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Tris(diethyldithiocarbamato)(4-methoxyphenyl)tellurium(IV), p-MeOC$_6$H$_4$Te(S$_2$CNEt$_2$)$_3$, and the Triclinic Modification of Tris(diethyldithiocarbamato)phenyltellurium(IV), PhTe(S$_2$CNEt$_2$)$_3$

Steinar Husebye
University of Bergen

Sergey V. Lindeman
Marquette University, sergey.lindeman@marquette.edu

Tris(diethyldithiocarbamato)(4-methoxyphenyl)tellurium(IV), p-MeOC$_6$H$_4$Te-(S$_2$CNEt$_2$)$_3$, and the Triclinic Modification of Tris(diethyldithiocarbamato)phenyltellurium(IV), PhTe(S$_2$CNEt$_2$)$_3$

STEINAR HUSEBYE

Department of Chemistry, University of Bergen, Allegaten 41, N-5007 Bergen, Norway

SERGEY V. LINDEMAN

Institute of Organoelement Compounds, 28 Vavilov Street, Moscow 117813, Russia

Abstract

The structures of the tellurium(IV) complexes [Te(C$_5$-H$_{10}$NS$_2$)$_3$(C$_7$H$_7$O)], (1), and [Te(C$_5$H$_{10}$NS$_2$)$_3$(C$_6$H$_5$)], (2) (the triclinic modification), have been investigated. In both structures the coordination of the Te atom is distorted pentagonal bipyramidal, with four S atoms from two near symmetrically bidentate dithiocarbamate ligands [Te—S 2.625 (1)–2.889 (1) Å] and a fifth S atom from the third unsymmetrically bidentate dithiocarbamate ligand [Te—S 2.585 (1)–2.602 (1) Å] in equatorial positions. The aryl group is axial [Te—C 2.148 (5)–2.160 (3) Å]; the second axial position is occupied by the second S atom of the unsymmetrically bidentate dithiocarbamate ligand [Te···S 3.235 (2)–3.241 (1) Å], the *trans* angle C—Te···S being 144.6–147.2 (1)°. In the structure of (2), the two crystallographically independent molecules have different orientations of the ethyl groups in all three ligands and slightly differing phenyl group orientations.

Comment

In the crystal structures of both (1) and (2), the Te atom has distorted pentagonal bipyramidal coordination geometry (Figs. 1 and 2); two dithiocarbamate groups behave as near symmetrically bidentate chelate ligands and are situated in the equatorial plane together with another strongly coordinated S atom from the third dithiocarbamate group. The second S atom of this group seems to be weakly coordinated and is axial, but with significant deviation from an ideal position *trans* to the aryl ligand, which occupies the second axial position.

Detailed investigation shows that the equatorial bidentate dithiocarbamate ligands are not quite symmetrically coordinated: the Te—S bonds quasi *trans* to the unique unsymmetrically coordinated dithio-

(1) R = MeO
(2) R = H
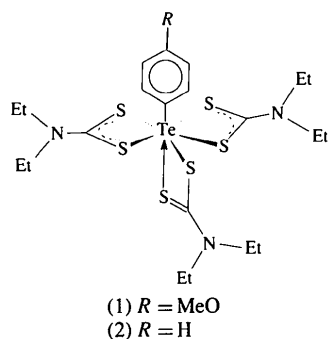
carbamate ligand [S—Te—S bond angles 146.51 (4) and 142.15 (4)° in (1) and 142.11 (3)–144.47 (3)° in the two crystallographically independent molecules of (2)] are slightly longer [2.812 (1) and 2.882 (1) Å in (1) and 2.769 (1)–2.889 (1) Å in (2)] than the quasi *cis* Te—S bonds [2.666 (1) and 2.666 (1) Å in (1) and 2.625 (1)–2.694 (1) Å in (2)]. The weakening of these bonds may be explained by the greater *trans* influence of the unique dithiocarbamate ligand, which bonds very strongly to the Te atom in the equatorial plane: the Te—S5 bonds are 2.590 (1) Å in (1) and 2.585 and 2.602 (1) Å in (2).

The same distribution of the equatorial Te—S bond lengths was found earlier in tris(dimethyldithio-carbamato)(4-methoxyphenyl)tellurium(IV), (3) (as the 1:1 chloroform solvate; Husebye, Maartmann-Moe & Steffensen, 1990), and in the monoclinic crystal modi-fication of (2) (Esperås & Husebye, 1972): the unique Te—S bond was the shortest [2.591 (1) and 2.606 (3) Å, respectively], the *cis* Te—S bonds were longer [2.646–2.706 (2) Å] and the *trans* Te—S bonds were weaker still [2.792–2.868 (2) Å].

