Crystal structure of *N*-benzyloxycarbonyl-DL-alanine 4-methylphenylester, $C_{18}H_{19}NO_4$

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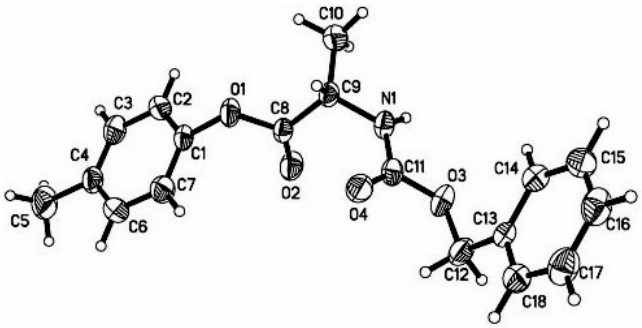

Abstract

$C_{18}H_{19}NO_4$, orthorhombic, $P2_12_12_1$ (no. 19), a = 5.352(1) Å, b = 8.916(2) Å, c = 34.269(7) Å, V = 1635.2 Å^3, Z = 4, $R_{gt}(F)$ = 0.042, $wR_{ref}(F^2)$ = 0.097, T = 293 K.

Source of material

N-benzyloxycarbonyl-DL-alanine (0.223 g, 1.0 mmol) was dissolved in acetonitrile (10 ml) and the solution was cooled to 0 °C. 4-Methylphenol (0.135 g, 0.9 mmol) and 4-dimethylaminopyridine (DMAP; 0.024 g, 0.2 mmol) were added followed by *N*,*N*′-dicyclohexylcarbodiimide (DCC; 0.227 g, 1.1 mmol) in acetonitrile (10 ml). The solution was stirred at 0 °C for 1 h and at room temperature for 8 h. The precipitate was filtered off and the filtrate was evaporated in vacuo, then the residue was purified by flash chromatography with ethyl acetate/petroleum ether (1:7, *v*/*v*) as eluent, to afford 0.237 g (yield 4 %) *N*-benzyloxycarbonyl-DL-alanine 4-methylphenyl ester as a colorless solid. It was recrystallized from ethyl acetate and petroleum ether, yielding the colorless block-like crystals 15 days later.

Experimental details

H atoms bound to C atoms were fixed geometrically and were refined with a riding model, with d(C—H) = 0.93 - 0.98 Å and with U_{iso}(H) = 1.2 U_{eq}(C) and U_{iso}(H) = 1.5 U_{eq}(C) for the methyl group. H1 bound to N is found in difference Fourier map and refined with d(N—H) = 0.85 Å and U_{iso}(H) = 1.0 U_{eq}(N).

Discussion

Both bond lengths of C8—O2 (1.176(3) Å) and C11—O4 (1.206(3) Å) in the title compound, are consistent with the value of the C=O double bond in the 4-nitroguaiacyl ester of *N*-benzyloxycarbonyl-L-isoleucine [1]. The average C—C bond length in the phenyl is shorter than the expected value of 1.39 Å [1,2]. The planar conformation of the peptide group is established from the torsion angles ∠O4–C11–N1–C9 = −12.3(4)° and ∠O3–C11–N1–C9 = 169.0(2)°. The conformation of the side chain is described by the torsion angles ∠C8–O1–C1–C7 = 82.8(3)° and ∠O3–C12–C13–C14 = −18.0(4)°. The aromatic rings (C1/C2/C3/C4/C6/C7) and (C13/C14/C15/C16/C17/C18) are not co-planar with a dihedral angle of 20°. There are two types of intra-molecular hydrogen bonds: C12–H12B···O4 (2.672(4) Å) and C14–H14···O3 (2.824(3) Å). The molecules are linked by intermolecular hydrogen bonds N1–H1···O4^i (symmetry code i: 1+x,y,z). The bond distance and angle between donor and acceptor are 3.267(4) Å and 175(3)°. There are also weak π-π stacking interactions between the aromatic rings with a centroid-to-centroid distance of 3.576 Å.

