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# Charge-Transfer Complexes of Indenophanes with π-Acceptors

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The charge-transfer (CT) spectra of the π-complexes formed by a number of π-acceptors with several indenophanes as well as indene as a model compound have been measured in methylene chloride at 20 °C. Association constants and transition energies of these complexes as well as ionization potentials of the π-donors have been determined. The data obtained indicate the existence of transannular electronic interactions in the indenophane nucleus. Furthermore, the pseudo-*para*- and *meta*[2.2]indenophane isomers (**3** and **4**) show a large difference in their π-base strength. A good linear relationship has been observed between the association constants and $\lambda_{max}$ of the long wavelength CT bands for the π-complexes of these π-donors with both tetracyanoethylene (*TCNE*) and 2,3-dichloro-5,6-dicyanobenzoquinone (*DDQ*). All CT complexes studied have a 1 : 1 stoichiometry.

*(Keywords: Charge-transfer spectra; π-Complexes; Indenophanes)*

## *Charge-transfer-Komplexe aus Indenophanen und π-Akzeptoren*

Die Charge-transfer-Spektren (CT-Spektren) von π-Komplexen aus Indenophanen bzw. der Modellverbindung Inden und verschiedenen π-Akzeptoren wurden in Methylenchlorid bei 20 °C bestimmt. Die Assoziationskonstanten und Übergangsenergien dieser Komplexe sowie die Ionisationspotentiale der π-Donatoren wurden ermittelt. Die Daten sprechen für das Vorliegen transannularer elektronischer Wechselwirkungen im Indenophan-System. Die isomeren pseudo-*para*- und -*meta*[2.2]indenophane **3** und **4** unterscheiden sich in ihrer π-Basizität deutlich. Es besteht eine gute lineare Korrelation zwischen den Assoziationskonstanten und $\lambda_{max}$ der langwelligen CT-Banden der verschiedenen π-Donatoren mit Tetracyanoethylen (*TCNE*) und 2,3-Dichlor-5,6-dicyano-*p*-benzochinon (*DDQ*). Alle untersuchten CT-Komplexe besitzen 1 : 1-Stöchiometrie.

## Introduction

The $\pi$-donor properties of indene (**1**) are established from its ability to form complexes with hexacarbonyl chromium[1, 2], 1,3,5-trinitrobenzene[3] and 2,4,7-trinitrofluorenone[4]. It has been reported that in the (indene) $Cr(CO)_3$ complex the benzene ring is complexed with $Cr(CO)_3$ and not the five-membered ring[1, 2]. Also, this complex is less stable relative to tricarbonyl chromium complexes of [2.2]paracyclophanes[5, 6].

A number of novel indenophanes (**2**–**4**, Fig. 1) have been prepared recently[7,8]. The objective of the present study was to compair the importance of transannular electronic interactions on the $\pi$-basicity of this interesting class of compounds with those of indene, as a model compound, and 4,5,12,13-tetramethyl[2.2]paracyclophane (**5**, Fig. 2), as a highly basic $\pi$-donor. In addition, we wished to apply the tool of CT complexation to differentiate between the $\pi$-base character of the two isomeric forms **3** and **4**. The relative base strength of the $\pi$-donors **1**–**4** were

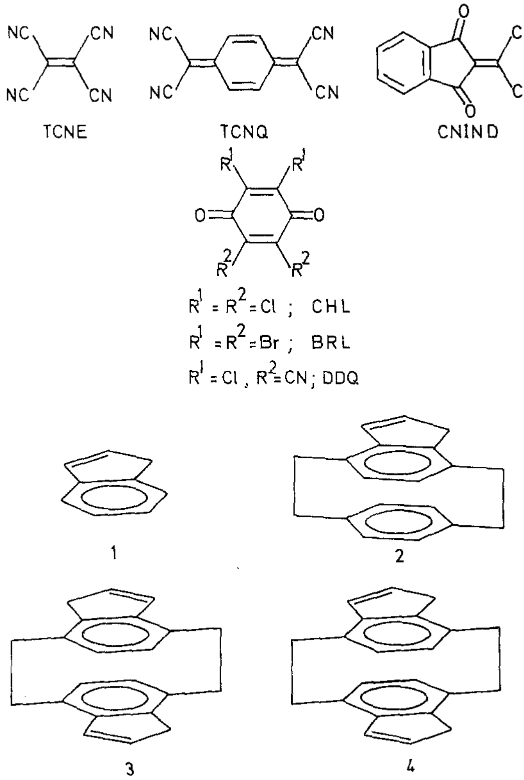


Fig. 1

determined by making use of the position of $\lambda_{max}$ of the long wavelength CT band of their complexes and the energy of transition of these CT bands. The association constants of formation of the CT complexes of the $\pi$-donors **1**–**4** with $\pi$-acceptors are a measure of the stability of these CT complexes.

