CRYSTAL STRUCTURES OF TETRAKIS(*p*-ETHYLPHENYL)TIN(IV) AND TETRAKIS(*p*-*t*-BUTYLPHENYL)TIN(IV)

Ivor Wharf* and Anne-Marie Lebuis

Department of Chemistry, McGill University, Montreal, Quebec, H3A 2K6,
Canada <wharf@chemistry.mcgill.ca>

ABSTRACT

Single-crystal X-ray studies of $(p\text{-}C_2H_5C_6H_4)_4Sn$ **(A)** and $[p\text{-}(CH_3)_3CC_6H_4]_4Sn$ **(B)** have been undertaken to determine the effect of increasing *para*-substituent size on the structures of tetra-aryltins. Molecules of **(A)** are almost tetrahedral at tin but have 2-fold symmetry. The $p\text{-}C_2H_5$ groups are perpendicular to the phenyl ring planes having the all *exo*-conformation in one-half of the molecule but equally disordered (*exo/endo*) in the other half. In contrast **(B)** crystallises in the unusual tetragonal space group $P4_2/n$, with molecules having -4 symmetry. Four *t*-butyl groups from four adjacent Ar_4Sn molecules form a tetrahedral array around parallel 4_2 axes resulting in strongly directional intermolecular forces and a highly ordered and robust diamantoid network structure for **(B)**.

INTRODUCTION

Symmetric tetra-aryl molecules (MAr_4) and ions (MAr_4^{q}) show a strong tendency to crystallise in tetragonal space groups with the molecules located on sites of -4 (S_4) symmetry,[1] which is the lowest energy molecular configuration for these species.[2-3] Earlier Kitaigorodskii[4] had predicted that such -4 symmetry molecules would closely pack in tetragonal space groups and two of these, $P\text{-}42_1c$ and $I\text{-}4$, account for most MAr_4 structures to date.[1] This arrangement is remarkably resilient, occurring even for some asymmetric $SnPh_{4\text{-}n}(o\text{-}Tol)_n$ structures.[5] However, Kitaigorodskii[4] also predicted that as *para*-hydrogens are replaced by larger substituents the packing efficiency of tetragonal space groups would decrease, ultimately leading to the use of less symmetric space groups with concomitant lower symmetry molecules even if these molecules would have higher energy than if they had –4 symmetry. This effect depends on the size of *M*, i.e. with M = Si, Ge, *p*-H replaced by CH_3 is sufficient (*Pc*).[6] For *M* = Sn, larger *para*-groups seem to be required, thus $CH_3S(O_2)$- gives *C2/c*,[7] while C_2H_5O- gives $P2_1/c$.[8] However, even though Cl and CH_3 are held to be isosteric,[9] $p\text{-}ClC_6H_4)Sn$ is not tetragonal (*P*-1)[10] The third space group proposed by Kitaigorodskii, $P4_2/n$, is little used and has only been found for MAr_4 solvates such as $[p\text{-}CH_3S(O)C_6H_4]_4Sn.H_2O$[11] and $(Ar)_4M.nC_2H_5COOH$ which appear to involve directed H-bonding in the crystal lattice.[11,12]

We now report the structures of two more $(p\text{-}XC_6H_4)_4Sn$, one **(A)** with X = C_2H_5 being isosteric with $(p\text{-}CH_3OC_6H_4)_4Sn$, and the other **(B)** having the sterically demanding *t*-butyl group as the *para*-substituent, in order to interrogate Kitaigorodskii's predictions further.

EXPERIMENTAL

All experimental procedures including microanalyses and solution NMR spectral measurements were as described previously.[13,14] Tetrakis(*p*-*t*-butylphenyl)tin(IV) **(B)** was prepared earlier,[15] *Slow* cooling of a hot chlorobenzene solution of **(B)** gave fine colourless needles.

