Isolation and structures of some selenium and tellurium derivatives of 1, 4, 5, 8, 9, 12-hexabromododecahydrotriphenylene as co-crystals of triphenylene

POONAM RAJESH PRASAD^a, HARKESH B SINGH^{a,*} and RAY J BUTCHER^b

^aDepartment of Chemistry, Indian Institute of Technology Bombay, Powai, Mumbai 400 076, India

^bDepartment of Chemistry, Howard University, Washington DC, 20059, USA

e-mail: chhbsia@chem.iitb.ac.in

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Abstract. The synthesis and characterization of low-valent organoselenium and tellurium derivatives of hexabromododecahydrotriphenylene has been attempted. The reaction of hexabromododecahydrotriphenylene with *in situ* generated disodium dichalcogenides (Na_2E_2 ; E = Se, Te) afforded insoluble chalcododecahydrotriphenylene derivatives, **20**, **21** respectively. Attempted aromatization of **20** and **21** using DDQ (2, 3-dichloro-5, 6-dicyano-1,4-benzoquinone) as an oxidizing agent afforded the co-crystals. The hexaselenophenyl derivative, **22** and the hexaselenocyanate derivative **23** were synthesized by the reaction of *in situ* generated sodium arylselenolate/potassium selenocyanate with hexabromododecahydrotriphenylene, respectively. The compounds were characterized by common spectroscopic tools and a few by single crystal x-ray crystallographic studies.

Keywords. Hexabromododecahydrotriphenylene; organoselenide; –telluride; selenocyanate.

1. Introduction

The design and synthesis of polycyclic aromatic hydrocarbons (PAHs) have attracted considerable interest due to their potential application in various fields such as organic photovoltaic cells, semiconductors, liquid-crystalline materials and polymer research.^{1–3} Among PAHs, fullerene is one of the most studied molecules because of its symmetric structure and interesting semiconductor properties. The smallest subunit of fullerene is the bowl-shaped corannulene (**1**) and a concentric zwitterion ‘annulene-within-an-annulene’ resonance structure (**1a**) might contribute to the electronic properties of **1** (chart 1).²

Similar to corannulene (**1**), the other simple symmetric structures of PAHs are correnes (**2**) and sumanene (**4**), which are not only attractive as siblings of fullerenes but attractive for their own physical and chemical properties.⁴ Triphenylene (**3**) is of special interest as a substrate for use as precursor for the synthesis of graphenes, buckminsterfullerenes, carbon nanotubes, as well as polycyclic heteroaromatics. It is known that the insertion of heteroatoms such as sulfur (**5–8**) into **3** enhances their electronic properties. Some other sulfur substituted PAHs synthesized for such studies are **9–15**.^{3–6} The main aim of introducing chalcogen

atoms into the frameworks of extended π -conjugated system of PAHs is to improve their inter-chain coupling and to suppress the *Peierls transition*.^{7–9} Among chalcogens, selenium and tellurium are more interesting due to their larger sizes and higher polarizability compared to sulfur. In the present study we report our attempts to insert heteroatoms like selenium and tellurium at the peripheral positions of the triphenylene rings using nucleophilic substitution reaction without any substitution on the triphenylene rings. During the course of the present study, Shao and co-workers¹⁰ have reported the insertion of sulfur and selenium heteroatoms at the peripheral positions of the triphenylene rings (**16–17**). In this case they succeeded in incorporating sulfur and selenium by electrophilic substitution reaction using *n*-BuLi as reagent followed by chalcogen (S, Se) insertion.

2. Experimental

2.1 Materials

Dry cyclohexanone (Spectrochem, India), ZrCl_4 (Sigma-Aldrich), bromine solution (Merck, India), potassium selenocyanate (Sigma-Aldrich), sodium borohydride (Merck, India), 2, 3-dichloro-5, 6-dicyanobenzoquinone (DDQ) (Sigma-Aldrich), selenium/tellurium powder

*For correspondence

Chart 1. A few polycyclic aromatic hydrocarbons (PAHs) and heteroaromatics.

(Sigma-Aldrich) were used as received. Dodecahydrotriphenylene (**18**)¹¹ and 1,4,5,8,9,12-hexabromododecahydrotriphenylene (**19**)¹¹ were prepared by following the literature procedures. The solvents were purified and dried by standard procedures and were freshly distilled prior to use.

2.2 Physical measurements

Melting points were recorded in capillary tubes. For most of the compounds, NMR spectra were recorded in CDCl₃ solvent and for some using CD₃ OD or DMSO-*d*₆. The ¹H (400 MHz), ¹³C (100 MHz), ⁷⁷Se (76.4 MHz) and ¹²⁵Te (126.3 MHz) spectra were recorded on a Bruker 400 MHz spectrometer. Chemical shifts cited were referenced with respect to TMS for (¹H and ¹³C) as internal standard and Me₂Se (for ⁷⁷Se), Me₂Te (for ¹²⁵Te) as external standards. Elemental analysis was performed on Carlo-Erba model 1106 and Eager 300 EA112 elemental analyzers. The IR spectra were recorded in the range of 400–4000 cm⁻¹ by using KBr pellets for solid samples and as neat film for liquid samples on a Thermo Nicolet Avatar 320 FT-IR spectrometer. ESI-MS were recorded at room temperature on a Q-TOF micro (YA-105) mass spectrometer with electrospray ionization mode of analysis. In the case of isotopic patterns, the value given is for the most intense peak. In column chromatography, silica gel was used as

a stationary phase whereas petroleum ether and ethyl acetate (2%) were used as the mobile phase.

