

FORMATION AND VISIBLE SPECTRA OF SOME MOLECULAR COMPLEXES  
OF ALIPHATIC AND AROMATIC PRIMARY AMINES WITH IODINE IN  
CHLORINE-CONTAINING ALIPHATIC SOLVENTS

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THE FORMATION AND THE SPECTRAL BEHAVIOUR OF CHARGE-TRANSFER COMPLEXES OF PRIMARY ALIPHATIC (HEXADECYLAMINE, DODECYLAMINE, OCTYLAMINE) AND AROMATIC AMINES (ANILINE, p-TOLUIDINE, p-Cl-ANILINE) WITH IODINE WERE STUDIED IN SIX CHLORINE-CONTAINING SOLVENTS. THE FORMATION CONSTANTS,  $K_f$ , OF THE COMPLEXES WERE DETERMINED AND CALCULATIONS WERE MADE ON THE ENERGETICAL RELATIONS OF THE COMPLEX MOLECULES.

*Introduction*

Several authors (e.g. [1]) have reported that an increase in the solvating power of a medium for a charge-transfer (CT) complex shifts the CT band to lower energy, but it is often found that an increase in solvent polarity results in a shift in the opposite direction [2]. A specific interaction between the CT complex and the surrounding solvent causing this blue shift should therefore also be considered to be significant in these systems [3]. We earlier [4] discussed the CT complex-forming ability of several aromatic secondary amines with iodine.

As a continuation of this work, we have now studied the formation and the spectral behaviour of molecular complexes of aliphatic [hexadecylamine (HAD), dodecylamine (DDA) and octylamine (OA)] and aromatic [aniline (An), p-toluidine

(pTol) and p-Cl-An (pClAn)] primary amines with iodine in chlorine-containing aliphatic solvents ( $\text{CCl}_4$ ,  $\text{CHCl}_3$ ,  $\text{CH}_2\text{Cl}_2$ ,  $(\text{Cl}-\text{CH}_2)_2$ ,  $(\text{Cl}_2=\text{CH})_2$  and  $(\text{Cl}_2=\text{C})_2$ , and we present the results in this paper.

### *Experimental*

The chemicals were BDH products of p.a. purity, while the solvents were spectroscopically pure; they were used without further purification. The experimental methods have been described elsewhere [4]. For determination of the stoichiometry, stock solutions ( $1.2 \cdot 10^{-2}$  mol/dm<sup>3</sup>) of the donors (D) and acceptor (A) were prepared. In every case, 1:1 complex formation was found. In determinations of the formation constants,  $K_f$ , the concentration of iodine was  $1.2 \cdot 10^{-3}$  mol/dm<sup>3</sup>, while those of the donors ranged from  $5 \cdot 10^{-4}$  to  $5 \cdot 10^{-2}$  mol/dm<sup>3</sup>. The  $K_f$  values were calculated by the least squares method, using the BENESI-HILDEBRAND [5] equation. Because of the absorption of the solvents, we made measurements only in the spectral range above 250 nm. The optical method used yields values of  $K_f$  and  $\epsilon_{\text{CT}}$  which are often concentration-dependent;  $1/\epsilon_{\text{CT}}$  and  $1/K_f \cdot \epsilon_{\text{CT}}$  are obtained from the plot, and therefore the evaluated  $K_f$  values are very sensitive to  $\epsilon_{\text{CT}}$ . However, the extinction coefficient is also concentration-dependent, a deviation from the BEER's law can be obtained, and thus the BENESI-HILDEBRAND plot does not give strictly true values of  $K_f$  and  $\epsilon_{\text{CT}}$ . The calculated values must therefore be treated carefully.

### *Results and Discussion*

Both the n-alkyl and the aromatic amines studied form molecular complexes as n-donors through the lone pair electron(s) on the nitrogen atom, while iodine acts as  $\sigma$ -acceptor; their complexes can be classified as  $n\sigma$  complexes.

