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1,2,2a,4a,5,6,7,8-Octahydro-5,8-methanocyclobut[*c*]indene-1,1,2,2-tetracarbonitrile, $C_{16}H_{12}N_4$

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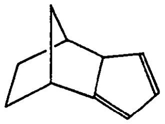
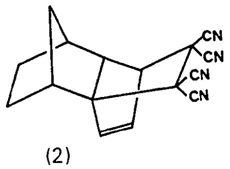
Abstract. $M_r = 260{\cdot}30$, monoclinic, $P2_1/n$, $a = 11{\cdot}415\,(2)$, $b = 15{\cdot}401\,(3)$, $c = 7{\cdot}751\,(1)$ Å, $\beta = 96{\cdot}90\,(1)°$, $V = 1352{\cdot}8\,(4)$ Å^3, $Z = 4$, $D_x = 1{\cdot}278$ g cm^{-3}, Cu $K\alpha$, $\lambda = 1{\cdot}54178$ Å, $\mu = 6{\cdot}43$ cm^{-1}, $F(000) = 544$, room temperature, $R = 0{\cdot}040$ for 1508 unique reflections with $I > 3\sigma(I)$. The tetracyanoethylene adduct contains a four-membered ring with three long C—C distances of 1·581 (3), 1·582 (3) and 1·596 (3) Å. Both N—C—C—C—N moieties are planar and almost perpendicular to the four-membered ring and to each other. Although there is little steric hindrance within the molecule, there is considerable angle strain as evidenced by the fourteen C(sp^3) valence angles of less than 104°.

Introduction. The least reactive isomer (1) of isodicyclopentadiene (Bartlett & Wu, 1984*a*) reacts with tetracyanoethylene (TCNE) at 273 K in acetonitrile to form adduct (2). In the presence of polar solvents (2) rearranges to form the title compound (3) (Bartlett & Wu, 1984*b*). Both steps in this reaction are solvent dependent.



(1)



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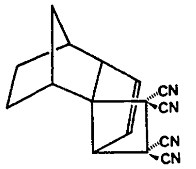

(3)

Experimental. Bipyramidal-shaped crystal, 0·6 × 0·3 × 0·3 mm, Syntex $P2_1$ diffractometer, θ:2θ scan, variable scan rate, $2\theta_{max} = 120°$, graphite-monochromated Cu $K\alpha$ radiation; lattice parameters from least squares of 15 medium-angle reflections with angles measured by centering routine associated with the diffractometer system (systematic absences $h + l = 2n + 1$ for $h0l$); monitored reflections showed no change in intensity greater than $3\sigma(I)$; 1842 independent reflections ($0 \le h \le 12$, $0 \le k \le 16$, $-8 \le l \le 8$), 1508 with intensities $>3\sigma(I)$; Lorentz and polarization but no absorption corrections; direct methods (*MULTAN*78: Main, Hull, Lessinger, Germain, Declercq & Woolfson, 1978) located all heavy atoms; H atoms located in difference synthesis but not refined, full-matrix least-squares anisotropic refinement; $\sum w(|F_o| - |F_c|)^2$ minimized, $w = 1/\sigma^2(F_o)$; 181 parameters refined, final $R = 0{\cdot}040$, $R_w = 0{\cdot}059$, $S = 2{\cdot}79$, $(\Delta/\sigma)_{av} = 0{\cdot}014$, $(\Delta/\sigma)_{max} = 0{\cdot}12$, highest peak in difference Fourier map 0·17 e Å^{-3}; locally written programs used for data reduction and initial block-diagonal least-squares refinement, *MULTAN*78 for direct-methods calculations and *XRAY*76 (Stewart, Machin, Dickinson, Ammon, Heck & Flack, 1976) for all other computations; atomic scattering factors for C, O and N from Cromer & Mann (1968), for H from Stewart, Davidson & Simpson (1965). Table 1 lists atomic positional parameters and U_{eq} values while Table 2 gives bond lengths and valence angles.†

