High symmetry crystal supramolecularity: –XPh_3 molecules in rhombohedral lattices, using multimolecular rather than bimolecular sixfold phenyl embraces†

Ian Dance* **and Marcia Scudder**

School of Chemistry, University of New South Wales, Sydney 2052, Australia.
E-mail: I.Dance@unsw.edu.au

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Molecules of the type Ph_3XYXPh_3 commonly crystallise in trigonal and rhombohedral lattices comprised of hexagonal arrays of sixfold phenyl embraces (HA6PE) which are bimolecular concerts of edge-to-face (EF) phenyl···phenyl interactions. In this paper we describe crystal structures containing molecules Ph_3XYXPh_3, also crystallising in the space group $R\bar{3}$ characteristic of the HA6PE lattice, but without the bimolecular $(EF)_6$ form of 6PE. Instead there are multimolecular concerts of EF and offset-face-to-face (OFF) motifs, building up hexagonal layers and in some cases generating high symmetry cavities. These crystals possess the same molecular symmetry as the HA6PE systems, and crystallise in the same space groups, but have different intermolecular motifs: they are effectively crystal supramolecular isomers of the HA6PE lattice. The specific crystalline compounds analysed are $Ph_3SiOSiPh_3 \cdot C_6H_6$, $Ph_3SiNCNSiPh_3$ and $Ph_3PNPPh_3{}^+[Nb(CO)_6]^-$. The crystal packing in $(MePh_3P)_2[Cu_4I_6]$, and in a high symmetry Ni_3 complex crystallised with Ph_3PO, both in space group $R\bar{3}c$ also characteristic of the HA6PE lattice, are supramolecular isomers of the HA6PE lattice because the bimolecular motif is $(OFF)_3$ rather than $(EF)_6$. The crystal packing analyses benefit by recognition of the asymmetric sectors of the intermolecular interactions and of cavities, in addition to the conventional asymmetric sectors of the molecular components.

Molecules containing the XPh_3 function are able to form attractive intermolecular motifs based on a concert of edge-to-face (EF) local interactions between phenyl rings. When formed between a pair of molecules this intermolecular motif is the sixfold phenyl embrace (6PE), $(EF)_6$, which is a widely occurring intermolecular motif[1–6] that can undergo further association and generate one-, two- and three-dimensional networks.[7–11] The 6PE can and does have S_6 ($\bar{3}$) point symmetry. Derivatisation of the phenyl groups need not interfere with these embrace motifs.[12] One of the three-dimensional networks is the hexagonal array of 6PE (HA6PE) in which the 6PE threefold axis and the molecules that form them are all parallel, generating a trigonal or rhombohedral lattice.[8,13] The 6PE form two-dimensional hexagonal arrays, and around the edges of these hexagons there are hexamolecular concerted embraces of phenyl rings, which may be $(EF)_6$ or $(OFF)_6$ (OFF is the offset-face-to-face configuration of a pair of phenyl groups) or may be more elaborate.[13] The HA6PE lattice occurs for a variety of molecules of the type Ph_3X and Ph_3XYXPh_3, and possesses a geometric variability that permits the inclusion of other species (such as anions where Ph_3PR^+ cations generate the array), and control of their site symmetry and charge state.

In our previous paper[14] we analysed the symmetry properties of the HA6PE lattice and other high symmetry molecular crystal structures in terms of the symmetry components that are important in the analysis of crystal supramolecularity: these four components are the molecular symmetry, the intermolecular motif symmetries, the crystal lattice symmetry (space group) and the symmetry of cavities generated within the lattice. We showed how these components may be combined in different ways for molecules containing the XPh_3 function.

In this paper we describe and analyse another set of molecular crystal structures, containing molecules of type Ph_3XYXPh_3, crystallising in the space group $R\bar{3}$ characteristic of the HA6PE lattice, but without the bimolecular 6PE. These are alternatives to the HA6PE lattice. The compounds in this set are listed in Table 1.

Results

The compounds in Table 1 fall into two groups: (1) those with an uncharged Ph_3XYXPh_3 molecule (Y absent or O) crystallising in the presence of an aromatic or heteroaromatic guest, with an acute rhombohedral cell ($\alpha \approx 62°$) and (2) two isostructural salts $Ph_3PNPPh_3{}^+[M(CO)_6]^-$ with an almost orthogonal cell ($\alpha \approx 92°$). We describe first the crystal packing of group 1, then demonstrate the contrast with the guest-free HA6PE lattice formed by a chemically related compound, $Ph_3SiNCNSiPh_3$, and finally describe the crystal packing of the salts in group 2.

