# Supramolecular Motifs: Concerted Multiple Phenyl Embraces between $Ph_4P^+$ Cations Are Attractive and Ubiquitous

**Ian Dance* and Marcia Scudder**

**Abstract**: Examination of the Cambridge Structural Database reveals that $Ph_4P^+$ cations in crystals associate through phenyl–phenyl nonbonded interactions which are attractive, concerted, and widespread. Intermolecular phenyl–phenyl conformations, which are offset-face-to-face (**off**), edge-to-face (**ef**) or vertex-to-face (**vf**), combine in five classes of supramolecular motifs for $\{Ph_4P^+\}_2$ pairs, namely the sextuple phenyl embrace (SPE) with $(\mathbf{ef})_6$ and offset sextuple phenyl embrace (OSPE) containing $(\mathbf{off})_1(\mathbf{ef})_2(\mathbf{ef}/\mathbf{vf})_2$, the translational quadruple phenyl embrace (TQPE) with $(\mathbf{ef})_4$, the parallel quadruple phenyl embrace (PQPE) with $(\mathbf{off})_1(\mathbf{vf})_2$, and the double phenyl embrace (DPE) with $(\mathbf{off})_1$. Typical intermolecular *attractive* energies (kJ per mol of $\{Ph_4P^+\}_2$) for these motifs are SPE 85, OSPE 57, TQPE 70, PQPE 41, DPE 34. There is strong interpenetration of the cations in these motifs: 489/770 structures in the CSD have $P\cdots P \leq 7$ Å (spherical $Ph_4P^+$ has a van der Waals diameter of 13.6 Å). Of the 812 instances of $P\cdots P \leq 7$ Å, 86% are SPE, 10% are OSPE, 2% are TQPE, and only 2% are unclassified. Average $P\cdots P$ separations in the PQPE and DPE are 8.3 Å. Centrosymmetry is prevalent in all except the TQPE, which has implications for the engineering of noncentric crystals.

**Keywords**
cations · crystal structures · phenyl rings · supramolecular chemistry · tetraphenylphosphonium ions

## Introduction

Research in supramolecular chemistry seeks to discover and understand the attractive motifs which determine the nonbonded associations of molecules in condensed phases, and to develop an ability to design and fabricate total supramolecular structures.[1] In this search there are two rich sources: the amazing materials and processes of evolved molecular biology provide the inspiration and incentive, while the recorded structures of molecular crystals, numbering about 130000, provide the fine detail of supramolecular architecture.

A supramolecular system of multimolecular dimensions is conceptualised as an elaborate concert of interactions. The key objective in advancing knowledge and understanding of these concerts is to progress from the primary level of intermolecular forces (essentially atom-based[2]) to secondary and tertiary levels, as in molecular biology, and to recognise larger and more elaborate ensembles in the full symphony. This paper describes concerted attractive supramolecular motifs involving tetraphenylphosphonium cations, $Ph_4P^+$.

Following examination of the Cambridge Structural Database[3,4] (CSD) we recently reported[5] that molecules containing $PPh_3$ ligands and compounds containing $Ph_4P^+$ cations commonly associate in crystals in a supramolecular pattern named the sextuple phenyl embrace (SPE, Figure 1). The SPE involves six of the well-known attractions between phenyl groups, arising because three phenyl groups on each molecule interleave with three from the other molecule in the interpenetration domain. A net attraction of 60–85 kJ mol$^{-1}$ was calculated for these SPE motifs. The $Ph_3P$ ligand occurs on the periphery of a large number of inorganic compounds, and the $Ph_4P^+$ cation is frequently used in the crystallisation of inorganic anions, and therefore these multiple phenyl embraces are of fundamental importance in supramolecular inorganic chemistry.[6] It is not appropriate to regard $Ph_4P^+$ cations in crystals as mutually repulsive, and there are many molecular crystals in which the attractive interactions between $Ph_4P^+$ cations dominate the crystal structure and possibly the molecular structures of anions.

