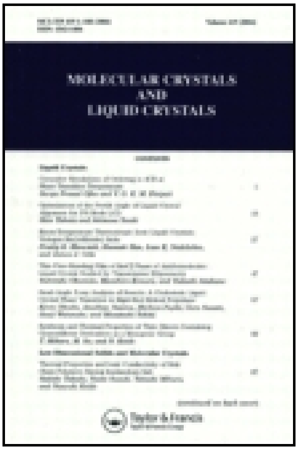

Molecular Crystals and Liquid Crystals Incorporating Nonlinear Optics

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl17

X-Ray and Theoretical Study of Cyclophane-tetracyanoethylene Charge Transfer Complexes

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Version of record first published: 13 Dec 2006.

To cite this article: Anne Renault , Claudine Cohen-addad , Janine Lajzerowicz , Enric Canadell & Odile Eisenstein (1988): X-Ray and Theoretical Study of Cyclophane-tetracyanoethylene Charge Transfer Complexes, Molecular Crystals and Liquid Crystals Incorporating Nonlinear Optics, 164:1, 179-195

To link to this article: http://dx.doi.org/10.1080/00268948808072122

Mol. Cryst. Liq. Cryst., 1988, Vol. 164, pp. 179–195
Reprints available directly from the publisher

Printed in the United States of America

X-Ray and Theoretical Study of Cyclophane-tetracyanoethylene Charge Transfer Complexes

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(*Received January 25, 1988*)

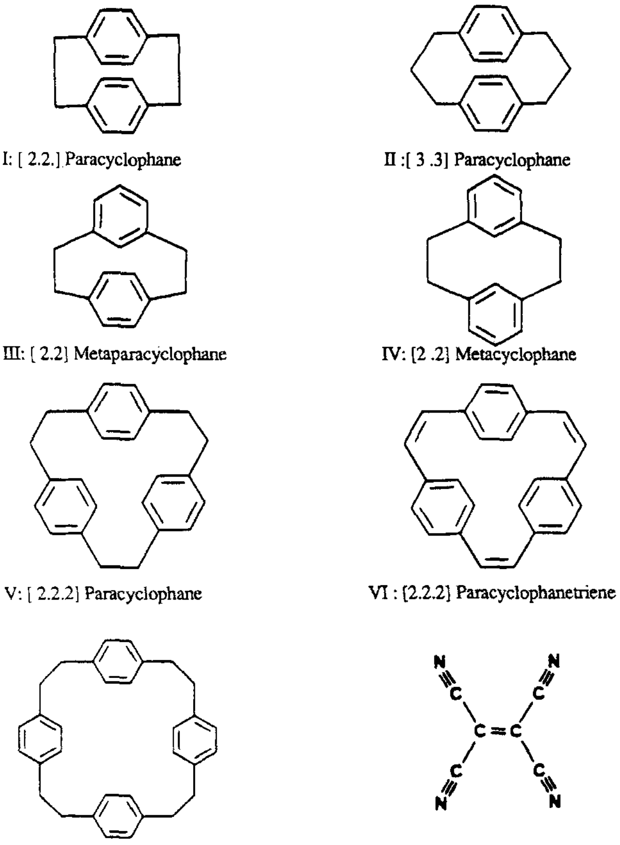
The crystal structures of a series of 1/1 complexes of tetracyanoethylene (TCNE) with cyclophanes containing two, three and four phenyl rings are compared. In all cases parallel and identical columns of alternately stacked donors and acceptors are found, as in complexes of planar molecules with TCNE. Complexes of several two phenyl ring cyclophanes are isostructural. When three phenyl rings are present in the donor molecule only two of them overlap with TCNE in the complex. A disorder of the TCNE molecule on two orientations is observed in several structures. Empirical intermolecular potential and extended Hückel calculations are used to explain these observations. It is found that interstack interactions determine the different orientations of TCNE with respect to the cyclophane while the intrastack ones determine the relative population of these orientational alternatives.

I. INTRODUCTION

Due to the existence of weakly interacting delocalized π-systems, cyclophanes present several remarkable physical and chemical properties.[1,2] In particular, they give charge-transfer complexes with tetracyanoethylene (TCNE). The 1:1 complexes which are usually formed in solution have been carefully studied by electron spectroscopy.[3–5] It is now well established that they present a charge-transfer band in the 400–600 nm range of the UV spectra characteristic of each complex.

