# Synthesis and crystal structure of cis-1-benzylidene-1,2,3,4-tetrahydronaphthalene, containing an unexpected conformation of the cyclohexenylidene ring

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#### Abstract

Two isomers of 1-benzylidene-1,2,3,4-tetrahydronaphthalene have been synthesized by the Wittig reaction, and the crystal structure of the cis-isomer has been solved. The compound  $C_{17}H_{16}$  crystallizes in the monoclinic space group  $P2_1/n$  with a = 9.796(2), b = 5.490(5), c = 23.215(3)Å,  $\beta = 95.11(2)^\circ$ , and Z = 4. The structure was determined by direct methods, and refined by full-matrix least squares to R = 0.047 for 1104 reflections. The cyclohexenylidene ring has the unusual envelope  $C_s^{2,10}$  conformation.

# Introduction

Earlier attempts to synthesize the title compound by the Wittig reaction and to separate the cis and transisomers were not successful (Witschard and Griffin, 1964; Bestmann *et al.*, 1968). We now report the synthesis and separation of isomers, their characterization, and a single-crystal X-ray study for cis-isomer (V). The appearance of the two isomers can be attributed either to cis-trans

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isomerism around the C(1)=C(11) double bond, or to structural isomerism, with a double bond transfer in the 1-2 position. The crystal and molecular structure of the trans isomer (Bukowska-Strzyżewska and Skoweranda, 1987) demonstrated an unexpected  $C_2^{9,10}$  conformation of the cyclohexenylidene ring and an out-of-plane deformation of the four bonds around the double C(1)-C(11) bond.

## Experimental

Melting points were determined with a Boetius apparatus, and were not corrected. The IR spectra were recorded on a Specord 72-IR spectrometer, and the <sup>1</sup>H-NMR spectra on a Tesla BS 467(60 MHz) spectrometer using TMS as an internal standard ( $\delta = 0$ ). The chromatographic analysis was performed by gas chromatography (GCHF 18.3 apparatus, steel column of 3 m length and  $\phi = 4$  mm packed by 5% DC 200 chromosorb W-AWDMC3 80-100 mesh; temperature 200°C; carrier gas N<sub>2</sub>). The quantitative separations were performed by column chromatography using Al<sub>2</sub>O<sub>3</sub> (layer length of 85 cm,  $\phi = 1.8$  cm). The purity of the separated compounds was controlled by thin layer chromatography (TLC), using Merck silica gel 60F 254 analytical sheets.

$$\begin{array}{c} 1\text{-}Benzylidene-1,2,3,4\text{-}tetrahydronaphthalene}\\ & \oplus & \oplus \\ [C_6H_5CH_2-P(C_6H_5)_3]Cl + C_2H_5ONa \rightarrow C_6H_5CH = P (C_6H_5)_3 + C_2H_5OH + NaCl \\ I & II \end{array}$$



38.9 g (0.1 mol) of I and 14.6 g (0.1 mol) of III were dissolved in 75 ml of hot absolute ethanol. To this boiling solution the solution of sodium ethoxide (2.3 g Na in 75 ml ethanol) was added drop by drop during 35 min. The reaction mixture was heated and stirred for 2 h. After cooling, NaCl was filtered off and  $C_2H_5OH$  evaporated under reduced pressure. The residue in 60 ml of ether was

allowed to stand overnight; the next day,  $(C_6H_5)_3PO$  was filtered off. The ether solution was washed with water and dried with MgSO<sub>4</sub>. The ether was evaporated and the residue was fractionally distilled, and the fraction 152-160°C (0.4 hPa) was collected. (The gas chromatography analysis indicated that the fraction contains isomers IV and V and the initial ketone III; the ratio of isomers V: IV was 19.68: 80.32). The isomers were separated by preparative column chromatography using cyclohexane as the eluent. The fastest moving band afforded IV + V (13.07 g), and the slowest gave IV (1.87 g); the common yield was 67.8%. The full chromatographic resolution was obtained by reducing the separated portion to 1 g. Isomer trans(IV): t.t. 49-50°C (crystallized from ethanol); IR(CHCl<sub>3</sub>): 3025, 2940, 1600, 1445 cm<sup>-1</sup>; <sup>1</sup>H-NMR(CDCl<sub>3</sub>)  $\delta$ (ppm): 1.74 (qui, 2H, -C-CH<sub>2</sub>-C-), 2.78 (t, 4H,  $\equiv$ C-CH<sub>2</sub>- and  $Ar-CH_2-$ ), 6.97-7.76 (m, 9H, Ar and 1H,  $\equiv$ CH); C<sub>17</sub>H<sub>16</sub>(220.3) calculated: C-92.68, H-7.32; found: C-92.84, H-7.28. Isomer cis(V): t.t. 67-68°C (crystallized from ethanol); IR(CHCl<sub>3</sub>): 3035, 2956, 1605, 1490, 1450 cm<sup>-1</sup>; <sup>1</sup>H-NMR(CDCl<sub>3</sub>)  $\delta$ (ppm): 1.94 (qui, 2H, -C-CH<sub>2</sub>-C-), 2.47(t, 2H,  $\equiv$ C-CH<sub>2</sub>-), 2.82(t, 2H, Ar-CH<sub>2</sub>-), 6.34(S, 1H,  $\equiv$ CH), 6.60-7.22 (m, 9H, Ar); C<sub>17</sub>H<sub>16</sub>(220.3) calculated: C-92.68, H-7.32; Found: C-92.56, H-7.30.