## Experimental

Indene (**1**) (Fluka AG purum) was distilled, b.p. 94–98°/65 Torr. [2]-Benzo[2]indenophane (**2**), pseudo-*para*[2.2]indenophane (**3**) and pseudo-*meta*[2.2]-indenophane (**4**) were synthesized according to the literature[7, 8].

Tetracyanoethylene (Janssen Chimica, Belgium), 2,3-dichloro-5,6-dicyanobenzoquinone, chloranil, bromanil (Merck, Federal Republic of Germany) and 7,7,8,8-tetracyanoquinodimethane (EGA-Chemie, Federal Republic of Germany) were used without further purification. 2-Dicyanomethylene-1,3-indanedione was prepared from 1,3-indanedione and tetracyanoethylene according to the published procedure[9].

Methylene chloride (Merck) was dried over phosphorus pentaoxide and distilled following Ref.[10].

Association constant of formation ($K$) and molar extinction coefficient ($\varepsilon$) of the CT complexes studied have been determined by utilizing the rearranged form[11] of the *Benesi-Hildebrand* equation[12]:

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

where $[A]$ and $[D]$ are the initial molar concentration of acceptor and donor respectively, $l$ the length of light path in cm and $d$ the optical density. This equation enables one to determine $K$ and $\varepsilon$ values independently for the complexes under the condition of constant $[A]$. The values of $\varepsilon$ and $K$ are determined from the gradient and negative intercept of the linear plot of $[A] + [D]$ against $[A][D]/d$.

The visible spectra were determined on a Beckman UV 5230 recording spectrophotometer in a matched pair of stoppered fused silica cells of 1.0 cm optical pathlength. All scans covered the range from 350 to 800 nm.

## Results and Discussion

Table 1 lists the wavelengths of the CT bands for twenty-four CT complexes together with values of the transition energies of the CT bands of these complexes. Analysis of the data in this Table reveals that indenophanes **3** and **4** form one CT band with all $\pi$-acceptors except *BRL*, however the $\pi$-donor 2 gives one CT band in complexation with both *DDQ* and *TCNE*, while with the other $\pi$-acceptors only shoulders were observed. In the case of indene one CT maximum with *DDQ* and two maxima with *TCNE* at 422 and 536 nm were observed, however with the other $\pi$-acceptors shoulders were visible in the spectra. Furthermore, these data indicate that the spectra all contain bands in regions which must be associated with CT complexes, since neither the components alone absorb in these regions. The values of the position of the long wavelength maximum of the $\pi$-donors **1**–**4** with all $\pi$-acceptors demonstrate that these $\pi$-donors fall in the following order with respect to their ability to release electrons to the $\pi$-acceptors involved: **4** > **3** > **2** > **1**. Examination of the relative $\pi$-base character of the indenophanes **2**–**4** and their model compound (indene) reveals that the latter forms CT complexes with the $\pi$-acceptors at shorter wavelengths with respect to the indenophanes. This observation is an indication of the existence of transannular electronic interactions in the indenophane molecule.

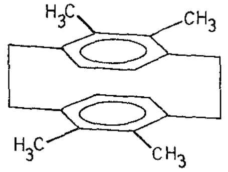
Table 1. *Maximum absorption wavelengths* $\lambda_{max}$ (nm) *and transition energies* $E_{ct}$ (kcal mol$^{-1}$) *for the CT complexes of $\pi$-donors* **1**–**4** *with $\pi$-acceptors*