Several studies have been devoted to complexes of TCNE with planar aromatic molecules in the solid state.[6] Mixed stack configuration have always been observed. Complexes with non planar systems[1a] have not attracted much attention although the crystal structure of the [3.3] paracyclophane-TCNE complex has been determined.[7]

In view of the structural versatility offered by cyclophanes (variable number of delocalized systems, different types of bridging groups), it is rather surprising that their ability to act as donors in TCNE complexes has not been more thoroughly considered. We would like to report here the results of such analysis. The systems considered in this work are those of Figure 1. In all cases, highly colored (red-



I: [2.2.] Paracyclophane

II :[3 .3] Paracyclophane

III: [2.2] Metaparacyclophane

IV: [2 .2] Metacyclophane

V: [2.2.2] Paracyclophane

VI : [2.2.2] Paracyclophanetriene

VII: [2.2.2.2] Paracyclophane

TCNE: Tetracyanoethylene

FIGURE 1 Molecules considered in this work.

orange to black) crystals were obtained after complexation. Crystal structure determinations have been done for all of them and we would like to analyse and compare them here.

We will focus on the following points:

First, how does the stacking mode depend on the substitution pattern—*i.e.*, para vs. meta substitution and number of bridging CH_2 groups (I to IV in Figure 1)—in the case of two-phenyl ring cyclophanes? Second, is it possible to obtain two-dimensional stackings when using cyclophanes containing more than two-phenyl-rings (V to VII)?† One could imagine that networks like **1** could be obtained with [2.2.2] paracyclophane (V). Third, what is the relative role played by inter and intrastack interactions in determining the structure adopted in every case? This is an essential step in the search for tailor-made complexes of this type.

1

In the first section we report our results concerning the main structural details of the crystal structures of TCNE complexes with I–VII. We then discuss these results from the view point of inter and intrastack interactions with the help of intermolecular potential and extended Hückel calculations.

II. STRUCTURAL RESULTS

A. The cyclophane donors (Table I)

The crystal symmetry of the cyclophane molecule is generally higher in the complexes than in the uncomplexed cyclophanes. In all the

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†From now on cyclophanes with two, three and four phenyl rings will be referred to as "2- 3- or 4-ring" respectively.

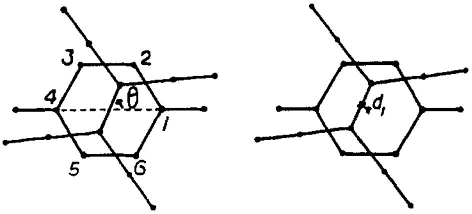
complexes,[7-10] except for V, the cyclophane molecule lies at a center of symmetry or on a mirror plane. This is in contrast with the corresponding uncomplexed cyclophanes[9,12-17] except for I. For the complexed two-ring donors I, II and IV, the out of the plane bendings of the phenyl rings are similar to those found in the uncomplexed cyclophanes. A decrease in the plane-to-plane distance between the two rings is observed in the complexes.

An important signature of the complexation of "3-ring" and "4-ring" donors is the significant redistribution of the torsion angles of the bridging groups. For example in the case of VII two different conformations are observed in the uncomplexed[17] and the complexed[11] situations (Table I).

B. Cyclophane-TCNE-cyclophane stack (Table II)

In every case, the TCNE molecule lies at a center of symmetry. It is sandwiched between two phenyl rings of two different cyclophane molecules and is parallel to these rings. Plane to plane distances range from 3.1 to 3.3 Å, the smallest values corresponding to the "2-ring" donors.

It is important to note that the orientation of TCNE, defined by θ(2) changes along the series of compounds. In addition, the overlap between the molecules in the ring-TCNE-ring sequence, characterized by the d_1 distance (2), also changes noticeably in the different complexes.



