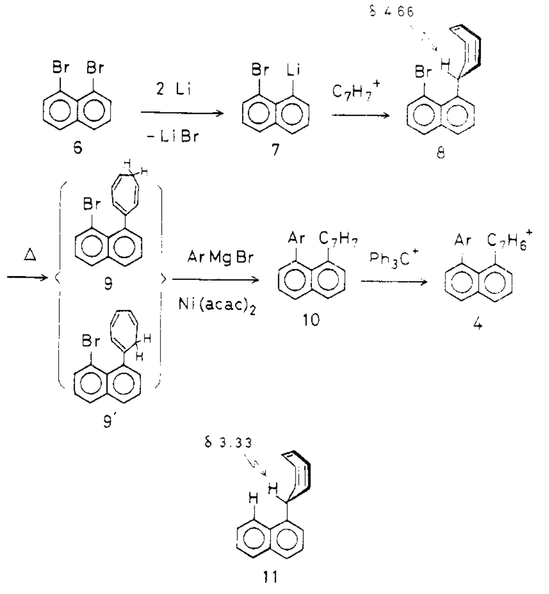


5

X = H (4a), p-CH$_3$ (4b),
m,m-(CH$_3$)$_2$ (4c), p-OCH$_3$ (4d),
p-CF$_3$ (4e), m,m-(CF$_3$)$_2$ (4f)

even in the tropylium analogue of triptycene (9,10-dihydro-9,10-(1,2-tripylio)anthracene (**2**))[3] which contains the donor and acceptor rings in an arrangement remote to each other. These two types of compounds represent the case in which interacting π systems are fixed in rigid carbon frameworks. On the other hand, the 1,8-diphenylnaphthalene system (**3**) provides another interesting case in which the two π systems attached at the peri positions[4] stand facing each other but possess some freedom in motion as compared with the above-mentioned systems: that is, the two phenyl groups can flip back and forth across the plane of the naphthalene ring,[5] can rotate with the energy barrier of 16 kcal/mol,[6] and are slightly splayed out repulsing each other.[7] From the X-ray crystallographic study,[7] the distance between the *ipso*-carbons of the facing phenyls and that between the *peri*-carbon atoms are shown to be 2.99 and 2.56 Å, respectively, to be compared with the distances between the facing phenyl rings in [2.2]paracyclophane (3.10 Å between the unsubstituted carbon atoms and 2.79 Å between the substituted ones) and in [3.3]paracyclophanes (3.31 and 3.14 Å, respectively).[8] Unlike the paracyclophanes, no skeletal deformation of the facing rings occurs in **3** so that the intrinsic electronic nature of the π system is preserved. A series of naphthalenes substituted with one or two phenyl groups at various positions have been synthesized, but upon comparison of their electronic spectra no distinct interaction was observed between the facing phenyl rings in **3**.[9]

Scheme I



Thus, in order to clarify the possible π–π interaction in this system, we have synthesized a series of 1-aryl-8-tropylionaphthalenes (**4a–f**) and examined the intramolecular charge-transfer interaction in them, in comparison with 1-tropylionaphthalene (**5**) as the reference compound. Heretofore, such interaction has been discussed primarily based on appearance of a new charge-transfer band in the electronic spectrum. Rather, we were interested in the physicochemical properties of the acceptor moiety, such as reduction potential and pK_{R^+} values, which should also strongly reflect the intramolecular electronic interaction. For the purpose of systematic examination of these properties, the system **4** has an advantage in that a variety of substituents can be easily introduced into the donor ring as will be described below.

Synthesis. The synthetic route for 1-aryl-8-tropylionaphthalenes **4a–f** is shown in Scheme I. In spite of the presence of a bulky bromo substituent at the peri position, 1-bromo-8-lithionaphthalene (**7**) smoothly reacted with the tropylium ion to give 1-bromo-8-(cyclohepta-2,4,6-trien-1-yl)naphthalene (**8**) in 60% yield. Due to considerable steric compression with the bromine atom, the ^{1}H NMR signal for the H-1 proton in the cycloheptatriene ring of **8** is shifted 1.33 ppm downfield as compared with the corresponding signal of the reference compound, 1-(cyclohepta-2,4,6-trien-1-yl)naphthalene (**11**). In order to minimize the steric hindrance at the subsequent aryl coupling process, cycloheptatriene **8** was then thermally isomerized by sigmatropic rearrangement to a mixture of isomers **9** and **9′**. As had already been shown by Roberts et al. in ready synthesis of 1,8-diarylnaphthalenes,[10] nickel(II) acetylacetonate was found to catalyze the coupling of the bromonaphthalenes **9** and **9′** and various arylmagnesium halides to give the 1-aryl-8-cycloheptatrienylnaphthalenes **10** in 25–61% yields. The subsequent hydride abstraction afforded, in 75–90% yields, the cation salts **4a–f** ClO_4^- as yellowish orange to dark red crystals which are stable in the air.

Characterization of 1-Aryl-8-tropylionaphthalenes (4a–f) and the Intramolecular Charge-Transfer Interaction. The structural assignment was made based on

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(4) For the review on the peri interaction in naphthalene derivatives, see V. Balasubramaniyan, *Chem. Rev.*, **66**, 567 (1966).

(5) R. L. Clough and J. D. Roberts, *J. Am. Chem. Soc.*, **98**, 1018 (1976).

