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THE CRYSTAL AND MOLECULAR STRUCTURE OF 3,4-QUINOXALINO-1-TELLURACYCLOPENTANE $C_{10}H_8N_2Te^{II}$

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Summary

The crystal and molecular structure of 3,4-quinoxalino-1-tellura(II)cyclopentane has been determined by X-ray diffraction at room temperature. The crystals are tetragonal, space group $I4_1/a$ with $a = b = 25.315(8)$, $c = 6.010(1)$ Å and $V = 3851.38$ Å^3. The density of 1.96 g cm^{-3} calculated on the basis of 16 molecules per unit cell is in agreement with the flotation value of 1.91 g cm^{-3}. The structure has been refined to a conventional R value of 0.0408 using 744 independent observed reflections obtained from four-circle diffractometer measurements. The structure consists of discrete molecules Te–C = 2.134 Å (av.), C–N = 1.343 Å (av.) and angle C–Te–C = 80.7° (e.s.d. 0.5) but the intermolecular Te–Te bonds (3.791 and 3.998 Å) are less than the sum of the Van der Waals' radii thus indicating the presence of secondary bonding. These short intermolecular contacts in the crystal structure are consistent with the anomalous physical properties observed.

Introduction

The study of the crystal structures of a variety of organotellurium compounds has revealed the presence of intermolecular bonds of various type and strength. These secondary bonds have been associated with such properties as the colour of crystals, the presence of dimers or chain like polymers in the structure and anomalous physical properties. For example, comparatively short intermolecular Te–N bonds were found in the crystal structure of 1,2-benzoisotellurazole which shows some anomalous physical properties but not in the crystal structure of 1,2-benzisoselenazole for which the corresponding physical properties are as expected [1]. This new compound 3,4-quinoxalino-1-tellura(II)cyclopentane which has an unexpectedly high melting point and low solubility in ether and is of interest for the preparation of charge transfer complexes [2] was investigated by X-ray methods to study the nature of the intermolecular reactions.

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Experimental

Preparation. $C_{10}H_8N_2Te^{II}$ was prepared by the reduction of 1,1-diiodo-3,4-quinoxalino-1-tellura(IV)cyclopentane with hydrazine hydrate and recrystallised from ether. The crystals grow as fine yellow needles which are stable in the presence of air and light. M.p. 158–160 °C. (Found: C, 41.6; H, 2.80; N, 9.50; Te, 44.2. $C_{10}H_8N_2Te$ calcd.: C, 42.3; H, 2.81; N, 9.87; Te, 44.9%.) The mass spectral analysis showed the parent ion and no species larger than the compound mass. A density column was prepared from tetrabromoethane and carbon tetrachloride and the density was found to be 1.91 g cm^{-3} at 20 °C.

X-Ray measurements. After preliminary oscillation and equiinclination Weissenberg photographs had been taken a crystal with dimensions 0.76 × 0.08 × 0.08 mm was mounted along the z axis on an Enraf–Nonius CAD-4 diffractometer. The automatic centering, indexing and least squares routines of the instrument were applied to 20 reflections to obtain lattice parameters using graphite-monochromated Mo-K_α radiation. The intensity data were collected in the ω-2θ scan mode, the scan range (ω°) was calculated from $(1.0 + 0.35 \tan \theta)$ and the scan speed varied from 0.5–2.5° min^{-1} depending on the intensity. 2030 reflections were scanned in the range $2 < \theta < 25°$. Three standard reflections were monitored every 2 h and the orientation of the crystal was checked every one hundred reflections. No decomposition or movement of the crystal was observed during the collection of reflection intensities. Lorentz and polarisation corrections were applied to the data and 744 independent observed reflections with $F > 7\sigma(F)$ were used in the structure analysis. The crystals were found to be tetragonal with $hk0$ present only when $h + k + l = 2n$, $hk0$ present only when $h = 2n$ and $00l$ present only when $l = 4n$ consistent with the space group $I4_1/a$ and the number of formula weights in the unit cell is 16.

