

Structural Studies of Highly Strained Hydrocarbons.

III. *The *T*–*C*–*C* Stereoisomer of Perhydrotriptycene

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$C_{20}H_{32}$ is monoclinic, space group $P2_1/c$ with $a = 8.904$ (3), $b = 15.226$ (3), $c = 12.410$ (2) Å, $\beta = 106.03$ (2)°, $Z = 4$, $D_m = 1.03$ (2), $D_x = 1.043$ g cm⁻³. The structure was refined to $R = 5.9\%$ for 2961 observed reflections. The bond and torsion angles of the central bicyclooctane nucleus reveal a high degree of strain imposed by the attached cyclohexane rings. The two rings *cis*-bonded and the one *trans*-bonded to the central nucleus show different conformations, the former being in the boat and the latter in a chair conformation. All bond lengths and angles agree well with the values obtained by force-field calculations.

Introduction

In recent years there has been a growing interest in the stereochemistry of high-symmetry strained compounds, for example cage compounds such as bicyclooctane (hereafter BCO) and its derivatives. The BCO system has been extensively investigated by vibrational spectroscopy (Brüesch & Günthard, 1966), X-rays (Cameron, Ferguson & Morris, 1968; Ermer & Dunitz, 1969), electron diffraction (Yokozeki, Kuchitsu & Morino, 1970) and force-field calculations (Ermer & Dunitz, 1969; Ermer 1976) to determine whether its actual conformation has D_{3h} or D_3 symmetry

On the other hand, little is known about homo-substituted bicyclooctanes or more complex systems such as the partially or fully hydrogenated derivatives of triptycene, $C_{20}H_{14}$ (Fig. 1). We have undertaken a systematic structural analysis of the stereoisomers obtained by catalytic hydrogenation of triptycene (Farina, Morandi, Mantica & Botta, 1977) because not only is the structure of this group of molecules interesting in view of their high degree of steric compression and their large flexibility, but also a comparison with the results of conformational analysis,

* Part II: Albinati, Brückner & Allegra (1977). *Acta Cryst.* B33, 229–231.

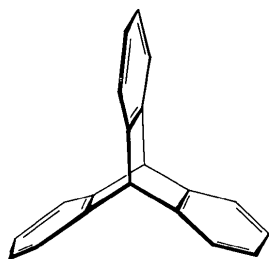


Fig. 1. A schematic representation of the triptycene molecule $C_{20}H_{14}$.

carried out by molecular mechanics, seemed to be particularly significant.

The catalytic hydrogenation of triptycene (on Pd or Ru) has been elucidated (Farina *et al.*, 1977; Morandi, Mantica, Botta, Gramegna & Farina, 1973) and proceeds in steps, one aromatic ring being hydrogenated at a time giving rise to a mixture of partially hydrogenated compounds and eventually, at thermodynamic equilibrium, to a mixture of fully hydrogenated isomers with *cis* and *trans* arrangements of the cyclohexane rings.

We have determined the structure of two isomers (Fig. 2), *A*–*C'*–*C* (I) (see part II of this series) and *C*–*C'*–*C* (II) (Brückner & Allegra, 1977).

The nomenclature adopted refers to the arrangement of the cyclohexane rings along each of the bridges of the BCO nucleus (Fig. 2): the isomer is *C* when both the C–C bonds of the BCO moiety point in the same

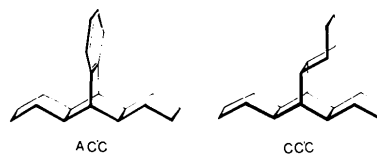


Fig. 2. Schematic drawings of the *A*–*C'*–*C* ($C_{20}H_{24}$) and *C*–*C'*–*C* ($C_{20}H_{32}$) stereoisomers.

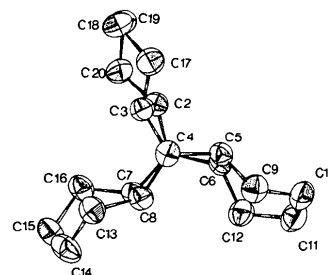


Fig. 3. An ORTEP drawing (Johnson, 1970) of the *T*–*C*–*C* molecule with the numbering scheme. H atoms have been omitted for clarity.

direction, T in the other case (the prime indicates for a given arrangement an opposite orientation, A indicates the presence of an aromatic ring).

