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Charge-Transfer Complexes of Benzo[*b*]thiophene with σ- and π-Electron Acceptors

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The spectrophotometric properties of the charge-transfer (CT) complexes of benzo[*b*]thiophene with iodine at 24 °C in different solvents such as cychlohexane, carbon tetrachloride, chloroform, dichloromethane, and 1,2-dichloroethane are studied. In addition the spectrophotometric and thermodynamic properties of the CT complexes of benzo[*b*]thiophene with tetracyanoethylene, chloranil, 2,3-dichloro-5,6-dicyano-*p*-benzoquinone and 7,7,8,8,-tetracyanoquinodimethane are studied. The results show that the equilibrium and the thermodynamic parameters and the wavelengths of the maximum absorption bands ($\lambda_{\max}$) of the complexes vary markedly with the solvent. The ionization potential and the donor sites of benzo[*b*]thiophene are also determined and discussed.

The formation of CT complexes between π- and n-donors with σ- and π-acceptors has been widely investigated.[1,2] Heterocyclic compounds have π and n electrons and therefore can give two different types of CT complexes.[3,4] It has been reported that n-types form strong complexes,[1] while the π-types appear to fall in the category of weak CT complexes.[5,6] Benzo[*b*]thiophene is an electron donor which has n (the lone pair of the sulfur atom) and π-electrons. Therefore, it is interesting to study the CT interactions of benzo[*b*]thiophene with σ- and π-electron acceptors. The spectral and thermodynamic characteristics of such complexes are discussed. The study is extended to investigate the solvent effect on the equilibrium parameters and the CT bands of the complexes. In addition, the donor sites and the ionization potential of benzo[*b*]thiophene are investigated.

Experimental

Benzo[*b*]thiophene (BT), Aldrich, was recrystallized twice from cyclohexane. Iodine (I_2), was purified by sublimation from potassium iodide. Chloranil (CHL) was recrystallized from benzene (mp = 247 °C). 2,3-Dichloro-5,6-dicyano-*p*-benzoquinone (DDQ), Aldrich, was recrystallized twice from benzene–chloroform (2 : 3), (mp = 213—215 °C). 7,7,8,8-Tetracyanoquinodimethane (TCNQ) and tetracyanoethylene (TCNE), Aldrich, were purified by vacuum sublimation (mp = 170 and 199 °C, respectively). All the solvents used were purified by the recommended methods.[7]

Absorption spectra were scanned on a Shimadzu (Model 240) spectrophotometer using 1 cm matched silica cells. Temperature control was achieved using a Haake model circulating water bath having an accuracy of ±0.01 °C. All measurements were made on freshly prepared solutions.

Results and Discussion

I. The CT Complexes of BT with σ-Acceptors (I_2).

The absorption spectra of mixed solutions with a fixed concentration of I_2 and varying concentrations of BT in cyclohexane solvent at 24 °C are shown in Fig. 1. It can be seen that neither the donor nor the acceptor absorbs at a wavelength where the complex absorbs. The absorption spectra of BT–I_2 system in other solvents are of similar nature, except for the position of the maximum CT band ($\lambda_{\max}$) of the complex, Table 1. The CT band can be interpreted as the CT transition from the molecular orbital of