The crystal packing of $Ph_3SiOSiPh_3 \cdot C_6H_6$ [CECXAJ02]

There are several determinations of this crystal structure. The original result[15] [CSD refcode CECXAJ] is less accurate and appreciably different from the other two,[16,17] and will be ignored. The results for CECXAJ02[17] are used here.

Fig. 1 shows part of the crystal packing of CECXAJ02, viewed perpendicular to the trigonal axis. The molecules have S_6 ($\bar{3}$) symmetry and are arranged in clear layers. The significant characteristic is that molecules in adjacent layers are not

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† Electronic supplementary information (ESI) available: additional figures (Fig. S1 and S2) described in the text. See http://www.rsc.org/suppdata/nj/b1/b104328p/

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Table 1 Compounds of the type $Ph_3X(Y)XPh_3$ crystallising in the space group $R\bar{3}$ and not forming bimolecular sixfold phenyl embraces

REFCODE	Component 1	Component 2	Rhombohedral cell dimensions, a/Å, α/°
HPGEBZ10	$Ph_3Ge–GePh_3$	Benzene	10.88, 64.02
VINXOF	$Ph_3Sn–SnPh_3$	Benzene	10.97, 63.35
REPNEF	$Ph_3Sn–SnPh_3$	Toluene	11.16, 63.85
CECXAJ02	$Ph_3Si–O–SiPh_3$	Benzene	11.05, 61.63
DOHDOT	$Ph_3Si–O–SiPh_3$	Piperidine	11.20, 60.19
TAFBAD	$Ph_3Si–O–SiPh_3$	Toluene	11.13, 62.48
BILNEP10	$Ph_3P–N–PPh_3{}^+$	$[Nb(CO)_6]^-$	9.83, 91.98
BUVGII	$Ph_3P–N–PPh_3{}^+$	$[Ta(CO)_6]^-$	9.81, 92.02

collinear and do not form bimolecular 6PEs between the layers. The benzene guest molecules are located in positions that block 6PE formation. However, it is evident from Fig. 1 that the phenyl groups of contiguous molecules occur in bilayers perpendicular to the trigonal axis. These bilayers are hexagonal nets of molecules pointing alternately up and down, and participating in multimolecular EF interactions. Part of one bilayer is shown in Fig. 2, with the EF interactions marked. Well-developed hexamolecular $(EF)_6$ cycles occur. Each Ph_3Si participates in six such EF interactions with three neighbouring molecules.

The complete set of EF interactions in this crystal, together with the Si–O–Si intramolecular linkages, generates an effective three-dimensional scaffold. The molecules Ph_3XXPh_3 (X = Ge, Sn) form the same lattice (see Table 1) and intermolecular motifs, with a slight contraction in the distance between the bilayers. As outlined in the previous paper, high symmetry and effective supramolecular lattices such as this can generate cavities occupied by guest molecules, which occurs here with inclusion of benzene, piperidine, or toluene (see Table 1). The locations and surrounds of the benzene molecules in CECXAJ02 are shown in Fig. 3. Comparison of Fig. 3(a) with Fig. 2 shows that the benzene molecules lie against the face of one Ph_3Si (called the coaxial molecule), and each is surrounded equatorially by the lower halves of three $Ph_3SiOSiPh_3$ molecules with which the coaxial molecule forms EFs. The upper halves of these three molecules complete the enclosure of the cavity [Fig. 3(b)]. The site symmetry for the guest is 3. The upper and lower sections of the cavity are similar, with three oblique Ph closing the ends (from one $Ph_3SiOSiPh_3$ molecule at the bottom and three molecules at the top). In fact the array of 12 phenyl rings immediately surrounding the benzene molecule has pseudo-$\bar{3}$ symmetry, but this is not a crystallographic $\bar{3}$ site.

