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Synthesis and structural aspects of 1-naphthyltellurium(IV) trichloride (**1**), bis(mesityl)tellurium(IV) dichloride (**2**) and bis(chlorobis(2-thiophenyl)tellurium)oxide (**3**)



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ABSTRACT

Chlorination of bis(1-naphthyl)ditelluride (NpITeTeNpl; Npl = $1-C_{10}H_7$) with 3 equiv. of sulfuryl chloride (SO₂Cl₂) resulted in bright yellow crystals of 1-naphthyltellurium(IV) trichloride (1-NpITeCl₃; **1**). Bis(mesityl)tellurium(IV) dichloride, Mes₂TeCl₂, **2** (Mes = 2,4,6-Me₃C₆H₂) has been synthesized by the oxidative addition of sulfuryl chloride to bis(mesityl)telluride(II), prepared from detelluration of bis(mesityl)ditelluride with a freshly prepared electrolytic copper. Bis(chlorobis(2-thiophenyl)tellurium)oxide, (Tpn₂TeCl)₂O, **3** (Tpn = 2-C₄H₃S) have been obtained serendipitously as a product of reaction between bis(thiophenyl)tellurium(IV) dichloride (Tpn₂TeCl₂) and AgCN. All the three compounds **1–3** have been characterized crystallographically. In crystal lattice of **1**, an asymmetric unit consists of two independent molecules and both the molecules form a separate polymeric zig-zag chains *via* μ_2 -chloro bridging. These two polymeric chains are interlinked *via* C–H···Cl H-bonding interactions to form a one dimensional supramolecular array. In case of **2** a dimeric unit has been formed *via* intermolecular Te···Cl1 secondary bonding interactions, where both the tellurium atoms exhibit ψ -trigonal bipyramidal geometry.

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1. Introduction

The structural characteristics of several classes of organotellurium halides are known. In crystal structures reported for RTeX₃ species, the occurrence of intra- and intermolecular secondary bonding interactions (SBIs), altered by the presence of additional secondary bonds to tellurium together with the nature of the organic groups binding to the tellurium atoms and with the halogen, oxygen or other donor atoms of adjacent molecules, leads to supramolecular self-assembly [1–7]. The intermolecular SBIs of the type Te \cdots X and X \cdots X in various RTeX₃ leads to the formation of polymeric chains, dimers or monomers. It has been assumed that among RTeX₃ compounds there is a tendency for the chlorides to be polymeric, the bromides either polymeric or dimeric, the iodides to be dimeric and if R is particularly bulky, monomeric structures would be the rule. Here the size of the halogen should be the other determining factor and the preference for dimeric structures increases as size of the halogen increases [8-12]. The isomorphous PhTeCl₃ and PhTeBr₃ exist as polymers made up of infinite chains with bridging halides, but with no Te \cdots X secondary bonds [8,13]. In contrast to the polymeric chlorides and bromides, PhTeI₃ has been reported to exist as dimers, having either cis or trans oriented phenyl groups [9]. Recently, in the coordination chemistry of organotellurium compounds [14,15], the synthesis and the molecular structure of (α -naphthyl)TeI₃ and (α -naphthyl)TeBr₃ has been reported [16,17]. Though a large number of organotellurium trichlorides have been explored so far, only a few have been studied crystallographically [3,5,10,13,18,19] including the sterically encumbered supermesityltellurium(IV) trichloride [20]. The reason for less exploration of crystallographic studies of such compounds may be partially attributed to the difficulty encountered in recrystallization of these compounds, which are highly insoluble due to their polymeric structures.

The geometry of R_2TeX_2 type of compounds has also been predicted to be ψ -trigonal bipyramidal with two carbon atoms and an electron pair in the equatorial positions and two halo atoms in the axial positions. Crystal structures of this type of compounds have been reported [13,21–26] with a view to study SBIs. Presence of secondary Te…X bonds in many phenyl dihalides, R_2TeX_2 (X = F, Cl or Br) renders them to exist in the form of monomers [13,27,28]. Structural studies on a series of organotellurium



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diiodides have been reported [29–34]. However, the coordination about tellurium is usually expanded to octahedral by formation of intermolecular Te \cdots I bonds.