The behaviour of the  $n\sigma$  complexes is completely different from that of the other types; for example, their energy of formation is very high, the bonds are strongly localized, the self-absorption of the components varies considerably, *etc.*

When the solutions of the alkylamines studied as donors and iodine as acceptor are mixed, a new band develops in the visible range, between 330 and 430 nm.

Figure 1 shows the absorption spectra of OA, iodine and their mixtures in  $\text{CCl}_4$  (A) and  $\text{CHCl}_3$  (B) solutions.

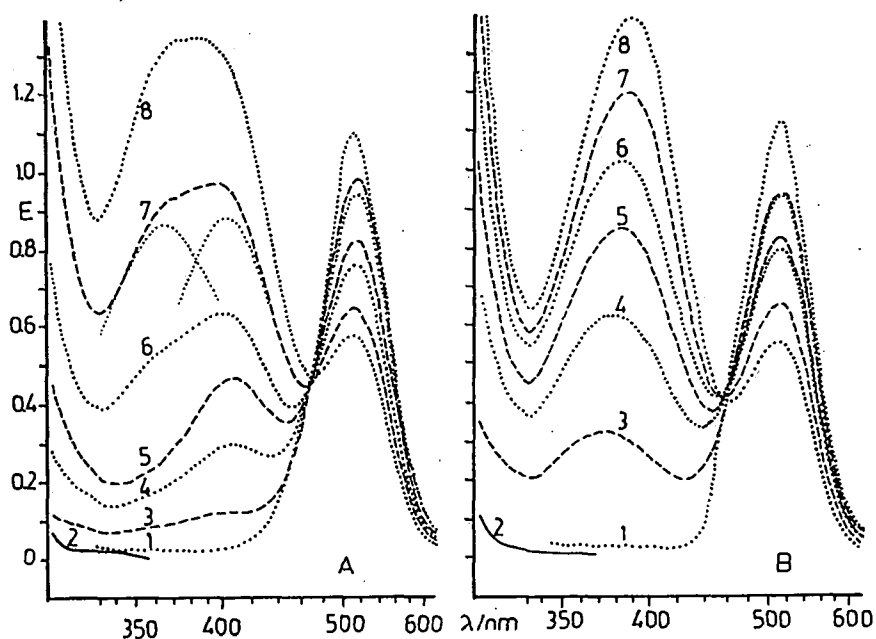


Figure 1: Absorption spectra of iodine (1), OA (2) and their mixtures in  $\text{CCl}_4$  (A) and  $\text{CHCl}_3$  (B) solution.  $[\text{I}_2]=1.2 \cdot 10^{-3} \text{ mol/dm}^3$ .  $[\text{OA}] =$  (A): (3):  $1.89 \cdot 10^{-4}$ , (4):  $4.72 \cdot 10^{-4}$ , (5):  $7.55 \cdot 10^{-4}$ , (6):  $9.44 \cdot 10^{-4}$ , (7):  $1.89 \cdot 10^{-3}$ , (8):  $2.36 \cdot 10^{-3}$ ; (B): (3):  $1.97 \cdot 10^{-4}$ , (4):  $4.93 \cdot 10^{-4}$ , (5):  $7.88 \cdot 10^{-4}$ , (6):  $9.85 \cdot 10^{-4}$ , (7):  $1.48 \cdot 10^{-3}$ , (8):  $1.97 \cdot 10^{-3} \text{ mol/dm}^3$ .  $d=1.0 \text{ cm}$ ,  $T=295 \text{ K}$ .

Besides the new band, an isosbestic point appears at about 480 nm, indicating equilibrium systems (Figure 2).

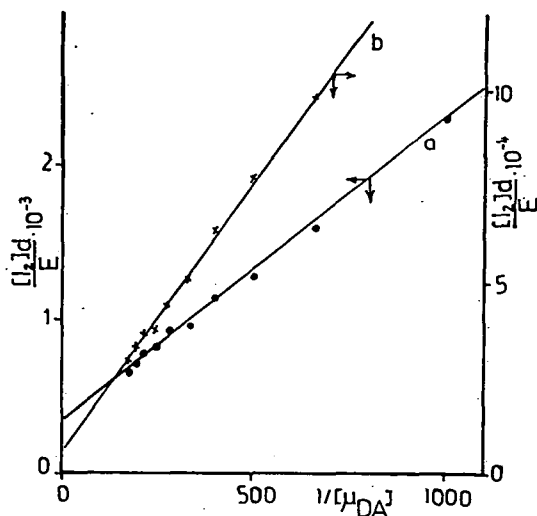


Figure 2. BENESI-HILDEBRAND plot on HDA - iodine systems,  
 a.) in  $\text{CCl}_4$  ( $r = 0.992$ ) b.) in  $\text{CHCl}_3$  ( $r = 0.994$ )