Tetrakis(p-ethylphenyl)tin(IV) (A)

The title compound was prepared by reacting excess Grignard reagent in THF (from *p*-bromoethylbenzene) with tin tetrachloride in the usual manner.[13] The reaction mixture was hydrolysed (10% aqueous HCl), extracted with benzene, and methanol added to precipitate the crude product, which was then recrystallised from ether. Yield 66%. m.p. 153-155°C. Analysis; Found: C, 71.10: H, 6.82: Calcd. for $C_{32}H_{36}Sn$: C, 71.26· H, 6.73%. NMR data [$CDCl_3$; $(CH_3)_4Sn$ (ext.); $(CH_3)_4Si$ (int.); δ(ppm); *J*(Hz)]: $\delta(^{119}Sn)$ -124.86, $\delta(^{13}C)$ 134.99 (*i*-C), 137.37 (*o*-C), 128.30 (*m*-C), 145.12 (*p*-C), 29.01 (CH_2), 15.60 (CH_3), $^{n}J(^{119}Sn\text{-}^{13}C)$, 535.9 (*n* = 1), 37.7 (*n* = 2), 51.8 (*n* = 3), 11.0 (*n* = 4). Recrystallisation from ethanol/THF (5/1) gave the colourless needles used here.

X-ray structure analyses

For both **(A)** and **(B)**, suitable crystals were selected from those available and examined using a *Rigaku* AFC6S diffractomer. Cell constants and space group for each crystal were obtained using 20 reflections in the θ ranges, **(A)** 25° - 30°, and **(B)** 27° - 30°. Data were collected at 230(2) K using the ω-2θ scan technique. Three standard intensities measured every 150 min showed 1.6% and 2.8% intensity decays for **(A)** and **(B)** respectively. Crystal data as well as other details of the data collection and structure refinement for **(A)** and **(B)** are given in Table 1.

Table 1. Crystal data and structure refinement[a] for compounds **(A)** and **(B)**

	Compound **(A)**	**(B)**
Colour/shape	colourless/needle	colourless/needle
Formula	$C_{32}H_{36}Sn$	$C_{40}H_{52}Sn$
Formula mass (M_r)	539.33	651.55
Crystal system	Monoclinic	Tetragonal
Space group	$C2/c$	$P4_2/n$
a, Å	19.4370(10)	16.661(2)
b, Å	7.159(2)	16.661(2)
c, Å	20.807(2)	6.446(2)
β^{b} (°),	92.256(6)	90
V, Å^3	2893.0(9)	1789.3(6)
Z/$D_{calc.}$ Mg/m^3	4/1.238	2/1.209
μ mm^{-1} [Cu$K\alpha$; λ=1.54056 Å]	7.121	5.838
θ Range for data collection (°)	4.25 to 69.38	3.75 to 70.00
Index ranges	$-23 \le h < 23$ $-8 < k \le 8$ $-25 < l < 25$	$-20 \le h \le 20$ $-16 < k \le 16$ $-7 < l < 7$
Reflections measured	10084	6425
Independent reflections [R_{int}]	2713 [0.0607]	1651 [0.0607]
Observed reflections [$I>2\sigma(I)$]	1968	1163
Data/parameters	2713/170	1651/103
Goodness-of-fit on F^2	1.033	1.136
R indices (R_1/wR_2) [$I>2\sigma(I)$]	0.0385/0.0817	0.0477/0.1150
R indices (R_1/wR_2) [all data]	0.0606/0.0921	0.0728/0.1370
Max. & min. peaks in final diff. map (eÅ^{-3})	0.211; -0.266	0.739/ -0.863

[a] $R_1 = \Sigma(||F_o| - |F_c||)/\Sigma(|F_o|)$; $wR_2 = [\Sigma\{w(F_o^2 - F_c^2)^2\}/\Sigma\{w(F_o^2)^2\}]^{1/2}$; GoF $= [\Sigma\{w(F_o^2 - F_c^2)^2\}/(\text{No of reflns} - \text{No of params})]^{1/2}$.

[b] $\alpha = 90°$, $\gamma = 90°$.

Both structures were solved by direct methods using SHELXS96[16] and difference map synthesis with SHELXL96.[17] All non-hydrogen atoms were anisotropic but H-atoms were isotropic and constrained to the parent site using a riding model with SHELXL96 defaults d(C-H) = 0.93 - 0.98 Å. The U_{iso} values were assigned values of 1.2 x U_{eq} values of each parent site (1.5 x U_{eq} for methyl). A final verification of possible voids was made using the VOID routine of PLATON.[18]

In **(A)** each tin atom lies on a site with 2 symmetry resulting in two phenyl rings in the asymmetric unit. With one of these rings, the p-CH_3CH_2- group is disordered over 2 sites of 50% occupation each; the C(sp^2)—CH_2 distance was made the same for both orientations. The acentric space group Cc was also considered, not only because of the disorder but also due to the intensity distribution of the reflections. The final model in this space group still showed disorder for two of the four independant phenyl rings. Verification of missed symmetry in this model showed that it contained an inversion centre and that the rings were related by a 2-fold axis through the molecule. Hence $C2/c$ is the correct space group for **(A)**.

