Acta Crystallographica Section B
Structural Science
ISSN 0108-7681

Structural similarities in tetraaryltins described by virtual non-crystallographic rotations or translations: Kitaigorodskii's morphotropism is revisited

Alajos Kálmán* and László Fábián‡

Institute of Structural Chemistry, Chemical Research Center, Hungarian Academy of Sciences, POB 17, 1525 Budapest, Hungary

‡ Present address: Cambridge Crystallographic Data Centre, Cambridge, UK.

Correspondence e-mail: akalman@chemres.hu

Received 10 October 2006
Accepted 8 March 2007

Dedicated to Dr Kálmán Sasvári, a pioneer of X-ray crystallography in Hungary on the occasion of his 95th birthday.

Recently Kálmán [(2005), *Acta Cryst.* B**61**, 536–547] revealed that *semirigid* molecules or their patterns held together *e.g.* by hydrogen bonds may perform non-crystallographic rotations (through 180, 90° *etc.*) around themselves whenever a substitution, ring enlargement or isomerization destroys the existing close packing, *i.e.* the novel substituent or the enlarged ring can no longer fit in the hollows formed between the molecules. In other words, the old and new arrangements of such chemically similar molecules can be converted into each other by virtual *rotations*. However, when a semirigid molecule without substitution, but under the influence of solvents, temperature *etc.*, is fully or partly rearranged in the solid state, the corresponding non-crystallographic rotation (hereinafter *ncr*) is real and gives rise to polymorphism. Such polymorphs are hallmarked by full or partial isostructurality and show that *ncr*s always occur together with isostructurality. First Kitaigorodskii [(1961), *Organic Chemical Crystallography*, New York: Consultants Bureau] reported on the structural similarity of three tetraaryltins, $(p\text{-}RC_6H_4)_4Sn$, R = H, CH_3, CH_3O, which is terminated by the larger C_2H_5O group. A revisit to these structures revealed that the tetragonal → monoclinic conversion termed by Kitaigorodskii as a '*morphotropic step*' is also performed by an *ncr*. Similarly, other tetraaryltins in the literature are related by *ncr*s or the *nc* translation of the semirigid tetrahedra, or they remain isostructural. Since one of the definitions of *morphotropism*, a word of Greek origin, is 'turn of form', the *ncr*s of semirigid molecules can be denoted – following Kitaigorodskii – by this word, whereas its alternative definition in the morphological crystallography of 'unidirectional changes' [applied by Groth (1870). *Ber. Chem. Ges.* **3**, 449–457] covers the non-crystallographic translations described first in this work.

1. Introduction

Non-crystallograpic rotations (*ncr*) were first observed in a series of organometallic compounds related by isostructurality (Kálmán *et al.*, 1993*a*,*b*). While $Me_3Si–SiPh_3$ and its analogs $Me_3Si–GePh_3$ and $Me_3Ge–SiPh_3$ form trigonal crystals (common space group $P\bar{3}$), the isomeric $Me_3Ge–SnPh_3$ and $Me_3Sn–GePh_3$ crystals are pseudohexagonal with the orthorhombic space group $Pna2_1$. In the former case the $Me_3E–E'Ph_3$ dumbbells related by a center of symmetry are antiparallel, whereas in the orthorhombic pair of structures they are stacked in a parallel array. In other words, every second dumbbell rotates through 180° around its center of gravity. Continuing these investigations, Kálmán & Párkányi (1997) found the crystals of $Me_3Ge–GePh_3$, $Me_3Sn–SnPh_3$ and some others such as $Me_3Sn–PbPh_3$ and $Me_3Pb–PbPh_3$ (Preut & Huber, 1976) to be trigonal again with the space group $P\bar{3}$. The

doi:10.1107/S0108768107010968

Table 1
Lattice parameters and space groups of *ortho*-, *meta*- and *para*-substituted tetraphenyl-tins $(R\mathrm{Ph})_4\mathrm{Sn}$.

R	Refcode	*a* (Å)	*b* (Å)	*c* (Å)	α (°)	β (°)	γ (°)	Space group
H	TPHESN03[a]	12.068 (3)	12.068 (3)	6.558 (2)	90	90	90	$P\bar{4}2_1c$
o-CH_3	BUGLOE[a]	12.021 (1)	12.021 (1)	8.054 (1)	90	90	90	$P\bar{4}2_1c$
m-CH_3	TMMPSN[b]	17.370 (13)	17.370 (13)	8.285 (9)	90	90	90	$I4_1/a$
p-CH_3	PTOLSN[c]	13.819 (8)	13.819 (8)	6.406 (4)	90	90	90	$I\bar{4}$
p-CH_3O	ZZZULI01[d]	14.180 (4)	14.180 (4)	6.303 (2)	90	90	90	$I\bar{4}$
p-CH_3S	FUWYIF[d]	13.553 (4)	13.553 (4)	7.442 (2)	90	90	90	$I\bar{4}$
o-CH_3O	HEVFIX01[e]	9.145 (6)	16.582 (5)	18.010 (8)	77.72 (3)	78.52 (5)	81.70 (4)	$P\bar{1}$
m-CH_3O	ZILFEF[e]	17.534 (5)	9.908 (4)	30.011 (13)	90	108.27 (3)	90	$C2/c$
p-C_2H_5O	ZZZHE01[f]	12.964 (2)	13.953 (2)	19.603 (2)	90	123.41 (2)	90	$P2_1/c$

