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Pressure and Solvent Shifts of Charge Transfer Absorption Band of Iodine Complexes

Seiji SAWAMURA, Yoshihiro TANIGUCHI, and Keizo SUZUKI*

Department of Chemistry, Faculty of Science and Engineering, Ritsumeikan University, Kita-ku, Kyoto 603

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Absorption spectra of the CT band of I_2 complexes were observed in several nonpolar solvents at 1 bar, and in heptane up to 4400 bar. All solvent shifts were red with an increase in $(n^2-1)/(2n^2+1)$, the refractive index (n) function of solvents, consistent with the solvent shift theory. On the other hand pressure caused a variety of shifts, that is, red shifts in benzene–, toluene–, and mesitylene–I_2 complexes, an inversion shift from red to blue in HMB–I_2 complex, and blue shifts in Et_3N–, n-Pr_3N–, and n-Bu_3N–I_2 complexes, though increase in pressure invariably raises the $(n^2-1)/(2n^2+1)$ value of solvent. The pressure shifts of I_2 complexes seem to be interpreted by a sum of two effects. One is the increased polarity of the solvent, which causes a red shift. The other is the decrease in the bond distance between a donor and an acceptor, which contributes to a blue shift in a strong CT complex and to a red shift in a week one. The pressure and solvent shifts of I_2 complexes were compared with those of π-donor–TCNE complexes.

Recently, we found the pressure shifts of charge transfer (CT) absorption band of n-donor (diethyl sulfide (Et_2S) and diethyl selenide (Et_2Se))–iodine (I_2) complexes in heptane, changing from red to blue at *ca.* 2500 bar.[1] Such an inversion shift is known only in the π-π complex between hexamethylbenzene (HMB) and tetracyanoethylene (TCNE).[2–4] The other CT bands of π-π complexes[2–5] and π-donor–I_2 complexes[6,7] in solution shifted only to red.

In the present work we have found blue shifts of well-defined CT band of amine–I_2 complexes in heptane. In polymer matrix the blue shift of CT band was reported by Offen and Nakashima[8] in two π-π complexes between *trans*-stilbene and phenanthrene as donors and 2,3-dichloro-5,6-dicyano-*p*-benzoquinone (DDQ) as an acceptor. However, it seems to be obscured by a strong overlap with another absorption band.

The red shift of CT band has been interpreted by an increase in the polarity of the solvent with increase in pressure.[6,9,10] Two different interpretations have been proposed for the blue shift: (1) Offen and Nakashima[8] tried to explain the blue shift of DDQ complexes by a decrease in the bond distance between a donor and an acceptor. (2) Nakayama *et al.*[4] ascribed the blue shift of HMB–TCNE complex to an increase in the polarity of solvent caused by pressure, the relevance of the interpretation being examined by a comparison of the pressure shift of CT band with the solvent shift.

In the present work we measured the pressure shifts of CT bands of I_2 complexes with several π- and n-donors up to 4400 bar. In order to interpret them, the observed pressure shifts, red, red to blue, or blue, were compared with the solvent shifts.

Experimental

I_2 was sublimed from a mixture of I_2, calcium oxide, and potassium iodide, and then was done under nitrogen atmosphere. TCNE was sublimed under reduced pressure (10 mmHg). The purification of diethyl ether (Et_2O), Et_2S, and Et_2Se was reported.[1] HMB was recrystallized twice from ethanol. Triethylamine (Et_3N), tripropylamine (n-Pr_3N), and tributylamine (n-Bu_3N) were shaken with acetic anhydride, dried over potassium hydroxide and sodium metal successively, and distilled over sodium metal (under reduced pressure for the last two amines, 34—36 °C/6 mmHg and 51—52 °C/2 mmHg, respectively). The other donors (benzene, toluene, and mesitylene) and the solvents (pentane, heptane, cyclohexane, carbon tetrachloride, decalin, and carbon disulfide) were purified by the usual method.[11] The method of measuring the absorption spectra under high pressure was reported[1]

