# Structure of the 1:1 Complex of 5,8-Dimethoxy-2,11-dithia[3.3]paracyclophane with Tetracyanoethylene

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**Abstract.** $C_{18}H_{20}O_2 \cdot C_6N_4$, $M_r = 460 \cdot 6$, monoclinic, $C2/c$, $a = 16 \cdot 989$ (5), $b = 9 \cdot 745$ (3), $c = 15 \cdot 443$ (5) Å, $\beta = 117 \cdot 40$ (5)°, $V = 2269$ (2) Å$^3$, $Z = 4$, $D_x = 1 \cdot 35$ Mg m$^{-3}$, Mo $K\alpha$, $\lambda = 0 \cdot 71093$ Å, $\mu = 0 \cdot 25$ mm$^{-1}$, $F(000) = 960$, room temperature. The structure was refined to $wR = 0 \cdot 027$ for 882 observed intensities. The structure is a racemate. The molecules of cyclophane and tetracyanoethylene are located on the twofold axis of symmetry and not on a centre of symmetry as observed in other cyclophane–TCNE complexes. Nevertheless, the stacking is identical to that of the other complexes; the donor and acceptor are alternately stacked in a sandwich arrangement along **b**.

**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 those of their complexes with TCNE were investigated: for example, [2.2]- and [3.3]paracyclophane, [2.2]-meta- and metaparacyclophane (Gantzel & Trueblood, 1965; Bernstein & Trueblood, 1971; Hope, Bernstein & Trueblood, 1972; Renault, Cohen-Addad, Lajzerowicz-Bonneteau, Dutasta & Crisp, 1987; Renault & Cohen-Addad, 1986; Cohen-Addad, Renault, Commandeur & Baret, to be published). In all these complexes the molecules were located on a centre of symmetry.

In the present work, the structure of the complex of 5,8-dimethoxy-2,11-dithia[3.3]paracyclophane (I)*

* (I) = 14,16-dimethoxy-3,10-dithiatricyclo[10.2.2.2$^{5,8}$]octa-deca-5,7,12,14,15,17-hexaene.

with TCNE is investigated in order to study the effect of dimethoxy groups which increase the donor character of the phenyl ring and of sulfur on complexing with TCNE. In that case, owing to the chirality of the cyclophane molecule, its position on a centre of symmetry should lead to a 50% solid solution of left and right molecules and this is unlikely.



(I)                    TCNE
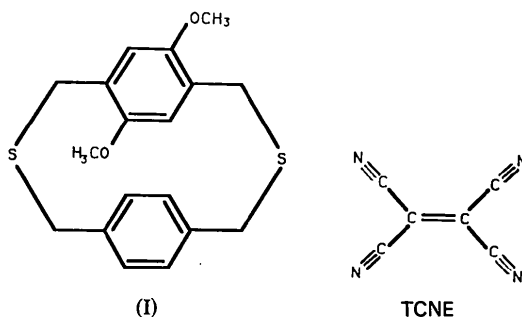
**Experimental.** *Synthesis.* 5,8-Dimethoxy-2,11-dithia-[3.3]paracyclophane was obtained by coupling 1,4-bis(bromomethyl)benzene and 1,4-bis(mercapto-methyl)benzene by potassium hydroxide in a mixture of toluene, *tert*-butanol and ethanol (2:1:1) at 343 K, under high-dilution conditions. The pure product was isolated from the mixture of oligomeric analogues by column chromatography (pentane–dichloromethane gradient) (yield: 48%).

Black crystals of (I)–TCNE were grown from a solution of (I) and TCNE in dichloromethane at 277 K.

Table 1. *Fractional coordinates* (× 10⁴) *and equivalent isotropic thermal parameters with e.s.d.'s in parentheses*

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

| | $x$ | $y$ | $z$ | $B_{eq}(\text{Å}^2)$ |
|---|---|---|---|---|
| S | 1727 (1) | 1134 (2) | 5025 (1) | 3·7 |
| C(1) | 931 (4) | 2528 (6) | 4623 (4) | 3·4 |
| C(2) | 1060 (4) | −422 (6) | 4617 (4) | 4·0 |
| C(3) | 512 (4) | −559 (6) | 3513 (4) | 2·9 |
| C(4) | −401 (4) | −614 (6) | 3097 (5) | 3·5 |
| C(5) | 917 (4) | −617 (6) | 2918 (5) | 3·3 |
| C(6) | 453 (4) | 2735 (5) | 3522 (4) | 2·5 |
| C(7) | −483 (4) | 2778 (6) | 3018 (4) | 2·8 |
| C(8) | 912 (4) | 2778 (6) | 2983 (4) | 3·0 |
| O | −904 (3) | 2745 (4) | 3593 (3) | 4·0 |
| C(9) | −1849 (4) | 2589 (8) | 3113 (5) | 4·5 |
| C(10) | 41 (4) | 5942 (6) | 2947 (4) | 3·9 |
| C(11) | −735 (4) | 5953 (7) | 3113 (5) | 4·0 |
| C(12) | 914 (4) | 6007 (6) | 3792 (4) | 3·8 |
| N(1) | −1312 (4) | 5987 (7) | 3286 (4) | 5·8 |
| N(2) | 1569 (3) | 6071 (6) | 4475 (4) | 5·1 |