In **(B)** the t-butyl group is disordered over two sites by ~180° rotation about the C(4)—C(7) bond. The major orientation refined to an occupancy of 0.84. Then for the minor orientation, the occupancy was fixed at 0.16 with the geometry restrained to be similar to that of the major orientation and thermal parameters were fixed to those of the major orientation.

ORTEP[19] views of the molecules of **(A)** and **(B)** are shown in Figs. 1 and 2, respectively.

RESULTS

Compound **(A)** is not tetragonal with -4 molecular symmetry but instead crystallises in the monoclinic space group $C2/c$ with the tin on a 2-fold axis (Fig. 1) as was found earlier for $[p\text{-}CH_3S(O_2)C_6H_4]_4Sn$.[7] However while unit cells for both compounds show similar distortions from "ideal" tetragonal symmetry (β = 92.26° or 93.80° respectively), compound **(A)** is much less distorted from -4 molecular symmetry with almost equal d(Sn—C) values and very little variation from the tetrahedral angle of 109.5° for all angles around tin. In addition the two values of the dihedral angle ϕ (the angle between the aryl ring plane and the CSnC plane containing the principal axis) 45.2(3)° and 45.8(3)° are effectively the same. In fact the most significant deviation from -4 molecular symmetry lies in the orientations assumed by the p-C_2H_5 groups.

For one half of the molecule, the substituents adopt the *exo*-conformation with the expected minimum energy perpendicular configuration found earlier for ethylbenzene itself. However for the other half of the molecule, the *para*-ethyl groups are equally disordered between the *exo*- and *endo*-conformations but with some distortions both with respect to the expected perpendicular configurations and the bond angles at the C_{para} and $\underline{C}H_2$ atoms (Table 2). These distortions are even more pronounced for the *endo*-ethyl groups which would suggest that this conformation is more demanding with regard to crystal packing. In fact the all-*exo*-conformation is adopted by nearly all other substituted Ar_4Sn systems, tetragonal or non-tetragonal.[13,21]

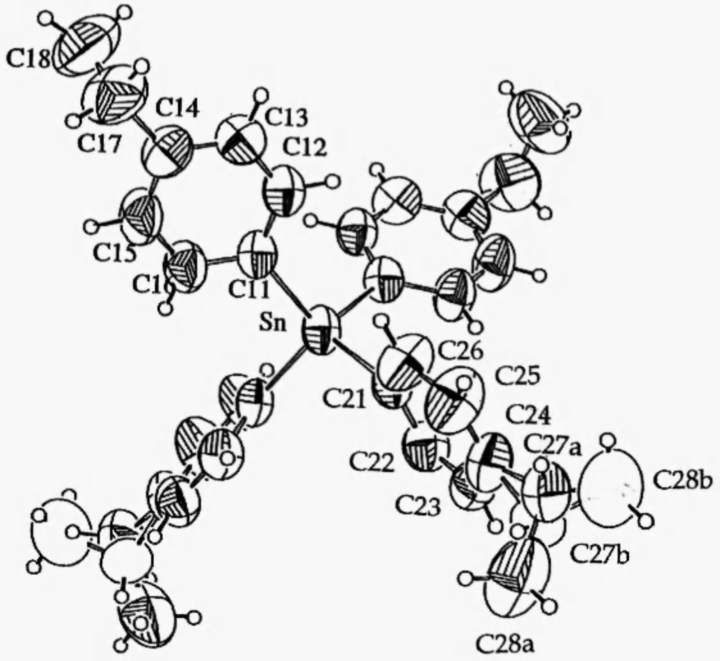

Figure 1. ORTEP view of (A) perpendicular to the 2 axis, showing the numbering scheme adopted. Ellipsoids drawn at the 30% probability level. Hydrogen atoms are represented by spheres of arbitrary size.

