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Molecular Associations of [2.2]Paracyclophane-arylhydrazones with Organic Acceptors, VIII

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Summary. Molecular complexes of mono and disubstituted [2.2]paracyclophanehydrazones with organic acceptors have been studied by means of thermodynamic and spectroscopic properties. Furthermore, the enhancement of the donor strength, induced by the hydrazono group, is viewed in the light of substituent as well as transannular effects.

Keywords. Charge-transfer complexes; Formation constant and stability constant; Hydrazones; Molecular association.

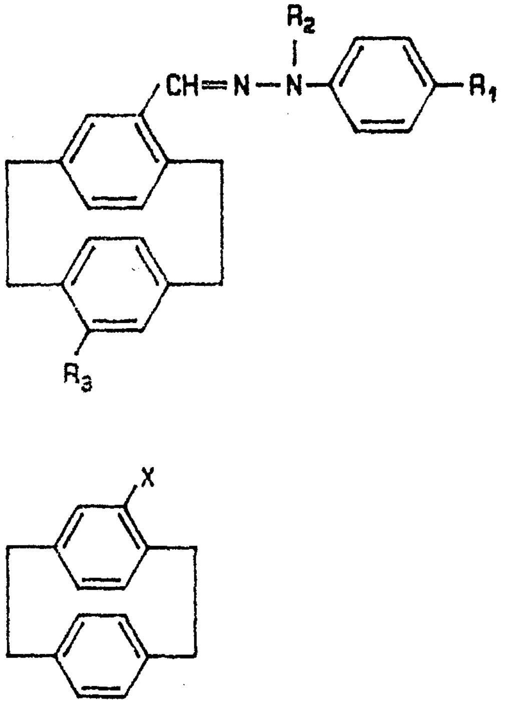
Molekulare Assoziation von [2.2]Paracyclophanarylhydrazonen mit organischen Akzeptoren, 8. Mitt.

Zusammenfassung. Es wurden Molekülkomplexe von mono- und disubstituierten [2.2]Paracyclophanarylhydrazonen mit organischen Akzeptoren mittels thermodynamischer und spektroskopischer Methoden untersucht. Zusätzlich wird der Anstieg in der Donorstärke, der von der Hydrazonogruppe induziert wird, im Hinblick auf Substituenten- und auch transannulare Effekte diskutiert.

Introduction

Cyclophanes are interesting ligands which can undergo complexation with a large number of organic and inorganic acceptors [1–5]. In particular, the formation of stable π-π* molecular complexes (MC) with acceptors like tetracyanoethylene (*TCNE*) or substituted quinones depends on the length of the alkyl bridges linking the aromatic nuclei and from the substituents present on their rings [6, 7]. The substituents may exhibit a transannular directive influence on the chemical behaviour as well as on the π-base strength. Complexes of substituted [2.2]paracyclophanes with organic acceptors have been reported and stable π-π* salts have been isolated and characterized. Recently, paracyclophanes bearing large substituents (like activated and deactivated azomethines, azines etc.) have been used as donors, the results showing that the effect of transannular electronic interactions does not play an important role on the MC bonding (the small transannular transmission to the neighbouring donor ring following the sequence:

pseudo-geminal> pseudo-*meta*> pseudo-*para*) [3, 8, 9]. Additionally steric effects influence the complexation in these systems. In order to gain further information on the role of Schiff bases on the complexation of paracyclophanes, some representative hydrazones of mono and bisformyl [2.2]paracyclophanes were reacted with common organic acceptors like tetracyanoethylene (*TCNE*), 2,3-dicyano-5,6-dichloro-1,4-benzoquinone (*DDQ*), chloranil (*CA*), 2,4,7-trinitro-9-fluorenone (*TNF*) and (2,4,7-trinitro-9-fluorenylidene)malononitrile (*DTF*) (Scheme 1). In Scheme 1 other donors, whose complexes with the cited acceptors have been already studied [2, 3, 5], are also listed and used as reference. The hydrazones were chosen in such a way to evidence both electronic and steric effects [10–12]. Furthermore, a qualitative relationship is observed between the association energies in complexes of the pseudo-geminal, pseudo-*meta* and pseudo-*para* bisformyl [2.2]paracyclophane methylphenylhydrazones supposing the isomeric transannular effect mentioned above.



