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Nature of Electrophiles and Electron Acceptors. Comparison of Their Molecular Complexes with Aromatic Donors

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The novel charge-transfer (CT) absorption bands observed with various arenes and mercuric trifluoroacetate are assigned to 1:1 electron donor–acceptor (EDA) complexes. Spectral data are also reported for the aromatic complexes of the halogen electrophiles Cl_2 and Br_2. Electron-poor organic compounds such as maleic anhydride, tetracyanoethylene, chloranil, tetracyanobenzene, and tetracyanopyrazine interact as π acceptors with the same series of arenes to afford persistent CT absorption bands which can be shown to arise from 1:1 EDA complexes. An empirical parameter, K_S, is introduced to provide comparative measures of the strengths of EDA complexes from the readily available spectral parameters. Analysis indicates that electrophiles cannot be distinguished from π acceptors solely on the basis of values of K_S for their EDA complexes with aromatic donors. Furthermore, the CT transition energies $h\nu_{CT}$ of electrophile and π-acceptor complexes show the same types of linear variations with the ionization potentials (I_D) of the aromatic donors, in accord with the predictions of the Mulliken theory. The variations in the slopes of the correlations, i.e., $\partial(h\nu_{CT})/\partial(I_D)$ are related to the changes in the mean separation r_{DA}, which are supported by intermolecular comparisons of the spectral data in Figure 8, as well as the intramolecular comparisons of the multiple CT bands in Figure 9. The structures of the EDA complexes with electrophiles are compared with those of other arene complexes.

There are a few sporadic and incomplete reports in the extant literature for the existence of electron donor–acceptor (EDA) complexes of aromatic compounds with inorganic species.[1–7] Similar EDA complexes of aromatic compounds are also known for a variety of electron-deficient organic compounds such as quinones, polycyanoalkenes, and polycyanoaromatics.[8] EDA complexes of aromatic donors with two classes of electron acceptors are thus known: electron-deficient organic compounds usually referred to as π acceptors and electronegative inorganic species usually referred to as electrophiles. Since the designation as an electrophile is often applied to kinetic processes (in connection with reactivity), whereas π acceptor is commonly used in a thermodynamic sense (in connection with stability of a complex), we wished to make a direct comparison of electrophiles and π acceptors under circumstances which are common to both. Mulliken theory[8] provides well for the intermolecular interactions in EDA complexes of π acceptors and arenes, and our primary task in this study is to ascertain the relationship of these complexes quantitatively to those derived from electrophiles.

Results

For the study of electrophiles, we chose the halogens Cl_2 and Br_2 and the mercuric complex $[Hg(O_2CCF_3)_2]$ as representatives of structurally diverse reagents. In each case, the experimental problem centers on the measurement of the transient charge-transfer (CT) absorption spectrum. For the study of π acceptors, we examined the same series of substituted-benzene donors with maleic anhydride, tetracyanoethylene, chloranil, tetracyanobenzene, and tetracyanopyrazine.

I. Charge-Transfer Absorption Spectra of Mercury(II) Complexes with Aromatic Compounds. When methylene chloride solutions of benzene or toluene and mercury(II) trifluoroacetate are mixed, there is an immediate increase in the absorbance in the ultraviolet region of the spectrum. The magnitude of enhanced absorption is larger than the sum of the absorbances of the individual components. Indeed, the *difference spectrum* measured under carefully calibrated conditions, as described in the Experimental Section, revealed the presence of a new absorption band arising from the interaction of the arene with mercuric trifluoroacetate. The difference spectrum in Figure 1 shows a rather broad unresolved absorption band with a maximum at about 270 nm for benzene and at roughly 280 nm for toluene. The actual presence of two bands (with maxima centered at 266 and 272 nm for benzene and at 273 and 280 nm for toluene) is revealed by the Gaussian deconvolution in Figure 1, as indicated by the dashed lines.[9] Similar broad absorption bands discerned with the homologous mono- and polyalkyl aromatics are characteristic of intermolecular, electron donor–acceptor or EDA complexes.[8]

The intensity of the absorption bands in Figure 1 is linearly related to the concentrations of both the aromatic component and mercuric trifluoroacetate, as shown in Figure 2. Since mercuric trifluoroacetate is monomeric in CH_2Cl_2 solutions, the new absorption band is due to a 1:1 complex with the aromatic compound, e.g., eq 1. The

$$PhCH_3 + Hg(O_2CCF_3)_2 \xrightleftharpoons{K_{DA}} [PhCH_3\ Hg(O_2CCF_3)_2] \tag{1}$$

linear correlations in Figure 2 correspond to formation

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[1] Keefer, R. M.; Andrews, L. J. *J. Am. Chem. Soc.* **1950**, *72*, 4677. Andrews, L. J.; Keefer, R. M. *Ibid.* **1951**, *73*, 462. Andrews, L. J.; Keefer, R. M. *Ibid.* **1952**, *74*, 4500.

[2] The immediate increase in the absorbance of $Hg(O_2CCF_3)_2$ attendant upon the addition of benzene has been reported by Fung et al., who speculatively proposed the formation of a complex during the substitution process (Fung, C. W.; Khorramdel-Vahed, M.; Ranson, R. J.; Roberts, R. M. G. *J. Chem. Soc., Perkin Trans. 2* **1980**, 267).

[3] Changes in the ^{13}C and ^1H NMR chemical shifts of arenes have been attributed to complexation with $Hg(O_2CCF_3)_2$ in liquid SO_2 at 197 K (Olah, G. A.; Simon, H. Y.; Parker, D. G. *J. Org. Chem.* **1976**, *41*, 1983).

[4] Arene complexes of mercury(II) have been recently isolated from the mixture of arenes and strong acid salts of mercury such as $Hg(SbF_6)_2$, $HgF(AsF_6)$, and $Hg(O_2CCF_3)_2$ in liquid SO_2 (Damude, L. C.; Dean, P. A. W. *J. Organomet. Chem.* **1979**, *181*, 1).

[5] Larock, R. C. *Angew. Chem., Int. Ed. Engl.* **1978**, *17*, 27 and references cited therein.

[6] Seyferth, D. *J. Organomet. Chem.* **1979**, *183*, 141.

[7] Fukuzumi, S.; Kochi, J. K. *J. Phys. Chem.* **1981**, *85*, 648.

[8] (a) Mulliken, R. S.; Person, W. B. "Molecular Complexes"; Wiley-Interscience: New York, 1969. (b) Foster, R. "Organic Charge-Transfer Complexes"; Academic Press: New York, 1969.

[9] Similar spectra, but with the maxima clearly resolved, are obtained from mercuric bromide and hexamethylbenzene. The twin CT bands for the mercuric complexes, arise from the splitting of LUMO as a result of bending (see ref 7).

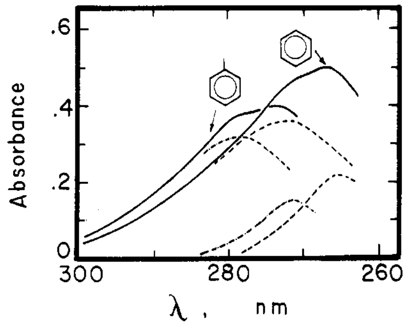

Figure 1. (a) Charge-transfer spectra of mercuric trifluoroacetate with benzene and toluene in CH_2Cl_2 solutions at 25 °C. The twin maxima are shown by the Gaussian deconvolution (dashed lines).

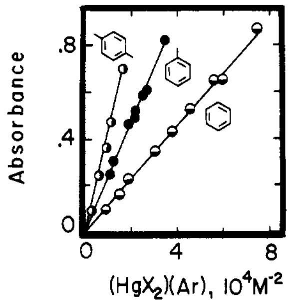

Figure 2. Linear dependence of the CT absorbance of the mercuric trifluoroacetate complexes with benzene, toluene, and *p*-xylene in CH_2Cl_2 with variations in the concentrations of both components.

constants of EDA complexes, in which $K_{DA}[PhCH_3] \ll 1$, according to the Benesi–Hildebrand expression, and thus the absorbance A is given by eq 2,[8] where ϵ is the extinction

$$A = \epsilon K_{DA}[PhCH_3][Hg(O_2CCF_3)_2] \qquad (2)$$

coefficient of the CT band. (Note that the linearity in Figure 2 is independent of the wavelengths monitored.)

The absorption maxima, λ_{max}, of the EDA complexes listed in Table I are generally red shifted with increases in the donor ability of the aromatic compounds, as measured by the lower values of the ionization potentials.[10-18] The electron-rich aromatic compounds such as styrene, methoxy-substituted benzenes, and polyalkylbenzenes reacted too rapidly with mercuric trifluoroacetate in CH_2Cl_2 solutions to observe their CT bands under our experimental conditions.

Table I. Charge-Transfer Spectral Data of $Hg(O_2CCF_3)_2$ Complexes with a Series of Substituted Benzenes

no.	compd	I_D,[a] eV	λ_{max}, nm	$h\nu_{CT}$, eV	log $\epsilon_{max}K$
1	PhH	9.23[b]	273	4.54	3.12
2	PhCl	9.08[c]	267	4.64	2.60
3	PhBr	9.05[c]	270	4.59	2.60
4	PhMe	8.82	278	4.46	3.34
5	PhEt	8.76	278	4.46	3.34
6	Ph-*n*-Pr	8.72	279	4.44	3.38
7	Ph-*n*-Bu	8.69	278	4.46	3.42
8	Ph-*i*-Pr	8.69	279	4.44	3.29
9	Ph-*t*-Bu	8.68	278	4.46	3.32
10	$PhOCH_3$	8.39[b]			
11	*o*-$Me_2C_6H_4$	8.56[d]	281	4.41	3.70
12	*m*-$Me_2C_6H_4$	8.56[d]	281	4.41	3.81
13	*p*-$Me_2C_6H_4$	8.44[e]	280	4.43	3.64
14	*p*-MeC_6H_4-*i*-Pr		280	4.43	3.49
15	*o*-MeC_6H_4Cl	8.83	272	4.56	2.94
16	*m*-MeC_6H_4Cl	8.83	273	4.54	2.74
17	*p*-MeC_6H_4Cl	8.69	~275[i]	4.51	2.77
18	*m*-MeC_6H_4Br	8.81	273	4.54	2.84
19	*p*-MeC_6H_4Br	8.67	~275[i]	4.51	2.73
20	1,3,5-$Me_3C_6H_3$	8.40	288	4.30	4.35
21	1,2,3,4-$Me_4C_6H_2$				
22	1,2,4,5-$Me_4C_6H_2$	8.05[e]			
23	Me_6C_6	7.85[d]	323[j]	3.84	4.56
24	Et_6C_6	7.65[f]	315	3.94	3.66
25	$PhCH{=}CH_2$	8.42[g]			
26	$PhCH{=}CHMe$				
27	$PhCH{=}CHBr$				
28	*m*-$(MeO)_2C_6H_4$	8.14[h]			
29	*p*-$(MeO)_2C_6H_4$	7.96[h]			

[a] From ref 11, unless noted otherwise. [b-h] From ref 11–17. [i] Not accurate. [j] From ref 7.