Even greater differences between the equatorial Te—S bonds were found in the analogous compound, tris-
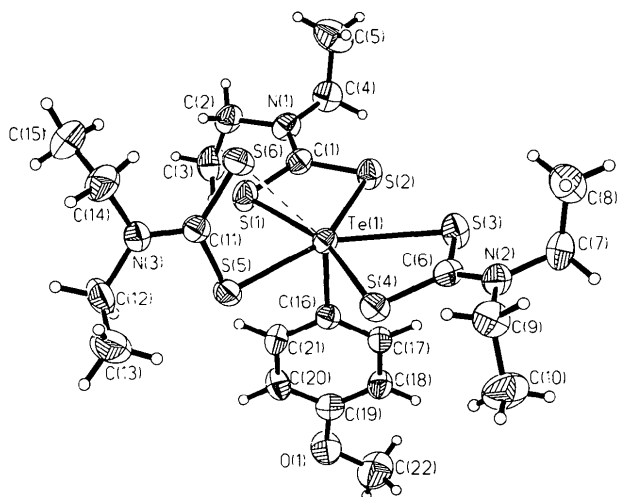

Fig. 1. Perspective view of (1) showing the labelling of the non-H atoms. Displacement ellipsoids are shown at the 50% probability level for non-H atoms; H atoms are represented by small spheres of arbitrary radii. The secondary Te···S coordination is shown by a dashed line.
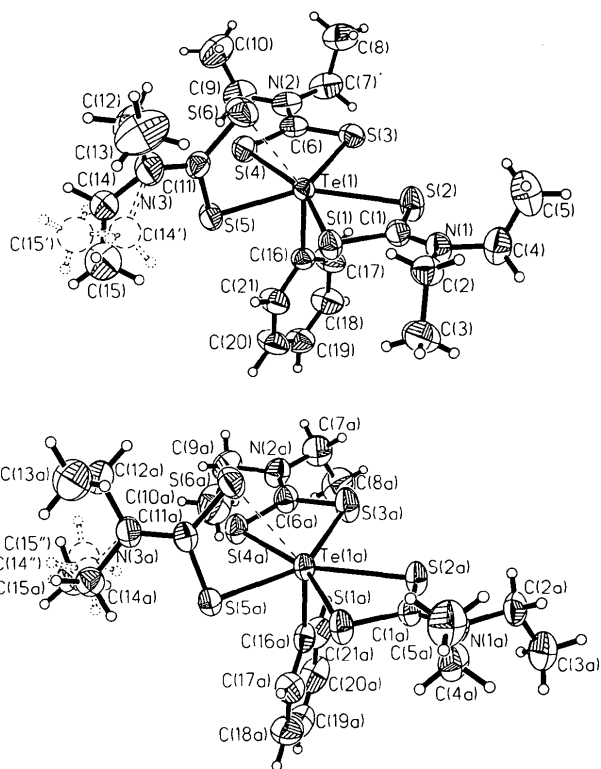

Fig. 2. Perspective views of the two crystallographically independent molecules of (2) in comparable orientations, showing conforma-tional differences and the labelling of the non-H atoms. Displace-ment ellipsoids are shown at the 50% probability level for non-H atoms; H atoms are represented by small spheres of arbitrary radii. The less populated positions of the disordered ethyl groups and the secondary Te···S coordination are shown by dashed lines.

(O,O'-diphenyldithiophosphato)phenyltellurium(IV), (4) (Wieber & Lang, 1994). In this compound, the unique Te—S bond is further shortened [to 2.481 (1) Å] and the *trans* Te—S bonds are lengthened [to 3.106 and 3.292 (1) Å], while the *cis* Te—S bonds are virtu-ally unchanged [2.613 and 2.659 (1) Å]. Nevertheless, the unique dithiophosphate ligand exhibits no notice-able *trans* influence on the equatorial dithiocarbamate ligands in bis(diethyldithiocarbamato)(O,O'-diethyldi-thiophosphato)phenyltellurium(IV), (5) (Dakternieks, Di Giacomo, Gable & Hoskins, 1988), in which the *trans* Te—S bonds [2.696 (4) and 2.700 (3) Å] are only a little longer than the *cis* bonds [2.674 (4) and 2.690 (3) Å] and the unique Te—S bond from the dithiophosphate ligand of 2.708 (4) Å is much longer than in (4). Evidently, the dithiocarbamate ligands have a greater *trans* influence than the dithiophosphate ligand. On the other hand, no observable difference is found between dimethyl- and diethyl-substituted dithiocarbamate ligands in this re-spect.

Likewise, hardly any difference in molecular geom-etry is found between phenyl- and *p*-methoxyphenyl-substituted complexes. The Te—C bond length is only slightly shorter in the *p*-methoxy derivatives (1) and

(3) [2.148 (5) and 2.153 (5) Å] than in the phenyl analogue (2) [2.159 (3) and 2.160 (3) Å in the present triclinic modification; in the monoclinic structure this bond length is 2.124 (11) Å, but its precision is not high] in accordance with the σ-acceptor effect of the methoxy group. This small difference does not have a noticeable effect on the *trans* axial secondary Te$\cdots$S interaction: the Te$\cdots$S distances are 3.235 (2) and 3.277 (2) Å in (1) and (3), 3.241 (1) and 3.235 (1) Å in the triclinic form of (2), and 3.228 (3) Å in the monoclinic form of (2).

The bonding character of this secondary interaction is open to question: the *trans* angle C—Te$\cdots$S is only 144.6 (1) in (1), 143.7 (1) in (3) and 144.6 (2)–147.2 (1)° in (2) (both modifications). In the case of the dithiophosphate complexes (4) and (5), the Te$\cdots$S distances are 3.374 (1) and 3.436 (4) Å, even though the C—Te$\cdots$S bond angles are slightly 'improved' at 156.6 (1) and 148.0 (4)°, respectively. On the one hand, these contacts are noticeably shorter than the sum of the van der Waals radii of Te and S (3.86 Å; Bondi, 1964). The great deviations from linearity in the C—Te$\cdots$S angle may be caused by the small value of the bite angle of these chelate ligands (for a symmetrically axial-equatorial coordinated dithiocarbamate ligand the *trans* angle C—Te—S cannot be much greater than 155° if one of the S atoms is required to lie in the equatorial plane). On the other hand, there is evidence here of some repulsion between the Te and S atoms: the *cis* C—Te—S bond angle for the unsymmetrically bidentate ligand is substantially less than 90° in all cases [85.0 (1) in (1), 84.2 (2)–87.2 (1) in (2) (both modifications) and 84.1 (1)° in (3)].

