The high yield of an alcohol product in the present reaction as contrasted with small contribution of H abstraction reaction in the gas-phase reaction  $CH_3CN + O(^{3}P)$  is possibly due to the participation of excited  $O(^{1}D)$  atoms, in addition to  $O(^{3}P)$  atoms in an overall  $CH_3CN + O$  matrix reaction. In the reaction of ethene with atomic oxygen in solid argon, the relative yield of vinyl alcohol was enhanced via H-atom abstraction or insertion of O(1D) atoms.23

The first step in the major reaction channel of the gas-phase  $CH_3CN + O(^{3}P)$  reaction<sup>4</sup> was reported to involve displacement of CH<sub>3</sub> by O(<sup>3</sup>P) and formation CH<sub>3</sub> and OCN (or CNO) radicals:

 $CH_3CN + O(^{3}P) \rightarrow CH_3 + OCN \text{ (or CNO)}$ 

The formation of CH<sub>3</sub>CNO via CH<sub>3</sub> and CNO radicals might require the rearrangement OCN  $\rightarrow$  CNO in the matrix cage followed by cage recombination of CH<sub>3</sub> and CNO. As recently reported,<sup>28</sup> the CNO radical is easily converted photolytically to the OCN radical, but the reverse rearrangement does not occur. This leads to the conclusion that CH<sub>3</sub>CNO is formed in simple bimolecular addition reaction of O atom to the nitrile nitrogen, the excess energy being quenched by the matrix cage, which contrasts the gas-phase reaction mechanism.<sup>4</sup>

It is of interest to conjecture on the branching ratio between HOCH<sub>2</sub>CN and CH<sub>3</sub>CNO in the matrix photolysis experiments. It is suggested that photolysis of ozone in close proximity to  $CH_3CN$  where the excited  $O(^1D)$  photoproduct can react before relaxation gives HOCH<sub>2</sub>CN preferentially, but longer diffusion of O atoms before reaction provides an opportunity for relaxation to O(<sup>3</sup>P) where the CH<sub>3</sub>CNO product is favored. This is supported by annealing experiments. When matrices were annealed, the CH<sub>3</sub>CNO monomer concentration was relatively constant even though the amount of CH<sub>3</sub>CNO-HOCH<sub>2</sub>CN complexes increased. (The Y bands showed little sensitivity to matrix annealing, but the 1311-cm<sup>-1</sup> Z band due to the complex increased in absorbance.) During matrix annealing the quenched  $O(^{3}P)$ 

(28) Bondybey, V. E.; English, J. H.; Mathews, C. W.; Contolini, R. J. Chem. Phys. Lett. 1981, 82, 208.

atoms diffuse through the matrix and react with CH<sub>3</sub>CN forming CH<sub>3</sub>CNO and keeping the CH<sub>3</sub>CNO monomer concentration approximately constant. The argon matrix is a convenient vehicle for studying different O-atom addition product in ozone photochemistry.

## Conclusions

Full arc photolysis of  $O_3$  in argon matrices containing acetonitrile leads to the formation of hydroxyacetonitrile and acetonitrile N-oxide as primary products, and there is also evidence for methyl isocyanate as a minor product. Hydroxyacetonitrile forms hydrogen-bonded complexes with acetonitrile and with acetonitrile *N*-oxide molecules as secondary products. The alcohol yield in the  $CH_3CN + O$  reaction is higher than in similar  $CH_4 + O$  and  $C_2H_4 + O$  matrix reactions, in accord with the lower dissociation energy of the CH bond in the CH<sub>3</sub>CN molecule as compared to methane or ethene. Hydroxyacetonitrile is formed by insertion of oxygen atom into a C-H bond or H-atom abstraction by oxygen atom followed by recombination of OH and CH<sub>2</sub>CN radicals. Acetonitrile N-oxide is believed to be formed by a simple bimolecular addition reaction of oxygen atom to the nitrile nitrogen. It is suggested that participation of excited  $O(^{1}D)$  atoms, in addition to O(<sup>3</sup>P), increases the relative yield of hydroxyacetonitrile as compared to acetonitrile N-oxide.

The vibrational spectra of different CH<sub>3</sub>CNO isotopomers evidence strong mixing of internal modes within the CH<sub>3</sub>CNO molecule. There is an extensive interaction between the N-O stretch, C=N stretch, C-C stretch, and CH<sub>3</sub> deformation modes. The hydroxyacetonitrile molecule exhibits Fermi resonance between the C≡N stretch mode and combination between C-O stretch and C-OH in-plane bending modes. The perturbation of the hydroxyacetonitrile COH group vibrations in the hydroxyacetonitrile-acetonitrile complex evidences formation of a medium-strength hydrogen-bonded complex.

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Registry No. O, 17778-80-2; CH<sub>3</sub>CN, 75-05-8; HOCH<sub>2</sub>CN, 107-16-4; CH<sub>3</sub>CNO, 7063-95-8; Ar, 7440-37-1.

# Ultraviolet/Visible Spectra of Halogen Molecule/Arene and Halogen Atom/Arene $\pi$ -Molecular Complexes<sup>1</sup>

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Ultraviolet/visible spectra have been recorded for chlorine, bromine, and iodine atom  $\pi$ -molecular complexes with a number of aromatic compounds. The visible spectra of the I'/arene complexes show charge-transfer (CT) bands whose transition energy correlates linearly with the vertical ionization potential of the corresponding arene. Comparison of the spectra of these complexes with the spectra of the corresponding  $Cl_2/arene$ ,  $Br_2/arene$ , and  $I_2/arene$  complexes leads to the conclusion that the I<sup>•</sup>/arene complexes are classical hexahapto  $\pi$ -molecular complexes. The CT transition energies of the Cl<sup>•</sup>/arene and the Br'/arene complexes correlate well with one another, yet the CT transition energies of these complexes are seemingly independent of the vertical ionization potential of the arene.

Thirty years ago, Russell<sup>3,4</sup> reported that the photochlorination of 2,3-dimethylbutane gave a greater ratio of tertiary to primary monochloride products in the presence of benzene and certain other arenes. This enhanced selectivity was attributed to the formation of a chlorine atom/arene  $\pi$ -complex which acted as a much more

<sup>(1)</sup> Issued as NRCC No. 29568.

 <sup>(2)</sup> NRCC Research Associate 1986–1988.
 (3) Russell, G. A. J. Am. Chem. Soc. 1957, 79, 2977–2978.
 (4) Russell, G. A. J. Am. Chem. Soc. 1958, 80, 4987–4996.

<sup>(5)</sup> Bühler, R. E.; Ebert, M. Nature (London) 1967, 214, 1220-1221.
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Figure 1. Ultraviolet/visible spectra of the chlorine atom complexes with benzene (a), mesitylene (b), and hexamethylbenzene (c).

complexes<sup>7</sup> on the basis that there was an (approximately) linear correlation between the energies of the absorption band maxima  $h\nu_{\rm CT}$  and the ionization potentials of the arenes.<sup>10</sup> More recently, we have observed the spectrum of the chlorine atom/benzene complex using laser flash photolysis and five different sources of chlorine atoms.<sup>11</sup>

There is, currently, a disagreement as to whether the species responsible for the higher selectivities of alkane photochlorinations in the presence of benzene and for the transient spectrum of the chlorine atom/benzene complex is a  $\pi$ -molecular complex<sup>8</sup> or a chlorocyclohexadienyl radical,  $\sigma$ -complex.<sup>11-14</sup> In an effort to



resolve this disagreement we have now studied the charge-transfer<sup>15</sup> absorption spectra of a number of other halogen atom/arene complexes. As originally suggested by Dewar and Thompson,<sup>5</sup> we have restricted our study to simple arenes of low polarity (benzene and alkylated benzenes, mainly) in order to reduce the importance of perturbations arising from ground-state electrostatic interactions. For such a restricted range of  $\pi$ -donors it is commonly assumed that the transition energies of the charge-transfer absorption band maxima,  $h\nu_{\rm CT}$ , will correlate well with the vertical ionization potentials of the aromatic donors  $I_D$ . Such correlations are observed for molecular halogen (I2, Cl2, Br2)/arene complexes and iodine atom/arene complexes. However, in contrast to earlier, much more limited, investigations and to our great surprise we have found that  $h\nu_{\rm CT}$  energies for chlorine atom/arene complexes and bromine atom/arene complexes show no correlation with the  $I_{\rm D}$  values of the arenes, these energies being instead nearly independent of  $I_{\rm D}$ .

