



The crystal packing and engineering prospects of Hellwinkel's salt: $[P(2,2'\text{-biphenyl})_2]^+ [P(2,2'\text{-biphenyl})_3]^-$

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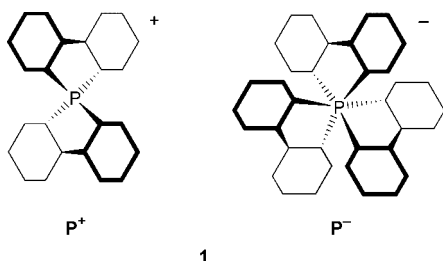
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The crystal structure of Hellwinkel's salt $[P(2,2'\text{-biphenyl})_2]^+ [P(2,2'\text{-biphenyl})_3]^-$ (**1**) is reported and the crystal packing analysed. The cation $[P(2,2'\text{-biphenyl})_2]^+$ (P^+) is analogous to Ph_4P^+ , and the anion $[P(2,2'\text{-biphenyl})_3]^-$ (P^-) is analogous to $[M(\text{bipy})_3]^-$ complexes, both of which form multiple aryl embraces in crystals, but not previously with each other. The chirality of P^- is potentially valuable for the resolution of chiral cations. The crystal supramolecularity of **1** is comprised of (1) a $P^- \cdots P^-$ sixfold aryl embrace with a calculated energy of $8.9 \text{ kcal mol}^{-1}$ attraction, (2) a tight homochiral embrace $P^+ \cdots P^-$ embrace using offset-face-to-face interactions between biphenyl ligands (calculated attraction $21.0 \text{ kcal mol}^{-1}$), (3) a parallel fourfold aryl embrace $P^+ \cdots P^+$ (calculated attraction $1.2 \text{ kcal mol}^{-1}$), and (4) several non-standard $P^+ \cdots P^-$ embraces (calculated attractions $13.9, 18.3 \text{ kcal mol}^{-1}$). Comparisons with related crystals are made. The prognosis for application of P^- to the resolution of phenylated molecules and cationic metal complexes with phenylphosphonium or phenylarsonium ligands is good.

Introduction

The salt $[P(2,2'\text{-biphenyl})_2]^+ [P(2,2'\text{-biphenyl})_3]^-$ **1** was prepared by Hellwinkel in 1965.^{1,2} In the following we will use the symbols P^+ for $[P(2,2'\text{-biphenyl})_2]^+$ and P^- for $[P(2,2'\text{-biphenyl})_3]^-$.



We are interested in **1** for four reasons. One relates to the general similarity of P^+ with Ph_4P^+ , which is commonly used for the crystallisation of anions, and which engages in multiple phenyl embraces of the type that we have investigated in detail.^{3,4} Multiple phenyl embraces between molecules are concerted combinations of local edge-to-face (EF) and the offset-face-to-face (OFF) geometries for a pair of aryl or heteroaryl rings: the sixfold phenyl embrace (6PE) is a concerted cycle (EF)₆, the parallel fourfold phenyl embrace (P4PE) is (OFF)(EF)₂, and the orthogonal fourfold phenyl embrace (O4PE) is (EF)₄. Crystal supramolecular extensions in one-, two- and three-dimensions have been described.⁵⁻⁷ The crucial difference in molecular geometry and conformation between P^+ and Ph_4P^+ is that the phenyl rings are linked in pairs in the former but are separate and largely unconstrained in the latter. Second, the 2,2'-biphenyl ligands in **1** are directly analogous to the 2,2'-bipyridyl (bipy) ligands in metal complexes, and chiral P^- is very similar in structure to $[M(\text{bipy})_3]^-$ complexes. We have previously described the high symmetry crystal lattices with infinite chains of sixfold aryl

