

Charge-Transfer Complexes of Mercaptobenzimidazoles with σ - and π -Electron Acceptors

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Résumé

Nous avons étudié par spectrophotométrie, le transfert de charge des complexes de 2-mercaptopbenzimidazole et de quelques-uns de ses dérivés alkylés avec l'iode, en tant qu'accepteur σ typique, et avec le tétracyanoéthylène (TCNE), le 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ) et le 2,3,5,6-tétrachloro-1,4-benzoquinone (CHL), en tant qu'accepteurs d'électrons π , dans des solutions de dichlorométhane, de 1,2-dichloroéthane et de chloroforme. Nous avons déterminé les données spectrales, les constants de formation et les fonctions thermodynamiques ΔH° , ΔG° et ΔS° . Nous discutons des caractéristiques spectrales et des constantes de formation en termes de structure de donneur moléculaire, d'affinité d'accepteur d'électron, et de polarité de solvant. Nous avons estimé les potentiels d'ionisation des donneurs à partir des énergies de transition CT de leurs complexes. Les résultats spectroscopiques suggèrent la présence de 2-mercaptopbenzimidazole dans un équilibre des tautomères thiol-thione impliqué dans la formation du complexe.

Abstract

The charge-transfer complexes of 2-mercaptopbenzimidazole and some of its alkyl derivatives with iodine, as a typical σ -acceptor; and with tetracyanoethylene (TCNE), 2,3-dichloro-5,6-

dicyano-1,4-benzoquinone (DDQ) and 2,3,5,6-tetrachloro-1,4-benzoquinone (CHL), as π -electron acceptors, were studied spectrophotometrically in dichloromethane, 1,2-dichloroethane and chloroform solutions. Spectral data, formation constants and thermodynamic functions ΔH° , ΔG° and ΔS° have been determined. Spectral characteristics and formation constants are discussed in the terms of donor molecular structure, electron acceptor affinity, and solvent polarity. The ionization potentials of the donors were estimated from the CT transition energies of their complexes. The spectroscopic results suggest the presence of 2-mercaptopbenzimidazole in the thiol-thione tautomers equilibrium that is involved in the complex formation.

Keywords: CT complexes, formation constant, ionization potential, 2-Mercaptopbenzimidazole, UV-Visible spectra

Introduction

Among the most widely used anti-thyroidal agents for the treatment of hyperthyroidism (Graves' disease) over the years are thiomides, such as *N*-methylimidazoline-2-thione (methimazole), 3-methyl-2-thioxo-4-imidazoline-1-carboxylate, and carbimazole, (1,2). 2-mercaptopbenzimidazole, a widely used antioxidant for rubbers and plastics (3), has also been used for this purpose (4). Thioamides inhibit the formation of 3,5,3'-triiodothyronine (T_3) and 3,5,3', 5'-triiodothyronine (T_4) hormones by depressing the incorporation of oxidized iodides in tyrosine, a precursor of T_3 and T_4 hormones (5-9). In addition, a good correlation between the anti-thyroid activity in vivo and the formation constants of iodine complexes with

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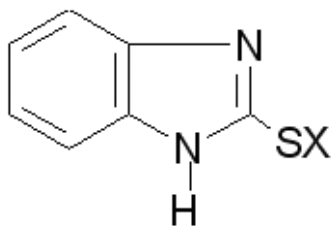
organic bases has been found (7). Therefore, there is an increasing interest in the study of the charge-transfer complexes of iodine with thioamides or thiones (10,11), not only for the clarification of the iodine-binding mechanism but also for the development of new anti-thyroidal agents. Moreover, the sulfur-iodine charge-transfer complexes have been shown to possess promising electrical properties, such as superconducting ability (12, 13).

In light of these important findings and the lack of sufficient data on 2-mercaptobenzimidazoles with π -acceptors, it was of interest to study the charge-transfer molecular complexes of 2-mercaptobenzimidazole and some of its alkyl derivatives, as electron donors, with iodine, as σ -acceptor, and π -electron acceptors viz. DDQ, TCNE and CHL. The spectral characteristics of the formed CT molecular complexes are examined and discussed in terms of the donor and acceptor molecular structure and the nature of the organic solvent used. The thermodynamic parameters of complex formation are also examined.