We have now carried out an X-ray study of the $T-C-C$ isomer (Fig. 3) to ascertain the solid-state conformation and compare the geometry predicted by conformational analysis with the actual one.

Crystals were obtained by evaporation from toluene. They are prismatic and stable in the air. A crystal $0.5 \times 0.2 \times 0.3$ mm was chosen for data collection. The space group according to the systematic absences ($h0l$: $l = 2n$; $0k0$: $k = 2n$) is $P2_1/c$ (No. 14). The cell parameters were obtained by least squares from the 2θ values of 20 reflections ($\lambda = 0.71069 \text{ \AA}$).

The intensities were collected on a four-circle Philips diffractometer up to $\sin \theta/\lambda = 0.595 \text{ \AA}^{-1}$, graphite-reflected Mo $K\alpha$, $\omega/2\theta$ scan (1.30°), counter opening 1.1° . Out of 2961 reflections measured, 1352 were considered observed [$I \geq 3\sigma(I)$].

Three standard reflections were measured every hour; no significant variation of the intensities was detected.

The data were corrected for Lorentz and polarization factors, but not for extinction or absorption.

The structure was solved with the program *MULTAN* (Main, Woolfson, Lessinger, Germain & Declercq, 1974).

The E map calculated with the phases giving the highest consistency indices (300 E 's, 2000 Σ_2 relationships) revealed all the non-hydrogen atoms. Block-

diagonal isotropic refinement gave an R for the observed reflections of 0.165 falling to 0.115 when anisotropic temperature factors were included; a

Table 2. Bond distances (\AA)

	The bond lengths corrected for TLS are given in parentheses.	
	Experimental	Calculated
C(1)—C(2)	1.534 (7)	(1.537) 1.550
C(1)—C(6)	1.542 (7)	(1.536) 1.555
C(1)—C(7)	1.549 (7)	(1.531) 1.554
C(2)—C(3)	1.537 (8)	(1.545) 1.535
C(2)—C(20)	1.532 (9)	(1.533) 1.535
C(3)—C(4)	1.537 (8)	(1.537) 1.557
C(3)—C(17)	1.513 (8)	(1.518) 1.536
C(4)—C(5)	1.557 (7)	(1.560) 1.557
C(4)—C(8)	1.531 (8)	(1.532) 1.557
C(5)—C(6)	1.561 (7)	(1.566) 1.561
C(5)—C(9)	1.520 (7)	(1.520) 1.544
C(6)—C(12)	1.524 (7)	(1.525) 1.546
C(7)—C(8)	1.578 (6)	(1.578) 1.557
C(7)—C(16)	1.495 (8)	(1.496) 1.547
C(8)—C(13)	1.549 (7)	(1.552) 1.542
C(9)—C(10)	1.530 (7)	(1.538) 1.542
C(10)—C(11)	1.522 (8)	(1.513) 1.544
C(11)—C(12)	1.533 (8)	(1.538) 1.538
C(13)—C(14)	1.512 (8)	(1.499) 1.542
C(14)—C(15)	1.531 (8)	(1.551) 1.545
C(15)—C(16)	1.557 (7)	(1.557) 1.539
C(17)—C(18)	1.526 (8)	(1.527) 1.549
C(18)—C(19)	1.525 (9)	(1.531) 1.550
C(19)—C(20)	1.530 (7)	(1.535) 1.548
(C—H)*	1.02 (3)	

* Average value.

Table 1. Fractional coordinates ($C \times 10^4$, $H \times 10^3$) and isotropic temperature factors

The e.s.d.'s on the last significant digit are in parentheses.