embraces (6AE, analogous to 6PE) that occur for complexes $[M(\text{bipy})_3]^{z+}$, $z = 3, 2$ and 0 .⁸ The attractive energy in these 6AE motifs is most favourable when $z = 0$. The ion P^- could engage in the same threefold symmetric 6AE interaction, either as pairs, $(P^-)_2$, or as infinite chains, $(P^-)_\infty$. Third, the salt **1** provides a combination of embracing entities that has not been achieved previously: it is analogous to a molecular crystal containing both Ph_4P^+ and $[M(\text{bipy})_3]^{z+}$, and the embrace motifs between such species are not yet known. Finally, P^- is chiral, and has the potential for interaction with chiral cations in the solid state and in solution. $(\pm)\text{-}P^-$ has been resolved by fractional crystallisation of its *N*-methylbrucinium salt.⁹ The ability of the enantiomers of P^- to achieve resolution will be related to the crystal supramolecular motifs it forms. We note that while the term crystal engineering is credited to Schmidt,¹⁰ and it is now widely used, there is a large opus of earlier crystal engineering implicit in the design of diastereomeric lattices for resolution of chiral molecules and ions by fractional crystallisation.¹¹

These considerations raised the question of the intermolecular interactions between P^+ and P^- in crystalline **1**. Here we report the crystal structure of **1** (Table 1) and an analysis of its crystal packing and crystal supramolecular motifs in the context of these related embrace motifs and possible applications of P^- to resolutions and chiral discriminations.

Synthesis

Compound **1** was prepared and isolated as previously described.¹

Calculation of inter-ion energies

Inter-ion energies were calculated using the summed atom-atom method, with van der Waals and electrostatic compo-

Table 1 Crystal data for **1**^a

| Properties | Values |
|--|--|
| Empirical formula | C ₆₀ H ₄₀ P ₂ |
| <i>M_r</i> | 822.92 |
| Crystal system, space group | Monoclinic, <i>P2₁/a</i> (no. 14) |
| <i>a</i> /Å | 16.3355(2) |
| <i>b</i> /Å | 16.3158(2) |
| <i>c</i> /Å | 16.9505(2) |
| β/° | 111.0154(8) |
| <i>V</i> /Å ³ | 4217.26(9) |
| <i>Z</i> | 4 |
| ρ _{calcd} /g cm ⁻³ | 1.296 |
| μ/cm | 1.4 |
| <i>F</i> (000) | 1720 |
| <i>R</i> , <i>R_w</i> | 0.038, 0.042 |
| <i>T</i> /K | 200 |
| No. of unique reflections | 9677 |
| No. of reflections observed | 6257 (<i>I</i> > 2σ(<i>I</i>)) |

^aYellow plates 0.30 × 0.28 × 0.15 mm. Click here for full crystallographic data (CCDC no. 1350/39).

nents expressed by eqns. (1) to (4).

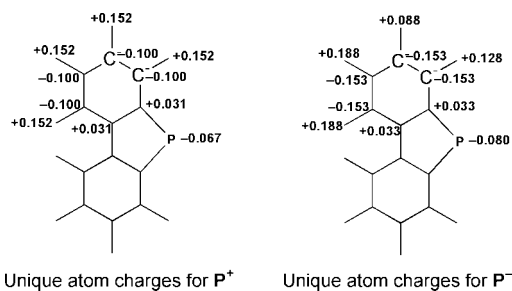
$$E_i^{\text{inter-ion}} = \sum_j E_{ij} \quad (1)$$

$$E_{ij} = e_{ij}^a \left[\left(\frac{d_{ij}}{d_{ij}^a} \right)^{-12} - 2 \left(\frac{d_{ij}}{d_{ij}^a} \right)^{-6} \right] + (q_i q_j) / (\epsilon d_{ij}) \quad (2)$$

$$d_{ij}^a = r_i^a + r_j^a \quad (3)$$

$$e_{ij}^a = \left(e_i^a e_j^a \right)^{0.5} \quad (4)$$

The parameters e^a and r^a for the Lennard-Jones potential describing the van der Waals energy are: P, $e^a = 0.20$ kcal mol⁻¹, $r^a = 2.1$ Å; C, $e^a = 0.093$ kcal mol⁻¹, $r^a = 1.945$ Å; H, $e^a = 0.02$ kcal mol⁻¹, $r^a = 1.6$ Å. The unique atom charges are presented in the following diagrams, and permittivity ϵ in eqn. (2) is distance-dependent, $\epsilon = d_{ij}$.