References: (*a*) Belsky *et al.* (1983); (*b*) Karipides & Oertel (1977); (*c*) Karipides & Wolfe (1975); (*d*) Wharf & Simard (1987); (*e*) Wharf & Simard (1995); (*f*) Wharf & Simard (1991).

'break' in the series of isostructural crystals, after Kitaigorodskii (1961), was termed *morphotropism*. This example and one of the definitions (Webster's, 1989) of this word of Greek origin ('turn of form') led to the recognition and systematization of *ncr*s (through 180, 90° *etc.*) performed by dimers, tetramers, helices *etc.* when a structure virtually converts into another form (Kálmán, 2005). This discovery stimulated the recognition of new forms of *ncr* in our laboratory: Deák & Tárkányi (2005) reported an *ncr* which links two close-packing forms of a $[\mathrm{Me_2Sn(PhN_2O_2)_2}]_2$ dimer crystallized either from solution or from a melt with slightly different triclinic unit cells. Bombicz described[1] four calixarene inclusion complexes; in one of them the host molecule is related *via ncr* to the others. Finally, it was discovered that a group of crystal structures (*ortho*-, *meta*- and *para*-substituted 2,4,6-triphenoxy-1,3,5-triazine derivatives; Báthori, 2006) are also isostructural or related by different forms of *ncr* (Báthori *et al.*, 2007).

Inasmuch as Groth (1870, 1906), in his morphological studies of H-atom substitutions, had denoted 'unidirectional changes' in the crystal habits (*i.e.* in the axial ratios: a': 1: c'), observed using an optical goniometer, with the same word morphotropy (Bernstein, 2005), two questions need to be answered:

(i) Does this word have two meanings semantically?

(ii) If so (Webster's, 1989), does Kitaigorodskii's morphotropism[2] cover the non-crystallographic rotation(s) as Kálmán & Párkányi (1997) adapted this term first to a 'break' in the isostructural series of $\mathrm{Me_3}E\text{–}E'\mathrm{Ph_3}$ derivatives or not?

A revisit to Kitaigorodskii's (1961) example gives the answer. He described an H-atom subsitution on $\mathrm{Ph_4Sn}$ by *p*-C_2H_5O groups, which terminates the tetragonal $\bar{4}$ symmetry assumed by three allied tetraaryltins (*R* = H, *p*-CH_3, *p*-CH_3O). Now we prove that the new crystal structure with lower (monoclinic) symmetry is reached by an *ncr*. In addition, the revisit has been extended to the corresponding *ortho* and *meta* isomers, of which study of the tetragonal → tetragonal $\mathrm{Ph_4Sn}$ → (*m*-$\mathrm{MePh})_4\mathrm{Sn}$ transition revealed a new form of non-crystallographic motions, the *translations*. This observation, however, extends the second meaning of morphotropism (unidirectional changes) from an early morphological application (Groth, 1870) to structural (X-ray) crystallography.

Since *ncr*s, in general, terminate the isostructurality of crystals, it is advisable to first summarize the main forms of the isostructurality. Lima-de-Faria *et al.* (1990) in *The Nomenclature of Inorganic Structure Types* classified the forms of *isotypism*. Following them, Kálmán *et al.* (1993*b*) suggested that the packing similarities exhibited by organic crystals should be denoted by the term *isostructurality*. This proposal has been slowly accepted (*cf.* Caira, 2004), in particular, 'the volumetric measure of isostructurality' (Fábián & Kálmán, 1999) is frequently used.

A high degree of isostructurality (same space group with similar unit cells) can be expected whenever the shapes of the related molecules are similar, *i.e.* exhibit only small differences on their surface. The descriptors of isostructurality (Fábián & Kálmán, 1999) are summarized in *Appendix A*. If substitution (or atomic replacement) occurs on more than one atomic site in the related molecules, only 'relaxed' packing similarities can then be recognized. This allows for a large variety of 'isostructural forms', including packing motifs which are related by non-crystallographic symmetries. Such crystals are termed homostructural. In addition, Fábián & Kálmán (2004) extended the study of isostructurality to two and even one dimensions. It was demonstrated that in two dimensions the layers of the molecules may retain isostructurality. For example, *trans*-2-hydroxycyclopentanecarboxamide (I) and its cycloheptane homolog (II) form similar helices of hydrogen-bonded molecules which exhibit either parallel or antiparallel stacking (Kálmán *et al.*, 2004). These helices are isostructural in two dimensions, but every second helix turns by 180°. The antiparallel layers result in a doubled unit cell along the orthorhombic *b* axis of (II) with the space group *Pbca*, while the parallel layers form the crystals of (I) with the non-standard space group $P2_1ca$. Their two-dimensional isostructurality (*via* an *ncr*) is obvious, but they are not isomorphous! It follows that the words 'isomorphic' and 'isomorphism' are misleading and insufficient to describe the structural similarities between organic crystals.

