Crystal structure of 1-(2-ethoxyethyl)-4-ethynyl-4-benzoyloxypiperidine hydrochloride, $C_{18}H_{24}ClNO_3$

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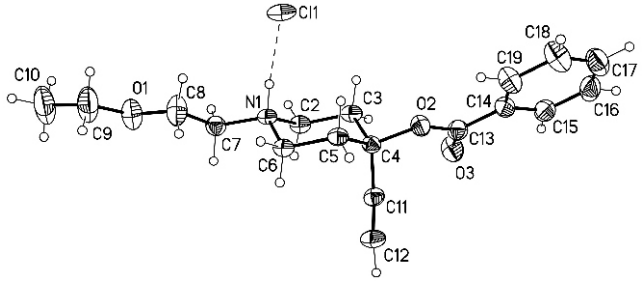

Abstract

$C_{18}H_{24}ClNO_3$, orthorhombic, $P2_12_12_1$ (no. 19), a = 8.953(1) Å, b = 9.986(1) Å, c = 21.257(1) Å, V = 1900.5 Å^3, Z = 4, $R_{gt}(F)$ = 0.038, $wR_{ref}(F^2)$ = 0.095, T = 293 K.

Source of material

1-(2-Ethoxyethyl)-4-ethynyl-4-benzoyloxypiperidine hydrochloride has been synthesized as described earlier [1]. Colorless, prism-shaped single crystals were obtained by slow evaporation of its solution in hot ethyl acetate.

Experimental details

The hydrogen atoms have been determined from the differential syntheses of electron densities, apart from H atoms at C9 and C10 atoms of an ethoxyethyl group, which positions have been calculated. No other constraints/restraints were needed to obtain a reasonable structure for non-hydrogen atoms. The structure refined down to an $R1$ value of 3.77 %. The Flack parameter x of 0.47(4) indicated a racemic twinning in this crystal. Refinements including this twinning improved the $R1$ value only slightly to 3.75 %.

Discussion

To obtain compounds with local anaesthetic activity, there have been synthesized different 4,4-disubstituted derivatives of piperidine, which possessed substituents ($C_2H_4OCH_3$, $C_2H_4OC_2H_5$, $C_3H_6OC_4H_9$) at N1 atom, and (C≡CH, C≡CCH=CH$_2$, C≡CPh) and (OCOCH$_3$,OCOC$_2$H$_5$, OCOPh) at a C4 atom substituents of piperidine cycle [1]. 1-(2-Ethoxyl)-4-ethynyl-4-benzoyloxypiperidine hydrochloride has been proved to be most efficient [2].

Geometric parameters of ethoxyethyl, ethynyl and benzoyloxyl substituents in the title crystal structure correspond to the conventional values, the bond lengths of C(sp^3)—C(sp^3) and C—N in the piperidine cycle, possessing average values of 1.519 Å and 1.495 Å, respectively, well agree with the standard values [3]. The piperidine cycle assumes a conformation of a slightly distorted chair. Nl and C4 atoms deviate from the best-fit plane of the other four atoms of the cycle by 0.659(1) Å and 0.678(1) Å, respectively. The ethoxyethyl group occupies an equatorial position and possesses a stretched conformation. The orientation of the ethynyl group is axial and that of the benzoyloxy group is equatorial. The title crystals are built of substituted piperidine cations $(C_{18}H_{24}NO_3)^+$ and Cl^- anions. Through hydrogen bond N–H···Cl (d(N1–H···Cl) = 2.10(1) Å, ∠N1–H···Cl = 170(1)°) the cations and anions form ionic pairs, which are associated into infinite columns along [010] by hydrogen bonds C–H···Cl (d(C12–H···Cl) = 2.38(2) Å, ∠C12–H···Cl = 175(1)°) and C–H···O (d(C7–H···O3) = 2.55(2) Å, ∠C7–H···O3 = 145(1)°). Interacting through van der Waals forces, these columns form the crystal structure.

