Electron Donor-Acceptor Compounds, 46[1]

Molecular Structures and Charge-Transfer Absorptions of [2.2]-, [3.3]-, and [4.4]Paracyclophanes with Tetracyanobenzene as Acceptor Unit

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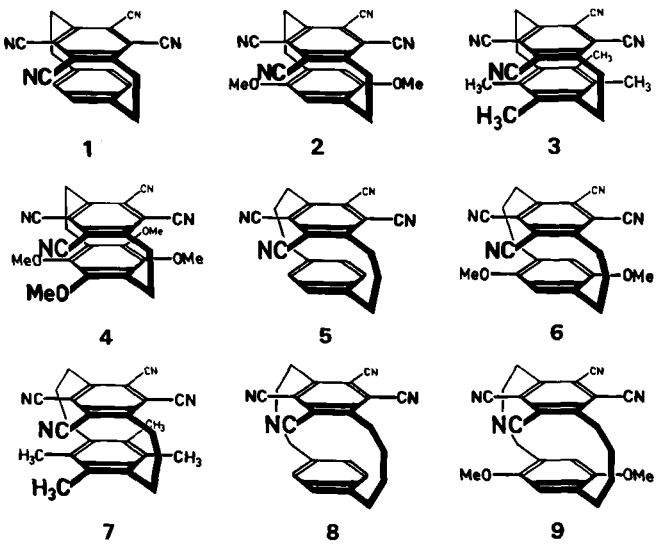
Based on X-ray analyses the molecular structures of the electron donor-acceptor [2.2]- and [3.3]paracyclophanes **1**, **2**, **4**, **6**, **10**, and **11** are discussed in terms of steric and electronic effects. The charge-transfer absorptions of **1**–**9** were measured and are dealt with in correlation to the variation of the strength of the electron donors and of the donor-acceptor distances in the series **1**–**9**.

Elektron-Donor-Acceptor-Verbindungen, 46[1]. – Molekülstrukturen und Charge-Tansfer-Absorptionen von [2.2]-, [3.3]- und [4.4]Paracyclophanen mit Tetracyanbenzol als Acceptor-Einheit

Die Molekülstrukturen der Elektron-Donor-Acceptor-[2.2]- und -[3.3]Paracyclophane **1**, **2**, **4**, **6**, **10** und **11** werden im Hinblick auf sterische und elektronische Effekte auf der Grundlage von Röntgen-Strukturanalysen diskutiert. Die Charge-Transfer-Absorptionen von **1**–**9** wurden bestimmt; sie werden in Beziehung zur Variation der Elektron-Donor-Stärke und des Donor-Acceptor-Abstands behandelt.

In the preceding paper[1] the syntheses of the 4,5,7,8-tetracyano[2.2]paracyclophanes **1**–**4**, of the 5,6,8,9-tetracyano[3.3]paracyclophanes **5**–**7** and of the 6,7,9,10-tetracyano[4.4]paracyclophanes **8** and **9** have been described. In this series of compounds the tetracyanobenzene (TCNB) unit as the common electron acceptor is facing various electron donors of different ionisation potential and with graduated donor-acceptor distances. In the present paper we deal with the X-ray structure analyses of some typical representatives of this series and with investigations concerning charge-transfer (CT) absorptions which we try to correlate with the molecular structures.



Molecular Structures of Tetracyanoparacyclophanes

X-Ray Structure Analysis[2]: Crystal and data collection parameters for **1**, **2**, **4**, **6**, **10**, and **11** are listed in Table 1. Intensity data were collected by using graphite-monochromated Mo-K_α radiation and applying $\Theta/2\Theta$ scan technique. The structures of **1**, **4**, **6**, **10**, and **11** were solved by direct methods (MULTAN) and were refined by full-matrix least-squares technique using anisotropic temperature factors for non-hydrogen atoms and isotropic temperature factors for hydrogen atoms. In the case of **2** the solution of the structure was not possible by direct method. Based on a Patterson synthesis and considering the structures of **1** and of *pseudogem*-tetramethoxy-[2.2]paracyclophane[3] a molecular model was constructed and introduced into the elementary cell. By variation of the *x* and *z* components for the centre of the molecule and by variation of the three Euler angles the location and orientation of the molecule of **2** was refined using anisotropic temperature factors for non-hydrogen and isotropic temperature factors for hydrogen atoms. The *R* values are listed in Table 1 (p. 554).