TABLE I: Charge-Transfer Spectral Data of Chlorine Atom Complexes with a Series of Substituted Benzenes

			UV		visibl	e
no.	arene	I <sub>D</sub> , <sup>a</sup> eV	$\lambda_{\max}^{b,c}$ nm	hν <sub>CT</sub> , eV	λ <sub>max</sub> , <sup>b,d</sup> nm	hν <sub>CT</sub> , eV
1	PhCl	9.07	320 (38)	3.87	498 (120)	2.49
2	PhH	9.23	319 (24)	3.89	486 (130)	2.55
3	PhMe	8.82	323 (27)	3.84	479 (140)	2.59
4	Ph-t-Bu	8.65	323 (36)	3.84	492 (120)	2.52
5	$1,2-Me_2C_6H_4$	8.56	326 (30)	3.80	498 (150)	2.49
6	$1,3-Me_2C_6H_4$	8.56	332 (27)	3.73	470 (120)	2.64
7	$1,4-Me_2C_6H_4$	8.44	326 (28)	3.80	485 (145)	2.56
8	1,4-t-Bu <sub>2</sub> C <sub>6</sub> H <sub>4</sub>	8.28	323 (30)	3.84	497 (135)	2.49
9	1,2,3-Me <sub>3</sub> C <sub>6</sub> H <sub>3</sub>	8.42	332 (35)	3.73	505 (150)	2.46
10	$1,2,4-Me_{3}C_{6}H_{3}$	8.27	333 (35)	3.72	478 (135)	2.59
11	$1,3,5-Me_{3}C_{6}H_{3}$	8.42	332 (40)	3.73	470 (120)	2.64
12	1,3,5- <i>t</i> -Bu <sub>3</sub> C <sub>6</sub> H <sub>3</sub>	8.19	333 (45)	3.72	506 (140)	2.45
13	1,2,3,4-Me <sub>4</sub> C <sub>6</sub> H <sub>2</sub>	8.14			509 (150)	2.44
14	$1,2,3,5-Me_4C_6H_2$	8.07			477 (135)	2.60
15	$1,2,4,5-Me_4C_6H_2$	8.05			509 (150)	2.44
16	Me <sub>5</sub> C <sub>6</sub> H	7.92			518 (150)	2.39
17	Me <sub>6</sub> C <sub>6</sub>	7.85			565 (160)	2.19
18	PhOMe	8.39	330 (45)	3.76	524 (190)	2.37

<sup>a</sup>See ref 16. <sup>b</sup>Bandwidth at half-height given in parentheses. <sup>c</sup>Symmetrical band. <sup>d</sup>Asymmetrical band, tails into the red end of the spectrum.



Figure 2. Visible spectrum of the iodine atom complex with p-xylene.

#### Results

Halogen atom/arene complexes were produced by 308- or 337-nm laser excitation of carbon tetrachloride solutions containing the molecular halogen and the arene. In the chlorine-containing solutions the laser radiation was absorbed by the molecular chlorine forming chlorine atoms which then complex with the arene. In the bromine- and iodine-containing solutions it is the molecular halogen/arene complexes that absorb the laser radiation, and the resultant photodissociation of these complexes may well yield half of the total halogen atom/arene complex directly. The complexes of molecular iodine with 1,3,5-tri-*tert*-butylbenzene, tetramethylbenzenes, pentamethylbenzene, and hexamethylbenzene had CT bands at quite long wavelengths. Photodissociation of these complexes was achieved by laser excitation at 337 nm.

As we reported previously for the chlorine atom/benzene complex,<sup>11</sup> the chlorine atom/arene complexes have electronic spectra consisting of an absorption in the visible and an absorption in the UV region (see Figure 1 for some representative spectra). The wavelengths of the visible and UV band maxima  $\lambda_{max}$  are given in Table I for the 18 chlorine atom/arene complexes examined together with the energies,  $h\nu_{CT}$ , associated with each of these transitions and the vertical ionization potentials,  $I_D$ , of the arenes.<sup>16</sup> Our  $\lambda_{max}$  values for the visible absorption bands of arenes 1–5 are in satisfactory agreement with the rather approximate values reported previously by Bühler.<sup>5,6,10b</sup> The UV bands for the complexes of the chlorine atom with arenes 13–17 could not be observed free from interference by overlapping absorptions which

<sup>(7)</sup> For two excellent and comprehensive reviews of  $\pi$ -molecular complexes<sup>8</sup> see: (a) Mulliken, R. S.; Person, W. B. Molecular Complexes; Wiley-Interscience: New York, 1969. (b) Foster, R. Organic Charge Transfer Complexes; Academic: New York, 1969. (8) Dewar and Thompson<sup>9</sup> have given a pungent critique of the other terms (8) Dewar and Thompson<sup>9</sup> have given a pungent critique of the other terms).

<sup>(8)</sup> Dewar and Thompson<sup>9</sup> have given a pungent critique of the other terms that have been used to describe complexes of this type such as  $\pi$ -complexes, charge-transfer complexes, donor-acceptor complexes, etc. In accordance with this, we prefer to stay with the neutral term,  $\pi$ -molecular complex, to describe the complexes reported in the present work since this avoids implications concerning their electronic structure.

<sup>(9)</sup> Dewar, M. J. S.; Thompson, C. C., Jr. Tetrahedron 1966, Suppl. 7, 97-114.

<sup>(10) (</sup>a) For 13 arenes ranging in ionization potential from benzene  $(I_D = 9.23 \text{ eV})$  to naphthacene  $(I_D = 6.88 \text{ eV})$ . (b)  $\lambda_{\text{max}}$  values given by Bühler<sup>6</sup> for the compounds also studied in this work were: Cl<sup>+</sup>/1, 490 ± 5 nm; Cl<sup>+</sup>/2, 490 ± 5 nm; Cl<sup>+</sup>/3, 475 ± 5 nm; Cl<sup>+</sup>/4, 480 ± 20 nm; Cl<sup>+</sup>/5, 505 ± 10 nm.

 <sup>10</sup> the components also statice in this work. C1 / 1, 4/0 ± 5 nm; C1 / 3, 475 ± 5 nm; C1 / 4, 480 ± 20 nm; C1 / 5, 505 ± 10 nm.
 (11) Bunce, N. J.; Ingold, K. U.; Landers, J. P.; Lusztyk, J.; Scaiano, J. C. J. Am. Chem. Soc. 1985, 107, 5464-5472.

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<sup>(13)</sup> Skell, P. S.; Baxter, H. N., III; Tanko, J. M.; Chebolu, V. J. Am. Chem. Soc. 1986, 108, 6300-6311.

<sup>(14)</sup> Walling, C. J. Org. Chem. 1988, 53, 305-308.

<sup>(15)</sup> The appearance of a charge-transfer spectrum does *not* automatically imply that charge transfer plays a dominant, or even a significant, role in the binding together of the complex.<sup>9</sup>

<sup>(16)</sup> Values for the ionization potentials have been taken from relatively recent data obtained by photoelectron spectroscopy. Arenes 2-17 from Howell, J. O.; Goncalves, J. M.; Amatore, C.; Klasinc, L.; Wightman, R. M.; Kochi, J. K. J. Am. Chem. Soc. 1984, 106, 3968-3976. Arenes I and 18 from Klasinc, L.; Kovac, B.; Güsten, H. Pure Appl. Chem. 1983, 55, 289-298.

