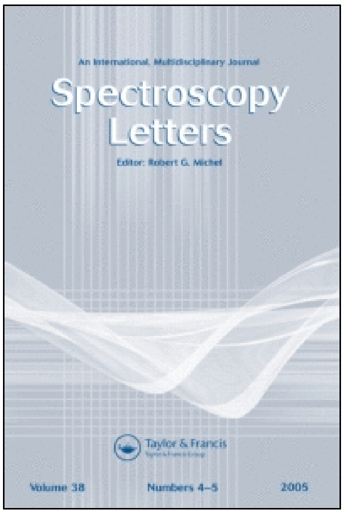

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Charge Transfer Molecular Complexes of Some Pyrazoles with σ- and π-Electron Acceptors

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ABSTRACT

Charge-transfer (CT) complexes of some pyrazoles with iodine as a σ-electron acceptor and with 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ), tetracyanoethylene (TCNE), chloranil (CHL) as a π-electron acceptors were investigated spectroscopically. The spectral characteristics and stability constants of the formed 1: 1 CT complexes were examined and discussed in terms of the donor molecular structure, the nature of the electron acceptor as well as the solvent polarity. It is deduced that the complexes with iodine exist in the ionic structure (pyrazole)$_2$ $I^{+}\cdot I_3^{-}$ whereas the complex with DDQ is mainly in the dissociated state (radical cation and anion; pyrazole$^{\cdot+}$, DDQ$^{\cdot-}$). On the other hand pyrazoles-TCNE, −CHL complexes are essentially of the

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nonbonding type (pyrazole-TCNE, −CHL). Moreover, it is concluded that the solvent polarity plays an important role in determining the stability of these kinds of CT complex. The ionization potentials of the donors were calculated based on the CT transition energies of their complexes.

Key Words: Molecular complexes; Charge-transfer complexes; Solvent effect; Stability; Pyrazoles.

INTRODUCTION

Several azoles have important applications. For instance, pyrazoles and their derivatives are widely used as antipyretic, anti-inflammatory, antidepressant, antibacterial and antifilarial[1,2] medicines. Accordingly, charge transfer (CT) molecular complexes of some azoles have been subjected to many studies,[3−7] among which are pyrazole, 3,5-dimethylpyrazole, 1,3,5-trimethylpyrazole with π-electron acceptors tetracyanoethylene (TCNE), tetracyanoquinodimethane (TCNQ)[3−5] as well as CT complexes of pyrazole and acetylpyrazoles with σ-electron acceptors (I_2, IBr).[6,7]

With respect to π-electron acceptors, the conclusions reported concerning the stoichiometry and the nature of the CT complexes formed are unclear. For example Utkina and his associates[3,5] showed that azoles form CT complexes with π acceptors (TCNE, TCNQ) with various component ratios (2:1, 1:1, 1:2). They also suggested that the resultant complexes are of the n−π type. On the other hand Turchaninov et al.[8] deduced that CT complexes of some pyrazoles and benzazoles with π-electron acceptor (chloranil) are of the π−π type. Moreover, Hassan et al.[9] deduced that the CT complexes of aminopyrazoles with π-electron acceptors (dicyanoethylenetrinitrofluorene (DTF), TCNE and CHL) are a mixture of the n−π* and π−π* type. On the other hand, it was indicated that the CT complexes of some azoles with I_2 are of the n−σ type.[6]

In order to throw more light about the identity, composition and nature of CT complexes of pyrazoles with π- and σ-electron acceptors, the work of the present article is devoted to carry out a detail systematic study of CT complexes of pyrazole (I), 3-methylpyrazole (II), 3,5-dimethylpyrazole (III) and 3,5-dimethyl-1-phenylpyrazole (IV) with a σ-electron acceptor (iodine) and with some π-electron acceptors (DDQ, TCNE, CHL). The spectral characteristics and stability of the resultant CT complexes were examined and discussed in terms of the donor molecular structure, the nature of the electron acceptor and the solvent polarity. The ionization potentials of the donors were calculated based on the CT energies of their CT complexes.

