(4-Nitrophenylsulfanyl)methyl)triphenylstannane and (4-nitrophenylsulfonylmethyl)triphenylstannane: $R_2^2(10)$ rings ($X$ is 10, 18 or 24) and $C—H⋯π$ interactions

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(4-Nitrophenylsulfanylmethyl)triphenylstannane and (4-nitrophenylsulfonylmethyl)triphenylstannane: \(R_2^2(10)\) rings (\(X\) is 10, 18 or 24) and C–H⋯π interactions

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In the crystal structures of (4-nitrophenylsulfanylmethyl)triphenylstannane, \([\text{Sn}(\text{C}_6\text{H}_5)_3(\text{C}_7\text{H}_6\text{NO}_2\text{S})]\), (I), and (4-nitrophenylsulfonylmethyl)triphenylstannane, \([\text{Sn}(\text{C}_6\text{H}_5)_3(\text{C}_7\text{H}_6\text{N}_2\text{O}_4\text{S})]\), (II), the molecules are linked by paired C–H⋯O hydrogen bonds into centrosymmetric dimers which combine to form sheets. In (I), two such dimers form to give \(R_2^2(10)\) and \(R_2^2(24)\) rings. In (II), similar dimers form, here with \(R_2^2(10)\) and \(R_2^2(18)\) rings, but with an additional dimer due to the presence of the sulfone group, giving \(R_2^2(10)\) rings. In both structures, C–H⋯π interactions lead to a doubling of the width of the sheets.

Comment

The intermolecular non-bonded interactions in a number of nitro, sulfanyl and sulfonyl aromatic derivatives have been investigated in the solid state (Kelly et al., 2002; Cannon et al., 2000, 2001; Glidewell et al., 2001; Wardell et al., 2000a,b). Continuing our studies, the structures of (4-nitrophenylsulfanylmethyl)triphenylstannane, (I), and (4-nitrophenylsulfonylmethyl)triphenylstannane, (II), have now been investigated and the results are presented here.

Both (I) (Fig. 1) and (II) (Fig. 2) crystallize in the triclinic space group \(\overline{P}1\) and form sheets via similar soft interactions.
metal-organic compounds

Molecules of (II) are also linked *via* intermolecular C—H⋯O interactions. In this case, the sulfone group leads to one further bond (Table 2). Considering the nitro acceptor interactions first, phenyl atom C5 at (x, y, z) acts as a hydrogen-bond donor to nitro atom O1 at (−x, 1 − y, −z), to give an $R_2^2(10)$ motif centred at (0,1/2,0). Similarly, atom C7 at (x, y, z) donates to the nitro atom O2 at (−x, 2 − y, −z), giving an $R_2^2(18)$ ring centred at (0,1,0), forming a chain along [010] (Fig. 5). Thus, the effect of the sulfone group is to alter the local conformation and thus the C—H⋯O bonding to the second nitro O atom. In (I), a phenyl H atom from the Ph$_3$Sn group acts as the donor, whereas in (II), the CH$_2$ group is the donor, effectively contracting the size of the $R_2^2(X)$ ring.

An extra hydrogen bond occurs due to the presence of the sulfone group. Phenyl atom C2 at (x, y, z) acts as a hydrogen-bond donor to sulfone atom O4 at (1 − x, 2 − y, −z), forming an $R_2^2(10)$ motif with an inversion centre at (1/2,1/2,0). These three dimers thus combine to form a sheet which propagates along [110] (Fig. 6), as in the structure of (I).

Figure 3
Part of the crystal structure of (I) showing dimers containing $R_2^2(10)$ and $R_2^2(24)$ rings [symmetry codes: (i) $3-x, 2-y, -z$; (ii) $2-x, 1-y, -z$].

Figure 4
The dimers formed from C—H⋯π interactions in (I) *via* the symmetry translation $(1-x, 2-y, 1-z)$.

Figure 5
Part of the crystal structure of (II) showing dimers containing $R_2^2(10)$ and $R_2^2(18)$ rings [symmetry codes: (i) $-x, 1-y, -z$; (ii) $-x, 2-y, -z$].

Figure 6
The chains formed by C—H⋯O interactions in (II).
As with (I), the phenyl groups in (II) form C–H⋯π interactions with neighbouring molecules within the sheet. In addition, atom C33 at (x, y, z) donates a hydrogen bond to the C21–C26 phenyl ring at (2 − x, 1 − y, 1 − z), with a distance of 3.361 Å between the H atom and the centroid (Fig. 7), which, as in (I), has the effect of doubling the width of the sheet.