Results

Solvent Shift. The dielectric constant or refractive index (n) of solvent has been often used as a measure of the property of solvent for interpretation of the solvent shift of the electronic spectrum. Theories given by Ooshika[12] and McRae[13] on solvent shift predicted that the wavenumber at absorption maximum ($\tilde{\nu}_{max}$) of electronic spectrum depends linearly on the value of $(n^2-1)/(2n^2+1)$ of nonpolar solvents. The linear relation between $\tilde{\nu}_{max}$ of CT band and $(n^2-1)/(2n^2+1)$ has been reported for several π-donor–TCNE[14,15] and π-donor–I_2[6] complexes. Pressure shifts to red in the latter complexes were interpreted by Ham[6] in comparison with the solvent shifts using the function of $(n^2-1)/(2n^2+1)$.

The $\tilde{\nu}_{max}$ values of I_2 complexes in several nonpolar solvents at 1 bar are plotted as a function of $(n^2-1)/(2n^2+1)$ of solvents, including that of HMB–TCNE complex, in Figs. 1 and 2. All CT bands shift linearly to red with increase in the $(n^2-1)/(2n^2+1)$ values of solvents. The red shift in HMB–TCNE complex observed by Voigt[14] was confirmed. The $\tilde{\nu}_{max}$ values of mesitylene–, and Et_2S–I_2 complexes in gaseous state fit the lines. The values of the slopes (Figs. 1 and 2) are given in Table 1 as C_{solv}, together with the data of π-donor–TCNE complexes. For the I_2 complexes with a series of π-donors (Table 1-A) the values of C_{solv} increase with an increase in the bond energy ($-\Delta H$). A similar trend is seen for n-donor–I_2 and π-donor–TCNE (Table 1-B and C, respectively) but not so marked in the latter.

Pressure Shift. Absorption spectra of the CT band of n-Bu_3N–I_2 complex under various pressures are shown in Fig. 3. The absorption maximum shifts toward blue with increase in pressure. Similar well-defined

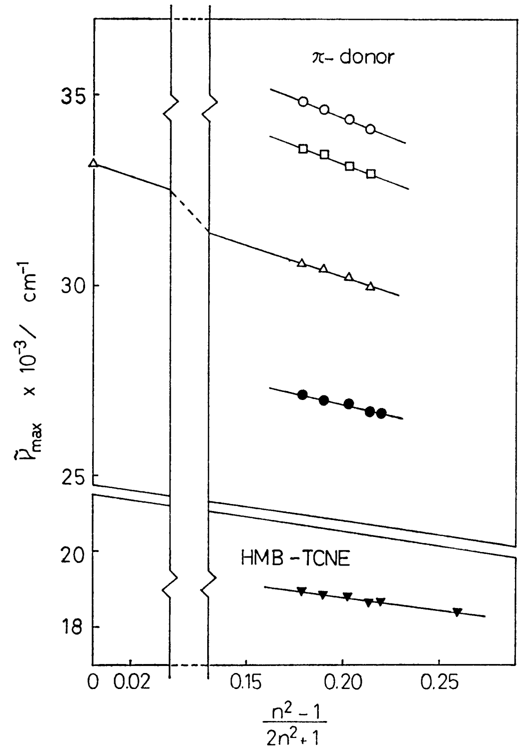

Fig. 1. Solvent shifts on CT absorption maxima of the I_2 complexes with π-donors, including HMB–TCNE complex. Donors are, ○: benzene, □: toluene, △: mesitylene, and ●: HMB in I_2 complexes. Solvents are pentane ($(n^2-1)/(2n^2+1)=0.179$), heptane (0.190), cyclohexane (0.203), carbon tetrachloride (0.214), decalin (0.220), and carbon disulfide (0.261), adding the data in gaseous state (0.000) of Ref. 16 for mesitylene–I_2 complex. The values of n of solvents were cited from Ref. 11.

absorption spectra were also observed in Et_3N– and n-Pr_3N–I_2 complexes, causing blue shifts.

