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Molecular Complexes of Cyclophanes, XVIII: Spectroscopic and Thermodynamic Studies on the Charge-Transfer Complexes Between 4-([2.2]Paracyclophanoyl)amines and π-Acceptors

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Abstract. The charge-transfer (CT) complexes of several substituted 4-([2.2]paracyclophanoyl)amines as donors with tetracyanoethylene (*TCNE*) and 2,3-dichloro-5,6-dicyanobenzoquinone (*DDQ*) as π-acceptors have been studied spectrophotometrically. The role of the molecular structure of the donors on their Lewis basicities, the site and type of CT interactions are discussed. The thermodynamic properties of some CT complexes as well as the solvent effect on the CT complexation are reported.

Keywords. Cyclophanes; Molecular complexes; Charge-transfer complexes.

Molekulare Komplexe von Cyclophanenen, 18. Mitt.: Spektroskopische und thermodynamische Untersuchungen der Charge-Transfer-Komplexe von 4-([2.2]Paracyclophanoyl)aminen mit π-Akzeptoren

Zusammenfassung. Es wurden die Charge-Transfer-Komplexe einiger substituierter 4-([2.2]Paracyclophanoyl)amine als Donoren mit Tetracyanoethylen (*TCNE*) und 2,3-Dichlor-5,6-dicyanobenzochinon (*DDQ*) als π-Akzeptoren spektrophotometrisch untersucht. Der Einfluß der Donor-Molekülstrukturen auf ihre Lewis-Basizitäten sowie Ort und Typ der CT-Wechselwirkung werden diskutiert. Es wird über die thermodynamischen Eigenschaften einiger CT-Komplexe und auch über Lösungsmitteleffekte bei der Komplexierung berichtet.

Introduction

The CT complexes between cyclophanes and electron acceptor were the subject of several interesting studies in the last three decades. In recent studies, the spectroscopic properties of the CT complexes of [2.2]paracyclophanecarbamates [1] and azomethines [2, 3] have been discussed.

In continuation of our investigstions on the CT complexes of nitrogen containing ligand cyclophanes, we wish in the present study to discuss the spectroscopic and thermodynamic properties of the CT complexes of some newly synthesized 4-([2.2]paracyclophanoyl)amines (I) (Scheme 1) with *TCNE* and *DDQ* as electron acceptors.

The aim of our study is:

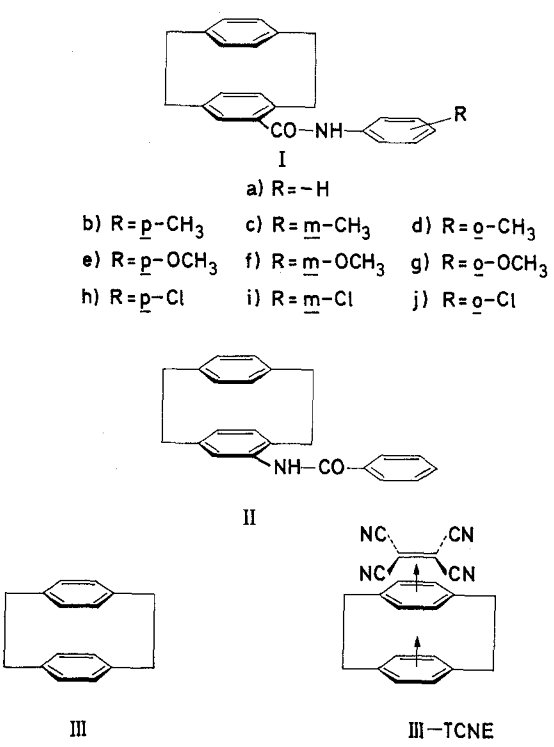
1) To determine the site and type of interactions in the donor system.

2) To explain the influence of the transannular electronic interactions on the basicities of the [2.2]paracyclophane-anilides **I** and **II**.

3) To study the thermodynamic properties of the CT complexes of **I** with π-acceptors.

