Acta Cryst. (1995). B**51**, 973–980

Studies in Aryltin Chemistry. IX. Structures of Tetra(*m*-methoxyphenyl)tin(IV) and Tetra(*o*-methoxyphenyl)tin(IV)*

BY I. WHARF

Department of Chemistry and Chemical Technology, Dawson College, 3040 *Sherbrooke St W., Montreal, Que, Canada H*3*Z* 1*A*4

AND M. G. SIMARD

Département de Chimie, Université de Montréal, CP 6128, *Succ. A, Montréal, Qué, Canada H*3*C* 3*J*7

(*Received* 12 *January* 1994; *accepted* 13 *March* 1995)

Abstract

The structures of tetra(*m*-methoxyphenyl)tin (1) and tetra(*o*-methoxyphenyl)tin (2) have been determined at 225 and 290 K, respectively. Crystal data: (1), m.p. 361.5–362.5 K, monoclinic, $C2/c$, $a = 17.534(5)$, $b = 9.908(4)$, $c = 30.011(13)$ Å, $\beta = 108.27(3)°$, $V = 4951(3)$ Å^3, $Z = 8$, $D_x = 1.468$ Mg m^{-3}, $\mu = 1.06$ mm^{-1}, $R = 0.021$ for 3989 observed reflections [$I \geq 3\sigma(I)$]; (2), m.p. 447–449 K, triclinic, $P\bar{1}$, $a = 9.145(6)$, $b = 16.562(5)$, $c = 18.010(8)$ Å, $\alpha = 77.72(3)$, $\beta = 78.52(5)$, $\gamma = 81.70(4)°$, $V = 2597(2)$ Å^3, $Z = 4$, $D_x = 1.399$ Mg m^{-3}, $\mu = 8.24$ mm^{-1}, $R = 0.037$ for 6993 observed reflections [$I \geq 3\sigma(I)$]. For (1), the molecular structure completely deviates from the usual $\bar{4}$ symmetry found for the *para*-analogue, but molecules of (2) have distorted $\bar{4}$ symmetries with the methoxy groups having the all-*exo* conformation. The occurrence of these unsymmetric structures is attributed to the need to maximize crystal lattice stability to offset, in the case of (1), the exigent packing requirements of the *meta*-CH_3O groups, and in the case of (2), the intrinsically high molecular energy compared with the tetraphenyl archetype.

Introduction

Tetra-aryl derivatives of Group 14 elements generally crystallize in close-packed tetragonal space groups ($P\bar{4}2_1$ or $I\bar{4}$) with the molecules having $\bar{4}$ symmetry (Charisée, Roller & Dräger, 1992; Wharf & Simard, 1987). Empirical force-field calculations (Hutchings, Andose & Mislow, 1975) for the molecules Ar_4M [M = C, Si; Ar = C_6H_5, *o*-$CH_3C_6H_4$, 2,6-$(CH_3)_2C_6H_3$] indicated that the ground state conformation of the molecule indeed has $\bar{4}$ symmetry [except $(C_6H_5)_4C$], while earlier less rigorous calculations (Kitaigorodskii, 1961), including both intra- and intermolecular nonbonded forces, predicted a $\bar{4}$ molecular ground state for all $(C_6H_5)_4M$ (M = C, Si, Sn, Pb) with the most favoured crystal structures having molecules closely packed in one of three tetragonal space groups ($P\bar{4}2_1c$, $I\bar{4}$ or $P4_2/n$). Using this model and experimental cell constants, Ahmed, Kitaigorodskii & Mirskaya (1971) were able to reproduce closely the experimentally determined molecular and cell parameters for $(C_6H_5)_4M$. Earlier, Kitaigorodskii (1961) had predicted that as *para*-hydrogens are replaced by larger substituents, the packing efficiency with tetragonal space groups would decrease and less symmetric crystal and molecular structures would then be preferred. This is indeed the case with the large *para*-substituents, $CH_3S(O_2)$ (Wharf, Simard & Lamparski, 1990) and C_2H_5O (Wharf & Simard, 1991). In contrast, we found earlier that for $(p\text{-}CH_3ZC_6H_4)_4Sn$ (Z = O, S), the space group ($I\bar{4}$) is the same as for $(p\text{-Tol})_4Sn$ (Tol = $CH_3C_6H_4$) (Karipides & Wolfe, 1975).

The effects of replacing *meta*- or *ortho*-hydrogens by larger substituents on the structures of Ar_4Sn have received less attention, although *prima facie*, the former change should cause increased intermolecular interactions while the latter would result in more significant steric crowding around the tin. Since both $(m\text{-Tol})_4Sn$ (Karipides & Oertel, 1977) and $(o\text{-Tol})_4Sn$ (Belsky, Simonenko, Reikhsfeld & Saratov, 1983) crystallize in tetragonal space groups, we have examined the structures of $(m\text{-}CH_3OC_6H_4)_4Sn$ (1) and $(o\text{-}CH_3OC_6H_4)_4Sn$ (2) to determine the effects of larger substituents at the *meta*- or *ortho*-positions.

Experimental

Syntheses

Both title compounds were prepared using the Grignard method and characterized as described previously (Wharf & Simard, 1987). For (1), the reaction mixture was treated with methanol to yield the crude product. This was recrystallized from tetrahydrofuran (THF) and then methanol/THF (1:1) to give white plates; m.p. 361.5–362.5 K. Analysis: found: C 61.46, H 5.17;

---

* The correspondence between the second structure in this paper and the first structure in the paper by J. N. Ross, J. L. Wardell, G. Ferguson & J. N. Low [*Acta Cryst.* (1994), C**50**, 1703–1709; received 18 March 1994, accepted 13 June 1994] was missed because of a subtle problem with the IUCr in-house registration software.

Acta Crystallographica Section B
ISSN 0108-7681 © 1995

calc. for $C_{28}H_{28}O_4Sn$: C 61.46, H 5.16%. For (2) the Grignard solution was filtered before the addition of tin tetrachloride. The reaction mixture was hydrolysed (10% aqueous HCl), extracted with benzene, and methanol added to precipitate the crude product which was recrystallized from acetone to give white plates; m.p. 447–449 K. Analysis: found: C 61.39, H 5.25; calc. for $C_{28}H_{28}O_4Sn$: C 61.46, H 5.16%.

Structure determination

Anomalous dispersion terms included for the Sn atoms were obtained from Cromer & Liberman (1970); atomic scattering factors for non-H atoms from Cromer & Mann (1968), and for H atoms from Stewart, Davidson & Simpson (1965). Crystal data, data collection and structure refinement details are in Table 1.

For (1), the structure was solved by the Patterson method and difference Fourier synthesis using *NRCVAX* (Gabe, LePage, Charland, Lee & White, 1989) and *ORTEP* stereodrawings (Johnson, 1965). Full-matrix least-squares refinement based on F's, all non-H atoms anisotropic, H atoms isotropic. Rotational disorder located at one of the methoxy groups, O(4), corresponds to four extra variables added in the refinement (coordinates and isotropic temperature factor). The occupancy ratio was initially refined, then fixed in the final cycles [occ. = 0.70 (major, *exo* conformation); occ. = 0.30 (minor, *endo* conformation)]. H atoms were initially calculated at idealized positions [d(C—H,D) = 0.95 Å, sp^2 or sp^3 hybridization], refined in the last cycles [H(48x) excepted, $U_{\rm iso}$ fixed at the average value 0.06 Å^2]. The secondary extinction coefficient was refined. The final Fourier map showed six peaks of 0.34–0.41 e Å^{-3} at 0.86–1.37 Å from Sn; one peak of 0.86 e Å^{-3} located in the vicinity of the disordered methoxy group was not introduced in the final solution. The background was 0.20 e Å^{-3}.

