Dipole Moments of Charge-Transfer Complexes between Iodine and Some Aliphatic Amines

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Abstract: The dipole moments of the charge-transfer complexes between iodine and several aliphatic amines were measured in benzene and dioxane. The following results were obtained: 6.2, 6.2–6.5, and 6.2 D. for the $(CH_3)_2CHNH_2$–I_2, $C_2H_5NH_2$–I_2, and $(C_2H_5)_2NH$–I_2 systems in benzene, respectively; 7.2, 7.0, and 6.1–6.7 D. for the $(CH_3)_2CHNH_2$–I_2, $(C_2H_5)_2NH$–I_2, and NH_3–I_2 systems in dioxane, respectively. It was found that the dipole moments of these systems greatly increase with the increment in the amine concentrations. This can be explained by considering that the contribution of the charge-transfer configuration in the ground states of these complexes increases with the increment in the dielectric constant of the environment. By analyzing the observed dipole moments by the aid of Mulliken's charge-transfer theory, it was found that the contribution of the charge-transfer configuration in the ground state amounts to 35–41% for the amine–iodine complexes under consideration. Furthermore, several energy quantities concerning the no-bond and charge-transfer configurations could be evaluated for the complexes.

Molecular complexes containing aliphatic amines as electron donors and iodine as electron acceptor have been studied extensively. Their equilibrium constants and heats of formation have been determined accurately in *n*-heptane solution.[1] The results show that aliphatic amines are in general very strong electron donors and form strong charge-transfer (abbreviated hereafter as CT) type complexes with iodine. This conclusion was also supported by the X-ray crystal analysis experiment made by Strømme,[2] which determined the N···I distance of the trimethylamine–iodine complex to be 2.27 A. This value is shorter than the van der Waals distance (3.65 A) and close to the sum (2.03 A) of the covalent radii of nitrogen and iodine.

From the above-mentioned facts, it may be inferred that the contributions of the CT structures are large in the ground states of the iodine complexes with aliphatic amines, and therefore their dipole moments are also very large. Actually Tsubomura and Nagakura determined the dipole moment of the triethylamine–iodine complex in dioxane to be 11.3 D.[3] This means that the contribution of the CT structure in the ground state of the complex amounts to 60%. There is a possibility, however, that the triethylamine–iodine system may exist as an ion pair in dioxane.[4]

Under these circumstances, it seems important to obtain experimental knowledge concerning the dipole moments of iodine complexes with other amines in dioxane and in the other solvents. We used ammonia, ethylamine, isopropylamine, and diethylamine as electron donors, and dioxane and benzene as solvents. In order to check whether the systems exist as CT complexes or as ion pairs, the electronic absorption spectra were also measured in parallel with the dipole moments.

Experimental Section

Materials. Dioxane was refluxed over sodium metal for more than 5 hr and was fractionally distilled immediately before use. Ammonia, ethylamine, diethylamine, iodine,[1] and benzene[5] were purified by the method reported previously. Isopropylamine was dried with KOH, and then was fractionally distilled twice with activated alumina.

Measurements of Dielectric Constants and Densities. The dielectric constants of solutions were measured with a resonance method apparatus, principally the same as that described in a previous paper.[6] A dielectric constant measurement cell with cylindrical platinum electrodes was used. The temperature was kept constant within 20 ± 0.3° during a series of measurements by using a dewar vessel containing oil. The densities of the solutions were measured by the use of an Ostwald-Sprengel pycnometer.

In a series of measurements, benzene or dioxane solutions containing a fixed concentration of an amine and various concentrations of iodine were used. The latter concentrations ranged from 0 to 0.07 *M* and did not exceed a tenth of that of amine in the solution. In actual experiment, mixed solvents containing benzene or dioxane and an amine were kept at a measurement temperature and then iodine was added just before the measurement, in order to avoid (or at least minimize) the effect of ion-pair formation and other chemical changes of the solutions upon the dielectric constant and density measurements.

Determination of Dipole Moments. In the evaluation of dipole moments from the observed dielectric constants and densities, it was assumed that all the iodine molecules in the solutions are complexed with amines, and that the concentrations of the free iodine, the iodine ion, the iodine complex with dioxane or benzene, and the ion-pair such as $R_3N^+I\cdots I_3^-$ (R = H or alkyl groups) are negligibly small. In actuality these assumptions were shown to be evident by measuring the electronic absorption spectra in parallel with the dipole moments and by analyzing the results. The details of this point are given in the Appendix.