Figures 4 and 5 show the pressure shifts of absorption maxima of several I_2 complexes as a function of $(n^2-1)/(2n^2+1)$ of heptane. Various pressure shifts were observed: red shifts in benzene–, toluene–, mesitylene–, and Et_2O–I_2 complexes, inversion shifts from red to blue in HMB–, Et_2S–, and Et_2Se–I_2 complexes, and blue shifts in Et_3N–, n-Pr_3N–, and n-Bu_3N–I_2 complexes. The values of the initial slope in Figs. 4 and 5 are given in Table 1 as C_{press}, with the values of π-donor–TCNE complexes given by Nakayama *et al.*[4]

In I_2 or TCNE complexes with benzene, toluene, and mesitylene (Table 1), each slope estimated from the pressure shift (C_{press}) is smaller than that estimated from the solvent shift (C_{solv}). The reverse is found in other CT complexes, except in the case of comparable values in Et_2O–I_2 complex. In the series of π-donor–I_2 complexes, C_{press} becomes large accompanied by an increase in the bond energy ($-\Delta H$). A similar relation between C_{press} and $-\Delta H$ is found in n-donor–I_2 complexes and π-donor–TCNE complexes, though less explicit in the former.

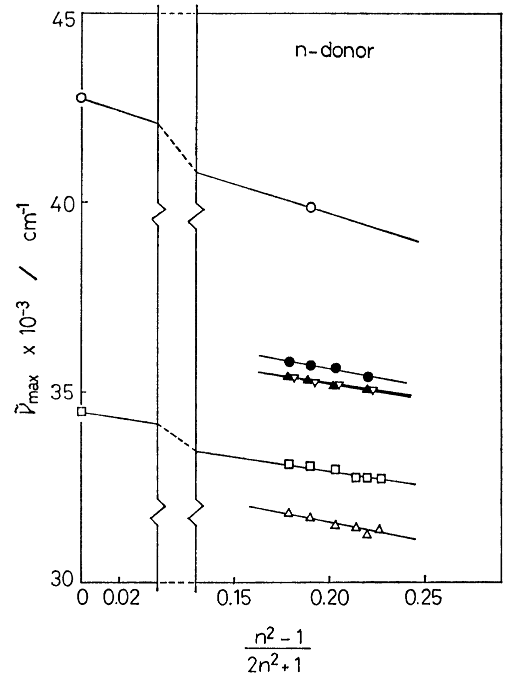

Fig. 2. Solvent shifts on CT absorption maxima of the I_2 complexes with n-donors. Donors are, ○: Et_2O, □: Et_2S, △: Et_2Se, ●: Et_3N, ▲: n-Pr_3N, and ▽: n-Bu_3N. Solvents are the same as Fig. 1, adding benzene (0.227) instead of carbon disulfide. Gaseous data for Et_2O– and Et_2S–I_2 complexes are cited from Refs. 16 and 17, respectively.

TABLE 1. SLOPES OF SOLVENT (C_{solv}) AND PRESSURE (C_{press}) SHIFT AND THE BOND ENERGY ($-\Delta H$) OF SEVERAL CT BANDS

Complex	C_{solv} / 10^3 cm^{-1}	C_{press}[a] / 10^3 cm^{-1}	$-\Delta H$ / kJ mol^{-1}
(A) π-Donor–I_2			
Benzene–I_2	−20±2	−29±3	6[b]
Toluene–I_2	−19±2	−24±2	8[c]
Mesitylene–I_2	−16±2	−22±3	12[b]
HMB–I_2	−12±2	−8±2	16[b]
(B) n-Donor–I_2			
Et_2O–I_2	−16±2	−17±4	18[d]
Et_2S–I_2	−9±2	−5±2	33[e]
Et_2Se–I_2	−10±2	−4±2	41[f]
Et_3N–I_2	−9±2	+3±2	50[g]
n-Pr_3N–I_2	−9±2	+8±3	51[g]
n-Bu_3N–I_2	−8±2	+4±2	52[g]
(C) π-Donor–TCNE			
Benzene–TCNE	−12[h]	−17	10[i]
Toluene–TCNE	—	−15	11[i]
Mesitylene–TCNE	−7[h]	−12	19[i]
HMB–TCNE	−5[h] −7±2	0	32[i]

