

Discussion. The space group *Pbcm* exhibits the same systematic absences as *Pca2₁*. However, with *Z* = 4 the site symmetry imposed by the space group is inconsistent with the symmetry of the molecule.

Fig. 1 is an *ORTEP* diagram (Johnson, 1976) of the molecule illustrating 50% probability ellipsoids for all non-H atoms and arbitrary spheres of radius about 0.4 Å for H atoms. Atomic positions are listed in Table 1 and distances and angles between all non-H atoms are shown in Table 2. The structure determined for compound (III) indicates that the structure of (I) has been correctly assumed in the literature and indirectly confirms the structure of the analogous maleic anhydride–benzene photoadduct.

Very recently, the complete structure of a derivative of (I), in which the imide ring fused to the four-membered ring was opened by prolonged hydrolysis, has been determined by X-ray crystallography (Pettit, Paull, Herald, Herald & Riden, 1983). Assuming no rearrangement occurred during the basic hydrolysis the same structure and stereochemistry was indicated by this study.

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Structure of the 1/1 Complexes of [2.2.2]Paracyclophane and [2.2.2.2]Paracyclophane with Tetracyanoethylene, C₂₄H₂₄·C₆N₄ (I) and C₃₂H₃₂·C₆N₄ (II)

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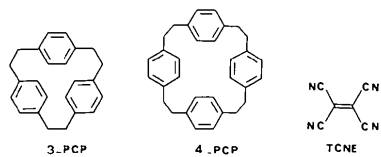
Abstract. (I): $M_r = 440.36$, triclinic, $P\bar{1}$, $a = 9.057$ (6), $b = 22.646$ (9), $c = 6.830$ (5) Å, $\alpha = 104.85$ (5), $\beta = 103.25$ (5), $\gamma = 106.35$ (5)°, $V = 1229$ Å³, $Z = 2$, $D_x = 1.15$ Mg m⁻³, $\lambda(\text{Cu K}\alpha) = 1.5418$ Å, $\mu = 0.545$ mm⁻¹, $F(000) = 464$, $T = 293$ K; (II): $M_r = 544.45$, monoclinic, $C2/c$, $a = 27.298$ (8), $b = 6.727$ (3), $c = 17.156$ (6) Å, $\beta = 105.25$ (5)°, $V = 3039$ Å³, $Z = 4$, $D_x = 1.18$ Mg m⁻³, $\lambda(\text{Cu K}\alpha) = 1.5418$ Å, $\mu = 0.548$ mm⁻¹, $F(000) = 1152$, $T = 293$ K. The structures were refined to *R* values of 0.085 (I) and 0.066 (II) for 2604 and 1438 observed intensities respectively. In (I), the three benzene rings of the paracyclophane molecules are related by a threefold pseudo-axis of symmetry. In (II), the paracyclophane

molecule lies on a centre of symmetry and is not planar. In both compounds, 1/1 complexes are formed with tetracyanoethylene molecules (TCNE) lying on centres of symmetry. Each TCNE is situated between symmetrically related paracyclophane molecules. In (I) only two of the three aromatic rings of each paracyclophane are involved in the charge transfer with TCNE. This leads to a one-dimensional charge transfer approximately along a lattice body diagonal and not to a two-dimensional one, as might be expected from the threefold pseudo-symmetry observed in the [2.2.2]-paracyclophane crystal structure. In (II) the charge-transfer direction is along a face diagonal in a sandwich arrangement.

Introduction. The cyclophanes have a molecular cavity able to complex metal ions; thus, [2.2.2]paracyclophane forms a stable complex with an Ag⁺ ion (Pierre, Baret, Chautemps & Armand, 1981; Cohen-Addad, Baret, Chautemps & Pierre, 1983). Cyclophanes also form π - π^* charge-transfer complexes with electron-acceptor molecules such as tetracyanoethylene (TCNE) (Keehn & Rosenfeld, 1983); this is the case with [m.n]paracyclophanes (*m*, *n* = 3 to 4) (Cram & Bauer, 1959), [2.2.2]paracyclophane and [2.2.2.2]paracyclophane (Imashiro, Yoshida & Tabushi, 1973). These complexes are coloured from yellow-orange to blue and show an intense UV absorption band, characteristic of the charge transfer.

