Molecular Complexes of Cyclophanes. XV. Charge-Transfer Complexes of Sterically Hindered[2.2]metapara- and [2.2]paracyclophanes with π-Acceptors

Aboul-fetouh E. Mourad*, Alaa El-Din A. Hassan, and Jörg Dannheim[†]
Chemistry Department, Faculty of Science, El-Minia University, El-Minia, Egypt
[†]Institut für Organische Chemie, Technische Universität Braunschweig, Hagenring 30, D-3300 Braunschweig, Federal Republic of Germany

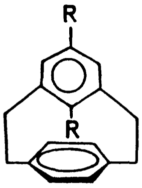
(Received April 18, 1988)

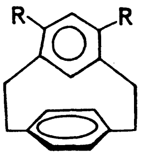
Synopsis. The charge-transfer (CT) complexes of some sterically hindered [2.2]metapara- and [2.2]paracyclophanes as π-donors with 2,3-dichloro-5,6-dicyano-*p*-benzoquinone (DDQ) and tetracyanoethylene (TCNE) as π-acceptors have been investigated by electronic as well as infrared spectroscopy. Electronic, steric, and transannular effects governing the formation and stability of the CT complexes studied are discussed.

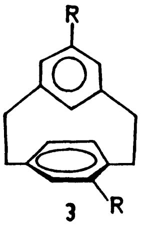
The transannular electronic interactions in the [2.2]paracyclophanes were the subject of several spectroscopic investigations in the last decades.[1–9] These studies dealt mainly with the question of how the electronic effects of substituents in one ring are transferred to the second ring of the [2.2]paracyclophane molecule.

This paper dealt with the visible and infrared spectra of intermolecular complexes of di-*t*-butyl[2.2]metaparacyclophanes (**1**—**3**), diisopropyl[2.2]paracyclophanes (**4**,**5**), 4-*t*-butyl[2.2]paracyclophane (**6**) as well as 4-trimethylsilyl[2.2]paracyclophane (**7**) and both acceptors DDQ and TCNE. A new absorption band due to neither donor **1**—**7** nor acceptor was observed in the visible region for the CT complexes studied. In two cases two new absorption bands were observed (Table 1). These two absorption bands may be explained as due to electron transition from two highest occupied π-molecular orbitals of an electron donor to the lowest vacant π-molecular orbital of an electron acceptor.

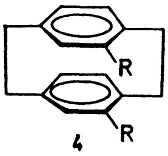
It has been reported that the λ_{max} values for the CT complexes were used as a measure of the π-base strengths of the donors used.[2)] Comparison of the λ_{max} values for the CT complexes of the donors **1**—**5** with both DDQ and TCNE demonstrates that the π-base strengths of the donors follow the order: 4>5>1>2>3. Also, [2.2]paracyclophanes (**4** and **5**) are more basic

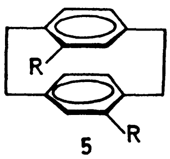

1


2


3

R= t-butyl


4


5

R= isopropyl

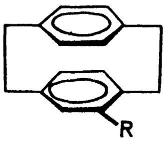

6) R = $C(CH_3)_3$
7) R = $Si(CH_3)_3$

Table 1. CT Spectral Data for Complexes between Donors **1**—**7** and DDQ, TCNE in Dichloromethane at 20 °C

Donor	Acceptor	λ_{max} nm	ε l mol^{-1} cm^{-1}	K l mol^{-1}	IP eV
1	DDQ	632	109	121.45	8.17
2	DDQ	597	100	93.71	8.31
3	DDQ	562	117	72.24	8.46
4	DDQ	659	98	137.56	8.07
5	DDQ	650	118	129.43	8.10
6	DDQ	597	144	95.26	8.31
7	DDQ	587	196	91.44	8.35
1	TCNE	563, 425	49	78.08	8.14, 9.09
2	TCNE	537, 425	69	65.27	8.28, 9.09
3	TCNE	499	86	52.56	8.52
4	TCNE	580	95	86.12	8.05
5	TCNE	575	108	81.03	8.08
6	TCNE	541	115	70.52	8.26
7	TCNE	532	136	67.36	8.31

than [2.2]metaparacyclophanes (**1**—**3**). In order to explain this trend of basicity two factors must be discussed; electronic and steric. In the metaparacyclophanes (**1**—**3**) the transannular electronic interactions are absent, since the two aromatic nuclei are perpendicular to each other,[10] and thus the unsubstituted part of compound **1** and **2** may be formally considered as *p*-xylene. The higher values of the $\lambda_{\max}$'s of the CT complexes of donors **1**—**3** with TCNE in Table 1 relative to *p*-xylene-TCNE complex ($\lambda_{\max}$=460 nm[11]) indicated that the substituted ring in **1** and **2** mainly formed complexes with the acceptors. Accordingly, the electronic effects of the *t*-butyl groups are prevailing over steric ones. The presence of two *t*-butyl groups in the *p*-position in **1** and in the *m*-position in **2** is responsible for the greater steric hindrance and consequently lower π-basicity of **2** relative to **1**.[1]

