Tetrahedron Letters,Vol.25,No.16,pp 1721-1724,1984 0040-4039/84 $3.00 + .00
Printed in Great Britain

COMPLEXATION OF ELECTRON DONOR-ACCEPTOR [2.2]PARACYCLOPHANES WITH TETRACYANOETHYLENE (TCNE) 1)

Lothar Schanne and Heinz A. Staab*

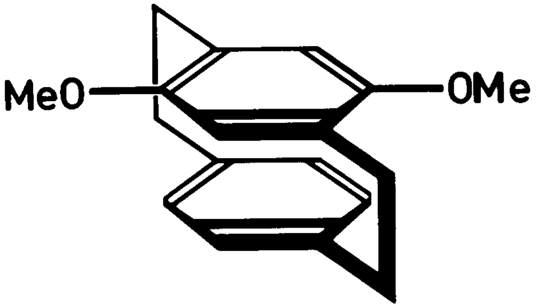
Abteilung Organische Chemie
Max-Planck-Institut für medizinische Forschung
Jahnstrasse 29, D-6900 Heidelberg

Summary: For a series of electron donor-acceptor cyclophanes the effect of the acceptor unit on the ionisation potential I_D of the donor part was measured by determining the transition energies of the charge-transfer absorption of intermolecular complexes with TCNE.

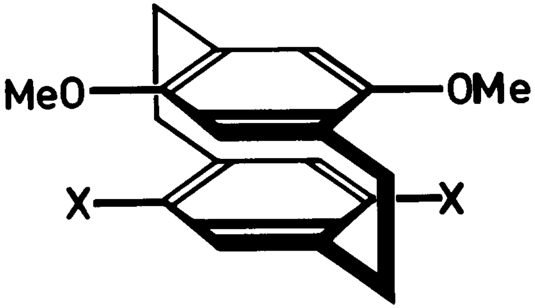
For a variety of weak charge-transfer (CT) complexes of a specific acceptor with a series of different donors the energy of the CT transition was found to depend on the ionisation potentials I_D of the donors approximately according to $h\nu = I_D - C_1$ 2). Since the I_D values are normally varied by substitution on the donor ring itself, however, sterical conditions affecting complexation are changed at the same time. Therefore, C_1 in the aforementioned equation is not constant in a strict sense. Nevertheless, fairly good linear correlations of ionisation potentials I_D and CT transition energies have been reported in literature for quite a number of such series 3).

The recent synthesis of a great variety of electron donor-acceptor cyclophanes 4) opens up the possibility to leave the donor part itself completely unchanged for intermolecular complexation with an acceptor, e. g. tetracyanoethylene (TCNE), and to vary the I_D of the donor over a wide range via transanular transmission by various substitutions in the second paracyclophane ring 5).

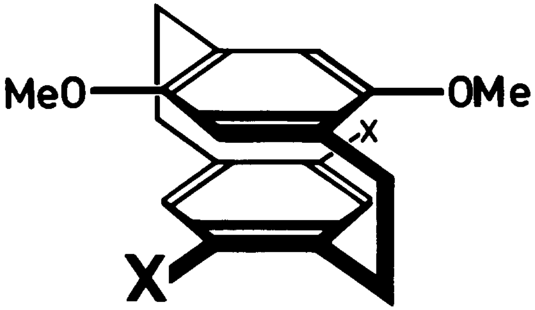
The compounds used for the approach mentioned are the tetra-substituted [2.2]paracyclophanes **2** - **17** in which as the donor side the 4,7-dimethoxy-substituted ring is kept constant whereas the second ring bears substituents in the 12- and 15-position having either pseudogeminal or pseudoortho orientation to the methoxy groups (even or odd numbers, resp.). Although 4,7-dimethoxy[2.2]paracyclophanes containing much stronger acceptor units like benzoquinones or tetracyanoquinodimethane (TCNQ) have been synthesized 4) these cyclophanes were not included into this study for methodical reasons (long wavelength absorption of the CT phane itself, intramolecular vs. intermolecular CT interactions) as well as for theoretical reasons 6). As standard, 4,7-dimethoxy[2.2]paracyclophane (**1**) was used instead of the open-chained 1,4-dimethoxy-2,5-dimethylbenzene which according to the first CT absorption with TCNE (λ_{max} = 720 nm, $\tilde{\nu}$ = 13890 cm^{-1}) is a considerably poorer donor than 1 (λ_{max} = 775 nm, $\tilde{\nu}$ = 12900 cm^{-1}; see below).



1



2: X = OMe
4: X = Me
6: X = COOMe
8: X = CON_3
10: X = CHO
12: X = COCl
14: X = CN
16: X = NO_2



3: X = OMe
5: X = Me
7: X = COOMe
9: X = CON_3
11: X = CHO
13: X = COCl
15: X = CN
17: X = NO_2

For the measurement of the absorption spectra of the TCNE complexes with the paracyclophanes 2 - 17 these compounds (1 - 10 mg) were dissolved in a saturated solution of TCNE in 2 ml chloroform. In Table 1 wavelengths and wavenumbers for the first CT absorption maxima are listed. Since line shape and width of these absorption bands (contrary to a second CT absorption around 400 - 550 nm) are very similar within the whole series it is justified to take the wavenumbers at the maxima as measures for the transition energies.