Crystal structure and crystal packing

The space group is *P2₁/a*, with one cation and one anion in the asymmetric unit, and no solvent in the lattice. The bond lengths and angles in P⁺ and P⁻ are normal, each of the five biphenylene ligands is coplanar to better than 0.1 Å, and the coordination stereochemistry of P⁻ is close to octahedral. The two biphenylene ligands in P⁺ are twisted slightly from orthogonality, with a dihedral angle between the ligand planes of 85.34°.

The principal interest in the structure is the crystal packing. We first describe the array of ions in the lattice and then focus on the details of each of the local inter-ion motifs. The ion centres are shown (as P atoms only) in Fig. 1: the cations P⁺ are coloured orange and the anions P⁻ magenta. The array of ions can be described as stacked layers, each layer being approximately hexagonal with oppositely charged ions alternating within each layer. The P–P separations for P⁺⋯P⁻ pairs in the layer are 6.56, 8.23 and 8.41 Å. There are two

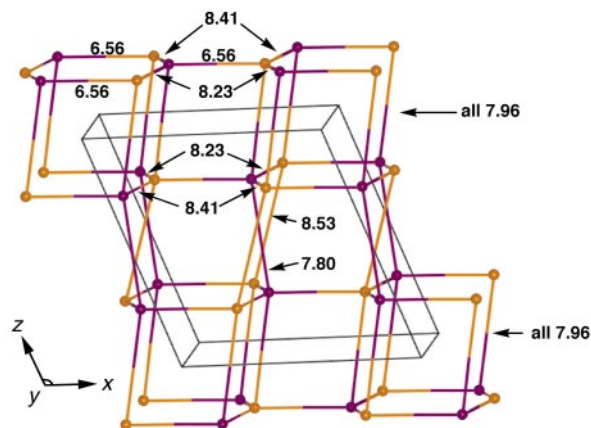


Fig. 1 The array of P atoms for the cations P⁺ (orange) and anions P⁻ (magenta) in the crystal lattice of **1**. The space group is *P2₁/a*. All P–P distances less than 9 Å are marked. These distance symbols are used to identify the inter-ion interaction motifs.

stacking modes relating adjacent layers: one set of adjacent layers is effectively eclipsed in projection normal to the layers, with oppositely charged ions all separated by P–P = 7.96 Å. The other juxtaposition of contiguous layers involves adjacent ions of the same sign, with P–P for P⁺⋯P⁺ at 8.53 Å and for P⁻⋯P⁻ at 7.80 Å. In this way the stack of layers is comprised of alternating homo-ion and hetero-ion interactions. Each ion, P⁺ or P⁻, is surrounded by one ion of the same charge and four of the opposite charge.

An important inter-ion motif is the association of two anions, P⁻⋯P⁻, at P–P = 7.80 Å. This motif is an excellent