In similar complexes where the aryl group is replaced by a halogen, the equatorial S atom in the unique ligand is lifted out of the equatorial plane as the axial S atom occupies a more perfect axial position. Since the *trans* influence of the halogen ligand is much smaller than that of the dithiocarbamate ligand, the Te—S$_{ax}$ bond is stronger than all the Te—S$_{eq}$ bonds. This situation is realized in complexes of the general formula Te(R^1R^2NCS$_2$)$_3$Cl with $R^1 = R^2 =$ Et [as the 1:1 dioxane solvate, (6)] (von Deuten, Schnabel & Klar, 1980), $R^1 = R^2 =$ CH$_2$CH$_2$OH [as the dihydrate, (7)] (Rao, Seshasayee, Aravamudan & Radha, 1983) and $R^1 =$ Me, $R^2 =$ CH$_2$CH$_2$OH [as the dihydrate, (8)] (Husebye & Thowsen, 1981), where there is strengthened axial coordination (Te—S 2.465–2.512 Å, *trans* Cl—Te—S angle 174.9–179.1°) and significantly weakened equatorial coordination (Te—S 2.801–2.874 Å, *cis* angle 108.3–114.1°). The structure of the Br analogue of (8), compound (9), is practically the same (Husebye, 1979).

A similar structure is also found for ML_3X metal complexes where L is a dithiocarbamate ligand and X is a halogen. This indicates that the strong *trans* influence of the aryl group is responsible for the lengthening of the Te—S$_{ax}$ bond in complexes (1)–(5). An additional

'push' may result from stereochemical activity of the lone pair of electrons on Te which are presumably located in the direction of the S2–S3–S6 face of the polyhedron.

It is of interest that in compounds (6)–(9) an 'inverse' Te—S bond length distribution in the equatorial plane is found: the Te—S bonds '*trans*' to the weakly coordinated equatorial S atom of the unsymmetrically bidentate ligand are shortened to 2.580–2.640 Å, while the '*cis*' Te—S bonds are lengthened to 2.690–2.773 Å.

Intermolecular interactions (crystal packing effects) do not induce substantial changes in the coordination sphere of the Te atom in the complexes investigated (excluding some variation in length for the weaker Te—S bonds; see above). However, the outer parts of these molecules are not as rigid and the aryl substituent shows a substantial rotational lability. For example, the S5—Te—C—CH torsion angles in (2) are −25.9 (3) and −42.1 (2)° in the triclinic form and 44.7° in the monoclinic form. The orientation of the terminal ethyl groups undergoes more dramatic changes, being quite different in both forms of (1), in the crystallographically independent molecules in the triclinic structure of (2) and in the monoclinic structure of (2) (see Figs. 1 and 2 and Tables 3 and 4).

Overall, the dithiocarbamate ligands have the usual π-conjugated structure: the C$_{sp^2}$—N bond lengths lie in the range 1.324–1.337 (4) Å, the twist along these bonds does not exceed 9.8 (3)° [except for 21.3 (3)° in the minor disordered component of the first crystallographically independent molecule of (2)] and the configuration of the N atoms is planar to within 0.017 (3) Å [but with substantial pyramidalization of 0.127 (4) and −0.232 (5) Å in the two disordered components of the first and of 0.137 and −0.128 (4) Å in the second crystallographically independent molecule of (2)].

The *p*-methoxyphenyl ligand in (1) has the usual flat π-conjugated structure; the torsion angle C—C—O—C is only 0.8 (9)°.

Experimental

Compounds (1) and (2) were prepared according to literature methods (Foss, 1953).

Compound (1)

Crystal data

[Te(C$_5$H$_{10}$NS$_2$)$_3$(C$_7$H$_7$O)]	Mo $K\alpha$ radiation
$M_r = 679.51$	$\lambda = 0.71069$ Å
Monoclinic	Cell parameters from 24
$P2_1/n$	reflections
$a = 10.859$ (2) Å	$\theta = 9$–10°
$b = 18.443$ (3) Å	$\mu = 1.401$ mm^{-1}
$c = 15.299$ (5) Å	$T = 293$ (2) K
$\beta = 92.66$ (2)°	Plate
$V = 3060.7$ (13) Å^3	0.45 × 0.35 × 0.15 mm
$Z = 4$	Yellow
$D_x = 1.475$ Mg m^{-3}	

Data collection

Enraf–Nonius CAD-4 diffractometer	$R_{int} = 0.0224$
	$\theta_{max} = 25.97°$
$\omega/2\theta$ scans	$h = 0 \rightarrow 13$
Absorption correction:	$k = 0 \rightarrow 22$
none	$l = -18 \rightarrow 18$
6309 measured reflections	3 standard reflections
5997 independent reflections	frequency: 120 min
3653 observed reflections	intensity decay: 4.5%
[$I > 2\sigma(I)$]	