TCNE-Complex of	$\lambda^{1}_{CT,\,max}$ [nm]	$\tilde{\nu}^{1}_{CT,\,max}$ [cm^{-1}]	ΔI_D [eV]
2	840	11910	- 0.123
3	787	12710	- 0.024
4	787	12710	- 0.024
5	770	12990	0.011
6	772	12950	0.006
7	772	12950	0.006
8	750	13330	0.053
9	758	13190	0.036
10	742	13480	0.072
11	742	13480	0.072
12	723	13830	0.116
13	732	13660	0.094
14	710	14090	0.148
15	727	13755	0.106
16	715	14000	0.136
17	715	14000	0.136

Table 1. Wavelengths and wavenumbers of the first CT absorption of TCNE complexes of **2** - **17** and ΔI_D values derived therefrom (with reference to **1**; see text for further details).

The first examples in Table 1 show that for **1**-derivatives with electron-donating groups in the second ring the TCNE complexation reveal a reduction of the ionisation potential which can be explained by assuming a transanular supply of electrons to the neighbouring donor ring which itself donates electrons to TCNE by CT complexation. For the majority of compounds listed in Table 1, however, the second aromatic ring linked to the dimethoxy-substituted donor part of **1** is substituted by electron-withdrawing groups. Although in all these cases we are dealing with relatively poor electron acceptors the increase of the effective ionisation potentials with regard to TCNE complexation is significant. The magnitude of this effect for the individual compounds follows closely the well-known order of the electron-withdrawing capacity of aromatic substituents.

The orientation dependence of CT interactions which has been studied extensively on the basis of absorption spectra of electron donor-acceptor cyclophanes [4)] is also reflected by the data of Table 1: of pairs of diastereomers in the majority of cases the pseudogeminal isomer shows the strongest effect on ΔI_D (there are, however, some cases where pseudogeminal and pseudo-ortho compounds within the limits of error of this method do not show the expected different effects). The approach reported here for [2.2]paracyclo=

phanes has also been applied to some [3.3]paracyclophanes as well as to [2.2]- and [3.3]metacyclophanes with analogous results. The significance of the results reported in Table 1 is supported by the fact that the determination of first oxidation potentials E_{ox} by cyclic voltammetry (against Ag/Ag$^+$, 0.1 M tetra-t-butylammonium perchlorate, acetonitril) shows a linear correlation to the ΔI_D values for a sample of compounds from Table 1. More extensive experimental work is in progress and will be published together with the attempt of a theoretical explanation $^{6)}$.

Charge-transfer from the donor to the acceptor in the course of an excitation from the ground to the excited state as observed in absorption spectroscopy is still the most prominent and thoroughly studied property of electron donor-acceptor systems. The question, however, to what an extent actually CT occurs in the ground state of electron donor-acceptor compounds is still a matter of controversial discussion. Therefore, any contribution to this problem which is not directly linked to CT absorption spectra seems to be of interest.

---

1) Electron Donor-Acceptor Compounds, Part 37. - Part 36: H. A. Staab, M. Jörns, C. Krieger and M. Rentea, Chem. Ber., in press.

2) G. Briegleb and J. Czekalla, Z. Elektrochem. **59**, 184 (1955); **63**, 6 (1959); see R. Foster, Organic Charge-Transfer Complexes, Academic Press, London - New York 1969 for further references.

3) See, for example, E. M. Voigt and C. Reid, J. Am. Chem. Soc. **86**, 3930 (1964).

4) H. A. Staab, G. H. Knaus, H.-E. Henke and C. Krieger, Chem. Ber. **116**, 2785 (1983); H. A. Staab, R. Reimann-Haas, P. Ulrich and C. Krieger, ibid. **116**, 2808 (1983); H. A. Staab, G. Gabel and C. Krieger, ibid. **116**, 2827 (1983); H. A. Staab, R. Hinz, G. H. Knaus and C. Krieger, ibid. **116**, 2835 (1983); H. A. Staab, C. P. Herz, C. Krieger and M. Rentea, ibid. **116**, 3813 (1983); H. A. Staab, B. Starker and C. Krieger, ibid. **116**, 3831 (1983); therein further references to earlier work.

5) Cf. D. J. Cram and R. H. Bauer, J. Am. Chem. Soc. **81**, 5971 (1959); L. A. Singer and D. J. Cram, ibid. **85**, 1080 (1963); M. Sheehan and D. J. Cram, ibid. **91**, 3553 (1969).

6) T. Geiger, H. Vogler and H. A. Staab, to be published.

(Received in Germany 6 February 1984)