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The influence of crystal packing effects upon the molecular structures of $Ph_3Sn(CH_2)_nSnPh_3$, n = 1 to 8, as determined by X-ray crystallography and DFT molecular orbital calculations. Supramolecular aggregation patterns sustained by C-H…π interactions

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Synthesis

The synthesis and characterisation of the n = (**1**) [D. Dakternieks, R. Altmann, K. Jurkschat and E. R. T. Tiekink, *Z. Kristallogr, - New Cryst. Struct*., 1998, **213**, 525], (**2**) [G. Reeske, M. Schurmann and K. Jurkschat, *Main Group Met. Chem*., 2001, **24**, 389] and (**4**) [D. Dakternieks, Y. Farhangi and E. R. T. Tiekink, *Z. Kristallogr, - New Cryst. Struct*., 1998, **213**, 397] compounds have been reported earlier. The details for the remaining compounds are given below.

$Ph_3Sn(CH_2)_3SnPh_3$ (**3**). Ammonia (800 mL) was condensed into a mechanically stirred solution of triphenyltin chloride (200 g, 519 mmol) at −78 ^oC. Sodium (23.9 g, 1.04 mol) was added in portions to form an orange solution and the mixture was stirred for 2 h at −78 ^oC. A solution of dichloropropane (29.3 g, 259 mmol) in THF (800 mL) was added dropwise over 1 h which produced a grey solution. The solution was stirred for an additional 2 h at −78 ^oC and then allowed to warm to room temperature. The remaining ammonia and THF were removed *in vacuo*. The crude product was placed in a Soxhlet apparatus and extracted with diethyl ether (500 mL) for 12 h. After removing the diethyl ether *in vacuo* the crude product was crystallised from ethanol to give pure (**3**) as a white powder (119 g, 62 %). m. p. 104 ^oC. ^1H NMR ($CDCl_3$): δ 1.42 (t, 4H, $SnCH_2$), 1.74 (quint, 2H, CH_2), 7.26-7.55 (m, 30H). ^{13}C NMR ($CDCl_3$): δ 16.25 [$SnCH_2$, $^1J(^{13}C\text{-}^{117/119}Sn)$ = 365/382 Hz, $^3J(^{13}C\text{-}^{117/119}Sn)$ = 66 Hz], 24.32 [CH_2, $^2J(^{13}C\text{-}^{117/119}Sn)$ = 21 Hz], 128.43, 128.75, 136.99 [$^2J(^{13}C_o\text{-}^{117/119}Sn)$ = 35 Hz], 138.85 [$^1J(^{13}C_i\text{-}^{117/119}Sn)$ = 464/483 Hz]. ^{119}Sn NMR ($CDCl_3$): δ −102.9 [$^1J(^{119}Sn\text{-}^{13}C_i)$ = 482 Hz]. Anal. Calcd. for $C_{39}H_{36}Sn_2$: C, 63.1; H, 4.9. Found: C, 63.2; H, 4.8.

$Ph_3Sn(CH_2)_5SnPh_3$ (**5**). A solution of $BrMg(CH_2)_5MgBr$ [prepared from magnesium (12.6 g, 519 mmol) and 1,5-dibromopentane (29.8 g, 130 mmol) in THF (200 mL)] was added to a solution of Ph_3SnCl (100 g, 259 mmol) in THF (250 mL) and the reaction mixture was maintained at reflux for 24 h. The reaction mixture was hydrolysed with satd. ammonium chloride (200 mL), extracted with diethyl ether (3 x 200 mL) and the combined extracts washed with a solution of KF (10 g) in water (200 mL), dried (Na_2SO_4) and the solvent removed *in vacuo*. The residue was recrystallised from chloroform/hexane (30/70) to afford (**5**) as a white solid (27.1 g, 90 %). m. p. 75 ^oC. ^1H NMR ($CDCl_3$): δ 1.42-1.72 (m, 10H), 7.26-7.56 (m, 30H). ^{13}C NMR ($CDCl_3$): δ 10.80 [$SnCH_2$, $^1J(^{13}C\text{-}^{117/119}Sn)$ = 386 Hz], 25.87 [CH_2, $^2J(^{13}C\text{-}^{117/119}Sn)$ = 22 Hz], 38.70 [CH_2, $^3J(^{13}C\text{-}^{117/119}Sn)$ = 62 Hz], 128.41, 128.75 [$^4J(^{13}C_p\text{-}^{117/119}Sn)$ = 11 Hz], 137.00 [$^2J(^{13}C_o\text{-}^{117/119}Sn)$ = 35 Hz], 139.02. ^{119}Sn NMR ($CDCl_3$): δ –99.3 [$^1J(^{119}Sn\text{-}^{13}C_i)$ = 480 Hz]. Anal. Calcd. for $C_{41}H_{40}Sn_2$: C, 63.9; H, 5.4. Found: C, 63.8; H, 5.5.