Refinement

Refinement on F^2

$R[F^2 > 2\sigma(F^2)] = 0.0328$

$wR(F^2) = 0.1631$

$S = 1.093$

5931 reflections

305 parameters

H atoms treated using a riding model, CH$_3$ orientation refined, fixed U_{iso}

$w = 1/[\sigma^2(F_o^2) + (0.0520P)^2 + 3.7927P]$

where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{max} = 0.010$

$\Delta\rho_{max} = 1.50$ e Å^{-3}

$\Delta\rho_{min} = -1.05$ e Å^{-3}

Extinction correction: none

Atomic scattering factors from *International Tables for Crystallography* (1992, Vol. C, Tables 4.2.6.8 and 6.1.1.4)

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters (Å^2) for (1)*

$$U_{eq} = (1/3)\Sigma_i\Sigma_j U_{ij}a_i^* a_j^* \mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	U_{eq}
Te1	0.19369 (3)	0.78926 (2)	0.42002 (2)	0.03191 (10)
S1	0.41436 (12)	0.82545 (8)	0.36421 (10)	0.0465 (3)
S2	0.30141 (12)	0.68551 (8)	0.31264 (9)	0.0430 (3)
S3	0.03769 (13)	0.66286 (8)	0.40998 (9)	0.0463 (3)
S4	−0.01896 (11)	0.79973 (7)	0.49949 (9)	0.0396 (3)
S5	0.20617 (13)	0.91931 (7)	0.48366 (9)	0.0425 (3)
S6	0.34206 (13)	0.81713 (8)	0.60521 (10)	0.0459 (3)
O1	−0.0245 (4)	0.9442 (2)	0.0805 (3)	0.0607 (11)
N1	0.5311 (4)	0.7234 (2)	0.2776 (3)	0.0417 (10)
N2	−0.1407 (4)	0.6767 (2)	0.5231 (3)	0.0400 (10)
N3	0.3441 (4)	0.9602 (2)	0.6203 (3)	0.0411 (10)
C1	0.4268 (4)	0.7424 (3)	0.3134 (3)	0.0371 (11)
C2	0.6365 (5)	0.7738 (3)	0.2748 (4)	0.0470 (13)
C3	0.6243 (6)	0.8247 (4)	0.1981 (4)	0.060 (2)
C4	0.5497 (5)	0.6525 (3)	0.2389 (4)	0.0491 (14)
C5	0.6158 (7)	0.6013 (4)	0.3030 (5)	0.077 (2)
C6	−0.0511 (4)	0.7092 (3)	0.4813 (3)	0.0370 (10)
C7	−0.1709 (5)	0.6000 (3)	0.5112 (4)	0.0519 (14)
C8	−0.1034 (7)	0.5526 (4)	0.5774 (4)	0.066 (2)
C9	−0.2173 (5)	0.7170 (3)	0.5847 (4)	0.0516 (14)
C10	−0.3253 (6)	0.7538 (5)	0.5381 (5)	0.078 (2)
C11	0.3041 (4)	0.9019 (3)	0.5755 (3)	0.0340 (10)
C12	0.3082 (6)	1.0345 (3)	0.5956 (4)	0.055 (2)
C13	0.1900 (7)	1.0581 (4)	0.6349 (5)	0.072 (2)
C14	0.4264 (6)	0.9528 (4)	0.6999 (4)	0.061 (2)
C15	0.5602 (6)	0.9530 (5)	0.6773 (6)	0.088 (3)
C16	0.1133 (4)	0.8404 (3)	0.3049 (3)	0.0336 (10)
C17	0.0200 (5)	0.8082 (3)	0.2551 (3)	0.0398 (12)
C18	−0.0289 (5)	0.8415 (3)	0.1805 (3)	0.0426 (12)
C19	0.0142 (5)	0.9073 (3)	0.1548 (3)	0.0416 (12)
C20	0.1080 (5)	0.9418 (3)	0.2040 (4)	0.0470 (13)
C21	0.1570 (5)	0.9079 (3)	0.2784 (3)	0.0428 (12)
C22	−0.1176 (7)	0.9122 (4)	0.0264 (4)	0.078 (2)