Experimental Part

4-([2.2]Paracyclophanoyl)amines **I a – j** were prepared according to the Schotten-Baumann method by addition of the acid chloride of 4-carboxy[2.2]paracyclophane to the appropriate amine in 10% aqueous sodium hydroxide solution [4]. N-Benzoyl-4-amino[2.2]paracyclophane (**II**) was prepared from 4-amino[2.2]paracyclophane and benzoyl chloride. Analytical and physical data of these anilides are recorded in Tables 1 and 2. Tetracyanoethylene (Aldrich) was recrystallized from chloroform and sublimed. 2,3-Dichloro-5,6-dicyanobenzoquinone (Aldrich) was recrystallized from benzene-chloroform (2 : 3). Methylene chloride, dichloroethane, chloroform, carbon tetrachloride and sym.-tetrachloroethane were purified following [5], dried, and distilled.



Scheme 1

For the determination of the stoichiometry by Job's method [6], stock solutions ($1 \cdot 10^{-2}$ mol/l) of *TCNE* and *DDQ* as well as donors **I** and **II** were prepared accurately. Association constant (*K*) values of the CT complexes were determined using the Benesi-Hildebrand equation [7] for a 1 : 1-complex:

$$\frac{[A]l}{d} = \frac{1}{K\varepsilon} \cdot \frac{1}{[D]} + \frac{1}{\varepsilon},$$

where $[A]$ and $[D]$ are the initial molar concentration of acceptor and donor respectively, l the length of the light path in cm, d is the optical density, ε is the apparent molar extinction coefficient and K

is the association constant for the equation *TCNE* (or *DDQ*) + Paracyclophane $\rightleftharpoons$ complex. The effect of temperature on the association constant and the stability of CT complexes in different solvents was determined by increasing the temperatures gradually from 10 to 35°C (±0.5°C) and decreasing it from 35 to 10°C.

Melting points are uncorrected. UV/VIS absorption spectra were recorded on a Perkin-Elmer Lambda 2 spectrophotometer equipped with a temperature-regulated cell holder. Matched quartz (stoppered) cells of 1 cm path length were used. All scans covered the range 350–800 nm. IR spectra were recorded on a Shimadzu 408 spectrometer. Elemental analyses were performed by the microanalysis unit at Cairo University.

Results and Discussion

Addition of either *TCNE* or *DDQ* to the donors **Ia–j** in methylene chloride gave coloured solutions absorbing in the visible region thus confirming the formation of CT complexes. The absorption bands of these CT complexes are broad and well separated from the transitions of either of the components. Also, the linear relationship between the maximum frequencies of the new bands for *TCNE*-complexes and those of *DDQ*-complexes (Fig. 1) further supports complex formation.

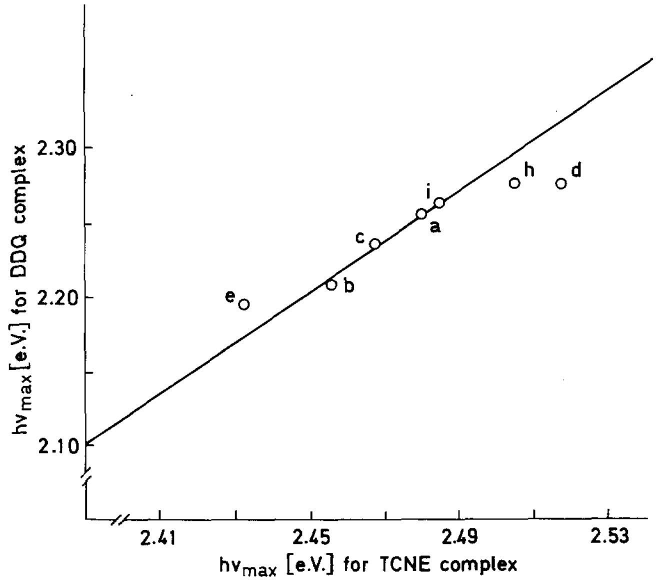


Fig. 1

Application of Job's method [6] for continuous variation for the two series of CT complexes gave symmetrical curves with a mole fraction of 0.5 indicating 1 : 1 stoichiometric ratio for all CT complexes studied under the range of the experimental conditions.