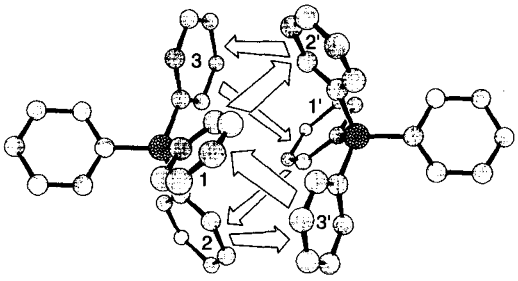

Fig. 1. A representative sextuple phenyl embrace, SPE, which is centrosymmetric and very close to colinear: the parallel rings are denoted 1 and 1', 2 and 2', 3 and 3'. Hydrogen atoms are omitted for clarity. The large arrows designate the six **ef** interactions, from hydrogen atoms (not shown) at the edge of one ring (arrow tail) to carbon atoms (arrow head) of a phenyl ring on the other molecule. Within each **ef** pair for phenyl rings, the donor hydrogen atoms occur at positions 2, 3 of the "donor" ring, and the carbon atoms at positions 3, 4 of the "acceptor" ring. [CSD refcode BADCAK.]

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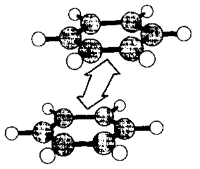
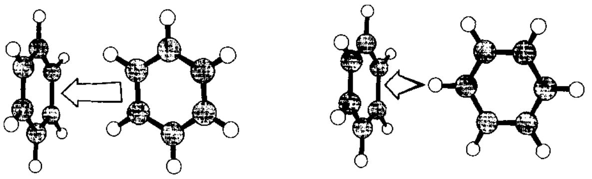
The source of the substantial attraction in these motifs is the attraction between phenyl groups, the phenyl factor, which has been documented and investigated for many other systems;[4, 6-21] the nature and magnitude of the attractive energy has been extensively probed both experimentally[22-24] and theoretically.[13, 16-21, 24] In addition to the dispersion attraction, there is a significant and structure-directing coulombic component arising from the $C^{\delta-}/H^{\delta+}$ polarisation. Three types of relevant pairwise phenyl–phenyl configurations are recognised, namely the offset-face-to-face (**off**), the edge-to-face (**ef**) and the vertex-to-face (**vf**), shown in Figure 2. In the **off** interaction the two approximately parallel phenyl rings are offset such that H atoms of one ring project onto C atoms of the other; in the **ef** interaction the rings are steeply canted such that two H atoms on the edge of one ring are directed towards C atoms of the other; in the **vf** interaction, a variant of **ef**, one C-H bond on one ring is directed close to the centre of the other, and the rings are again steeply canted.


offset face-to-face interaction **off**


edge-to-face interaction **ef**

vertex-to-face interaction **vf**

Fig. 2. The three specific attractive interactions between pairs of phenyl rings: offset-face-to-face **off**, edge-to-face **ef**, vertex-to-face **vf**.

While the SPE is the most prevalent concerted supramolecular motif in $Ph_4P^+$ salts and in $Ph_3P$-ligated complexes, there are others. In this paper we report on the full set of identifiable concerted phenyl embraces between pairs of $Ph_4P^+$ cations in crystals.[25] In the CSD (1994) there are 875 compounds containing the unsubstituted $Ph_4P^+$ cation, of which 770 entries have coordinates which permit analysis of supramolecular interactions.

## Methods

The graphical version of the Cambridge Structural Database [3,4], 1994 release, was used. The first collection of structures containing $Ph_4P^+$ with significant interactions was selected according to the intermolecular P···P separation. This large set was then analysed according to the angles between the P–C bonds on each molecule and the P···P vector, which revealed the broad classes of interaction and the number of phenyl groups in the interaction domain. At this stage bogus and unreliable structures were eliminated, mainly on the basis of abnormal geometry. Further geometrical analyses were based on 1) the intermolecular separations of phenyl rings (centroid to centroid), 2) the intermolecular inclinations of phenyl rings (angle between normals to ring planes) and 3) the angles between C-P-C planes on different cations. Concurrent with each of these numerical analyses, graphical display of the intermolecular interactions confirmed qualitatively the characteristics and generalities of interaction geometries. The specific geometrical characteristics of each of the multiple phenyl embraces, and thus the search criteria, are included in the descriptions below.