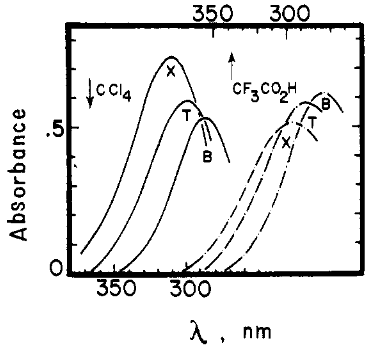

Figure 3. Comparison of the charge-transfer spectra of bromine complexes of benzene (B), toluene (T), and *o*-xylene (X) in carbon tetrachloride (—) and trifluoroacetic acid (-·-) solutions at 25 °C.

II. Charge-Transfer Absorption Spectra of Halogen Complexes with Aromatic Compounds in CCl_4 and CF_3CO_2H Solutions. Bromine. In carbon tetrachloride solution, bromine is known to rapidly form a rather persistent EDA complex with toluene.[6a] However, in trifluoroacetic acid, the CT absorption is transient,

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(10) The values of the ionization potentials are chosen from the relatively recent data obtained with photoelectron spectroscopy (PES) in ref 11–17. The values reported by the different research groups generally agree to within 0.05 eV for most compounds.[18] For example, the values of I_D for chlorobenzene and bromobenzene (the PES spectra of which are relatively broad compared to other alkyl-substituted benzenes) have been variously reported as 9.08 and 9.05,[11] 9.10 and 9.05,[18h] and 9.06 and 9.05,[18a] respectively.

(11) (a) Watanabe, K.; Nakayama, T.; Mottl, J. *J. Quant. Spectrosc. Radiat. Transfer* **1962**, *2*, 369. (b) Kobayashi, T.; Nagakura, S. *Bull. Chem. Soc. Jpn.* **1974**, *47*, 2563.

(12) Sell, J. A.; Kuppermann, A. *Chem. Phys.* **1978**, *33*, 367.

(13) Bralsford, R.; Harris, P. V.; Price, W. C. *Proc. R. Soc. London, Ser. A.* **1960**, *258*, 459.

(14) Bock, H.; Kaim, W. *Chem. Ber.* **1978**, *111*, 3552.

(15) Estimated from the value of benzene (I_1), methylbenzene (I_2), ethylbenzene (I_3), and hexamethylbenzene (I_4) by the relationship $I_4 - (I_3 - I_2)(I_1 - I_4)/(I_1 - I_2) = 7.65$.

(16) Rabalais, J. W.; Colton, R. J. *J. Electron Spectrosc. Relat. Phenom. Spect.* **1972**, *1*, 83.

(17) Anderson, G. M., III; Kollman, P. A.; Domelsmith, L. N.; Houk, K. N. *J. Am. Chem. Soc.* **1979**, *101*, 2344.

(18) (a) Turner, D. W.; Baker, C.; Baker, A. D.; Brundle, C. R. "Molecular Photoelectron Spectroscopy"; Wiley-Interscience: London, 1970. (b) Bock, H.; Wagner, G.; Kroner, J. *Chem. Ber.* **1972**, *105*, 3850. (c) Asbrink, L.; Edquist, O.; Lindholm, E.; Selin, L. E. *Chem. Phys. Lett.* **1970**, *5*, 192. (d) Haselbach, E.; Heilbronner, E. *Helv. Chim. Acta* **1970**, *53*, 689. (e) Watanabe, K. *J. Chem. Phys.* **1957**, *26*, 542. (f) Koenig, T.; Tuttle, M. *J. Org. Chem.* **1974**, *39*, 1308. (g) Maier, J. P.; Turner, D. W. *J. Chem. Soc., Faraday Trans. 2* **1973**, *69*, 196. (h) Mohraz, M.; Maier, J. P.; Heilbronner, E.; Bieri, G.; Shiley, R. H. *J. Electron Spectrosc. Relat. Phenom.* **1980**, *19*, 429. (i) Kobayashi, T.; Yokota, K.; Nagakura, S. *Ibid.* **1973**, *3*, 449. (j) Murrell, J. N.; Suffolk, R. J. *ibid.* **1972**, *1*, 471. (k) Dewar, M. J. S.; Worley, S. D. *J. Chem. Phys.* **1969**, *50*, 654.

Table II. Charge-Transfer Spectral Data of Halogen (Br_2, Cl_2, I_2) Complexes with a Series of Substituted Benzenes in CCl_4 and CF_3CO_2H

	Br_2/CCl_4		Br_2/CF_3CO_2H		Cl_2/CCl_4		I_2/CCl_4	
compd[a]	λ_{max}, nm	$h\nu_{CT}$, eV	λ_{max}, nm	$h\nu_{CT}$, eV	λ_{max}, nm	$h\nu_{CT}$, eV	λ_{max}, nm	$h\nu_{CT}$, eV
1	287	4.32[b]	276	4.49	261	4.75[b]	292	4.25[c]
2	280	4.43[b]	271	4.57			283	4.38
3	285	4.35[b]	273	4.54			288	4.30[c]
4	299	4.15[b]	288	4.30	272	4.56	304	4.08[c]
5	299	4.15	288	4.30	271	4.57	304	4.08
6	299	4.15	289	4.29	271	4.57	305	4.06
7	299	4.15	289	4.29	272	4.56	305	4.06
8	300	4.13	288	4.30	272	4.56	304	4.08
9	299	4.15	288	4.30	269	4.61	305	4.06
10	332	3.73			300	4.13	347	3.57
11	310	4.00[b]	297	4.17	278	4.46	317	3.91[c]
12	312	3.97[b]			280	4.43[b]	318	3.90[c]
13	300	4.13[b]	290	4.27	277	4.48	304	4.08[c]
14	303	4.09	291	4.26	276	4.49	305	4.06
15	293	4.23	281	4.41			298	4.16
16	290	4.27	282	4.40			298	4.16
17	285	4.35	<280	>4.43			291	4.26
18	293	4.23	283	4.38			298	4.16
19	292	4.25	280	4.43			295	4.20
20	327	3.79			290	4.27	334	3.71[c]
21	328	3.78			288	4.30	333	3.72
22	329	3.77			287	4.32	333	3.72
23	369	3.36			320	3.87	376	3.30[c]
24	363	3.41					379	3.27[c]
25	315	3.94					333	3.72[c]
26	330	3.76					349	3.55
27	301	4.12					310	4.00
28							352	3.52
29							403	3.08

[a] Identified in Table I. [b,c] Similar values are reported in ref 19–21.

owing to a further, slow substitution reaction leading to bromotoluenes. Nonetheless, the absorption spectrum of the EDA complex can be measured, and it is compared in Figure 3 with that obtained in CCl_4 solution. Although the band shapes are similar in both solvents, the absorption maxima are slightly blue shifted in CF_3CO_2H solution. In both solvents, the new absorption bands are due to 1:1 complexes of bromine and toluene (eq 3; see Figure 13 in

$$PhCH_3 + Br_2 \xrightleftharpoons[CCl_4 \text{ or } CF_3CO_2H]{K_{DA}} [PhCH_3Br_2] \qquad (3)$$

the Experimental Section). The CT spectral data for the bromine complexes with other aromatic compounds are listed in Table II.[19] The dimethoxybenzenes react too rapidly with bromine (even in CCl_4 solution) to observe their CT absorptions. Those aromatic compounds which show high reactivity with mercuric trifluoroacetate in methylene chloride are too reactive to measure the absorption spectra of the bromine complexes in this solvent.

It is noteworthy that the absorption maxima, λ_{max}, in Table II are all blue shifted in trifluoroacetic acid compared to those in carbon tetrachloride. However, the magnitude of the *blue shift is constant*, irrespective of the aromatic compound, as shown by the correlation of the points in Figure 4 to the line arbitrarily drawn with a slope of unity.

Chlorine. The CT spectra of chlorine complexes have only been reported for benzene and *m*-xylene.[6b] In order to carry out the comparison with mercuric trifluoroacetate and bromine complexes, the CT spectra of chlorine complexes with various aromatic compounds were measured by the difference technique.[20] The CT spectral data are included in Table II, together with those of the more commonly known iodine complexes.[21]

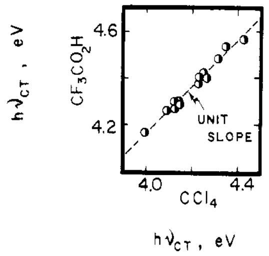

Figure 4. Constancy of the solvent-induced blue of the CT absorption band $h\nu_{CT}$ in trifluoroacetic acid relative to carbon tetrachloride. Note that the line is arbitrarily drawn with a slope of unity.

III. Charge Transfer Absorption Spectra of π Acceptors with Aromatic Compounds. Benzene and its derivatives are known to form persistent but rather weak 1:1 (EDA) complexes with various π-electron acceptors such as maleic anhydride (MA),[22] tetracyanobenzene (TCNB),[23] tetracyanoethylene (TCNE),[24] and chloranil

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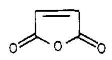
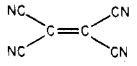
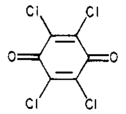
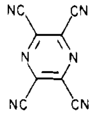
(19) Similar values are reported in ref 6a.

(20) The values reported by Andrews and Keefer[6b] are approximately 20 nm larger than the values found in this study. However, the CT absorptions are severely overlapped with the benzene and *m*-xylene absorptions under their conditions, i.e., concentrated solutions of donors. In this study, dilute solutions of benzenes were used in conjunction with relatively high concentrations of Cl_2 (0.11 M), and difference spectra were measured in order to eliminate the interference arising from the overlap of donor absorbances. The absorbance overlap with Cl_2 is negligible.

(21) (a) Similar values are reported in ref 6c and 21b–d. (b) Tamres, M.; Virzi, D. R.; Searles, S. *J. Am. Chem. Soc.* **1953**, *75*, 4358. (c) Ham, J. S.; Platt, J. R.; McConnell, H. *J. Chem. Phys.* **1951**, *19*, 1301. (d) Ketelaar, J. A. A. *J. Phys. Radium* **1954**, *15*, 197.

(22) (a) Andrews, L. J.; Keefer, R. M. *J. Am. Chem. Soc.* **1953**, *75*, 3776. (b) Barb, W. G. *Trans. Faraday Soc.* **1953**, *49*, 143.

Table III. Charge Transfer Spectral Data of EDA Complexes of Benzene Derivatives with MA, TCNB, TCNE, and TCNP in CH_2Cl_2 and Chloranil in CCl_4

	$h\nu_{CT}$, eV				
compd					
1	4.56[a]	4.02[b]	3.19[c]	3.65[d]	3.68
2	>4.52		3.27[c]	4.02	3.73
3	>4.43		3.16[c]	4.04	3.72
4	4.44[a]	3.94[b]	2.99[c]	3.31[d]	3.54
5	4.46[a]		3.01[c]	3.31	3.53
6	4.44	3.92	2.97	3.30	3.52
7	4.46		2.97	3.28	3.53
8	4.46[a]		2.97[c]	3.33	3.53
9	4.46[a]		2.99[c]	3.35[d]	3.52
10	4.04	3.50	2.43,[c] 3.19	2.74, 3.59	2.92, 3.65
11	4.33[a]	3.73	2.82[c]	3.06[d]	3.33
12	4.33	3.73	2.80[c]	3.06[d]	3.32
13	4.36[a]	3.72	2.65,[c] 3.10	2.89,[d] 3.54	2.95, 3.42
14	4.40	3.72	2.61, 3.10	2.86, 3.54	2.95, 3.39
15	4.43		3.05	3.47	3.61
16	4.40		3.05	3.49	3.61
17	4.35		2.80	3.14	3.26
18	4.35		3.00	3.49	3.60
19	4.36		2.74	3.08	3.22
20	4.10[a]	3.59[b]	2.64[c]	2.89[d]	3.08
21	3.97	3.35	2.38, 2.75	2.55, 2.95	2.69, 3.06
22	4.04[a]	3.35[b]	2.38,[c] 2.75	2.54,[d] 2.95	2.69, 3.06
23	3.54[a]	3.10[b]	2.27[c]	2.38[d]	2.59
24	3.80	3.73	2.23[c]	2.64	3.10
25	4.20	3.78	2.57,[c] 3.18	2.90, 3.55	3.02, 3.61
26	4.00	3.77	2.32, 3.08	2.63, 3.40	2.76, 3.60
27	>4.20		2.65, 3.14	3.02, 3.40	3.18, 3.61
28	4.00	3.18	2.26, 2.72	2.48, 2.88	2.67, 3.10
29	3.53	2.85[b]	1.96, 3.24	2.26, 3.54	2.43, 3.68

[a-d] Similar values are reported in the literature: *a*, ref 22; *b*, ref 23; *c*, ref 24; *d*, ref 24g,h and 25.