Table 1. Data collection and handling.

Crystal:	colourless prism, size 0.30 × 0.35 × 0.50 mm
Wavelength:	Mo K_α radiation (0.71073 Å)
μ:	2.14 cm^{-1}
Diffractometer, scan mode:	KUMA/OXFORD KM-4, $\theta/2\theta$
$2\theta_{max}$:	58.82°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	12537, 1253
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\ \sigma(I_{obs})$, 9417
$N(param)_{refined}$:	285
Programs:	SHELXS-97, SHELXL-97 [4], ORTEP-3 [5], PLATON [6]

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

Atom	Site	x	y	z	U_{iso}
H(9A)	4*a*	0.5524	0.8826	–0.0064	0.143
H(9B)	4*a*	0.4762	1.0168	–0.0261	0.143
H(10A)	4*a*	0.4883	1.0035	0.0846	0.212
H(10B)	4*a*	0.3231	1.0033	0.0602	0.212
H(10C)	4*a*	0.3996	0.8686	0.0801	0.212
H(1N)	4*a*	0.244(1)	0.833(1)	–0.2110(5)	0.059(3)
H(2A)	4*a*	0.103(2)	0.595(1)	–0.1948(6)	0.062(4)
H(2B)	4*a*	0.023(2)	0.729(1)	–0.1968(6)	0.062(4)
H(3A)	4*a*	0.003(1)	0.629(1)	–0.2959(5)	0.044(3)
H(3B)	4*a*	0.087(1)	0.760(1)	–0.3047(6)	0.055(3)
H(5A)	4*a*	0.363(1)	0.761(1)	–0.3095(6)	0.057(4)
H(5B)	4*a*	0.445(1)	0.626(1)	–0.3089(5)	0.045(3)
H(6A)	4*a*	0.375(1)	0.588(1)	–0.2042(6)	0.055(4)
H(6B)	4*a*	0.458(1)	0.725(1)	–0.2087(5)	0.047(3)
H(7A)	4*a*	0.253(2)	0.664(1)	–0.1078(5)	0.063(3)
H(7B)	4*a*	0.157(2)	0.792(1)	–0.1114(6)	0.063(4)
H(8A)	4*a*	0.463(2)	0.797(2)	–0.1104(8)	0.101(7)
H(8B)	4*a*	0.387(2)	0.926(2)	–0.1252(9)	0.126(8)
H(12)	4*a*	0.250(2)	0.250(2)	–0.2750(7)	0.094(5)
H(15)	4*a*	–0.035(1)	0.479(1)	–0.5131(6)	0.052(4)

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Table 2. Continued.

Atom	Site	*x*	*y*	*z*	U_{iso}
H(16)	4*a*	–0.039(2)	0.535(2)	–0.6183(7)	0.082(5)
H(17)	4*a*	0.146(2)	0.680(2)	–0.6532(9)	0.100(6)
H(18)	4*a*	0.321(2)	0.772(2)	–0.5836(9)	0.121(8)
H(19)	4*a*	0.303(2)	0.723(2)	–0.4791(7)	0.080(5)