The calculations of intermolecular energies used standard atom–atom methodology, with the Lennard-Jones equation $E_{ij}^{vdW} = e_{ij}^{a}[(d_{ij}^{a}/d_{ij})^{12} - 2(d_{ij}^{a}/d_{ij})^{6}]$ for the van der Waals components and the equation $E_{ij} = \{q_i \cdot q_j)/(\varepsilon \cdot d_{ij})$ for the coulombic components, for atoms i, j with partial charges $q_i$, $q_j$, separated by $d_{ij}$: $d_{ij}^{a}$ is the distance at which the interaction energy is most negative (attractive) with the magnitude $e_{ij}^{a}$; $d_{ij}^{a} = r_i^{a} + r_j^{a}$; $e_{ij}^{a} = (e_i^{a} \cdot e_j^{a})^{0.5}$; the intermolecular dielectric constant $\varepsilon$ was set as $d_{ij}$. The relevant parameters $r^{a}$ (Å) and $e^{a}$ (kJ mol$^{-1}$) for H, C and P are, respectively, (1.50, 0.17), (2.00, 0.21) and (2.07, 0.84), and the atom partial charges used for $Ph_4P^+$ are $H^{+0.15}$, $C^{-0.1}$, $P^{+0.4}$ [26,27]. The intermolecular energies reported are for representative examples of each of the motifs. In the energy minimisations the intramolecular bonded force constants of the cvff force field [28] were used, except that the C-P-C angle bending constant was increased by an arbitrary factor in order to maintain these C-P-C angles close to 109.5: for 1090 $Ph_4P^+$ cations in the CSD the standard deviation of the C-P-C angle from its mean of 109.5 is <0.1°.

## Results

**Description of the multiple phenyl interactions**: The following sections describe first the geometries of the recognisable and distinct motifs for $\{Ph_4P^+\}_2$ pairs, then the frequencies of occurrence and the interaction energies. The motifs are named according to the total number of phenyl rings which are involved in the interaction domain and contribute to the intermolecular energy of the $\{Ph_4P^+\}_2$ pair.

**The sextuple phenyl embrace, SPE**: This concerted interaction involving six phenyl rings in the interaction domain is shown in Figure 1. The fourth phenyl group on each $Ph_4P^+$ is directed away from the interaction domain such that there is near colinearity of the distal C–P vectors on the two P atoms. This *trans* colinearity of the P–Ph rings external to the interaction domain is the most recognisable characteristic of the SPE in crystal packing diagrams, and is the property searchable through the CSD. A scattergram of this colinearity (expressed as half the sum of the $^{distal}C-P\cdots P$ and $P\cdots P-C^{distal}$ angles) versus the P···P distance shows[5] a distinct concentration of points in the colinearity range 160–180° and distance range 5.7–7.0 Å, all of which are SPE motifs. Note that the actual example of an SPE shown in Figure 1 is not exactly colinear. The average P···P distance is 6.37 Å.

In most SPEs the six rings occur as three exactly parallel pairs (1,1′; 2,2′; 3,3′ in Fig. 1), a consequence of a centre of symmetry midway between the P atoms; in the remainder of the SPEs these pairs are approximately parallel. Analysis of 700 SPEs in the CSD reveals that the average intercentroid distance between each pair of parallel rings is 7.0 Å. While these parallel pairs are a geometrical characteristic of the SPE they are not the main source of the attraction, which derives from the six **ef** interactions shown as large arrows 1⇒2′, 2′⇒3, 3⇒1′ etc. in Figure 1. For the ring pairs involved in the **ef** interactions the intercentroid distances are approximately 5.0 Å, and the normals to the ring planes are inclined at approximately 65°. Within the class of SPEs there is some variability of torsion around the six P–C bonds involved, and so close approach to local threefold symmetry (or $S_6$ if the centre of inversion is present) in the interaction domain is not required and is not observed. Threefold crystallographic symmetry is not possible with *ordered* $Ph_4P^+$ cations, and crystallographic disorder is rare because the multiple phenyl embraces are strongly ordering influences.