	x	y	z	$B (\text{\AA}^2)$		x	y	z	$B (\text{\AA}^2)$
C(1)	6062 (3)	2947 (2)	2269 (2)		HC(7)	431 (2)	231 (1)	277 (2)	2.2 (5)
C(2)	6803 (3)	2856 (2)	2267 (2)		HC(8)	571 (2)	253 (1)	452 (2)	3.2 (5)
C(3)	7005 (3)	4287 (2)	3420 (2)		HC(9)	795 (3)	194 (2)	519 (2)	6.1 (7)
C(4)	7122 (3)	3544 (2)	4273 (2)		HC(9)	957 (2)	246 (1)	565 (2)	3.4 (5)
C(5)	8235 (3)	2823 (2)	4050 (2)		HC(10)	1055 (4)	161 (2)	451 (3)	6.2 (9)
C(6)	7395 (3)	2355 (2)	2926 (2)		H'C(10)	1012 (3)	99 (2)	521 (2)	5.7 (7)
C(7)	4735 (3)	2937 (2)	2850 (2)		HC(11)	809 (3)	32 (2)	394 (3)	6.7 (8)
C(8)	5495 (3)	3153 (2)	4125 (2)		H'C(11)	869 (4)	74 (2)	310 (3)	9.0 (9)
C(9)	8809 (4)	2182 (2)	5013 (2)		HC(12)	619 (4)	140 (2)	349 (3)	8.5 (9)
C(10)	9563 (4)	1381 (2)	4620 (3)		H'(C12)	626 (3)	112 (2)	243 (2)	5.2 (7)
C(11)	8432 (4)	874 (2)	3698 (3)		HC(13)	492 (3)	371 (2)	546 (2)	3.4 (6)
C(12)	6977 (3)	1408 (2)	3100 (2)		H'C(13)	430 (3)	431 (1)	436 (2)	3.1 (5)
C(13)	4366 (3)	3704 (2)	4593 (2)		HC(14)	279 (3)	260 (2)	439 (2)	7.5 (8)
C(14)	2742 (4)	3316 (2)	4209 (3)		H'C(14)	204 (4)	365 (2)	433 (3)	7.0 (9)
C(15)	2047 (4)	3369 (2)	2930 (3)		HC(15)	138 (4)	283 (2)	260 (3)	8.1 (9)
C(16)	3343 (3)	3493 (2)	2323 (2)		H'C(15)	123 (3)	387 (2)	268 (2)	6.8 (8)
C(17)	8276 (4)	4977 (2)	3598 (3)		HC(16)	277 (3)	336 (2)	155 (2)	4.2 (6)
C(18)	7794 (4)	5676 (2)	2687 (3)		H'C(16)	370 (3)	418 (1)	238 (2)	3.5 (5)
C(19)	7318 (4)	5299 (2)	1499 (3)		HC(17)	856 (3)	525 (2)	436 (3)	7.0 (8)
C(20)	6149 (4)	4535 (2)	1352 (3)		H'C(17)	928 (3)	471 (2)	366 (2)	7.3 (8)
HC(1)	552 (3)	273 (1)	152 (2)	2.8 (5)	HC(18)	688 (3)	605 (2)	274 (3)	7.7 (9)
HC(2)	787 (2)	374 (1)	225 (2)	2.8 (5)	H'C(18)	873 (3)	611 (2)	287 (3)	7.7 (8)
HC(3)	587 (3)	464 (2)	326 (2)	6.6 (8)	HC(19)	671 (3)	580 (2)	100 (2)	6.1 (7)
HC(4)	763 (2)	374 (1)	505 (2)	2.6 (5)	H'C(19)	824 (4)	501 (2)	141 (3)	6.7 (8)
HC(5)	920 (2)	314 (1)	402 (2)	3.2 (5)	HC(20)	508 (3)	476 (2)	137 (2)	5.0 (7)
HC(6)	818 (3)	224 (2)	261 (2)	4.3 (6)	H'C(20)	576 (3)	426 (2)	59 (2)	6.2 (8)

difference map then revealed all the H atoms. Block-diagonal refinement continued with anisotropic temperature factors for the C and isotropic for the H atoms.

The function minimized was $\Sigma w(K^{-1}|F_o| - |F_c|)^2$ and the weights of Cruickshank, Pilling, Bujosa, Lovell & Truter (1961) were used. The scattering factors for C were taken from Cromer & Mann (1968), for H from Stewart, Davidson & Simpson (1965). The refinement was terminated when the shifts in the parameters were less than the e.s.d.'s.

The final $R = \Sigma (|F_o| - |F_c|) / \Sigma |F_o|$ is 0.058 for the observed reflections.

A final difference map showed no significant features.

The programs used were the Univac version for structure factor, Fourier and least-squares calculations (Immirzi, 1967*a,b*; 1973).

The final atomic parameters are given in Table 1, bond lengths and angles, and torsion angles in Tables 2 and 3.*

Because of the low R and the reasonable values for

* Lists of structure factors, anisotropic thermal parameters and the values of the T,L,S tensors have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 32848 (15 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

the thermal parameters, an analysis of the molecular motion in terms of a rigid-body model (Schomaker & Trueblood, 1968) was attempted with a program written by Filippini & Gramaccioli (1969).