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[1] In a joint paper from Budapest, Freiberg and Stockholm (Gruber *et al.*, 2006).

[2] Although Kitaigorodskii (1961) used the term morphotropism only once in the subject index referring to page 223, the essence of his observation reads as follows: 'as *para*-H atoms are replaced by larger substituents, the packing efficiency with tetragonal space groups would decrease and crystal structures of lower symmetry would then be preferred'.

Table 2
Lattice parameters of the isostructural tetrakis(pentafluorophenyl)silicon, germanium and tin(IV) and tetrakis(3-methylphenyl)tin(IV).

Compound	Refcode	a (Å)	b (Å)	c (Å)	V (Å^3)	D_x (Mg m^{-3})	Space group
$(C_6F_5)_4Si$	PFPSIL[a]	17.165 (12)	17.165 (12)	8.125 (8)	2393.93		$I4_1/a$
$(C_6F_5)_4Ge$	PFPHGE10[b]	17.277 (13)	17.277 (13)	8.122 (7)	2424.37	2.030	$I4_1/a$
$(C_6F_5)_4Sn$	TFUPSN[b]	17.738 (11)	17.738 (11)	8.094 (5)	2546.67	2.052	$I4_1/a$
$(m\text{-}CH_3C_6H_4)_4Sn$	TMMPSN4[c]	17.370 (13)	17.370 (13)	8.285 (9)	2499.72	1.284	$I4_1/a$

References: (*a*) Karipides & Foerst, 1978); (*b*) Karipides *et al.* (1974); (*c*) Karipides & Oertel (1977).

2. Data collection and retrieval from CSD

Kitaigorodskii's (1961) observation was based on two-dimensional structure determinations (Zhdanov & Ismail-Zade, 1949). The accurate (including H positions) structure determinations of tetraaryltins were published much later. First tetrakis(4-methylphenyl)tin (Karipides & Wolfe 1975), then tetrakis(3-methylphenyl)tin (Karipides & Oertel, 1977) and finally tetrakis(2-methylphenyl)tin (Belsky *et al.*, 1983) were published. In addition, Wharf & Simard (1987, 1991, 1995) reported those tetraaryltin structures (*o*-MeO, *m*-MeO, *p*-MeO, *p*-MeS and *p*-EtO) which enabled us to shed more light on Kitaigorodskii's (1961) morphotropism. The crystallographic parameters of these structures retrieved from the Cambridge Structural Database (CSD; Allen, 2002) are listed in Table 1. Since the lattice parameters of Ph_4Sn have been measured several times, data reported by Belsky *et al.* (1983) are listed. Finally, it is worth noting that Ph_4Sn is isostructural with the homologous tetraphenyl compounds (Ahmed *et al.*, 1971) of C, Si and Pb (Ph_4Ge was reported by Karipides & Haller, 1972) with the common space group $P\bar{4}2_1c$. These crystals are isostructural when in pairs, but the size and shape (tetrahedron → bisphenoid) of Ph_4C and Ph_4Pb are so different that they are homostructural rather than isostructural (Kálmán & Párkányi, 1997).

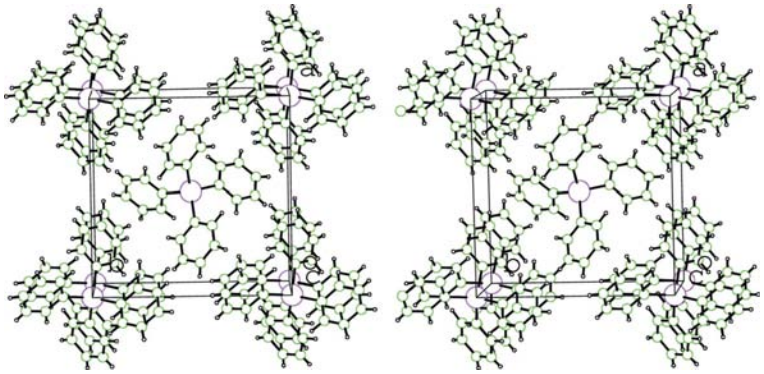

Figure 1
Stereoview of the unit cell of tetrakis(phenyl)tin (TPHESN) perpendicular to the *c* axis (space group $P\bar{4}2_1c$). It is isostructural with tetrakis(2-methylphenyl)tin (BUGLOE).

