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***rel*-(2*R*,5*R*)-1-Benzoyl-2-*tert*-butyl-3-methyl-5-(2,2,3,3,4,4,5,5,5-nonafluoropentyl)-imidazolidin-4-one at 100 K**

RENÉ BÜCHEL, ROLF AEBI AND REINHART KEESE\*

*Institut für Organische Chemie, Universität Bern, Freiestrasse 3, CH-3012 Bern, Switzerland*

PALOTH VENUGOPALAN

*Laboratorium für chemische und mineralogische Kristallographie, Universität Bern, Freiestrasse 3, CH-3012 Bern, Switzerland*

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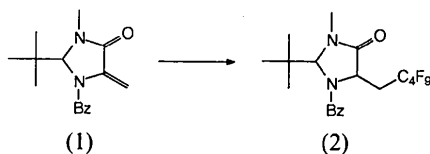
**Abstract**

The imidazolidinone ring of the title compound,  $C_{20}H_{21}F_9N_2O_2$  (2), adopts an envelope conformation with the *tert*-butyl and nonafluoropentyl groups in a *trans* arrangement with respect to the ring. The angles at each N atom total nearly  $360^\circ$ , indicating a very small degree of pyramidalization at the two amides. The torsional angles  $C(1)-N(2)-C(2)-O(1)$ ,  $C(3)-N(1)-C(4)-O(2)$  and  $C(1)-N(1)-C(4)-O(2)$  deviate from  $180$  or  $0^\circ$  by  $7.1$ ,  $25.5$  and  $10.4^\circ$ , respectively. This is consistent with considerable conjugative stabilization in both amide groups.

**Comment**

1-Benzoyl-2-*tert*-butyl-3-methyl-5-(2,2,3,3,4,4,5,5,5-nonafluoropentyl)imidazolidin-4-one (2) was synthesized in order to study the perfluoroalkylation of heterocycles and with the intention of eventually obtaining optically active  $\alpha$ -perfluoroalkylated amino acids.

The structural determination of the title compound (2) was undertaken to establish whether the addition of the perfluorinated alkyl group to 1-benzoyl-2-*tert*-butyl-3-methyl-5-methyleneimidazolidin-4-one (1) yields a *cis* or a *trans* product. Moreover, the conformation and the packing of the perfluorinated alkyl group in the crystal was of interest.



Compound (2) (m.p. 392 K) was obtained in 25% yield by reaction of perfluorobutyl iodide with racemic (1) in the presence of tributylstannane and

azoisobutyronitrile under UV irradiation (Beckwith & Chai, 1990). Crystals were obtained from dichloromethane [for experimental details see Büchel (1994)].

Bond distances and angles have normal values except for the C—F distances which vary between 1.252 (14) and 1.365 (10) Å due to the high displacement parameters of the F atoms. We also noticed that due to the strong electron-withdrawing (negative inductive) effect of the  $C_4F_9$  group,  $C(16)-C(17)$  is the shortest C—C bond [1.498 (10) Å] in the chain.

The imidazolidinone ring adopts a nearly perfect envelope conformation with C(1) being the out-of-plane atom [0.22 (1) Å]; asymmetry parameter  $\Delta_s^{Cl} = 1.3^\circ$  (Duax, Weeks & Rohrer, 1976). This corroborates the fact that both N atoms are approximately planar [pyramidalization of both N(1) and N(2) is low: 0.10 and  $-0.05$  Å].

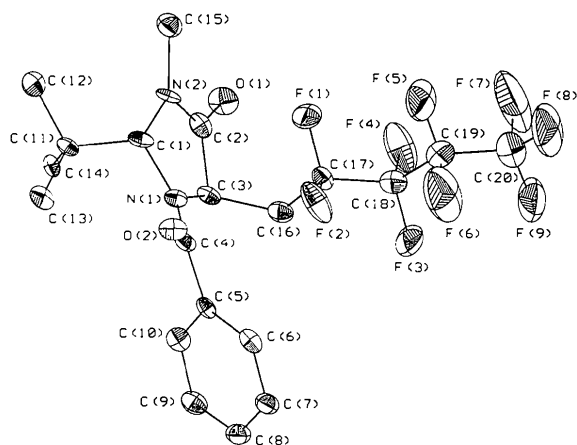


Fig. 1. View of *rel*-(2*R*,5*R*)-1-benzoyl-2-*tert*-butyl-3-methyl-5-(2,2,3,3,4,4,5,5,5-nonafluoropentyl)imidazolidin-4-one (2) with displacement ellipsoids, representing 50% probability density (100 K), and atomic numbering (PEANUT; Hummel, Hauser & Bürgi, 1990).