**The offset sextuple phenyl embrace, OSPE**: This is a variant of the SPE, less frequently encountered. A typical example is shown in Figure 3. It is recognised as a slippage or offset of the face of three phenyl rings on one cation relative to the face of three phenyl rings on the other cation, but all six phenyl rings are still involved in significant attractive interactions between the cations. In the OSPE the two distal P–C vectors are still parallel, but no longer almost colinear. Our extraction of OSPEs from the database targeted sextuple phenyl embraces in which the $^{distal}C-P\cdots P$ and $P\cdots P-C^{distal}$ angles are both in the range 140–160° and the $P\cdots P$ distance is less than 7 Å. There are 78 examples in the CSD, with an average $P\cdots P$ distance of 6.75 Å, and the minimum $P\cdots P$ distance was 6.3 Å. The distribution of $P\cdots P$ distances was not a normal distribution, and so instances of the OSPE could exist with the $P\cdots P$ distance greater than 7 Å. Most (53/78) of the OSPEs have three pairs of intermolecular parallel rings (like most SPEs), but there is necessary variation in the intercentroid distances in these pairs. The intercentroid distance for one pair of parallel rings decreases from about 7 Å in SPE to about 5.5 Å, while the other two increase in length to between 8 and 10 Å. In Figure 3, the offset is clear, the parallel rings being 1 and 1′ (shortest), 2 and 2′, 3 and 3′. In general, the OSPEs with larger offsets (i.e., lower $^{distal}C-P\cdots P$ angles) have shorter 1⇔1′ intercentroid distances. The effects on the energies of these interactions are described below.

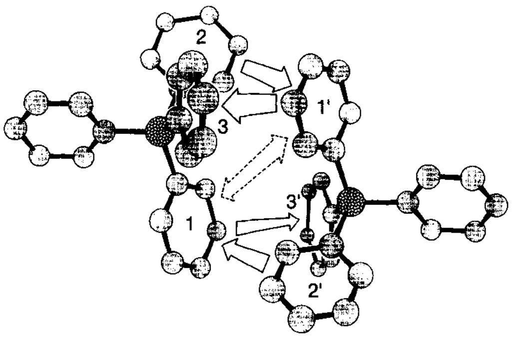


Fig. 3. A representative offset sextuple phenyl embrace, OSPE. The dotted double arrow signifies an approach of rings 1 and 1′ to the offset-face-to-face (**off**) interaction, the interactions 2⇒1′ and 2′⇒1 are edge-to-face (**ef**), and the interactions 1′⇒3 and 1⇒3′ approach the vertex-to-face (**vf**) geometry. [CSD refcode BUMYUD.]

In the OSPEs with the shorter 1⇔1′ intercentroid distances, the local interaction between rings 1 and 1′ approaches **off**. This is indicated in Figure 3 by the dashed double-ended arrow. There are also **ef** interactions (2⇒1′ and 2′⇒1), while the 1′⇒3 and 1⇒3′ interactions approach the vertex-to-face conformation in which the hydrogen atom on one vertex of the "donor" phenyl ring is approximately equidistant from all six carbon atoms of the "acceptor" ring.[29]

In the minority of OSPEs where the rings are not in three parallel pairs, there is a variety of edge-to-face interactions between the six rings, and no virtual symmetry. The OSPE obviously cannot permit close approach to threefold symmetry in the interaction domain.

We have detected only a few instances where five phenyl rings (3+2) form a significant interaction domain between two $Ph_4P^+$ cations, but interaction domains containing four phenyl rings (2+2) are frequent and significant. There are two important and general subclasses, the translational quadruple embrace (TQPE) and the parallel quadruple embrace (PQPE), and a number of other quadruple phenyl embraces which do not fit either of these patterns.

**The translational quadruple phenyl embrace, TQPE**: The fundamental phenyl embrace involving four phenyl rings in the phenyl–phenyl interaction domain is illustrated in Figure 4. There are four intermolecular edge-to-face interactions, signified by the arrows in Figure 4. In this motif the interacting $Ph_4P^+$ cations cannot be related by a centre of symmetry, but the prominent relationship between them is translation: this is obvious in Figure 4 and provides the distinguishing name, the translational quadruple phenyl embrace. For the majority of the TQPEs in the CSD, the $P\cdots P$ vector is parallel to an edge of the unit cell, and in these cases the TQPE becomes an infinite linear sequence of quadruple phenyl embraces.[30]

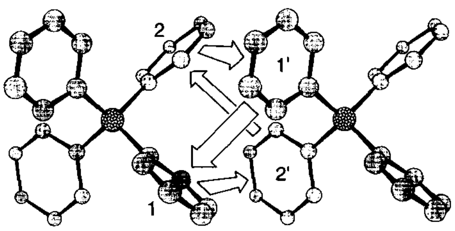


Fig. 4. A representative translational quadruple phenyl embrace, TQPE. Each of the interactions marked with an arrow is edge-to-face, **ef**. The two $Ph_4P^+$ cations shown are related by translation. [CSD refcode DEMYEZ.]