Table 3 includes the spectroscopic data of the CT complexes with both *TCNE* and *DDQ*. Analysis of these data reveals that the *DDQ*-complexes absorbed at longer wavelengths than those of *TCNE*, due to the relatively high electron affinity of *DDQ* [8]. Taking into consideration the position of λ_{max} of the CT complex as a measure of the basicity of the donor, the data indicate also that the electron donating character of donors **I** decreases in the order; anisyl > tolyl > phenyl > chlorophenyl. Since the *ortho*-substituted donors are more sterically hindered than the others, the donor character of the former are in general weaker than the *para*-

Table 1. Physical and analytical data for 4-([2.2]paracyclophanoyl)amines **I a – j** and N-benzoyl-4-amino[2.2]paracyclophane (**II**)

Compound	M.p. (°C)*	Analysis calculated (found) (%)		
		C	H	N
I a	184–185	84.37	6.46	4.27
		(84.30	6.40	4.10)
I b	191–192	84.45	6.75	4.11
		(84.40	6.80	4.10)
I c	174–175	(84.50	6.70	4.10)
I d	142	(84.55	6.72	4.08)
I e	178	80.67	6.44	3.92
		(80.70	6.43	3.90)
I f	156–157	(80.80	6.40	3.80)
I g	139–140	(80.60	6.40	3.85)
I h	184–185	76.35	5.53	3.87
		(76.30	5.50	3.90)
I i	169–170	(76.32	5.51	3.85)
I j	99–100	(76.29	5.49	3.83)
I I	177	84.37	6.46	4.27
		(84.32	6.44	4.25)

* All compounds were recrystallized from cyclohexane

Table 2. ^{1}H-NMR (δ, *TMS*, $CDCl_3$) and IR (KBr, cm^{-1}) of **I a – j** and **II**

Compound	$-CH_2-CH_2-$	(*Ar*-H, –NH)	Other protons	IR (KBr, cm^{-1})	
				NH (br.)	CO
I a	3.50 – 3.00 (m, 8 H)	7.80 – 6.50 (m, 13 H)	–	3 300	1 635
I b	3.20 – 3.00 (m, 8 H)	7.70 – 6.35 (m, 12 H)	2.35 (s, 3 H, $-CH_3$)	3 275	1 650
I c	3.20 – 2.90 (m, 8 H)	7.45 – 6.30 (m, 12 H)	2.37 (s, 3 H, $-CH_3$)	3 300	1 650
I d	3.30 – 3.00 (m, 8 H)	7.80 – 6.40 (m, 12 H)	2.30 (s, 3 H, $-CH_3$)	3 300	1 640
I e	3.50 – 3.00 (m, 8 H)	7.70 – 6.50 (m, 12 H)	3.90 (s, 3 H, $-OCH_3$)	3 250	1 650
I f	3.30 – 3.00 (m, 8 H)	7.50 – 6.40 (m, 12 H)	3.80 (s, 3 H, $-OCH_3$)	3 300	1 650
I g	3.50 – 3.00 (m, 8 H)	8.00 – 6.40 (m, 12 H)	3.80 (s, 3 H, $-OCH_3$)	3 450	1 670
I h	3.20 – 2.90 (m, 8 H)	7.60 – 6.40 (m, 12 H)	–	3 300	1 650
I i	3.20 – 2.96 (m, 8 H)	7.78 – 6.30 (m, 12 H)	–	3 300	1 655
I j	3.20 – 2.80 (m, 8 H)	7.90 – 6.40 (m, 12 H)	–	3 450	1 680
II	3.45 – 2.80 (m, 8 H)	7.95 – 6.35 (m, 13 H)	–	3 305	1 646

Table 3. Spectral data for 1 : 1 CT complexes between **I a – j** and **II** with *TCNE* and *DDQ* in methylene chloride at 22°C