For (2), the structure was solved by the Patterson method and difference Fourier synthesis using *NRCVAX* (Gabe, LePage, Charland, Lee & White, 1989) and *ORTEP* stereodrawings (Johnson, 1965). Full-matrix least-squares refinement based on F's, all non-H atoms anisotropic, H atoms isotropic. H atoms were initially calculated at idealized positions [d(C—H,D) = 0.95 Å, sp^2 or sp^3 hybridization], isotropically refined in the last cycles. The secondary extinction coefficient was refined. The final Fourier map showed ten peaks of 0.36–0.55 e Å^{-3} at 1.04–1.42 Å from Sn. The background was ≤ 0.33 e Å^{-3}. Complete atom positions and thermal parameters are given in Table 2.*

Table 1. *Crystal data, data collection and refinement parameters*

	(1)	(2)
Crystal data		
Chemical formula	$[Sn(C_7H_7O)_4]$	$[Sn(C_7H_7O)_4]$
Chemical formula weight	547.22	547.22
Cell setting	Monoclinic	Triclinic
Space group	$C2/c$	$P\bar{1}$
a (Å)	17.534 (5)	9.145 (6)
b (Å)	9.908 (4)	16.562 (5)
c (Å)	30.011 (13)	18.010 (8)
α (°)	90	77.72 (3)
β (°)	108.27 (3)	78.52 (5)
γ (°)	90	81.70 (4)
V (Å^3)	4951 (3)	2597 (2)
Z	8	4
D_x (Mg m^{-3})	1.468	1.399
Radiation type	Mo $K\alpha$	Cu $K\alpha$
Wavelength (Å)	0.70930	1.54056
No. of reflections for cell parameters	25	25
θ range for cell parameters (°)	25–35	44–48
μ (mm^{-1})	1.06	8.24
Temperature (K)	225	290
Crystal color	White	White
Crystal form	Parallelepiped	Parallelepiped
Crystal size (mm)	0.48 (001, $00\bar{1}$) × 0.46 ($1\bar{1}\bar{1}$, $\bar{1}11$) × 0.40 (100, $\bar{1}00$)	0.38 (100, $\bar{1}00$) × 0.19 ($0\bar{1}0$, 011) × 0.11 (001, $00\bar{1}$)
Crystal source	Slow evaporation of a thf/methanol solution	Slow evaporation of a methanol solution
Data collection		
Diffractometer	Enraf–Nonius	Enraf–Nonius
Data collection method	$\omega/2\theta$ scans	$\omega/2\theta$ scans
Absorption correction	None	Gaussian by integration from crystal shape (10 × 10 × 10)
$T_{\rm max}$		0.51
$T_{\rm min}$		0.13
No. of measured reflections	8399	19 394
No. of independent reflections	4342	9862
No. of observed reflections	3989	6993
Criterion for observed reflections	$I \geq 3\sigma(I)$	$I \geq 3\sigma(I)$
$R_{\rm int}$	0.023	0.023
$\theta_{\rm max}$ (°)	50.0	140
Range of h, k, l	$-20 \rightarrow h \rightarrow 19$ $0 \rightarrow k \rightarrow 11$ $0 \rightarrow l \rightarrow 35$	$-10 \rightarrow h \rightarrow 11$ $0 \rightarrow k \rightarrow 20$ $-21 \rightarrow l \rightarrow 31$
No. of standard reflections	3	4
Frequency of standard reflections (min)	60	60
Intensity decay (%)	±0.8	±0.7
Refinement		
Refinement on	F	F
R	0.021	0.037
wR	0.029	0.038
S	2.20	1.64
No. of reflections used	3989	6993
No. of parameters used	420	820
Weighting scheme	$w = 1/[\sigma^2(F) + 0.0001F^2]$	$w = 1/[\sigma^2(F)) + 0.0001F^2]$
$(\Delta/\sigma)_{\rm max}$	0.15	0.19
$\Delta\rho_{\rm max}$ (e Å^{-3})	0.87	0.55
$\Delta\rho_{\rm min}$ (e Å^{-3})	−0.49	−0.65
Extinction correction	Zachariasen (1967)	Zachariasen (1967)
Extinction coefficient	0.462 (13)	1.136 (18)
Source of atomic scattering factors	Cromer & Mann (1968) for non-H atoms and Stewart, Davidson & Simpson (1965) for H atoms	Cromer & Mann (1968) for non-H atoms and Stewart, Davidson & Simpson (1965) for H atoms

---

[*] Lists of structure factors, anisotropic thermal parameters, H-atom coordinates, complete geometry and least-squares planes data have been deposited with the IUCr (Reference: BK1035). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 2. *Fractional atomic coordinates and equivalent isotropic displacement parameters* (Å^2)

