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Structure of *cis-cisoid-cis*-Tricyclo[8.6.0.0^{2,9}]hexadecane, $C_{16}H_{28}$

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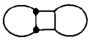
Abstract. $M_r = 220\cdot4$, monoclinic, $C2/c$, $a = 19\cdot723$ (3), $b = 5\cdot269$ (3), $c = 12\cdot957$ (2) Å, $\beta = 97\cdot79$ (1)°, $U = 1334\cdot1$ (8) Å^3, $Z = 4$, $D_x = 1\cdot097$ g cm^{-3}, Cu $K\alpha$, $\lambda = 1\cdot5418$ Å, $\mu = 4\cdot5$ cm^{-1}, $F(000) = 496$, $T = 295$ K, $R = 0\cdot055$ for 1090 observed reflections with $I > 2\cdot5\sigma(I)$. The central cyclobutane ring is found to be significantly puckered with $\varphi = 23\cdot9$ (2) and $24\cdot3$ (2)° about the two non-bonded C–C vectors. The cyclooctane rings are each in a boat-like conformation with smallest asymmetry parameter value $\Delta C_s = 19\cdot4$ (2)° for C(4).

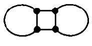
Introduction. The photodimerization of cycloalkenes such as cyclohexene is catalyzed by copper(I) triflate (trifluoromethanesulfonate) (Salomon, Folting, Streib & Kochi, 1974). Five stereoisomers of cyclodimers having a central ring may be formed: *ttt* = *trans-transoid-trans*; *tct* = *trans-cisoid-trans*; *ct* = *cis-trans*; *ctc* = *cis-transoid-cis* and *ccc* = *cis-cisoid-cis*:


ttt


tct


ct


ctc


ccc

As part of an investigation on the mechanism for this type of cyclodimerization of C_6–C_8 cycloalkenes, it was found necessary to correlate ^{1}H and ^{13}C NMR spectroscopic properties with these structures (Spee, Evers & Mackor, 1982; Timmermans, de Ruiter, Tinnemans & Mackor, 1983). The *ct* stereoisomer is asymmetric and easily recognized by NMR spectroscopy. The other four have at least C_2 symmetry. A tentative assignment was made on the basis of a comparison of the NMR data (Spee, Evers & Mackor, 1982), assuming that a larger number of *cis*(*oid*) substituents results in a larger interaction between these substituents giving a less-puckered cyclobutane ring. Such a relation was suggested by the available experimental data for the cyclohexene dimer tricyclo-[6.4.0.0^{2,7}]dodecane (Salomon, Folting, Streib & Kochi, 1974). These authors report a relatively large puckering angle $\varphi = 41$ (2)° for the least-hindered *ttt* isomer on the basis of an X-ray study and state that this angle is approximately zero for the *ccc* isomer.

This paper reports the structure determination of the *ccc* isomer of the cyclooctene dimer that was carried out to obtain firm experimental data for its cyclobutane-ring puckering. The consequences of finding a significantly puckered cyclobutane ring for the previously given spectral assignments and correlations (Spee, Evers & Mackor, 1982) will be reported elsewhere (Timmermans, Mackor & Spek, 1985).

Experimental. Crystals prepared by Leitich (1982). Colorless crystals obtained by recrystallization from methanol. Enraf–Nonius CAD-4F diffractometer, Ni-filtered Cu $K\alpha$ radiation; plate-shaped crystal 0·075 × 0·30 × 0·88 mm glued on a glass fiber. 1266 unique reflections, $\omega/2\theta$ scan; $4\cdot5 < \theta < 70°$; h −24→23; k 0→6, l 0→15. Two reference reflections showed small intensity variations ($60\bar{2}$: r.m.s. dev. 1·7%; $\bar{6}02$: r.m.s. dev. 2·5%). Cell dimensions from setting angles of 13 reflections ($12 < \theta < 21°$) in four alternative settings (de Boer & Duisenberg, 1984). Correction for Lorentz and polarization effects. Structure solved by direct methods, refined on F by full-matrix least-squares techniques with anisotropic thermal parameters for non-hydrogen atoms. Hydrogen atoms located from difference Fourier synthesis and refined with one overall isotropic temperature factor. $R = 0\cdot055$, $wR = 0\cdot059$; $w = 1$; 1090 observed reflections with $I > 2\cdot5\sigma(I)$; $S = 1\cdot03$; 116 refined parameters; max. $\Delta/\sigma = 0\cdot6$. Min. and max. residual densities in final difference Fourier map −0·24 and 0·20 e Å^{-3}. The final values of the refined parameters are given in Table 1.† Scattering factors from Cromer & Mann (1968). Calculations

