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The Study of π–π Interaction in Layered [3.3]Orthocyclophanes. Charge-Transfer Complexes of [3.3]Orthocyclophanes with Tetracyanoethylene

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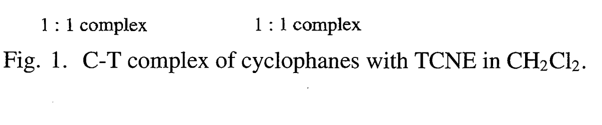
Dibenzo[3.3]orthocyclophanes ([3.3]OCPs) with a bicyclo[4.4.1]undecane substructure form charge-transfer (C-T) complexes with tetracyanoethylene (TCNE). 3,4 : 8,9-Dibenzobicyclo[4.4.1]undecane (**9**) and its 11-methylene derivative **8** are flexible molecules and take a chair-boat conformation. Complexes **8**- and **9**-TCNE exhibit the absorption maximum at ca. 420 nm, which coincides with the value for the TCNE complex of *o*-xylene. On the other hand, acetal **5**, methylcarbinol **6**, and dimethylmethylene derivative **7** are rigid, layered [3.3]OCPs with stacked benzene rings. Compounds **5**, **6**, and **7** form a 1 : 1 complex with TCNE in solution. The absorption maxima of the complexes at ca. 500 nm suggest an enhanced C-T complexation due to a π–π through-space interaction in **5**, **6**, and **7**. A 2 : 1 complex of rigid [3.3]OCP **7** with TCNE crystallized from dichloromethane, while OCP **8** gave a red crystalline 2 : 3 complex with TCNE. X-ray crystallographic analyses of these two complexes is given.

C-T complexes of cyclophanes with TCNE have been studied in order to evaluate the π basicity of the cyclophane rings and to demonstrate transannular interactions in such systems.[1] To this effect, the complexes of para- and metacyclophanes (PCPs and MCPs) have been extensively studied (Fig. 1).[2—9]

Thus, Cram and Bauer[2] established the order of the π base strength for [*m.n*]PCPs and compared them to those of open-chain arenes. Additionally, Singer and Cram[3] investigated transannular substituent effects in [2.2] and [3.3]PCP-TCNE complexes **1a**, **b**. Furthermore, Misumi et al.[4] reported that the absorption maxima of C-T complexes of multilayered PCPs with a TCNE shift to longer wavelengths with increasing number of layers. In the field of MCPs, Hayashi and Sato[5] showed that [2.2]MCP affords a 1 : 1 complex **2** with TCNE, which is stabilized due to a π–π interaction.



1a n = 2 λ_{max} 521 nm
1b n = 3 λ_{max} 599 nm
1 : 1 complex

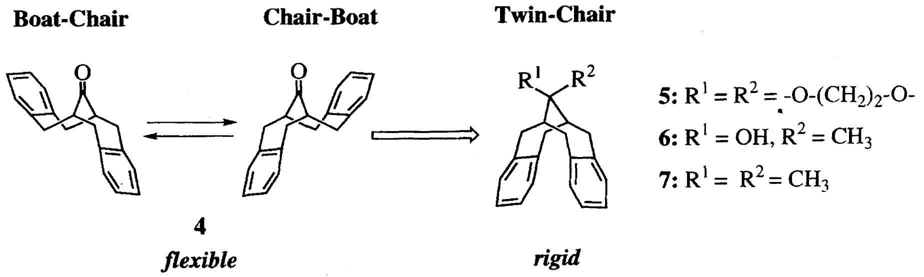
2 λ_{max} 486 nm
1 : 1 complex

3

Fig. 1. C-T complex of cyclophanes with TCNE in CH$_2$Cl$_2$.

Relatively little is known about TCNE-complexes of orthocyclophanes (OCPs). Usually, OCPs are of less interest in studying the π–π interaction. Many known [2.2] and [3.3]OCPs possess a flexible structure, and they do not show any π–π interaction.[10] However, there are a few marked examples of OCPs that have rigid structures with layered π systems.[11—14] It must be noted that in most MCPs and PCPs the aromatic rings are distorted, which unavoidably affects their electronic structures. The aromatic rings of OCPs, however, are virtually non-distorted, thus making them interesting candidates for studying the π–π interaction of closely layered, rigidly-held aromatic systems.

A typical OCP with layered aromatic rings, which has been studied recently by the authors,[15] is the dibenzobicyclo-[4.4.1]undecane system in its twin-chair conformation. The twin-chair conformation is realized by introducing the bulky substituents onto the methylene bridge of 3,4 : 8,9-dibenzobicyclo[4.4.1]undeca-3,8-dien-11-one (**4**), as exemplified by acetal **5**, the corresponding thioacetal,[14] the tertiary alcohol **6**, and the dimethyl compound **7** (Scheme 1). Compound **5** and the thioacetal as well as **6** and **7** show a transannular interaction between the two benzo rings, as is evidenced by a long wavelength shift observed in their UV/vis spectra.[14,16] The present article reports on C-T complexes of a series of these [3.3]OCP-TCNE complexes **3**.