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† Lists of structure factors, H-atom parameters, torsion angles and thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 39149 (21 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Table 1. *Atomic coordinates* (×10⁴) *and equivalent isotropic thermal parameters* (Å² ×10³) *for compound* (3)

	x	*y*	*z*	U_{eq}*
C(1)	4646 (2)	2468 (1)	2767 (3)	44 (1)
C(2)	4105 (2)	1676 (1)	3700 (3)	44 (1)
C(3)	4835 (2)	1031 (1)	2621 (3)	46 (1)
C(4)	5230 (2)	1845 (2)	1587 (3)	53 (1)
C(5)	6508 (2)	2064 (2)	1845 (4)	68 (2)
C(6)	6740 (2)	2661 (2)	3038 (4)	64 (2)
C(7)	5679 (2)	2958 (2)	3849 (3)	54 (1)
C(8)	5313 (3)	3917 (2)	3632 (4)	74 (2)
C(9)	5400 (3)	4224 (2)	1786 (4)	81 (2)
C(10)	4417 (2)	3696 (2)	687 (4)	79 (2)
C(11)	3824 (2)	3202 (2)	2070 (3)	62 (1)
C(12)	3984 (3)	3828 (2)	3626 (5)	85 (2)
C(13)	4386 (2)	1646 (1)	5600 (3)	51 (1)
N(13)	4611 (2)	1653 (2)	7068 (3)	74 (1)
C(14)	2825 (2)	1575 (2)	3266 (3)	52 (1)
N(14)	1834 (2)	1501 (2)	2914 (3)	76 (2)
C(15)	5787 (2)	592 (2)	3708 (3)	51 (1)
N(15)	6518 (2)	267 (2)	4608 (3)	74 (1)
C(16)	4117 (2)	409 (2)	1529 (3)	57 (1)
N(16)	3576 (2)	−41 (2)	594 (3)	85 (2)

* $U_{eq} = \frac{1}{3}[U_{11}(aa^*)^2 + U_{22}(bb^*)^2 + U_{33}(cc^*)^2 + 2U_{12}aba^*b^*\cos\gamma + 2U_{13}aca^*c^*\cos\beta + 2U_{23}bcb^*c^*\cos\alpha]$.

Table 2. *Interatomic distances* (Å) *and valence angles* (°) *for compound* (3)

C(1)—C(2)	1·581 (3)	C(6)—C(7)	1·501 (4)
C(1)—C(4)	1·532 (4)	C(7)—C(8)	1·539 (4)
C(1)—C(7)	1·558 (3)	C(8)—C(9)	1·522 (5)
C(1)—C(11)	1·526 (3)	C(8)—C(12)	1·523 (5)
C(2)—C(3)	1·596 (3)	C(9)—C(10)	1·554 (4)
C(2)—C(13)	1·470 (3)	C(10)—C(11)	1·536 (4)
C(2)—C(14)	1·468 (3)	C(11)—C(12)	1·538 (4)
C(3)—C(4)	1·582 (3)	C(13)—N(13)	1·136 (3)
C(3)—C(15)	1·459 (3)	C(14)—N(14)	1·137 (3)
C(3)—C(16)	1·463 (3)	C(15)—N(15)	1·137 (3)
C(4)—C(5)	1·487 (3)	C(16)—N(16)	1·131 (4)
C(5)—C(6)	1·308 (4)		

C(2)C(1)C(4)	90·7 (2)	C(3)C(4)C(5)	116·5 (2)
C(2)C(1)C(7)	116·1 (2)	C(4)C(5)C(6)	111·5 (2)
C(2)C(1)C(11)	118·4 (2)	C(5)C(6)C(7)	113·9 (2)
C(4)C(1)C(7)	105·6 (2)	C(1)C(7)C(6)	102·9 (2)
C(4)C(1)C(11)	123·1 (2)	C(1)C(7)C(8)	103·2 (2)
C(7)C(1)C(11)	103·0 (2)	C(6)C(7)C(8)	118·0 (3)
C(1)C(2)C(3)	89·0 (2)	C(7)C(8)C(9)	110·7 (2)
C(1)C(2)C(13)	115·6 (2)	C(7)C(8)C(12)	99·9 (2)
C(1)C(2)C(14)	114·2 (2)	C(9)C(8)C(12)	101·7 (3)
C(3)C(2)C(13)	116·1 (2)	C(8)C(9)C(10)	103·2 (3)
C(3)C(2)C(14)	112·5 (2)	C(9)C(10)C(11)	103·1 (2)
C(13)C(2)C(14)	108·5 (2)	C(1)C(11)C(10)	108·1 (2)
C(2)C(3)C(4)	88·3 (1)	C(1)C(11)C(12)	100·2 (2)
C(2)C(3)C(15)	112·7 (2)	C(10)C(11)C(12)	102·5 (2)
C(2)C(3)C(16)	114·8 (2)	C(8)C(12)C(11)	94·8 (3)
C(4)C(3)C(15)	115·0 (2)	C(2)C(13)N(13)	177·6 (3)
C(4)C(3)C(16)	113·6 (2)	C(2)C(14)N(14)	179·3 (7)
C(15)C(3)C(16)	110·9 (2)	C(3)C(15)N(15)	177·4 (4)
C(1)C(4)C(3)	91·3 (2)	C(3)C(16)N(16)	175·5 (3)
C(1)C(4)C(5)	105·5 (2)		