Donor	Acceptor	λ_{max} [nm]	E [e.V]	ε_{max} ($l\ mol^{-1}\ cm^{-1}$)	K ($l\ mol^{-1}$)	I.P. [e.V]
Ia	*TCNE*	500	2.480	276	$2.831 \pm 4 \cdot 10^{-2}$	8.510
Ib		508	2.455	244	$3.900 \pm 1 \cdot 10^{-2}$	8.477
Ic		503	2.467	286	$3.397 \pm 1 \cdot 10^{-2}$	8.494
Id		493	2.518	400	$2.586 \pm 2 \cdot 10^{-2}$	8.560
Ie		510	2.431	200	$5.179 \pm 1 \cdot 10^{-2}$	8.445
If		475 (sh)	–	–	–	–
Ig		488	2.545	500	$2.222 \pm 2 \cdot 10^{-2}$	8.817
Ih		498	2.492	333	$2.647 \pm 1 \cdot 10^{-2}$	8.543
Ii		499	2.485	250	$2.769 \pm 3 \cdot 10^{-2}$	8.517
Ij		495 (sh)	–	–	–	–
II		515	2.408	833	$8.267 \pm 2 \cdot 10^{-2}$	8.414
Ia	*DDQ*	550	2.255	375	$8.530 \pm 6 \cdot 10^{-2}$	8.524
Ib		558	2.224	286	$11.666 \pm 3 \cdot 10^{-2}$	8.480
Ic		553	2.244	333	$9.000 \pm 2.5 \cdot 10^{-2}$	8.511
Id		545	2.275	392	$8.014 \pm 2 \cdot 10^{-2}$	8.549
Ie		565	2.195	308	$13.000 \pm 5 \cdot 10^{-2}$	8.450
If		540 (sh)	–	–	–	–
Ig		538	2.339	400	$7.500 \pm 1 \cdot 10^{-2}$	8.628
Ih		545	2.275	308	$8.000 \pm 7 \cdot 10^{-2}$	8.548
Ii		549	2.259	333	$8.273 \pm 5 \cdot 10^{-2}$	8.529
Ij		535 (sh)	–	–	–	–
II		670	1.851	125	$21.932 \pm 7 \cdot 10^{-2}$	8.028

and *meta*-isomers. However, in case of the anisyl derivative **Ie – g** the resonance effect overcompensates the steric one, and accordingly the *ortho*-isomer is more basic than the *m*-isomer. In the chlorophenyl derivatives **Ih – j** the donors are affected to a great extent by the inductive effect of the chlorine atom.

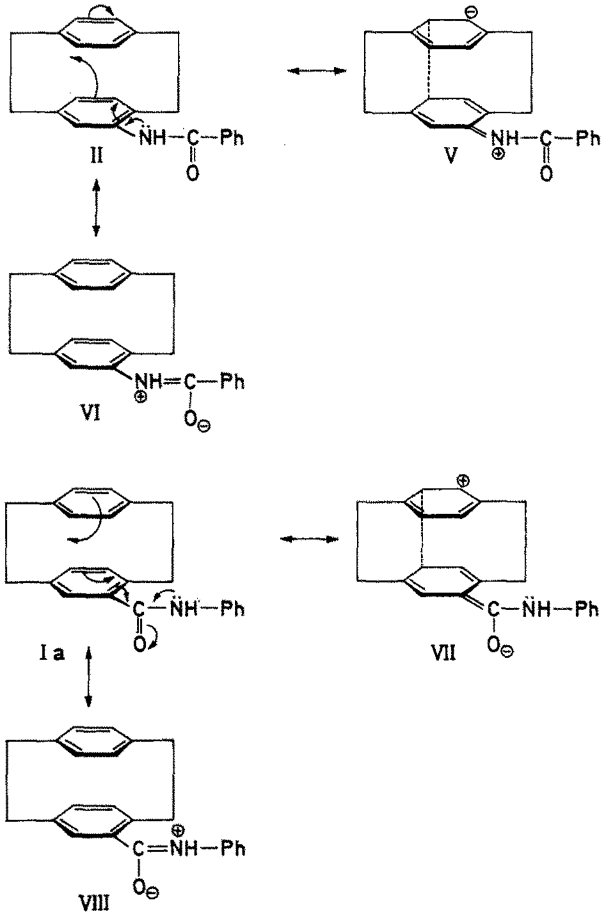
Plotting $\log K$ values of the CT complexes against the Hammett substituent constant (σ) of the different substitutents results in a linear fit with a slope $\rho = -4.432$ ($r = 0.97$) in case of the *TCNE*-complexes and $\rho = -4.342$ ($r = 0.99$) for *DDQ*-complexes. This is a good measure of electronic inductive and resonance effects involved in the CT complex formation.