The Sn centre in (I) is four-coordinate; the bond angles, in the range 106.27 (10)–114.64 (8)5, indicate a slightly distorted tetrahedral geometry. The Sn–C bond lengths are in the expected region and fall in a narrow range, 2.138 (2)–2.172 (2) Å. The bond lengths in (II) show a greater range, 2.172 (2) Å, with those involving the phenyl groups being between 2.172 (2) Å. The bond angles subtended at Sn in (II) range from 101.15 (5) to 111.76 (6)°, a little within the sum of the van der Waals radii of 3.70 Å.

Figure 7
The dimers formed by C–H⋯π interactions in (II) via the symmetry translation (1 − x, 2 − y, 1 − z).

The closest Sn–O sulfone separation is Sn–O4 3.5906 (12) Å, a little within the sum of the van der Waals radii of 3.70 Å.

A number of related triphenyl–Sn and –Ge structures have been reported, along with one related iododiphenyltin compound (CSD database, Release 5.23; Allen & Kennard, 1993). These are Ph3GeCH2SO2C6H5 (CSD refcode GESYIM; Howie & Wardell, 1994), Ph3Sn(CH2)2SO2C6H4Me-4 (YEZVII; Cox & Wardell, 1994), Ph3Sn(CH2)2CH(SC6H4NO2-2)CH2Cl (ZIKHOQ; Aupers & Wardell, 1995), Ph3Sn(CH2)2SO2C6H4Me-4 [(III), n = 2, YEZVEE; Cox & Wardell, 1994], Ph3Sn(CH2)2SO2C6H4Me-4 [(III), n = 4, YEZVII; Cox & Wardell, 1994], Ph3Sn(CH2)2SO2C6H4Me-4 [(III), n = 3, ZAVHIN; Howie & Wardell, 1994], IPh3Sn(CH2)3SO2C6H4Me-4 (ZAVHOT; Howie & Wardell, 1994). Ph3Sn-CHCICH2SC6H5NO2-2-Me-4 (PAGHEK; Howie et al., 1992), Ph3SnCH(SCN)CH2C6H5NO2-2 (PAGHIO; Howie et al., 1992), (cyclohexyloxyl)SnCH2C6H5Bu-4 (JERICM; Cox et al., 1990), Ph3Ge(CH2)SO2C6H5 (NOJXEP; Wardell & Cox, 1996), Ph3SnC(SMe)=CH2C6H5 (GODLOA and GODLUG; Bruhn et al., 1999), Ph3SnC(SCH2Ph)CH2C6H5 (POMXUK; Block et al., 1994) and Ph3SnCH2C6H5Me-4 (ZUWQIR; Cox et al., 1995).

Of these, the first four (GESYIM, ZIKHOQ, YEZVII and YEZVII) have C–H⋯O bonds which can be considered in relation to (I) and (II). The latter four compounds (GODLOA, GODLUG, POMXUK and ZUWQIR) display C–H⋯S interactions, while the rest do not form hydrogen bonds, as detected by PLATON (Spek, 2002).

Ph3GeCH2SO2C6H4 (GESYIM), a Ge analogue to (II), forms hydrogen bonds via the CH2 group as donor to a sulfone O atom, thus forming simple C(4) chains along [001]. No rings are formed. Ph3Sn(CH2)2CH(SC6H5NO2-2)CH2Cl (ZIKHOQ), in which the nitro group is ortho to S, again has CH2 as the donor to one nitro O atom as acceptor, forming R21(16) dimers. The other H atom of the CH2 group donates to the other nitro O atom, forming a chain of dimers along [001]. Ph3Sn(CH2)2SO2C6H4Me-4 (YEZVEE) again donates a hydrogen bond via the CH2 group adjacent to S to a sulfone O atom; in addition, a phenyl H atom acts as a donor to the same O atom, forming R21(13) groups which link to give C(8) chains along [010]. In the related compound Ph3Sn(CH2)3SO2C6H4Me-4 (YEZVII), similar hydrogen bonding occurs, although here via the third CH2 group from S, to give an R22(16) motif, linking to give C(12) chains along [010]. Both motifs are enlarged by the extra CH2 groups in the latter compound.

