Crystal structure of (2*R*, 3*R*, 4*S*)-5-dibromomethyl-3,4-dihydro-3,4-dihydroxy-3,4-O-isopropylidene-2-(*N*-succinimido)-2*H*-pyrrole-1-oxide, $C_{12}H_{14}Br_2N_2O_5$

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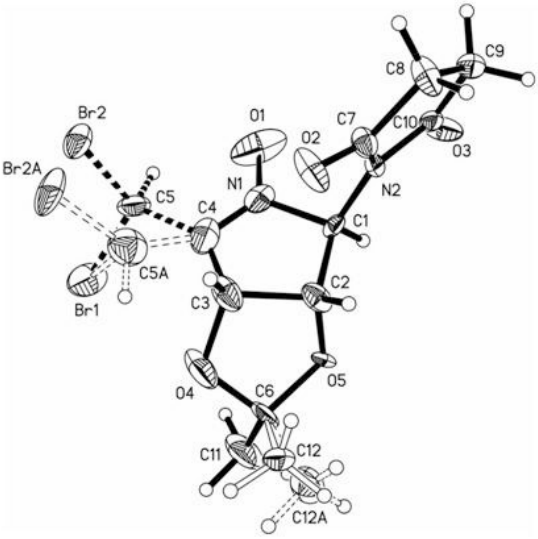

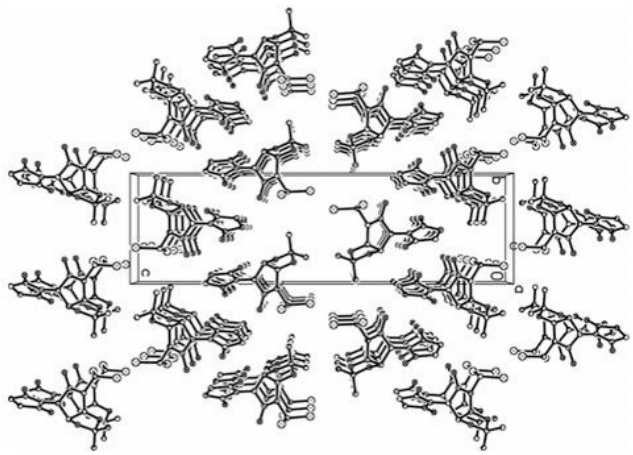

Abstract

$C_{12}H_{14}Br_2N_2O_5$, orthorhombic, $P2_12_12_1$ (no. 19), a = 5.7982(4) Å, b = 8.5837(6) Å, c = 29.676(2) Å, V = 1477.0 Å^3, Z = 4, $R_{gt}(F)$ = 0.0558, $wR_{ref}(F^2)$ = 0.1248, T = 100 K.

Source of material

The title compound was obtained in a reproducible way as a by-product of the reaction between an isomeric mixture of (*E/Z*)-4,5-dideoxy-2,3-O-isopropylidene-*D*-erythro-4-pentenose O-tert-butyldimethylsilyloximes with *N*-bromosuccinimide (NBS) in acetonitrile [1-4]. Isolation by column chromatography (ethyl acetate/petroleum ether) followed by recrystallization from ethyl acetate/petroleum ether gave the title product in the form of colourless crystals.

Analysis: m.p. 133-135°C, $[\alpha]_D20$ = -14 (c = 1.00, CH_2Cl_2).

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Table 1. Data collection and handling.

Crystal:	colourless blocks, size 0.08×0.15×0.22 mm
Wavelength:	Mo K_α radiation (0.71073 Å)
μ:	55.11 cm^{-1}
Diffractometer, scan mode:	Bruker Kappa Apex II Duo, ω and φ
$2\theta_{max}$:	50.24°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	8954, 2614
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\ \sigma(I_{obs})$, 1970
$N(param)_{refined}$:	223
Programs:	SHELXS-97 [5]

Experimental details

H atoms were located in the difference fourier map, but refined with fixed individual displacement parameters, using a riding model with d(C–H) ranging from 0.93 to 0.98 Å. In addition, methyl groups were allowed to rotate but not to tip. The population parameters of the disordered atoms were refined free. The Flack parameter is 0.01(2) [6], which is in accordance with the absolute configuration resulting from the synthetic pathway.

Discussion

The title compound (figure, top) crystallizes with two independent molecules in the asymmetric unit of the acentric space group $P2_12_12_1$. The bond distances N1–O1 of the N-oxide with 1.279(9) Å and of the formal N1=C4 double bond with 1.264(11) Å are identical with respect to their standard deviations. The pyrrole ring system shows a slight envelope conformation where C3 is 0.24 Å out-of-plane. A typical envelope conformation is evident in the dioxolane moiety where O5 is 0.52 Å out-of-plane. The bromomethyl moiety and one of the methyl groups of the dioxolane ring system are disordered with alternative atom positions. The cell plot (figure, bottom) shows an antiparallel organization of the molecules which yields in a layer-type stacking along the *c*-axis. There are three types of layers: The first one is formed by the succinimido moieties and the second one is built up by the pyrroles. Finally the last one is a bilayer-type formed by the dibromomethyl fragments.

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

Atom	Site	Occ.	x	y	z	U_{iso}
H(1)	4*a*		0.5695	–0.0286	0.1768	0.021
H(2)	4*a*		0.2967	–0.2810	0.1681	0.031
H(3)	4*a*		0.0067	–0.1746	0.1220	0.040
H(5)	4*a*	0.65	0.1740	0.2673	0.1023	0.038

Table 2. continued.