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In several structures, the TCNE presents an orientational disorder in its plane, around its center. The two orientations are related by a nearly 90° rotation, and their occupancy varies from one compound to another. Evidence for this disorder is shown by difference electron density maps calculated in the TCNE plane (Figure 2). Such a disorder has already been observed in II-TCNE[7] and also in pyrene-TCNE.[18] When disorder occurs, residual peaks are observed in the plane of the TCNE molecule on the normal to the central C═C molecular

TABLE I

Effect of the complexation on the cyclophane conformation

	I		II		III	
	uncomplexed	complexed	uncomplexed	complexed	uncomplexed	complexed
α_1	12.6°	11.2°	6.4°	6.1°	15.8°	15.1°
 α_2	12.6°	12.9°	6.4°	6.5°	15.8°	15.4°
d_c (Å)	3.09	3.03	3.27	3.21	2.36	2.32
	V		VI		VII	
	uncomplexed	complexed	uncomplexed	complexed	uncomplexed	complexed
T_1 (°)	40,12,−39	18,43,23	−4,5,9	6,6,0	69,68,69,68	81,−72,81,−72
T_2 (°)	90,90,90	$\underline{97}$,$\underline{83}$,97	50,84,59	$\underline{76}$,52,$\underline{76}$	33,83,34,85	22,$\underline{75}$,22,$\underline{25}$

Standard deviations on distances <0.01 Å; standard deviations on angles <1°
α_1,α_2: bending deformations of the rings as defined in Ref. 1a.
d_c: distance between the two rings.
T_1: torsion angles in the bridges
T_2: angles between phenyl ring planes and a plane defined by their centers of gravity; underlined values correspond to the phenyl rings associated to TCNE.

TABLE II

Structural parameters of the donor-acceptor sandwich in the I to VII cyclophane-TCNE complexes.

compounds	D(Å)	*d*(Å)	d_1(Å)	*p*(TCNE disorder) %	θ_1(°)	θ_2(°)
I	3.14	3.21	0.5	93–7	52,142	0
II	3.20	3.25	0.4	75–25	45,135	1
IV	3.25	3.18	0.1	no disorder	25	22
V[a] TCNE 1	3.30	3.32	0.3	no disorder	87	29
TCNE 2	3.31	3.32	0.3	95–5	81,171	32
VI	3.30	3.29	0.5	58–42	34,123	34
VII	3.29	3.30	0.5	no disorder	75	8

Standard deviation ≤0.01 Å and ≤1°

a: values corresponding to the two independent molecules in the cell.

D: Phenyl ring-TCNE distance.

d: Shortest distance between phenyl ring carbons and TCNE carbons bonded to nitrogen.

d_1: distance between the center of the phenyl ring and the projection on its plane of the associated TCNE center (see **2**).

p: occupancy of the two TCNE orientations.

θ_1: angle between phenyl ring and TCNE (major orientation, minor orientation when disordered) as defined on **2**.

θ_2: angle between the normal to TCNE and the stacking axis as defined on Figure 3.