2.3 Synthesis of hexaselenododecahydrotriphenylene (**20**)

A stirred solution of disodium diselenide {generated *in-situ* by the reaction of sodium (0.19 g, 8.42 mmol) and selenium (0.66 g, 8.42 mmol) in dry THF in the presence of catalytic amount of naphthalene} was treated with precursor **19** (1.00 g, 1.4 mmol) dissolved in DMF (5 mL) and DMSO (10 mL). The reaction mixture was stirred at room temperature for 12 h. The resulting mixture was poured into water to get a yellow precipitate. This was collected by vacuum filtration, washed with water and ethanol and dried under vacuum to get a yellow solid. The crude product was insoluble (*vide infra*) in all common solvents including DMSO and was used as such for further reactions. Yield: 0.5 g (28%), M.p.: > 250°C. Anal. Calc. for C₁₈H₁₈Se₆: C, 30.53; H, 2.56. Found: C, 28.06; H, 2.09%.

2.4 Synthesis of tetratellurododecahydrotriphenylene (**21**)

It was synthesized from the reaction of disodium ditelluride (generated *in-situ*) with **19** (1.00 g, 1.4 mmol) in DMF (5 mL) and DMSO (10 mL), following the procedure used for the preparation of compound **20**. The crude product was insoluble (*vide infra*) in all common solvents including DMSO and was used as such for further reactions. Yield: 0.4 g (38%) M.p.: > 250°C. Anal. Calc. for C₁₈H₁₈Te₄: C, 29.03; H, 2.44. Found: C, 28.03; H, 1.90%.

2.5 Synthesis of hexaselenophenyldodecahydrotriphenylene (**22**)

To an ethanolic solution of diphenyl diselenide (0.51 g, 1.63 mmol) was added an excess of sodium borohydride (0.12 g, 3.26 mmol) at 0°C. To this, a solution of **19** (0.39 g, 0.54 mmol) in DMF (5 mL) was added and the reaction mixture allowed to stir for additional 6 h (monitored by TLC) at room temperature. The reaction mixture was then poured into water and the organic layer was extracted with diethyl ether and dried over sodium sulfate. The organic layer was evaporated to afford **22** as yellow oil. The oil was triturated with petroleum ether and diethyl ether (2:1) to give a white solid. Yield: 0.20 g (33%). M.p. 237–239°C. ¹H NMR (400 MHz, CDCl₃): δ (ppm): 7.59–7.24 (m, 30H), 5.59 (s, 6H), 2.87–2.80 (d, 6H), 1.99–1.97(d, 6H); ¹³C NMR (75

MHz, CDCl_3): δ 25.2, 42.0, 127.8, 129.4, 131.0, 134.3, 134.7; ^{77}Se NMR (CDCl_3): δ 462. ES-MS m/z calcd. for $\text{C}_{54}\text{H}_{48}\text{Se}_6$: 1170; found: 1016 $[\text{M-SePh}]^+$; 636 $[\text{M-Se}_3\text{Ph}_4+\text{Na}]$. Anal.Calc. for $\text{C}_{54}\text{H}_{48}\text{Se}_6$: C, 55.40; H, 4.13. Found C, 54.68; H, 4.12%.

2.6 Synthesis of hexaselenocyanatedodecahydrotriphenylene (23)

To a stirred solution of **19** (0.50 g, 0.70 mmol) in dry tetrahydrofuran (30 mL) was added KSeCN (0.61 g, 4.20 mmol) and the solution stirred for 10 h at room temperature. The resultant reaction mixture was then poured into water. The precipitate was filtered, washed with water and finally washed with methanol to get a pale yellow solid of **23**. Yield: 0.21 g (34%). M.p. 224–226°C. ^1H NMR (400 MHz, CDCl_3), δ (ppm): 5.8 (s, 6H), 2.84 (d, $J = 12$ Hz, 6H), 2.50 (d, $J = 12$ Hz, 6H); ^{13}C NMR (75 MHz, CDCl_3), δ (ppm): 25.23, 26.22, 44.31, 67.13, 104.39, 134.42; ^{77}Se NMR (CDCl_3): δ 411. ES-MS m/z calcd. for $\text{C}_{24}\text{H}_{18}\text{Se}_6\text{N}_6$: 864; found: 883 $[\text{M} + \text{K}]^+$; IR (KBr, cm^{-1}): 2148.4 ($\nu_{\text{C}\equiv\text{N}}$); Anal.Calc. for $\text{C}_{24}\text{H}_{18}\text{Se}_6\text{N}_6$: C, 33.36; H, 2.10; N, 9.72. Found C, 34.13; H, 1.95; N, 7.562%.