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† Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 39735 (10 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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carried out on either the Cyber-175 of the University of Utrecht with programs of the *APOLLO* (data reduction), *MULTAN*80 (Main *et al.*, 1980) and *EUCLID* (Spek, 1982) packages or the in-house Eclipse S/230 mini-computer with a locally modified version of *SHELX*76 (Sheldrick, 1976).

Discussion. Fig. 1 gives a view of the dimer including the adopted numbering scheme. Relevant data on the geometry are given in Table 2. The monoclinic unit cell contains four discrete molecules with C_2 symmetry coinciding with a crystallographic twofold axis. The observed conformation deviates considerably from the conceivable C_{2v} symmetry. The central cyclobutane ring is significantly puckered and the cyclooctane rings are each in a boat-type conformation with torsion angles ranging from 24·3 to 104·8° and lowest asymmetry parameter value $\Delta C_s = 19·4$ (2)° for C(4) and C(8).

The cyclobutane ring-puckering angle φ, as defined by Moriarty (1974), along the non-bonded C(2)–C(2$^{\mathrm{i}}$) and C(3)–C(3$^{\mathrm{i}}$) is 24·3 (2) and 23·9 (2)° respectively. These values are in the usual range $20 < \theta < 35°$ (Allen, 1984). The cyclobutane-ring puckering may also be illustrated by the observed ring torsion angles: 17·1 (2) and −16·9 (2)°, average 17·01 (8)°. Whereas the torsion angles in this ring are found to be

Table 1. *Final atomic coordinates and equivalent isotropic thermal parameters*

	x	y	z	U_{eq}(Å^2)†
C(1)	0·5803 (1)	0·1311 (5)	0·7002 (2)	0·0383 (7)
C(2)	0·5496 (1)	0·3908 (4)	0·7197 (2)	0·0315 (6)
C(3)	0·5261 (1)	0·4352 (4)	0·8292 (2)	0·0314 (6)
C(4)	0·5567 (1)	0·2841 (5)	0·9239 (2)	0·0395 (7)
C(5)	0·6275 (1)	0·3791 (6)	0·9706 (2)	0·0473 (8)
C(6)	0·6810 (1)	0·3831 (5)	0·8955 (2)	0·0446 (8)
C(7)	0·6899 (1)	0·1292 (5)	0·8413 (2)	0·0493 (8)
C(8)	0·6582 (1)	0·1121 (6)	0·7268 (2)	0·0471 (8)
H(11)	0·567 (1)	0·092 (3)	0·616 (2)	0·052 (2)
H(12)	0·560 (1)	0·000 (3)	0·739 (2)	0·052 (2)
H(21)	0·586 (1)	0·519 (3)	0·699 (2)	0·052 (2)
H(31)	0·532 (1)	0·624 (3)	0·849 (2)	0·052 (2)
H(41)	0·522 (1)	0·295 (3)	0·981 (2)	0·052 (2)
H(42)	0·558 (1)	0·098 (3)	0·903 (2)	0·052 (2)
H(51)	0·624 (1)	0·555 (3)	1·005 (2)	0·052 (2)
H(52)	0·645 (1)	0·261 (3)	1·032 (2)	0·052 (2)
H(61)	0·669 (1)	0·514 (3)	0·842 (2)	0·052 (2)
H(62)	0·729 (1)	0·438 (3)	0·937 (2)	0·052 (2)
H(71)	0·669 (1)	−0·008 (3)	0·883 (2)	0·052 (2)
H(72)	0·742 (1)	0·095 (3)	0·836 (2)	0·052 (2)
H(81)	0·674 (1)	−0·051 (3)	0·697 (2)	0·052 (2)
H(82)	0·678 (1)	0·254 (3)	0·686 (2)	0·052 (2)

† $U_{eq} = \frac{1}{3}\sum_i\sum_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j$.

