

Orientalional Disorder in [2.2]Metaparacyclophane and in its Charge-Transfer Complex with Tetracyanoethylene: Crystal Structures and NMR Studies in Solution

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(Received 7 January 1987; accepted 8 May 1987)

Abstract

[2.2]Metaparacyclophane, $C_{16}H_{16}$, (I), undergoes an order-disorder phase transition at 316 K. In the ordered low-temperature structure, studied at 166 K, the space group is $P2_12_12_1$ [$M_r = 208.3$, $a = 11.063$ (4), $b = 11.470$ (4), $c = 18.437$ (7) Å, $V = 2339$ (3) Å³, $Z = 8$, $D_x = 1.18$ Mg m⁻³, Mo $K\alpha$, $\lambda = 0.71093$ Å, $\mu = 0.072$ mm⁻¹, $F(000) = 896$, $R = 0.059$ for 991 reflexions] and there are two independent molecules. In the high-temperature phase, studied at 328 K, the space group is $Pbam$ [$a = 11.370$ (7), $b = 11.736$ (8), $c = 9.213$ (8) Å, $V = 1229$ (3) Å³, $Z = 4$, $D_x = 1.13$ Mg m⁻³, Mo $K\alpha$, $\mu = 0.068$ mm⁻¹, $F(000) = 448$, $R = 0.087$ for 137 reflexions] and the two independent cyclophane molecules occupy on their sites four positions related by a twofold axis and a center of symmetry. Low- and high-temperature structures are closely related to the structure of [2.2]paracyclophane (tetragonal). The charge-transfer complex, [2.2]metaparacyclophane-tetracyanoethylene (1/1), $C_{16}H_{16}.C_6N_4$, (II), crystallizes in the space group $P\bar{1}$ [$M_r = 336.4$, $a = 9.563$ (4), $b = 8.732$ (5), $c = 7.171$ (3) Å, $\alpha = 110.30$ (5), $\beta = 96.70$ (5), $\gamma = 120.00$ (5)°, $V = 454$ (2) Å³, $Z = 1$, $D_x = 1.23$ Mg m⁻³, Mo $K\alpha$, $\mu = 0.081$ mm⁻¹, $F(000) = 176$, $T = 293$ K, $R = 0.067$ for 513 reflexions]. The cyclophane molecule is disordered, the two half-weight molecules being related by a center of symmetry. The averaged structure is isomorphous with those of the complexes of [2.2]- and [3.3]paracyclophane with tetracyanoethylene (TCNE). It is composed of columns in which cyclophane and TCNE molecules are stacked alternately along the a axis. The ¹H and ¹³C NMR spectra of [2.2]metaparacyclophane in solution are completely assigned by one- and two-dimensional techniques. The complete analysis of the

system of the bridge protons is reported and correlated to the structural parameters.

Introduction

This work is part of a series of structural studies of paracyclophanes and their complexes with electron-acceptor molecules such as tetracyanoethylene (TCNE) (Cohen-Addad, Le Bars, Renault & Baret, 1984; Renault & Cohen-Addad, 1985, 1986).

Several crystal structures of cyclophanes containing two benzene rings have been investigated (Keehn & Rosenfeld, 1983) and among them those of [2.2]paracyclophane, [2₂]PCP (Londsdale, Milledge & Rao, 1960; Hope, Bernstein & Trueblood 1972), of [3.3]paracyclophane, [3₂]PCP (Gantzel & Trueblood, 1965), and of [2.2]metacyclophane, [2₂]MCP (Kai, Yasuoka & Kosai, 1977).

[2.2]Metaparacyclophane, [2₂]MPCP (Fig. 1), is of particular interest because of its asymmetry. The stereochemistry of this molecule has been theoretically discussed (Boyd, 1968; Vögtle & Neumann, 1972). In the solid state, a previous study of [2₂]MPCP at room temperature led to a nearly tetragonal structure in which positional parameters could not be refined satisfactorily and large displacement parameters were observed (Crisp, 1968; Maverick, 1985). Since this might be caused by a molecular disorder we undertook a study of the crystal structure as a function of temperature.

In addition, cyclophanes, as donor molecules, form mixed-stack charge-transfer crystals with TCNE (acceptor). In the structures of [2₂]PCP-TCNE and [3₂]PCP-TCNE complexes (Renault & Cohen-Addad, 1986; Bernstein & Trueblood, 1971), the component molecules are alternatively stacked along the needle axis and each TCNE is close to two cyclophane

molecules related by a center of symmetry. In the present work, the structure of $[2_2]$ MPCP-TCNE was undertaken in order to observe the effect of the asymmetry of the $[2_2]$ MPCP molecule on the charge-transfer stacking within the crystal.

In the course of this study we carried out NMR experiments on $[2_2]$ MPCP in solution. Others have discussed the conformational flipping of the *meta* ring at high temperature (Hefelfinger & Cram, 1971; Akabori, Hayashi, Nawa & Shiomi, 1969) and also the transannular electronic interactions between aromatic rings (Tokita, Takemura, Kondo & Mori, 1980). Previous assignments of the ^{13}C chemical shifts of the compound are based on selective decoupling techniques and on comparison with data from the substituted parent compounds (Takemura, Tokita, Kondo & Mori, 1977). The NMR parameters of the aliphatic bridge protons of cyclophanes have seldom been discussed. It seemed desirable to achieve the complete assignment of the proton and ^{13}C NMR spectra by applying one- and two-dimensional techniques.

Experimental

Synthesis and crystallization

$[2_2]$ MPCP, (I), was prepared according to the method previously described (Hefelfinger & Cram, 1971). Colorless crystals were grown from acetone solution by slow evaporation at room temperature; dark-red crystals of $[2_2]$ MPCP-TCNE (II) were grown from a solution of TCNE and (I) in

dichloromethane at 277 K. All crystals were kept in capillaries in order to prevent sublimation.