Table 2. *Selected geometric parameters (Å, °) for (1)*

Te1—C16	2.148 (5)	S3—C6	1.717 (5)
Te1—S5	2.5897 (14)	S4—C6	1.726 (6)
Te1—S1	2.6658 (14)	S5—C11	1.752 (5)
Te1—S4	2.6662 (13)	S6—C11	1.674 (5)
Te1—S2	2.8119 (14)	O1—C19	1.373 (6)
Te1—S3	2.8817 (14)	O1—C22	1.406 (8)
Te1—S6	3.235 (2)	N1—C1	1.327 (6)
S1—C1	1.726 (5)	N2—C6	1.330 (6)
S2—C1	1.719 (5)	N3—C11	1.336 (6)
C16—Te1—S5	85.04 (13)	C1—N1—C4	122.9 (5)
C16—Te1—S1	87.96 (13)	C1—N1—C2	121.5 (4)
S5—Te1—S1	81.75 (5)	C4—N1—C2	115.6 (4)
C16—Te1—S4	90.84 (13)	C6—N2—C7	122.7 (5)
S5—Te1—S4	78.04 (4)	C6—N2—C9	121.6 (5)
C16—Te1—S2	89.10 (13)	C7—N2—C9	115.7 (4)
S5—Te1—S2	146.51 (4)	C11—N3—C12	122.9 (4)
S1—Te1—S2	65.09 (4)	C11—N3—C14	121.1 (5)
C16—Te1—S3	95.53 (13)	C12—N3—C14	116.0 (4)
S5—Te1—S3	142.15 (4)	N1—C1—S2	121.8 (4)
S4—Te1—S3	64.12 (4)	N1—C1—S1	120.4 (4)
C16—Te1—S6	144.63 (13)	S2—C1—S1	117.8 (3)
S5—Te1—S6	60.55 (4)	N2—C6—S3	121.7 (4)
S1—Te1—S6	79.76 (5)	N2—C6—S4	120.3 (4)
S4—Te1—S6	89.76 (4)	S3—C6—S4	117.9 (3)
S2—Te1—S6	114.58 (4)	N3—C11—S6	122.9 (4)
S3—Te1—S6	116.29 (4)	N3—C11—S5	115.7 (4)
C1—S1—Te1	90.7 (2)	S6—C11—S5	121.4 (3)
C1—S2—Te1	86.1 (2)	C17—C16—C21	118.4 (5)
C6—S3—Te1	84.8 (2)	C17—C16—Te1	121.7 (4)
C6—S4—Te1	91.7 (2)	C21—C16—Te1	119.9 (4)
C11—S5—Te1	98.7 (2)	C18—C19—O1	125.6 (5)
C11—S6—Te1	78.7 (2)	C18—C19—C20	120.1 (5)
C19—O1—C22	117.7 (5)	O1—C19—C20	114.2 (5)
S2—Te1—S1—C1	−3.4 (2)	C14—N3—C11—S6	0.4 (7)
S4—Te1—S3—C6	−7.1 (2)	C12—N3—C11—S5	0.6 (7)
S6—Te1—S5—C11	4.5 (2)	C11—N3—C12—C13	87.4 (6)
C4—N1—C1—S2	−2.8 (7)	C11—N3—C14—C15	89.3 (7)
C2—N1—C1—S1	−4.1 (7)	S5—Te1—C16—C17	−143.2 (4)
C1—N1—C2—C3	−83.8 (6)	S1—Te1—C16—C17	134.9 (4)
C1—N1—C4—C5	−96.3 (6)	S4—Te1—C16—C17	−65.3 (4)
C7—N2—C6—S3	−0.4 (7)	S2—Te1—C16—C17	69.8 (4)
C9—N2—C6—S4	1.3 (7)	S3—Te1—C16—C17	−1.3 (4)
C6—N2—C7—C8	92.6 (6)	C22—O1—C19—C18	0.8 (9)
C6—N2—C9—C10	86.1 (7)		

Compound (2)

Crystal data

[Te(C$_5$H$_{10}$NS$_2$)$_3$(C$_6$H$_5$)]

$M_r = 649.48$

Triclinic

$P\bar{1}$

$a = 11.1827$ (7) Å

$b = 16.0827$ (15) Å

$c = 17.3830$ (13) Å

$\alpha = 108.300$ (7)°

$\beta = 100.623$ (6)°

$\gamma = 96.120$ (6)°

$V = 2871.6$ (4) Å^3

$Z = 4$

$D_x = 1.502$ Mg m^{-3}

Mo $K\alpha$ radiation

$\lambda = 0.71069$ Å

Cell parameters from 24 reflections

$\theta = 10-11°$

$\mu = 1.487$ mm^{-1}

$T = 293$ (2) K

Plate

$0.35 \times 0.3 \times 0.12$ mm

Yellow

Data collection

Enraf–Nonius CAD-4 diffractometer

$\omega/2\theta$ scans

Absorption correction: none

16686 measured reflections

16686 independent reflections

10630 observed reflections

[$I > 2\sigma(I)$]

$\theta_{max} = 29.96°$

$h = 0 \rightarrow 15$

$k = -22 \rightarrow 22$

$l = -24 \rightarrow 23$

3 standard reflections frequency: 120 min intensity decay: 3.5%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.0327$
$wR(F^2) = 0.1085$
$S = 1.066$
16662 reflections
569 parameters
H atoms treated using a riding model, CH3 orientation refined, fixed U_{iso}

$w = 1/[\sigma^2(F_o^2) + (0.0496P)^2]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.056$
$\Delta\rho_{max} = 0.86$ e Å^{-3}
$\Delta\rho_{min} = -0.95$ e Å^{-3}
Extinction correction: none
Atomic scattering factors from *International Tables for Crystallography* (1992, Vol. C, Tables 4.2.6.8 and 6.1.1.4)

Table 3. *Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters* (Å²) *for* (2)

U_{iso} for C14, C15, C14', C15', C14a, C15a, C14" and C15", $U_{eq} = (1/3)\Sigma_i\Sigma_j U_{ij}a_i^* a_j^* \mathbf{a}_i.\mathbf{a}_j$ for all others.

