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

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 θ 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).

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.

DRÜCK, U. & GUTH, H. (1982). *Z. Kristallogr.* 161, 103–110.

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 Kluwer Academic Publishers, Dordrecht.)

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.* C43, 480–488.

ROLLETT, J. S. (1965). *Computing Methods in Crystallography*, p. 114. Oxford: Pergamon Press.

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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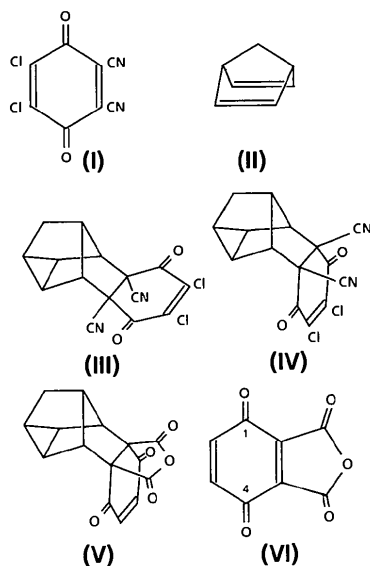*School of Chemistry, The University, Bristol BS8 1TS, England*

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}, λ(Mo Kα) = 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 stereo-selective 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

endo selectivity (Tabushi, Yamamura, Yoshida & Togashi, 1975), has now been found to react readily with (I). A single-crystal X-ray study was necessary in order to establish the stereochemistry as (III) or (IV).

Table 1. *Atomic coordinates* $(\times 10^4)$ *and equivalent isotropic thermal parameters* $(\text{Å}^2 \times 10^3)$

Equivalent isotropic U defined as one third of the trace of the orthogonalized U_{ij} tensor.

	x	y	z	U_{eq}
Cl(1)	2507 (1)	264 (1)	9316 (1)	58 (1)
Cl(2)	−824 (1)	−1248 (1)	9614 (1)	63 (1)
C(1)	2391 (4)	−1104 (3)	8945 (2)	38 (1)
C(2)	1001 (4)	−1753 (3)	9091 (2)	36 (1)
C(3)	980 (4)	−2979 (3)	8872 (2)	34 (1)
C(4)	2178 (4)	−3390 (2)	8093 (2)	29 (1)
C(5)	3772 (4)	−2601 (2)	7865 (2)	30 (1)
C(6)	3952 (4)	−1532 (2)	8479 (2)	35 (1)
C(7)	1158 (4)	−3392 (2)	7162 (2)	31 (1)
C(8)	335 (4)	−2252 (3)	6982 (2)	35 (1)
C(9)	1856 (4)	−1483 (2)	6775 (2)	35 (1)
C(10)	3428 (4)	−2244 (3)	6839 (2)	33 (1)
C(11)	2595 (4)	−3318 (2)	6416 (2)	33 (1)
C(12)	1677 (5)	−2890 (3)	5562 (2)	39 (1)
C(13)	741 (4)	−1924 (3)	5999 (2)	37 (1)
C(14)	2696 (4)	−4553 (2)	8327 (2)	35 (1)
C(15)	5421 (4)	−3216 (3)	7904 (2)	40 (1)
O(3)	26 (3)	−3620 (2)	9257 (2)	54 (1)
O(6)	5319 (3)	−1048 (2)	8531 (2)	53 (1)
N(14)	3047 (4)	−5466 (2)	8505 (2)	52 (1)
N(15)	6707 (4)	−3678 (3)	7915 (3)	61 (1)

Experimental. Bicyclo[2.2.1]hepta-2,5-diene (3·42 g) was added to a suspension of 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (2·46 g) in benzene (80 ml), and the mixture was stirred at room temperature for 5 d, by which time the colour of the resulting solution had changed from red to yellow. The solution was filtered (to remove polymer) and the filtrate was evaporated under reduced pressure, and the residue was recrystallized from methanol–ether to give the cyclo-adduct (2·00 g, 58%), m.p. 468–469 K, which analysed correctly for $C_{15}H_8Cl_2N_2O_2$ and showed the expected signals in the ^1H NMR spectrum.

