Structure of (10*SR*,5*RS*,9*SR*)-10α-Ethyl-5,6,7,8,9,10-hexahydro-5α,9α-methanobenzocyclooctene-10β-carboxamide

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Abstract. $C_{16}H_{21}NO$, $M_r = 243.35$, $P\bar{1}$, $a = 8.689$ (2), $b = 9.124$ (3), $c = 10.270$ (3) Å, $\alpha = 93.83$ (3), $\beta = 107.28$ (3), $\gamma = 117.73$ (4)°, $Z = 2$, $D_c = 1.210$ Mg m^{-3}, $R = 0.046$ for 2596 observed reflexions $|I > 2\sigma(I)|$. The cyclohexene moiety appears in a half-chair and the cyclohexane in a chair conformation. These rings are *cis* fused. The interatomic distances and angles are in agreement with the given atom type and hybridization. Both enantiomers related by the centre of inversion form hydrogen-bonded dimers, with $N-H\cdots O = 2.881$ (2) Å acting between carboxamide groups.

Introduction. Weissenberg photographs recorded with Cu $K\alpha$ radiation indicated space group $P1$ or $P\bar{1}$. The presence of three chiral atoms in the molecule and statistical calculations included in *MULTAN* (Main, Lessinger, Woolfson, Germain & Declercq, 1977) implied the non-centrosymmetric space group $P1$. However, the C(10) epimer of the title compound crystallizes in $P2_1/c$ with right and left enantiomers in the unit cell (Kojić-Prodić, Ružić-Toroš & Golič, 1980). Thus, the solution of the present structure was begun and successfully refined in $P\bar{1}$. A pinacoidal crystal 0.52 × 0.52 × 0.40 mm was selected and intensities collected on an Enraf–Nonius CAD-4 diffractometer with Mo $K\alpha$ radiation. 3226 independent reflexions were recorded in the ω–2θ mode in the range $4 < 2\theta < 56°$. 2596 with $I > 2\sigma(I)$ were used in the calculations. The data were corrected for background, Lorentz and polarization effects but not for absorption $|\mu(\text{Mo }K\alpha) = 0.169$ mm$^{-1}|$.

Overall temperature ($B = 3.08$ Å^2) and scale factors were determined (Wilson, 1942) and used to compute normalized structure amplitudes by the *NORMAL* routine included in *MULTAN* 77. In these calculations all reflexions (3226) were used. The structure was solved with *MULTAN* 77 (Main, Lessinger, Woolfson, Germain & Declercq, 1977). The solution was based on 200 reflexions with $|E| \geq 1.90$. The E map

corresponding to the solution with the best figure of merit (ABS FOM = 1.062, PSI ZERO = 178.4, RESID = 14.42) revealed 17 non-hydrogen atoms out of 18 in the molecule. The remaining C atom belonging to the ethyl group was located from the resulting Fourier synthesis. Refinement was by full-matrix least squares minimizing $\sum w||F_o| - |F_c||^2$. A weighting scheme of type 3 from XRAY (Stewart, Machin, Dickinson, Ammon, Heck & Flack, 1976) was used. The weights were assigned as: $w = w_1 w_2$, where $w_1 = 1$ for $|F_o| \leq 30$ and $w_1 = 30/|F_o|$ for $|F_o| > 30$; $w_2 = 1$ for sin $\theta \geq 0.20$ and $w_2 = (\sin \theta)/0.20$ for sin $\theta < 0.20$. Anisotropic refinement and a subsequent weighted difference synthesis located the H atoms. A scale factor, atomic coordinates, isotropic thermal parameters of the H atoms and anisotropic thermal parameters of the heavy atoms (228 variables in all) were refined. The positional and thermal parameters of H(N)1, H(N)2, H(16)1, H(16)2, and H(16)3 were not refined; for these atoms the isotropic thermal parameters were those of the bonded atoms. Anisotropic