Crystal data. $C_{10}H_8N_2Te$, $M = 283.784$, Tetragonal, $a = b = 25.315(8)$, $c = 6.010(1)$ Å, $V = 385.38$ Å, $D_m = 1.91$ g cm^{-3}, $Z = 16$, $D_c = 1.96$ g cm^{-3}, $F(000) = 2143.14$, $\lambda(\text{Mo-}K_\alpha) = 0.71069$ Å, $U = 30.47$ cm^{-1}.

Solution and refinement of the structure. The atomic parameters for tellurium were found by direct methods using SHELX 76 [3] and confirmed by analysis of the

TABLE 1

ATOMIC COORDINATES WITH STANDARD DEVIATIONS IN PARENTHESES ($\times 10^4$)

Atom	x	y	z
Te	5749(0)	2500(0)	6217(0)
C(1)	6404(5)	2759(5)	8200(25)
C(2)	6768(5)	2307(5)	8167(25)
C(3)	6754(4)	1960(5)	6344(30)
C(4)	6365(5)	2082(6)	4593(26)
N(1)	7043(4)	1535(4)	6187(25)
N(2)	7096(4)	2230(4)	9812(21)
C(5)	7418(5)	1795(5)	9734(25)
C(6)	7772(5)	1675(6)	11491(29)
C(7)	8072(5)	1242(6)	11326(36)
C(8)	8060(6)	891(6)	9639(33)
C(9)	7729(6)	994(5)	7915(28)
C(10)	7390(5)	1439(5)	7939(26)

Patterson map. The positions of the carbon and nitrogen atoms were found by using a difference map. Anisotropic temperature factors were calculated for all non-hydrogen atoms. The positional and temperature factor parameters for tellurium, carbon and nitrogen were refined by four cycles of blocked full-matrix least squares refinement with hydrogen atoms included in the calculation in their theoretical positions. The weighting scheme used was $w = 1.3438/\sigma^2 F$ and the refinement converged to $R = 0.0408$ and $R_w = 0.038$. The fractional atomic coordinates are listed in Table 1. Tables of thermal parameters and structure factors are available from the authors on request.

Results and discussion

The unit cell dimensions and space group of 3,4-quinoxalino-1-telluracyclopentane differ from those of the related compounds that have been studied [1,5–7]. The structure consists of one discrete repeating molecule (Fig. 1) whose bond lengths and

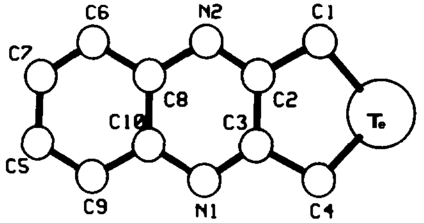

Fig. 1. Molecule of $C_{10}H_8N_2Te$ with atom labelling scheme.

TABLE 2

BOND DISTANCES (Å) AND ANGLES (°) in $C_{10}H_8N_2Te$

Te–C(1)	2.145(13)	C(1)–Te–C(4)	80.7(0.5)
Te–C(4)	2.123(14)	C(2)–C(1)–Te	103.9(0.9)
C(1)–C(2)	1.469(16)	C(3)–C(2)–C(1)	118.8(1.3)
C(2)–C(3)	1.405(19)	C(3)–C(2)–N(2)	120.9(1.2)
C(2)–N(2)	1.305(16)	N(2)–C(2)–C(1)	120.3(1.3)
C(3)–C(4)	1.473(19)	C(4)–C(3)–C(2)	116.3(1.1)
C(3)–N(1)	1.304(14)	C(4)–C(3)–N(1)	119.8(1.5)
N(1)–C(10)	1.392(18)	N(1)–C(3)–C(2)	123.9(1.5)
N(2)–C(5)	1.370(15)	C(3)–C(4)–Te	105.5(1.0)
C(5)–C(6)	1.419(19)	C(3)–N(1)–C(10)	116.3(1.4)
C(6)–C(7)	1.337(17)	N(2)–C(5)–C(6)	121.5(1.4)
C(7)–C(8)	1.349(23)	N(2)–C(5)–C(10)	120.7(1.4)
C(8)–C(9)	1.359(20)	C(6)–C(5)–C(10)	117.7(1.3)
C(9)–C(10)	1.417(18)	C(5)–N(2)–C(2)	118.1(1.2)
C(10)–C(5)	1.407(18)	C(5)–C(6)–C(7)	118.7(1.7)
		C(6)–C(7)–C(8)	125.7(1.8)
		C(7)–C(8)–C(9)	117.4(1.4)
		C(8)–C(9)–C(10)	121.3(1.5)
		N(1)–C(10)–C(5)	120.0(1.2)
		N(1)–C(10)–C(9)	120.8(1.4)
		C(9)–C(10)–C(5)	119.1(1.4)