$$B_{\text{iso}} = (1/3)\Sigma_i\Sigma_j B_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	B_{iso}
Compound (1)				
Sn	0.310720 (8)	0.017905 (14)	0.886303 (5)	2.114 (6)
O(1)	0.11775 (10)	−0.30013 (17)	0.95837 (6)	3.20 (7)
O(2)	0.23616 (10)	0.55085 (16)	0.85337 (6)	3.25 (8)
O(3)	0.09361 (11)	−0.24669 (18)	0.74470 (6)	3.93 (8)
O(4)	0.52231 (16)	−0.27220 (21)	0.82822 (7)	5.88 (12)
C(11)	0.24584 (13)	−0.03330 (21)	0.93336 (7)	2.24 (9)
C(12)	0.20410 (13)	−0.15521 (21)	0.92924 (7)	2.30 (9)
C(13)	0.16081 (12)	−0.18441 (22)	0.95953 (7)	2.40 (9)
C(14)	0.15917 (14)	−0.09288 (25)	0.99406 (8)	2.92 (10)
C(15)	0.20051 (16)	0.02685 (24)	0.99865 (9)	3.05 (10)
C(16)	0.24382 (14)	0.05701 (23)	0.96838 (8)	2.67 (10)
C(17)	0.11392 (15)	−0.39380 (26)	0.92209 (9)	3.45 (11)
C(21)	0.33944 (13)	0.22796 (21)	0.89467 (7)	2.27 (9)
C(22)	0.27788 (13)	0.31910 (21)	0.87302 (8)	2.42 (9)
C(23)	0.29292 (14)	0.45587 (22)	0.87462 (8)	2.43 (9)
C(24)	0.36928 (15)	0.50489 (21)	0.89842 (8)	2.61 (10)
C(25)	0.42971 (14)	0.41517 (25)	0.92024 (8)	2.83 (9)
C(26)	0.41530 (13)	0.27766 (23)	0.91817 (8)	2.57 (10)
C(27)	0.16299 (18)	0.50026 (25)	0.82202 (11)	4.13 (12)
C(31)	0.23794 (14)	−0.00640 (21)	0.81444 (8)	2.40 (9)
C(32)	0.18944 (14)	−0.11812 (22)	0.80030 (7)	2.55 (9)
C(33)	0.13934 (13)	−0.13220 (23)	0.75415 (8)	2.67 (10)
C(34)	0.13845 (15)	−0.03381 (26)	0.72156 (8)	3.20 (11)
C(35)	0.18819 (16)	0.07713 (28)	0.73550 (9)	3.67 (12)
C(36)	0.23723 (15)	0.09150 (24)	0.78105 (8)	3.20 (11)
C(37)	0.04156 (17)	−0.26787 (33)	0.69818 (9)	4.62 (14)
C(41)	0.41511 (12)	−0.10565 (20)	0.89830 (7)	2.23 (9)
C(42)	0.43764 (14)	−0.14758 (22)	0.86024 (7)	2.65 (9)
C(43)	0.50342 (15)	−0.23271 (23)	0.86669 (9)	3.20 (11)
C(44)	0.54700 (14)	−0.27545 (24)	0.91120 (9)	3.35 (11)
C(45)	0.52483 (14)	−0.23351 (25)	0.94894 (8)	3.22 (10)
C(46)	0.45893 (14)	−0.14943 (23)	0.94269 (8)	2.84 (10)
C(47)*	0.56782 (25)	−0.38386 (44)	0.83061 (17)	4.95 (21)
C(48)*	0.50392 (54)	−0.22474 (99)	0.78525 (29)	4.03 (42)
Compound (2)				
Sn(1)	0.25660 (4)	0.27909 (2)	0.20290 (2)	3.957 (14)
Sn(2)	0.99341 (4)	0.77425 (2)	0.30005 (2)	3.623 (13)
O(11)	0.0837 (4)	0.4539 (2)	0.1654 (2)	5.08 (18)
O(12)	0.0773 (4)	0.1346 (2)	0.2867 (2)	6.70 (22)
O(13)	0.4062 (4)	0.1890 (2)	0.0700 (2)	6.55 (21)
O(14)	0.4944 (4)	0.3263 (2)	0.2852 (2)	5.60 (20)
O(21)	1.1486 (4)	0.6023 (2)	0.3572 (2)	5.15 (18)
O(22)	1.1769 (4)	0.9072 (2)	0.1942 (2)	5.63 (19)
O(23)	0.8494 (4)	0.8803 (2)	0.4238 (2)	5.37 (18)
O(24)	0.7555 (4)	0.6970 (2)	0.2410 (2)	5.38 (19)
C(111)	0.0903 (5)	0.3477 (3)	0.2738 (3)	4.1 (2)
C(112)	0.0327 (5)	0.4282 (3)	0.2434 (3)	4.0 (2)
C(113)	−0.0680 (6)	0.4769 (3)	0.2886 (3)	4.7 (3)
C(114)	−0.1138 (6)	0.4442 (3)	0.3655 (3)	5.2 (3)
C(115)	−0.0617 (6)	0.3649 (3)	0.3980 (3)	5.4 (3)
C(116)	0.0404 (6)	0.3174 (3)	0.3518 (3)	4.9 (3)
C(117)	0.0316 (7)	0.5353 (3)	0.1297 (3)	5.9 (3)
C(121)	0.3279 (6)	0.1591 (3)	0.2673 (3)	4.6 (3)
C(122)	0.2212 (6)	0.1027 (3)	0.2964 (3)	5.1 (3)
C(123)	0.2631 (7)	0.0211 (3)	0.3318 (3)	6.4 (3)
C(124)	0.4125 (8)	−0.0023 (3)	0.3378 (4)	7.9 (4)
C(125)	0.5170 (7)	0.0509 (4)	0.3099 (4)	7.8 (4)
C(126)	0.4744 (6)	0.1319 (3)	0.2755 (3)	6.0 (3)
C(127)	−0.0321 (8)	0.0811 (4)	0.2988 (4)	8.3 (4)
C(131)	0.1699 (5)	0.2561 (3)	0.1079 (3)	4.4 (2)
C(132)	0.2606 (6)	0.2105 (3)	0.0566 (3)	4.6 (2)
C(133)	0.2076 (7)	0.1881 (3)	−0.0021 (3)	6.2 (3)
C(134)	0.0608 (8)	0.2130 (4)	−0.0103 (4)	7.7 (4)
C(135)	−0.0313 (7)	0.2584 (4)	0.0380 (4)	7.9 (4)
C(136)	0.0212 (6)	0.2796 (3)	0.0974 (4)	6.2 (3)
C(137)	0.5094 (7)	0.1464 (4)	0.0193 (4)	8.5 (4)
C(141)	0.4484 (5)	0.3471 (3)	0.1584 (3)	3.7 (2)
C(142)	0.5399 (5)	0.3589 (3)	0.2083 (3)	4.1 (2)
C(143)	0.6658 (6)	0.4024 (3)	0.1805 (3)	5.2 (3)
C(144)	0.6997 (6)	0.4335 (3)	0.1019 (3)	5.4 (3)
C(145)	0.6131 (6)	0.4235 (3)	0.0522 (3)	5.0 (3)
C(146)	0.4879 (5)	0.3800 (3)	0.0804 (3)	4.3 (2)
C(147)	0.5979 (8)	0.3168 (5)	0.3360 (4)	9.5 (5)
C(211)	1.1627 (5)	0.6955 (3)	0.2403 (3)	3.6 (2)
C(212)	1.2117 (5)	0.6177 (3)	0.2802 (3)	4.1 (2)
C(213)	1.3142 (6)	0.5618 (3)	0.2435 (5)	4.7 (2)
C(214)	1.3704 (6)	0.5854 (3)	0.1655 (3)	5.2 (3)
C(215)	1.3271 (6)	0.6623 (3)	0.1246 (3)	4.9 (2)
C(216)	1.2234 (5)	0.7169 (3)	0.1620 (3)	4.1 (2)
C(217)	1.1963 (7)	0.5261 (3)	0.4036 (3)	6.5 (3)
C(221)	0.9273 (5)	0.8797 (3)	0.2161 (3)	4.0 (2)
C(222)	1.0378 (6)	0.9296 (3)	0.1734 (3)	4.4 (2)
C(223)	1.0063 (7)	0.9971 (3)	0.1166 (3)	6.1 (3)
C(224)	0.8618 (8)	1.0148 (4)	0.1029 (4)	7.8 (4)
C(225)	0.7496 (7)	0.9683 (4)	0.1442 (4)	7.3 (4)
C(226)	0.7837 (6)	0.8997 (3)	0.2002 (3)	5.4 (3)
C(227)	1.2965 (7)	0.9535 (4)	0.1534 (4)	7.8 (4)
C(231)	1.0835 (6)	0.8094 (3)	0.3878 (3)	4.1 (2)
C(232)	0.9920 (6)	0.8558 (3)	0.4388 (3)	4.3 (2)
C(233)	1.0451 (6)	0.8751 (3)	0.4995 (3)	5.3 (3)
C(234)	1.1920 (7)	0.8482 (3)	0.5088 (3)	6.1 (3)
C(235)	1.2859 (6)	0.8037 (3)	0.4584 (3)	5.5 (3)
C(236)	1.2318 (6)	0.7836 (3)	0.3987 (3)	4.6 (2)
C(237)	0.7376 (7)	0.9103 (4)	0.4813 (4)	7.4 (4)
C(241)	0.8062 (5)	0.7073 (3)	0.3597 (3)	4.0 (2)
C(242)	0.7150 (5)	0.6798 (3)	0.3198 (3)	4.3 (2)
C(243)	0.5920 (6)	0.6362 (3)	0.3587 (3)	5.8 (3)
C(244)	0.5655 (6)	0.6198 (3)	0.4380 (4)	6.6 (3)
C(245)	0.6560 (7)	0.6452 (3)	0.4789 (3)	6.2 (3)
C(246)	0.7759 (6)	0.6887 (3)	0.4396 (3)	5.0 (2)
C(247)	0.6587 (8)	0.6782 (4)	0.1954 (4)	7.8 (4)

* Corresponding to the disordered methoxy group [occ. C(47) = 0.70; occ. C(48) = 0.30].

