

Retention of $\bar{4}$ Symmetry in Compounds Containing MAR_4 Molecules and Ions

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Abstract

A search of the Cambridge Structural Database shows that MAR_4 molecules usually retain the low-energy $\bar{4}$ conformation in the crystal. MAR_4^q ions also usually occupy sites if the counterion can conform to $\bar{4}$ (or higher) symmetry. The ability of the aryl groups to fit well around an empty $\bar{4}$ site is crucial to the symmetry retention. Molecules (and ions) in the tetragonal structures pack in columns that parallel the *c* axis; the columnar cross sections are approximately square. Aryl groups in adjacent columns can interleave to form a sort of herringbone arrangement. The tetragonal packing of columns is sufficiently favorable that it sometimes occurs even if the molecules must be disordered. The columnar motif is also found in some lower-symmetry structures of MAR_4 molecules and MAR_4^q ions; these structures may be pseudosymmetric.

1. Introduction

Many authors have noted that symmetric tetraaryl molecules often, perhaps even usually, crystallize in tetragonal space groups with the molecules located on sites of $\bar{4}$ (*i.e.* S_4) symmetry (see *e.g.* Ahmed, Kitaigorodsky & Mirskaya, 1971; Bel'skii, 1975; Karipides, 1978; Wharf & Simard, 1987). Simple salts of tetraaryl (and tetrapyridyl) ions behave similarly provided the counterion is also capable of conforming to 4 or $\bar{4}$ symmetry (Mueller, 1980; Knop, Cameron, Bakshi, Kwiatkowski, Choi & Adhikesavalu, 1993). Although some of the tabulations of such structures are fairly recent, we believe there is more to be said about the range of compounds that follow this rule and about its basis.

2. Experimental

Structures containing fragments of the type shown below were located in the March 1995 version (140 268 entries; MDAT 950220) of the Cambridge Structural Database (Allen, Kennard & Taylor, 1983). Entries were required to include atomic coordinates and to be error-free.



The list of hits was sorted by hand. Molecules and ions for which the four aryl rings were not equivalent were deleted, as were salts in which the counterion could not conform to $\bar{4}$ symmetry. Some structures in the recent literature or otherwise known to us were included in the compilation.

Lists of structures are shown in Tables 1 (molecules) and 2 (salts). Some tetrabenzyl-like molecules and ions are listed in Table 3. Refcodes and full references have been deposited.†

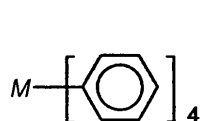
3. Results

Most MAR_4 molecules crystallize in tetragonal groups on sites of $\bar{4}$ symmetry. MAR_4^q ions usually crystallize on sites of $\bar{4}$ symmetry provided the counterions are highly symmetric. Crystallization in lower-symmetry groups is less common and is usually associated with large substituents. The fraction of the MAR_4 structures in low symmetry groups can be expected to rise, however, as more complicated derivatives are examined.

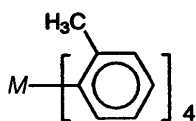
Molecules and ions crystallizing in tetragonal groups usually occupy a single set of special positions. Compounds having the same space group are therefore isostructural. Exceptions are $\text{Sn}(4\text{-bromophenyl})_4$ ($I\bar{4}$; Fronczek, 1996) and $\text{Si}(2\text{-dimethylaminomethylphenyl})_4$ ($I4_1/a$; Auner, Probst, Hahn & Herdtweck, 1993). Molecules in these two structures occupy sites of both symmetry $\bar{4}$ and symmetry 2 ($Z' = 3/4$).

The range of molecules within each isostructural group is astounding. For molecules of general shape the addition of a methyl or halo substituent to a phenyl ring usually changes the crystal packing, but in this class of compounds the crystal packing is often conserved. Space group $P\bar{4}2_1c$ (15 occurrences) accommodates molecules with molecular volumes (V/Z) that vary from 422 to 595 Å³ (see supplementary material†). If the molecules from Table 3 are included, the range is 422–928 Å³! The cell dimensions *a* and *c* vary over the ranges 10.92–15.20 and 6.53–8.09 Å (see supplementary material†). The phenyl rings can be changed into thienyl ligands (see Table 1), although a necessary twofold rotational disorder of each ring is then introduced.