Molecular Structure of 4,5,7,8-Tetracyano[2.2]paracyclophane (**1**): Figure 1 A shows the molecular structure of **1** in a top-view perpendicular to the planes of the aromatic rings. The bond lengths given in this figure do not deviate significantly from normal values with the exception of the central bonds in the bridges which, obviously due to transanular π-π repulsion, are considerably elongated. There is only a slight deviation from an ecliptic arrangement of the two rings, the axes through the bridge-head atoms of which form an angle of 4° with each other. In Figure 1 B a side-view of **1** is presented which shows the boat-type deformation of the aromatic rings which is similar to that of [2.2]paracyclophane itself[4]. The deviation from planarity is somewhat stronger for the acceptor ring whereas the bridge bonds to the bridge-head atoms deviate from the corresponding triangle planes stronger on the unsubstituted side. The exocyclic bonds on the ring atoms deviate from the sp^2 plane of these atoms into the direction towards the neighbouring ring. This deviation for the cyano groups on the carbon atoms C(4), C(5), C(7), and C(8) amounts to 6.7° in the av-

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erage [inclination of C(4)–C(4′) against the plane C(3)···C(4)···C(5), etc.]. The corresponding deviation for the C–H bonds of the unsubstituted ring is 7.6°. The transanular distance between bridge-head C atoms in **1** (274 pm) is somewhat shorter than in [2.2]paracyclophane (278 pm)[2]

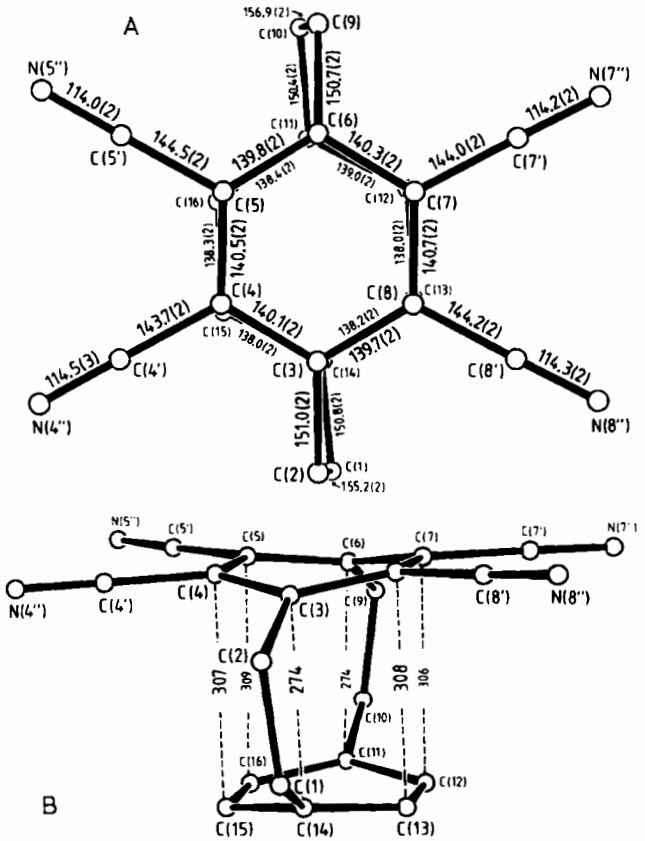


Figure 1. Molecular structure of **1** in a top-view in the projection on the aromatic rings (A) with bond lengths (in pm, standard deviations in brackets), and in a side-view (B) with transanular distances (in pm)

In the crystal lattice the molecules of **1** form stacks along the *a*-axis in which the donor side of one molecule is facing the acceptor side of the neighbour. The axis through the ring centres is inclined against the *a*-axis by 14° reducing the intermolecular donor-acceptor overlap; the shortest intermolecular distances within the stacks are in the order of 330 pm.

Molecular Structure of 4,5,7,8-Tetracyano-12,15-dimethoxy[2.2]paracyclophane (**2**): As Figure 2 demonstrates in the top-view (A) with bond lengths and in the side-view (B) with transanular distances the molecular structure of **2** is very similar to that of **1**: The *para* axes intersect at an angle of 3°; the deviation from planarity of the aromatic rings is in the same order as in **1**; the transanular distances are almost precisely the same as for **1**. This means that the stronger donor-acceptor interaction in **2** does not lead to any significant structural changes. The methoxy substituents in **2** are nearly coplanar to the bottom plane of the rings. The packing in the crystal is also similar to **1** with the molecules within the stacks being displaced against each other; as a consequence, the shortest intermolecular distances are not observed between the π systems of the aromatic rings but between the substituents on these rings.