Experimental

The compounds investigated in the present study are 2-mercaptobenzimidazole, 2-(ethylmercapto)-benzimidazole, 2-(methylmercapto)benzimidazole, and 2-(benzylmercapto)benzimidazole. 2-Mercaptobenzimidazole was supplied by Aldrich chemical Co., while the other compounds were synthesized according to the recommended method described in the literature (14). The purity of all synthesized derivatives of 2-mercaptobenzimidazole was checked using thin layer chromatography, elemental analysis and $^1\text{H NMR}$ spectra.

The structure of these compounds is represented schematically below:



- X = H 2-mercaptobenzimidazole, (I).
 X = $-\text{C}_2\text{H}_5$ 2-(ethylmercapto)benzimidazole, (II).
 X = $-\text{CH}_3$ 2-(methylmercapto)benzimidazole, (III).
 X = $-\text{CH}_2-\text{C}_6\text{H}_5$ 2-(benzylmercapto)benzimidazole, (IV).

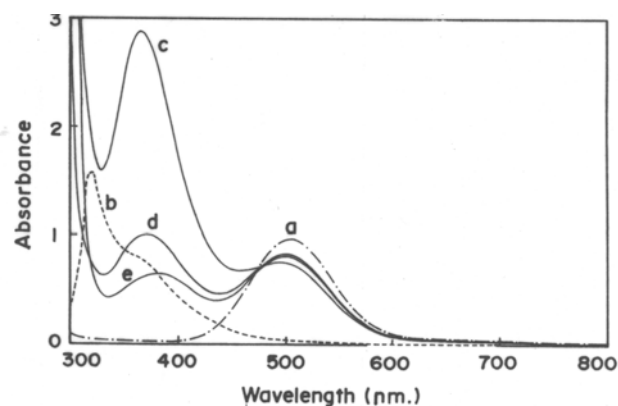


Figure 1. Electronic absorption spectra of CT complexes of mercaptobenzimidazoles with iodine in CH_2Cl_2 solutions at 25°C . (a) Free iodine ($1 \times 10^{-4} \text{ mol dm}^{-3}$), (b) I- I_2 CT complex, $[\text{I}] = 4 \times 10^{-5} \text{ mol dm}^{-3}$, (c) II- I_2 CT complex, $[\text{II}] = 4 \times 10^{-3} \text{ mol dm}^{-3}$, (d) III- I_2 CT complex, $[\text{III}] = 4 \times 10^{-3} \text{ mol dm}^{-3}$, (e) IV- I_2 CT complex, $[\text{IV}] = 4 \times 10^{-3} \text{ mol dm}^{-3}$. Iodine concentration was, also, in cases (b-e) $1 \times 10^{-4} \text{ mol dm}^{-3}$.

The σ -electron acceptor (iodine, BDH) was purified by re-sublimation from potassium iodide. The π -acceptors: TCNE, DDQ, and CHL (Aldrich or Merck reagent grade) were crystallized twice from chlorobenzene, dry dichloromethane, and dry benzene, respectively.

Solvents were of spectral grade (BDH). Stock solutions of donors and acceptors were freshly prepared in a dry and deoxygenated solvent prior to use in order to avoid any contamination. Electronic absorption spectra were scanned on a Shimadzu 2401PC spectrophotometer using 1 cm matched quartz cells. Temperature control was achieved using a Julabo F30 ultrathermostat with an accuracy of $\pm 0.05^\circ\text{C}$. Computations of formation constants (K_{CT}) and molar extinction coefficients (ϵ_{CT}) were performed on a Compaq PC computer with the aid of a BASIC program based on unweighted linear least-squares fits. The thermodynamic parameters were obtained by means of a computer program based on Van't Hoff plots.

