

Fig. 2. Packing diagram viewed down the z axis showing hydrogen bonding between molecules in the unit cell.

196.42 and 25.72° respectively. The conformation about the C(4')–C(5') bond is *gauche-gauche* with torsion angles $\varphi_{OO}[O(5')-C(5')-C(4')-O(4')]$ and $\varphi_{OC}[O(5')-C(5')-C(4')-C(3')]$ –67.5 (5) and 51.0 (5)° respectively.

Dioxolane ring. The dioxolane ring assumes O(3')-*endo* geometry with torsional angle C(10)–O(2')–C(2')–C(3') = 6.0 (4)° and O(3') displaced by –0.530 (4) Å. The pseudorotation parameters for the dioxolane ring are $P = -45.49$ and $\tau_{m,max} = 38.43$ °.

Molecular packing. The crystal structure shows no base stacking in contrast to other guanosine-containing crystals where stacking of bases is normally observed.

The structure is stabilized by three hydrogen bonds as shown in Fig. 2. Molecules related by $(x - \frac{1}{2}, -y + \frac{1}{2}, -z + 1)$ form two hydrogen bonds [N(1)–H...N(7) = 2.801 (4) Å, 166.0°; N(2)–H...O(6) = 2.887 (4) Å, 167.9°]. The third bond [N(2)–H...O(1) = 2.941 (5) Å, 170.5°] involves the O(1) atom of the solvent Me₂SO molecule related by $x - 1, y, z$.

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References

- CROMER, D. T. & WABER, J. T. (1965). *Acta Cryst.* **18**, 104–109.
 GAUTHAM, N., SESHADRI, T. P. & VISWAMITRA, M. A. (1983). *Acta Cryst.* **C39**, 456–458.
 GAUTHAM, N., SESHADRI, T. P., VISWAMITRA, M. A. & SALISBURY, S. A. (1983). *Acta Cryst.* **C39**, 459–461.
 IUPAC–IUB JOINT COMMISSION ON BIOCHEMICAL NOMENCLATURE (1983). *Eur. J. Biochem.* **131**, 9–15.
 KATTI, S. K., SESHADRI, T. P. & VISWAMITRA, M. A. (1981). *Acta Cryst.* **B37**, 407–410.
 MAIN, P., FISKE, S. J., HULL, S. E., LESSINGER, L., GERMAIN, G., DECLERCQ, J.-P. & WOOLFSON, M. M. (1980). *MULTAN80. A System of Computer Programs for the Automatic Solution of Crystal Structures from X-ray Diffraction Data*. Univs. of York, England, and Louvain, Belgium.
 SHELDRIK, G. M. (1976). *SHELX76*. Program for crystal structure determination. Univ. of Cambridge, England.
 STEWART, R. F., DAVIDSON, E. R. & SIMPSON, W. T. (1965). *J. Chem. Phys.* **42**, 3175–3187.
 VISWAMITRA, M. A. & GAUTHAM, N. (1984). *Proc. Indian Acad. Sci.* **93**, 3, 261–269.

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Structure of the 1/1 Complex of [2.2]Metacyclophane* with Tetracyanoethylene

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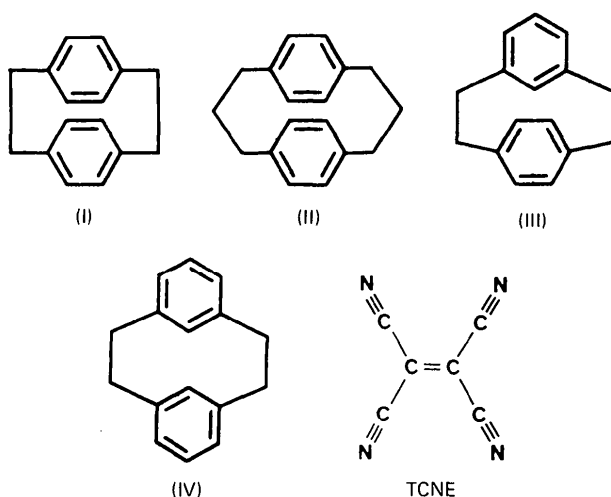
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Abstract. C₁₆H₁₆·C₆N₄, $M_r = 336.4$, triclinic, $P\bar{1}$, $a = 9.380$ (4), $b = 8.700$ (5), $c = 6.888$ (4) Å, $\alpha = 102.20$ (5), $\beta = 99.60$ (5), $\gamma = 119.70$ (5)°, $V = 452$ (1) Å³, $Z = 1$, $D_x = 1.23$ Mg m⁻³, $\lambda(\text{Mo K}\alpha) = 0.71093$ Å, $\mu = 0.081$ mm⁻¹, $F(000) = 176$, $T = 243$ K. The structure was refined to a wR value of

