

4.* X-RAY STRUCTURE OF 2-PHENYLBENZOTELLURAZOLE

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The crystal and molecular structure of 2-phenylbenzotellurazole is determined by x-ray methods. The heterocyclic fragment of the molecule is planar. The dihedral angle between planes of the heterocycle and the 2-phenyl substituent is 31.2° . Somewhat shortened Te-N intermolecular contacts (3.43 \AA) are seen in the crystal. These do not substantially affect the physical properties of the compound.

Data on five-membered nitrogen-tellurium-containing heterocycles are limited [2]. Only benzisotellurazole [3] and 1,2,5-telluradiazole [4] have been studied by x-ray methods. In the present report, we describe the crystal and molecular structure of a representative of the new benzotellurazole heterocyclic system [5-7], 2-phenylbenzotellurazole (I).

The molecular structure and bond lengths and angles in it are shown in Fig. 1. The atomic coordinates appear in Table 1. The heterocyclic fragment of 2-phenylbenzotellurazole is planar. The atoms of this fragment deviate from the plane by 0.001 - 0.017 \AA : Te, 0.016 ; N, 0.006 ; C₍₁₎, 0.002 ; C₍₂₎, 0.011 ; C₍₃₎, 0.006 ; C₍₄₎, 0.010 ; C₍₅₎, 0.001 ; and C₍₆₎, 0.017 \AA . The dihedral angle between the planes of the heterocyclic and phenyl rings is 31.2° . Such twisting of the phenyl substituent around C₍₇₎ relative to the plane of the remaining part of the molecule minimizes the steric hindrance. The intramolecular Te-H₍₁₃₎ distance is 2.93 \AA . However, this intramolecular contact should be much closer (Te-H₍₁₃₎ 2.72 \AA) according to the planar model of I.

The Te-C bond lengths (2.080 and 2.123 \AA) are comparable to analogous distances in other five- [2] and six-membered [8] tellurium-containing heterocycles (2.07 - 2.12 \AA).

The angles around the heteroatoms in I differ considerably from corresponding angles in benzoxazole (5-nitro-2-cyclohexylaminobenzoxazole [9]) and benzothiazole (2-(2'-hydroxyphenyl)benzothiazole [10]) derivatives. The C₍₁₎-N-C₍₇₎ angle increases in the series benzoxazole (103.8°), benzothiazole (110.8°), and benzotellurazole (116.9°). Conversely, the C₍₂₎-X-C₍₇₎ angle for the group VIA X heteroatoms decreases much more significantly in the same order: benzoxazole (103.8°), benzothiazole (88.6°), and benzotellurazole (78.6°). The decrease of the C-C-C angle and the increase of the C-N-C angle is caused by a lengthening of the X-C bond on increasing the size of the X heteroatom in the order X = O, S, Te. Moreover, the angle at the tellurium atom in 2-phenylbenzotellurazole (I) differs insignificantly from analogous angles in a number of other five-membered tellurium-containing heterocycles: α -tellurophenecarboxylic acid (81.5°) [11], dibenzotellurophene (81.7°) [12], benzisotellurazole (80.0°) [3], and 1,2,5-telluradiazole (82.5°) [4]. The bond lengths and angles in the annelated benzene ring and the 2-phenyl substituent have standard values.

The short intermolecular contacts between the nitrogen and tellurium atoms are especially interesting. Similar Te-N contacts observed in benzisotellurazole (2.40 \AA) [3] and 1,2,5-telluradiazole (2.76 \AA) [4] (the sum of van der Waals radii for tellurium and nitrogen is 3.70 \AA [13]) are probably responsible for the anomalously high melting point and low solubility in ordinary organic solvents of tellurium-containing heterocycles in comparison to other

*For Communication 3, see [1].