Scheme 1.

Results and Discussion

Synthesis. Dimethyl 11-oxo-3,4 : 8,9-dibenzobicyclo-[4.4.1]undeca-3,8-diene-1,6-dicarboxylate was prepared by reaction of 1,2-bis(bromomethyl)benzene with dimethyl 3-oxoglutarate under a phase-transfer-catalysis with the base sodium hydroxide, as previously reported.[14] The hydrolysis and pyrolysis of the obtained dicarboxylate gave **4**.[15] Ketone **4** was reduced to the methylene compound **9** upon a treatment with $LiAlH_4$–$TiCl_3$.[17] In order to transform the functional group at the bridge into a bulkier group, **4** was converted to acetal **5** and *t*-alcohol **6** in a fair yield.[14] The alcohol **6** was dehydrated with 20% sulfuric acid in ethanol under reflux, to give olefin **8**.[18] The spirocyclopropane **10** was synthesized by the Simmons–Smith reaction of **8**.[18] The dimethyl compound **7** can be obtained by the hydrogenation of **10** (Scheme 2).[16]

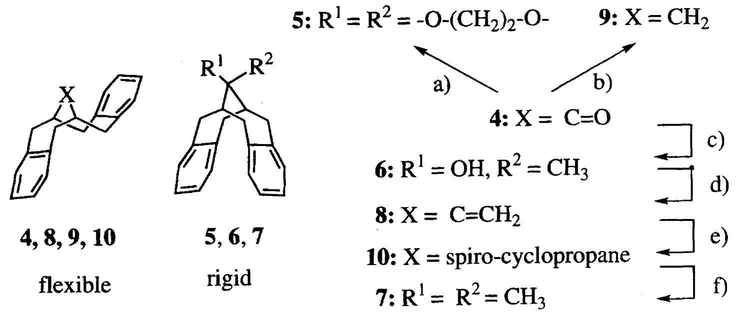
UV/vis Absorption Spectra of the C-T Complexes of [3.3]OCPs with TCNE. Generally, the TCNE complexes of the OCPs (**4**, **5**, **6**, **7**, **8**, and **9**) have been prepared by adding a solution of 0.02 M (1 M = 1 mol dm^{-3}) TCNE in dichloromethane to a solution of 0.02 M [3.3]OCPs in dichloromethane in various ratios.

a) TCNE Complexes of Flexible [3.3]OCPs. Of the possible conformers of flexible dibenzobicyclo[4.4.1]-undeca-3,8-dien-11-one **4**, the twin-chair conformer is not prefered, due to an electronic repulsion between the π-electrons of the two layered benzo-units. Ketone **4** exists in an equilibrium of chair-boat and boat-chair conformers.[17] Similarly, [3.3]OCPs **8** and **9** are flexible, and exist as chair-boat and boat-chair conformers. With TCNE, **8** and **9** give light-orange C-T complexes in dichloromethane. The absorbance spectra and Job plot of C-T complexes of flexible [3.3]OCPs (**4**, **8**, and **9**) with TCNE are shown in Fig. 2.

The absorption maxima of the C-T bands of **8**– and **9**–TCNE complexes (λ_{max}, 426 and 424 nm) correspond to that found for a single arene–TCNE complex, where the substituents of the benzo units due to the bridges are not quite equivalent to two methyl substituents (*o*-xylene–TCNE complex; λ_{max} 430 nm[19]). The positions of the maxima, the shapes of the curves, and the relative intensities of the absorption bands were virtually unchanged when the concentrations of TCNE and the [3.3]OCPs were varied. On the other hand, **4** formed a light-yellow C-T complex of TCNE with an absorption maximum at 392 nm. This value is shorter than the absorption maximum of the C-T complex of *o*-xylene with TCNE, indicating that the presence of the carbonyl group impedes the formation of an arene–TCNE charge-transfer complex in **4**. Whether this is due to a repulsion between TCNE and the lone-pair electrons of the carbonyl group or due to another type of interaction with the ketone is not yet fully understood. It is difficult to ascertain the stoichiometry of the TCNE complexes of **4** and **8** in solution from the Job plot,[20] since the presence of 1 : 1 and 1 : 2 complex-species (Fig. 3) gives rise to two peaks, which overlap.

b) TCNE Complexes of Rigid, Layered [3.3]OCPs. Layered [3.3]OCPs **5**, **6**, and **7** form purple C-T complexes with TCNE in dichloromethane. It can be deduced from the corresponding Job plots that they form 1 : 1 complexes (Fig. 4).

Similar absorption spectra were observed for all TCNE



a) HO(CH$_2$)$_2$OH / TsOH / Benzene
b) $LiAlH_4$ / $TiCl_3$ / THF
c) CH_3MgI / Et_2O
d) 20% H_2SO_4 / EtOH
e) CH_2I_2 / Zn / CuCl / Et_2O
f) H_2 / PtO_2 / AcOH, 4kg/cm^2

Scheme 2.