Table 1. *Final atomic coordinates* (× 10⁴) *and isotropic thermal parameters* (× 10²) *for non-hydrogen atoms*

	x	y	z	U (Å²)
O	11216 (1)	6093 (1)	6847 (1)	5.60
N	8802 (2)	6126 (1)	5296 (1)	5.06
C(1)	8940 (2)	9313 (2)	6500 (1)	4.41
C(2)	7910 (2)	10107 (2)	6129 (1)	5.37
C(3)	6494 (2)	9770 (2)	6613 (1)	5.58
C(4)	6145 (2)	8664 (2)	7475 (1)	4.97
C(5)	6740 (2)	6701 (2)	8856 (1)	4.53
C(6)	5081 (2)	4920 (2)	8019 (2)	5.19
C(7)	5582 (2)	4129 (2)	6990 (1)	4.58
C(8)	7434 (2)	4204 (2)	7705 (1)	5.06
C(9)	9054 (2)	5975 (1)	8619 (1)	4.11
C(10)	9840 (1)	7385 (1)	7820 (1)	3.30
C(11)	8443 (2)	6592 (2)	9672 (1)	4.55
C(12)	8620 (1)	8187 (1)	7381 (1)	3.20
C(13)	7200 (2)	7882 (1)	7887 (1)	3.62
C(14)	10015 (2)	6503 (1)	6595 (1)	3.84
C(15)	11866 (2)	8755 (2)	8827 (1)	4.08
C(16)	13027 (2)	10186 (2)	8260 (2)	5.10

$C_{16}H_{21}NO$

Table 2. Positional ($\times 10^3$) and thermal ($\times 10^2$) parameters for the H atoms

	x	y	z	U (Å^2)
H(1)	994 (2)	957 (2)	617 (2)	4·7 (5)
H(2)	820 (2)	1090 (2)	554 (2)	5·8 (5)
H(3)	575 (3)	1033 (2)	634 (2)	6·2 (5)
H(4)	510 (3)	837 (2)	780 (2)	5·8 (5)
H(5)	634 (2)	718 (2)	951 (2)	5·3 (5)
H(6)1	480 (3)	417 (2)	869 (2)	6·4 (6)
H(6)2	391 (2)	498 (2)	751 (2)	5·9 (5)
H(7)1	566 (2)	474 (2)	620 (2)	4·9 (5)
H(7)2	458 (2)	293 (2)	655 (2)	6·1 (5)
H(8)1	779 (2)	376 (2)	700 (2)	5·8 (5)
H(8)2	725 (3)	342 (2)	836 (2)	5·9 (5)
H(9)	1010 (2)	582 (2)	912 (2)	4·2 (4)
H(11)1	812 (2)	575 (2)	1025 (2)	5·2 (5)
H(11)2	950 (2)	774 (2)	1031 (2)	4·9 (5)
H(15)1	1253 (2)	811 (2)	915 (2)	5·4 (5)
H(15)2	1177 (3)	924 (2)	966 (2)	6·0 (5)
H(16)1	1262	1111	807	5·8
H(16)2	1435	1085	891	5·8
H(16)3	1301	962	736	5·8
H(N)1	778	631	500	4·5
H(N)2	893	550	450	4·5

Fig. 1. The atom numbering and bond lengths (Å); the chiral atoms are marked by an asterisk.

Table 3. Bond angles (°)