Experimentally observed dielectric constants (ϵ_{123}) and densities (d_{123}) of the solutions were found to be linearly dependent upon the weight fractions (w_3) of molecular complexes for a series of measurements using the same mixed solvent, as is shown in Figure 1 for the dielectric constants of the benzene solutions.

$$\epsilon_{123} = \epsilon_{12}^0 + Aw_3 \qquad (1)$$

$$d_{123} = d_{12}^0 + Bw_3 \qquad (2)$$

Here ϵ_{12}^0 and d_{12}^0 are respectively the dielectric constant and density of the mixed solvent containing a fixed concentration of an amine. *A* and *B* are the proportionality constants and were determined by the slopes of straight lines.

The specific polarizations of the solution and the mixed solvent are given by the aid of Clausius-Mossotti's equation

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(1) H. Yada, J. Tanaka, and S. Nagakura, *Bull. Chem. Soc. Japan*, **33**, 1660 (1960).

(2) O. Strømme, *Acta Chem. Scand.*, **13**, 268 (1959).

(3) H. Tsubomura and S. Nagakura, *J. Chem. Phys.*, **27**, 819 (1957).

(4) K. Toyoda and W. B. Person, *J. Am. Chem. Soc.*, in press. S. N. expresses his sincere thanks to Professor Person for his kindness in showing his manuscript before publication.

(5) S. Nagakura and H. Baba, *ibid.*, **74**, 5693 (1952).

(6) S. Nagakura and A. Kuboyama, *Rept. Inst. Sci. Technol. Univ. Tokyo*, **4**, 242 (1950).

$$p_{123} = \frac{\epsilon_{123} - 1}{\epsilon_{123} + 2}\frac{1}{d_{123}} = (1 - w_2 - w_3)p_1 + w_2p_2 + w_3p_3 \quad (3)$$

$$p_{12}{}^0 = (1 - w_2{}^0)p_1 + w_2{}^0p_2 \quad (4)$$

Here w_2 and $w_2{}^0$ are the weight fractions of amine in solution and in mixed solvent, respectively. p_1, p_2, and p_3 represent the specific polarizations of solvent, amine, and complex, respectively. Equations 1–4 lead to the following equation

$$p_3 = p_{12}{}^0\left[1 + \frac{3A}{(\epsilon_{12}{}^0 + 2)(\epsilon_{12}{}^0 - 1)} - \frac{B}{d_{12}{}^0}\right] - (p_{12}{}^0 - p_1) + \left[w_2{}^0 + \frac{M_2}{M_3}(1 - w_2{}^0)\right](p_2 - p_1) \quad (5)$$

where M_2 and M_3 are molecular weights of amine and complex, respectively. In eq 5, the first term corresponds to the ordinary Halverstadt–Kumler equation,[7] and residual terms are corrections for the decrease of free amine concentration by the complex formation. Generally speaking, the latter terms are negligibly small compared with the former one.

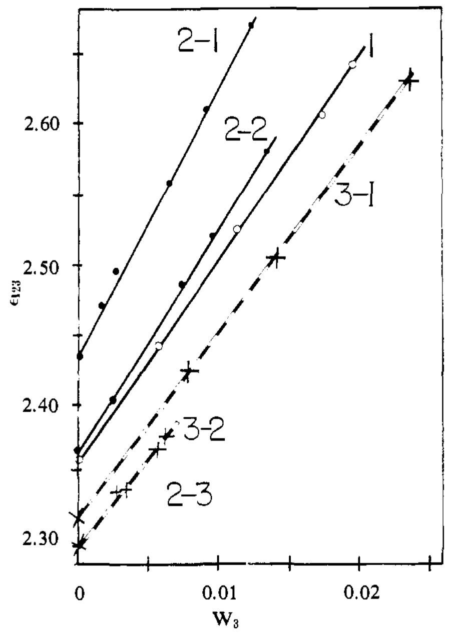

Figure 1. The relation between the dielectric constant of solutions (ϵ_{123}) and the weight fraction of complexes (w_3): (1) isopropylamine–iodine in benzene; (2-1, 2-2, 2-3) ethylamine–iodine in benzene for three ethylamine concentrations; (3-1, 3-2) diethylamine–iodine in benzene for two diethylamine concentrations.