angles are given in Table 2. The intramolecular Te–C distances 2.145(13) and 2.123(14) Å are in good agreement with the sum of the single bond radii 2.140 Å [4] but longer than those reported for benzisotellurazole-1,2 (2.08(1), 2.09(1) Å) [1] and dibenzotellurophene (2.089(5), 2.084(5) Å) [5]. The average of the C–N bonds (1.34 Å) are again longer than those in benzoisotellurazole (1.27(2), 1.28(2) Å) [1] but shorter than those found in one molecule of the (2-phenylazophenyl-*C,N'*)tellurium(II) chloride structure (1.45(3), 1.43(3) Å) [6]. The C–Te–C angle 80.7(0.5)° is less than those found for dibenzotellurophene (81.7(2)°) [5] and 1,1-diiodo-3,4-benzo-1-telluracyclopentane (86.0(5)°) [7]. The other intramolecular distances and angles are in agreement with the expected values.

The two aromatic moieties of the quinoxaline residue are almost planar. The distances of the non-hydrogen atoms from the least squares planes is small, the largest being 0.0348 Å, and the angle between the planes is calculated to be 0.809°. The tellurium bonded residue is distorted from planarity and is tilted so that the tellurium atom is displaced 0.6801 Å from the least squares plane of the molecule lying below C(2) and C(5) (Fig. 1). The angle between the tellurium bonded residue plane and the quinoxaline residue is 22.07° (Table 3).

The packing arrangement of the molecules viewed along the *c* axis is shown in Fig. 2 where the screw axis and glide plane symmetry may be observed. The tellurium atoms are seen to be arranged in layers and there are short intermolecular bonds between some tellurium atoms e.g. between the symmetry related positions x, y, z and $1-x, \frac{1}{2}-y, z$ (3.791 Å) and x, y, z and $\frac{1}{4}+y, \frac{3}{4}-x, \frac{3}{4}-z$ (3.998 Å),

TABLE 3

DEVIATIONS OF ATOMS FROM LEAST-SQUARES PLANES [a]

Atom	Plane 1	Plane 2	Plane 3	Plane 4	Plane 5
Te	−0.2276	−1.0124	−1.0770	−0.6801	−1.0341
C(1)	0.2531	−0.0605	−0.1075	0.1963	−0.0720
C(2)	−0.1422	−0.0123	−0.0433	0.1641	−0.0171
C(3)	−0.1419	0.0125	−0.0193	0.1832	0.0054
C(4)	0.2585	−0.0187	−0.0677	0.2290	−0.0348
N(1)	−0.5275	−0.0012	−0.0196	0.1014	−0.0029
N(2)	−0.4922	0.0010	−0.0153	0.1127	0.0049
C(5)	−0.8872	0.0101	0.0085	0.0481	0.0191
C(6)	−1.3239	−0.0200	−0.0052	−0.0549	−0.0023
C(7)	−1.7091	−0.0226	0.0059	−0.1257	0.0006
C(8)	−1.7606	−0.0383	−0.0099	−0.1512	−0.0170
C(9)	−1.3406	0.0005	0.0134	−0.0439	0.0136
C(10)	−0.9276	−0.0101	−0.0126	0.0226	−0.0034
Dihedral angles					
{Plane 1}–{Plane 2}			21.69°		
{Plane 2}–{Plane 3}			0.809°		
{Plane 1}–{Plane 5}			22.07°		