2.7 Synthesis of selenotriphenylene (24–25)

The crude solid of **20** (1.0 g) was suspended in dry chlorobenzene (20 mL) containing DDQ and refluxed for 12 h. After this, it was allowed to cool to the room temperature. The reaction mixture was washed with aqueous Na_2SO_3 solution until the solution became colourless. The organic layer was dried over Na_2SO_4 and concentrated under reduced pressure to afford a residue, which was purified by chromatography on silica gel using petroleum ether and ethyl acetate (2%) to get a mixture of products. The isolation of these compounds was very difficult due to their similar polarity and sensitivity to decomposition to form **3**. Hence the compounds were characterized as mixture (vide infra). Yield: 0.22 g. M.p. > 250°C (decomp.); ^1H NMR (400 MHz, CDCl_3) mixture of **3**, **24** and **25**, δ (ppm): 8.65–8.64 (m, 2H), 8.63–8.51 (m, 2H), 8.40 (d, 2H), 8.07 (d, 2H), 7.76 (d, 2H), 7.6 (m, 2H); ^{13}C NMR (75 MHz, CDCl_3), δ (ppm): 118.0, 118.16, 123.4, 123.6, 124.0, 124.1, 124.3, 127.2, 127.3, 127.4, 127.5, 127.6, 127.7, 130.0, 130.1, 130.3, 130.5, 130.5, 130.6, 133.4; 133.6, 138.8, 139.0; ^{77}Se NMR (CDCl_3): δ (ppm): 498, 459; ES-MS m/z calcd. for $\text{C}_{36}\text{H}_{18}\text{Se}_3$: 689; found: 690 $[\text{M}+1]$; 611 $[\text{C}_{18}\text{H}_8\text{Se}_2 + \text{C}_{18}\text{H}_{12} + \text{H}]^+$.

The experiment was repeated two more times and similar results were obtained. The three elemental

analysis values of the mixtures of compounds **3** and **24**, **25** before crystallization (from powder) are given below:

- (i) Anal.Calc. for $\text{C}_{54}\text{H}_{30}\text{Se}_3$: C, 70.83; H, 3.30. Found: C, 70.50; H, 4.07%.
- (ii) Anal.Calc. for $\text{C}_{54}\text{H}_{30}\text{Se}_3$: C, 70.83; H, 3.30. Found: C, 73.61; H, 3.76%.
- (iii) Anal.Calc. for $\text{C}_{54}\text{H}_{30}\text{Se}_3$: C, 70.83; H, 3.30. Found: C, 73.57; H, 3.07%.

After column chromatography and repeated crystallizations, the elemental analysis data obtained on crystals are given below. The elemental analysis data and other data (vide infra) showed it to be co-crystal of compounds **3** and **24**.

- (i) Anal.Calc. for $\text{C}_{18}\text{H}_{11.64}\text{Se}_{0.36}$: C, 84.33; H, 4.57. Found: C, 84.51; H, 4.36%.
- (ii) Anal.Calc. for $\text{C}_{18}\text{H}_{11.59}\text{Se}_{0.41}$: C, 83.07; H, 4.49. Found: C, 83.88; H, 4.82%.

2.8 Synthesis of tellurotriphenylene (26)

Similarly, the crude solid of **21** (1.0 g) was suspended in dry chlorobenzene (20 mL) containing DDQ and refluxed for 12 h and following a procedure similar to that used for the synthesis of **24–25**. The yellow solid obtained was purified by column chromatography and it always eluted as a mixture of two components **3** and **26**. Yield: 0.14 g. M.p. > 250°C (decomp.). ^1H NMR (400 MHz, CDCl_3) mixture of **3** and **26**, δ (ppm): 8.65–8.64 (m, 2H), 8.57 (d, 2H), 8.02 (d, 2H), 7.60 (d, 2H); ^{125}Te NMR (CDCl_3): δ 625; ES-MS: m/z (%) 479 $[\text{M}]^+$. (i) Anal.Calc. for $\text{C}_{72}\text{H}_{46}\text{Te}$: ($\text{C}_{18}\text{H}_{12}$: $\text{C}_{18}\text{H}_8\text{Te}$, 3:1) C, 83.25; H, 4.46; Found: C, 84.28; H, 4.68%.

The experiment was repeated twice and different results were obtained.

Anal. calcd for $\text{C}_{72}\text{H}_{46}\text{Te}$ ($\text{C}_{18}\text{H}_{12}$: $\text{C}_{18}\text{H}_8\text{Te}$, 8:1): C, 89.25; H, 4.90; Found C, 89.48; H, 5.06%.

2.9 X-ray data collection and structure refinement

The single crystal x-ray diffraction measurements compounds **3**, **3–24 a, b, c** (as co-crystal) and **3–26** (as co-crystals) were performed by using an Oxford Diffraction Gemini Diffraction measurements device with graphite monochromated $\text{MoK}\alpha$ radiation ($\lambda = 0.7107$ Å). The structures were determined by routine heavy-atom method using SHELXS 97¹² (Fourier methods) and refined by full-matrix least-squares with the non-hydrogen atom anisotropic and hydrogen atoms with fixed isotropic thermal parameters of 0.07 Å by means of SHELXS 97 program.¹³ Scattering factors were from

common sources.¹⁴ The crystallographic data for **3**, co-crystals of **3–24(a, b, c)** and co-crystal of **3–26** are given in table 1.