Telluroxides of the type R_2 TeO (R = C₆H₅, C₆F₅, p-MeOC₆H₄) [35-38] constitute another important class of Te(IV) compounds. They have been characterized structurally very well and used to prepare oligotelluroxanes [39,40] and macrocyclic multi-telluranes [41]. In recent past these compounds have also been used in organic synthesis as oxidizing agents as well as catalysts and also in some organometallic reactions as oxygen transfer reagents [42–50]. Hydrolysis of bis(organyl)tellurium dihalides is the main synthetic strategy for the synthesis of such compounds. The hydrolysis products of aryltellurium trihalides are not well characterized whereas initial studies have revealed that the hydrolysis of phenyland substituted phenyltellurium trihalides in neutral aqueous medium results in the formation of partially hydrolyzed products such as RTe(O)X (R = C₆H₅, p-EtOC₆H₄) (X = Cl and Br). However, the formation of RTe(OH)₃, RTeO(OH) and (RTeO)₂O takes place when hydrolysis is carried out under alkaline conditions. More recently, Comasseto et al. reported that tellurinic anhydride, $(RTeO)_2O$ (R = C₆H₅, p-EtOC₆H₄) can also be prepared by the alkaline hydrolysis in the presence of a phase transfer catalyst [51]. Partial or complete hydrolysis of organotellurium trihalides has been reported in a few cases, but the structural characterization of products obtained has not been reported. However, very recently Beckmann and coworkers have demonstrated the isolation and structural characterization of RTe(O)OH and RTe(O)Cl by kinetic stabilization with a bulky *m*-ter phenyl substituent which exist as dimers in the solid state [52].

In the light of these previous results, we extend our studies to the molecular structures and intermolecular bondings in organotellurium trichloride, dichloride and heteroaryl telluroxane. In this article we report the preparation and structural characterization and packing arrangement of the polymeric 1-NpITeCl₃ (1), monomeric structure of Mes₂TeCl₂ (2) and (Tpn₂TeCl)₂O (3).

2. Results and discussion

2.1. Synthesis

Compound **1** (1-NplTeCl₃) has been synthesized (Scheme 1) by the oxidative addition of the sulfuryl chloride to the bis(1-naphthyl)ditelluride, prepared similarly as reported in literature [53]. Its bright yellow crystals have been obtained by recrystallization of the compound in dichloromethane.

Compound **2** has been synthesized by the oxidative addition of SO_2Cl_2 to the solution of bis(mesityl)telluride(II) in hexane. Bis(mesityl)telluride(II) has been prepared by literature methods (detelluration of the corresponding ditelluride, Mes_2Te_2) [44]. The sequential reactions for the synthesis of **2** are presented in Scheme 2. Colorless crystals of Mes_2TeCl_2 (**2**) has been obtained from its dichloromethane solution.



The third compound $(Tpn_2TeCl)_2O(3)$ has been obtained serendipitously in an attempt to recrystallize the reaction product of bis(thiophenyl)tellurium(IV) dichloride $[Tpn_2TeCl_2]$ and AgCN. Attempt was made to synthesize the bis(2-thiophenyl)tellurium(IV) dicyanide by a metathetical reaction between Tpn_2TeCl_2 and AgCN (excess) in dichloromethane at room temperature. The colorless crystals of reaction product have been characterized as **3**. It may be assumed that the moisture present in the solid AgCN partially hydrolyze (Scheme 3) the Tpn_2TeCl_2 to the $Tpn_2TeCl(OH)$ which undergo self condensation (Scheme 3) to yield the telluroxane, **3**.