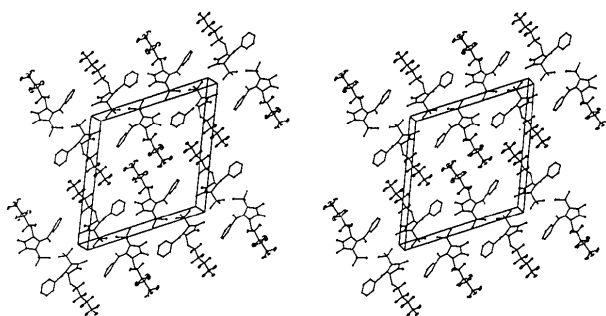


Fig. 2. Stereoscopic projection of *rel*-(2*R*,5*R*)-1-benzoyl-2-*tert*-butyl-3-methyl-5-(2,2,3,3,4,4,5,5,5-nonafluoropentyl)imidazolidin-4-one (2) along *b* with the *a* axis horizontal (PEANUT; Hummel, Hauser & Bürgi, 1990).

The *tert*-butyl group is in an equatorial position and has no steric interaction with the phenyl group [bond angles N(1)—C(1)—C(11) and N(2)—C(1)—C(11) are 112.2 (6) and 112.6 (6)°, respectively]. The phenyl ring forms a 68.0° angle with the imidazolidinone ring and a 43.3° angle with the carbonyl group at N(1). A search of the Cambridge Structural Database showed that the latter angle is in the normal range for benzamide systems (Chakrabarti & Dunitz, 1982).

The four C atoms of the terminal *n*-perfluorobutyl group are in one plane, indicating an antiplanar conformation [maximum deviation of an atom from the base plane through the four atoms being 0.04 (1) Å]. This is comparable to the three known X-ray structures containing *n*-C<sub>4</sub>F<sub>9</sub> groups (Sereda, Antipin, Timofeeva, Struchkov & Shelyazhenko, 1987*a*; Sereda, Antipin, Timofeeva & Struchkov, 1988). The plane of the four C atoms of the C<sub>4</sub>F<sub>9</sub> group is nearly perpendicular to the plane of the five-membered ring [84.0 (5)°].

Fig. 2 shows the packing viewed along **b** with the *a* axis horizontal. The molecules are packed in alternating layers, with antiparallel perfluoroalkyl chains and imidazolidinone groups.

## Experimental

### Crystal data

C<sub>20</sub>H<sub>21</sub>F<sub>9</sub>N<sub>2</sub>O<sub>2</sub>  
*M<sub>r</sub>* = 492.38  
 Monoclinic  
*P*2<sub>1</sub>/*a*  
*a* = 19.350 (10) Å  
*b* = 5.885 (3) Å  
*c* = 20.368 (10) Å  
 $\beta$  = 111.90 (4)°  
*V* = 2152 (2) Å<sup>3</sup>  
*Z* = 4  
*D<sub>x</sub>* = 1.5197 Mg m<sup>-3</sup>

### Data collection

Enraf–Nonius CAD-4 diffractometer  
 $\omega$  scans  
 Absorption correction: none  
 2584 measured reflections  
 1803 independent reflections  
 1348 observed reflections  
 [*I* > 3 $\sigma$ (*I*)]

### Refinement

Refinement on *F*  
*R* = 0.052  
 $wR$  = 0.065  
*S* = 1.826  
 1348 reflections  
 362 parameters  
 $w = 1/[\sigma^2(F) + 0.000719F^2]$

Mo *K* $\alpha$  radiation  
 $\lambda = 0.71069$  Å  
 Cell parameters from 22 reflections  
 $\theta = 4.0$ – $13.9^\circ$   
 $\mu = 0.15$  mm<sup>-1</sup>  
*T* = 100 K  
 Block  
 0.42 × 0.29 × 0.14 mm  
 Colourless