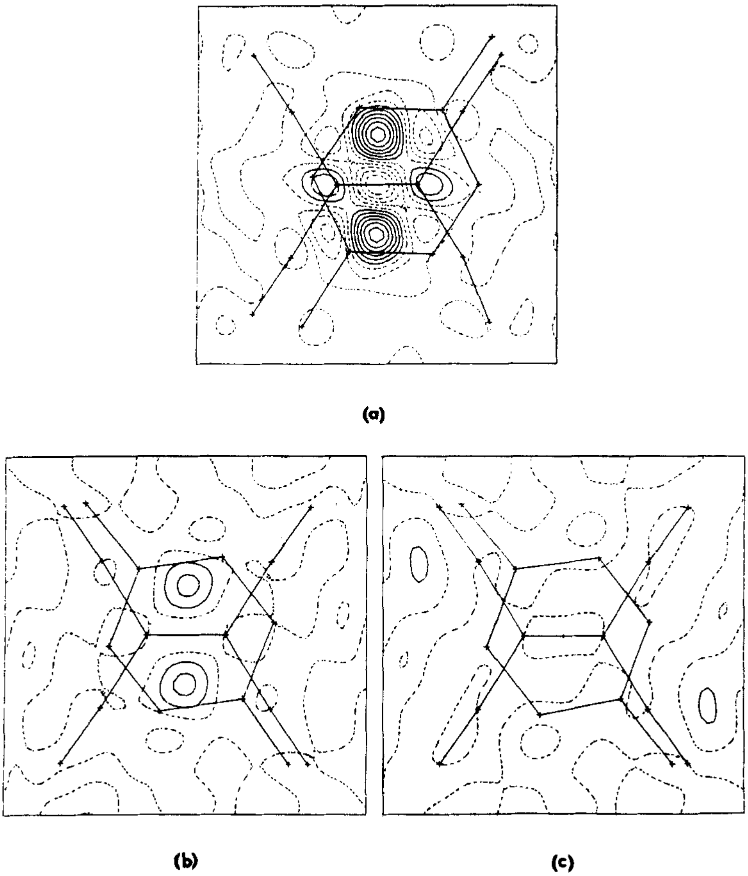


FIGURE 2 Difference electron density maps showing orientational disorder TCNE. Sections in the TCNE plane: (a) In VI-TCNE, only one of the two orientations (58%) of TCNE is introduced in the structure factor calculation. Strong residual peaks appear; (b) In I-TCNE, the major orientation (93%) is introduced in the calculation. Weak peaks appear; (c) In I-TCNE, the two orientations (93–7%) are introduced in the calculation. The residual peaks disappear.

bond. These peaks correspond to the central carbon atoms of a second TCNE molecule rotated by 90° with respect to the first one around an axis normal to its plane and passing through its center. As the molecule is nearly "square," this rotation results in a superposition of the cyano groups. Occupancy factors and orientations of the two positions were refined with a rigid body model, and the final difference electron density maps did not show any residual peak.

Two examples are given in Figure 2: VI-TCNE[8] with a strong disorder (42%–58%) and I-TCNE[8] with a weak disorder (93%–7%). In the last case both the geometry and the R index are correct when performing a normal refinement of an ordererd structure. Nevertheless a difference electron density map reveals the weak TCNE disorder.

C. Mode of stacking

Complexes of the four "2-ring" cyclophanes (I, II, III and IV) are isostructural:space group $P\bar{1}$, Z = 1, similar cell parameters, donors and acceptors sitting at centers of symmetry[7,8] (for III[9] the cyclophane molecule has no center of symmetry and a disorder of the molecule on two orientations related by a center of symmetry is observed in the complex). In the structures of I- and II-TCNE, the donors and the acceptors alternate in a stacking mode of parallel and identical chains perpendicular to the TCNE molecular planes (Figure 3a). In the VII-TCNE complex[11] (Figure 3a), only two of the four phenyl rings are involved in the sandwich association with TCNE and the stacking is very similar to that observed in the "2-ring" complexes.

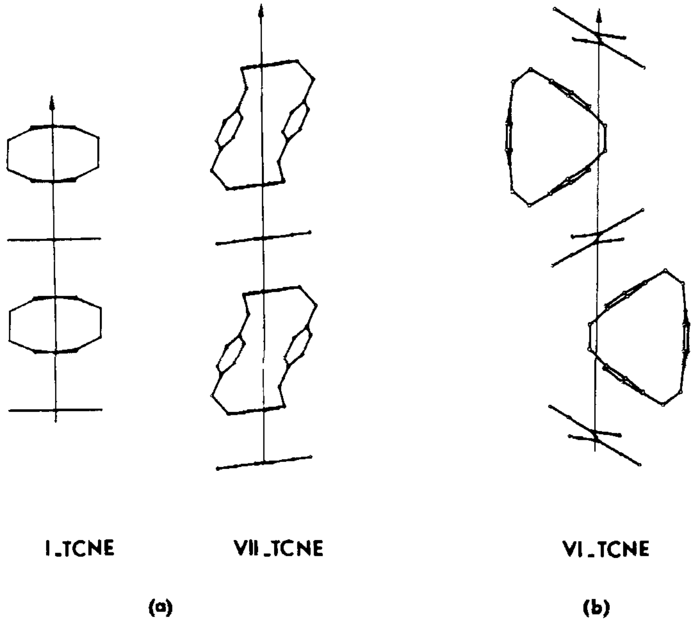


FIGURE 3 Molecular packing: (a) I- and VII-TCNE complexes; (b) VI-TCNE complex.