Since the self-absorption of anilines is not negligible in the region of importance, we find only an inflection at around 340–370 nm. We therefore used the donor at the same concentration as in the mixtures as a blank; in this case the isosbestic point is also observed.

We attribute the new band to the formation of a CT complex. In quantum mechanical terms [16], the wave functions for the ground and excited states are

$$\psi_N = a\psi_0(D, A) + b\psi_1(D^+ - A^-) \quad \text{and} \quad \psi_E = a^*\psi_1(D^+ - A^-) - b^*\psi_0(D, A)$$

respectively, with  $a \approx a^*$ ,  $b \approx b^*$  and  $a^2 \gg b^2$ .

Thus, when light is absorbed, an intermolecular CT occurs, and the transition takes place from the structure  $\psi_0(A, D)$  ("no-bond" function) to the structure  $\psi_1(A^- - D^+)$  ("dative" function), i.e. it is an intermolecular CT transition involving a one-electron jump from D to A.

It is just possible, however, that this new band corresponds to the hypsochromically shifted visible band of iodine [6,7], and the true CT band lies in the shorter wavelength region. This blue shift of the iodine band is attributed by MULLIKEN [8] to a greater exchange repulsion between the  $\sigma_u$  excited MO of iodine and the adjacent donor, and an isobestic point may be observed between the free and complexed iodine bands [9]. On the other hand, the  $I_3^-$  ion also exhibits an absorption maximum at around 365 nm [10]. Thus, in the wavelength region mentioned, absorptions of different origins are present and the exact position of the CT band is very difficult to establish. The BENESI-HILDEBRAND [5] method is still applicable here, in spite of the fact that the absorption is a superposition of the CT band and the shifted iodine band, because both arise from the complex; the appropriate plot in every case gives a straight line with reasonable agreement, indicating the formation of 1:1 complexes.

With regard to the effects of the solvents used on the spectral structure of both the iodine and the amine-iodine systems, we can divide the solvent molecules into three groups:

a.) In solutions in the inert  $CCl_4$ , the interaction is probably due to van der Waals forces only; the  $\lambda_{max}$  values measured in the vapour phase [11] and in  $CCl_4$  solution differ only slightly ( $\lambda_{max}$ : 520 and 516 nm).

b.) In solutions in  $CHCl_3$ ,  $CH_2Cl_2$ ,  $(Cl-CH_2)_2$  and  $(Cl_2=CH)_2$ , there are attractive forces due to polarization of the iodine molecule and other species by the electrical field of the solvent molecules [12], and  $\lambda_{max}$  is somewhat lower (498-510 nm).

c.) In the case of solutions in  $(\text{Cl}_2=\text{C})_2$ , the spectrum of iodine changes completely, and there is no evaluable change in the presence of aniline donors.

It seems likely that  $(\text{Cl}_2=\text{C})_2$  forms a CT complex with iodine that is more stable than the aniline–iodine complexes. In accordance with literature data [20], we measured the CT band of the tetrachloroethylene–iodine system in *n*-hexane solution at 279 nm (4.44 eV),  $\epsilon_{\text{CT}} = 15950$ , from which an ionization potential of  $I_D = 9.27$  eV may be calculated.

The tendency is observed that, the higher the relative permittivity of the solvent molecule, the greater is the hypsochromic shift of the visible band of iodine; the data on  $(\text{Cl}_2=\text{CH})_2$  and  $(\text{Cl}_2=\text{C})_2$  deviate strongly from the linear  $\lambda_{\text{max}}$  vs.  $\epsilon$  correlation (Figure 3).