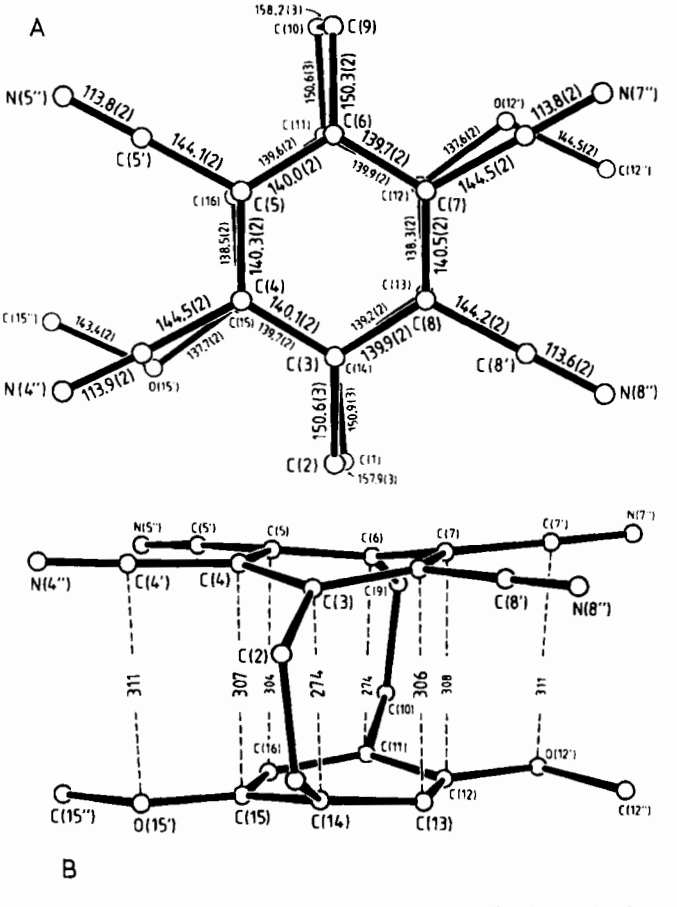


Figure 2. Molecular structure of **2** in a top-view in the projection on the aromatic rings (A) with bond lengths (in pm, standard deviations in brackets) and in a side-view (B) with transanular distances (in pm)

Molecular Structure of **4**: Figure 3A shows in a view onto the aromatic rings that, in contrast to **1** and **2**, in the completely substituted [2.2]paracyclophane **4** the aromatic rings are not centered but show a considerable lateral displacement by 54 pm leading to an interplanar distance of only 301 pm for the central parts of the two rings. The bond lengths of **4** are normal with the exception of the bonds O(12′)–C(12″) and O(15′)–C(15″) which appear considerably shortened due to strong thermal vibrations of the methyl carbon atoms. The most remarkable feature of the structure of **4** is the extent to which the methoxy groups are rotated out of the plane of the donor ring (Figure 3B): the torsional angles are 69° for C(13)–C(12)–O(12′)–C(12″), −126° for C(12)–C(13)–O(13′)–C(13″), 87.9° for C(16)–C(15)–O(15′)–C(15″), and −118.3° for C(15)–C(16)–O(16′)–C(16″). By this strong deviation of the methoxy substituents from coplanarity with the aromatic rings the normal electron-donating mesomeric effect of the methoxy groups is almost completely cancelled which is remarkably reflected by the charge-transfer properties of **4** (see below). In the crystal lattice the torsion of the methoxy groups out

of the ring plane results in a bulky arrangement of the molecules of **4** in which no intermolecular donor-acceptor interaction is possible.

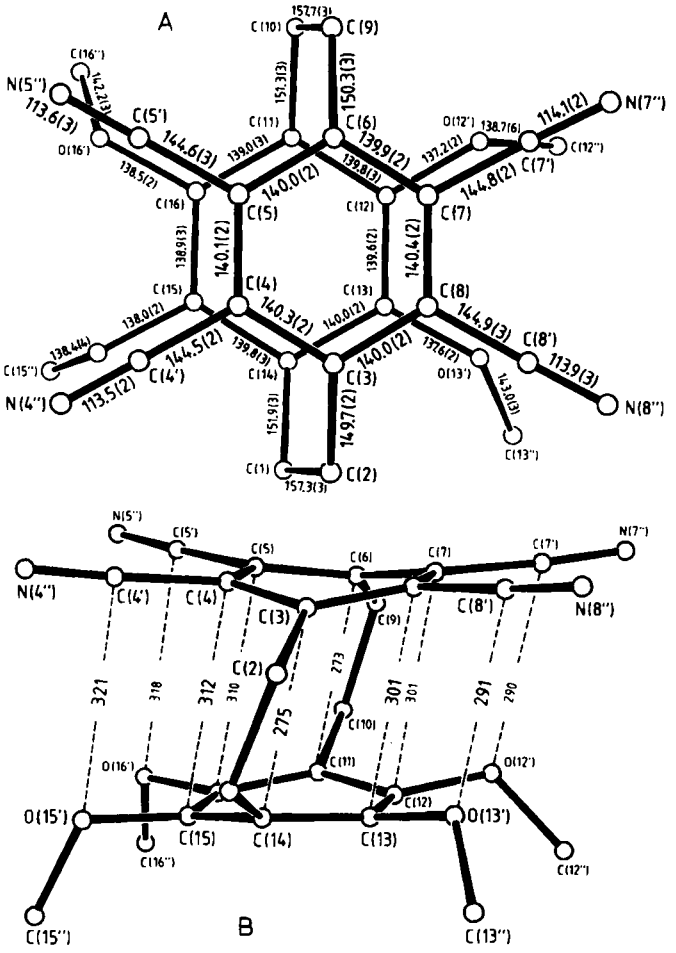


Figure 3. Molecular structure of **4** in a top-view onto the aromatic rings (A) with bond lengths (in pm, standard deviations in brackets) and in a side-view (B) with transanular distances (in pm)