[a] Plane 1 Plane defined by Te, C(1), C(2), C(3) and C(4) $0.4260x+0.6988y-0.5744z+8.7094=0$ Plane 2 Plane defined by C(2), C(3), N(1), N(2), C(5) and C(10) $0.7029x+0.5321y-0.4720z+12.8464=0$ Plane 3 Plane defined by C(5), C(6), C(7), C(8), C(9) and C(10) $0.7119x+0.5253y-0.4661z+13.0214=0$ Plane 4 Plane defined by Te, C(1), C(2), C(3), C(4), N(1), N(2), C(5), C(6), C(7), C(8), C(9) and C(10) $0.6590x+0.5674y-0.4937z+12.0177=0$ Plane 5 Plane defined by C(2), C(3), N(1), N(2), C(5), C(6), C(7), C(8), C(9) and C(10) $0.7073x+0.5297y-0.4682z+12.9305=0$.

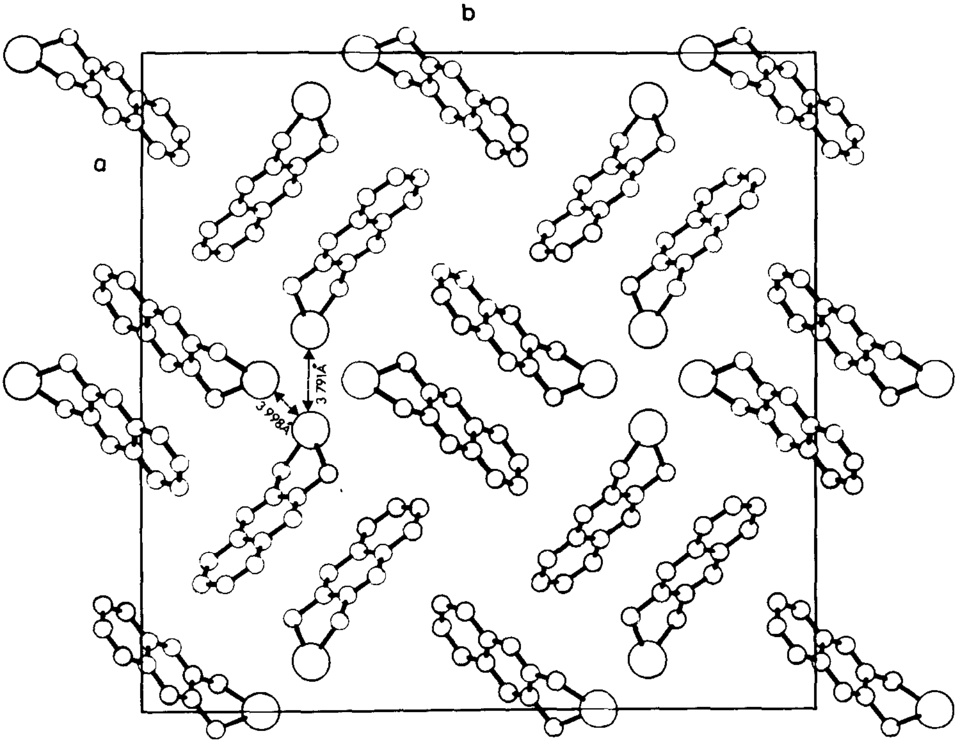

Fig. 2. Unit cell packing of $C_{10}H_8N_2Te$ viewed along the crystallographic *c* axis.

Fig. 2. These Te–Te distances are less than the sum of the Van der Waals' radii (4.40 Å) [4] and thus indicate weak bonding. Shorter intermolecular contacts involving tellurium in relation to crystal packing and properties have been reported for some other compounds e.g. tetratellurotetracene (3.701 Å) [8], polymorph B of bis(2-naphthyl ditelluride), (3.707 Å) [9] and diphenyl telluroxide (3.537 Å) [10].

The intermolecular Te–N distances 4.095 Å provide no evidence for secondary bonding between the atoms as has been found in 1,2-benzoisotellurozole where the shortest intermolecular Te–N distance is 2.46 Å [1] and the sum of the Van der Waals' radii are 3.70 Å [4]. However, the short intermolecular contacts between the tellurium atoms explains the high melting point and low solubility of the compound and may help in the segregation of donor and acceptor stacks when used in the preparation of charge transfer complexes.

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