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EXPERIMENTAL

Materials and Solutions

The pyrazoles (pyrazole I, 3-methylpyrazole II) were supplied by Merck Chem. Co. with high purity and were used as received. On the other hand, 3,5-dimethylpyrazole III and 3,5-dimethyl-1-phenylpyrazole IV were prepared as previously described.[10] The purity of the prepared compounds was checked by elemental analysis and thin-layer chromatography.

Donor III ($C_5H_8N_2$) requires C 62.47, H 8.38, N 29.14; found C 62.28, H 8.30, N 28.92; m.p.107°C. Donor IV ($C_{11}H_{12}N_2$) requires C 76.71, H 7.02, N 16.27; found C 76.65, H 6.96, N 16.16; b.p. 273°C.

The π-electron acceptors DDQ, TCNE and CHL (Aldrich or Merck reagent grade) were recrystallized form dry methylene chloride, chlorobenzene and dry benzene, respectively. Resublimed analytical reagent grade iodine was used and its concentration in solution was checked spectrophotometrically. All solvents used were of spectral grade (BDH or Merck). Stock solutions of the donors or acceptors were freshly prepared in a dry and deoxygenated solvent prior to use.

Several attempts were made to prepare solid CT complexes of each of the donors (I–IV) with π-acceptors (in a 1:1 molar ratio) and with iodine (in a molar ratio 1:1 or 1:2), however all these trials failed.

Physical Measurements

The electronic absorption spectra of the studied CT complex solutions were recorded with a Perkin-Elmer Lambda 40 recording spectrophotometer using 1 cm matched silica cells. The apparatus was equipped with a temperature-controlled cell holder, which was adjusted by a Julabo FP 40 thermostat with an accuracy ± 0.01°C. All computations were performed on an Apple II_e microcomputer with the aid of two programs based on unweighted linear least-squares fits.

RESULTS AND DISCUSSION

Spectral Characteristics and Formation Constants (K_{CT})

The electronic spectra of the CT complexes of the pyrazoles (I–IV) with the π-electron acceptors (DDQ, TCNE, CHL) and with the σ-electron acceptor (I_2) in CH_2Cl_2 solutions were recorded in the temperature range 10–25°C within the wavelength range 230–700 nm (Figures 1–4 and

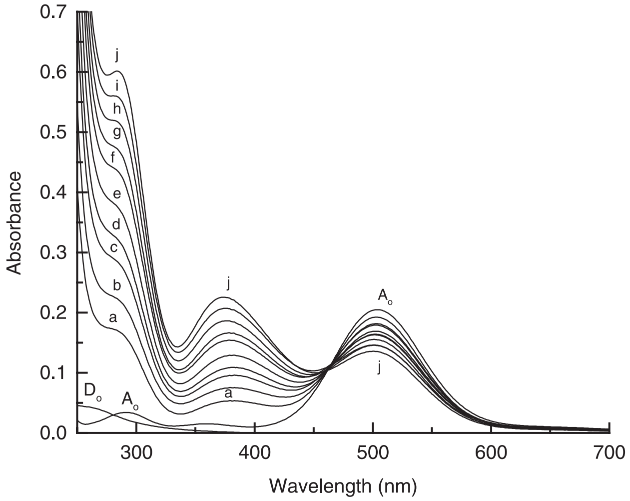

Figure 1. Electronic absorption spectra of the CT molecular complex solutions of 3,5-dimethyl-pyrazole (III) with iodine ($[A_o] = 2 \times 10^{-4}$ mol dm^{-3}) in CH_2Cl_2 at different temperatures, [III] = 2, 3, 4, 5, 6, 7, 8, 9, 10, 11 × 10^{-3} mol dm^{-3} for a, b, c, d, e, f, g, h, i, j, respectively.