In contrast to (A), compound **(B)** is tetragonal (Fig. 2) but with the unexpected space group $P4_2/n$Four *t*-butyl groups from four adjacent Ar_4Sn molecules fit around 4_2 axes parallel to the molecular -4 axes (Fig. 3) giving rise to a diamantoid network like those found earlier in structures involving H-bonding.[11,12]

Further indication that $[p\text{-}(CH_3)_3CC_6H_4]_4Sn$ is a network solid rather than simply close-packed like other Ar_4Sn is given by its mp. 374-6°C, much higher than that of Ph_4Sn (238°C), and its very low solubility in many solvents even compared with Ph_4Sn. The *t*-butyl groups are disordered but both orientations have the *t*-butyl moiety in the minimum energy planar form as found earlier for *t*-butylbenzene and 1-*t*-butyl-4 -ethylbenzene, where one methyl is coplanar with the phenyl ring while the two other methyl groups are at dihedral angles of ± 60° to the ring plane. In **(B)** the major occupancy (0.84) model very closely adheres to this ideal geometry (Table 3) with the in-plane CH_3 groups having the all *endo*-conformation. The minor occupancy model is not as well adjusted with the "in-plane" methyl group 10° away from the "ideal" geometry. The ratio (minor/major) = (0.16/0.84) corresponds to an energy difference of ~4 kJ/mol which is twice the barrier to rotation of an unhindered aromatic *t*-butyl group. It is therefore most likely due to specific inter- and intramolecular interatomic repulsions. However these do not appear to involve the quartet of *tert*-butyl units grouped around the 4_2 axis which give rise to the unexpected diamantoid network structure.

DISCUSSION

The packing in molecular crystals is usually so as to **maximise density** and **minimise free volume** - Kitaigorodskii's Principle of Close Packing. This close-packing is usually accomplished by molecules being complementary in shape like die and coin as proposed by Pauling and Delbreuck (cf. the "bumps and hollows" of Kitaigorodskii[illegible]). Thus most molecular compounds crystallise with unsymmetric molecules in low-symmetry space groups, the most common being $P2_1/c$ and P-1.[illegible] In contrast, symmetric (-4) $M\text{Ph}_4$ achieve the same goal even when crystallising in a highly symmetric tetragonal space group presumably because (a) distortion of the relatively rigid (4) $M\text{Ph}_4$ molecule would require energy, (b) two adjacent $M\text{Ph}_4$ on the same principal axis fit well around a second empty -4 site on this axis in a manner described by Dance as the translational quadruple phenyl embrace (TQPE),[25] giving rise to columns of interlocked $M\text{Ph}_4$ molecules, and (c) these parallel columns can then fit together to give a closely packed square array in the crystal.

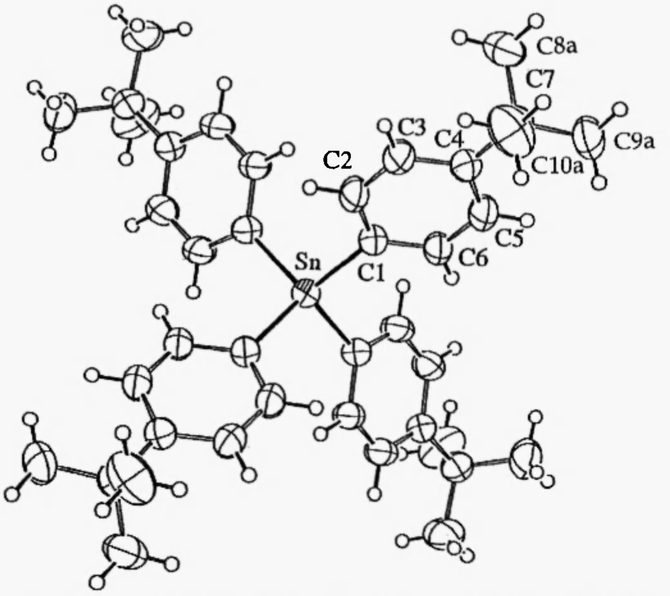

Figure 2. ORTEP view of (**B**) (major orientation) perpendicular to the -4 axis, showing the numbering scheme adopted. Ellipsoids drawn at the 40% probability level. Hydrogens are represented by spheres of arbitrary size.