Comparison with the HA6PE lattice: $Ph_3SiNCNSiPh_3$ [TPSICI] and $Ph_3SiOSiPh_3 \cdot C_6H_6$ [CECXAJ02]

The space group of the lattices just described, $R\bar{3}$, is the same as that of many of the HA6PE lattices. A question at this point concerns the relationships between the supramolecular arrangements and crystal packing of two lattices with the same high symmetry. We illustrate that relationship for two chemically similar molecules, $Ph_3SiNCNSiPh_3$ [in TPSICI][18] and $Ph_3SiOSiPh_3$ [CECXAJ02].[17]

Fig. 4 shows that in TPSICI the $Ph_3SiNCNSiPh_3$ molecules are coaxial and form axial sequences of 6PE at each end of the molecule. Both the molecule and the 6PE are at $\bar{3}$ sites in the crystal. The interactions between the $\cdots Ph_3SiNCNSiPh_3 \cdots 6PE \cdots Ph_3SiNCNSiPh_3 \cdots 6PE \cdots$ axial sequences are EF, occurring in multimolecular hexagonal nets. There are two types of these, illustrated in Fig. 5. The two

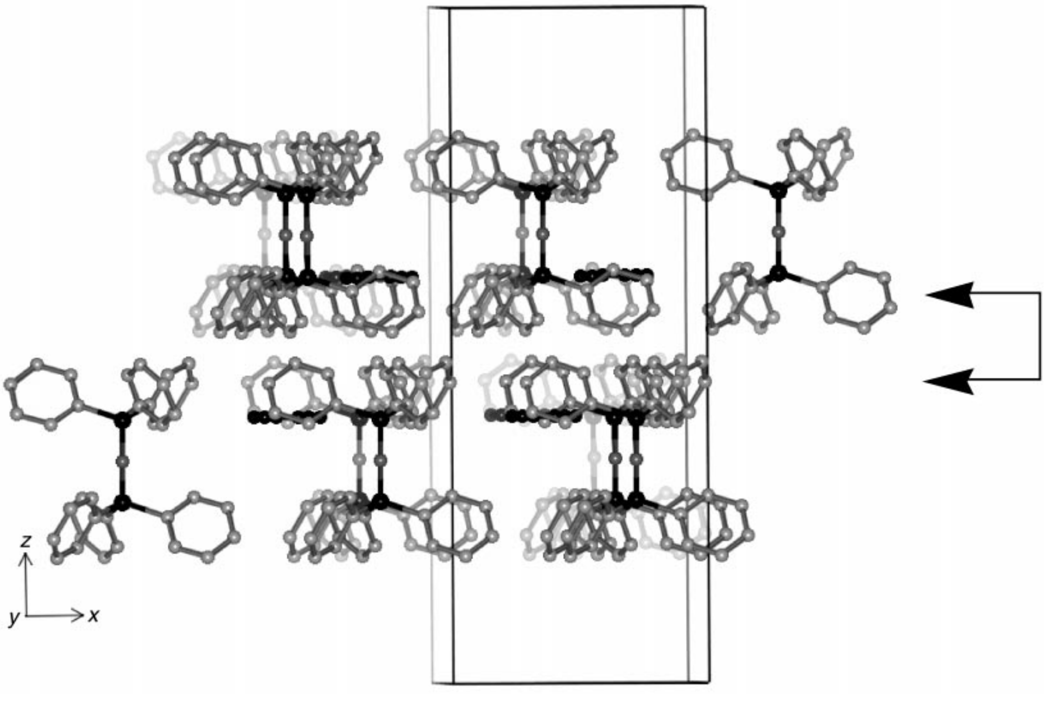


Fig. 1 Side view of part of the crystal packing of $Ph_3Si–O–SiPh_3 \cdot C_6H_6$ [CECXAJ02]: Si and benzene C are black (not all of the benzene molecules are included). The linear Si–O–Si geometry and the S_6 symmetry of the molecule is evident. Note that the Ph_3Si sections of adjacent molecules along the trigonal direction are not collinear and do not form 6PEs. Instead, a benzene molecule is located over each Ph_3Si section. The bilayer of phenyl groups discussed in the text is identified by the arrows.