From the value of p_3 evaluated by eq 5, the dipole moments of complexes (μ_N) were calculated by the Debye equation

$$\mu_N = 0.0128\sqrt{(M_3p_3 - P_{EA})T} \quad (6)$$

where P_{EA} is the sum of the electronic and atomic polarizations of the complex, and was evaluated as the sum of the atomic refractions.[8] The evaluated dipole moments are given in Table I.

For the isopropylamine–iodine and diethylamine–iodine systems in dioxane, the value of p_3 was evaluated by the following equation.

$$p_3 = [p_{123} - (1 - w_2 - w_3)p_1 - w_2p_2]/w_3 \quad (7)$$

The dipole moments determined from eq 6 and 7 are also shown in Table I.

Table I. Dipole Moments (μ_N in Debye Units) and Dielectric Constants of Mixed Solvents ($\epsilon_{12}{}^0$)

Donor	Solvent	$\epsilon_{12}{}^0$	μ_N, D.
Isopropylamine	Benzene	2.358	6.2
	Dioxane		7.2
Ethylamine	Benzene	2.443	6.6
		2.365	6.5
		2.314	6.2
Diethylamine	Benzene	2.317	6.2
		2.295	6.2
	Dioxane		7.0
Ammonia	Dioxane	2.307	6.7
		2.273	6.2
		2.251	6.1

Results and Discussion

The linear relationship between the weight fractions of the complex and the dielectric constants or the densities of the solutions seem to show that, under the present experimental conditions, the dipole–dipole interaction between the complexes is negligibly small, and time-dependent processes, for example, leading to ion-pair formation, give no serious effect upon the measurements. Furthermore, these linearities seem to offer evidence that all of the iodine molecules in the solution are completely complexed with amine.

The dipole moments of the iodine complexes with isopropylamine and diethylamine were measured in both benzene and dioxane. Furthermore, the dipole moments were determined for the solutions with various concentrations of each amine. The inspection of Table I shows that the dipole moments of the complexes are larger by 0.8–1.0 D. in dioxane than in benzene. This tendency is generally observed with dipole moment measurements. For example, the dipole moment of *p*-nitroaniline is 6.17 and 6.81 D. in benzene and dioxane, respectively.[5] In this case, the difference of the dipole moment between the two solutions is 0.64 D. and may be regarded as being of the same order of magnitude as that in the case of the amine–iodine system.

The dipole moments of the complexes increased with the increment of amine concentration in the mixed solvent. Since the dielectric constant of the mixed solvent increases with the increment in the amine concentration, this tendency seems to mean that the dipole moment of the complex increases with the increase in the solvent dielectric constant. This may be interpreted by considering the greater stabilization of the CT structure with the increase in dielectric constants of the media. This point will be discussed later somewhat quantitatively.

According to Mulliken's CT theory,[9] the wave functions of the ground (Ψ_N) and excited (Ψ_E) states of the CT complex can be written approximately as the linear combination of the no-bond structure $\psi_0(D \cdots A)$ and CT structure $\psi_1(D^+\text{–}A^-)$ wave functions.

$$\Psi_N = a\psi_0(D \cdots A) + b\psi_1(D^+\text{–}A^-)$$

$$\Psi_E = -b^*\psi_0(D \cdots A) + a^*\psi_1(D\text{–}A^-)$$

The dipole moment of the ground state, μ_N, can be represented by the following equation on the assumption that the dipole moment of the no-bond structure is

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[7] I. F. Halverstadt and W. D. Kumler, *J. Am. Chem. Soc.*, 64, 2988 (1942).

[8] Strictly speaking, we must use the P_{EA} value for the complex which may be somewhat different from that obtained as the sum of the corresponding quantities for the component molecules. This point was discussed in detail by Toyoda and Person (see ref 4) who concluded that the change of the P_{EA} value due to the CT interaction gives only negligibly small effect to the evaluation of dipole moments.

[9] R. S. Mulliken, *J. Am. Chem. Soc.*, 74, 811 (1952).