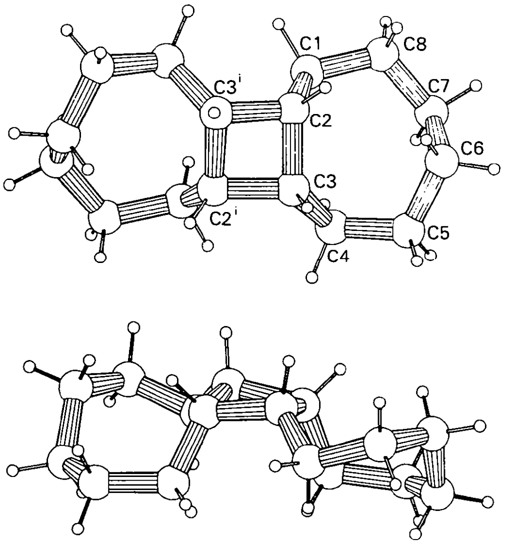

Fig. 1. *PLUTO* drawings of *cis-cisoid-cis*-tricyclo[8.6.0.0^{2,9}]-hexadecane illustrating the puckering and adopted numbering scheme.

Table 2. *Data on the geometry of* $C_{16}H_{28}$

Bond distances (Å)

C(1)–C(8)	1·531 (4)	C(2)–H(21)	1·04 (2)
C(1)–C(2)	1·531 (3)	C(3)–H(31)	1·03 (2)
C(2)–C(3$^{\mathrm{i}}$)	1·559 (3)	C(4)–H(41)	1·08 (2)
C(2)–C(3)	1·569 (3)	C(4)–H(42)	1·02 (2)
C(3)–C(4)	1·517 (3)	C(5)–H(51)	1·03 (2)
C(4)–C(5)	1·530 (4)	C(5)–H(52)	1·03 (2)
C(5)–C(6)	1·529 (4)	C(6)–H(61)	0·98 (2)
C(6)–C(7)	1·532 (4)	C(6)–H(62)	1·06 (2)
C(7)–C(8)	1·532 (4)	C(7)–H(71)	1·02 (2)
C(1)–H(12)	0·97 (2)	C(7)–H(72)	1·05 (2)
C(1)–H(11)	1·10 (2)	C(8)–H(81)	1·01 (2)
		C(8)–H(82)	1·02 (2)

Bond angles (°)

C(2)–C(1)–C(8)	115·3 (2)	H(41)–C(4)–H(42)	106 (2)
C(1)–C(2)–C(3)	117·1 (2)	C(3)–C(4)–H(41)	108 (1)
C(1)–C(2)–C(3$^{\mathrm{i}}$)	116·4 (2)	C(3)–C(4)–H(42)	108 (1)
C(3)–C(2)–C(3$^{\mathrm{i}}$)	87·8 (2)	C(5)–C(4)–H(42)	111 (1)
C(2)–C(3)–C(2$^{\mathrm{i}}$)	89·7 (2)	C(6)–C(5)–H(51)	110 (1)
C(2$^{\mathrm{i}}$)–C(3)–C(4)	120·3 (2)	C(6)–C(5)–H(52)	109 (1)
C(2)–C(3)–C(4)	121·2 (2)	C(4)–C(5)–H(51)	111 (1)
C(3)–C(4)–C(5)	113·0 (2)	C(4)–C(5)–H(52)	107 (1)
C(4)–C(5)–C(6)	115·1 (2)	H(51)–C(5)–H(52)	104 (2)
C(5)–C(6)–C(7)	114·3 (2)	C(5)–C(6)–H(61)	110 (1)
C(6)–C(7)–C(8)	116·0 (2)	H(61)–C(6)–H(62)	106 (2)
C(1)–C(8)–C(7)	118·6 (2)	C(7)–C(6)–H(61)	109 (1)
C(8)–C(1)–H(12)	109 (1)	C(7)–C(6)–H(62)	109 (1)
C(2)–C(1)–H(12)	110 (1)	C(5)–C(6)–H(62)	109 (1)
H(11)–C(1)–H(12)	108 (2)	C(6)–C(7)–H(72)	111 (1)
C(2)–C(1)–H(11)	106·2 (9)	C(6)–C(7)–H(71)	107 (1)
C(8)–C(1)–H(11)	108 (1)	C(8)–C(7)–H(71)	109 (1)
C(3$^{\mathrm{i}}$)–C(2)–H(21)	116 (1)	C(8)–C(7)–H(72)	101 (1)
C(1)–C(2)–H(21)	104 (1)	H(71)–C(7)–H(72)	112 (2)
C(3)–C(2)–H(21)	116 (1)	C(1)–C(8)–H(81)	109 (1)
C(2$^{\mathrm{i}}$)–C(3)–H(31)	108 (1)	C(1)–C(8)–H(82)	106 (1)
C(4)–C(3)–H(31)	107 (1)	C(7)–C(8)–H(81)	108 (1)
C(2)–C(3)–H(31)	109 (1)	C(7)–C(8)–H(82)	109 (1)
C(5)–C(4)–H(41)	110 (1)	H(81)–C(8)–H(82)	106 (2)