In the solid state, very few complexes have been investigated. Among them, the crystal structures of [3.3]paracyclophane-TCNE and of [2.2](1,5)-naphthalenoparacyclophane-TCNE were determined (Bernstein & Trueblood, 1971; Irngartinger & Goldman, 1979).

The crystal structure of [2.2.2]paracyclophane (3-PCP, formula below) reveals a geometry in which the three benzene rings are parallel to a threefold pseudo-axis of symmetry and related by this axis. It appeared that the solid-state complex of this molecule with TCNE† (compound I) would be interesting to study because it might lead to the formation of benzene ring-TCNE entities related by the same pseudo-symmetry and, consequently, to a two-dimensional charge-transfer complex. Concurrently, the crystal-structure determination of the [2.2.2.2]paracyclophane (4-PCP)-TCNE complex† (compound II) was undertaken.



Experimental. Synthesis: 3-PCP and 4-PCP prepared by P. Baret, P. Chautemps and J. L. Pierre (Laboratoire d'Etudes Dynamiques et Structurales de la Sélectivité, Grenoble) according to methods already described (Tabushi, Yamada, Yoshida & Oda, 1971; Thulin, Wennerström & Högberg, 1975).

Compound (I): [2.2.2]paracyclophane-TCNE (1/1) bright orange, crystal 0.4 × 0.45 × 0.5 mm, compound (II): [2.2.2.2]paracyclophane-TCNE (1/1) bright orange, crystal 0.3 × 0.3 × 0.35 mm obtained by slow evaporation at 277 K from a solution of TCNE and

† Chemical formulae according to the *Chemical Abstracts* nomenclature: (I): Tetracyclo[14.2.2^{4,7}.2^{10,13}]tetracos-4,6,10,12-, 16,18,19,21,23-nonaene-ethenetetracarboxitrile (1/1). (II): Pentacyclo[20.2.2^{4,7}.2^{10,13}.2^{16,19}]dotriaconta-4,6,10,12,16,18,22,24-, 25,27,29,31-dodecaene-ethenetetracarboxitrile (1/1).

paracyclophane in chloroform. Measurements with a Siemens diffractometer, Ni-filtered Cu K α radiation, five-points method (Troughton, 1969), ω -scan, no absorption correction. Lattice parameters refined with 10 (I) and 13 (II) reflexions. Number of reflexions with $I > 3\sigma(I)$: (I) 2604 (measured 3640), $\sin\theta/\lambda < 0.56 \text{ \AA}^{-1}$, *hkl*, $\bar{h}kl$, $\bar{h}\bar{k}l$, $h\bar{k}l$; (II) 1438 (measured 2245), $\sin\theta/\lambda < 0.56 \text{ \AA}^{-1}$, *hkl*, $\bar{h}kl$. Standard reflexions: (I) 060, 412, 322 (4% variation); (II) 315, 912, 10,0,8 (4% variation). Multisolution direct method (Germain, Main

Table 1. Atomic coordinates ($\times 10^4$) with standard deviations in parentheses and equivalent isotropic temperature factors of [2.2.2]paracyclophane-TCNE (I) and [2.2.2.2]paracyclophane-TCNE (II)

Standard deviations on B_{eq} : 0.5–0.6 Å² (I), 0.3–0.4 Å² (II).