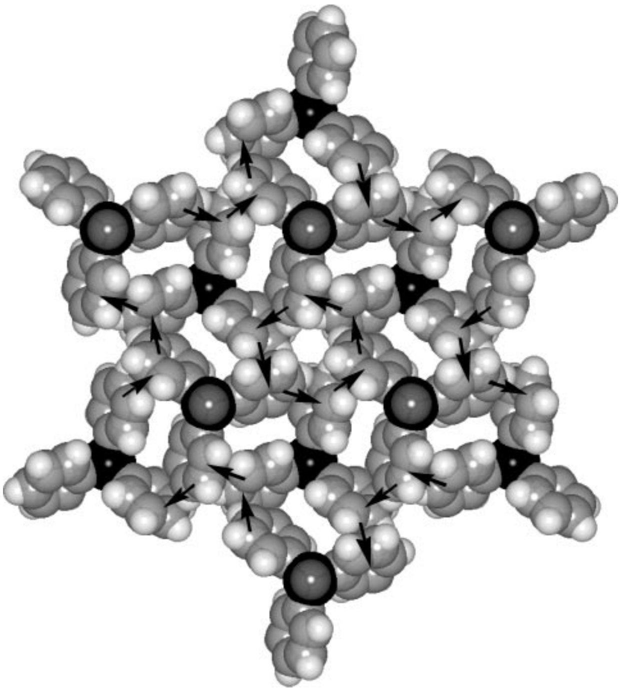
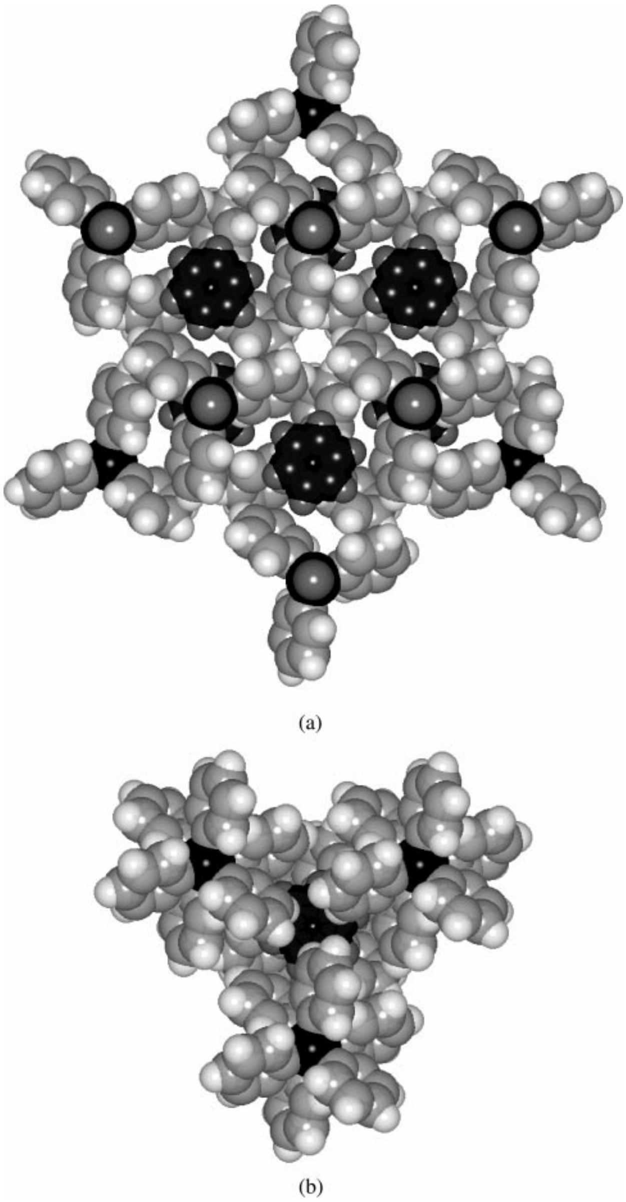


Fig. 2 Ph_3SiO sections of molecules in a bilayer of $Ph_3SiOSiPh_3 \cdot C_6H_6$ [CECXAJ02]. Each molecule has been truncated at the distal $SiPh_3$ group: molecular axes alternate up and down from the layer. The arrows show the locations of the EF interactions. Centres of inversion occur between nearest molecules. Guest benzene molecules are omitted for clarity.

different hexagonal nets of EF arise from different axial positions of the molecules relative to the median plane of the net and contain different sequences of EF. One type [Fig. 5(a)] is a double counter-cyclical $(EF)_6$ net with $\bar{3}$ site symmetry, symmetrically but not metrically analogous to that shown at the centre of Fig. 2. The other [Fig. 5(b)] is enlarged, with site symmetry 3.

We can conclude that the two lattice types, without 6PE [CECXAJ02] and with 6PE [TPSICI], use Ph···Ph interactions effectively. As discussed in the previous paper,[14] the concept of the asymmetric segment of intermolecular interactions is useful in understanding crystal supramolecularity. In both of the crystals considered here the crystallographic asymmetric unit contains one phenyl group, but the asymmetric segments of intermolecular interactions are quite different, as illustrated in Fig. 6. All of the surrounding participants in EF interactions are evident. In CECXAJ02 ($Ph_3SiOSiPh_3 \cdot C_6H_6$) the unique phenyl ring functions as one acceptor and one donor in EF interactions (see also Fig. 2) with other molecules, but is also involved in EF with four benzene molecules. In the HA6PE lattice, $Ph_3SiNCNSiPh_3$, the unique phenyl ring interacts with six surrounding phenyl rings, three as EF donors and three as EF acceptors.