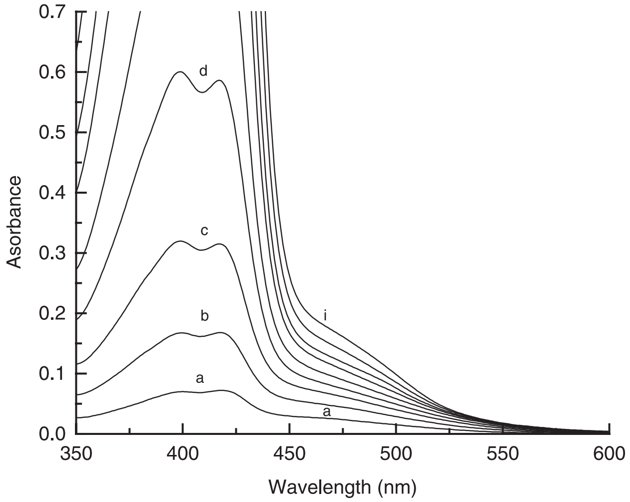

Figure 2. Electronic absorption spectra of the CT molecular complex solutions of 3,5-dimethyl-pyrazole (III) with TCNE (2×10^{-3} mol dm^{-3}) in CH_2Cl_2 at different temperatures, [III] = 0.008, 0.016, 0.024, 0.032, 0.040, 0.048, 0.056, 0.064, 0.072 × 10^{-3} mol dm^{-3} for a, b, c, d, e, f, g, h, i, respectively.

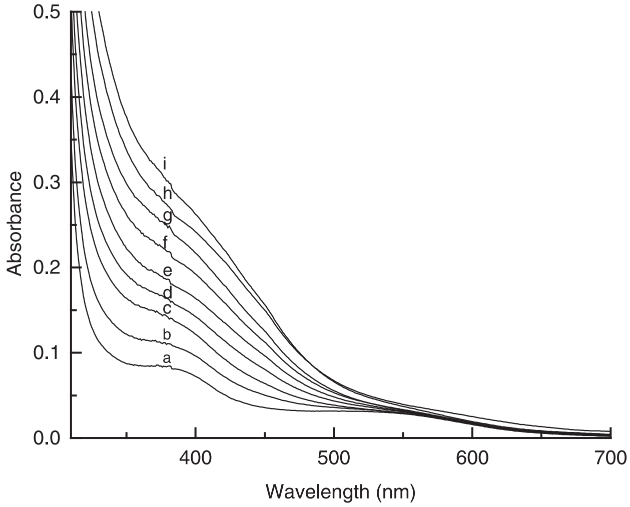

Figure 3. Electronic absorption spectra of the CT molecular complex solutions of 3,5-dimethyl-pyrazole (III) with CHL (6×10^{-3} mol dm^{-3}) in CH_2Cl_2 at different temperatures, [III] = 0.02, 0.03, 0.04, 0.05, 0.06, 0.07, 0.08, 0.09, 0.10×10^{-3} mol dm^{-3} for a, b, c, d, e, f, g, h, i, respectively.

Table 1). In cases of the CT complexes with π-electron acceptors DDQ or CHL the same acceptor concentration as in the test solution was used as a blank. However, in the case of TCNE or iodine CT complexes the solvent was used as a blank (except in case of 3,5-dimethyl-1-phenylpyrazole where the same donor concentration was employed as a blank). This was done so as to eliminate any possible overlap that may arise from the acceptor or the donor absorption spectrum with that of the corresponding CT complexes.

The spectra of dichloromethane solutions of iodine with each of the pyrazoles (I–IV) displayed two strong absorption bands with maximum absorption in the wavelength range 286–293 and 365–390 nm (cf. Figure 1). However, the intensities of these two bands increase with time and reach constant values after about 2–3 h depending on the nature of the donor. In this respect, it should be noted that in case of the donors pyrazole (I) and 3-methyl-pyrazole (II), the shorter wavelength band appears as a weak shoulder because of its overlap with the strong absorption band of the uncomplexed donor at 230, 260 and 235, 287 nm, respectively. From previous work,[11–13] these two bands are characteristic for the formation of the triiodide ion, which is characterized by two strong absorptions at 292