Results

Selected bond lengths and angles for compounds (1) and (2) are given in Tables 3 and 4, respectively, with numbering schemes in Figs. 1 and 2. In addition, refined H-atom positions (deposited) give for (1): d(C—H) = 0.89–1.10 Å [av. 0.97 (5); B_{iso} = 1.6–6.3 Å^2 (av. 4.0)] and for (2): d(C—H) = 0.92–1.02 Å [av. 0.97 (2); B_{iso} = 4.5–11.0 Å^2 (av. 7.5)]. Both (1) and (2) crystallize in non-tetragonal space groups $C2/c$ and $P\bar{1}$, respectively. Stereoviews of the unit cells showing the crystal packing are shown in Figs. 3 and 4 for (1) and (2), respectively. For (1), the Sn atoms lie on general positions and, therefore, the molecules are asymmetric, as are those of (2).

Discussion

The symmetries of Ar$_4M$ molecules, even those with 'ideal' tetrahedral C$_4M$ skeletons, vary depending on the aryl ring orientations. These can be expressed by the dihedral angle φ (the angle between the aryl ring plane and the CSnC plane containing the principal axis). In addition, the geometry around the central atom can be summarized by values of d(Sn—C) and the angles θ and β (Fig. 5). When the aryl groups have *meta-* or *ortho-*substituents, the molecular symmetry will also depend on whether the substituents are *exo* (directed away from the equatorial plane, $0 < \varphi < 90°$) or *endo* ($90 < \varphi < 180°$).

Table 3. *Selected geometric parameters* (Å, °) *for* (1)

Sn—C(11)	2.134 (2)	Sn—C(31)	2.148 (2)
Sn—C(21)	2.138 (2)	Sn—C(41)	2.137 (2)
O(1)—C(13)	1.367 (3)	O(3)—C(33)	1.367 (2)
O(1)—C(17)	1.416 (3)	O(3)—C(37)	1.424 (2)
O(2)—C(23)	1.373 (2)	O(4)—C(43)	1.355 (3)
O(2)—C(27)	1.423 (2)	O(4)—C(47)	1.353 (5)
		O(4)—C(48)	1.314 (9)
C(48)···C(48^{i})	2.08 (2)	C(48)···H(48B^{i})	1.71
C(48)···H(48A^{i})	1.87	C(48)···H(48C^{i})	2.29
H(48A)···H(48A^{i})	1.94	H(48B)···H(48B^{i})	1.76
H(48A)···H(48B^{i})	1.12	H(48B)···H(49C^{i})	2.07
H(48A)···H(48C^{i})	2.29	H(48C)···H(48C^{i})	2.10
H(47A)···H(48A^{i})	2.22	H(22)···H(47C^{ii})	2.19 (5)
C(11)—Sn—C(21)	107.97 (8)	C(21)—Sn—C(41)	112.35 (8)
C(11)—Sn—C(31)	111.46 (9)	C(31)—Sn—C(41)	108.23 (8)
C(11)—Sn—C(41)	111.01 (8)	C(23)—O(2)—C(27)	116.0 (2)
C(13)—O(1)—C(17)	117.5 (2)	O(2)—C(23)—C(22)	123.7 (2)
O(1)—C(13)—C(12)	124.8 (2)	O(2)—C(23)—C(24)	116.1 (2)
O(1)—C(13)—C(14)	115.3 (2)	C(43)—O(4)—C(47)	119.3 (3)
C(33)—O(3)—C(37)	118.7 (2)	O(4)—C(43)—C(42)	118.0 (2)
O(3)—C(33)—C(32)	115.8 (2)	O(4)—C(43)—C(44)	121.8 (2)
O(3)—C(33)—C(34)	124.4 (2)	C(43)—O(4)—C(48)	133.0 (5)
C(21)—Sn—C(31)	105.73 (8)		

C(17)—O(1)—C(13)—C(12)	−3.3 (1)
C(27)—O(2)—C(23)—C(22)	−10.7 (1)
C(37)—O(3)—C(33)—C(32)	−179.5 (3)
C(47)—O(4)—C(43)—C(42)	−159.7 (3)
C(48)—O(4)—C(43)—C(42)	18.7 (4)
C(17)—O(1)—C(13)—C(14)	176.7 (2)
C(27)—O(2)—C(23)—C(24)	168.7 (2)
C(37)—O(3)—C(33)—C(34)	0.4 (1)
C(47)—O(4)—C(43)—C(44)	19.8 (2)
C(48)—O(4)—C(43)—C(44)	−161.8 (5)

Symmetry codes: (i) $1 - x, y, \frac{3}{2} - z$; (ii) $x - \frac{1}{2}, \frac{1}{2} + y, z$.

Table 4. *Selected geometric parameters* (Å, °) *for* (2)

