Multiple phenyl interactions. Part 1: relative frequencies of six-fold phenyl embraces (6PE) in crystalline compounds containing the fragment XPh_3 ($X = $ any tetrahedral atom)

Thomas Steiner

Institut für Chemie—Kristallographie, Freie Universität Berlin, Takustraße 6, D-14195, Berlin, Germany. E-mail: steiner@chemie.fu-berlin.de

Received (in Montpellier, France) 15th November 1999, Accepted 12th January 2000

Using the Cambridge Structural Database, the frequencies of occurrence are determined for 6-fold phenyl embraces (6PEs) between all fragments $–XPh_3$, where X can be any tetrahedral atom. The relative frequencies are high for the family of cations Ph_4X^+, highest of all for Ph_4P^+ where 1121 6PEs are found for 1647 cations. For $R–XPh_3$ units ($R \neq Ph$) with group IV and V central atoms, the relative frequencies are much lower, ranging between 13 and 28% depending on R–X. It is very low, about 2%, for the Ph_4B^- anion and $R–XPh_3$ groups with X = B, Al and Ga. The formation of the hetero-pairs $R_1–XPh_3\cdots Ph_3Y–R_2$ ($X \neq Y$) is neither strongly favoured nor disfavoured over the formation of homo-pairs.

In 1995, Dance and Scudder showed that $–PPh_3$ groups and Ph_4P^+ cations frequently aggregate in the particular way shown in Fig. 1.[1] The triphenyl groups are interleaved in such a way that the edge of each phenyl ring interacts with the face of another phenyl ring, and the central atoms approach to a distance of 5.8–6.8 Å. The two remaining bonds at the central atoms are roughly collinear, and point in opposite directions. Because there is a total of six concerted edge-to-face interactions between phenyl groups, the motif was called 'sextuple phenyl embrace' (SPE), a term that has later been changed by the authors to 'six-fold phenyl embrace' (6PE).[2] It is of some interest to compare the 6PE with the benzene-type configuration of concerted edge-to-face interactions. In crystalline benzene, each face of the aromatic ring is involved in an edge-to-face contact and the smallest circular unit of the resulting array is formed by four benzene molecules (Fig. 2), clearly contrasting the 6PE. Apart from the 6PE, $–PPh_3$ groups and Ph_4P^+ ions can form a number of other multiple phenyl embraces involving four or two phenyl rings, but the 6PE is the most distinct and abundant one.[4] Many Ph_4P^+ ions and $R(PPh_3)_n$ molecules form more than one 6PE, and this can lead to supramolecular arrangements such as linear columns and zigzag chains.[5,6] Multiple aryl interactions of aromatic tridendate ligands in organometallic compounds have also been recently recognized.[7]

The 6PE can also be formed by groups other than $–PPh_3$. There is no need for the central atom to be phosphorus, as long as it has a tetrahedral valence geometry and carries three (or four) phenyl rings. Examples of 6PEs formed by pairs of $–XPh_3$ groups are tabulated in ref. 6 for the group V and IV elements, X = P, As, Sb, C, Si, Sn and Pb. There is also no need for the two interacting triphenyl groups to be chemically identical. Examples for unlike triphenyl groups forming 6PEs have been reported for the pairs $–SiPh_3\cdots Ph_3P–$[8] and $–CPh_3\cdots Ph_3P–$.[9] Furthermore, 6PEs can also be formed with phenyl rings carrying substituents like methyl and methoxy groups.[6] The general case of the 6PE is, therefore, $R_1–XPh_3\cdots Ph_3Y–R_2$, where Ph can also be a substituted phenyl ring.

It can be suggested that the 6PE might be useful in the design of crystal structures. However, controlled use of a particular pattern of intermolecular interactions requires more than just knowing that it can be formed in principle. It is also necessary to have an idea about the *chance* that the pattern is actually formed, when the relevant chemical functionalities are present in a supramolecular system. If this chance (*i.e.*, the probability of formation) is high, it is relatively easy to use the pattern in crystal design. With falling probability of formation, it becomes increasingly difficult to control the pattern in