*R*<sub>int</sub> = 0.02  
 $\theta_{\max} = 23^\circ$   
 $h = -21 \rightarrow 21$   
 $k = 0 \rightarrow 6$   
 $l = 0 \rightarrow 22$   
 3 standard reflections  
 frequency: 60 min  
 intensity variation: <1%

( $\Delta/\sigma$ )<sub>max</sub> = 0.004  
 $\Delta\rho_{\max} = 0.604$  e Å<sup>-3</sup>  
 $\Delta\rho_{\min} = -0.419$  e Å<sup>-3</sup>  
 Atomic scattering factors  
 from *International Tables*  
 for *X-ray Crystallography*  
 (1974, Vol. IV)

Table 1. Fractional atomic coordinates and equivalent isotropic displacement parameters (Å<sup>2</sup>)

$$U_{eq} = (1/3)\sum_i \sum_j U_{ij} a_i^* a_j^* \cdot a_i \cdot a_j$$

	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> <sub>eq</sub>
O(1)	0.0628 (3)	-0.1874 (8)	0.2136 (2)	0.0331 (21)
O(2)	-0.1554 (2)	0.4952 (8)	0.1709 (2)	0.0220 (20)
N(1)	-0.0950 (3)	0.1623 (9)	0.1731 (3)	0.0180 (21)
N(2)	0.0095 (3)	0.1295 (9)	0.1486 (3)	0.0186 (22)
C(1)	-0.0614 (4)	0.2480 (13)	0.1240 (4)	0.0194 (29)
C(2)	0.0130 (4)	-0.0481 (13)	0.1910 (4)	0.0215 (30)
C(3)	-0.0554 (3)	-0.0410 (12)	0.2114 (3)	0.0176 (28)
C(4)	-0.1455 (3)	0.2947 (13)	0.1889 (3)	0.0209 (30)
C(5)	-0.1912 (3)	0.1806 (11)	0.2242 (3)	0.0165 (30)
C(6)	-0.2076 (4)	0.2957 (13)	0.2762 (4)	0.0214 (32)
C(7)	-0.2544 (4)	0.2031 (13)	0.3052 (4)	0.0252 (30)
C(8)	-0.2866 (4)	-0.0049 (13)	0.2817 (4)	0.0283 (26)
C(9)	-0.2719 (4)	-0.1223 (13)	0.2303 (4)	0.0252 (31)
C(10)	-0.2236 (4)	-0.0300 (12)	0.2019 (4)	0.0224 (29)
C(11)	-0.1094 (3)	0.1933 (11)	0.0462 (3)	0.0169 (29)
C(12)	-0.0737 (4)	0.2923 (14)	-0.0025 (4)	0.0250 (32)
C(13)	-0.1867 (4)	0.2979 (13)	0.0252 (4)	0.0250 (32)
C(14)	-0.1185 (4)	-0.0639 (12)	0.0357 (4)	0.0212 (29)
C(15)	0.0754 (4)	0.2073 (15)	0.1372 (5)	0.0290 (32)
C(16)	-0.0293 (4)	-0.0376 (13)	0.2923 (4)	0.0246 (31)
C(17)	0.0162 (4)	0.1620 (12)	0.3303 (3)	0.0229 (27)
C(18)	0.0587 (4)	0.1225 (13)	0.4090 (4)	0.0335 (34)
C(19)	0.1011 (5)	0.3209 (17)	0.4533 (4)	0.0482 (42)
C(20)	0.1528 (6)	0.2741 (23)	0.5304 (5)	0.0704 (53)
F(1)	0.0654 (2)	0.2287 (7)	0.3018 (2)	0.0470 (20)
F(2)	-0.0275 (2)	0.3478 (7)	0.3250 (2)	0.0514 (19)
F(3)	0.0141 (3)	0.0337 (11)	0.4372 (2)	0.0887 (27)
F(4)	0.1115 (3)	-0.0362 (8)	0.4129 (2)	0.0717 (23)
F(5)	0.1350 (3)	0.4421 (9)	0.4214 (3)	0.0790 (26)
F(6)	0.0490 (3)	0.4647 (12)	0.4604 (3)	0.1111 (33)
F(7)	0.2118 (4)	0.1661 (14)	0.5260 (3)	0.1308 (37)
F(8)	0.1811 (4)	0.4501 (13)	0.5643 (3)	0.1137 (35)
F(9)	0.1229 (4)	0.1512 (15)	0.5628 (3)	0.1471 (44)