3. Results and Discussion

3.1 Synthesis

The precursor, 1, 4, 5,8, 9, 12-hexabromododecahydrotriphenylene **19**, was prepared by the reaction of dodecahydrotriphenylene **18** with bromine following the literature procedure.^{11,15} Organochalcogen derivatives **20** and **21** were synthesized by the reaction of **19** with *in situ* generated Na₂E₂ (E = Se and Te) at room temperature (scheme 1). Compounds **20** and **21** were obtained as yellow and as black solids, respectively. The crude products could not be purified further and characterized properly owing to their poor solubility in the common organic solvents and were used as obtained for further reactions. Wei *et al.* have also obtained a similar insoluble product during the reaction of **19** with sodium sulfide.¹¹ The elemental analysis indicated the formation of the desired products **20** and **21**. The FT-IR spectra of **20** and **21** showed a different pattern as compared to precursor **19**. Compound **22** was synthesized by the

reaction of PhSeNa with **19** at 0°C. The elemental analysis suggested the formation of compound **22**. The synthesis of the selenocyanate derivative, **23** was accomplished by the addition of KSeCN to a tetrahydrofuran solution of **19** at room temperature (scheme 1).

The ¹H NMR spectrum of **22** exhibits signals in the range of 7.41–7.25 ppm corresponding to the aromatic protons, a signal at 5.53 ppm for CH protons adjacent to the selenium atoms and other signals in the range of 2.57–1.98 ppm for (CH₂) protons. The CH protons adjacent to the selenium atoms are shifted upfield (5.53 ppm) when compared to the CH protons adjacent to bromine atoms in precursor **19** (6.13 ppm). Similarly, in the case of selenocyanate **23**, the CH protons appeared in the upfield region (5.78 ppm) as compared to the precursor **19** and the alicyclic protons were observed in the region of 3.59–2.47 ppm. The ⁷⁷Se NMR signal for **22** was observed at 462 ppm which is slightly more (~50 ppm) downfield shifted as compared to that expected for monoselenides.¹⁶ This value of 462 ppm is also downfield shifted as compared to bis(2-formylphenyl)selenide (393 ppm).¹⁷ For selenocyanate **23**, the ⁷⁷Se NMR chemical shift was 411 ppm, which is close to the chemical shifts reported for the related RSeC≡N derivatives.¹⁸ The ¹³C NMR spectrum of **22** shows seven peaks expected for the seven carbons, which are

Table 1. Crystal data and structure refinement for co-crystals of **3**, **3–24 (a,b,c)** and **3–26**.

Parameter	3	3-24a	3-24b	3-24c	3-26
Formula	C18 H18	C18 H11.64 Se0.36	C18 H11.70 Se0.30	C18 H11.59 Se0.41	C18 H11.98 Te0.02
Formula Weight	228.28	256.17	251.55	259.44	230.79
Temperature	123(2) K	296(2) K	123(2) K	123(2) K	123(2) K
Wavelength (Å)	1.54184	1.54178	1.54184	1.54184	0.71073
Crystal System	Orthorhombic	Orthorhombic	Orthorhombic	Orthorhombic	Orthorhombic
Space Group	P2 ₁ 2 ₁ 2 ₁	P2 ₁ 2 ₁ 2 ₁	P2 ₁ 2 ₁ 2 ₁	P2 ₁ 2 ₁ 2 ₁	P2 ₁ 2 ₁ 2 ₁
a (Å)	5.26628(17)	5.2507(5)	5.27903(15)	5.2728(3)	5.25999(1)
b (Å)	12.9714(4)	13.804(2)	13.2092(9)	13.3470(11)	12.9652(4)
c (Å)	16.6563(5)	16.782(2)	16.7456(6)	16.7410(11)	16.6417(4)
α (°)	90	90	90	90	90
β (°)	90	90	90	90	90
γ (°)	90	90	90	90	90
Volume (Å ³)	1137.81(6)	1216.4(3)	1167.70(9)	1178.17(14)	1134.91(5)
Z	4	4	4	4	4
D (Mg/m ³)	1.333	1.399	1.431	1.463	1.351
Abs. Coef. (mm ⁻¹)	0.572	1.786	1.645	1.996	0.126
Crystal Size (mm)	0.4 × 0.28 × 0.17	0.49 × 0.15 × 0.06	0.45 × 0.12 × 0.08	0.48 × 0.15 × 0.10	0.50 × 0.23 × 0.13
Total Reflections	7640	8010	2717	2687	31286
Unique Ref. (Rint)	2324 (0.0375)	2489 (0.0349)	1832 (0.0287)	1899 (0.0208)	7319 (0.0472)
Abs. Correction	Multi-scan	Multi-scan	Multi-scan	Analytical	Analytical
Tmin & Tmax	0.956, 1.000	0.702, 1.000	0.622, 1.000	0.560, 0.828	0.898, 0.962
R1, wR2	0.055, 0.151	0.080, 0.248	0.062, 0.167	0.0389, 0.112	0.0639, 0.1501
Diff. peak & hole (e.Å ³)	0.95, −0.195	0.73, −0.21	0.37, −0.41	0.28, −0.13	0.48, −0.34