Torsion angles (°)

C(1)–C(2)–C(3)–C(4)	24·3 (3)
C(2)–C(3)–C(4)–C(5)	78·1 (3)
C(3)–C(4)–C(5)–C(6)	−57·0 (3)
C(4)–C(5)–C(6)–C(7)	−53·8 (3)
C(5)–C(6)–C(7)–C(8)	104·8 (3)
C(6)–C(7)–C(8)–C(1)	−64·7 (3)
C(7)–C(8)–C(1)–C(2)	67·9 (3)
C(8)–C(1)–C(2)–C(3)	−91·6 (3)
C(2$^{\mathrm{i}}$)–C(3)–C(2)–C(3$^{\mathrm{i}}$)	17·1 (2)
C(3$^{\mathrm{i}}$)–C(2$^{\mathrm{i}}$)–C(3)–C(2)	−17·0 (2)
C(8)–C(1)–C(2)–C(3$^{\mathrm{i}}$)	166·6 (2)
C(5)–C(4)–C(3)–C(2$^{\mathrm{i}}$)	−171·6 (2)

Symmetry code: (i) $1 - x, y, \frac{3}{2} - z$

approximately equal, this does not apply for the ring bond angles. It turns out that the ring puckering is mainly accomplished by the distortion of the valence angle at C(2) by 2·2 (2)° since the angle at C(3) remains approximately 90°.

As a result of the cyclobutane-ring puckering, C(1) becomes an axial substituent with an angle of 26·6 (2)° between the C(1)—C(2) bond and the normal to the least-squares plane through C(2), C(3), C(2^{i}) and C(3^{i}), whereas C(4) becomes an equatorial substituent with corresponding angle 58·3 (2)°. The observed ring puckering avoids very short H···H contacts for H atoms attached to C(4) and C(1^{i}) that would arise in the case of a flat ring as may be seen from space-filling models.

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Structure of *N,N'*-Di-*tert*-butylethanediimine, $C_{10}H_{20}N_2$, at 98 K and Comparison with the Geometry Calculated by Molecular Mechanics

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Abstract. $M_r = 168·29$, monoclinic, $P2_1/n$, $a = 9·662$ (2), $b = 10·643$ (2), $c = 11·472$ (2) Å, $\beta = 110·15$ (1)°, $U = 1107·5$ (4) Å^3, $Z = 4$, $D_x = 1·009$ g cm^{-3}, λ(Mo $K\alpha$) = 0·71069 Å, $\mu = 0·32$ cm^{-1}, $F(000) = 376$, $T = 98$ K, $R = 0·0461$ for 2593 observed reflections. The low-temperature structure contains two independent molecules that are located on $\bar{1}$ symmetry sites. The ethanediimine moiety is in the *trans* conformation. The detailed geometry with its distortion in the *tert*-butyl bond angles is well reproduced by molecular-mechanics calculations.

Introduction. The gas-phase structure of the title compound, which sublimes at room temperature, was studied by Hargittai & Seip (1976) with electron diffraction (ED) techniques. At 353 K a mixture of 80% *gauche* ($\varphi = 65°$) and 20% *trans* ($\varphi = 180°$) conformers around the central C—C bond was found, both with an *E* configuration about the imine bonds. In all cases one C—C bond of the *tert*-butyl moiety is eclipsed with the nearest C=N bond.

In solution a torsion angle (φ) of 90–140° was derived from dipole-moment measurements on this compound (Exner & Kliegman, 1971) and experimental difference of ^{1}H NMR spectra with and without

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