To study the structural factors which are responsible for complex formation and to determine the complexation centre in the CT complexes of donors **I** with the π-acceptors, a comparison including the CT complexes of N-benzoyl-4-amino-[2.2]paracyclophane (**II**) [2.2]paracyclophane [**III**] [9] and benzanilide [10] was made. Table 4 contains the λ_{max} values of **I a**, **II**, **III**, and benzanilide with *TCNE*. Accordingly, the basic character decreases in the order **III** > **II** > **I a** > benzanilide. It has been reported that the **III**-*TCNE* complex absorbs at longer wavelength than the open-chain related system, e. g. *p*-xylene-*TCNE* complex [11]. This is attributed to the existence of transannular electronic interactions in the paracyclophane system, i.e. the two benzene rings act as one unit. Therefore the net electron density of both rings is shifted towards the π-acceptor involved as indicated in Scheme 1.

Table 4. Values of the wavelengths of maximum absorption of the CT complexes of *TCNE* with **I a**, **II**, **III**, and benzanilide in methylene chloride

Donor	λ_{max} (nm)
4-([2.2]paracyclophanoyl)aniline (**I a**)	500
N-Benzoyl-4-amino-[2.2]paracyclophane (**II**)	515
[2.2]paracyclophane (**III**)	521
Benzanilide	575 (sh)

Substitution of one hydrogen atom in **III** by NHCO*Ph* should increase the transannular electronic interactions resonance due to the resonance between the lone pair of the nitrogen atom and the paracyclophane nucleus (**V**, Scheme 2). On the other hand, this resonance is diminished by overlays between the −NH and the carbonyl group (**VI**) so that the electron donating character of **II** is weaker than **III**. The basicity of donor **I a** should be weaker than that of **II**, due to the electron delocalization indicated in **VII**. The resonance between the −NH and



Scheme 2

carbonyl group in **I a** (**VIII**) results in a partial reduction of the electron-withdrawing effect of the carbonyl group. It is worth noting that the weak electron donating character of benzanilide is due to the absence of transannular electronic interactions.

One may suggest that the unsubstituted ring in the donors **I** is the preferred complexing centre. This can reasonably be explained as being due to the reduction of the donor capability of the benzene ring substituted with an electron-withdrawing carbonyl group. In addition, the π-acceptor does not complex with −HN*Ph*, since this substituent is considered as the complexing centre in the benzanilide-*TCNE* complex and the latter is weak and absorbs only as a shoulder [10]. Accordingly, the electronic transition is most likely to be of the π-π* type. In case of donor **II**, the two halfs of the [2.2]paracyclophane nucleus may be considered as a complexing site, however, the steric hindrance in the substituted half reinforces the suggestion that the unsubstituted half is the most preferable donating site, and the electronic transition is suggested to be of π-π* type.