Scheme 1. Reagents and conditions: (i) Br_2 , dry CCl_4 ; (ii) Na_2Se_2 , THF, 24 h, r.t.; (iii) Na_2Te_2 , THF, 24 h, r.t.; (iv) PhSeNa , dry EtOH; (v) KSeCN , dry THF, 10 h, r.t.

significantly upfield shifted compared to the precursor **19**. In the FT-IR spectrum of compound **23**, the absorption at 2148 cm^{-1} is assigned to $\nu\text{C}\equiv\text{N}$ stretching. In the mass spectrum of **23**, the molecular ion peak was observed at m/z 887 $[\text{M} + \text{Na}]^+$. However, in the case of selenocyanate **22**, the molecular ion peak was not observed and the base peak observed at m/z 1016 corresponded to $[\text{M-SePh}]^+$ where ($\text{M} = \text{C}_{54}\text{H}_{48}\text{Se}_6$) and m/z 636 corresponding to the $[\text{C}_{30}\text{H}_{28}\text{Se}_3 + \text{Na}]^+$.

Aromatization of **20–21** to obtain organoselenide **24–25** and -telluride **26** was attempted using DDQ as the oxidizing agent. The resulting derivatives **24–25** and

telluride **26** were obtained as mixture containing **3** in very low yields respectively (scheme 2). However, when the reaction mixture was refluxed for a short period of time, most of the starting material was found to have remained unreacted. The purification of the aromatized organochalcogenides (**24–25** and **26**) was extremely difficult by usual methods (recrystallization and column chromatography) due to their similar polarity and sensitive nature of the compounds which decompose to triphenylene (**3**). It is worth mentioning that Klemm *et al.* have also reported to get a mixture of **3**, **6** and **7** during the preparation of **7** in low

Scheme 2. Reagents and conditions: (i) DDQ, PhCl, reflux, 10 h.

yields by the direct reaction of triphenylene (**3**) with hydrogen sulfide in the presence of heterogeneous catalyst at high temperature (500–550°C).¹⁹ Similarly, Imamura's group prepared trithiosumane (**5**) in 2% yield by flash vacuum pyrolysis (FVP)²⁰ and very recently Wei and co-workers synthesized the polycyclic pentathioaromatic (**9**) by a modified procedure in 20% yield.¹¹ Here, it might be difficult to introduce selenium or tellurium at the peripheral positions of triphenylene **3** rings simultaneously owing to their larger size. The existence of the mixture of compounds was inferred from the elemental analysis. The elemental analysis showed different values for each preparation. In the elemental analysis data, the carbon percentage was very high (C = 80–89%) and indicated the presence of the hydrocarbon (triphenylene **3**) as the major impurity. Several attempts were made to isolate pure **24** and **25** (selenide) or **26** (telluride), however, every time elemental analysis showed different values. This observation was further corroborated by single crystal x-ray structure analysis (*vide infra*). After crystallization, the elemental analysis ratio was different than the ratio found for the powdered (crude) samples. In the mass spectrum of the mixture of selenides, the molecular ion peaks were observed at m/z 315 $[M+Na]^+$ for **24** and at m/z 392 $[M+Na]^+$ for **25**. It also showed the combined peak for **24**+**25** at 690 $[M+1]^+$. However, the single crystal x-ray structure analysis indicated the presence of only one selenium compound **24** (*vide infra*) along with **3**. Though in the case of the tellurium derivative, the molecular ion peak observed at m/z 447 for $[M]^+$ which indicated that two tellurium atoms were present at the peripheral positions of the triphenylene rings, i.e. formation of **27**, the single crystal X-ray structure analysis again indicated the presence of only one tellurium compound (**26**) in small ratio (*vide infra*) along with **3**.

The 1H NMR spectrum of the mixture of **3**, **24** and **25** (powder) showed the expected three sets of peaks in the region of 8.65–7.57 ppm corresponding to the **3** (8.55 and 7.56 ppm), **24** (8.39 and 8.05 ppm) and **25** (8.65 and 7.78 ppm). It was further corroborated by ^{13}C NMR spectrum. The ^{13}C NMR spectrum (after long time data accumulation) also showed expected twenty one peaks related to all three compounds (**3**, **24** and **25**). It was further confirmed by ^{77}Se NMR spectrum. In the ^{77}Se NMR, two peaks were observed at 498 and 459 ppm. Similar to the selenides **24** and **25**, compounds **3**, and **26** also showed a complex pattern in the 1H NMR spectrum, however, the ^{125}Te NMR spectrum showed a single at 625 ppm. This is slightly upfield shifted (~37 ppm) compared to the reported monotelluride, bis[2-(phenylazo)phenyl-*C, N*]telluride (667 (667 ppm)).²¹

3.2 X-ray crystallographic study

The crystal data for the 5 compounds are listed in table 1. The structures of 4 co-crystals of triphenylene with various amounts mono-selenium and tellurium substituted triphenylene are reported as well as a low temperature structure of triphenylene itself.