0.062 for 589 observed intensities. The structure is isomorphous to those of the related compounds, charge-transfer complexes of [2.2]paracyclophane, [3.3]paracyclophane and [2.2]metaparacyclophane with tetracyanoethylene (TCNE). The molecules of [2.2]metacyclophane and TCNE are on centers of symmetry and are alternately stacked along the a axis, as in the three compounds mentioned above.

* [2.2]Metabenzenophane.

Introduction. Cyclophanes (donors) form mixed-stack charge-transfer crystals with acceptor tetracyanoethylene (TCNE). In previous studies, structures of several cyclophanes containing two benzene rings, and of their complexes with TCNE, were investigated: [2.2]paracyclophane (I), [3.3]paracyclophane (II), [2.2]metaparacyclophane (III) (Gantzel & Trueblood, 1965; Bernstein & Trueblood, 1971; Hope, Bernstein & Trueblood, 1972; Renault & Cohen-Addad, 1986; Renault, Cohen-Addad, Lajzerowicz-Bonneteau, Dutasta & Crisp, 1987). The structure of [2.2]-metacyclophane (IV) has also been determined (Kai, Yasuoka & Kosai, 1977). In the present work, the structure of the complex of [2.2]metacyclophane with TCNE is investigated in order to compare it with the structures of the above related compounds and to study the effect of complexation on the cyclophane conformation.



Experimental. [2.2]Metacyclophane was obtained in good yield by a two-step synthesis:

- coupling of 1,3-bis(bromomethyl)benzene and 1,3-bis(mercaptomethyl)benzene by potassium hydroxide in ethanol gave 2,11-dithia[3.3]metacyclophane;
- photoextrusion of sulfur by irradiation of the dithiacyclophane in triethyl phosphite with a high-pressure mercury lamp under a nitrogen atmosphere led to [2.2]metacyclophane (IV).

Orange-red crystals of (IV)-TCNE were grown from a solution of (IV) and TCNE in dichloromethane at 277 K. During experiments, the crystals were kept in capillaries in order to prevent sublimation.

Differential scanning calorimetry

A Perkin-Elmer DSC-2C instrument was used over the range 100–400 K. A peak corresponding to a reversible phenomenon was observed for (IV)-TCNE at 323 K.

X-ray measurements

X-ray studies were first performed on (IV)-TCNE with an Explorer Camera as a function of the temperature. Any evidence of structural phase transition could not be shown. Therefore, in order to avoid any disorder problems, it was decided only to study the structure at low temperature. X-ray data collected at 223 K on a Nicolet P3F four-circle diffractometer. Low-temperature device made of a regulated cold N₂ gas flow. Crystal 0.2 × 0.2 × 0.2 mm. Graphite-monochromatized Mo K α radiation, ω -scan mode, no absorption correction. Lattice parameters refined with 23 reflexions, $11 < 2\theta < 17^\circ$. 589 independent reflexions with $I/\sigma(I) > 3.0$ (1200 measured reflexions), $(\sin\theta)/\lambda \leq 0.52 \text{ \AA}^{-1}$, $hkl, \bar{h}kl, \bar{h}\bar{k}l, h\bar{k}l$, $h: -9$ to 9 , $k: -8$ to 8 , $l: 0$ to 7 . Standard reflexions: $2\bar{1}1, \bar{2}1\bar{1}, 3\bar{1}0$ (2% variation). Structure solved with multiresolution direct methods (Germain, Main & Woolfson, 1971), least-squares refinement minimizing $\sum w(F_o - F_c)^2$ (Busing & Levy, 1962). Positional and anisotropic displacement parameters refined for the heavy atoms, H-atom positional parameters calculated (not refined), isotropic temperature factors for H estimated (not refined). Weighting scheme approximately linear, obtained empirically by plotting $(F_o - F_c)^2$ as a function of F_o (Rollett, 1965). Final $R = 0.058$, $wR = 0.062$ for 589 reflexions, $(\Delta/\sigma)_{\max} = 0.3$, final $\Delta\rho < 0.2 \text{ e \AA}^{-3}$. Atomic scattering factors from *International Tables for X-ray Crystallography* (1974).