### X-ray determination

Crystals suitable for X-ray diffraction were obtained by crystallization from ethanol solution. Preliminary cell dimensions were determined photographically. Accurate unit-cell dimensions were obtained by the least-squares fit to the  $\theta$  values of 25 reflections ( $10 \le \theta \le 30^\circ$ ) measured on the Enraf-Nonius CAD4 diffractometer. The intensity data were collected using graphitemonochromated Mo K $\alpha$  radiation and the  $\omega$ -2 $\theta$  scan technique. The three monitor reflections, measured after every 75 reflections, showed a slight systematic intensity reduction, and the appearance of the crystal indicated that sublimation had occurred. The measured intensities were corrected for the intensity variation (from 1.00 to 1.10), and the data were corrected for Lorentz and polarization effects, but not for absorption. Crystal data and experimental details are listed in Table 1.

#### Solution and refinement of the structure

The structure was solved by direct methods, using the multisolution MUL-TAN 78 program system (Main *et al.*, 1978). An *E* map phased on the set having the highest FOM and lowest residual revealed correctly all 17 carbon atoms and three hydrogen atoms. Four cycles of full-matrix least-squares refinement, including a scale factor and individual isotropic thermal parameters, gave R =0.120. Individual anisotropic thermal parameters were then introduced, and after

Molecular formula	$C_{17}H_{16}$
M <sub>r</sub>	220.33
Space group	$P2_1/n$
a(Å)	9.796(2)
b(Å)	5.490(5)
c(Å)	23.215(3)
$\beta(\text{deg})$	95.11(2)
$V(\text{\AA}^3)$	1243(1)
Z	4
F(000)	472
$D_x(\mathrm{Mg} \mathrm{m}^{-3})$	1.18
$D_m(Mg m^{-3})$	1.17
$\mu(Mo K\alpha) (mm^{-1})$	0.33
Radiation	Μο Κα
Temperature (°C)	22
Scan mode	$\omega - 2\theta$
Crystal size (mm)	0.4  imes 0.25  imes 0.15
$2\theta$ range	0-60°
Reflections measured	2602
Reflections with $I \ge 3\delta(I)$	1104
R	0.047
$R_w$	0.050

Table 1. Crystal data and experimental parameters

three cycles R dropped to 0.096. At this stage a three-dimensional difference Fourier synthesis was computed, which revealed the positions for the all hydrogen atoms. Peaks higher than those corresponding to the hydrogen atoms were not observed. Further refinement (all hydrogen atoms were included with isotropic temperature factors) gave R = 0.047 and  $R_w = 0.050$ . The function  $(|F_o| - F_c|)^2$  was minimized, and in the final cycles of calculation a weighting scheme based on counting statistics was used with  $w = [\delta|F_o|^2 + 0.0017|F_o|^2]^{-1}$ . An empirical isotropic extinction correction was introduced, and the parameter was refined to the value 0.0046(15). The final difference Fourier map did not show any peaks higher than 0.15 e Å<sup>-3</sup>. Tables 2, 3 and 4 list the final atomic positional and thermal parameters. Most of the computations were performed with SHELX-76 crystal structure determination program (Sheldrick, 1976) on a AMSTRAD 1512 minicomputer.