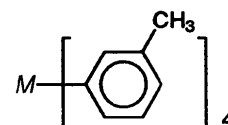
† Lists of refcodes and full literature citations have been deposited with the IUCr (Reference: CR0522). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. Structures of MAR_4 molecules $P\bar{4}2_1c$ (all $\bar{4}$)

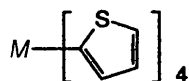
C, Si, Ge, Sn, Pb, Os



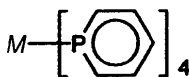
Sn, Pb, Mo



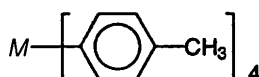
Pb



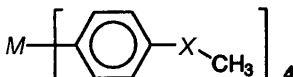
Si, Ge, Sn, Pb (disordered)



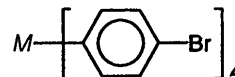
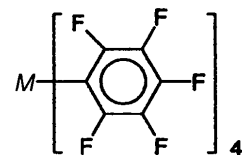
Ni

 $I\bar{4}$ ($\bar{4}$ except as noted)

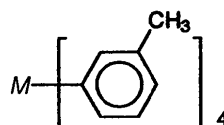
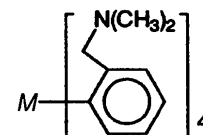
Sn, Pb



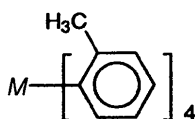
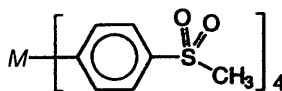
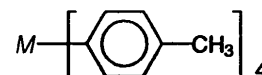
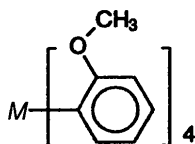
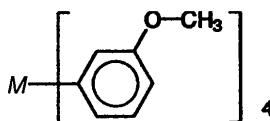
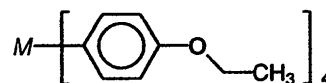
Sn/O, Sn/S

C; Si ($\bar{4}$ and 2) $I4_1/a$ ($\bar{4}$ except as noted)

Si, Ge, Sn

Sn, Sn with *m*-CF₃Si ($\bar{4}$ and 2)

Other space groups:

Ru, Os (*Pba*2; 2);
Ge ($P\bar{1}$; 1); Re ($P2_1/n$; 1)Sn ($C2/c$; 2)Si, Ge (*Pc*; 1)Sn ($P\bar{1}$; 2*1)Sn ($C2/c$; 1)Sn ($P2_1/c$; 1)

The other tetragonal space groups that occur for MAR_4 molecules are $I\bar{4}$ (six occurrences; molecular volumes 575–684 Å³) and $I4_1/a$ (six occurrences; molecular volumes 599–663 Å³ for $Z' = 1/4$ and 818 Å³ for $Z' = 3/4$).

Salts of MAR_4^q cations and anions usually crystallize in tetragonal groups provided the counterion can conform to 4 or $\bar{4}$ symmetry. Salts with square-pyramidal

counterions of the type MXY_4^q often crystallize in $P4/n$ (Mueller, 1980) with the counterions on 4 symmetry sites and the MAR_4^q ions on $\bar{4}$ sites. Salts of more symmetrical counterions usually crystallize in $I\bar{4}$ (see Table 2) or groups of even higher symmetry.

Parallels can be drawn between the MAR_4^q structures and the structures of simple salts. The ionic arrangement in the K⁺, Rb⁺ and NH₄⁺ salts of BPh₄⁻ is that of NaCl

Table 2. Selected ionic compounds containing MAR_4^q ions and counterions that can conform to $\bar{4}$ symmetry