(a)

(b)

Fig. 3 The surroundings of the benzene in CECXAJ02. (a) Locations of benzene in the multimolecular EF two-dimensional net (*cf.* Fig. 2). The top halves of the upper $Ph_3SiOSiPh_3$ molecules have been truncated to reveal the equatorial surrounds. (b) One cavity containing benzene with the upper halves of the three surrounding molecules included. The site symmetry in the guest cavity is exactly 3, but approaches $\bar{3}$.

The crystal packing of $Ph_3PNPPh_3^+[Nb(CO)_6]^-$ [BILNEP10][19]

The crystal packing is described in terms of the net of $Ph_3PNPPh_3^+$ ions and the resulting cavities containing the $[Nb(CO)_6]^-$ ions. Fig. 7 shows a side view of the approximately orthogonal cell, still in space group $R\bar{3}$. The cations and anions, each with S_6 ($\bar{3}$) symmetry, alternate along the trigonal axes: 6PE formation is impossible in this arrangement. The PPh_3 ends of the cations form monolayers (contrast the bilayers in Fig. 1) and within these layers there are well-developed multimolecular motifs forming a hexagonal net. As shown in Fig. 8, there are both EF and OFF interactions between adjacent cations in this two-dimensional net. This is very effective and the local geometry appears to be better than that of CECXAJ02 (Fig. 2). The dimensions of the hexamolecular net in BILNEP10 are larger than in CECXAJ02 (related to the different angles α, see Table 1) and it accommodates an anion at its centre. Note that full extension of the net in Fig. 8 has each phenyl group involved in one OFF and two EF motifs.

The $[Nb(CO)_6]^-$ ion in BILNEP10 forms many O···H–C hydrogen bonds with phenyl groups of cations in contiguous layers (as shown in Fig. S1 of the ESI). While each is probably relatively weak, the large number (30) of them resulting from the high $\bar{3}$ symmetry of the anion and surrounding cations probably makes a substantial contribution to the lattice energy.

$(OFF)_3$ variant of the HA6PE lattice

In the context of this description of rhombohedral lattices that are different from the HA6PE lattice due to the absence of the bimolecular 6PE, it is appropriate to draw attention to two

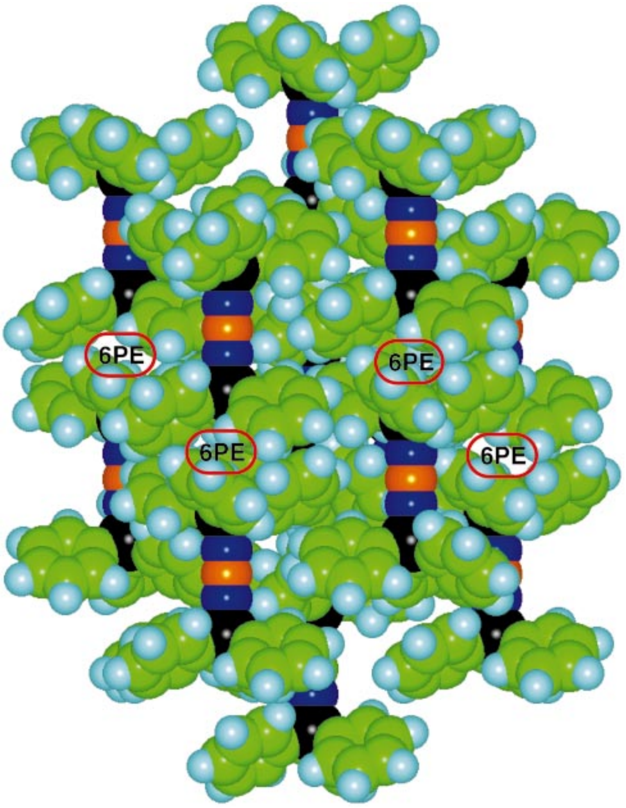


Fig. 4 Crystal packing in $Ph_3SiNCNSiPh_3$ [TPSICI] viewed perpendicular to the trigonal axis, space group $R\bar{3}$: Si black, N blue, cyanamide C orange. Locations of complete 6PE are marked. The molecules and the 6PE are at $\bar{3}$ sites. The axial sequences $\cdots Ph_3SiNCNSiPh_3\cdots$6PE$\cdots Ph_3SiNCNSiPh_3\cdots$6PE$\cdots$ are evident.