NMR

NMR spectra were obtained on a Bruker WP80SY (^1H , 80.13 MHz; ^{13}C , 20.15 MHz) and a Bruker AM300 (^1H , 300.1 MHz; ^{13}C , 75.5 MHz) spectrometer. The samples were run in 5 mm o.d. sample tubes. Chemical-shift references were tetramethylsilane (Me_4Si) or the appropriate solvent relatively to Me_4Si . For the measurement of ^1H - ^{13}C shift correlated 2D NMR, spectral widths of 1000 and 8475 Hz were used for dimensions δ_1 and δ_2 . The number of acquisition data points was 512 and digital resolution for the δ_2 axis was 8.3 Hz. Digital resolution for the δ_1 axis was 2.0 Hz. The INADEQUATE spectrum was obtained on a solution of 200 mg of $[2_2]$ MPCP in 3 ml of CDCl_3 in a 10 mm o.d. sample tube. The experiment was conducted at 100.13 MHz on a Bruker AM400 spectrometer. The 2D spectrum was obtained from a $128 \times 1\text{K}$ data matrix. Each FID was obtained from 512 scans with delay of 3 s between scans. The double quantum coherence was obtained from a 6 ms delay corresponding to an average coupling constant of 42 Hz. The spin systems in the one-dimensional proton spectrum were analyzed with the PANIC program (Bruker NMR software).

Differential scanning calorimetry

A Perkin-Elmer DSC-2C instrument was used over the temperature range 100 to 400 K. For (I), a peak assigned to a reversible phase transition was observed at 316 K.

X-ray data collection and treatment

The experimental conditions are summarized in Table 1. Low-temperature studies were performed with a regulated cold N_2 gas flow apparatus mounted on an Explorer camera or on a four-circle diffractometer. No absorption correction was made.

Computational procedures were as follows:

For direct methods, the multisolution *MULTAN* program was used (Germain, Main & Woolfson, 1971).

For least-squares refinements, the quantity $\sum w(F_o - F_c)^2$ was minimized. For the ordered structure (166 K), *ORXFLS* was used (Busing & Levy, 1962) and positional and anisotropic parameters for the C atoms were refined by full-matrix least squares. For H atoms, calculated positions and isotropic displacement parameters (equivalent to those for bonded atoms) were introduced but not refined. A weighting scheme was obtained by plotting $(F_o - F_c)^2$ versus F_o (Rollett, 1965). For the two disordered structures, a rigid-body refinement was applied using *ORION* (André, Fourme & Renaud, 1971). The

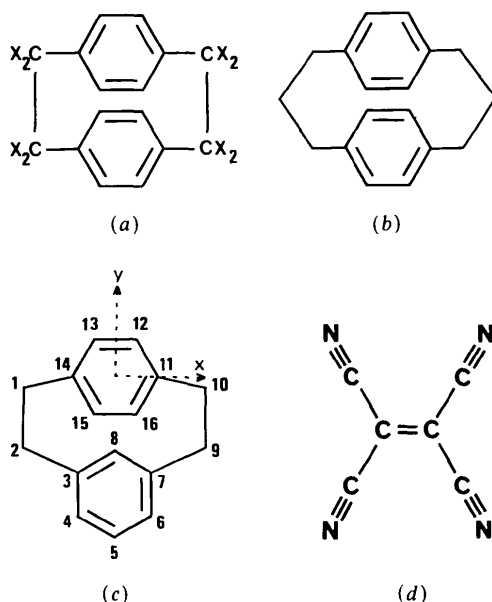


Fig. 1. (a) $[2_2]$ Paracyclophane ($X = \text{H}$) and octafluoro derivative ($X = \text{F}$); (b) $[3_2]$ paracyclophane; (c) $[2_2]$ metaparacyclophane, Cartesian system attached to the molecule and atom numbering; (d) tetracyanoethylene.

Table 1. *Experimental parameters and data treatment*

	[2 ₂]MPCP	[2 ₂]MPCP	[2 ₂]MPCP-TCNE
Temperature	166 K	328 K (transition at 316 K)	293 K
Space group	<i>P</i> 2 ₁ 2 ₁ 2 ₁	<i>Pbam</i>	<i>P</i> 1̄
Cell parameters (Å, °)	<i>a</i> = 11.063 (4), <i>b</i> = 11.470 (4), <i>c</i> = 18.437 (7)	<i>a</i> = 11.370 (7), <i>b</i> = 11.736 (8), <i>c</i> = 9.213 (8)	<i>a</i> = 9.563 (4), <i>b</i> = 8.732 (5), <i>c</i> = 7.171 (3), <i>α</i> = 110.30 (5), <i>β</i> = 96.70 (5), <i>γ</i> = 120.00 (5)
<i>Z</i>	8	4	1
Number of independent molecules	2	2	1
Diffractometer	Nicolet <i>P3F</i>	Enraf-Nonius CAD-4	Nicolet <i>P3F</i>
Radiation		Mo <i>Kα</i> (graphite-monochromatized)	
Scan mode	<i>ω</i>	<i>ω</i>	<i>ω</i>
Crystal size (mm)	0.2 × 0.2 × 0.3	0.2 × 0.2 × 0.3	0.2 × 0.2 × 0.2
Number of reflexions for lattice parameters	25	25	25
Maximum (sin <i>θ</i>)/ <i>λ</i> for data collection (Å ⁻¹)	0.55	0.53	0.48
<i>hkl</i> range	0 → 12, 0 → 12, 0 → 20	0 → 12, 0 → 12, 0 → 9	9̄ → 9, 7̄ → 7, 0 → 7
Number of measured reflexions	1900	508	938
Number of observed reflexions	991 [<i>I</i> / <i>σ</i> (<i>I</i>) ≥ 2]	137 [<i>I</i> / <i>σ</i> (<i>I</i>) ≥ 3]	513 [<i>I</i> / <i>σ</i> (<i>I</i>) ≥ 3]
Check reflexions and variation	024, 024, 310 (2%)	310, 310, 311 (10%)*	310, 310, 301 (2%)
Refinement	Independent atoms	Rigid body	Rigid body
<i>wR</i>	0.043†	0.082‡	0.073‡
Conventional <i>R</i>	0.059	0.087	0.067
Number of varied parameters	145	14	53
(<i>Δ</i> / <i>σ</i>) _{max}	0.7	0.5	0.8
Residual <i>Δρ</i> (e Å ⁻³)	<0.2	<0.2	<0.2
Scattering factors			

International Tables for X-ray Crystallography (1974)

* Decay corresponding to a partial sublimation and corrected by scaling.