a) Estimated from the straight line through the two points at 1 and 1100 bar in Figs. 4 and 5. Values for (C) complexes were estimated with data taken from Ref. 4 at 1 and 1500 bar in CCl_4. b) Ref. 18. c) Ref. 19. d) Ref. 20. e) Ref. 21. f) Ref. 22. g) Ref. 23. h) Ref. 14. i) Ref. 24.

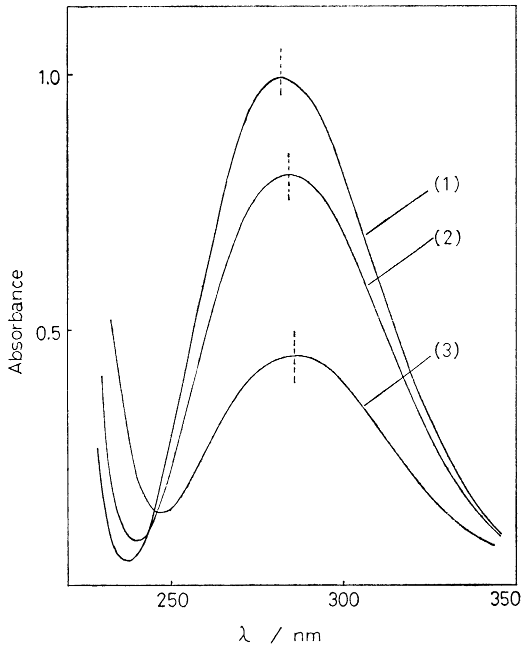

Fig. 3. Absorption spectra of CT band of n-Bu$_3$N–I$_2$ complex in heptane. n-Bu$_3$N: 5×10^{-4} mol dm^{-3}, I$_2$: 3.5×10^{-5} mol dm^{-3}. (1) 4.4 kbar, (2) 2.2 kbar, (3) 1 bar. Dotted lines show the absorption maxima at each pressure.

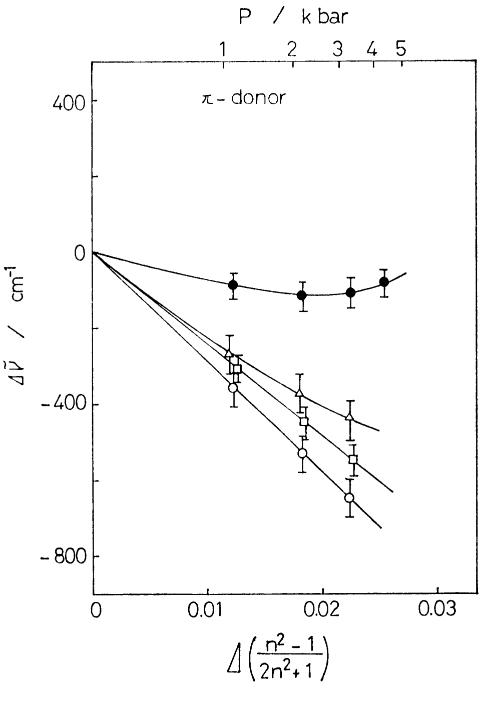

Fig. 4. Pressure shifts of CT absorption maxima of the I$_2$ complexes with π-donors in heptane. The marks of π-donors are the same as in Fig. 1. $\Delta\tilde{\nu}=\tilde{\nu}_{\max}$ (at P bar) $-\tilde{\nu}_{\max}$ (at 1 bar). The value of n of heptane under high pressure was cited from the dielectric constant (ε) of heptane in Ref. 25 using the relation of Maxwell ($\varepsilon=n^2$). $\Delta[(n^2-1)/(2n^2+1)]=(n_P^2-1)/(2n_P^2+1)-(n_1^2-1)/(2n_1^2+1)$.