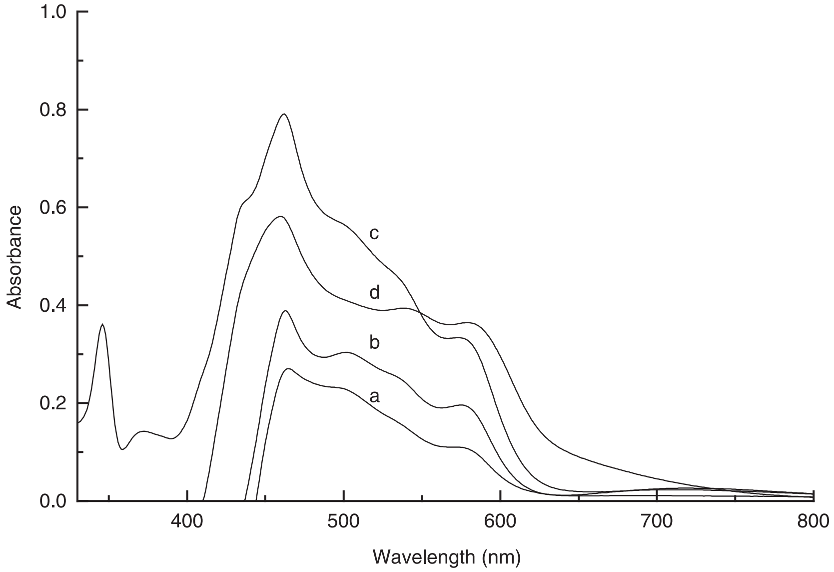

Figure 4. Electronic absorption spectra of dichloromethane CT complex solutions of DDQ with pyrazoles (I–IV): a) 0.080 mol dm^{-3} pyrazole + 3×10^{-3} mol dm^{-3} DDQ; b) 0.015 mol dm^{-3} 3-methylpyrazole + 3×10^{-3} mol dm^{-3} DDQ; c) 0.030 mol dm^{-3} 3,5-dimethylpyrazole + 2×10^{-3} mol dm^{-3} DDQ; d) 0.037 mol dm^{-3} 3,5-dimethyl-1-phenylpyrazole + 2×10^{-3} mol dm^{-3} DDQ.

and 365 nm. Thus the two observed absorption bands could be assigned to the absorption of the resultant triiodide ion (I_3^-). Since the results of the molar ratio method[14] is in accordance with the formation of a 1:1 CT complex in each case (cf. Figure 5), one can conclude that the pyrazoles-I_2 CT complexes exist mainly in solution in the form of the ionic structure $D_2I^+ \cdot I_3^-$. Convincing evidence for this assignment is that lowering the temperature, in the range 10–25°C, does not affect the intensity ratio of the observed two bands. Thus, one can deduce that the two CT bands should have the same enthalpies of formation (cf. Table 1) and therefore they are of the same nature (i.e. absorption of formed I_3^-). Accordingly, the formation of ionic complex $D_2I^+ \cdot I_3^-$ in solution may proceed by ionization of the initially formed molecular complex $D{-}I_2$.

$$2D - I_2 \rightarrow D_2I^+ + I_3^-$$

A similar suggestion was made previously for 1:1 pyridine (py), hexamethylene-tetramine (hx) and imidazole (im)-iodine CT complexes

Table 1. Spectral characteristics and thermodynamic parameters of the CT complexes of pyrazoles (I–IV) with various electron acceptors in methylene chloride at different temperatures as well as the ionization potentials of these donors.