The structure of triphenylene has previously been reported²² but this structure was based on film data at room temperature whereas the present study reports the structure based on diffractometer data at 123 K. Co-crystals of triphenylene with other arene type molecules have previously been reported²³ and result in interesting architectures.²⁴ Since this is a more accurate structure of the important arene, triphenylene (figure 1), some comparison with the earlier results should be made. In the original paper of Ahmed & Trotter²³ it was noted that the aromatic molecule as a whole was significantly non-planar while the central ring was basically planar. In addition, the non-planarity shown by the outer six-membered rings showed a pattern where the two rings were displaced in one direction from this central plane while the other ring was displaced in the opposite direction. In the original paper the unique ring was labelled as A while the other two rings were labelled as B and C. In the present structure the A ring is C3 C4 C11 C12 C13 & C14 while B corresponds to C1 C2 C7 C8 C9 & C10 and C to C5 C6 C15 C16 C17 & C18 (figure 1). For the central ring composed of C1 through C6, the rms deviation of the 6 fitted atoms is 0.0065(16) Å while each individual outer ring is also planar (rms

Figure 1. Molecular structure of **3**.

deviations of 0.0045(15), 0.0074(15) and 0.0033(15) Å for A, B, and C, respectively). The dihedral angles between the outer rings and central ring are 1.30(15)°, 2.42(16)° and 2.19(15)°, for A, B and C, respectively. The central ring shows a pronounced pattern of alternating short and longer bonds with the shorter C-C bonds being those which are part of the outer rings. The C-C bond lengths for each outer ring also show a pattern with the C-C bonds involving the carbon atoms of the central ring being significantly longer (1.409(3)°) than those involving only outer rings (1.381(3)°). As was noticed in the original report, the closest π - π stacking involve ring A with rings B and C in neighbouring molecules (in this case, ring A corresponds to C3 C4 C11 C12 C13 and C14; ring B to C1 C2 C7 C8 C9 and C10; ring C to C5 C6 C15 C16 C17 C18).

For the substituted triphenylenes there are three mono-Se substituted derivatives (**3-24a**, **3-24b**, **3-24c**) (as well as one mono-Te) substituted triphenylene (**3-26**). For the Se derivatives, the structure of **3-24a** was carried out at room temperature (RT) with 0.36 Se substitution while there were two (**3-24b** and **3-24c**) low temperature (LT) structures (123 K) with 0.30 and 0.41 Se substitution. In addition, there was one (**3-26**) LT structure with Te substitution (0.02). The effect of the substitution for each can be found by comparison of the cell constants, metrical parameters and π - π stacking interactions of each with the un-substituted triphenylene structure. Each structure will

Figure 2. Molecular structure of **24**: Selected bond (Å) lengths and bond angles (°): Se(1)-C(7A) 1.751(6), Se(1)-C(1A) 1.904(5), C(7)-Se(1)-C(1A) 100.8(2), C(6)-C(1A)-Se(1) 98.5(3), C(2)-C(1A)-Se(1) 141.5(4).

be discussed in turn starting with **3-24a** (figure 2). A direct comparison of cell constants is made difficult for this structure due to the differences in temperature between the two structures. Obviously it is generally expected that at the higher temperature the cell volume should be larger than at low temperature and this is observed. A more meaningful comparison will be made for the LT Se structures. As far as the Se substitution for this structure is concerned, all the spectroscopic evidence points to a mono substitution of the triphenylene skeleton. However, in the X-ray structure the mono Se substitution shows up in two positions at a ratio of 3.79:1.00 and this substitution has a dramatic effect on the conformation adopted by the triphenylene skeleton. As in the un-substituted derivative, both the central ring and the three outer rings are planar (rms deviations from planarity of 0.0074(23), 0.0098(23) 0.0119(30) and 0.0053(30) Å, respectively for the central ring and three outer rings). However, while in the un-substituted derivative there are clearly rings A, B and C based on distortions from planarity, in the present case all the carbon atoms form one outer ring (C13 C14 C15 C16 and C17) deviate from the central in the same direction but this is not true for the other two outer rings. In the case of the ring composed of C1 C2 C3 C4 C5 and C6, the atoms C2 and C3 deviate substantially in the opposite direction while in the other ring (C7 C8 C9 C10 C11 and C12) the outermost two atoms, C10 and C11 have only small deviations but in opposite directions (0.0061(66) and -0.0239(77) Å, respectively). There are similar changes in the bond lengths. While in the central ring there is a similar pattern of alternating shorter and longer C-C bond lengths, in the outer rings the pattern is not so clearly established. This is especially the case with the ring composed of C1 through C6 where all the C-C bonds are all of similar length. One noticeable effect of the substitution is the fact that the dihedral angles between the planes of the outer rings and the central ring (0.78(25)° for C1 to C6, and 1.40(27)° and 1.40(58)° for the other two rings) are much smaller than in the un-substituted derivative. As far as the packing is concerned it appears that the substitution has not had a major effect on the π - π stacking compared to the un-substituted derivative (table 2).

The X-ray analysis of the second Se derivative (**3-24b**) (this is dealt with first as it has the lower Se substitution) was carried out at LT (123 K). The extent of the substitution was 0.30 Se per triphenylene molecule. As in the RT derivative previously discussed the substitution pattern shows two positions for the Se in an atom ratio of 1.92:1. Since this structure was carried out at the same temperature as for the

Table 2. Intermolecular and interplanar distances.