† Weighting scheme defined in the text.

‡ *w* = 1; high *R* values owing to disorder.

[2₂]MPCP molecule is assumed to be a rigid group with a coordinate system *S* which is defined in the following way (Fig. 1): the center of the *para*-substituted ring is the origin; the *XY* plane is defined by the four non-substituted C atoms C(12), C(13), C(15), C(16) with the *X* axis perpendicular to the C(12)---C(16) direction. The position of the molecular group in the cell is described by the crystallographic coordinates *u*₁, *u*₂, *u*₃ of the origin of *S*, and the three orientational angles *θ*₁, *θ*₂, *θ*₃. With *S* at the start in coincidence with the conventional orthogonal system (*ABC*) related to the crystallographic system (*abc*), *θ*₁, *θ*₂, *θ*₃ are the angles around *A*, *B* and *C* which bring *S* to its actual orientation in the cell. The following parameters were refined: position of the origin of the group, orientational angles and one isotropic displacement parameter for the group.

Results and discussion

Compound (I)

(a) *Phase transition. Space groups and cell parameters* of low- and high-temperature (LT and HT) phases are reported in Table 1. The LT phase has a pseudo-fourfold axis, as shown by the pseudo-extinction 00*l*, *l* = 4*n* + 2. Above the transition, new extinctions appear (0*kl*, *k* = 2*n* + 1, *h*0*l*, *h* = 2*n* + 1) leading to space groups *Pba*2 or *Pbam*; *c* is divided by two and the pseudo-fourfold axis is still present. From the comparison of LT and HT crystal parameters it can be assumed that, in the HT phase, an orientational disorder of [2₂]MPCP exists around *c*. In the space group *Pba*2 each molecule occupies its site in two

positions related by the twofold axis *c*, with equal occupancies (0.5); there are two independent sites. In the space group *Pbam* the disorder would be described by four orientations on each of two independent sites, each with an occupancy of 0.25. As the LT-phase space group, *P*2₁2₁2₁, is a subgroup of *Pbam* and not of *Pba*2, *Pbam* was chosen for the HT structure.

The LT superstructure reflections decrease continuously as a function of temperature and are weak at room temperature before disappearing at the transition. This phenomenon may explain the difficulties encountered when refining the room-temperature structure which was probably partly disordered (Crisp, 1968); it indicates also that even at rather low temperatures a slight disorder may persist.

(b) *Low-temperature structure* (166 K). Starting from previous results at room temperature (Crisp, 1968), we refined the structure with independent atoms (results in Table 1).

Correlations were found between the two independent molecules, leading to some slightly negative values for displacement parameters. Separate treatment of the two molecules removed these difficulties. These correlations could be explained either by the existence of the pseudo-fourfold axis relating the two independent sites or by a slight disorder which may be present even at 166 K. At this point, two scale factors were introduced in a further refinement, separating the LT superstructure reflections from the others. The parameters and geometries remained unchanged, the two scale factors remained almost identical (0.3% variation), yet the correlations disappeared.

Table 2. Compound (I) at 166 K: fractional atomic coordinates ($\times 10^4$)

E.s.d.'s are given in parentheses. Unprimed: molecule A; primed: molecule B.

	x	y	z	B_{eq}^* (\AA^2)
C(1)	2130 (16)	-219 (14)	3937 (8)	5.1
C(2)	3530 (12)	-358 (14)	3719 (7)	5.0
C(3)	3823 (13)	300 (11)	3034 (8)	4.0
C(4)	4090 (12)	1489 (14)	3055 (7)	4.5
C(5)	4138 (10)	2126 (9)	2426 (10)	3.7
C(6)	3849 (11)	1629 (10)	1766 (7)	3.6
C(7)	3596 (10)	462 (11)	1732 (6)	1.9
C(8)	3677 (11)	-216 (9)	2357 (8)	2.8
C(9)	3047 (13)	-79 (13)	1042 (7)	4.5
C(10)	1679 (12)	66 (14)	1005 (8)	5.3
C(11)	1171 (10)	-4 (12)	1773 (7)	2.9
C(12)	1077 (13)	-1072 (11)	2099 (8)	4.2
C(13)	1190 (13)	-1245 (12)	2835 (10)	4.5
C(14)	1394 (14)	-192 (14)	3255 (9)	3.8
C(15)	1191 (10)	872 (12)	2951 (8)	2.8
C(16)	1084 (11)	960 (10)	2199 (7)	2.9
C(1')	7531 (14)	-554 (13)	1453 (7)	4.9
C(2')	8029 (13)	681 (14)	1249 (8)	5.6
C(3')	7483 (13)	1109 (11)	538 (7)	3.7
C(4')	6331 (17)	1626 (12)	526 (9)	5.0
C(5')	5767 (11)	1839 (11)	-137 (12)	5.2
C(6')	6247 (14)	1448 (12)	-760 (8)	3.5
C(7')	7397 (12)	917 (11)	-754 (7)	3.6
C(8')	8031 (9)	862 (9)	-116 (7)	2.7
C(9')	7841 (14)	312 (13)	-1429 (8)	5.2
C(10')	7380 (14)	-977 (13)	-1492 (7)	5.8
C(11')	7301 (13)	-1516 (11)	-738 (7)	3.1
C(12')	8318 (12)	-1781 (10)	-347 (10)	3.3
C(13')	8423 (13)	-1657 (12)	397 (10)	4.0
C(14')	7407 (12)	-1230 (12)	772 (8)	3.1
C(15')	6312 (12)	-1261 (9)	390 (7)	2.4
C(16')	6254 (13)	-1328 (10)	-354 (7)	3.9

$$* B_{eq} = 8\pi^2(U_1 U_2 U_3)^{2/3}.$$

The coordinates are given in Table 2, distances and angles in Table 3.*

The conformations and numbering schemes of the two independent molecules are shown in Fig. 2. Both are nearly mirror symmetric, as calculated by Boyd (1968) and as already observed in triple-layered metaparacyclophanes (Koizumi, Toyoda, Kasai & Misumi, 1985). Some bond lengths reported in Table 3 show discrepancies from conventional values. This was also the case in the room-temperature structure (Crisp, 1968); in that study some discrepancies were even larger [see Appendix in Crisp (1968)].