Colourless crystal (0·6 × 0·6 × 0·6 mm) from methanol, Nicolet $P3m$ diffractometer, 25 reflections centred $(14 < \theta < 15°)$, graphite-monochromated Mo $K\alpha$; for data collection $2 < \theta < 25°$, ω scans, data measured over 16 X-ray h with no detectable decay or movement; 1358 unique data used for structure solution, and for refinement 1243 reflections with $F > 3\sigma(F)$ retained $(0 < h < 10, \ 0 < k < 15, \ 0 < l < 18)$. Direct methods and difference Fourier methods, blocked-cascade least-squares refinement on F, $w = [\sigma^2(F) + 0·0005(F^2)]^{-1}$, anisotropic thermal parameters for all non-hydrogen atoms, H atoms were constrained to ride on attached C with $C-H = 0·96$ Å. Determination of the 'handedness' of the structure was carried out using an η refinement (Sheldrick, 1985); this gave a value of 0·77 (22). Absorption corrections were not applied. $R = 0·0363$, $wR = 0·0517$, $S = 1·64$, data:variable ratio 6·76:1, max. peak and min. trough in final ΔF synthesis 0·33 and 0·25 e Å^{-3} respectively, max. shift in final cycle 0·04σ; complex neutral scattering factors for C, H, Cl, N, O from *International Tables for X-ray Crystallography* (1974). Computer programs *SHELXTL* (Sheldrick, 1985).

Table 2. *Bond lengths* (Å) *and bond angles* (°)

Cl(1)–C(1)	1·702 (3)	Cl(2)–C(2)	1·709 (3)
C(1)–C(2)	1·337 (5)	C(1)–C(6)	1·472 (5)
C(2)–C(3)	1·480 (5)	C(3)–C(4)	1·536 (4)
C(3)–O(3)	1·194 (4)	C(4)–C(5)	1·580 (4)
C(4)–C(7)	1·559 (4)	C(4)–C(14)	1·469 (4)
C(5)–C(6)	1·547 (4)	C(5)–C(10)	1·562 (4)
C(5)–C(15)	1·469 (4)	C(6)–O(6)	1·204 (4)
C(7)–C(8)	1·510 (4)	C(7)–C(11)	1·551 (4)
C(8)–C(9)	1·517 (4)	C(8)–C(13)	1·504 (4)
C(9)–C(10)	1·515 (4)	C(9)–C(13)	1·506 (4)
C(10)–C(11)	1·547 (4)	C(11)–C(12)	1·510 (4)
C(12)–C(13)	1·490 (5)	C(14)–N(14)	1·140 (4)
C(15)–N(15)	1·135 (5)		
Cl(1)–C(1)–C(2)	122·4 (3)	Cl(1)–C(1)–C(6)	115·2 (2)
C(2)–C(1)–C(6)	122·4 (3)	Cl(2)–C(2)–C(1)	122·4 (3)
Cl(2)–C(2)–C(3)	115·1 (2)	C(1)–C(2)–C(3)	122·3 (3)
C(2)–C(3)–C(4)	117·2 (3)	C(2)–C(3)–O(3)	121·8 (3)
C(4)–C(3)–O(3)	120·9 (3)	C(3)–C(4)–C(5)	116·0 (2)
C(3)–C(4)–C(7)	109·0 (2)	C(5)–C(4)–C(7)	102·5 (2)
C(3)–C(4)–C(14)	107·0 (2)	C(5)–C(4)–C(14)	112·6 (2)
C(7)–C(4)–C(14)	109·5 (2)	C(4)–C(5)–C(6)	115·5 (2)
C(4)–C(5)–C(10)	102·9 (2)	C(6)–C(5)–C(10)	109·8 (2)
C(4)–C(5)–C(15)	112·3 (2)	C(6)–C(5)–C(15)	107·6 (2)
C(10)–C(5)–C(15)	108·5 (2)	C(1)–C(6)–C(5)	117·9 (3)
C(1)–C(6)–O(6)	122·0 (3)	C(5)–C(6)–O(6)	120·0 (3)
C(4)–C(7)–C(8)	111·1 (2)	C(4)–C(7)–C(11)	103·6 (2)
C(8)–C(7)–C(11)	97·6 (2)	C(7)–C(8)–C(9)	103·8 (2)
C(7)–C(8)–C(13)	107·7 (3)	C(9)–C(8)–C(13)	59·8 (2)
C(8)–C(9)–C(10)	104·9 (2)	C(8)–C(9)–C(13)	59·7 (2)
C(10)–C(9)–C(13)	107·5 (2)	C(5)–C(10)–C(9)	110·8 (2)
C(5)–C(10)–C(11)	103·0 (2)	C(9)–C(10)–C(11)	97·3 (2)
C(7)–C(11)–C(10)	94·1 (2)	C(7)–C(11)–C(12)	104·4 (2)
C(10)–C(11)–C(12)	104·1 (2)	C(11)–C(12)–C(13)	98·0 (2)
C(8)–C(13)–C(9)	60·5 (2)	C(8)–C(13)–C(12)	107·7 (3)
C(9)–C(13)–C(12)	107·5 (3)	C(4)–C(14)–N(14)	177·9 (3)
C(5)–C(15)–N(15)	178·3 (4)		

ing factors for C, H, Cl, N, O from *International Tables for X-ray Crystallography* (1974). Computer programs *SHELXTL* (Sheldrick, 1985).
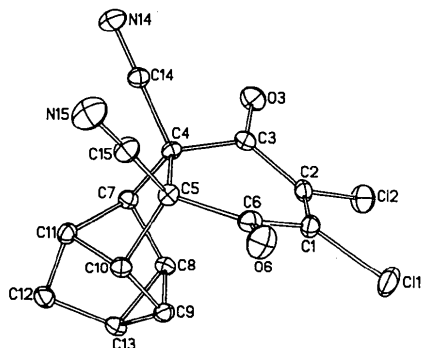
$C_{15}H_8Cl_2N_2O_2$

Fig. 1. View of the title compound showing the atom numbering.