Table II. The Calculated Values of Various Quantities

Donor	μ_N	a	b	$b^2 + abS$	β_0	β_1	X_0	X_1	W_0	W_1	Solvent	$h\nu_{CT}$, ev	ΔH, ev
Ammonia	6.1	0.74	0.49	0.35	−2.14	−2.58	−1.19	2.75	0.98	2.46	Dioxane	5.41	0.21
	6.7	0.72	0.52	0.38	−2.22	−2.58	−1.32	2.90	1.11	2.32	Dioxane		
Ethylamine	6.2	0.74	0.49	0.35	−1.99	−2.40	−1.10	2.56	0.79	2.16	Benzene	5.04	0.32
	6.6	0.72	0.51	0.37	−2.05	−2.40	−1.20	2.67	0.88	2.05	Benzene		
Isopropylamine	6.2	0.74	0.49	0.36	−2.00	−2.41	−1.13	2.64	0.79	2.08	Benzene	5.02	0.35
	7.4	0.68	0.55	0.41	−2.14	−2.37	−1.40	2.93	1.05	1.76	Dioxane		
Diethylamine	6.2	0.74	0.49	0.34	−1.86	−2.25	−1.02	2.37	0.60	1.92	Benzene	4.77	0.42
	7.0	0.70	0.53	0.39	−1.99	−2.25	−1.23	2.61	0.81	1.73	Dioxane		

negligibly small compared with that of the CT structure (μ_1)[10]

$$\mu_N = \mu_1(b^2 + abS) \qquad (8)$$

where S is the overlap integral between ψ_0 and ψ_1. Furthermore, the normalization conditions $a^2 + b^2 + 2abS$ and $a^{*2} + b^{*2} - 2a^*b^*S = 1$ must be satisfied. If the values of S and μ_1 are known, one can evaluate a, b, and the contribution of the CT structure in the ground state, $100(abS + b^2)$, from the observed dipole moment.

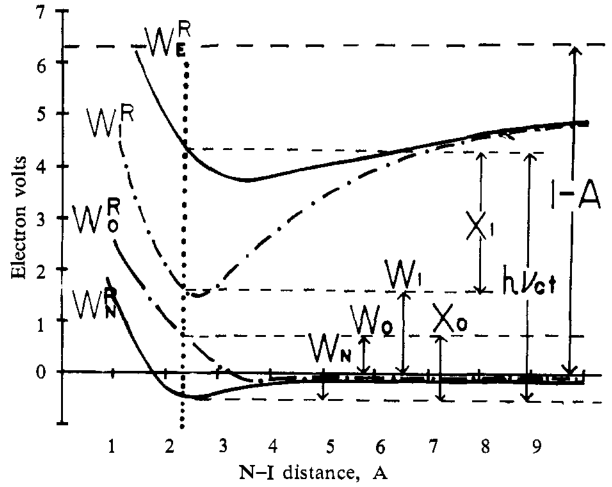

Figure 2. The schematic relation of various energy quantities for the diethylamine–iodine complex in dioxane.

Concerning the ground state (W_N) and excited state (W_E) energies, the following equations can be obtained[11,12]

$$W_N = W_0 + X_0 \qquad (9)$$

$$W_E = W_1 + X_1 \qquad (10)$$

where

$$X_0 = k\beta_0/(1 + kS); \quad X_1 = k^*\beta_1/(1 - k^*S) \qquad (11)$$

$$k^* = b^*/a^* = (k + S)/(1 + kS); \quad k = b/a \qquad (12)$$

$$\beta_1 = k^*\beta_0/k \qquad (13)$$

W_0 and W_1 are the energies of the no-bond and CT structures in the stable geometrical configuration of the complex, respectively. X_0 and X_1 are the resonance interaction energies in the ground and excited states, respectively. β_0 and β_1 are the resonance integrals. The CT transition energy ($h\nu_{CT}$) and the heat of formation (ΔH) can be given by the following equations.

$$h\nu_{CT} = W_E - W_N = [(1 + 2kS + S^2)/k(1 + kS)(1 - S^2)]^*(-\beta_0) \qquad (14)$$

$$\Delta H = -W_N \qquad (15)$$

The relation among the above-mentioned energy quantities is schematically shown in Figure 2, taking the iodine–diethylamine–benzene system as an example.