In these "2-ring" and "4-ring" complexes the stacking axis is parallel to the crystal needle axis.

The structures of "3-ring" complexes (V et VI) although not isostructural present a comparable stacking[15,16] (Figure 3b). Only two of the three phenyl rings are involved in the association with TCNE. Donors and acceptors are alternately stacked in columns whose axis is not perpendicular to the molecular planes of TCNE.

From these results, it can be concluded that the non-planar structure of cyclophanes does not seem to play any leading structural role in the complexation with TCNE. Whatever the cyclophane, the mode of stacking observed in the complex is the one dimensional analog of the one observed in the complexes with planar molecules. The sequence in the stacks is AD-DAD-DA for the cyclophane instead of DADAD for the planar molecules.

III. THE ROLE OF INTER AND INTRASTACK INTERACTIONS ON DETERMINING THE CRYSTAL STRUCTURES

As shown in the preceding section, the crystal structures of these systems are built from one-dimensional stacks. In understanding the structural details (TCNE orientation, occupancy ratios in disordered cases. . .), it is essential to consider the two types of interactions at work, *i.e.*, donor-acceptor interactions *within* the stacks and classical type non-bonded interactions *between* the stacks. To gain some insight into this problem, we have performed extended Hückel tight-binding and molecular calculations for the crystal structure and fragments of it, as well as classical potential energy calculations for the crystal structure.

A. Computational details

The van der Waals interaction between a molecule and its surrounding ones can be described by the sum of pairwise interactions between the n atoms i of the given molecule and the j atoms of the surrounding molecules:[19]

$$\sum_{ij}^{n} \mathrm{A} \exp[-\mathrm{B}r_{ij}] - \mathrm{C}/r_{ij}^{6}$$

where r_{ij} is the interatomic distance. The empirical parameters, A, B, C are taken from reference 20 and the calculations are performed by using the PACKRB computer program.[21] The interaction energy of one TCNE molecule with the surrounding TCNE and cyclophane molecules is calculated but the interaction between the cyclophanes is not taken into account because we are only interested in the orientation of the TCNE molecules. The energy is thus calculated as a function of $\theta(2)$. Interatomic distances r_{ij} up to 8 A are included in the calculations.

The tight-binding and molecular calculations are of the extended Hückel type.[22] Both single- and double-ζ[23] atomic orbitals for C and N are used. Exponents and parameters for the single-ζ calculations are the standard ones.[22b] The exponents ζ_μ and ζ'_μ and weighting coefficients c_μ and c'_μ used in double-ζ calculations are: 1.831, 1.153, 0.7616 and 0.2630 for C2*s*; 2.730, 1.257, 0.2595 and 0.8025 for C2*p*; 2.261, 1.424, 0.6978 and 0.3304 for N2*s* and 3.249, 1.249, 0.2881 and 0.7783 for N2*p*. A modified Wolfsberg-Helmholz formula is used to calculate the non-diagonal $H_{\mu\nu}$ values.[24]

B. Discussion

The results of the van der Waals interaction energy calculations concerning the TCNE orientation θ and the occupancy ratios are reported in Table III. There is an almost perfect agreement between the calculated and experimental values of θ. In all cases two different minima corresponding to θ values differing by about 90° are obtained. This can be explained by the "square" geometry of TCNE molecules. In contrast the calculated energy differences between minima are consistently too low so that the calculated occupancy ratios (Table III) are very far from the crystallographic values. The only exception is VI-TCNE. Energy curves for I-TCNE are shown in Figure 4. It can be seen that the contribution to the potential energy interaction within the sandwich, (one TCNE with the two associated cyclophanes) is about one half of the total energy interaction near the minima. The corresponding potential energy curve (Figure 4b) is very shallow especially between θ and $\theta + 90$. These results are similar for every complex. It can also be observed that the energy barriers separating the two minima in the complete calculation are very high (Figure 4a). Although these values have no absolute meaning, they seem to indicate a static rather than a dynamic disorder in the crystal structure. This hypothesis was confirmed for VI-TCNE: The 44–56% TCNE disorder observed in the structure at room temperature does not significantly change at low temperature (153K:42–58%). This series of results suggest that the classical energy interactions between stacks impose the TCNE orientations but not the occupancy ratios.