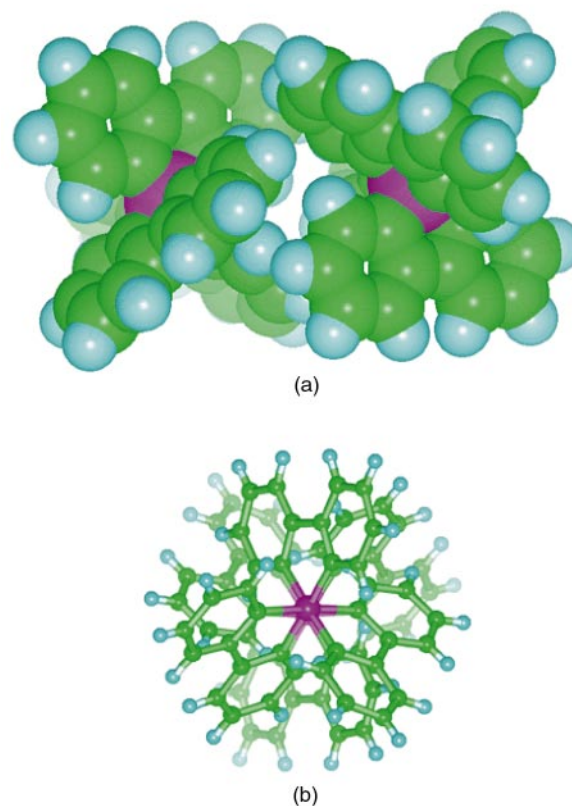


Fig. 2 The centrosymmetric sixfold aryl embrace (6AE) between a pair of P⁻: (a) space-filled side view; (b) skeletal end view showing the eclipsed ions. One end of each biphenyl ligand forms an edge-to-face (EF) interaction across the interaction domain with another ligand, and the cycle of six EF primary motifs is concerted. This is the 7.80 Å motif of Fig. 1. The H⋯C distances in the EF interactions range from 2.83 to 3.3 Å.

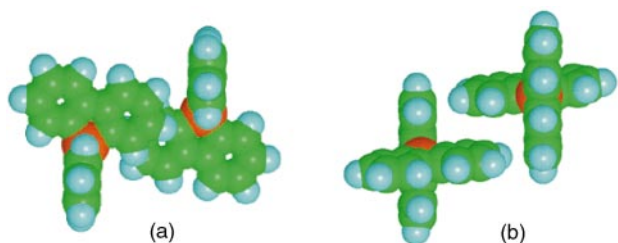


Fig. 3 Two orthogonal views of the parallel fourfold aryl embrace (P4AE) between two P^+ ions. This is the 8.53 Å motif of Fig. 1. The interplanar separation in the OFF is 3.55 Å, and the H...C distances in the EF motifs are ~3.3 Å.

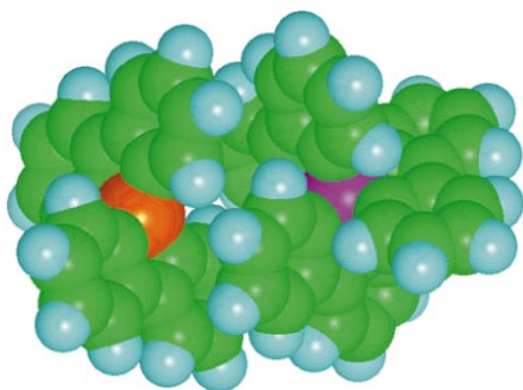


Fig. 4 The embrace between P^+ (left, orange) and P^- (right, magenta) at $P-P = 6.56$ Å. The (non-crystallographic) twofold axes of both P^+ and P^- are close to collinear with the motif axis, which is horizontal in this view. There are two OFF primary motifs, at the upper and lower regions of the interaction domain in this view. Note that the two ions are homochiral: they have the same helicity. Click image or here to access a 3D representation.

sixfold aryl embrace (6AE), shown in detail in Fig. 2. One end of each biphenyl ligand forms an EF interaction across the interaction domain, generating the characteristic cycle of concerted (EF)₆. The 6AE is crystallographically centrosymmetric and closely approaches S_6 symmetry (Fig. 2(b)). Fig. 2 shows that the EF motifs are very well-formed, with H atoms on the edge directed over the C atoms of the face. Both ends of P^- are equivalent along the molecular threefold axis, and therefore P^- could form 6AE at both ends (as do the $[M(\text{bipy})_3]$ complexes), but does not in **1**.