TABLE 1. Atomic Coordinates in I ($\times 10^5$ for Te, $\times 10^4$ for N and C, $\times 10^3$ for H)

Atom	x	y	z	Atom	x	y	z
Te	12014(2)	11163(4)	24333(2)	C ₍₁₁₎	3733(4)	-3954(7)	539(3)
N	3662(3)	1980(5)	2830(2)	C ₍₁₂₎	2840(4)	-4238(7)	1005(3)
C ₍₁₎	3202(3)	3478(6)	3312(2)	C ₍₁₃₎	2596(4)	-2742(7)	1610(3)
C ₍₂₎	2016(3)	3510(6)	3271(3)	H ₍₃₎	60	504	368
C ₍₃₎	1498(4)	5025(7)	3728(3)	H ₍₄₎	184	765	460
C ₍₄₎	2204(4)	6497(7)	4248(3)	H ₍₅₎	392	759	471
C ₍₅₎	3397(4)	6464(7)	4311(3)	H ₍₆₎	480	493	392
C ₍₆₎	3901(4)	4949(7)	3852(3)	H ₍₉₎	467	61	145
C ₍₇₎	2951(4)	653(6)	2368(3)	H ₍₁₀₎	508	-199	36
C ₍₈₎	3246(3)	-965(6)	1772(3)	H ₍₁₁₎	390	-507	6
C ₍₉₎	4161(4)	-711(7)	1322(3)	H ₍₁₂₎	235	-559	90
C ₍₁₀₎	4398(4)	-2197(8)	705(3)	H ₍₁₃₎	191	-296	195

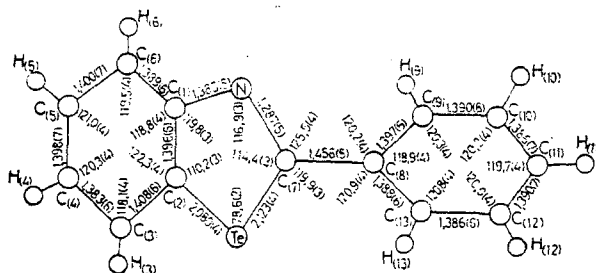


Fig. 1. Geometry of 2-phenylbenzotellurazole.

benzisochoalcogenoazoles and 1,2,5-chalcogenodiazoles. Intermolecular Te-N contacts (3.43 Å) that are longer than those in the aforementioned tellurium-containing heterocycles are also seen in 2-phenylbenzotellurazole.

These relatively weak contacts, shortened in comparison to the sum of van der Waals radii for tellurium and nitrogen by about 0.3 Å, do not have a substantial effect on the physical properties of 2-phenylbenzotellurazole. The melting point of this compound (118-120°C [5]) is almost the same as for its selenium analog (116°C [14]). It is very soluble in ordinary organic solvents.

EXPERIMENTAL

2-Phenylbenzotellurazole was synthesized by the method given in [6].

The x-ray structural study of I was carried out on a Syntex P2₁ diffractometer ($\theta/2\theta$ scanning, Mo K α radiation, graphite monochromator, $2\theta_{\max} = 60^\circ$).

Yellow crystals of I, C₁₃H₉NTe, are monoclinic: $a = 11.870(1)$, $b = 6.557(6)$, $c = 14.403(2)$ Å, $\beta = 103.107(9)^\circ$, $V = 1091.9(2)$ Å³, $\rho_{\text{exp}} = 1.83(3)$ g/cm³, $\rho_{\text{calc}} = 1.87$ g/cm³, $\mu_{\text{Mo}} = 27.9$ cm⁻¹, $Z = 4$, space group P2₁/a.

Intensities of 3009 reflections were measured. Of these, 2451 with $I \geq 1.96$ were used in the calculations. All calculations were performed on a Nova-1200 minicomputer using XTL programs.

The structure of I was solved by the heavy atom method and refined by anisotropic full-matrix least squares for all nonhydrogen atoms. The hydrogen atom positions were calculated for sp²-hybridized carbon atoms and C-H distances of 1.05 Å. The final R-factor was 0.030.

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