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TABLE II: Charge-Transfer Spectral Data of Bromine and Iodine Atom Complexes with a Series of Substituted Benzenes

		Br <sup>+</sup>		I+	•
no.	arene	$\lambda_{max}$ , <sup><i>a,b</i></sup> nm	$h\nu_{\rm CT},  {\rm eV}$	$\lambda_{\max}^{a,c}$ nm	$h\nu_{\rm CT},  {\rm eV}$
1	PhCl	539 (185)	2.30	445 (145) <sup>d</sup>	2.79
2	PhH	$534 (155)^d$	2.32	488 (115)	2.54
3	PhMe	535 (185)	2.32	529, 480 (175) <sup>e</sup>	2.34, 2.58
4	Ph-t-Bu	537 (160)	2.31	542, 479 (175) <sup>e</sup>	2.29, 2.59
5	$1,2-Me_2C_6H_4$	555 (185)	2.23	563 (165)	2.20
6	$1,3-Me_2C_6H_4$	527 (175)	2.35	562 (165)	2.21
7	$1,4-Me_2C_6H_4$	521 (165)	2.38	595, 487 (250)e	2.08, 2.55
8	$1,4-t-Bu_2C_6H_4$	531 (165)	2.33	627, 503 (230) <sup>e</sup>	1.98, 2.47
9	1,2,3-Me <sub>3</sub> C <sub>6</sub> H <sub>3</sub>	559 (185)	2.22	593 (125) <sup>d</sup>	2.09
10	$1,2,4-Me_3C_6H_3$	544 (210)	2.28	609, 538 (200) <sup>e</sup>	2.04, 2.30
11	1,3,5-Me <sub>3</sub> C <sub>6</sub> H <sub>3</sub>	525 (165)	2.36	584 (125)	2.12
12	1,3,5-t-Bu <sub>3</sub> C <sub>6</sub> H <sub>3</sub>	565 (165)	2.19	633 (130)	1.96
13	$1,2,3,4-Me_4C_6H_2$	583 (150)	2.13	618 (200)	2.00
14	$1,2,3,5-Me_4C_6H_2$	536 (160)	2.31	657, 582 (200) <sup>e</sup>	1.88, 2.13
15	$1,2,4,5-Me_4C_6H_2$	548 (195)	2.26	703, 569 (245) <sup>e</sup>	1.76, 2.18
16	Me <sub>5</sub> C <sub>6</sub> H	565 (210)	2.19	670 (220)	1.85
17	Me <sub>6</sub> C <sub>6</sub>	600 (255)	2.07	738 (200)	1.70
18	PhŎMe	ca, 580 (300)	2.14	626 (135), 458 (80)	1.98, 2.71

<sup>a</sup> Bandwidth at half-height given in parentheses. <sup>b</sup>Asymmetrical band, tails into the red end of the spectrum unless otherwise stated. "Asymmetrical band, tails into the blue end of the spectrum unless otherwise stated. "Symmetrical band. "Width of complete twin band. Spectrum was measured in chloroform.

arise from the corresponding polymethylated benzyl radicals. These radicals are formed by hydrogen atom abstraction from a methyl group in the arene. For each of the remaining 13 chlorine atom/arene complexes, the lifetimes of the UV and visible absorption bands were identical, which implies that these two bands are probably due to a single transient species. It would therefore appear that methylated benzenes containing fewer than four methyl groups do not give a sufficient yield of benzylic radicals for these radicals to be detected by UV absorption in these systems.

The wavelengths of the absorption maxima in the visible region of the spectrum together with the corresponding transition energies are given in Table II for 18 bromine atom/arene complexes and 18 iodine atom/arene complexes. Where comparison is possible, the present  $\lambda_{max}$  values are in agreement with the literature data for bromine atom/arene complexes<sup>17</sup> and for iodine atom/arene complexes.<sup>21</sup> It was not possible to discover whether the bromine atom/arene and iodine atom/arene complexes also possess a UV absorption band. In both systems "photobleaching" occurs at short wavelengths ( $\lambda \leq 340$  nm for bromine and  $\lambda \leq 400$  nm for iodine). That is, any increase in the UV absorbance due to the formation of Br'/arene and I'/arene complexes is small compared with the decrease in the UV absorbance of the  $Br_2/arene$  and  $I_2/arene$ complexes, respectively. It is interesting to note that the iodine atom complexes with certain arenes, e.g., p-xylene<sup>27</sup> (see Figure 2), gave twin absorption bands in the visible region of the spectrum.

## Discussion

Transition Energies of Charge-Transfer Bands. Relatively

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(20) Yamamoto, N.; Kajikawa, T.; Sato, H.; Tsubomura, H. J. Am. Chem Soc. 1969, 91, 265-267.

(21) There are somewhat more data on I<sup>\*</sup>/arene than on Br<sup>\*</sup>/arene complexes;<sup>22-26</sup> the reported  $\lambda_{max}$  values are: I<sup>\*</sup>/2, 465 nm,<sup>20</sup> 495 nm,<sup>23</sup> 500 nm;<sup>25</sup> I<sup>\*</sup>/3, 515 nm,<sup>23</sup> 520 nm;<sup>23</sup> I<sup>\*</sup>/5, 570 nm;<sup>23,26</sup> I<sup>\*</sup>/7, 520 nm;<sup>23,27</sup> I<sup>\*</sup>/11, 590 nm.<sup>23,25</sup>

. (22) Rand, S. J.; Strong, R. L. J. Am. Chem. Soc. **1960**, 82, 5–9. (23) Strong, R. L.; Rand, S. J.; Britt, J. A. J. Am. Chem. Soc. **1960**, 82,

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 (26) Strong, R. L.; Perano, J. J. Am. Chem. Soc. 1967, 89, 2535-2538.
 (27) Strong et al.<sup>23</sup> noted that the I'/7 CT band was at a lower wavelength than they expected and was quite broad, possibly because of CT transitions from two slightly different donor orbitals of p-xylene.



Figure 3. Plot of  $h\nu_{CT}(I_2/arene)$  against the (first) ionization potential of the aromatic donor (O). For those complexes that show twin CT bands, the second (higher energy) band has also been plotted against the second ionization potential  $(\Box)$ . The solid line was obtained by leastsquares analysis of all the data (slope = 0.62, correlation coefficient = 0.86). The dotted line is the least-squares line based only on the points for the symmetrically substituted arenes: benzene (2), 1,3,5-trimethylbenzene (11), and 1,3,5-tri-tert-butylbenzene (17).

weak interactions between an electron acceptor (A) and an electron donor (D) are described in Mulliken's<sup>7</sup> valence-bond model in terms of a wave function of the form

$$\psi_{\rm N}({\rm AD}) = a\psi_0({\rm A,D}) + b\psi_1({\rm A}^--{\rm D}^+)$$
 (1)

The charge-transfer band arises from an electronic excitation from the neutral ground state,  $\psi_N$ , to the polar excited singlet state,  $\psi_{\rm E}$ :

$$\psi_{\rm E}(\rm AD) = a^* \psi_1(\rm A^--\rm D^+) - b^* \psi_0(\rm A,\rm D)$$
(2)

For weak interactions this transition is effectively an intermolecular charge transfer transition involving a one-electron jump from D to A, i.e.

$$\psi_0(\mathbf{A},\mathbf{D}) \xrightarrow{h\nu_{\mathbf{CT}}} \psi_1(\mathbf{A}^- - \mathbf{D}^+)$$
(3)

with the same mean separation of A and D  $(r_{AD})$  in the excited ion pair as in the ground-state acceptor-donor complex.<sup>7</sup> The energy associated with this CT transition,  $hv_{CT}$ , depends on the electron affinity of the acceptor  $E_A$  and the vertical ionization potential of the arene donor,  $I_D$ . To a first approximation this energy difference can be represented by<sup>7</sup>

$$h\nu_{\rm CT} = I_{\rm D} - E_{\rm A} - W \tag{4}$$

<sup>(17)</sup> There is very little data available for Br<sup>•</sup>/arene complexes.<sup>18-20</sup> Comparison is possible for  $Br^*/2$  for which  $\lambda_{max}$  values of 535, 540, and 550 nm are given in ref 19 and a value of 555 nm in ref 20 and for  $Br^*/3$  for which <sup>A</sup>max is given as 575 nm in ref 20.
 (18) Strong, R. L. J. Phys. Chem. 1962, 66, 2423–2426.