$I\bar{4}2m$ (all $\bar{4}2m$)		
$[NH_4][BPh_4]$	$K[BPh_4]$	$Rb[BPh_4]$
$P\bar{4}2_1c$ (both $\bar{4}$)		
$Li[InPh_4]$	$Na[InPh_4]$	
$I\bar{4}$ (all $\bar{4}$)		
$[PPh_4]Br$	$[PPh_4]I$	$[PPh_4][TeH]$
$[PPh_4][PF_6]$	$[PPh_4][CrO_3(H_2O)]$	$[PPh_4][CrO_3(OH)]$
$[AsPh_4][ClO_4]$	$[AsPh_4][IO_4]$	$[AsPh_4][FeCl_4]$
$[SbPh_4][ClO_4]$	$[BiPh_4][ClO_4]$	
$[LiPy_4][ClO_4]$	$[CuPy_4][ClO_4]$	$[AgPy_4][ClO_4]$
$[Cu(N-Melm-N')_4][ClO_4]_2$		
$[PPh_4][BPh_4]$ ($2\bar{4}$)	$[AsPh_4][BP_4]$ ($2\bar{4}$)	$[SbPh_4][BPh_4]$ ($2\bar{4}$)
$I4_1/a$ ($\bar{4}$ except as noted)		
$[Cu(BzNCH_2CH_2NBz)_2]^- [BPh_4]$	$[Li(H_2O)_4][B(3,5-bis(CF_3)Ph)_4]$	$[Li(H_2O)_4][BPh_4]$ (1)
$I4_1/acd$ ($\bar{4}$)		
$[Co(4-MePy)_4][PF_6]_2$		
Other space groups		
$[NMe_4][BPh_4]$	$[PPh_4]Cl$ ($P2_1/n$; 1)	$[PPh_4]Br$ ($P\bar{1}$; 1)
($Cmcm$; mm)		
$[P(2-propyl)_4][BPh_4]$		
($P2_12_12_1$; 2)		

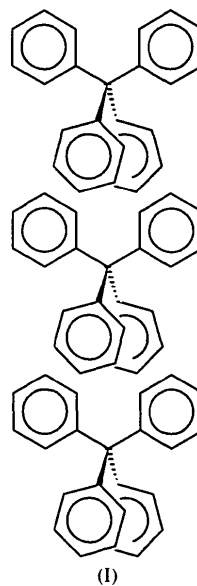
(see also Knop *et al.*, 1993), although the space group is $I\bar{4}2m$ ($Z' = 1/8$). [Alternatively these salts can be viewed as having close-packed MPh_4 structures (but with a $\bar{4}2m$ BPh_4^- conformation) in which the cations occupy 'octahedral holes', which have $\bar{4}$ symmetry.] The structure of $Na[InPh_4]$ (Hoffmann & Weiss, 1973) is also similar to that of rock salt, but the space group is $P\bar{4}2_1c$, the $InPh_4^-$ symmetry is only $\bar{4}$ and the anions at 0, 0, 0 and 1/2, 1/2, 1/2 are not related by translation. A second group of structures has the ionic arrangement of zinc blende [cubic ZnS (see also Knop *et al.*, 1993)]. These $I\bar{4}$, $Z' = 1/4$, structures can be viewed as close-packed MPh_4 structures in which the tetrahedral 'holes' at 1/2, 0, 1/4 and 0, 1/2, 3/4 are filled by counterions.

Notable exceptions to the rule that simple MAR_4^q salts crystallize in tetragonal groups are $[PPh_4]Cl$ (Richardson, Ball & Boorman, 1986; $P2_1/n$, $Z' = 1$) and a second form of $[PPh_4]Br$ (Schweizer, Baldacchini & Rheingold, 1989; $P\bar{1}$, $Z' = 1$).

4. Discussion

Several factors specific to this class of compound combine to favor crystallization with $\bar{4}$ symmetry. First, the low-energy conformation of the relatively rigid, and approximately equi-dimensional, tetraphenyl fragment has $\bar{4}$ symmetry (Hutchings, Andose & Mislow, 1975*a,b*; Dunitz, 1979). Distortion of the molecule or ion to a lower-symmetry conformation requires energy. Second, two adjacent MPh_4 molecules (or ions) fit easily around an empty $\bar{4}$ site [see (I)]. Most tetragonal groups with a $\bar{4}$ site have at least two sets of $\bar{4}$ sites and the rest have 4, $\bar{4}2m$ or 222 sites; crystallization in such

