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Structural Studies of Highly Strained Hydrocarbons. II. The *A—C′—C* Stereoisomer of Dodecahydrotriptycene

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Abstract. $C_{20}H_{26}$, triclinic, $P\bar{1}$, $Z = 2$, $a = 11{\cdot}101$ (3), $b = 10{\cdot}077$ (3), $c = 6{\cdot}696$ (2) Å, $\alpha = 86{\cdot}09$ (6), $\beta = 93{\cdot}81$ (6), $\gamma = 84{\cdot}96$ (6)° (from least-squares refinement of diffractometer data); $V = 742{\cdot}77$ Å^3, $D_x = 1{\cdot}19$, $D_m = 1{\cdot}17$ (3) g cm^{-3}. Crystals of quality suitable for X-ray analysis were obtained by slow evaporation from a benzene solution. The molecule contains two cyclohexane rings in the boat conformation *cis* bonded to a bicyclooctane cage.

Introduction. As part of a study of highly strained hydrocarbons, undertaken to determine their conformational properties in the solid state, we have studied the crystal structure of the title compound, which is a stable intermediate in the hydrogenation of triptycene. With the nomenclature of Brückner & Allegra (1976) this compound is the *A—C′—C* stereoisomer, where *A* refers to the presence of an aromatic ring and *C′* and *C* (in clockwise succession) refer to the arrangement of the cyclohexane rings along each of the bridges of the bicyclooctane moiety (Fig. 1). The prime indicates an anticlockwise orientation for one cyclohexane ring, as can be seen along the C_3 axis of the bicyclooctane cage.

The structure is also interesting with regard to the clarification of the nature of the intermediate steps in the hydrogenation reaction leading to a mixture of perhydrotriptycene isomers (Morandi, Mantica, Botta, Gramegna & Farina, 1973; Farina, Morandi, Mantica & Botta, 1976). Compared with other partially hydrogenated products (Farina *et al.*, 1976), this compound shows a remarkable resistance to complete hydrogenation.

The intensities of 2587 reflexions were collected up to $2\theta = 50°$ (graphite-monochromated Mo $K\alpha$ radiation) with a Philips automated four-circle diffractometer and the $\omega/2\theta$ scan technique (scan speed 0·10° s^{-1}, scan range 1·20°). Two background counts (4 s each) for each reflexion were averaged. Three standard reflexions were measured every hour to check stability. No significant variations were observed. No absorption or extinction corrections were found necessary. 1915 reflexions with $I > 2{\cdot}5\sigma(I)$ were considered observed.

The structure was solved with *MULTAN* 74 (Main, Woolfson, Lessinger, Germain & Declercq, 1974); all the C atoms were found on the *E* map and all the H atoms on a difference map. Block-diagonal refinement

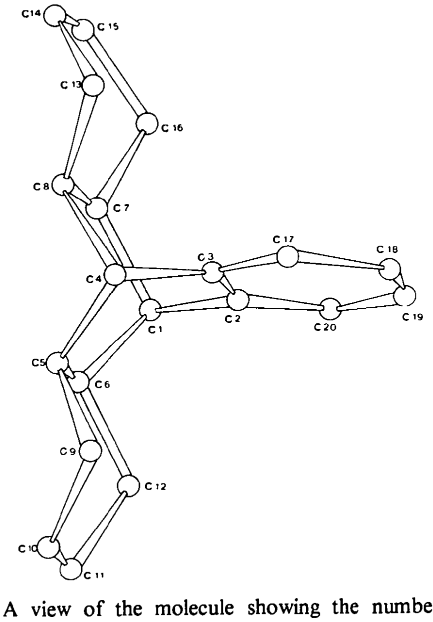

Fig. 1. A view of the molecule showing the numbering of the atoms.

with anisotropic temperature factors for the C atoms and isotropic for the H atoms, and weights chosen after Cruickshank, Pilling, Bujosa, Lovell & Truter (1961) gave a final R of 0·042 for the observed reflexions and 0·062 with the unobserved included. The scattering factors of Cromer & Mann (1968) for C and Stewart, Davidson & Simpson (1965) for H were used. A final difference map showed no significant features.