Figure 4. Plot of  $h\nu_{CT}(Cl_2/arene)$  (O) and  $h\nu_{CT}(Br_2/arene)$  (D) against the corresponding  $h\nu_{CT}(I_2/arene)$ . For those  $I_2/arene complexes that$ show twin CT bands, the lower energy band was chosen for the construction of this plot.

where W is the dissociation energy of the charge-transfer excited state, i.e.,  $e^2/r_{AD}$ . Therefore, for a series of arene donors, each interacting with a single acceptor, a plot of  $h\nu_{\rm CT}$  vs  $I_{\rm D}$  should be linear.28

Molecular Halogen/Arene  $\pi$ -Molecular Complexes. For the molecular iodine/arene complexes a plot of  $h\nu_{\rm CT}$  vs  $I_{\rm D}$  shows a reasonably linear correlation (see Figure 3)<sup>31</sup> as has been reported by earlier workers.<sup>7,29,30</sup> Nevertheless, even with the restricted range of arene structural types employed in the present work not all the points fall on a single straight line. (The solid line in Figure 3 is the best straight line through the experimental points; slope = 0.62, correlation coefficient = 0.86.) In plots of this type the deviations of individual points from the best straight line are usually attributed to the influence of steric factors, of specific patterns of substitution, and of heteroatom-containing substituents on  $r_{AD}$  and hence on  $h\nu_{CT}$ . It seems to us, therefore, much better to consider deviations from a line drawn through only those points corresponding to the symmetrically substituted arenes and, more restictively, through the points for benzene and for arenes substituted with methyl groups since methyl groups will have the minimal steric influence on  $r_{AD}$ . The dotted line shown in Figure 3 has therefore been drawn through the points for benzene (2), 1,3,5-trimethylbenzene (11), and hexamethylbenzene (17) (slope = 0.69, correlation coefficient = 0.999). The excellent fit of these three points to a straight line is, we presume, a consequence of symmetrical substitution and of a monotonic increase in  $r_{AD}$  along the series 2, 11, 17. It can be seen that only the point (points, vide infra) for anisole falls below this line. The asymmetrically methyl-substituted benzenes all give points above the dotted line as do the three *tert*-butyl substituted benzenes 4, 8, and 12 and chlorobenzene (1). It is particularly noteworthy not only that the

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symmetrically substituted 1,3,5-tri-tert-butylbenzene (12) lies above this line but also that tert-butylbenzene (4) and 1,4-ditert-butylbenzene (8) are displaced further from this line than toluene (3) and 1,4-dimethylbenzene (7), respectively. Following the lead of Fukuzumi and Kochi,<sup>30</sup> we therefore suggest that for all those  $I_2$ /arene complexes for which the  $h\nu_{CT}$  energy is greater than would be expected from the 2-11-17 dotted line, the primary cause is a sterically induced increase in  $r_{AD}$ . All these I<sub>2</sub>/arene  $\pi$ -molecular complexes would appear to involve only weak CT interactions in the ground state.<sup>32</sup>

Plots of  $h\nu_{CT}$  vs  $I_D$  for Cl<sub>2</sub>/arene and Br<sub>2</sub>/arene complexes have points that deviate from the two 2-11-17 lines in direction and in magnitude in a manner that is virtually identical with the deviations seen in Figure 3 for the  $I_2$ /arene complexes. This similarity is illustrated in Figure 4 in which  $hv_{CT}$  energies for the  $Cl_2$ /arene and  $Br_2$ /arene complexes have been plotted against the  $h\nu_{\rm CT}$  energies for the I<sub>2</sub>/arene complexes. Substituent-induced changes in  $r_{AD}$  must therefore be very similar for  $Cl_2/arene$ , Br<sub>2</sub>/arene, and I<sub>2</sub>/arene complexes, which certainly implies strongly that the structures of molecular halogen/arene complexes must be similar.

In principle, there are three possible structures for the molecular halogen/arene complexes, i.e., the degenerate resting structures R, the axial structure A, and the oblique structure  $O.^7$  Simple



symmetry considerations,<sup>33</sup> involving electron donation from the HOMO of benzene to the LUMO of the acceptor, led to the conclusion that the I2/benzene CT complex would adopt structures R, since structures A and O require electron donation from a lower  $\pi$ -MO of benzene. However, X-ray structural investigations of Br<sub>2</sub>/benzene<sup>34</sup> and Cl<sub>2</sub>/benzene<sup>35</sup> complexes, have shown that the structure A was the most probable, though structure O could not be ruled out.<sup>7,36</sup> Both structures A and O (which may merely reflect thermally excited motion of the benzene ring relative to the axis of the halogen molecule) have one halogen atom located above the center of the ring.37

The complexes formed between  $I_2$  and 1,2,4,5-tetramethylbenzene (15) and between  $I_2$  and anisole (18) showed two CT absorption bands. The occurrence of multiple bands in CT absorption spectra is, in fact, a fairly common phenomenon.7b Multiplicity may arise from electron donation from more than one energy level in the donor, from acceptance at more than one energy level of the acceptor, from differences in the interaction energy, or from combinations of these possibilities. Frequently it is due to electron transitions from more than one level of the donor as first suggested by Orgel<sup>38</sup> for polymethylbenzene complexes of chloranil. Double CT bands are observed in complexes in which the degeneracy of the  ${}^{2}E_{1g}$  ground state of the  $C_{6}H_{6}^{+}$ ion is removed by substitution and the degree of splitting should increase as the electron-donating property of the substituent(s) increases and should be largest for 1,4-di- and 1,2,4,5-tetra-substituted donors.<sup>7b,38</sup> These predictions have been largely confirmed for CT complexes with acceptors such as electron-deficient organic molecules<sup>7b,30,39-41</sup> and molecular iodine,<sup>42</sup> and it has been shown

(37) Such a perfect central location would appear to be rather unlikely for

<sup>(28)</sup> According to eq 4 the slope of a plot of  $h\nu_{CT}$  vs  $I_D$  for a single acceptor will be unity provided  $r_{AD}$  remains constant. However, a full theoretical treatment' suggests that even in this case the plot would actually be curved if a sufficiently large range of  $I_D$  values could be covered. Bühler<sup>39</sup> has argued that the  $h\nu_{CT}$  vs  $I_D$  plots for the molecular halogen/arene complexes and for halogen atom/arene complexes should be described by curves and it is for this reason that the slopes of the best straight lines through the experimental data points have slopes that are less than unity. The validity of this theoretical points have slopes that are less than unity. The validity of this theoretical approach has, however, been seriously questioned by Fukuzumi and Kochi,<sup>30</sup> who have interpreted the occurrence of slopes less than unity in  $h\nu_{CT}$  vs  $I_D$  plots as being due to variations in the mean separation,  $r_{AD}$ , between the aromatic  $\pi$ -donor and the acceptor.

 <sup>(29)</sup> Bühler, R. E. J. Phys. Chem. 1972, 76, 3220-3228.
 (30) Fukuzumi, S.; Kochi, J. K. J. Org. Chem. 1981, 46, 4116-4126. (31) Although the data from which Figure 3 (and Figure 4) was constructed were largely already available (the most complete information being contained in ref 30 and in references cited therein), the CT spectra for the  $I_2$ /arene complexes were specially measured in the present work. Values of  $\lambda_{max}$  and  $h\nu_{CT}$  for these complexes are available as supplementary material (See paragraph at end of paper regarding supplementary material).

<sup>(32)</sup> There is probably complete charge transfer upon excitation; see ref (32) Inferences cited therein.
(33) Mulliken, R. S. J. Am. Chem. Soc. 1952, 74, 811-824.
(34) Hassel, O.; Stromme, K. O. Acta Chem. Scand. 1958, 12, 1146.
(35) Hassel, O.; Stromme, K. O. Acta Chem. Scand. 1959, 13, 1781-1786.
(36) Mulliken, R. S. J. Chim. Phys. 1964, 61, 20-38.

the nonsymmetrically substituted arenes examined in this work, and deviations from this central position are probably partly responsible for some of the deviations in the plot of hv<sub>CT</sub>(I<sub>2</sub>/arene) vs I<sub>D</sub> shown in Figure 3. (38) Orgel, L. E. J. Chem. Phys. 1955, 23, 1352-1353.