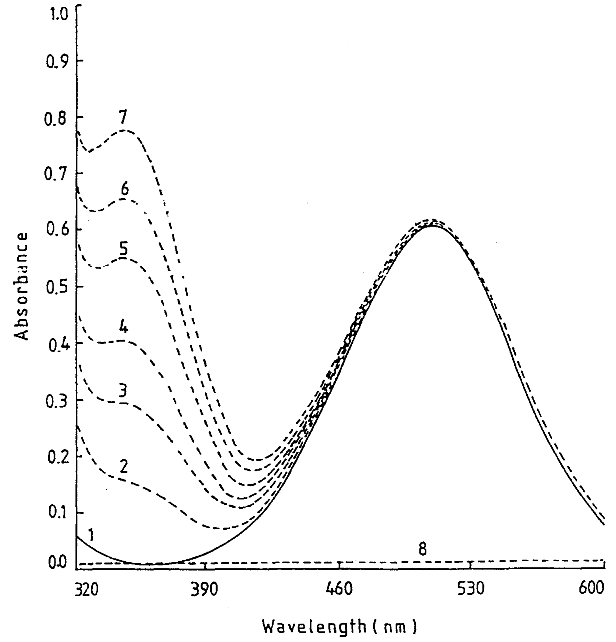

Fig. 1. The absorption spectra of I_2–BT system in cyclohexane at 24 °C. Concentration of I_2 (solid line) = 6.48×10^{-4} mol L^{-1}, concentration of BT: (1) 0.0, (2) 6.97×10^{-2}, (3) 13.94×10^{-2}, (4) 20.9×10^{-2}, (5) 27.87×10^{-2}, (6) 34.8×10^{-2}, and (7) 41.82×10^{-2} mol L^{-1}. (8) represents the spectra of pure BT of concentration: 41.82×10^{-2} mol L^{-1}.

Table 1. Spectrophotometric Results of the BT Complexes with I_2 in Different Solvents at 24 °C, the Dielectric Constant (ε) and the Refractive Index of the Solvents (n)

Solvent	λ_{max} nm	K_{CT} L mol^{-1}	ε_{CT} L mol^{-1} cm^{-1}	ε[a]	n[a]
Cyclohexane	347	1.15±0.06	3352±26	2.00	1.4262
Carbon tetrachloride	357	0.88±0.04	4335±124	2.20	1.4601
Chloroform	354	0.74±0.10	2792±227	4.70	1.4459
Dichloromethane	350	0.63±0.02	3736±76	8.90	1.4241
1,2-Dichloroethane	350	0.55±0.02	4095±113	10.63	1.4448

a) Ref. 13.

the donor to the σ-orbital of I_2. The spectrophotometric data are employed to calculate the equilibrium constant (K_{CT}) and the molar extinction coefficient (ε_{CT}) for BT–I_2 complexes in different solvents using the Scott modifications[8] of the Benesi–Hildebrand equation.[9] This equation is based on the assumptions of 1 : 1 (Acceptor : Donor) complex formation and $[D]_0 \gg [A]_0$ and can be written as follows:

$$\frac{[A]_0[D]_0}{A} = \frac{[D]_0}{\varepsilon_{CT}} + \frac{1}{K_{CT}\varepsilon_{CT}}, \quad (1)$$

where $[A]_0$ and $[D]_0$ are the initial molar concentrations of the acceptor and the donor, respectively. A is the absorbance of the CT complex. The plots of $[A]_0$ $[D]_0/A$ against $[D]_0$ at four different wavelengths of the CT band are found to be linear in all cases. The average values of K_{CT} and ε_{CT} in different solvents were calculated and are presented in Table 1. The linearity of the modified Benesi–Hildebrand plots and the approximate constancy of the determined K_{CT} at different wavelengths indicate the formation of 1 : 1 stoichiometric complex between I_2 and BT. It is obvious that the K_{CT} values run in the following sequence: cychlohexane > carbon tetrachloride > chloroform > dichloromethane > 1,2-dichloroethane. This can be interpreted as a competitive solvent interaction with both the I_2 and BT. Bhowmik et al.[10] have reported equilibrium constants for the interaction of I_2 with cyclohexane, carbon tetrachloride, and 1,2-dichloroethane as 0.082, 0.143, and 0.232 dm^3 mol^{-1}, respectively. Also chloroform, dichloroethane and even carbon tetrachloride have shown hydrogen bond formation with some donors.[11] The values of ε_{CT} show irregular behavior. They are not consistent with the CT variation of K_{CT} in different solvents. Similar behavior was previously obtained.[6,10]

Examination of the data given in Table 1 clearly indicates that the CT complex in a non-polar solvent, cyclohexane, absorbs at a shorter wavelength than in polar halogenated hydrocarbon solvents. Since the excited states of the CT complexes are considerably more polar than the ground state, the energy of the CT band is thought to decrease as the polarity of the solvent increases.[11] No correlation is observed between λ_{max} and the dielectric constant of the solvents. However, a plot of λ_{max} against the refractive index function,[12] $n^2-1/2n^2+1$, gives a straight line whose correlation coefficient equals 0.8814. Therefore, it would be reasonable to suggest that the refractive index of the solvents (n) may have a pronounced effect on the shifts of the CT absorption bands.