$$B_{eq} = (U_1 U_2 U_3)^{1/3}.$$

	x	y	z	$B_{eq}(\text{Å}^2)$
Compound (I)				
C(1)	1278 (6)	3895 (2)	1045 (9)	4.2
C(2)	1031 (6)	3757 (2)	2777 (9)	4.7
C(3)	1857 (7)	3416 (3)	3726 (8)	4.9
C(4)	2951 (6)	3208 (2)	2916 (11)	4.6
C(5)	3213 (7)	3361 (3)	1184 (12)	5.5
C(6)	2378 (8)	3704 (3)	277 (9)	5.3
C(7)	3758 (9)	2809 (3)	3915 (16)	7.1
C(8)	2892 (9)	2180 (3)	3675 (14)	6.9
C(9)	1280 (7)	1792 (3)	1926 (11)	4.8
C(10)	1218 (7)	1626 (3)	-196 (13)	5.3
C(11)	-279 (8)	1294 (2)	-1846 (9)	5.1
C(12)	-1702 (6)	1119 (2)	-1397 (9)	4.5
C(13)	-1620 (7)	1274 (3)	687 (10)	5.1
C(14)	-156 (8)	1608 (3)	2331 (9)	5.3
C(15)	-3310 (8)	781 (3)	-3184 (11)	6.3
C(16)	-4409 (8)	1154 (3)	-3293 (14)	6.9
C(17)	-3623 (6)	1863 (3)	-2970 (11)	4.6
C(18)	-3536 (6)	2339 (4)	-1239 (10)	5.7
C(19)	-2740 (7)	3006 (3)	-873 (9)	5.3
C(20)	-1990 (6)	3192 (2)	-2236 (10)	4.4
C(21)	-2124 (7)	2713 (3)	-4038 (10)	5.5
C(22)	-2939 (7)	2064 (3)	-4386 (10)	5.6
C(23)	-1024 (8)	3900 (3)	-1774 (14)	6.6
C(24)	338 (9)	4237 (3)	-32 (14)	6.9
N(25)	-3452 (7)	-478 (3)	-160 (10)	6.9
C(26)	-2063 (7)	-265 (3)	268 (9)	4.8
C(27)	-343 (6)	8 (2)	768 (8)	4.2
C(28)	661 (7)	307 (3)	2982 (10)	4.7
N(29)	1452 (6)	540 (3)	4725 (8)	6.3
N(30)	5579 (6)	4448 (2)	8483 (8)	5.5
C(31)	5189 (6)	4680 (2)	7285 (8)	4.2
C(32)	4683 (5)	4990 (2)	5776 (7)	4.0
C(33)	3454 (6)	5265 (2)	5996 (8)	4.4
N(34)	2492 (6)	5479 (3)	6174 (8)	6.3
Compound (II)				
C(1)	2381 (1)	6761 (7)	-1375 (2)	4.3
C(2)	1968 (2)	7355 (7)	-1976 (3)	5.0
C(3)	1541 (2)	6203 (8)	-2229 (2)	4.7
C(4)	1508 (1)	4350 (7)	-1906 (2)	4.0
C(5)	1924 (2)	3727 (7)	-1305 (3)	4.7
C(6)	2347 (2)	4910 (8)	-1035 (3)	5.0
C(7)	1028 (2)	3113 (8)	-2195 (2)	4.9
C(8)	703 (1)	2972 (7)	-1590 (3)	4.7
C(9)	938 (1)	1678 (6)	-869 (2)	3.7
C(10)	1022 (1)	-341 (7)	-974 (2)	4.1
C(11)	1255 (2)	-1534 (6)	-334 (2)	4.3
C(12)	1410 (1)	-804 (7)	451 (2)	3.8
C(13)	1321 (1)	1185 (7)	558 (2)	3.9
C(14)	1091 (1)	2403 (6)	-84 (3)	4.1
C(15)	1654 (2)	-2156 (8)	1143 (3)	4.9
C(16)	2158 (2)	-3091 (7)	1095 (3)	5.7
C(17)	-8 (1)	890 (6)	165 (2)	3.6
C(18)	-216 (1)	2569 (7)	-339 (2)	3.8
C(19)	182 (1)	1205 (6)	1025 (2)	4.0
N(1)	-377 (1)	3897 (6)	-737 (2)	5.2
N(2)	334 (1)	1402 (7)	1695 (2)	5.4

& Woolfson, 1971), least-squares refinement minimizing $\sum w(F_o - F_c)^2$ (Busing & Levy, 1962). Positional and anisotropic thermal parameters refined for non-H atoms; H-atom positional parameters calculated (not refined); isotropic temperature factors for H estimated

Table 2. *Interatomic distances (Å) and valence angles (°)*

Symmetry code: (i) $-x, -y, -z$; (ii) $\frac{1}{2} - x, \frac{1}{2} - y, -z$.