Benzene rings are boat shaped (Table 4). The intermolecular arrangement is shown in Fig. 3.

(c) *High-temperature structure.* A rigid-body refinement was performed in which a model molecule of $[2_2]$ MPCP was built from both LT structure results and theoretical calculations (Boyd, 1968). In this model, the molecule is assumed to have a mirror plane perpendicular to the X axis as shown in Fig. 1. Its coordinates in \AA are given in Table 5.

As indicated in (a), in the space group $Pb3m$, two groups corresponding to the two independent

* Lists of H-atom coordinates, anisotropic displacement parameters, crystallographic coordinates within molecular groups, mean-plane equations and F_o and F_c have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 43972 (19 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 3. 166 K structure of compound (I): interatomic distances (\AA), valence and torsion angles ($^\circ$)

E.s.d.'s are given in parentheses.

	Molecule A	Molecule B
C(1)-C(2)	1.61 (2)	1.57 (2)
C(1)-C(14)	1.50 (2)	1.48 (2)
C(2)-C(3)	1.51 (2)	1.52 (2)
C(3)-C(4)	1.40 (2)	1.41 (2)
C(3)-C(8)	1.39 (2)	1.38 (2)
C(4)-C(5)	1.37 (2)	1.39 (2)
C(5)-C(6)	1.38 (2)	1.34 (2)
C(6)-C(7)	1.37 (2)	1.41 (2)
C(7)-C(8)	1.39 (2)	1.37 (2)
C(7)-C(9)	1.54 (2)	1.51 (2)
C(9)-C(10)	1.52 (2)	1.57 (2)
C(10)-C(11)	1.53 (2)	1.52 (2)
C(11)-C(12)	1.37 (2)	1.37 (2)
C(11)-C(16)	1.36 (2)	1.38 (2)
C(12)-C(13)	1.38 (2)	1.38 (2)
C(13)-C(14)	1.45 (2)	1.41 (2)
C(14)-C(15)	1.36 (2)	1.40 (2)
C(15)-C(16)	1.40 (2)	1.38 (2)
C(14)-C(1)-C(2)	108 (1)	108 (1)
C(1)-C(2)-C(3)	112 (1)	111 (1)
C(2)-C(3)-C(8)	121 (1)	121 (1)
C(2)-C(3)-C(4)	121 (1)	121 (1)
C(8)-C(3)-C(4)	118 (1)	118 (1)
C(3)-C(4)-C(5)	120 (1)	120 (1)
C(4)-C(5)-C(6)	121 (1)	121 (1)
C(5)-C(6)-C(7)	119 (1)	120 (1)
C(6)-C(7)-C(8)	120 (1)	119 (1)
C(6)-C(7)-C(9)	121 (1)	119 (1)
C(8)-C(7)-C(9)	119 (1)	121 (1)
C(3)-C(8)-C(7)	121 (1)	121 (1)
C(7)-C(9)-C(10)	113 (1)	113 (1)
C(9)-C(10)-C(11)	109 (1)	110 (1)
C(10)-C(11)-C(12)	119 (1)	122 (1)
C(10)-C(11)-C(16)	121 (1)	117 (1)
C(11)-C(12)-C(13)	124 (1)	125 (1)
C(12)-C(11)-C(16)	118 (1)	117 (1)
C(12)-C(13)-C(14)	115 (1)	117 (1)
C(1)-C(14)-C(13)	121 (1)	122 (1)
C(1)-C(14)-C(15)	117 (1)	121 (1)
C(13)-C(14)-C(15)	120 (1)	116 (1)
C(14)-C(15)-C(16)	119 (1)	123 (1)
C(11)-C(16)-C(15)	121 (1)	119 (1)
C(2)-C(3)-C(4)-C(5)	-168 (1)	-170 (1)
C(5)-C(6)-C(7)-C(9)	169 (1)	170 (1)
C(7)-C(9)-C(10)-C(11)	-34 (2)	-35 (2)
C(10)-C(11)-C(12)-C(13)	148 (1)	143 (1)
C(12)-C(13)-C(14)-C(1)	-149 (1)	-151 (1)
C(14)-C(1)-C(2)-C(3)	36 (2)	37 (2)

molecules were introduced with an occupancy factor of 0.25 and isotropic thermal parameters. In the starting set, the groups were given the positions and orientations found for the two molecules in the LT structure. Some correlations were observed between θ_1 and θ_3 angles of the same group. Refining them separately in several cycles, we obtained the final R values reported in Table 1. The parameters are given in Table 6. On each site, of local symmetry $2/m$, the molecules take four orientations; this leads to a time-averaged occupancy of high symmetry.

The molecular disorder is shown in Fig. 3. In space group $Pba2$, a refinement led to very similar results and it is not possible to distinguish between the two groups from refinement criteria.

Normal intermolecular contacts are observed for both LT and HT phases.

