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Note

Molecular structure and absolute configuration of (+)-(1R, 2S, 6R, 7S, 1′R)-5-(1′-phenylethylamino)-*endo*-tricyclo[5.2.1.0^{2,6}]deca-4,8-dien-3-one

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The crystal and molecular structure of (+)-(1R, 2S, 6R, 7S, 1′R)-5-(1′-phenylethylamino)-*endo*-tricyclo[5.2.1.0^{2,6}]deca-4,8-dien-3-one is described. Based on the known absolute configuration (R) of the α-phenylethylamine moiety the X-ray analysis revealed the absolute configuration of the title compound. The structure was refined to $R_1 = 0.0298$ for 1950 reflections (with $I > 2\sigma(I)$). Crystal data: $C_{18}H_{19}NO$, monoclinic, space group $P2_1$, $a = 6.7406(4)$, $b = 9.959(2)$, $c = 11.3123(8)$Å, $\beta = 102.969(5)$, $V = 740.0(2)$Å^3, and $Z = 2$.

KEY WORDS: Crystal structure; tricyclodecadienone; enaminone; resolution.

Introduction

The *endo*-tricyclo[5.2.1.0^{2,6}]deca-4,8-dien-3-one system **1** has proven to be an extremely useful synthon for a wide range of naturally occurring cyclopentanoids and other pharmacologically important compounds.[1] A most convenient and direct route to **1** constitutes the Diels-Alder reaction of cyclopenten-1,3-dione with cyclopentadiene, yielding racemic 5-hydroxytricyclodecadienone **2**. Amination of (±)-**2** with the optically pure (R)-(+)-α-phenylethylamine furnished in high yield the corresponding diastereomeric enaminones **3a** and **3b** in a 1:1-ratio (Scheme 1.)[2]

The diastereomers could be separated by column chromatography on silica gel. In order to establish the absolute configuration of the respective isomers, an X-ray diffraction analysis of one of the diastereomers ($[\alpha]^{20}{}_{d} = +178°$ (c = 1, $CHCl_3$), mp. 222–224°C) was undertaken.

Experimental

The crystal data and a summary of the data collection and structure refinement are given in Table 1. The atomic positional and vibrational parameters are given in Table 2. The structure was solved by the program CRUNCH.[3] All nonhydrogen atoms were refined with anisotropic temperature factors. All hydrogen atoms were taken from a difference Fourier map and were freely refined.

Discussion

The structure and atomic numbering are presented in Fig. 1. Selected bond distances and angles are given

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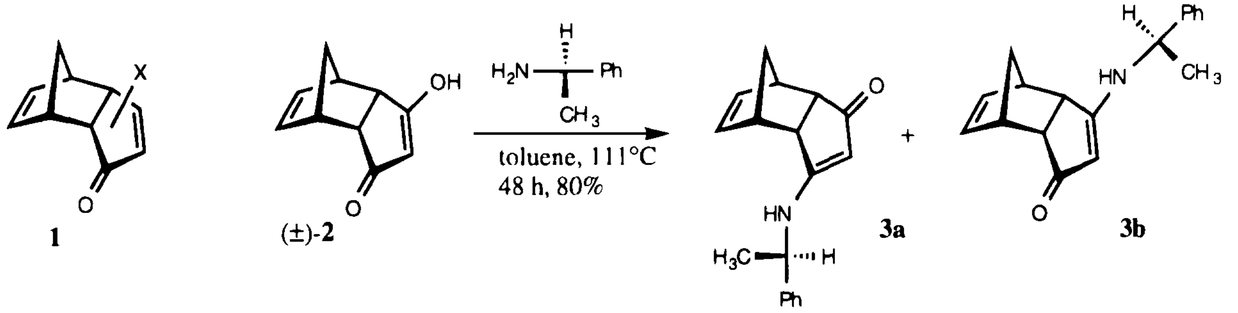

Scheme 1.