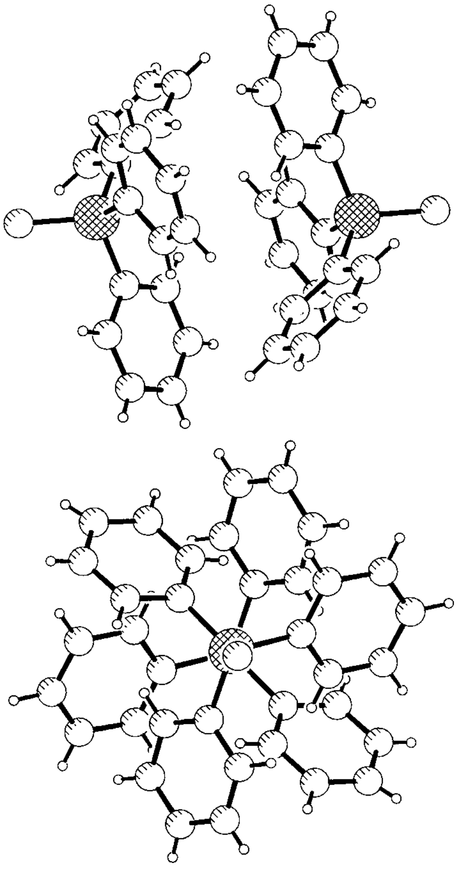

Fig. 1 A representative six-fold phenyl embrace, 6PE, shown in two perpendicular views. There is a total of six edge-to-face phenyl–phenyl interactions. The typical 6PE is centrosymmetric or close to centrosymmetric.

DOI: 10.1039/a909054a

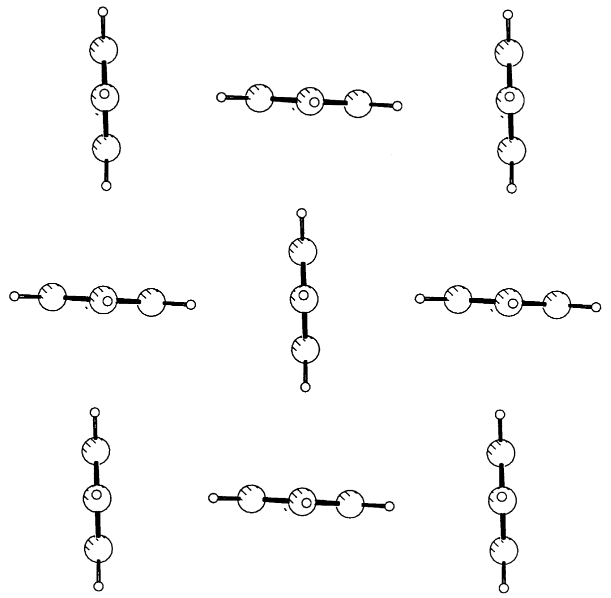

Fig. 2 Concerted edge-to-face interactions in benzene (neutron diffraction crystal structure of orthorhombic benzene at −135 °C, determined by Bacon, Curry and Wilson,[3] CSD code BENZEN01).

practice. Global probabilities of formation can be obtained by analyzing the intermolecular interactions of all published crystal structures, using as a tool the Cambridge Structural Database (CSD).[10] Such an analysis has recently been performed for 75 hydrogen bonded ring motifs in organic crystal structures.[11] It was shown that the probability of formation varies widely between different motifs, ranging from close to 100% for the strongest and most robust patterns to values <1% for others, and depend strongly on the competitive situation. Very high probabilities are rare, and typical values for well-known 'good' cyclic hydrogen bond motifs are in the range 20–60% (averaged over all competitive situations). In the present study, the probabilities of formation are determined for 6PEs with all possible central atoms. For the sake of simplicity, only XPh_3 groups with underivatized Ph rings are considered. Apart from the probabilities, the study obtains several other pieces of information on 6PEs that have not been published before.