(d) *Comparison with structures of $[2_2]$ PCP and related compounds.* LT and HT structures of (I) are strongly related to the structure of $[2_2]$ PCP (Hope *et al.*, 1972). From the pseudo-tetragonal cell

Table 4. 166K structure of compound (I): phenyl-ring characteristics and comparison with [2₂]metacyclophane and [2₂]paracyclophane

	meta-Substituted ring		[2 ₂]Metacyclophane*
	[2 ₂]MPCP	[2 ₂]MPCP	
α ₁ (°)	12 (A)	12 (B)	15.4
α ₂ (°)	12	11	
β ₁ (°)	9	10	11.8
δ(°)	4	6	3.4

	para-Substituted ring		[2 ₂]Paracyclophane†
	[2 ₂]MPCP	[2 ₂]MPCP	
α ₃ (°)	13 (A)	9 (B)	13
α ₄ (°)	14	15	
β ₂ (°)	13	20	11
β ₃ (°)	15	11	

Plane-to-plane distance q (Å)		
[2 ₂]MPCP = 3.08	[2 ₂]Metacyclophane = 2.69	[2 ₂]Paracyclophane = 3.09

α₁ = angle between the 3, 4, 6, 7 plane and the 2-3 bond vector.
 α₂ = angle between the 3, 4, 6, 7 plane and the 7-9 bond vector.
 β₁ = angle between the 3, 7, 8 and 3, 4, 6, 7 planes.
 δ = angle between the 4, 5, 6 and 3, 4, 6, 7 planes.
 α₃ = angle between the 12, 13, 15, 16 and 11, 12, 16 planes.
 α₄ = angle between the 12, 13, 15, 16 and 13, 14, 15 planes.
 β₂ = angle between the 11, 12, 16 plane and the 11-10 bond vector.
 β₃ = angle between the 13, 14, 15 plane and the 1-14 bond vector.

* From Kai *et al.* (1977).

† From Hope *et al.* (1972).

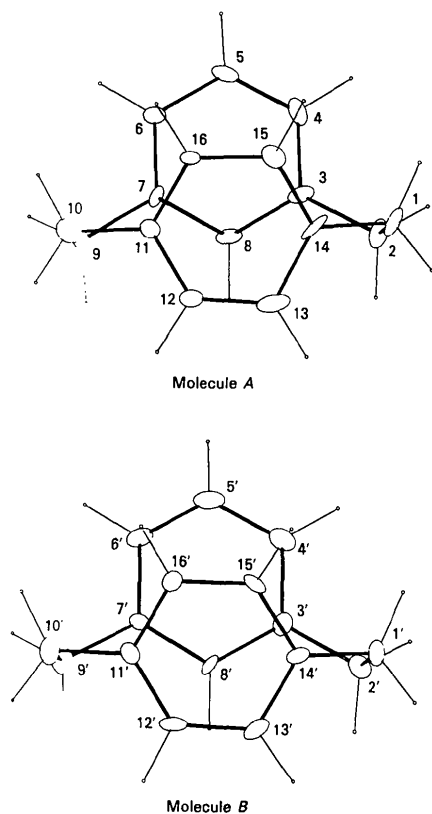


Fig. 2. Compound (I) at 166 K: plane projection defined by C(12), C(15), C(16) for molecule A and C(12'), C(15'), C(16') for molecule B. The thermal ellipsoids are drawn at 50% probability.

represented with dashed lines in Fig. 3, the structure of [2₂]MPCP is similar to that of [2₂]PCP, as shown in the figure. The following parameters: $a' = \frac{1}{2}(a + b) = 7.968$ (5), $c' = c/2 = 9.128$ (3) Å (LT); $a' = \frac{1}{2}(a + b) = 8.170$ (8), $c' = c = 9.213$ (3) Å (HT) are close to the cell parameters of [2₂]PCP ($a = 7.781$, $c = 9.290$ Å).

A comparison can also be made with the structures of an octafluoro derivative of [2₂]PCP (Hope *et al.*, 1972) and of [3₂]PCP (Gantzel & Trueblood, 1965). These structures, monoclinic ($P2_1/n$) and practically isomorphous, present an arrangement similar to that observed in the [2₂]PCP structure (cell parameters are: $a = 7.994$, $b = 7.986$, $c = 10.855$ Å, $\beta = 97.85^\circ$

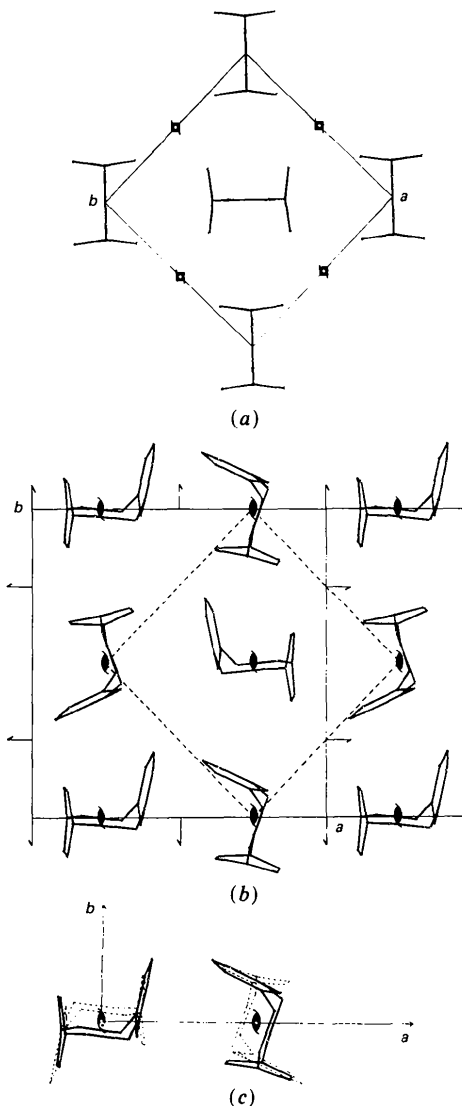


Fig. 3. Compound (I): cell projections on the *ab* plane and comparison with [2₂]paracyclophane. (a) [2₂]Paracyclophane; the fourfold axes are shown. (b) LT structure of compound (I); half the cell in the *c* direction is shown. (c) HT structure of compound (I) and disorder; because of the symmetry, the four orientations are superimposed on two positions in the projection.