Molecular Structure of 5,6,8,9-Tetracyano-14,17-dimethoxy[3.3]paracyclophane (**6**): For [2.2]paracyclophanes the strong steric strain leads to a very rigid structure leaving rather restricted scope for additional effects on the conformation of the molecules. In contrast, for [3.3]paracyclophanes due to the nearly strainfree and more flexible structure a stronger influence of specific repulsive or attractive interactions on the molecular conformations might be expected, especially since the interplanar distance between the rings is still short enough for transanular electronic and steric interactions to be effective. Whereas the [2.2]paracyclophanes of which molecular structures have been determined (to our knowledge with the only exception of the fully substituted compound **4**) show an arrangement of the rings which is very close to ecliptic, the aromatic rings in the [3.3]paracyclophane series are not nearly as rigidly fixed in a face-to-face arrangement: For the unsubstituted [3.3]paracyclophane a strong parallel-shift of the rings against each other, along the axis through the bridge-head atoms as well as perpendicular to it, has been observed[5]; on the other hand, for a variety of substituted [3.3]paracyclophanes nearly ecliptic orientations of the two rings have been determined[6]. In this context, the molecular structure of **6** and, for comparison, the structures of the related [3.3]paracyclophanes **10** and **11** were of interest.

Figure 4 shows the molecular structure of **6** in the projection onto the planes of the aromatic rings (A) and in a side-view (B). The lateral parallel-shift between donor and acceptor planes occurs mainly perpendicular to the axis through the bridge-head atoms.

Whereas the cyclophane bridge C(1) – C(2) – C(3) is fixed, there is a disorder effect for the central atom C(11) of the other bridge: its position is found to about 60% in a *syn* arrangement ("boat conformation") with respect to the other bridge and to about 40% in an *anti*-arrangement ("chair conformation"). The bond lengths of **6** show (with the exception of the disorder area) no abnormalities, and they agree in spite of the strong differences in molecular deformations very well with the bond lengths of the correspondingly substituted [2.2]paracyclophane **2**. As also found for **2** the methoxy substituents in **6** are nearly coplanar to the aromatic ring.

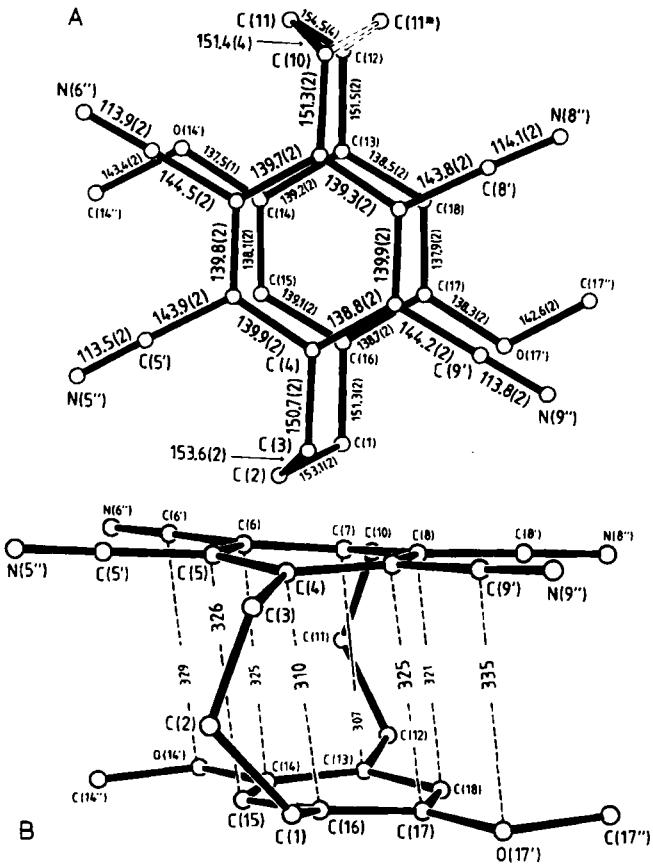


Figure 4. Molecular structure of **6** in a top-view perpendicular to the aromatic rings (A) with bond lengths (in pm, standard deviations in brackets) and in a side-view (B) with transanular distances (in pm)

In the crystal lattice of **6** (Figure 5) the molecules form stacks along the *b*-axis with the acceptor side of one molecule facing the donor ring of the neighbour. The axis per-

Table 1. Crystal and data collection parameters for **1**, **2**, **4**, **6**, **10**, and **11**