Results and Discussion

Spectral Characteristics of the formed CT Complexes

The electronic absorption spectra of the CT complexes in CH_2Cl_2 solutions for the mercaptobenzimidazoles- I_2 system were taken in the wavelength range 300-600 nm. Typical examples are shown in Figure 1.

Charge-transfer complexes of 2-mercaptobenzimidazole derivatives (II-IV) with iodine displayed a

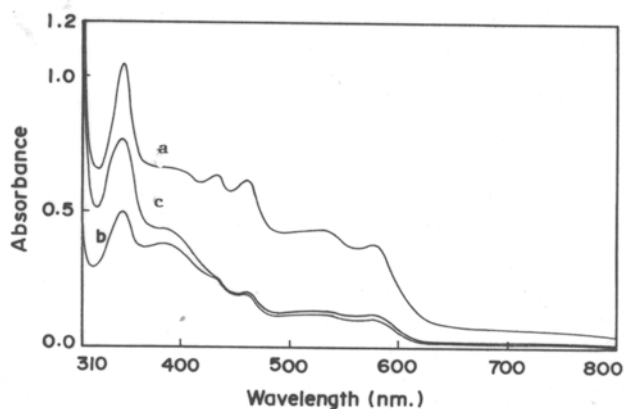


Figure 4. Electronic absorption spectra of CT complex solutions of Mercaptobenzimidazoles (II-IV) with DDQ in CH_2Cl_2 at 25°C . $[\text{DDQ}] = 1 \times 10^{-4} \text{ mol dm}^{-3}$. (a) II-DDQ Complex, $[\text{II}] = 4 \times 10^{-3} \text{ mol dm}^{-3}$, (b) III-DDQ Complex, $[\text{III}] = 4 \times 10^{-3} \text{ mol dm}^{-3}$, (c) IV-DDQ Complex, $[\text{IV}] = 4 \times 10^{-3} \text{ mol dm}^{-3}$.

23).

Using CHL as a π -acceptor with donor II in dichloromethane at 25°C , one broad CT band appeared in the wavelength range 390-800 nm with $\lambda_{\text{max}} = 530 \text{ nm}$ (Figure 3). This could be ascribed to a single intermolecular CT transition from the HOMO of the donor

to the LUMO of CHL.

On mixing dichloromethane solutions of the donors (II, III, IV) with DDQ as a π -acceptor, the electronic absorption spectra of the CT complex solution show a group of absorption bands at 432, 460, 531 and 575 nm (Figure 4). These absorption bands are characteristic for the absorption of the radical anion DDQ^- (24, 25). Thus one can deduce that the donor (II, III, IV)-DDQ CT complexes exist predominantly in the dissociated state (D^+ , A^-) i.e. it is of strong nature. However, as soon as the solution of the donor (I) and the acceptor (DDQ) is mixed, a green colour is observed instantaneously and then a white precipitate is rapidly formed at any concentration of the donor and acceptor. Thus, all attempts to record the electronic spectra of the CT complex of donor (I) with DDQ failed.

From the above described discussion of the electronic absorption spectra of the donor 2-(ethylmercapto)-benzimidazole (II) with π -acceptors, one can deduce that the CT complexes with π -acceptors (DDQ and TCNE) exist in the dissociated state (radical cations and anions, D^+ , A^-), while those with CHL are mainly of the nonbonding structure (D , A).

Table 1. Spectral characteristics, thermodynamic parameter values and the formation constants (K_{CT}) for the CT complexes of 2-mercaptobenzimidazole derivatives with iodine at different temperatures in dichloromethane. The ionization potentials of the donors are also included.