Atom	Site	Occ.	*x*	*y*	*z*	U_{iso}
H(5A)	4*a*	0.35	0.0462	–0.0377	0.0645	0.057
H(8A)	4*a*		–0.0566	–0.0270	0.2917	0.041
H(8B)	4*a*		0.0641	–0.1943	0.2976	0.041
H(9A)	4*a*		0.3851	–0.0823	0.3198	0.031
H(9B)	4*a*		0.2597	0.0847	0.3164	0.031
H(11A)	4*a*		0.5633	–0.2844	0.0134	0.085
H(11B)	4*a*		0.7710	–0.2823	0.0490	0.085
H(11C)	4*a*		0.6265	–0.1268	0.0395	0.085
H(12A)	4*a*	0.42	0.4225	–0.5072	0.1082	0.060
H(12B)	4*a*	0.42	0.6632	–0.4831	0.0828	0.060
H(12C)	4*a*	0.42	0.4331	–0.5133	0.0544	0.060
H(12D)	4*a*	0.58	0.2393	–0.4437	0.1107	0.062
H(12E)	4*a*	0.58	0.4684	–0.5210	0.0906	0.062
H(12F)	4*a*	0.58	0.2618	–0.4730	0.0576	0.062

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

Atom	Site	Occ.	*x*	*y*	*z*	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Br(1)	4*a*		0.1916(2)	0.1660(1)	0.02990(3)	0.0760(7)	0.0503(6)	0.0336(5)	0.0251(6)	0.0216(5)	0.0164(5)
O(1)	4*a*		0.333(1)	0.2241(7)	0.1608(3)	0.072(5)	0.023(3)	0.094(5)	0.003(4)	0.050(5)	0.019(4)
N(1)	4*a*		0.294(1)	0.0834(8)	0.1488(2)	0.024(4)	0.034(4)	0.027(4)	0.008(4)	0.015(3)	0.010(3)
C(1)	4*a*		0.399(1)	–0.0441(8)	0.1757(2)	0.011(4)	0.017(4)	0.025(4)	0.005(3)	–0.003(3)	0.000(3)
O(2)	4*a*		–0.0381(9)	–0.1562(8)	0.2073(2)	0.023(3)	0.068(4)	0.017(3)	–0.021(3)	0.000(2)	0.002(3)
N(2)	4*a*		0.309(1)	–0.0420(6)	0.2209(2)	0.019(3)	0.021(3)	0.012(3)	0.003(3)	–0.001(3)	0.002(3)
C(2)	4*a*		0.347(1)	–0.1908(9)	0.1492(2)	0.035(5)	0.024(4)	0.017(4)	–0.009(4)	0.002(3)	0.000(3)
O(3)	4*a*		0.6106(9)	0.0921(7)	0.2537(2)	0.024(3)	0.049(4)	0.038(3)	–0.005(3)	0.005(3)	–0.024(3)
C(3)	4*a*		0.165(1)	–0.137(1)	0.1143(2)	0.021(3)	0.057(4)	0.023(3)	–0.007(3)	–0.001(3)	–0.005(3)
O(4)	4*a*		0.245(1)	–0.2000(8)	0.0727(2)	0.036(3)	0.088(4)	0.018(3)	0.000(4)	–0.002(2)	–0.011(3)
C(4)	4*a*		0.181(2)	0.032(1)	0.1156(3)	0.039(5)	0.074(7)	0.023(5)	0.028(6)	0.014(4)	0.016(5)
O(5)	4*a*		0.5430(9)	–0.2222(6)	0.1211(2)	0.035(3)	0.031(3)	0.016(3)	0.016(3)	–0.007(2)	–0.016(2)
C(5)	4*a*	0.65	0.094(1)	0.175(2)	0.0888(4)	0.044(7)	0.022(8)	0.029(7)	0.011(6)	0.006(5)	–0.006(5)
Br(2)	4*a*	0.803	–0.2213(2)	0.2025(2)	0.10164(5)	0.0195(5)	0.0403(8)	0.0376(8)	0.0057(5)	0.0007(5)	0.0072(7)
C(5A)	4*a*	0.35	0.054(2)	0.069(5)	0.078(1)	0.05(1)	0.05(1)	0.04(1)	–0.001(9)	0.004(9)	0.002(9)
Br(2A)	4*a*	0.197	–0.2650(8)	0.1124(9)	0.0771(2)	0.017(3)	0.067(5)	0.054(4)	0.012(3)	0.005(2)	0.027(4)
C(6)	4*a*		0.452(2)	–0.284(1)	0.0793(3)	0.078(7)	0.023(5)	0.015(4)	0.006(5)	–0.018(4)	–0.010(4)
C(7)	4*a*		0.100(1)	–0.1050(9)	0.2334(2)	0.017(4)	0.034(5)	0.017(4)	–0.002(4)	0.000(3)	0.002(4)
C(8)	4*a*		0.080(2)	–0.090(1)	0.2836(3)	0.030(5)	0.052(6)	0.020(4)	–0.010(4)	–0.004(4)	0.003(4)
C(9)	4*a*		0.296(1)	–0.0122(9)	0.2998(2)	0.031(5)	0.023(4)	0.024(4)	0.005(4)	–0.003(4)	–0.006(3)
C(10)	4*a*		0.430(1)	0.0231(9)	0.2577(3)	0.025(5)	0.019(4)	0.023(4)	0.009(4)	–0.009(4)	–0.010(4)
C(11)	4*a*		0.618(2)	–0.241(1)	0.0420(3)	0.049(6)	0.097(9)	0.024(5)	0.012(6)	0.001(4)	–0.022(5)
C(12A)	4*a*	0.42	0.497(6)	–0.464(3)	0.0814(8)	0.05(1)	0.04(1)	0.04(1)	–0.007(8)	–0.013(8)	–0.004(8)
C(12)	4*a*	0.58	0.346(4)	–0.445(2)	0.0851(6)	0.05(1)	0.033(8)	0.042(8)	0.019(7)	–0.018(7)	–0.022(6)

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