Sn(1)—C(111)	2.140 (5)	Sn(2)—C(211)	2.146 (4)
Sn(1)—C(121)	2.160 (5)	Sn(2)—C(221)	2.154 (4)
Sn(1)—C(131)	2.146 (5)	Sn(2)—C(231)	2.137 (4)
Sn(1)—C(141)	2.148 (5)	Sn(2)—C(241)	2.151 (5)
O(11)—C(112)	1.383 (6)	O(21)—C(212)	1.376 (6)
O(11)—C(117)	1.422 (6)	O(21)—C(217)	1.420 (6)
O(12)—C(122)	1.376 (7)	O(22)—C(222)	1.375 (6)
O(12)—C(127)	1.385 (7)	O(22)—C(227)	1.417 (7)
O(13)—C(132)	1.382 (6)	O(23)—C(232)	1.372 (6)
O(13)—C(137)	1.400 (7)	O(23)—C(237)	1.420 (7)
O(14)—C(142)	1.377 (6)	O(24)—C(242)	1.371 (6)
O(14)—C(147)	1.413 (7)	O(24)—C(247)	1.426 (7)
Sn(1)···O(11)	3.100 (3)	Sn(2)···O(21)	3.059 (3)
Sn(1)···O(12)	3.051 (4)	Sn(2)···O(22)	3.051 (4)
Sn(1)···O(13)	3.075 (4)	Sn(2)···O(23)	3.101 (3)
Sn(1)···O(14)	3.131 (4)	Sn(2)···O(24)	3.131 (3)
C(111)—Sn(1)—C(121)	111.2 (2)	C(232)—O(23)—C(237)	119.1 (4)
C(111)—Sn(1)—C(131)	111.2 (2)	C(242)—O(24)—C(247)	118.4 (4)
C(111)—Sn(1)—C(141)	110.0 (2)	O(11)—C(112)—C(111)	114.3 (4)
C(121)—Sn(1)—C(131)	106.6 (2)	O(11)—C(112)—C(113)	123.8 (4)
C(121)—Sn(1)—C(141)	108.9 (2)	O(12)—C(122)—C(121)	114.4 (4)
C(131)—Sn(1)—C(141)	108.9 (2)	O(12)—C(122)—C(123)	124.9 (5)
C(112)—O(11)—C(117)	118.1 (4)	O(13)—C(132)—C(131)	114.3 (4)
C(122)—O(12)—C(127)	119.5 (5)	O(13)—C(132)—C(133)	123.6 (5)
C(132)—O(13)—C(137)	119.1 (5)	O(14)—C(142)—C(141)	115.3 (4)
C(142)—O(14)—C(147)	118.5 (4)	O(14)—C(142)—C(143)	123.6 (4)
C(211)—Sn(2)—C(221)	107.6 (2)	O(21)—C(212)—C(211)	114.0 (4)
C(211)—Sn(2)—C(231)	108.7 (2)	O(21)—C(212)—C(213)	124.3 (4)
C(211)—Sn(2)—C(241)	110.7 (2)	O(22)—C(222)—C(221)	114.5 (4)
C(221)—Sn(2)—C(231)	112.4 (2)	O(22)—C(222)—C(223)	123.6 (4)
C(221)—Sn(2)—C(241)	111.8 (2)	O(23)—C(232)—C(231)	114.8 (4)
C(231)—Sn(2)—C(241)	105.6 (2)	O(23)—C(232)—C(233)	123.9 (4)
C(212)—O(21)—C(217)	118.3 (4)	O(24)—C(242)—C(241)	115.0 (4)
C(222)—O(22)—C(227)	118.5 (4)	O(24)—C(242)—C(243)	123.7 (4)

C(117)—O(11)—C(112)—C(111)	−179.6 (6)
C(127)—O(12)—C(122)—C(121)	167.1 (7)
C(137)—O(13)—C(132)—C(131)	−176.9 (7)
C(147)—O(14)—C(142)—C(141)	164.3 (7)
C(217)—O(21)—C(212)—C(211)	−177.3 (7)
C(227)—O(22)—C(222)—C(221)	179.1 (7)
C(237)—O(23)—C(232)—C(231)	165.4 (7)
C(247)—O(24)—C(242)—C(241)	−173.8 (7)
C(117)—O(11)—C(112)—C(113)	0.9 (4)
C(127)—O(12)—C(122)—C(123)	−12.8 (4)
C(137)—O(13)—C(132)—C(133)	3.8 (4)
C(147)—O(14)—C(142)—C(143)	−17.0 (4)
C(217)—O(21)—C(212)—C(213)	3.4 (4)
C(227)—O(22)—C(222)—C(223)	−2.6 (4)
C(237)—O(23)—C(232)—C(233)	−15.0 (4)
C(247)—O(24)—C(242)—C(243)	7.4 (4)

Thus, where all aryl rings are rotated to the same degree, *e.g.* the anticlockwise all-*exo* conformation shown in Fig. 5, the molecule has $\bar{4}$ symmetry, if d(Sn—C), θ and β have unique values (Table 5).

For both (1) and (2), the central C_4Sn geometries (Table 5) show the molecules are asymmetric with apparently similar distortions from the 'ideal' $\bar{4}$ symmetry. However, study of the conformations of the aryl rings in the two structures enables more fruitful structural comparisons to be made with each other or with the $\bar{4}$ symmetries listed in Table 5. For example, the view of (1) down the putative principal axis taken through the centres of angles C(11)—Sn—C(41) and C(21)—Sn—C(31) (Fig. 6) shows the molecule has no symmetry whatsoever, with two of the four aryl groups *endo* rather than *exo*, and large variations in the dihedral angles. Equally irregular structures are apparent when the molecule is viewed down the two other principal axes. In contrast, the equivalent view of either of the two molecules forming the asymmetric unit of (2) (Fig. 7) shows both to have pseudo-$\bar{4}$-symmetry with all CH_3O groups *exo* [$\varphi \simeq 61°$ (av.)], thus closely resembling the $\bar{4}$ structure of (*o*-Tol)$_4$Sn.

The loss of $\bar{4}$ symmetry when a *meta*- or *ortho*-CH_3 group is replaced by a methoxy group is clearly related to the more exacting steric requirements of the CH_3O group, which remains coplanar with the phenyl ring as in (*p*-$CH_3OC_6H_4$)$_4$Sn (Wharf & Simard, 1987). This preferred planarity, which is ascribed to $2p_O$–π_{ring} conjugation with a barrier to internal rotation about the O—Csp^2 bond of *ca* 25 kJ mol^{-1} (Schaeffer *et al.*, 1984), however, still allows for two methoxy group orientations when there are no adjacent substituents on the phenyl ring (Schaeffer, Salman, Wildman & Penner, 1985). In fact, in (1) the close packing in the cell (Fig. 3) prevents this disorder occurring, with *m*-CH_3O groups on rings (1) and (2) directed towards the centre of the molecule and on ring (3) away from the central tin atom. Only for ring (4) is the disorder expected for a methoxy group almost coplanar with a phenyl ring observed (Fig. 1). However, the short intermolecular interatomic distances required (Table 3) when both neighbouring ring (4) units on adjacent molecules have the CH_3O

groups oriented towards the central tin would suggest this arrangement does not occur in practice. Thus, the occupancy ratio (67:33) predicted on this basis for CH_3O on ring (4) is almost the same as that found (70:30). Indeed, the exigent packing requirements of the minor occupancy arrangement of the CH_3O group may account for the distortions observed from its usual geometry, *e.g.* $C_{sp^2}OCH_3$ = 133° compared with the usual 119°, the larger distance between adjacent non-bonded carbons, 2.94 Å compared with 2.8 Å (av.) usually observed, and the shorter (O—CH_3) bond length.

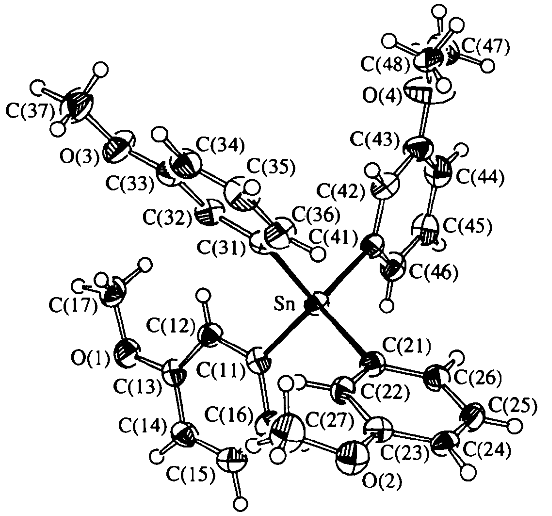


Fig. 1. *ORTEP* (50% probability level) drawing of the molecule forming the asymmetric unit in (1), showing the disorder present for one of the methoxy groups.