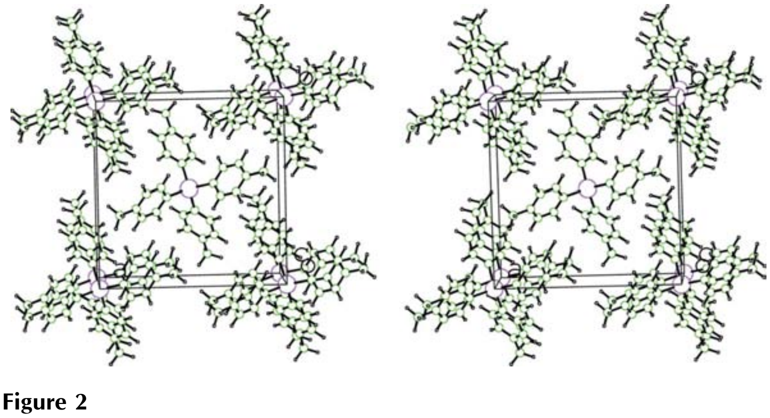

Figure 2
Stereoview of the unit cell of tetrakis(4-methylphenyl)tin (PTOLSN) perpendicular to the *c* axis (space group $I\bar{4}$).

3. Discussion

The crystals listed in Tables 1 and 2, and the $Ph_4C \rightarrow Ph_4Pb$ row form three groups around the three tetragonal space groups $P\bar{4}2_1c$ (No. 112), $I4_1/a$ (No. 88) and $I\bar{4}$ (No. 82). Within each group the members are isostructural. From a topological point of view, the close packing of each crystal is governed by the self-complementary surfaces (Brock & Dunitz, 1994) of the molecules. The self-complementarity of the Ph_4Sn molecules possessing S_4 symmetry (Fig. 1) is not altered by the four methyl groups entering the *ortho* position. The consequent increase in volume of the asymmetric unit is 26.1 Å^3 and the unit cell only expands along the *c* axis (Δc = 1.5 Å). This provides extra space around the methyl groups without molecular rearrangement. In contrast, the unit cells of the isostructural *p*-methyl (Fig. 2) and *p*-methoxy derivatives increase in a different way (Table 1). The tetragonal $a_1 = a_2$ axes are increased, while the *c* axis remains nearly constant. The bulky *p*-methylthio goup (Wharf & Simard, 1987) slightly shortens the $a_1 = a_2$ axes of the *p*-methyl derivative, but this is counterbalanced by an increase of the *c* axis (Δc = 1.1 Å). However, after this change in the unit cell of $(p\text{-MeSPh})_4Sn$ (Table 1) it remains isostructural with the *p*-methyl and *p*-methoxy analogs.

The structures listed in Table 1 reveal that hydrogen substitutions on Ph_4Sn, except the *ortho*-

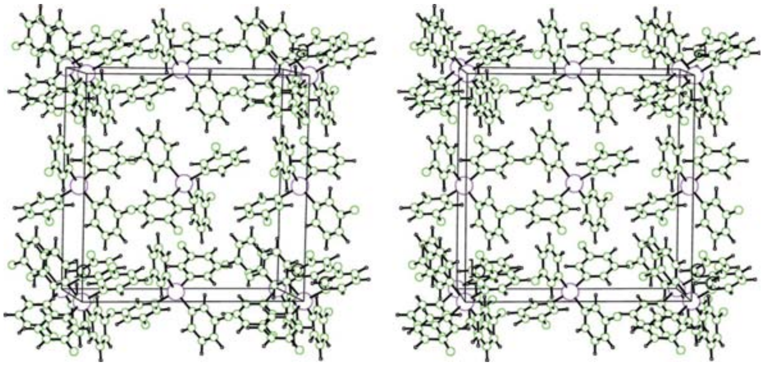

Figure 3
Stereoview of the unit cell of tetrakis(3-methylphenyl)tin (TMMPSN) perpendicular to the c axis. (space group $I4_1/a$).

methyl derivative, alter the basic structure in three different ways:

(i) by an *ncr* (through 180°) of the molecule with S_4 symmetry at $\frac{1}{2},\frac{1}{2},\frac{1}{2}$ around the a_1 or a_2 axis perpendicular to the c axis,

(ii) by shifts ($\pm\frac{1}{4}$ and $\frac{1}{2}$) of the molecules parallel to the $\bar{4}$ axis and/or

(iii) by an *ncr* of the molecules (through *ca* 55°) so that one of the Sn—C bonds is oriented in the direction of the $\bar{4}$ axis.

(i) In the unit cell of Ph_4Sn one molecule sitting in the center at $\frac{1}{2},\frac{1}{2},\frac{1}{2}$ is the mirror image of the eight others at 0,0,0 (Fig. 1). They are related by c glide planes, whereas in the body-centred unit cell (Fig. 2) of the p-methyl derivative (space group $I\bar{4}$), the molecule at $\frac{1}{2},\frac{1}{2},\frac{1}{2}$ is related to the other at 0,0,0 by screw axes $2_1(\frac{1}{4},\frac{1}{4},Z)$. Consequently, the central molecule of the primitive unit cell of Ph_4Sn is related to that in the centred unit cell of (p-MePh)$_4$Sn (Fig. 2) by *virtual rotations* either by 180° perpendicular to or by 90° around the $\bar{4}$ axis.