(CA).[24g,h,25] However, the extant literature contains only limited data of such CT spectra, being available only for a randomly chosen set of the benzene derivatives included in Table I and II.[22-25] Thus the CT spectral data summarized in Table III were measured under standard conditions to allow a direct comparison with the EDA complexes of the halogen and mercury(II) electrophiles. The CT spectral parameters derived from the novel acceptor tetracyanopyrazine (TCNP) are also included.

The absorption maxima of the π-acceptor complexes in Table III are generally red shifted relative to those of the mercury(II) and halogen complexes in Tables I and II, respectively. As a result, there is less overlap of the CT band with the absorptions of the components, and a wider spectral region can be examined. The latter allowed the two well-separated CT bands to be observed for the EDA complexes of TCNE, CA, and TCNP, as shown in Figure 5.

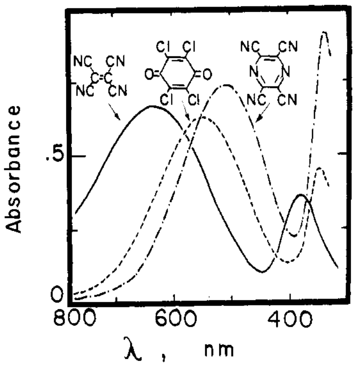


Figure 5. Resolution of the twin CT absorption bands of the EDA complexes of *p*-dimethoxybenzene with tetracyanoethylene, chloranil, and tetracyanopyrazine.

The formation constants for the EDA complexes with these π acceptors were determined by the Benesi–Hildebrand method by utilizing the absorbance change given by eq 4,[26] where $[A]_0$ and $[Ar]_0$ are the initial concentrations of the acceptor and aromatic donor, respectively, in a cell of unit path length. The results in Table IV were obtained with various amounts of the aromatic donor in excess.

$$\frac{[A]_0}{A} = \frac{1}{\epsilon K_{DA}} \frac{1}{[Ar]_0} + \frac{1}{\epsilon} \qquad (4)$$

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(23) (a) Iwata, S.; Tanaka, J.; Nagakura, S. *J. Am. Chem. Soc.* **1966**, *88*, 894. (b) Hayashi, H.; Iwata, S.; Nagakura, S. *J. Chem. Phys.* **1969**, *50*, 993. (c) Bailey, A. S.; Henn, B. R.; Langdon, J. M. *Tetrahedron* **1963**, *19*, 161. (d) Foster, R.; Thomson, T. J. *Trans. Faraday Soc.* **1963**, *59*, 2287.

(24) (a) Merrifield, R. E.; Phillips, W. D. *J. Am. Chem. Soc.* **1958**, *80*, 2778. (b) Hanstein, W.; Berwin, H. J.; Traylor, T. G. *Ibid.* **1970**, *92*, 829. (c) Voigt, E. M.; Reid, C. *Ibid.* **1964**, *86*, 3930. (d) Rosenberg, H. M.; Hale, D. *J. Phys. Chem.* **1965**, *69*, 2490. (e) Dewar, M. J. S.; Rogers, H. *J. Am. Chem. Soc.* **1962**, *84*, 395. (f) Dewar, M. J. S.; Thomson, C. C., Jr. *Tetrahedron, Suppl.* **1966**, *7*, 97. (g) Briegleb, G.; Czekalla, J.; Reuss, G. *Z. Phys. Chem. (Wiesbaders)* **1961**, *30*, 316. (h) Bryce-Smith, D.; Connett, B. E.; Gilbert, A. *J. Chem. Soc. B* **1968**, 816. (i) Kochi, J. K.; Tang, R. T.; Bernath, T. *J. Am. Chem. Soc.* **1973**, *95*, 7114.

(25) Murrell, J. N. *Q. Rev., Chem. Soc.* **1961**, *15*, 191.

(26) Benesi, H. A.; Hildebrand, J. H. *J. Am. Chem. Soc.* **1949**, *71*, 2703. (a) Buhler, R. E. *J. Phys. Chem.* **1972**, *76*, 3220. (b) Yada, H.; Tanaka, J.; Nagakura, S. *Bull. Chem. Soc. Jpn.* **1960**, *33*, 1660. (c) Mulliken, R. S.; Person, W. B. *Annu. Rev. Phys. Chem.* **1962**, *13*, 107. (d) Person, W. B. *J. Chem. Phys.* **1963**, *38*, 109.

(27) (a) Michaelian, K. H.; Rieckhoff, K. E.; Voigt, E. M. *J. Phys. Chem.* **1977**, *81*, 1489. (b) Ewall, R. X.; Sonnessa, A. J. *J. Am. Chem. Soc.* **1970**, *92*, 2845.

Table IV. Formation Constants of EDA Complexes of Benzene Derivatives with TCNB, TCNE, and TCNP in CH_2Cl_2 and Chloranil in CCl_4 at 25 °C

	K_{DA}, M^{-1}			
compd	TCNE	chloranil	TCNP	TCNB
1	0.19	0.35[c]	0.12	0.25[a]
2	0.68	0.87	0.10	
3	0.11	0.83	0.24	
4	0.24	0.67[c]	0.48	
5	0.25	0.56	0.32	
6	0.16	0.63	0.34	
7	0.85	0.48	0.58	
8	0.20	0.56	0.59	
9	0.14	0.10	0.30	
10	0.41[b]	1.0	0.98	
11	0.53[b]	0.97[c]	0.97	0.21
12	0.46[b]	1.1[c]	0.72	0.40
13	0.58[b]	1.2[c]	0.51	0.24
14	0.22	0.50	0.41	0.23
15	0.14	0.37	0.28	
16	0.10	0.72	0.29	
17	0.15	0.33	0.23	
18	0.16	0.40	0.51	
19	0.14	0.44	0.27	
20	1.1[b]	1.4	0.91	0.52
21	2.2	4.1[c]	2.0	
22	3.2[b]	3.1[c]	1.5	
23	21.0[b]	8.6[c]	3.4	0.35
24	0.18	0.92	0.49	
25	0.34	0.65	0.44	0.17
26	0.51	1.1	0.84	0.18
27	0.14	0.38	0.39	
28	0.94	2.0	1.3	
29	1.4	2.0	1.1	

[a] $-\Delta H = 0.4$ kcal mol^{-1}.[23a] [b] Similar values are reported in ref 27. [c] Similar values are reported in ref 25.

Discussion

I. Comparative Strengths of EDA Complexes of Aromatic Donors with Electrophiles and Electron Acceptors. The thermodynamic formation constant K_{DA} is a commonly used measure of the strength of an electron donor–acceptor complex. Thus the values of K_{DA} in Table IV reveal the influence of aromatic substituents on the stability of EDA complexes with various π acceptors. However, for the very weak and transient EDA complexes such as those derived from the halogen and mercury(II) electrophiles in Tables II and I, respectively, the magnitude of K_{DA} cannot be independently determined by the usual techniques, including the Benesi–Hildebrand procedure. In order to provide a basis for comparing EDA complexes of various strengths, we require a measure which is common to all complexes such as data derived from the CT spectra. Indeed, the product of the formation constant and the extinction coefficient, $K_{DA}\epsilon_{max}$, is a readily measurable quantity for very weak as well as moderately strong EDA complexes, as given in eq 2 and 4, respectively.

We define parameter K_S to be a measure of the strength of an EDA complex, i.e., eq 5, where $\Delta\nu_{1/2}$ is the width of

$$K_S = \tfrac{1}{2}\, \epsilon_{max} K_{DA} \Delta\nu_{1/2} \tag{5}$$

the CT absorption band at half its maximum height. [The theoretical basis for eq 5 is presented separately in the Experimental Section.] The magnitudes of K_S for the aromatic complexes with both electrophiles and acceptors employed in this study are tabulated in Table IX (supplementary material; see Experimental Section).

The values of K_S for a typical π-acceptor TCNE are compared in Figure 6a with K_S for the mercury(II) electrophile $Hg(O_2CCF_3)_2$ by using the same series of aromatic compounds. There is clearly a parallel behavior between the electrophile and the π acceptor, as also shown in Figure 6b for the comparison of the bromine electrophile and the maleic anhydride π acceptor. Furthermore, similar linear relationships of K_S exist between other pairs of electrophile and π-acceptor complexes with aromatic compounds.[28] Thus by taking K_S (defined in eq 5) as a measure of the stability of an EDA complex, we conclude that there is no particular distinction in the ground-state properties of EDA complexes with electrophiles relative to those with π acceptors. Since the stabilization of aromatic complexes with π acceptors such as TCNE derive from a charge-transfer origin,[24] it is reasonable that similar interactions are extant with the halogen and mercury(II) electrophiles. In other words, electrophiles cannot be distinguished from π acceptors solely on the basis of the strengths of the EDA complexes with aromatic donors.

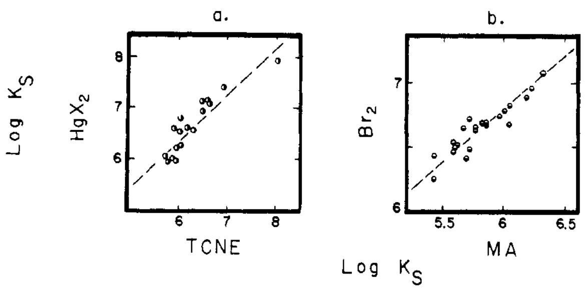

Figure 6. Typical linear correlations of K_S for aromatic complexes with π acceptors (abscissa) and K_S for the corresponding aromatic complexes with electrophiles (ordinate): left, $Hg(O_2CCF_3)_2$ vs. tetracyanoethylene; right, Br_2 vs. maleic anhydride.