	R_1	R_2	R_3
1	O*Me*	H	H
2	H	H	H
3	NO_2	H	H
4	H	*Me*	H
5	H	H	CH = N – NH – *Ph*
6	H	*Me*	CH = N – N(*Me*) – *Ph*

	X	Ref.
7	CH = N – C_6H_4 – O*Me*(*p*)	[3]
8	CH = N – C_6H_5	[3]
9	CH = N – C_6H_4 – NO_2(*p*)	[3]
10	O*Me*	[2, 6]
11	H	[2, 6]
12	NO_2	[2, 6]

Scheme 1

Results and Discussion

On mixing dichloromethane solutions of the hydrazone and the acceptor, coloured solutions were obtained absorbing in a region where the reactants do not. Not all complexes were stable, affording some sort of adduct in time (Scheme 2). Table 1 reports λ_{max} values for the whole series of the complexes, while Table 2 lists λ_{max} as well as transition energies (E_T) for the complexes of donors **1**–**12** with *TCNE*. The MC transitions show a random dependence from the electron affinity of the acceptor, as visualized in Fig. 1. Nevertheless for complexes of the unsubstituted donors **2**, **4**–**6**, the following sequence of electron acceptor character may be derived: *DDQ* > *TCNE*> *DTF*> *CA* > *TNF*. This is in some disagreement with the literature data (*TCNE*>*DDQ*>*DTF*, *CA*>*TNF*) [13, 14]. Complexes of donors **1** and **5**

Table 1. λ_{max} of complexes of donors **1**–**6** with various acceptors using dichloromethane as solvent at 25°C

Donor	*DDQ*	*TCNE*	*DTF*	*TNF*	*CA*
1	768	583	813	617 s	740
2	828	782	725	580 s	635
3	547 s	520 s	617 s	564 s	640
4	886	834	773	608 s	719
5	570 s	770	690	600 s	660 s
6	886	832	769	600 s	719

Table 2. Complexes of [2.2]paracyclophanes with *TCNE* in CH_2Cl_2 at 25°C, *p*-xylene as reference (λ_{max} = 460 nm; E_T = 62.1 kcal mol^{-1})

Donor	λ_{max} (nm)	E_T (kcal mol^{-1})	Donor	λ_{max} (nm)	E_T (kcal mol^{-1})
1	583	49.0	**7**	520	55.0
2	782	36.6	**8**	515	55.3
3	520	55.0	**9**	500 sh	57.2
4	834	34.3	**10**	570	50.2
5	770	37.1	**11**	521	54.9
6	832	34.4	**12**	457	60.7

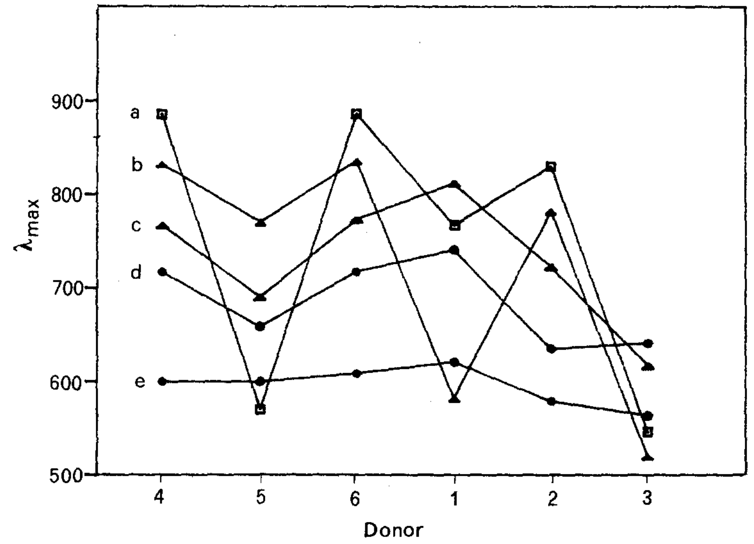
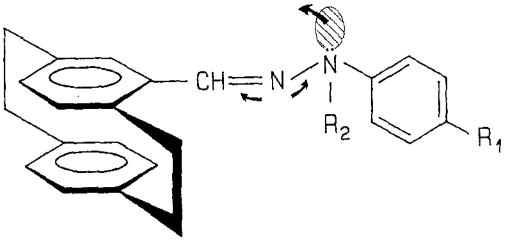