TABLE III

Potential energy calculations for cyclophane-TCNE complexes.

compounds	θ obs	θ cal(°)	ΔE (Kcal/mol)	*p*cal (%)	*p*obs (%)
I-TCNE	52,142	53,143	−0.07	47−53	97−3
II-TCNE	45,135	46,135	−0.02	49−51	75−25
IV-TCNE	25	23,111	−0.04	48−52	100−0
V[a] TCNE 1	87	90,184	0.31	62−38	100−0
TCNE 2	81,171	83,176	0.27	61−39	95−5
VI-TCNE	34,123	32,122	0.23	60−40	58−42
VII-TCNE	75	78,171	0.61	74−26	100−0

a: values corresponding to the two independent molecules.
θobs: the observed (see Table II) TCNE orientations (one or two when disordered).
θcal: theoretical angles of the two TCNE orientations corresponding to the energy minima.
ΔE: difference between the two energy minima.
*p*cal: theoretical occupancy values of the two TCNE orientations.
*p*obs: observed occupancy values.

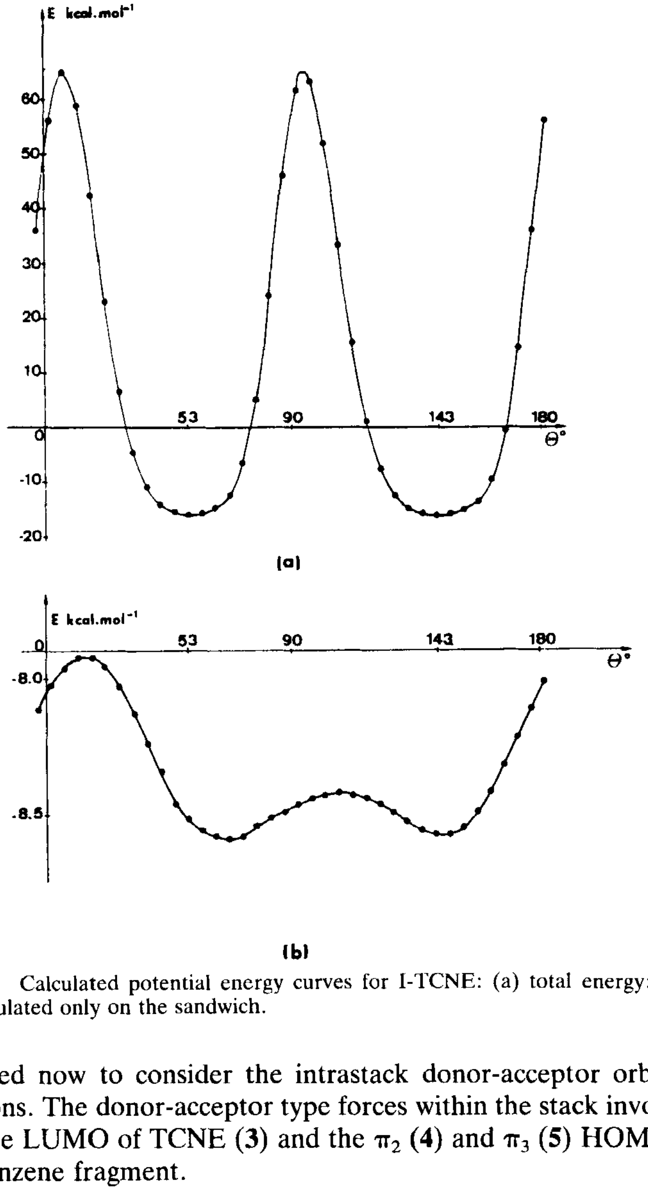
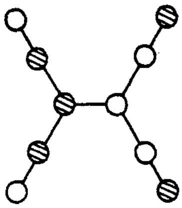


FIGURE 4 Calculated potential energy curves for I-TCNE: (a) total energy; (b) energy calculated only on the sandwich.

We need now to consider the intrastack donor-acceptor orbital interactions. The donor-acceptor type forces within the stack involve mainly the LUMO of TCNE (**3**) and the π_2 (**4**) and π_3 (**5**) HOMO's of the benzene fragment.