All calculations were carried out with programs written by Immirzi (1967, 1973). The final atomic parameters are in Table 1, and a perspective view of the molecule is in Fig. 1.*

An analysis in terms of rigid-body motion (Schomaker & Trueblood, 1968) was attempted with a program written by Filippini & Gramaccioli (1969). The r.m.s. deviation between observed and calculated U_{ij}, corrected for the number of degrees of freedom, is 0·0026 compared with a value of 0·0029 Å^2 for the average r.m.s. deviation of the observed U_{ij}, showing that the rigid-body model accounts for most of the thermal motion.

All the rigid-body-corrected bond lengths are within 2 e.s.d.'s of the uncorrected ones. Bond lengths and angles are reported in Table 2.

Discussion. Fig. 1 shows that the molecule possesses non-crystallographic C_{2v} symmetry. The aromatic ring shows no unusual features and the bond lengths [mean C—C 1·387 (2) Å] and angles are normal.

The C(5)—C(6) and C(7)—C(8) lengths [mean 1·560 (2) Å] are equal to those of the equivalent bonds in the C—C'—C stereoisomer [hereafter (I)] (Brückner & Allegra, 1976); the mean of the bond angles within the cyclohexane rings is 112·17 (8)° compared with 110·8 (4)° in (I). Angles of the type C_a—C_b—C_c (where C_a and C_b belong to the bicyclooctane cage and C_c is

Table 1. *Final positional* ($\times 10^4$, *for* H $\times 10^3$) *and thermal parameters*

The anisotropic temperature factor is expressed as $T = \exp[-\frac{1}{4}(B_{11}a^{*}h^2 + B_{22}b^{*2}k^2 + B_{33}c^{*2}l^2 + B_{12}a^{*}b^{*}hk + B_{13}a^{*}c^{*}hl + B_{23}b^{*}c^{*}kl)]$.
The e.s.d.'s are given in parentheses and refer to the last significant figures.

	x	y	z	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
C(1)	7064 (1)	1522 (2)	5429 (2)	2·33 (6)	2·52 (7)	2·42 (7)	−0·20 (10)	0·13 (10)	−0·06 (10)
C(2)	7628 (1)	2533 (1)	6658 (2)	2·19 (6)	2·26 (6)	2·80 (7)	0·07 (10)	−0·35 (11)	−0·06 (11)
C(3)	7231 (1)	2542 (1)	8593 (2)	2·23 (6)	2·28 (6)	2·55 (7)	0·30 (10)	−0·57 (11)	−0·06 (10)
C(4)	6353 (1)	1517 (2)	9017 (2)	2·45 (7)	2·53 (7)	2·39 (7)	−0·15 (10)	0·16 (10)	0·03 (10)
C(5)	6972 (1)	116 (2)	8690 (2)	2·57 (7)	2·32 (7)	2·83 (7)	−0·29 (11)	−0·05 (11)	0·20 (11)
C(6)	7392 (1)	113 (2)	6514 (2)	2·18 (6)	2·32 (6)	2·91 (7)	0·02 (10)	−0·15 (11)	−0·43 (11)
C(7)	5664 (1)	1836 (1)	5319 (2)	2·41 (7)	2·18 (7)	2·53 (7)	−0·42 (10)	−0·39 (11)	−0·57 (10)
C(8)	5228 (1)	1797 (2)	7488 (2)	2·26 (6)	2·38 (6)	2·68 (7)	−0·31 (10)	0·15 (10)	0·02 (10)
C(9)	8463 (1)	3393 (2)	6054 (3)	2·42 (7)	2·83 (7)	3·65 (8)	−0·45 (11)	−0·07 (12)	0·97 (12)
C(10)	8885 (2)	4278 (2)	7367 (3)	2·67 (7)	2·89 (7)	4·86 (10)	−1·46 (12)	−1·18 (14)	0·87 (13)
C(11)	8480 (2)	4309 (2)	9263 (3)	3·23 (8)	2·72 (7)	4·77 (10)	−0·43 (12)	−3·05 (14)	−1·03 (13)
C(12)	7651 (2)	3441 (2)	9899 (3)	3·04 (8)	2·74 (7)	3·03 (8)	0·19 (11)	−1·38 (12)	−0·75 (12)
C(13)	8740 (2)	−347 (2)	6477 (3)	2·49 (7)	3·52 (8)	3·76 (8)	0·42 (12)	0·52 (12)	−0·69 (13)
C(14)	9088 (2)	−1682 (2)	7701 (3)	2·93 (8)	3·12 (8)	5·08 (10)	1·29 (13)	−0·90 (14)	−0·74 (14)
C(15)	8650 (2)	−1690 (2)	9824 (3)	4·12 (9)	3·36 (8)	4·67 (10)	1·80 (14)	−1·07 (15)	1·23 (15)
C(16)	8017 (2)	−345 (2)	10266 (3)	3·77 (8)	3·15 (8)	3·15 (8)	0·95 (13)	−1·19 (13)	0·45 (13)
C(17)	5227 (1)	3161 (2)	4123 (2)	3·01 (7)	2·47 (7)	2·59 (7)	−0·26 (11)	−0·13 (11)	0·18 (11)
C(18)	3853 (2)	3460 (2)	4117 (3)	2·78 (7)	2·80 (7)	3·74 (8)	0·07 (11)	−1·37 (12)	0·25 (12)
C(19)	3399 (2)	3371 (2)	6228 (3)	2·48 (7)	3·78 (8)	4·16 (9)	0·85 (12)	−0·06 (13)	0·39 (14)
C(20)	4435 (2)	3066 (2)	7866 (3)	2·85 (7)	3·24 (8)	3·04 (8)	0·62 (12)	0·57 (12)	−0·48 (12)