Fig. 1. Schematic drawing of λ_{max} values for complexes of donors **1**–**6** in dichloromethane at 25°C with the following acceptors: *a DDQ, b TCNE, c DTF, d CA*, and *e TNF*

with *DDQ* and of donor **1** with *DTF* absorb at anomalous high energies probably as a consequence of the existence of the predicted π-π* transition together with some other effects, like hydrogen bonding by the carbonyl or the nitro group of *DDQ* and *DTF*, respectively. The λ_{max} values reported in Table 2 allow some conclusions to be drawn for complexes of donors **1–12** with *TCNE*: (i) the influence of the amino nitrogen on the transition energy, in the sense of lowering the corresponding values via direct or mesomeric participation, is exhibited by a red shift of 30–50 nm; (ii) the anomalous low value of the λ_{max} in the complex **1**/*TCNE* may be a consequence of a competitive and predominant reaction; (iii) the inductive effect of the methyl group induces an expected lowering of the ionization potential of the donor [10]; (iv) no contribution to the value of E_T comes from the additional presence of a pseudo-*para* hydrazono group.



$$D + A \rightleftharpoons D{-}A \rightleftharpoons D^{\dot{+}} + A^{\dot{-}} \xrightarrow{a} \text{PRODUCTS}$$

Scheme 2

Owing to the low solubility of many reactants in the solvents used and to the instability of many complexes, it was possible to evaluate the formation constants (K_f) only for the systems **4**/*DDQ* and **4**/*CA* (Fig. 2 reports Benesi-Hildebrand plots for complexes **4**/*DDQ* and **4**/*CA* in dichloromethane). The K_f values indicate the presence of a strong complex in the first (K_f = 78 l mol^{-1}) and a weak one in the

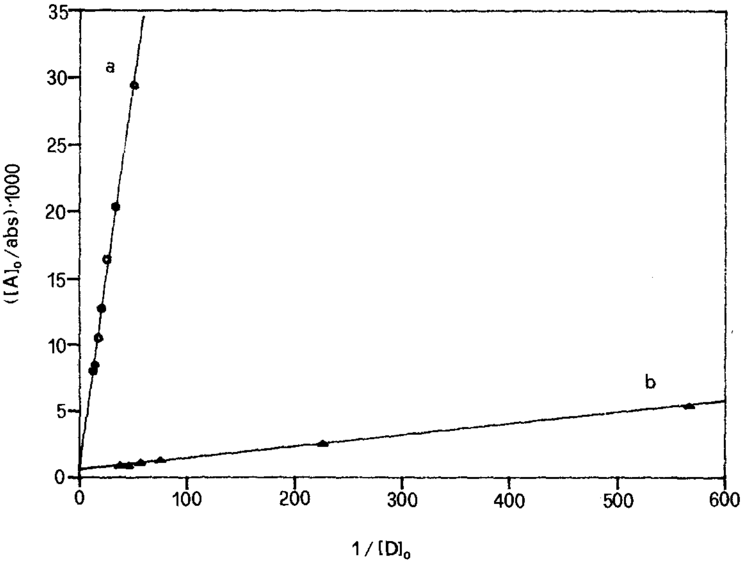


Fig. 2. Benesi-Hildebrand plots for complexes **4**/*CA* (a) and **4**/*DDQ* (b) in dichloromethane at 25°C

second case (K_f=2.4 l mol^{-1}). The donor capability of the hydrazone group becomes evident when it is compared with the azomethine linkage. For example, a K_{app} of 6.7 or a K_f of 10.0 l mol^{-1} are evaluated in complexes between the monoazomethine, **8** or the corresponding pseudo-*para*-azomethine with *DDQ*, respectively [3, 8], that are, at least, sevenfold lower than K_f value quoted in the system **4**/*DDQ*. At this point, it is not surprising that a weaker acceptor like Chloranil does not form any detectable interaction with [2.2]paracyclophaneazomethines [3].