2.2. Spectroscopic studies

All the three tellurium(IV) compounds are sharp melting, bright vellow to colorless crystalline solids and soluble in chlorinated solvents viz. chloroform and dichloromethane. In the ¹H NMR spectra of these compounds the ring protons of the naphthyl, mesityl as well as thiophene moiety appear in the aromatic region. The appearance of two different signals for the protons of two o-methyl groups of 2 in the aliphatic region indicates restricted rotation of the benzene ring about the Te-C(Mes) bond in Mes_2TeCl_2 . The ¹³C NMR chemical shifts for the ring carbons (of naphthyl, mesityl and thiophene moiety) have been found to be in the range 125–144 ppm. A single ¹²⁵Te NMR resonance (deshielded in comparision to that of 2) has been observed (see Table 1) for both the tellurium(IV) derivatives **1** (δ 1373 ppm) and **3** (δ 871 ppm), indicating the presence of only one Te containing species in their solutions. The magnitude of deshielding is very high (560 ppm) in case of **1** (see Table 1), probably due to three electronegative chlorine atoms attached directly to the Te(IV) metal centre in 1.

2.3. Crystal structures

The molecular structures of 1, 2 and 3 have been elucidated with the help of X-ray diffraction on their single crystals and are shown in Figs. 1-3 with selected bond parameters collected in the caption to each figure.

Two crystallographically independent molecules are present in the asymmetric unit of the crystal lattice of **1** and each molecule conforms to the usual ψ -trigonal bipyramidal geometry in which Cl atom at the equatorial site is closest of the three attached to each Te atom [d(Te1,Cl12), 2.334(1) Å and d(Te2,Cl22), 2.341(2) Å]. The axial Te-Cl bonds are unequal and substantially longer compared to Σ r_{cov}(Te,Cl) value of 2.36 Å [58]. Such an almost linear Te(IV)Cl₂ fragment among organotellurium(IV) diand trihalides is routinely described as a three-centre four-electron bond (3c-4e), similar to that introduced by Rundle and Pimentel for trihalide anions [59–62] and explains the hypervalency of tellurium atom without violating the octet rule or invoking ionic bonding. As two of the four electrons are occupied in a non-bonding molecular orbital, only one bonding pair is available for the two Te–Cl bonds in **1** (1-NplTeCl₃) as well, thereby accounting for their bond orders typically less than 1.0 for a single electron pair bond (2c-2e) between the same elements. The involvement of one of the axial Cl atoms in strong intermolecular Te ... Cl secondary bonding interaction (SBI) may be responsible for the significant disparity in the Te-Cl_{axial} bond distances, found in both the molecules of 1. Separate polymeric zig-zag (helical) chains are formed by units of each of the independent molecules via μ_2 -chloro bridging (Fig. S1) in the crystal lattice. The intermolecular secondary bonds $[d(Te1 \cdots Cl11') = 2.875(2) \text{ Å}, d(Te2 \cdots Cl21') = 2.888(1) \text{ Å}]$ that are (Supporting information: Fig. S1) only slightly longer (\sim 5%) than the two axial Te–Cl bonds [d(Te1...Cl11) = 2.673(1) Å, d(Te2...Cl21) = 2.674(1) Å], are significantly shorter than Σ r_{vdw}(Te,Cl) value of 3.90 Å [63]. Thus, in the crystalline state of 1, the environment of the five coordinate central tellurium atom





 Table 1

 Chemical shifts (δ ¹²⁵Te, in ppm) of organotellurium(IV) compounds.

Compound	R = 1-naphthyl(1-Npl)	R = mesityl(Mes)
R ₂ TeF ₂	-	1206 [54]
R_2TeCl_2	-	813 [55]
R ₂ TeBr ₂	-	744 [56]
R_2TeI_2	-	389 [56]
RTeCl ₃	1373	-
RTeBr ₃	1348 [17]	469 [57]
RTeI ₃	-	-

appears to be square pyramidal with naphthyl moiety at the apical site with its plane perpendicular to the distorted square basal plane. The nearly coplanar four Cl atoms along with the Te atom {deviation from the mean plane is limited to 0.1788 Å (Cl12 atom) and 0.019 Å (Cl23 atom) in molecules I and II respectively} occupy