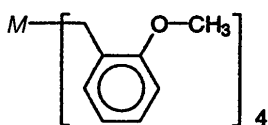
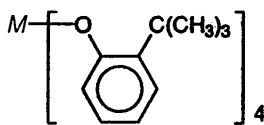
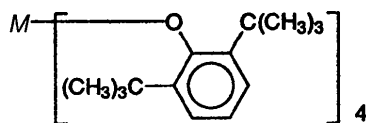
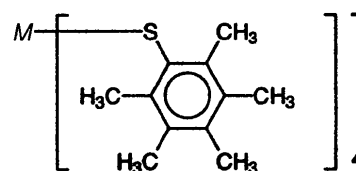
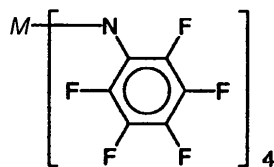
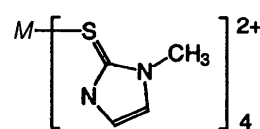
a group cannot occur unless packing around both the occupied and the empty sites is favorable. Thirdly, the axes located within and between the fragments are collinear; tetraphenyl molecules and ions can therefore be expected to form columns parallel to *c*. Finally, the cross sections of these columns are roughly square and are not changed much by *ortho* substituents (see Fig. 1). Since the interactions between the columns are rather nonspecific,[†] the columns can fit together in a square array.



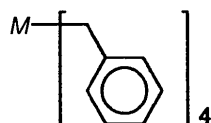
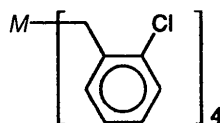
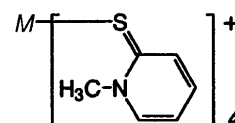
The importance of the columnar motif in salts of EPh_4^+ cations ($E = P, As$ or Bi) was pointed out by Mueller (1980); Knop *et al.* (1993) also noted the importance of the columnar motif in the salts of BPh_4^- with small monocations. The arrangement of a pair of ions within the columnar motif has been termed the 'translational quadruple phenyl embrace (TQPE)' by Dance & Scudder (1996), who analyzed pairwise PPh_4^- interactions.

In which space groups can such columns crystallize? Most space groups having $\bar{4}$ axes also include mirror planes, fourfold axes or 222 sites, all of which are detrimental to crystal packing unless occupied (Brock & Dunitz, 1994); the number of tetragonal space groups in which MAR_4 molecules and MAR_4^q salts are likely to crystallize is therefore limited. The tetragonal space groups that occur for molecules are $P\bar{4}2_1c$, $I\bar{4}$ and $I4_1/a$ (see Fig. 1). In $P\bar{4}2_1c$ adjacent columns are related by glide planes parallel to the edges of the squares and 2_1 axes perpendicular to *c*; column corners meet around axes 2. In $I\bar{4}$ adjacent columns are related by the centering operation (or 2_1 axes parallel to *c*) and column corners meet around axes $\bar{4}$. In $I4_1/a$ adjacent

[†] Robbins, Jeffrey, Cheswick, Donohue, Cotton, Frenz & Murillo (1975) characterized tetraphenylmethane as 'an overcrowded molecule in a loosely packed crystal environment'.

Table 3. Structures of some $M(\text{benzyl})_4$ -like molecules and ions $P\bar{4}2_1c$ (both $\bar{4}$)Sn ($\bar{4}$)Ti ($\bar{4}$) $I\bar{4}$ (both $\bar{4}$)U ($\bar{4}$)Fe, with NEt_4^+ ($\bar{4}$) $I4_1/a$ (both $\bar{4}$)Si ($\bar{4}$)Co, with 2 ClO_4^- ($\bar{4}$)

Other space groups:

Ge ($P2_1/n$; 1)Pb ($P2_1/n$; 1)Cu, Ag with BF_4^- ($P2_1/c$; 1)

columns are related by inversion centers and column corners meet around 4_1 axes. The groups that occur for $M\text{Ar}_4^q$ salts are $I\bar{4}$, $P\bar{4}2_1c$, $I\bar{4}2m$ and $I4_1/acd$. In the $I\bar{4}$ structures, which dominate the list, both types of ions form columns having $\bar{4}$ symmetry.