Discussion. The atomic parameters are listed in Table 1; interatomic distances, valence, torsion and dihedral angles in Table 2.*

As in the uncomplexed molecule, the cyclophane molecule lies on a center of symmetry and has an *anti* conformation. The benzene rings are not planar and adopt a boat conformation: C(8) and C(7) are respectively at 0.11 (1) and 0.007 (1) Å from the plane defined by the atoms C(3), C(4), C(6) and C(7). The deviations from the planar conformation are given in Table 2 and are similar to those found in the uncomplexed cyclophane (Kai *et al.*, 1977). A slight decrease in the plane-to-plane distance between the two rings is observed in the complex, the C(8)-C(8') distance varying from 2.633 (2) in (IV) to 2.60 (1) Å in the complex.

The TCNE molecule lies on a center of symmetry between two cyclophane molecules. The overlap between TCNE and the benzene rings is shown in Fig. 1; the relative orientation of donor and acceptor can be characterized by the θ angle defined in Table 2. The

* Lists of H-atom coordinates, anisotropic displacement parameters, mean-plane equations and F_o and F_c have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 44713 (7 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. Fractional atomic coordinates ($\times 10^4$) and equivalent isotropic thermal parameters

E.s.d.'s are given in parentheses. $B_{eq} = 8\pi^2(U_1U_2U_3)^{2/3}$.

	x	y	z	$B_{eq}(\text{\AA}^2)$
C(1)	4212 (10)	-3383 (10)	-1229 (15)	4.8
C(2)	2488 (9)	-3477 (10)	-1670 (16)	4.8
C(3)	2713 (8)	-1812 (9)	-77 (13)	3.2
C(4)	2403 (11)	-1913 (14)	1778 (18)	4.4
C(5)	2985 (14)	-284 (21)	3376 (15)	5.3
C(6)	4016 (12)	1442 (14)	3238 (13)	4.1
C(7)	4356 (9)	1606 (9)	1362 (11)	3.2
C(8)	3558 (8)	-73 (9)	-325 (10)	2.4
C(9)	-56 (8)	-353 (9)	-992 (9)	2.7
C(10)	-1019 (9)	-2352 (11)	-2060 (11)	3.4
C(11)	847 (9)	883 (9)	-2083 (10)	2.9
N(1)	-1796 (8)	-3928 (9)	-2936 (10)	4.5
N(2)	1543 (8)	1827 (9)	-2970 (10)	4.4

Table 2. Interatomic distances (\AA), valence, torsion and dihedral angles ($^\circ$)

E.s.d.'s are given in parentheses. Symmetry code: (i) $1-x, -y, -z$; (ii) $-x, -y, -z$.

β_1 : angle between the C(3),C(4),C(6),C(7) and C(3),C(8),C(7) planes.

β_2 : angle between the C(3),C(4),C(6),C(7) and C(4),C(5),C(6) planes.

θ : angle between the C(9)-C(9ⁱⁱ) and C(3)-C(7) directions.