Donor	λ_{max} (nm)	E_{CT} (eV)	IP (eV)	K_{CT} ($\text{dm}^3 \text{ mol}^{-1}$), $^\circ\text{C}$				ϵ_{CT} ($\text{dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$) at 25°C	$-\Delta\text{H}$ (K cal mol^{-1})	$-\Delta\text{S}$ (cal mol^{-1})	$-\Delta\text{G}$ (K cal mol^{-1})	(b/a) ²
				10	15	20	25					
I	360sh ^a 317	3.43 3.89	8.15 8.86	12341±561	10723±460	7589±833	6899±540	5115±1833	7.03±1.44	6.11±0.93	8.82	0.089
II	365	3.38	8.08	2186±374	1712±253	1442±162	1354±285	3008±97	5.41±0.91	3.80±0.55	4.30	0.070
III	370	3.34	8.01	1307±111	1190±128	1030±137	794±89	1617±101	5.48±0.95	5.02±1.20	4.01	0.071
IV	376	3.28	7.93	663±48	545±91	415±39	397±2.9	1007±26	6.08±1.03	8.60±3.60	3.56	0.081

^aWavelength at which the calculations were carried out. ΔG is calculated at 20°C

Table 2. Spectral characteristics and the formation constants (K_{CT}) for the CT complexes of 2-(ethylmercapto)benzimidazole with several electron acceptors at different temperatures in dichloromethane. The ionization potentials of the donors are also included.

Electron Acceptor	λ_{max} (nm)	E_{CT} (eV)	IP (eV)	K_{CT} ($\text{dm}^3 \text{ mol}^{-1}$), $^\circ\text{C}$				ϵ_{CT} ($\text{dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$) at 25°C			
				10	15	20	25	10	15	20	25
Iodine	365	3.38	8.08	2186±374	1712±253	1442±162	1354±285	3008±97	2775±88	2534±80	2017±91
TCNE	590 ^a 490	2.09	8.01	--	--	--	38±1.2	--	--	--	80±10
CHL	530	2.33	7.89	--	--	--	31±1.8	--	--	--	18±2.0

^aWavelength at which the calculations were carried out.

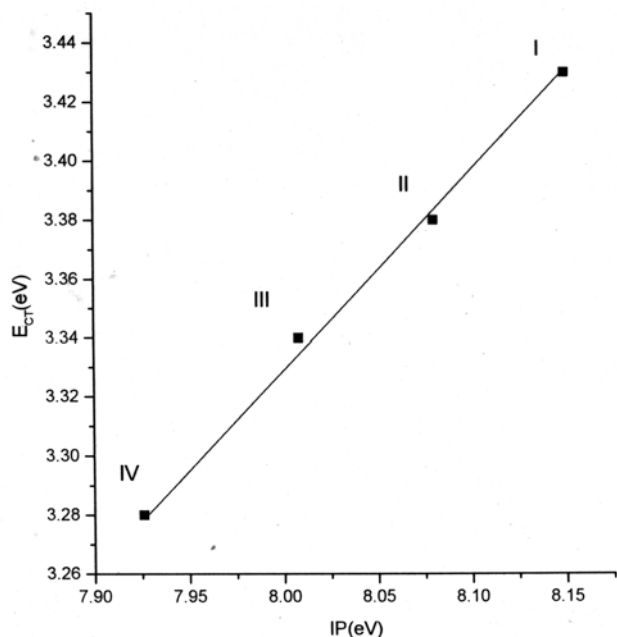


Figure 5. Plot of CT transition energies of mercaptobenzimidazoles- I_2 complexes versus donor ionization potentials.

The ionization potentials (IP) of 2-mercaptobenzimidazole derivatives (I-IV) with I_2 as well as those of II with TCNE and CHL have been estimated from the empirical equations reported by Aloisi and Pingnataro (26) and are compiled in Tables 1 and 2. These empirical equations are:

$$IP \text{ (eV)} = 2.90 + 1.89 \times 10^{-4} \nu_{I_2} \text{ cm}^{-1}$$

$$IP \text{ (eV)} = 5.21 + 1.65 \times 10^{-4} \nu_{TCNE} \text{ cm}^{-1}$$

$$IP \text{ (eV)} = 5.00 + 1.53 \times 10^{-4} \nu_{CHL} \text{ cm}^{-1}$$

where ν is the wavenumber corresponding to the charge-transfer band. The obtained IP values (7.89 - 8.86 eV) are comparable with those previously estimated for the CT complexes of TCNE and other compounds containing the thioamido group in which the sulphur atom of thiocarbonyl group is the donor site (27-29). Thus one can deduce that the mercaptobenzimidazole donor orbital involved in the CT transition is of n-type.