	x	y	z	U_{iso}/U_{eq}
Te1	0.88030(2)	0.71428(1)	0.02341(1)	0.03458(5)
S1	1.04183(7)	0.65704(5)	0.11552(5)	0.0461(2)
S2	1.10619(8)	0.83190(5)	0.09974(6)	0.0568(2)
S3	0.85671(7)	0.87343(5)	-0.01752(5)	0.0490(2)
S4	0.67149(7)	0.70864(5)	-0.08345(5)	0.0498(2)
S5	0.76471(7)	0.55537(5)	-0.00666(4)	0.0461(2)
S6	0.71649(10)	0.67733(6)	0.14874(6)	0.0631(2)
N1	1.2435(2)	0.7733(2)	0.2074(2)	0.0504(6)
N2	0.6423(3)	0.8512(2)	-0.1256(2)	0.0558(7)
N3	0.6408(3)	0.5037(2)	0.0891(2)	0.0644(8)
C1	1.1415(3)	0.7568(2)	0.1472(2)	0.0437(6)
C2	1.2677(3)	0.7125(2)	0.2553(2)	0.0529(7)
C3	1.3386(4)	0.6441(3)	0.2155(3)	0.0719(10)
C4	1.3402(3)	0.8518(3)	0.2275(2)	0.0667(10)
C5	1.3251(5)	0.9274(3)	0.2981(3)	0.0907(14)
C6	0.7157(3)	0.8159(2)	-0.0796(2)	0.0459(6)
C7	0.6785(4)	0.9428(3)	-0.1245(2)	0.0670(10)
C8	0.6416(4)	1.0125(3)	-0.0570(3)	0.0810(12)
C9	0.5212(4)	0.8027(3)	-0.1767(2)	0.0730(11)
C10	0.4222(4)	0.8111(4)	-0.1302(3)	0.0954(15)
C11	0.7022(2)	0.5748(2)	0.0817(2)	0.0426(6)
C12	0.5783(3)	0.5110(3)	0.1580(2)	0.0661(10)
C13	0.6513(5)	0.4991(5)	0.2311(3)	0.109(2)
C14†	0.5991(4)†	0.4179(3)	0.0174(3)	0.0510(10)
C15†	0.6899(6)†	0.3562(5)	0.0222(5)	0.079(2)
C14'‡	0.6915(10)	0.4088(8)	0.0564(7)	0.058(2)
C15'‡	0.5884(12)	0.3543(9)	-0.0149(8)	0.077(3)
C16	0.9563(2)	0.6585(2)	-0.0833(2)	0.0383(5)
C17	0.9910(4)	0.7106(2)	-0.1276(2)	0.0605(9)
C18	1.0351(4)	0.6735(2)	-0.1981(2)	0.0637(9)
C19	1.0438(3)	0.5864(2)	-0.2243(2)	0.0567(8)
C20	1.0112(4)	0.5347(2)	-0.1796(2)	0.0651(10)
C21	0.9686(3)	0.5703(2)	-0.1086(2)	0.0563(8)
Te1a	1.33397(2)	0.77143(1)	-0.43179(1)	0.03774(5)
S1a	1.31901(8)	0.94099(5)	-0.34888(5)	0.0493(2)
S2a	1.17495(8)	0.79092(5)	-0.32515(5)	0.0492(2)
S3a	1.25442(10)	0.60270(5)	-0.42720(6)	0.0610(2)
S4a	1.39324(8)	0.63762(5)	-0.54550(5)	0.0493(2)
S5a	1.46368(7)	0.85495(5)	-0.50361(5)	0.0461(2)
S6a	1.63164(8)	0.81839(6)	-0.36699(5)	0.0536(2)
N1a	1.1899(2)	0.9596(2)	-0.2319(2)	0.0478(6)
N2a	1.3228(3)	0.4758(2)	-0.5421(2)	0.0534(6)
N3a	1.7015(2)	0.8523(2)	-0.4937(2)	0.0491(6)
C1a	1.2239(3)	0.9034(2)	-0.2947(2)	0.0415(6)
C2a	1.1186(3)	0.9285(2)	-0.1798(2)	0.0563(8)
C3a	0.9818(4)	0.9165(3)	-0.2103(3)	0.0837(13)
C4a	1.2252(3)	1.0569(2)	-0.2079(2)	0.0605(9)
C5a	1.3454(4)	1.0932(3)	-0.1467(3)	0.0806(12)
C6a	1.3229(3)	0.5623(2)	-0.5087(2)	0.0467(6)
C7a	1.2580(4)	0.4101(2)	-0.5138(3)	0.0656(9)
C8a	1.1250(4)	0.3832(3)	-0.5545(3)	0.0936(15)
C9a	1.3856(4)	0.4407(2)	-0.6104(2)	0.0664(9)
C10a	1.3034(5)	0.4173(4)	-0.6929(3)	0.105(2)
C11a	1.6106(3)	0.8421(2)	-0.4556(2)	0.0403(6)
C12a	1.8286(3)	0.8419(2)	-0.4626(2)	0.0592(8)
C13a	1.9155(4)	0.9280(3)	-0.4247(3)	0.0823(13)
C14a§	1.6827(5)	0.8828(4)	-0.5671(4)	0.0492(13)
C15a§	1.6470(7)	0.7987(5)	-0.6458(4)	0.069(2)
C14"¶	1.6776(8)	0.8479(6)	-0.5821(5)	0.046(2)
C15"¶	1.6393(9)	0.7534(7)	-0.6451(6)	0.062(2)
C16a	1.1762(3)	0.7634(2)	-0.5281(2)	0.0433(6)
C17a	1.1593(3)	0.8353(2)	-0.5535(2)	0.0569(8)
C18a	1.0616(4)	0.8265(3)	-0.6196(2)	0.0723(11)
C19a	0.9808(3)	0.7475(3)	-0.6582(2)	0.0710(11)
C20a	0.9965(3)	0.6777(3)	-0.6332(2)	0.0724(11)
C21a	1.0936(3)	0.6839(2)	-0.5686(2)	0.0576(8)

† Occupancy = 0.67.
‡ Occupancy = 0.33.
§ Occupancy = 0.60.
¶ Occupancy = 0.40.