Contrary to what happens in complexes of hydrazones [10] and cyclophanes when used as separate donor moieties, no linear correlation is found between the λ_{max} in complexes of [2.2]paracyclophane hydrazones with two different acceptors, leading to the hypothesis that a different donor center may interact in function of the particular acceptor. It is known that the transannular charge delocalization in paracyclophanes enhances the donor strength [14]: surprisingly, in our case, the presence of a second hydrazono group does not appear to improve the donor character (the energy of the CT transition has the same value of the one of the corresponding monohydrazone), suggesting that, also in this case, the formation of 1/1-D/A complexes is favored [15].

Unfortunately, owing to the low solubility of donors **5** and **6**, it was impossible to achieve more detailed informations through the evaluation of the equilibrium constants.

The role of the hydrazono group is also emphasized in Table 3 where the association process is viewed by means of the analysis of the participation of each fragment forming the final donor molecule: under the concentration values of the donors, used so far, the hydrazono moiety not only allowed the formation of the complex (*CA* as acceptor) but also introduced an appreciable λ_{max} red shift with respect to cyclophane itself (*DDQ* as acceptor).

As already observed in bisazomethine derivatives [8], the reciprocal disposition of the two hydrazono groups with respect to the cyclophane moiety influences the donor strength that decreases in the order: pseudo-geminal> pseudo-*meta*> pseudo-*para*.

UV-Vis solid state absorptions of the complexes of donor **4** with various acceptors (obtained by grinding together the reactants) follow the same sequence found in solution spectra, testifying that lattice interactions are negligible with

Table 3. Complexation by different donor skeletons (CH_2Cl_2, 25°C)

Donor	λ_{max} (nm)	
	DDQ	*CA*
p-Xylene	515	no MC
11	560	no MC
BAPH[a]	797	632
2	828	650
4	886	736
8	570	–

[a] Benzaldehydephenylhydrazone

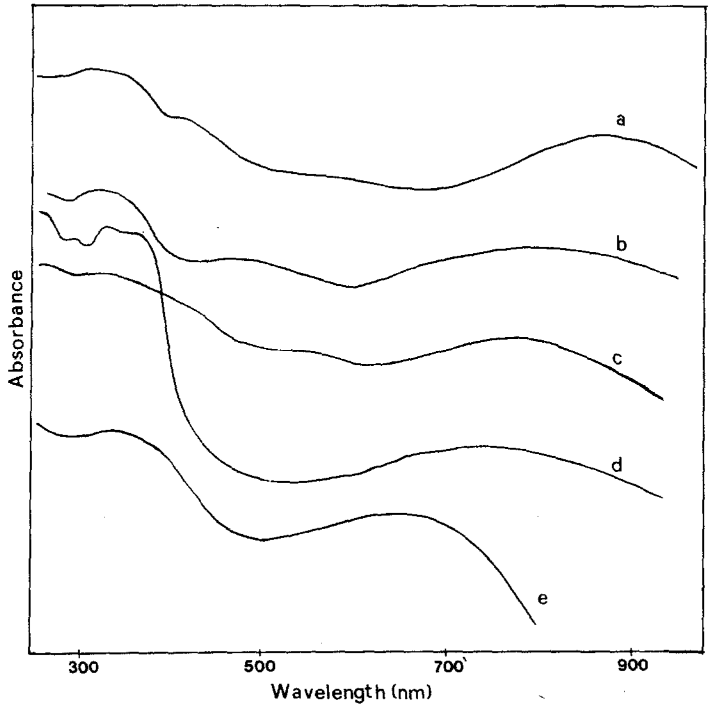


Fig. 3. UV-Vis solid state spectra for complexes of donor **4** with *a DDQ*, *b TCNE*, *c DTF*, *d CA*, and *e TNF*

respect to the binding energy as a whole (Fig. 3). The same considerations can be made from the results of FT-IR (DRIFT) determinations resulting in small frequency changes of the characteristic absorptions of donor and acceptor molecules [16, 17]. In particular, in complexes **4**/π^*-acceptor, the 10% intensity increase of the $C=N$ stretching mode of the donor in the complex gives an approximate idea of the charge-transfer percentage (νMe, 2816 cm^{-1}, stretching mode used as internal standard). No correlation can be established between the change in band intensity and the electron affinity of the acceptor.

Some contribution to the association energy could arise from dative forms supposedly due to the presence (in all complexes) of the e.s.r. signal of the acceptor radical anion, strong enough to be formed only by the ionizing power of the solvent [11, 18].