Table 2. Selected bond lengths (Å) and angles (°) for tetrakis(*p*-ethylphenyl)tin(IV) (**A**)

Sn — C(11)	2.129(4)	C(14)—C(17)	1.525(8)
C(17)—C(18)	1.412(10)	Sn — C(21)	2.125(4)
C(24)—C(27*a*)	1.58(2)	C(24)—C(27*b*)	1.57(2)
C(27*a*)—C(28*a*)	1.61(3)	C(24)—C(27*b*)	1.57(2)
C(11)-Sn-C(11)^a	110.3(2)	C(21)-Sn-C(21)^a	109.2(2)
C(11)-Sn-C(21)	110.3(2)	C(11)-Sn-C(21)^a	108.4(2)
C(14)-C(17)-C(18)	113.4(6)	C(13)-C(14)-C(17)	123.0(6)
C(15)-C(14)-C(17)	120.0(6)	C(24)-C(27*a*)-C(28*a*)	97.8(14)
C(23)-C(24)-C(27*a*)	133.7(14)	C(25)-C(24)-C(27*a*)	109.2(14)
C(24)-C(27*b*)-C(28*b*)	104(2)	C(23)-C(24)-C(27*b*)	112.7(11)
C(25)-C(24)-C(27*b*)	129.7(12)		

C(13)-C(14)-C(17)-C(18)	87.2(9)
C(15)-C(14)-C(17)-C(18)	-92.5(9)
C(23)-C(24)-C(27*a*)-C(28*a*)	-57(3)
C(25)-C(24)-C(27*a*)-C(28*a*)	128(2)
C(23)-C(24)-C(27*b*)-C(28*b*)	108(2)
C(25)-C(24)-C(27*b*)-C(28*b*)	-81(3)

[a] -x, y, -z+3/2 ; (*a*,*b*) occupancy (0.50, 0.50).

Table 3. Selected bond lengths (Å) and angles (°) for tetrakis(p-t-butylphenyl)tin(IV) (**B**)

Sn — C(1)	2.138(5)	C(4)—C(7)	1.535(7)
C(7)—C(8*a*)	1.537(10)	C(7)—C(9*a*)	1.525(9)
C(7)—C(10*a*)	1.518(10)	C(7)—C(8*b*)	1.65(5)
C(7)—C(9*b*)	1.46(5)	C(7)—C(10*b*)	1.47(5)
C(1)-Sn-C(1)[a]	111.4(3)	C(1)-Sn-C(1)[b]	108.50(13)
C(4)-C(7)-C(8*a*)	109.1(5)	C(4)-C(7)-C(9*a*)	112.6(5)
C(4)-C(7)-C(10*a*)	109.7(5)	C(4)-C(7)-C(8*b*)	104.8(14)
C(4)-C(7)-C(9*b*)	109(2)	C(4)-C(7)-C(10*b*)	112(2)
C(3)-C(4)-C(7)-C(8*a*)	60.5(8)		
C(5)-C(4)-C(7)-C(8*a*)	-119.7(7)		
C(3)-C(4)-C(7)-C(9*a*)	178.9(6)		
C(5)-C(4)-C(7)-C(9*a*)	-1.2(9)		
C(3)-C(4)-C(7)-C(10*a*)	-59.4(8)		
C(5)-C(4)-C(7)-C(10*a*)	120.4(7)		

[a] -x+3/2, -y+3/2, z ; [b] y, -x+3/2, -z+3/2 .

Adding *para*-substituents to the above packing model will tend to disrupt the close-packing, particularly between the columns, although this effect may be somewhat mitigated by the substituents adopting the all *exo*-conformation i.e. directed towards the central axis of the molecule. Of like importance is the preferred orientation of the substituent with respect to the phenyl ring which may be due to electronic (p-X = CH_3O or CH_3CH_2O) or simply steric factors (p-X = CH_3CH_2). In the former case the alkoxy group prefers to be copla-nar with the phenyl ring and this is almost true for (p-$CH_3OC_6H_4)_4Sn$[13] (10° dihedral angle) while with the more obtrusive p-CH_3CH_2O substituent the molecule itself is unsymmetric, crystallising in the ubiquitous $P2_1/c$ space group as predicted by Kitaigorodskii[4], but the substituent is coplanar with the phenyl ring for three of the aryl groups and only ~10° out-of-plane for the fourth ring. Thus the whole molecule distorts before losing the preferred conformation of the *para*-substituent. The same is true for (**A**). Each p-CH_3CH_2 substituent retains the lowest energy conformation (~90°) to the phenyl ring with the molecule being distorted from -4 symmetry, even though the change is slight and the unit-cell is not far from tetragonal.