the basal plane. Formation of similar square pyramidal, TeX₄Y units in the solid state has been observed invariably for the anions $[TeX_4Y]^-$ (Y = X = Cl [64] or Y = aryl group, X = Cl, Br [65]) and among the oligomeric or polymeric supramolecular motifs in the solid state of similar organotellurium trichlorides [3,10,66] as well as organotellurium tribromides [8] including the bromo analog of 1 [17]. In the case of neutral organotellurium trichlorides and -tribromides formation of planar TeX₄ units takes place when the central Te atom is approached by a chloro or bromo ligand of an adjacent molecule in a direction trans to the equatorial Cl(Br)-Te bond in preference to that of the C-Te bond resulting in two quasi linear X-Te-X alignments. Formation of such a planar covalent TeX₄ moiety among 12-Te-5 hypervalent species may be said to represent a five-centre eight-electron bonding (5c-8e) system where three doubly degenerate molecular orbitals are constituted by two atomic orbitals from the Te atom and one each from four halogen atoms. All the four Te-Cl bonds are weaker than a normal



Fig. 1. Molecular structure of 1. Selected interatomic distances (Å) and angles (°) for the two independent molecules: Te1-C1A 2.115(5) {2.116(5)}, Te1-Cl11 2.673(1) {2.674(1)}, Te1-Cl12 2.334(1) {2.341(2)}, Te1-Cl13 2.382(1) {2.376(2)}, C1A-Te1-Cl11 87.70(14) {87.99(14)}, C1A-Te1-Cl12 96.09(15) {95.14(15)}, C1A-Te1-Cl13 91.80(14) {92.30(15)}, Cl11-Te1-Cl12 83.82(5) {84.68(6)}, Cl11-Te1-Cl13 171.93(5) {172.27(6)}, Cl12-Te1-Cl13 88.22(6) {87.60(7)}.



Fig. 2. Molecular structure of 2. Selected interatomic distances (Å) and angles (°): Te-C1A 2.147(3), Te-ClB 2.142(2), Te-Cl1 2.5368(7), Te-Cl2 2.4979(8), C1A-Te-C1B 115.34(9), Cl1-Te-Cl2 174.98(2).



Fig. 3. Molecular structure of 3. Selected interatomic distances (Å) and angles (°) with higher occupencies of the atoms are shown for the clarity: Te1-C9A 2.186(13), Te1-C13A 2.086(15), Te2-C1A 2.067(21), Te2-C5B 2.110(16), Te1-O1 1.988(6), Te2-O1 1.971(7), Te1-Cl1 2.691(2), Te2-Cl2 2.611(3), C9A-Te1-C13A 102.8(5), C1A-Te2-C5B 97.0(7), Te1-O1-Te2 136.6(4), Cl1-Te1-O1 170.1(2), Cl2-Te2-O1 170.6(2).

2c–2e bond because of the eight electrons that occupy bonding and non bonding molecular orbitals, only four account for such Te–Cl bonds. However, the formation of such halo-bridged square pyramidal CTeX₄ units (formed by intermolecular Te···X SBIs) has not observed in the crystal structures of the iodo analog of 1-naphthyltellurium(IV) trichloride [16], mesityltellurium tribromide [57], 2biphenylyltellurium tribromide [1] and also among those of the functionalized aryltellurium trihalides possessing intramolecular Te···A SBI with the central Te atom [7,67–68]. The Addison's tau values [69] for the compound **1**, **2** and **3** are 1.23, 1.0 and 1.12 & 1.23 respectively which also proved that compound **2** is perfectly trigonal bipyramidal and **2** and **3** are ψ -trigonal bipyramidal. A diverse combination of crystal packings has been observed among organotellurium trihalides and it is not surprising because a slight variation in the steric and electronic features of the ligands bound to the Te(IV) atom could lead to subtle modifications in the supramolecular motifs (Fig. 4).

The asymmetric unit in the crystal lattice of **2** is consist of only one independent molecule which conforms to the usual ψ -trigonal bipyramidal geometry around Te atom. The axial positions are occupied by more electronegative chlorine atom while the *ipso* carbon atoms of the mesityl moieties together with a lone pair are placed in the equatorial positions. The steric demand of the mesityl ligand in this molecule enlarges the equatorial angle [115.34(9)°] which is comparable to 113.5(2)° in Mes₂TeBr₂ [56]. A zero dimensional dimeric unit has been realized *via* C–H···Cl intermolecular interactions (Fig. S2).