Table 2. *Interatomic distances* (Å), *valence angles* (°) *and torsion angles* (°) *with e.s.d.'s in parentheses*

| | | | |
|---|---|---|---|
| C(1)–S | 1·813 (6) | C(6)–C(8) | 1·379 (7) |
| C(2)–S | 1·823 (6) | C(7)–C(8ⁱ) | 1·372 (7) |
| C(2)–C(3) | 1·527 (8) | C(7)–O | 1·374 (7) |
| C(3)–C(4) | 1·380 (8) | O–C(9) | 1·433 (6) |
| C(4)–C(5ⁱ) | 1·400 (8) | C(10)–C(10ⁱ) | 1·321 (11) |
| C(3)–C(5) | 1·380 (8) | C(10)–C(11) | 1·456 (9) |
| C(1)–C(6) | 1·523 (7) | C(10)–C(12) | 1·457 (7) |
| C(6)–C(7) | 1·413 (7) | C(11)–N(1) | 1·129 (7) |
| | | C(12)–N(2) | 1·129 (6) |

| | | | |
|---|---|---|---|
| C(1)–S–C(2) | 104·9 (2) | C(6)–C(7)–C(8ⁱ) | 120·0 (5) |
| S–C(2)–C(3) | 114·9 (4) | C(6)–C(7)–O | 115·6 (5) |
| C(2)–C(3)–C(4) | 120·0 (6) | C(8ⁱ)–C(7)–O | 124·2 (5) |
| C(2)–C(3)–C(5) | 120·8 (6) | C(7ⁱ)–C(8)–C(6) | 121·7 (5) |
| C(4)–C(3)–C(5) | 119·2 (6) | C(7)–O–C(9) | 117·5 (4) |
| C(3)–C(4)–C(5ⁱ) | 120·7 (6) | C(11)–C(10)–C(10ⁱ) | 121·0 (8) |
| C(3)–C(5)–C(4ⁱ) | 119·9 (5) | C(12)–C(10)–C(10ⁱ) | 120·7 (8) |
| S–C(1)–C(6) | 114·4 (4) | C(11)–C(10)–C(12) | 118·2 (5) |
| C(1)–C(6)–C(8) | 121·3 (5) | C(10)–C(11)–N(1) | 176·6 (8) |
| C(1)–C(6)–C(7) | 120·4 (6) | C(10)–C(12)–N(2) | 176·5 (5) |
| C(7)–C(6)–C(8) | 118·1 (5) | | |

| | | | |
|---|---|---|---|
| C(6)–C(1)–S–C(2) | −69·4 (5) | C(1)–S–C(2)–C(3) | 62·7 (5) |

Symmetry code: (i) −x, y, ½−z.

During the experiment, crystals were kept in capillaries in order to prevent sublimation.

*X-ray measurements.* X-ray data collected at room temperature on a Nicolet *P3F* four-circle diffractometer, with a crystal 0·3 × 0·25 × 0·25 mm. Graphite-monochromatized Mo Kα radiation, ω-scan mode, no absorption correction. Lattice parameters refined with reflexions 13° < 2θ < 26°. 882 independent reflexions with $I/\sigma(I) > 2\cdot5$ (1751 measured reflexions), (sinθ)/λ < 0·55 Å⁻¹, *hkl*, *h̄kl*, *h*: −15 to 15, *k*: 0 to 10, *l*: 0 to 15, standard reflexions: 1̄31, 13̄1, 4̄21 (1·5% variation); structure solved with multisolution direct method (Germain, Main & Woolfson, 1971), least-squares refinement minimizing $\sum w(F_o - F_c)^2$ (Bus-

ing & 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 $R = 0\cdot049$, $wR = 0\cdot027$ for 882 reflexions, $(\Delta/\sigma)_{max} = 0\cdot1$, final $\Delta\rho < 0\cdot2$ e Å⁻³. Atomic scattering factors from *International Tables for X-ray Crystallography* (1974).*