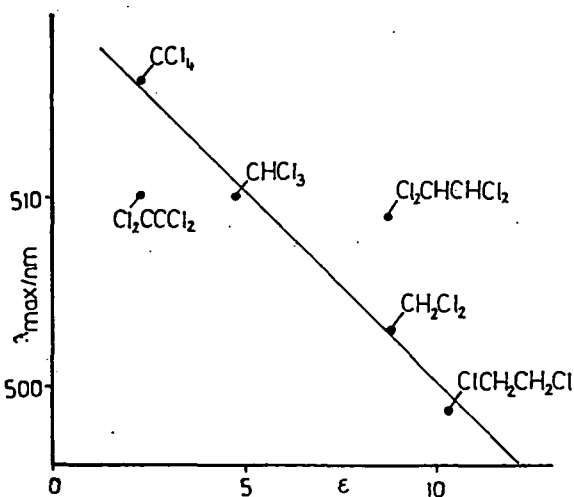


Figure 3. Plot of  $\lambda_{\text{max}}$ /nm of the iodine band measured in different solvent vs. the relative permittivities of solvent molecules.

In the case of anilines, the equilibrium measurements show that the *para*-X substituent plays an important role in the complex formation. If  $X = H$ , it is easy to follow the spectral change when the blank also contains the aniline in appropriate concentration; a similar set of curves may be measured as presented in Fig. 1. The CT band shifts bathochromically as compared with those for the alkylamine complexes. If an electron-withdrawing substituent is present in the *para* position, the spectral change is much smaller than in the An-iodine system, suggesting that the complex formation under otherwise the same experimental circumstances and at the same D/A ratios, is limited. It appears that an electron-withdrawing substituent decreases the charge density in the aromatic ring and also on the nitrogen atom to such an extent that the probability of CT is reduced. On the other hand, in the presence of an electron-donating substituent ( $X = OCH_3$ ), similarly as in the An.I<sub>2</sub> system, a well-defined spectral change is measurable; the determined formation constants are higher than those of An.I<sub>2</sub> (Table I).

The intensity of the CT bands,  $\epsilon_{CT}$ , does not vary in a systematic way with  $K_f$ , which has usually been ascribed to contact CT during molecular collisions, where the internuclear distance is too great for complex formation to contribute to the intensity of the CT band.

The  $\nu_{CT}$  values do not show a correlation either with the TAFT-KAMLET [13] parameters or with the McRAE [14] and other [15] equations; only the plot of  $\nu_{CT}$  vs. the acceptor number, AN, of the solvents results in a linear correlation. For the HDA.I<sub>2</sub> and An.I<sub>2</sub> systems, the empirical equations are  $\nu_{CT} = 128.AN + 23820$  ( $r = 0.989$ ) and  $\nu_{CT} = 61.AN + 27250$  ( $r = 0.916$ ), respectively; i.e. with higher AN, the CT bands shift hypsochromically.