Discussion. Fig. 1 is an *ORTEP* (Johnson, 1971) drawing of the title compound. The cyclopentene system is *cis* fused to the norbornane moiety. The five-membered ring is nearly planar [maximum deviation 0·04 (1) Å] with C(5)—C(6) = 1·308 (4) Å. The four-membered ring is slightly puckered [maximum deviation from planarity 0·04 (1) Å], and the four- and five-membered rings form an interplanar angle of 118·1 (6)°. The C(1)—C(2), C(2)—C(3) and C(3)—C(4) bond distances associated with the TCNE moiety are 1·581 (3), 1·596 (3) and 1·582 (3) Å, respectively, which reflects the electron-withdrawing character of the four cyano groups and the strain in the four-membered ring. The two N—C—C—C—N units are planar [maximum deviation 0·02 (1) Å] and are almost perpendicular, interplanar angle = 88·0 (5)°. The plane containing C(2) makes an angle of 91·2 (5)° with the four-membered ring while that containing C(3) makes an angle of 92·4 (5)°. The four C(sp^3)—C(sp) distances in the TCNE unit of 1·459 (3) to 1·470 (3) Å can be compared with the 1·445 (4) to 1·451 (4) Å range observed for 1,1,2,2-tetracyanocyclopropane (Wang & Stucky, 1973) and the 1·463 (6) to 1·511 (6) Å range for a TCNE reaction product (Karle, Flippen, Huisgen & Schug, 1975). The four C≡N distances of 1·131 (4) to 1·137 (2) Å may be compared with the 1·134 (3) to 1·141 (3) Å and 1·109 (6) to 1·146 (6) Å ranges observed for the two structures cited above.

The cyclohexane ring is held in a boat conformation by the methylene bridge. The interplanar angles involving C(11)C(1)C(7)C(8) *A*, C(8)C(12)C(11) *B*, and C(8)C(9)C(10)C(11) *C* are *A*,*B* = 121·1 (5), *B*,*C* = 125·0 (5) and *A*,*C* = 113·9 (6)°. Other than H(4)···H(10a) = 2·28 (4) Å and H(11)···C(14) = 2·44 (4) Å there are no unusually short intramolecular contacts. Although there is little steric hindrance within the molecule, the fusion of small rings with fourteen C(sp^3) valence angles of less than 104° leads to considerable strain. There is a short intermolecular contact of 2·22 (4) Å between H(5) of one molecule and H(12*A*) of another and five additional hydrogen-atom contacts which lie between 2·45 (4) and 2·70 (4) Å.

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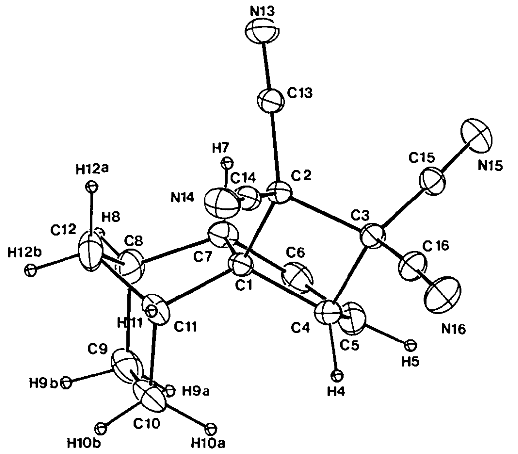

Fig. 1. *ORTEP* drawing of compound (3). Thermal ellipsoids are drawn at the 50% probability level.