II. The CT Complexes of BT with π-Acceptors. The absorption spectra of solutions containing a fixed concentration of TCNE, CHL, and TCNQ and varying concentrations of BT in dichloromethane at different temperatures were measured. The TCNE–BT system was also studied in carbon tetrachloride, chloroform and 1,2-dichloroethane solvents at 24 °C. The complex of DDQ with BT was studied in dichloromethane at 24 °C only. New bands in the visible region (462—630 nm) are observed immediately. In each system, neither the donor nor the acceptor absorbs at the region at which the complex absorbs. λ_{max} of the CT for bands in different systems are reported in Table 2. The complexes of TCNE, Fig. 2, and DDQ show two CT bands which can be attributed to the intermolecular CT transition from two energy levels of BT to the same orbital of the acceptor. For CHL–BT, Fig. 3, and TCNQ–BT systems, only one CT band is observed.

The spectrophotometric data obtained are employed to calculate K_{CT} and ε_{CT}. Since the concentration ranges of BT in each system are not much larger than that of the electron acceptor, see the relevant Figs. 2 and 3 and Table 2, the formation of 1 : 2 (Acceptor : Donor) complex is therefore not expected. Hence, under the assumption $[D]_0 > [A]_0$ the following Rose and Drago equation[14] is used:

$$\frac{[A]_0[D]_0}{A} = \frac{1}{K_{CT}\varepsilon_{CT}} + \frac{1}{\varepsilon_{CT}}([A]_0 + [D]_0). \quad (2)$$

$[A]_0$, $[D]_0$, and A are as defined above in Eq. 1. The plots of $[A]_0$ $[D]_0/A$ against ($[A]_0+[D]_0$) at four different wavelengths of the CT band are linear and indicate that the stoichiometric ratio of the CT complexes under examination is 1 : 1.[15] The average values of K_{CT} and ε_{CT} in different solvents and at different temperatures are presented in Table 2.

It is seen that the values of K_{CT} of BT with different acceptors at 24 °C follow the order expected from the electron affinity, E^A of the acceptors except TCNE (E^A of DDQ, TCNQ, CHL, and TCNE are 1.95, 1.7, 1.37 and 2.2 eV, respectively[16]). The deviation of TCNE–BT system would be attributed to its different CT transition. In this system, the bonding involves a transfer of π-bonding electron from the donor to the vacant π-antibonding orbitals associated with the alkenic linkage in TCNE. However, for CT complex

Table 2. Spectrophotometric and Thermodynamic Results for CT Complexes of BT with Different π-Electron Acceptors

Acceptor	Solvent	$\frac{[D]_0}{[A]_0}$ ratio	Temp	λ_{max}	K_{CT}	ε_{CT}	$\Delta H°$	$\Delta S°$	$\Delta G°$	b^2/a^2
			°C	nm	dm^3 mol^{-1}	dm^3 mol^{-1} cm^{-1}	kcal mol^{-1}	cal mol^{-1} K^{-1}	kcal mol^{-1}	
TCNE	Carbon tetrachloride	3.14—42.78	24	462, 537	4.46±0.45	1694±54				
	Chloroform	4.89—19.45	24	468, 537	3.75±0.25	588±36				
	Dichloromethane	7.51—27.04	13	473, 525	3.17±0.07	461±5	3.79	10.97	0.53	0.062
			19		2.96±0.15	440±12				
			24		2.45±0.17	547±33				
	1,2-Dichloroethane	13.05—60.93	24	473—513	1.30±0.01	657±10				
CHL	Dichloromethane	8.79—43.97	10	500	2.77±0.09	312±31	3.97	11.97	0.45	0.038
			15.5		2.44±0.07	328±19				
			20		2.19±0.06	332±23				
DDQ	Dichloromethane	2.74—19.80	24	505, 630	12.26±0.84	397±66				
TCNQ	Dichloromethane	10.07—60.44	10	560	5.81±0.19	444±28	5.23	15.16	0.76	0.102
			17		4.03±0.19	401±42				
			25		3.60±0.18	416±40				
			30.5		2.97±0.19	488±27				