There is no strict correlation between the formation constants and the solvent

Table I

Measured and calculated characteristics on the iodine complexes studied

Donor		S <sub>1</sub>	S <sub>2</sub>	S <sub>3</sub>	S <sub>4</sub>	S <sub>5</sub>	S <sub>6</sub>
<u>HDA</u>	$\lambda_{CT}/nm$	≈401	374	378	380	361	362
	$\mu_{EN}^*$	3.01	4.94	3.11	4.04	5.71	
	$I_D^{**}$	7.69	7.97	7.93	7.91	8.13	8.11
	$K_f^{***}$	310	200	620	525	75	
	$\epsilon_{CT}^{****}$	1890	5070	2020	3400	6800	
<u>DDA</u>	$\lambda_{CT}/nm$	365,401	385	378	380	361	365
	$\mu_{EN}$	5.25	2.90	4.60	4.79	6.32	
	$I_D$	8.08,7.69	7.86	7.93	7.91	8.19	8.08
	$K_f$	130	645	450	530	62	
	$\epsilon_{CT}$	5760	1760	4420	4800	8330	
<u>QA</u>	$\lambda_{CT}/nm$	360,410	390	377	373	360	365
	$\mu_{EN}$	4.71	3.09	4.29	5.85	599	
	$I_D$	8.13,7.60	7.80	7.94	8.06	8.13	8.08
	$K_f$	100	650	880	470	95	
	$\epsilon_{CT}$	4630	2000	3850	7140	7500	
<u>pTol</u>	$\lambda_{CT}/nm$	357	356	358	360	355	354
	$\mu_{EN}$	1.33	1.58	1.52	2.02	1.76	
	$I_D$	8.16	8.18	8.17	8.13	8.19	
	$K_f$	225	240	245	210	185	
	$\epsilon_{CT}$	370	520	480	850	650	
<u>An</u>	$\lambda_{CT}/nm$	360	348	350	352	350	≈340
	$\mu_{EN}$	1.64	2.03	1.97	2.14	1.37	
	$I_D$	8.13	8.27	8.25	8.23	8.25	
	$K_f$	200	140	200	180	130	
	$\epsilon_{CT}$	560	860	810	950	390	
<u>pClAn</u>	$\lambda_{CT}/nm$	380	350	362	362	358	≈350
	$\mu_{EN}$	1.83	1.68	2.18	2.01	1.26	
	$I_D$	7.91	8.25	8.16	8.11	8.16	≈8.25
	$K_f$	40	60	1010	744	310	
	$\epsilon_{CT}$	700	590	990	840	330	

S<sub>1</sub>:CCl<sub>4</sub>, S<sub>2</sub>:CHCl<sub>3</sub>, S<sub>3</sub>:CH<sub>2</sub>Cl<sub>2</sub>, S<sub>4</sub>:ClCH<sub>2</sub>CH<sub>2</sub>Cl, S<sub>5</sub>:Cl<sub>2</sub>CHCHCl<sub>2</sub>, S<sub>6</sub>:Cl<sub>2</sub>CCl<sub>2</sub>;  
 \*[22] p.63, \*\*[22] p. 76, \*\*\* dm<sup>3</sup>mol<sup>-1</sup>,\*\*\*\* from BENESI-HILDEBRAND plot, dm<sup>3</sup>mol<sup>-1</sup>cm<sup>-1</sup>



parameters, but certain tendencies are recognizable. With an increase in the solvent polarity ( $\pi^*$ ) or acceptor number, the  $K_f$  value also increases. In the case of chloroform, the values differ, which may be due to both the hydrogen-bond and the iodine-complex-forming abilities of the solvent. It seems that  $K_f$  increases with the lengthening of the alkyl chain. The formation constants of the complexes of the anilines are generally lower than those of the *n*-alkylamine complexes.

It is known that the lower the ionization potential of the donor,  $I_D$ , the smaller the transition energies of the CT bands [16,17]. It has been proposed [18] that  $\nu_{CT}$  is related to  $I_D$  and the electron affinity of the acceptor,  $E_A$  (for iodine, 1.8 eV [16]):

$$h \nu_{CT} = I_D - E_A - \Delta \quad (a)$$

where  $\Delta$  is the stabilization energy of the ion pair. Several other correlations can also be found in the literature, for example

$$h \nu_{CT} = I_D - D + 2 \beta / (I_D - D) \quad (b)$$

where  $\beta$  is the exchange integral between electron-donating and electron-acceptor orbitals [19]. The experimental and calculated values agree well if it is assumed that  $\beta$  and  $D$  are 1.3 and 6.0 eV, respectively. The binding energy is given by the formula  $\beta / (I_D - D)$  [19-21]. BRIEGLEB [22] has applied the equation

$$h \nu_{CT} = I_D - C_1 + C_2 / (I_D - C_1) \quad (c)$$

where for iodine complexes  $C_1(E_A - E_C + W_O) = 5.2$  and  $C_2(\beta_O^2 + \beta_I^2) = 1.5$  eV; (b) and (c) are analogous. Several empirical equations can also be found, for example

$$I_D = 2.90 + 1.89 \cdot 10^{-3} \cdot \nu_{CT} \quad (d)$$

reported by ALOISI and PIGNATARO [23].