A related characteristic of the TQPE is that the C-P-C planes involving the interacting rings on each cation are mutually perpendicular or very close to perpendicular. This property provides a valuable search criterion, and there are 116 TQPEs in the CSD where the angle between the normals to the C-P-C planes lies in the range 80–90°. The $P\cdots P$ distances average 7.6 Å, but there is no clear peak in the distribution of $P\cdots P$ distances, which range from 6.7 to 9.0 Å (the upper limit of the search). In those QPEs where the C-P-C planes are exactly perpendicular, the range of $P\cdots P$ distances reduces to 6.7–7.9 Å. The $P\cdots P$ distances for the TQPE are necessarily longer than those of the SPE, because the phenyl groups are directed more closely to the $P\cdots P$ vector and into the interaction domain. For each of the intermolecular pairs of phenyl rings involved in the **ef** interactions, the intercentroid distances and the interplanar angles average 5.0 Å and 65°, which are the same as the **ef** interactions in the SPE.

**The parallel quadruple phenyl embrace, PQPE**: This motif is illustrated in Figure 5. A distinctive geometrical characteristic is that the two intramolecular C-P-C planes for the four rings involved in the interaction are parallel or almost parallel (in contrast to the perpendicular planes of the TQPE). There are 713 interactions in the CSD where the angle between the normals to these planes is less than 10°. The $P\cdots P$ distances are usually longer than in the TQPE, with a mean value of 8.3 Å, and are rarely less than 7 Å. In addition to the C-P-C planes being parallel, the interacting phenyl rings usually also form two

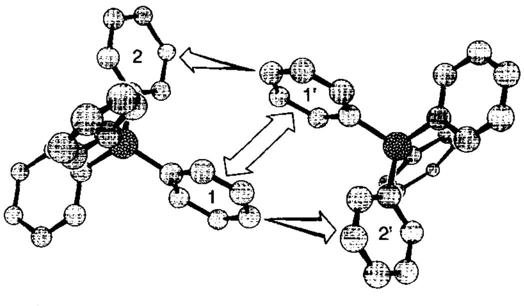


Fig. 5. A representative parallel quadruple phenyl embrace, PQPE. The **off** interaction occurs between rings 1 and 1′, while the interactions from 1⇒2′ and 1′⇒2 are intermediate between **vf** and **ef**; the primes signify parallel rings, in this case related by a centre of inversion. [CSD refcode BUMYUD.]

parallel pairs—hence the name parallel quadruple phenyl embrace. For the closer of the two parallel pairs of rings, the mean intercentroid distance is 5.4 Å, but the range is wide, from 3.7 to 8.0 Å. At the lower end of the range, where the parallel rings are only approximately 4 Å apart, an **off** interaction occurs—this is marked in Figure 5. The other pair of interactions in the PQPE is **ef** or **vf**. Of the 713 PQPEs, 89% have the defining C-P-C planes exactly perpendicular, indicating symmetry which is most probably a centre of inversion.

In addition to the 116 TQPEs and the 713 PQPEs, there are 378 further examples of quadruple phenyl embraces, in which the angle between the C-P-C planes lies in the range 10–80°: in these variants of the QPE the inter-phenyl ring interactions are variable.

**The double phenyl embrace, DPE**: In the double phenyl embrace only two phenyl rings with an **off** relationship are in the interaction domain, as illustrated in Figure 6. There are 25 examples of the DPE in the CSD (with a search limit of 9 Å for the P···P distance). The mean P···P distance is 8.3 Å, and the mean intercentroid distance between the rings is 3.9 Å (range 3.7–4.6 Å). All instances of the DPE are centrosymmetric.

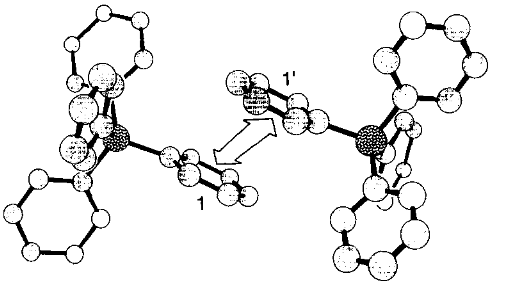


Fig. 6. A representative double phenyl embrace, DPE. Offset face-to-face interaction occurs between rings 1 and 1', with an intercentroid distance of 3.9 Å. The prime signifies a centre of inversion. [CSD refcode JAGBUO.]