(a) Compound (I)

C(1)–C(2)	1.348 (8)	C(17)–C(22)	1.366 (9)
C(1)–C(6)	1.350 (8)	C(18)–C(19)	1.405 (9)
C(2)–C(3)	1.392 (8)	C(19)–C(20)	1.355 (8)
C(3)–C(4)	1.376 (9)	C(20)–C(21)	1.371 (8)
C(4)–C(5)	1.368 (9)	C(21)–C(22)	1.371 (8)
C(5)–C(6)	1.385 (9)	C(20)–C(23)	1.504 (8)
C(4)–C(7)	1.507 (8)	C(23)–C(24)	1.360 (9)
C(7)–C(8)	1.366 (10)	C(24)–C(1)	1.498 (8)
C(8)–C(9)	1.507 (8)	N(25)–C(26)	1.148 (7)
C(9)–C(10)	1.384 (9)	C(26)–C(27)	1.425 (7)
C(9)–C(14)	1.364 (9)	C(27)–C(28)	1.439 (8)
C(10)–C(11)	1.402 (9)	C(27)–C(27 ^b)	1.334 (10)
C(11)–C(12)	1.367 (8)	C(28)–N(29)	1.132 (7)
C(12)–C(13)	1.355 (8)	N(30)–C(31)	1.124 (6)
C(13)–C(14)	1.382 (8)	C(31)–C(32)	1.448 (7)
C(12)–C(15)	1.508 (8)	C(32)–C(32 ^b)	1.321 (9)
C(15)–C(16)	1.477 (10)	C(32)–C(33)	1.438 (7)
C(16)–C(17)	1.496 (8)	C(33)–N(34)	1.126 (6)
C(17)–C(18)	1.350 (9)		
C(2)–C(1)–C(6)	118.0 (5)	C(15)–C(16)–C(17)	115.7 (5)
C(6)–C(1)–C(24)	120.7 (7)	C(16)–C(17)–C(18)	121.4 (7)
C(2)–C(1)–C(24)	121.3 (6)	C(16)–C(17)–C(22)	122.0 (7)
C(1)–C(2)–C(3)	121.3 (5)	C(18)–C(17)–C(22)	116.6 (5)
C(2)–C(3)–C(4)	120.7 (5)	C(17)–C(18)–C(19)	121.9 (6)
C(3)–C(4)–C(5)	117.4 (5)	C(18)–C(19)–C(20)	120.5 (5)
C(3)–C(4)–C(7)	119.2 (8)	C(19)–C(20)–C(21)	117.9 (5)
C(5)–C(4)–C(7)	123.4 (8)	C(21)–C(20)–C(23)	121.0 (6)
C(4)–C(5)–C(6)	120.7 (6)	C(19)–C(20)–C(23)	121.1 (6)
C(1)–C(6)–C(5)	121.9 (6)	C(20)–C(21)–C(22)	120.5 (5)
C(4)–C(7)–C(8)	120.9 (5)	C(17)–C(22)–C(21)	122.5 (6)
C(7)–C(8)–C(9)	121.2 (5)	C(20)–C(23)–C(24)	121.0 (5)
C(8)–C(9)–C(14)	122.8 (7)	C(1)–C(24)–C(23)	121.8 (5)
C(8)–C(9)–C(10)	119.7 (7)	C(27)–C(27)–C(26)	121.4 (6)
C(10)–C(9)–C(14)	117.5 (5)	C(27)–C(27)–C(28)	119.9 (6)
C(9)–C(10)–C(11)	120.4 (5)	C(26)–C(27)–C(28)	118.8 (4)
C(10)–C(11)–C(12)	120.9 (5)	N(25)–C(26)–C(27)	178.8 (4)
C(11)–C(12)–C(13)	118.0 (5)	N(29)–C(28)–C(27)	179.6 (6)
C(11)–C(12)–C(15)	120.4 (6)	C(32)–C(32)–C(31)	120.9 (6)
C(13)–C(12)–C(15)	121.6 (6)	C(32)–C(32)–C(33)	120.9 (6)
C(12)–C(13)–C(14)	121.8 (5)	C(33)–C(32)–C(31)	118.1 (4)
C(9)–C(14)–C(13)	121.3 (6)	N(30)–C(31)–C(32)	178.8 (5)
C(12)–C(15)–C(16)	115.8 (5)	N(34)–C(33)–C(32)	179.8 (6)

(b) Compound (II)