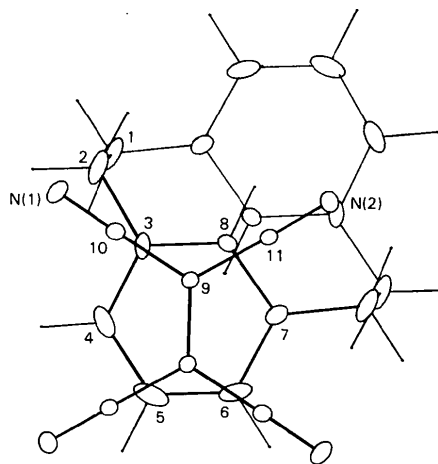
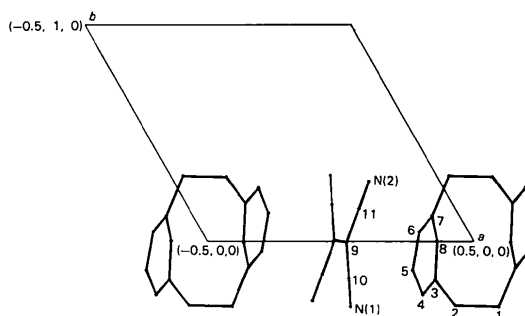
C(1)-C(2)	1.552 (10)	C(6)-C(7)	1.401 (11)
C(1)-C(7)	1.498 (10)	C(7)-C(8)	1.397 (9)
C(2)-C(3)	1.514 (10)	C(3)-C(8)	1.383 (9)
C(3)-C(4)	1.368 (11)	C(9)-C(9 ⁱⁱ)	1.337 (11)
C(4)-C(5)	1.375 (13)	C(9)-C(10)	1.436 (9)
C(5)-C(6)	1.359 (13)	C(9)-C(11)	1.445 (9)
C(2)-C(1)-C(7)	111.1 (6)	C(6)-C(7)-C(8)	116.6 (7)
C(1)-C(7)-C(8)	118.8 (7)	C(7)-C(8)-C(3)	121.8 (7)
C(1)-C(7)-C(6)	123.1 (7)	C(8)-C(3)-C(4)	119.0 (7)
C(1)-C(2)-C(3)	109.8 (6)	C(9 ⁱⁱ)-C(9)-C(10)	120.9 (7)
C(2)-C(3)-C(8)	118.7 (7)	C(9 ⁱⁱ)-C(9)-C(11)	120.6 (7)
C(2)-C(3)-C(4)	121.1 (8)	C(10)-C(9)-C(11)	118.5 (6)
C(3)-C(4)-C(5)	119.5 (8)	C(9)-C(10)-N(1)	178.6 (8)
C(4)-C(5)-C(6)	121.4 (8)	C(9)-C(11)-N(2)	178.8 (7)
C(5)-C(6)-C(7)	120.5 (7)		

$$C(3)-C(2)-C(1)-C(7) \quad 59.9 (10)$$

$$\beta_1 = 9.3 (8) \quad \beta_2 = 6.1 (8) \quad \theta = 34.8 (6)$$

TCNE molecule is nearly parallel to the associated benzene rings, their mean planes making an angle of $3.1 (8)^\circ$. The corresponding plane-to-plane distance of $3.26 (1) \text{\AA}$ is longer than that found in (I)-TCNE and (II)-TCNE complexes (respectively 3.14 and 3.20\AA). The structure is isomorphous to those of (I), (II) and (III) complexes with TCNE. As in all these structures, the donor, cyclophane, and acceptor, TCNE, are stacked alternately in a sandwich arrangement in columns parallel to the a axis (Fig. 2). Because of the *meta* substitution and of the *anti* conformation of the cyclophane, the molecules cannot be oriented perpendicularly to the a axis; this axis makes an angle of 20° with the normal to the benzene ring.

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Fig. 1. Plane projection defined by C(9), C(9ⁱⁱ) and C(11). The thermal ellipsoids are drawn at 50% probability.Fig. 2. Projection on the ab plane.

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References

- BERNSTEIN, J. & TRUEBLOOD, K. N. (1971). *Acta Cryst.* B27, 2078-2089.
- BUSING, W. R. & LEVY, H. A. (1962). ORXFLS-3. Report ORNL-TM-271. Oak Ridge National Laboratory, Tennessee, USA.
- GANTZEL, P. K. & TRUEBLOOD, K. N. (1965). *Acta Cryst.* 18, 958-968.
- GERMAIN, G., MAIN, P. & WOOLFSON, M. M. (1971). *Acta Cryst.* A27, 368-376.
- HOPE, H., BERNSTEIN, J. & TRUEBLOOD, K. N. (1972). *Acta Cryst.* B28, 1733-1743.
- International Tables for X-ray Crystallography* (1974). Vol. IV. Birmingham: Kynoch Press. (Present distributor D. Reidel, Dordrecht.)
- KAI, Y., YASUOKA, N. & KOSAI, N. (1977). *Acta Cryst.* B33, 754-762.
- RENAULT, A. & COHEN-ADDAD, C. (1986). *Acta Cryst.* C42, 1529-1533.
- RENAULT, A., COHEN-ADDAD, C., LAJZEROWICZ-BONNETEAU, J., DUTASTA, J. P. & CRISP, M. J. (1987). *Acta Cryst.* B43, 480-488.
- ROLLETT, J. S. (1965). *Computing Methods in Crystallography*, p. 112. Oxford: Pergamon Press.