#### Discussion

The view of the molecule, with endocyclic torsion angles indicated, is given in Figure 1. Bond lengths and angles are listed in Table 5. The double bond of 1.332(4)Å links C(1) and C(11) atoms. The molecule has a cis configuration. The cyclohexenylidene ring adopts a slightly deformed envelope

	x	.v	Z
C(1)	-769(3)	407(5)	1188(1)
C(2)	-2246(3)	-396(8)	1097(2)
C(3)	-2323(5)	-3012(9)	1296(2)
C(4)	-1856(4)	-3304(8)	1925(2)
C(5)	-148(3)	-1814(7)	2718(2)
C(6)	831(4)	-238(7)	2952(2)
C(7)	1292(3)	1583(7)	2615(1)
C(8)	798(3)	1764(6)	2045(1)
C(9)	-181(3)	141(5)	1796(1)
C(10)	-688(3)	-1654(6)	2145(1)
C(11)	-107(3)	1140(6)	742(1)
C(12)	1378(3)	1539(6)	706(1)
C(13)	1846(4)	3479(7)	409(1)
C(14)	3229(4)	3778(9)	337(2)
C(15)	4161(4)	2094(8)	556(2)
C(16)	3724(4)	163(8)	852(2)
C(17)	2347(3)	-141(7)	931(1)

**Table 2.** Positional parameters  $(\times 10^4)$  for the nonhydrogen atoms

conformation  $C_s^{2,10}$  instead of the expected  $C_s^{3,9}$  conformation. The asymmetry parameter (Duax and Norton, 1975)  $\Delta C_s^{2,10} = 5.3$ ,  $\Delta C_s^{3,9} = 36.5$ . This unexpected conformation probably results from intramolecular steric hindrance. A slightly shortened (according to Kitaigorodsky, 1973) contact H(8)...C(12) of

**Table 3.** Anisotropic temperature factors  $(\text{\AA}^2 \times 10^3)$  in the form: exp  $[-2\pi^2(U_{11}h^2a^{*2} + U_{22}k^2b^{*2} + U_{33}l^2c^{*2} + 2U_{23}klb^*c^* + 2U_{13}lhc^*a^* + 2U_{12}hka^*b^*)]$ 

	<i>U</i> <sub>11</sub>	U <sub>22</sub>	U <sub>33</sub>	U <sub>23</sub>	<i>U</i> <sub>13</sub>	<i>U</i> <sub>12</sub>
C(1)	43(2)	51(2)	56(2)	-5(1)	3(1)	8(1)
C(2)	43(2)	87(3)	74(2)	-12(2)	-2(2)	1(2)
C(3)	59(3)	87(3)	102(3)	-10(3)	4(2)	-22(2)
C(4)	63(2)	63(2)	100(3)	3(2)	13(2)	-12(2)
C(5)	62(2)	65(2)	66(2)	14(2)	23(2)	3(2)
C(6)	61(2)	83(3)	51(2)	0(2)	11(2)	9(2)
C(7)	59(2)	70(2)	52(2)	-8(2)	6(2)	-7(2)
C(8)	52(2)	55(2)	51(2)	1(2)	9(1)	-7(2)
C(9)	40(2)	50(2)	52(2)	-2(1)	9(1)	7(1)
C(10)	46(2)	49(2)	68(2)	0(2)	16(1)	4(2)
C(11)	54(2)	56(2)	50(2)	0(2)	-5(1)	8(2)
C(12)	58(2)	55(2)	39(1)	-2(2)	2(1)	0(2)
C(13)	73(2)	71(2)	62(2)	17(2)	3(2)	3(2)
C(14)	82(3)	82(3)	64(2)	12(2)	16(2)	-21(2)
C(15)	62(2)	92(3)	63(2)	-5(2)	17(2)	-10(2)
C(16)	58(2)	81(3)	67(2)	-1(2)	8(2)	13(2)
C(17)	57(2)	61(2)	56(2)	6(2)	10(1)	6(2)

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	x	у	z	U	
H(21)	-278(4)	53(7)	131(2)	9(1)	
H(22)	-257(3)	-31(5)	69(1)	6(1)	
H(31)	-319(4)	-355(7)	124(2)	9(1)	
H(32)	-165(5)	-405(9)	109(2)	12(2)	
H(41)	-271(4)	-307(7)	219(2)	11(1)	
H(42)	-162(3)	-505(7)	202(1)	8(1)	
H(5)	-46(3)	-297(7)	296(1)	8(1)	
H(6)	121(3)	-31(6)	335(2)	8(1)	
H(7)	193(3)	282(6)	277(1)	7(1)	
H(8)	112(3)	311(6)	185(1)	6(1)	
H(11)	-63(3)	131(5)	365(1)	5(1)	
H(13)	117(4)	469(7)	28(2)	8(1)	
H(14)	346(4)	509(8)	13(2)	11(1)	
H(15)	512(4)	227(7)	48(1)	9(1)	
H(16)	434(5)	-111(8)	102(2)	10(1)	
H(17)	204(3)	-150(6)	113(1)	7(1)	

Table 4. Hydrogen atom positional parameters ( $\times 10^3$ ) with isotropic temperature factors (Å  $^2\times 10^2)$ 



Fig. 1. View of the molecule of cis-1-benzylidene-1,2,3,4-tetrahydronaphthalene with endocyclic torsion angles (deg). The torsion angles convention according to Klyne and Prelog (1960).