II. Comparative CT Transition Energies of Aromatic Complexes with Electrophiles and π Acceptors. We now inquire whether electrophiles can be distinguished from π acceptors on the basis of their charge-transfer excited states. According to Mulliken, the CT absorption band arises from the electronic excitation from the neutral ground-state Ψ_N of the EDA complex to the polar excited singlet state Ψ_X as described by eq 6 and 7, respectively,[7,8]

$$\Psi_N = a\Psi_0(DA) + b\Psi_1(D^+A^-) \tag{6}$$

$$\Psi_X = a^*\Psi_1(D^+A^-) - b^*\Psi_0(DA) \tag{7}$$

where $|a|^2$ and $|a^*|^2$ are close to unity for weak complexes of the types examined in this study. The CT transition can thus be schematically represented as a vertical process (eq 8) in which the asterisk identifies an excited ion pair

$$[ArE] \xrightarrow{h\nu_{CT}} [Ar^+\ E^-]^* \tag{8}$$

with the same mean separation r_{DA} as that in the EDA complex. The nature of the CT excited state has been experimentally confirmed to be the polar ion-pair state in eq 8 by applying spectroscopic methods with pulsed-laser excitation.[29] Thus in aromatic complexes with π acceptors such as tetracyanobenzene and pyromellitic anhydride, the absorption spectra of the excited EDA complexes were shown to consist of the superposition of the spectral bands of the aromatic donor cation and the acceptor anion. Such observations have been made both in rigid media at 77°K as well as in dilute fluid solutions at room temperature.[29,30]

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(28) In the correlation with chloranil, the value for hexaethylbenzene deviates significantly from the correlation. However, compare the same deviation in Figure 7.

(29) (a) Mataga, N.; Ottolenghi, M. In "Molecular Association"; Foster, R., Ed.; Academic Press: New York, 1979; Vol. 2, p 31. (b) Ottolenghi, M. *Acc. Chem. Res.* **1973**, *6*, 153. (c) Potashnik, R.; Ottolenghi, M. *Chem. Phys. Lett.* **1970**, *6*, 525. (d) Masuhara, H.; Mataga, N. *Ibid.* **1970**, *6*, 608. (e) Masuhara, H.; Mataga, N. *Bull. Chem. Soc. Jpn.* **1972**, *45*, 43. (f) Masuhara, H.; Tsujino, N.; Mataga, N. *Ibid.* **1973**, *46*, 1088. (g) Kobayashi, T.; Matsumoto, S.; Nagakura, S. *Chem. Lett.* **1974**, 235.

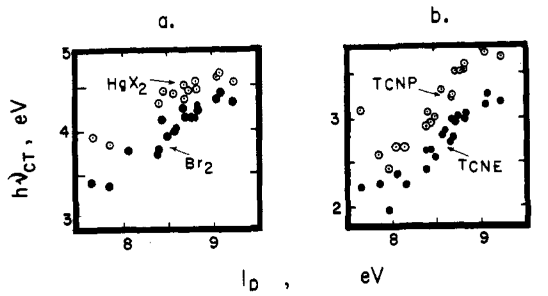

Figure 7. Variation of the CT transition energy $h\nu_{CT}$ with the ionization potential (I_D) of the aromatic donor: left, electrophiles $Hg(O_2CCF_3)_2$ (⊙) and Br_2 (●) from Tables I and II; right, π acceptors TCNP (⊙) and TCNE (●) from Table III.

Table V. Variation in the Slopes of the Correlation of $h\nu_{CT}$ and I_D with the Electrophile or π Acceptor

electrophile or π acceptor	$\partial(h\nu_{CT})/\partial I_D$	ρ[a]	no. of aromatic compds
$Hg(O_2CCF_3)_2$	0.5	0.93	21
TCNB	0.6	0.72	14
Cl_2	0.6	0.89	14
MA	0.7	0.91	23
Br_2	0.7	0.93	23
TCNE	0.8	0.94	25
TCNP	0.9	0.87	25
CA	1.0	0.92	25

[a] Correlation coefficient.

The energy associated with the CT transition in eq 8 is given in the first-order expression[8] shown in eq 9, where

$$h\nu_{CT} = I_D - E_A - e^2/r_{DA} \qquad (9)$$

I_D is the vertical ionization potential of the aromatic donor and E_A is the electron affinity of the electrophile or π acceptor. The variation of the CT transition energy with the ionization potential of the aromatic donor is obtained from the differentiation of eq 9, i.e., eq 10, in which

$$\frac{\partial(h\nu_{CT})}{\partial I_D} = 1 + \left(\frac{e^2}{{r_{DA}}^2}\right)\frac{\partial r_{DA}}{\partial I_D} \qquad (10)$$

$\partial r_{DA}/\partial I_D$ relates to the variation in the mean separation with changes in the ionization potential. Therefore, if we consider a series of substituted benzenes interacting with a particular electrophile or π acceptor, it follows from eq 10 that $h\nu_{CT}$ will be linearly related to I_D with a slope of unity provided r_{DA} remains constant, as is commonly assumed.[8b] Indeed, the CT transition energies for the aromatic complexes of Br_2 and $Hg(O_2CCF_3)_2$ are related to the ionization potentials of the aromatic donors, as shown in Figure 7a.[31] Furthermore, the relationship is not restricted to electrophiles since the same trend in the data is noted in Figure 7b for π acceptors such as tetracyanopyrazine and tetracyanoethylene. A detailed comparative examination shows striking similarities between the electrophile and π-acceptor complexes. Similar relationships of $h\nu_{CT}$ and I_D are also obtained for the other electrophiles and π acceptors included in Tables II and III. If each set of data is analyzed by a linear least-squares treatment, we note that the apparent slopes of the overall plots vary considerably from unity, as listed in Table V. Although the correlation coefficients are not uniformly high, it is clear that the deviation in the slope from unity is the greatest with $Hg(O_2CCF_3)_2$ and the least with chloranil, the others falling in the intermediate range in more or less random fashion, irrespective of whether they are electrophiles or π acceptors. Thus the results in Table V suggest that the mean separation r_{DA} is not constant in eq 9 but varies in a series of substituted benzenes, the magnitude depending on the particular electrophile or π acceptor. Such a change in r_{DA} can be shown directly in the following two ways which involve either an intermolecular or an intramolecular comparison.

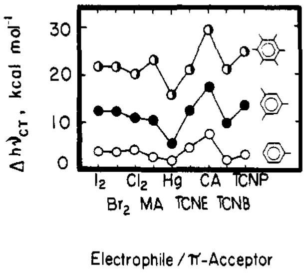

Figure 8. Variations in the relative CT transition energies $\Delta h\nu_{CT}$ (using benzene as the reference arene) with the various electrophiles and π acceptors designated in the abscissa: ○, toluene; ●, mesitylene; ◐, hexamethylbenzene.

(A) Intermolecular Comparison of r_{DA}. The CT transition energy for a substituted benzene complex can be compared with that of the corresponding benzene complex. In such an intermolecular comparison, it follows from eq 9 that the difference in the CT transition energies $\Delta h\nu_{CT}$ can be expressed as eq 11, where ΔI_D is the difference in the ionization potentials of the substituted benzene and benzene. (Note that the electron affinity is cancelled out in this comparative procedure with benzene as the reference aromatic compound.) If the mean separation were invariant, values of $\Delta h\nu_{CT}$ would also be invariant since ΔI_D would be constant in a series of complexes with a particular aromatic donor. However, experimentally we find that values of $\Delta h\nu_{CT}$ do vary widely with the electrophile and π acceptor, as shown in Figure 8. Furthermore, the variations in $\Delta h\nu_{CT}$ observed with toluene, parallel those with mesitylene and hexamethylbenzene. According to eq 9, such variations must reflect changes in the mean separation r_{DA} associated with different electrophiles and π acceptors, without any distinction between them.

$$\Delta h\nu_{CT} = \Delta I_D - \Delta(e^2/r_{DA}) \qquad (11)$$

(B) Intramolecular Comparison of r_{DA}. The appearance of twin CT bands in EDA complexes of methylbenzenes with chloranil was first explained by Orgel,[32] who attributed the splitting to the removal of the degeneracy in the HOMO orbital of benzene upon nuclear substitution. The two CT bands are thus associated with the transitions from two such occupied orbitals in the donor to the acceptor. This assignment has been confirmed in chloranil and TCNE complexes with polycyclic aromatics by Briegleb and coworkers.[24g] They showed that the energy difference $\Delta' h\nu_{CT}$ between the first and second CT bands is equal to the calculated energy difference between

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[30] (a) There is controversy as to whether the geometry of the Franck–Condon state is different from that of the singlet fluorescent state and whether the ionic contribution in the Franck–Condon state is much less than complete.[30b,c] However, the fact that the absorption spectrum of the excited TCNB–toluene complex is quite close to that of the TCNB anion even at 4.2 K[29a] strongly suggests that an almost pure ionic state is generated during the Franck–Condon transition, without further structural changes. (b) Iwata, S.; Tanaka, J.; Nagakura, S. *J. Am. Chem. Soc.* **1966**, *88*, 894. (c) Masuhara, H.; Mataga, N. *Z. Phys. Chem.* (*Wiesbaden*) **1972**, *80*, 113.

[31] It is important to note that a plot of $h\nu_{CT}$ for $Hg(O_2CCF_3)_2$-aromatic complexes against that for Br_2-aromatic complexes is linear.

[32] Orgel, L. E. *J. Chem. Phys.* **1955**, *23*, 1352.

Table VI. Differences in the CT Transition Energies between the First and the Second CT Bands of Some Substituted Benzenes with Different Acceptors

no.	aromatic donor	$\Delta' I_D$, eV	$\Delta' h\nu_{CT}$, eV TCNE	chloranil	TCNP
10	$PhOCH_3$	0.83[a]	0.76	0.85	0.73
13	p-$Me_2C_6H_4$	0.61[b]	0.45	0.65	0.47
22	1,2,4,5-$Me_4C_6H_2$	0.50[b]	0.37	0.41	0.37
25	$PhCH{=}CH_2$	0.78[c]	0.61	0.65	0.59
26	$PhCH{=}CHMe$	0.66[c]	0.76	0.77	0.84
28	m-$(MeO)_2C_6H_4$	0.58[d]	0.46	0.40	0.43
29	p-$(MeO)_2C_6H_4$	1.20[d]	1.28	1.28	1.25

[a] Reference 10. [b] Reference 14. [c] Reference 16. [d] Reference 17.

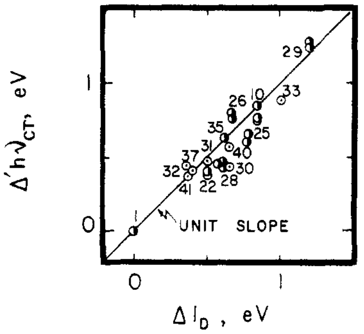

Figure 9. Intramolecular comparison of the CT transition energies using the multiple-absorption bands: $\Delta' h\nu_{CT}$ from the difference between the first and second CT bands and $\Delta' I_D$ from the difference between the first and second I_D of the aromatic donor. Numbers refer to the entries in Tables VI and VII. The line is arbitrarily drawn with a slope of unity to emphasize the fit of the data.

the first and second highest occupied molecular orbitals (HOMO) of the aromatic donor.

We have also observed twin CT absorption bands in Figure 5 for the EDA complexes of p-dimethoxybenzene with TCNE and TCNP, in addition to chloranil. Furthermore, similar pairs of CT bands are listed in Table III for these acceptors with other substituted benzenes such as anisole, p-xylene, p-cymene, 1,2,3,4-tetramethylbenzene, durene, and the styrene derivatives. The difference $\Delta' h\nu_{CT}$ in the CT transition energies of the twin bands are listed in Table VI for the various acceptors. It is noteworthy that the values of $\Delta' h\nu_{CT}$ are independent of the acceptor, to within the experimental error of ±0.1 eV. Furthermore, the striking linear correlation in Figure 9 represents the relationship shown in eq 12,[33] where $\Delta' I_D$ is the energy

$$\Delta' h\nu_{CT} = \Delta' I_D \qquad (12)$$

difference between the first and second vertical ionization potentials in the aromatic donor, measured independently from the photoelectron spectra. For completeness, the CT transition energies previously reported for the TCNE complexes of various silicon-substituted benzenes included in Table VII (see supplementary material) are also plotted in Figure 9. Since the mean separation r_{DA} of the complex is the same for the first and second CT bands,[33] eq 12 merely represents an intramolecular comparison, which is equivalent to eq 11 derived from an intermolecular comparison.