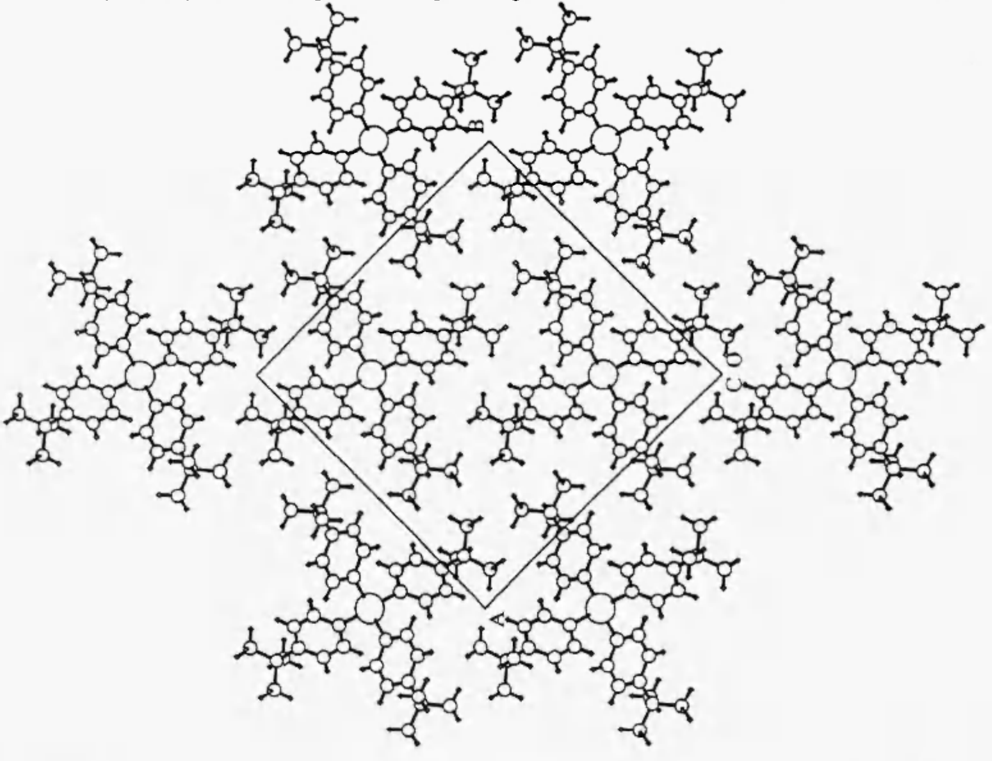

Figure 3. View (PLATON) of the unit cell of (**B**) (major orientation only) looking down the c axis.

Thus the whole molecule distorts before losing the preferred conformation of the *para*-substituent. The same is true for **(A)**. Each *p*-CH_3CH_2 substituent retains the lowest energy conformation (~90°) to the phenyl ring with the molecule being distorted from -4 symmetry, even though the change is slight and the unit-cell is not far from tetragonal.

The tetragonal structure of **(B)** appears to contradict this trend deduced from Kitaigorodskii's model[4] which considers a crystal as collection of molecules packed in the most efficient manner with the intermolecular interactions being much weaker than the covalent bonds of the molecule. Amore recent approach is to consider a crystal as a supermolecule in which mutual recognition of molecules which may already have high symmetry, allows the formation of supramolecular arrays, that is, crystals. Crystal engineering is the rational design of new ordered supramolecular arrays with potentially useful physical and chemical properties. One approach is that of *molecular tectonics*[27] where sticky molecules of high symmetry (*tectons*) self-assemble to highly organised structures, often containing large voids containing guest molecules, such as $(Ar)_4\mathit{M}.\mathit{n}C_2H_5COOH$. These use directed hydrogen bonds in the lattice, and [*p*-$CH_3S(O)C_6H_4]_4Sn.H_2O$ would also seem to fit in this catagory. However well organised structures occur without the need for directed intermolecular forces and **(B)**, isomorphous with [*p*-$CH_3S(O)C_6H_4]_4Sn.H_2O$, is one of these. The assembly of these networks has been analysed by dissecting them into *supramolecular synthons* and *molecular synthons*, the former being the structural units which enable the mutual recognition of symmetric molecules to yield the the supermolecular network of the crystal. Thus (*p*-$BrC_6H_4)_4C$ [*I4*] has molecules (-4 symmetry) assembled with tetrahedral Br_4 clusters acting as *supramolecular synthons.* The crystal structure of (*p*-$CH_3C_6H_4)_4Sn$[29] can be described likewise. In **(B)** (Fig. 3), four methyls, one from each *t*-butyl group, also provide tetrahedral $(CH_3)_4$ clusters as *supramolecular synthons* around the 4_2 axes while there are multiple intermolecular methyl-phenyl attractions also possible. The result is the formation of a very robust ordered lattice with the molecules retaining the lowest energy -4 symmetry conformation even though they are assembled using only weak, non-directional van der Waals type interactions.