Bond lengths (Å)				
C(2) - C(1)	1.509(5)	C(9) - C(1)	1.483(4)	
C(11) - C(1)	1.332(4)	C(3) - C(2)	1.512(6)	
C(4) - C(3)	1.498(6)	C(10) - C(4)	1.512(5)	
C(6) - C(5)	1.368(5)	C(10) - C(5)	1.391(5)	
C(7) - C(6)	1.370(5)	C(8) - C(7)	1.372(5)	
C(9) - C(8)	1.396(4)	C(10) - C(9)	1.395(4)	
C(12) - C(11)	1.481(4)	C(13) - C(12)	1.370(5)	
C(17) - C(12)	1.391(5)	C(14) - C(13)	1.390(6)	
C(15) - C(14)	1.366(6)	C(16) - C(15)	1.353(5)	
C(17) - C(16)	1.387(5)			
	Bond ang	gles (deg)		
C(9) - C(1) - C(2)	113.0(3)	C(11) - C(1) - C(2)	120.5(3)	
C(11) - C(1) - C(9)	126.4(3)	C(3) - C(2) - C(1)	108.0(3)	
C(4) - C(3) - C(2)	112.3(4)	C(10) - C(4) - C(3)	114.9(3)	
C(10) - C(5) - C(6)	122.3(4)	C(7) - C(6) - C(5)	119.3(4)	
C(8) - C(7) - C(6)	119.9(4)	C(9) - C(8) - C(7)	121.5(4)	
C(8) - C(9) - C(1)	121.7(3)	C(10) - C(9) - C(1)	119.5(3)	
C(10) - C(9) - C(8)	118.6(3)	C(5) - C(10) - C(4)	119.8(3)	
C(9) - C(10) - C(4)	121.7(3)	C(9) - C(10) - C(5)	118.4(3)	
C(12) - C(11) - C(1)	129.6(3)	C(13) - C(12) - C(11)	121.2(3)	
C(17) - C(12) - C(11)	121.4(3)	C(17) - C(12) - C(13)	117.2(3)	
C(14) - C(13) - C(12)	121.7(4)	C(15) - C(14) - C(13)	120.2(4)	
C(16) - C(15) - C(14)	119.2(4)	C(17) - C(16) - C(15)	121.1(4)	
C(16) - C(17) - C(12)	120.6(4)			

Table 5. Bond lengths (Å) and angles (deg)

2.81(3)Å is observed. The valence angles C(1)-C(11)-C(12) of 129.6(3)° and C(9)-C(1)-C(11) of 126.5(3)° are significantly greater than 120°.

The four torsion angles around the C(1)=C(11) bond, namely  $\omega_{2-1-11-12} = -166.7(3)$ ,  $\omega_{9-1-11-H(11)} = 177(2)$ ,  $\omega_{9-1-11-12} = 9.6(5)$ , and  $\omega_{2-1-11-H(11)} = 7(2)^\circ$ , indicate the out-of-plane deformation of the



group. These deformations may be described in terms of two out-of-plane bendings  $\chi_1$  and  $\chi_{11}$  and one twist  $\tau_{1-11}$  around the double bond (Winkler and Dunitz, 1971; Bürgi and Shefter, 1975):  $\tau_{1-11} = 8(2)^{\circ}$ ,  $\chi_1 = 3.7(3)$ ,  $\chi_{11} = -7(2)^{\circ}$ . All three deformations are working cooperatively in the out-of-plane deformations of this group.

The phenyl ring condensed with the cyclohexenylidene ring is not perfectly planar; the intraring torsion angles ranging from 0.6(8) to  $3.0(4)^{\circ}$ . Inside the aromatic ring the normal bond lengths and angles are observed, whereas inside

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Fig. 2. The packing in the unit cell viewed along b.

the cyclohexenylidene ring (similar as in the trans isomer in Bukowska-Strzyżewska *et al.*, 1987) the shortened  $C_{sp}^3 - C_{sp}^3$  bond lengths of 1.499(6) and 1.513(7) Å and unexpected bond angles C(2)-C(1)-C(9) of 113.0(3), C(2)-C(3)-C(4) of 112.3(4) and  $C(3)-C(4)-C(10) = 114.9(3)^{\circ}$  are found. The packing arrangement (Fig. 2) does not indicate any shortened intermolecular contacts.

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Structure factor data have been deposited with the British Library, Boston Spa, Wetherby, West Yorkshire, UK as supplementary publication No 60583 (8 pages).