The root mean square deviation between the observed and calculated U_{ij} 's, corrected for the number of degrees of freedom, is 0.00030 compared with 0.00042 Å² for the average r.m.s. deviation of the observed U_{ij} 's, showing that this model accounts for most of the thermal motion and the molecule behaves as a rigid body. The corrected bond lengths are not significantly different from the uncorrected ones but are reported in Table 2 for comparison.

The conformational-energy calculations are part of a more general work devoted to the structural analysis of the whole series of stereoisomers of perhydrotriptycene. We have used a Fortran program (Boyd, 1968), and a set of force-field parameters (Boyd, Sanwal, Shary-Tehrany & McNally, 1971) with modified Buckingham potentials for non-bonded interactions and intrinsic rotation and bond-angle strain potentials added. A more detailed description of the calculations and the parameters will be given elsewhere.

Discussion

An overall view of the molecule is given in Fig. 3. The mean bond length in the BCO cage is 1.547 (7) Å,

Table 3. Bond angles and torsion angles (°)

The e.s.d.'s on the last significant digit are in parentheses.

	Observed	Calculated		Observed	Calculated
C(1)–C(2)–C(3)	108.9 (1)	108.81	C(4)–C(8)–C(7)	109.5 (1)	109.37
C(1)–C(2)–C(20)	122.4 (1)	120.72	C(4)–C(8)–C(13)	115.9 (1)	114.18
C(1)–C(6)–C(5)	108.5 (1)	108.77	C(5)–C(4)–C(8)	109.3 (2)	108.62
C(1)–C(6)–C(12)	116.9 (1)	114.59	C(5)–C(6)–C(12)	112.0 (1)	112.21
C(1)–C(7)–C(8)	107.2 (1)	109.41	C(5)–C(9)–C(10)	110.0 (1)	110.44
C(1)–C(7)–C(16)	116.1 (1)	114.47	C(6)–C(1)–C(7)	109.0 (2)	108.66
C(2)–C(1)–C(6)	105.1 (1)	103.45	C(6)–C(5)–C(9)	112.2 (1)	112.45
C(2)–C(1)–C(7)	113.1 (1)	112.96	C(6)–C(12)–C(11)	110.8 (1)	111.51
C(2)–C(3)–C(4)	107.1 (1)	108.29	C(7)–C(8)–C(13)	110.3 (1)	112.64
C(2)–C(3)–C(17)	108.8 (1)	108.54	C(7)–C(16)–C(15)	110.9 (1)	111.56
C(2)–C(20)–C(19)	108.5 (1)	107.70	C(8)–C(7)–C(16)	113.3 (1)	112.23
C(3)–C(2)–C(20)	108.9 (1)	109.82	C(8)–C(13)–C(14)	109.5 (1)	110.36
C(3)–C(4)–C(5)	108.9 (1)	109.60	C(9)–C(10)–C(11)	112.8 (1)	112.11
C(3)–C(4)–C(8)	108.8 (1)	106.90	C(10)–C(11)–C(12)	112.9 (1)	112.89
C(3)–C(17)–C(18)	109.2 (1)	108.09	C(13)–C(14)–C(15)	112.5 (1)	112.17
C(4)–C(3)–C(17)	120.4 (1)	118.98	C(14)–C(15)–C(16)	111.4 (1)	112.90
C(4)–C(5)–C(6)	108.0 (1)	109.82	C(17)–C(18)–C(19)	113.5 (1)	113.28
C(4)–C(5)–C(9)	114.0 (1)	113.79	C(18)–C(19)–C(20)	113.3 (1)	113.17
C(1)–C(2)–C(3)–C(4)	–25.7 (2)		C(7)–C(8)–C(13)–C(14)	45.1 (2)	
C(1)–C(6)–C(5)–C(4)	18.3 (1)		C(7)–C(16)–C(15)–C(14)	–40.9 (2)	
C(1)–C(7)–C(8)–C(4)	–16.2 (1)		C(8)–C(7)–C(16)–C(15)	59.7 (2)	
C(2)–C(3)–C(17)–C(18)	–60.8 (2)		C(8)–C(13)–C(14)–C(15)	64.8 (3)	
C(2)–C(20)–C(19)–C(18)	51.9 (2)		C(9)–C(5)–C(6)–C(12)	15.3 (1)	
C(3)–C(2)–C(20)–C(19)	60.7 (3)		C(9)–C(10)–C(11)–C(12)	–17.8 (1)	
C(3)–C(17)–C(18)–C(19)	51.8 (2)		C(13)–C(8)–C(7)–C(16)	15.2 (1)	
C(5)–C(6)–C(12)–C(11)	58.9 (2)		C(13)–C(14)–C(15)–C(16)	–19.9 (2)	
C(5)–C(9)–C(10)–C(11)	61.8 (2)		C(17)–C(3)–C(2)–C(20)	–67.2 (3)	
C(6)–C(5)–C(9)–C(10)	43.1 (3)		C(17)–C(18)–C(19)–C(20)	48.6 (2)	
C(6)–C(12)–C(11)–C(10)	–41.0 (2)				