| | **1** | | **2** | | **3** | | **4** | |
|---|---|---|---|---|---|---|---|---|
| Acceptor | $\lambda_{max}$ | $E_{ct}$ | $\lambda_{max}$ | $E_{ct}$ | $\lambda_{max}$ | $E_{ct}$ | $\lambda_{max}$ | $E_{ct}$ |
| *DDQ* | 595 | 48.03 | 650 | 43.97 | 655 | 42.98 | 685 | 41.72 |
| *TCNE* | 422 | 67.73 | 575 | 49.70 | 595 | 48.03 | 614 | 46.55 |
| | 536 | 53.32 | | | | | | |
| *CHL* | 500 (sh) | 57.16 | 515 (sh) | 55.50 | 535 | 53.42 | 550 | 51.96 |
| *BRL* | 475 (sh) | 60.17 | 520 (sh) | 54.96 | 527 (sh) | 54.23 | 535 (sh) | 53.42 |
| *TCNQ* | 550 (sh) | 51.96 | 575 (sh) | 49.70 | 650 | 43.97 | 682 | 41.91 |
| *CNIND* | 525 (sh) | 54.44 | 535 (sh) | 53.42 | 557 | 51.31 | 561 | 50.94 |

It is clear that either **3** or **4** must be more basic than **2**, since the former compounds contain two indene molecules, while the latter contains an indene and benzene moiety, respectively, and indene is a strong $\pi$-base relative to benzene, which forms a weak CT complex with *TCNE*[13].

Although **3** and **4** have nearly the same structure and differ only in the position of one double bond, they show a definite shift in the absorption of their CT complexes with the $\pi$-acceptors (Table 1). It is of interest to discuss this behaviour in the light of transannular electronic interactions: as is apparent from Fig. 2, the two double bonds of the five-membered rings in **4** are involved in the intraannular electron delocalization in the indenophane molecule; in the other isomer **3**, however, only one double bond can participate in conjugation. Accordingly, the basicity of **4** should be higher than that of **3**.

Comparison of the values of $\lambda_{max}$ for the CT complexes between indenophane (**4**) and both *DDQ* and *TCNE* with the CT complexes of 4,5,12,13-tetramethyl[2.2]paracyclophane (**5**) with the same $\pi$-acceptors shows that **5** forms CT complexes with *TCNE* and *DDQ* at $\lambda_{max}$ = 570 and 630 nm respectively[14], while the CT complexes of **4** with these acceptors absorb at 614 and 685 nm respectively. From these data it may be



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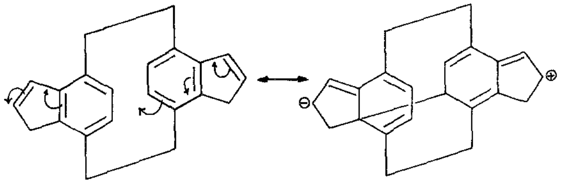

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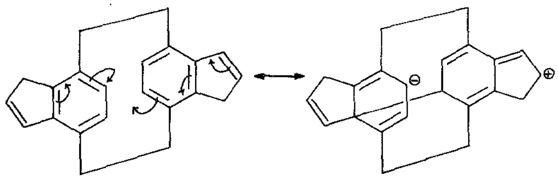

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Fig. 2

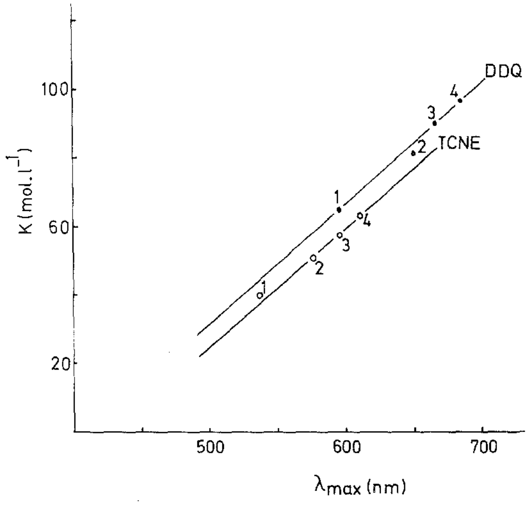

Fig. 3. Plot of association constant ($K$) vs. $\lambda_{\text{max}}$ of the long wavelength CT band for CT complexes of $\pi$-donors **1**–**4** with *DDQ* and *TCNE* (the numbering as in Fig. 1)