Since Ph_4Sn and (o-MePh)$_4$Sn are isostructural, the o- and p-methyl isomers directly represent a *par excellence* case of *ncr*. Their structural relationship can be described without space-group symmetries. In the center of the unit cell of (p-*Me*Ph)$_4$Sn the molecule has the same orientation as those in the eight corners, whereas in (o-MePh)$_4$Sn the upper edge of the central tetrahedron is perpendicular to those sitting on the eight corners. This difference is only an *ncr* of the central tetrahedron (bisphenoid) through 90° around or through 180° perpendicular to the c axis in either of the unit cells. This demonstrates a novel case of homostructurality where the *primitive* and *centred* unit cells and the close packing are rather similar,[3] but the space groups are different. As shown by $\Pi = 0.061$ (see *Appendix A*), the unit cell of the p isomer is slightly compressed along the c axis with respect to that of the o isomer (Table 1). At the same time, this reveals a 'unidirectional change' in the axial ratios a/c from 1.494 (*ortho*) to 2.057 (*para*), which repeatedly underscores the ambivalent meaning (*cf.* Webster's, 1989) of morphotropism: unidirectional changes in crystal habits (Groth, 1870) *versus* a turn of forms (Kálmán, 2005).

(ii) m-Methyl substitution also maintains both S_4 molecular and $\bar{4}$ crystal symmetries. The (m-MePh)$_4$Sn bisphenoids form a centred unit cell with the space group $I4_1/a$ (Fig. 3), which was listed by Kitaigorodskii (1961) among the unfavorable tetragonal space groups for molecules of S_4 symmetry. According to him, in this space group the adjacent molecules, related by mirror planes, diminish the close packing. This is obviously a mistake since in the space group $I4_1/a$ there are no mirror planes. The viability of the space group $I4_1/a$ is substantiated by the isostructurality of (m-MePh)$_4$Sn (Karipides & Oertel, 1977) with $(C_6F_5)_4Sn$, and with the homologous $(C_6F_5)_4Ge$ (Karipides *et al.*, 1974) and $(C_6F_5)_4Si$ (Karipides & Foerst, 1978). The small difference in the volumes of the asymmetric units (23.5 Å^3, 0.9% of the larger unit cell together with $\Pi = 0.013$) demonstrates that semirigid molecules such as (m-MePh)$_4$Sn and $(C_6F_5)_4Sn$, with a substantial difference (4 CH_3 groups *vs* 20 F atoms) in their chemical structures, may exhibit homostructurality.

The question is what kind of rearrangement may convert the basic $P\bar{4}2_1c$ close packing into another tetragonal array (Fig. 3) exhibited by the m-methyl isomer with the space group $I4_1/a$? The answer: a non-crystallographic migration ($\Delta z = \pm\frac{1}{4}$ and $\frac{1}{2}$) of molecules along the c axis. In both Ph_4Sn and (o-MePh)$_4$Sn the crystal lattice is formed by two tetragonal layers (Fig. 1). They are separated by the crystallographic translation $\frac{1}{2},\frac{1}{2},\frac{1}{2}$ and differ in the *orientation* of their bisphenoids. This array, represented by red and green layers stacked upon each other, is depicted in Fig. 4(a). This pattern, from a perpendicular view, shows the red and green layers (now triangles) in a parallel array (Fig. 4b). (On p-methyl substitution the green layer turns upside down. The two red layers together form a centred close packing with the space group $I\bar{4}$, depicted in Fig. 4c.) In contrast, on m-methyl substitution the two overlapping triangles from layer A (Fig. 4b) move upward by $\Delta z = \frac{1}{4}$, while the other two are shifted by $\Delta z = -\frac{1}{4}$ in the opposite direction. Thus, they occupy the four corners of a super 'bisphenoid'. Simultaneously, the central molecule of the green layer B migrates by $\Delta z = \frac{1}{2}$ into the center of this super bisphenoid (borne from layer A), while it forms a tetragonal pyramid together with the other green triangles. *Mutatis mutandis* two (green) tetragonal pyramids fused together by their common peak form the eight corners of a body-centred unit cell demonstrated by (m-MePh)$_4$Sn (Fig. 3). In this new array the nine triangles (Fig. 4d) are distributed on four layers in a stacking perpendicular to the c axis, the length of which hardly changes (~ 8 Å). Shifts of the molecular bisphenoids along the c axis are followed by an expansion of the unit cell in the (001) plane resulting in $a' = a(2^{1/2})$. This suggests that non-crystallographic translations (*nct*) are also to be regarded as a

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[3] This is a crystallographic paradox, since the volume of the centred unit cell (I) is at least doubled with respect to a primitve (P) unit cell.

form of morphotropism in accordance with the second meaning of the word: unidirectional change(s).