C(2)–C(1) C(12)	122·4 (2)	C(8)–C(9)–C(11)	108·8 (2)
H(1) C(1)– C(2)	119 (1)	C(8)–C(9) H(9)	106·5 (9)
H(1)–C(1) C(12)	118 (1)	C(10)–C(9)–C(11)	109·6 (2)
C(1)–C(2)–C(3)	119·6 (2)	H(9)–C(9)–C(10)	106 (1)
C(1) C(2)–H(2)	120 (2)	H(9)–C(9) C(11)	110 (1)
H(2)–C(2) C(3)	121 (2)	C(9)–C(10)–C(12)	112·1 (1)
C(2) C(3) C(4)	119·3 (2)	C(9)–C(10) C(15)	106·9 (1)
C(2) C(3) H(3)	120 (1)	C(9) C(10)–C(14)	105·0 (1)
H(3)–C(3) C(4)	121 (1)	C(12)–C(10)–C(14)	114·4 (1)
C(3) C(4)– C(13)	122·0 (2)	C(12) C(10) C(15)	110·9 (1)
C(3)· C(4) H(4)	120 (1)	C(14)–C(10) C(15)	107·0 (1)
H(4) C(4) C(13)	118 (1)	C(5)–C(11) C(9)	108·0 (1)
C(6) C(5)–C(11)	110·5 (2)	C(5) C(11)–H(11)1	110 (1)
C(6) C(5) C(13)	110·6 (1)	C(5) C(11)–H(11)2	111 (1)
C(11) C(5) C(13)	110·4 (1)	C(9) C(11)–H(11)1	108 (1)
H(5)–C(5) C(6)	107·3 (8)	C(9) C(11) H(11)2	110 (1)
H(5) C(5) C(11)	111 (1)	H(11)1 C(11)–H(11)2	109 (1)
H(5) C(5) C(13)	107 (1)	C(1) C(12)–C(10)	121·0 (2)
C(5) C(6) C(7)	110·2 (2)	C(1)–C(12) C(13)	117·4 (2)
C(5) C(6) H(6)1	108·7 (9)	C(10) C(12)–C(13)	121·5 (1)
C(5)–C(6) H(6)2	111 (1)	C(4) C(13) C(5)	118·6 (2)
H(6)1–C(6) C(7)	108 (2)	C(4) C(13) C(12)	119·4 (2)
H(6)2 C(6) C(7)	111 (1)	C(5)–C(13)–C(12)	122·0 (2)
H(6)1 C(6)–H(6)2	108 (2)	O C(14) C(10)	118·9 (1)
C(6)–C(7)–C(8)	111·7 (1)	O C(14)–N	122·0 (2)
C(6) C(7) H(7)1	110 (1)	C(10) C(14)–N	119·0 (2)
C(6) C(7) H(7)2	110 (1)	H(N)1 N–C(14)	129
C(8) C(7) H(7)1	110 (1)	H(N)2–N –C(14)	117
H(7)1 C(7) H(7)2	107 (1)	C(10) C(15)–C(16)	117·9 (1)
C(8) C(7) H(7)2	109 (1)	C(10)–C(15)–H(15)1	105·9 (8)
C(7)–C(8)–C(9)	114·5 (2)	C(10)–C(15)–H(15)2	107 (1)
C(7) C(8) H(8)1	110 (1)	H(15)1–C(15) C(16)	109 (1)
C(7)–C(8) –H(8)2	108 (1)	H(15)2–C(15)–C(16)	109 (1)
H(8)1 –C(8) –C(9)	111·1 (9)	H(15)1–C(15)–H(15)2	106 (2)
H(8)2 C(8)–C(9)	105·9 (8)	C(15)–C(16)–H(16)1	117
H(8)1 C(8)–H(8)2	106 (2)	C(15)–C(16)–H(16)2	111
C(8) C(9) C(10)	116·5 (1)	C(15) C(16)–H(16)3	106

Table 4. Displacements from least-squares planes (Å)

Atoms included in the calculation of the planes are denoted by an asterisk.

Plane I		Plane II	
C(5)*	−0·004 (2)	C(5)*	−0·020 (2)
C(10)*	0·004 (2)	C(6)*	0·019 (2)
C(12)*	−0·009 (2)	C(8)*	−0·019 (2)
C(13)*	0·009 (2)	C(9)*	0·019 (2)
C(9)	−0·239 (2)	C(7)	−0·606 (2)
C(11)	0·578 (2)	C(11)	0·746 (2)

Scattering factors given by Cromer & Mann (1968) and (for H) Stewart, Davidson & Simpson (1965) were used.

The calculations were carried out on a Univac 1110 computer at the University Computing Centre in Zagreb with XRAY (Stewart, Machin, Dickinson, Ammon, Heck & Flack, 1976).

Atom coordinates are listed in Tables 1 and 2.*

Discussion. The present structure determination is part of an investigation of the 10,10-disubstituted ethyl-5,6,7,8,9,10-hexahydro-5,9-methanocyclooctenes (Mutak, 1979). Some derivatives in this class of

thermal parameters are in the usual range: maximum values of U_{22} for O and N of 0·070 (1) and 0·066 (1) Å^2 were obtained, respectively. The final $R = 0·046$ and $R_w = 0·043$ for 2596 reflexions with $I > 2\sigma(I)$.

Table 5. *Torsion angles* (°)