Table 4. *Selected geometric parameters* (Å, °) *for* (2)

Te1—C16	2.160(3)	Te1a—C16a	2.159(3)
Te1—S5	2.5854(11)	Te1a—S5a	2.6023(10)
Te1—S1	2.6247(11)	Te1a—S4a	2.6633(12)
Te1—S4	2.6761(12)	Te1a—S1a	2.6944(11)
Te1—S2	2.8088(15)	Te1a—S2a	2.7688(10)
Te1—S3	2.8889(10)	Te1a—S3a	2.7944(11)
Te1—S6	3.2415(12)	Te1a—S6a	3.2354(13)
S1—C1	1.720(3)	S1a—C1a	1.724(3)
S2—C1	1.704(3)	S2a—C1a	1.712(3)
S3—C6	1.715(3)	S3a—C6a	1.715(3)
S4—C6	1.721(3)	S4a—C6a	1.721(3)
S5—C11	1.756(3)	S5a—C11a	1.765(3)
S6—C11	1.665(3)	S6a—C11a	1.681(3)
N1—C1	1.337(4)	N1a—C1a	1.327(3)
N2—C6	1.334(4)	N2a—C6a	1.328(3)
N3—C11	1.324(4)	N3a—C11a	1.335(4)
C16—Te1—S5	87.18(8)	C16a—Te1a—S5a	86.66(8)
C16—Te1—S1	90.71(8)	C16a—Te1a—S4a	86.28(8)
S5—Te1—S1	79.51(4)	S5a—Te1a—S4a	77.95(3)
C16—Te1—S4	87.59(8)	C16a—Te1a—S1a	90.50(9)
S5—Te1—S4	78.33(4)	S5a—Te1a—S1a	79.64(3)
C16—Te1—S2	88.19(8)	C16a—Te1a—S2a	86.91(7)
S5—Te1—S2	144.47(3)	S5a—Te1a—S2a	144.01(3)
S1—Te1—S2	65.34(3)	S1a—Te1a—S2a	65.05(3)
C16—Te1—S3	91.34(8)	C16a—Te1a—S3a	93.87(9)
S5—Te1—S3	142.11(3)	S5a—Te1a—S3a	143.05(3)
S4—Te1—S3	63.78(4)	S4a—Te1a—S3a	65.25(3)
C16—Te1—S6	147.21(7)	C16a—Te1a—S6a	146.64(7)
S5—Te1—S6	60.23(3)	S5a—Te1a—S6a	60.63(3)
S1—Te1—S6	80.50(3)	S4a—Te1a—S6a	80.85(4)
S4—Te1—S6	89.04(3)	S1a—Te1a—S6a	89.89(4)
S2—Te1—S6	115.67(3)	S2a—Te1a—S6a	123.02(3)
S3—Te1—S6	116.12(3)	S3a—Te1a—S6a	108.11(4)
C1—S1—Te1	90.75(10)	C1a—S1a—Te1a	89.53(10)
C1—S2—Te1	85.03(10)	C1a—S2a—Te1a	87.32(10)
C6—S3—Te1	85.63(11)	C6a—S3a—Te1a	86.33(11)
C6—S4—Te1	92.56(11)	C6a—S4a—Te1a	90.50(10)
C11—S5—Te1	99.34(10)	C11a—S5a—Te1a	97.26(9)
C11—S6—Te1	79.13(10)	C11a—S6a—Te1a	78.08(10)
C1—N1—C2	121.3(3)	C1a—N1a—C2a	121.9(3)
C1—N1—C4	122.1(3)	C1a—N1a—C4a	122.2(3)
C4—N1—C2	116.6(3)	C2a—N1a—C4a	115.9(2)
C6—N2—C9	121.6(3)	C6a—N2a—C7a	121.4(3)
C6—N2—C7	121.2(3)	C6a—N2a—C9a	121.7(3)
C9—N2—C7	117.1(3)	C7a—N2a—C9a	121.7(3)
C11—N3—C12	121.4(3)	C11a—N3a—C12a	122.7(3)
C11—N3—C14	121.7(3)	C11a—N3a—C14"	122.6(4)
C12—N3—C14	114.6(3)	C12a—N3a—C14"	112.3(4)
C11—N3—C14'	117.6(4)	C11a—N3a—C14a	121.7(3)
C12—N3—C14'	113.7(5)	C12a—N3a—C14a	115.4(3)
N1—C1—S2	122.0(2)	N1a—C1a—S2a	121.3(2)
N1—C1—S1	119.8(2)	N1a—C1a—S1a	121.1(2)
S2—C1—S1	118.2(2)	S2a—C1a—S1a	117.5(2)
N2—C6—S3	122.0(3)	N2a—C6a—S3a	121.3(2)
N2—C6—S4	120.0(3)	N2a—C6a—S4a	120.8(2)
S3—C6—S4	118.0(2)	S3a—C6a—S4a	117.9(2)
N3—C11—S6	123.3(2)	N3a—C11a—S6a	123.1(2)

