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cis-1,2,3,4,4a,5,6,8a-Octahydro-3,3-dimethyl-1-(1-propyl)quinol-2-one

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Abstract. $C_{14}H_{23}NO$ (m.p. 55–56 °C), monoclinic, $P2_1/c$, $a = 10{\cdot}315\ (4)$, $b = 8{\cdot}598\ (2)$, $c = 15{\cdot}341\ (10)$ Å, $\beta = 100{\cdot}00\ (9)°$; $Z = 4$, $D_x = 1{\cdot}097$ g cm^{-3}; $F(000) = 488$. All H atoms were located and the model was refined to an R of 0·040. A *cis*-fused configuration was observed for the bicyclic skeleton.

Introduction. Colourless prismatic crystals were kindly provided by Professor W. Oppolzer (Department of Organic Chemistry, University of Geneva). Because of easy sublimation a crystal with an average cross-section of 0·3 mm was sealed in a Lindemann capillary. The cell parameters and intensities were obtained at 20°C on an automatic four-circle Philips PW 1100 diffractometer (graphite monochromator, Mo $K\alpha$ radiation). 1849 reflexions were scanned over two quadrants in the θ–2θ mode (scan width 1·0°; scan speed 0·02° s^{-1}) within the range $3° \leq \theta \leq 18°$. A monitor reflexion measured at intervals of about 80 reflexions revealed a slight decrease in intensity and this was taken into account in the data reduction. After averaging over pairs of equivalent reflexions, 795 structure amplitudes had $|F| \geq 3\sigma_F$ and were used in the analysis. The phase problem was solved with *LSAM* (Main, Woolfson & Germain, 1972). The E map revealed the locations of all the non-hydrogen atoms. Positional parameters and anisotropic temperature factors were refined by full-matrix least squares. The function minimized was $\Sigma\, \omega \Delta F^2$, where $\omega = 1/\sigma_F^2$. All H atoms were subsequently located from a difference synthesis and refined isotropically. The final R based on 795 reflexions was 0·040. The final positional parameters are listed in Table 1. The bond lengths and angles are given in Table 2.* The numbering system is given in Fig. 1.

Table 1. *Final positional parameters with standard deviations*

Values are $\times 10^4$ for non-hydrogen atoms and $\times 10^3$ for hydrogen atoms.

	x	*y*	*z*
C(1)	3646 (3)	3093 (4)	4283 (3)
C(2)	3985 (3)	3255 (4)	5272 (3)
C(3)	3253 (4)	4083 (5)	5728 (3)
C(4)	2021 (4)	4937 (5)	5340 (3)
C(5)	1890 (3)	5047 (4)	4337 (3)
C(6)	2212 (3)	3500 (4)	3925 (2)
C(7)	1335 (3)	2170 (4)	4123 (2)
C(8)	1620 (3)	679 (4)	3648 (2)
C(9)	3089 (4)	377 (6)	3731 (2)
N(10)	3969 (3)	1513 (4)	4008 (2)
C(11)	5375 (3)	1198 (4)	4019 (3)
C(12)	5757 (4)	1484 (5)	3122 (3)
C(13)	7198 (4)	1078 (5)	3108 (3)
C(14)	989 (3)	−710 (4)	4042 (3)
C(15)	1067 (3)	771 (5)	2650 (3)
O(16)	3469 (2)	−923 (3)	3534 (2)
H(1)	420 (3)	389 (3)	397 (2)
H(2)	495 (3)	266 (4)	555 (2)
H(3)	347 (2)	414 (3)	638 (2)
H1(4)	111 (3)	430 (3)	547 (2)
H2(4)	208 (3)	613 (4)	567 (2)
H1(5)	265 (2)	580 (3)	421 (2)
H2(5)	88 (3)	539 (4)	410 (2)
H(6)	207 (3)	364 (3)	319 (2)
H1(7)	36 (3)	245 (3)	390 (2)
H2(7)	151 (3)	197 (4)	486 (2)
H1(11)	603 (3)	189 (4)	452 (2)
H2(11)	557 (3)	−2 (4)	424 (2)
H1(12)	569 (3)	265 (5)	297 (2)
H2(12)	517 (3)	82 (4)	269 (2)
H1(13)	787 (4)	168 (5)	363 (3)
H2(13)	736 (4)	124 (5)	237 (3)
H3(13)	733 (3)	−13 (4)	329 (2)
H1(14)	136 (3)	−79 (4)	472 (2)
H2(14)	117 (3)	−178 (4)	372 (2)
H3(14)	4 (3)	−54 (4)	402 (2)
H1(15)	114 (4)	−28 (5)	236 (2)
H2(15)	159 (3)	180 (4)	232 (2)
H3(15)	7 (3)	86 (4)	260 (2)