(iii) Finally, 'with the increasing size of the *p* or *m* substituents the close packing of the $\bar{4}$ ground-state molecules becomes less feasible' (Wharf & Simard, 1995). In contrast to the *p*-MeO substitution (ZZZULI01, Table 1), H → MeO replacement in *meta* positions (ZILFEF) and the H → EtO substitution in *para* positions (ZZZHE01) lead to tetragonal → monoclinic rearrangements. It can be seen from Figs. 5 and 6 that one of the Sn—C(aryl) bonds rotates by *ca* 55° towards the direction of the *c* axis. Since these molecules cannot assume trigonal (C_3) symmetry, lower molecular and lattice symmetries are realized with pseudo-threefold rotors. The resulting crystals are monoclinic with space groups $P2_1/c$ and $C2/c$, respectively. The volume of the asymmetric unit of the *m*-MeO derivative ($C2/c$) is smaller by 15 Å^3 than that of the *p* isomer in the tetragonal lattice. Consequently, with lower symmetries the close packing is improved. The analogous rearrangement of the *o*-MeO derivative (HEVFIX01) in an oblique unit cell (space group $P\bar{1}$, $Z' = 2$) is less clearly visible. At any rate both tetragonal → monoclinic transitions are governed by *ncr*s and one of them was termed a 'morphotropic step' by Kitaigorodskii (1961).

There is a puzzle, however. Why did Kitaigorodskii denote this rearrangement with the word morphotropism? The answer probably is that Kitaigorodskii, who had to know about Groth's (1870, 1906) morphological studies,[4] simply adapted Groth's (1870) term in a more general sense than could be gained before the birth of X-ray crystallography in 1912. Reading Kitaigorodskii book it becomes obvious that he clearly distinguished the macroscopic and microscopic symmetries: the former refers to the external shape, while the latter depends on the internal structure. To avoid a lengthy explanation he did not refer[5] to Groth's work, which might have helped to shed light upon Groth's earlier morphotropy.