Discussion. Table 1 lists the atomic coordinates for the non-hydrogen atoms, and Table 2 the bond lengths and bond angles.* A perspective view of the structure is presented in Fig. 1, which also shows the crystallographic numbering. The stereochemistry of the

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* Lists of structure factors, anisotropic thermal parameters and H-atom parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 51140 (12 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

cycloadduct, hereby established as (IV), is analogous to that reported for the adduct (V) from bicyclo[2.2.1]-hepta-2,5-diene (II) and the quinone anhydride (VI) (Kanematsu, Morita, Fukushima & Osawa, 1981). The exclusive formation of (V), in which the cyclohexene-dione ring takes up the *endo* configuration in preference to the anhydride ring, was explained on the basis of secondary orbital interactions, which in (VI) could involve either of the pairs of carbonyl C atoms, but would be expected to be greater at C(1) and C(4) where the LUMO coefficients are larger.

References

BROWN, R., BRUCE, J. M., HUDSON, D. W. & MILLS, O. S. (1974). *J. Chem. Soc. Perkin Trans.* 2, pp. 132–135.
DÜRR, H., RUGE, B. & WEISS, B. (1974). *Justus Liebigs Ann. Chem.* pp. 1150–1161.
International Tables for X-ray Crystallography (1974). Vol. IV. Birmingham: Kynoch Press. (Present distributor Kluwer Academic Publishers, Dordrecht.)
KANEMATSU, K., MORITA, S., FUKUSHIMA, S. & OSAWA, E. (1981). *J. Am. Chem. Soc.* **103**, 5211–5215.
POINTER, D. J., WILFORD, J. B. & HODDER, O. J. R. (1971). *J. Chem. Soc. B*, pp. 2009–2014.
SHELDRICK, G. M. (1985). *SHELXTL*. Revision 5.1. Univ. of Göttingen, Federal Republic of Germany.
TABUSHI, I., YAMAMURA, K., YOSHIDA, Z. & TOGASHI, A. (1975). *Bull. Chem. Soc. Jpn*, **48**, 2922–2926.

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Structure of 1,4-Dioxa-10,13-dithia-7,16-diazacyclooctadecane-6,17-dione

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Abstract. $C_{12}H_{22}N_2O_4S_2$, $M_r = 322\cdot44$, monoclinic, $P2_1/c$, $a = 7\cdot760$ (2), $b = 21\cdot425$ (5), $c = 9\cdot658$ (2) Å, $\beta = 91\cdot17$ (2)°, $V = 1605\cdot3$ (6) Å³, $Z = 4$, $D_x = 1\cdot334$ g cm⁻³, $\lambda(\text{Mo }K\bar{\alpha}) = 0\cdot71069$ Å, $\mu = 2\cdot96$ cm⁻¹, $F(000) = 688\cdot0$, $T = 296$ K, final $R = 0\cdot035$ for 2152 observed reflections. The conformation of the 18-membered ring is characterized by the exodentate orientation of sulfur atoms and the *gauche* torsion angles for all C—S—C—C units and *anti* torsion angles for the S—C—C—S and S—C—C—N fragments. The planar amide groups are *trans* with exo- and endo-dentate carbonyl oxygens involved in inter- and intramolecular C=O···H—N interactions, respectively.

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Introduction. The structural chemistry of unsubstituted and substituted crown-ether-type ligands has received considerable attention (Dale, 1980; Dobler, 1981; Hilgenfeld & Saenger, 1982; Truter, 1973). However, very little work has been reported on the structures of oxa- and thia-substituted macrocyclic amides (Samuel & Weiss, 1970; Ganin, Lukyanenko, Dvorkin, Popkov, Simonov, Bogatskii & Malinovskii, 1981; Simonov, Malinovskii, Ganin, Dvorkin, Bogatskii, Lukyanenko & Popkov, 1981; Ganin, Sobolev, Bel-skii, Simonov, Lukyanenko, Popkov & Malinovskii, 1984). Compounds of this type are of interest owing to their metal ion complexation properties and their ability to transport cations across membranes (Tümmler, Maass, Weber, Wehner & Vögtle, 1977). The replacement of