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}
Cl(1)	4*a*	0.27488(4)	1.01501(3)	–0.25857(2)	0.0636(2)	0.0341(1)	0.0982(3)	0.0018(1)	0.0097(2)	0.0138(2)
N(1)	4*a*	0.2417(1)	0.74653(8)	–0.19504(4)	0.0399(6)	0.0313(4)	0.0504(5)	0.0013(4)	0.0000(5)	0.0048(4)
C(2)	4*a*	0.1002(1)	0.6784(2)	–0.21542(6)	0.0332(6)	0.0456(8)	0.0595(9)	0.0014(6)	0.0030(5)	0.0033(6)
C(3)	4*a*	0.0880(1)	0.6714(1)	–0.28590(6)	0.0336(6)	0.0383(7)	0.0655(9)	–0.0016(6)	–0.0046(6)	0.0045(6)
C(4)	4*a*	0.2230(1)	0.60051(9)	–0.31495(5)	0.0408(6)	0.0363(5)	0.0455(6)	–0.0045(5)	–0.0028(5)	0.0049(4)
C(5)	4*a*	0.3643(1)	0.6707(1)	–0.29299(6)	0.0381(7)	0.0369(7)	0.0517(8)	–0.0038(6)	0.0035(5)	0.0054(6)
C(6)	4*a*	0.3747(1)	0.6777(1)	–0.22268(6)	0.0318(6)	0.0382(7)	0.0558(8)	–0.0018(5)	–0.0006(5)	0.0051(6)
C(7)	4*a*	0.2481(2)	0.7577(1)	–0.12509(6)	0.0546(9)	0.0532(7)	0.0480(7)	0.0022(7)	0.0027(6)	0.0018(5)
C(8)	4*a*	0.3726(2)	0.8444(2)	–0.10169(8)	0.086(1)	0.103(1)	0.055(1)	–0.025(1)	–0.0020(9)	–0.010(1)
C(9)	4*a*	0.4604(3)	0.9320(2)	–0.00595(8)	0.124(2)	0.152(2)	0.083(1)	–0.009(2)	–0.039(1)	–0.027(1)
C(10)	4*a*	0.4154(3)	0.9544(3)	0.06088(9)	0.139(2)	0.206(3)	0.080(1)	0.040(2)	–0.043(1)	–0.042(2)
C(11)	4*a*	0.2304(1)	0.4574(1)	–0.29924(5)	0.0409(6)	0.0389(6)	0.0594(7)	–0.0052(5)	–0.0014(6)	–0.0008(5)
C(12)	4*a*	0.2463(2)	0.3457(1)	–0.28392(6)	0.0520(8)	0.0395(6)	0.088(1)	–0.0013(7)	–0.0044(7)	0.0059(6)
C(13)	4*a*	0.1147(2)	0.5617(1)	–0.41799(6)	0.0526(8)	0.0500(7)	0.0581(8)	–0.0023(6)	–0.0086(6)	–0.0030(6)
C(14)	4*a*	0.1281(2)	0.5969(1)	–0.48561(6)	0.0591(8)	0.0562(7)	0.0536(8)	0.0105(7)	–0.0077(7)	–0.0005(6)
C(15)	4*a*	0.0275(2)	0.5408(2)	–0.52738(8)	0.072(1)	0.0640(9)	0.065(1)	0.0115(9)	–0.0133(8)	–0.0080(8)
C(16)	4*a*	0.0329(2)	0.5730(2)	–0.59026(8)	0.085(1)	0.096(1)	0.061(1)	0.036(1)	–0.019(1)	–0.0189(9)
C(17)	4*a*	0.1380(2)	0.6592(2)	–0.61149(9)	0.088(1)	0.115(2)	0.057(1)	0.040(1)	0.001(1)	0.009(1)
C(18)	4*a*	0.2377(2)	0.7163(2)	–0.57108(8)	0.086(1)	0.122(1)	0.070(1)	–0.002(1)	–0.002(1)	0.023(1)
C(19)	4*a*	0.2336(2)	0.6847(2)	–0.50764(7)	0.075(1)	0.089(1)	0.0591(9)	–0.005(1)	–0.0076(8)	0.0123(8)
O(1)	4*a*	0.3466(1)	0.8610(1)	–0.03690(5)	0.0857(8)	0.1203(8)	0.0600(7)	–0.0027(7)	–0.0125(6)	–0.0126(7)
O(2)	4*a*	0.2232(1)	0.61992(7)	–0.38323(3)	0.0527(5)	0.0520(4)	0.0465(5)	–0.0109(4)	–0.0035(4)	0.0041(3)
O(3)	4*a*	0.0184(1)	0.4917(1)	–0.39615(4)	0.0670(6)	0.0804(6)	0.0690(6)	–0.0268(6)	–0.0102(5)	0.0045(5)

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