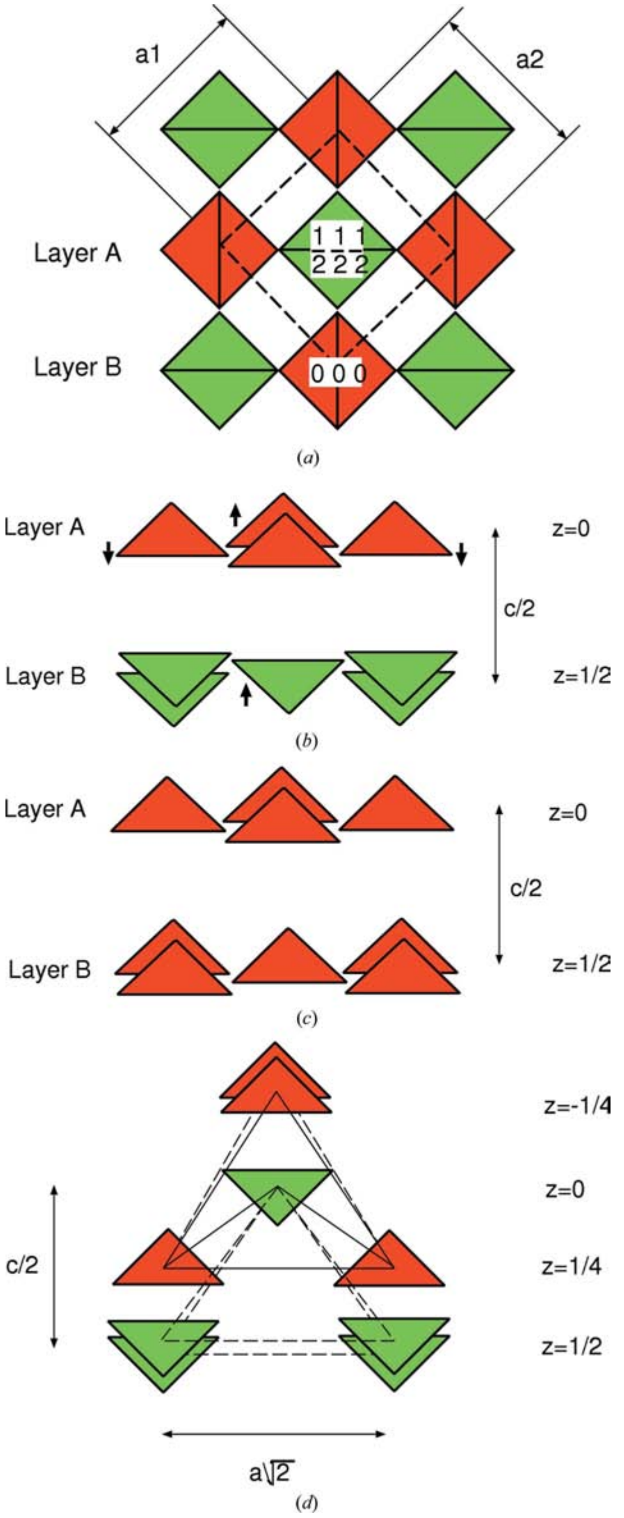

Figure 4
A topological description of the $P\bar{4}2_1c \rightarrow I4_1/a$ rearrangement by nine (XPh)$_4$Sn bisphenoids. (*a*) Tetragonal layers *A* (red) and *B* (green) perpendicular to the *c* axis (space group $P\bar{4}2_1c$). (*b*) Layers *A* and *B* in a parallel array. The orientation of the triangles (up and down) shows the inverse relationship between the red and green bisphenoids. (*c*) Non crystallographic rotation of layer *B* through 180° results in a second red layer; the new space group is $I\bar{4}$. (*d*) The formation of the space group $I4_1/a$ by the migration of the triangles along the *c* axis. The red pairs (Fig. 4*b*) split into two layers by $\Delta z = \pm\frac{1}{4}$ motions, while a migration of the central green triangle by $\Delta z = \pm\frac{1}{2}$ forms the fourth layer.

4. Summary

Although on different technical levels,[6] both Groth (1870, 1906) and Kitaigorodskii (1961) wanted to elucidate the forms of 'crystal responses' to H-atom substitutions. While Groth's 'morphotropy' refers to changes in axial ratios estimated by reflecting goniometers, Kitaigorodskii, using early X-ray data, denoted a tetragonal → monoclinic rearrangement as morphotropism. Finally, after fact-gatherings on *ncr*s (Kálmán, 2005), the present study of tetraaryltin structures

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[4] Groth's last fundamental work (Groth, 1921) has served as a guide book of crystallography for several decades. His concept of 'morphotropie' was also known and cited *e.g.* by Bidló & Nikolics (1973) in the book 'Crystallograpic investigations of organic compounds' (published in Hungarian). This suggests that Kitaigorodskii also knew about Groth's morphotropy.

[5] In the theoretical part of Kitaigorodskii's seminal book (Kitaigorodskii, 1961) the citations are rare, the first 240 pages refer only to 33 articles, mainly without author's names! This may explain why Groth is not mentioned at all.

[6] According to Desiraju (2003): 'when an entity (such as a crystal) is defined by an observed property, its very existence depends on the method of observation. Crystals were first observed by eye, then by microscope, then by X-rays'.

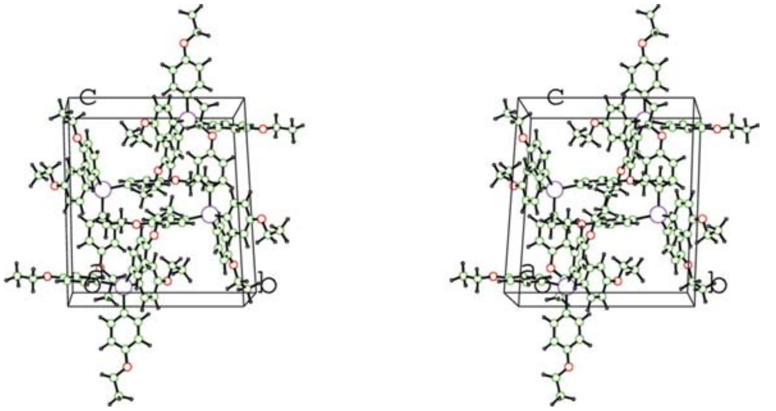

Figure 5
Stereoview of the unit cell of tetrakis(4-ethoxyphenyl)tin (ZZZHE01) projected onto the *bc* plane (space group $P2_1/c$).

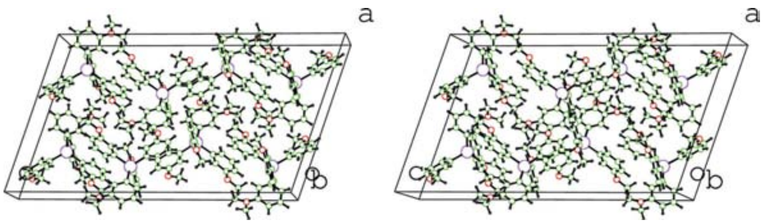

Figure 6
Stereoview of the unit cell of tetrakis(3-methoxyphenyl)tin (ZILFEF) perpendicular to the orthogonal *b* axis (space group $C2/c$).

convinced us that the ambivalent meaning of morphotropism equally covers both forms of non-crystallographic changes. Thus, we may say that morphotropism in general is the crystallographic answer to chemical effects on *semirigid* molecules which occur either in solution or in the melt (or even in the solid state). Such effects are as follows:

(i) atomic replacement in the core of the molecules (Kálmán & Párkányi, 1997),

(ii) change in the size of the molecules (ring enlargement: Kálmán *et al.*, 2002*a*,*b*; Fábián *et al.*, 2005),

(iii) substitution on, or isomerization of molecules (tetraaryltins, present work).