The geometrical configuration of the complex is necessary for the evaluation of S and μ_1. Concerning the trimethylamine–iodine complex, it was determined by Strømme[2] as is shown in Figure 3. We assumed that this geometrical configuration can approximately be applied to the other amine–iodine complexes, and that in the CT structure a negative charge is located on the center of the iodine molecule and a positive charge is on the nitrogen atom. From these assumptions, μ_1 was estimated to be 17.7 D. For the overlap integral, the reasonable value of $S = 0.3$ was adopted to all the complexes.[1,12,13] By combining the observed μ_N, $h\nu_{CT}$, and ΔH values in addition to μ_1 and S mentioned above with eq 8–15, we can estimate various quantities tabulated in Table II. According to the present estimation given in Table II, the contribution of the CT structure in the ground state amounts to 35–41% for the amine–iodine complexes under consideration.

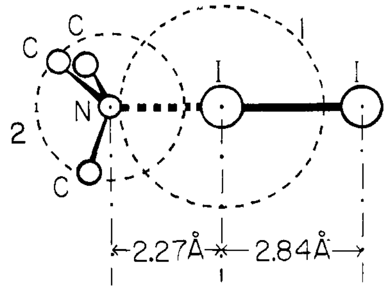

Figure 3. The spacial configuration for the trimethylamine–iodine complex. Circles 1 and 2 are the van der Waals radii for I and N, respectively.

The large positive values of W_0 indicate that the no-bond structures are strongly repulsive. It is reasonable because the N–I distance in the amine–iodine complex is considerably shorter than the van der Waals distance between N and I. This means that the resonance

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[10] Actually μ_1 and μ_0 are respectively 17.7 and 1.5~0.9 D. Therefore, the above assumption may be considered to be satisfied.

[11] R. S. Mulliken and W. B. Person, *Ann. Rev. Phys. Chem.*, **13**, 107 (1962).

[12] G. Briegleb, "Elektronen-Donator-Acceptor-Komplexe," Springer-Verlag, Berlin, 1961.

[13] W. B. Person, *J. Chem. Phys.*, **38**, 109 (1963).

Table III. Equilibrium Constants (K_1), Maximum Wavelengths (λ), and Molar Extinction Coefficient for the Isopropylamine–Iodine and Diethylamine–Iodine Systems in Various Solvents

Donor	Solvent	λ_{CT}, mμ	$\epsilon_{CT} \times 10^{-4}$	K_1[a]	λ_{vis}, mμ	$\epsilon_{vis} \times 10^{-3}$
Isopropylamine	Dioxane	253	3.55	57,800	375	2.0
	Benzene			1,770	380	2.7
	n-Heptane	248	2.3	1,000	412	1.5
Diethylamine	Dioxane	263	2.90	146,000	385	2.2
	n-Heptane	260	2.50	6,900	410	

[a] The K_1 values for the benzene and dioxane solutions were obtained at 22.5°. The observed A_λ values for various d values are shown in Table IV.

stabilization energy $|X_0|$ is considerably larger than the observed heat of formation.

Table II shows that W_1 decreases and $b^2 + abS$, $|\beta_0|$, $|X_0|$, $|X_1|$, and $|W_0|$ become larger with the increment in the amine concentration of the mixed solvent and by changing solvent from benzene to dioxane.

Previously, Nagakura, *et al.*, proposed $\beta = -2.32$ ev for primary amines and ammonia, $\beta = -2.20$ ev for secondary amines, and $\beta = -2.09$ ev for tertiary amines, where β is the approximate average of β_0 and β_1.[1,13] Person proposed the values $W_0 = 0.97$ ev and $X_0 = -1.15$ ev for the ammonia–iodine complex, and $\beta_0 = -2.5$ ev for all the amine–iodine complexes with the aid of spectroscopic consideration.[13] The W_0 and X_0 values estimated by Person are satisfactorily coincident with the corresponding values by the present authors. But the β_0 value estimated by Person seem to be somewhat too large, because from the condition that $h\nu_{CT} \geq -2\beta_0/\sqrt{1 - S^2}$, $\beta_0 = -2.5$ ev will give complex "k" values except for the ammonia–iodine complex.

Appendix

In order to check whether or not all the iodine molecules in the solutions are complexed with amine and whether or not the concentrations of I_3^- and other ionic species are negligibly small, we measured the electronic absorption spectra parallel with the dipole moments. Furthermore, the equilibrium constants between iodine and amines in dioxane or in benzene were evaluated by analyzing the electronic absorption spectra. Absorption spectra were measured with a Cary recording spectrophotometer Model 14.

