Review Article:

Charge-Transfer Interactions in Cyclophanes

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Abstract. Charge-transfer interactions in cyclophane systems are reviewed. The majority of the work covered involves intramolecular complexation, with both donor and acceptor moieties existing within the same molecule. Studies have also been performed on intermolecular complexes, mainly tetracyanoethylene:cyclophane complexes. Host–guest complexes involving charge-transfer are also discussed. Other areas covered include solvent effects, substituent effects, and theoretical calculations.

Key words. Charge-transfer complexes, cyclophane, host–guest complexes, donor-acceptor complexes.

1. Introduction

1.1. BASIC THEORY

In 1952 Mulliken proposed his theory of charge-transfer [1] in an effort to explain the existence of weak molecular complexes possessing both electron donor and acceptor properties. Mulliken designated those complexes formed by the weak interaction of electron donor molecules with electron acceptor molecules as charge-transfer complexes. A wide variety of compounds are known to form these complexes, ranging from simple systems such as the benzene-iodine complex first reported by Benesi and Hildebrand [2] to the multilayered donor-acceptor cyclophanes studied by Staab [31] and Misumi [30, 32]. A number of books [3] and reviews [4] have been published which provide a wealth of information, both theoretical and practical, on the subject of charge-transfer and molecular complexes.

Mulliken theorized that in the ground state of the complex normal physical forces such as van der Waals attractions between the complex components are predominant. Additional binding energy is contributed to the complex by a small amount of charge transferred from the donor to the acceptor. When the ground state complex absorbs light of a suitable wavelength, it is promoted to the excited state. In the excited state the electron, which in the ground state was only slightly shifted towards the acceptor, is almost completely transferred to the acceptor. This electronic transition can be observed in ultraviolet (UV)-visible spectrophotometry, which is the method of choice for studying charge-transfer complexation.

There is some confusion in the literature as to when the term 'charge-transfer complex' is appropriate. In many systems designated as such, charge-transfer forces are only a minor contributor to the binding forces in the ground state of the complex,

even though a charge-transfer absorption is observed in the electronic spectrum. Dewar and coworkers [5] object to this use of the term, holding that π-molecular complexes of this nature are best regarded as normal van der Waals aggregates. They point out that even though most known examples of systems designated as 'charge-transfer' or 'donor-acceptor' complexes show obvious charge-transfer bands in their electronic spectra, this is due to artificial selection since nearly all the work done in this area makes use of spectroscopic techniques. According to Dewar, information concerning the importance of charge-transfer forces can best be obtained from measurements of stability constants of complexes formed by unsubstituted aromatic hydrocarbons. Measurements of this kind are reported for a number of complexes, and results do not indicate any major contribution to binding by charge-transfer forces. For the purposes of this review, however, it is convenient to designate as charge-transfer complexes those systems which have been shown to produce an absorption band ascribable to charge-transfer in the UV-visible spectrum, regardless of the nature of the 'major' binding forces in the complexes.

1.2. SOLVENT EFFECTS

The charge-transfer (CT) absorption band is generally broad and intense, with extinction coefficients as high as 50 000 being observed. Most extinction coefficients for CT absorptions range from 1000 to 5000. It has been shown [6] that longer wavelengths for the CT band indicate a greater stability of the complex and a more complete transfer of the electron from donor to acceptor. The position of the charge-transfer absorption has been correlated with a number of properties of the complex components, including the ionization potential of the donor (I^D), the electron affinity of the acceptor (E^A), and Hammett σ values (with aromatic systems). The position of the charge-transfer absorption of most complexes has been shown to be solvent-dependent. When the complex possesses a neutral ground state and a polar excited state, a change from a less to a more polar solvent causes a red shift (to longer wavelengths) of the CT band [7]. An explanation for this observation has been given [3e]:

Solvating molecules will orient themselves about the complex so that the energy is minimized in the ground state. By the Franck–Condon Principle there will be no solvent reorientation at the instant of excitation. Through the polarization of solvent molecules by the solute dipole(s), the increase in solute dipole in the excited state (for neutral ground-state components) will result in the upper state being more stabilized than the ground state by this non-specific solvent interaction.

A more polar solvent will be better able to stabilize the polar excited state, resulting in a lowering of energy for the excited state. A smaller gap between ground and excited states necessitates a longer wavelength of light for the charge-transfer transition, and hence, a greater red shift. These changes in the charge-transfer spectrum due to solvent differences are large and so readily observable that it has been suggested [8] that the position of the CT band may be used as an estimate of the ionizing power of the solvent. The absorption band shifts due to solvation have been roughly correlated with the dielectric constant of the solvent.

The solution concentration of the CT complex can be calculated by measuring the intensities of absorption bands characteristic to the complex and using variations on the Benesi–Hildebrand equation (Equation 1) for analysis of the results.

Equation 1 – the Benesi–Hildebrand equation:

$$l[A]/A = 1/K\varepsilon[D] + 1/\varepsilon$$

Here l = path length; $[A], [D]$ = conc. of acceptor, donor; A = absorbance; ε = extinction coefficient.

The Benesi–Hildebrand analysis starts from the assumption that there is only one equilibrium present in solution, and that the absorbance (λ) monitored is due only to the complex. For $[D]_0 \gg [A]_0$, a plot of $l[A]/A$ vs. $1/[D]$ normally gives a straight line with a slope of $1/K\varepsilon$ and a y-intercept of $1/\varepsilon$. This fails for very strong complexes ($[A]_0 \sim [A]_{complexed}$). There are a number of variations on this equation, dependent upon the experimental conditions. In general, this equation is a very powerful tool for obtaining meaningful results from the raw experimental data. It should be noted that the association constant and extinction coefficient of the CT complex are increasingly being evaluated by computer-assisted nonlinear least-squares fitting procedures which remove the necessity for experimental boundary conditions [49].

Kobayashi and coworkers [9] have examined CT complexes between naphthalene derivatives and nitrated benzene compounds in the presence of γ-cyclodextrin (a cyclic octasaccharide). γ-Cyclodextrin (γ-CD) can apparently accommodate both donor and acceptor molecules within its cavity, resulting in weak CT bands becoming intensified. Charge-transfer absorptions are produced in some cases where complexation is normally not observed in the absence of γ-CD, such as that observed between 1-napthylacetic acid and picric acid; when the solvent was changed from water to a 1:1 water:methanol (less polar) mixture, the position of the CT band shifted from 510 to 500 nm. This observation is in agreement with the known solvent sensitivity of charge-transfer absorptions as discussed earlier.

2. Intramolecular charge-transfer

2.1. COMPARATIVE STUDIES

There has been considerable discussion concerning the relative orientation of the donor and acceptor moieties of charge-transfer complexes in solution. Detailed crystal structures have been obtained for a number of CT complexes, but solid-phase geometry is not necessarily the same as that in solution. Intermolecular distances between donor and acceptor in the solid state are in the order of 3.5 Å; this is longer than a covalent bond, but shorter than the usual van der Waals distances. One method of gaining more information on the geometry of complexes is to design a system with both donor and acceptor contained within the same molecule and having relatively restricted degrees of freedom. The cyclophane framework, where one or more aromatic systems are connected by one or more bridges, fits these requirements quite well, and has been utilized as a base structure by many researchers. The reader is referred to the Keehn/Rosenfeld monographs *Cyclophanes I* and *II* [51] and to Smith's book on bridged aromatic compounds [52] for further discussion.

The simplest donor-acceptor cyclophane is [2.2]paracyclophane quinone (Structure A, Figure 1), reported by Cram and coworkers in 1966 [10]. This compound
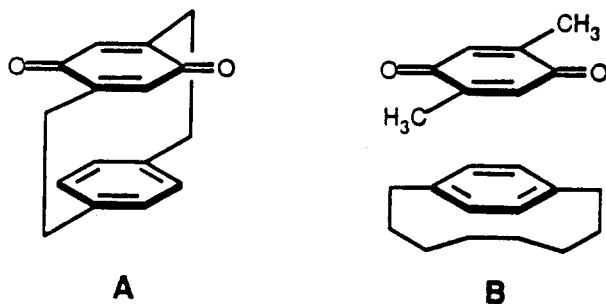
Fig. 1.   Structures for a simple donor-acceptor cyclophane and the corresponding intermolecular system.

has an ultraviolet absorption spectrum which includes a band at 340 nm ($\varepsilon = 597$). The authors suggest that this band is due to an intramolecular charge-transfer transition. The absorption presumably cannot be associated with deformation of the benzene ring, since it does not appear in the spectrum of [8]paracyclophane-2,5-dimethylbenzoquinone (Structure **B**, Figure 1) and [8]paracyclophane is known to have a 'bent' benzene ring. The 340 nm absorption is also absent in the spectrum of [4.4]paracyclophane quinone, which had been previously synthesized by Cram [11]. The [4.4] cyclophane possesses a spectrum comparable with the model 2,5-dimethylbenzoquinone. 2,5-Dimethylbenzoquinone shows a strong absorption between 265 and 274 nm which shifts to slightly longer wavelengths in the [4.4] system. A
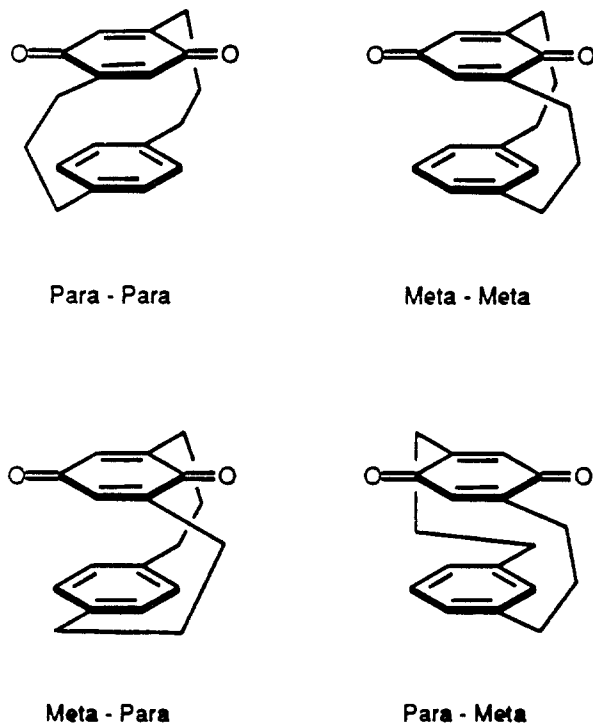

Fig. 2.   Structures for a series of [3.3]meta- and paracyclophane quinones.

Table I. Comparison of the CT absorption for a series of [n.n] paracyclophane quinones in acetonitrile, 25°C

n	λ, nm
2	340
3	406
4	288

shoulder in the model spectrum at ~ 290 nm becomes a slight maximum (288 nm) in the spectrum of the cyclophane. This provides evidence for a very weak inter-ring electronic interaction in the paracyclophane quinone system.

Other groups have studied similar cyclophane systems. Shinmyozu and coworkers [12] have compared a series of [3.3]meta- and paracyclophane quinones (Figure 2). They concluded that the *para-para* cyclophane system, which has a parallel and near center-on-center stacking of donor and acceptor, adopts the most suitable conformation for intramolecular CT transitions in these [3.3]cyclophane quinones. They also compared the position of the charge-transfer absorption for [2.2], [3.3], and [4.4]paracyclophane quinone (Table I), and concluded that the [3.3] system forms the most stable intramolecular charge-transfer complex [12b], presumably because it can attain the optimum intramolecular donor-acceptor distance.