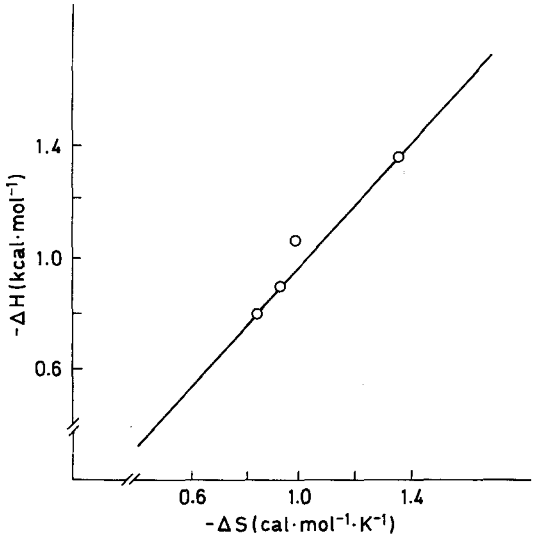


Fig. 2

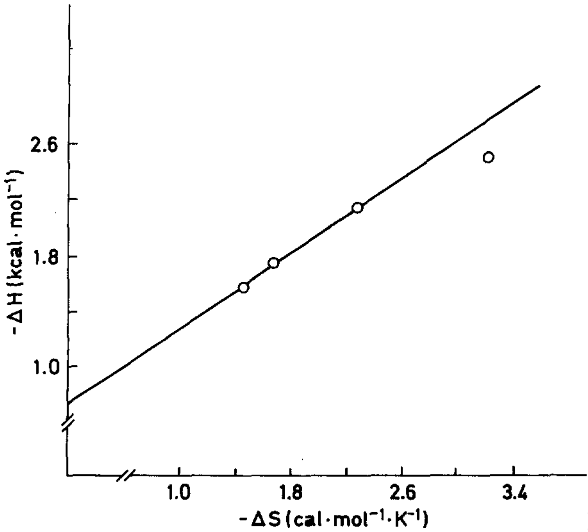


Fig. 3

Table 5. Thermodynamic and spectrophotometric data of the CT complexes between **I a**, **I b**, **I e**, and **I h** with *TCNE* and *DDQ* in methylene chloride

Donor	Acceptor	*K*					$-\Delta G$ (kcal mol^{-1})	$-\Delta H$ (kcal mol^{-1})	$-\Delta S$ (cal mol^{-1} K^{-1})
		10°C	20°C	25°C	30°C	35°C			
Ia	*TCNE*	$3.233 \pm 2.5 \cdot 10^{-2}$	$2.899 \pm 1.3 \cdot 10^{-2}$	$2.755 \pm 1.8 \cdot 10^{-2}$	$2.692 \pm 4.5 \cdot 10^{-2}$	$2.570 \pm 5.1 \cdot 10^{-2}$	$0.607 \pm 4.0 \cdot 10^{-3}$	$0.881 \pm 1.1 \cdot 10^{-2}$	$0.929 \pm 5.0 \cdot 10^{-2}$
Ib		$4.366 \pm 1.9 \cdot 10^{-2}$	$4.101 \pm 3.3 \cdot 10^{-2}$	$3.813 \pm 1.7 \cdot 10^{-2}$	$3.750 \pm 4.4 \cdot 10^{-2}$	$3.650 \pm 5.2 \cdot 10^{-2}$	$0.794 \pm 2.0 \cdot 10^{-3}$	$1.092 \pm 1.0 \cdot 10^{-2}$	$1.013 \pm 4.0 \cdot 10^{-2}$
Ie		$5.631 \pm 4.1 \cdot 10^{-2}$	$5.250 \pm 3.4 \cdot 10^{-2}$	$5.000 \pm 2.5 \cdot 10^{-2}$	$4.815 \pm 1.9 \cdot 10^{-2}$	$4.666 \pm 3.4 \cdot 10^{-2}$	$0.959 \pm 2.5 \cdot 10^{-3}$	$1.366 \pm 1.0 \cdot 10^{-2}$	$1.378 \pm 3.5 \cdot 10^{-2}$
Ih		$3.000 \pm 4.3 \cdot 10^{-2}$	$2.684 \pm 3.9 \cdot 10^{-2}$	$2.591 \pm 2.8 \cdot 10^{-2}$	$2.357 \pm 3.2 \cdot 10^{-2}$	$2.323 \pm 2.2 \cdot 10^{-2}$	$0.568 \pm 9.1 \cdot 10^{-3}$	$0.813 \pm 2.0 \cdot 10^{-2}$	$0.831 \pm 3.0 \cdot 10^{-2}$
Ia	*DDQ*	$8.885 \pm 4.5 \cdot 10^{-2}$	$8.612 \pm 3.5 \cdot 10^{-2}$	$8.378 \pm 4.8 \cdot 10^{-2}$	$8.175 \pm 3.9 \cdot 10^{-2}$	$7.840 \pm 2.5 \cdot 10^{-2}$	$1.251 \pm 1.1 \cdot 10^{-3}$	$1.741 \pm 1.5 \cdot 10^{-2}$	$1.663 \pm 4.2 \cdot 10^{-2}$
Ib		$12.133 \pm 3.1 \cdot 10^{-2}$	$11.789 \pm 4.1 \cdot 10^{-2}$	$11.558 \pm 2.8 \cdot 10^{-2}$	$11.308 \pm 1.9 \cdot 10^{-2}$	$10.769 \pm 2.2 \cdot 10^{-2}$	$1.433 \pm 2.0 \cdot 10^{-3}$	$2.102 \pm 5.0 \cdot 10^{-2}$	$2.267 \pm 2.5 \cdot 10^{-2}$
Ie		$13.464 \pm 2.8 \cdot 10^{-2}$	$13.200 \pm 2.5 \cdot 10^{-2}$	$12.800 \pm 2.5 \cdot 10^{-2}$	$12.650 \pm 5.0 \cdot 10^{-2}$	$12.500 \pm 3.0 \cdot 10^{-2}$	$1.497 \pm 2.7 \cdot 10^{-3}$	$2.452 \pm 1.5 \cdot 10^{-2}$	$3.239 \pm 4.0 \cdot 10^{-2}$
Ih		$8.450 \pm 4.3 \cdot 10^{-2}$	$8.196 \pm 3.9 \cdot 10^{-2}$	$7.800 \pm 4.4 \cdot 10^{-2}$	$7.583 \pm 2.9 \cdot 10^{-2}$	$7.428 \pm 3.5 \cdot 10^{-2}$	$1.213 \pm 7.0 \cdot 10^{-3}$	$1.656 \pm 5.0 \cdot 10^{-2}$	$1.501 \pm 2.2 \cdot 10^{-2}$