Table 2. Selected geometric parameters (Å, °)

O(1)—C(2)	1.218 (8)	C(9)—C(10)	1.381 (12)
O(2)—C(4)	1.230 (9)	C(11)—C(12)	1.519 (12)
N(1)—C(1)	1.470 (10)	C(11)—C(13)	1.525 (10)
N(1)—C(3)	1.476 (8)	C(11)—C(14)	1.530 (10)
N(1)—C(4)	1.380 (10)	C(16)—C(17)	1.498 (10)
N(2)—C(1)	1.451 (8)	C(17)—F(1)	1.345 (9)
N(2)—C(2)	1.341 (9)	C(17)—F(2)	1.362 (8)
N(2)—C(15)	1.452 (11)	C(17)—C(18)	1.523 (9)
C(1)—C(11)	1.542 (9)	C(18)—F(3)	1.310 (11)
C(2)—C(3)	1.529 (11)	C(18)—F(4)	1.365 (10)
C(3)—C(16)	1.534 (10)	C(18)—C(19)	1.516 (11)
C(4)—C(5)	1.491 (11)	C(19)—F(5)	1.295 (12)
C(5)—C(6)	1.390 (11)	C(19)—F(6)	1.364 (12)
C(5)—C(10)	1.387 (9)	C(19)—C(20)	1.541 (12)
C(6)—C(7)	1.366 (12)	C(20)—F(7)	1.338 (15)
C(7)—C(8)	1.376 (11)	C(20)—F(8)	1.252 (14)
C(8)—C(9)	1.369 (12)	C(20)—F(9)	1.256 (15)
C(3)—N(1)—C(4)	127.4 (5)	F(1)—C(17)—C(18)	107.9 (6)
C(1)—N(1)—C(4)	119.8 (6)	F(1)—C(17)—F(2)	104.5 (6)
C(1)—N(1)—C(3)	111.4 (5)	C(17)—C(18)—C(19)	118.0 (7)
C(2)—N(2)—C(15)	120.8 (6)	C(17)—C(18)—F(4)	105.3 (6)
C(1)—N(2)—C(15)	124.5 (6)	C(17)—C(18)—F(3)	109.7 (6)
C(1)—N(2)—C(2)	114.2 (6)	F(4)—C(18)—C(19)	105.4 (7)
N(1)—C(1)—N(2)	101.6 (5)	F(3)—C(18)—C(19)	110.2 (7)
N(2)—C(1)—C(11)	112.6 (6)	F(3)—C(18)—F(4)	107.6 (7)
N(1)—C(1)—C(11)	112.2 (6)	C(18)—C(19)—C(20)	118.1 (8)
O(1)—C(2)—N(2)	127.6 (7)	C(18)—C(19)—F(6)	106.5 (7)
N(2)—C(2)—C(3)	108.3 (6)	C(18)—C(19)—F(5)	112.9 (7)
O(1)—C(2)—C(3)	124.0 (6)	F(6)—C(19)—C(20)	103.1 (7)
N(1)—C(3)—C(2)	102.1 (5)	F(5)—C(19)—C(20)	110.6 (8)
C(2)—C(3)—C(16)	108.8 (6)	F(5)—C(19)—F(6)	104.1 (7)
N(1)—C(3)—C(16)	117.1 (6)	C(19)—C(20)—F(9)	112.8 (9)
C(3)—C(16)—C(17)	117.3 (6)	C(19)—C(20)—F(8)	113.5 (9)
C(16)—C(17)—C(18)	114.0 (6)	C(19)—C(20)—F(7)	105.2 (8)