(6) H. O. House, W. J. Campbell, and M. Gall, *J. Org. Chem.*, **35**, 1815 (1970).

(7) R. A. Ogilvie, Ph.D. Thesis, Massachusetts Institute of Technology (1971), cited in H. O. House, D. G. Koepsell, and W. J. Campbell, *J. Org. Chem.*, **37**, 1003 (1972), and R. L. Clough, W. J. Kung, R. E. Marsh, and J. D. Roberts, *ibid.*, **41**, 3603 (1976).

(8) (a) C. J. Brown, *J. Chem. Soc.*, 3265 (1953); (b) P. K. Gantzel, C. L. Coulter, and K. N. Trueblood, *Angew. Chem.*, **72**, 755 (1960); (c) P. Gantzel and K. N. Trueblood, *Acta Crystallogr.*, **18**, 958 (1965).

(9) H. O. House, R. W. Magin, and H. W. Thompson, *J. Org. Chem.*, **28**, 2403 (1963).

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

Table I. ^{1}H NMR Spectral Data for 1-Phenylnaphthalene (12), 1-Tropylionaphthalene (5), and 1-Aryl-8-tropylionaphthalene Cations (4a–f)

	chemical shift, δ, in ppm from Me_4Si^a			
compd	tropylium	naphthyl	phenyl	substituent
12^b		7.9–7.6 (m)	7.38 (s)	
5	9.19 (s)	8.2–7.6 (m)		
4a	8.68 (s)	8.3–7.7 (m)	7.01 (s)	
4b	8.67 (s)	8.3–7.7 (m)	6.89 (s)	2.17 (s)
4c	8.65 (s)	8.4–7.7 (m)	6.66 (s)^c 6.61 (s)^d	2.09 (s)
4d	8.70 (s)	8.4–7.7 (m)	6.89 (q)	3.87 (s)
4e	8.76 (s)	8.4–7.7 (m)	7.33 (s)	
4f	8.82 (s)	8.4–7.5 (m)	7.65 (s)^c 7.54 (s)^d	

^{a} Measured in CF_3CO_2H ^{b} Measured in CCl_4, ref 9. ^{c} Ortho protons. ^{d} Para proton.

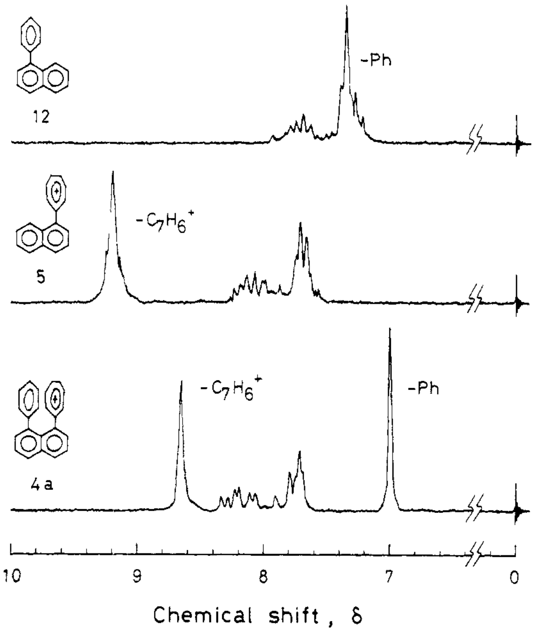

Figure 1. The 60 MHz ^{1}H NMR spectra for 1-phenylnaphthalene (12; in CCl_4), 1-tropylionaphthalene (5; in CF_3CO_2H), and 1-phenyl-8-tropylionaphthalene (4a; in CF_3CO_2H).

spectral data shown in Table I and in the Experimental Section. The ^{1}H NMR spectra provide valuable information about the conformation of two aromatic substituents at the peri position. As a representative example, the spectrum for the 1-phenyl-8-tropylionaphthalene (4a) is shown in Figure 1 together with those for the reference compounds, 1-phenyl- (12) and 1-tropylionaphthalenes (5). Due to mutual shielding of the facing aromatic rings, the signals for phenyl and tropylium ring protons in 4a are shifted upfield by 0.37 and 0.51 ppm, respectively, as compared with 12 and 5. This phenomenon, which has also been observed in the case of 1,8-diphenylnaphthalene (0.53 ppm upfield shift for the phenyl signal compared with that of 12),[9] is taken as strong evidence for the face-to-face arrangement of the phenyl and tropylium rings.

In the electronic spectra in acetonitrile shown in Figure 2, the cation 4a exhibits an absorption band at 373 nm, which is absent in the spectrum of either reference compound 12 or 5. This band shows a marked bathochromic shift to 392 nm upon changing the solvent to less polar dichloromethane. This fact, together with the constancy of the absorption coefficient regardless of the change in concentration, suggests that this absorption arises from the intramolecular charge-transfer interaction between the donor's HOMO and the acceptor's LUMO.[11] This assignment is further supported by the substituent effect as is shown in Figure 3; i.e., with the increasing order of electron-donating nature of the substituent on the phenyl group, the band shifts to the longer wavelengths with relative increase in intensity. On the other hand, the absorption at the longest wavelength, which is supposed to arise from the electronic interaction between the tropylium and naphthalene rings, is much less affected by the substituents on the phenyl ring.

