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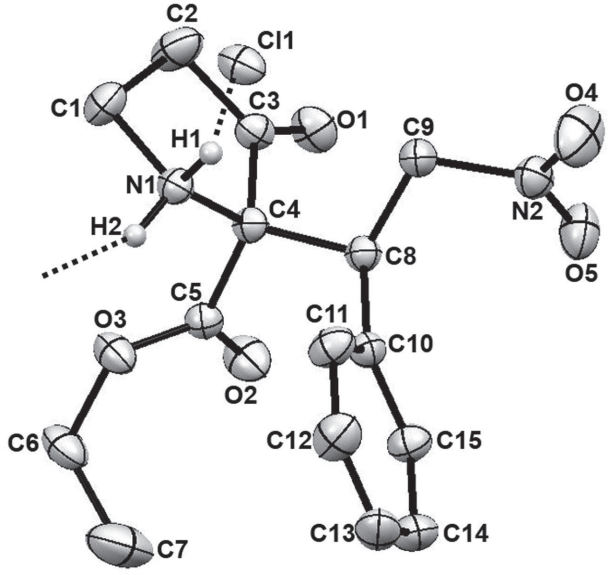
Crystal structure of 2-(ethoxycarbonyl)-2-(2-nitro-1-phenylethyl)-3-oxopyrrolidinium chloride, $C_{15}H_{19}N_2O_5Cl$



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Abstract

$C_{15}H_{19}N_2O_5Cl$, triclinic, $P\bar{1}$ (no. 2), $a = 8.2232(9)$ Å, $b = 8.5833(10)$ Å, $c = 12.5916(13)$ Å, $\beta = 100.713(5)°$, $V = 833.39$ Å^3, $Z = 2$, $R_{gt}(F) = 0.0331$, $wR_{ref}(F^2) = 0.0870$, $T = 173$ K.

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The crystal structure is shown in the figure. For clarity hydrogen atoms not involved in hydrogen bonds are omitted. Tables 1–3 contain details of the measurement method and a list of the atoms including atomic coordinates and displacement parameters.

Table 1: Data collection and handling.

Crystal:	Colorless, block, size 0.19×0.21×0.22 mm
Wavelength:	Mo K_α radiation (0.71073 Å)
μ:	2.55 cm^{-1}
Diffractometer, scan mode:	Nonius Kappa CCD diffractometer, 1.2° φ scans and ω scans
$2\theta_{max}$:	55.76°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	29079, 3956
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\,\sigma(I_{obs})$, 3343
$N(param)_{refined}$:	217
Programs:	OLEX2 [7], SHELX [8]

Table 2: Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2).

Atom	Site	x	y	z	U_{iso}
H(1)	2*i*	0.153(2)	0.474(2)	0.411(2)	0.038(4)
H(2)	2*i*	−0.012(2)	0.476(2)	0.345(1)	0.033(4)
H(1A)	2*i*	0.1811	0.7386	0.4393	0.039
H(1B)	2*i*	0.0747	0.7215	0.3148	0.039
H(2A)	2*i*	0.3416	0.7883	0.2863	0.048
H(2B)	2*i*	0.4218	0.7057	0.3817	0.048
H(6A)	2*i*	−0.2503	0.4221	0.0100	0.044
H(6B)	2*i*	−0.3653	0.4571	0.0978	0.044
H(7A)	2*i*	−0.3025	0.1473	0.0119	0.090
H(7B)	2*i*	−0.4806	0.1981	−0.0162	0.090
H(7C)	2*i*	−0.4069	0.1794	0.1064	0.090
H(8)	2*i*	0.2324	0.2095	0.1805	0.026
H(9A)	2*i*	0.4382	0.3693	0.3448	0.032
H(9B)	2*i*	0.3192	0.2939	0.4180	0.032
H(11)	2*i*	0.0310	0.1945	0.4137	0.038
H(12)	2*i*	−0.1941	−0.0171	0.4115	0.045
H(13)	2*i*	−0.3098	−0.2287	0.2521	0.043
H(14)	2*i*	−0.1981	−0.2303	0.0945	0.041
H(15)	2*i*	0.0271	−0.0194	0.0958	0.034

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Source of material

1-*tert*-Butyl-2-ethyl-3-oxopyrrolidine-1,2-dicarboxylate (0.1 g, 0.39 mM), nitrostyrene (0.069 g, 0.47 mM) and L-proline (20 mol %) in DMSO (2 mL) was stirred for 72 h at RT. The

Table 3: Atomic displacement parameters (Å^2).