	x	y	z	B (Å^2)		x	y	z	B (Å^2)
H(C1)	737 (1)	156 (1)	403 (2)	2·5 (3)	H′(C14)	1000 (2)	−188 (2)	777 (3)	5·4 (5)
H(C4)	607 (1)	153 (2)	1049 (2)	3·0 (4)	H(C15)	803 (2)	−242 (2)	1001 (3)	5·1 (5)
H(C5)	631 (1)	−56 (1)	885 (2)	2·6 (3)	H′(C15)	932 (2)	−192 (2)	1077 (3)	5·3 (5)
H(C6)	690 (1)	−54 (1)	572 (2)	2·3 (3)	H(C16)	860 (2)	34 (2)	1030 (3)	3·6 (4)
H(C7)	532 (1)	109 (1)	458 (2)	2·0 (3)	H′(C16)	767 (2)	42 (2)	1168 (3)	4·3 (4)
H(C8)	471 (1)	96 (1)	767 (2)	2·3 (3)	H(C17)	562 (2)	390 (2)	470 (2)	2·8 (3)
H(C9)	874 (1)	335 (2)	469 (2)	3·1 (4)	H′(C17)	548 (2)	312 (2)	270 (2)	3·2 (4)
H(C10)	947 (2)	489 (2)	695 (3)	4·1 (5)	H(C18)	361 (2)	439 (2)	343 (3)	4·1 (4)
H(C11)	872 (2)	494 (2)	1018 (3)	3·6 (5)	H′(C18)	346 (2)	278 (2)	330 (2)	3·3 (4)
H(C12)	736 (2)	348 (2)	1127 (3)	3·6 (4)	H(C19)	290 (2)	422 (2)	653 (3)	5·1 (5)
H(C13)	896 (2)	−45 (2)	502 (3)	3·6 (4)	H′(C19)	284 (2)	263 (2)	628 (3)	4·8 (5)
H′(C13)	922 (2)	36 (2)	704 (3)	4·0 (4)	H(C20)	409 (2)	294 (2)	924 (3)	3·7 (4)
H(C14)	873 (2)	−240 (2)	696 (3)	4·8 (5)	H′(C20)	492 (2)	383 (2)	795 (3)	3·1 (4)

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* A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 32003 (12 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

on the *cis*-bonded cyclohexane ring) are significantly smaller (mean 112·6 ± 0·5°) than the corresponding ones in (I) (mean 115·8 ± 1°), a discrepancy that may be due to the smaller steric hindrance of the aromatic ring compared to the bulkier cyclohexane moiety. Moreover, the orientation of both cyclohexane rings with respect to the aromatic ring may account for its resistance to hydrogenation; we can assume that the latter is protected from the incoming H by the shielding of the H atoms of the cyclohexane rings [H(C12)–C(2); H(C9)–C(3); H′(C13)–C(3); H′(C16) –C(2); mean 3·2 (1) Å].