C(16)—C(17)—F(2)	111.1 (6)	F(8)—C(20)—F(9)	112.3 (9)
C(16)—C(17)—F(1)	112.4 (6)	F(7)—C(20)—F(9)	109.5 (10)
F(2)—C(17)—C(18)	106.3 (6)	F(7)—C(20)—F(8)	102.8 (10)
C(3)—N(1)—C(4)—O(2)	154.5 (7)		
C(1)—N(1)—C(4)—O(2)	-10.4 (10)		
C(1)—N(1)—C(3)—C(2)	9.3 (7)		
C(3)—N(1)—C(1)—N(2)	-14.9 (7)		
C(1)—N(2)—C(2)—O(1)	172.9 (7)		
C(2)—N(2)—C(1)—N(1)	15.9 (8)		
C(1)—N(2)—C(2)—C(3)	-10.8 (8)		
O(1)—C(2)—C(3)—N(1)	177.2 (7)		
N(2)—C(2)—C(3)—N(1)	0.7 (7)		
O(1)—C(2)—C(3)—C(16)	52.9 (9)		
C(2)—C(3)—C(16)—C(17)	62.5 (8)		
N(1)—C(3)—C(16)—C(17)	-52.4 (9)		
N(1)—C(4)—C(5)—C(10)	-43.8 (10)		
C(3)—C(16)—C(17)—F(1)	-39.6 (9)		
C(3)—C(16)—C(17)—F(2)	77.1 (8)		
C(3)—C(16)—C(17)—C(18)	-162.8 (6)		
C(16)—C(17)—C(18)—C(19)	-174.8 (7)		
F(2)—C(17)—C(18)—F(3)	75.2 (7)		
C(17)—C(18)—C(19)—C(20)	-171.6 (8)		

The positional parameters of all H atoms were refined with a common isotropic displacement factor. Refinement was by full-matrix least squares.

Data collection: *CAD-4 Software* (Enraf-Nonius, 1989). Cell refinement: *CAD-4 Software*. Data reduction: *SDP* (Frenz, 1984). Program(s) used to solve structure: *SHELXS86* (Sheldrick, 1985). Program(s) used to refine structure: *SHELX76* (Sheldrick, 1976). Molecular graphics: *PEANUT* (Hummel, Hauser & Bürgi, 1990). Software used to prepare tables for publication: *PARST* (Nardelli, 1983).

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Lists of structure factors, anisotropic displacement parameters, H-atom coordinates, complete geometry and intermolecular contacts less than 3.5 Å have been deposited with the IUCr (Reference: SH1082). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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## Product of a Paterno–Büchi Reaction of Pentafluorobenzaldehyde and 1-Acetoxycyclododecene

CAROLYN PRATT BROCK AND DAVID S. WATT

*Department of Chemistry, University of Kentucky, Lexington, KY 40506-0055, USA*

HIROYUKI MORITA

*Department of Chemistry and Biological Engineering, Toyama University, Toyama 930, Japan*

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## Abstract

The stereochemistry of 14-pentafluorophenyl-13-oxabicyclo[10.2.0]tetradecan-1-yl acetate, C<sub>21</sub>H<sub>25</sub>F<sub>5</sub>O<sub>3</sub>, the photoaddition product of pentafluorobenzaldehyde to 1-acetoxycyclododecene, has been established. The aryl and acetoxy substituents are *cis*, and the ring fusion is *trans*.

## Comment

In the course of the development of a synthesis of the 3-acetoxoxetane subunit in the antineoplastic agent taxol (Wani, Taylor, Wall, Coggan & McPhail, 1971), we examined the prospects for using a Paterno–Büchi reaction of enol acetates and benzaldehydes to introduce this particular moiety. The stereoselectivity of the photoaddition of various benzaldehydes was investigated in several acyclic and cyclic enol acetates. As expected (Paterno & Chietti, 1909; Büchi, Imman & Lipinsky, 1954; Jones, 1981), the aryl and acetoxy groups have a *cis* relationship in the products, a finding supported by chemical-shift data in the <sup>1</sup>H NMR spectra. In the case of 1-acetoxycyclododecene, the enol acetate (1) was a mixture of *E/Z* isomers and the photoaddition with pentafluorobenzaldehyde, (2), could lead to a product in which the acetoxy group and the bridgehead methine