<sup>(39)</sup> Briegleb, G.; Czekalla, J.; Reuss, G. Z. Phys. Chem. (Munich) 1961, 30. 316-332.

TABLE III: Comparison of the Differences between the First and Second Vertical Ionization Potentials of Some Arenes,  $\Delta I_D$ , and the Differences in Transition Energies between the First and Second CT Bands of These Arenes,  $\Delta h \nu_{CT}$ , with Different Acceptors

arene		$\Delta h \nu_{CT}$ , eV				
	$\Delta I_{\rm D}$ , <sup><i>a</i></sup> eV	I*b	$I_2^c$	TCNE <sup>d,e</sup>	CA <sup>f.g</sup>	TCNP <sup>g,h</sup>
PhMe	0.31	0.24	i	0.37		
Ph-t-Bu	0.48	0.30	i	0.34		
1,4-Me <sub>2</sub> C <sub>6</sub> H <sub>4</sub>	0.61	0.47	i	0.51		
				0.45	0.65	0.47
$1,4-t-Bu_2C_6H_4$	0.50	0.49	i	0.58		
1,2,4-Me <sub>3</sub> C <sub>6</sub> H <sub>3</sub>	0.45	0.26	i	0.45		
1,2,4,5-Me <sub>4</sub> C <sub>6</sub> H <sub>2</sub>	0.50	0.42	0.47	0.37	0.41	0.37
PhOMe	0.81	0.73	0.64	0.76	0.85	0.73
	arene PhMe Ph-t-Bu 1,4-Me <sub>2</sub> C <sub>6</sub> H <sub>4</sub> 1,2,4-Me <sub>3</sub> C <sub>6</sub> H <sub>3</sub> 1,2,4,5-Me <sub>4</sub> C <sub>6</sub> H <sub>2</sub> PhOMe	arene $\Delta I_{D}$ , eVPhMe0.31Ph-t-Bu0.481,4-Me_2C_6H_40.611,4-t-Bu_2C_6H_40.501,2,4-Me_3C_6H_30.451,2,4,5-Me_4C_6H_20.50PhOMe0.81	arene $\Delta I_{D}$ , $^{a}$ eV $I^{*b}$ PhMe0.310.24Ph-t-Bu0.480.301,4-Me_2C_6H_40.610.471,4-t-Bu_2C_6H_40.500.491,2,4-Me_3C_6H_30.450.261,2,4,5-Me_4C_6H_20.500.42PhOMe0.810.73	arene $\Delta I_{D}$ , $^{a}$ eV $I^{*b}$ $I_{2}^{c}$ PhMe0.310.24 $i$ Ph-t-Bu0.480.30 $i$ 1,4-Me_{2}C_{6}H_{4}0.610.47 $i$ 1,4-t-Bu_{2}C_{6}H_{4}0.500.49 $i$ 1,2,4-Me_{3}C_{6}H_{3}0.450.26 $i$ 1,2,4,5-Me_{4}C_{6}H_{2}0.500.420.47PhOMe0.810.730.64	$\begin{tabular}{ c c c c c c } \hline & & & & & & & & & & & & & & & & & & $	$\begin{tabular}{ c c c c c } \hline & & & & & & & & & & & & & & & & & & $

<sup>a</sup> From ref 44-49. <sup>b</sup> This work (see Table II). <sup>c</sup> This work (see supplementary material). <sup>d</sup> Tetracyanoethylene. <sup>e</sup> Data from ref 30 and 41 and from Mobley, M. J.; Rieckhoff, K. E.; Voigt, E.-M. J. Phys. Chem. 1978, 82, 2005-2012. <sup>f</sup> Chloranil. <sup>g</sup> Data from ref 30. <sup>h</sup> Tetracyanopyrazine. <sup>i</sup> The lower wavelength band may be calculated to lie under the  $\pi \to \pi^*$  band of the aromatic donor; hence  $\Delta h\nu_{CT}$  cannot be measured.



**Figure 5.** Plot of  $hv_{CT}(1^{\circ}/arene)$  against the (first) ionization potential of the aromatic donor (O). For those complexes that show twin CT bands, the second (higher energy) band has *also* been plotted against the *second* ionization potential ( $\Box$ ).

that the energy difference between the first and second CT transitions in the complex  $\Delta h \nu_{\rm CT}$  is approximately equal to the energy difference between the first and second highest occupied MO's of the aromatic donor  $\Delta I_{\rm D}$ .<sup>43</sup> The twin bands we observed in the I<sub>2</sub>/15 and I<sub>2</sub>/18 complexes fit into this general pattern (see Table III). Moreover, when the  $h\nu_{\rm CT}$  energies for the higher energy CT bands of the I<sub>2</sub>/15 and I<sub>2</sub>/18 complexes are plotted against the second ionization potentials of the corresponding arenes (shown as squares in Figure 3), the points fit the main, lower energy  $h\nu_{\rm CT}$  vs first ionization potential correlation (shown as circles in Figure 3) just about as well as do the lower energy I<sub>2</sub>/15 and I<sub>2</sub>/18 points.

Iodine Atom/Arene  $\pi$ -Molecular Complexes. Many of the I<sup>•</sup>/arene complexes also show twin CT bands, the energy difference between these bands again being approximately equal to the difference in energy between the first and second ionization potentials of the arene (see Table III).<sup>50</sup> A plot of  $h\nu_{CT}$  vs  $I_D$  using

- (40) Voigt, E. M. J. Am. Chem. Soc. 1964, 86, 3611-3617.
- (41) Holder, D. D.; Thompson, C. C. J. Chem. Soc., Chem. Commun. 1972, 277-279.
  - (42) de Maine, P. A. D. J. Chem. Phys. 1957, 26, 1189-1191.
- (43) Relevant values of  $\Delta I_D$  are  $0.57^{16}$  (1),  $0.31^{44}$  (3),  $0.48^{45}$  (4),  $0.44^{44}$  (5),  $0.45^{44}$  (6),  $0.61^{44}$  (7),  $0.50^{46}$  (8),  $0.45^{47}$  (10),  $0.28^{48}$  (13),  $0.30^{47}$  (14),  $0.50^{44}$  (15), and  $0.81^{49}$  (18).
  - (44) Bock, H.; Kaim, W. Chem. Ber. 1978, 111, 3552-3572.
- (45) Bischof, P. K.; Dewar, M. J. S.; Goodman, D. W.; Jones, T. B. J.
- Organomet. Chem. 1974, 82, 89–98. (46) Kaim, W.; Tesmann, H.; Bock, H. Chem. Ber. 1980, 113, 3221–3234.
  - (47) Klessinger, M. Angew. Chem., Int. Ed. Engl. 1972, 11, 525-526.
- (48) Santiago, C.; Gandour, R. W.; Houk, K. N.; Nutakul, W.; Cravey,
- W. E.; Thummel, R. P. J. Am. Chem. Soc. 1978, 100, 3730-3737.
- (49) Anderson, G. M., III; Kollman, P. A.; Domelsmith, L. N.; Houk, K. N. J. Am. Chem. Soc. 1979, 101, 2344-2352.



Figure 6. Plot of  $h\nu_{CT}(Cl^*/arene)$  against the (first) ionization potential of the aromatic donor.

the data for both the lower and the higher energy CT bands when available yields an excellent straight line for the I<sup>•</sup>/arene complexes<sup>52</sup> (slope = 0.70, correlation coefficient = 0.97) (see Figure 5). Indeed, with few exceptions the individual points deviate from the best line by smaller amounts than is the case for the I<sub>2</sub>/arene plot (see Figure 3). This implies that sterically induced variations in  $r_{AD}$  are less significant for I<sup>•</sup>/arene complexes than for I<sub>2</sub>/arene complexes. Our results imply that for I<sup>•</sup>/arene complexes involving benzene and symmetrically substituted alkyl benzenes, at the very least, the iodine atom lies directly above the center of the ring, i.e., I<sup>•</sup>/C<sub>6</sub>H<sub>6</sub> would appear to be a classical, hexahapto complex H.