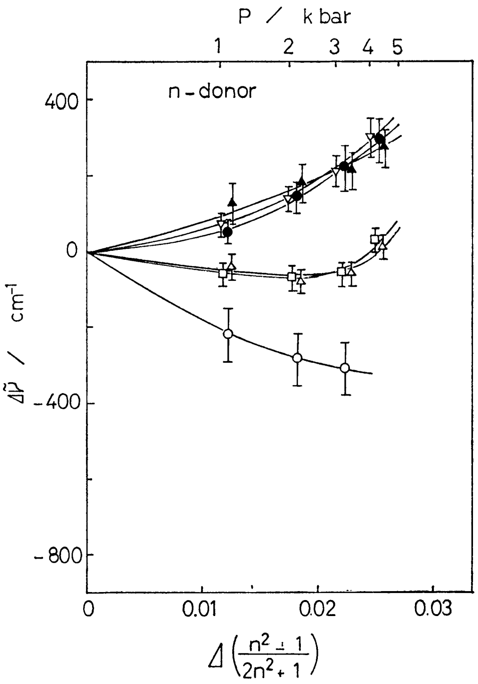

Fig. 5. Pressure shifts of CT absorption maxima of the I$_2$ complexes with n-donors in heptane. The marks are the same as in Fig. 2. $\Delta\tilde{\nu}$ and $\Delta[(n^2-1)/(2n^2+1)]$ are defined in Fig. 4. The data of Et$_2$O–, Et$_2$S–, and Et$_2$Se–I$_2$ complexes are cited from Ref. 1.

Discussion

Linear red shift of CT bands in Figs. 1 and 2 are in line with the solvent shift theory as in the case of π-donor–TCNE[14,15] and π-donor–I$_2$[6] complexes. The result that C_{solv} values (Table 1-A, B, and C) increase accompanied by an increase in $-\Delta H$ would be interpreted by the solvent shift theory regarding $-\Delta H$ as a measure of the CT interaction, since the excited state of CT band becomes less polar and the dipole moment of the ground state increases with increasing CT interaction.[26,27]

In Figs. 4 and 5 the values of $(n^2-1)/(2n^2+1)$ of heptane are 0.190 at 1 bar 0.216 at 4400 bar. The values are covered by those in Figs. 1 and 2, *viz.*, 0.179 for pentane to 0.261 for carbon disulfide. If the pressure shifts of CT bands are attributed to only the increasing polarity of solvent, red shifts similar to those given in Figs. 1 and 2 can be expected in Figs. 4 and 5, respectively. In HMB–, Et$_2$S–, and Et$_2$Se–I$_2$ complexes, however, the observed inversion shifts differ from the expected ones, the blue shifts of Et$_3$N–, n-Pr$_3$N–, and n-Bu$_3$N–I$_2$ complexes (Fig. 5) being a striking contrast to the red shifts (Fig. 2). The solvent shift of HMB–TCNE complex (Fig. 1) is not in line with the inversion shift caused by increase in pressure. Though the increasing polarity of the solvent caused by compression may contribute to a red shift, another effect causing a blue shift should participate in at least HMB–, Et$_2$S–, Et$_2$Se–, Et$_3$N–, n-Pr$_3$N–, and n-Bu$_3$N–I$_2$ complexes, and HMB–TCNE complex.