In case of $(Tpn_2TeCl)_2O$ (3), an asymmetric unit also contains one crystallographically independent molecule in the crystal lattice and ring atoms of each of thiophenyl moieties in the molecule



Fig. 4. One dimensional array was realized *via* C7B–H7BA····Cl12 interactions in between the two independent molecules of **1**. Only relevant hydrogen atoms are shown for clarity.

are twofold disordered with occupancies 57:43, 58:42 for the rings attached to Te1 and 69:31, 44:56 for rings attached to Te2. The geometry around each Te atom is pseudo-trigonal bipyramidal and the axial sites are occupied by the more electronegative chloro and oxo ligands while the carbon atoms of the thiophenyl moieties together with a lone pair are placed in the equatorial positions. The equatorial C-Te-C angles are 102.8(5)° for Te1 and 97.0(7)° for Te2 atom and are significantly smaller than the putative value of 120° for a trigonal bipyramidal geometry owing to the stereochemical activity of the lone pair on the central Te atom. The Te1-O1-Te2 angle is 136.6(4)°. The Te1–Cl1 bond [2.691(2) Å] is slightly longer than Te2-Cl2 bond [2.611(3)Å]. It is presumably due to the involvement of Cl1 atom in the intermolecular secondary bonding interaction. Formation of one-dimensional supramolecular array has been observed in this case via bifurcated Te.-Cl1 intermolecular interactions $[d(Te1 \cdots Cl1) = 3.300(2) \text{ Å}, d(Te2 \cdots Cl1) =$ 3.293(2) Å] which are appreciably shorter than Σr_{vdw} (Te,Cl) value of 3.90 Å (Fig. 5).

2.4. Conclusion

Oxidative addition of the sulfuryl chloride to bisnaphthylditelluride and bismesityltelluride gave 1-naphthyltellurium(IV) trichloride (1) and bismesityltellurium(IV) dichloride (2) respectively. Compound **3** (Tpn₂TeCl)₂O has been obtained serendipitously in crystalline form by the reaction between bis(thiophenyl)tellurium(IV) dichloride (Tpn₂TeCl₂) and AgCN. The crystal structures of these three compounds have been crystallographically studied. In case of **1**, a polymeric chain was observed *via* bridging Cl atom. In **1** and **2** supramolecular architects were formed through C–H···Cl H-bonding interaction. 1D supramolecular array has been realized in case of **3** *via* bifurcated Te···Cl1 intermolecular interactions.

3. Experimental

3.1. General procedures

All solvents were purified and dried before use. Te powder was purchased from Sigma Aldrich (USA). The starting materials 2-bromo naphthlene, 2-bromo mesitylene and 2-bromo thiophene were used as procured from Merck KGaA, Germany. Melting points were recorded in capillary tubes and are uncorrected. ¹H NMR spectra were recorded at 300.13 MHz in CDCl₃ on a Bruker DRX300 spectrometer using Me₄Si as the internal standard. ¹³C{¹H} (100.54 MHz) and ¹²⁵Te{¹H} (126.19 MHz) NMR spectra were recorded in CDCl₃ on a JEOL Eclipse Plus 400 NMR spectrometer, using Me₄Si and Me₂Te respectively as internal standards. Microanalyses were carried out using a Carlo Erba 1108 analyzer.