Table 2. *Bond distances* (Å), *bond angles* (°) *and internal rotation angles* (°)

C(1)–C(2)	1·505 (2)	C(1)–C(2)–C(3)	113·00 (7)
C(1)–C(6)	1·552 (2)	C(1)–C(6)–C(5)	109·04 (6)
C(1)–C(7)	1·555 (2)	C(1)–C(7)–C(8)	109·36 (6)
C(2)–C(3)	1·397 (2)	C(1)–C(6)–C(12)	112·08 (7)
C(2)–C(20)	1·385 (2)	C(1)–C(7)–C(16)	112·98 (7)
C(3)–C(4)	1·506 (2)	C(1)–C(2)–C(20)	126·78 (9)
C(3)–C(17)	1·390 (2)	C(2)–C(1)–C(6)	108·56 (6)
C(4)–C(5)	1·550 (2)	C(2)–C(1)–C(7)	108·25 (6)
C(4)–C(8)	1·554 (2)	C(2)–C(3)–C(4)	113·20 (6)
C(5)–C(6)	1·559 (2)	C(3)–C(4)–C(5)	108·64 (6)
C(5)–C(9)	1·533 (3)	C(3)–C(4)–C(8)	108·89 (6)
C(6)–C(12)	1·530 (2)	C(4)–C(3)–C(17)	126·93 (9)
C(7)–C(8)	1·560 (2)	C(4)–C(5)–C(6)	109·30 (6)
C(7)–C(16)	1·532 (2)	C(4)–C(8)–C(7)	108·85 (6)
C(8)–C(13)	1·533 (2)	C(4)–C(5)–C(9)	112·87 (7)
C(9)–C(10)	1·528 (3)	C(4)–C(8)–C(13)	112·63 (7)
C(10)–C(11)	1·532 (3)	C(5)–C(6)–C(12)	112·40 (7)
C(11)–C(12)	1·531 (3)	C(6)–C(1)–C(7)	108·48 (6)
C(13)–C(14)	1·531 (3)	C(6)–C(5)–C(9)	111·81 (7)
C(14)–C(15)	1·531 (3)	C(7)–C(8)–C(13)	112·38 (6)
C(15)–C(16)	1·528 (2)	C(8)–C(7)–C(16)	111·63 (6)
C(17)–C(18)	1·392 (3)		
C(18)–C(19)	1·376 (3)		
C(19)–C(20)	1·383 (3)		
C–H (ave.)	1·01 (2)		

C(1)–C(6)–C(5)–C(4)	0·81 (5)
C(1)–C(7)–C(8)–C(4)	2·40 (6)
C(5)–C(4)–C(8)–C(7)	63·04 (7)
C(5)–C(6)–C(1)–C(7)	61·49 (6)
C(5)–C(6)–C(12)–C(11)	51·84 (6)
C(5)–C(9)–C(10)–C(11)	54·67 (6)
C(6)–C(1)–C(7)–C(8)	59·65 (8)
C(6)–C(5)–C(4)–C(8)	61·27 (8)
C(6)–C(5)–C(9)–C(10)	52·92 (7)
C(6)–C(12)–C(11)–C(10)	50·73 (6)
C(7)–C(8)–C(13)–C(14)	51·80 (7)
C(7)–C(16)–C(15)–C(14)	51·92 (8)
C(8)–C(7)–C(16)–C(15)	54·10 (8)
C(8)–C(13)–C(14)–C(15)	54·68 (7)
C(9)–C(5)–C(6)–C(12)	0·02 (6)
C(9)–C(10)–C(11)–C(12)	2·53 (8)
C(13)–C(8)–C(7)–C(16)	2·11 (9)
C(13)–C(14)–C(15)–C(16)	2·61 (8)

This protection mechanism of the reactive sites is in agreement with the observation that the cyclohexane rings hydrogenate one at a time and also that another intermediate can be isolated; this compound possesses only one double bond joining C(2) and C(3), which are the most stereochemically protected, and, of the partially hydrogenated compounds, it is the most resistant to hydrogenation (Farina *et al.*, 1976).

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