crystal structures that are also rhombohedral but contain a bimolecular $(OFF)_3$ motif in place of the bimolecular $(EF)_6$ motif of the standard 6PE. Fig. 9 (and Fig. S2 of the ESI) shows that $(MePh_3P)_2[Cu_4I_6]$ [MPPICU] contains pairs of $MePh_3P^+$ cations around $\bar{3}$ sites (in space group $R\bar{3}c$) engaged in a well-formed bimolecular $(OFF)_3$ embrace, and that these embraces generate puckered hexagonal layers surrounding anion sites, as is characteristic of the HA6PE lattice. The hexamolecular motif that generates the hexagonal layers is $(OFF)_6$, and this crystal structure is remarkably devoid of EF local interactions. The $[Cu_4I_6]_2^-$ ion is twofold disordered to conform to its 32 site symmetry. The HA6PE lattice with the $(OFF)_3$ variant of the bimolecular embrace occurs also in the crystal structure of the unusually symmetric Ni_3 complex shown in Fig. 10, crystallised with Ph_3PO [BTZANI]. Again the space group is $R\bar{3}c$.

Discussion

The crystal packings described here for molecules Ph_3XYXPh_3 are exceptions to the HA6PE principle, which has previously been demonstrated for a variety of chemical types. The lattice symmetry (rhombohedral, $R\bar{3}$) is the same as that common in HA6PE lattices, as is the molecular shape and symmetry (S_6). Only the intermolecular interactions are different and in one sense the results reported here represent crystal packing isomerism, or polymorphism. Compounds in this class do crystallise in other ways, which we will describe separately.

What do we learn from these crystal structures? Certainly the possibility of effective concerted multimolecular interactions involving EF and OFF motifs is demonstrated. An alternative to the $(EF)_6$ intermolecular motif involving two molecules (the 6PE) is the $(EF)_6$ motif involving six molecules, both with S_6 ($\bar{3}$) symmetry. The quality of the EF interactions is no less for the hexamolecular motif than for the bimolecular motif. Further, crystal packing with concerted hexamolecular cycles of EF interactions can be effective geometrically, as illustrated in Fig. 2 and 8, and there is no reason to expect that the energies of the multimolecular motifs are less than those of the bimolecular motifs. The number density of these EF motifs determines their contributions to the total lattice energy, and this can be assessed by examination of the asym-

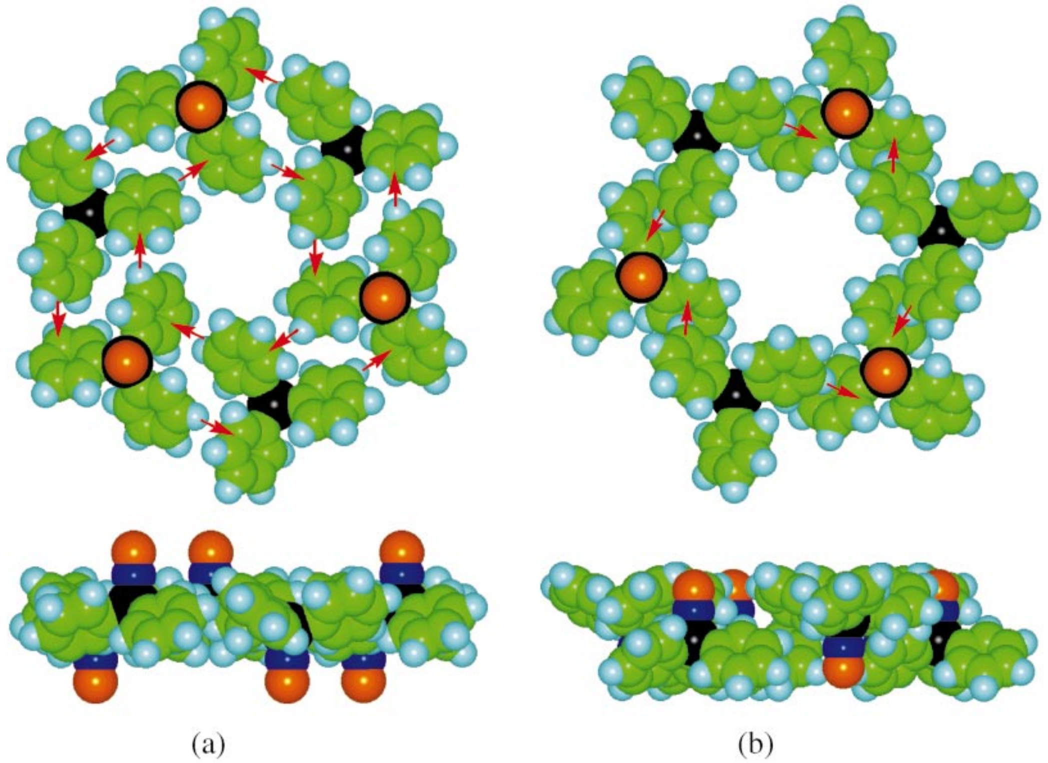
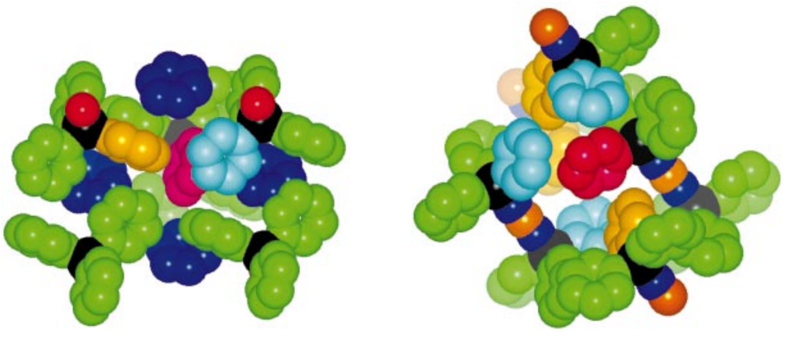