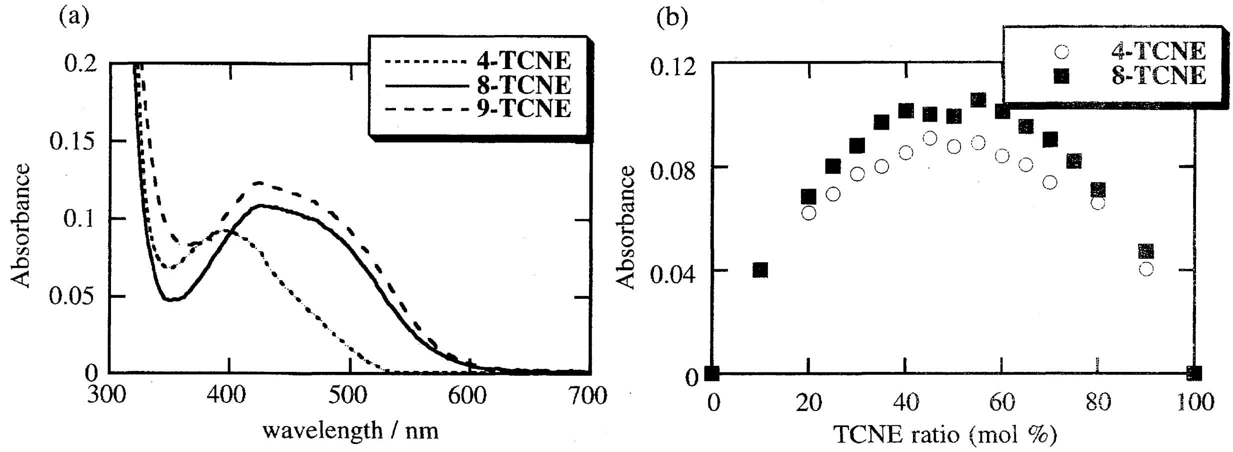


Fig. 2. (a) UV/vis spectra of **4**–, **8**–, and **9**–TCNE complexes (**4**, **8**, and **9** : 0.01 M, TCNE : 0.01 M) and (b) Job plot of **4**– and **8**–TCNE complexes (0.02 M).

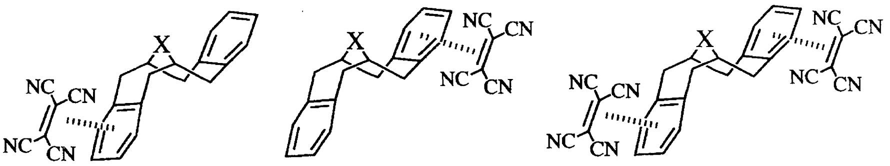


Fig. 3. 1 : 1 and 1 : 2 Complexes of flexible [3.3]OCPs (X = O, CH_2, C=CH_2).

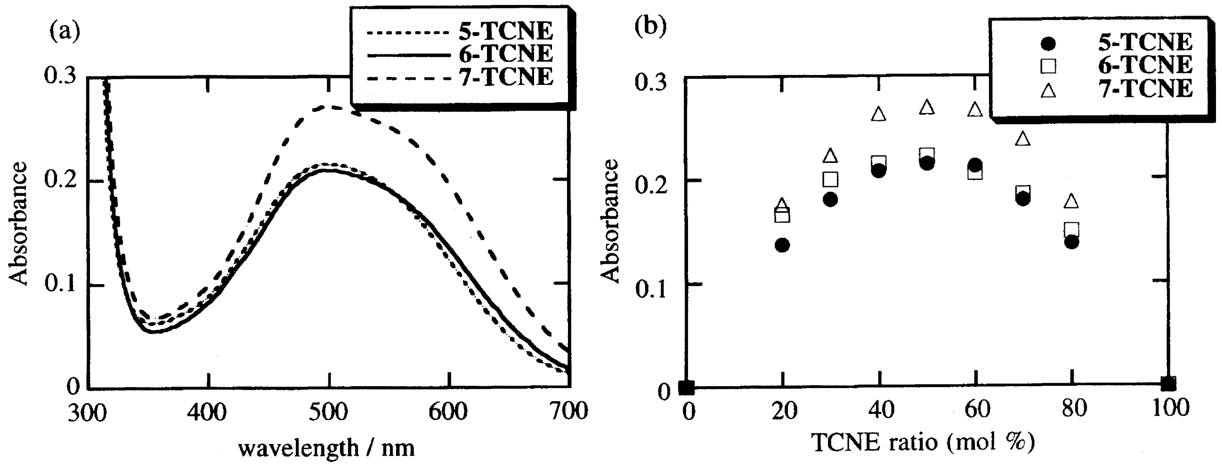


Fig. 4. (a) UV/vis spectra of **5**–, **6**–, and **7**–TCNE complexes (**5**, **6**, and **7**: 0.01 M, TCNE: 0.01M) and (b) Job plot of **5**–, **6**–, and **7**–TCNE complexes (0.02 M).

complexes of layered [3.3]OCPs **5**, **6**, and **7**, both in the position of the absorption maxima and the shape of the curve [λ_{max} 502 (**5**–TCNE), 502 (**6**–TCNE), and 500 nm (**7**–TCNE)]. The presence of the lone-pair electrons of the σ-bonded oxygen atoms of the acetal and alcohol functionalities in **5** and **6** does not hinder the formation of C-T complexes. The relative position of the absorption maximum reflects a significant enhancement of π-basicity in the layered [3.3]OCPs **5**, **6**, and **7** in comparison to the flexible [3.3]OCPs **4**, **8**, and **9**. These findings strongly support the possibility of a transannular release of electron density to the complexed ring.