	1	2	4	6	10	11
Formula	$C_{20}H_{12}N_4$	$C_{22}H_{16}N_4O_2$	$C_{24}H_{20}N_4O_4$	$C_{24}H_{20}N_4O_2$	$C_{22}H_{22}N_2O_2$	$C_{20}H_{12}N_4S_2$
Molecular Mass	308.3	368.4	428.5	396.4	346.4	372.5
a [pm]	660.5(2)	864.0(2)	924.3(3)	1739.4(2)	967.8(1)	1389.6(1)
b [pm]	2697.2(8)	1207.4(2)	1636.3(4)	674.3(1)	1385.2(2)	951.0(2)
c [pm]	918.8(2)	1830.6(3)	1432.7(3)	1740.9(2)	1351.5(2)	1339.5(2)
β [°]	108.84(5)	110.14(4)	98.85(2)	102.92(2)	99.23(1)	101.64(2)
Space group	$P2_1/n$	$P2_1/c$	$P2_1/c$	$P2_1/n$	$P2_1/c$	$P2_1/a$
Z	4	4	4	4	4	4
D_x [gcm^{-3}]	1.32	1.36	1.33	1.32	1.29	1.43
Max. sin θ/λ [nm^{-1}]	6.72	6.72	6.62	6.96	6.62	6.62
No. of reflections measured	3953	4355	5186	5646	4298	4382
No. of reflections with $I \geq 1.96\ \sigma(I)$	3071	3106	3744	3530	3158	3091
R	0.050	0.047	0.051	0.051	0.045	0.050

	1	2	4	6	10	11
crystal size [mm]	0.5 x 0.2 x 0.2	0.4 x 0.4 x 0.2	0.3 x 0.3 x 0.3	0.3 x 0.2 x 0.15	0.4 x 0.4 x 0.25	0.5 x 0.5 x 0.35
crystallized from	acetone	chlorobenzene	acetonitrile	chlorobenzene	trichloromethane	chlorobenzene/ethanol

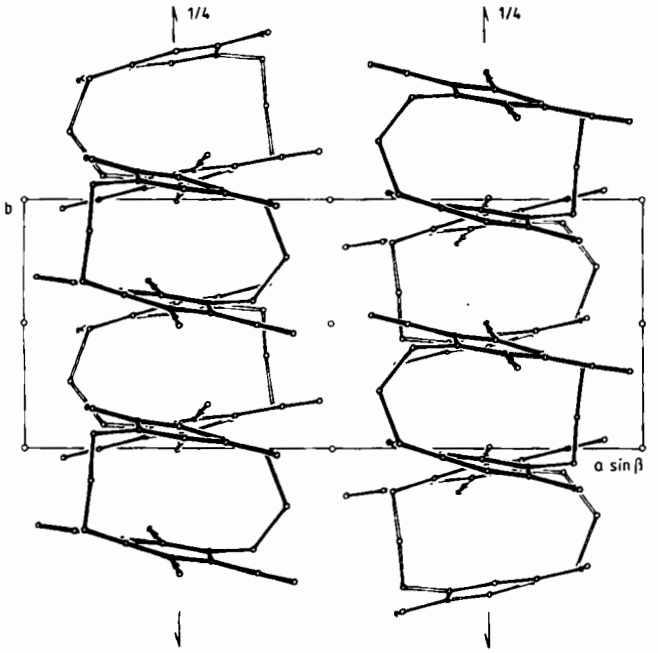


Figure 5. Crystal packing of **6** in the projection along the *c*-axis

pendicular to the ring planes shows an inclination to the *b*-axis of 12.5°. The lateral displacement of the molecules against each other is smaller than in **2** and allows a considerable intermolecular donor-acceptor overlap with an intermolecular distance between the ring planes which with 337 pm is not much longer than the intramolecular donor-acceptor distance (Figure 4B).

Molecular Structure of pseudogem-5,8-Dicyano-14,17-dimethoxy[3.3]paracyclophane (**10**): For comparison with **6** the molecular structure of **10**[7] differing from **6** only by the absence of two cyano substituents on C(6) and C(9) was determined as was the structure of the tetracyano-substituted dithia[3.3]paracyclophane **11**. Figure 6 shows the structure of **10** in a view perpendicular to the ring planes (A) and in a side-view (B). As compared to **6** the fully ecliptic orientation of the aromatic rings of **10** is remarkable. It would certainly be tempting to correlate this difference with the electron-acceptor strength which, of course, is much higher for the TCNB-containing **6**. This would require that donor-acceptor interaction would be optimal not in an ecliptic but in a lateral-shifted arrangement which brings donor and acceptor closer together although some overlap between donor and acceptor has to be sacrificed. Indeed, the transanular distance between the central parts of the

donor and the acceptor rings is considerably shorter in **6** than in **10**. In view of other results from the series of donor-acceptor [3.3]paracyclophanes[5,6] it seems more likely, however, that the degree of the parallel shift of the aromatic rings is determined by intermolecular interactions in the crystal lattice.