Benzene[14] and dioxane[15] are known to form CT complexes with iodine. Therefore, in the iodine–amine–benzene or –dioxane systems there exist the following equilibria where D, A, C, S, and E represent amine,

$$D + A \rightleftharpoons C;\quad K_1 = c/(\bar{a} - c - e)(d - c) \quad (16)$$

$$S + A \rightleftharpoons E;\quad K_2 = e/(\bar{a} - c - e)(s - e) \simeq e/(\bar{a} - c - e)S \quad (17)$$

iodine, amine–iodine complex, solvent, and solvent–iodine complex, respectively. The small letters d, $\bar{a}$, c, s, and e are the concentrations of the corresponding species in moles/liter, respectively. K_1 and K_2 are the equilibrium constants of the amine–iodine and solvent–iodine complexes in solution.

On the assumption that K_1 and K_2 are independent from the solvent, we can easily show by the aid of the K_1 and K_2 values obtained in an inert solvent, say *n*-heptane, that all the iodine molecules are complexed with amine under the present experimental conditions of the dielectric constant measurements.

For the amine–iodine complexes, however, it seems probable that the solvent effect is considerably large, because of their large dipole moments. Therefore, we undertook to evaluate again K_1 in benzene and dioxane solutions from the analysis of the observed electronic absorption spectra.

The absorbance (A_λ) of the solution per 1-cm light path length at the wavelength λ can be represented by the following equation on the assumption that $\epsilon_D = \epsilon_A = 0$.

$$A_\lambda = \epsilon_C c + \epsilon_E e \quad (18)$$

Here ϵ_D, ϵ_A, ϵ_C, and ϵ_E are the molar extinction coefficients of D, A, C, and E, respectively. From eq 16, 17, and 18, the following equations can be obtained.[16]

$$\frac{1 + sK_2}{K_1} = \frac{A_\lambda - \epsilon_E'\bar{a}}{\epsilon_C - \epsilon_E'} - (\bar{a} + d) + \bar{a}d\,\frac{\epsilon_C - \epsilon_E'}{A_\lambda - \epsilon_E'\bar{a}} \quad (19)$$

$$\epsilon_E' = \frac{sK_2}{1 + sK_2}\epsilon_E \quad (20)$$

The studies of the benzene–iodine[14] and dioxane–iodine[15] complexes in inert solvents have shown that the equilibrium constants and molar extinction coefficients of these systems are almost independent from the donor concentrations. Hence, by the aid of the values of K_2 and ϵ_E obtained in the inert solvents, the evaluation of K_1 and ϵ_C can be carried out accurately by eq 19 and 20.

K_1 and ϵ_C were evaluated graphically by the aid of the method developed by Rose and Drago;[17] namely, by plotting the relationship between $1/K_1$ and ϵ_C given by eq 19 for each set of a, d, and A_λ, and by reading the intersection of the curves corresponding to various sets of a, d, and A_λ values. In actuality the above-mentioned plots were found to intersect with one another in a small region for each of the isopropylamine–iodine–dioxane, isopropylamine–iodine–benzene, and diethylamine–iodine–dioxane systems. This shows that the equilibrium of the 1:1 CT complex formation shown by eq 16 exists for the systems. The evaluated K_1, ϵ_C, and other spectroscopic data are tabulated in Table III. In this table the corresponding spectroscopic data and the equilibrium constant in the *n*-heptane solution are also given for the purpose of comparison. The amine concentrations and the observed absorbance values are tabulated in Table IV.

Tables III and IV show that, as compared with the values obtained in *n*-heptane solution, the CT bands shift to longer wavelengths in dioxane, with the increase

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(14) H. A. Benesi and J. H. Hildebrand, *J. Am. Chem. Soc.*, **71**, 2703 (1949).

(15) J. A. A. Ketelaar, C. van de Stolpe, A. G. Oudsmit, and W. D. Zcubas, *Rec. Trav. Chim.*, **71**, 1104 (1952).

(16) M. Tamres, *J. Phys. Chem.*, **65**, 654 (1961).

(17) N. J. Rose and R. S. Drago, *J. Am. Chem. Soc.*, **81**, 6138 (1959).