The  $I_D$  values (Table I) calculated *via* (c) and (d) agree well;  $I_D(\text{An})$  is between the values published:  $I_D(\text{An}) = 7.70$  [24], 7.85 [25], 7.95 [26], and 8.23 [27] eV. The anilines possess higher  $I_D$  values than the *n*-alkylamines (7.60-8.00 and 8.10-8.40 eV,

respectively). The difference is probable due to the fact that the anilines cannot be classified as either  $n$ - or  $\pi$ -donors, as a consequence of the resonance between the amino group and the benzene ring;  $n\pi$  mixed orbitals form. It has been concluded [28] that the CT in the complex between  $N,N$ - $Me_2An$  and iodine occurs mainly from the lone pair electrons of the nitrogen atom. On the other hand, in  $An$ , the ionizing electron may possibly be due to one of the non-bonding electrons [27]. In the primary alkylamines studied, there is no such resonance possibility; a "pure"  $n$ -orbital is the donor orbital. The data presented in Table I demonstrate that the  $I_D$  values do not change considerably with the solvent. As regards our data and those previously published [29], it seems that, with lengthening of the alkyl chains,  $I_D$  decreases; for example, for  $CH_3NH_2$ ,  $CH_3CH_2NH_2$  and  $n$ - $CH_3CH_2CH_2CH_2NH_2$ ,  $I_D$  is 8.97, 8.86 and 8.71 eV, respectively [29]. A plot of  $\Delta H$  against the ionization potential of structurally related donors shows a regular relationship; with increasing  $I_D$ ,  $\Delta H$  decreases somewhat.

Using the spectral data discussed above, it is possible to calculate the energy levels of the complexes as described in [22]. The calculated energies ( $W_N$ : energy of the ground state,  $W_O$ : van der Waals energy in the ground state,  $R_N$ : resonance energy in the ground state,  $E_C$ : Coulombic energy acting between the ions,  $W_E$ : energy of the excited state,  $R_E$ : resonance energy in the excited state) are listed in Table II, while the energy level diagrams for  $HDA.I_2$  and  $An.I_2$  are presented in Figure 4. The calculations give only very approximate results, but these are suitable for a qualitative comparison of the changes and of the behaviour. Let us suppose that the maximum value of the dipole moment of the molecular complex,  $\mu_1$ , after the electron transition  $D \rightarrow A$ , if the distance is  $d_{DA} = 3.2 \cdot 10^{-10}$  m [22], is  $51.03 \cdot 10^{-30}$  C·m. In the knowledge of  $\mu_1$  and the transition moment,  $\mu_{EN}$  [22], and if the overlap integral is small (S

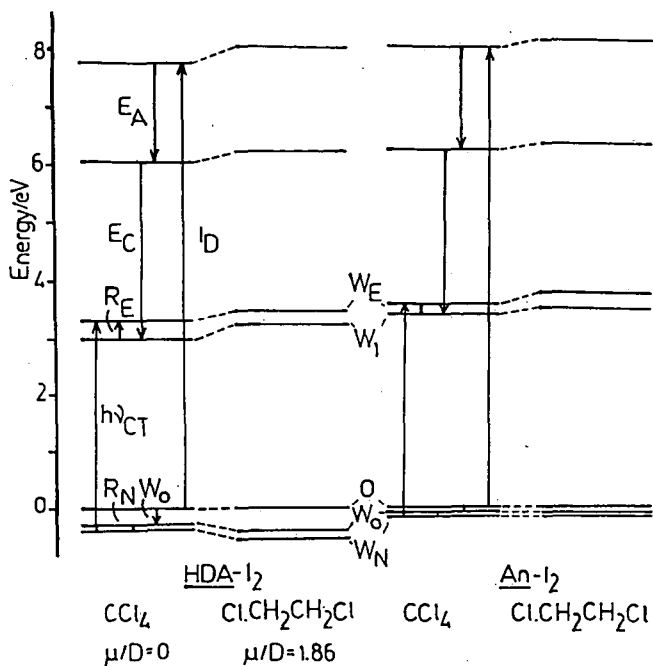


Figure 4: Energy level diagrams of HDA.I<sub>2</sub> (A) and An.I<sub>2</sub> (B) complexes, calculated with spectral data obtained in CCl<sub>4</sub> and (Cl-CH<sub>2</sub>)<sub>2</sub> solutions; the energy values are summarized in Table II.