Most donor-acceptor cyclophanes incorporate a *p*-benzoquinone moiety. However, Miyahara and coworkers [13] have synthesized the [2.2] and [3.3]paracyclophane quinones shown in Figure 3, utilizing the normally unstable *o*-benzoquinone group. They found that these cyclophanes appeared to be stabilized by an intramolecular CT transition with an absorption band at ~ 500 nm. This band was absent in the simple 3,6-dimethyl-*o*-benzoquinone. The band shifted to longer wavelength when the solvent was changed from cyclohexane to chloroform, following the expected pattern for a charge-transfer transition.

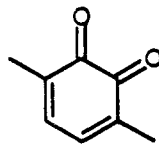## 2.2. INTRAMOLECULAR QUINHYDRONES

One of the most prolific researchers in the area of donor-acceptor cyclophanes is Staab and his group. They initially studied systems designated as 'intramolecular quinhydrones' [14]. Quinhydrone itself has long been known as the greenish-black, crystalline 1 : 1 charge-transfer complex between *p*-benzoquinone and hydroquinone. Although hydrogen bonding probably does exist between the donor and acceptor components of quinhydrone, it is not the sole means of association as hydroquinone dimethyl ether is also known to form a colored adduct with *p*-benzoquinone [15].

Staab and coworkers first synthesized the [2.2] intramolecular quinhydrones [14a, b] shown in Figure 4. There are two possible orientations of donor and acceptor components, resulting in the formation of pseudo-ortho (C) and pseudo-geminal (D) isomers. These isomers show strikingly different UV spectra (C, 515 nm, $\varepsilon = 170$; D, 492 nm, $\varepsilon = 1600$), illustrating the apparent orientation dependence of CT transitions in these types of cyclophanes. Staab has based much of his
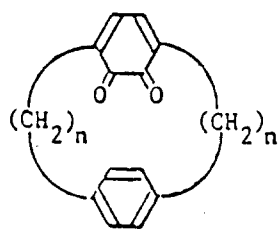
1 (n=2)

2 (n=3)

9
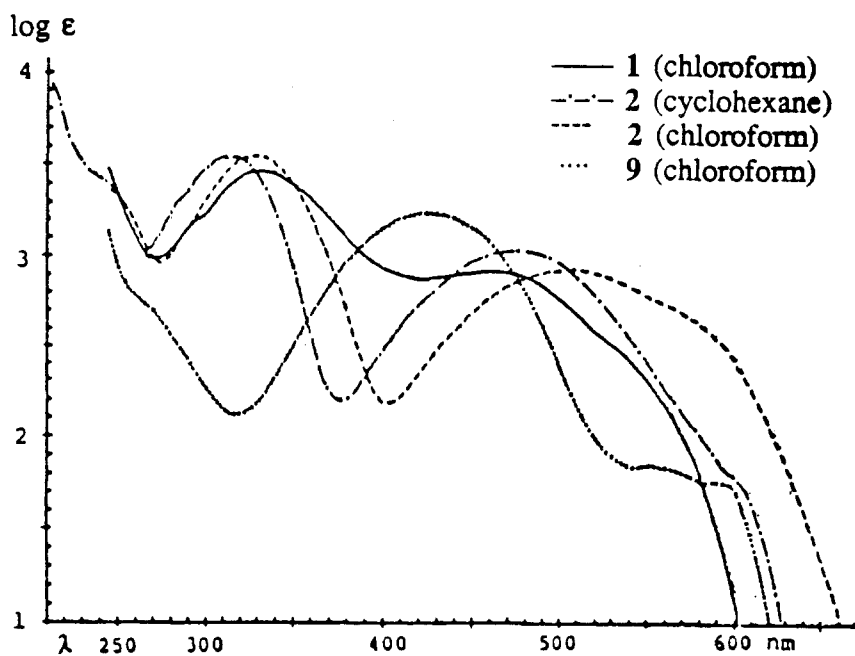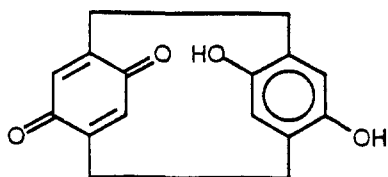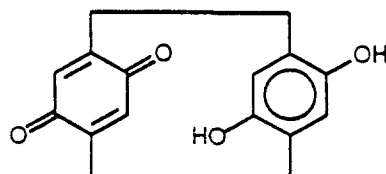

Fig. 3. Structures and electronic spectra for a series of *o*-benzoquinonoid compounds in varying solvents.

Fig. 4. Structures for two isomeric [2.2] intramolecular quinhydrones.

research on the contention that the effectiveness of the charge-transfer transition in these types of molecules is largely based on the relative orientation of donor and acceptor. It is thought that systems in which the donor and acceptor are in a pseudo-geminal type of relationship will attain better orbital overlap and hence more effective charge transfer than systems where donor and acceptor are in a pseudo-ortho orientation. The results of his work (*vide infra*) tend to support this hypothesis. Simple molecular orbital calculations have been carried out [14c] in an attempt to explain the observed differences in the spectra of the two isomers. Qualitative conclusions were obtained using one-electron theory which agreed well with the experimental data. Vogler [16] has also performed theoretical calculations on these donor-acceptor cyclophanes. His method involves a four-orbital model utilizing the HOMO of the donor and the LUMO of the acceptor, and produces results that are quite close to the actual data as observed by Staab.

Two other intramolecular quinhydrones have been synthesized which have even shorter transannular distances than [2.2]paracyclophane quinone. Staab and coworkers [14e] investigated a tetrabridged cyclophane quinhydrone (Structure E, Figure 5) while Stobbe *et al.* [17] synthesized the unsaturated form of [2.2]paracyclophane quinhydrone (F). [2.2]Paracyclophane has a transannular distance of ~ 2.74 Å, while E has a transannular distance of 2.67 Å (measured between ring carbons by single-crystal X-ray analysis). The UV-visible spectrum of E shows a broad, intense CT absorption at 491 nm ($\varepsilon = 1280$). The similarity in lineshape and position of this absorption to the CT band of pseudo-geminal [2.2]paracyclophane quinhydrone (D, 492 nm, $\varepsilon = 1600$) is surprising in view of the shorter transannular distances and the completely rigid mutual orientation of donor and acceptor enforced by the fourfold bridging. (Earlier work suggests that the [3.3] system is the most favorable for intramolecular CT transitions, as it is flexible enough to achieve the best mutual donor-acceptor geometry.) The olefin-bridged cyclophane shows a CT transition at 517 nm ($\varepsilon = 138$), similar to that shown by pseudo-ortho structure C (Figure 4), which is to be expected because of the similar orientations of donor and acceptor.

As mentioned earlier, hydroquinone bis methyl ether also forms a charge-transfer complex with *p*-benzoquinone. Accordingly, Staab has studied the corresponding intramolecular complexes [14f, g]. The two isomers (pseudo-ortho and pseudo-geminal) of [2.2]paracyclophane quinhydrone bis methyl ether show almost
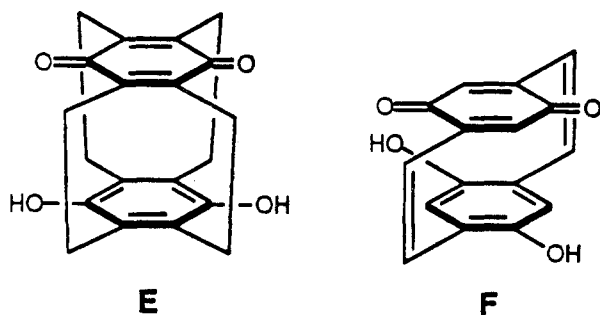

E   **F**

Fig. 5. Structures for intramolecular quinhydrones with very short transannular distances.
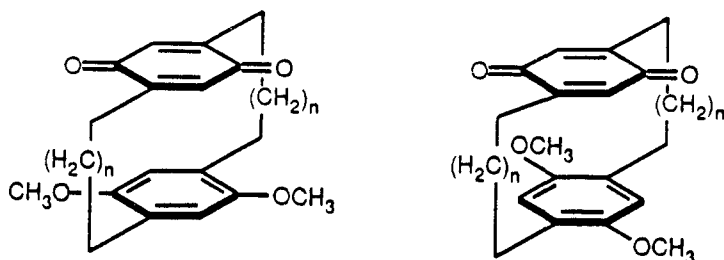
Fig. 6.   General structures for a series of isomeric intramolecular quinhydrones ($n = 1-4$).

identical UV spectra to quinhydrones **C** and **D**. This tends to support the contention that hydrogen bonding is not the major binding force in quinhydrone complexes.

Staab has extended his studies of intramolecular paracyclophane quinhydrones to the [3.3], [4.4], [5.5], and [6.6] homologs [14m, n] (Figure 6). The electronic spectra of the pseudo-geminal and pseudo-ortho [3.3] isomers resemble those of the analogous quinhydrones in the [2.2] series. The differences in the CT absorptions between the two isomers are, however, much more pronounced for the [3.3] cyclophanes (see Table II). As n increases and the cyclophanes become more flexible, the efficiency of the intramolecular charge-transfer transition decreases. When $n = 3$ (the [5.5] system), a rapid equilibrium between the two isomers is observed, and when $n = 4$ (the [6.6] homolog) the barrier to rotation is so low that only one compound is observed.

Having extensively investigated the paracyclophane quinhydrones, Staab then turned his attention to the corresponding metaparacyclophane quinhydrone bis-methyl ethers [14h, o]. Again, two isomers are possible, depending upon which ring has the *meta* and which the *para* linkage, as shown in Figure 7. Staab determined that the strain found in the [2.2]metaparacyclophanes is considerably reduced in the [3.3] systems. As a result, the molecular structures of the two systems are quite different. It is interesting to note that **H** ($n = 0$) crystallizes in such a fashion that enantiomeric single crystals can be isolated. The X-ray crystal structure shows that the metabridged quinone is much more deformed than the para-bridged aromatic portion of the molecule. A single-crystal X-ray structure was also obtained for **H** ($n = 1$). The longer bridges in the [3.3] system appear to have substantial effects on

Table II.   Comparison of CT absorption data for a series of intramolecular quinhydrones (Fig. 6) in chloroform, 25°C

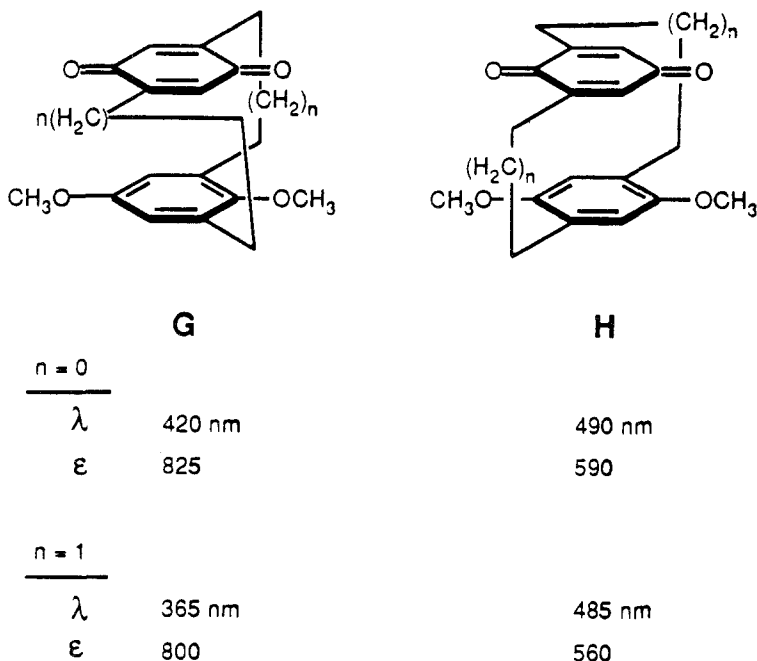| n	isomer	λ, nm	ε
0	gem	483	1330
	ortho	498	142
1	gem	462	3210
	ortho	500	105
2	—not reported—		
3	(rapid interconv.)	435	59
4	(one compound)	425	43

Fig. 7. Structures and UV data for a series of isomeric metaparacyclophane quinhydrones.

the orientation of the molecule. First, the overlap between the quinone acceptor and the aromatic donor appears to be considerably less than in the [2.2] compound; furthermore, the two rings are not nearly as deformed, due to the reduction in bond angle strain. Attempts were made to interpret the electronic spectra of these systems using molecular orbital theory, but the complex and unsymmetrical structure of the metaparacyclophane system precluded use of the simple HMO model which worked well for the [2.2] and [3.3]paracyclophane quinhydrones.