Table 1 The structural data set

Fragment	n_{Struct}	n_{Frag}	$\bar{d}$(X–C)/Å	$\bar{\alpha}$(C–X–C)/°
Group III central atom				
Ph_4B^-	1157	1336	1.661(1)	109.47(4)
$R–BPh_3$ (R ≠ Ph)	36	40	1.639(2)	111.8(2)
$R–AlPh_3$	4	9	2.03(1)	110.9(6)
$R–GaPh_3$	3	5	1.99(1)	114.9(8)
Ph_4In^-	1	1	2.22	109.5
Group IV central atom				
$R–CPh_3$	266	370	1.536(1)	111.0(1)
$R–SiPh_3$	276	461	1.878(1)	108.8(1)
$R–GePh_3$	65	109	1.952(2)	109.3(2)
$R–SnPh_3$	242	333	2.144(1)	109.1(1)
$R–PbPh_3$	24	36	2.205(4)	109.9(5)
Group V central atom				
Ph_4P^+	1121	1647	1.792(1)	109.46(3)
Ph_4As^+	392	514	1.906(1)	109.4(1)
Ph_4Sb^+	11	13	2.097(3)	109.3(6)
Ph_4Bi^+	3	3	2.20(1)	109.7(1.7)
$C–PPh_3{}^+$	505	657	1.795(1)	108.81(5)
other $R–PPh_3$	135	196	1.798(1)	107.71(9)
$X{=}PPh_3$ (organic)	328	456	1.801(1)	107.20(5)
$M–PPh_3$	4756	8501	1.827(1)	103.67(2)
$R–AsPh_3$ (R ≠ Ph)	189	314	1.930(2)	104.6(2)
$R–SbPh_3$ (R ≠ Ph)	68	146	2.126(2)	100.2(2)
$R–BiPh_3$ (R ≠ Ph)	8	11	2.204(5)	109.3(1.5)
Other central atoms				
$R–SPh_3$	1	1	1.81	102.1
Ph_4Os	1	1	2.00	109.6
Ph_4Mg^{2-}	1	1	2.29	109.5

[a] Only central atoms with tetrahedral valence geometry are considered. Given are the numbers of crystal structures and relevant fragments, n_{Struct} and n_{Frag}, respectively, and the mean X–C(Ph) distances and (Ph)C–X–C(Ph) angles.

Data analysis

The study is based on update 5.16 of the CSD (October 1998, 190 307 entries, organic and organometallic crystal structures). Because it is not structural details that count in the study, but only whether or not a 6PE is formed in a given crystal structure, no quality criteria (such as *R* values) were used. In the first step of analysis, all $–XPh_3$ triphenyl groups with tetrahedral central atoms present in the CSD were identified and subsets were formed for each X. Only phenyl groups without substituents, $X–(C_6H_5)$, were considered. In Table 1, the frequencies, mean X–C(Ph) distances and mean (Ph)C–X–C(Ph) angles are listed for all such triphenyl groups. The tetraphenyl species, Ph_4X, are treated as separate cases and for the far most frequent central atom, P, further subdivision is performed (Ph_4P^+, $C–PPh_3{}^+$, $M–PPh_3$, other $R–PPh_3$, $R{=}PPh_3$).

In the second step of analysis, the CSD subsets were screened for 6PEs formed between homo-pairs, $–XPh_3\cdots Ph_3X–$. To identify the 6PEs, the method of Dance and Scudder was followed closely,[1] with the exception that the distance range was expanded. First, all intermolecular contacts between $–XPh_3$ units were extracted up to an X···X distance of 10 Å, and for each contact, the four $A–X_1\cdots X_2$ and four $X_1\cdots X_2–B$ angles were tabulated (A are the four atoms bonded to X_1, and B the four atoms bonded to X_2). The largest of the A–X···X and the largest of the X···X–B angles define the A–X and X–B bonds that point farthest away from the connecting line X···X (compare Fig. 1). Their mean value is called the 'A–X···X–B colinearity',[1] and for the 6PE is close to 180°. Then, scatterplots were produced of the A–X···X–B collinearity drawn against the X···X separation. These scatterplots allow us to determine the distance range of the 6PE for each kind of X, and also give an idea to what degree the 6PE is geometrically distinct from other configurations. Typical examples of such scatterplots are shown in Fig. 3. The clusters of data points at short distances and high collinearities represent 6PEs. The clusters are quite distinct, but there is also a transition region to other interaction geometries. Although only weakly populated, this transition region makes it impossible to characterize the region of 6PEs sharply. To allow direct comparison with the results of Dance and Scudder,[1,4] their cutoff limit in collinearity, 160°, is also applied here. Using this angular cutoff, the absolute frequencies of 6PEs and their range of X···X separations was determined (Table 2). The relative frequencies were calculated as the number of symmetry-independent 6PEs divided by the number of XPh_3 fragments present in the CSD subset.

Finally, this procedure was also performed for all possible hetero-pairs $R_1–XPh_3\cdots Ph_3Y–R_2$. However, it turned out that surprisingly few crystal structures contain triphenyl groups with different central atoms. In consequence, the corresponding part of Table 2 contains only a few entries.