Molecular complex	λ_{max} (nm)	E_{CT} (eV)	I.P (eV)	pK_a	$K_{CT}(dm^3mol^{-1})$, °C				ε_{CT} $dm^3mol^{-1}cm^{-1}$, 10°C	−ΔH° k cal.mol^{-1}	$(b/a)^2$
					10	15	20	25			
I–I_2	290 sh.	4.28		2.64	9.90 ± 0.27	8.58 ± 0.51	7.02 ± 0.11	6.10 ± 0.06	2452 ± 46	5.54 ± 0.28	0.057
	390	3.18	7.52		8.84 ± 0.36	7.73 ± 0.25	6.51 ± 0.14	5.54 ± 0.03	1212 ± 34	5.27 ± 0.23	0.073
II–I_2	286	4.34		3.73	13.69 ± 0.79	11.82 ± 0.84	9.40 ± 0.51	8.01 ± 0.31	6837 ± 366	6.15 ± 0.38	0.062
	385	3.22	7.58		13.41 ± 1.05	11.16 ± 2.01	9.48 ± 0.76	7.84 ± 0.38	2272 ± 164	5.94 ± 0.15	0.081
III–I_2	287	4.32		4.55	78.52 ± 2.19	60.89 ± 1.78	49.05 ± 2.53	39.80 ± 2.11	6245 ± 164	7.56 ± 0.17	0.077
	376	3.29	7.68		35.15 ± 2.36	27.14 ± 1.83	22.07 ± 1.07	17.72 ± 0.39	3823 ± 253	7.58 ± 0.21	0.100
IV–I_2	293	4.23		2.27	26.27 ± 0.28	21.72 ± 0.69	17.35 ± 0.69	14.54 ± 0.63	10306 ± 107	6.79 ± 0.19	0.070
	365	3.39	7.83		26.76 ± 0.93	21.79 ± 0.93	17.51 ± 0.63	14.50 ± 0.66	4447 ± 154	6.89 ± 0.10	0.089
III–TCNE	470	2.64	8.72	4.55	5.09 ± 0.18	4.68 ± 0.39	4.26 ± 0.12	3.92 ± 0.21	273 ± 10	2.94 ± 0.06	0.049
III–CHL	390	3.18	8.92	4.55	2.95 ± 0.09	2.66 ± 0.08	2.46 ± 0.11	2.30 ± 0.12	205 ± 6	2.77 ± 0.16	0.038

sh. = shoulder.

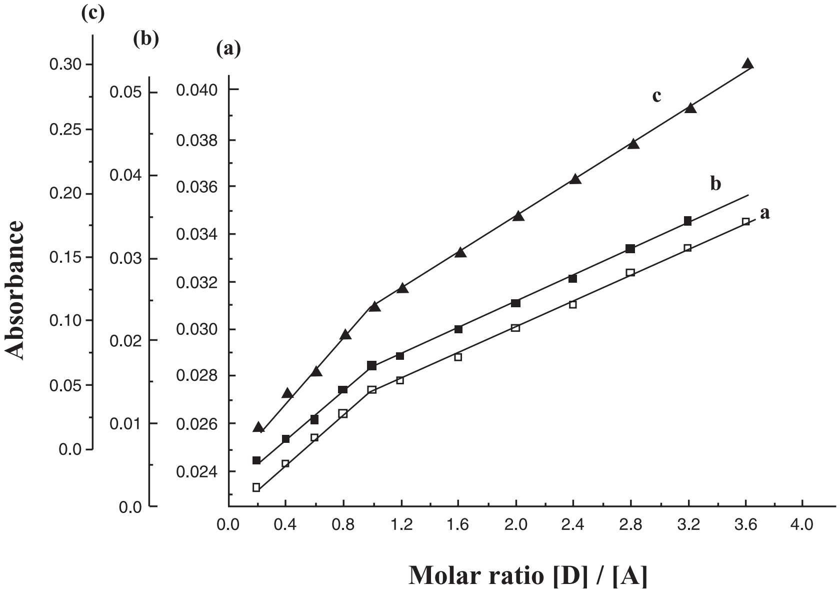

Figure 5. Molar ratio method for the CT complexes of 3,5-dimethylpyrazole (III) with π- and σ-electron acceptors. a) III–CHL CT complex ($\lambda_{max}=390$ nm), b) III–TCNE CT complex ($\lambda_{max}=470$ nm), c) III–I_2 CT complex ($\lambda_{max}=376$ nm).

which exist mainly in solution or in the solid state in the form of the ionic structure $(py)_2\ I^{+}\cdot I_3^{-}$, $(hx)_2\ I^{+}\cdot I_3^{-}$ and $(im)_2\ I^{+}\cdot I_3^{-}$, respectively.[15–18] Further evidence of the above mechanism concerning the formation of the ionic complex $D_2I^{+}\cdot I_3^{-}$ is from the results of the molar ratio method of 3,5-dimethylpyazole-I_2 CT complex (as representative example), which clearly reveal the 1:1 stoichiometric ratio of these complexes.