(iv) rearrangement in heteromolecular systems (Gruber *et al.*, 2006).

(v) the solvent effect which results in polymorphism: (Pineaar *et al.*, 1990*a*,*b*; Kálmán *et al.*, 2003; Fábián *et al.*, 2004).

However, whenever non-crystallographic motions do not result in a rearrangement then the related molecules retain their *isostructurality*. Thus, isostructurality and morphotropism are alternative phenomena. Partial rearrangements may also retain isostructurality in two (Kálmán *et al.*, 2003) or even in one dimension (Fábián & Kálmán, 2004). Accordingly, two structures which are related by morphotropism can be superimposed with a high degree of *isostructurality* (*Appendix A*) if the 'revealed' *virtual* non-crystallograpic motions are properly taken into account.[7]

Finally, it should be emphasized that *ncr*s occasionally govern a novel form of the polymorphism of semirigid molecules which has been overlooked so far. For example, the close packings of the monoclinic crystals of 3-nitrophenol (space group $P2_1/n$; Pandarese *et al.*, 1975) and its orthorhombic dimorph (space group $P2_12_12_1$; Hamzaoui *et al.*, 1996) are related by *ncr* (through 180°) of every second (achiral) molecule. Hopefully, after this work the number of recognized forms of morphotropic polymorphs such as cyclitol (Bhosekar *et al.*, 2005) or $[\mathrm{Me_2Sn(PhN_2O_2)_2}]_2$ (Deák & Tárkányi, 2005) will increase in the future.

5. Conclusions

(i) Semirigid molecules with small chemical differences frequently form fairly similar close packing. Such crystals are termed isostructural. Thus, isostructurality is a preserved molecular harmony in crystals.

(ii) The relaxed forms of isostructurality are denoted by the word homostructurality.

(iii) The ambivalent meaning of morphotropism (turn of form *versus* unidirectional change), independent from Groth's (1870) and Kitaigorodskii's (1961) usage, equally covers both forms of *non-crystallographic changes* (*a*) virtual rotations and/or (*b*) virtual translations between allied structures.

(iv) Polymorphs of semirigid molecules occasionally are related by *ncr*s. These crystals retain isostructurality in two-dimensions (Kálmán *et al.*, 2003) or even in three-dimensions (Fábián *et al.*, 2004). This underscores the fact that morphotropism is not only an alternative phenomenon of isostructurality, but is inseparable; it may also link isostructurality and polymorphism.

APPENDIX *A*
Descriptors of isostructurality

A1. Unit-cell similarity index (Kálmán *et al.*, 1993*b*)

$$\Pi = [(a + b + c)/(a' + b' + c')] - 1, \qquad (1)$$

where *a*, *b*, *c* and *a*′, *b*′, *c*′ are the orthogonalized unit-cell parameters of the related crystals. Similar unit cells are demonstrated by $\Pi \simeq 0$. For an appropriate comparison of the

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[7] These together fulfill Groth's (1906) legacy which reads as follows: 'In general, the question as to the relation between the crystal structures of two substances, which stand in definite chemical relationship to one another and which are known in corresponding states, will be answered when it can be stated what change the crystal structure of the one substance undergoes when those changes in the chemical molecules, by which it is transformed into the second substance, are imagined to be carried out.'

unit cells, the orthogonalization method of Löwdin (1950) was adapted (Fábián & Kálmán, 1999).

A2. Isostructurality index (Kálmán *et al.*, 1993*b*)

$$I_i(n) = \left| \left[\frac{\sum (\Delta R_i)^2}{n} \right]^{1/2} - 1 \right| \times 100, \quad (2)$$

where n is the number of distance differences (ΔR_i) between the crystal coordinates of identical non-H atoms within the same section of the asymmetric units of the related (A and B) structures. It is worth noting that $I_i(n)$ takes into account both the differences in the geometry of the molecules and the positional differences caused by rotational and translational operations.

A3. Volumetric measure of isostructurality (Fábián & Kálmán, 1999)

$$I_v = 2V_{\cap}/(V_1 + V_2) \times 100\%, \quad (3)$$

where V_1 and V_2 are the volumes of the compared fragments while $V_{\cap}$ is the intersection of these volumes. I_v is calculated for the whole unit cell as opposed to the I_i index. It starts from 100% for identical structures and decreases to *ca* 30%. A lower value than 30% has no significance, since the independent molecules located in their unit cells at random have at least such a degree of overlap.

We thank Professor Joel Bernstein (Ber Sheva) for his invaluable information on the work of Groth published in 1906, which enabled us to search after his other seminal works. Thanks are also due to Dr Petra Bombicz for her assistance. This work was supported by the Hungarian Research Fund Grant T049712.

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