In TCNE complexes of PCPs, the absorption maxima were observed at 521 nm for **1a**$^{2)}$ and at 599 nm for **1b**,$^{2)}$ whereas the absorption maximum of the C-T band of the [2.2]MCP–TCNE complex **2** was reported to be at 486 nm.$^{5)}$ In cyclophanes, there is a direct relationship between the wavelengths of the C-T bands and π-basicities.$^{2)}$ Thus, the order of decreasing π-basicity may be given as: [3.3]PCP > [2.2]PCP > layered [3.3]OCPs **5**, **6**, and **7** > [2.2]MCP. This means that the interaction of the two benzo rings in the layered [3.3]OCPs is smaller than that in the [2.2]PCPs and the [3.3]PCPs. This overlap is given by geometric restrictions in the molecule.

Figure 5 shows geometrical data provided by a known X-ray crystallographic analysis of [2.2]PCP,$^{21)}$ [3.3]PCP,$^{22)}$ and [3.3]OCP **5**.$^{14)}$ An X-ray crystallographic analysis of the [3.3]OCP **5** supports the fact that in such compounds the interaction of the π-systems may be smaller than that in the [2.2]PCP and the [3.3]PCP, due to geometrical reasons. The

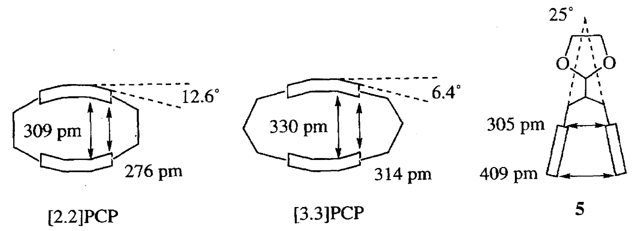


Fig. 5. Angles and distances in the cyclophanes.

mean distance between the two benzo rings of **5** (357 pm) is larger than the corresponding distances in either the [2.2]PCP or the [3.3]PCP. Additionally, the aromatic rings of **5** exhibit an angle of 25° from parallel. From this, it can be deduced that the overlap of the π-electrons and the π-basicities of the layered [3.3]OCP **5** is smaller than those of the PCPs.

X-Ray Crystal Structures of [3.3]OCP–TCNE Complexes. In the solid state, very few complexes of cyclophanes with TCNE have been investigated.[23—27] The complexes of [2.2]PCPs **1a**,[23] [3.3]PCPs **1b**,[24,25] and [2.2]MCPs **2**[26] with TCNE have been found to exhibit a sandwich-type stacking. In these systems, the donor cyclophanes and TCNE as an acceptor are stacked in an alternate arrangement, and afford 1 : 1 complexes. In the present work, the structures of the complexes of [3.3]OCPs with TCNE in the crystalline state were investigated in order to compare them with the structures of the above-mentioned compounds and to study the effect of complexation on the conformation of the [3.3]-OCPs.

a) X-Ray Crystal Structure of the Flexible [3.3]OCP 8 and 8-TCNE Complex. Crystallization from a 1 : 1 solution of **8** and TCNE in dichloromethane gave fine wine-red crystals of a C-T complex of **8**. The X-ray crystal structure of the C-T complex of **8** is shown in Fig. 6.

The distances between atoms of the nearest-neighboring benzo ring and TCNE are also given in Fig. 6. The benzo ring annelated to that side of the [4.4.1]undecane unit of **8**, which is in the boat conformation, is coordinated to two TCNE molecules having different surroundings. The shortest interatomic distance between one benzo ring of **8** and a TCNE molecule is 305 pm. This value is slightly smaller than that found for other C-T complexes of the type TCNE–arene, reported previously.[28] The shortest interatomic distance between the benzo ring of **8** and the upper coordinated TCNE molecule is 373 pm. These findings indicate that the *exo*-methylene bridge of **8** prevents coordination of the upper coordinated TCNE molecule to the benzo ring.