= 0.1), it is possible to look for the optimum values of the coefficients  $a, a^*$ ,  $b, b^*$  and so calculate the parameters listed in Table II.

Thus, it seems that, for the complexes studied, the solvent effect is not particularly considerable.  $W_O - W_N$  and  $W_1 - W_E$  are the resonance energies, and it generally holds that  $W_1 - W_E > W_O - W_N$ . For our complexes, these energies lie in the ranges 24–40 and 10–14 kJ/mol, respectively; the energy values for the aniline complexes are somewhat higher. Since  $W_N = \Delta H$  [22], i.e. the heats of formation for HDA.I<sub>2</sub> and An.I<sub>2</sub> (solvents: CCl<sub>4</sub>,  $\mu=0$  C·m, and (Cl-CH<sub>2</sub>)<sub>2</sub>,  $\mu=6.20 \cdot 10^{-30}$  C·m) are

31.0, 54.6 and 10.9, 16.4 kJ/mol, respectively, the solvent dependence in the cases of the alkylamine complexes are more definite.

BHATTACHARYA and BASU [30] have estimated the stabilization energy of the ion pair  $D^+ - A^-$  for a series of iodine complexes of polynuclear aromatic hydrocarbons from  $\nu_{CT}$ , by using equation (a) and  $E_A = 1.80$  eV for iodine. The fact that their  $\Delta$  value (3.256 eV) is higher than the electrostatic energy between two charges separated by  $3-4 \cdot 10^{-10}$  m is offered as evidence that polarization and/or covalent forces make some contribution to the binding energy between D and A in the activated state, but the effect of the solvent cannot be excluded. Our  $\Delta$  values lie in the interval 2.8–3.0 eV; (the effect of the solvent is not determined and the change is not unambiguous).

The calculated binding energies  $E_B$  (Table II) are 0.2–0.4 and 0.08–0.10 eV for e two complexes, respectively [ $E_B = (\beta_o^2 + \beta_i)/(I_D - D)$ ,  $D = 6.0$  eV [19]]. The published  $E_B$  values [*e.g.* 19, 20], and presumably also our own data, are generally higher than the actual energy, because the two molecules forming the complex have been pulled together against no-bond state repulsive forces. The calculated  $E_B$  for published  $E_B$  values [*e.g.* 19, 20], and presumably also our own data, are generally higher than the actual energy, because the two molecules forming the complex have been pulled together against no-bond state repulsive forces. The calculated  $E_B$  for benzene. $I_2$  and dioxane. $I_2$ , for example, are 0.5 and 0.36 eV [19], while the experimental ones are 0.06 [21] and 0.15 eV [20], respectively. Our values agree well with the van der Waals energy  $W_o$  in the ground state (Table II). The data show that the resonance energy in the ground state is *arc.* 20–30 and 10–20 per cent, respectively, of the heat of formation  $\Delta H$ , which is in accordance with other observations [see *e.g.* 22].

The quotient  $100 b^2/(a^2 + b^2)$  is a measure of the participation of the ionic

structure in the ground state. For the discussed two complexes, 2.3, 4.9 and 0.4, 0.8 can be calculated. The low values for the complex  $An \cdot I_2$  are noteworthy similar low values have also been published for the complexes of styrene, diphenylbutadiene, *etc.* with *s*-trinitrobenzene, for example [22]. With increase in the dipole moment of the solvent, the probability of the presence of the ionic structure also increases. It is interesting that the presence of the ionic structure in the excited state of the two complexes discussed, relative to their ground states, decreases and increases, respectively (see Table II).