Table 2. *Charge-transfer spectral data for CT complexes between the π-donors* **1–4** *and the π-acceptors in* $CH_2Cl_2$ *at 20 °C*

| Acceptor | Donor | $\lambda_{max}$ (nm) | $\varepsilon_{max}$ ($l\,mol^{-1}\,cm^{-1}$) | $E_{ct}$ (eV) | $K$ ($mol\,l^{-1}$) | *i.p.* (eV) |
|---|---|---|---|---|---|---|
| *DDQ* | **1** | 595 | 1 660 | 2.09 | 64.95 | 8.31 |
| *DDQ* | **2** | 650 | 160 | 1.91 | 79.13 | 8.10 |
| *DDQ* | **3** | 665 | 930 | 1.87 | 90.91 | 8.05 |
| *DDQ* | **4** | 685 | 1 010 | 1.82 | 97.11 | 7.98 |
| *TCNE* | **1** | 422 | 2 800 | 2.95 | 40.62 | 9.12 |
| | | 536 | | 2.32 | | 8.29 |
| *TCNE* | **2** | 575 | 2 260 | 2.16 | 51.28 | 8.08 |
| *TCNE* | **3** | 595 | 308 | 2.09 | 58.82 | 7.98 |
| *TCNE* | **4** | 614 | 340 | 2.03 | 64.10 | 7.90 |
| *CHL* | **3** | 535 | 200 | 2.32 | 29.41 | 7.86 |
| *CHL* | **4** | 550 | 265 | 2.26 | 33.30 | 7.78 |
| *TCNQ* | **3** | 650 | 190 | 1.91 | 12.05 | — |
| *TCNQ* | **4** | 682 | 210 | 1.82 | 14.93 | — |
| *CNIND* | **3** | 557 | 400 | 2.23 | 23.26 | 7.65 |
| *CNIND* | **4** | 561 | 235 | 2.22 | 24.26 | 7.64 |

concluded that in spite of the fact that **5** contains four methyl groups which render the molecule to be highly basic through hyperconjugative effects, the conjugative effect is apparently more effective.

The values of $\lambda_{max}$, molar extinction coefficient ($\varepsilon$), energy of transition ($E_{ct}$) and association constant ($K$) of the CT complexes as well as the ionization potentials of the π-donors **1–4** obtained in the present study are presented in Table 2.

The correlation between association constants and $\lambda_{max}$'s for the CT complexes between **1–4** and both *DDQ* and *TCNE* is illustrated in Fig. 3. A reasonably good linear relationship is evident. From this result it seems fair to say that the sequence of $K$ values further supports the order of decreasing π-basicity of the π-donors **1–4** measured by the values of $\lambda_{max}$.

The transition energies of the CT bands (Tables 1 and 2) are another measure of the basic character of **1–4**.

On the basis of the position of CT absorption maxima of the CT complexes between the indenophane **4** and the six π-acceptors (Table 1), the ability of these π-acceptors to accept electrons decreases in the following order: *DDQ* > *TCNQ* > *TCNE* > *CNIND* > *CHL* > *BRL*. However, a more reasonable order may be derived on the basis of $K$ values of these complexes (Table 2), the sequence being: *DDQ* > *TCNE* > *CHL* > *CNIND* > *TCNQ*. This order is in agreement with the reported electron affinity values of the π-acceptors[15,16].