(a) (b)

Fig. 5 (a) and (b) The two different hexagonal nets of multimolecular EF interactions in $Ph_3SiNCNSiPh_3$ [TPSICI], each shown in axial projection and side elevation. Molecules are truncated at cyanamide C (orange). EF interactions are marked with red arrows.



(a) CECXAJ02

(b) TPSICI

Fig. 6 The asymmetric segments of intermolecular interactions in (a) CECXAJ02 and (b) TPSICI. A phenyl ring of the crystallographic asymmetric unit is coloured red; phenyl rings that provide an edge in an EF to the target ring are coloured yellow, and phenyl rings that receive an EF from the target ring are coloured cyan; in (a) the guest benzene molecules are blue and in (b) the cyanamide C atoms are orange. In (a) the benzene molecules above and below the target phenyl ring are facial receptors in EF interactions to it, and the two benzenes on the left and right are edge donors in EF interactions. In (b) there are C–H···C (cyanamide) hydrogen bonds, not marked.

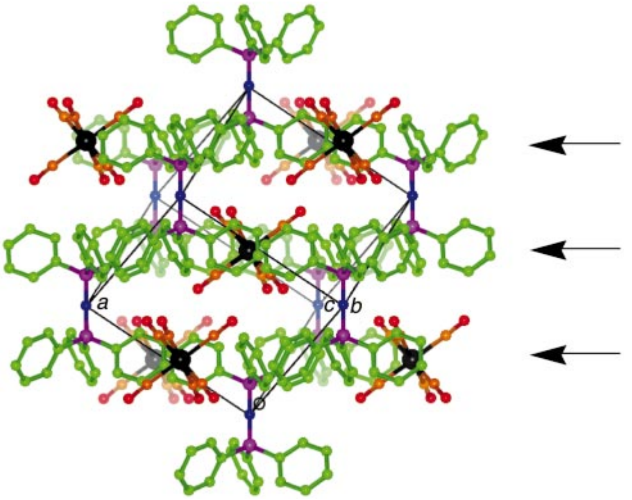


Fig. 7 View of the crystal structure of $Ph_3PNPPh_3{}^+[Nb(CO)_6]^-$ [BILNEP10] perpendicular to the trigonal axis, space group $R\bar{3}$: P magenta, Nb black, O red, CO carbon orange. Note the monolayers of phenyl groups (arrowed) and the location of anions in these layers.