The π_2 and the π_3 orbitals lead to different preferential orientations θ of the TCNE molecule: $\theta = 0°$ for π_2 (**4**) and $\theta = 90°$ for π_3 (**5**). Because of the C_6 axis, there is no real preference for benzene itself, since the degenerate π_2 and π_3 can mix to give equivalent interactions with the LUMO of TCNE. However when some substitution is done



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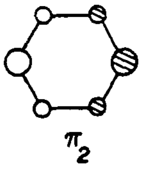

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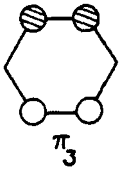

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at the 1-, 4-positions the degeneracy between π_2 and π_3 is removed and this results in some orientational preference. The overlap integrals $S\pi_2$-LUMO and $S\pi_3$-LUMO as a function of θ are reported in Figure 5. The important fact is that the overlap decreases rather slowly in the first part of the curve (θ close to 0° for π_2 ant to 90° for π_3) and then falls very quickly in the second part. Since the interaction energies are proportional to the square of the overlap they become small for values less/more (π_2/π_3) than $\approx 45°$.

Let us start by considering the I-TCNE complex case. As a result of the interplay of "through-space" and "through-bond" interactions, the HOMO of I derives from π_2 but the in-phase combination of π_3 orbitals lies very near in energy.[25] This is the result of the mixing of a bridge empty orbital into the HOMO.[25a] Thus, on energy grounds, both π_2 and π_3-type orbitals should interact similarly with the TCNE LUMO. However the overlap with the π_2-type one is severely reduced because of the bending of the benzene fragments. Remembering that the crystal packing imposes $\theta = 52°$ for the most populated position and referring back to the results of Figure 5, we conclude that the orbital effectively engaged in the interaction with the TCNE LUMO in the crystal, is the π_3 based one. In agreement with the previous analysis, the band structure of I-TCNE (assuming all TCNE in the 93% populated position) shows a completely flat valence band, made of the HOMO orbital of I and a slightly dispersive conduction band, made of the TCNE LUMO and the π_3-type orbitals. The band gap is calculated to be 1.28 eV and the system should be insulating as in fact revealed by the resistivity measurements.

Let us come back to the question of the occupancy ratio. The two orientations of TCNE in this complex correspond to $\theta = 52°$ and 142°. Since the π_3-type orbital is the one at work, in the first case (52°) we are still in the zone of important overlap whereas in the

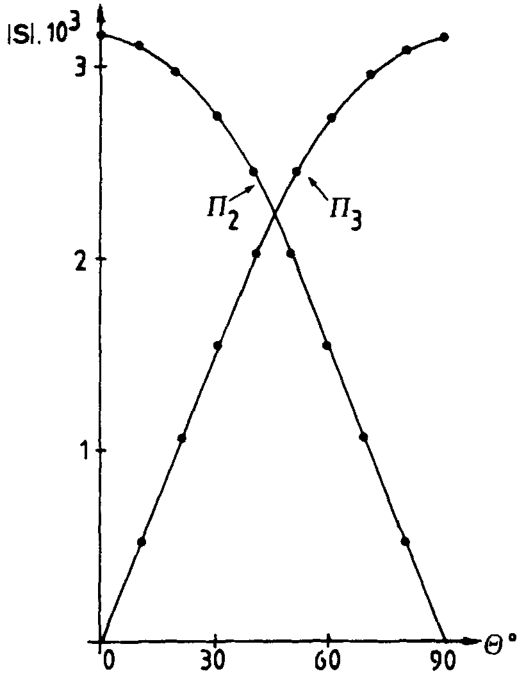
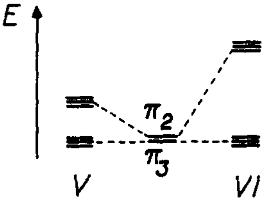


FIGURE 5 Overlap integrals between the TCNE LUMO and the π_2 and π_3 orbitals as a function of θ.

second case (142°), we are in the small overlap region. The computed overlap values $(S_{(52°)}/(S_{(142°)} = 1.6)$ substantiate these simple ideas. It is then normal that the position at 52° is the more populated one. Were it not for the non-planarity of the benzene rings, the second position would be more populated. In fact, in II-TCNE[7] where the nonplanarity of the benzenes is reduced, the disorder increases to 75–25% in agreement with this analysis.