Table 1. Data collection and handling.

Crystal:	colorless block, size 0.13 × 0.25 × 0.50 mm
Wavelength:	Mo K_α radiation (0.71073 Å)
μ:	0.90 cm^{-1}
Diffractometer, scan mode:	Bruker SMART CCD, φ/ω
$2\theta_{max}$:	52.02°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	6853, 3160
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\ \sigma(I_{obs})$, 1641
$N(param)_{refined}$:	215
Programs:	SHELXS-97 [3], SHELXL-97 [4], SHELXTL [5]

Table 2. Atomic coordinates and displacement parameters (in Å^2).

Atom	Site	x	y	z	U_{iso}
H(2)	4*a*	0.9783	0.1688	0.0144	0.076
H(3)	4*a*	0.8743	0.0454	–0.0429	0.083
H(5A)	4*a*	0.3719	–0.0811	–0.0731	0.160
H(5B)	4*a*	0.4336	–0.2358	–0.0537	0.160
H(5C)	4*a*	0.6420	–0.1480	–0.0763	0.160
H(6)	4*a*	0.2897	–0.1363	0.0096	0.088
H(7)	4*a*	0.3901	–0.0129	0.0669	0.079
H(9)	4*a*	0.7990	0.2806	0.1429	0.059
H(10A)	4*a*	1.2042	0.3728	0.1475	0.103
H(10B)	4*a*	1.1459	0.3423	0.1034	0.103
H(10C)	4*a*	1.3109	0.2291	0.1271	0.103
H(12A)	4*a*	0.7243	–0.1645	0.2612	0.084
H(12B)	4*a*	0.5203	–0.0860	0.2355	0.084
H(14)	4*a*	0.9152	0.1662	0.2811	0.074
H(15)	4*a*	0.8238	0.3120	0.3347	0.088
H(16)	4*a*	0.4656	0.2703	0.3693	0.093
H(17)	4*a*	0.1966	0.0832	0.3508	0.096
H(18)	4*a*	0.2846	–0.0600	0.2968	0.079
H(1)	4*a*	1.128(5)	0.111(3)	0.1821(7)	0.054(9)

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Table 3. Atomic coordinates and displacement parameters (in Å^2).