From the above results we can conclude that the lowering of the MC transition energy caused by the hydrazono groups in the cyclophane molecule is a relevant parameter; a second hydrazono group does not introduce a further lowering; the data are less correlable than those of complexes of simple hydrazones, probably due to the lack of a simple additive cooperation between the fragments of the substituted cyclophane molecule.

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Experimental

UV-Vis determinations were carried out on a Perkin-Elmer Model 554 spectrophotometer equipped with a MgW-K2R thermostating system. For UV-Vis solid state spectra the spectrometer was equipped with a Perkin Elmer integrating sphere. IR spectra were obtained using a Nicolet Fourier Transform Infrared 20-SX Spectrometer equipped with a Spectra Tech. Multiple Internal Reflectance "Collector" for solid state determinations. Mass spectra were obtained with a Hewlett Packard model 5895B Spectrometer while e.s.r. spectra were recorded on a Varian E-4 ESR Spectrometer using a deareated two-leg inverted cell [19].

Compounds **1**–**6** were prepared from mono and bisformyl derivatives [20, 21] with arylhydrazines following known methods [22].

All acceptors were Aldrich reagents and were purified as follows: tetracyanoethylene was sublimed at reduced pressure (1–2 mm Hg); chloranil was twice crystallized from acetone and vacuum dried; 2,4,7-trinitro-9-fluorenone and (2,4,7-trinitro-9-fluorenylidene)malononitrile were purified according to Ref. [11], 2,3-dicyano-5,6-dichloro-1,4-benzoquinone was crystallized from benzene.

All solvents were Carlo Erba RP-ACS grade reagents and were purified according to the literature [22].

General Procedure for the Synthesis of All Cited Complexes

Equimolar solutions of donor and acceptor were mixed in dichloromethane at room temperature with stirring and the λ_{max} of the MC bands were measured.

*Formation Constants of the Complexes of Hydrazone **4** with DDQ and CA*

The formation constants of hydrazone **4** with *DDQ* and *CA* were measured spectrophotometrically in dichloromethane solution. According to the Benesi-Hildebrand method [23], the concentration dependence of the absorbance of the charge-transfer band (d) for a 1 : 1 complex is given by:

$$[\mathrm{A}]_o/d = 1/K\varepsilon[D]_o + 1/\varepsilon$$

under conditions in which the total concentration of the electron donor $[D]_o$ is in large excess with respect to the total concentration of the acceptor $[A]_o$ and for 1 cm light path. K_f is the formation constant and ε is the extinction coefficient of the complex at the monitoring wavelength. Plots of $[A]_o/d$ against $1/[D]_o$ for solutions in which $[D]_o >> [A]_o$ should be linear.

*Ultraviolet-Visible Spectrophotometric Measurements on the Complex **4**/DDQ (or CA) in Dichloromethane*

From stock solutions of freshly prepared hydrazone (approximately $2.95 \cdot 10^{-2} M$) and *DDQ* (approx. $1.53 \cdot 10^{-3} M$) (hydrazone approx. $1.20 \cdot 10^{-1} M$ and *CA* approx. $5.85 \cdot 10^{-3} M$), eight samples were prepared by mixing 0.250, 0.500, 0.750, 1.00, 1.25, 1.50, 1.75, 2.00 cm^3 of donor solution and 1 cm^3 of *DDQ* (or *CA*) solution. Five different samples of each mixture were prepared for a total of 40, on which the determination of absorbance (*d*), at the λ_{max} of the complex was performed at 25.0°C. A linear correlation was obtained plotting $[A]_o l/d$ against $1/[D]_o$, where $[A]_o$ and $[D]_o$ indicate the total concentration of the acceptor and of the donor, $l = 1$ cm is the light path and d is the absorbance (optical density). In all cases the correlation coefficients (r) were greater than 0.998.

*Reaction of Donors **2** and **4** with TCNE*

Equimolar amounts of donor **2** (or **4**) and *TCNE* in dichloromethane were allowed to react for 24 h. After this period the red solution was concentrated under vacuum and cromatographed on silica gel column (cyclohexane/ethylacetate 7/3). The red compound was identified by comparison with an authentic sample following a well established procedure [24].

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