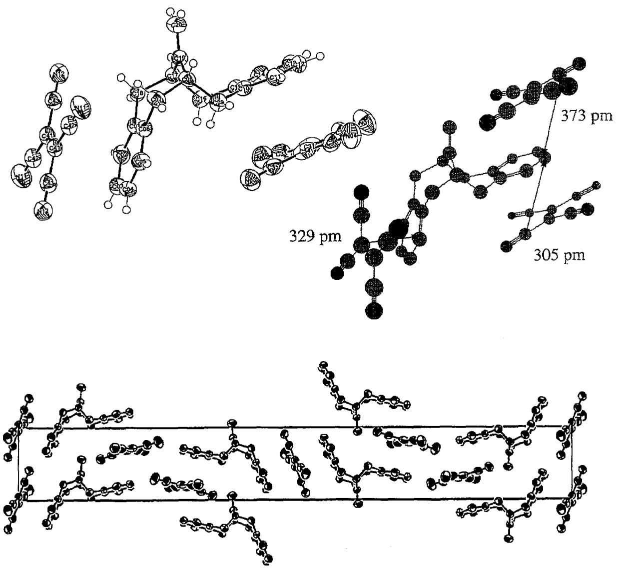


Fig. 6. ORTEP drawing of C-T complex of **8** with TCNE.

One molecule of TCNE is stacked between the facing benzo units of two [3.3]OCPs. Both of these benzo units are annelated to that side of the bicyclo[4.4.1]undecane substructure, which is in the chair form. Thus, an isolated D–A–D assembly is formed. The remaining benzo unit, which is annelated to the boat conformation side of bicyclo[4.4.1]-undecane, interacts with TCNE in D–A–D–A··· stacks. On the whole, TCNE molecules coordinate both benzo rings of the [3.3]OCP **8**, and a 2 : 3 complex is formed.

In order to assess the effect of TCNE complexation on the conformation and the crystal packing of the flexible [3.3]-OCPs, an X-ray crystal structural analysis of **8**, itself, was performed (Fig. 7).

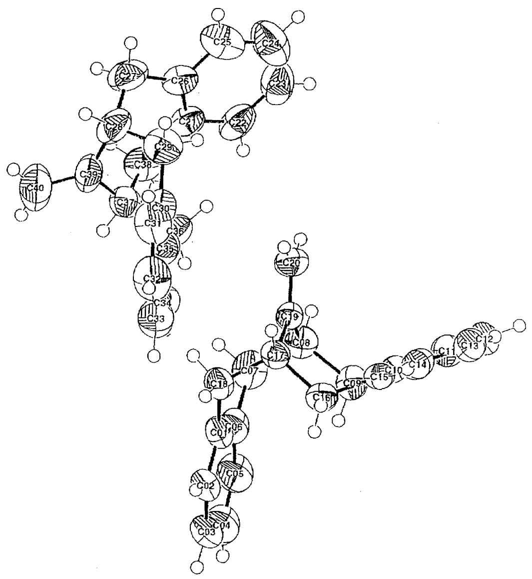
From the X-ray crystal structure it can be seen that **8** exists in a chair-boat conformation in the crystal, just as its C-T complex. The crystal system changes drastically from trigonal in **8** to monoclinic in the TCNE complex. An increase in the angle between the two benzo rings of the OCP has been observed. The angle is changed from 117° and 120° in **8** to 128° in the C-T complex of **8** (Fig. 8).

b) X-Ray Crystal Structure of the Layered [3.3]OCP 7 and 7–TCNE. A 1 : 1 solution of layered [3.3]OCP **7** and TCNE affords a crystalline purple C-T complex. The X-ray diffraction structure of a single crystal of the C-T complex of **7** is shown in Fig. 9

This crystalline complex shows sandwich Donor–Acceptor–Donor assemblies. The TCNE molecule lies on a center of symmetry (point of inversion of a D–A–D assembly unit) between two OCP molecules. In contrast to [2.2]PCP,[23] [3.3]PCP,[24,25] and [2.2]MCP,[26] which form 1 : 1 TCNE complexes **1a**, **1b**, and **2**, [3.3]OCP **7** and TCNE form a 2 : 1 complex. The stacking of the C-T complexes of **7** is similar to that observed for other structures, such as for the anthracenophane–TCNE complex.[27] The largest distance between the two benzo rings of the [3.3]OCP **7** is as small as 421 pm. This makes coordination of the TCNE within the cavity of **7** impossible. The shortest interatomic distance between the π system of the [3.3]OCP **7** and TCNE is 345 pm, and is slightly larger than that found for other C-T complexes of cyclophanes (320 pm in **1a**,[23] 325 pm in **1b**,[25] and 326 pm in **2**[26]).

An X-ray crystal-structural analysis of [3.3]OCP **7**, itself, was performed for a comparison. The structure of **7** is shown in Fig. 10

A slight, but insignificant, increase in the plane-to-plane distances and in the angle between the two benzo rings is observed in the complex, the angle varying from 27° in **7** to



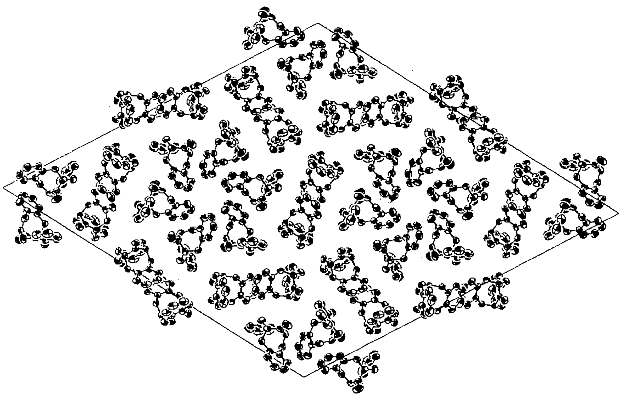


Fig. 7. ORTEP drawing of **8**.