Furthermore, examination of the calculated ionization potential of 2-(ethylmercapto)benzimidazole as an electron donor, estimated from the CT energies of its complexes with the electron acceptors (I_2 , TCNE and CHL), reveals that there is not a significant difference between the calculated ionization potential values (see Table 2). This suggests that the same molecular donor orbital is involved in the interaction with the electron acceptors. It should be pointed out that the plot of the

E_{CT} (CT transition energies) values of 2-mercaptobenzimidazoles- I_2 complexes versus ionization potentials of the donors (IP) is approximately linear (Figure 5). This confirms that the observed new absorption bands of the 2-mercaptobenzimidazoles- I_2 complexes are of CT nature (30).

Determination of Formation Constants of the CT Complexes

Formation constants (K_{CT}) and molar extinction coefficients (ϵ_{CT}) of the studied 2-mercaptobenzimidazoles electron donors (I-IV) with σ - and π -electron acceptors (I_2 , TCNE and CHL) in CH_2Cl_2 were determined spectrophotometrically in the temperature range 10-25 °C for I_2 and at 25 °C for TCNE and CHL. The Seal, Sil and Mukherjee (31) method (derived from the Benesi-Hildebrand equation (32) and its modified form (33) to evaluate K_{CT} and ϵ_{CT} independently) under the condition $[D]_0 > [A]$, was used to calculate the formation constants (K_{CT}) and extinction coefficients (ϵ_{CT}). The equations derived for this method can be written in the following forms:

$$([A]_0 + [D]_0/[D]_0)A = [A]_0\epsilon_{CT} - A/K_{CT}[D]_0 \quad (1)$$

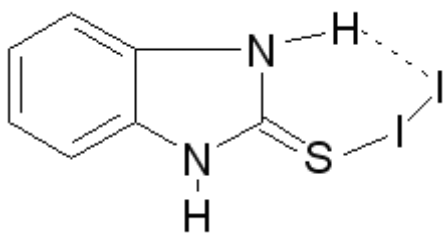
$$[A]_0 + [D]_0 = [A]_0[D]_0\epsilon_{CT} - 1/K_{CT} \quad (2)$$

where $[D]_0$ is the initial concentration of donor, $[A]_0$ is the initial concentration of acceptor, A is the measured absorbance, and ϵ_{CT} is the extinction coefficient at a given wavelength. Generally, all calculations were carried out by using a linear least-squares method. The results obtained are collected in Tables 1 and 2. It can be seen in Table 1 that the numerical K_{CT} values of CT complexes of mercaptobenzimidazoles (II-IV) with iodine follows the order:

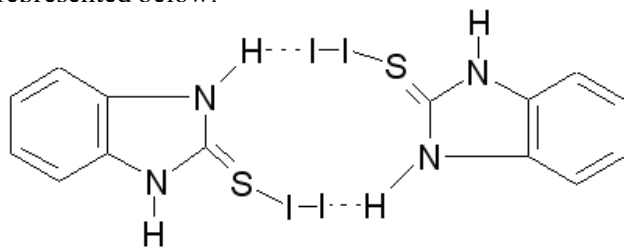
$$II > III > IV$$

This behaviour can be attributed to the inductive effect of alkyl groups, which increases the electron donating ability of the sulphur atom in the same direction (i.e. S-ethyl > S-methyl > S-benzyl). A similar behaviour was reported previously for compounds containing N-alkyl groups (34).