To complete their investigation of simple intramolecular quinhydrones, Staab and coworkers then examined the charge-transfer behavior of a number of metacyclophane quinhydrones [14p]. Once again, two isomers of each compound are possible, in this case as rotational isomers (Figure 8). In both the [2.2] and the [3.3]
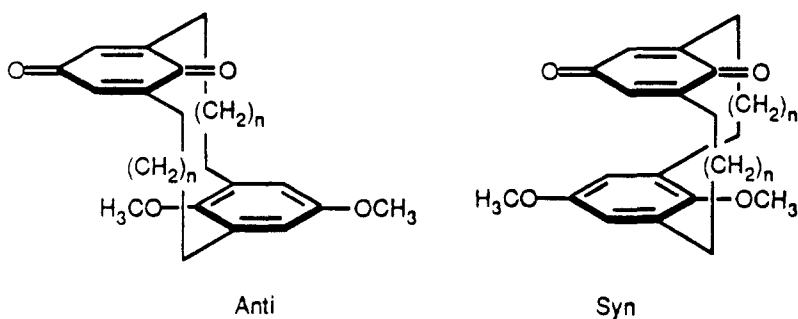

Fig. 8. Rotational isomers for a series of metacyclophane quinhydrones ($n = 0, 1$).

systems the UV spectra of the two isomers are surprisingly similar, in spite of completely different donor-acceptor overlap. The [3.3] *anti* isomer was observed to rearrange completely to the *syn* isomer at 120°C. In view of the large steric strain in the *syn* isomer (evident from ring deformations observed by X-ray analysis) and the sterically less crowded structure of the *anti* isomer, the complete isomerization of *anti* to *syn* suggests a considerably stronger ground state stabilization by electron donor-acceptor interactions for the *syn* isomer. This result agrees well with HMO calculations on the charge-transfer ground state stabilization observed for quinhydrone [18]. These calculations show that a translocated donor-acceptor orientation such as in the *anti* isomer would provide only about 50% of the ground state stabilization present in the eclipsed orientation found in the *syn* isomer. However, these calculations do not account for the extreme similarities observed in the UV spectra of both isomers. This suggests that there is not necessarily a correlation between ground state stabilization by CT interaction and the wavelengths and/or the intensities of the CT absorption.

Having studied all the possible variations for connecting donor and acceptor with methylene bridges in the intramolecular quinhydrone systems, Staab and coworkers turned to replacing one or both methylene bridges with polyether bridges (Figure 9) [19]. It was anticipated that, due to the width and flexibility of the macrocycles, the donor and acceptor moieties would not be optimally arranged for charge-transfer transitions. However, because of the partial crown ether structure of these molecules, complexation of cations with suitable ionic radius should result in a greater rigidity of the macrocycle and in a mutual approach of the donor and acceptor portions of the molecule. These conformational changes would then be expected to cause changes in the CT absorptions of the molecules. The first series investigated was that resulting from replacing one bridge of [3.3]paracyclophane quinhydrone bis methyl ether with polyether chains of varying length. The method of investigation involved comparison of the electronic spectra of the macrocycles with the spectra obtained upon addition of Na^+ ion. With the lower analogues (I, $n = 1,2$), the addition of sodium ion does not produce any significant effects on the CT absorption. For $n = 3$, the addition of sodium ion caused an increase in ε of 550 units and a bathochromic shift of 16 nm. The final analog ($n = 4$) also showed some
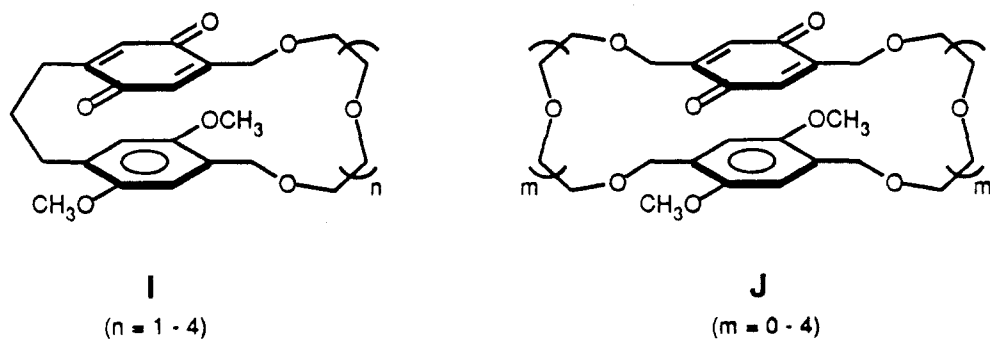

Fig. 9. Structures for a series of intramolecular quinhydrones with one or both bridges replaced by polyether linkages.
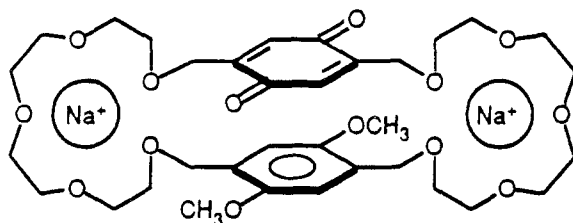
Fig. 10. Proposed manner of complexation with sodium ion for compound **J** ($m = 3$).

changes upon the addition of sodium ion, but the effects (ε increases by 162) are significantly less than when $n = 3$. The effect of added potassium ion was also investigated, but was not as large as that caused by sodium ion complexation. The second series, where both bridges have been replaced by polyether linkages, showed similar effects. For the compounds where $m = 0-2$ no significant changes were observed in the CT absorption intensity upon addition of sodium ion. As before, when $m = 3$ large effects were seen in the presence of Na$^+$, with a bathochromic shift of 30 nm and ε increasing by 378 units. Presumably in these compounds ($m = 3$), the polyether bridges are mimicking 15-crown-5 (a good sodium ion complexer) in a manner such as that shown in Figure 10. The larger analogues ($m = 4$) should mimic 18-crown-6, and better results should be observed in the presence of potassium ion. This was the case in the doubly-bridged compound (**J**, $m = 4$), with a bathochromic shift of 25 nm and a change in ε of 217 units being observed upon addition of K$^+$ ions.

Although quinhydrone is one of the most extensively studied charge-transfer complexes, there are other systems equally worth investigating. Accordingly, Staab and coworkers [20] modified their intramolecular quinhydrones by replacing the p-benzoquinone portion with a tetracyanoquinodimethane fragment. TCNQ is a very efficient electron acceptor, and these systems were expected to show intense charge-transfer transitions. The compounds studied were those based on [2.2] and [3.3]paracyclophane quinhydrone. As in the intramolecular quinhydrone cases, there are two possible donor-acceptor orientations, and Staab was again interested in observing the orientation dependence of the CT interactions. The structures shown in Figure 11 were studied using UV-visible spectroscopy. As for the quinhydrone systems, a strong orientation dependence of the CT transition was observed, as listed in Table III. When the data for the TCNQ-based cyclophanes
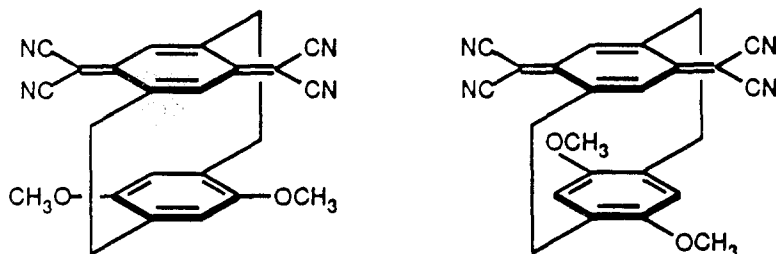

Fig. 11. Structures for two isomeric TCNQ-based donor-acceptor cyclophanes.

Table III. CT absorption data for TCNQ-based donor-acceptor cyclophanes (Fig. 11) in chloroform, 25°C

	[2.2]		[3.3]	
	λ, nm	ε	λ, nm	ε
gem	695	3225	705	3450
ortho	730	258	670	117

are compared to that for the corresponding intramolecular quinhydrone, it can be seen that the CT absorptions for the TCNQ systems are, in all cases, much more intense. There is also a much more pronounced intensity difference between the TCNQ isomers. The extinction coefficient for the pseudo-geminal isomer is 12.5 times higher than for the pseudo-ortho isomer in the [2.2] system, and approximately 30 times higher in the [3.3] analog. This reinforces the well-documented fact that TCNQ is a more efficient electron acceptor than p-benzoquinone.

Staab has also studied a number of systems where the benzoquinone portion of his intramolecular quinhydrone was replaced by a substituted benzene moiety [21–23]. Some of these systems were examined for intramolecular CT activity as before [21, 22], again with an interest towards observing the orientation dependence of the CT transitions (Figure 12). Both the cyano- and nitro-substituted compounds

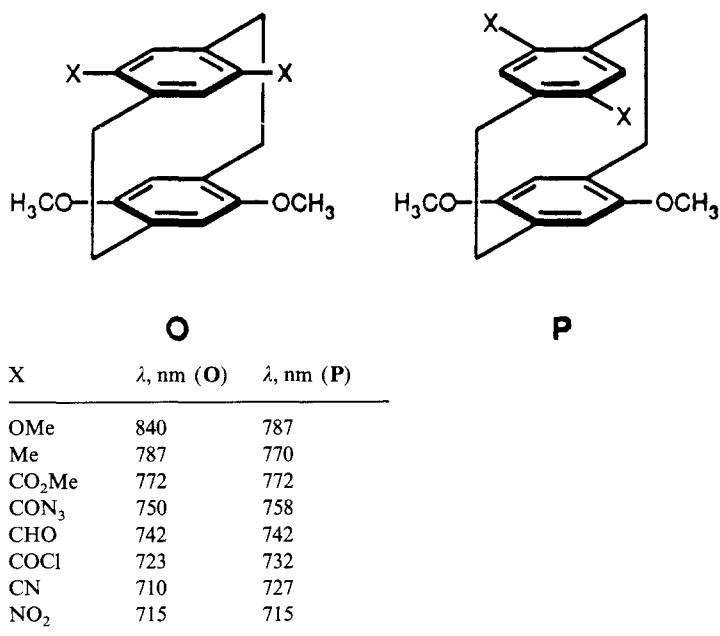| X	λ, nm (O)	λ, nm (P)
OMe	840	787
Me	787	770
CO_2Me	772	772
CON_3	750	758
CHO	742	742
COCl	723	732
CN	710	727
NO_2	715	715

Fig. 12. Maxima of CT transitions for the TCNE complexes of the two isomers for a series of substituted cyclophanes.
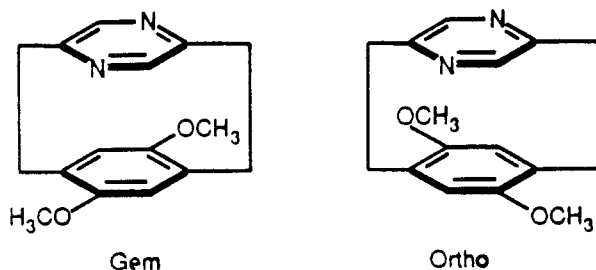
Fig. 13. Structures for two isomeric pyrimidine-based donor-acceptor cyclophanes.

showed a strong dependence on orientation when measuring the intensity of the CT transition, with the pseudo-geminal isomer providing a much stronger absorption than the pseudo-ortho isomer in both cases.