Table 1. Crystal data and structure refinement for **3a**

Compound	$C_{18}H_{19}NO$
Color/shape	Colorless/regular plate
Empirical formula	$C_{18}H_{19}NO$
Formula weight	265.34
Temperature	293(2)K
Crystal system	Monoclinic
Space group	$P2_1$
Unit cell dimensions (25 reflections, 18° $< \theta <$ 24°)	a = 6.7406(4) Å b = 9.959(2) Å c = 11.3123(8) Å β = 102.969(5)°
Volume	740.0(2) Å^3
Z	2
Density (calculated)	1.191 g cm^{-3}
Absorption coefficient	0.073 mm^{-1}
Diffractometer/scan	Enraf-Nonius CAD4/ θ-2θ scan
Radiation/wavelength	Mo$K\alpha$ (graphite monochrom.) /0.71073 Å
F(000)	284
Crystal size	0.42 × 0.39 × 0.20 mm
θ-range for data collection	2.76 to 26.29°
Index ranges	$-8 \leq h \leq 6$, $-12 \leq k \leq 9$, $-13 \leq l \leq 14$
Reflections collected	2548
Independent/observed refls.	2227 [R_{int} = 0.0083]/1950 ([$I > 2\sigma(I)$])
Absorption correction	Semi-empirical from psi-scans[5]
Range of rel. transm. factors	0.98 and 1.04
Refinement method	Full-matrix, least-squares on F^2
Computing	SHELXL[6]
Data/restraints/parameters	2227/1/258
Goodness-of-fit on F^2	1.093
SHELXL-93 weight parameters	0.0358, 0.0669
Final R indices [$I > 2\sigma(I)$]	R_1 = 0.0298, wR_2 = 0.0694
R indices (all data)	R_1 = 0.0377, wR_2 = 0.0739
Extinction coefficient	0.079(5)
Largest diff. peak and hole	0.121 and −0.117 e.Å^{-3}

Table 2. Atomic coordinates (× 10^4) and equivalent isotropic displacement parameters (Å^2 × 10^3) for **3a**[a]

	x	y	z	U_{eq}
N(1)	−9162(2)	−747(2)	−1693(1)	49(1)
O(1)	−16074(2)	−2126(2)	−2522(2)	84(1)
C(1)	−14036(3)	−2711(2)	−4725(2)	51(1)
C(1′)	−8874(3)	200(2)	−683(2)	52(1)
C(2)	−13271(3)	−2911(2)	−3334(2)	45(1)
C(2′)	−6957(4)	1020(3)	−642(2)	67(1)
C(3)	−14249(3)	−2039(2)	−2535(2)	56(1)
C(4)	−12760(3)	−1174(2)	−1854(2)	57(1)
C(5)	−10913(3)	−1362(2)	−2145(2)	44(1)
C(6)	−11046(3)	−2419(2)	−3099(2)	42(1)
C(7)	−10833(3)	−1954(2)	−4388(2)	51(1)
C(8)	−12232(4)	−791(3)	−4750(2)	61(1)
C(9)	−14114(3)	−1231(2)	−4952(2)	61(1)
C(10)	−12102(3)	−3076(3)	−5146(2)	59(1)
C(20)	−8841(3)	−522(2)	505(2)	51(1)
C(21)	−10301(3)	−270(2)	1158(2)	60(1)
C(22)	−10247(4)	−947(3)	2249(2)	75(1)
C(23)	−8746(5)	−1855(3)	2677(2)	81(1)
C(24)	−7295(4)	−2123(3)	2042(2)	81(1)
C(25)	−7344(4)	−1465(3)	962(2)	68(1)

[a] U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor.

in Table 3. From the data in Table 3 it can be seen that the interatomic distances in the enaminone moiety differ markedly from the standard bond lengths found for isolated C=O, C−C, C=C, and C−N bonds (1.22, 1.46, 1.34, and 1.40, respectively). However, it is clear that the enaminone moiety is in fact a conjugated system which explains the deviations found. Further geometrical calculations revealed neither unusual geometric features, nor unusual short intermolecular contacts. Calculations with PLATON[4] revealed no higher symmetry and no solvent accessible areas.