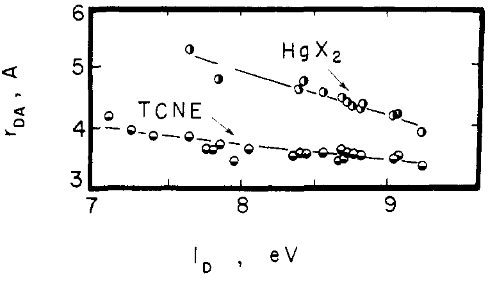

Figure 10. Steric effects in $Hg(O_2CCF_3)_2$ and TCNE complexes with a series of benzene derivatives from Table VIII.

(C) Alternatives to the Variations in r_{DA}. The intermolecular and intramolecular comparisons presented in both of the foregoing sections suggest that the reduced slopes in Table V are due to variations of the mean separation in aromatic complexes with various electrophiles and π acceptors. However, before embracing this notion too strongly, we must consider an alternative explanation which is commonly used to explain the dependence of $h\nu_{CT}$ on I_D with slopes of less than unity.[35]

It is possible that the charge separation in eq 8 is not complete owing to a significant contribution from the "no-bond" wave function $\Psi_0(DA)$ in the excited state given by eq 7. Under these circumstances the first-order expression for the CT transition energy in eq 9 is inappropriate, and a more general solution of the secular equation, such as that in eq 13,[35] is required, where $C_1 = E_A + e^2/r_{DA}$

$$h\nu_{CT} = \frac{I_D - C_1}{1 - S_{01}^2}\left[1 + \frac{4\beta_0\beta_1}{I_D - C_1}\right]^{1/2} \qquad (13)$$

and β_0 and β_1 are the matrix elements $(H_{01} - S_{01}H_{00})$ and $(H_{01} - S_{01}H_{11})$, respectively, in which S_{01} is the overlap integral. However, there are three independent types of experimental evidence which do not support the formulation in eq 13.[36] The first relates to the dependence of $h\nu_{CT}$ on I_D in Figure 7. Since the second derivative of eq 13 with respect to I_D is positive,[37] $h\nu_{CT}$ will show a concave dependence on I_D, according to eq 13. In fact, the observations in Figure 7 show an opposite trend. The second evidence relates to the erratic dependence of $\Delta h\nu_{CT}$ on the electrophile or the π acceptor in Figure 8. According to eq 13, the value of $\Delta h\nu_{CT}$ must be the largest for the electrophile or π acceptor with the smallest electron affinity.[38] In fact, mercuric trifluoroacetate which has the smallest value of E_A gives the smallest value of $\Delta h\nu_{CT}$ in Figure 8.[39] The third piece of evidence relates to the

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[33] Different molecular configurations corresponding to the first and the second CT bands have been discussed for TCNE complexes with substituted benzenes.[34] However, the differences in the mean separation due to such differences in configurations in the same pair of compounds should be negligible, especially when compared with those between different pairs of compounds (compare Figure 7 and 8 with Figure 9).

[34] (a) Mobley, M. J.; Rieckhoff, K. E.; Voigt, E. M. *J. Phys. Chem.* **1977**, *81*, 809. (b) Holder, D. D.; Thompson, C. C. *J. Chem. Soc., Chem. Commun.* 1972, 277. (c) Michaelian, K. H.; Rieckhoff, K. E.; Voigt, E. M. *Proc. Natl. Acad. Sci. U.S.A.* **1975**, *72*, 4196.

[35] (a) Buhler, R. E. *J. Phys. Chem.* **1972**, *76*, 3220. (b) Yada, H.; Tanaka, J.; Nagakura, S. *Bull. Chem. Soc. Jpn.* **1960**, *33*, 1660. (c) Mulliken, R. S.; Person, W. B. *Annu. Rev. Phys. Chem.* **1962**, *13*, 107. (d) Person, W. B. *J. Chem. Phys.* **1963**, *38*, 109.

[36] (a) The use of eq 13 has been also criticized by Tamres and Strong in their review (Tamres, M.; Strong, R. L. In "Molecular Association"; Foster, R., Ed.; Academic Press: New York, 1979; Vol. 2, p 389). (b) See also: Fukuzumi, S.; Kochi, J. K. *J. Phys. Chem.* **1980**, *84*, 608, 2246.

[37] In eq 13, the resonance energies β_0 and β_1 are both <0, and the square of the overlap integral $S_{0,1}^2$ is $\ll 1$. It follows that $\partial^2(h\nu_{CT})/\partial I_D^2$ is >0.

[38] Since $h\nu_{CT}$ is a monitonically decreasing function with E_A, i.e., $\partial(h\nu_{CT})/\partial E_A < 0$, the value of $\Delta h\nu_{CT}$ must be the largest for the smallest value of E_A. Note that $\partial(h\nu_{CT})/\partial I_D = -\partial(h\nu_{CT})/\partial E_A$.

[39] (a) The electron affinity E_A of $Hg(O_2CCF_3)_2$ is estimated to be approximately 1.0 eV.[39c] Compare the values of E_A for TCNE (1.7 eV), I_2 (1.6 eV), Br_2 (1.5 eV).[36b] For others, see reference 39b. At this juncture, detail discussions based on E_A cannot be carried out owing to the inaccuracy of the data. (b) Briegleb, G. *Angew. Chem.*, Int. *Ed. Engl.* **1964**, *3*, 617. (c) Fukuzumi, S.; Kochi, J. K. *J. Am. Chem. Soc.*, **1981**, *103*, 2783.

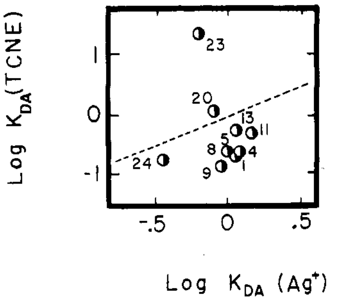


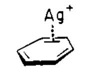
Figure 11. Comparison of the formation constants of the TCNE and the silver(I) complexes with a series of substituted benzenes. Note that the dashed line is arbitrarily drawn through the origin with a slope of unity to emphasize the lack of correlation.

multiple CT bands in Figure 9. The first derivative of eq 13 with respect to I_D is less than unity.[40] In fact, the plot of the data in Figure 9 coincides within experimental error to the solid line, arbitrarily drawn with a slope of unity. Although the foregoing evidence is somewhat qualitative, largely owing to the lack of quantitative measures of the resonance integrals, the experimental fit of the data accords well with eq 9. Thus these aromatic complexes are best described as uniformly involving weak CT interactions in the ground state and complete charge transfer upon excitation.[41,42]

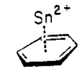
III. Comparative Structures of Arene Complexes with Electrophiles and π Acceptors. The formation constants of the EDA complexes of arenes with the electrophiles examined in this study are too small to allow a direct crystallographic study of their molecular structures. Interestingly, the mean separation in $Hg(O_2CCF_3)_2$ complexes are the largest among the various electrophiles and π acceptors, judging by the minimum values of $\Delta h\nu_{CT}$ in Figure 8 and by the smallest slopes in Table V. In order to assess this effect quantitatively, we evaluated the mean separations in the aromatic complexes of $Hg(O_2CCF_3)_2$ from eq 9, and these are given in Table VIII (see supplementary material).[43] The variations in r_{DA} for the $Hg(O_2CCF_3)_2$ complexes with the ionization potential of the aromatic donor are compared in Figure 10 with those in the TCNE complexes. In both series there is a trend for r_{DA} to increase as I_D decreases. However, the effect is significantly larger for $Hg(O_2CCF_3)_2$ relative to TCNE. For example, the difference between r_{DA} in the benzene and hexaethylbenzene complexes of $Hg(O_2CCF_3)_2$ is 1.41 Å, whereas it is only 0.55 Å for the TCNE complexes. The larger values of r_{DA} in the $Hg(O_2CCF_3)_2$ complexes may be attributed to ligand interference in the CT interaction from the π-HOMO of benzene to the mercury-centered π_u^* LUMO of the acceptor.[45] This point is elaborated in the following analysis.

According to Mulliken theory, the CT spectral transition in EDA complexes arises via electron donation from the aromatic moiety to the electrophile or π acceptor acting as an electron acceptor.[8] Such a CT interaction is to be distinguished from the synergistic bonding commonly described for the related aromatic complexes with silver(I), in which back-donation from the occupied d orbitals of silver(I) into the unoccupied π* antibonding donor orbitals represents an additional factor.[46] The resulting contrast in the stabilities of the complexes is illustrated in Figure 11, which shows the complete lack of correlation between the measured formation constants of aromatic complexes with TCNE and with silver(I).[47] Furthermore, the formation constants for mercury(II)–aromatic complexes (were they available) would also show no correlation with the formation constants of the corresponding silver(I)–aromatic complexes, judging by the linear relationships in Figure 6a. The difference between mercury(II) and silver(I) in complex formation with aromatic compounds may be attributed to differences in the extent of back-bonding. Thus back-donation of d electrons from silver(I) is expected to be more important than that from mercury(II), owing to a significant difference in the ionization potentials [$I_D(Hg^{2+})$ = 34.20 eV, $I_D(Ag^+)$ = 21.49 eV].[48] The bonding in copper(I) and gold(I) complexes is similar to that in the silver(I) complex, as also indicated by their ionization potentials of 20.50 and 20.29 eV, respectively.[46,48-50]

Since the structures of the $Hg(O_2CCF_3)_2$ complexes with benzene derivatives cannot be determined directly, we compare the properties of these complexes with those in which the molecular structures are known from X-ray crystallographic analyses. For example, the crystal structures of silver(I)–arene complexes have been studied extensively.[46a,51] The silver atom is known to be preferentially located above and between two adjacent unsubstituted carbons when such positions are available, as schematically shown in the molecular structure A. Such



A.



B.

a dihapto arrangement of benzene is quite different from the structure of tin(II)–benzene complexes in which the tin atom resides on the 6-fold axis, as shown in B.[52]

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(40) Compare footnotes 37 and 38.

(41) The complete transfer of charge in the excited state is shown by the elegant studies in ref 29 and 30.

(42) Such a formulation allows us to focus clearly on the variations of r_{DA} to explain CT phenomena which otherwise would be difficult to account for. For example, the ionization potential of hexaethylbenzene (7.65 eV) is slightly less that that of hexamethylbenzene (7.85 eV). Nonetheless, the CT transition energies of the hexaethylbenzene complexes are all consistently larger than those of the corresponding hexamethylbenzene complexes, as illustrated in Figure 7. The increases in r_{DA} which arise from increased steric effects in hexaethylbenzene readily accommodate the inverse behavior. Such an inversion of I_D and $h\nu_{CT}$ is also observed between benzene (9.23 eV) and chlorobenzene (9.08 eV), as shown in Figure 7 and listed in Tables I–III. The increase in $h\nu_{CT}$ from benzene to chlorobenzene is also readily attributed to an increase in r_{DA}. For the other aromatics, the decrease in I_D accompanying substitution usually exceeds the variation in r_{DA}. The overall effect can lead to an increase in r_{DA} by an amount sufficient to allow a resultant smooth correlation of $h\nu_{CT}$ and I_D.