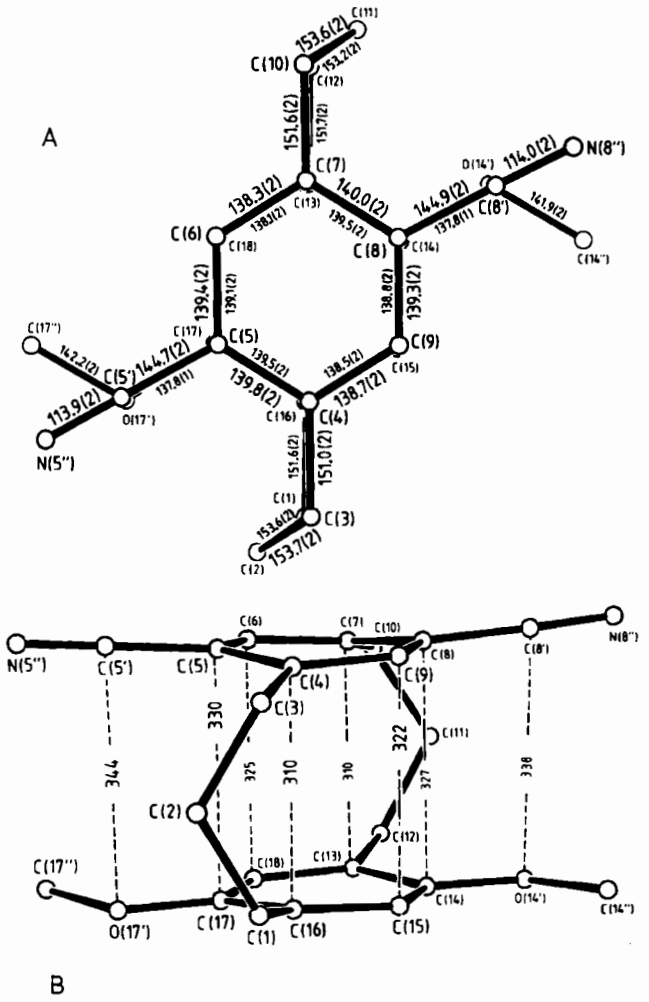
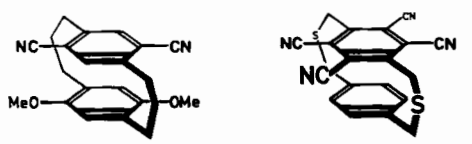


Figure 6. Molecular structure of **10** in a top-view onto the aromatic rings (A) with bond lengths (in pm; standard deviations in brackets) and in a side-view (B) with transanular distances (in pm)



10 **11**

Molecular Structure of 5,6,8,9-Tetracyano-2,11-dithia-[3.3]paracyclophane (**11**): With this structure a 2,11-dithia-[3.3]paracyclophane is contrasted to the molecular structures of carbocyclic [3.3]paracyclophanes. The structure of **11** (Figure 7) shows that substitution of $-CH_2-$ by $-S-$ in the cyclophane bridges has two immediate consequences: the longer carbon-sulfur bonds [C(1)–S(2): 181.6 (3) pm, S(2)–C(3): 182.2 (2) pm] as compared to the corresponding carbon-carbon bonds [C(1)–C(2): 153.6 (2), C(2)–C(3): 153.1 (2) pm in **6**], and the smaller C(1)–S(2)–C(3) angle (104.3°) in comparison to C(1)–C(2)–C(3) (117.2° in **6**). With regard to the transanular distance between the aromatic rings these two effects are working in an opposite direction. Still, the transanular distance between the bridge-head atoms C(4)···C(16) is elongated to 321 pm as compared to 310 pm in **6**. Consequently, the out-of-plane deformation of the aromatic rings is smaller than in carbocyclic [3.3]paracyclophanes. The lateral shift between the two rings is 9 pm in the axis through the bridge-head atoms and 61 pm perpendicular to this axis. The two ring planes are not parallel to each other but are tilted for 3.6° resulting in smaller transanular distances for C(5)···C(17) and C(6)···C(18) as compared to C(8)···C(14) and C(9)···C(15). With the exception of the bond lengths in the disorder area around S(11) there are no significant deviations from regular bond lengths. In the crystal lattice of **11**, as for the carbocyclic paracyclophanes, we find the usual stacking of the molecules with the acceptor side of one cyclophane facing the donor side of the neighbouring molecule. There is considerable intermolecular donor-acceptor overlap with distances between 340 and 360 pm.