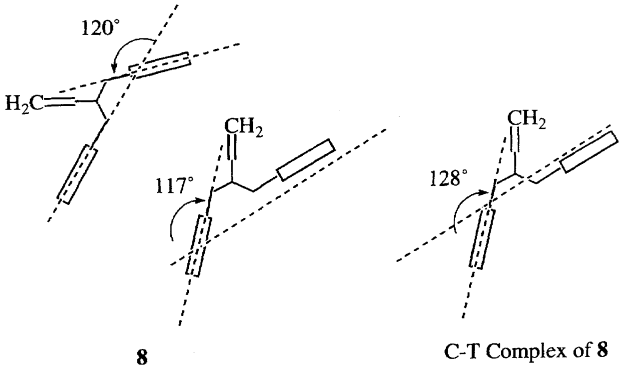


Fig. 8. Angles between benzene rings of **8**.

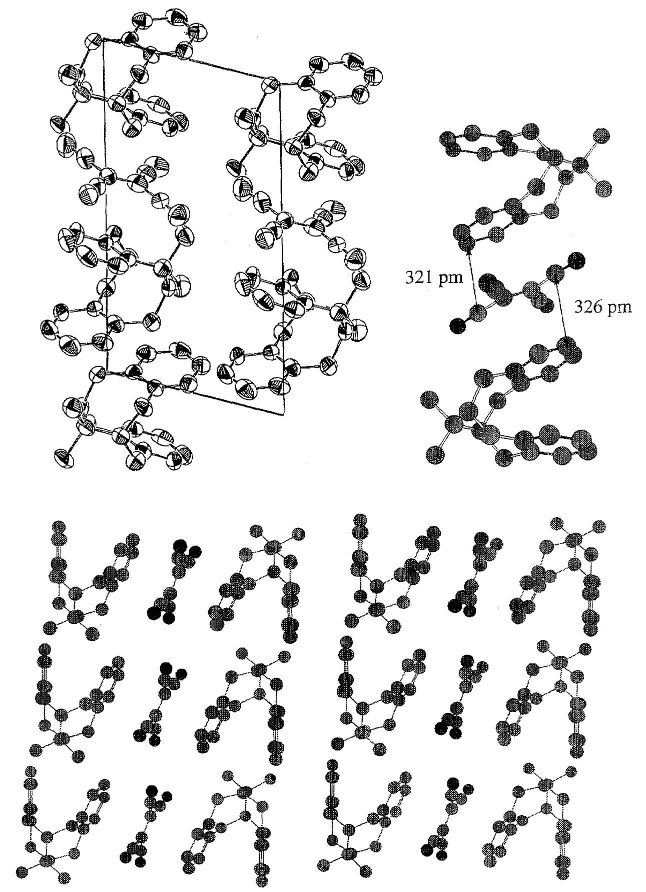


Fig. 9. ORTEP drawing of C-T complex of **7** with TCNE.

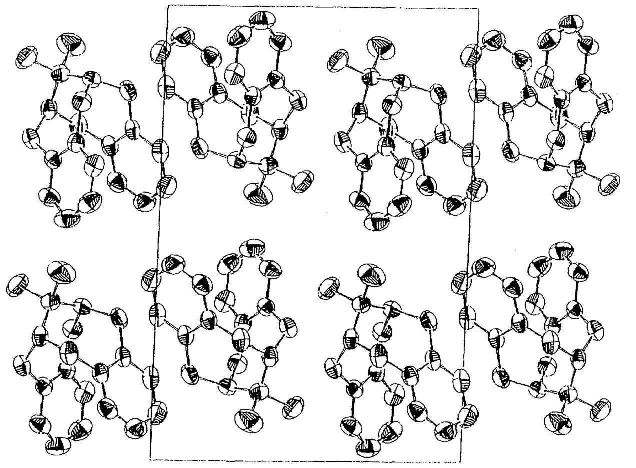
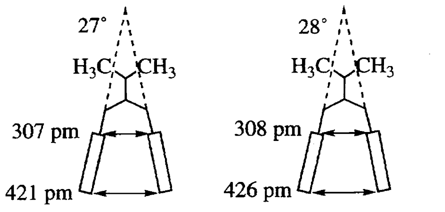


Fig. 10. ORTEP drawing of **7**.