As another variation on the theme of replacing the benzoquinone portion of his donor-acceptor cyclophanes, Staab introduced a pyrimidine ring into the system (Figure 13) [24b]. As usual, there are two possible orientations of the pyrimidine ring, resulting in two isomers. Once again, the pseudo-geminal isomer showed a more intense CT absorption (440 nm, $\varepsilon = 405$) as compared to the pseudo-ortho compound (460 nm, $\varepsilon = 103$).

Taking a different approach, Staab examined a series of systems all having the same acceptor unit but varying in strengths of the donor units and in donor-acceptor distance [24a]. These compounds are shown in Figure 14. From the colors of these complexes, some qualitative conclusions could be drawn about the
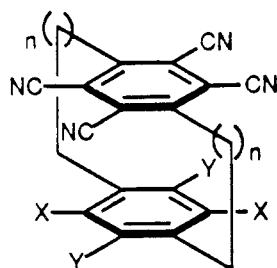
Compound	n	X	Y	λ, nm	$\log \varepsilon$
K	2	H	H	395	–
L		OMe	H	520	2.38
M		CH$_3$	CH$_3$	440	–
N		OMe	OMe	380	–
O	3	H	H	–	–
P		OMe	H	508	2.54
Q		CH$_3$	CH$_3$	–	–
R	4	H	H	–	–
S		OMe	H	495	1.95

Fig. 14. Maxima of intramolecular CT transitions for a series of donor-acceptor cyclophanes varying in the strength of the donor unit and in donor-acceptor distance.
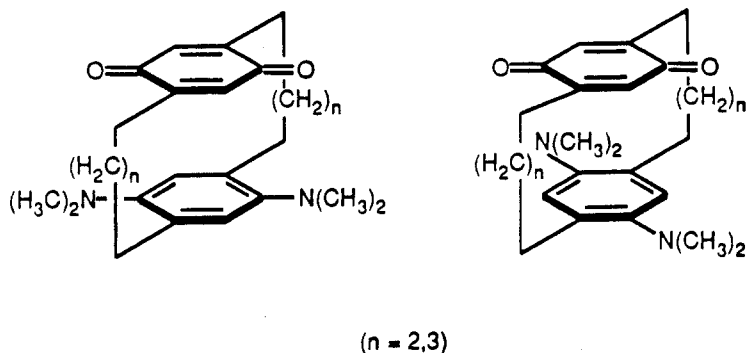
(n = 2,3)

Fig. 15.   Structures for a series of isomeric TMPD-based donor-acceptor cyclophanes.

strengths of the different donors and about the importance of the donor-acceptor distance. In the [2.2] series, compound **K** was yellow while **M** was red, **L** violet, and **N** orange-red. It seems that darker colors indicate stronger electron donors. In the case of structure **N**, the tetramethoxy ring would be expected to be a strong electron donor, but it appears to encounter steric interactions which decrease its donating ability. With respect to ring sizes, the [2.2] structure **L** was violet while the [3.3] analog **P** was dark red and the [4.4] system **S** was orange. This result implies that the [2.2] system has the most effective donor-acceptor distance. The absorption data shown in Figure 14 support these qualitative observations and conclusions.

A final example of the simple donor-acceptor cyclophanes studied by Staab is shown in Figure 15 [25]. In this system, the role of the electron donor is played by a tetramethyl-p-phenylenediamine (TMPD) moiety. TMPD is known to be a very strong electron donor, so these compounds are expected to show significant charge-transfer activity. Table IV shows the wavelengths of the CT absorptions observed for the TMPD-based cyclophane quinones. When the solvent was changed from dichloromethane to cyclohexane a blue shift of 40–50 nm was observed for each compound. These results illustrate once again both the orientation dependence and the sensitivity to solvent polarity of the CT transition in donor-acceptor cyclophanes.

Staab has also investigated a number of other systems showing charge-transfer activity. Some of these utilize a naphthoquinone moiety in place of the benzo-quinone fragment [26] while others can be categorized as new electron donors [27]. One of these new systems is shown in Figure 16. Upon subjection of **T** to cyclic

Table IV.   CT absorption data for TMPD-based donor-acceptor cyclophanes (Fig. 15) in methylene chloride, 25°C

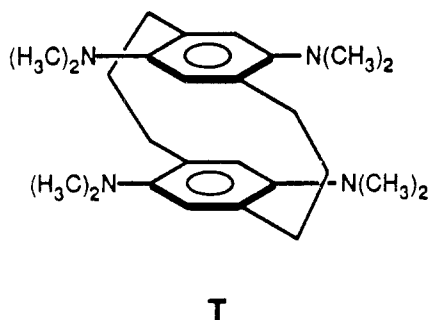| n	isomer	λ, nm	ε
1	gem	577	1930
	ortho	595	160
2	gem	538	2455
	ortho	537	76

Fig. 16.   Structure for a 'double TMPD' system categorized as a new electron donor.

voltammetry, four oxidation steps were observed, with the first oxidation step having $E_1^{ox} = -0.242$ V (compared to $E_1^{ox} = -0.216$ V for TMPD). The fact that the 'double TMPD' system has a first oxidation step that is more negative than that for TMPD implies that **T** should be an even stronger electron donor than TMPD. This new electron donor cyclophane forms a 1:2 crystalline complex with TCNQ.

2.3. MULTILAYERED CYCLOPHANES

A more complex series of cyclophanes has been investigated by Misumi and coworkers. These compounds are known as multilayered cyclophanes, the simplest of which is based on [2.2]paracyclophane. Misumi has studied compounds containing between two and six stacked benzene rings [28], shown in Figure 17. When the electronic spectra of compounds **U–Y** were inspected, strong bathochromic and hyperchromic effects were observed as the number of layers increased. These shifts are particularly noticeable as the number of layers increases from two to three and from three to four, while the absorption curves become markedly structureless. These effects are explained mainly by transannular π-electron interactions, and to a lesser extent by the increased distortion of the aromatic rings. X-ray crystallography has shown that the outer benzene rings are bent into a pseudo-boat shape, while the inner rings exist as a pseudo-twist-boat.

Having examined the effects of layering in the parent benzenoid cyclophanes, Misumi then turned to more substituted systems, beginning with a series of structural effects on CT complexation in multilayered donor-acceptor systems. The first modification involves the replacement of one of the aromatic rings in the triply layered cyclophane with a p-benzoquinone moiety [29]. These quinonoid cyclophanes are shown in Figure 18. The electronic spectra of these systems were compared with that of [2.2]paracyclophanequinone. It was observed that the charge-transfer absorptions for **AA** and **BB** appeared at longer wavelengths than for the double-layered system, indicating that donors in the triply layered systems had more π-donor character; there was also a large difference in the appearance of the UV spectra of **AA** and **BB**. **AA** showed an absorption at 395 nm ($\varepsilon = 2330$) while the CT absorption for **BB** appeared at 435 nm ($\varepsilon = 320$). It can be theorized that the lower benzene ring in **AA** is donating electrons to the center aromatic ring, increasing its π-donor character relative to **BB**.
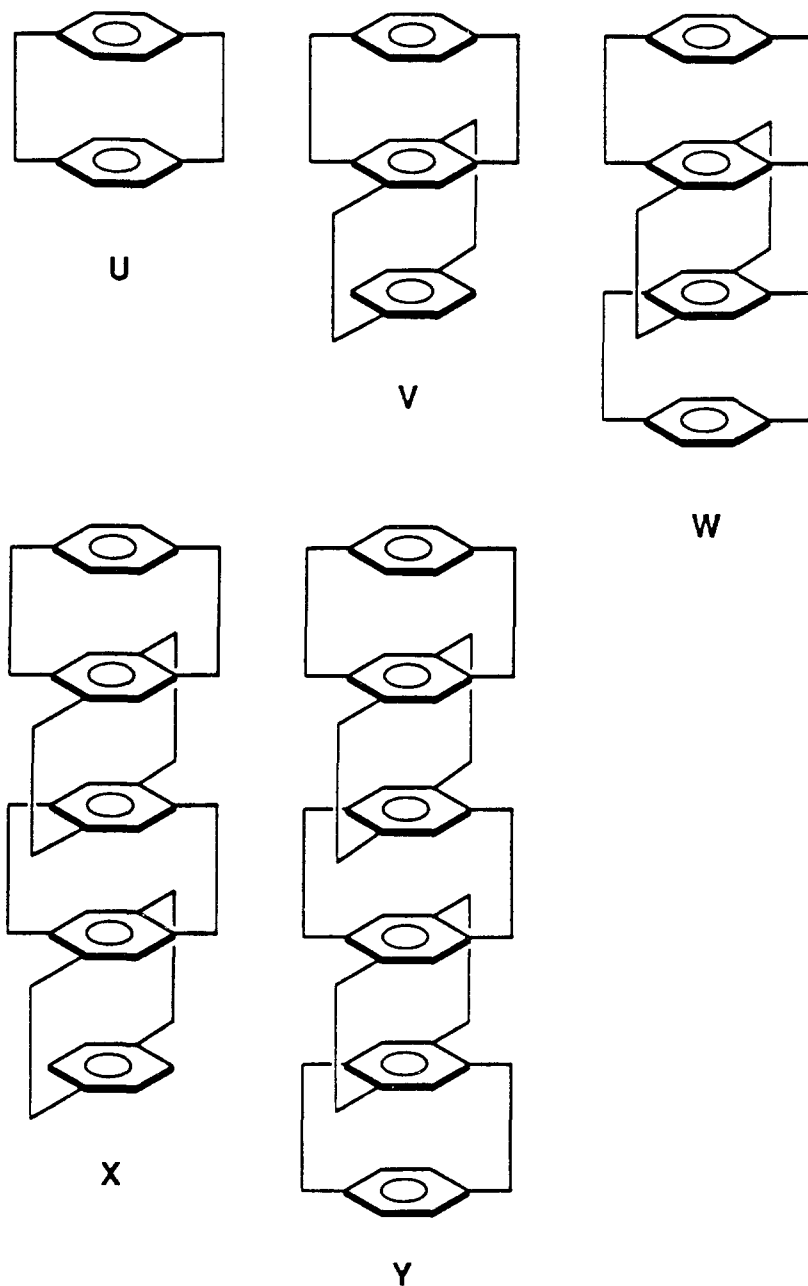
Fig. 17. Structures for a series of simple multilayered cyclophanes.