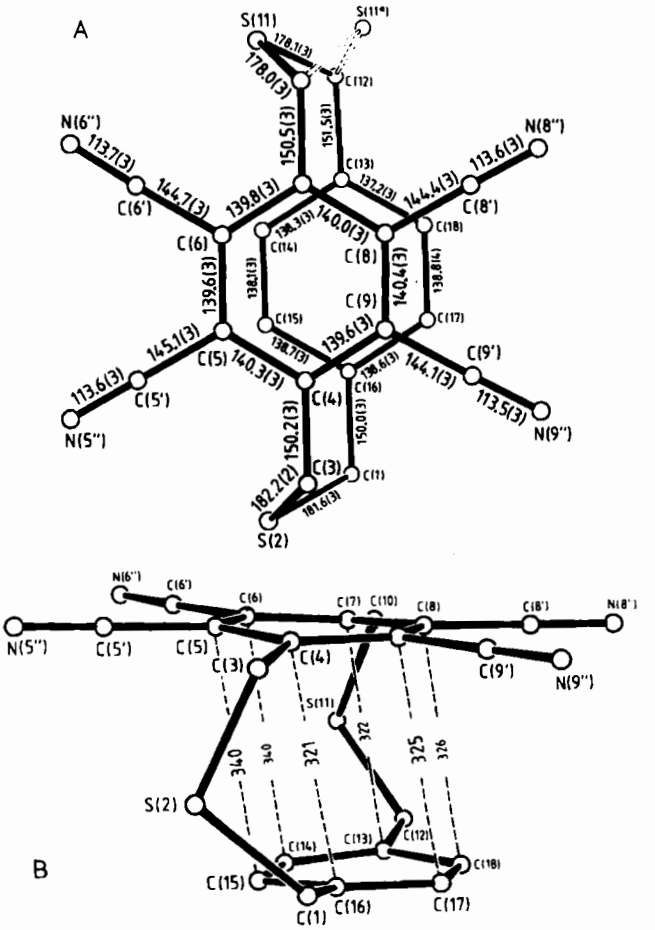
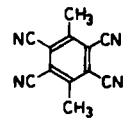
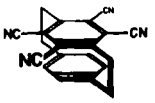
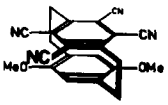
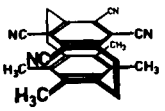
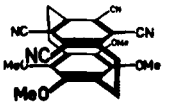
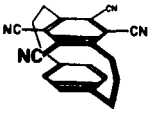
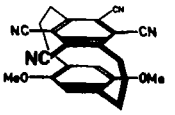
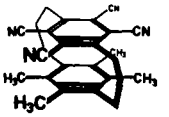
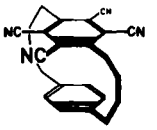
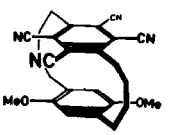


Figure 7. Molecular structure of **11** in a top-view perpendicular to the plane C(5)···C(6)···C(8)···C(9) (A) with bond lengths (in pm; standard deviations in brackets), and in a side-view (B) with transanular distances (in pm)

Table 2. Absorptionsspectra of TCNB-substituted [2.2]-, [3.3]-, and [4.4]paracyclophanes (in trichloromethane)

Compound	λ[nm] (lg ε)
12 	253sh(4.06), 259.5(4.20), 268(4.12) 309.5sh(3.45), 320(3.77), 333(3.91)
1 	257.5(4.03), 265(4.08), 286(3.72), 348sh(3.46) 350(3.46), 395sh(2.64)
2 	270sh(3.92), 301(3.65), 352(3.49), 520(2.38)
3 	260sh(3.95), 268sh(3.83), 298(3.40), 329(3.70) 352sh(3.21), 440(2.73)
4 	260sh(3.97), 268(3.84), 306(3.59), 320sh(3.56) 380sh(3.12)
5 	250sh(4.05), 258(4.13), 266(4.06), 280sh(3.46) 287(3.51), 311(3.38), 416(3.11)
6 	254sh(4.01), 263(4.06), 271sh(4.01) 303(3.61), 379(3.20), 508(2.54)
7 	254(3.96), 261(4.01), 270(3.98) 302sh(3.33), 314(3.53), 330sh(3.32), 434(2.76)
8 	253(4.03), 260(4.10), 268(4.10) 312sh(3.40), 326(3.62), 335(3.66), 364sh(2.59)
9 	252sh(3.92), 262(4.05), 270(4.06) 298(3.53), 312sh(3.38), 326(3.56), 336(3.54) 495(1.95)

Charge-Transfer Absorptions of the Tetracyanoparacyclophanes 1–9

The [2.2]paracyclophanes **1**–**4**, the [3.3]paracyclophanes **5**–**7**, and the [4.4]paracyclophanes **8** and **9** all have the same TCNB acceptor unit. They differ, however, in the strengths of the donor components and in the donor-acceptor distance. Thus, the series of compounds presented in this paper offers the possibility to study the effect of these two parameters on charge-transfer (CT) absorptions in geometrically well-defined systems. In the series **1**–**9** the dependence of the charge-transfer absorption on donor strengths and donor-acceptor distances is at first sight very easily recognized visibly by the colour of the compounds: Within the [2.2]paracyclophane series the compound with the weakest donor part (**1**) is only yellow; increasing the donor strength by four methyl groups (**3**) changes the colour to red; introducing two methoxy groups as strong donor substituents (**2**) results in a deep-violet colour; adding two more methoxy groups and, in this way, hindering sterically the mesomeric effect of all the methoxy substituents shifts the colour back to orange-red. Keeping the dimethoxy-substituted donor constant and changing the donor-acceptor distance leads from [2.2]- to [3.3]- and [4.4]paracyclophanes to colour changes from deep-violet (**2**) to dark-red (**6**) and orange (**9**).