The homo-cation $P^+ \cdots P^+$ embrace ($P \cdots P$ 8.53 Å, Fig. 1) is a parallel fourfold aryl embrace, P4AE, shown in Fig. 3. This

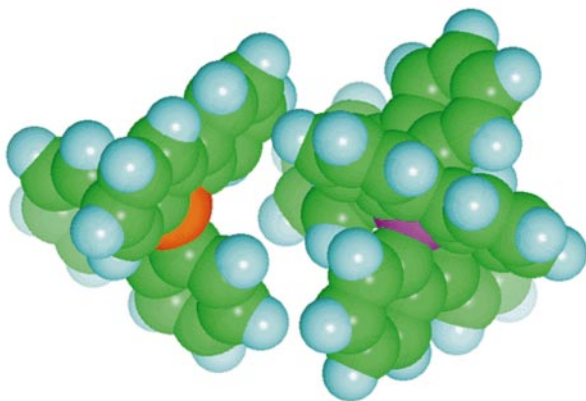


Fig. 5 The 7.96 Å motif in **1**. The threefold axis of P^- is close to the motif axis, which is horizontal in this view. There are two well-developed primary EF motifs, at the front of this picture. The ions are heterochiral.

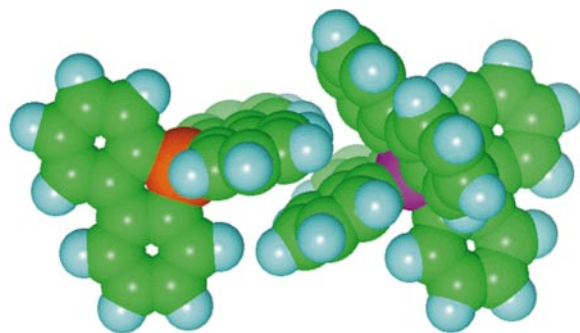


Fig. 6 The $P^+ \cdots P^-$ embrace, OFF + EF, at 8.23 Å.

centrosymmetric embrace is comprised of one OFF motif in which the H atoms of one ring are over C atoms of the other (see Fig. 3(a)), and two EF motifs.

In addition to these embraces of each ion with another ion of the same charge, each ion is surrounded by four ions of the opposite charge, at $P \cdots P$ distances of 6.56, 7.96, 8.23 and 8.41 Å.

Fig. 4 shows the close motif at 6.56 Å. The P^- ion is oriented with a twofold axis close to the motif $P^+ \cdots P^-$ axis, and a twofold axis of P^+ is also close to collinear with these two axes. This allows the two ligand planes of P^+ to become almost parallel with two ligand planes of P^- , and generates two pseudo-OFF primary motifs. This parallelism of the ligand planes and absence of EF primary motifs permits the two ions to approach each other more closely than other motifs where EF's occur, and accounts for the relatively short P-P distance. The secondary motif here is effectively (OFF)₂, which is analogous to the threefold (OFF)₃ embrace between MePh_3P^+ and $[\text{Cr}(\text{oxalate})_3]^{3-}$.¹² This embrace type with parallel ligand flanges is very rare,¹³ and is geometrically awkward to the extent of being impossible for two $[M(\text{bipy})_3]$ or $[M(\text{phen})_3]$. It is the flatter array of the two biphenylene ligands in P^+ that allows this (OFF)₂ motif in **1**. An important consequence of the (OFF)₂ motif is that the two species involved in the embrace are homochiral, in contrast to the heterochiral 6AE. The crystal lattice is centrosymmetric, and so is a racemate containing homochiral embraces of both helicities.

The 7.96 Å embrace is shown in Fig. 5. Apart from two good EF motifs there is no good development of concerted primary motifs in this secondary motif. The two ions are heterochiral.

The two other interior motifs, at 8.23 and 8.41 Å, are portrayed in Figs. 6 and 7. Both have one biphenyl ligand of P^+ inserted between two biphenyls of P^- , allowing one OFF and one EF primary motif in each case.