Elaborating the substitution patterns further, Misumi next synthesized a series of cyclophanes, based on the ubiquitous quinhydrone charge-transfer complex. Staab has already shown (vide supra) that charge-transfer transitions in these types of double-layered compounds show a definite dependence on donor-acceptor orientation. In a similar manner, Misumi was interested in investigating the sensitivity of

Fig. 18. Structures for two triply-layered quinonoid cyclophanes.

triple- and quadruple-layered compounds to this variable [30]. Accordingly, a series of triple- and quadruple-layered donor-acceptor cyclophanes was synthesized. A representative sampling is shown in Figure 19. (It should be noted that Staab and coworkers earlier synthesized some of these compounds [31] with intent to study the same features and effects). Both Misumi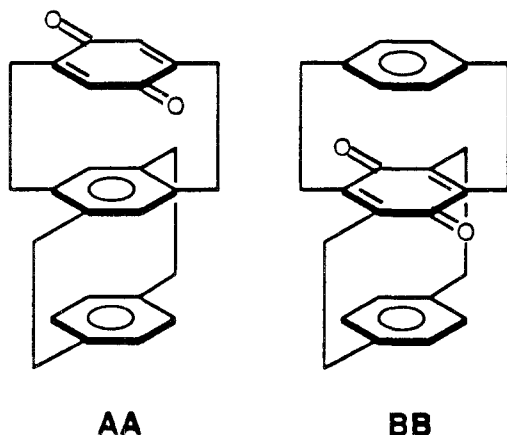 and Staab concluded that, for these multilayered quinhydrones, there did not seem to be any dependence of the CT absorption upon donor-acceptor orientation. The internal benzene rings seem to act as conductors rather than as insulators, resulting in indirect electron transfer. As the number of layers in the molecules increased, the charge-transfer bands shifted to correspondingly longer wavelengths, providing more evidence for this theory. Within a particular series, the electronic spectra of the various isomers were practically identical.

A third series of multilayered cyclophanes was formulated utilizing a tetra-cyanoquinodimethane fragment instead of the p-benzoquinone unit (Figure 20) [32]. As in the simple paracyclophane systems based on this moiety, these compounds were expected to show intense charge-transfer absorptions due to the high electron acceptor efficiency of TCNQ. As a comparison, the triply layered compound *sans* methoxy substituents (**LL**) was also synthesized. The electronic spectra of these compounds exhibit very broad absorption bands, sometimes tailing to over 1000 nm. A number of features of these spectra are of interest. The absorption maximum of the double-layered TCNQ cyclophane **HH** is shifted to longer wavelength than those of the three triple-layered cyclophanes, while the absorptions of the latter compounds are longer than that of the former. The fact that the CT bands of **II**–**KK** showed marked red shifts and tailing to long wavelengths compared to that of model system **LL** clearly indicates that the dimethoxybenzene fragment is functioning as a strong π-donor through the sandwiched inner benzene ring.

2.4. OTHER SYSTEMS

Although the paracyclophane framework is usually based on substituted benzene rings, other aromatic systems have also been utilized. One interesting example
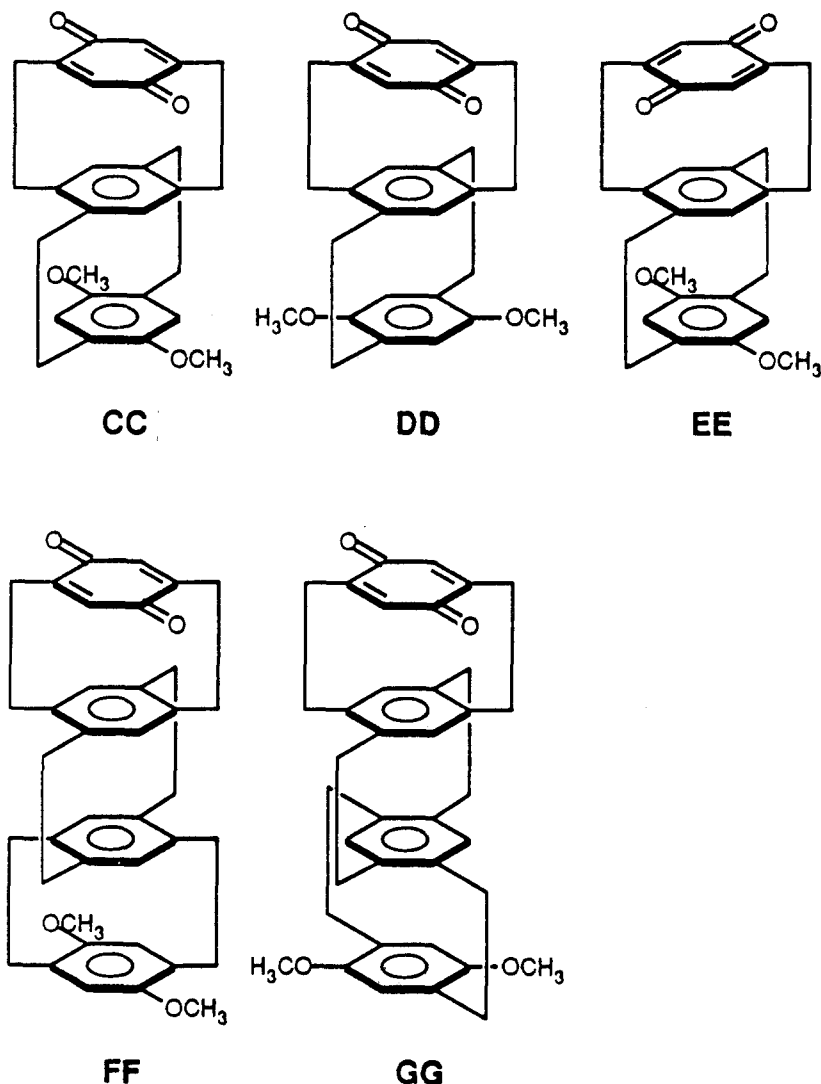
Fig. 19.   Structures for a series of multilayered donor-acceptor cyclophanes.

involves the use of the tropylium cation as an integral part of the cyclophane. Misumi and coworkers have studied a number of compounds of this type [33]. They first synthesized the system based on [2.2]paracyclophane and its triply layered analog (Figure 21). Both compounds exhibited a band in the electronic spectrum that was ascribed to intramolecular charge-transfer, with **MM** having an absorption at 354 nm and **NN** at 434 nm. Although these wavelengths are short compared to those observed for CT transitions in other systems, they were described as due to charge-transfer for a number of reasons. First, there is no corresponding band in the UV spectrum of the dimethyl tropylium cation, implying that the observed absorptions in the cyclophanes are due to some intramolecular interaction. Secondly, a shift to longer wavelengths of these absorption bands was observed
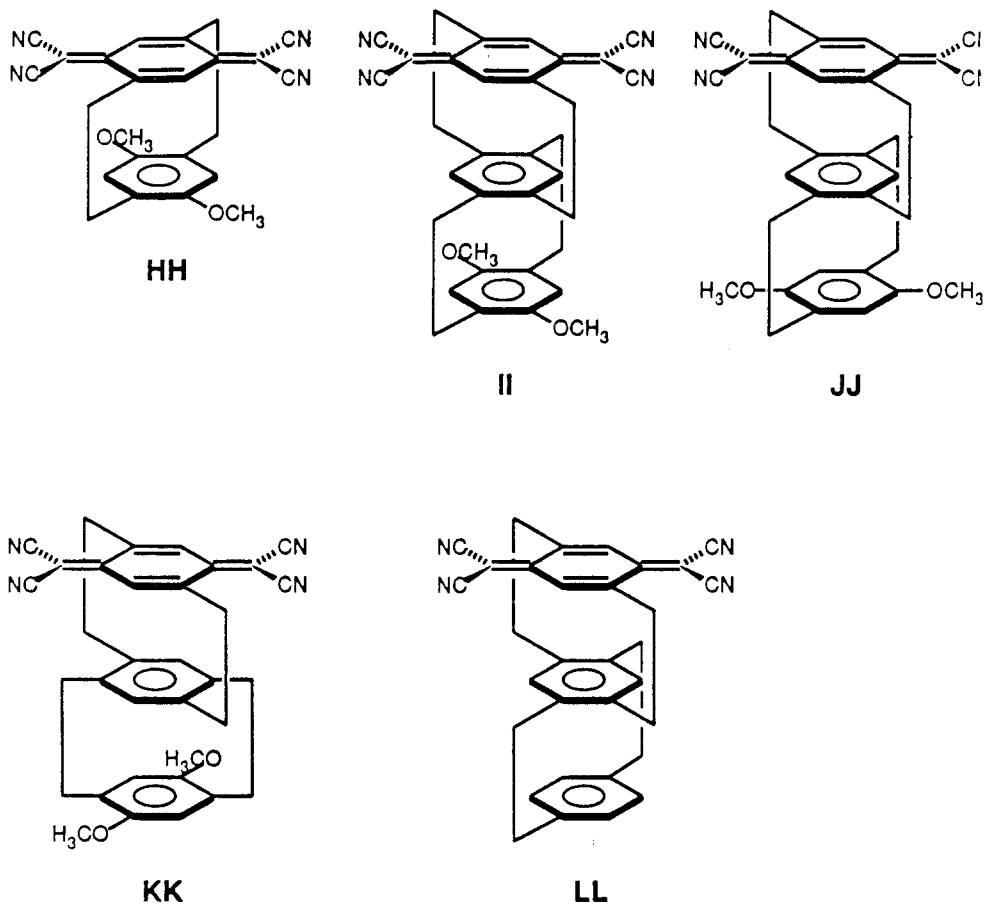
Fig. 20. Structures for a series of TCNQ-based multilayered donor-acceptor cyclophanes.
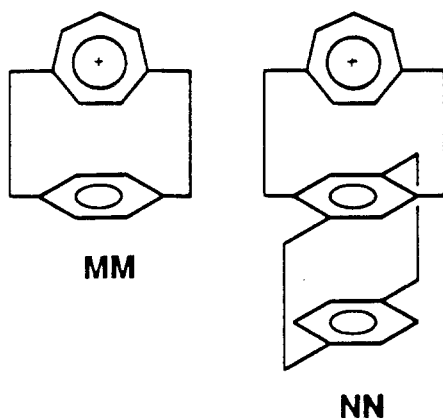
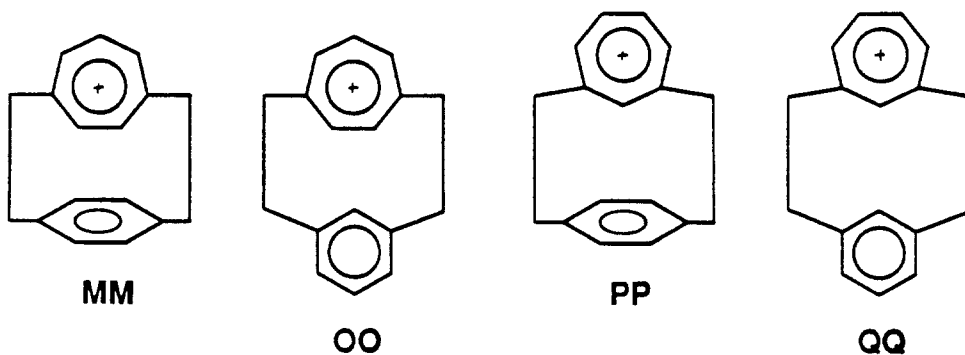Fig. 21. Structures for two tropylium cation-based cyclophanes.