(43) According to eq 9, the mean separation in angstroms is given by $r_{DA} = 14.4(I_D - E_A - h\nu_{CT})^{-1}$.

(44) Bock, H.; Alt, H. *J. Am. Chem. Soc.* **1970**, *92*, 1569.

(45) (a) Griffiths, T. R.; Anderson, R. A. *J. Chem. Soc., Faraday Trans. 2* **1979**, *75*, 957. (b) Griffiths, T. R.; Anderson, R. A. *Inorg. Chem.* **1979**, *18*, 2506. (c) This is also confirmed by the bonding between Hg(II) and nitrogen in the bis(pyridine)–$Hg(O_2CCF_3)_2$ complex: Halfpenny, J.; Small, R. W. H.; Thorpe, F. G. *Acta Crystallogr., Sect. B* **1978**, *B34*, 3075.

(46) (a) Beverwijk, C. D. M.; Van der Kerk, G. J. M.; Leusink, A. J.; Noltes, J. G. *Organomet. Chem. Rev., Sect. A* **1970**, *5*, 215. (b) Mulliken, R. S. *J. Chim. Phys.* **1964**, *61*, 20.

(47) Ogimachi, N.; Andrews, L. J.; Keefer, R. M. *J. Am. Chem. Soc.* **1956**, *78*, 2210.

(48) Hosoya, H.; Nagakura, S. *Bull. Chem. Soc. Jpn.* **1964**, *37*, 249.

(49) (a) Salomon, R. G.; Kochi, J. K. *J. Am. Chem. Soc.* **1973**, *95*, 1889. (b) Salomon, R. G.; Kochi, J. K. *J. Organomet. Chem.* **1974**, *64*, 135. (c) Komiya, S.; Kochi, J. K. *Ibid.* **1977**, *135*, 65.

(50) In more general cases such as hydrogen bonding, the interactions in the EDA complexes consist of many factors, including electrostatic, polarization, exchange repulsion, and coupling, in addition to the charge-transfer contributions. Compare: Morokuma, K. *Acc. Chem. Res.* **1977**, *10*, 294.

(51) (a) Rundle, R. E.; Goring, J. H. *J. Am. Chem. Soc.* **1950**, *72*, 5337. (b) Smith, H. G.; Rundle, R. E. *Ibid.* **1958**, *80*, 5075. (c) Turner, R. W.; Amma, E. L. *Ibid.* **1966**, *88*, 3243. (d) Griffith, E. A. H.; Amma, E. L. *Ibid.* **1971**, *93*, 3167. (e) Taylor, I. F., Jr.; Hall, E. A.; Amma, E. L. *Ibid.* **1969**, *91*, 5745. (f) Taylor, I. F., Jr.; Amma, E. L. *J. Cryst. Mol. Struct.* **1975**, *5*, 129. (g) Hunt, G. W.; Lee, T. C.; Amma, E. L. *Inorg. Nucl. Chem. Lett.* **1974**, *10*, 909.

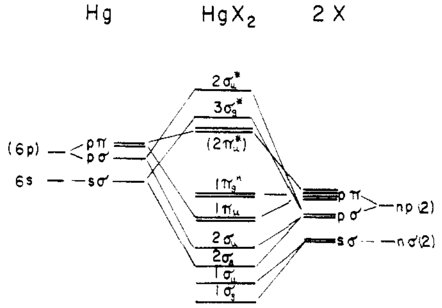
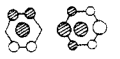


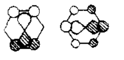
Figure 12. Correlation diagram for the orbitals in mercury(II) complexes HgX_2 with slightly distorted $D_{\infty h}$ symmetry.[62] The antibonding orbitals are indicated by an asterisk and the nonbonding orbitals as n.

Structures similar to the silver(I)–benzene complex A have been reported for copper(I)–benzene complexes.[53] Other aromatic complexes with metal ions such as lead(II),[54] gallium(I),[55] and thallium(I)[55] are known to have structures similar to B.[56,57]

These structural results accord with the predictions based on symmetry considerations for CT interactions.[8,58] Thus the LUMOs of silver(I) and copper(I) are 5s and 4s orbitals, respectively, which are orthogonal to the HOMOs of benzene in C_{6v} symmetry (with the metal located on the 6-fold axis), as shown in orbital representation C. The CT interaction is not possible without the movement of the metal to a position of lower symmetry, as in A. However, for tin(II), lead(II), gallium(I), and thallium(I), the metal LUMOs are p orbitals, which have the same symmetry (e_1) as the HOMOs of benzene in C_{6v} symmetry, as shown in D. Thus the molecular structure B is the most favorable for CT interactions in these metal–arene complexes, in accord with the reported structures.[59]

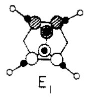

C.

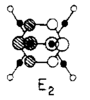
vs


D.

Since the mercury ions Hg^{2+} and Hg^+ both have the 6s orbital as the lowest acceptor orbital, a molecular structure similar to A is expected for the arene complexes.[60] However, for the mercury(II) compound $Hg(O_2CCF_3)_2$, the LUMO is not the 6s orbital as in the free ion but the 6p orbital, owing to the strong interaction with the ligands, as shown by the orbital correlation diagram in Figure 12.[62] (The antibonding nature of the LUMO of HgX_2 is also known by the spontaneous dissociative processes which accompany electron capture.[39c,63])

The foregoing consideration of orbital symmetry leads to the conclusion that the molecular structure of the $Hg(O_2CCF_3)$–benzene complexes are described better by B than by A. A consideration of the spectroscopic results leads to essentially the same conclusion in the following way. Previous studies have shown that the intensity of the symmetry-forbidden $^1A_{1g}$–$^1B_{2u}$ transition at 255 nm in benzene is increased by 75% in the silver(I) complex as a result of the lower symmetry in the molecular structure A.[64] Such a perturbation of the electronic structure of benzene by silver(I) complexation is also observed as a shorter C–C bond length at the centers nearest to the silver atom.[51b] By contrast, there is no apparent increase in the intensity of the symmetry-forbidden π–π* band of hexamethylbenzene at 273 nm upon complexation with $Hg(O_2CCF_3)_2$.[7] Either the orbital interaction between mercury(II) and hexamethylbenzene is symmetrical as in B or the interaction is as indicated in A but is too weak to be detected. To partially resolve this point, we draw attention to the parallel relationship observed between the $Hg(O_2CCF_3)_2$ and the TCNE complexes in Figure 6a. The TCNE–benzene complex is known to have the symmetric configurations E_1 and E_2, depending upon the benzene orbitals, $e_{1g}(A)$ and $e_{1g}(S)$, respectively.[34,65] It should be noted that the orbital symmetry in E is the same as that in D, despite the structural distinction between the metal complex and TCNE. The similarity of the $Hg(O_2CCF_3)_2$ complexes to the TCNE complexes, coupled with the dissimilarity between $Hg(O_2CCF_3)_2$ and silver(I) complexes, thus supports the conclusion that the molecular structure of the $Hg(O_2CCF_3)$–benzene complex is symmetrical, as in B, in which the orbital correlation is represented by D.[66]


E_1


E_2

Summary and Conclusion

The properties of the electron donor–acceptor complexes of various aromatic compounds are compared for electrophiles [Cl_2, Br_2, and $Hg(O_2CCF_3)_2$] and π acceptors (maleic anhydride, tetracyanoethylene, chloranil, tetracyanobenzene and tetracyanopyrazine). A parameter, K_S, is introduced to allow a comparison to be made of the relative strengths of weak EDA complexes from the readily measured spectral parameters associated with the charge-transfer transitions in these complexes. The linear correlation of the strengths of $Hg(O_2CCF_3)_2$ and TCNE com-

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[52] (a) Weininger, M. S.; Rodesiler, P. F.; Amma, E. L. *Inorg. Chem.* **1979**, *18*, 751. (b) Rodesiler, P. F.; Auel, T.; Amma, E. L. *J. Am. Chem. Soc.* **1975**, *97*, 7405. (c) Luth, H.; Amma, E. L. *Ibid.* **1969**, *91*, 7515. (d) Weininger, M. S.; Rodesiler, P. F.; Gash, A. G.; Amma, E. L. *Ibid.* **1972**, *94*, 2135.

[53] (a) Dines, M. B.; Bird, P. H. *J. Chem. Soc., Chem. Commun.* **1973**, *12*. (b) Rodesiler, P. F.; Amma, E. L. *Ibid.* **1974**, 599.

[54] (a) Gash, A. G.; Rodesiler, P. F.; Amma, E. L. *Inorg. Chem.* **1974**, *13*, 2429. (b) Auel, T.; Amma, E. L. *J. Am. Chem. Soc.* **1968**, *90*, 5941.

[55] Rundle, R. E.; Corbett, J. D. *J. Am. Chem. Soc.* **1957**, *79*, 757.

[56] (a) Albright, T. A.; Hofmann, P.; Hoffmann, R. *J. Am. Chem. Soc.* **1977**, *99*, 7546 and references cited therein. (b) Coates, G. E.; Green, M. L. H.; Wade, K. "Organometallic Compounds", 3rd ed.; Methuen: London, 1968; Vol. 2, p 165.

[57] A variety of transition-metal–arene complexes such as $(C_6H_6)Cr(CO)_3$ and $(C_6H_6)Mo(CO)_3$ are also known with η^6 benzene ligands, as in B (see ref 56).

[58] Mulliken, R. S. *J. Am. Chem. Soc.* **1952**, *74*, 811.

[59] (a) It should be noted, however, that these simple symmetry considerations involving the HOMO–LUMO interaction failed to predict the crystal structure of benzene–halogen complexes[59b–e] (see discussions in ref 46b). (b) Hassel, O.; Strømme, K. O. *Acta Chem. Scand.* **1958**, *12*, 1146. (c) Hassel, O.; Strømme, K. O. *Ibid.* **1959**, *13*, 1781. (d) Hassel, O. *Mol. Phys.* **1958**, *1*, 241. (e) Hassel, O.; Rømming, C. *Q. Rev., Chem. Soc.* **1962**, *16*, 1.

[60] Arene complexes of Hg_2^{2+} [61a] and Hg^{2+} [61b,c] as strong acid salts of AsF_6^- and SbF_6^- are best described as involving localized bonding between the mercury atom and one C–C linkage of the arene similar to that in A. See the ^{13}C and ^1H NMR studies in liquid SO_2 reported in ref 61.

[61] (a) Dean, P. A. W.; Ibbott, D. G.; Stothers, J. B. *Can. J. Chem.* **1976**, *54*, 166. (b) Damude, L. C.; Dean, P. A. W. *J. Chem. Soc., Chem. Commun.* **1978**, 1083. (c) Damude, L. C.; Dean, P. A. W. *J. Organomet. Chem.* **1979**, *181*, 1. (d) See also: Olah, G. A.; Yu, S. H.; Parker, D. G. *J. Org. Chem.* **1976**, *41*, 1983.

[62] A d orbital is not included in the diagram, since the use of a d orbital for ds hydridization will not affect the HOMO and LUMO discussed here. The degeneracy of $2\pi_u^*$, $^1\pi_g^n$, and $^1\pi_u$ is only slightly removed in the complex with the benzene derivatives. [See ref. 7.]

[63] Nazhat, N. B.; Asmus, K.-D. *J. Phys. Chem.* **1973**, *77*, 614.