Table 5. Orthogonal coordinates (Å) of the model molecule of [2₂]MPCP used for rigid-body refinement

	X	Y	Z
C(1)	-2.73	0.05	0.87
C(2)	-2.52	-0.14	2.41
C(3)	-1.22	0.55	2.87
C(4)	-1.20	1.91	3.17
C(5)	0.00	2.57	3.37
C(6)	1.20	1.91	3.17
C(7)	1.22	0.55	2.87
C(8)	0.00	-0.14	2.84
C(9)	2.52	-0.14	2.41
C(10)	2.73	0.05	0.87
C(11)	1.38	0.00	0.17
C(12)	0.71	-1.20	0.00
C(13)	-0.71	-1.20	0.00
C(14)	-1.38	0.00	0.17
C(15)	-0.71	1.20	0.00
C(16)	0.71	1.20	0.00
H(1a)	-3.19	1.02	0.69
H(1b)	-3.36	-0.76	0.50
H(2a)	-3.36	0.31	2.94
H(2b)	-2.46	-1.21	2.63
H(4)	-2.07	2.42	3.23
H(5)	0.00	3.53	3.66
H(6)	2.07	2.42	3.23
H(8)	0.00	-1.16	2.80
H(9a)	3.36	0.31	2.94
H(9b)	2.46	-1.21	2.63
H(10a)	3.19	1.02	0.69
H(10b)	3.36	0.31	2.94
H(12)	1.21	-2.07	0.04
H(13)	-1.21	-2.07	0.04
H(15)	-1.21	2.07	0.04
H(16)	1.21	2.07	0.04

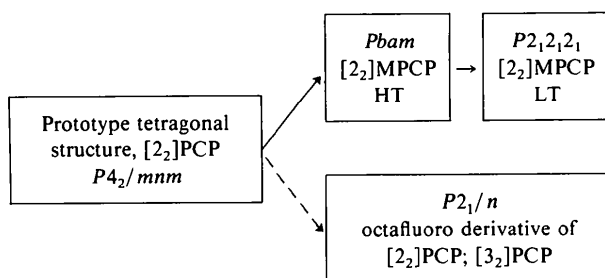
Table 6. High-temperature structure of compound (I): parameters of the molecular groups

Coordinates in Å are given in Table 5 and crystallographic coordinates have been deposited.

	Molecule A	Molecule B
θ_1	140.1 (3)	157.6 (3)
θ_2	83.6 (8)	82.9 (5)
θ_3	139.9 (3)	-125.3 (3)
u_1	-0.138 (2)	0.508 (2)
u_2	-0.030 (2)	-0.143 (2)
u_3	0.497 (4)	0.028 (4)
B_8 (Å ²)	9.3 (5)	9.1 (5)
m	0.25	0.25

and $a = 9.715$, $b = 8.138$, $c = 8.524$ Å, $\beta = 90.70^\circ$, respectively).

The relationships between all these structures are summarized in the following way:



Compound (II)

The structure was solved by *MULTAN*. Because of the particular geometry of the molecules, the use of molecular groups in the normalization process led to a complicated non-interpretable Fourier map.

Table 7. Parameters of the rigid group, fractional atomic coordinates of TCNE ($\times 10^3$) and interatomic distances (Å) and bond angles ($^\circ$) for TCNE

E.s.d.'s are given in parentheses. Coordinates in Å are given in Table 4; crystallographic coordinates for metaparacyclophane have been deposited.

[2 ₂]MPCP					
Parameters of the rigid group					
θ_1	93.7 (1) ^o	u_1	-0.162 (2)	m	0.5
θ_2	-73.9 (1) ^o	u_2	-0.513 (1)	B	4.5 (1) Å ²
θ_3	92.2 (1) ^o	u_3	0.013 (1)		

TCNE					
	x	y	z	B_{eq} * (Å ²)	
C(17)	501 (2)	467 (2)	68 (1)	4.5	
C(18)	588 (2)	604 (2)	297 (1)	4.8	
C(19)	416 (2)	252 (2)	-6 (1)	5.6	
N(1)	655 (2)	703 (2)	474 (1)	6.6	
N(2)	356 (2)	94 (2)	44 (1)	8.4	

Distances and angles

C(17)-C(17 ⁱ)	1.29 (3)	C(18)-N(1)	1.13 (1)
C(17)-C(18)	1.46 (1)	C(19)-N(2)	1.10 (2)
C(17)-C(19)	1.47 (2)		
C(18)-C(17)-C(17 ⁱ)	121 (1)	C(17)-C(18)-N(1)	177 (2)
C(19)-C(17)-C(17 ⁱ)	120 (1)	C(17)-C(19)-N(2)	174 (1)
C(18)-C(17)-C(19)	118 (1)		

Symmetry code: (i) $1 - x, 1 - y, -z$.

$$* B_{eq} = 8\pi^2(U_1U_2U_3)^{2/3}$$

When the chemical formula only was introduced in the normalization, the correct structure was obtained. Statistics on the whole data led to a centrosymmetric structure. Both cyclophane and TCNE were found to be on a center of symmetry. This leads to a disorder of [2₂]MPCP on its site, with two orientations related by the center of symmetry.

A rigid-body refinement was performed, in which the molecule of [2₂]MPCP was treated as a group with an isotropic displacement factor and TCNE described by independent atoms with anisotropic displacement parameters. *R* values are given in Table 1, coordinates, distances and angles in Table 7. The center of symmetry relating the two orientations of the [2₂]MPCP molecule is located on the mirror plane of the molecule. Then the disorder can be described by a twofold axis perpendicular to the mirror. It is geometrically identical to that found in the HT phase of [2₂]MPCP. However, because of steric hindrance in the complex, the disorder is more probably static rather than dynamic. Owing to the [2₂]MPCP disorder, the effect of the complexation on its conformation cannot be discussed. If the disorder which affects the donor sublattice is taken into account, the acceptor, TCNE, is in charge transfer with either two *para*-substituted or two *meta*-substituted rings or one *para*- and one *meta*-substituted one. The overlap between TCNE and the benzene rings is shown in Fig. 4. The TCNE molecules are almost parallel to the associated phenyl rings with dihedral angles of 4° (*para* ring) and 9° (*meta* ring). The plane-to-plane averaged distances are 3.3 Å, similar to those found in [2₂]PCP-TCNE and other cyclophane-TCNE complexes (Renault & Cohen-Addad, 1986). The shortest

interatomic distances are C(15)---C(19) 3.13 (1) and C(5)---C(19) 3.11 (1) Å. The relative orientations of donor and acceptor can be characterized by the angle between the C=C double bond of TCNE and the disubstituted axis of the rings [C(3)---C(7) and C(11)---C(14)]. Its value is 65° in both cases. The stacking of the molecules is shown in Fig. 5.