Discussion. It has been shown that steric control over several centres of chirality is possible in intramolecular Diels–Alder reactions (review: Oppolzer, 1977). In particular, intramolecular cycloaddition of dieneamides could be directed towards the formation of either *cis*- or *trans*-fused octahydroquinolinones in a highly stereoselective way (Oppolzer & Fröstl, 1975). In further studies with substituted dieneamides (Oppolzer & Fröstl, 1977) a 3 : 1 mixture of diastereoisomeric octahydroquinolinones was obtained, but to neither component could a *cis* or *trans* configuration be unequivo-

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* Lists of structure factors and thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 32538 (11 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

Table 2. *Molecular parameters*

Bond distances (Å) (mean e.s.d. 0·005 Å)

C(1)–C(2)	1·503	C(8)–C(9)	1·522
C(1)–C(6)	1·527	C(8)–C(14)	1·533
C(1)–N(10)	1·478	C(8)–C(15)	1·541
C(2)–C(3)	1·322	C(9)–N(10)	1·351
C(3)–C(4)	1·499	C(9)–O(16)	1·239
C(4)–C(5)	1·524	N(10)–C(11)	1·472
C(5)–C(6)	1·533	C(11)–C(12)	1·515
C(6)–C(7)	1·520	C(12)–C(13)	1·530
C(7)–C(8)	1·527		

Bond angles (°) (mean e.s.d. 0·3 °)

C(2)–C(1)–C(6)	112·5	C(7)–C(8)–C(15)	111·2
C(2)–C(1)–N(10)	110·4	C(9)–C(8)–C(14)	108·6
C(6)–C(1)–N(10)	111·2	C(9)–C(8)–C(15)	106·4
C(1)–C(2)–C(3)	121·9	C(14)–C(8)–C(15)	108·8
C(2)–C(3)–C(4)	125·2	C(8)–C(9)–N(10)	120·5
C(3)–C(4)–C(5)	110·6	C(8)–C(9)–O(16)	119·1
C(4)–C(5)–C(6)	112·0	N(10)–C(9)–O(16)	120·4
C(1)–C(6)–C(5)	108·5	C(1)–N(10)–C(9)	125·6
C(1)–C(6)–C(7)	109·2	C(1)–N(10)–C(11)	115·9
C(5)–C(6)–C(7)	113·1	C(9)–N(10)–C(11)	118·5
C(6)–C(7)–C(8)	111·2	N(10)–C(11)–C(12)	111·8
C(7)–C(8)–C(9)	112·0	C(11)–C(12)–C(13)	112·5
C(7)–C(8)–C(14)	109·7		

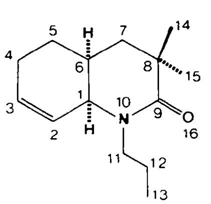

Fig. 1. The atom-numbering system.

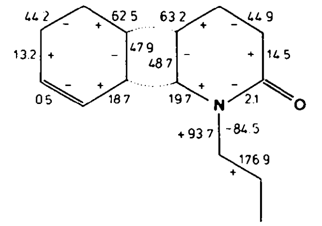

Fig. 2. An exploded view of the bicyclic skeleton showing the torsion angles (°) in the component rings. The mean e.s.d. is 0·4°.

cally assigned by standard procedures. The present determination was undertaken to identify the major diastereoisomer.

The octahydroquinolinone ring system is *cis*-fused with a torsion angle H(1)–C(1)–C(6)–H(6) of 46·5°. Both component rings are in a half-chair conformation and have similar shapes, as reflected by the torsion angles (Fig. 2). The amido fragment [C(1), C(11), N(10), C(9), C(8), O(16)] is reasonably planar (e.s.d. 0·030 Å) with a maximum deviation of 0·038 Å for C(11); C(6) is shifted by 0·452 Å from the best plane, whereas C(7) is displaced by 0·285 Å in the opposite direction. As expected the olefinic backbone C(1)–C(2)–C(3)–C(4) is also planar (e.s.d. 0·002 Å). C(5) and C(6) are forced out of the plane in opposite directions, at distances of 0·319 and 0·444 Å respectively. The planes defined by the amido and olefinic fragments are inclined to each other at an angle of 114·7°. The *n*-propyl chain, together with N(10) to which it is bonded, assumes the favoured *trans*-planar configuration. This plane makes an angle of 86·3° with that of the amido group. The slight departure from perpendicularity can be explained by repulsions between H(2)···H1(11) and O(16)···H2(11), separated by 2·19 and 2·38 Å respectively, which add up to induce a torsion of the N(10)–C(11) bond. The predominant non-bonded interaction between the two ring components of the octahydroquinolinone backbone occurs through the pseudo-axial H1(4) and the axial H2(7) at a distance of 2·27 Å; the latter is also in van der Waals contact with H1(14) of the pseudo-equatorial methyl group.