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

* Lists of structure factors, H-atom coordinates, anisotropic displacement parameters and mean-plane equations have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 51117 (8 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.
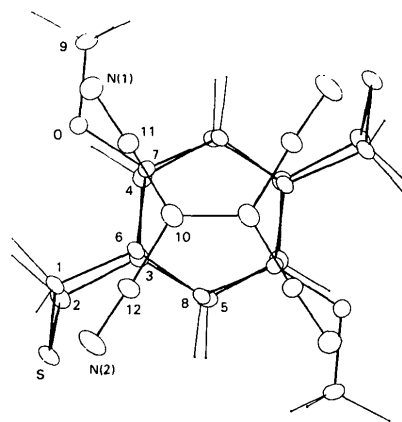


Fig. 1. Projection in the C(10)–C(10ⁱ)–C(11) plane. The thermal ellipsoids are drawn at 50% probability. [(i) −x, y, ½−z.]
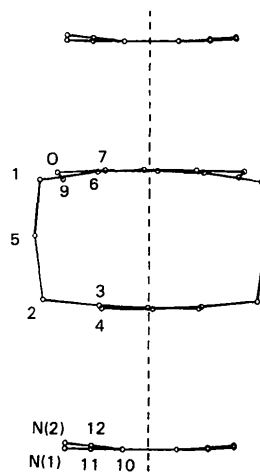


Fig. 2. Stacking along **b**: projection perpendicular to the C(10)–C(10ⁱ)–C(11) plane.

$$C_{18}H_{20}O_2.C_6N_4$$

Both molecules of cyclophane and TCNE are on the twofold axis. The two rings of the cyclophane molecule are planar and perpendicular to b with the following equations

– phenyl ring $Y = -0.596$ Å [max. deviation to the plane C(3) at 0.05 Å];
– 'methoxy' ring $Y = 2.687$ Å [C(6): 0.025 Å].

The geometry of TCNE is similar to that observed in other structures (Drück & Guth, 1982); the C—C—N group is slightly bent. The molecular plane is perpendicular to b $[Y = 5.839$ Å, with N(2) at 0.08 Å from the plane]. No orientational disorder of the TCNE molecule is observed. The relative orientation of the donor and the acceptor can be defined by the $\theta$ value between the central C=C bond of TCNE and the axis of disubstitution on the phenyl rings. These values are 23.7 (6) and 28.1 (6)° for the 'methoxy' and phenyl rings, respectively. The plane-to-plane distances between TCNE and the cyclophane rings are 3.15 (1) and 3.33 (1) Å for the 'methoxy' and phenyl rings, respectively. The reduction of the distance for the first ring is in agreement with the fact that methoxy groups increase its donor character.

The conformation and the overlap of the molecules are shown in Fig. 1. As suggested above, the molecules are not located on a centre of symmetry but have a twofold axis of symmetry. The structure corresponds to a racemate. This is the first example of such a symmetry in a cyclophane–TCNE complex. Nevertheless, the stacking is identical to that observed in other similar complexes. Donor, cyclophane, and acceptor, TCNE, are stacked alternately in a sandwich arrangement along b which is the needle axis of the crystal (Fig. 2). The length of this charge-transfer axis (9.745 Å) has nearly the same value as those observed in the other complexes (Renault & Cohen-Addad, 1986).

The authors are indebted to Professor J. Lajzerowicz, to Professor J. L. Pierre and to Dr A. Renault for very enlightening discussions.

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# Structure of the [2 + 2 + 2] Cycloadduct of Bicyclo[2.2.1]hepta-2,5-diene with 2,3-Dichloro-5,6-dicyano-1,4-benzoquinone

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**Abstract.** 11,12-Dichloro-10,13-dioxopentacyclo-[7.4.0.0$^{2,7}$.0$^{3,5}$.0$^{4,8}$]tridec-11-ene-1,9-dicarbonitrile, $C_{15}H_8Cl_2N_2O_2$, $M_r = 319.15$, orthorhombic, $P2_12_12_1$, $a = 7.741$ (2), $b = 11.794$ (4), $c = 14.434$ (6) Å, $V = 1317.79$ (75) Å$^3$, $Z = 4$, $D_x = 1.61$ g cm$^{-3}$, $\lambda$(Mo $K\alpha$) $= 0.71073$ Å, $\mu = 4.96$ cm$^{-1}$, $F(000) = 647.91$, $T = 295$ K, $R = 0.036$ for 1243 unique observed reflections. In the formation of this [2 + 2 + 2] cycload-
duct either the cyclohexenedione ring or the cyano groups could adopt endo stereochemistry; the X-ray study showed that the former is preferred.

**Introduction.** 2,3-Dichloro-5,6-dicyano-1,4-benzoquinone (I) is a highly reactive site- and stereoselective dienophile (Pointer, Wilford & Hodder, 1971; Brown, Bruce, Hudson & Mills, 1974; Dürr, Ruge & Weiss, 1974). Bicyclo[2.2.1]hepta-2,5-diene (II), which cycloadds to dienophiles in a [2 + 2 + 2] mode with