[2₂]MPCP and TCNE molecules are stacked alternately in columns along the *a* axis in a sandwich arrangement. This is identical to the stacking observed in the structures of [3₂]PCP-TCNE and [2₂]PCP-TCNE (Bernstein & Trueblood, 1971; Renault & Cohen-Addad, 1986). The three structures are isomorphous (considering a cell with the *a* axis as the *a* + *b* diagonal in the two latter compounds). The TCNE-TCNE distances are very similar in the three cases with values of 9.56, 9.63 and 9.37 Å for [2₂]MPCP-,

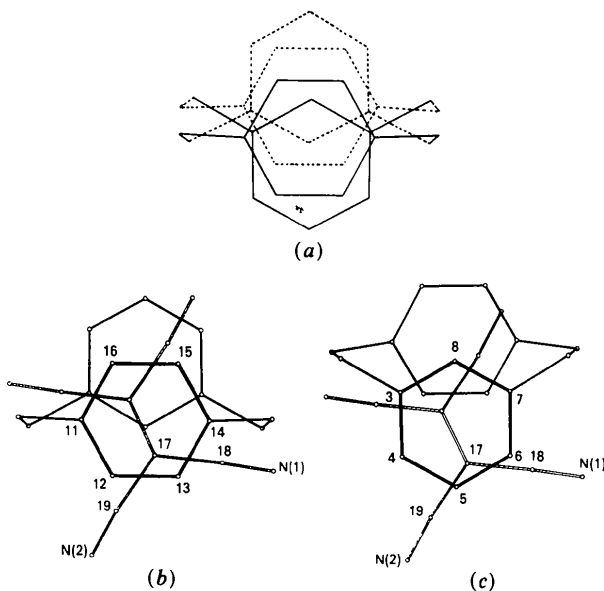


Fig. 4. Structure of compound (II). (a) Disorder of the [2₂]metaparacyclophane molecule, projection on the *XY* plane. (b) Overlap between TCNE and the *para*-substituted ring, plane projection defined by C(12), C(15), C(16). (c) Overlap between TCNE and the *meta*-substituted ring, plane projection defined by C(4), C(6), C(7).

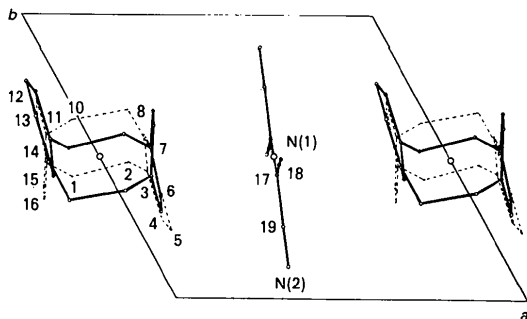
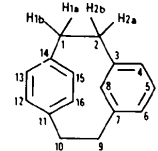


Fig. 5. Structure of compound (II): projection on the *ab* plane.

Table 8. ¹H and ¹³C NMR data for [2₂]MPCP

<i>J</i> (H,H)(Hz)				
1 <i>a</i> , 1 <i>b</i>	-12.1			
1 <i>a</i> , 2 <i>a</i>	0.6			
1 <i>a</i> , 2 <i>b</i>	7.6			
1 <i>b</i> , 2 <i>a</i>	7.0			
1 <i>b</i> , 2 <i>b</i>	10.9			
2 <i>a</i> , 2 <i>b</i>	-12.1			
δ H(p.p.m.)		δ ¹³ C(p.p.m.)		¹ <i>J</i> (¹³ C,H)(Hz)
H(1 <i>a</i>)	3.12	C(1)	38.28	129.7
H(1 <i>b</i>)	2.51	C(2)	37.09	129.2
H(2 <i>a</i>)	2.73	C(3)	140.91	—
H(2 <i>b</i>)	2.15	C(4)	125.19	162.0
H(4)	6.70	C(5)	127.37	159.0
H(5)	6.90	C(8)	133.69	156.0
H(8)	5.37	C(13)	130.23	162.0
H(13)	7.13	C(14)	138.82	—
H(15)	5.79	C(15)	128.84	158.5

[3₂]PCP- and [2₂]PCP-TCNE complexes, respectively.

Very weak diffuse intensities leading to a parameter *a*' = 2*a* were observed on films; it may correspond to a local order of the [2₂]MPCP molecule but this effect was too small to be studied. These intensities do not vary with the temperature. But we observed that crystallization at low temperature led to a more important effect, the superstructure reflexions becoming more intense.

As in (I), normal intermolecular distances were observed.

NMR

In the following discussion we will use the molecular numbering defined for the X-ray structure study. For the molecule under study, the number of signals characterized by different chemical shifts in the proton-decoupled ¹³C NMR spectrum is compatible with *C_s* symmetry. In solution, the molecule can be described as in the solid state with a symmetry plane passing through C(5), C(8) and the middle of the C(12)—C(13) and C(15)—C(16) bonds, and perpendicular to the aromatic rings.

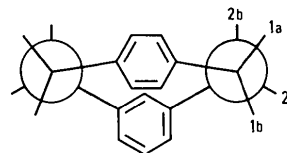
The 300 MHz proton NMR spectrum of [2₂]MPCP shows well separated resonances for each proton. The aromatic protons are readily distinguished and unambiguously assigned after analysis (Table 8). The location of H(13) and H(15) was confirmed later on by homonuclear Overhauser enhancement (NOE) experiments. The *ABCD* system of the methylene protons is analyzed by means of homonuclear decoupling experiments followed by an iterative analysis. The results are given in Table 8. The relative spatial locations of the methylene groups are determined by NOE difference spectroscopy. Irradiation of the signal at 5.79 p.p.m. causes a strong enhancement of the multiplet at 2.51 p.p.m. and allows the latter to be assigned to the methylene proton close in space to the H(15) aromatic proton. This fixes the location of the CH(1*a*)H(1*b*) methylene group bond to the *para* aromatic ring. Similarly, NOE between

the signals at 6.70 and 2.73 p.p.m. demonstrates the close spatial relationship of the remaining CH(2a)H(2b) methylene protons and the *meta* aromatic ring. Furthermore, irradiation of H(13) shows enhancement of the H(8) signal, indicative of the proximity of H(13) and H(8).