Let us consider the 3-ring systems V and VI. Our calculations for the isolated VI show that the "vertical" benzene (corresponding to the angle equal to 84° in Table I) does not contribute to the HOMO and LUMO orbitals. This is in agreement with the fact that the delocalization of the negative charge in the corresponding anion does not involve the "vertical" benzene.[26] In both cyclophanes, the three orbitals deriving from π_2 are found higher in energy—although only marginally more in V (**6**)—because they interact with the occupied orbitals of the bridges, whereas the orbitals derived from π_3 are left almost unaltered.



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Since the bending of the benzene in the 3-ring system is almost nil, it could be expected that the π_2-type orbitals will now play the major role in the donor-acceptor interactions. Nevertheless an important consequence of the interaction with the bridge orbitals is that these π_2-type orbitals are less concentrated on the benzene fragment. For instance, about 35% and 20% of the HOMO in VI and V respectively are found in the non-interacting region. Since the π_3-type orbitals are almost unaltered the overlap is better with these orbitals. Our model calculations show that they are indeed the π_3-type orbitals which interact with the TCNE LUMO, favoring thus $\theta = 90°$. The potential energy calculation for V-TCNE lead to minima near 90° and 180°. Besides an inherent tendency for the 90° orientation due to the interstack interactions, the donor-acceptor orbital interaction is maximized for the first orientation while it is minimized for the second one. This is coherent with the two θ values near 90° (81° and 87°) observed for the two TCNE present in the unit cell. As pointed out before, the ΔE value of the potential energy difference between the two disordered alternatives is low in the case of VI-TCNE and is almost exactly equal to the observed value (Table III). This means that the donor-acceptor interactions in this case are so small that they cannot alter the requirements of the crystal packing. In agreement with this fact, the calculated band structure for VI-TCNE (assuming $\theta = 34°$) shows almost completely flat valence and conduction bands and a band gap of 1.5 eV. The system should be an insulator. In fact, this is the only case among those we have examined where the orbital interactions do not play any important role. Why is that so? From the two positions allowed by the crystal packing, the first one ($\theta = 34°$) lies in the low overlap π_3-LUMO zone (Figure 5). The second one ($\theta = 123°$) although not at the optimum value, still lies in the high-overlap region ($\theta = 57°$ in Figure 5). Nevertheless, we note that the crystal packing also imposes a d_1 value (**2**) of 0.50 Å, among the greatest we have found. Such displacement combined with a not too favourable θ, severely decreases the overlap and consequently, in both cases we are in the very small overlap region which leads to very weak donor-acceptor interactions.

In VII-TCNE the calculated orientation ratio is again too small if only non-orbital interactions are considered. The two possible orientations (78° and 171°) are those which nearly optimize and minimize respectively the interaction of the TCNE LUMO with the π_3 type orbitals (Figure 5). We then conclude that again these orbitals play the role of the donor and definitively determine the only orientation observed.

IV. CONCLUDING REMARKS

The solid state complexes of cyclophanes with TCNE described in the present work are of the 1/1 type. Whatever the cyclophane, the three-dimensional arrangement is made of parallel and identical columns of alternately stacked donors and acceptors as observed in complexes of planar molecules with TCNE. It seems that the complexes are of two different types as far as the interplay of the inter and intrastack interactions is concerned. In only one case ([2.2.2] paracyclophanetriene VI), the interstack interactions alone completely determine the crystal structure. In all other cases, the interstack interactions determine θ but the intrastack orbital interactions impose the occupation of the different allowed positions. It should be emphasized that since the crystal packing imposes the θ values, the donor-acceptor interactions cannot be maximized in the solid state. As a consequence the donor ability of a given cyclophane can be very different in the solid or liquid states. For instance, according to our calculations VI should be the best donor in solution but it is the worst one in the crystal.

Acknowledgment

We especially thank Prof. P. Baret and Dr. J. P. Dutasta for their contribution to this work. We also wish to thank Dr. P. Batail for helpful discussions.

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