Having described the main embrace motifs, it is necessary to examine higher levels of association and check for extended embraces in the crystal packing. Fig. 8 (with the same orientation as Fig. 1) shows that the crystal structure is essentially layered parallel to the *ab* plane. There are two

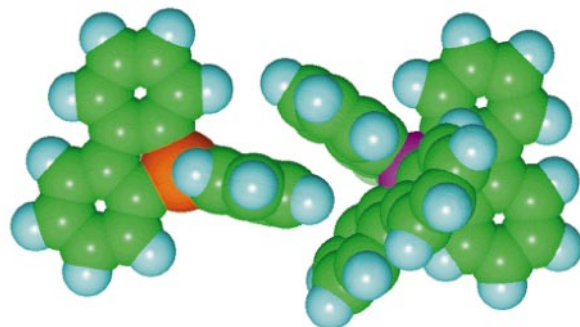


Fig. 7 The $P^+ \cdots P^-$ embrace, OFF + EF, at 8.41 Å.

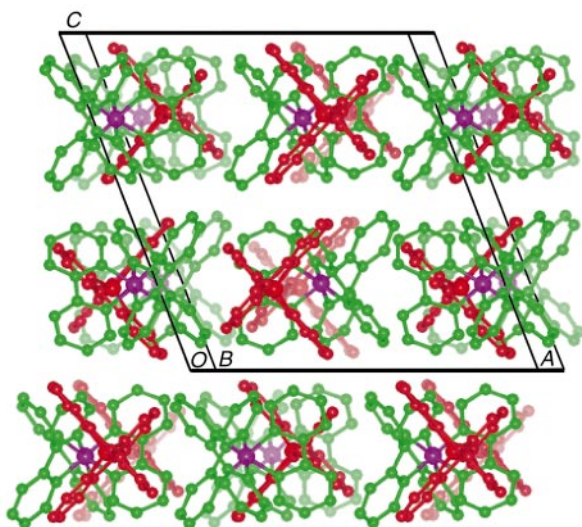


Fig. 8 The layers parallel to ab in crystalline **1**: cations P^+ have C red; anions P^- have P magenta and C green; H atoms are omitted. The 6AE $P^- \cdots P^-$ motif and the P4AE $P^+ \cdots P^+$ motif occur between the upper two layers, across $z = 0.5$, and the 7.96 $P^+ \cdots P^-$ motif occurs between the lower two layers, across $z = 0$.

different interfaces between the layers: one involves the 7.96 Å motifs, and the other the 6AE and P4AE embraces. All $P^+ \cdots P^-$ motifs except the 7.96 Å are within the layers.

The energies of the secondary motifs have been calculated using our standard procedures: the results are contained in Table 2. The hetero-ion $P^+ \cdots P^-$ motifs where the coulombic contributions augment the van der Waals attractions are more attractive than the homo-ion motifs, but both homo-ion motifs are attractive, at -8.9 kcal mol $^{-1}$ for the 6AE ($P^- \cdots P^-$) and -1.2 kcal mol $^{-1}$ for the P4AE ($P^+ \cdots P^+$). We note that the tight hetero-ion (OFF) $_2$ embrace is particularly stable, at -21.0 kcal mol $^{-1}$. The layering in the crystal is consistent with these energies, in that the three most attractive secondary motifs occur within the layers and the interlayer motifs are appreciably less attractive.

Discussion

The sizes of the P^+ and P^- ions in **1** are not markedly different, and, in the absence of local supramolecular motifs, a cubic array (fcc or bcc) of ions with hetero-charge primary contacts would be expected. However, multiple aryl embraces, as secondary motifs comprised of concerts of the primary OFF and EF motifs, play a significant role in the crystal packing of **1**. The 6AE between two P^- ions is very well-developed, and calculated to contribute an attractive energy that is of the order of half the attractive energy for hetero-charged $P^+ \cdots P^-$ motifs, and it is evident that the optimum crystal packing in **1**† has incorporated both homo-charged and hetero-charged motifs. We note that infinite chains of P^- linked by 6AE, analogous to