3.2. Syntheses

3.2.1. Synthesis of 1-naphthyltellurium(IV) trichloride, 1-NplTeCl₃ (1) Dropwise addition of a solution of SO₂Cl₂ (0.16 mL, 2.0 mmol) in dichloromethane (5 mL) to a stirred red solution of bisnaphthylditelluride (0.26 g, 0.50 mmol) in the same solvent (10 mL) at 0 °C followed by stirring at room temp (2 h), resulted in the precipitation of **1** as a bright yellow solid that was recrystallized from dichloromethane to afford bright yellow single crystals. Yield: 0.33 g (91%). M.p.: 180 °C (lit. 175–180 °C [70]). Anal. Calc. for C₁₀₋ H₇Cl₃Te (361.12): C, 33.26; H, 1.95. Found: C, 33.14; H, 1.87%. ¹H NMR: δ 7.65 (t, 1H), 7.72 (t, 1H), 7.81 (t, 1H), 8.05 (d, 1H), 8.14 (d, 2H), 8.69 (s, 1H) ppm. ¹³C{¹H} NMR: δ 124.7, 127.1, 127.3, 127.5, 128.3, 129.7, 129.8, 130.0, 133.1, 133.3 (aromatic carbons) ppm. ¹²⁵Te{¹H} NMR: δ 1373 ppm.

3.2.2. Synthesis of bis(mesityl)tellurium(IV) dichloride, $Mes_2TeCl_2(2)$

Sulfuryl chloride (0.08 mL, 1.0 mmol) in hexane (5 mL) was added dropwise to a cooled (0 °C) solution of bis(mesityl)telluride (0.366 g, 1.0 mmol) in hexane (5 mL) and the reaction mixture was stirred for 5 min to obtain a white precipitate. It was filtered and recrystallized from dichloromethane to yield colorless needles of **2**. Yield: 0.41 g (89%). M.p.: 179 °C (lit. 178–179 °C [71]). *Anal.* Calc. for C₁₈H₂₂TeCl₂ (436.87): C, 49.49; H, 5.08. Found: C, 49.42; H, 5.21%. ¹H NMR: δ 2.33 (s, 3H, *p*-Me), 2.56 (s, 3H, *o*-Me), 2.91 (s, 3H, *o*-Me), 7.01 (s, 1H, *m*-H mesityl ring), 7.05 (s, 1H, *m*-H mesityl ring) ppm. ¹³C{¹H} NMR: δ 20.9 (*p*-Me), 24.0 (*o*-Me), 24.9 (*o*-Me), 130.5, 130.9, 135.1, 140.6, 141.8, 144.4 (aromatic carbons) ppm.

3.2.3. Isolation of bis(chlorobis(2-thiophenyl)tellurium)oxide; (Tpn₂TeCl)₂O (**3**)

A solution of Tpn₂TeCl₂ (0.36 g, 1.0 mmol) [34] in 25 ml chloroform was stirred with AgCN (0.27 g, 2.0 mmol) for 36 h. The reaction mixture was filtered and the filtrate was passed through a short silica column. Filtrate was concentrated to ~5 mL and hexane was added to afford a white solid that was recrystallized from dichloromethane/hexane (10:1) to give colorless crystals of **3**. Yield: 0.21 g (62%). M.p.: 168 °C. *Anal.* Calc. for C₁₆H₁₂Cl₂OS₄Te₂ (674.63): C, 28.49; H, 1.79. Found: C, 28.43; H, 1.68%. ¹H NMR: δ 7.23 (t, 1H), 7.79 (d, 1H), 8.15 (d, 1H) ppm. ¹³C{¹H} NMR: δ 128.7, 135.7, 138.2, 140.1 (aromatic carbons) ppm. ¹²⁵Te{¹H} NMR: δ 871 ppm.



Fig. 5. 1D supramolecular array realized via Te...Cl intermolecular secondary bonding interactions in the crystal lattice of 3. Hydrogen atoms are omitted for clarity.

Table 2 Crystal data and structure refinement details of 1, 2 and 3.