The electronic spectrum for a dichloromethane solution of 3,5-dimethylpyrazole-TCNE CT complex shows two main absorption bands, where the shorter wavelength band appears as a doublet ($\lambda_{max}=398$ and 417 nm), while the longer one is located at 470 nm (cf. Figure 2). The shorter band and its position can be compared with that previously reported for 1,1,2,3,3-pentacyanopropenide anion ($PCNP^{-}$),[19] formed by the reaction of TCNE with water traces of the solvent in the presence of a base (3,5-dimethylpyrazole) base hydrolysis.[20] Accordingly, the doublet band that appeared at 398 and 417 nm could be assigned to absorption of $PCNP^{-}$.[21,22] A similar interpretation has been suggested for the 1,4,8,11-tetramethyl-1,4,8,11-tetraazacyclotetradecane (TMTACTD)-TCNE complex.[23] On the other hand, the longer absorption band (470 nm) could be ascribed to intermolecular CT formation.

As a conclusion the spectrum of the 3,5-dimethylpyrazole-TCNE CT complex solution could be ascribed to absorption of formed $PCNP^-$ (the doublet band at 398, 417 nm)[21,22] and to intermolecular 1: 1 CT complex formation (the longer wavelength band at 470 nm) and not to the formation of CT complexes with various component ratios (2:1, 1:1 and 1: 2) as reported previously.[3,5]

From the quantitative point of view, the concentration of the formed $PCNP^-$ was estimated using the reported value of its ε_{max} (22600 dm^3 mol^{-1} cm^{-1}).[19,20] It was found that its concentration lies within the range 3.17×10^{-6} to 1.34×10^{-4}, 2.94×10^{-6} to 1.22×10^{-4}, 2.50×10^{-6} to 1.12×10^{-4} and 1.46×10^{-6} to 1.05×10^{-4} mol dm^{-3} in CH_2Cl_2 at temperatures 10, 15, 20, 25°C respectively. Accordingly, the remaining TCNE concentration was calculated. It is evident that the formation of $PCNP^-$ could not affect the remaining TCNE concentration and consequently the formation constant.

On applying CHL as a π-acceptor with donor III, one broad CT band appeared in the wavelength range 310–700 nm with λ_{max} at 390 nm (cf. Figure 3), which could be ascribed to a single intermolecular charge-transfer transition from HOMO on the donor to the LUMO on CHL.

Within the wavelength range 300–900 nm, the recorded spectra of the DDQ CT complex solutions (in deoxygenated methylene chloride) with donors I–IV display a series of absorption bands at 345, 369–74, 435–38 sh., 460–62, 539–40 sh., 575–78 nm (cf. Figure 4). These spectroscopic features are in good agreement with those previously reported for the anion radical $DDQ^{\cdot -}$ (346, 435, 456, 508, 547 and 584 nm).[24–26] Thus, one can deduce that the pyrazoles-DDQ CT complexes are of the strong kind (i.e., dissociate to radicals $DDQ^{\cdot -}$ and pyrazoles$^{\cdot +}$). Recently a similar assignment was reported for the interaction of DDQ with other donors.[27]

The formation constants (K_{CT}) and molar extinction coefficients (ε_{CT}) of the presently studied CT complexes in CH_2Cl_2 were determined spectrophotometrically in the temperature range 10–25°C using both the Benesi–Hildebrand and Scott equations[28,29] under the conditions $[D_o] > [A_o]$. All of the calculations were done by use of the method of linear least-squares. The mean K_{CT} and ε_{CT} values obtained are given in Table 1.