equal within the e.s.d.'s to 1.542 (4) Å found in free BCO by electron diffraction (Yokozeki *et al.*, 1970) and 1.541 Å found in bicyclo[2.2.2]octane-1,4-dicarboxylic acid (hereafter III) (Ermer & Dunitz, 1969) by X-ray diffraction.

The C—C bond length in the BCO nucleus where a *cis*-cyclohexane ring is bonded [mean 1.566 (8) Å] is longer than that where a *trans*-bonded ring occurs [mean 1.537 (6) Å], as predicted by the force-field calculations (1.557 and 1.535 Å respectively).

The mean value of the C—C bond in the cyclohexane rings is 1.535 (6) Å, comparable with 1.531 (2) in (I) and 1.55 (2) Å in (II). The highly strained nature of this compound is reflected by the systematic deviations of most bond angles from the 110–113° range usually found in hydrocarbons, and also of the torsion angles around the C—C bonds from the value characterizing the staggered conformation, usually 180° (*trans*) and ±60° (*gauche* and *gauche'*).

The mean of the angles within the BCO cage is 108.6° compared with 110.17(±2)° in (I) or 108.0(±3)° in (II) and a theoretical value of 110(±2)° from conformational calculations; the values in parentheses refer to the spread of values. For the ideal D_{3h} conformation of BCO found in (III) the mean is 109.9° and the mean obtained by electron diffraction is 109.7 (7)° (Yokozeki *et al.*, 1970).

The mean of the angles of the *cis*-bonded cyclohexane ring is 111.6 (4)°, for the *trans*-bonded ring 110.4 (4)°.

For the angles of the type $C_a-C_b-C_c$ (where C_a and C_b belong to the BCO nucleus and C_c is on the *cis*-bonded cyclohexane ring) the mean is 115.7(±1)° comparable with the 115.8(±1.5)° for the $C-C'-C$ isomer but significantly greater than the 112.6(±0.5)° in $A-C'-C$. If C_c is on the *trans*-bonded ring a value of 110.4(±2)° is found. This difference might be due to a smaller steric hindrance of the aromatic ring as compared with the bulkier cyclohexane ring.

The calculated values for the bond angles (Table 3) are in fair agreement with those observed; in particular the systematic distortion of the bond angles is well reproduced. The cyclohexane ring *trans*-bonded to the BCO moiety is in its normal chair conformation while the *cis*-bonded rings are in a boat conformation. This is a general rule for these compounds and has been confirmed by the force-field calculations as the lowest-energy conformation.

As shown by the values of the torsion angles, the BCO cage no longer possesses D_{3h} symmetry as found approximately in (I) or rigorously in (III) and in unsubstituted BCO; the C(1)—C(7)—C(8)—C(4) dihedral angle is 16.2 (3)° compared with 2.4 (1)° in (I) and 0.1 (7)° in (III). The other two angles C(1)—C(6)—C(5)—C(4) and C(1)—C(2)—C(3)—C(4) have respective values of 18.3 (4) and 25.7 (3)° [the corresponding values in (III) are 0.6 (7) and 0.4 (7)°],

indicating the strain imposed on the central nucleus by the substituents.

These values may be compared with the largest possible distortion of BCO from D_{3h} symmetry obtained by gas-phase electron diffraction. A torsion angle (around the threefold axis) of 12.0(±1.5)° is obtained (Yokozeki *et al.*, 1970) and is caused by a twisting motion around the D_{3h} symmetry axis. The potential function which best fits the electron diffraction data shows two minima for the D_{3h} and D_3 conformations separated by a small barrier of about 10 cal mol⁻¹ giving to the BCO cage a quasi D_{3h} conformation.

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