28° in the complex (Fig. 11). The arrangement of [3.3]OCP **7** in the crystal is compared with that of the C-T complex. With TCNE, D–A–D D–A–D assemblies are formed. This means that there is an insertion of TCNE between the columns of the cyclophanes. Otherwise, the arrangement of the cyclophanes, themselves, is not altered. This is in contrast to the result found for the flexible [3.3]OCP **8**.

Solid-State Reflectance Spectra of the C-T Complexes of [3.3]OCP with TCNE. There is a correlation between the solid-state reflectance spectra and the UV/vis spectra of the solution. While the shapes of the curves are not the same, the order of the reflectance maxima has not changed (**4**–TCNE 420 nm, **7**–TCNE 425 and 559 nm, **8**-TCNE 422 nm) (Fig. 12). In the layered cyclophane **7**, the long-wavelength shift is more pronounced than in the flexible cyclophanes (**4** and **8**). From this finding, we can say that a through-space π–π interaction in **7**–TCNE can be observed in the solid state. Unfortunately, a simple correlation between the position of $\lambda_{\max}$ in the solid-state reflectance spectra



7 C-T Complex of **7**

Fig. 11. Angles and distances between benzene rings of **7**.

and the distances between the donor molecules and TCNE observed in the X-ray crystallographic analyses cannot be formulated.

Conclusion

C-T complexes of flexible and rigid, layered [3.3]OCPs with TCNE have been studied. The rigid, layered [3.3]-OCPs, which possess bulky functionalities on the methylene bridge of the bicyclo[4.4.1]undecane subunit, form 1 : 1 C-T complexes in solution. In the crystal, however, they form 2 : 1 complexes. In solution, a transannular interaction within the molecule is evidenced by a C-T absorption maximum at about 500 nm. On the other hand, the C-T bands of the complexes of the flexible [3.3]OCPs with TCNE at about 420 nm indicate that in these cases there is no through-space π–π interaction within the molecules. Here, a 2 : 3 ([3.3] OCP–TCNE) C-T complex could be observed in the crystal.

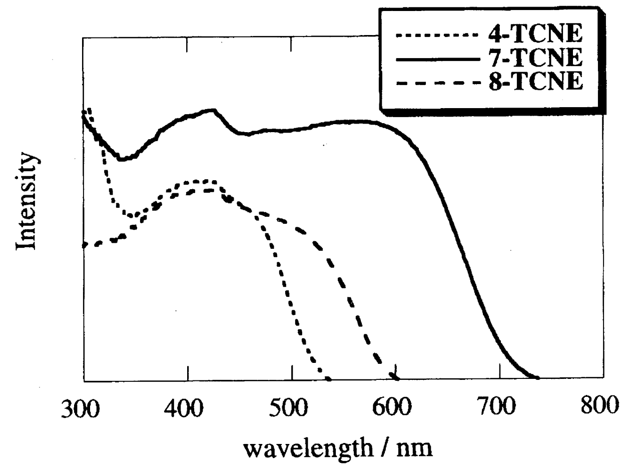


Fig. 12. Solid-state reflectance spectra of **4**–, **7**–, and **8**–TCNE complexes.

Experimental

The UV/vis spectra of the [3.3]OCP–TCNE complexes were

Table 1. Summary of the Crystal Data of **7** and **7**–TCNE

Compound	**7**	**7**–TCNE (2 : 1)
Formula	$C_{21}H_{24}$	$(C_{21}H_{24})_2 \cdot C_6N_4$
Formula weight	276.421	680.934
Crystal system	Monoclinic	Triclinic
Space group	$P2_1/a$	$P1$
a/Å	16.677(3)	9.409(5)
b/Å	8.275(2)	13.743(5)
c/Å	11.395(2)	7.519(5)
$\alpha/^\circ$		104.391(5)
$\beta/^\circ$	91.850(10)	95.457(5)
$\gamma/^\circ$		93.973(5)
V/Å^3	1571.72(0.55)	933.13(0.86)
Z	4	1
D_c/g cm^{-3}	1.1682	1.2117
μ/cm^{-1}	0.484	0.540
Crystal size/mm	0.50 × 0.30 × 0.10	0.53 × 0.33 × 0.23
θ range	3.88—64.98	4.74—64.94
Index ranges h	−19—19	−11—11
k	−9—0	−16—0
l	−13—0	−8—8
F(000)	600.0	364.0
No. Refl. Measd.	2820	3307
No. Unique Refl.	2676	3307
No. Refl.	2275, $F > 2\sigma(F)$	2442, $F > 2\sigma(F)$
No. of parameters	191	469
R	0.0436	0.0764
R_w	0.1215	0.1947
Largest Diff. Peak/Hole (e Å^{-3})	0.160/−0.128	0.439/−0.280
Weighting scheme	$w = 1/[\sigma^2(F_o^2)+(0.0711P)^2$ $+0.2718P]$, $P = (F_o^2+2F_c^2)/3$	$w = 1/[\sigma^2(F_o^2)+(0.1669P)^2$ $+0.1426P]$, $P = (F_o^2+2F_c^2)/3$
Direct methods	SIR 92	SIR 92