Atom	Site	*x*	*y*	*z*	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
C(1)	4*a*	0.6934(5)	0.0875(3)	0.04545(8)	0.058(2)	0.054(2)	0.036(2)	0.008(2)	–0.008(2)	–0.002(1)
C(2)	4*a*	0.8386(6)	0.1069(3)	0.01344(9)	0.070(2)	0.068(2)	0.053(2)	–0.013(2)	–0.009(2)	–0.000(2)
C(3)	4*a*	0.7755(7)	0.0327(3)	–0.02079(8)	0.083(2)	0.083(2)	0.042(2)	0.008(2)	0.002(2)	0.002(2)
C(4)	4*a*	0.5705(7)	–0.0586(3)	–0.02259(9)	0.088(2)	0.059(2)	0.047(2)	0.002(2)	–0.018(2)	–0.004(2)
C(5)	4*a*	0.4979(9)	–0.1381(3)	–0.0598(1)	0.163(4)	0.088(2)	0.069(2)	–0.004(3)	–0.036(3)	–0.017(2)
C(6)	4*a*	0.4296(7)	–0.0745(3)	0.0103(1)	0.084(2)	0.066(2)	0.070(2)	–0.018(2)	–0.015(2)	–0.002(2)
C(7)	4*a*	0.4889(6)	–0.0012(3)	0.04475(9)	0.070(2)	0.076(2)	0.051(2)	–0.006(2)	0.001(2)	0.000(2)
C(8)	4*a*	0.8748(5)	0.0989(3)	0.10806(7)	0.054(2)	0.058(2)	0.035(2)	0.000(2)	–0.003(1)	0.001(1)
C(9)	4*a*	0.9380(6)	0.2098(3)	0.14004(7)	0.060(2)	0.054(2)	0.033(2)	0.001(2)	–0.001(1)	–0.000(1)
C(10)	4*a*	1.1713(6)	0.2965(3)	0.12846(9)	0.076(2)	0.073(2)	0.057(2)	–0.013(2)	–0.004(2)	0.001(2)
C(11)	4*a*	0.7842(6)	0.0763(3)	0.19570(8)	0.059(2)	0.059(2)	0.038(2)	0.006(2)	0.000(2)	–0.006(1)
C(12)	4*a*	0.6705(6)	–0.0688(3)	0.25073(9)	0.103(3)	0.061(2)	0.045(2)	–0.005(2)	0.004(2)	0.008(2)
C(13)	4*a*	0.6105(6)	0.0358(3)	0.28399(7)	0.060(2)	0.051(2)	0.040(2)	–0.003(2)	–0.003(2)	0.011(1)
C(14)	4*a*	0.7696(6)	0.1487(3)	0.29519(8)	0.067(2)	0.063(2)	0.055(2)	–0.006(2)	0.002(2)	0.008(2)
C(15)	4*a*	0.7149(7)	0.2360(3)	0.3271(1)	0.095(3)	0.056(2)	0.069(2)	–0.005(2)	–0.006(2)	–0.003(2)
C(16)	4*a*	0.5022(8)	0.2113(4)	0.3477(1)	0.106(3)	0.070(2)	0.056(2)	0.022(2)	0.007(2)	–0.010(2)
C(17)	4*a*	0.3420(6)	0.1004(4)	0.3367(1)	0.072(2)	0.104(3)	0.064(2)	0.011(2)	0.010(2)	0.008(2)
C(18)	4*a*	0.3961(6)	0.0142(3)	0.30455(9)	0.066(2)	0.075(2)	0.057(2)	–0.010(2)	0.000(2)	0.004(2)
N(1)	4*a*	0.9776(5)	0.1351(3)	0.17690(7)	0.053(2)	0.072(2)	0.035(1)	0.005(1)	–0.002(1)	0.001(1)
O(1)	4*a*	0.7509(4)	0.1707(2)	0.07927(5)	0.090(2)	0.054(1)	0.042(1)	0.013(1)	–0.019(1)	–0.0060(9)
O(2)	4*a*	0.9292(4)	–0.0290(2)	0.10763(5)	0.113(2)	0.050(1)	0.057(1)	0.016(1)	–0.019(1)	–0.004(1)
O(3)	4*a*	0.8628(4)	–0.0108(2)	0.22549(5)	0.083(2)	0.077(1)	0.041(1)	0.016(1)	0.004(1)	0.011(1)
O(4)	4*a*	0.5674(4)	0.0986(2)	0.18810(6)	0.061(1)	0.074(1)	0.064(1)	–0.002(1)	–0.002(1)	0.011(1)

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References

1. Urbanczyk-Lipkowska, Z.; Krajewski, J. W.; Gluzinski, P.: Structure of the 4-Nitroguaiacyl Ester of *N*-Benzyloxycarbonyl-L-isoleucine. Acta Crystallogr. **B36** (1980) 2447-2450.
2. Rajalakshmi, K.; Jain, N.; Deepthi, S.; Krishnamurthy, H. G.; Pattabhi, V.: 7-Hydroxy-4-(4-methoxyphenyl)-3,4-dihydrocoumarin. Acta Crystallogr. **C55** (1999) 813-815.
3. Sheldrick, G. M.: SHELXS-97. Program for the Solution of Crystal Structures. University of Göttingen, Germany 1997.
4. Sheldrick, G. M.: SHELXL-97. Program for the Refinement of Crystal Structures. University of Göttingen, Germany 1997.
5. Sheldrick, G. M.: SHELXTL. Structure Determination Software Suite. Version 6.14. Bruker AXS, Madison, Wisconsin, USA 2000.