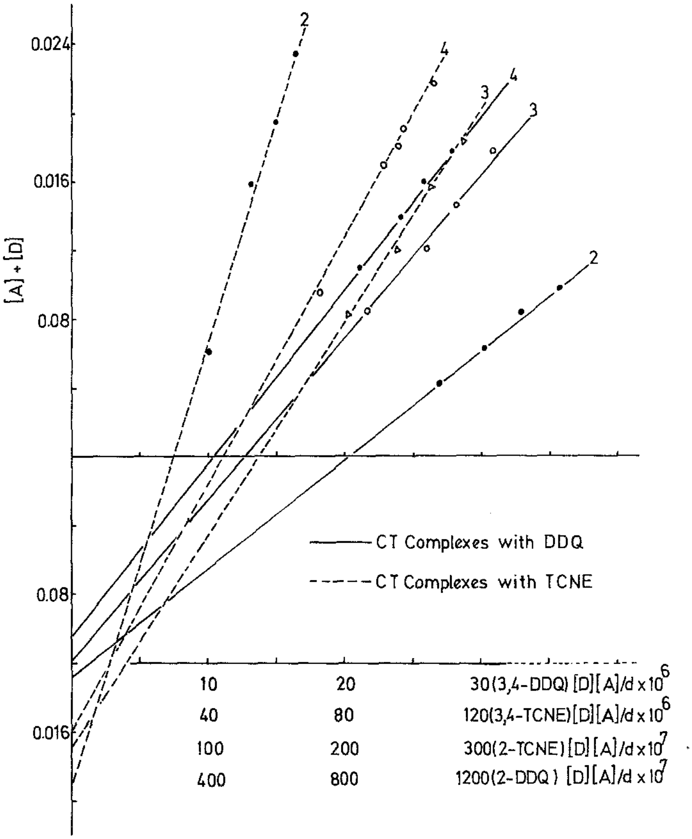

Fig. 4. Spectral determination of association constants and molar extinction coefficients of the CT complexes

The geometric structure of the CT complexes studied may be designated as one in which the benzene ring of the indenophane molecule is mainly complexed with the $\pi$-acceptor. This suggestion is supported by the fact that the benzene ring is the more basic center. Furthermore, as reported previously, in the (indene) $Cr(CO)_3$ complex the benzene ring is complexed with the tricarbonyl chromium ligand[1, 2].

The ionization potential (*i.p.*) values (Table 2) were determined by the following equation[15]:

$$i.p.\quad (\text{eV}) = a + b\,\tilde{\nu}_{\text{ct}},$$

where the coefficients $a$ and $b$ depend only on the electron acceptors. The ionization potentials of the $\pi$-donors correlated well with the energies of

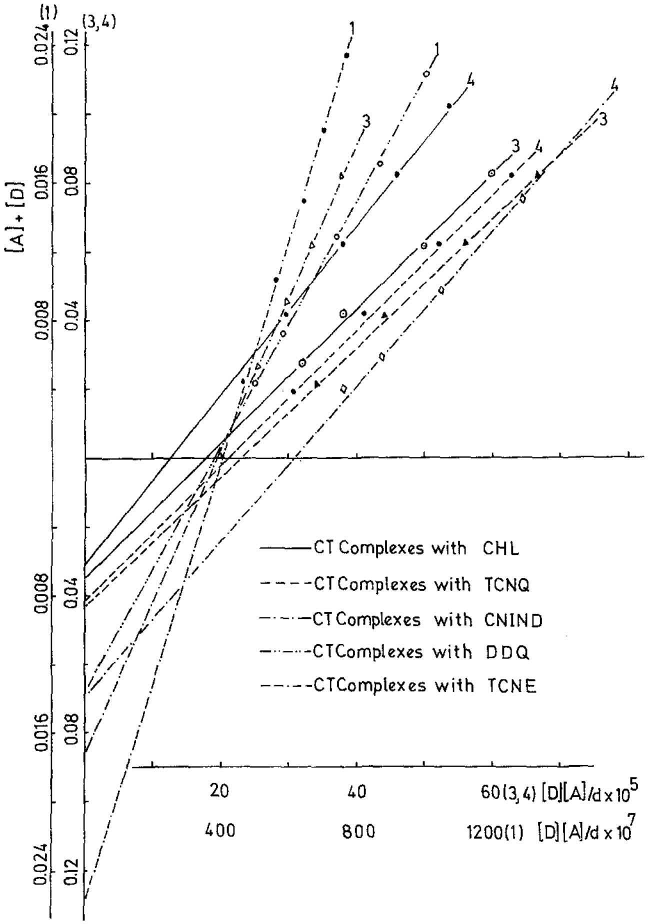

Fig. 5. Spectral determination of association constants and molar extinction coefficients of the CT complexes

transition ($E_{ct}$) of their CT complexes (Table 2). This result is in agreement with that reported by *McConnel* et al.[17].

The stoichiometry of the CT complexes of **1**–**4** with the different $\pi$-acceptors was determined by applying *Job*'s method[18] of continuous variation, which provides symmetrical curves with maxima at mole fraction 0.5, indicating a 1 : 1 stoichiometric ratio. Typical plots of the rearranged *Benesi-Hildebrand* equation for determination of the association constants as well as molar extinction coefficients of the CT complexes are presented in Figs. 4 and 5.

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