The remaining possible tetragonal space groups are $P\bar{4}$, $P4_2/n$ and $I\bar{4}2d$. Groups $P\bar{4}$ and $P4_2/n$ have twofold axes ($[0, 1/2, z]$ etc.) which are probably unfavorable; group $P\bar{4}$ also requires that the molecules form strict layers at $z = 0$ and $1/2$. Group $I\bar{4}2d$ has two sets of twofold axes perpendicular to c . The space groups that are actually observed are those with the least 'extra' symmetry. Indeed, the frequency of $P\bar{4}2_1c$ structures is surprising given the presence of glide planes and additional twofold axes. The occurrences of $I\bar{4}2m$ (three structures), with its mirror plane, and $I4_1/acd$ (one structure), with its set of 222 sites, are even more unexpected.

Crystallization in tetragonal groups is sufficiently favorable that it may occur even if the molecules or counterions must be disordered. The compound $\text{SnPh}_3(\text{CSSCH}_3)$ (Kunze, Bolz & Winter, 1981) crystallizes in $P\bar{4}2_1c$ with cell constants ($a = 11.843$, $c = 6.77$ Å) similar to those of SnPh_4 [$a = 12.058$, $c = 6.581$ Å (Belsky, Simonenko, Reichsfeld & Saratov, 1983)]. The salts $[\text{PPh}_4][\text{C}_{60}]\text{X}$, $\text{X} = \text{Cl}$ (Bilow & Jansen, 1994) and $\text{X} = \text{I}$ (Penicaud, Perez-Benitez, Gleason, Munoz & Escudero, 1993) crystallize in $I4/m$ with $Z' = 1/8$ and the PPh_4^+ ions on $\bar{4}$ sites; the C_{60} anions are disordered around $4/m$ sites and the I^- sites are only partially occupied. The salt $[\text{PPh}_4][\text{PBr}_2\text{S}_2]$ crystallizes in $I\bar{4}$ with $Z' = 1/4$ and the necessary disorder of anions around $\bar{4}$ sites (Mueller & Mohammed, 1984); the salts $[\text{PPh}_4][\text{VO}_2\text{F}_2]$ (Fairhurst, Hughes, Leigh, Sanders & Weisner, 1994), $[\text{AsPh}_4][\text{VO}_2\text{Cl}_2]$ (Mueller

& Mohammed, 1984) and $[\text{AsPh}_4][\text{WOF}_5]$ (Massa, Herman & Dehnicke, 1982) are isostructural. Crystals of $[\text{PPh}_4][\text{InI}_3(\text{C}_2\text{H}_5)_3]$ are in the group $I4_1/a$, with $Z' = 1/4$ and a disordered anion (Khan, Peppe & Tuck, 1985).

Another indication that $\bar{4}$ symmetry is favorable is the pseudosymmetry of some of the orthorhombic, monoclinic and triclinic MAr_4 structures. A pseudo-tetragonal cell for $\text{Sn}(2\text{-methoxyphenyl})_4$ has been described (Wharf & Simard, 1995); the tetragonal symmetry is broken because the layers are offset. The major difference between the two $Pba2$ structures (see Table 1) and the tetragonal structures is the arrangement of the molecular columns (see Fig. 2); in $Pba2$ each is surrounded by six, rather than four, other columns. A similar packing arrangement is found in the structure of $\text{Si}(\text{cyclohexyl})_4$ (Karipides, 1978), which is pseudohexagonal ($C2/c$, $Z' = 1/2$; $a = 17.646$, $c = 17.793$ Å, $\beta = 120.86^\circ$; $b = 8.533$ Å). The structure of $\text{SiPh}_3(p\text{-tolyl})$ (Charisse, Gauthey & Draeger, 1993; $Pbca$ with $Z' = 1$) is formed from molecular columns (parallel a) that are arranged in approximate squares, but

the cell is elongated (and doubled) along c ($b = 16.26$, $c = 2 \times 17.26$, $a = 7.16$ Å) to accommodate the 'extra' methyl groups (see Fig. 2).