SUPPLEMENTARY DATA

Crystallographic data are on deposit at the Cambridge Crystallographic Data Centre, bearing deposition numbers, **(A)** CCDC No.146676, and **(B)** CCDC No. 146677.

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REFERENCES

1. M. L. Lloyd and C.P. Brock , *Acta Cryst*., 1997, **B53**, 780.
2. M.G. Hutchings, J.D. Andose and K. Mislow, *J. Am. Chem. Soc*., 1975, **97**, 4553.
3. M.G. Hutchings, J.D. Andose and K. Mislow, *J. Am. Chem. Soc*., 1975, **97**, 4562.
4. A.I. Kitaigorodskii, *Organic Chemistry Crystallography,* Consultants Bureau, New York, 1961, pp 124-128, 404-406.
5. M. Charisse, A. Zickgraf, H. Stenger, E. Bräu, C. Desmarquet, M. Dräger, S. Gerstmann, D. Dakternieks and J. Hook, *Polyhedron*, 1998, **17**, 4497.
6. M. Charissé, S. Roller and M. Dräger, *J. Organomet. Chem*., 1992, **427**, 23.
7. I. Wharf, M.G. Simard and H. Lamparski, *Can. J Chem*., 1990, **68**, 1277.
8. I. Wharf and M.G. Simard, M.G. *Acta Cryst*., 1991, **C47**, 1314.
9. G.R. Desiraju and J.A.R.P.Sarma, *Proc. Ind. Acad. Sci. (Chem. Sci.)*, 1986, **96**, 599.
10. S.W. Ng, *Acta Cryst*., 1997, **C53**, 273.
11. M. Simard, D. Su, and J. Wuest, *J. Am. Chem. Soc*., 1991, **113**, 4696.
12. X. Wang, M. Simard and J. Wuest, *J. Am. Chem. Soc*., 1994, **116**, 12119.
13. I. Wharf and M.G. Simard, *J. Organomet. Chem*., 1987, **332**, 85.
14. I. Wharf, *Inorg. Chim. Acta*, 1989, **159**, 41.
15. I. Wharf, M.G. Simard and K. McGinn, *Acta Cryst*., 1995, **C51**, 236.
16. G.M. Sheldrick, SHELXS96. Program for the Solution of Crystal Structures. Univ. of Göttingen, Germany, 1996.
17. G.M. Sheldrick, SHELXS96. Program for Structure Analysis. Univ. of Göttingen, Germany, 1995.
18. A.L. Spek, *Acta Cryst*., 1990, **A46**, C34. PLATON-94 version, July 1996.
18. C.K. Johnston, *ORTEPII, Rep. ORNL-5138*, Oak Ridge National Laboratory, Tennessee, USA, 1976.
20. P.J. Breen, E.R. Bernstein and J.I. Seeman, *J. Chem. Phys*., 1987, **87**, 3269.
21. I. Wharf and M.G. Simard, *Acta Crystallogr*., 1995, **B51**, 973.
22. J.I. Seeman, H.V. Secor, P.J. Breen, V.H. Grassian and E.R. Bernstein, *J. Am. Chem. Soc*., 1989, **111**, 3140.

23. L. Pauling and M. Delbreuck, *Science*, 1940, **92**, 77.
24. C.P. Brock and J.D. Dunitz, *Chem. Mater.* 1994, **6**, 1118.
25. I. Dance and M. Scudder, *Chem. Eur. J.* 1996, **2**, 481.
26. G.R. Desiraju, Ed: *Perspectives in Supramolecular Chemistry: The Crystal as a Supramolecular Entity, Vol. 2*, Wiley, Chichester, 1996.
27. D. Su, X. Wang, M. Simard and J.D. Wuest, *Supramolecular Chemistry*, 1995, **6**, 171.
28. D.S. Reddy, D.C. Craig and G.R. Desiraju, *J. Am. Chem. Soc.*, 1996, **118**, 4090.
29. A. Karipides and K. Wolfe, *Acta Crystallogr.*, 1975, **B31**, 605.

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