As is apparent from comparison of Figures 5 and 6, the DPE can be considered to be a subset of the PQPE, in which the ends of rings 1 and 1′ are directed between phenyl rings on the other cation, rather than towards rings 2′ and 2 in the **vf** or **ef** interaction of the PQPE.

**Occurrence and distribution of the phenyl embrace motifs**: Of the 770 compounds in the CSD containing $Ph_4P^+$ (and with available coordinates), 489 crystal structures give rise to 812 different instances of P···P separations less than 7 Å. Although we have not made a rigorous assessment, it is our observation that no more than about 2% of these instances have interaction geometries which cannot be classified as one of the motifs we have described here. Of the 812 instances, 86% are SPE, 10% are OSPE and 2% are TQPE. At larger P···P separation the TQPE is more prominent, while as already described, the DPE and PQPE have idealised geometries which require a P···P separation around 8.3 Å. Obviously, at increasing P···P separations there are increasing numbers of interactions which are different from the classes we have described, but in many of these instances the reasons for the variations are apparent when more of the crystal structure than the pair of $Ph_4P^+$ is examined, as we will describe in detail in an analysis of extended multiple phenyl embraces in crystals.[30] We note that contacts are also possible in which one phenyl ring from the first $Ph_4P^+$ group interacts with two or three phenyl rings from the other, and where two phenyl rings from one $Ph_4P^+$ group interact with three from the other. These interaction types are rare, but occurrences have been found.

**Interaction energies**: The van der Waals and coulombic components of the nonbonded interaction energies between the $Ph_4P^+$ cations have been evaluated by means of standard atom-based calculations for a representative example of each of the motifs: the geometries and the CSD references are those of the figures. These energies are presented in Table 1 as matrices which show the intermolecular ring–ring energies, for the rings labelled as in the figures. The P···P energy at a distance of 7 Å is negligible, about +4 kJ mol$^{-1}$, and the sum of the intermolecular P···ring energies is always less than about +4 kJ mol$^{-1}$ and relatively unimportant in comparison with the ring–ring energies.

Table 1. Calculated interaction energies (van der Waals plus coulombic) in kJ mol$^{-1}$ for intermolecular pairs of rings in the multiple phenyl embraces, with geometries defined by the CSD refcodes in parentheses.

| Interaction energies of intermolecular ring pairs | | | | | $E_{total}$ |
|---|---|---|---|---|---|
| SPE (BADCAK) | | | | | −85.8 |
| ring no. | 1′ | 2′ | 3′ | 4′ | |
| 1 | −3.1 | −14.0 | −10.6 | −0.6 | |
| 2 | −14.0 | −1.9 | −13.3 | −0.4 | |
| 3 | −10.6 | −13.3 | −2.0 | −0.5 | |
| 4 | −0.6 | −0.4 | −0.5 | 0 | |
| OSPE (BUMYUD) | | | | | −56.8 |
| ring no. | 1′ | 2′ | 3′ | 4′ | |
| 1 | −8.7 | −6.7 | −11.4 | −0.8 | |
| 2 | −6.7 | −1.1 | −3.5 | −0.4 | |
| 3 | −11.4 | −3.5 | −0.8 | −0.3 | |
| 4 | −0.8 | −0.4 | −0.3 | 0 | |
| TQPE (DEMYEZ) | | | | | −70.0 |
| ring no. | 1′ | 2′ | 3′ | 4′ | |
| 1 | −14.2 | −14.2 | −2.7 | −0.6 | |
| 2 | −14.2 | −14.2 | −0.6 | −2.7 | |
| 3 | −0.6 | −2.7 | 0 | 0 | |
| 4 | −2.7 | −0.6 | 0 | 0 | |
| PQPE (BUMYUD) | | | | | −41.4 |
| ring no. | 1′ | 2′ | 3′ | 4′ | |
| 1 | −20.8 | −7.8 | −1.7 | −0.6 | |
| 2 | −7.8 | −0.2 | −0.1 | 0 | |
| 3 | −1.7 | −0.1 | 0 | 0 | |
| 4 | −0.6 | 0 | 0 | 0 | |
| DPE (JAGBUO) | | | | | −34.1 |
| ring no. | 1′ | 2′ | 3′ | 4′ | |
| 1 | −12.5 | −6.3 | −0.8 | −3.6 | |
| 2 | −6.3 | 0 | 0 | −0.1 | |
| 3 | −0.8 | 0 | 0 | 0 | |
| 4 | −3.6 | −0.1 | 0 | 0 | |