The unexpectedly high K_{CT} values for compound (I) compared with those involving the electron donors (II-IV) are interpreted by assuming an intramolecular H-bonding between the NH hydrogen and the terminal iodine as depicted in the following scheme (35):



Alternatively, as a result of the presence of the thione tautomer, dimerization was considered to be possible through intermolecular hydrogen bonding between the NH hydrogen and iodine (11), i.e. via (NH...I-I-S=) as represented below:



This behaviour was previously reported for alkylthioureas (27), as well as alkyl- and aryl-substituted imidazole-2-thiones (36). From Job's method of continuous variation (37), a stoichiometry of 1:1 was obtained for the CT complexes of donors (I-IV) with iodine as illustrated in Figure 6. In this method, a series of solutions was prepared by mixing equimolar solutions of donor and acceptor in varying proportion while keeping the total molar concentration constant. The stoichiometry of the CT complexes was determined graphically by plotting the mole fraction of donor on the abscissa against the absorbance on the ordinate. Graphical representation of the results obtained by this method show symmetrical curves with a maximum at a mole fraction

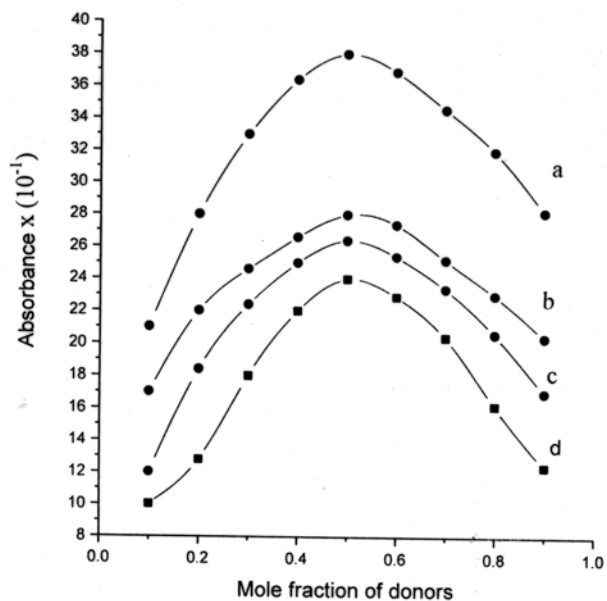


Figure 6. Job's method of continuous variation for the CT complexes of mercaptobenzimidazoles with iodine in CH_2Cl_2 at 25°C . (a) I-I₂ CT complex, λ_{CT} 360 nm, total concentration = $1 \times 10^{-5} \text{ mol dm}^{-3}$, (b) II-I₂ CT complex, λ_{CT} 365 nm, total concentration = $4 \times 10^{-4} \text{ mol dm}^{-3}$, (c) III-I₂ CT complex, λ_{CT} 370 nm, total concentration = $4 \times 10^{-4} \text{ mol dm}^{-3}$, (d) IV-I₂ CT complex, λ_{CT} 376 nm, total concentration = $4 \times 10^{-4} \text{ mol dm}^{-3}$.

≈ 0.5 , indicating the formation of 1:1 CT complexes in all cases.

Furthermore, examination of the K_{CT} values of the CT complexes of donor (II) with the various acceptors (I₂, TCNE and CHL) reveals that their stability decreases on going from I₂ \rightarrow TCNE \rightarrow CHL (see Table 2). This is consistent with the decrease in the electron affinity of the applied electron acceptors in the same direction.

Table 3. Spectral characteristics, thermodynamic parameter values and the formation constants (K_{CT}) for the CT complexes of 2-(ethylmercapto)benzimidazole with iodine and TCNE at different temperatures in various solvents.

