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syn-1,5-Dimethylbicyclo[3.2.1]oct-8-yl *N*-Phenylcarbamate

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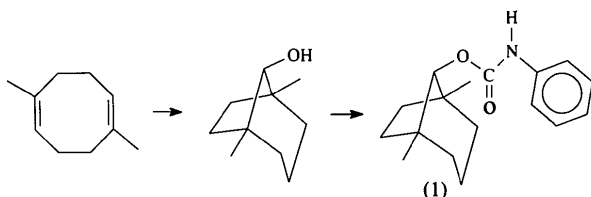
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Abstract

The *N*-phenylcarbamate residue in *syn*-1,5-dimethylbicyclo[3.2.1]oct-8-yl *N*-phenylcarbamate, C₁₇H₂₃NO₂, is in an axial position with respect to the cyclohexane chair, while the five-membered ring has an envelope and the cycloheptane moiety a boat conformation.

Comment

N-Phenylcarbamates of cyclic alcohols are useful targets for biotransformations by fungi (Vigne, Archelas, Fourneron & Furstoss, 1986, 1987; Vigne, Archelas & Furstoss, 1988; Pietz & Haufe, 1995). In order to gain insight into the sterical requirements for the substrates of the enzymatic system it is essential to obtain exact information on the geometry of rigid molecules. The title compound, (1), provides a good model substrate for studying the selective oxygenation of non-activated positions by microorganisms.



Compound (1) was synthesized according to the scheme above (for details see *Experimental*). The X-ray crystallographic analysis shows that the product is

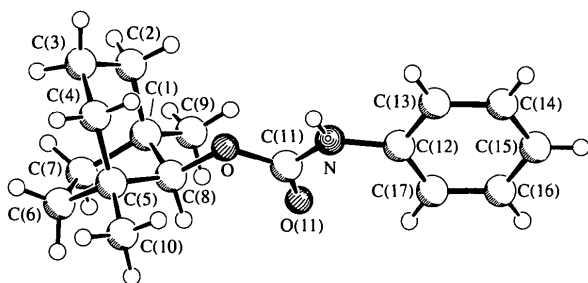


Fig. 1. SCHAKAL92 (Keller, 1992) plot of (1) with the atomic numbering scheme.

the *syn*-orientated *N*-phenylcarbamate of the bicyclic alcohol. The three ring systems of the 1,5-dimethylbicyclo[3.2.1]oct-8-yl residue have the following conformations: the five-membered ring is envelope, the six-membered ring is chair and the seven-membered ring is boat.

Experimental

The title compound was prepared as described by Whitesell, Matthews & Solomon (1976) and Haufe, Wolf & Schulze (1986).

Crystal data

C₁₇H₂₃NO₂
M_r = 273.26
Monoclinic
*P*2₁/*c*
a = 10.134 (1) Å
b = 18.154 (1) Å
c = 8.518 (1) Å
 β = 103.44 (1)°
V = 1524.2 (2) Å³
Z = 4
D_x = 1.191 Mg m⁻³
D_m not measured

Data collection

Enraf–Nonius CAD-4
diffractometer
 $\omega/2\theta$ scans
Absorption correction:
none
5382 measured reflections
2586 independent reflections
2196 observed reflections
[*I* > 2σ(*I*)]

Refinement

Refinement on *F*²
R(*F*) = 0.038
wR(*F*²) = 0.103
S = 1.004
2586 reflections
187 parameters
 $w = 1/[\sigma^2(F_o^2) + (0.051P)^2 + 0.330P]$
where $P = (F_o^2 + 2F_c^2)/3$
(Δ/σ)_{max} = <0.001

Cu *K*α radiation
 λ = 1.54178 Å
Cell parameters from 25
reflections
 θ = 22.87–42.70°
 μ = 0.61 mm⁻¹
T = 293 K
Irregular
0.5 × 0.4 × 0.1 mm
Colourless

*R*_{int} = 0.032
 θ_{max} = 64.96°
h = 0 → 11
k = -21 → 21
l = -10 → 9
3 standard reflections
monitored every 250
reflections
intensity decay: none

$\Delta\rho_{max}$ = 0.27 e Å⁻³
 $\Delta\rho_{min}$ = -0.17 e Å⁻³
Extinction correction:
 $F_c^* = kF_c[1 + (0.001\chi \times F_c^2 \lambda^3 / \sin 2\theta)]^{-1/4}$
Extinction coefficient:
 $\chi = 0.0097$ (4)
Atomic scattering factors
from *International Tables
for Crystallography* (1992,
Vol. C)

Table 1. Fractional atomic coordinates and equivalent isotropic displacement parameters (Å²)

	$U_{eq} = (1/3)\sum_i \sum_j U_{ij} a_i^* a_j^* \mathbf{a}_i \cdot \mathbf{a}_j$			
	<i>x</i>	<i>y</i>	<i>z</i>	<i>U_{eq}</i>
C(1)	0.7452 (1)	0.1185 (1)	-0.1373 (2)	0.045 (1)
C(2)	0.6482 (2)	0.1747 (1)	-0.0915 (2)	0.057 (1)
C(3)	0.6082 (2)	0.1555 (1)	0.0649 (2)	0.064 (1)
C(4)	0.7295 (2)	0.1326 (1)	0.1969 (2)	0.055 (1)
C(5)	0.8232 (1)	0.0782 (1)	0.1381 (2)	0.045 (1)