As reported in Table 1, the CT complexes of **4** with DDQ and TCNE absorb at 659 and 580 nm respectively. The CT complexes of its analogue 4,13-di-*t*-butyl[2.2]paracyclophane (**4**, R=*t*-butyl) with the same acceptors absorb at 663 and 595 nm respectively.[12] These results reveal that the *t*-butyl-substituted cyclophane is more basic than the isopropyl-substituted one. In other words, the electron-releasing character is stronger than the steric one. Accordingly if we compare the basicity of di-*t*-butyl-substituted [2.2]metaparacyclophanes (**1**—**3**) with that of diisopropyl-substituted [2.2]paracyclophanes (**4** and **5**) the former basicity is expected to be larger than that of the latter. Contrary to the expectation the latter was larger than the former as shown in Table 1. This behavior arises undoubtly from transannular electronic interactions within paracyclophanes **4** and **5** .

The existence of steric hindrance in a donor-acceptor system tends to inhibit the interections between the electron-poor π-orbitals of acceptor with the electron-rich π-orbitals of donor, and hence the basic character of donor will be decreased with increasing the steric hindrance, i.e., the absorption of its CT complexes will be shifted to shorter wavelengths. Consequently, on the basis of steric requirements, the CT complexes of **4** with DDQ and TCNE should absorb at shorter wavelengths than those of **5**, since the two isopropyl groups in **4** are pseudo-geminally oriented, and hence more sterically hindered than in the pseudo-ortho case (**5**) On the contrary, the donor **4** exerts higher basic character than **5** as reported in Table 1 for the values of $\lambda_{\max}$. This may be explained as due to the difference in exiton splitting of the electronic states of the two donor molecules.

The association constants for complex formaation indicate a marked sensitivity to substituent effects and follow the same sequence as the corresponding $\lambda_{\max}$ values. A linear correlation between the association constants and the position of the $\lambda_{\max}$ of the long wavelength CT band has been observed for the two series of complexes.

It is worthwhile to point out that the low K values of the CT complexes of 4-trimethylsilyl[2.2]paracyclophane (**7**) with DDQ and TCNE and the absorption at relatively shorter wavelengths than the CT complexes of 4-*t*-butyl[2.2]paracyclophane (**6**) with the same acceptors are in agreement with the low electronegativity of the silicon atom with respect to the carbon one.

It has been reported that for a series of CT complexes the relationship between K and ε values is generally linear,[13] and when the electron donor is sterically hindered the ε values will be reduced.[11] The CT complexes in the present work reveal no regular relationship between K and ε values. This behavior is believed to be due to the steric hindrance in the donor molecules, which decreases in the following order:

2>**1**>**3** and **4**>**5**>**6**.

The empirical relation derived by Aloisi and Pignataro[14] were used to determine the ionization potentials (IP) of the free donors (**1**—**7**) and their values are given in Table 1; they are another measure of the relative π-basicities of these electron donors. The high IP values in case of the DDQ-complexes is due to the high electron affinity of DDQ with respect to TCNE.[15]

The infrared spectra of some CT complexes as well as their free components are summarized in Table 2. The data reveals that in case of the CT complexes with

Table 2. IR Spectra (KBr) of Some Free Donors and Acceptors and Their CT Complexes (cm^{-1})

Complex	Free acceptor	Compl. acceptor	Free donor	Compl. donor
2-DDQ	2225(CN)	Very weak	1353, 1240,	1360, 1250
	1670(CO)	1690, 1660	925(CMe$_3$)	930
	1555(C=C)	1550	790, 720(ArH)	800, 728
	1175(C-Cl)	1160		
2-TCNE	2260, 2220(CN)	2240, 2200	1100(CMe$_3$)	1105
	1085, 960, 920	1077, 950, 910	880, 790, 728	885, 800, 732
	(C-CN)		(ArH)	
5-DDQ	2225(CN)	Very weak	2850(aliph. CH)	2857
	1670(CO)	1685, 1660	1370, 1350	1378, 1360
	1175, 800(C-Cl)	1170, 793	(CHMe$_2$)	
			882, 840(ArH)	890, 845
5-TCNE	2260, 2220(CN)	2245, 2208	2850(aliph. CH)	2855
	1110, 1085, 960	1105, 1080, 952	1370, 1350	1375, 1356
	(C-CN)		(CHMe$_2$)	
			840, 720(ArH)	845, 727

DDQ the C=O at 1670 cm^{-1} splits into two bands, whereas that of the C≡N group is weaken. In case of the TCNE-complexes, the two bands characteristic of the C≡N groups show a red shift. Comparison of the infrared spectra of the CT complexes with those of the free components reveals an apparent shift of the bands of the acceptor to lower wavenumbers. However those of the donor are shifted to higher values indicating a decrease in the electron density in the donor part of the CT complex. This behavior is characteristic of π-π^* transitions.[16]

In conclusion, the spectroscopic studies of this type of donor-acceptor interactions revealed the important role played by both electronic effects of the electron-releasing groups and the transannular electronic interactions of the π-electron clouds of the two aromatic rings with one another in [2.2]paracyclophane relative to the eteric factors.