The primary result from Table 1 is that the net attractive energy in these multiple phenyl embraces is substantial, and results from the intermolecular attractions of the phenyl rings in the interaction domain. These formal cations are strongly attractive, not repulsive. The P···P and P···ring energies are relatively constant and small, but the intermolecular ring–ring energies are the major contributors, and are variable with the details of the motif. The **ef** and **vf** interactions between pairs of phenyl rings contribute from 6.7 to 14.2 kJ mol$^{-1}$ attractive energy per pair. The **off** interactions contribute 20.8 kJ mol$^{-1}$ attractive energy in the PQPE depicted, and 12.5 kJ mol$^{-1}$ in the DPE depicted. These phenyl–phenyl energies in **ef**, **vf** and **off** conformations are relatively sensitive to geometrical details, because the local attractive and repulsive coulombic components from $H^{\delta+}$ and $C^{\delta-}$ are substantial (vide infra).

The SPE is the most attractive interaction because it engages six of the favourable **ef** interactions. It is not surprising that the SPE is the most abundant of the multiple phenyl embraces. The DPE has the smallest attraction, and is the least abundant motif.

Further insight into the contributions to and ranges of the energies in these multiple phenyl embraces comes from energy minimisation calculations. In these calculations the intramolecular C-P-C angles were restrained to maintain close tetrahedral geometry, but the C-P-C-C torsional angles were treated normally in the force field, so that intramolecular conformations as well as intermolecular conformations could change. For two different examples of the SPE which appear similar in their crystal structures (CSD refcodes COVBOE and BADCAK), minimisation produces two slightly different $\{Ph_4P^+\}_2$ structures, both slightly offset SPE: one has $C-P\cdots P$ and $P\cdots P-C$ angles of 173° and the other of 166°. The intermolecular inter-ring energies of the minimised structures are similar, $-82.8$ and $-84.4\,kJ\,mol^{-1}$, respectively (compared with $-73.6$ and $-85.8\,kJ\,mol^{-1}$ prior to minimisation). Two different OSPEs (CSD refcodes BUMYUD and BEKYIZ, starting energies $-56.8$ and $-54.7\,kJ\,mol^{-1}$, respectively) also minimised to the same two slightly offset SPEs. A QPE (DEMYEZ, $-70.0\,kJ\,mol^{-1}$) underwent minor geometrical changes but could not improve its interaction energy. Two multiple phenyl embraces based on **off** phenyl–phenyl interaction geometry, namely a PQPE (CSD refcode JAGBUO, with intermolecular ring–ring total energy of $-30.1\,kJ\,mol^{-1}$ in the crystal structure) and a DPE (JAGBUO, starting energy $-33.9\,kJ\,mol^{-1}$), both minimised to the same PQPE structure with energy $-51.4\,kJ\,mol^{-1}$.

While these energy minimisation calculations reveal the components and variabilities of the multiple phenyl embraces in pairwise $\{Ph_4P^+\}_2$ motifs, we do not attach significance to the optimised geometries, because the context of our analysis is the crystal lattice and the total supramolecular environment of the $\{Ph_4P^+\}_2$ moiety.

## Discussion and Conclusion

The widespread occurrence of $Ph_4P^+$ cations in crystals is a consequence of the wisdom of synthetic chemists, who know that $Ph_4P^+$ and related phenylated cations provide quality crystals with favourable lattice energies leading to lower solubilities, and is tacit recognition of advantageous supramolecularity in their molecular crystals. In this paper we have identified and characterised the motifs which provide those advantages. All of the multiple phenyl embraces between $Ph_4P^+$ cations involve $P\cdots P$ separations that are very much less than 13.6 Å, which is twice the van der Waals radius of $PPh_4$ regarded as a sphere, and there is a large degree of supramolecular interpenetration.[31] The intramolecular conformations of $EPh_4$ and $Ph_4P^+$ have been analysed previously:[7, 32] we have not attempted to correlate the intramolecular conformations with the extramolecular motifs described in this paper, nor to calibrate the barriers to intramolecular conformational change against the extramolecular interaction energies.