$Ph_3Sn(CH_2)_6SnPh_3$ (**6**). In a similar manner to (**5**), compound (**6**) was prepared from magnesium (12.6 g, 518 mmol), 1,6-dichlorohexane (31.7 g, 130 mmol) and Ph_3SnCl (100 g, 259 mmol). Crystallisation from chloroform/hexane (30/70) afforded (**6**) as a white solid (77.1 g, 76 %). m. p. 84 ^oC. ^1H NMR ($CDCl_3$): δ 1.23-1.68 (m, 12H), 7.26-7.64 (m, 30H). ^{13}C NMR ($CDCl_3$): δ 10.99 [$SnCH_2$, $^1J(^{13}C\text{-}^{117/119}Sn)$ = 380/397 Hz], 26.34 [CH_2, $^2J(^{13}C\text{-}^{117/119}Sn)$ = 22 Hz], 33.50 [CH_2, $^3J(^{13}C\text{-}^{117/119}Sn)$ = 60 Hz], 128.39, 128.72, 137.06 [$^2J(^{13}C_o\text{-}^{117/119}Sn)$ = 35 Hz], 139.06. ^{119}Sn NMR ($CDCl_3$): δ –99.1 [$^1J(^{119}Sn\text{-}^{13}C_i)$ = 480 Hz]. Anal. Calcd. for $C_{42}H_{42}Sn_2$: C, 64.3; H, 5.4. Found: C, 64.5; H, 5.2.

$Ph_3Sn(CH_2)_7SnPh_3$ (**7**). In a similar manner to (**5**), compound (**7**) was prepared from magnesium (3.80 g, 155 mmol), 1,7-dibromoheptane (10.0 g, 38.8 mmol) and Ph_3SnCl (29.9 g, 77.5 mmol). Crystallisation from chloroform/hexane (30/70) afforded (**7**) as a white solid (23.1 g, 74 %). m. p. 131-132 ^oC. ^1H NMR ($CDCl_3$): δ 1.25-1.66 (m, 14H), 7.27-7.60 (m, 30H). ^{13}C NMR ($CDCl_3$): δ 11.28 [$SnCH_2$, $^1J(^{13}C\text{-}^{117/119}Sn)$ = 380/397 Hz], 26.71 [CH_2, $^2J(^{13}C\text{-}^{117/119}Sn)$ = 22 Hz], 34.29 [CH_2, $^3J(^{13}C\text{-}^{117/119}Sn)$ = 61 Hz], 28.68, 128.63, 128.96 [$^4J(^{13}C_p\text{-}^{117/119}Sn)$ = 10 Hz], 137.23 [$^2J(^{13}C_o\text{-}^{117/119}Sn)$ = 35 Hz], 139.34 [$^1J(^{13}C_i\text{-}^{117/119}Sn)$ = 459/480 Hz]. ^{119}Sn NMR ($CDCl_3$): δ –98.4 [$^1J(^{119}Sn\text{-}^{13}C_i)$ = 479 Hz, $^1J(^{119}Sn\text{-}^{13}C)$ = 399 Hz]. Anal. Calcd. for $C_{43}H_{44}Sn_2$: C, 64.7; H, 5.5. Found: C, 64.9; H, 5.2.

$Ph_3Sn(CH_2)_8SnPh_3$ (**8**). In a similar manner to (**5**), compound (**8**) was prepared from magnesium (9.30 g, 383 mmol), 1,8-dibromooctane (26.0 g, 957 mmol) and Ph_3SnCl (73.8 g, 191 mmol) and was obtained as a colourless oil which crystallised on standing (44.7 g, 57 %). m. p. 101 ^oC. ^1H NMR ($CDCl_3$): δ 1.19-1.73 (m, 16H), 7.27-7.64 (m, 30H). ^{13}C NMR ($CDCl_3$): δ 11.07 [$SnCH_2$, $^1J(^{13}C\text{-}^{117/119}Sn)$ = 380/397 Hz], 26.46 [CH_2, $^2J(^{13}C\text{-}^{117/119}Sn)$ = 22 Hz], 28.82, 34.12 [CH_2, $^3J(^{13}C\text{-}^{117/119}Sn)$ = 60 Hz], 128.40, 128.73, 137.00 [$^2J(^{13}C_o\text{-}^{117/119}Sn)$ = 35 Hz], 139.11 [$^1J(^{13}C_i\text{-}^{117/119}Sn)$ = 459/480 Hz]. ^{119}Sn NMR ($CDCl_3$): δ –98.9 [$^1J(^{119}Sn\text{-}^{13}C_i)$ = 478 Hz]. Anal. Calcd. for $C_{44}H_{46}Sn_2$: C, 65.1; H, 5.7. Found: C, 65.0; H, 5.8.