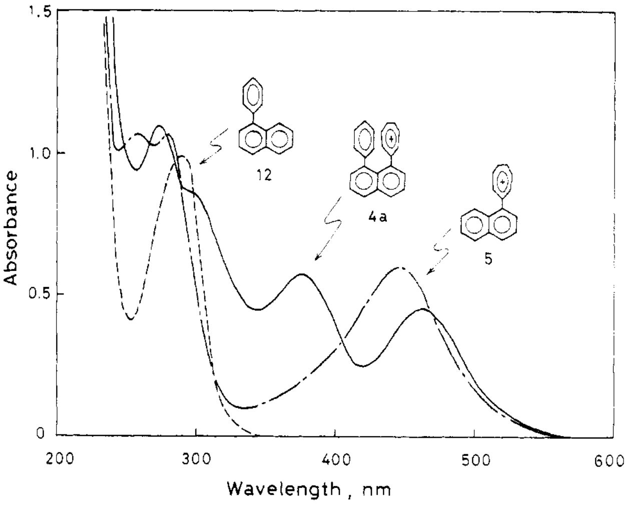

Figure 2. The electronic spectra for 1-phenylnaphthalene (12; ---), 1-tropylionaphthalene (5; — —), and 1-phenyl-8-tropylionaphthalene (4a; —) in CH_3CN; concentration, 1.00 × 10^{-4} M; cell path, 1 cm.

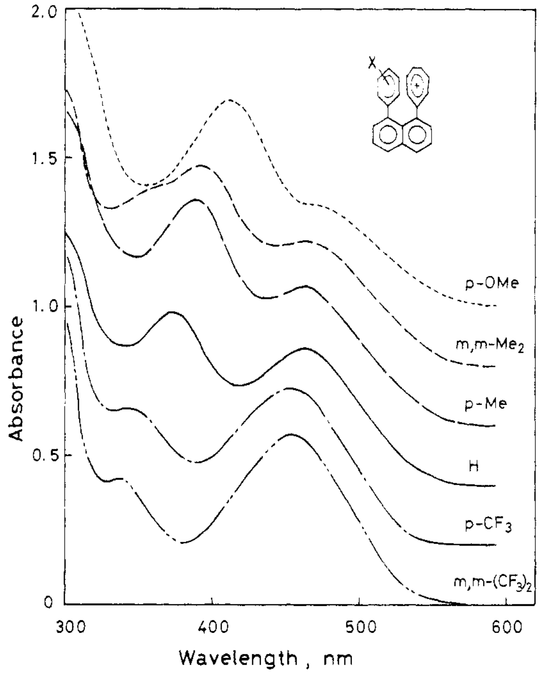

Figure 3. The electronic spectra for the 1-aryl-8-tropylionaphthalenes 4a–f in CH_3CN; concentration, 1.00 × 10^{-4} M; cell path, 1 cm. The absorbance for each spectrum is shifted by 0.2 with respect to the spectrum for 4f.

The transition energy (E_{CT}) for the intramolecular charge-transfer band observed in the present system 4a

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(11) Examination on MO's of benzene and tropylium ion indicates that the HOMO–LUMO interaction between these molecules is possible, though not very effective. On the other hand, it has been shown that the tropylium ion and aromatic hydrocarbons including benzene form charge-transfer complexes based on the spectral evidence.[12]

Table II. The pK_{R^+} and Reduction Potential Data for the Tropylium ($C_7H_7^+$), 1-Tropylionaphthalene (5), and 1-Aryl-8-tropylionaphthalene Cations (4a-f)

cation	pK_{R^+}[a] in 50% EtOH	V vs. SCE[b]
$C_7H_7^+$	2.91	-0.120
5	2.25	-0.113
4a	4.35	-0.295
4b	4.40	-0.300
4c	4.51	-0.317
4d	4.42	-0.289
4e	3.06	-0.217
4f	2.11	-0.178

[a] Measured spectrophotometrically at 25 °C. Uncertainty limit, ±0.05. [b] Reduction potential determined by cyclic voltammetry in dichloromethane with tetrabutylammonium perchlorate as a supporting electrolyte; scan rate, 100 mV/s. Uncertainty limit, ±0.005 V.

(λ_{max} 392 nm in dichloromethane) is apparently smaller than that for the reported charge-transfer band between benzene and tropylium ion (λ_{sh} 305 nm in 1,2-dichloroethane[12]) by 0.90 eV. According to Mulliken's theory on donor-acceptor complexes,[13] the value of E_{CT} is correlated with the donor's ionization potential (IP) and the acceptor's electron affinity (EA) as E_{CT} = IP - EA + constant.[14] If we assume that the IP for the benzene ring substituted with the 1-naphthyl group can be approximated by that for biphenyl (8.27 eV[15]), the IP for the donor unit in **4a** is supposed to be lowered by 0.98 eV as compared with that for benzene (9.25 eV[15]). On the other hand, the EA for the acceptor unit is estimated to be about 0.01 eV greater than that for the tropylium ion from the reduction potential data of the cation **5** in Table II (vide infra). Thus, from the above correlation, the E_{CT} for the intramolecular complex **4a** is predicted to be 0.99 eV less than that for the benzene-tropylium ion complex and seems to be in fairly good agreement with the observed value.

Effect of the Intramolecular Charge-Transfer Interaction upon the Stability and Reduction Potential. Now that the presence of the intramolecular charge-transfer interaction in 1-phenyl-8-tropylionaphthalene (**4a**) was confirmed by electronic spectroscopy, it is of particular interest to examine how this interaction will affect the thermodynamic stability and the electron affinity of the tropylium ring. Thus, the pK_{R^+} value was determined spectrophotometrically in 50% aqueous ethanol, which was chosen because of its good solubility for both the cations **4a-f** and their neutralized species. As is shown by the pK_{R^+} data in Table II, the stability of the tropylium ion is decreased by substitution with the 1-naphthyl group. Since the tropylium ring is supposedly forced to take a conformation nearly perpendicular to the naphthalene system due to the steric repulsion of the *peri*-hydrogen, only the electron-withdrawing inductive effect of the naphthyl group must be operating to destabilize the cation **5**. On the contrary, it is noted that the introduction of a phenyl group to the peri-position of the naphthalene ring results in an increase in the pK_{R^+} value by more than 2 pK units in spite of the severe steric congestion brought about between the two peri substituents. This remarkable increase in pK_{R^+} is considered to indicate the thermodynamic stabilization of the tropylium ring in **4a** due to the through-space π-electron supply from the facing phenyl ring.[16]

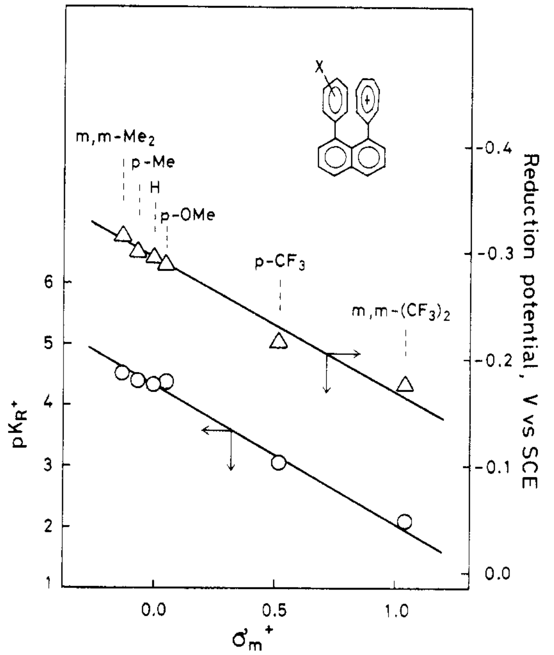

Figure 4. Plots of pK_{R^+} (○) and reduction potential (△) for the 1-aryl-8-tropylionaphthalenes **4a-f** against the substituent constant, σ_m^+.

An even more direct piece of evidence for the through-space interaction is given by the reduction potential, which is closely related to the electron affinity of the tropylium ion moiety. The peak potential data for the reduction wave observed by cyclic voltammetry[17] are also given in Table II. The increase in the reduction potential of **4a** by 0.182 V as compared with the reference cation **5**, again, clearly demonstrates the decrease in electron affinity of the tropylium moiety due to the considerable π-electron supply from the donor ring.

Substituent Effect. In their study on the charge-transfer complexation between 4-substituted [2.2]- and [3.3]paracyclophanes and tetracyanoethylene, Cram and co-workers have reported the transannular substituent effect of electron-withdrawing substituents upon the π basicity of the unsubstituted benzene ring.[18] In the

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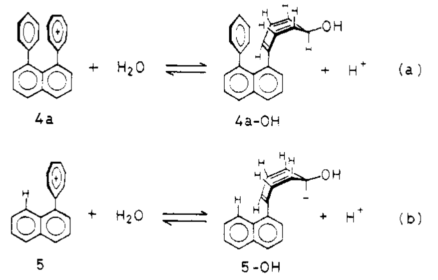
(12) M. Feldman and S. Winstein, *J. Am. Chem. Soc.*, **83**, 3338 (1961).

(13) R. S. Mulliken, *J. Am. Chem. Soc.*, 74, 811 (1952); *J. Phys. Chem.*, **56**, 801 (1952).

(14) (a) G. Briegleb and J. Czekalla, *Angew. Chem.*, **72**, 401 (1960); G. Briegleb, *ibid.*, **76**, 326 (1964); (b) M. Feldman and S. Winstein, *Theor. Chim. Acta*, 10, 86 (1968).

(15) *Natl. Stand. Ref. Data Ser., Natl. Bur. Stand.*, **No. 26** (June 1969).

(16) By definition, the pK_{R^+} value corresponds to the free energy difference between the cation and the neutralized covalent compound (isomeric mixtures of the alcohol, e.g. **4a-OH** or **5-OH**, or the corresponding dicycloheptatrienyl ether) in the equilibrium (a) and (b) shown below.



Since the relief of the steric congestion is considered to be greater in the transformation from **4a-OH** to **4a** than in that from **5-OH** to **5**, the observed increase in the pK_{R^+} of **4a** might be partly ascribed to this effect.

(17) Although the reduction wave for each cation was irreversible at the scan rate of 100 mV/s due to rapid dimerization of the generated radical species, values of the peak potential are supposed to be sufficiently valid for the comparison among the structurally related cations when determined under the same conditions.

present system, both the electron-donating and -withdrawing effects of substituents of the phenyl ring are expected to be transmitted to the acceptor ring mainly by the through-space electronic interaction. Thus, as is shown by the pK_{R^+} and reduction potential data in Table II, the methyl substituent stabilizes the tropylium ring and lowers its electron affinity (i.e., decreases the π acidity), while the trifluoromethyl group acts strongly in the opposite direction. Judging from such a sensitive change in the electronic nature of the tropylium ring, the transmission of the substituent effect through the σ bond along the phenyl and naphthyl periphery, if present, seems to contribute only to a minor extent. It is of particular interest that the methoxy group, which is known to exert the conjugative stabilization effect upon the cationic carbon, exhibits only little stabilizing effect and rather increases the electron affinity of the tropylium ring. Furthermore, a better linear correlation is obtained in the plots of pK_{R^+} and reduction potential data against $\sigma_m{}^{+}$[19] (correlation coefficient, 0.9925 and 0.9885 for the plots of pK_{R^+} and reduction potential, respectively; see Figure 4) rather than $\sigma_p{}^{+}$[19] (correlation coefficient, 0.9489 and 0.9309, respectively). These facts suggest that the through-space substituent effect in the present system is inductive in nature.

The sensitivity of the π acidity of the tropylium ring to the substituent effect is measured by the slope (ρ value) for the Hammett-type plot of the reduction potential data in Figure 4. When the unit of the ordinate (V) is converted to kcal/mol, the ρ value is calculated to be about 3.0 and is apparently smaller than the values corresponding to the sensitivity of the π basicity of the [2.2]- (ρ, 8.0[18a]) or [3.3]paracyclophanes (ρ, 6.8[18b]) to the transannular substituent effect of electron-withdrawing substituents. The substituent effect observed in the present system (i.e., the effect upon the electron affinity of the facing ring) acts in the opposite direction to that in the case of tetracyanoethylene–paracyclophane complexation[18] (i.e., the effect upon the ionization potential of the facing ring), and also the methods for detection of these effects are different. Although, from these reasons, it might not be quite adequate to directly compare these ρ values, the smaller ρ value found in the present system would be related to the less effective overlapping of the p orbitals of two interacting rings due to the less rigid face-to-face geometry and the difference in size of the two facing rings.

Also, in the ^{1}H NMR spectral data shown in Table I (vide supra), the small but similar substituent effect is observed upon the chemical shift of the tropylium ring protons: the ring-proton signal is shifted upfield by the introduction of methyl groups ($\Delta\delta$ = 0.01 ppm for p-CH_3 and 0.03 ppm for m,m-$(CH_3)_2$) and downfield by the introduction of methoxy ($\Delta\delta$ = −0.02 ppm) and trifluoromethyl groups ($\Delta\delta$ = −0.08 ppm for p-CF_3 and −0.14 ppm for m,m-$(CF_3)_2$). These shifts are in accordance with the inductively transmitted substituent effect affecting the positive charge on the tropylium ring.

Thus, the results of the present study, regarding the substituent effect upon the reduction potential as well as the proton chemical shift of the tropylium ring, are taken as the direct evidence for the importance of σ overlap of p orbitals in transmitting the substituent effect between two aromatic rings facing each other, as has already been suggested by Singer and Cram.[18a]

Experimental Section

Melting and boiling points are uncorrected. Elemental analyses were performed by the Microanalytical Center, Kyoto University, Kyoto. Infrared spectra were recorded with a Hitachi Model 215 spectrometer. UV–vis spectra were determined with a Hitachi Model 200-10 spectrometer using a 1-cm quartz cell. ^{1}H NMR spectra (60 MHz) were taken on a Hitachi Model R-24 spectrometer with Me_4Si as an internal standard.

All reagents were of a reagent-grade quality unless otherwise noted. Tropylium fluoroborate,[20] trityl fluoroborate and perchlorate,[21] 1,8-dibromonaphthalene,[22] and 1-iodo-3,5-bis(trifluoromethyl)benzene[23] were prepared according to the literature. 1-Phenylnaphthalene (**12**) was obtained by the method described by Roberts et al.:[10] UV λ_{max} (CH_3CN) 225 nm (log ϵ 4.75), 288 (3.99); the ^{1}H NMR spectrum agreed with the reported spectrum.[9]

1-(Cyclohepta-2,4,6-trien-1-yl)naphthalene (11) and Its Thermal Isomerization. To a stirred solution of 1-naphthylmagnesium bromide, prepared from 1-bromonaphthalene (11.3 g; 54.6 mmol) and magnesium (1.40 g; 57.6 mmol) in 60 mL of ether–THF (2:3), there was added a solution of 7-ethoxycyclohepta-1,3,5-triene (5.10 g; 37.4 mmol) in 25 mL of ether over 1 h with heating to reflux. After being refluxed for 7 h, the mixture was hydrolyzed with 2 N HCl, and the aqueous solution was extracted with ether. The combined organic solution was washed with 10% NaCl, dried over $MgSO_4$, and evaporated under reduced pressure. Distillation of the crude product afforded **11** as colorless oil (5.84 g; 71.5%): bp 170–175 °C (0.01 mmHg); IR (neat) ν 3050 (m), 3025 (m), 1595 (m), 1505 (m), 1430 (w), 1390 (m), 1020 (w), 800 (s), 775 (s), 735 (m), and 700 cm^{-1} (s); ^{1}H NMR (CCl_4) δ 7.80–7.25 (m, 7 H), 6.67 (t, 2 H), 6.20 (dm, 2 H), 5.48 (dd, 2 H), 3.33 (t, 1 H).

Anal. Calcd for $C_{17}H_{14}$: C, 93.54; H, 6.46. Found: C, 93.30; H, 6.44.

The 7-substituted cycloheptatriene **11** was sealed in an ampule under vacuum and heated at 160 °C for 1.5 h to effect thermal isomerization. The product was shown to be a mixture of 3- (83%) and 1-substituted cycloheptatriene (17%) by the integrated ratio of ^{1}H NMR signals (in CCl_4) for the methylene protons at δ 2.74 (d, 0.34 H) and 2.42 (t, 1.66 H). Other protons appeared at 7.75–7.20 (m, 7 H), 6.60 (d, 1.2 H), 6.21 (dm, 2.0 H), and 5.30 (m, 1.8 H).

1-Tropylionaphthalene Fluoroborate (5-BF_4^-). To a stirred suspension of trityl fluoroborate (5.00 g; 15.1 mmol) in 12 mL of acetonitrile, there was added a solution of the mixture of 3- and 1-(1-naphthyl)cyclohepta-1,3,5-trienes (3.28 g; 15.0 mmol) in 4 mL of acetonitrile. After the solution was stirred at 60 °C for 10 min and at room temperature for 1 h, 90 mL of absolute ether was added to cause the formation of yellow precipitates, which were collected and recrystallized from acetonitrile–ethyl acetate to give **5-BF_4^-** as bright orange needles (3.48 g; 76.2%): mp 149.5–152 °C dec; IR (KBr) ν 3000 (w), 1600 (m), 1530 (m), 1515 (m), 1485 (s), 1445 (m), 1250 (m), 1080 (br s), 1030 (s), 815 (m), 780 (s), and 760 cm^{-1} (m); UV–vis λ_{max} (CH_3CN) 220 nm (log ϵ 5.00), 258 (4.06), 279 (4.06), 290 sh (3.93), 446 (3.78).

Anal. Calcd for $C_{17}H_{13}BF_4$: C, 67.14; H, 4.31. Found: C, 67.31; H, 4.17.

1-Bromo-8-(cyclohepta-2,4,6-trien-1-yl)naphthalene (8) and Its Thermal Isomerization. A solution of 1,8-dibromonaphthalene (**6**) (3.40 g; 11.9 mmol) in 26 mL of anhydrous ether was added dropwise, over 45 min, to small pieces of lithium (0.175 g; 25.2 mmol) suspended in 7 mL of anhydrous ether with stirring under a nitrogen atmosphere. The rate of addition was controlled to maintain gentle refluxing due to the exothermic reaction which had been initiated by brief external heating. After the mixture was refluxed for 45 min, tropylium fluoroborate (2.14 g; 12.0 mmol) was added portionwise to the resulting solution of 1-bromo-8-lithionaphthalene (**7**) with vigorous stirring at room temperature.

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(18) (a) L. A. Singer and D. J. Cram, *J. Am. Chem. Soc.*, **85**, 1080 (1963); (b) M. Sheehan and D. J. Cram, *ibid.*, **91**, 3553 (1969).

(19) It was assumed that additivity holds for the substituent effects of the methyl and trifluoromethyl groups in the present system. The values for σ^+ were taken from H. C. Brown and Y. Okamoto, *J. Am. Chem. Soc.*, **80**, 4979 (1958).

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The mixture was stirred for 5 h, let stand overnight, and then treated with 30 mL of 2 N HCl. Ordinary workup afforded 3.14 g of the crude product, from which was isolated **8** (2.10 g; 59.5%) as viscous oil by preparative TLC over silica gel (Merck, PF$_{254}$) developed with *n*-hexane–benzene (9:1): IR (neat) ν 3005 (m), 1595 (m), 1560 (m), 1495 (w), 1360 (m), 1240 (m), 1190 (m), 1070 (w), 975 (m), 815 (s), 760 (s), 740 (s), and 700 cm^{-1} (s); ^{1}H NMR (CCl$_4$) δ 7.80–7.00 (m, 6 H), 6.57 (t, 2 H), 6.17 (dm, 2 H), 5.18 (dd, 2 H), 4.66 (t, 1 H).

The 7-substituted cycloheptatriene **8** was sealed in an ampule under vacuum and heated at 175 °C for 2 h. The resulting viscous oil was assigned to be a mixture of **9** and **9′** on the basis of the ^{1}H NMR spectrum and the analogy with the isomerization of **11** stated above: ^{1}H NMR (CCl$_4$) δ 7.80–7.10 (m, 6 H), 6.65–5.20 (m, 5 H), 3.10–2.00 (m, 2 H).

1-Aryl-8-tropylionaphthalene Perchlorates. 1-Phenyl-8-tropylionaphthalene Perchlorate (4a-ClO$_4^-$). A solution of phenylmagnesium bromide was prepared from bromobenzene (1.11 g; 7.05 mmol) and magnesium (0.180 g; 7.40 mmol) in 7 mL of ether and then quickly transferred into a dropping funnel using a pipet. Under a nitrogen atmosphere, the Grignard reagent was added dropwise, over 10 min, to a stirred solution of an isomeric mixture of 1-bromo-8-cycloheptatrienylnaphthalenes (**9** and **9′**) (1.38 g; 4.66 mmol) and nickel(II) acetylacetonate (0.017 g; 0.065 mmol) in 5 mL of ether at room temperature. After the mixture was heated under reflux for 2 h, it was hydrolyzed with 2 N HCl and worked up to give 1.59 g of the crude product. Preparative TLC of the product over silica gel developed with *n*-hexane–benzene (1:1) afforded 1-cycloheptatrienyl-8-phenylnaphthalene (**10a**) (0.549 g; 40.1%) as viscous oil: ^{1}H NMR (CCl$_4$) δ 7.80–7.05 (m, 11 H), 6.33–4.80 (m, 5 H), 2.70–1.35 (m, 2 H).

Trityl perchlorate (0.316 g; 0.922 mmol) was added to a stirred solution of **10a** (0.258 g; 0.876 mmol) in 1.5 mL of anhydrous acetonitrile–dichloromethane (1:1). The resulting mixture of dark red solution and crystals was refluxed for 10 min. After addition of 3 mL of ethyl acetate, the mixture was cooled to 0 °C. The precipitates were collected, washed with anhydrous ether, and dried in vacuo to give **4a**-ClO$_4^-$ (0.264 g; 76.6%) as yellow-orange needles: mp 186–187 °C dec; IR (KBr) ν 3010 (w), 1597 (m), 1530 (w), 1480 (s), 1440 (s), 1260 (m), 1180 (m), 1090 (br vs), 835 (s), 780 (s), 750 (s), and 700 cm^{-1} (s); UV–vis $\lambda_{\max}$ (CH$_3$CN) 225 nm (log ϵ 4.86), 271 (4.05), 300 (sh, 3.91), 373 (3.76), 464 (3.65); $\lambda_{\max}$ (CH$_2$Cl$_2$) 273 nm (log ϵ 4.04), 310 (sh, 3.85), 392 (3.75), 500 (3.62).

Anal. Calcd for C$_{23}$H$_{17}$ClO$_4$: C, 70.32; H, 4.36. Found: C, 70.09; H, 4.60.

1-(*p*-Methylphenyl)-8-tropylionaphthalene Perchlorate 4b-ClO$_4^-$). Similarly, 1-cycloheptatrienyl-8-(*p*-methylphenyl)-naphthalene (**10b**) was obtained in 39.0% yield by the coupling of the mixture of **9** and **9′** with (*p*-methylphenyl)magnesium bromide. The hydride abstraction with trityl perchlorate afforded **4b**-ClO$_4^-$ as dark red powder in 75.4% yield: mp 153–154 °C dec; IR (KBr) ν 3010 (w), 1598 (m), 1510 (m), 1480 (s), 1440 (m), 1260 (m), 1180 (m), 1080 (br vs), 835 (s), 820 (s), 780 (s), 745 (s), and 720 cm^{-1} (m); UV–vis $\lambda_{\max}$ (CH$_3$CN) 224 nm (log ϵ 4.87), 273 (4.06), 302 (4.03), 389 (3.89), 463 (3.65).

Anal. Calcd for C$_{24}$H$_{19}$ClO$_4$: C, 70.85; H, 4.71. Found: C, 70.67; H, 4.82.

1-(*m*,*m*-Dimethylphenyl)-8-tropylionaphthalene Perchlorate (4c-ClO$_4^-$). 1-Cycloheptatrienyl-8-(*m*,*m*-dimethylphenyl)naphthalene (**10c**) was obtained in 24.9% yield by the coupling of the mixture of **9** and **9′** with (*m*,*m*-dimethylphenyl)magnesium bromide. The hydride abstraction afforded **4c**-ClO$_4^-$ as brownish red powder in 84.7% yield: 198–199 °C dec; IR (KBr) ν 3010 (w), 1598 (m), 1510 (m), 1480 (s), 1440 (m), 1260 (m), 1180 (w), 1090 (br vs), 855 (m), 830 (s), 775 (s), 740 (s), and 710 cm^{-1} (s); UV–vis $\lambda_{\max}$ (CH$_3$CN) 224 nm (log ϵ 4.84), 274 (4.16), 305 (sh, 3.92), 391 (3.83), 465 (3.62).

Anal. Calcd for C$_{25}$H$_{21}$ClO$_4$: C, 71.34; H, 5.03. Found: C, 71.07; H, 4.92.

1-(*p*-Methoxyphenyl)-8-tropylionaphthalene Perchlorate (4d-ClO$_4^-$). 1-Cycloheptatrienyl-8-(*p*-methoxyphenyl)naphthalene (**10d**) was obtained in 60.6% yield by the coupling of the mixture of **9** and **9′** with (*p*-methoxyphenyl)magnesium bromide. The hydride abstraction gave **4d**-ClO$_4^-$ as dark red powder in 90.4% yield: mp 203–204 °C dec; IR (KBr) ν 3010 (w), 1603 (m), 1592 (m), 1505 (m), 1480 (s), 1435 (m), 1295 (m), 1260 (sh), 1250 (s), 1180 (w), 1080 (br vs), 830 (s), 820 (s), 775 (s), and 745 cm^{-1} (s); UV–vis $\lambda_{\max}$ (CH$_3$CN) 222 nm (log ϵ 4.76), 290 (4.06), 306 (sh, 4.01), 411 (3.84), 490 (3.44).

Anal. Calcd for C$_{24}$H$_{19}$ClO$_5$: C, 68.17; H, 4.53. Found: C. 67.99; H, 4.46.

1-(*p*-(Trifluoromethyl)phenyl)-8-tropylionaphthalene Perchlorate (4e-ClO$_4^-$). 1-Cycloheptatrienyl-8-(*p*-(trifluoromethyl)phenyl)naphthalene (**10e**) was obtained in 34.3% yield by the coupling of the mixture of **9** and **9′** with (*p*-(trifluoromethyl)phenyl)magnesium bromide. The hydride abstraction afforded **4e**-ClO$_4^-$ as yellowish brown powder in 83.3% yield: mp 197–198 °C dec; IR (KBr) ν 3010 (w), 1615 (m), 1600 (w), 1530 (m), 1515 (m), 1485 (s), 1440 (m), 1410 (m), 1320 (s), 1170 (s), 1080 (br vs), 1020 (w), 850 (m), 830 (s), 780 (s), and 750 cm^{-1} (s); UV–vis $\lambda_{\max}$ (CH$_3$CN) 223 nm (log ϵ 4.88), 265 (4.12), 291 (4.09), 345 (3.63), 453 (3.72).

Anal. Calcd for C$_{24}$H$_{16}$ClF$_3$O$_4$: C, 62.55; H, 3.50. Found: C, 62.38; H, 3.38.

1-(*m*,*m*-Bis(trifluoromethyl)phenyl)-8-tropylionaphthalene Perchlorate (4f-ClO$_4^-$). 1-Cycloheptatrienyl-8-(*m*,*m*-bis(trifluoromethyl)phenyl)naphthalene (**10f**) was obtained in 41.6% yield by the coupling of the mixture of **9** and **9′** with (*m*,*m*-bis(trifluoromethyl)phenyl)magnesium iodide. The hydride abstraction gave **4f**-ClO$_4^-$ as yellowish orange needles in 82.5% yield: mp 144–145 °C dec; IR (KBr) ν 3020 (w), 1605 (w), 1520 (m), 1485 (s), 1440 (w), 1370 (m), 1280 (s), 1260 (s), 1180 (s), 1140 (m), 1090 (br vs), 1000 (w), 838 (s), 780 (s), and 685 cm^{-1} (s); UV–vis $\lambda_{\max}$ 223 nm (log ϵ 4.69), 273 (4.12), 291 (sh, 4.04), 333 (3.63), 455 (3.76).

Anal. Calcd for C$_{25}$H$_{15}$ClF$_6$O$_4$: C, 56.78; H, 2.86. Found: C, 56.88; H, 3.15.

p*K*$_{\mathbf{R^+}}$ Measurement. The pK_{R^+} values were determined in 50% aqueous ethanol at 25 °C according to the spectrophotometric method reported by Breslow and Chang.[24] The cations, **4a–f**, **5**, and the tropylium ion, 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 spectrum upon acidifying the neutralized solution. The UV–vis spectrum was recorded on each cation in 15–20 solutions of buffers spaced through a pH range of about two 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. The measurements were carried out with a Hokuto-Denko Model HA 104 potentiostat equipped with a Hokuto-Denko Model HB 107A function generator. A three-electrode cell was used, consisting of platinum wire working and auxiliary electrodes and a saturated calomel reference electrode. The reference electrode was connected to the bulk of the solution by a capillary salt bridge filled with the sample solution. All the sample solutions were 1 mM in cation **4** and 0.1 M in tetrabutylammonium perchlorate as a supporting electrolyte in dichloromethane. The voltammograms obtained at the scan rate of 100 mV/s were recorded on a Hitachi Model 057 X-Y recorder.

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Registry No. *m*,*m*-bis(trifluoromethyl)phenyl iodide, 328-73-4; **4a** perchlorate, 70480-17-0; **4b** perchlorate, 70480-15-8; **4c** perchlorate, 70479-65-1; **4d** perchlorate, 70479-67-3; **4e** perchlorate, 70479-69-5; **4f** perchlorate, 70479-71-9; **5** fluoroborate, 70479-73-1; **6**, 17135-74-9; **7**, 70416-25-0; **8**, 70416-26-1; **9**, 70416-27-2; **9′**, 70416-28-3; **10a** isomer 1, 70416-29-4; **10a** isomer 2, 70416-30-7; **10b** isomer 1, 70416-31-8; **10b** isomer 2, 70416-32-9; **10c** isomer 1, 70416-33-0; **10c** isomer 2, 70416-34-1; **10d** isomer 1, 70428-83-0; **10d** isomer 2, 70416-35-2; **10e** isomer 1, 70416-36-3; **10e** isomer 2, 70416-37-4; **10f** isomer 1, 70416-38-5; **10f** isomer 2, 70416-39-6; **11**, 56360-04-4; **12**, 605-02-7; 1-bromonaphthalene, 90-11-9; 7-ethoxycyclohepta-1,3,5-triene, 1714-39-2; 1-(cyclohepta-2,4,6-trien-3-yl)naphthalene, 59891-53-1; bromobenzene, 108-86-1; *p*-methylphenyl bromide, 106-38-7; *m*,*m*-dimethylphenyl bromide, 556-96-7; *p*-methoxyphenyl bromide, 104-92-7; *p*-(trifluoromethyl)phenyl bromide, 402-43-7; tropylium, 26811-28-9.

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