[64] (a) Murrell, J. N.; Carter, S. *J. Chem. Soc.* **1964**, 6185. (b) Reichman, B.; Eliezier, I. *J. Chem. Phys.* **1973**, *59*, 5219.

[65] (a) Boeyens, J. C. A.; Herbstein, F. H. *J. Phys. Chem.* **1965**, *69*, 2153. (b) Prout, C. K.; Wright, J. D. *Angew. Chem.* **1968**, *80*, 688. (c) See also ref 34 for an alternative structure.

[66] The CT bands of the $Hg(O_2CCF_3)_2$ complexes in Figure 1 are much broader than those of the silver(I) complexes.[64] This supports the nonspecific interactions in the $Hg(O_2CCF_3)_2$ complexes, in contrast to the bonding in the silver(I) complexes.

plexes, as well as those of Br_2 and maleic anhydride complexes in Figure 6, indicate that electrophiles and π acceptors are not distinguished on the basis of K_S. Furthermore, the CT transition energies $h\nu_{CT}$ of electrophile and π-acceptor complexes in Figure 7 show the same types of linear variations with the ionization potentials of the aromatic donors, in accord with the first-order expression of the Mulliken formulation in eq 9. However, the slopes of the variation, i.e., $\partial(h\nu_{CT})/\partial I_D$, deviate from unity, as predicted on the assumption that the mean separations r_{DA} are invariant with changes in the aromatic donor. Intermolecular comparisons of the spectral data in Figure 8 and the intramolecular comparisons of the multiple CT bands in Figure 9 do not support this assumption. Indeed, the formulation of a constantly changing mean separation accounts for all the experimental observations. The $Hg(O_2CCF_3)_2$ complexes have particularly large mean separations, among the various electrophiles and π acceptors examined. The structure of the $Hg(O_2CCF_3)_2$ complexes are discussed in the context of the crystallographically known molecular structures of silver(I)–arene and tin(II)–arene complexes.

Experimental Section

Materials. Benzene, monosubstituted benzenes, and disubstituted benzenes (Aldrich Chemical Co.) were purified by repeatedly shaking them with portions of cold concentrated H_2SO_4 until the lower layer was colorless. The aromatic layer was washed with aqueous $NaHCO_3$, followed by several washings with water, and dried over $CaCl_2$. It was then distilled from sodium. Mesitylene was initially sulfonated by dissolving it in concentrated H_2SO_4. Mesitylenesulfonic acid was precipitated by addition of concentrated HCl at 0 °C, washing with cold concentrated HCl, and recrystallization from $CHCl_3$. It was then hydrolyzed by boiling it in 20% HCl, and the separated mesitylene was dried over $CaCl_2$ and distilled from sodium. Tetramethylbenzene, hexamethylbenzene, and hexaethylbenzene were purified by recrystallization from absolute ethanol. Styrenes were distilled under reduced pressure. Mercury trifluoroacetate, iodine, and bromine used in this study were described previously.[36b,39c] Chlorine (Matheson Gas Products) was distilled directly and used without further purification. Tetracyanoethylene, chloranil, tetracyanobenzene, tetracyanopyrazine, and maleic anhydride were resublimed in vacuo. The solvents (methylene chloride and carbon tetrachloride) were reagent grade materials obtained commercially and purified according to standard methods.[67] Trifluoroacetic acid was fractionally distilled after treatment with P_2O_5.

Spectral Measurements of the CT Absorption Bands. For the spectral measurement of the EDA complexes of $Hg(O_2CCF_3)_2$ with benzene derivatives, the difference spectra were recorded under carefully calibrated conditions on a Cary 14 spectrophotometer with the compartment thermostatted at 25 °C. In a typical procedure, the spectrum of the solution of $Hg(O_2CCF_3)_2$ (5.0×10^{-3}–2.0×10^{-2} M) in methylene chloride was first measured against a reference prepared with the same solvent. Next the same concentration of the aromatic component was added to both the sample and the reference cuvettes, and the spectrum was quickly measured to avoid complications arising from the subsequent substitution reaction. The maximum concentration of the aromatic component was limited to below 10^{-2} M, which corresponded to the concentration at which the slit of the spectrometer would open to its maximum width (3.0 mm). The first spectrum was subtracted from that obtained in the second operation to afford the spectrum of the EDA complex.[7,36b]

The high extinction coefficient for the $Hg(O_2CCF_3)_2$ complex with hexamethylbenzene ($\epsilon_{max} = 2.34 \times 10^3\ M^{-1}\ cm^{-1}$) coupled with the relatively large formation constant ($K_{DA} = 15.6\ M^{-1}$), allowed an extensive search for additional absorption bands at shorter wavelengths, i.e., in the region where the π–π* band of hexamethylbenzene exists [λ_{max} 273 nm (log ϵ_{max} 2.35)].[7] However, no other bands were found in the difference spectrum. Therefore, the intensity of the π–π* band of hexamethylbenzene remained invariant in the EDA complex.

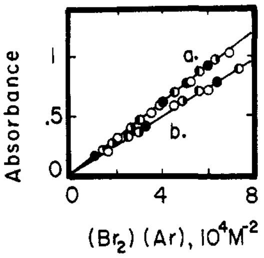

Figure 13. Variation in the CT absorbance with changes in the concentrations of benzene (○), toluene (●), ethylbenzene (◑), and *n*-propylbenzene (◐). [Bromine] was (a) 1.04×10^{-2} M in CF_3CO_2H and (b) 4.8×10^3 M in CCl_4.

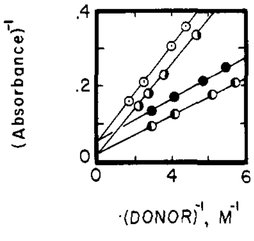

Figure 14. Benesi–Hildebrand plots for the determination of the formation constants of typical EDA complexes: ⊙, 3.0×10^{-3} M TCNE and *n*-butylbenzene; ◑, 3.0×10^{-3} M TCNP and isopropylbenzene; ●, 3.0×10^{-3} M chloranil and *p*-dimethoxybenzene; ◐, 2.5×10^{-3} M TCNP and *m*-xylene.

For the measurement of CT spectra of other electrophiles and acceptors with the benzene derivatives listed in Table II and III, essentially the same procedures as those employed for the $Hg(O_2CCF_3)_2$ complexes were followed at 25 °C. The intensities of the CT bands of the 1:1 complexes of bromine and benzene derivatives are insensitive to the solvents used (CCl_4 and CF_3CO_2H). The intensities are linearly correlated with the concentrations of Br_2 and the benzene derivatives, as shown in Figure 13.

Formation Constants of the EDA Complexes. The formation constants of the EDA complexes of electrophiles such as $Hg(O_2CCF_3)_2$, Br_2, and Cl_2 with the aromatic compounds were uniformly difficult, if not impossible, to measure as a result of their limited values. The problem was compounded by the transient nature of the CT absorption bands owing to the competing substitution reactions which precluded the use of high arene concentrations. However, the formation constants of the EDA complexes of the π-acceptors (TCNB, TCNE, chloranil, and TCNP) are larger, and the CT absorption bands are persistent. Thus, the formation constants could be obtained from the Benesi–Hildebrand equation (eq 4) by by measuring the CT absorbances at various initial concentrations of the aromatic donor in the range between 0.1 and 0.5 M. The values of K_{DA} determined from the slopes and the intercepts in Figure 14 are listed in Table IV.

Strengths of EDA Complexes. For the very weak and transient EDA complexes, the formation constants cannot be evaluated by the usual procedures (vide supra). For purposes of comparison of the strengths of such complexes, a parameter, K_S, is introduced in eq 5 and is defined in terms of $\Delta\nu_{1/2}$, the width at half maximum height of the CT band in units of reciprocal centimeters, and the quantity $\epsilon_{max}K_{DA}$, which represents the slope of the CT absorbance change in eq 2 with variations in the donor and acceptor concentrations. In order to provide the theoretical justification for the use of eq 5, we rely on Mulliken theory to draw a parallel relationship between the spectral parameters $\epsilon_{max}\Delta\nu_{1/2}$ and the heat of formation ΔH_{DA} of the EDA complex as follows.

First, the heat of formation of the complex can be related to the magnitude of the CT contribution in the ground state (i.e., b^2 in eq 6) by the relationship in eq 14.[36b] For weak complexes

$$-\Delta H_{DA} = b^2/a^2h\nu_{CT} \qquad (14)$$

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[67] Perrin, D. D.; Armarego, W. L.; Perrin, D. R. "Purification of Laboratory Chemicals"; Pergamon Press: Elmsford, New York, 1966.

of the type described in this study, $a^2 \simeq 1$ and $h\nu_{CT}$ is relatively constant in relationship to b^2. In other words, the heat of formation ($-\Delta H_{DA}$) is approximately proportional to b^2 for weak EDA complexes. (Note that the ratio of the coefficients b^2/a^2 corresponds to the resonance energy β^2, as described in an earlier study.[36b])

Second, the oscillator strength f of the CT absorption band is experimentally evaluated from the expression shown in eq 15,[8]

$$f = (4.32 \times 10^{-9}) \int \epsilon \, d\nu \simeq (4.32 \times 10^{-9}) \epsilon_{max} \Delta\nu_{1/2} \qquad (15)$$

and it is theoretically expressed in terms of the transition moment μ_{CT} by eq 16. The combination of eqs 15 and 16 yields eq 17,

$$f = (4.70 \times 10^{-7}) \nu_{max} \mu_{CT}^2 \qquad (16)$$

$$\epsilon_{max} \Delta\nu_{1/2} \simeq (1.09 \times 10^2) \mu_{CT}^2 \nu_{max} \qquad (17)$$

which may be reexpressed in terms of the mean separation r_{DA} as eq 18 since the transition moment is directly related to the dipole moment of the CT state $\Psi_1(D^+A^-)$, i.e., $\mu_{CT} \simeq -aber_{DA}$.[8]

$$\epsilon_{max} \Delta\nu_{1/2} \simeq (1.09 \times 10^2) a^2 b^2 e^2 r_{DA}^2 \nu_{max} \qquad (18)$$

The right side of eq 18 is approximately proportional to b^2, since $a^2 \simeq 1$ and $r_{DA}^2 \nu_{max}$ is relatively constant relative to b^2. [For example, by using the data in Tables III and VIII, $r_{DA}^2 \nu_{max}$ varies by only 11% in proceeding from the TCNE complex of benzene, at one extreme, to the TCNE complex of hexamethylbenzene, at the other extreme. On the other hand, b^2, which is proportional to $-\Delta H_{DA}$ according to eq 14, varies by 240% in proceeding from the TCNE–benzene complex (3.3 kcal mol^{-1}) to the TCNE–hexamethylbenzene complex (7.8 kcal mol^{-1}).[68]]

By applying the Mulliken theory, it is thus possible to show the parallel relationship between the thermodynamic ΔH_{DA} and the spectral $\epsilon_{max} \Delta\nu_{1/2}$ through eq 14 and 18, respectively. The parameter K_S, which merely combines $\epsilon_{max} \Delta\nu_{1/2}$ with K_{DA} in eq 5, therefore must also relate to the strength of the EDA complex. The values of K_S are listed in Table IX (see supplementary material) for the EDA complexes of a series of benzene derivatives with all the electrophiles and π acceptors examined in this study.[69]

