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MOLECULAR AND CRYSTAL STRUCTURE OF 1-BROMO-1-BUTYL-3H-2,1-BENZOXATELLUROLE

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The molecular and crystal structure of 1-bromo-1-butyl-3H-2,1-benzoxatellurole was determined by x-ray diffraction structural analysis. Without taking account of secondary interactions, the molecule contains a tetracoordinated tellurium atom with bisphenoidal bond configuration. The angle between the axial bromine and oxygen atoms is 172.1°. The intermolecular Te···Br contacts (3.592 Å) connect the individual dimers into planar dimers, which expands the coordination about the tellurium atom to octahedral.

We have recently synthesized [1, 2] and studied some reactions of tetracoordinated derivatives of a new heterocyclic system, namely, 3H-2,1-benzoxatellurole [2]. In the present work, we studied the molecular and crystal structure of one of these compounds, namely, 1-bromo-1-butyl-3H-2,1-benzoxatellurole (I).

The molecular structure of I, numbering of the atoms, and bond lengths are given in Fig. 1, while the bond angles are given in Table 1.

Without taking account of intermolecular interactions, the tellurium atom has trigonal–bipyramidal bond configuration at the tellurium atom common for tetracoordinated tellurium derivatives (tellurium tetrahalides, σ-telluranes R_2TeX_2 and $RTeX_3$, where X = halogen) [3]. The most electronegative substituents (the bromine and oxygen atoms) are found at the apical positions and the angle between the Te–O and Te–Br bonds is 172.1°. This value is somewhat greater than those found for the angles between the most electronegative substituents of structurally similar 1,1-dichloro-3,3-bis(trifluoromethyl)-5-methyl-

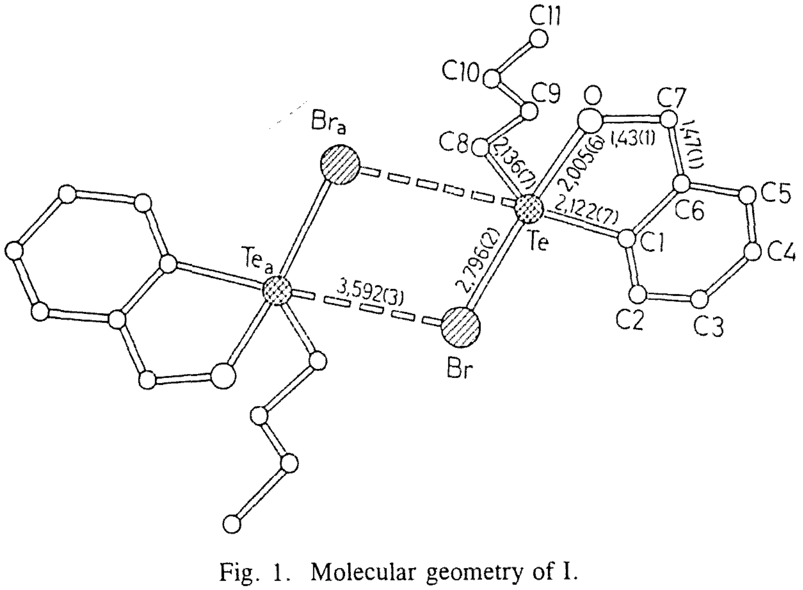

Fig. 1. Molecular geometry of I.

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TABLE 1. Bond Angles ω (deg) in Heterocycle I

Bond angle	ω	Bond angle	ω
Br—Te—O	172,1(2)	$C_{(1)}$—$C_{(2)}$—$C_{(3)}$	118,5(8)
Br—Te—$C_{(1)}$	90,3(2)	C(2)—$C_{(3)}$—$C_{(4)}$	119,9(7)
O—Te—$C_{(1)}$	82,4(3)	C(3)—$C_{(4)}$—$C_{(5)}$	121,0(8)
Br—Te—$C_{(8)}$	87,2(2)	C(4)—$C_{(5)}$—$C_{(6)}$	121,3(9)
O—Te—$C_{(8)}$	90,6(3)	$C_{(1)}$—$C_{(6)}$—$C_{(5)}$	116,3(7)
$C_{(1)}$—Te—$C_{(8)}$	98,7(3)	$C_{(1)}$—$C_{(6)}$—$C_{(7)}$	120,0(7)
Te—O—$C_{(7)}$	116,1(4)	$C_{(5)}$—$C_{(6)}$—$C_{(7)}$	123,7(8)
Te—$C_{(1)}$—$C_{(2)}$	127,8(6)	O—$C_{(7)}$—$C_{(6)}$	112,3(7)
Te—$C_{(1)}$—$C_{(6)}$	109,1(5)	Te—$C_{(8)}$—$C_{(9)}$	115,7(5)
$C_{(2)}$—$C_{(1)}$—$C_{(6)}$	123,0(7)	$C_{(8)}$—$C_{(9)}$—$C_{(10)}$	111,0(7)
		$C_{(9)}$—$C_{(10)}$—$C_{(11)}$	112,3(7)