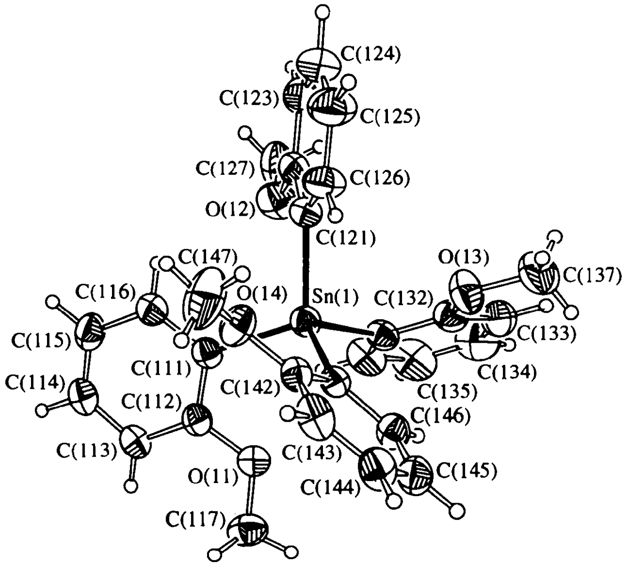


Fig. 2. *ORTEP* (40% probability level) drawing of molecule *A* in the asymmetric unit of (2).

In compound (2), as in (o-Tol)$_4$Sn, there are no significant intermolecular contacts. However, the bending towards the tin of the CH_3O groups (Table 4), caused by the repulsions between methyls almost coplanar with the adjacent phenyl ring atoms, forces the O atoms close to the Sn (av. S—O = 3.09 Å). The similar short Sn—O distances in (o-$CH_3OC_6H_4$)$_3$SnI [3.02 Å (av.) (Howie, Ross, Wardell & Low, 1994)] and (o-$CH_3OC_6H_4$)$_2$SnBr$_2$ [2.91 Å (av.) (Ross & Wardell, 1994)] have been taken as evidence for weak Sn···O intramolecular interactions. However, the trend in *d*(Sn···O) values could equally well be ascribed to the increased Lewis acidity of tin or better packing of the O atoms around tin as aryl groups are replaced by halogens.

The consequences of substituent position on Ar$_4$Sn structures as hydrogen is replaced by CH_3 and then CH_3O groups are now apparent. In the *para*-position, the effect is minimal with the larger CH_3O group and its enforced coplanarity readily accommodated in a structure which retains the $\bar{4}$ molecular ground state and the close packing required to minimize free volume in molecular crystals (Brock & Dunitz, 1994).

With the *meta*-substituents, the consequences are dire with, first, the loss of close packing in (m-Tol)$_4$Sn ($I4_1/a$) and then in (1), the complete loss of crystal and molecular symmetry (Fig. 6). Thus, the extramolecular steric requirements of *meta*-CH_3O groups require the loss of $\bar{4}$ molecular symmetry so that the asymmetric molecules have the necessary bumps and hollows (Kitaigorodskii, 1961) to provide the close packing which can then achieve the structure with overall maximum stability.

In the case of *ortho*-substituents, intramolecular effects appear to predominate with (o-Tol)$_4$Sn ($P\bar{4}2_1c$) retaining $\bar{4}$ symmetry as predicted for (o-Tol)$_4$Si, while

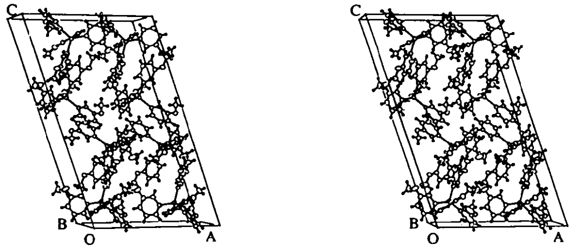


Fig. 3. Stereoview for (1).

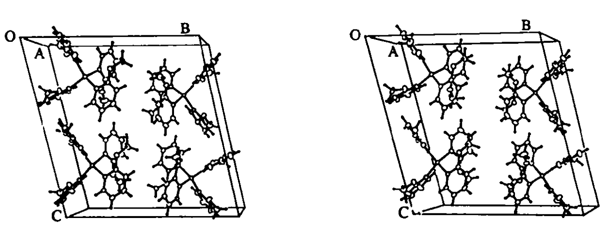


Fig. 4. Stereoview for (2).

in (2), the deviation (Fig. 7) from this symmetry is relatively small. However, (*o*-Tol)$_4$Ge ($P\bar{1}$) (Belsky, Simonenko & Reikhsfeld, 1984) also has the loss of molecular symmetry as well as bending of the *o*-CH_3 groups away from the central metal atom. Thus, the close packing of these sterically crowded identical Ar_4M may require a molecular distortion causing a slight increase in the already high molecular energy (compared with Ph_4M), but yielding molecules with complementary surfaces, such as die and coin (Pauling & Delbrück, 1940), which are needed to achieve the maximum crystal stability.

Both (*o*-Tol)$_4$Ge and (2) have like molecules packing across inversion centres. In addition, in (2) the two independent molecules in the asymmetric unit which clearly bear a close resemblance appear to pack across a pseudo-inversion centre (Fig. 4) which, calculated as the centroid of the non-H atoms of the asymmetric unit, is located at a general position [0.628 (5), 0.522 (9), 0.252 (14)]. Whether this position actually represents a pseudo-inversion centre according to the accepted criteria (Desiraju, Calabrese & Harlow, 1991) was not determined but more evident is the pseudo-translation

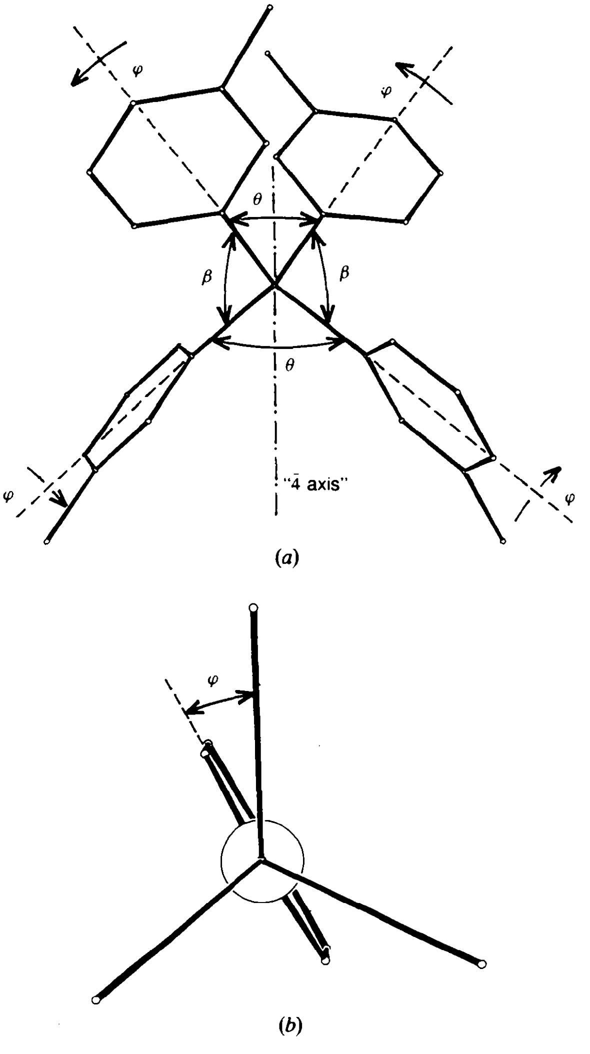


Fig. 5. Views of idealized (*m*-XC_6H_4)$_4$Sn with $\bar{4}$ symmetry: (*a*) perpendicular to the $\bar{4}$ axis showing bond angles θ and β; (*b*) down a Sn—C bond showing the dihedral angle φ.