(50) In the case of toluene, the twin bands overlap strongly and the shorter wavelength band appears as a shoulder on the longer wavelength band. Although  $\Delta I_D$  for o- and *m*-xylene and chlorobenzene are greater than that for toluene,<sup>43</sup> only single CT bands were observed for iodine atom complexes of these arenes. Examination of the bandwidths at half-height shows that these three complexes have bands which are wider than that of the I'/benzene complex. The increase in the bandwidths of these complexes suggests, therefore, that there are two closely overlapping bands which cannot be resolved. This also appears to be true for the chlorine atom and bromine atom complexes with anisole (18). It is clear from our own and others' work<sup>51</sup> that the CT bandwidths generally increase as  $\lambda_{max}$  increases. Considering that the  $\lambda_{max}$  for Cl'/18 lies between those of Cl'/16 and Cl'/17 (see Table I), its bandwidth would be expected to lie in the range from 150 to 160 nm. However, the bandwidth for Cl'/18 is 190 nm, suggesting that this complex probably has two unresolved CT bands. The same appears to be true for Br'/18.

(51) Briegleb, G.; Czekalla, J. Z. Phys. Chem. (Munich) 1960, 24, 37-54.

(52) Previous workers have interpreted data on I/arene complexes both in terms of a linear<sup>7,23,25</sup> and a nonlinear<sup>29</sup> relationship between  $h\nu_{CT}$  and  $I_D$ .



Figure 7. Plot of  $h\nu_{CT}(Br^{*}/arene)$  against  $h\nu_{CT}(Cl^{*}/arene)$ . The solid line was obtained by least-squares analysis of all the data (slope = 0.69, correlation coefficient = 0.87). The dotted line is the least-squares line based only on the points for the symmetrically substituted arenes: 2, 11, and 17.

Chlorine Atom/Arene and Bromine Atom/Arene  $\pi$ -Molecular Complexes. No multiple bands were observed in the visible region of the spectrum for any Cl<sup>•</sup>/arene or Br<sup>•</sup>/arene complex.<sup>53</sup> Although a UV band was detected in the Cl\*/arene complexes (see Table I), we are unable to say whether or not such bands are also present in Br<sup>•</sup>/arene and I<sup>•</sup>/arene complexes (see Results). The wavelength of the UV band for Cl<sup>•</sup>/arene complexes shows very little dependence on the nature of the arene, as has been found for the UV bands of other  $\pi$ -molecular complexes.<sup>7,42</sup>

A plot of  $hv_{CT}$  for Cl<sup>•</sup>/arene complexes against  $I_D$  for the arene gives the "buckshot" pattern shown in Figure 6. The deviations of the points from the line of best fit (not shown; slope = 0.14, correlation coefficient = 0.48) are actually comparable in magnitude (ca.  $\pm 0.2$  eV for  $h\nu_{CT}$ ) to the deviations observed in the  $h\nu_{\rm CT}$  vs  $I_{\rm D}$  plot for the  $I_2$ /arene complexes (see Figure 3). However, for the Cl<sup>•</sup>/arene complexes the  $h\nu_{CT}$  energies range only over 0.45 eV (from 2.19 eV for 17 to 2.64 eV for 6 and 11) whereas the  $hv_{CT}$  energies for I<sub>2</sub>/arene complexes range over 1.08 eV. It is clear that there is no correlation between  $h\nu_{\rm CT}$  and  $I_{\rm D}$ for the complexes formed between Cl<sup>•</sup> atoms and the range of arenes studied in the present work.54

A plot of  $h\nu_{\rm CT}$  for Br<sup>•</sup>/arene complexes against  $I_{\rm D}$  for the arene gives a buckshot pattern very similar to that found for the Cl<sup>•</sup>/arene complexes.<sup>55</sup> Indeed, a plot of  $h\nu_{CT}$  for the Br<sup>•</sup>/arene complexes against  $h\nu_{\rm CT}$  for the corresponding Cl<sup>•</sup>/arene complexes gives an acceptable linear correlation (correlation coefficient = (0.87) with the best line having a slope of (0.69) (see Figure 7). Although some arenes give points that deviate substantially from the best line, there can be no doubt that the general effect of the arene's substituents on the energies of the Cl<sup>•</sup>/arene and Br<sup>•</sup>/arene CT bands are substantially similar. We presume again that the primary reason for the deviations is that an asymmetrical distribution of the substituents or a change in their size  $[H, CH_3,$  $C(CH_3)_3$  could produce nonequivalent alterations in the relative  $r_{AD}$  for particular Cl<sup>•</sup>/arene and Br<sup>•</sup>/arene complexes. In this connection, we note that the symmetric arenes benzene (2), 1,3,5-trimethylbenzene (11), and hexamethylbenzene (17) yield points that, within experimental error, again lie on a single line (shown as the dotted line in Figure 7). In a relative sense, arenes that give points which, for example, lie above the dotted line form Cl<sup>•</sup>/arene complexes that are stronger (smaller  $r_{AD}$ ) and/or

Br<sup>•</sup>/arene complexes that are weaker (larger  $r_{AD}$ ) than would be expected.

Since the energies of the CT bands for Cl'/arene and Br'/arene complexes do not correlate with  $I_D$ , we have searched, albeit unsuccessfully, for other properties of the arenes that might correlate with  $h\nu_{CT}$  for these complexes. For example, it is well-known that in Ag<sup>+</sup>/arene complexes the silver ion is located above and between two adjacent unsubstituted carbons, when such positions are available, in a dihapto structure D.<sup>7,33,56-59</sup> Com-



D

parison of the  $h\nu_{\rm CT}$  energies for the Cl<sup>•</sup>/arene or Br<sup>•</sup>/arene complexes with the equilibrium constants  $K_1$  for formation of Ag<sup>+</sup>/arene complexes in equimolar ethanol/water at 25 °C<sup>56</sup> showed some similarities;<sup>60</sup> however, the differences<sup>61</sup> were more obvious than the similarities. Similarly, we explored the possibility that  $h\nu_{\rm CT}$  energies for the Cl<sup>•</sup>/arene complexes would correlate with the basicity of the arene<sup>62</sup> in view of the proposal of Skell<sup>12,13</sup> that chlorine atoms form a  $\sigma$ -complex with benzene, just as protons are known to do. However, the correlation of  $h\nu_{CT}$  with arene basicity was, if anything, worse than its correlation with  $I_{\rm D}$ .

Symmetry considerations would lead one to conclude that the  $\pi$ -molecular complexes formed between benzene and Cl<sup>•</sup>, Br<sup>•</sup>, and I' atoms should all have the same structure. These atoms all have LUMO's which are p orbitals which would favor the hexahapto structure, H, that is probably adopted by  $I^{\bullet}/C_{6}H_{6}$  (vide supra). The absence of a correlation between  $h\nu_{\rm CT}$  and  $I_{\rm D}$  for the Cl<sup>•</sup>/arene and Br'/arene complexes raises the interesting possibility that these complexes might have a structure different from that of the I<sup>•</sup>/arene complexes. However, we could obtain no evidence that would support either of the two most likely alternative structures, viz., a dihapto  $\pi$ -molecular complex or a  $\sigma$ -complex (vide supra). We therefore conclude that Cl<sup>•</sup>/arene and Br<sup>•</sup>/arene complexes are most likely to have the same hexahapto structure as the I<sup>•</sup>/arene complexes.

The absence of the expected correlation between  $h\nu_{CT}$  and  $I_D$ for the Cl\*/arene and Br\*/arene complexes having hexahapto structures could be accounted for in one or both of the following

<sup>(53)</sup> However, for Cl<sup>+</sup>/18 and Br<sup>+</sup>/18 it seems likely that there are two closely overlapping bands which are not resolved.50

<sup>(54)</sup> This conclusion does not agree with the early contention of Bühler<sup>5,6</sup> (54) This conclusion does not agree with the early contention of Bühler.<sup>50</sup> that  $h\nu_{CT}$  energies for Cl<sup>+</sup>/arene complexes correlate linearly with the arene's  $I_D$ , nor is it in agreement with Bühler's<sup>29</sup> more recent analysis of literature data which leads him to conclude that  $(h\nu_{CT})^2$  should be quadratically dependent on  $I_D$ . We note only that Bühler's literature data covered a slightly wider range of  $I_D$  values<sup>10a</sup> and a considerably wider range of arene structures. (55) Our results do not support the contention of Bossy et al.<sup>19</sup> that  $h\nu_{CT}$  energies for Br'/arene complexes correlate linearly with the arene's  $I_D$ , nor do they support Bühler's<sup>29</sup> quadratic relationship. In Bossy's work<sup>19</sup> the range of  $I_D$  values and structures was greater than we employed (from 8.1 eV for naphthalene to ca. 10.34 eV for pure bromocyclohexane).