N3—C11—S5	115.7 (2)	N3a—C11a—S5a	116.0 (2)
S6—C11—S5	121.0 (2)	S6a—C11a—S5a	120.9 (2)
C17—C16—C21	119.3 (3)	C17a—C16a—C21a	119.0 (3)
C17—C16—Te1	120.2 (2)	C17a—C16a—Te1a	120.8 (2)
C21—C16—Te1	120.6 (2)	C21a—C16a—Te1a	120.1 (2)

S2—Te1—S1—C1	4.88 (10)
S4—Te1—S3—C6	0.16 (9)
S6—Te1—S5—C11	-3.02 (10)
C4—N1—C1—S2	-9.1 (5)
C2—N1—C1—S1	-7.0 (4)
C1—N1—C2—C3	90.7 (4)
C1—N1—C4—C5	95.9 (4)
C7—N2—C6—S3	-0.8 (4)
C9—N2—C6—S4	3.1 (4)
C6—N2—C7—C8	-87.6 (4)
C6—N2—C9—C10	84.6 (5)
C12—N3—C11—S6	0.9 (5)
C14—N3—C11—S5	-15.4 (5)
C14'—N3—C11—S5	34.9 (6)
C11—N3—C12—C13	-93.3 (5)
C11—N3—C14—C15	97.0 (5)
C11—N3—C14'—C15'	-114.2 (8)
S5—Te1—C16—C17	152.9 (3)
S1—Te1—C16—C17	-127.7 (3)
S4—Te1—C16—C17	74.5 (3)
S2—Te1—C16—C17	-62.4 (3)
S3—Te1—C16—C17	10.8 (3)
S2a—Te1a—S1a—C1a	4.44 (10)
S4a—Te1a—S3a—C6a	0.41 (11)
S6a—Te1a—S5a—C11a	9.95 (9)
C2a—N1a—C1a—S2a	6.1 (4)
C4a—N1a—C1a—S1a	3.5 (4)
C1a—N1a—C2a—C3a	-91.3 (4)
C1a—N1a—C4a—C5a	-88.6 (4)
C7a—N2a—C6a—S3a	3.4 (5)
C9a—N2a—C6a—S4a	1.7 (4)
C6a—N2a—C7a—C8a	84.1 (4)
C6a—N2a—C9a—C10a	-91.3 (5)
C12a—N3a—C11a—S6a	1.4 (4)
C14"—N3a—C11a—S5a	-17.6 (5)
C14a—N3a—C11a—S5a	6.6 (4)
C11a—N3a—C12a—C13a	-107.0 (4)
C11a—N3a—C14a—C15a	-93.8 (5)
C11a—N3a—C14"—C15"	-77.4 (8)
S5a—Te1a—C16a—C17a	-42.1 (2)
S4a—Te1a—C16a—C17a	-120.2 (2)
S1a—Te1a—C16a—C17a	37.5 (2)
S2a—Te1a—C16a—C17a	102.5 (2)
S3a—Te1a—C16a—C17a	174.9 (2)

The C14–C15 ethyl group in (2) is disordered in both independent molecules. Two positions were refined isotropically for each molecule with occupancy factor ratios of 0.67/0.33 and 0.6/0.4, respectively. Refinement was carried out on F^2 for all reflections except for 66 [structure (1)] and 24 [structure (2)] with very negative F^2 or flagged for potential systematic errors (*e.g.* extinction).

For both compounds, program(s) used to solve structures: *SHELXS*86 (Sheldrick, 1985); program(s) used to refine structures: *SHELXL*93 (Sheldrick, 1993).

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates, bond distances and angles involving non-H atoms and torsion angles have been deposited with the IUCr (Reference: MU1172). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Benz[4,5]isoquino[1,2-*b*]quinazoline-7,9-dione and a Rearrangement Product of its Hydrolysis, 2-(1,8-Naphthalene-dicarboximido)benzamide

Sergey V. Lindeman, Igor I. Ponomarev and Alexandr L. Rusanov

Institute of Organoelement Compounds, 28 Vavilov Street, Moscow 117813, Russia

Abstract

Benz[4,5]isoquino[1,2-*b*]quinazoline-7,9-dione, (1), $C_{19}H_{10}N_2O_2$, was isolated as a product of the reaction between naphthalic anhydride and anthranylamide after crystallization from dimethylformamide. Recrystallization from concentrated (95%) formic acid resulted in 2-(1,8-naphthalenedicarboximido)benzamide, (2), $C_{19}H_{12}N_2O_3$, as a rearrangement product of hydrolysis [alternative systematic name: 2-(1,3-dioxo-2,3-dihydro-1*H*-benz[*de*]isoquinol-2-yl)benzamide]. The two crystallographically independent molecules of (1) [(1*a*) and (1*b*)] are substantially non-planar as a result of strong intramolecular steric repulsion between their *cis*-arranged carbonyl groups [the O···O distances are 2.584 (3) and 2.664 (3) Å, and the dihedral angles between the naphthalene and benzene nuclei are 8.75 (7) and 14.46 (7)°, respectively]. Molecule (2) is also sterically hindered with an approximately orthogonal orientation of the naphthalenedicarboximide and *o*-phenylene groups [dihedral angle 87.05 (4)°] and absence of π-conjugation between the *o*-phenylene and amide groups [dihedral angle 40.02 (6)°].