Atom	Site	*x*	*y*	*z*	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Cl(1)	2*i*	0.24337(4)	0.47941(4)	0.58480(2)	0.0242(2)	0.0428(2)	0.0225(2)	0.0037(1)	0.0060(1)	0.0046(1)
O(1)	2*i*	0.3818(1)	0.5069(1)	0.16648(8)	0.0297(5)	0.0402(6)	0.0362(5)	0.0066(4)	0.0156(4)	0.0130(4)
O(2)	2*i*	0.0185(1)	0.3238(1)	0.04996(8)	0.0336(5)	0.0517(6)	0.0214(5)	0.0130(5)	0.0071(4)	0.0016(4)
O(3)	2*i*	−0.1367(1)	0.4202(1)	0.16694(7)	0.0233(4)	0.0451(6)	0.0232(4)	0.0114(4)	0.0044(4)	0.0036(4)
O(4)	2*i*	0.4942(2)	0.0941(2)	0.4191(1)	0.0776(9)	0.0458(7)	0.0420(6)	0.0277(6)	−0.0006(6)	0.0181(5)
O(5)	2*i*	0.4218(1)	0.0468(1)	0.24075(9)	0.0508(6)	0.0412(6)	0.0396(6)	0.0242(5)	0.0146(5)	0.0081(5)
N(1)	2*i*	0.0985(1)	0.4969(1)	0.34737(9)	0.0229(5)	0.0253(5)	0.0202(5)	0.0056(4)	0.0059(4)	0.0031(4)
N(2)	2*i*	0.4272(1)	0.1260(1)	0.3338(1)	0.0301(6)	0.0273(6)	0.0340(6)	0.0078(5)	0.0060(5)	0.0105(5)
C(1)	2*i*	0.1594(2)	0.6786(2)	0.3605(1)	0.0403(8)	0.0218(6)	0.0343(7)	0.0067(5)	0.0105(6)	0.0016(5)
C(2)	2*i*	0.3230(2)	0.6932(2)	0.3196(1)	0.0432(8)	0.0266(7)	0.0458(9)	−0.0034(6)	0.0165(7)	0.0011(6)
C(3)	2*i*	0.2988(2)	0.5373(2)	0.2339(1)	0.0228(6)	0.0253(6)	0.0268(6)	0.0037(5)	0.0045(5)	0.0100(5)
C(4)	2*i*	0.1455(2)	0.4104(1)	0.24573(9)	0.0209(5)	0.0225(6)	0.0194(5)	0.0041(4)	0.0071(4)	0.0031(4)
C(5)	2*i*	0.0008(2)	0.3792(2)	0.1412(1)	0.0232(6)	0.0233(6)	0.0228(6)	0.0043(5)	0.0060(5)	0.0060(5)
C(6)	2*i*	−0.2865(2)	0.3896(2)	0.0747(1)	0.0248(7)	0.0528(9)	0.0305(7)	0.0121(6)	−0.0005(5)	0.0080(6)
C(7)	2*i*	−0.3769(2)	0.2134(3)	0.0413(2)	0.0360(9)	0.066(1)	0.064(1)	−0.0067(8)	−0.0061(8)	0.014(1)
C(8)	2*i*	0.1964(2)	0.2466(1)	0.2511(1)	0.0213(5)	0.0220(6)	0.0220(6)	0.0045(4)	0.0063(4)	0.0035(4)
C(9)	2*i*	0.3523(2)	0.2728(2)	0.3457(1)	0.0243(6)	0.0238(6)	0.0291(6)	0.0060(5)	0.0036(5)	0.0047(5)
C(10)	2*i*	0.0500(2)	0.1110(2)	0.2537(1)	0.0226(6)	0.0215(6)	0.0248(6)	0.0043(5)	0.0055(5)	0.0051(5)
C(11)	2*i*	−0.0158(2)	0.1092(2)	0.3484(1)	0.0358(7)	0.0271(7)	0.0293(7)	0.0025(5)	0.0127(6)	0.0022(5)
C(12)	2*i*	−0.1495(2)	−0.0172(2)	0.3471(1)	0.0401(8)	0.0333(7)	0.0419(8)	0.0043(6)	0.0223(7)	0.0090(6)
C(13)	2*i*	−0.2180(2)	−0.1431(2)	0.2528(1)	0.0267(7)	0.0283(7)	0.0511(9)	0.0011(5)	0.0117(6)	0.0096(6)
C(14)	2*i*	−0.1521(2)	−0.1437(2)	0.1593(1)	0.0305(7)	0.0273(7)	0.0363(7)	−0.0005(5)	0.0025(6)	0.0008(6)
C(15)	2*i*	−0.0182(2)	−0.0176(2)	0.1600(1)	0.0303(7)	0.0272(6)	0.0255(6)	0.0035(5)	0.0064(5)	0.0035(5)

reaction progress was monitored by TLC. ($R_f = 0.3$ using 15% ethyl acetate/hexane). The reaction was quenched with water and the product was extracted using dichloromethane. The solvent was completely evaporated and the residual oil was purified using a silica column. Pure fractions were concentrated and treated with 20% trifluoroacetic acid in DCM and stirred for 4 h. The solution was basified with saturated $NaHCO_3$. The organic layer was separated and then concentrated to dryness. Yield 72%. m.p = 449 K. Crystals suitable for X-ray analysis were grown in methanolic HCl and ethyl acetate.

Experimental details

X-ray single crystal diffraction data were collected on a Nonius κ-CCD diffractometer. Temperature was controlled by an Oxford Cryostream cooling system (Oxford Cryostat). Absorption correction was performed using SADABS [1]. All hydrogen atoms, except H3, were placed in idealised positions and refined in riding models with U_{iso} assigned the values to be 1.2 or 1.5 times those of their parent atoms and the constraint distances of C—H ranging from 0.95 Å to 1.00 Å. The hydrogen atoms H1 and H2 were located in the electron difference maps and refined freely.

Discussion

Oxopyrrolidine moieties have a proline backbone and are used in a wide range of applications such as ACE inhibitors, antibacterial, antitumor and asymmetric catalysis [2–5]. Here we report for the first time the single crystal structure of a 4-oxopyrrolidine derivative. The five membered oxopyrrolidine ring N(1)–C(1) bond is twisted with the pseudorotation parameters P (188.6(1)°), τ (M) (34.3(1)°) [6], puckering amplitude Q of 0.3246(14) Å, and φ is 26.5(3)°. The nitrogen of oxopyrrolidine is protonated and two adjacent molecules with quaternary nitrogen are interconnected through N(+)-H$\cdots$Cl(−) hydrogen bonds to form a cyclic motif classified by the graph set descriptor $R^2_4(8)$ in which the chloride ions are hydrogen bonded to the hydrogen of quaternay nitrogen of oxopyrrolidine moieties in a bifurcated manner. Such dimeric units grow further along the *a* axis.

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