Several ionic MAr_4^q salts crystallize in structures that can be viewed as superstructures of the more common arrangements. Crystals of $[\text{Li}(\text{H}_2\text{O})_4][\text{BPh}_4]$ (Bakshi, Sereda, Knop & Falk, 1994) have ions on general positions in space group $I4_1/a$. The hydrogen-bonding requirements of the cations apparently preclude their being located on $\bar{4}$ sites, but the columnar motif of the anions is retained. The structure is strongly pseudosymmetric. The compound $[\text{AsPh}_4]\text{Cl}_3$ crystallizes in $I\bar{4}$ with cations on all four independent $\bar{4}$ sites and the anion on a general position (Bogaard, Peterson & Rae, 1981). The cations in one of the two independent stacks are, as expected, almost eclipsed, but there is a ca 45° rotation around the $\bar{4}$ axis between adjacent molecules in the second stack. {In the related salt $[\text{SbPh}_4]\text{I}_3$ the columns of cations are retained, but their site symmetry of the cations is reduced from $\bar{4}$ to 2 (Bricklebank, Godfrey, Lane, McAuliffe & Pritchard, 1994; $P2/n$, $Z' = 1/2$.)}

Tetragonal groups are also found for some molecular complexes (or co-crystals). The 1:1 co-crystal of CPh_4 with CBr_4 (Reddy, Craig & Desiraju, 1996) crystallizes in $I\bar{4}$ with $Z' = 1/4$ and cell constants very similar to those of tetra(4-bromophenyl)methane. Simard and Wuest (Simard, Su & Wuest, 1991; Wang, Simard & Wuest, 1994) have made and studied a series of tetraaryl molecules that assemble into diamantoid networks linked by hydrogen bonding. Two of the structures are tetragonal ($P4_2/n$, $Z' = 1/4$), presumably because the very large cavities are filled by molecules (e.g. a propionic acid) that are the right size to fill the voids and that can be arranged favorably around 'empty' $\bar{4}$ sites.

Two catenated complexes of Cu^1 also have MAr_4 units located on $\bar{4}$ (or higher) sites. The compound composed of tetrakis(4-cyanophenyl)methane, Cu^+BF_4^- , and two

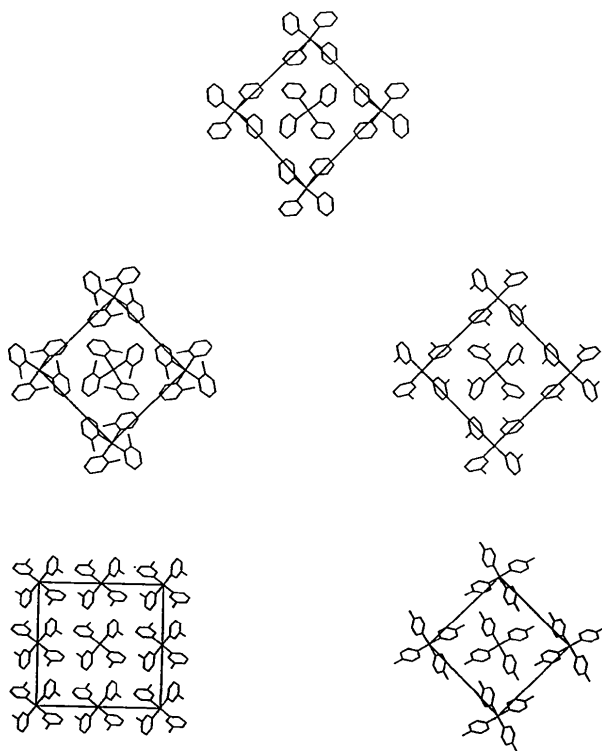


Fig. 1. Examples of tetragonal structures of MAr_4 molecules showing the interactions between the columns of molecules. The top drawing shows the MPh_4 structure in $P4_2/n$ found for $M = \text{C, Si, Ge, Sn, Pb}$ or Os ; the next two diagrams show how this structure is perturbed when *ortho*- ($M = \text{Sn, Pb}$ or Mo) or *meta*-methyl substituents ($M = \text{Pb}$) are added. The $I4_1/a$ structure for $\text{Sn}(m\text{-tolyl})_4$ is shown in the fourth drawing. (Note that the cell constant a is larger by $2^{1/2}$ for the $I4_1/a$ structures than for comparable $P4_2/n$ and $I\bar{4}$ structures.) The last drawing shows the $I\bar{4}$ structure of $\text{Pb}(p\text{-tolyl})_4$.