Thermodynamic Studies

The effect of temperature on the CT complexation of donors **I a**, **b**, **e**, **h** with *TCNE* and *DDQ* reveals that the absorbance of these complexes decreases with increasing temperature. Upon decreasing the temperature again, the original absorbance values were restored with no significant change. The values of iteratively computed K of the former complexes at different temperatures in methylene chloride were used to compute ΔG, ΔH, and ΔS; the results are summarized in Table 5.

Comparison of the results in Table 5 reveals that the CT complexation of these donors with *DDQ* is more exothermic than with *TCNE*. This could again be explained to be due to the relatively high electron affinity of *DDQ* with respect to *TCNE* [8].

Plotting ΔH against ΔS for the donors and both π-acceptors in methylene chloride gave a linear relationship (Figs. 2 and 3). This is in agreement with the results reported for other systems [12, 13]. It is particularly interesting that increasing the electron-donating property of R, the ΔH, values become more negative (i.e. better stabilization of the CT complexes) and a corresponding decrease in ΔS was observed. The simultaneous slight decrease in these terms indicates the slight effect of the substitutent on the stability of the CT complexes studied

Solvent Effects

The solvent plays an important role in the CT complexation by affecting both thermodynamic as well as spectrophotometric properties [14–17]. Thermodynamic and spectrophotometric properties of 4-([2.2]paracyclophanoyl)aniline-*TCNE* complexes in different solvent such as methylene chloride, 1,2-dichloroethane, chloroform, carbon tetrachloride, and *sym*-tetrachloroethane, are reported in Table 6. The chlorinated solvents were chosen since they are more suitable than any others such as ethyl acetate, acetonitrile and aromatic hydrocarbons.