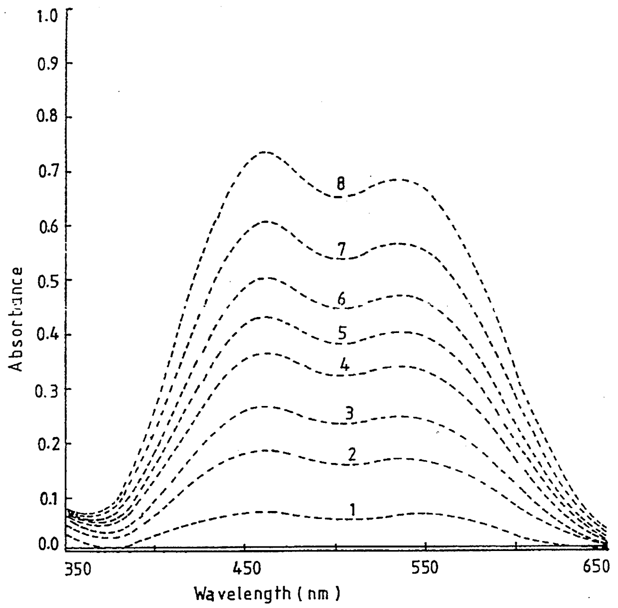

Fig. 2. The absorption spectra of TCNE–BT system in carbon tetrachloride at 24 °C. Concentration of TCNE (solid line) = 1.33×10^{-3} mol L^{-1}, concentration of BT: (1) 0.417×10^{-2}, (2) 1.22×10^{-2}, (3) 1.97×10^{-2}, (4) 2.71×10^{-2}, (5) 3.64×10^{-2}, (6) 4.20×10^{-2}, (7) 4.95×10^{-2}, and (8) 5.69×10^{-2} mol L^{-1}. Pure donor shows no absorbance.

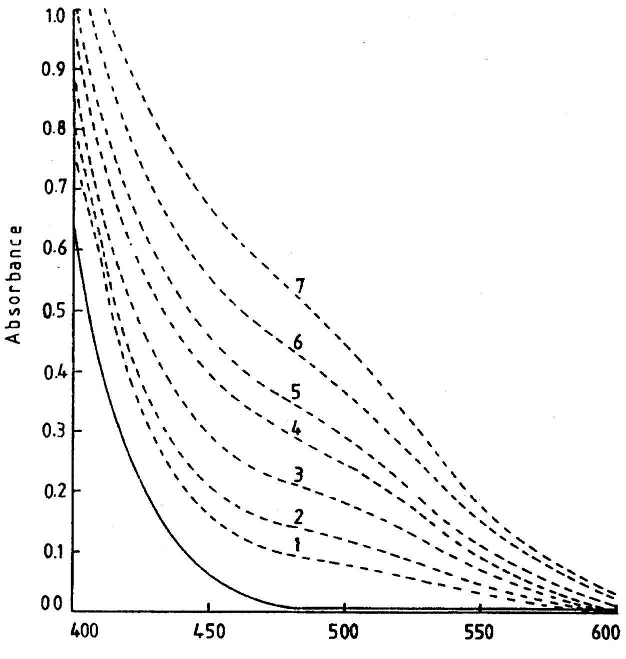

Fig. 3. The absorption spectra of CHL–BT system in dichloromethane at 10 °C. Concentration of CHL (solid line) = 4.197×10^{-3} mol L^{-1}, concentration of BT: (1) 3.69×10^{-2}, (2) 5.54×10^{-2}, (3) 9.23×10^{-2}, (4) 12.92×10^{-2}, (5) 14.77×10^{-2}, (6) 18.46×10^{-2}, and (7) 22.15×10^{-2} mol L^{-1}. Pure donor shows no absorbance.

of BT with the aromatic acceptors DDQ, TCNQ, and CHL, the relevant transfer would be to the π-antibonding orbitals associated with the aromatic ring of the acceptor.