As a plausible effect causing a blue shift, a decrease in the bond distance (R_{DA}) between a donor and an acceptor proposed by Offen and Nakashima[8] may be taken into account. The effect is interpreted by means of the Mulliken's equation[27] for the CT transition energy $hc\tilde{\nu}_{CT}$:

$$hc\tilde{\nu}_{CT} = \frac{\sqrt{4\beta_0\beta_1+\Delta^2}}{1-S_{01}^2} \qquad (1)$$

$$\begin{aligned} \beta_0 &= W_{01} - W_0S_{01} \\ \beta_1 &= W_{01} - W_1S_{01} \qquad (2) \\ \Delta &= W_1 - W_0 \end{aligned}$$

where W_0 and W_1 are the energy of no-bond and dative structure, respectively, and W_{01} is the interaction matrix which is approximately proportional to the overlap integral S_{01}. $|\beta_0|$ and $|\beta_1|$ increase with increase in S_{01}. When R_{DA} decreases by compression, S_{01} increases and so $\beta_0\beta_1$ does. Δ is the energy accompanied by the transfer of an electron from a donor to an acceptor. It is approximately expressed as follows, decreasing with reduction in R_{DA}.

$$\Delta \approx I_D - E_A - \frac{e^2}{R_{DA}} \qquad (3)$$

where I_D is the ionization potential of a donor, E_A the electron affinity of an acceptor, and e the charge of an electron. The denominator $(1-S_{01}^2)$ and the first term in the square root $(4\beta_0\beta_1)$ in Eq. 1 might contribute to a blue shift and the second term in the square root (Δ^2) to a red shift with increasing pressure, the shifts overlapping the red shift caused by an increase in the polarity of the solvent.

TABLE 2. REASONABLE VALUES OF $4\beta_0\beta_1$ AND Δ^2 FOR I_2 COMPLEXES

Complex	$\frac{4\beta_0\beta_1{}^{a)}}{\text{eV}^2}$	$\frac{\Delta^2}{\text{eV}^2}$
Et_3N–I_2[b)]	12—42	0—1
Benzene–I_2[c)]	1—7	13—21

a) $4\beta_0\beta_1=4\beta_0(\beta_0-\Delta S_{01})$, deduced from Eq. 2. b) Mulliken's "Reasonable Values"[28] are S_{01}=0.4—0.5, $(I_D-\Delta)$ =6.5—7.5 eV, and $-\beta_0$=1.7—3 eV. I_D=7.50 eV.[29] c) Mulliken's "Reasonable Values"[28] are S_{01}=0—0.15, $(I_D-\Delta)$ =4.7—5.7 eV, and $-\beta_0$=0.5—1.0 eV. I_D= 9.24 eV.[30]

In a strong CT complex of a large $-\Delta H$ value such as Et_3N-I_2 complex, the value of $4\beta_0\beta_1$ should be large as compared with Δ^2 in view of the CT theory.[27] The reverse holds for a weak CT complex such as benzene–I_2. The values of $4\beta_0\beta_1$ and Δ^2 given in Table 2 are roughly estimated from the values of I_D and Mulliken's "Reasonable Values" for S_{01}, $I_D-\Delta$, and β_0 of the I_2 complexes from Eq. 2. In Et_3N-I_2 complex Δ^2 is negligible as compared with $4\beta_0\beta_1$. Thus in a strong CT complex the contribution to a blue shift by the term of $4\beta_0\beta_1$ with reducing R_{DA} is expected to be effective. The observed blue shift may be attributed to this effect. On the other hand, in a weak CT complex a decrease in R_{DA} may contribute to a red shift since $4\beta_0\beta_1$ is small or negligible as compared with Δ^2. The excessive red shift caused by pressure as compared with the solvent shift in I_2 or TCNE complexes with benzene, toluene, and mesitylene, may be due to such a contribution of Δ^2.

In conclusion, the observed pressure shifts of CT bands could be interpreted by a sum of two effects, the increased polarity of the solvent causing a red shift, and the decrease in R_{DA} contributing to a blue shift in a strong CT complex and to a red shift in a weak one.

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