Analysis of the data in Table 6 reveals that the thermodynamic and spectrophotometric dats are affected by the variation of the solvent. For example the observed increase in K values measured in chloroform suggests that the complex is better solvated by chloroform than by other solvents. This can be ascribed to the presence of a certain competition between donor and solvent via formation of a hydrogen bond between the nitrogen-lone pair of the donor and the hydrogen atom of $CHCl_3$. Since 1,2-dichloroethane, methylene chloride, and *sym*-tetrachloroethane are of comparable polarity their effect on complex formation is similar. Compared to the other chlorinated solvents carbon tetrachloride shows a strange behaviour since it behaves as a weak acceptor [18], and thus competes with *TCNE* for the formation of CT complexes with donors; hence lower values of K were obtained.

Acknowledgement

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Table 6. Effect of solvent on maximum absorption wavelengths λ_{max} [nm] and association constants K [$l\,mol^{-1}$] of the 4-([2.2]paracyclophanoyl)aniline-*TCNE* complex

Solvent	Dielectric constant	λ_{max}	ε_{max} [$l\,mol^{-1}\,cm^{-1}$]	K					$-\Delta G$ (kcal mol^{-1})	$-\Delta H$ (kcal mol^{-1})	$-\Delta S$ (cal-mol^{-1}K^{-1})
				10°C	20°C	25°C	30°C	35°C			
Methylene chloride	8.900[a]	500	276	$3.233 \pm 2.5 \cdot 10^{-2}$	$2.899 \pm 3.0 \cdot 10^{-2}$	$2.755 \pm 2.0 \cdot 10^{-2}$	$2.670 \pm 1.5 \cdot 10^{-2}$	$2.416 \pm 2.0 \cdot 10^{-2}$	$0.607 \pm 2.3 \cdot 10^{-3}$	$0.881 \pm 1.5 \cdot 10^{-2}$	$0.930 \pm 5.2 \cdot 10^{-2}$
Chloroform	4.800[a]	505	381	$4.700 \pm 5.0 \cdot 10^{-2}$	$4.045 \pm 3.0 \cdot 10^{-2}$	$4.300 \pm 4.5 \cdot 10^{-2}$	$4.000 \pm 2.5 \cdot 10^{-2}$	$3.900 \pm 1.5 \cdot 10^{-2}$	$0.846 \pm 3.4 \cdot 10^{-3}$	$1.188 \pm 5.0 \cdot 10^{-2}$	$1.158 \pm 1.8 \cdot 10^{-2}$
Carbon tetrachloride	2.200[a]	490	125	$1.792 \pm 4.0 \cdot 10^{-2}$	$1.739 \pm 3.5 \cdot 10^{-2}$	$1.677 \pm 2.5 \cdot 10^{-2}$	$1.636 \pm 2.0 \cdot 10^{-2}$	$1.500 \pm 3.5 \cdot 10^{-2}$	$0.309 \pm 4.5 \cdot 10^{-3}$	$0.486 \pm 1.3 \cdot 10^{-2}$	$0.599 \pm 4.0 \cdot 10^{-2}$
sym-Tetrachloroethane	8.200[a]	495	577	$2.448 \pm 2.5 \cdot 10^{-2}$	$3.140 \pm 3.0 \cdot 10^{-2}$	$1.999 \pm 4.0 \cdot 10^{-2}$	$1.900 \pm 1.5 \cdot 10^{-2}$	$1.867 \pm 3.5 \cdot 10^{-2}$	$0.407 \pm 4.8 \cdot 10^{-3}$	$0.607 \pm 9.0 \cdot 10^{-2}$	$0.671 \pm 7.0 \cdot 10^{-2}$
1,2-Dichloroethane	10.650[b]	497.5	400	$2.562 \pm 3.5 \cdot 10^{-2}$	$2.143 \pm 4.0 \cdot 10^{-2}$	$2.001 \pm 4.0 \cdot 10^{-2}$	$1.964 \pm 5.0 \cdot 10^{-2}$	$1.967 \pm 3.0 \cdot 10^{-2}$	$0.416 \pm 6.1 \cdot 10^{-3}$	$0.701 \pm 5.0 \cdot 10^{-2}$	$0.854 \pm 1.2 \cdot 10^{-2}$

[a] Ref. [4]

[b] Ref. [18]

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