C(1)–C(2)	1.371 (5)	C(9)–C(10)	1.398 (6)
C(1)–C(6)	1.388 (6)	C(10)–C(11)	1.374 (6)
C(1)–C(16 ^h)	1.516 (6)	C(11)–C(12)	1.392 (5)
C(2)–C(3)	1.371 (6)	C(12)–C(13)	1.381 (6)
C(3)–C(4)	1.377 (6)	C(12)–C(15)	1.503 (6)
C(4)–C(5)	1.385 (5)	C(13)–C(14)	1.384 (6)
C(4)–C(7)	1.519 (6)	C(15)–C(16)	1.536 (7)
C(5)–C(6)	1.378 (6)	C(17)–C(17 ^b)	1.331 (8)
C(6)–C(1)	1.388 (6)	C(17)–C(19)	1.444 (5)
C(7)–C(8)	1.536 (6)	C(17)–C(18)	1.445 (6)
C(8)–C(9)	1.511 (6)	C(18)–N(1)	1.140 (5)
C(9)–C(14)	1.388 (5)	C(19)–N(2)	1.123 (5)
C(2)–C(1)–C(6)	116.4 (4)	C(10)–C(9)–C(8)	120.1 (4)
C(2)–C(1)–C(16 ^h)	121.0 (4)	C(11)–C(10)–C(9)	121.4 (4)
C(6)–C(1)–C(16 ^h)	122.6 (4)	C(10)–C(11)–C(12)	121.8 (4)
C(3)–C(2)–C(1)	122.3 (4)	C(13)–C(12)–C(11)	116.8 (4)
C(2)–C(3)–C(4)	121.7 (4)	C(13)–C(12)–C(15)	122.6 (4)
C(3)–C(4)–C(5)	116.4 (4)	C(11)–C(12)–C(15)	120.6 (4)
C(3)–C(4)–C(7)	120.5 (4)	C(12)–C(13)–C(14)	121.8 (4)
C(5)–C(4)–C(7)	123.1 (4)	C(13)–C(14)–C(9)	121.5 (4)
C(6)–C(5)–C(4)	121.8 (4)	C(12)–C(15)–C(16)	115.0 (4)
C(5)–C(6)–C(1)	121.2 (4)	C(17)–C(17)–C(19)	121.6 (4)
C(4)–C(7)–C(8)	114.5 (4)	C(17)–C(17)–C(18)	120.0 (4)
C(9)–C(8)–C(7)	113.2 (3)	C(19)–C(17)–C(18)	118.4 (3)
C(14)–C(9)–C(8)	116.7 (4)	N(1)–C(18)–C(17)	179.5 (4)
C(14)–C(9)–C(8)	123.1 (4)	N(2)–C(19)–C(17)	178.2 (4)

(not refined). Weighting scheme approximately linear obtained empirically by plotting $(F_o - F_c)^2$ as a function of F_o (Rollett, 1965). Final R values: (I) 2604 reflexions, $R = 0.085$, $R_w = 0.106$, $(\Delta/\sigma)_{\max} = 0.44$, final $\Delta\rho < 0.3 \text{ e } \text{Å}^{-3}$; (II) 1438 reflexions, $R = 0.066$, $R_w = 0.081$, $(\Delta/\sigma)_{\max} = 0.48$, final $\Delta\rho < 0.3 \text{ e } \text{Å}^{-3}$. Atomic scattering factors from *International Tables for X-ray Crystallography* (1974).

Discussion. Final atomic parameters are given in Table 1,* bond distances and angles in Table 2. Fig. 1 shows the conformations of the two complexes.

Conformation of the paracyclophane molecules

In (I), the conformation of the paracyclophane molecule is the same as that observed in 3-PCP and in its complex with Ag^+ (Cohen-Addad *et al.*, 1983). The aromatic rings are not distorted [maximum deviation, 0.02 (6) Å] and are parallel to a threefold pseudo-axis of symmetry and related by this axis (Fig. 2). This is illustrated by the angles between the benzene rings [60 (1)°] and the angles of almost 90° between them and the P plane defined by the barycentres of the rings. The methylene groups exhibit a disorder phenomenon analogous to that observed in 3-PCP. This leads to a shortening effect of the C–C bonds and to high values of the thermal parameters (6 to 7 Å²), the long axes of thermal ellipsoids – 0.5 to 0.6 Å – being perpendicular to the P plane defined above. The torsion angles