Fig. 22.   Structures for a series of tropylium cation-based cyclophanes, synthesized to study the effects of differing geometries on the absorption spectra.

in polar solvents, in accordance with the known behavior of charge-transfer transitions.

Misumi was also interested in the effects of geometry on the absorption spectra of the [2.2]tropyliocyclophanes [33b]. Accordingly, the compounds shown in Figure 22 were synthesized and their UV spectra compared. The four compounds all showed absorptions due to charge-transfer, each shifting towards shorter wavelengths by ~15 nm when the solvent was changed from dichloromethane to acetonitrile. However, the spectra appeared quite dissimilar, with **PP** showing the most intense CT absorption. Misumi concluded that the geometry of the tropyliocyclophanes has a large influence on the observed charge-transfer transitions.

Keehn and O'Connor have also studied tropylium-based cyclophanes. They independently synthesized compound **MM** (Figure 22) [34b] and compared its behavior to that of compound **RR** (Figure 23) [34a]. The spectra of these two systems were fairly similar, both showing evidence of intramolecular charge-transfer. It is interesting to note that the component pieces of **RR** (dimethylcycloheptatriene and dimethyltropylium cation) show no intermolecular charge-transfer when placed in solution, but connection of the two fragments within a cyclophane framework allows intramolecular charge-transfer to be observed.

Luhowy and Keehn prepared a related cyclophane (Figure 24) and studied the effects of protonation upon its charge-transfer activity [35]. No definite CT transition could be detected in compound **SS**, but addition of trifluoroacetic acid
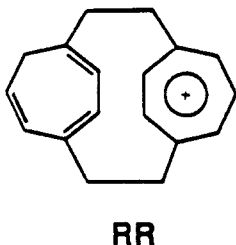
Fig. 23.   A tropylium cation-cycloheptatriene cyclophane.

Fig. 24. Proposed intramolecular electronics for the sequential protonation of an azulene-based cyclophane.

protonated **SS** to give **TT**, which did show charge-transfer activity. This protonation was very facile, presumably because of the stability of **TT**. A second protonation produced **UU**, but was difficult to perform because of the repulsive electronic interactions present in **UU**.

A final novel example of intramolecular charge-transfer in a cyclophane framework was presented by VerHoeven and coworkers [36]. They synthesized a series of compounds utilizing a pyromellitic diimide fragment as the electron acceptor, varying the lengths of the methylene bridges (Figure 25). In the cases where X = methyl, they observed that the conformational mobility of the intramolecular complex was severely limited by the interconnecting polymethylene chains. In the symmetrical molecule ($m = n = 6$), the charge-transfer absorption was not as intense as in the asymmetrical one ($n = 3$, $m = 8$). An X-ray study of the asymmetric

X	n	m
CH_3	6	6
	3	8
OCH_3	6	6
	4	8
	5	5

Fig. 25. Structures for a variety of intramolecular complexes based on a pyromellitic diimide acceptor.

system revealed that the centers of the donor and acceptor portions of the molecule are shifted away from each other by approximately 3 Å. This implies that the relative orientations of donor and acceptor are important for effective charge-transfer to occur, and that the more flexible asymmetric cyclophane is better able to attain the optimum geometry. Similar results were obtained when the series X = methoxy was examined. Comparison of the position and intensity of the CT absorption for each of the three systems led to the conclusion that the distance between donor and acceptor is not as important as their orientation with respect to each other.

3. Intermolecular charge-transfer

3.1. TETRACYANOETHYLENE COMPLEXES

Intramolecular charge-transfer complexation as applied to cyclophanes having been discussed, the next topic to be considered covers intermolecular charge-transfer between cyclophanes and electron donors or acceptors. The discovery of tetracyanoethylene (TCNE) [37] and of its ability to enter into charge-transfer complexes with aromatic hydrocarbons [38] sparked an interest in studying the behavior of simple cyclophanes in the presence of TCNE by investigation of the changes in the π-base strengths of [m.n]paracyclophanes as m and n are varied. Correlation between the association constant (K_a) of the complex and λ_{max} of the charge-transfer band allowed the relative π-base strengths of aromatic hydrocarbons to be measured. Similar techniques were applied in the investigations on cyclophanes.

   Cram and coworkers [39] have studied various aspects of charge-transfer complexation between the [m]paracyclophanes or the [m.n]paracyclophanes and TCNE, comparing these complexes to those formed with simple hydrocarbons. Their first studies [39a] had three main objectives: (1) to determine if the complexes of the [m.n]paracyclophanes involve one or two moles of TCNE; (2) to obtain correlations between the structure of the cyclophane π-bases and the energies of their charge-transfer absorptions; and (3) to determine the effect of the solvent on the energies of these transitions. Crystalline complexes of TCNE with [6.6], [4.4], and [3.4]paracyclophane were prepared by slow evaporation of solutions containing the two components. These crystals were analyzed and determined to be 1:1 complexes. The electronic spectra of these crystalline complexes were identical to those obtained when the two components were dissolved separately and then mixed. These spectra all contain bands in the 380–600 nm region which must be associated with a complex, since neither component alone absorbs in this region.

   The spectra of the TCNE complexes of 18 [m.n]paracyclophanes and 3 [m]paracyclophanes were obtained, and the position of the longest wavelength band determined. These values were compared to those of 19 different hydrocarbons (Table V). Unfortunately, insufficient amounts of the paracyclophanes were available for determination of the association constants (K_a) and ε values of the complexes at the time these studies were completed.

   For TCNE complexes of related hydrocarbons such as a series of methylated benzenes, a relationship exists between the position of λ_{max} of the longest wavelength band and the K_a of the complex. If the complexes are arranged in order of

Table V. Position of longest wavelength band of hydrocarbon: TCNE complexes in methylene chloride, 23°C

Paracyclophane	λ	Hydrocarbon	λ
[3.3]	599	Hexamethylbenzene	545
[3.4]	538	Pentamethylbenzene	520
[1.7]	527	Durene	480
[2.2]	521	1,6-Bis(4-propylphenyl)hexane	470
[3.6]	520	1,4-Bis(4-ethylphenyl)butane	468
[1.8]	515	1,3-Bis(4-ethylphenyl)propane	466
[2.3]	511	1,4-Bis(n-pentyl)benzene	463
[1.9]	509	Mesitylene	461
[1.10]	506	1,2-Bis(4-ethylphenyl)ethane	460
[1.11]	501	p-Xylene	460
[4.6]	492	m-Xylene	440
[9]	492	o-Xylene	430
[12]	491	Toluene	406
[6.6]	490	Benzene	384
[1.12]	490	p-Terphenyl	564
[10]	486	Diphenyl	500
[5.6]	485	Cyclohexane	422
[5.5]	485		
[4.5]	485		
[2.4]	483		
[4.4]	476		

decreasing λ_{max}, the order is essentially the same as that of decreasing K_a. Since the paracyclophanes bear a homologous relationship to each other with little steric difference, it is likely that the order of decreasing λ_{max} for the paracyclophane-TCNE complexes is approximately the same as the order of decreasing K_a for these complexes. Therefore, the ordering of the paracyclophanes shown in Table V is likely that of decreasing strength as π-bases. The order of arrangement in Table V can be rationalized on the basis of the effects of a number of structural features on the ability of the cyclophanes to act as electron donors. The most important structural features and their presumed effects are listed in Table VI. Evidence for the first effect listed is the observation that all of the paracyclophane-TCNE complexes absorb at longer wavelengths than any of the open-chain model compounds. In the [m.n]paracyclophanes, the second benzene ring can donate electrons to the first, which then complexes with TCNE. In the [m]paracyclophanes it is

Table VI. Effect of structural features of cyclophanes on electron-donating ability

Structural factor	Effect on electron-donating ability
Transannular delocalization of charge in paracyclophane	Increase
Inhibition of delocalization due to methylene bridges holding rings apart	Decrease
Inhibition of same due to non-planar benzene rings	Decrease

possible that the methylene groups that lie over the face of the aromatic ring can enter into hyperconjugation with the ring, helping to stabilize the partial positive charge formed upon complexation with TCNE.

The second effect can be observed in the fact that the [6.6] complex absorbs at longer wavelength than the [4.4] complex. Molecular models imply that in the smaller system the methylene bridges are just long enough to hold the benzene rings apart, while the larger system is flexible enough to allow the rings to twist towards each other. In general, closer proximity of the π-systems of the two rings should allow a greater ability to stabilize positive charge. As has been observed by other researchers, the [3.3] system appears to possess the optimum geometry for π overlap.

Cram's final objective, investigating solvent effects on these complexes, was studied using the [3.4]paracyclophane-TCNE complex in 14 different solvents. The results of these experiments are shown in Table VII. As can be seen in the Table, the position of the long wavelength absorption varies by as much as 90 nm with solvent changes. In the first six solvents listed, none of which contain basic nitrogen or oxygen atoms which could complex TCNE, the position of the long wavelength band moves to shorter wavelengths as the polarity of the solvent decreases.

Association constants for a number of the paracyclophane-TCNE complexes were obtained in later investigations [39c] by the use of the Benesi-Hildebrand equation for analysis of the data (vide supra). The ordering of the cyclophanes studied with respect to the association constants of their TCNE complexes gave the same arrangement as that shown in Table V, confirming the relationship between K_a and λ_{max}. The π-base strengths of the paracyclophanes as determined by the K_a values of their TCNE complexes follow the order [3.3] > [3.4] > [2.2] > [4.4] > [6.6] $\sim$ open chain models. If [2.2]paracyclophane is disregarded, the sequence correlates with the distances of the two benzene rings from one another; the closer the two rings, the stronger the π-base. This indicates that the nonbound benzene ring

Table VII.   Solvent effects on the [3.4]paracyclophane-TCNE complex

Solvent	λ, nm	Dielectric constant[a]	T, °C
chloroform	540	4.8	20
methylene chloride	538	9.1	20
carbon tetrachloride	537	2.2	20
benzene	532	2.3	20
cyclohexane	527	2.0	20
n-pentane	520	1.8	20
acetic acid	505 (sh.)	6.2	20
ether	502	4.3	20
n-propanol	493	20.1	29
ethanol	490	24.3	25
ethyl acetate	483	6.0	20
methanol	468	33.6	20
acetonitrile	459	37.5	20
t-butanol	450	10.9	30

[a] A. A. Maryott and E. R. Smith: 'Table of Dielectric Constants of Pure Liquids', Natl. Bur. Standards 512 (1951).

releases electrons to the bound ring, enhancing the π-base character of the bound ring. The question as to why [3.3]paracyclophane is about twice as strong a π-base as [2.2]paracyclophane must also be addressed. The answer must lie in some difference in geometry between the two molecules. [2.2]Paracyclophane is known to have badly warped benzene rings, which would force a decrease in the delocalization of the π electrons. This may well be a major factor in the determination of π-base strengths (see third effect in Table VI).

Another aspect of these complexes that was investigated was the effect of substituents on one of the aromatic rings towards complexation [39b, c]. To this end a series of substituted [2.2] and [3.3]paracyclophanes was prepared, and the electronic spectra obtained (Table VIII). A rough linear correlation was observed between λ_{max} and K_a, and between δE_t (the difference in the transition energy of the charge-transfer absorption between the substituted and unsubstituted cyclophanes) and the Hammett σ_m constant. From the data in Table VIII it can be observed that, although [3.3]paracyclophane is the stronger π-base, the [2.2] system shows a greater sensitivity to transannular substituent effects. In general, however, the effects of transannular substitution are very similar to those observed by other researchers: electron-donating substituents increase π-base strength while electron-withdrawing substituents decrease it.