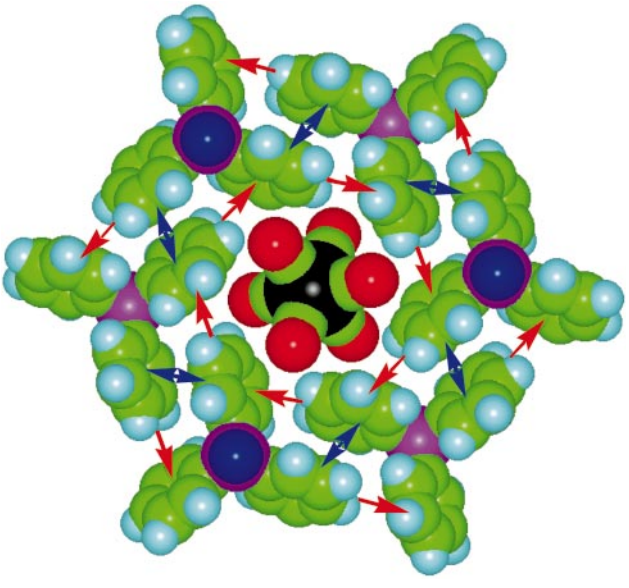


Fig. 8 The hexamolecular motif that extends to form the two-dimensional net of embraces in $Ph_3PNPPh_3{}^+[Nb(CO)_6]^-$ [BILNEP10]. Red arrows are EF interactions, blue arrows are OFF interactions.

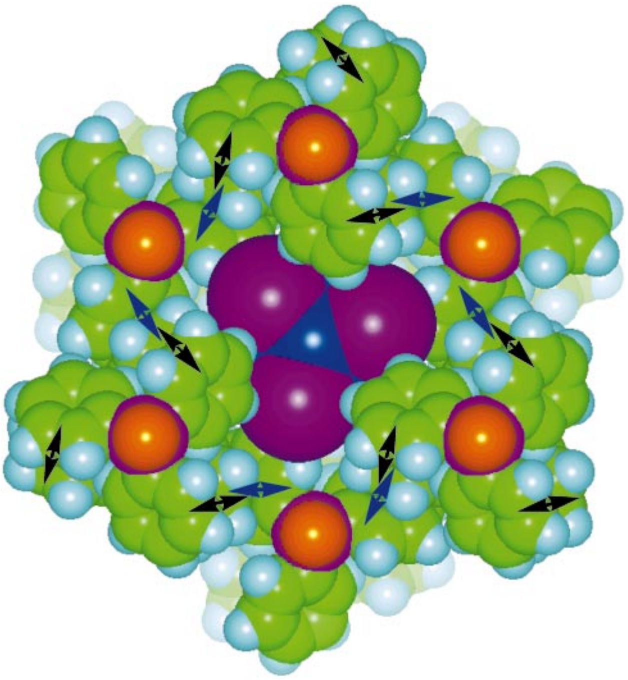


Fig. 9 Axial view of the structure of $(MePh_3P)_2[Cu_4I_6]$ [MPPICU]; Cu blue, I purple, methyl C orange (methyl H omitted); space group $R\bar{3}c$. The OFF motifs of bimolecular $(OFF)_3$ embraces are marked with black arrows, and the hexamolecular $(OFF)_6$ motif marked with blue arrows. Note the absence of EF interactions.

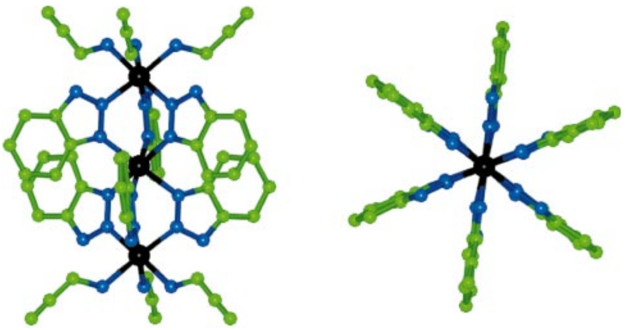


Fig. 10 Side and axial views of the Ni_3 complex crystallised with Ph_3PO in BTZANI: Ni black, C green, N blue, H omitted.

metric segment of interactions around the crystallographic asymmetric unit, as in Fig. 6. Both of the structure types reported here have other species associated with the lattice-forming Ph_3XYXPh_3 molecules, which is less common in the HA6PE crystals formed by Ph_3XYXPh_3 molecules.[13]

The crystal structure types described here allow possibilities for the engineering of crystal lattices containing similar species. In $Ph_3PNPPh_3{}^+[Nb(CO)_6]^-$ [BILNEP10] the combination of the hexagonal net of EF and OFF interactions between cations (Fig. 8) and the C–H···O interaction between cations and anion suggests other chemical systems that could be predicted (engineered) to crystallise similarly.

As previously,[13,20] we note the issue of whether crystal packing affects molecular geometry, that is whether the crystal packing described here is the reason for the linear Si–O–Si and P–N–P centres of molecules in Table 1.

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