Table 2. Summary of the Crystal Data of **8** and **8**–TCNE

Compound	**8**	**8**–TCNE (1 : 1.5)
Formula	$(C_{20}H_{20})_6$	$C_{20}H_{20}\cdot(C_6N_4)_{1.5}$
Formula weight	1562.268	452.517
Crystal system	Trigonal	Monoclinic
Space group	$R3$	$P2_1/n$
a/Å	40.485(5)	7.328(2)
b/Å	40.485(5)	50.542(17)
c/Å	9.587(5)	7.155(2)
$\alpha/^\circ$		
$\beta/^\circ$		116.24(2)
$\gamma/^\circ$		
V/Å^3	13608.23(7.48)	2376.93(1.29)
Z	6	4
D_c/g cm^{-3}	1.1438	1.2645
μ/cm^{-1}	0.479	0.616
Crystal size/mm	$0.40\times0.33\times0.26$	$0.23\times0.23\times0.23$
θ range	3.78—64.94	3.50—64.93
Index ranges h	−41—0	−8—0
k	−41—0	−59—0
l	−11—11	−7—8
F(000)	5040.0	944.0
No. Refl. Measd.	5392	4363
No. Unique Refl.	5147	4040
No. Refl.	3062, $F>2\sigma(F)$	1711, $F>2\sigma(F)$
No. of parameters	362	316
R	0.0930	0.0643
R_w	0.2679	0.1408
Largest Diff. Peak/Hole (e Å^{-3})	0.753/−0.467	0.359/−0.254
Weighting scheme	$w=1/[\sigma^2(F_o^2)+(0.2286P)^2$, $P=(F_o^2+2F_c^2)/3$	$w=1/[\sigma^2(F_o^2)+(0.0659P)^2$ $+2.6019P]$, $P=(F_o^2+2F_c^2)/3$
Direct methods	SIR 92	SIR 92

recorded on a Hitachi 220A spectrophotometer. Reflectance spectroscopy were recorded on a JASCO V-570 (ISV-470) spectrophotometer. X-Ray crystallographic analyses were carried out on an Enraf–Nonius FR-590 diffractometer.

Synthesis of the Dibenzobicyclo[4.4.1]undecane Derivatives. 3,4 : 8,9-Dibenzobicyclo[4.4.1]undeca-3,8-dien-11-one (**4**),[16] 3,4 : 8,9-dibenzobicyclo[4.4.1]undeca-3,8-dien-11-one ethylene acetal (**5**),[13] 11-hydroxy-3,4 : 8,9-dibenzobicyclo[4.4.1]undeca-3,8-dien-11-ol (**6**),[13] 11,11-dimethyl-3,4 : 8,9-dibenzobicyclo[4.4.1]undeca-3,8-diene (**7**),[15] 11-methylidene-3,4 : 8,9-dibenzobicyclo[4.4.1]undeca-3,8-diene (**8**),[17] and 3,4 : 8,9-dibenzobicyclo[4.4.1]undeca-3,8-diene (**9**)[16] were prepared as previously reported.

Preparation of the Charge-Transfer Complexes of [3.3]OCPs 4, 5, 6, 7, 8, and 9 with TCNE. Commercial TCNE was recrystallized from chlorobenzene and sublimed twice under reduced pressure. Dichloromethane was of spectroscopic grade and used without further purification. The complexes were prepared in dichloromethane at 298 K. For preparing a Job plot,[20] the concentration of the two solutions used for the reactions was 0.02 M in [3.3]OCPs **4**, **5**, **6**, **7**, **8**, and **9**, respectively, and 0.02 M in TCNE.

The crystalline 2 : 1 complex of the [3.3]OCP **7** and TCNE and the 2 : 3 complex of the [3.3]OCP **8** and TCNE were prepared as follows. Equimolar quantities of [3.3]OCP and TCNE were weighed into a flask, and dichloromethane (5 cm^3) was added to give an orange or purple solution. Single crystals were obtained by slow evaporation of the solvent in a refrigerator at normal pressure.

X-Ray Crystallographic Analysis of Structure Determination and Refinement. All crystallographic measurements were carried out at 296 K, except for **7**–TCNE (at 293 K), on an Enraf–Nonius FR-590 diffractometer operating in the ω–2θ scan mode, using graphite-monochromated Cu $K\alpha$-irradiation (λ = 1.54184 Å). The structures were solved by direct methods using SIR 92[29] and refined by a full-matrix least squares calculation for F^2 using SHELXL93.[30] The refinement was essentially the same for the four compounds in that all-non-hydrogen atoms were refined with anisotropic displacement parameters. All hydrogen atoms were included in the refinement, but were restrained to ride on the atom to which they were bonded.

The final R-factors and other crystallographic information are summarized in Tables 1 and 2. The atomic coordinates, thermal parameters, bond lengths and angles for all of the compounds and salts have been deposited at the Cambridge Crystallographic Data Centre. For details concerning the deposition scheme, see "Notice to Authors of Papers."

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