* Lists of structure factors, anisotropic thermal parameters, calculated H-atom parameters, torsion angles and mean-plane equations have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 39642 (33 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

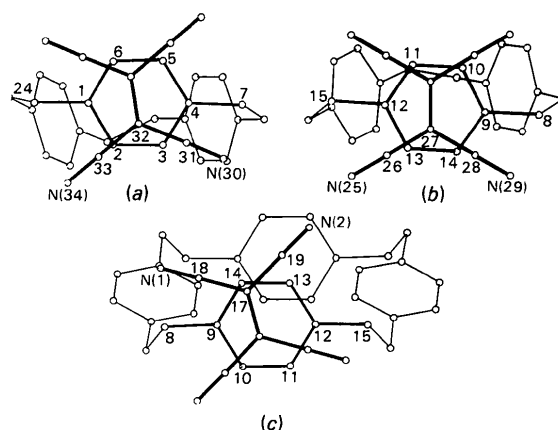


Fig. 1. Conformation of [2.2.2]paracyclophane–TCNE: (a) Projection on the plane C(1)C(2)C(6). (b) Projection on the plane C(11)C(12)C(13), and conformation of [2.2.2]paracyclophane–TCNE. (c) Projection on the plane C(9)C(13)–C(14).

involving methylene bridges are similar to those found in previous studies (Cohen-Addad *et al.*, 1983).

In (II) (Fig. 3), the four aromatic rings are also planar [maximum deviation, 0.01 (4) Å] and situated about a centre of symmetry in a non-planar arrangement. Two of them make an angle of 22 (1)° with the plane defined by the centre of symmetry and the barycentres of the rings. The two others make an angle of 75 (1)° with this plane.

This conformation is less planar than the one found in the related molecule [2.2.2.2]paracyclophane-tetraene (Ljungström, Lindqvist & Wennerström, 1978). No disorder of the methylene bridges is observed and this is in agreement with NMR spectra of 3-PCP

and 4-PCP (Tabushi, Yamada & Kuroda, 1975; Olsson, Tanner, Thulin, Wennerström & Liljefors, 1981). These studies have shown that the barrier of rotation of the ethylene protons is much lower in 3-PCP than in 4-PCP.

TCNE molecules, stacking and charge transfer

In both (I) and (II), the TCNE geometry is identical to that observed in other structures (Bernstein & Trueblood, 1971). In both cases each TCNE molecule lies on a centre of symmetry between two paracyclophane molecules. The overlap between TCNE and the benzene rings is shown in Fig. 1. The angle between the TCNE mean plane and the associated benzene rings is 2° in both (I) and (II). The plane-to-plane distances are 3.3 Å, and the shortest interatomic distances are: (I) C(13)–C(26), C(2)–C(33) 3.321 (7) Å; (II) C(14)–C(17) 3.302 (5) Å. These values, characteristic of TCNE complexes, are similar to those found in [3.3]paracyclophane–TCNE and in [2.2](1,5)-naphthalenoparacyclophane–TCNE (Bernstein & Trueblood, 1971; Prout & Kamenar, 1973; Irngartner & Goldman, 1979).

The relative orientation of donor and acceptor can be characterized by the angle between the C=C double bond in TCNE and the line defined by the two substituted *para*-carbon atoms of the associated benzene rings. In (I), the two independent TCNE molecules have almost identical orientations with angles of 81 and 87°. In (II) this angle is equal to 75°. These results differ from the value of 45° observed in the crystal structure of [3.3]paracyclophane–TCNE (Bernstein & Trueblood, 1971).

The charge-transfer transitions have been investigated in TCNE complexes with *para*-substituted arenes and paracyclophanes in solution (Imashiro *et al.*, 1973; Holder & Thompson, 1972; Mobley, Rieckhoff & Voigt, 1977). They have been interpreted in terms of the molecular conformations corresponding to a maximum overlap for the two highest occupied donor molecular orbitals with the lowest empty TCNE one. One of these conformations is actually observed in (I). However, it was shown that the variation in energy induced by the relative motion of donor and acceptor was small (Kuroda, Amano, Ikemoto & Akamatu, 1967). In the crystal, we believe that steric interactions are the dominating orientational forces stabilizing the TCNE molecules.