As mentioned earlier in this discussion, the energy of the CT transition has been correlated with the ionization potential of the donor, I^D. Since the I^D values are normally varied by substitution on the donor ring, steric conditions which also affect complexation are changed at the same time. However, the donor-acceptor cyclophane framework can be exploited in such a fashion that steric considerations are no longer a factor. It should be possible to leave the donor ring itself completely unchanged and to vary the ionization potential of the donor over a wide range *via* transannular transmission by various substituents on the second paracyclophane ring. Staab has investigated this area [23] with a series of donor-acceptor

Table VIII. Substituent effects on the position of the CT absorption in [2.2] and [3.3] systems (CH_2Cl_2, 25°C)

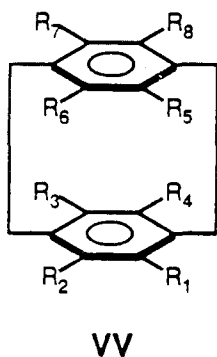| Substituent	λ[3.3]	λ[2.2]
NH_2	710	697
OCH_3	638	570
OH	620	552
C_2H_5	612	540
CH_3	603	–
H	599	521
$COCH_3$	575	496
Br	572	510
OAc	572	507
COOH	571	497
NHAc	560	534
$COOCH_3$	552	–
CN	548	475
NO_2	543	457

cyclophanes and examined their intermolecular complexation behavior with TCNE (Figure 12). These experiments show that for compounds with electron-donating groups on the second ring, the TCNE complexation exhibits a reduction in the ionization potential (this was calculated by comparing results from the substituted systems to the parent cyclophane, X = H). This result can be explained by assuming a transannular supply of electron density to the donor ring which then itself donates electrons to TCNE via charge-transfer. Most of the compounds studied were substituted with electron-withdrawing groups on the second aromatic ring. Although in all cases these are relatively weak electron acceptors, the increase in ionization potential with regard to TCNE complexation is significant. The magnitude of this effect for the individual compounds closely follows the well-known order of the electron-withdrawing ability of these substituents.

Finally, Renault and coworkers [40] have studied a series of cyclophane:TCNE complexes in the solid state. The cyclophanes studied include: [2.2] and [3.3]paracyclophane, [2.2]metaparacyclophane, [2.2]metacyclophane, [2.2.2]paracyclophane, [2.2.2]paracyclophanetriene, and [2.2.2.2]paracyclophane. Complexation of these compounds with TCNE produced highly colored complexes, ranging from reddish-orange to black crystals. X-ray crystallographic analyses were performed on all of the complexes. Renault observed stacking of TCNE and the various cyclophanes in the crystal structures, with all of the complexes showing a 1:1 ratio of TCNE to cyclophane. Extended Huckel calculations were also performed with respect to the HOMO-LUMO interactions within the stacks. They concluded that the donor ability of a given cyclophane can be very different in the solid or liquid states; for example, [2.2.2]paracyclophanetriene is calculated to be the best electron donor in solution, but is observed to be the worst donor in the crystal state.

Although TCNE-cyclophane complexes have been the most widely studied, other electron acceptors have also been investigated as potential cyclophane complexers. Mourad and Nour-el-Din [41a] have studied the complexes of a series of substituted [2.2]paracyclophanes with 2,3-dichloro-5,6-dicyano-p-benzoquinone (DDQ), chloranil (CHL), and tetracyanoquinodimethane (TCNQ) as the electron acceptors (Figure 26). Complexes were observed between DDQ and VVa–f, but only VVf showed any complexation with TCNQ or CHL. This reflects the relative strengths of the electron acceptors. All complexes observed were determined to be 1:1 cyclophane:acceptor complexes.

These same workers [41b] also studied some tribridged [2.2.2]cyclophanes, comparing a methyl-substituted compound to an unsubstituted one. They compared the formation constants of the complexes formed between these cyclophanes and four different electron acceptors (TCNE, DDQ, CHL, and bromanil (BRL)), and concluded that the stability of the complex depends on the nature of both donor and acceptor. From the data obtained, they decided that the substituted cyclophane is a better donor than the unsubstituted one, and that the electron acceptors fall in the order DDQ > TCNE > CHL > BRL.

Having investigated di- and tribridged cyclophanes, Mourad then went on to study tetra- and pentabridged systems [42, 43], comparing their donor abilities to the earlier compounds (Figure 27). The complexation behavior of these systems with TCNE, DDQ, CHL, BRL, and 2-dicyanomethyleneindane-1,3-dione (CNIND) was

Fig. 26. Structures for a series of substituted [2.2]paracyclophanes used for intermolecular complexation with CHL, DDQ and TCNQ.

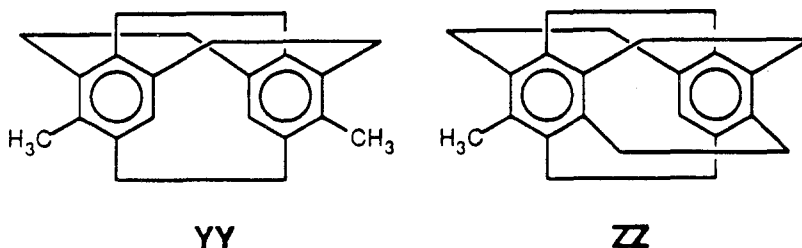| Compound	R_1	R_2	R_3	R_4	R_5	R_6	R_7	R_8
a	CHO	H	H	H	H	H	CHO	H
b	CHO	H	H	H	H	H	H	H
c	H	H	H	H	H	H	H	H
d	CHO	H	CH_3	CH_3	CH_3	CH_3	H	H
e	CH_3	H	H	H	H	H	CH_3	H
f	CH_3	CH_3	H	H	H	H	CH_3	CH_3

Fig. 27. Structures for tetra- and pentabridged cyclophanes complexed with a series of acceptors.

studied. It was determined that more bridges caused an increase in complexing ability. The TCNE complexes absorbed at longer wavelengths than the CNIND complexes, implying that TCNE is the better electron acceptor of the pair. Mourad and coworkers have further investigated related systems [44, 45], studying substituent effects on complexation and further examining CNIND as an electron acceptor.

3.2. HOST–GUEST COMPLEXES

Previous work involving cyclophane complexation has usually involved formation of complexes where the electron acceptor is located outside the cavity formed by the cyclophane framework, with the second aromatic ring acting only as an electron donor to increase the π-basicity of the cyclophane. A different approach to

Table IX. Polyether CT complexation data with
DDQ (methylene chloride, 25°C)

Compound	K_a	λ, nm	ε
benzo-15-crown-5	2.6	635	2383
dibenzo-18-crown-6	4.8	625	2033
dibenzo-24-crown-8	7.5	622	1759

intermolecular charge-transfer complexation was taken by Malini and Krishnan
[46], who investigated the DDQ complexes of a series of macrocyclic polyethers.
With these crown ether systems, the complexation is of the type generally labelled
'host–guest', where one component of the complex is surrounded by the other. The
systems investigated by Malini and Krishnan are listed in Table IX. All complexes
studied were determined to be 1:1 crown ether:DDQ. The association constants
(K_a) show a linear increase with the number of oxygens in the crown ether. It
should be noted that polyethers not containing benzene rings also formed CT
complexes with DDQ, as determined by the change in color when the solutions
were mixed, but the absorption maxima were coincident with the DDQ absorption
so K_a values for those systems could not be calculated.

Stoddart and coworkers also investigated a charge-transfer complex involving a
polyether [53], observing that 'diquat' (a bipyridyl dication) binds tightly to
dibenzo[30]crown ethers.

Pierre has studied a different type of polyether system [47], examining complexa-
tion with TCNQ (Figure 28). He observed that the equilibrium constant for
complexation was strongly influenced by the presence of potassium ion. Addition of
one equivalent of K^+ increased the observed equilibrium constant from 58 to
1890 L M^{-1}, presumably by binding to the polyether chain and causing a confor-
mational change bringing the two aromatic rings into close proximity. The presence
of two equivalents of potassium ion, however, decreased the equilibrium constant to
43 L M^{-1}. Apparently the oxygens of the methoxy substituents can become in-
volved in potassium binding and inhibit formation of the charge-transfer complex.

Another example of the application of charge-transfer complexation to 'host–
guest' chemistry is provided by Ferguson and Diederich [48]. When studying the
molecule shown in Figure 29, they considered it (the host) as an electron donor,
and expected charge-transfer to play a role in the complexation behavior of the
system. Three types of guest molecules were utilized in their experiments: (1)
naphthalenes with two donor substituents; (2) naphthalenes with one donor and
one acceptor substituent; and (3) naphthalenes with two acceptor substituents.
Table X gives the observed equilibrium constants for a series of guest molecules. It
can be concluded that the naphthalenes with electron-withdrawing substituents
formed the strongest complexes, demonstrating that electronic complementarity
between host and guest is very important in the study of aromatic guests in organic
solvents.

Another example of charge-transfer 'host–guest' complexes was presented by
Stoddart and coworkers [54]. They prepared cyclobis(paraquat-p-phenylene), a
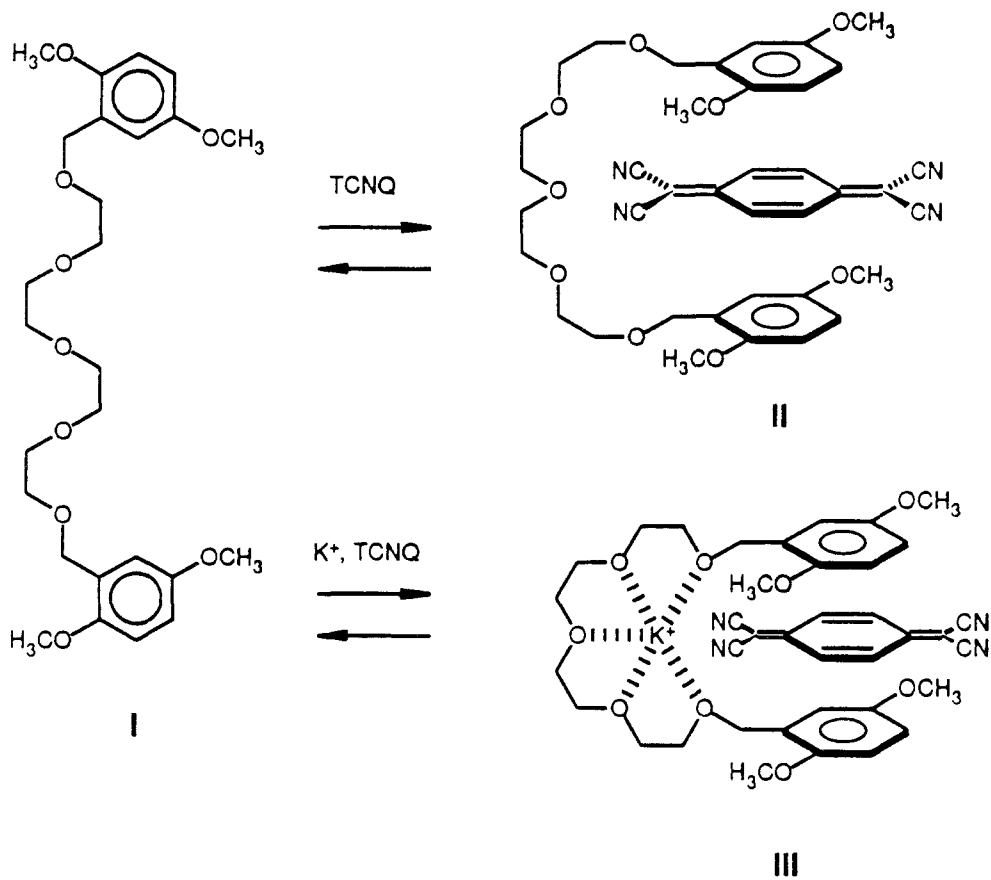tetracationic multipurpose receptor possessing a π-deficient cavity (see Figure 30),