<sup>(56)</sup> Ogimachi, N.; Andrews, L. J.; Keefer, R. M. J. Am. Chem. Soc. 1956, 78, 2210-2213.

<sup>(57)</sup> Beverwijk, C. D. M.; Van der Kerk, G. J. M.; Leusink, A. J.; Noltes, J. G. Organomet. Chem. Rev., Sect. A 1970, 5, 215-280.

<sup>(58)</sup> For crystal structures of various silver(I) aromatic complexes, see: Rundle, R. E.; Goring, J. H. J. Am. Chem. Soc. 1950, 72, 5337. Smith, H. G.; Rundle, R. E. Ibid. 1958, 80, 5075-5080. Turner, R. W.; Amma, E. L. Ibid. 1966, 88, 3243-3247. Taylor, I. F., Jr.; Hall, E. A.; Amma, E. L. Ibid. 1969, 91, 5745-5749. Griffith, E. A. H.; Amma, E. L. Ibid. 1971, 93, 3167-3172. Taylor, I. F., Jr.; Amma, E. L. J. Cryst. Mol. Struct. 1975, 5, 129-135. Hunt, G. W.; Lee, T. C.; Amma, E. L. Inorg. Nucl. Chem. Lett. 1974, 10, 909-913.

<sup>(59)</sup> Cu<sup>+</sup>/arene complexes also adopt a dihapto structure; see: Dines, M. B.; Bird, P. H. J. Chem. Soc., Chem. Commun. 1973, 12. Rodesiler, P. F.; Amma, E. L. *Ibid.* **1974**, 599–600. (60) For example, <sup>56</sup> o-xylene forms a stronger complex with  $Ag^+$  ( $K_1 =$ 

<sup>1.43</sup>  $M^{-1}$ ) than *m*-xylene (1.35  $M^{-1}$ ) or *p*-xylene (1.14  $M^{-1}$ ) while the CT transition energies for o-xylene complexes with Cl\* and Br\* are lower than for the corresponding complexes formed by the other two xylenes. (61) For example,<sup>56</sup> the methyl-substituted benzenes form much stronger

<sup>(61)</sup> For example, "the methyl-substituted benzenes form finder stronger complexes with Ag<sup>+</sup> than do the corresponding *tert*-butyl-substituted com-pounds:  $K_1 = 1.19$  and 0.90 M<sup>-1</sup> for toluene and *tert*-butylbenzene, respec-tively, 1.14 and 0.62 M<sup>-1</sup> for the corresponding 1,4-dialkylated benzenes, and 0.80 and 0.32 M<sup>-1</sup> for the corresponding 1,3,5-trialkylated benzenes, and 0.80 and 0.32 M<sup>-1</sup> for the corresponding 1,3,5-trialkylated benzenes, while the CT transition energies for Cl<sup>+</sup> and Br<sup>+</sup> atom complexes with methyl-substituted benzenes are always greater than for their complexes with the corresponding *tert*-butyl-substituted compounds.

<sup>(62)</sup> As measured by log  $K_b$  for the equilibrium: arene + 2 HF  $\rightleftharpoons$  arene-H<sup>+</sup> + HF<sub>2</sub> in liquid HF at 0 °C.<sup>63</sup>

<sup>(63)</sup> Brouwer, D. M.; Mackor, E. L.; MacLean, C. In *Carbonium Ions*; Olah, G. A., Schleyer, P. V. R., Eds.; Wiley-Interscience: New York, 1970; Vol. 2, Chapter 20, pp 837-897.

ways. First, there may be a relatively larger increase in  $r_{AD}$  as one proceeds along the series from benzene to hexamethylbenzene for the two smaller halogen atoms than for the larger iodine atom,<sup>64</sup> which would make the range of CT transition energies smaller for the Cl<sup>•</sup>/arene and Br<sup>•</sup>/arene complexes than for the I<sup>•</sup>/arene complexes (see eq 4).<sup>66</sup> Second, as Bühler has suggested,<sup>29</sup> there might be a greater amount of mixing of  $\psi_0(A,D)$ and  $\psi_1(A^--D^+)$  in the ground and excited states of the Cl<sup>•</sup> and Br<sup>•</sup> complexes with arenes of low  $I_D$  than is the case for the corresponding I<sup>•</sup>/arene complexes, perhaps as a consequence of the greater electron affinities of the smaller halogen atoms.<sup>68</sup> This would make charge transfer occur to a lesser extent in the spectroscopic transitions of the Cl<sup>\*</sup>/arene and Br<sup>\*</sup>/arene complexes than in the transitions of the I<sup>•</sup>/arene complexes.<sup>69</sup>

## Summary

The CT transition energies,  $h\nu_{\rm CT}$ , for the  $\pi$ -molecular complexes formed between Cl<sub>2</sub>, Br<sub>2</sub>, and I<sub>2</sub> and a carefully chosen range of arenes correlate fairly well with the ionization potentials,  $I_{\rm D}$ , of the arenes. Deviations of specific arene complexes from the correlations are essentially identical for  $Cl_2$ ,  $Br_2$ , and  $I_2$  and are attributed to nonuniform (relative to  $I_{\rm D}$ ) variations in  $r_{\rm AD}$  which arise from steric factors, asymmetrical patterns of substitution, and the presence of polar substituents. The  $\pi$ -molecular complexes formed between the iodine atom and these arenes yield a noticeably better correlation between  $h\nu_{\rm CT}$  and  $I_{\rm D}$  than do the molecular halogen/arene complexes. It is concluded that I'/arene complexes have a structure in which the I<sup>•</sup> atom is centered (at least for symmetrically substituted arenes) above the plane of the aromatic ring. The  $h\nu_{CT}$  energies for the Cl<sup>•</sup>/arene and Br<sup>•</sup>/arene  $\pi$ -molecular complexes correlate well with one another but do not show a correlation with the  $I_{\rm D}$  of the arene. It is nevertheless concluded that Cl\*/arene and Br\*/arene complexes are most likely to have structures similar to the structure of the I'/arene complexes, and possible reasons for the failure of the  $h\nu_{\rm CT}/I_{\rm D}$  correlation with Cl<sup>•</sup> and Br<sup>•</sup> are considered.

# **Experimental Section**

Chlorine Atom and Bromine Atom Complexes. The laser flash photolysis apparatus has been described previously.<sup>70</sup> A Lumonics TE-860-2 excimer laser operated with Xe/HCl mixtures (308 nm) was employed for excitation. Two streams, one carrying a de-

(66) This argument has been previously employed by Fukuzumi and Ko-chi<sup>30,67</sup> to account for the fact that plots of  $h\nu_{CT}$  energies vs  $I_D$  for numerous  $\pi$ -electron donor/acceptor and  $\sigma$ -electron donor/acceptor molecular complexes have slopes less than unity. For example, the  $h_{PCT}$  vs  $I_D$  plots for the following complexes have the slopes indicated: Br<sub>2</sub>/arene, 0.7;<sup>30</sup> Cl<sub>2</sub>/arene, 0.6;<sup>30</sup> 1,2,4,5-tetracyanobenzene/arene, 0.6;<sup>30</sup> Hg(O<sub>2</sub>CCF<sub>3</sub>)<sub>2</sub>/arene, 0.5;<sup>30</sup> I<sub>2</sub>/dialkylmercury, 0.4;<sup>67</sup> I<sub>2</sub>/tetraalkyltin, 0.4;<sup>67</sup> HgCl<sub>2</sub>/tetraalkyltin, 0.2;<sup>67</sup> O

the Cl<sup>\*</sup>/arene complexes we find that a plot of  $h_{VCT}$  vs  $I_D$  has a slope of 0.14. (67) Fukuzumi, S.; Kochi, J. K. (a) J. Phys. Chem. **1980**, 84, 608–616. (b) Ibid. **1980**, 84, 617–624. (c) Ibid. **1981**, 85, 648–654.