In (I), only two of the benzene rings of each paracyclophane molecule are involved in the association with TCNE (*A* and *B* rings in Fig. 2). The threefold pseudo-symmetry is not maintained for the benzene ring–TCNE entity and, consequently, there is no two-dimensional but a one-dimensional stacking between TCNE molecules (Fig. 2). It is approximately directed along a body diagonal, $\mathbf{a} + \mathbf{b} + \mathbf{c}$, which is the needle axis of the crystals. The shortest distance

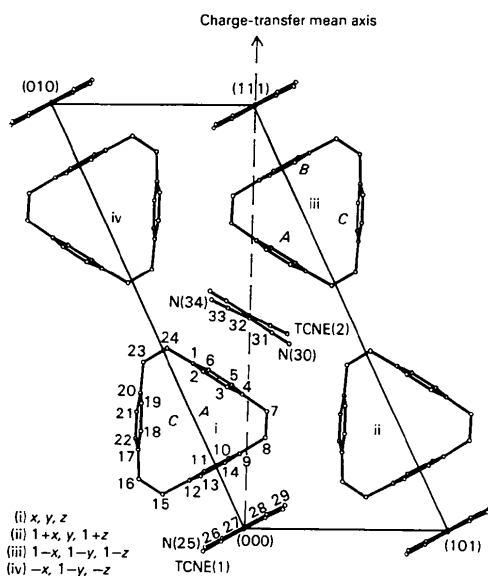


Fig. 2. Intermolecular arrangement in [2.2.2]paracyclophane–TCNE: projection on the plane *P* defined by the phenyl ring barycentres.

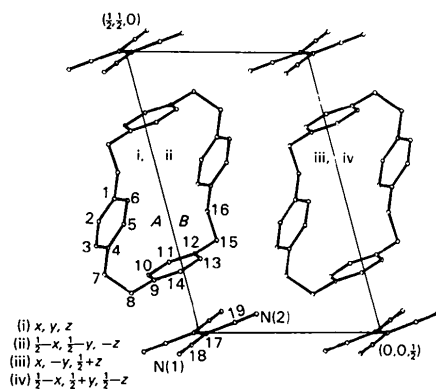


Fig. 3. Intermolecular arrangement in [2.2.2.2]paracyclophane–TCNE: projection on the *ac* plane.

between TCNE molecules along this axis is 10.23 (1) Å. Electrical conduction measurements along the charge-transfer axis did not lead to an observable value. A resistivity higher than 1.5 GΩ cm⁻¹ was found.

In (II), each of the two TCNE molecules related by a centre of symmetry is associated with one of the two non-symmetrically equivalent benzene rings of the paracyclophane molecule (*B* in Fig. 3). This leads to a one-dimensional sandwich-type stacking along a face diagonal, *a* + *b* (Fig. 3). The shortest TCNE–TCNE distance along this axis is 14.15 Å. This sandwich arrangement is identical to that observed in [3.3]-paracyclophane–TCNE (Bernstein & Trueblood, 1971). Contrary to this previous study, no disorder of the TCNE molecules was found in the present compounds. Both of them show normal intermolecular distances involving van der Waals interactions. Other structure studies are in progress.

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Structure of Bis(*o*-chlorophenylaminocarbonylmethyl) Disulphide,* C₁₆H₁₄Cl₂N₂O₂S₂

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Abstract. *M_r* = 401.33, monoclinic, *P*2₁/*c*, *a* = 9.394 (5), *b* = 17.84 (1), *c* = 10.576 (5) Å, β = 91.9 (1)°, *V* = 1771 (1) Å³, *Z* = 4, *D_m* = 1.5, *D_x* =

1.495 g cm⁻³, λ(Mo Kα) = 0.71073 Å, μ = 6.0 cm⁻¹, *F*(000) = 824, *T* = 293 K. Final *R* = 0.031 for 1403 observed reflections. The molecules adopt a folded conformation with non-parallel phenyl rings and are arranged in columns along the screw axis as a result of intermolecular hydrogen bonds [N–H...O distances of

* *N,N'*-Bis(*o*-chlorophenyl)-2,2'-dithiodiacetamide.

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