The assignment of the ^{13}C NMR spectrum can be obtained by using the two-dimensional ^1H - ^{13}C shift correlation method (Bax & Morris, 1981; Benn & Günther, 1983). From the correlation peaks we are able to identify the proton-bearing C atoms. The aliphatic part of the shift correlation map allows the assignment of the methylene C-atom signals. Moreover, the 2D spectrum shows which protons form methylene pairs, and this agrees with the conclusion depicted above from the analysis of the *ABCD* proton system. The results are reported in Table 8 together with the $^1J(^{13}\text{C}, ^1\text{H})$ coupling values determined from the gated decoupling ^{13}C spectrum. The quaternary C-atom resonances are assigned by using a two-dimensional ^{13}C homonuclear correlated NMR experiment. The INADEQUATE sequence gives 2D spectra with correlation peaks corresponding to coupling of directly bonded ^{13}C - ^{13}C atoms (Benn & Günther, 1983; Bax, Freeman & Frenkiel, 1981). The low-field quaternary C atom is directly connected to C(4) and C(8) whereas the other is connected to C(13) and C(15). They are respectively assigned to the *meta* C(3) and *para* C(14) atoms (Table 8). These results are in agreement with the assignments reported by Takemura *et al.* (1977).

The molecular structure of MPCP in the solid state shows that it is considerably strained and that the aryl rings are strongly bent. The assignment of the stereochemistry of $[2_2]\text{MPCP}$ in solution is relatively straightforward. Steric hindrance leads to a conformation similar to the one observed in the solid state. At room temperature the rigidity of the molecule is evidenced by the non-equivalence of the H(15) and H(13) protons and the C(15) and C(13) C atoms. The high field shifts observed for the H(8) and H(15) aromatic protons are due to the ring-current effects of the opposite benzene ring extended over them (Akabori *et al.*, 1969). The conformational mobility of the *meta* ring is detectable only at high temperature. In this connection, the analysis of the methylene-bridge protons gives rise to the conformation around the C(1)-C(2) bond, which can be correlated to the structural parameters determined in the solid state. Although ring bending and steric compression may affect the conformational dependence of the geminal and vicinal H,H coupling constants, Karplus relationships (Karplus, 1963) support the results shown in Table 8. The geminal H,H couplings are equal and in the range of what can be expected for this compound (Hopf, Mlynek, El-Tamany & Ernst, 1985). Of the vicinal H,H couplings, one value is close to zero [$^3J(1a, 2a) = 0.6$ Hz], indicative of a

torsional angle H(1a)CCH(2a) close to 90° . Torsional angles between the four protons of the C(1)-C(2) bridge have been calculated from the solid-state molecular structure determination. For this purpose, the H atoms were positioned on the basis of an ideal geometry. Therefore the torsion-angle values are only approximately estimated.



An average value of 85° is obtained for the H(1a)CCH(2a) dihedral angle, in accordance with the corresponding $^3J(1a, 2a)$ determined in solution. The largest dihedral angle, 156° , is found for H(1b)CCH(2b), for which $^3J(1b, 2b)$ is 10.9 Hz. The two remaining dihedral-angle values (33 and 38°) are also in agreement with the corresponding 3J values [$^3J(1a, 2b) = 7.6$ Hz and $^3J(1b, 2a) = 7.0$ Hz, respectively]. Despite the caution that must be used in the application of the Karplus relationship, our results are consistent with the existence of similar structures in the solid state and in solution at room temperature. Between $[2_2]\text{MPCP}$ and its complex with TCNE, no significant changes in the spectral pattern were observable at room temperature.

Concluding remarks

In the solid state, disorder of $[2_2]\text{metaparacyclophane}$ is observed for both structures of the non-complexed cyclophane and that of its charge-transfer complex with TCNE. This disorder is geometrically similar in the two structures, but probably of dynamic nature in the first case and static in the second case. The LT and HT structures of $[2_2]\text{MPCP}$ (pseudo-tetragonal) are strongly related to that of $[2_2]\text{PCP}$. This analogy is strengthened in the corresponding cyclophane-TCNE complexes which are isomorphous. In solution, complementary 1D and 2D NMR studies allow the unambiguous assignment of the ^1H and ^{13}C resonances of $[2_2]\text{MPCP}$. The analysis of the methylenic protons gives $J(\text{H,H})$ coupling-constant values in agreement with the conformation observed in the solid state. The $[2_2]\text{MPCP}$ -TCNE complex gives no significant changes in the spectral pattern.

Thanks are due to Professor P. Baret for his interest in this work. We are indebted to Professor K. N. Trueblood and to Dr E. Maverick for communication of preliminary results and very enlightening comments. M. Bardet and G. D'Assenza are gratefully acknowledged for their skillful technical assistance. X-ray data were collected within the Groupement Grenoblois de Diffractométrie. The 300 and 400 MHz

spectra were recorded at the Centre Grenoblois de Résonance Magnétique.

Note added in proof: Corresponding to the recommendations of a referee, we report that an analysis of the anisotropic atomic displacement (Shoemaker & Trueblood, 1984), recently performed on the LT structure of [2₂]MPCP (Maverick, 1987), indicates residual disorder in both molecules. Poor agreement is obtained with a rigid-body motion model. The rigid-bond test (Hirshfeld, 1976) shows differences of mean-square-displacement amplitudes along bonded directions of up to seven times the r.m.s. standard deviation of U_{obs} .

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