|					
C(12)—C(13)—C(5)—C(6)	−97·2 (2)	C(11)—C(9)—C(10)—C(14)	−168·3 (1)	H(6)1—C(6)—C(7)—C(8)	−68 (1)
C(12)—C(13)—C(5)—C(11)	25·5 (2)	C(11)—C(9)—C(10)—C(15)	78·3 (2)	H(6)2—C(6)—C(7)—C(8)	174 (1)
C(11)—C(5)—C(6)—C(7)	−59·9 (2)	C(9)—C(10)—C(12)—C(13)	11·0 (2)	H(7)1—C(7)—C(8)—C(9)	72 (1)
C(13)—C(5)—C(6)—C(7)	62·7 (2)	C(14)—C(10)—C(12)—C(13)	130·5 (1)	H(7)2—C(7)—C(8)—C(9)	−171 (1)
C(5)—C(6)—C(7)—C(8)	50·8 (2)	C(15)—C(10)—C(12)—C(13)	−108·4 (1)	H(8)1—C(8)—C(9)—C(10)	56 (1)
C(6)—C(7)—C(8)—C(9)	−49·6 (2)	C(9)—C(10)—C(14)—O	−69·5 (2)	H(8)2—C(8)—C(9)—C(10)	171 (2)
C(7)—C(8)—C(9)—C(10)	−70·2 (2)	C(9)—C(10)—C(14)—N	107·1 (2)	H(9)—C(9)—C(10)—C(15)	−40 (1)
C(7)—C(8)—C(9)—C(11)	54·1 (2)	C(9)—C(10)—C(15)—C(16)	174·1 (2)	H(N)1—N—C(14)—C(10)	−1
C(8)—C(9)—C(10)—C(12)	80·4 (2)	C(9)—C(11)—C(5)—C(6)	65·0 (2)	H(N)2—N—C(14)—C(10)	−178
C(11)—C(9)—C(10)—C(12)	−43·5 (2)	C(5)—C(11)—C(9)—C(8)	−60·2 (2)	H(16)1—C(15)—C(16)—C(10)	−71
C(8)—C(9)—C(10)—C(14)	−44·4 (2)	C(10)—C(12)—C(13)—C(5)	−2·1 (2)	H(16)2—C(15)—C(16)—C(10)	169
C(8)—C(9)—C(10)—C(15)	−157·8 (2)	H(5)—C(5)—C(6)—C(7)	179 (1)	H(16)3—C(15)—C(16)—C(10)	53
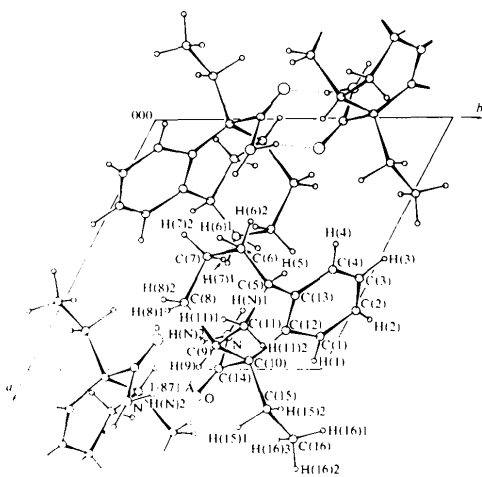
Fig. 2. Projection of the crystal structure along **c**. The enantiomers are hydrogen bonded by N—H(N)2···O of 2·881 (2) Å forming dimers. The value of the N—H(N)2—O angle is 167°.

compounds possess analgesic properties (Kojić-Prodić, Ružić-Toroš & Golič, 1980).

The structural formula with the atom numbering and intramolecular distances is given in Fig. 1. Bond angles are listed in Table 3. The conformation of the molecule is shown in Tables 4 and 5. The molecular packing is illustrated in Fig. 2. The C—C lengths between C(sp^3) atoms range from 1·512 (3) to 1·558 (2) Å. Bond lengths in the phenyl ring are in the range 1·373 (3) to 1·399 (2) Å. Interatomic distances in the carboxamide group, C(14)—O of 1·229 (3) and C(14)—N of 1·332 (2) Å, are in the usual range.

The valence angles involving only C(sp^3) atoms range from 105·0 (1) to 117·9 (1)°. The bond angles for the C(sp^2) atoms range from 117·4 (2) to 122·4 (2)°. All values of bond distances and angles are close to those found in the C(10) epimer (Kojić-Prodić, Ružić-Toroš & Golič, 1980).

The geometry of the present molecule can be considered in two ways: (1) by dividing the ring part in two moieties, cyclohexane and cyclohexene, or (2) as a cyclooctene ring. C(5), C(6), C(7), C(8), C(9), C(11) form a cyclohexane ring in a chair conformation. C(5), C(11), C(9), C(10), C(12), C(13) are in a cyclohexene ring with a typical half-chair conformation. C(5), C(10), C(12), C(13) form plane I (Table 4) and C(9) and C(11) are displaced from this plane by −0·239 (2) and 0·578 (2) Å. C(5), C(6), C(8), C(9) lie in plane II (Table 4) and C(7) and C(11) are displaced from it by −0·606 (2) and 0·746 (2) Å. Therefore, the conformation can be described by means of *cis*-fused six-membered rings. The conformation of the cyclooctene ring with corresponding torsion angles is shown in Table 5.

The appearance of the right and left enantiomers is the consequence of an inversion operation in $P\bar{1}$. These enantiomers form hydrogen-bonded dimers with N—H(N)2···O = 2·881 (2) Å and N—H(N)2—O = 167°.

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