C(6)	0.7412 (2)	0.0132 (1)	0.0465 (2)	0.056 (1)
C(7)	0.6917 (2)	0.0391 (1)	-0.1298 (2)	0.057 (1)
C(8)	0.8729 (1)	0.1133 (1)	-0.0010 (2)	0.039 (1)
C(9)	0.7718 (2)	0.1369 (1)	-0.3022 (2)	0.062 (1)
C(10)	0.9391 (2)	0.0546 (1)	0.2760 (2)	0.065 (1)
O	0.9376 (1)	0.1834 (1)	0.0509 (1)	0.043 (1)
C(11)	1.0404 (1)	0.2042 (1)	-0.0145 (1)	0.038 (1)
O(11)	1.0740 (1)	0.1720 (1)	-0.1236 (1)	0.053 (1)
N	1.0973 (1)	0.2662 (1)	0.0584 (1)	0.044 (1)
C(12)	1.2050 (1)	0.3071 (1)	0.0221 (1)	0.038 (1)
C(13)	1.2259 (2)	0.3773 (1)	0.0869 (2)	0.048 (1)
C(14)	1.3258 (2)	0.4218 (1)	0.0524 (2)	0.057 (1)
C(15)	1.4055 (2)	0.3972 (1)	-0.0465 (2)	0.058 (1)
C(16)	1.3870 (2)	0.3270 (1)	-0.1073 (2)	0.061 (1)
C(17)	1.2882 (1)	0.2812 (1)	-0.0730 (2)	0.050 (1)

Table 2. Selected geometric parameters (Å, °)

C(1)—C(8)	1.527 (2)	C(5)—C(8)	1.530 (2)
C(1)—C(9)	1.527 (2)	C(5)—C(6)	1.546 (2)
C(1)—C(2)	1.530 (2)	C(6)—C(7)	1.541 (2)
C(1)—C(7)	1.546 (2)	C(8)—O	1.452 (2)
C(2)—C(3)	1.519 (2)	O—C(11)	1.345 (2)
C(3)—C(4)	1.518 (2)	C(11)—O(11)	1.211 (2)
C(4)—C(5)	1.534 (2)	C(11)—N	1.348 (2)
C(5)—C(10)	1.518 (2)	N—C(12)	1.413 (2)
O—C(8)—C(1)	114.92 (11)	C(10)—C(5)—C(8)	112.49 (12)
C(1)—C(8)—C(5)	103.94 (11)	C(10)—C(5)—C(4)	110.84 (13)
O(11)—C(11)—O	124.40 (12)	C(8)—C(5)—C(4)	108.95 (11)
O—C(11)—N	109.43 (10)	C(10)—C(5)—C(6)	113.85 (13)
C(11)—N—C(12)	127.38 (11)	C(8)—C(5)—C(6)	99.35 (10)
C(8)—C(1)—C(9)	114.40 (12)	C(4)—C(5)—C(6)	110.79 (12)
C(8)—C(1)—C(2)	109.12 (11)	C(7)—C(6)—C(5)	105.93 (11)
C(9)—C(1)—C(2)	110.47 (13)	C(6)—C(7)—C(1)	106.63 (11)
C(8)—C(1)—C(7)	98.93 (11)	O—C(8)—C(5)	109.60 (10)
C(9)—C(1)—C(7)	112.39 (12)	C(11)—O—C(8)	117.26 (10)
C(2)—C(1)—C(7)	111.02 (12)	O(11)—C(11)—N	126.16 (12)
C(3)—C(2)—C(1)	112.88 (13)	C(17)—C(12)—N	123.89 (12)
C(4)—C(3)—C(2)	112.18 (13)	C(13)—C(12)—N	116.79 (12)
C(3)—C(4)—C(5)	112.97 (13)		

The positions of the H atoms of (1) could be found from difference Fourier maps, but refinement resulted in slightly deformed arrangements. Thus, for final refinement, H atoms were set at calculated positions [except for H(N)].

Data collection and cell refinement were carried out with CAD-4 EXPRESS (Enraf-Nonius, 1993). All calculations were performed with SHELXS86 (Sheldrick, 1985) and SHELXL93 (Sheldrick, 1993). Molecular graphics were obtained with SCHAKAL92 (Keller, 1992).

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Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: JZ1075). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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A 1:1 Molecular Complex of 1,5-Diphenylbiuret and Phenyl Carbamidonitrile

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Abstract

Crystals of the title compound, 1,5-diphenylbiuret-*N*-cyano-*N'*-phenylurea (1/1), C₁₄H₁₃N₃O₂·C₈H₇N₃O, were obtained from both ethanol and ethyl acetate solutions of phenyl carbamidonitrile. The structure of the complex features pairs of diphenylbiuret and phenyl carbamidonitrile molecules linked by hydrogen bonds. Excluding a tilted phenyl group, the molecule of 1,5-diphenylbiuret has a large, approximately coplanar, fragment in which all C—N bonds are partial double bonds.

Comment

In the course of our research on the relationship of the structure and properties of conjugated polynitriles, the monomeric structure of phenyl carbamidonitrile, (I), has been reported (Yang, Huang, Chen & Tang, 1995). While growing the crystals of (I) from both ethanol and ethyl acetate solutions of (I), we accidentally obtained crystals of a 1:1 complex of (I) with 1,5-diphenylbiuret, (II). It appears that a condensation-like reaction occurred in the solution. The melting point of the 1:1 complex (439–442 K) is much higher than the melting point of (I) (405–407 K).