Table II

Calculated energetical parameters (eV) on the  $HDA \cdot I_2$  and  $An \cdot I_2$  complexes

	HDA · I <sub>2</sub>		An · I <sub>2</sub>	
	CCl <sub>4</sub>	ClCH <sub>2</sub> CH <sub>2</sub> Cl	CCl <sub>4</sub>	ClCH <sub>2</sub> CH <sub>2</sub> Cl
CT <sub>max</sub>	3.09	3.26	3.44	3.52
I <sub>D</sub>	7.69	7.91	8.13	8.25
h <sub>EN</sub>	3.01	4.04	1.64	2.14
a	0.970	0.970	0.980	0.980
a*	0.985	0.985	0.990	0.990
b	0.150	0.220	0.060	0.090
b*	0.120	0.180	0.100	0.110
R <sub>N</sub>	-0.071	-0.155	-0.013	-0.030
R <sub>E</sub>	0.178	0.250	0.088	0.108
E <sub>C</sub>	-2.80	-2.85	-2.89	-2.93
W <sub>1</sub>	3.09	3.26	3.44	3.52
W <sub>E</sub>	3.27	3.51	3.53	3.63
W <sub>o</sub>	-0.250	-0.410	-0.100	-0.140
W <sub>N</sub>	-0.321	-0.565	-0.113	-0.170
E <sub>B</sub>	-0.20	-0.40	-0.08	-0.11
ΔH/kJ/mol	31.0	54.6	10.9	16.4
100b <sup>2</sup> /(a <sup>2</sup> +b <sup>2</sup> )	2.3	5.1	0.4	0.8
100* <sup>2</sup> /(a* <sup>2</sup> +b* <sup>2</sup> )	1.5	3.3	1.0	1.2

In connection with the shape of the CT bands, it is interesting to observe the effects of solvents on it. While the measured CT bands always show asymmetry on the shorter wavelength side in  $\text{CHCl}_3$ ,  $\text{CH}_2\text{Cl}_2$ , *etc.* solutions, in  $\text{CCl}_4$  solution the bands are extremely broad and their complexity is obvious. Gaussian analysis results in two sub-bands at 365 and 401 nm; the distance between the two maxima is  $2500\text{ cm}^{-1}$ . The relative intensities of the bands depend on the ratio  $D/A$ ; the intensity of the 365 nm band,  $\epsilon_{365}$ , increases more rapidly than that of the  $\epsilon_{401}$  band, and the plot of the ratio  $\epsilon_{401}/\epsilon_{365}$  vs.  $\log[\text{alkylamine}]$  gives a linear correlation (Figure 5).

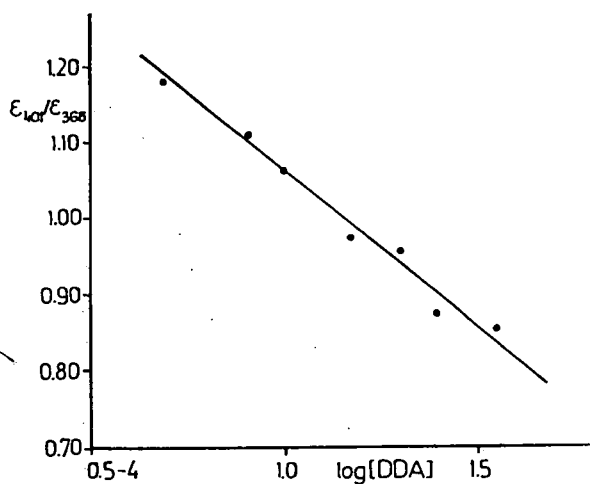


Figure 5: Plot of intensity ratios  $\epsilon_{401}/\epsilon_{365}$  vs.  $\log[\text{DDA}]$ . Solvent:  $\text{CCl}_4$

There may be many reasons for this band splitting. We consider it likely that, as a consequence of splitting of the ground state of the donor cation, the donor component has two ionization energies with close lying values; this supposition, however, requires further theoretical consideration. The complexity of the band is still more obvious

with shortening of the alkyl chain. A similar complexity of the CT bands has been described for several CT complexes [21–33].

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