The analyses described here are restricted to $\{Ph_4P^+\}_2$ pairs in crystals. This requires some justification, because the intermolecular contacts to each cation external to the interaction domain between the pair subtend a greater solid angle at each $Ph_4P^+$ than do the intrapair interactions, and it could be expected that the extrapair interactions could dominate the intrapair interactions. However, the analyses of crystal structures in the CSD reveal well-defined patterns, and tight attractive intrapair motifs. In the range $P\cdots P \leq 7$ Å, all but 2% of the interactions can be classified as multiple phenyl embraces, contributing up to approximately 80 $kJ\,mol^{-1}$ attractive energy per pair. It must be concluded that these are ubiquitous supramolecular motifs, that they are dominant in their crystal lattices, and consequently that they can be deployed for crystal engineering.

What then of the extra-$\{Ph_4P^+\}_2$ interactions? As we shall demonstrate in an examination of extended arrays of $Ph_4P^+$ cations in crystals,[30] there is not necessarily competition between intra-$\{Ph_4P^+\}_2$ and extra-$\{Ph_4P^+\}_2$ interactions, and indeed remarkable concert appears in extended multiple phenyl embraces.

We have examined all structures in the CSD containing $Ph_4P^+$ for which there are coordinates available. The conclusion that we reach is that most structures containing $Ph_4P^+$ take part in one or more of the concerted interactions which we have defined here. What about the exceptions? We have observed that these tend to fall into two categories. Occasionally a large structure containing few $Ph_4P^+$ cations will pack so that the $Ph_4P^+$ groups are not near each other. In other instances there are interactions with phenyl rings from other sources, such as OPh, SPh, SbPh, and ligands such as $Ph_2P(CH_2)_nPPh_2$. There are also attractive interactions involving H atoms from sources other than phenyl, such as terminal methyl groups. As we will describe in a future paper, these H–phenyl interactions are surprisingly common and strong.

The pictures of the multiple phenyl embraces show that on the phenyl rings there are positions which are directed away from the $P\cdots P$ axis, positions where distal substituents should not interfere with the embrace. Such compounds should also engage in the multiple phenyl embraces described here.

Finally, we draw attention to the fact that a substantial proportion of the multiple phenyl embraces are centrosymmetric: 86% of the SPE, that is 88% of $\{Ph_4P^+\}_2$ with separations less than 7 Å, are centrosymmetric. It is reasonable to postulate that the centrosymmetric embraces provide a driving force for formation of a centrosymmetric lattice when anions are crystallised with $Ph_4P^+$, even though the cation is not centrosymmetric. In crystal engineering applications where a centrosymmetric lattice is undesirable, such as the crystallisation of materials with second-order nonlinear optical properties, it would be unwise to use $Ph_4P^+$ cations, or analogues which could form these multiple phenyl embraces.

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[25] The *intramolecular* dimensions of metal-coordinated PPh$_3$ are sufficiently different from those of Ph$_4$P$^+$ to necessitate separate analysis of the concerted phenyl embraces.

[26] Atom partial charges which have been used for benzene are +0.153 (H), −0.153 (C) [16] or +0.115 (H), −0.115 (C) [20]: the coulombic components of the intermolecular energy are relatively insensitive to the magnitudes of the charges in this range.

[27] The parameters for C, H used in this paper yield intermolecular energies of 9.6, 11.3, 15.8 kJ mol$^{-1}$ (C$_6$H$_6$)$_2$ for the three independent **ef** interactions in crystalline benzene, and 7.5 kJ mol$^{-1}$ for the **vf** interaction of (C$_6$H$_6$)$_2$ (centroid–centroid = 4.96 Å) discussed by Hobza et al. [21]. Experimental and theoretical (high-quality ab initio calculations) estimates of the intermolecular attraction between benzene molecules are approx. 10 kJ mol$^{-1}$ (C$_6$H$_6$)$_2$ for dimers, oligomers, and bulk benzene [13,16,20,21,24]. The calculations in this paper probably yield a small overestimate of the phenyl–phenyl intermolecular energies.

[28] Program Discover, Biosym/MSI, San Diego (USA).

[29] The terms acceptor and donor, and the arrows in figures, are conveniently used here in the same sense as hydrogen bonding, but the interaction is largely nonvectorial coulombic.

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