The stability of a molecular complex strongly depends on the nature of both donor orbitals (n or π) as well as the acceptor ones.[30,31] In fact, with pure π-donors the TCNE CT complex has K_{CT} values greater than the iodine (e.g. naphthalene 3.29 and 0.25 dm^3 mol^{-1}; hexamethylbenzene 148 and 1.35 dm^3 mol^{-1}, respectively).[30,32] This situation is reversed with pure n-donors where iodine gives higher formation constants (e.g. pyridine 97 and 0.77 dm^3 mol^{-1},[33,34] tetrahydrothiophene 252 and 0.60 dm^3 mol^{-1},[35,36] respectively). Regarding the K_{CT} values of 3,5-dimethylpyrazole-I_2, –TCNE and –CHL CT complexes listed in Table 1 makes it difficult to decide whether the donating orbital is an n or π orbital (i.e., the obtained K_{CT} values are small for a pure n–σ CT complexes and are relatively large for a π–σ one). Therefore, it could be suggested that the donor orbital has both n and π character. This conclusion is in good agreement with that previously suggested for the CT complexes of aminopyrazoles with π-electron acceptors (dicyanoethylenetrinitrofluorene (DTF), TCNE and CHL).[9] Further, such behaviour has been reported for the CT complexes of other donors.[37–40] Generally, the relatively low K_{CT} values of TCNE and CHL CT complexes suggest that the formed CT complexes are of a weak type, i.e., the nonbonding structure (D, A) has greater contribution in the ground state stabilization.

The results given in Table 1 reveal that the stability of the CT complexes of pyrazoles (I–IV) with a halogen σ-electron acceptor I_2 runs along the order: pyrazole < 3-methylpyrazole < 3,5-dimethyl-1-phenylpyrazole < 3,5-dimethylpyrazole. With the exception of the donor 3,5-dimethyl-1-phenylpyrazole, this sequence is in good agreement with their basic properties, where the pK_a values are 2.64, 3.73 and 4.55 for donors I, II and III, respectively.[41] On the other hand, the low K_{CT} value for 3,5-dimethyl-1-phenylpyrazole (IV) relative to that of 3,5-dimethylpyrazole (III) can mainly be attributed to the expected decrease of the electron donating ability of donor IV, owing to the electron withdrawing character of its phenyl moiety and steric hindrance (i.e., low K_{CT}).

The K_{CT} values of the CT complexes of donor III with different acceptors (I_2, TCNE and CHL) in methylene chloride have been performed in the temperature range 10–25°C. The obtained mean K_{CT} values along with the spectral characterization of such CT complexes are shown in Table 1. It is evident that the stability of the CT complexes formed decrease in the order: I_2 > TCNE > CHL. The high stability of the 3,5-dimethylpyrazole CT complex with iodine, compared to that of its complexes with the applied π-electron acceptors (TCNE, CHL) is in accordance with the expected nature of the formed CT complex, since the former is of (n, π)-σ type whereas the others are of the (n, π)-π type. Further, the greater stability of the same donor (III) with TCNE, compared to that with CHL, is consistent with the higher electron affinity of TCNE relative to that of CHL (electron affinity of TCNE and CHL is 1.68 and 1.37, respectively).[42,44]

Spectrophotometric determination of the K_{CT} values of the 3,5-dimethylpyrazole-DDQ CT complex was not possible owing to the fact that the recorded spectra of this complex do not exhibit a well-defined CT band. However, the spectra of this complex is perturbed by those of the radical anion $DDQ^{\cdot -}$ as described before.

Thermodynamic Parameters of the CT Complexes

The computed K_{CT} values for a series of temperatures (10–25°C) were utilized to determine the enthalpy change ($\Delta H°$) connected with the formation of the CT complexes using Van't Hoff equation plots.[45] The results are given in Tables 1, 2. It is evident that the numerical ($\Delta H°$) values of the CT complexes of 3,5-dimethylpyrazole with the present acceptors run along the order: $I_2 > TCNE > CHL$. This order is in agreement with their stability constants.

According to Mulliken[46–50] the ratio between the coefficients of the dative bond to the non-bond wave functions ($\psi_{D^+-A^-}$ and ψ_{D-A}, respectively), $(b/a)^2$, was calculated using the relation: $-\Delta H°/h\nu = (b/a)^2$. The ratios for I_2 CT complexes (0.057–0.100, Table 1) are compared to those of many strong CT complexes.[51] However, the estimated ratio for III-TCNE, –CHL CT complexes are 0.049, 0.038, respectively. These values are in accordance with the suggested weak nature of such CT complexes.