Experimental

Reagents. *The electron donors* **1—7** *were prepared* according to the procedure described in Ref 17. Tetracyanoethylene and 2,3-dichloro-5,6-dicyano-*p*-benzoquinone (Janssen Chimica) were used without further purification. Dichloromethane (Merck) was dried over phosphorus pentaoxide and distilled as described in Organicum.[18]

Physical Measurements. Association constants (K) and molar extinction coefficients (ε) of the CT complexes studied have been determined by utilizing the Rose-Drago equation:[19,20]

$$K^{-1} = \frac{C_D C_A(\varepsilon - \varepsilon_A)}{d - d_A} - C_D - C_A + \frac{d - d_A}{\varepsilon - \varepsilon_A},$$

where C_D and C_A are the initial concentrations of donor and acceptor respectively, ε_A is the molar absorbance of the acceptor, d_A is the absorbance at the initial concentration of the acceptor, and d corresponds to the total absorbance at any given wavelength for a cell of 1.0 cm path length.

The visible spectra were scanned on a Beckman UV 5230 recording spectrophotometer in stoppered silica cells (1.0 cm). All scans covered the range from 350 to 800 nm. The infrared spectra were recorded on a Perkin-Elmer 157 G spectometer.

A. M. is grateful to the Alexander von Humboldt Foundation for the award of a fellwoship for 1986—1987 and to Prof. H. Hopf for providing working facilities at Braunschweig. J. D. thanks the Volkswagenwerk Foundation for financial support.

References

1) D. J. Cram and R. H. Bauer, *J. Am. Chem. Soc.*, **81**, 5971 (1959).

2) L. A. Singer and D. J. Cram, *J. Am. Chem. Soc.*, **85**, 1080 (1963).

3) D. J. Cram and D. I Wilkinson, *J. Am. Chem. Soc.*, **82**, 5721 (1960).

4) A. E. Mourad, A. M. Nour-el-Din, and M. R. Mahmoud, *Spectrochim. Acta, Part A*, **38**, 993 (1982).

5) A. E. Mourad and A. M. Nour-el-Din, *Spectrochim. Acta, Part A*, **39**, 533 (1983).

6) A. E. Mourad and A. M. Nour-el-Din, *Gazz. Chim. Ital.*, **113**, 213 (1983).

7) A. E. Mourad, F. W. Raulfs, and H. Hopf, *Monatsh. Chem.*, **116**, 701 (1985).

8) A. E. Mourad, E. H. Eltamany, and H. Hopf, *Z. Phys. Chem. (Leipzig)*, **267**, 507, 937 (1986).

9) A. E. Mourad, A. M. Nour-el-Din, and H. A. Abdel-Nabi, *Gazz. Chim. Ital.*, **116**, 381 (1986).

10) H. J. Lindner, *Tetrahedron*, **32**, 753 (1976).

11) R. E. Merrifield and W. D. Phillips, *J. Am. Chem. Soc.*, **80**, 2778 (1958).

12) A. E. Mourad and J. Dannheim, unpublished.

13) R. S. Mulliken, *J. Am. Chem. Soc.*, **74**, 811 (1952); *J. Phys. Chem.*, **56**, 801 (1952).

14) G. G. Aloisi and S. Pignataro, *J. Chem. Soc., Faraday Trans. 1*, **69**, 534 (1972).

15) R. Foster, "Organic Charge Transfer Complexes," Academic Press, London (1969).

16) R. M. Issa, M. Gaber, A. L. El-Ansary, and H E. Rizk, *Bull. Soc. Chim. Fr.*, **1985**, 173.

17) J. Dannheim, "Diplomarbeit," TU Braunschweig (1986).

18) Organicum, "Practical Handbook of Organic Chemistry," 1st ed., Pergamon Press, Oxford (1973).

19) N. J. Rose and R. S. Drago, *J. Am. Chem. Soc.*, **81**, 6138 (1959).

20) B. K. Seal, A. K. Mukherjee, and D. C. Mukherjee, *Bull. Chem. Soc. Jpn.*, **52**, 2088 (1979).