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Registry No. **1**·$Hg(D_2CCF_3)_2$, 78716-15-1; **1**·Br_2, 6142-76-3; **1**·Cl_2, 25077-31-0; **1**·I_2, 1772-22-1; **1**·MA, 25472-37-1; **1**·TCNB, 7431-46-1; **1**·TCNE, 1446-08-8; **1**·CA, 2234-63-1; **1**·TCNP, 78716-16-2; **2**·$Hg(O_2CCF_3)_2$, 78716-17-3; **2**·Br_2, 78716-18-4; **2**·I_2, 3879-17-2; **2**·MA, 78716-19-5; **2**·TCNE, 38758-28-0; **2**·CA, 78716-20-8; **2**·TCNP, 78716-21-9; **3**·$Hg(O_2CCF_3)_2$, 78716-22-0; **3**·Br_2, 28245-72-9; **3**·I_2, 3797-16-8; **3**·MA, 78716-23-1; **3**·TCNE, 38758-29-1; **3**·CA, 78716-24-2; **3**·TCNP, 78716-25-3; **4**·$Hg(O_2CCF_3)_2$, 78716-26-4; **4**·Br_2, 16734-75-1; **4**·Cl_2, 78716-27-5; **4**·I_2, 2605-02-9; **4**·MA, 40027-13-2; **4**·TCNB, 7378-82-7; **4**·TCNE, 2590-60-5; **4**·CA, 2473-74-7; **4**·TCNP, 78716-28-6; **5**·$Hg(O_2CCF_3)_2$, 78716-29-7; **5**·Br_2, 78716-30-0; **5**·Cl_2, 78716-31-1; **5**·I_2, 39573-42-7; **5**·MA, 15471-10-0; **5**-TCNE, 18852-73-8; **5**·CA, 14533-49-4; **5**·TCNP, 78716-32-2; **6**·$Hg(O_2CCF_3)_2$, 78716-33-3; **6**·Br_2, 78716-34-4; **6**·Cl_2, 78716-35-5; **6**·I_2, 60944-81-2; **6**·MA, 78716-36-6; **6**·TCNB, 78716-37-7; **6**·TCNE, 26515-97-9; **6**·CA, 78716-38-8; **6**·TCNP, 78716-39-9; **7**·$Hg(O_2CCF_3)_2$, 78716-40-2; **7**·Br_2, 78716-41-3; **7**·Cl_2, 78716-42-4; **7**·I_2, 60944-83-4; **7**·MA, 78716-43-5; **7**·TCNE, 26397-25-1; **7**·CA, 78716-44-6; **7**·TCNP, 78716-45-7; **8**·$Hg(O_2CCF_3)_2$, 78716-46-8; **8**·Br_2, 78716-47-9; **8**·Cl_2, 78716-48-0; **8**·I_2, 60944-82-3; **8**·MA, 15589-40-9; **8**·TCNE, 26819-20-5; **8**·CA, 78716-49-1; **8**·TCNP, 78716-50-4; **9**·$Hg(O_2CCF_3)_2$, 78716-51-5; **9**·Br_2, 78716-52-6; **9**·Cl_2, 78716-53-7; **9**·I_2, 60944-85-6; **9**·MA, 78716-54-8; **9**·TCNE, 17557-14-1; **9**·CA, 78716-55-9; **9**·TCNP, 78716-56-0; **10**·$Hg(O_2CCF_3)_2$, 78716-57-1; **10**·Br_2, 78716-58-2; **10**·Cl_2, 78716-59-3; **10**·I_2, 62093-94-1; **10**·MA, 62641-11-6; **10**·TCNB, 7371-19-9; **10**·TCNE, 19074-20-5; **10**·CA, 3921-67-3; **10**·TCNP, 78716-60-6; **11**·$Hg(O_2CCF_3)_2$, 78716-61-7; **11**·Br_2, 16840-57-6; **11**·Cl_2, 78716-62-8; **11**·I_2, 2789-26-6; **11**·MA, 78716-63-9; **11**·TCNB, 22627-38-9; **11**·TCNE, 2590-61-6; **11**·CA, 2473-75-8; **11**·TCNP, 78716-64-0; **12**·$Hg(O_2CCF_3)_2$, 78716-65-1; **12**·Br_2, 78716-66-2; **12**·Cl_2, 78716-67-3; **12**·I_2, 2605-03-0; **12**·MA, 78716-68-4; **12**·TCNB, 22627-39-0; **12**·TCNE, 2590-62-7; **12**·CA, 2760-13-6; **12**·TCNP, 78716-69-5; **13**·$Hg(O_2CCF_3)_2$, 78716-70-8; **13**·Br_2, 78716-71-9; **13**·Cl_2, 25077-33-2; **13**·I_2, 2768-91-4; **13**·MA, 26977-63-9; **13**·TCNB, 22627-40-3; **13**·TCNE, 2590-63-8; **13**·CA, 2473-76-9; **13**·TCNP, 78716-72-0; **14**·$Hg(O_2CCF_3)_2$, 78716-73-1; **14**·Br_2, 78716-74-2; **14**·Cl_2, 78716-75-3; **14**·I_2, 78716-76-4; **14**·MA, 78716-77-5; **14**·TCNB, 78716-78-6; **14**·TCNE, 78716-79-7; **14**·CA, 78716-80-0; **14**·TCNP, 78716-81-1; **15**·$Hg(O_2CCF_3)_2$, 78739-35-2; **15**·Br_2, 78716-82-2; **15**·I_2, 78716-83-3; **15**·MA, 78716-84-4; **15**·TCNE, 78716-85-5; **15**·CA, 78716-86-6; **15**·TCNP, 78716-87-7; **16**·$Hg(O_2CCF_3)_2$, 78716-88-8; **16**·Br_2, 78716-89-9; **16**·I_2, 78716-90-2; **16**·MA, 78716-91-3; **16**·TCNE, 18852-63-6; **16**·CA, 78716-92-4; **16**·TCNP, 78716-93-5; **17**·$Hg(O_2CCF_3)_2$, 78716-94-6; **17**·I_2, 78716-95-7; **17**·Br_2, 78739-58-9; **17**·MA, 78716-96-8; **17**·TCNE, 69168-82-7; **17**·CA, 78716-97-9; **17**·TCNP, 78716-98-0; **18**·$Hg(O_2CCF_3)_2$, 78716-99-1; **18**·Br_2, 78717-00-7; **18**·I_2, 78717-01-8; **18**·MA, 78717-02-9; **18**·TCNE, 18852-64-7; **18**·CA, 78717-03-0; **18**·TCNP, 78717-04-1; **19**·$Hg(O_2CCF_3)_2$, 78717-05-2; **19**·Br_2, 78717-06-3; **19**·I_2, 78717-07-4; **19**·MA, 78717-08-5; **19**·TCNE, 18852-72-7; **19**·CA, 78717-09-6; **19**·TCNP, 78717-10-9; **20**·$Hg(O_2CCF_3)_2$, 78717-11-0; **20**·Br_2, 78717-12-1; **20**·Cl_2, 78717-13-2; **20**·I_2, 2768-92-5; **20**·MA, 26977-64-0; **20**·TCNB, 7371-18-8; **20**·TCNE, 2590-66-1; **20**·CA, 2200-21-7; **20**·TCNP, 78717-14-3; **21**·$Hg(O_2CCF_3)_2$, 78717-15-4; **21**·Br_2, 78717-16-5; **21**·Cl_2, 78717-17-6; **21**·I_2, 2768-93-6; **21**·MA, 78717-18-7; **21**·TCNB, 78717-19-8; **21**·TCNE, 2590-68-3; **21**·CA, 2603-59-0; **21**·TCNP, 78717-20-1; **22**·$Hg(O_2CCF_3)_2$, 78717-21-2; **22**·Br_2, 78717-22-3; **22**·Cl_2, 78717-23-4; **22**·I_2, 2472-90-4; **22**·MA, 28737-48-6; **22**·TCNB, 7371-16-6; **22**·TCNE, 1223-67-2; **22**·CA, 2473-78-1; **22**·TCNP, 78717-24-5; **23**·$Hg(O_2CCF_3)_2$, 77001-38-8; **23**·Br_2, 78717-25-6; **23**·Cl_2, 78717-26-7; **23**·I_2, 24317-90-6; **23**·MA, 14495-52-4; **23**·TCNB, 7431-47-2; **23**·TCNE, 2605-01-8; **23**·CA, 850-23-7; **23**·TCNP, 78717-27-8; **24**·$Hg(O_2CCF_3)_2$, 78717-28-9; **24**·Br_2, 78717-29-0; **24**·I_2, 78717-30-3; **24**·MA, 78717-31-4; **24**·TCNB, 78739-36-3; **24**·TCNE, 78717-32-5; **24**·CA, 78717-33-6; **24**·TCNP, 78717-34-7; **25**·$Hg(O_2CCF_3)_2$, 78717-35-8; **25**·Br_2, 77836-19-2; **25**·I_2, 78717-36-9; **25**·MA, 30766-37-1; **25**·TCNB, 78717-37-0; **25**·TCNE, 7431-42-7; **25**·CA, 52644-95-8; **25**·TCNP, 78717-38-1; **26**·Br_2, 78717-39-2; **26**·I_2, 78717-40-5; **26**·MA, 78717-41-6; **26**·TCNB, 78717-42-7; **26**·TCNE, 52644-88-9; **26**·CA, 78717-43-8; **26**·TCNP, 78717-44-9; **27**·Br_2, 78717-45-0; **27**·I_2, 78717-46-1; **27**·MA, 78717-47-2; **27**·TCNE, 70086-45-2; **27**·CA, 78717-48-3; **27**·TCNP, 78717-49-4; **28**·$Hg(O_2CCF_3)_2$, 78717-50-7; **28**·I_2, 78717-51-8; **28**·MA, 78717-52-9; **28**·TCNB, 78717-53-0; **28**·TCNE, 54615-98-4; **28**·CA, 3921-68-4; **28**·TCNP, 78717-54-1; **29**·$Hg(O_2CCF_3)_2$, 78717-55-2; **29**·I_2, 62789-30-4; **29**·MA, 78717-56-3; **29**·TCNB, 7439-82-9; **29**·TCNE, 19199-93-0; **29**·CA, 2200-23-9; **29**·TCNP, 78717-57-4.

Supplementary Material Available: Tables VII–IX of CT spectral data (3 pages). Ordering information is given on any current masthead page.

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(68) Briegleb, G.; Czekalla, J.; Reuss, G. *Z. Phys. Chem.* (*Wiesbaden*) **1961**, *30*, 333. See also ref 24g.

(69) The strength parameter K_S is measured in units of M^{-2} cm^{-2}, which is equivalent to the units of K_{DA} (i.e., M^{-1}), when a multiplicative factor of mc^2/e^2N in units of M cm^2 is included. The constant mc^2/e^2N is the proportionality constant to be used in relating the dimensionless oscillator strength f and $\epsilon_{max}\Delta\nu_{1/2}$ in eq 15, where $f = (2.30 \times 10^3)\pi^{-1}(mc^2/e^2N)\epsilon_{max}\Delta\nu_{1/2} = (4.32 \times 10^{-9})\epsilon_{max}\Delta\nu_{1/2}$. The terms m, c, and N are the mass of the electron, the speed of light, and Avogadro's number. (Mataga, N.; Kubota, T. "Molecular Interactions and Electronic Spectra"; Marcel Dekker: New York, 1970; p 113).

(70) Traven, V. F.; West, R. *J. Am. Chem. Soc.* **1973**, *95*, 6824.