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rel-(1*R*,4*S*,5*S*,8*R*)-1,2,3,4,5,6,7,8-Octahydro-1,4:5,8-dimethanonaphthalene-2,2,3,3-tetracarbonitrile, $C_{16}H_{12}N_4$

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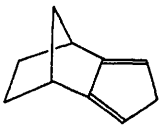
(*Received* 26 *September* 1983; *accepted* 20 *December* 1983)

Abstract. $M_r = 260{\cdot}30$, monoclinic, $P2_1/c$, $a = 18{\cdot}123\ (5)$, $b = 13{\cdot}509\ (3)$, $c = 12{\cdot}073\ (2)$ Å, $\beta = 109{\cdot}35\ (3)°$, $V = 2789\ (1)$ Å^3, $Z = 8$, $D_x = 1{\cdot}240$ g cm^{-3}, Cu $K\alpha$, $\lambda = 1{\cdot}54178$ Å, $\mu = 6{\cdot}24$ cm^{-1}, $F(000) = 1088$, room temperature, two independent molecules per asymmetric unit, $R = 0{\cdot}043$ for 2497 unique reflections with $I > 3\sigma(I)$. The central π system in the *anti*-sesquinorbornene derivative deviates from planarity by approximately 4°. This is attributed primarily to an interaction between the central π bond and the π system of the cyano groups. The electron-withdrawing character of the cyano groups may account for the elongation of three C—C bonds in each molecule which range from 1·591 (3) to 1·609 (4) Å.

Introduction. Isodicyclopentadiene (1) reacts rapidly with tetracyanoethylene (TCNE) in benzene to yield a mixture of isomers (2) and (3) (Bartlett & Wu, 1984). When the reaction is followed by ^{1}H or ^{13}C NMR it is found that (3) forms exclusively at the beginning, then slowly rearranges to (2). An 87:13 equilibrium mixture of 3:2 was obtained. To our knowledge, this is the first example in which a dienophile preferentially cycloadds to the *exo* face of (1) (Sugimoto, Kobuke & Furukawa, 1976; Paquette, Carr, Böhm & Gleiter, 1980; Watson, Galloy, Bartlett & Roof, 1981).

Experimental. Pyramidal-shaped crystal, 0·38 × 0·30 × 0·25 mm, Syntex $P2_1$ diffractometer, θ:2θ scan, variable scan rate, $2\theta_{\max} = 120°$, graphite-monochromated Cu $K\alpha$ radiation; lattice parameters from least squares of 15 medium-angle reflections with angles measured by centering routine associated with the diffractometer system (systematic absences $l = 2n + 1$ for $h0l$ and $k = 2n + 1$ for $0k0$); monitored reflection showed no change in intensity greater than $3\sigma(I)$; 3810 independent reflections ($0 \leq h \leq 19$, $0 \leq k \leq 14$, $-12 \leq l \leq 12$), 2497 with $I > 3\sigma(I)$; Lorentz and polarization, no absorption corrections; direct methods (*MULTAN78*: Main, Hull, Lessinger, Germain, Declercq & Woolfson, 1978) located all heavy atoms; hydrogen atom positions located in difference map but not refined in full-matrix least-squares anisotropic refinement; $\sum w(|F_o| - |F_c|)^2$ minimized, $w = 1/\sigma^2(F_o)$; 361 parameters refined; $R = 0{\cdot}043$, $R_w = 0{\cdot}048$, $S = 1{\cdot}92$, $(\Delta/\sigma)_{\text{av}} = 0{\cdot}057$, $(\Delta/\sigma)_{\max} = 0{\cdot}21$; highest peak in final difference map 0·15 e Å^{-3}; locally written programs used for data reduction and initial block-diagonal least-squares refinement, *MULTAN78* for direct-methods calculations and *XRAY76* (Stewart,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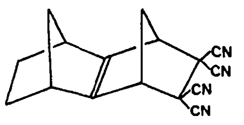

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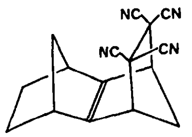

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