	1...1	slippage	A...A	slippage	B...B	slippage	C...C	slippage	Cg...Cg
3	3.4	4.022	3.31	4.096	3.352	4.062	3.356	4.058	3.714
3-24a*	3.465	3.945	3.469	3.942					3.846
3-24b	3.388	4.02			3.388	4.049	3.37	4.063	
3-24c	3.429	4.005			3.362	4.062	3.394	4.035	
3-26	3.4	4.022	3.356	4.058	3.31	4.096	3.352	4.022	3.714

* B & C
not determined

un-substituted molecule a comparison of the effect on crystal data can be made. The largest change in cell constants is for the *b* axis where the length has changed from 12.9714(4) to 13.2092(9) Å. There are similar but less dramatic lengthening of both *a* and *c*. Consequently there is a significant increase in overall cell volume from 1137.81(6) Å³ to 1167.70(9) Å³ and an increase in overall crystal density from 1.333 to 1.431. Both the central ring and three outer rings are planar (rms deviations of 0.0040(26), 0.0065(29), 0.0071(30) and 0.0023(30) Å, respectively). An analysis of the deviations of the three outer rings from co-planarity with the central ring shows a similar pattern to the un-substituted triphenylene and thus atoms C2 C3 C7a C8 C9 and C10a correspond to ring A, C1 C6 C15 C16 C17 and C18a correspond to B, while C4 C5 C11a C12 C13 C14 correspond to C. The dihedral angles between the central rings and the outer rings are 1.13(27), 2.14(28) and 1.77(27)° to A, B and C, respectively. As far as the metrical parameters are concerned, the central ring shows the same pattern of alternating short and long C-C bond lengths (1.464 vs 1.409 Å). In comparison with the structure of triphenylene it can be seen that the C-C bond lengths C11a C12 and C17 C18a (1.344(7) and 1.355(7) Å) have been shortened from the corresponding bonds (1.384(4) and 1.383(4) Å) due to the Se substitution. As far as the packing is concerned it appears that the substitution has not had a major effect on the $\pi - \pi$ stacking compared to the un-substituted derivative.

The structure of the third Se derivative (**3-24c**) was also carried out at 123 K and the extent of Se substitution was greater at 0.41 Se per triphenylene. As in the LT derivative previously discussed, the substitution pattern shows two positions for the Se in an atom ratio of 2.13:1. Since this structure was also carried out at the same temperature as for the un-substituted molecule a direct comparison of the effect on crystal data can be made. As in the previous LT example, the largest change in cell constants is for the *b* axis where the length has changed from 12.9714(4)

to 13.3470(11) Å. There are similar but less dramatic lengthening of both the *a* and *c* axes. Consequently there is a significant increase in overall cell volume from 1137.81(6) Å³ to 1178.14(14) Å³ and an increase in overall crystal density from 1.333 to 1.463. Both the central ring and three outer rings are planar (rms deviations of 0.0033(14), 0.0033(14), 0.0026(16) and 0.0085(16) Å, respectively). An analysis of the deviations of the three outer rings from co-planarity with the central ring shows a similar pattern to the un-substituted triphenylene and thus atoms C1 C6 C15a C16 C17 C18a correspond to ring A, C4 C5 C11 C12 C13 C14a correspond to B, while C2 C3 C7a C8 C9 C10 correspond to C. The dihedral angles between the central rings and the outer rings are 0.98(15), 1.94(15) and 2.07(15)° to A, B and C, respectively. As far as the metrical parameters are concerned the central ring shows the same pattern of alternating short and long C-C bond lengths (1.464 vs. 1.409 Å). Otherwise there is very little difference between the two LT structures. As far as the packing is concerned, it appears that the substitution has not had a major effect on the $\pi - \pi$ stacking compared to the un-substituted derivative (figures 3 and 4).

For the structure of the LT tellurium derivative (**3-26**), the extent of substitution is very small (0.02) but clearly seen in the NMR and MS data (vide supra). In this case there is only one site seen in the structure analysis (figure 5). Unlike the other four structures, this structure was collected with Mo radiation. The cell constants are not significantly different from the un-substituted derivative. Both the central ring and three outer rings are planar (rms deviations of 0.0049(7), 0.0036(7), 0.0025(7) and 0.0064(7) Å, respectively). An analysis of the deviations of the three outer rings from co-planarity with the central ring shows a similar pattern to the un-substituted triphenylene and thus atoms C5 C6 C15 C16 C17 C18 correspond to ring A, C3 C4 C11 C12 C13 C14 correspond to B, while C1 C2 C7 C8 C9 and C10 correspond to C. The dihedral angles between the central rings and the outer rings are 1.28(7), 2.11(7) and 2.53(7)° to A, B, and

Figure 3. Packing diagram showing only **24** Se $\cdots$ Se distance 3.291(3) Å, Se $\cdots$ H distance 2.80 Å [1/2 + x, 1/2 - y, 1 - z], Se $\cdots$ Se $\cdots$ Se angle 106.5(4)°.