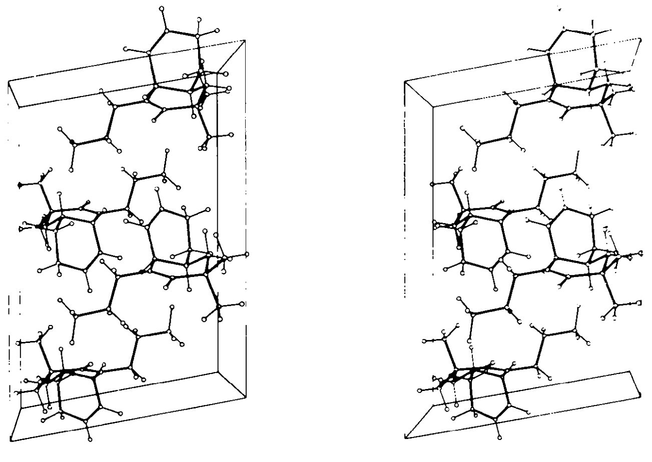

Fig. 3. A stereoscopic view of the contents of one unit cell. The origin is in the upper-left, rear corner; **a** points to the right and **c** downwards. The basic molecule with position (*x*,*y*,*z*) is the left molecule of the enantiomeric pair at the centre of the cell.

A stereoscopic view of the contents of one unit cell is shown in Fig. 3. The molecules touch almost exclusively *via* H···H contacts, with no distances substantially shorter than van der Waals diameters. There is only one short separation of 2·47 Å between O(16) in (x,y,z) and H(2) of the neighbouring molecule related by the centre of symmetry at ($\frac{1}{2},0,\frac{1}{2}$).

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2,2-Diphenylpent-4-ynenitrile (PHIPN)

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Abstract. $C_{17}H_{13}N$, orthorhombic, $Pn2_1a$, $Z = 4$, FW 231·31; $a = 9·8857\ (7)$, $b = 7·6927\ (5)$, $c = 17·1299\ (36)$ Å, $V = 1302·7\ (5)$ Å^3; $D_x = 1·177$, $D_m = 1·18$ g cm^{-3} (KI solution); $\lambda(\text{Mo } K\bar{\alpha}) = 0·7107$ Å, $\mu = 0·74$ cm^{-1}; dimensions: 0·70 × 0·5 × 0·4 mm; final $R = 0·05$. H atoms were located and refined isotropically. The C≡N and C≡C distances are 1·126 (4) and 1·180 (5) Å respectively, and the angles C—C≡N and C—C≡C are 178·8 (4) and 177·9 (3)°.

Introduction. A Philips 1100 automated diffractometer with monochromated Mo $K\bar{\alpha}$ radiation was used for collecting the 2025 unique reflexions up to 30° (2θ) in the $\omega/2\theta$ scan mode. 1519 intensities which were greater than twice the e.s.d. from counting statistics were considered as observed. Lorentz and polarization effects, but not absorption, were corrected. The noncentrosymmetric space group was decided from the distribution of the E values.

The structure was solved by direct (*MULTAN* 74, Main, Woolfson, Lessinger, Germain & Declercq, 1974) and Fourier methods. After least-squares refinement to an R of 0·14 a difference map revealed all the H atoms (which were refined with the other atoms) in the mixed mode (XRAY 70, Stewart, Kundell & Baldwin, 1970). The weighting scheme was derived from the ΔF *vs* F_o) and ΔF *vs* $\sin\theta/\lambda$ plots. It showed no dependence on $\sin\theta/\lambda$ and was: $w = 0·75/\sigma_F^2$ with $\sigma_F = 0·53 - 0·08|F_o|$ if $|F_o| < 3·6$, and $\sigma_F = 0·12 + 0·04|F_o|$ if $|F_o| > 3·6$. This scheme yielded $R = 0·05$ and $R_2 = 0·06$* with no trends in $\langle w\Delta^2F\rangle$. A final ΔF synthesis revealed no peaks outside the ±0·15 e Å^{-3} range.

Atomic scattering factors from *International Tables for X-ray Crystallography* (1962) were used for all the atoms.

Discussion. The stereochemistry of PHIPN and its derivatives with Cu$^{\text{I}}$, Ag$^{\text{I}}$ and Au$^{\text{I}}$ is being studied at the Institute of Inorganic Chemistry 'Elhuyar' (CSIC, Madrid) (Barral, Moreno & Santos, 1975). As a starting point a crystallographic study of the title compound has been undertaken.

Tables 1, 2 and 3 list the coordinates, the H thermal parameters and the derived bond lengths and angles. The numbering of the atoms is presented in Fig. 1. The angles involving phenyl H atoms range from 116 to 124°.

The geometry of the C(2)—C(1)≡N(6) group [1·486 (4), 1·126 (4) Å and 178·8 (4)°] agrees with the data in the literature (Kokkou & Rentzeperis, 1975; Ikemoto, Chikaishi, Yakushi & Kuroda, 1972). The acetyl group, C(3)—C(4)≡C(5), values of 1·450 (4), 1·180 (5) Å and 177·9 (9)°, also agree with reported

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