Results

The data set

According to Table 1, tetrahedral groups $–XPh_3$ are found frequently with group III, IV and V central atoms, and in addition for single examples of the central atoms S, Os and

Table 2 Absolute and relative frequencies of 6PE formation (relative frequency = $n_{\text{fragments}}/n_{\text{6PE}}$); d = X···X

Contact	$n_{\text{fragments}}$	n_{6PE}	Relative frequency	d range/Å	$\bar{d}$/Å
Homo-pairs					
Ph_4B^-	1336	24	0.02	6.2–7.4	6.85(7)
R–BPh_3 (R ≠ Ph)	40	1	0.02	6.2	6.2
R–$AlPh_3$	9	0	0	—	—
R–$GaPh_3$	4	0	0	—	—
Ph_4In^-	1	0	0	—	—
R–CPh_3	370	63	0.17	5.7–7.3	6.37(5)
R–$SiPh_3$	461	77	0.17	5.5–7.7	6.53(5)
R–$GePh_3$	109	16	0.15	5.5–7.7	6.3(1)
R–$SnPh_3$	333	57	0.17	5.2–7.7	6.34(8)
R–$PbPh_3$	36	3	0.08	5.6–6.6	6.0(3)
Ph_4P^+	1647	1026	0.62	5.7–7.0	6.37(1)
Ph_4As^+	514	267	0.52	5.7–7.1	6.31(2)
Ph_4Sb^+	13	5	0.38	6.1–7.3	6.8(2)
Ph_4Bi^+	3	1	0.33	7.1	7.1
C–$PPh_3{}^+$	657	127	0.19	5.8–7.4	6.45(3)
other R–PPh_3	196	33	0.17	5.6–7.4	6.56(8)
X=PPh_3 (organic)	456	61	0.13	6.2–7.3	6.74(3)
O=PPh_3	69	19	0.28	6.2–7.1	6.75(5)
M–PPh_3	8501	1935	0.23	6.1–8.0	7.07(1)
R–$AsPh_3$	314	62	0.20	6.0–8.0	7.11(5)
R–$SbPh_3$	146	37	0.25	7.1–8.0	7.51(4)
R–$BiPh_3$	11	0	0	—	—
R–SPh_3	1	0	0	—	—
Ph_4Os	1	0	0	—	—
Ph_4Mg^{2-}	1	0	0	—	—
Hetero-pairs					
Ph_4B^-···Ph_3P–R (all)	35	0	0	—	—
Ph_4B^-···Ph_4As^+	1	0	0	—	—
Ph_4B^-···Ph_4Sb^+	1	0	0	—	—
$BPh_4{}^-$···Ph_3As–R	1	0	0	—	—
$BPh_4{}^-$···Ph_3Sn–R	1	0	0	—	—
$BPh_4{}^-$···Ph_3C–R	3	0	0	—	—
R–CPh_3···Ph_3Sn–R	1	0	0	—	—
R–CPh_3···Ph_3P–R	2	1[a]	0.5	—	—
R–$SiPh_3$···Ph_3Ge–R	1	0	0	—	—
R–$SiPh_3$···Ph_3Sn–R	1	0	0	—	—
R–$SiPh_3$···Ph_3Pb–R	1	0	0	—	—
R–$SiPh_3$···Ph_4P^+	2	2	1.0	6.6	6.6
R–$SiPh_3$···Ph_3P–R	17	4[b]	0.24	6.8	6.8
R–$GePh_3$···Ph_3Sn–R	1	0	0	—	—
R–$SnPh_3$···Ph_3P–R	4	0	0	—	—
R–$PbPh_3$···Ph_4P^+	1	0	0	—	—
Ph_4P^+···Ph_3P–R	12	1	0.08	6.9	6.9
Ph_4P^+···$PbPh_3$–R	1	0	0	—	—
Ph_4As^+···Ph_3P–R	6	1	0.17	7.0	7.0
R–PPh_3···Ph_3As–R	1	0	0	—	—

[a] In the cocrystal of triphenylmethanol–triphenylphosphinoxide,[9] which is not yet in the CSD. [b] All four 6PEs occur in one crystal structure.[8]

Mg. With group III central atoms, they are frequent only in the form of tetraphenylborate ions, Ph_4B^-. With group IV central atoms, –XPh_3 groups are found for the whole group from C to Pb, and with group V central atoms, they occur for all atoms from P to Bi. