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Charge-transfer Interaction of a Series of Trifluoromethylated Benzenes in the Ground and Excited States

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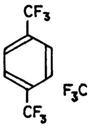
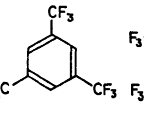
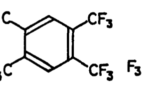
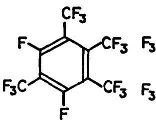
Charge-transfer interaction of a series of trifluoromethylated benzenes with several donor molecules was investigated by measuring electronic absorption and fluorescence spectra. Half-wave reduction potentials of acceptors were determined by cyclic voltammetry. Charge-transfer absorption bands were observed for several systems. Thermal one-electron transfer reactions were observed for solutions of hexakis(trifluoromethyl)benzene and several aromatic amines even in nonpolar solvents. Charge-transfer fluorescence was observed for solutions of hexakis(trifluoromethyl)benzene or tetrakis(trifluoromethyl)benzene and weak donor molecules such as benzene, toluene, or *p*-xylene.

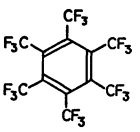
Spectroscopic studies on the charge-transfer (CT) interaction between donor and acceptor molecules have extensively been made both in the ground and excited states.[1] Acceptors in those studies were mainly aromatic molecules possessing electron withdrawing groups such as halogeno, cyano, nitro, and carbonyl groups. Trifluoromethyl group is known to have a strong electron withdrawing property.[2] However, no study has been made with aromatic acceptor molecule possessing trifluoromethyl group from the viewpoint of CT-interaction. We have measured electronic absorption and fluorescence spectra of the following acceptor molecules (A_2—A_6) with various donor molecules. We have also measured half-wave reduction potentials of these acceptors by cyclic voltammetry.


A_2


A_3


A_4


A_{4F}


A_6

The names of the acceptor molecules are abbreviated to A_2, A_3, A_4, A_{4F}, and A_6 as specified above. We have found that the above molecules behave as a new family of acceptors both in the ground and excited states.

Experimental

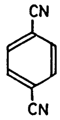
Materials. Hexakis(trifluoromethyl)benzene (A_6) was synthesized *via* a trimerization reaction of bis(trifluoromethyl)acetylene.[3] 1,3-Difluoro-2,4,5,6-tetrakis(trifluoromethyl)-benzene (A_{4F}) was obtained by a pyrolysis of A_6.[4] 1,2,4,5-Tetrakis(trifluoromethyl)benzene (A_4), 1,3,5-tris(trifluoromethyl)benzene (A_3), and 1,4-bis(trifluoromethyl)benzene (A_2) were synthesized *via* reactions of the corresponding carboxylic acids with sulfur tetrafluoride.[5] All of them were purified by vacuum distillation. Aniline, *N,N*-dimethylaniline, *N,N*-diethylaniline, and *N,N*-dibutylaniline were purified by vacuum distillation. *N,N,N′,N′*-Tetramethyl-*p*-phenylenediamine and *N,N*-dimethyl-*p*-phenylenediamine were obtained by neutralizing their dihydrochlorides with aqueous ammonia, followed by extracting them with diethyl ether. The crude materials obtained after evaporating diethyl ether were finally purified by vacuum sublimation. Benzene, toluene, and *p*-xylene were purified by treating them with sulfuric acid, dried over calcium chloride, refluxed over sodium for at least 8 h, and distilled twice. Hexane was purified by treating it with sulfuric acid, and dried over calcium chloride. It was then passed through a column composed successively of acidic, neutral, and basic aluminas, refluxed over sodium for more than 8 h, and finally distilled. Acetonitrile was purified by passing it through a column composed successively of acidic, neutral, and basic aluminas, refluxed over calcium hydride for more than 8 h, and finally distilled.

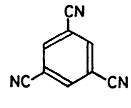
Cyclic Voltammetry. Cyclic voltammetry was run on an apparatus made by us. Acetonitrile was used as a solvent. Tetrabutylammonium perchlorate (0.1 mol dm^{-3}) was used as the supporting electrolyte; the concentration of the acceptor molecule was 1.0×10^{-3} mol dm^{-3}. An Ag/Ag$^+$ electrode, comprising an acetonitrile solution of silver nitrate (0.1 mol dm^{-3}) was used as a reference electrode.

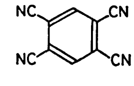
Electronic Absorption and Fluorescence Spectra. Electronic absorption spectra were measured on a Shimadzu UV-200 double beam spectrophotometer. Fluorescence spectra were measured on a Hitachi MPF-3 fluorescence spectrometer.

Results and Discussion

Cyclic Voltammetry. An cyclic voltammetry on A_4, A_{4F}, and A_6 in acetonitrile solution was conducted to obtain their reduction potentials. The reduction potentials of 1,2,4,5-tetracyanobenzene (TCNB), 1,3,5-tricyanobenzene (TCB), and *p*-dicyanobenzene (DCB) were also measured for comparison. An Ag/Ag$^+$ electrode was used as a reference electrode. Table 1 summarizes the half-wave reduction potentials of A_6, A_{4F}, A_4, TCNB, TCB, and DCB. This table shows that the absolute reduction potentials decrease in the order DCB>TCB>A_4>A_{4F}>TCNB≈A_6. The absolute reduction potentials increase with decreasing number of substituent CF_3 groups. From a comparison of the absolute reduction potentials of the CF_3-substituted benzenes with those of the corresponding CN-substituted benzenes, it is clear that the cyano group is a stronger electron withdrawing group than the trifluoromethyl group. The reduction potentials of A_3


DCB


TCB


TCNB

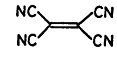

TCNE

TABLE 1. HALF-WAVE REDUCTION POTENTIALS OF ACCEPTORS

Acceptor	($E_{1/2}$ *vs.* Ag/Ag$^+$)/V
A_6	−1.03
A_{4F}	−1.41
A_4	−1.66
TCNB	−1.06
TCB	−1.32
DCB	−2.00

and A_2 could not be measured due to occurrence of an interference with the cathodic current by the electrolyte.

Charge-transfer Interaction of Trifluoromethylated Benzenes with Weak Aromatic Donor Molecules. CT-interaction of A_4 and A_6 with such a weak aromatic donor molecule as benzene, toluene, or *p*-xylene was investigated by measuring electronic absorption spectra. Figure 1 shows the absorption spectra of cyclohexane solutions of A_6, *p*-xylene, and a mixture of A_6 and *p*-xylene. Subtracting the absorbances of the component molecules from that of the mixture of A_6 and *p*-xylene, a new absorption band shown by the broken lines was obtained as a shoulder. This absorption band is ascribable to a CT-band. CT-absorption bands were also observed as shoulders on the absorption bands of the component molecules in cyclohexane solution for the following systems: A_6–benzene, A_6–toluene, A_4–benzene, A_4–toluene, and A_4–*p*-xylene.

In order to examine the stoichiometry of the CT-complexes in these systems, the absorbance of the CT-band as a function of donor concentration was analysed on the basis of the modified Benesi-Hildebrand equation.[6)]

$$\frac{L[A]_0}{I-\varepsilon_A[A]_0L-\varepsilon_D[D]_0L}=\frac{1}{K(\varepsilon_C-\varepsilon_A)}\frac{1}{[D]_0}+\frac{1}{\varepsilon_C-\varepsilon_A}, \quad (1)$$

where, I, ε_D, ε_A, ε_C, $[D]_0$, $[A]_0$, L, and K denote the absorbance, the molar extinction coefficients of the donor, acceptor, and CT-complex, the initial concentrations of the donor and acceptor molecules, the path length, and the equilibrium constant for the CT-complex, respectively. The Benesi-Hildebrand equation[7)] could not be used owing to overlap of the absorption band of CT-complex with those of the component molecules. Plots of $L[A]_0/(I-\varepsilon_A L[A]_0-\varepsilon_D L[D]_0)$ against $1/[D]_0$ gave straight lines for all of the above systems. Thus, the compositions of the CT-complexes are one to one in these systems.

Charge-transfer Interaction of A_2, A_3, A_4, and A_6 with Strong Donor Molecules. *N,N,N′,N′*-tetramethyl-*p*-phenylenediamine (TMPD) and *N,N*-dimethyl-*p*-phenylenediamine (DMPD) are known to be strong donor molecules. The CT-interaction of A_2, A_3, A_4, and A_6 with TMPD and DMPD was studied by measuring absorption spectra of mixed solutions of donor and acceptor molecules. In the case of benzene solutions of A_2, A_3, and A_4 with TMPD, new absorptions ascribable to CT-bands were observed as shoulders of the component molecules. The CT-band shifted to the longer wavelength region with increasing electron accepting power of the acceptors. However, when tetrahydrofuran (THF) was used as a solvent, one-electron transfer reaction as well as CT-complex formation was observed in the same donor–acceptor systems. Figure 2 shows the absorption spectra of THF solutions of TMPD mixed with A_2, A_3, or A_4. Besides the CT-absorption bands around at 400—500 nm, characteristic vibrational structures ascribable to the TMPD cation radical (λ_{max}=570, 620 nm)[8)] were observed.

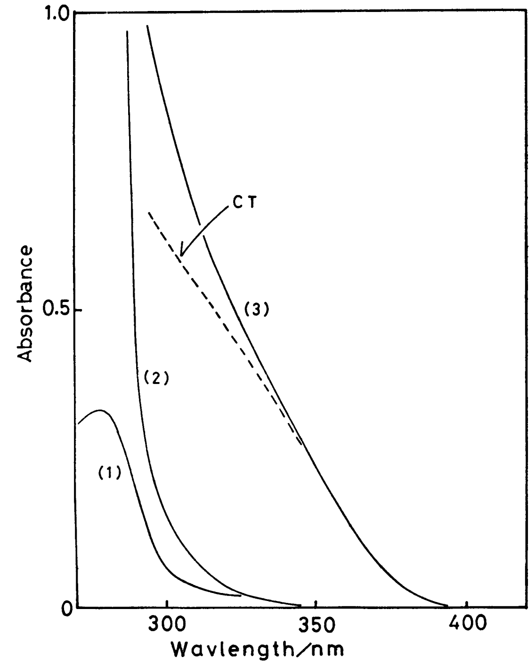


Fig. 1. Electronic absorption spectra of the cyclohexane solutions of (1) A_6, (2) *p*-xylene, and (3) the mixture of *p*-xylene and A_6. The broken line shows the charge-transfer absorption band. $[A_6]=1.23\times10^{-3}$ mol dm^{-3}, [*p*-xylene] = 6.53 mol dm^{-3}.

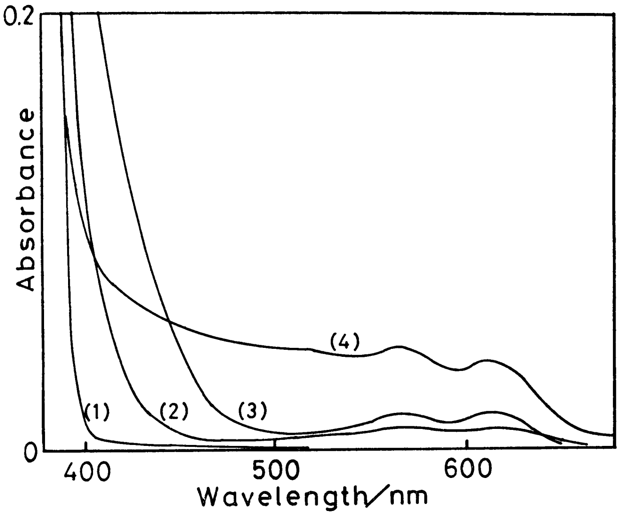


Fig. 2. Electronic absorption spectra of the THF solutions of TMPD and TMPD mixed with acceptors. [TMPD] = 0.0743 mol dm^{-3}. (1) TMPD, (2) TMPD-A_2 (0.136 mol dm^{-3}), (3) TMPD-A_3 (0.11 mol dm^{-3}), (4) TMPD-A_4 (0.0139 mol dm^{-3}).

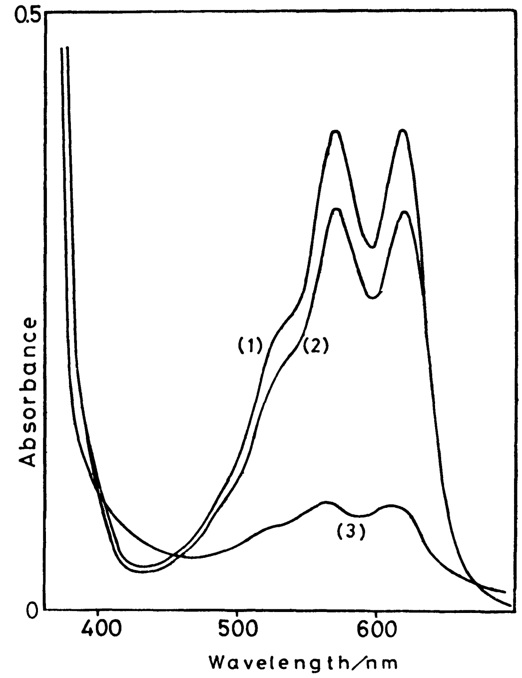


Fig. 3. Electronic absorption spectra of A_6–TMPD system in various solvents. $[A_6]=3.9\times10^{-3}$ mol dm^{-3}, $[\mathrm{TMPD}]=3.4\times10^{-3}$ mol dm^{-3}. (1) THF, (2) benzene, (3) cyclohexane.

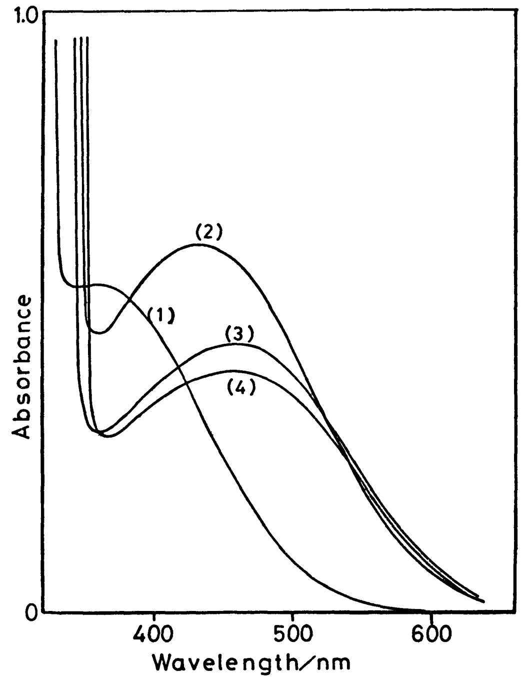


Fig. 4. Charge-transfer absorption spectra of A_6 mixed with liquid donors. $[A_6]=1.8\times10^{-3}$ mol dm^{-3}. (1) A_6–aniline, (2) A_6–*N*,*N*-dimethylaniline, (3) A_6–*N*,*N*-diethylaniline, (4) A_6–*N*,*N*-dibutylaniline.

These findings indicate that A_2, A_3, and A_4 form CT-complexes with strong donors such as TMPD and DMPD in nonpolar solvent. However, in a slightly more polar solvent like THF, these systems allowded not only CT-complex formation but also one-electron transfer from donor to acceptor molecule.

To our surprise, one-electron transfer from TMPD or DMPD to A_6 occurred not only in THF but also in such nonpolar solvents as benzene and cyclohexane. Figure 3 shows the absorption spectra of the TMPD–A_6 system in THF, benzene, or cyclohexane. The absorptions due to the TMPD cation radical were clearly observed in benzene and in cyclohexane. A similar phenomenon was also observed for the DMPD–A_6 system in benzene; the absorption of the DMPD cation radical ($\lambda_{\mathrm{max}}=508$, 532 nm)[9] as well as that of a dimer cation radical $(\mathrm{CDMPD}^+)_2$, ($\lambda_{\mathrm{max}}=680$ nm)[9] was observed. Tetracyanoethylene (TCNE) is known to be one of the strongest electron acceptor molecules. However, we observed only CT-absorption band even in the TMPD–TCNE system in benzene or cyclohexane. A_6 is, of course, a much weaker electron acceptor than TCNE, judging from its half-wave reduction potential. In spite of this, A_6 behaves as if it were a stronger acceptor than TCNE at least in the nonpolar solvents. We can now give no explanation for these unusual phenomena.

Upon mixing TMPD with A_6, or DMPD with A_6 in such a polar solvent as methanol or acetonitrile, one-electron transfer from donor to acceptor was observed.

Charge-transfer Interaction of A_6 with Aniline and Its Derivatives without Use of Solvents. CT-interaction of liquid donor molecules with A_6 was investigated without use of any solvents. Figure 4 shows the CT-absorption bands observed by mixing A_6 directly with aniline, *N*,*N*-dimethylaniline (DMA), *N*,*N*-diethylaniline (DEA), and *N*,*N*-dibutylaniline (DBA). The absorption bands observed at 380—600 nm are ascribable to CT-bands. The peak positions of the CT-bands shifted to the longer wavelength region with increasing length of alkyl groups attached to the amino-nitrogen: $\lambda_{\mathrm{max}}=365$ nm (aniline–A_6); $\lambda_{\mathrm{max}}=435$ nm (DMA–A_6); $\lambda_{\mathrm{max}}=465$ nm (DEA–A_6); $\lambda_{\mathrm{max}}=465$ nm (DBA–A_6). These findings can be accounted for in terms of the decrease in the ionization potentials of aniline derivatives due to the hyperconjugation of alkyl groups.

Fluorescence Spectra of Donor–Acceptor Systems. Fluorescence spectra of cyclohexane or hexane solutions of the following systems were measured at room temperature in order to examine the CT-interaction in the excited state: A_4–benzene (in cyclohexane), A_4–toluene (in hexane), A_4–*p*-xylene (in hexane), A_6–benzene (in hexane), A_6–toluene (in hexane), A_6–*p*-xylene (in cyclohexane). Selective excitation of the CT-bands was impossible in these systems except for the A_6–*p*-xylene system due to overlap of the absorption of CT-complex with those of the component molecules. However, the absorbances due to the CT-complexes were much higher than those of the component molecules at the following excitation wavelengths: A_4–benzene, 280 nm; A_4–toluene, 296 nm; A_4–*p*-xylene, 310 nm; A_6–benzene, 325 nm; A_6–toluene, 325 nm; A_6–*p*-xylene, 330 nm. The concentration of the acceptors was kept constant, and that of the donor molecules was varied widely.

Figure 5 shows the fluorescence spectra of the A_4–toluene system as a typical example. The charac-

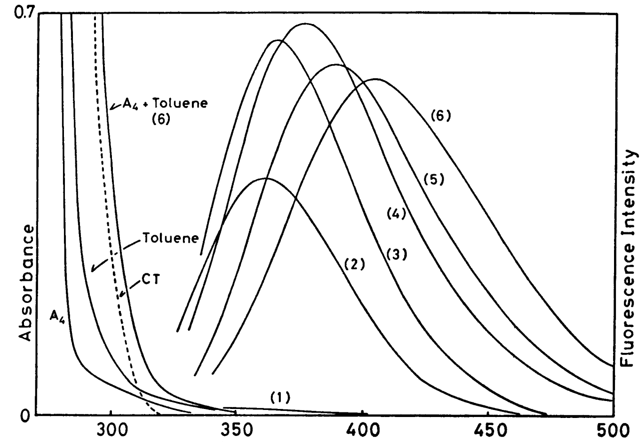


Fig. 5. Absorption and fluorescence spectra of A_4–toluene system in hexane excited at 296 nm. The fluorescence intensities were corrected on the basis of the absorbances at 296 nm. $[A_4]=2.32\times10^{-3}$ mol dm^{-3}. The concentrations of toluene are as follows (mol dm^{-3}); (1) 0, (2) 0.374, (3) 0.751, (4) 1.88, (5) 3.74, (6) 7.51.

teristic points of the system are as follows: (1) new fluorescence bands appeared at the longer wavelength region than the fluorescences of the component molecules; (2) the peak positions of the new fluorescences shifted to the longer wavelength region with increasing donor concentration. These fluorescence bands are ascribed to the CT-fluorescence, since the excitation spectra correspond to the CT-absorption bands. The fluorescence spectra of Fig. 5 were normalized on the basis of the absorbance at the excitation wavelength. The relative intensities of the fluorescences in the A_4–toluene system increased initially and then decreased as the donor concentration increased. The above two characteristic phenomena were also observed in the other systems. However, the dependence of the fluorescence intensity on the donor concentration was somewhat different between the A_4–donor systems and the A_6–donor systems. The fluorescence intensities in the latter systems decreased monotonously with increasing donor concentration.

Discussion on CT-Fluorescence. The fluorescence due to CT-complex was observed in the above systems.$^{10)}$ It is well known that the Stokes shift of CT-fluorescence is much larger than those of usual organic compounds.$^{11)}$ The Stokes shifts in the present systems could not be obtained correctly, since the absorption peak positions of the CT-complexes were hidden under the absorptions of the component molecules. However, a rough estimation of Stokes shifts gave values larger than 8×10^3 cm^{-1} in agreement with the above-mentioned tendency.

Let us discuss on the red-shift of the CT-fluorescence with increasing donor concentration. The ground states of the 1:1 CT-complexes are assumed to have mainly no-bond structures, because benzene, toluene, and *p*-xylene are weak donor molecules. The first excited states of the CT-complexes are assumed to have more polar structure than the ground states. The situations of the present systems are quite similar to that of the TCNB–toluene system;$^{12)}$ the red shift of the CT-fluorescence was also observed as the concentration of toluene increased. Mataga and Murata accounted for the large Stokes shift and red shift of the CT-fluorescence in terms of two factors:$^{12)}$ (1) the reorientation of the excited CT-complex from the Franck-Condon states to a stabler configuration in the excited CT-states; (2) the reorientation of the Franck-Condon ground states to the stablest configuration of the CT-complex in the ground state.

In the case of the present systems, two possibilities can be considered for the red shift of the CT-fluorescence with increasing donor concentration. One possibility is the same as that mentioned above in connection with the TCNB–toluene system. In this case, as the donor concentration increases, the energy stabilization of CT-complex in the excited states and the energy destabilization in the ground state are induced more and more effectively as a result of the electronic interaction between the CT-complex and donor molecules; this fact accounts for the red shift of CT-fluorescence. The other possibility is that the red shift of CT-fluorescence arises from CT-excited states with different stoichiometries, *e.g.*, different donor to acceptor ratios such as one to one, two to one, three to one,. . , *etc.* We cannot conclude which of these two possibilities is applicable to the present systems.

Summary

CT-interaction of a series of trifluoromethylated benzenes with several donor molecules was investigated in the ground and excited states. The trifluoromethylated benzenes acted as electron acceptors to induce CT-complex formation and/or one-electron transfer in the ground state. One-electron transfer reaction was observed for strong donor–A_6 systems even in nonpolar solvents. Fluorescences due to CT-complexes were observed for weak donors–A_4 systems and for weak donor–A_6 systems. The trifluoromethylated benzenes in the present study have been found to be a new family of electron acceptor molecules for study on the electron donor–acceptor interaction.

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6) Equation 1 is derived as follows: The following two

relations 1 and 2 are set by definition:

$$I/L = \varepsilon_{\mathrm{C}}[DA] + \varepsilon_{\mathrm{D}}([D]_0-[DA]) + \varepsilon_{\mathrm{A}}([A]_0-[DA]), \quad (1)$$

$$K = [DA]/([D]_0-[DA])([A]_0-[DA]) \quad (2)$$

$$\approx [DA]/[D]_0([A]_0-[DA]), \quad (3)$$

where $[DA]$ denotes the concentration of CT-complex. Since the experiments were performed under the condition $[D]_0 \gg [A]_0$, the equilibrium constant of the CT-complex can be approximated to Relation 3. Cancelation of $[DA]$ from Relations 1 and 3 gives Eq. 1. In the case of $\varepsilon_{\mathrm{D}}=\varepsilon_{\mathrm{A}}=0$, Eq. 1 gives the Benesi-Hildebrand equation.

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