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Crystal structure of (2*RS*)-2-bromomethyl-4,4-dimethyl-3,4-dihydro-2*H*-pyrrole 1-oxide hemi(hydrobromide), $C_7H_{12}BrNO \cdot \frac{1}{2}HBr$

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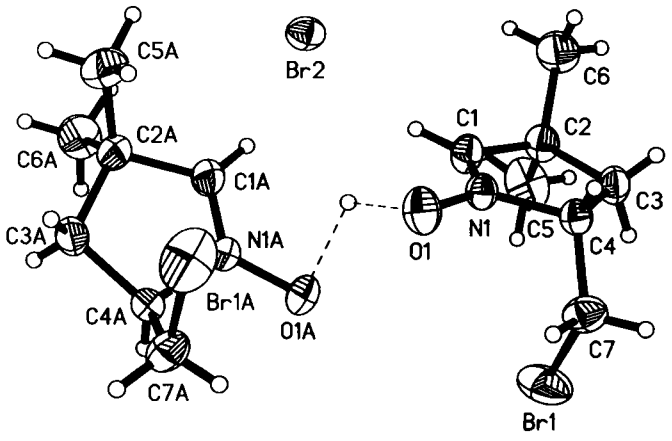

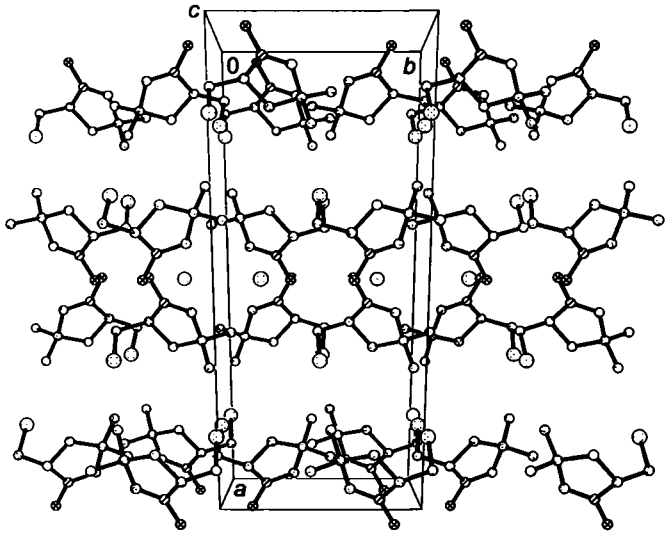

Abstract

$C_7H_{12.50}Br_{1.50}NO$, monoclinic, *C*12/*c*1 (no. 15), a = 22.249(2) Å, b = 8.571(1) Å, c = 11.083(1) Å, β = 117.037(8)°, V = 1882.5 Å^3, Z = 8, $R_{gt}(F)$ = 0.043, $wR_{ref}(F^2)$ = 0.116, T = 293 K.

Source of material

The title compound has been obtained by bromocyclization of 2,2-dimethyl-4-pentenal oxime [1-7]. The crystallization of the product from dichloromethane furnished the title nitrone in the form of colorless crystals (m.p. 326-327 K).

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Discussion

In the asymmetric unit we found one molecule of the pyrroline *N*-oxide and half a molecule of hydrobromide, where the hydrogen H1A and the bromine ion Br2 are in special positions in the crystal with population factors of 0.5 (figure, top). The intermolecular oxygen distance of the *N*-oxides is 2.429(6) Å, which is rather short. Between these oxygen atoms we found the half-populated hydrogen H1A with equal distances of 1.59(5) Å to each oxygen O1, which is very long as compared to usual O···H bonds. The O1–H1A···O1 angle is 100(4)°. The N1–O1 distance of 1.342(4) Å shows a slight lengthening which is forced by the hydrogen bond situation of H1A. The double bond N1=C1 is characterized by the distance of 1.265(5) Å. The pyrroline ring system shows a perfectly flat conformation (r.m.s.d. = 0.0088 Å) which is remarkable. In the packing diagram of the cell plot (figure, bottom) we observe alternate polar and non-polar layers in the *b*,*c* plane along the *a* axis. The non-polar layers are formed by the carbon atoms of the pyrroline moieties. The polar layers are built up by two types, one formed by the covalently bonded bromine atoms and the other one by the *N*-oxide atoms and the bromine ions.