The solvent effect on K_{CT} was tested for the TCNE–BT system. The values of K_{CT} are markedly affected by the variation of the solvent used. They decrease in the following sequence: carbon tetrachloride > chloroform > dichloromethane > 1,2-dichloroethane. This behavior could be explained on the basis of a competitive solvent effect, as discussed in the previous section.

The influence of the solvent on λ_{max} of TCNE–BT system, which has two CT bands, is clearly seen. The CT band at 537 nm exhibits a hypsochromic shift; in contrast, the second one at 462 nm exhibits a bathochromic shift when the solvent was changed from carbon tetrachloride, chloroform, dichloromethane and then to 1,2-dichloroethane. The values of K_{CT} decrease in the same sequence. Accordingly, it can be concluded that as the complex becomes weak, the degree of splitting of the two CT bands decreased. This can be justified when one considers DDQ–BT system, which has a higher K_{CT} in comparison with that of the TCNE complex, a higher degree of splitting between the two CT bands is observed. Similar behavior was obtained by Rosenberg et al.[17] in the case of CT complexes of 1,2 : 4,5-benzenetetracarboxylic dianhydride with methylbenzenes.

III. Donor Sites and the Ionization Potential of BT. There are two complexing sites of BT: the lone electron pair (n) on the sulfur atom and the π-electrons of the aromatic rings. It is known that the strength of the CT complexes of I_2 with n-donors is large.[1] However, as can be seen from the values of K_{CT} for I_2–BT system, the interaction is relatively low. The author has studied the CT complex formation of similar heterocyclic donors such as thiophene[5] and thianthrene[6] with I_2 and some π-acceptors. We concluded that both donors are of π-nature. This nature of thiophene was substantiated from other studies.[18—20] Therefore, one can suggest that the CT transition for BT to both I_2 and π-acceptors takes place from the highest occupied π-orbitals. The lone electron pair of the sulfur atom could be hybridized in the π-electronic configuration of BT. The ionization potential (I_p) of BT can be determined from the energies of CT bands, in dichloromethane as solvent, using the following equations:[1,3,21]

$$I_p\,(\mathrm{eV}) = 2.90 + 1.89 \times 10^{-4}\,\bar{\nu}_{I_2}\ \mathrm{cm}^{-1}, \tag{3}$$

$$I_p\,(\mathrm{eV}) = 5.76 + 1.52 \times 10^{-4}\,\bar{\nu}_{\mathrm{DDQ}}\ \mathrm{cm}^{-1}, \tag{4}$$

$$I_p\,(\mathrm{eV}) = 5.21 + 1.65 \times 10^{-4}\,\bar{\nu}_{\mathrm{TCNE}}\ \mathrm{cm}^{-1}, \tag{5}$$

where $\bar{\nu}$ is the maximum wavenumber corresponding to the first CT band and the subscripts indicate the appropriate electron acceptor. The broadness of CT bands in the complexes of BT with CHL and TCNQ causes some difficulty in evaluating λ_{max}. The values of I_p obtained using Eqs. 3, 4, and 5 are 8.3, 8.69, and 8.74 eV. The average value is equal to 8.57 eV.

IV. Thermodynamic Parameters of CT Complexes. The evaluation of K_{CT} at different temperatures was used to calculate the enthalpy (ΔH°) and entropy of formation (ΔS°). These values were calculated from van't Hoff plots. The Gibbs' free energy (ΔG°) is also determined. Thermodynamic parameters thus calculated are summarised in Table 2. The small negative values of ΔH° suggest that the complexes are weak. This is consistent with the formation of weak CT complexes. The relatively stronger CT complex (TCNQ–BT) shows larger negative values, as expected.

The strength of the interaction of BT with TCNE, CHL, and TCNQ in dichloromethane can be determined using the relation:[22]

$$\frac{b^2}{a^2} = \frac{\Delta H^\circ}{h\nu} \tag{6}$$

where the quantities a and b are the coefficients of the no-bond and dative states, respectively. The ratios show that the magnitude of interaction of the aromatic acceptors follows the order TCNQ > CHL. This is substantiated by the decrease of the K_{CT} of their complexes and by the decrease of the E^A of the acceptors in the same order. The deviation in case of TCNE system could be attributed to the reasons mentioned in Section II.

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