Table 5. *Molecular parameters for substituted tetraaryltins*

Compound (Space group)	Molecular angles (°)* φ	θ	β	*d*(SN—C) (Å)
(C_6H_5)Sn† ($P\bar{4}2_1c$)	56.5	110.5	108.9	2.143 (5)
(*p*-$CH_3C_6H_4$)$_4$Sn† ($I\bar{4}$)	48.4	114.4	107.0	2.147 (6)
(*p*-$CH_3OC_6H_4$)$_4$Sn† ($I\bar{4}$)	52.1	112.5	108.0	2.136 (4)
(*m*-$CH_3C_6H_4$)$_4$Sn† ($I4_1/a$)	40.7	109.3	109.5	2.150 (3)
(*m*-$CH_3OC_6H_4$)$_4$Sn‡ (*C*2/*c*)	70.2		108.0	2.134 (2)
	−142.8	111.0	111.5	2.137 (2)
	41.2		112.4	2.138 (2)
	−160.4	105.7	108.2	2.148 (2)
(*o*-$CH_3C_6H_4$)$_4$Sn§ ($P\bar{4}2_1c$)	52.8	113.7	107.4	2.145 (3)
(*o*-$CH_3OC_6H_4$)$_4$Sn¶ *A* ($P\bar{1}$)	59.0	110.0	111.2	2.140 (5)
	67.5		108.9	2.148 (5)
	61.0	106.6	111.2	2.160 (5)
	59.1		108.9	2.146 (5)
B	50.6	110.7	107.6	2.146 (4)
	67.7		111.8	2.151 (5)
	60.1	112.4	108.7	2.154 (4)
	64.4		105.6	2.137 (4)

* See text, Fig. 5.

† Data from Wharf & Simard (1987).

‡ Assignment: φ, Fig. 6; θ, β, *d*(Sn—C), Table 3.

§ Calculated from the data of Belsky, Simonenko, Reikhsfeld & Saratov (1983).

¶ Assignment: φ, Fig. 7; θ, β, *d*(Sn—C), Table 4.

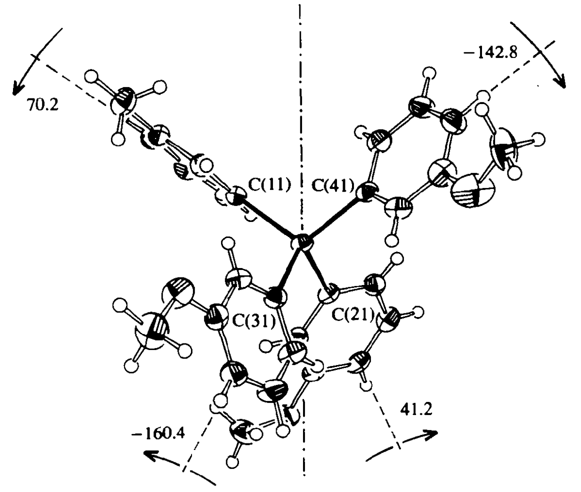
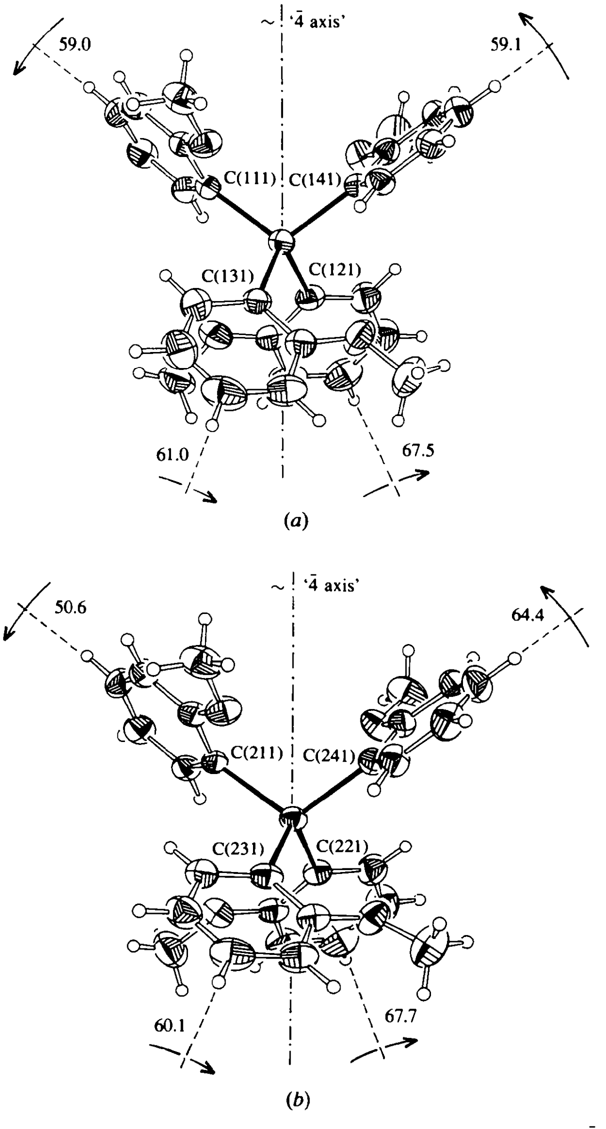


Fig. 6. View of molecule (1) perpendicular to the axis bisecting angles C(11)—Sn—C(41) and C(21)—Sn—C(31).

[0.256 (2), 0.044 (3), 0.497 (5)] determined from the positions of the two molecules in the asymmetric unit of (2) (Table 2). This translation $(\frac{1}{4}, 0, \frac{1}{2})$ requires space-group extinctions for reflections $h/2 + 1 = 2n + 1$ and $h = 2n$ (Stout & Jensen, 1968), and inspection of the structure-factor table (Table 2, S7, deposited material) indeed shows these reflections are systematically weak. The almost tetragonal pseudo-symmetry thus generated for (2), by assuming molecules *A* and *B* are essentially identical, is made clear with the projection obtained by viewing the unit cell down the pseudo-$\bar{4}$ axis of molecule *A* (Fig. 8*a*). Thus, the distortion from tetragonal symmetry is small for both the molecular and crystal lattice pictures. However, the complete view of the quasi-tetragonal unit cell which can be assembled (Fig. 8*b*) shows the parallel layers of molecules are displaced approximately 17° from the overlapping (90°) positions expected for exact tetragonal packing. Presumably, the less regular packing actually used provides even more crystal lattice stabilization to further compensate for the high molecular energy of (2).