Table 2 Calculated energies [kcal mol $^{-1}$] of the secondary motifs in **1**

| Secondary motif | Motif label | van der Waals energy | Coulombic energy | Total energy |
|-------------------------------|-------------|----------------------|------------------|--------------|
| $P^- \cdots P^-$, 6AE | 7.80 | -13.1 | +4.2 | -8.9 |
| $P^+ \cdots P^+$, P4AE | 8.53 | -6.3 | +5.1 | -1.2 |
| $P^+ \cdots P^-$, (OFF) $_2$ | 6.56 | -14.4 | -6.6 | -21.0 |
| $P^+ \cdots P^-$ | 7.96 | -8.6 | -5.3 | -13.9 |
| $P^+ \cdots P^-$ | 8.23 | -11.2 | -7.1 | -18.3 |
| $P^+ \cdots P^-$ | 8.41 | -11.5 | -6.8 | -18.3 |

†We are exploring for polymorphs of **1**.

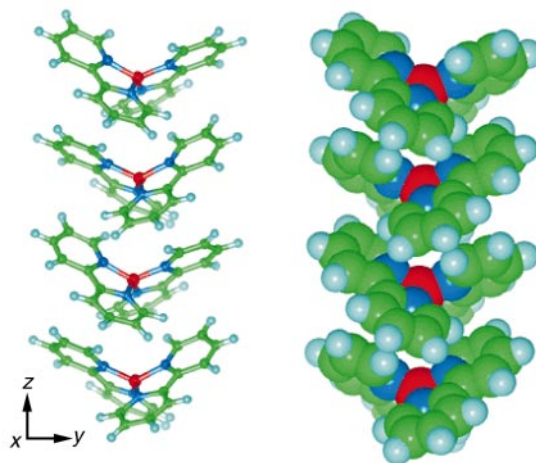


Fig. 9 The stack of molecules $Si(bipy)_2 3$ (in crystalline BIPYSI), in skeletal and space-filling representations. In each bipy ligand, each pyridyl ring functions as 'donor' and 'acceptor' in two edge-to-face EF local motifs. The edge is inclined at about 70° to the face. There are four such EF motifs between each pair of molecules.

the infinite chains of 6AE for complexes $[M(bipy)_3]^{z+}$,⁸ do not occur. This alternative packing would require corresponding chains of cations P^+ , calculated to be less attractive, and these chains may not be commensurate with the anion chain, or allow good inter-ion embraces between chains.

The crystal packing of **1** can be compared with that of $Ph_4P^+ Ph_4B^-$ **2**, in which the oppositely charged ions are much closer in shape and size.¹⁴ The tetragonal lattice of **2** is dominated by translational columns of orthogonal fourfold phenyl embraces (O4PE) with alternation of oppositely charged ions along the columns. Less significant attractive motifs occur between the columns and influence the registry between columns.¹⁵ The net supramolecular energies between homo-charged XPh_4^\pm ions are not repulsive, as is often assumed.¹⁶

The enantio-isomerism of the crystal supramolecular motifs in **1** is of particular interest to us, since P^- could be used for the resolution of cations by fractional crystallisation of diastereomers. The 6.56 hetero-charged motif is homo-chiral, while the 7.80 homo-charged 6AE motif is heterochiral. Our analysis shows that both the 6AE between two P^- and a hetero-charged 6AE or similar embrace involving P^- are predicted to be

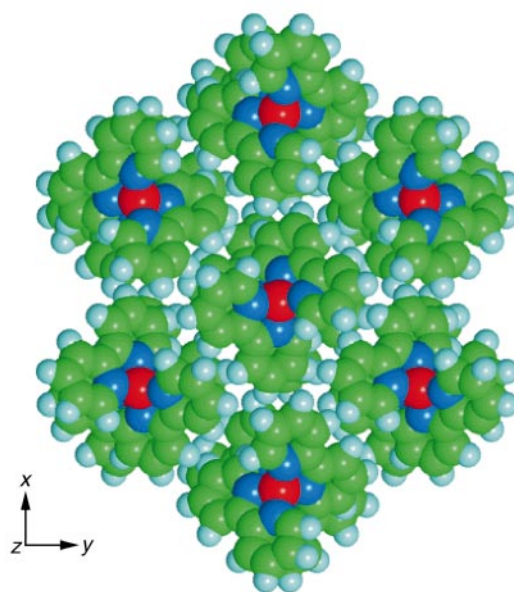


Fig. 10 The pseudo-hexagonal array of stacks of $Si(bipy)_2 3$ in crystalline BIPYSI.