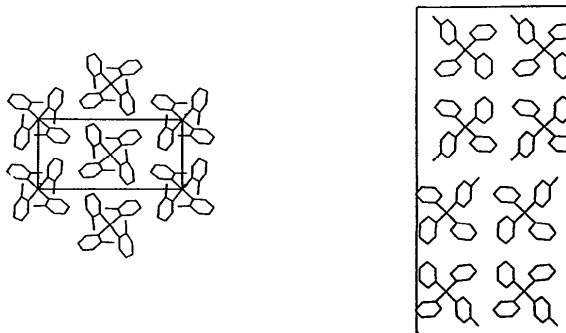


Fig. 2. Two other examples of MAr_4 structures in which the columnar motif is important. The structure on the left $[\text{M}(o\text{-tolyl})_4]$, $M = \text{Ru}$ or Os ; $Pba2$ has a hexagonal rather than square arrangement of molecular columns. The structure on the right $[\text{SiPh}_3(o\text{-tolyl})]$; $Pbca$ has a square array of molecular columns, but there is a small displacement of the molecules along a (horizontal axis) at $z = 0$ and $1/2$ (c axis vertical).

nitrobenzene solvent molecules crystallizes in $I\bar{4}m2$ with $Z' = 1/8$ (Hoskins & Robson, 1989). The compound $[\text{Cu}(4,4'\text{-bipyridyl})_2]\text{PF}_6$ crystallizes in $P4/n$ with the Cu^1 ions on $\bar{4}$ sites and the anions on sites of symmetry 4 (MacGillivray, Subramanian & Zaworotko, 1994).

5. Conclusions

Crystallographers have come to expect the loss of molecular symmetry (except inversion) upon crystallization. It can be argued, however, that molecules will crystallize on sites of the highest possible symmetry unless there is an energy penalty (unfavorable intramolecular interactions; unfavorable crystal packing) for doing so. A basis for this argument is the shape of the energy curves describing intermolecular atom-atom contacts. These curves are very steep on the repulsive side and shallow on the attractive side, so that contacts between neighboring molecules are nearly always repulsive. If an MAr_4 molecule were to lie on a general position rather than a $\bar{4}$ site, then the number of independent pairwise atom-atom contacts between molecules would be increased by a factor of four. The average energy of four different contacts in a low-symmetry structure would quite likely be greater than the energy of a single contact in a tetragonal structure.

Fig. 3 demonstrates why stacks of MAr_4 fragments are possible when similar stacks of planar molecules are not. If the plane normal of a flat molecule is parallel to a translation (Fig. 3a), like-like interactions within the stack and interactions between edges are unfavorable. Stacks of planar molecules are indeed common, but the angle between the plane normal and the translation vector is nearly always substantial and the plane normals of molecules in adjacent stacks are seldom parallel. The familiar herringbone arrangement is the result (Fig. 3b). Stacks of tetraaryl molecules (Fig. 3c) avoid these disadvantages. Stacks related by translations (*e.g.* **a** and/or **b**) in directions perpendicular to the stack axis (*e.g.* **c**) give herringbone arrangements of the peripheral aryl groups provided the stacks are offset (*e.g.* by $c/2$).

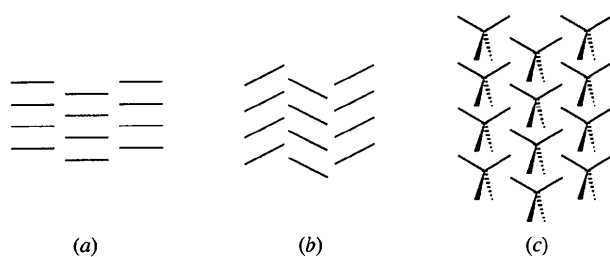


Fig. 3. Schematic drawing of (a) a possible packing of planar molecules that is seldom observed because of like-like interactions and edge effects that are unfavorable; (b) the commonly occurring herringbone arrangement that is derived from (a) by increasing the angle between the plane normal and the translation vector; (c) a possible packing arrangement of stacks of molecules.

Since MAr_4 molecules and ions can be expected to favor crystallization in tetragonal space groups they may be used as design elements in crystal engineering. The absence of an inversion center in two of the favored space groups ($I\bar{4}$ and $P\bar{4}2_1c$) means that such crystals could have nonlinear optical properties.

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