oxygenated solution of halogen in CCl<sub>4</sub> and another a deoxygenated solution of arene in CCl<sub>4</sub>, were mixed in a T-piece just before entering the photolysis cell. The concentration of halogen in the first stream was 0.118 M for chlorine and  $1.2 \times 10^{-3}$  M for bromine. The arene concentration in the second stream depended on the arene: benzene, 2 M; chlorobenzene, 1 M; anisole, 0.5 M; tert-butylbenzene, 1 M; 1,4-di-tert-butylbenzene, 0.5 M; 1,3,5-tri-tert-butylbenzene, 0.1 M; toluene, 1 M; xylenes, 1 M; trimethylbenzenes, 0.5 M; tetramethylbenzenes, 0.5 M; pentamethylbenzene, 0.1 M; and hexamethylbenzene, 0.1 M. A double-head peristaltic pump was used to move the two streams with equal flow rates. Teflon tubing was used everywhere except for the pump heads in which we used Viton washed with CCl<sub>4</sub>.

The (visible) band maximum for the  $Cl^{\bullet}/C_{6}H_{6}$  complex is very slightly greater (by ca. 5 nm) in neat  $C_6H_6$  than for 0.1 M  $C_6H_6$  in  $CCl_4$ .<sup>69</sup> Measurements of  $\lambda_{max}$  for the Cl<sup>•</sup> atom complexes with three alkylated benzenes at various arene concentrations showed that any similar variation was less than the uncertainties involved in determining  $\lambda_{max}$  (ca.  $\pm 2-3$  nm). The complexes examined and the arene concentrations chosen were  $Cl^{\bullet}/m$ -xylene, 4, 2, 1, 0.5, 0.2, 0.1 M; Cl<sup>•</sup>/1,3,5-trimethylbenzene, 0.5, 0.25, 0.1, 0.05 M; and Cl<sup>•</sup>/1,3,5-tri-*tert*-butylbenzene, 0.25, 0.1, 0.05, 0.025 M. Similarly,  $\lambda_{max}$  was the same for 0.5 M 1,3,5-trimethylbenzene in  $CCl_4/n$ -pentane (1:1 v/v) as in  $CCl_4$  and for 0.1 M 1,3,5tri-tert-butylbenzene in CCl<sub>4</sub>/CHCl<sub>3</sub> (1:1 v/v) as in CCl<sub>4</sub>.

Iodine Atom Complexes. The spectra of these complexes were measured in a static cell with CCl<sub>4</sub> as solvent; all solutions were deoxygenated. The complexes were generated by excitation at 308 nm unless otherwise stated. The iodine concentration was  $1.0 \times 10^{-4}$  M and the arene concentrations were benzene, 2 M; chlorobenzene, 2 M; anisole, 0.5 M; tert-butylbenzene, 2 M; 1,4-di-tert-butylbenzene, 2 M; toluene, 2 M; xylenes, 2 M; and trimethylbenzenes, 1 M.

The iodine atom complexes of 1,3,5-tri-tert-butylbenzene, tetramethylbenzenes, pentamethylbenzene, and hexamethylbenzene were produced by excitation at 337 nm using a Molectron UV-24 nitrogen laser. The iodine concentration was  $5.0 \times 10^{-3}$ M and the arene concentrations were 1,3,5-tri-tert-butylbenzene, 4 M; tetramethylbenzenes, 2.5 M; pentamethylbenzene, 3 M; and hexamethylbenzene, 2 M. The spectrum of the iodine atom complex with hexamethylbenzene was measured with chloroform as solvent due to the limited solubility of the arene in CCl<sub>4</sub>.

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Registry No. 1.Cl, 117308-66-4; 1.Br, 117308-82-4; 1.I, 117308-99-3; 2-Cl, 85754-18-3; 2-Br, 117308-83-5; 2-I, 117309-00-9; 3-Cl, 117308-67-5; 3.Br, 34475-57-5; 3.I, 117309-01-0; 4.Cl, 117308-68-6; 4.Br, 117308-84-6; 4·I, 117309-02-1; 5·Cl, 117340-32-6; 5·Br, 117308-85-7; 5-I, 117309-03-2; 6-Cl, 117308-69-7; 6-Br, 117308-86-8; 6-I, 117309-04-3; 7.Cl, 117308-70-0; 7.Br, 117308-87-9; 7.I, 117309-05-4; 8.Cl, 117308-71-1; 8·Br, 117308-88-0; 8·I, 117309-06-5; 9·Cl, 117308-72-2; 9·Br, 117308-89-1; 9-I, 117309-07-6; 10-Cl, 117308-73-3; 10-Br, 117308-90-4; 10-I, 65018-34-0; 11-Cl, 117308-74-4; 11-Br, 117308-91-5; 11-I, 117309-08-7; 12·Cl, 117308-75-5; 12·Br, 117308-92-6; 12·I, 117309-09-8; 13-Cl, 117308-76-6; 13-Br, 117308-93-7; 13-I, 117309-10-1; 14-Cl, 117308-77-7; 14-Br, 117308-94-8; 14-I, 117309-11-2; 15-Cl, 117308-78-8; 15-Br, 117308-95-9; 15-I, 117309-12-3; 16-Cl, 117308-79-9; 16-Br, 117308-96-0; 16-I, 117309-13-4; 17-Cl, 117308-80-2; 17-Br, 117308-97-1; 17.I, 117309-14-5; 17.Cl, 117308-81-3; 18.Br, 117308-98-2; 18.I, 117309-15-6.

Supplementary Material Available: Table IV giving the wavelengths and transition energies of all 18  $I_2$ /arene complexes (1 page). Ordering information is given on any current masthead page.

<sup>(64)</sup> The atomic radii of Cl<sup>\*</sup>, Br<sup>\*</sup>, and I<sup>\*</sup> are respectively 1.80, 1.95 and 2.15 Å while the C-C bond length in benzene is 1.395 Å. $^{65}$ 

<sup>(65)</sup> Handbook of Chemistry and Physics, 67th ed.; Weast, R. C., Ed.; CRC Press: Boca Raton, FL, 1986-1987.

<sup>(68)</sup> The electron affinities of Cl<sup>\*</sup>, Br<sup>\*</sup>, and I<sup>\*</sup> are 3.613, 3.663, and 3.063 eV, respectively.<sup>65</sup>

<sup>(69)</sup> A referee has suggested that  $h\nu_{\rm CT}$  for the Cl<sup>•</sup>/arene and Br<sup>•</sup>/arene complexes might show a dependence on solvent polarity. There is indeed, a complexes might show a dependence on solvent polarity. In set is indeed, a solvent effect on  $\lambda_{max}$ , but it is barely greater than the uncertainties involved in measuring  $\lambda_{max}$  (ca.  $\pm 2-3$  nm). Thus, for the Cl<sup>+</sup>/C<sub>6</sub>H<sub>6</sub> complex the following  $\lambda_{max}$  values were obtained: 0.1 M C<sub>6</sub>H<sub>6</sub> in CCl<sub>4</sub>, 485 nm; 0.1 M C<sub>6</sub>H<sub>6</sub> in CH<sub>3</sub>CN, 480 nm; neat C<sub>6</sub>H<sub>6</sub>, 490 nm. We will not attempt to interpret such trivial changes and note only that Fukuzumi and Kochl<sup>57</sup>c in their study of the HgCl<sub>2</sub>/tetraalkyltin molecular complexes ( $h_{PCT}$  vs  $I_D$  slope = 0.2) found no change in  $\lambda_{max}$  between CH<sub>2</sub>Cl<sub>2</sub>/hexane (1:2 v/v) as solvent and CH<sub>3</sub>CN or CH<sub>3</sub>OH as solvents.

<sup>(70)</sup> Scaiano, J. C. J. Am. Chem. Soc. 1980, 102, 7747-7753.