Table 1. Data collection and handling.

Crystal:	colorless plate, size 0.15 × 0.30 × 0.60 mm
Wavelength:	Cu K_α radiation (1.54178 Å)
μ:	79.95 cm^{-1}
Diffractometer, scan mode:	Siemens P4, ω
$2\theta_{max}$:	134.96°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	2026, 1636
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\,\sigma(I_{obs})$, 1549
$N(param)_{refined}$:	97
Programs:	SHELXS-97 [8], SHELXL-97 [9], SHELXTL-Plus [10]

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

Atom	Site	x	y	z	U_{iso}
H(1)	8*f*	0.4493	0.0692	0.2832	0.040
H(1A)	4*e*	½	0.2420	¼	0.082
H(3A)	8*f*	0.3075	0.2845	0.3251	0.041
H(3B)	8*f*	0.3509	0.2214	0.4733	0.041
H(4)	8*f*	0.4340	0.3762	0.5056	0.033
H(5A)	8*f*	0.2701	0.0185	0.2006	0.088
H(5B)	8*f*	0.3235	–0.0400	0.1556	0.088
H(5C)	8*f*	0.2991	0.1339	0.1305	0.088
H(6A)	8*f*	0.3427	–0.0746	0.4359	0.079
H(6B)	8*f*	0.4175	–0.0163	0.5150	0.079
H(6C)	8*f*	0.3973	–0.1331	0.3939	0.079
H(7A)	8*f*	0.4277	0.5724	0.3551	0.045
H(7B)	8*f*	0.3653	0.5757	0.3850	0.045

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}
Br(1)	8*f*	0.32688(3)	0.50560(7)	0.14827(5)	0.0482(4)	0.0722(5)	0.0446(4)	0.0000(2)	0.0097(3)	0.0240(2)
N(1)	8*f*	0.4480(2)	0.2727(4)	0.3576(3)	0.024(2)	0.029(2)	0.030(2)	–0.003(1)	0.014(1)	–0.002(1)
C(1)	8*f*	0.4278(2)	0.1359(5)	0.3173(4)	0.032(2)	0.033(2)	0.040(2)	–0.001(2)	0.022(2)	–0.004(2)
O(1)	8*f*	0.5028(1)	0.3439(4)	0.3621(3)	0.029(1)	0.046(2)	0.047(2)	–0.011(1)	0.021(1)	–0.006(1)
C(2)	8*f*	0.3662(2)	0.0917(4)	0.3296(4)	0.035(2)	0.029(2)	0.040(2)	–0.006(2)	0.021(2)	–0.004(2)
C(3)	8*f*	0.3512(2)	0.2429(5)	0.3877(4)	0.038(2)	0.028(2)	0.046(2)	–0.000(2)	0.028(2)	–0.001(2)
C(4)	8*f*	0.4068(2)	0.3598(4)	0.4081(4)	0.030(2)	0.027(2)	0.028(2)	–0.001(1)	0.016(2)	–0.002(1)
C(5)	8*f*	0.3095(3)	0.0469(8)	0.1912(5)	0.051(3)	0.075(4)	0.048(3)	–0.025(3)	0.020(3)	–0.020(3)
C(6)	8*f*	0.3824(3)	–0.0459(5)	0.4277(6)	0.076(4)	0.028(2)	0.068(3)	–0.002(2)	0.045(3)	0.005(2)
C(7)	8*f*	0.3871(2)	0.5165(5)	0.3414(5)	0.036(2)	0.028(2)	0.045(2)	–0.002(2)	0.016(2)	0.004(2)
Br(2)	4*e*	½	–0.20968(6)	¼	0.0447(4)	0.0276(4)	0.0375(4)	0	0.0173(3)	0

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