Based on the known absolute configuration (R) of the α-phenylethylamine moiety the X-ray analysis revealed absolute structure **3a** for the diastereomer

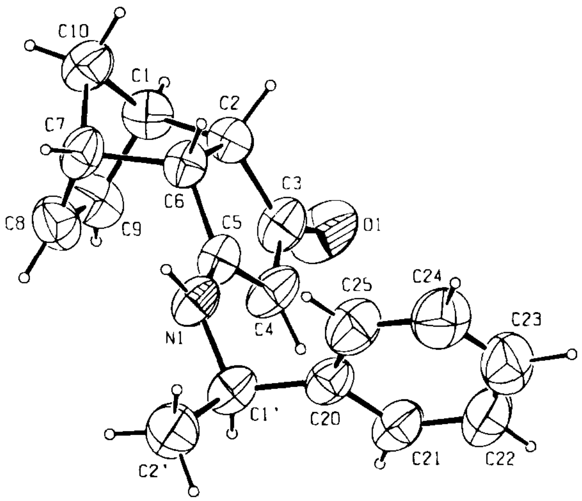

Fig. 1. ORTEP[7] drawing of the molecule with atomic numbering. Thermal ellipsoids are at 50% probability.

with $[\alpha]d^{20} = +178°$ ($c = 1$, $CHCl_3$). The diastereomer with $[\alpha]d^{20} = +117°$ ($c = 0.51$, $CHCl_3$) therefore has the absolute configuration **3b**. Although no diastereoselectivity is observed in the formation of **3a** and **3b** from (±)-**2**, the successful separation of these diastereomers constitutes the first optical resolution of the tricyclodecadienone system starting from 5-hydroxy-*endo*-tricyclodecadienone.

Table 3. Selected bond lengths [Å] and angles [°] for **3a**

O(1)–C(3)	1.236(2)
C(3)–C(4)	1.413(3)
C(4)–C(5)	1.370(2)
N(1)–C(5)	1.326(2)
C(5)–N(1)–C(1')	123.4(2)
O(1)–C(3)–C(4)	128.5(2)
O(1)–C(3)–C(2)	122.5(2)
C(4)–C(3)–C(2)	109.0(2)
C(5)–C(4)–C(3)	111.0(2)
N(1)–C(5)–C(4)	128.5(2)
N(1)–C(5)–C(6)	120.5(2)
C(4)–C(5)–C(6)	111.0(2)

Supplementary material. Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication CCDC-1003/5370. Copies of available material can be obtained, free of charge, on application to the Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK, (fax: +44-(0) 1223-336033 or e-mail: deposit@ccdc.cam.ac.uk).

References

1. Zhu, J.; Yang, J.Y.; Klunder, A.J.H.; Liu, Z.Y.; Zwanenburg, B. *Tetrahedron* **1995**, *51*, 5847, and references cited therein.
2. Bakkeren, F.J.A.D.; Ramesh, N.G.; De Groot, D.; Klunder; A.J.H.; Zwanenburg, B. *Tetrahedron Lett.* **1996**, *37*, 8003.
3. Gelder, R. de; Graaff, R.A.G. de; Schenk, H. *Acta Crystallogr.* **1993**, *A49*, 287.
4. Spek, A.L. *Acta Crystallogr.* **1990**, *A46*, C-34.
5. North, A.C.T.; Philips, D.C.; Mathews, F.S. *Acta Crystallogr.* **1968**, *A24*, 351.
6. Sheldrick, G.M. *SHELXL-93. Program for the Refinement of Crystal Structures*; University of Gottingen: Germany, 1993.
7. Spek, A.L. *PLATON-93. Program for Display and Analysis of Crystal and Molecular Structures*; University of Utrecht: The Netherlands, 1995.