Fig. 28. Proposed conformations for complexation of **I** with TCNQ in the absence and presence of potassium ion.
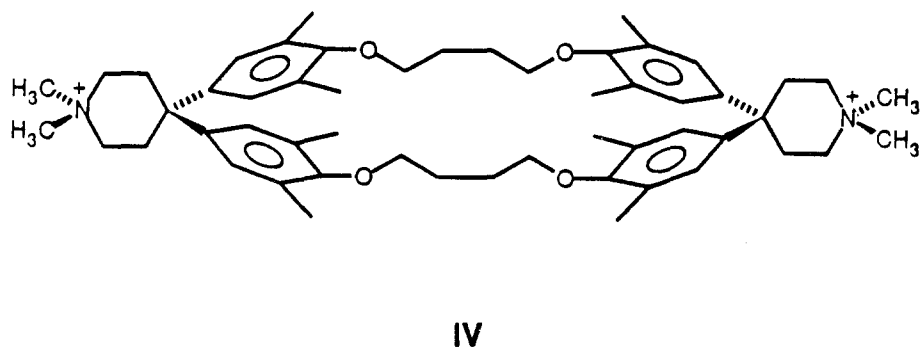

Fig. 29. Structure for a novel host molecule used as an electron donor in complexes with disubstituted naphthalenes.

Table X. Equilibrium constants for complexes of **IV** and 2,6-disubstituted naphthalene guests in CD_3OD, 30°C

2-Substituent	6-substituent	K_a
CH_2OH	CH_2OH	20
OH	OH	24
NH_2	NH_2	33
OCH_3	OCH_3	47
CH_3	CH_3	67
CH_3	CHO	98
NH_2	NO_2	102
OCH_3	NO_2	109
OCH_3	CN	117
OCH_3	COOH	135
OH	CN	157
OAc	OAc	109
$COOCH_3$	$COOCH_3$	188
COOH	COOH	210
NO_2	NO_2	213
CN	CN	277

and paired it with a series of isomeric dimethoxy benzenes. In all cases highly colored (red or orange) solutions were obtained, and the UV data was consistent with the presence of stabilizing CT interactions. They obtained X-ray data on the solid complexes, which still exhibited CT activity.

Hunig and coworkers prepared a series of similar paraquat-based cyclophanes [55], varying the length of the π system and the nature of the bridges (see Figure 31). One of the best electron donors used in their studies was 2,7-dihydroxynaphthalene. They report K_a values ranging from 20 to 95 M^{-1} in deuteromethanol/D_2O solution.
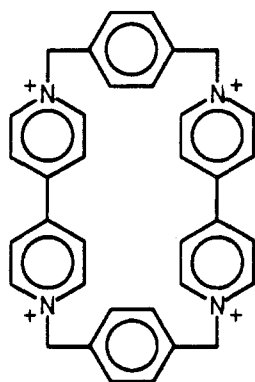

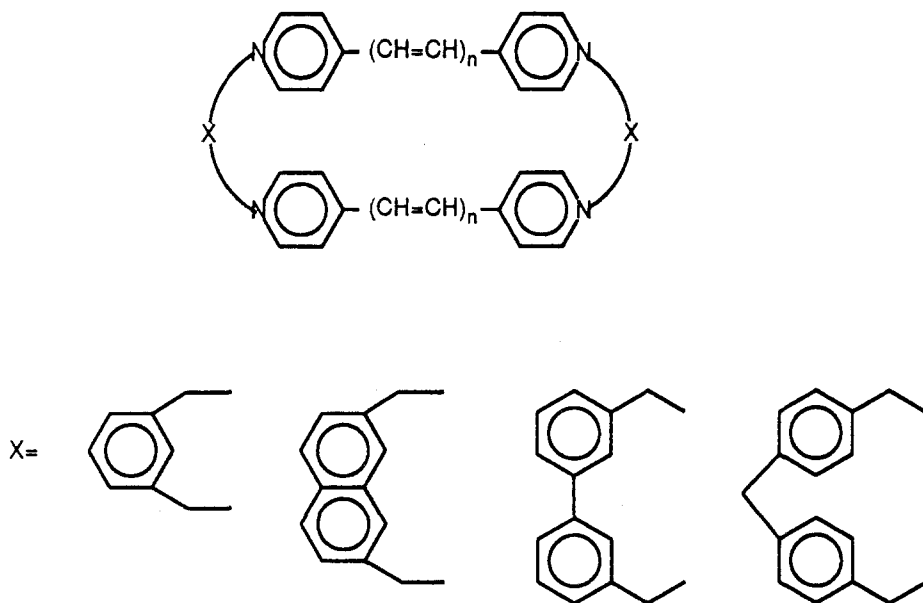Fig. 30.   Structure for cyclobis(paraquat-p-phenylene), a tetracationic receptor.

Fig. 31. Structures for a series of paraquat-based cyclophanes, varying the length of the π system (n = 0, 1) and the nature of the bridges.

Whitlock and coworkers have also attempted to utilize charge-transfer complexation in 'host–guest' cyclophane complexes [49]. Two potential host molecules were studied (Figure 32), one based on anthraquinone and one on anthracene. The anthraquinone-based cyclophane was viewed as an electron acceptor, while the anthracene-based system was considered an electron donor. Complexation studies were performed using guests chosen for their electronic complementarity to the designated host. Substituted benzenes such as TMPD were used with V and various
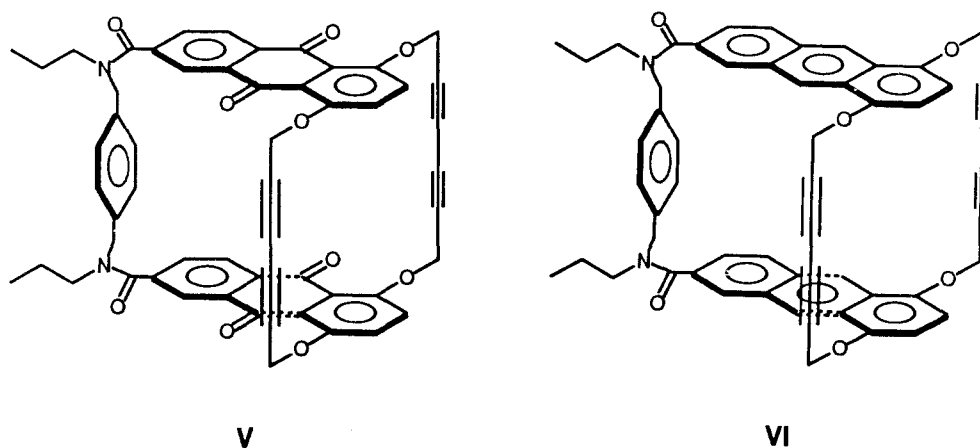

Fig. 32. Structures for two potential host molecules, one possessing an electron-poor cavity (V) and the other an electron-rich cavity (VI).

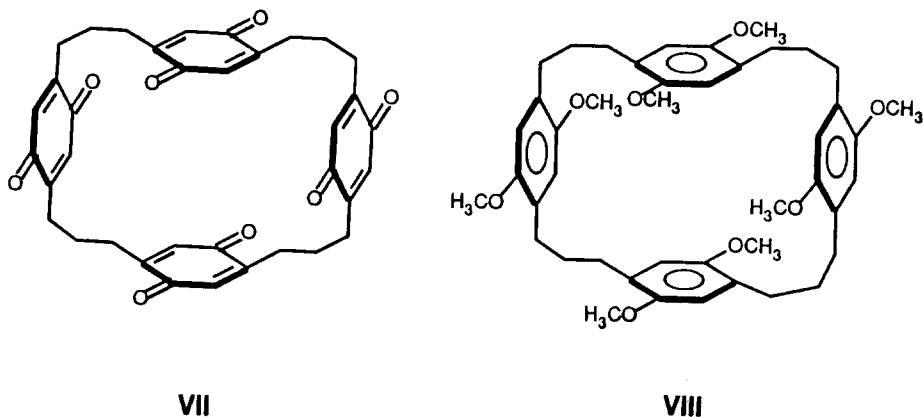VII   VIII

Fig. 33.   Structures for two unsuccessful host molecules, one possessing an electron-poor cavity (VII) and the other an electron-rich cavity (VIII).

benzoquinones such as CHL were paired with VI. However, no charge-transfer complexation was detected.

Shinmyozu and coworkers [50] also found donor-acceptor interactions to be ineffective in another cyclophane system, [3.3.3.3]p-benzoquinonophane (an electron-poor cavity) and its reduced form, 5, 8, 14, 17, 23, 26, 32, 35-octamethoxy [3.3.3.3]paracyclophane (an electron-rich cavity). These compounds are shown in Figure 33.
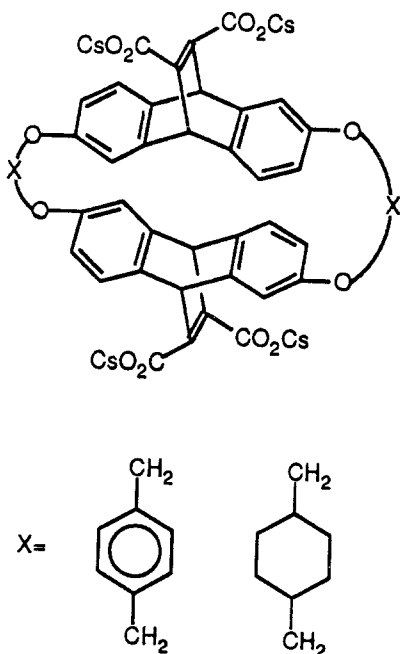

Fig. 34.   Structures for a series of water-soluble cyclophanes possessing hydrophobic binding sites.

This review is mainly concerned with charge-transfer interactions in organic media; however, it should be mentioned that these types of studies are also performed in aqueous solution. Representative work includes that of Dougherty and coworkers [56, 57]. Their research involves the synthesis of water-soluble cyclophanes containing hydrophobic binding sites (Figure 34) which are paired with electron-deficient quinolines and isoquinolines. Very large binding constants are reported, with CT interactions being invoked to explain the observed data.

4. Conclusion

A large amount of work has been reported in the area of charge-transfer complexes with cyclophane systems. The majority of this work involves intra-molecular complexation, with the donor and acceptor existing within the same molecule. Studies have also been carried out on intermolecular complexes, mainly TCNE : cyclophane complexes. The newest area of interest involves 'host–guest' complexation, with the cyclophane acting as the donor (or acceptor) and the guest being chosen for its electronic complementarity to the host. This is a field with great potential for growth; new areas of inquiry are continually being proposed and investigated.

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