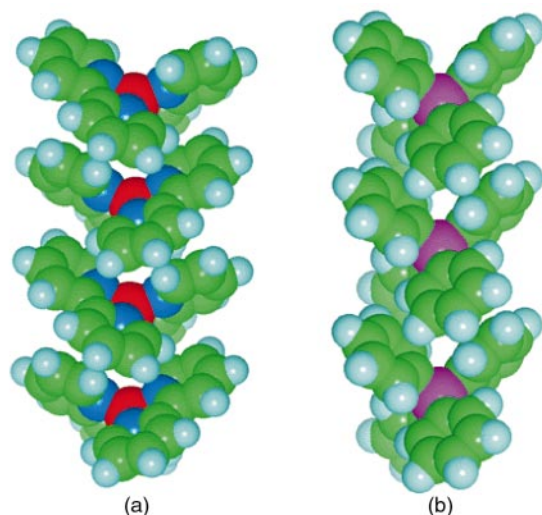


Fig. 11 Comparison of the stacks of Si(bipy)₂ with (EF)₄ secondary motifs between molecules (a) and a typical stack of O4PE formed by Ph₄P⁺ (b). The two figures are drawn on the same scale. The repeat distances are 5.1 Å in (a) and 7.1 Å in (b).

particularly stable. The prognosis is good for application of P⁻ to the resolution of phenylated molecules and of metal complexes with phenylphosphonium or phenylarsonium ligands. Metal complexes containing Ph₃P ligands commonly form 6PE secondary motifs.¹⁷

The crystal supramolecularity of the P⁺ ion can be understood further by inspection of the crystal structure of the closely related compound Si(bipy)₂ **3** [CSD refcode BIPYSI].¹⁸ The molecular stereochemistry of this compound is partially flattened tetrahedral: the dihedral angle between the ligand planes is about 75° in **3**, and 85° in **1**. Molecules of **3** are stacked parallel to the *c* axis in the space group *Pbca*, as shown in Fig. 9, such that the Si–Si distance is 5.07 Å and the Si–Si–Si angle is 175.5°. This stack is shown in Fig. 9, and the pseudo-hexagonal array of stacks is shown in Fig. 10.

These stacks of Si(bipy)₂ allow EF primary motifs between molecules: there are four EF motifs between each pair of molecules. Each pyridyl ring functions as both donor (at the edge) and acceptor (at the face) in EF motifs. This stack is thereby analogous to the linear infinite chain of orthogonal fourfold phenyl embraces (O4PE) previously described in detail for molecules of the type XAr₄.⁵ The two stack motifs are compared and contrasted in Fig. 11. In each case there are four aryl groups and four EF motifs in the embrace domain: the difference is due to the constraining linkage of pairs of rings in Si(bipy)₂, in contrast to the conformational freedom of the rings in XAr₄. The consequence of this is that the EF

interactions in the Si(bipy)₂ stack have a lesser inclination of the two rings in each EF, while in XAr₄ the EF interactions can be more strongly canted and approach orthogonality. This in turn affects the repeat distance along the stack, as is evident in Fig. 11: the repeat distance in the O4PE stack shown in Fig. 11(b) is 7.1 Å, which contrasts the 5.1 Å repeat for Si(bipy)₂ (Fig. 11(a)).

The columnar motif demonstrated by Si(bipy)₂ in BIPYSI is feasible for P⁺ in its crystals with other anions. A conceivable alternative crystal structure for **1** is a column of P⁺ as in Fig. 11(a) with a parallel infinite column of P⁻ engaged in 6AE at either end, as are known for [M(bipy)₃]⁺.⁸ However, these columns would be incommensurate. Further experiments with P⁺ and P⁻ are in progress.

Acknowledgements

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