Table S(1) Summary of intermolecular interactions (A-H…B; Å, º) operating in the crystal structures of (**1**) – (**8**)

A	H	B	H…B	A…B	A-H…B	Symmetry operation
n = 1 (**1**)						
C12	H12	Cg(C41-C46)	2.98	3.862(7)	154	1-*x*, 2-*y*, -*z*
C24	H24	Cg(C41-C46)	2.95	3.716(9)	139	1-*x*, 1-*y*, -*z*
C34	H34	Cg(C91-C96)	2.85	3.745(8)	157	1-*x*, ½+*y*, ½-*z*
C43	H43	Cg(C31-C36)	2.87	3.615(8)	136	*x*, 1½-*y*, -½+*z*
C53	H53	Cg(C111-C116)	2.91	3.542(6)	125	1-*x*, ½+*y*, ½-*z*
C103	H103	Cg(C121-C126)	2.96	3.597(8)	126	-*x*, -½+*y*, ½-*z*
C115	H115	Cg(C71-C76)	2.96	3.547(8)	121	-*x*, -½+*y*, ½-*z*
C123	H123	Cg(C71-C(76)	2.92	3.593(8)	129	*x*, ½-*y*, ½+*z*
C36	H36	Cg(C51-C56)	2.83	3.753(6)	164	*x*, *y*, *z*
C76	H76	Cg(C101-C106)	2.97	3.811(7)	149	*x*, *y*, *z*

n = 2 (**2**)

C44	H44	Cg(C11-C16)	2.75	3.497(4)	135	1-*x*, 1-*y*, -*z*
C55	H55	Cg(C61-C66)	2.86	3.618(4)	137	-1+*x*, *y*, *z*
C95	H95	Cg(C71-C76)	2.83	3.598(5)	139	2-*x*, -*y*, 1-*z*

n = 3 (**3**)

C14	H14	Cg(C11-C16)	2.86	3.657(11)	142	½-*x*, ½+*y*, 2-*z*
C26	H26	Cg(C11-C16)	2.93	3.800(9)	153	*x*, -1+*y*, *z*
C34	H34	Cg(C41-C46)	2.93	3.643(10)	133	½-*x*, ½+*y*, 1-*z*
C52	H52	Cg(C41-C46)	2.94	3.643(9)	132	*x*, -1+*y*, *z*
C66	H66	Cg(C51-C56)	2.90	3.693(9)	142	*x*, 1+*y*, *z*
C72	H72	Cg(C81-C86)	2.81	3.601(9)	142	*x*, 1+*y*, *z*
C86	H86	Cg(C91-C96)	3.00	3.701(9)	132	*x*, -1+*y*, *z*

n = 4 (**4**)

C1	H1b	Cg(C21-C26)	3.19	3.880(6)	130	-*x*, -*y*, -*z*

C13	H13	Cg(C31-C36)	3.18	3.746(8)	119	*x*, *y*, 1+*z*
C24	H24	Cg(C31-C36)	3.13	3.915(8)	139	1+*x*, *y*, *z*
C26	H26	Cg(C11-C16)	3.13	3.882(6)	135	*x*, *y*, -1+*z*
n = 5 (**5**)						
C3	H3a	Cg(C61-C66)	2.98	3.821(5)	143	1-*x*, -½+*y*, ½-*z*
C22	H22	Cg(C31-C36)	2.88	3.711(4)	147	-*x*, -*y*, -*z*
n = 6 (**6**)						
C23	H23	Cg(C11-C16)	2.68	3.557(5)	154	1-*x*, -*y*, 1-*z*
n = 8 (**8**)						
C25	H25	Cg(C31-C36)	2.94	3.647(5)	132	*x*, -1+*y*, *z*
C33	H33	Cg(C31-C36)	2.86	3.711(5)	150	-*x*, ½+*y*, 1½-*z*