C, respectively. As far as the metrical parameters are concerned the central ring shows the same pattern of alternating short and long C-C bond lengths (1.4625 vs. 1.4099 Å). Otherwise there is very little significant

difference between the substituted and un-substituted structures. As far as the packing is concerned it appears that the substitution did not have a major effect on the $\pi - \pi$ stacking compared to the un-substituted

Figure 4. Packing diagram of the co-crystallized triphenylene.

Figure 5. Molecular structure of **26**: Selected bond (Å) lengths and bond angles (°): Te-C7 1.951(5), Te-C7 1.956(5), C18-Te-C7 97.2(2).

derivative (figure 6). The packing diagram of molecule **3–26** shows Te...Te intermolecular interaction with bond distances of 2.963(6) Å which are shorter than the sum of van der Waals radii of Te (4.30 Å). The Te...Te bond distance (2.963(6) Å) is significantly

shorter than that observed for dimethoxytellurophene (3.803–4.04 Å).²⁵ As seen in the table of $\pi \dots \pi$ Interactions (table 1), there are very little significant differences in the packing between the un-substituted triphenylene and mono-Te derivative, reflecting the fact that the overall structure has not been perturbed by the low occupancy of Te (0.02). The perpendicular separation of the central planes is 3.400(6) Å and the centroid to centroid distance for both is 3.714(6) Å. For the RT structure (**3–24a**), there is increased separation of the planes as well as centroid to centroid distances. For the two LT Se structures (**3–24b** and **3–24c**), again there is a minor increase in interplanar separation.

4. Conclusion

Synthesis of organoselenium and –tellurium containing polyaromatic hydrocarbon derivatives has been attempted. Due to the larger size of selenium and tellurium, it is difficult to introduce them at the peripheral positions of triphenylene. Elemental analysis and single crystal X-ray structure analysis of organoselenium compound indicates that these always synthesize as a mixture of three components **3** and **24** and it is too difficult to separate them. Similar, results were also observed for the tellurium derivative **26** (**3** and **26** mixture). Alongside, the synthesis of monoselenide **22** and selenocyanate **23** derivatives has been achieved.

Figure 6. Two-dimensional packing diagram of **26**.

Supplementary Information

CCDC-1004393(3), CCDC-990989(3–24a), CCDC-990990(3–24b), CCDC-990991(3–24c), CCDC-990992(3–26) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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References

1. Wu Y-T and Siegel J S 2006 *Chem. Rev.* **106** 4843
2. Tsefrikas V M and Scott L T 2006 *Chem. Rev.* **106** 4868
3. Van Dijk J T M, Hartwijk A, Bleeker A C, Lugtenburg J and Cornelisse J 1996 *J. Org. Chem.* **61** 1136
4. Sakurai H, Daiko T, Sakane H, Amaya T and Hirao T *J. Am. Chem. Soc.* **127** 11580
5. Sakurai H, Daiko T and Hirao T 2003 *Science* **301** 1878
6. Higashibayashi S and Sakurai H 2008 *J. Am. Chem. Soc.* **130** 8592
7. Tanaka H N T and Mikawa H 1982 *Chem. Lett* 1841
8. Murschall R G H and Monch W 1982 *Chem. Lett* 727
9. Murschall R, Gant H and Mönch W 1982 *Solid State Commun.* **42** 787
10. Li X, Zhu Y, Shao J, Wang B, Zhang S, Shao Y, Jin X, Yao X, Fang R and Shao X 2014 *Angew. Chem. Int. Ed.* **53** 535
11. Wei J, Jia X, Yu J, Shi X, Zhang C and Chen Z 2009 *Chem. Commun.* 4714
12. Sheldrick G M *SHELXS-97, Program for Crystal Structure Solution* University of Göttingen, 1997
13. Sheldrick G M *SHELXL-97, Program for Crystal Structure Refinement*; University of Göttingen, 1997
14. *International Tables for X-ray Crystallography* Vol 4 1974 (Birmingham: Kynoch Press)
15. Wei J, Gao Y, Ma X, Jia X, Shi X and Chen Z 2010 *Chem. Commun.* **46** 3738
16. Selvakumar K, Singh H B, Goel N, Singh U P and Butcher R J 2011 *Dalton Trans.* **40** 9858
17. Panda A, Menon S C, Singh H B and Butcher R J 2001 *J. Organomet. Chem.* **62** 87
18. Müller J and Terfort A 2006 *Inorg. Chim. Acta* **359** 4821
19. Klemm L H, Hall E, Cousins L and Klopfenstein C E 1987 *J. Heterocyclic Chem* **24** 1749
20. Imamura K, Takimiya K, Otsubo T and Aso Y 1999 *Chem. Commun.* 1859
21. Srivastava K, Shah P, Singh H B and Butcher R J 2011 *Organometallics* **30** 534
22. Ahmed F R and Trotter J 1963 *Acta Cryst* **16** 503
23. Zyss J, Ledoux-Rak I, Weiss H -C, Blasser D, Boesse R, Thallapally P K, Thalladi V R and Desiraju G R 2003 *Chem. Matt.* **15** 3063
24. Collings J C, Roscoe K P, Thomas R L, Batsanov A S, Stimson L M, Howard J A K and Marder T B 2001 *New J. Chem.* **25** 1410
25. Patra A, Wijsboom Y H, Leitun G and Bendikov M 2009 *Organic Letters* **11** 1487