Acceptor	Solvent	D	λ_{max} (nm)	E_{CT} (eV)	K_{CT} ($\text{dm}^3 \text{ mol}^{-1}$), $^\circ\text{C}$				ϵ_{CT} ($\text{dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$) at 25°C	$-\Delta H$ (K cal mol ⁻¹)	$-\Delta S$ (cal mol ⁻¹)	$-\Delta G$ (K cal mol ⁻¹)	(b/a) ²
					10	15	20	25					
I ₂	C ₂ H ₄ Cl ₂	10.65	365	3.38	2971±153	2226±312	1875±215	1760±285	1970±28	5.87±1.13	4.95±1.2	4.42	0.076
	CH ₂ Cl ₂	9.08	365	3.38	2186±374	1712±253	1442±162	1354±285	2017±91	5.41±0.91	3.8±0.55	4.30	0.070
	CHCl ₃	4.80	360	3.43	1043±124	856±156	721±130	677±90	3251±92	4.95±0.69	3.68±0.97	3.87	0.063
TCNE	C ₂ H ₄ Cl ₂	10.65	590	2.09					54±2.9	125±3.0			
	CH ₂ Cl ₂	9.08	590	2.09					38±1.2	80±10			

ΔG is calculated at 20°C

Solvatochromic effect

The electronic absorption spectra of II-I₂ and II-TCNE CT complexes have been investigated in different solvents of various polarities (CHCl₃, CH₂Cl₂ and C₂H₄Cl₂) in a temperature range of 10-25 °C for the II-I₂ system and in CH₂Cl₂ and C₂H₄Cl₂ at 25 °C for the II-TCNE system. Spectral characteristics of the formed CT complexes are listed in Table 3. The obtained results reveal that the formation constant of the CT complex between II and iodine increases as the dielectric constant of the solvent is increased. This behaviour can be interpreted on the basis of the high stabilization of the group electronic state of the complex upon increasing the solvent polarity. This is due to the increase in the interaction between the dipole of the solvent and that of the complex. This is, in turn, consistent with the strong nature of the investigated CT complexes (i.e. n-σ kind). Similar behaviour has been observed for quinolines-I₂ complexes (38) and oxazolones-I₂ complexes (39). The fact that the K_{CT} values found for the complex between II and TCNE in C₂H₄Cl₂ is higher than that in CH₂Cl₂ is convincing evidence for the above interpretation. In this respect, it is worth mentioning that the solvents employed do not show specific interaction with the formed CT complexes.

Thermodynamic parameters of the CT complexes

The thermodynamic parameters (ΔH°, ΔS° and ΔG°) associated with the CT complex formation of 2-mercaptobenzimidazoles with iodine were determined and are compiled in Table 1. The enthalpy (ΔH°) and entropy (ΔS°) changes of the complex formation were determined from the obtained K_{CT} values at different temperatures using Van't Hoff's equation (40), $R \ln K_{CT} = -\Delta H^\circ/T + \Delta S^\circ$, where T is the absolute temperature. The Gibbs free energy (ΔG°) of the complex formation was evaluated according to the well known equation: $\Delta G = -RT \ln K$.

The results obtained reveal that the formed CT complexes are better stabilized as the temperature is lowered. This indicates that the CT complex formation of the investigated system is exothermic.

The obtained values of ΔH°, ΔS° and ΔG° are in accordance with those reported for strong n-σ complexes (38, 41). This is confirmed by the examination of the following equation: $b^2/a^2 = -\Delta H^\circ/h\nu$, where b and a are the coefficients of the dative bond and nonbonding wave functions of the CT complex,

respectively, and ν is the wave frequency (42). Indeed, the obtained values of b^2/a^2 are comparable to those for many strong CT complexes (43, 44).

Conclusion

The spectroscopic data demonstrated the n-σ and n-π nature of the CT complexes of 2-mercaptobenzimidazoles with iodine, as σ-acceptor and π-electron acceptors, respectively. All these complexes have a 1:1 stoichiometry. The values of the formation constants reflect that the 2-mercaptobenzimidazoles are strong n-donors. The 2-mercaptobenzimidzoles-DDQ systems were characterized by the formation of the DDQ anion radical, DDQ⁻. It was found that the values of K_{CT} depend on the nature of the formed CT complex, the polarity of the solvent, and the electron affinity of the acceptors. In the case of the 2-mercaptobenzimidazole-iodine system, the spectroscopic results suggest the presence of both thiol and thione tautomers involved in the complex formation.

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