Table IV. Observed Absorbance Values

Isopropylamine–iodine (2.707×10^{-5} *M*) in dioxane		Isopropylamine–iodine (1.932×10^{-4} *M*) in benzene		Diethylamine–iodine (3.228×10^{-5} *M*) in dioxane	
Amine concn, *M*	A_λ at 270 mμ	Amine concn, *M*	A_λ at 380 mμ	Amine concn, *M*	A_λ at 270 mμ
1.926×10^{-2}	0.573	2.751×10^{-3}	0.336	5.169×10^{-4}	0.805
1.926×10^{-3}	0.538	5.501×10^{-3}	0.384	2.585×10^{-4}	0.648
0.963×10^{-3}	0.488	5.501×10^{-2}	0.482	1.293×10^{-4}	0.498
0.481×10^{-3}	0.423			5.169×10^{-5}	0.346
0.963×10^{-4}	0.168			2.585×10^{-5}	0.258

in molar extinction coefficients, and that the iodine bands shift to shorter wavelengths and become stronger in dioxane than in benzene. These results can be interpreted by considering the fact that the CT structure is more stabilized in these two solvents than in *n*-heptane. According to the present results, the equilibrium constants of the isopropylamine–iodine and diethylamine–iodine systems are abnormally large in dioxane compared with those in benzene and *n*-heptane.[18]

By the aid of the K_1 value obtained with the dioxane and benzene solutions, it can be concluded that all the iodine molecules are complexed with amine under the conditions used in the dielectric constant measurements.

Next, let us consider whether or not the I_3^- or I^- ions exist in the benzene or dioxane solutions used for the dielectric constant measurements. The iodine and amine concentrations in these solutions are 0.03 and 0.2–0.6 *M*, respectively. Therefore their electronic absorptions could not be measured in the ultraviolet region below 300 mμ, even by the use of 0.01-cm light path length cell because of their strong absorptions in that wavelength region. Therefore we restricted our attention to the shifted iodine band.

The system containing 0.618 *M* of isopropylamine and 0.0226 *M* of iodine in dioxane shows the absorption peak at λ_{vis} 372 mμ with the peak molar extinction coefficient ϵ_c 2900. These values correspond to those for the dilute solution given in Table III, λ_{vis} 375 mμ and ϵ_c 2000. The similar phenomena were observed with the other systems such as the iodine–isopropylamine–benzene and diethylamine–iodine–dioxane system.

Popov and Swensen[19] have studied the electronic absorption of the triiodide ion in acetonitrile and ethylene dichloride. The result showed that the absorption spectrum of the triiodide ion appears at 360 mμ with ε 25,500 in acetonitrile (in this solvent the triiodide ion exist as a free ion), at 362 mμ with ε 25,000 in ethylene dichloride (in this solvent the triiodide ion exists as an ion pair with the tetramethylammonium ion). In view of the fact that the maximum wavelength and intensity of the triiodide ion spectrum may conceivably be insensitive to the environment, it may be concluded that the 372-mμ band (ε 2900) observed with the isopropylamine–iodine–dioxane system cannot be ascribed to the triiodide ion but can be assigned to the shifted iodine band of the CT complex. The same is the case for the bands observed with the isopropylamine–iodine–benzene and diethylamine–iodine–dioxane system. Therefore it may safely be said that the concentration of the triiodide ion is negligibly small under the present experimental conditions adopted in the dielectric constant measurement.[20] From this and the results of the consideration of equilibrium constants, it seems to be conclusive that almost all the iodine molecules are complexed with amine in the solution used for the dielectric constant measurements.

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(18) The free-energy difference between the *n*-heptane and dioxane solution can be obtained for the diethylamine–iodine complex as follows: $\Delta F = -RT \ln K_1$ (*n*-heptane) $+ RT \ln K_1$ (dioxane) $= 1.8$ kcal/mole. This seems not to be unreasonable.

(19) A. I. Popov and R. F. Swensen, *J. Am. Chem. Soc.*, 77, 3724 (1955).

(20) The iodine–amine complexes with large dipole moments may reasonably expected to be more stable in dioxane and benzene than in *n*-heptane. Actually the complexes are unstable in the *n*-heptane solutions with such high concentrations as those of the dioxane or benzene solutions used in the dielectric constant measurements.