Concluding remarks

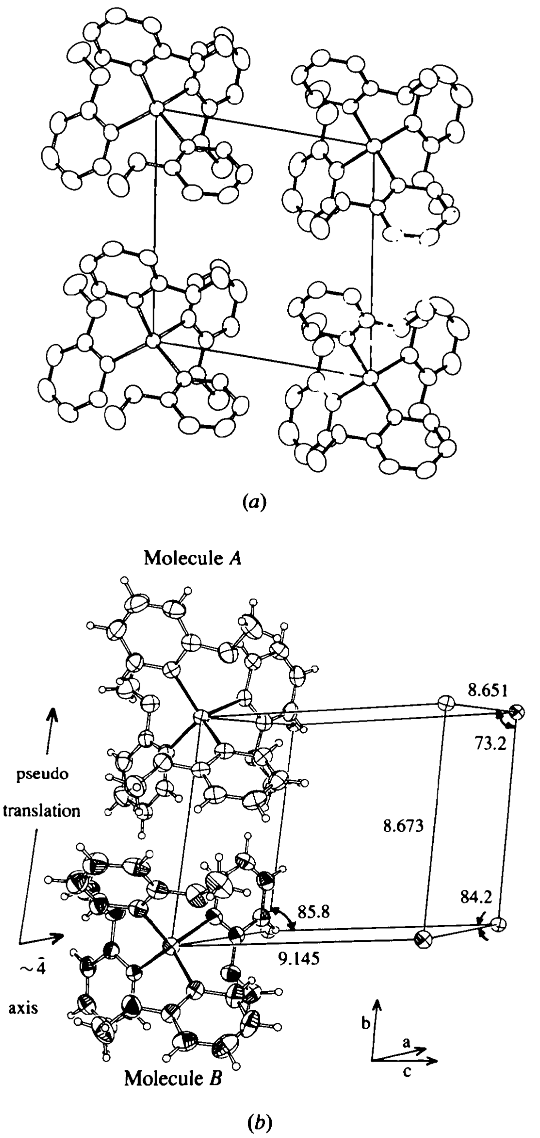
The overall stability of Group 14 tetra-aryls clearly reflects the need to attain the lowest-energy molecular conformation consonant with the close-packing required to achieve maximum lattice stability. With increasing



(*a*)

(*b*)

Fig. 7. Views of molecules *A* and *B* of (2) perpendicular to the pseudo-$\bar{4}$ axis.



(*a*)

(*b*)

Fig. 8. (*a*) Projection of the unit cell of (2) looking down the pseudo-$\bar{4}$ axis of molecule *A*. The pseudo-$\bar{4}$ axis for molecule *B* is approximately 15° away from the perpendicular. (*b*) View of the pseudo-tetragonal unit cell in (2) showing the distortion from tetragonal symmetry.

size of *para*- or *meta*-substituents, close packing of $\bar{4}$ ground state molecules becomes less feasible. This then induces a lowering of both molecular and lattice symmetry so as to re-establish close packing. This effect is more pronounced with *meta*-substituents with the molecular structure of (1) clearly deviant from the $\bar{4}$ ground state. With *ortho*-substituents, the packing requirements of Ar_4M are less problematic. However, the greater steric crowding in the molecules produces an increase in their absolute potential energy (compared with the tetraphenyl archetype), which can then be compensated, as in (2), by a relatively small deviation from $\bar{4}$ symmetry so as to enable more efficient crystal packing to occur. Thus, following on from the pioneering work of Kitaigorodskii (1961), the molecular mechanics calculations now needed must take into account both intra- and intermolecular interactions when predicting the most stable structure for a given Group 14 tetra-aryl derivative in the solid state.

The Fonds FCAR (Programme ACC) of the Gouvernement du Québec is thanked for support as well as the Department of Chemistry, McGill University, and, in particular, Professor Onyszchuk for the facilities where part of this work was carried out.

References

AHMED, N. A., KITAIGORODSKII, A. I. & MIRSKAYA, K. V. (1971). *Acta Cryst.* **B27**, 867–870.

BELSKY, V. K., SIMONENKO, A. A. & REIKHSFELD, V. O. (1984). *J. Organomet. Chem.* **265**, 141–143.

BELSKY, V. K., SIMONENKO, A. A., REIKHSFELD, V. O. & SARATOV, E. (1983). *J. Organomet. Chem.* **244**, 125–128.

BROCK, C. P. & DUNITZ, J. D. (1994). *Chem. Mater.* **6**, 1118–1127.

CHARISÉE, M., ROLLER, S. & DRÄGER, M. (1992). *J. Organomet. Chem.* **427**, 23–31.

CROMER, D. T. & LIBERMAN, D. (1970). *J. Chem. Phys.* **53**, 1891–1898.

CROMER, D. T. & MANN, J. B. (1968). *Acta Cryst.* **A24**, 321–324.

DESIRAJU, G. R., CALABRESE, J. C. & HARLOW, R. L. (1991). *Acta Cryst.* **B47**, 77–86.

GABE, E. J., LEPAGE, Y., CHARLAND, J.-P., LEE, F. L. & WHITE, P. S. (1989). *J. Appl. Cryst.* **22**, 384–387.

HOWIE, R. A., ROSS, J.-N., WARDELL, J. L. & LOW, J. N. (1994). *Acta Cryst.* **C50**, 229–231.

HUTCHINGS, M. G., ANDOSE, J. D. & MISLOW, K. (1975). *J. Am. Chem. Soc.* **97**, 4553–4561.

JOHNSON, C. K. (1965). ORTEP. Report ORNL-3794. Oak Ridge National Laboratory, Tennessee, USA.

KARIPIDES, A. & OERTEL, M. (1977). *Acta Cryst.* **B33**, 683–687.

KARIPIDES, A. & WOLFE, K. (1975). *Acta Cryst.* **B31**, 605–608.

KITAIGORODSKII, A. I. (1961). *Organic Chemical Crystallography*, pp. 124–128, 404–406. New York: Consultants Bureau.

PAULING, L. & DELBRÜCK, M. (1940). *Science*, **92**, 77–79.

ROSS, J.-N. & WARDELL, J. L. (1994). *Acta Cryst.* **C50**, 1207–1209.

SCHAEFFER, T., LAATIKAINEN, R., WILDMAN, T. A., PEELING, J., PENNER, G. H., BALEJA, J. & MARAT, K. (1984). *Can. J. Chem.* **62**, 1592–1597.

SCHAEFFER, T., SALMAN, S. R., WILDMAN, T. A. & PENNER, G. H. (1985). *Can. J. Chem.* **63**, 782–786.

STEWART, R. F., DAVIDSON, E. R. & SIMPSON, W. T. (1965). *J. Chem. Phys.* **42**, 3175–3187.

STOUT, G. H. & JENSEN, L. H. (1968). *X-ray Structure Determination, A Practical Guide*, Appendix D, pp. 443–444. New York: MacMillan.

WHARF, I. & SIMARD, M. G. (1987). *J. Organomet. Chem.* **332**, 85–94.

WHARF, I. & SIMARD, M. G. (1991). *Acta Cryst.* **C47**, 1314–1315.

WHARF, I., SIMARD, M. G. & LAMPARSKI, H. (1990). *Can. J. Chem.* **68**, 1277–1282.

ZACHARIASEN, W. H. (1967). *Acta Cryst.* **23**, 558–564.