Ionization Potentials of the Donors

The ionization potentials (I.P.) of the highest filled molecular orbitals of the donors I–IV were estimated from CT energies of their complexes with the acceptors (I_2, TCNE, CHL) making use of the empirical equations reported by Aloisi and Pignataro.[52] The calculated I.P. values for molecular orbitals participating in CT interaction of pyrazoles are listed in Table 1. The values obtained (7.52–8.92 eV) are comparable with those previously estimated for the CT complexes of chloranil with the donors, pyrazole, 3-methylpyrazole and 3,5-dimethylpyrazole (I.P. = 9.15, 9.09, 8.77 eV, respectively)[8] and with that of pyrazole-chloranilic acid CT complex (I.P = 8.71 eV).[53]

THE EFFECT OF THE SOLVENT POLARITY ON THE STABILITY OF THE FORMED CT COMPLEXES

To elucidate the role of solvent polarity on the stability of the formed CT complexes of pyrazoles (I–IV) with the applied electron acceptors, the CT molecular complex of 3,5-dimethylpyrazole (III) with I_2 had been studied in different solvents of various polarities ($C_2H_4Cl_2$, CH_2Cl_2, $CHCl_3$

Table 2. Spectral characteristics and thermodynamic parameters of the CT complexes of 3,5-dimethylpyrazole (III) with I_2 (σ-electron acceptor) in various solvents at different temperatures as well as the ionization potentials of this donor.

Solvent	λ_{max} (nm)	E_{CT} (eV)	I.P. (eV)	K_{CT} (dm^3mol^{-1}),°C				ε_{CT} $dm^3mol^{-1}cm^{-1}$, 10°C	−ΔH° k cal.mol^{-1}	$(b/a)^2$
				10	15	20	25			
CCl_4	287	4.32								
	395	3.14	7.46	22.61 ± 0.80	19.50 ± 0.66	16.48 ± 0.96	13.75 ± 0.99	3138 ± 110	5.56 ± 0.24	0.077
$CHCl_3$	281	4.41		36.30 ± 1.63	28.80 ± 0.76	24.17 ± 0.64	20.10 ± 0.84	5381 ± 234	6.54 ± 0.24	0.065
	392	3.16	7.49	25.93 ± 1.62	21.47 ± 1.61	17.50 ± 0.81	14.36 ± 0.91	2006 ± 123	6.63 ± 0.13	0.092
CH_2Cl_2	287	4.32		78.52 ± 2.19	60.89 ± 1.78	49.05 ± 2.53	39.80 ± 2.11	6245 ± 164	7.56 ± 0.17	0.077
	376	3.29	7.68	35.15 ± 2.36	27.14 ± 1.83	22.07 ± 1.07	17.72 ± 0.39	3823 ± 253	7.58 ± 0.21	0.100
$C_2H_4Cl_2$	290	4.27		146.37 ± 1.71	100.78 ± 1.65	69.85 ± 1.51	48.09 ± 1.03	12389 ± 107	12.42 ± 0.14	0.130
	367	3.38	7.80	148.66 ± 2.27	101.03 ± 1.61	70.54 ± 1.45	47.52 ± 1.27	5495 ± 65	12.67 ± 0.24	0.160

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and CCl_4) at the temperature range 10–25°C. Spectral characteristics, and the computed formation constant (K_{CT}) values of these CT complexes are cited in Table 2. It is evident that the formation constant of the charge-transfer complex increases as the dielectric constant of the solvent is increased (CCl_4, $D = 2.238 \rightarrow CHCl_3$, $D = 4.806 \rightarrow CH_2Cl_2$, $D = 9.080 \rightarrow C_2H_4Cl_2$, $D = 10.650$). This trend can be interpreted on the basis that the CT complex is of strong type and exists in the ionic form $D_2^{+}\cdot I_3^{-}$, i.e., there is a high contribution of the ionic structure wave function $\psi_{D^{+}-A^{-}}$ to the ground state wave function of the CT complex. Accordingly, the ionic structure (pyrazole)$_2$ $I^{+}\cdot I_3^{-}$ would be more stabilized in a polar solvent of high dielectric constant owing to increasing dipole–dipole or dipole-induced dipole interactions. Accordingly one can deduce that the solvent polarity plays an important role in determining the stability of such CT complexes. A similar behavior and interpretation was reported for other donor-iodine CT complexes.[18,54]

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