These qualitative observations are reflected in a quantitative way by the absorption data listed in Table 2. In weak intermolecular electron donor-acceptor complexes there is only a relatively small disturbation of the electronic structures of the components. In these cases the short-wavelength part of the absorption spectra corresponds to the addition of the absorptions of the components, and only the CT absorption is added at longer wavelength. In the [2.2]- and [3.3]paracyclophane series there is, however, a stronger interaction between the π systems which leads already for the unsubstituted parent compounds to significant changes in the absorption spectra[8]. These "phane-specific" effects consist of broadening of the absorption bands, loss of vibronic structure of the absorptions, and the appearance of new absorptions at longer and/or shorter wavelength. Of course, these phane-specific effects are also operating in the substituted paracyclophanes dealt with in this paper. As is seen from the data in Table 2 only for the [4.4]paracyclophanes **8** and **9** the absorption at shorter wavelength can be rationalized by a correlation to the additive absorption of the components as is seen by comparison with the data of **12**. Since the identification of CT absorptions for the donor-acceptor paracyclophanes is clearly possible either by their distinctive absorption bands at long wavelengths or by measurements of the solvent dependence of the fluorescence (see below) we do not attempt to deal with the remaining absorptions in detail.

Whereas for **1** the CT transition gives rise only to an absorption shoulder at 395 nm, the strengthening of the donor part by the introduction of four methyl groups in **3** leads to a distinct CT absorption band at 440 nm. **2**, with the dimethoxybenzene unit, shows a CT absorption with a strong bathochromic shift to 520 nm (all data for trichloromethane solutions). By adding two more methoxy groups all four methoxy groups are rotated out of the coplanar arrangement with the aromatic ring as shown clearly by the X-ray analysis; consequently the electron-donating +M effect is inoperative leading for **4**, as compared to **2**, to a strong hypsochromic shift of the CT absorption which appears as an absorption shoulder only at 380 nm. Going from [2.2]paracyclophanes to [3.3]paracyclophanes with the same substitution pattern, e.g. from **2** to **6** or from **3** to **7**, only minor changes in the absorption wavelengths are observed. With the further increase in donor-acceptor distances in the corresponding [4.4]paracyclophanes, due to the reduced donor-acceptor overlap, hypsochromic shifts as well as reduced absorption intensities are observed. For the three homologous tetracycanodimethoxyparacyclophanes the following data were measured: **2**: λ_{max} = 520 nm (lg ε 2.38), **6**: λ_{max} = 508 nm (lg ε 2.54), **9**: λ_{max} = 495 nm (lg ε 1.95).

As one would expect for CT transitions leading to a highly polar first excited singlet state the fluorescence of these donor-acceptor cyclophanes shows a strong red-shift with increasing polarity of the solvents. For **1** and **3** the solvent dependence of the fluorescence wave-numbers is shown in Table 3. From these data the difference of the dipole moments of ground state and first excited singlet state has approximately been determined[9].

Table 3. Solvent dependence of fluorescence of **1** and **3**

Solvent	Fluorescence maxima ν_F [cm^{-1}]	
	1	**3**
Cyclohexane	21645	18350
Tetrachloromethane	21370	18020
Diethyl ether	20200	17095
Trichloromethane	19800	16670
Dichloromethane	19455	16395
Acetone	18450	–[a]
Acetonitrile	18020	–[a]

[a] No fluorescence detectable.

Data on the solvent dependence of the phosphorescence of TCNB-paracyclophanes and the determination of the CT character of the triplet state by the method of optical detection of magnetic resonance (ODMR) have been reported separately[10].

CAS Registry Numbers

1: 105537-09-5 / **2**: 105537-10-8 / **3**: 105537-11-9 / **4**: 105537-12-0 / **5**: 105537-21-1 / **6**: 105537-22-2 / **7**: 105537-23-3 / **8**: 105537-30-2 / **9**: 105537-31-3 / **10**: 64783-72-8 / **11**: 105537-14-2 / **12**: 80717-49-3

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[2] Further information concerning the X-ray structure analyses of **1**, **2**, **4**, **6**, and **10** including the tables of atomic coordinates, thermal parameters, bond lengths as well as bond and torsional angles may be requested from Fachinformationszentrum Energie Physik Mathematik, D-7514 Eggenstein-Leopoldshafen 2, with the indication of the registry number CSD 52167, the author's names, and the references to this publication.

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