	1	2	3
Empirical formula	C ₁₀ H ₇ Cl ₃ Te	C ₁₈ H ₂₂ Cl ₂ Te	$C_{16}H_{12}Cl_2OS_4Te_2$
Formula mass (g mol ⁻¹)	361.11	436.86	674.60
Т (К)	123(2)	123(2)	123(2)
Wavelenth, λ (Å)	0.71073	0.71073	1.54178
Crystal system	monoclinic	monoclinic	monoclinic
Crystal size (mm)	$0.53 \times 0.47 \times 0.35$	$0.49 \times 0.31 \times 0.25$	$0.3034 \times 0.2404 \times 0.0160$
Space group	$P 2_1/c$	P 21/c	C 2/c
a (Å)	19.6060(16)	10.7833(4)	19.0326(8)
b (Å)	7.3478(3)	21.6413(7)	8.0139(2)
c (Å)	17.3811(17)	8.2536(3)	29.0158(12)
α (°)	90	90	90
β (°)	115.988(12)	111.034(4)	109.663(4)
γ (°)	90	90	90
$V(Å^3)$	2250.8(3)	1797.76(11)	4167.6(3)
Z	8	4	8
ρ_{calc} (Mg m ⁻³)	2.131	1.614	2.150
Absorption coefficient (mm^{-1})	3.310	1.944	28.239
F(000)	1360	864	2544
h, k, l ranges collected	$-31 \rightarrow 30$	$-15 \rightarrow 10$	-22 → 23
	$-11 \rightarrow 11$	$-20 \rightarrow 32$	$-9 \rightarrow 6$
	$-28 \rightarrow 27$	$-10 \rightarrow 12$	$-35 \rightarrow 36$
Reflection collected	43876	12674	13966
Independent reflections	9590 $[R_{int} = 0.0531]$	5882 [<i>R</i> _{int} = 0.0291]	$4158 [R_{int} = 0.0556]$
θ range (°)	5.24-35.22	5.03-32.69	3.23-74.04
Completeness to θ_{max} (%)	99.0	99.1	99.8
Absorption correction	Semi-empirical from equivalents		Analytical
Maximum, minimum transmission	1.00000, 0.45619	1.00000, 0.58408	0.645, 0.019
Refinement method	Full-matrix least-squares on F^2		
Data/restraints/parameters	9590/0/254	5882/0/197	4158/296/290
Goodness-of-fit (GOF) on F^2	1.139	1.054	1.057
Final R indices $(I > 2\sigma(I))$	$R_1 = 0.0498, wR_2 = 0.1044$	$R_1 = 0.0310, wR_2 = 0.0722$	$R_1 = 0.0573, wR_2 = 0.1535$
R indices (all data)	$R_1 = 0.0630, wR_2 = 0.1109$	$R_1 = 0.0486, wR_2 = 0.0759$	$R_1 = 0.0626$, $wR_2 = 0.1601$
Largest diff peak and hole ($e Å^{-3}$)	1.930 and -1.075	0.922 and -0.557	2.745 and -1.578
Extinction coefficient		0.0001(3)	

3.2.4. Crystallography

Single crystals of **1** and **2** suitable for X-ray crystallography were grown by slow evaporation of its dichloromethane solution while **3** by mixture of dichloromethane/hexane solution. Intensity data were collected on an Oxford Diffraction Gemini CCD diffractometer with graphite-monochromated Mo K α (0.71073 Å) radia-

tion for **1** and **2** while at 1.54178 Å for **3**. Data were reduced and corrected for absorption using spherical harmonics, implemented in SCALE3 ABSPACK scaling algorithm in the CrysAlisPro, Oxford Diffraction Ltd., Version 1.171.33.34d program. The structures were solved by direct methods and difference Fourier synthesis using SHELXS-97 [72]. Full-matrix least-squares refinements on F^2 ,

using all data, were carried out with anisotropic displacement parameters applied to non-hydrogen atoms. Hydrogen atoms attached to carbon were included in geometrically calculated positions using a riding model and were refined isotropically. Crystal data and structure refinement details are given in Table 2. The molecular structures are depicted in Figs. 1 and 3, showing 30% (1 and 3) and Fig. 2 (compd. 2), showing 50% probability displacement ellipsoids, omitting H atoms for clarity, and captioned with the geometrical parameters relevant to the primary geometry were generated using the program ORTEP-3 version 2.02 [73].

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Appendix A. Supplementary data

CCDC 871494, 871496 and 946567 contains the supplementary crystallographic data for 1, 2 and 3. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk. Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/ 10.1016/j.poly.2013.06.044.

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