The products of the reactions of o-sulfanylalkylstannanes, R3Sn(CH2)nSR', with oxidants depend greatly on n and on the oxidant. For example, (II) was obtained by H2O2 oxidation of (I), whereas the reaction of the related compound Ph3Sn(CH2)3SC6H5Me-4 [(IV), n = 1] with NaIO4 led to cleavage of the molecule with formation of Ph3SnCH2I and 4-MeC6H5SO2H (Taylor & Wardell, 1976; see also Peterson, 1971). The use of 3-ClC6H4CO3H with (IV), with n = 1, also resulted in cleavage (Wardell, unpublished observation). In contrast, oxidations of (IV) with n = 3 or 4 proceeded readily to the sulfones (III) with n = 3 or 4, or the corresponding sulfoxides, depending on the molar ratios of the reagents (Wardell & Wigzell, 1983). Particularly sensitive to oxidants is compound (IV), with n = 2. The reaction of (IV) with n = 2 with either NaIO4 or 3-ClC6H4CO3H led to loss of ethylene (Wardell & Wigzell, 1983). Compound (IV) with n = 2 was, however, obtained by the addition of Ph3SnH to H2C=C=SO2C6H4Me-4 (Wardell & Wigzell, 1983). The contrast between the Ge and Sn compounds is clear from the reactions of Ph3CH=CSR' (M is Ge or Sn) with 3-ClC6H4CO3H or Br2. The Br2–R3SnCH2SR' reactions invariably result in Sn–C bond cleavage, while the Ge compounds can be oxidized to Ph3GeCH2SO2R' (m = 1 or 2) by either Br2 in MeOH or 3-ClC6H4CO3H (Taylor & Wardell, 1976; Wardell & Cox, 1996).
Compound (I) was prepared from Ph₃SnCH₂I, HSC₆H₄NO₂ and NaOEt (2 mmol scale) in EtOH (20 ml). After refluxing for 2 h, the mixture was cooled, all volatiles removed and the residue recrystallized from EtOH (m.p. 416-418 K). Analysis found: C 58.4, H 5.5, S 6.3, N 3.1%; calculated for C₅₇H₇₆NO₂Sn: C 58.0, H 4.1, S 6.2, N 2.7%. Spectroscopic analysis, ¹H NMR (250 Hz, CDCl₃, δ p.p.m.): 2.88 [s, 2H, J(¹¹⁹Sn-¹⁹²H) = 48.8 Hz, CH₃], 7.41 (m, 11H, m-H + p-H of Ph₃Sn + 2H from C₆H₄), 7.60 [m, 6H, J(¹¹⁹Sn-¹⁹²H) ∼ 75 Hz, o-H of PhSn], 8.10 (d, 2H, J = 8.8 Hz, C₆H₄); ¹³C NMR (63.3 Hz, CDCl₃, δ, p.p.m.): 52.2 (CH₂), 123.8 (C₆), 124.6 (C₈), 128.9 (m-C of PhSn), 129.7 (o-C of PhSn), 136.7 (i-C of PhSn), 144.0 (C₁), 152.7 (C₂); ¹⁹⁵Sn NMR (93.3 Hz, CDCl₃, δ, p.p.m.): -118; IR (KBr, cm⁻¹): 1578 and 1339 (NO₂); Raman (cm⁻¹): 1587, 1331.

Compound (II) was obtained by H₂O₂ oxidation (30% solution in O₂ii 0.95 2.57 3.439 (3) 152
M₁ = 550.18
Triclinic, P₁

5030 independent reflections with
5061 reflections with I > 2σ(I)
ρmax = 0.001
ρmin = 28.9°
h = -9 → 8
k = -13 → 13
l = -23 → 23

Refractive
Refractometry on F²
R(F²) > 2σ(F²) = 0.018
wR(F²) = 0.046
S = 1.10
5261 reflections
289 parameters
H-atom parameters constrained

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<td>w = 1/[σ²(Fo)² + (0.0246P)²]</td>
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<td>0.054237P²</td>
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<td>w = P(Fo)² + 2P²</td>
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<tr>
<td>Δρmax = 0.38 e Å⁻³</td>
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<td>Δρmin = -0.61 e Å⁻³</td>
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Table 2
Hydrogen-bonding geometry (Å, °) for (II).

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<th>H···A</th>
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<td>3.204 (2)</td>
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<tr>
<td>C7-H7···O2ii</td>
<td>0.99</td>
<td>2.36</td>
<td>3.3163 (19)</td>
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Symmetry codes: (i) 1 - x, 2 - y, -z; (ii) -x, 1 - y, -z; (iii) -x, 3 - y, -z.

Structure (II) was solved using Patterson methods (SHELXS86; Sheldrick, 1990) in P₁, and then the coordinates were converted to P₁. All H atoms were placed in geometrically calculated positions, with C—H distances of 0.95 (phenyl) and 0.99 Å (CH₂), and refined using a riding model.

For compound (I), data collection: DENZO (Otwinowski & Minor, 1997) and COLLECT (Hooft, 1998); cell refinement: DENZO and COLLECT; data reduction: DENZO and COLLECT; program(s) used to solve structure: SHELXS86. For compound (II), data collection: SMART (Bruker, 1999); cell refinement: SAINT (Bruker, 1999); data reduction: SAINT; program(s) used to solve structure: SHELX97 (Sheldrick, 1990). For both compounds, program(s) used to refine structure: SHELXL97 (Sheldrick, 1997); molecular graphics: ORTEX in OSCAIL (McArdle, 1994, 2000) and ORTEP-3 for Windows (Farrugia, 1997); software used to prepare material for publication: SHELXL97.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: SK1559). Services for accessing these data are described at the back of the journal.

References