TABLE 2. Atomic Coordinates ($\times 10^4$) and Equivalent Temperature Parameters ($A^2 \times 10^3$)

Atom	x	y	z	U_{eq}
Te	3756(1)	5131(1)	2064(1)	16(1)
Br	6552(1)	5846(1)	1642(1)	31(1)
O	1711(7)	4757(3)	2514(6)	26(2)
$C_{(1)}$	3958(9)	5875(4)	4051(8)	19(2)
$C_{(2)}$	5138(9)	6446(5)	4694(8)	23(2)
$C_{(3)}$	5009(10)	6888(5)	5986(9)	26(3)
$C_{(4)}$	3728(10)	6736(5)	6610(9)	28(3)
$C_{(5)}$	2575(10)	6171(5)	5964(9)	28(3)
$C_{(6)}$	2636(9)	5713(5)	4639(8)	21(2)
$C_{(7)}$	1406(9)	5102(5)	3874(9)	26(3)
$C_{(8)}$	2242(10)	5861(5)	164(9)	28(3)
$C_{(9)}$	1068(10)	6406(5)	615(9)	24(2)
$C_{(10)}$	171(9)	6943(5)	-782(9)	24(2)
$C_{(11)}$	-1107(11)	7465(5)	-401(10)	35(3)

3H-2,1-benzoxathiol (II) (167.6°) [4] and 3,3,3′,3′-tetra(trifluoromethyl)-1,1-spirobis[3H-2,1-benzoxatellurole] (III) (160.5°) [5]. The Te−O bond length (2.005 Å) is somewhat less than in spirane III (2.077 Å) but is identical to the $Te-O_{ax}$ bond length found for 3,3,3′,3′,4,4,4′,4′-octamethyl-1,1-spirobis[2,5,1-dioxatellurole] determined by x−ray diffraction structural analysis [6]. On the other hand, the Te−C bond lengths ($Te-C_{aliph}$ 2.136 Å, $Te-C_{arom}$, 2.122 Å) are similar to those found in spirane III.

Heterocyclic fragment in I is virtually planar (the deviations of the atoms in the heterocycle from the plane do not exceed 0.02 Å), while geometric parameters of this fragment are almost identical to those for such fragments in spirane III.

The Te−Br bond length in the benzoxatellurole is 2.796 Å, which is greater than the length of the analogous bonds in $TeBr_4$ and σ-telluranes $ArTeBr_3$ and Ph_2TeBr_2, which lie in the range from 2.49 to 2.68 Å [3]. Virtually planar dimers are formed in the crystal of I due to intermolecular Te···Br(a) interactions (3.592 Å, the sum of the van der Waals radii is 4.15 Å) [7]. Only the butyl groups extrude from the plane of this dimer at an angle of 79.9° to it. Taking account of these bonds, the coordination of the tellurium atom may be seen as octahedral with the unshared electron pair in the vacant equatorial position.

We should note that such intermolecular interactions are characteristic for halogen-containing σ-telluranes, which most often exist in the crystalline state in dimeric or polymeric forms due to Te···Br bridging bonds [3]. However, in the present compound, the Te···Br bonds are much longer than the Te···Br bonds found in $TeBr_4$ (3.05 Å) and aryltellurium tribromides (2.88-2.93 Å) [3].

EXPERIMENTAL

The synthesis of 1-bromo-1-butyl-3H-2,1-benzoxatellurole was carried out as described in our previous work [2].

The unit cell parameters of monoclinic crystals of $C_{11}H_{15}BrOTe$ (I) at −120°C are as follows: a = 8.456(4), b = 17.169(11), c = 8.781(4) Å, β = 109.55(4)°, V = 1201(2) Å^3, space group $P2_1/c$, d_{calc} = 2.05 g/cm^3, Z = 4.

The unit cell parameters and reflection intensities were measured on a P3/PC automatic diffractometer using λMoK_α radiation and $\theta/2\theta$ scanning, $2\theta \leq 56°$.

The structure was solved by the direct method and refined anisotropically by the method of least squares for 2607 reflections with $I > 4\sigma/I$. The positions of the hydrogen atoms were determined geometrically and then refined in the "rider" approximation with fixed U_{iso} 0.08 Å^2. The final R factors: R = 0.051, R_w = 0.062, GOOF = 3.3.

All the calculations were carried out using the SHELTXL programs. The coordinates of the nonhydrogen atoms and their equivalent temperature parameters are given in Table 2.

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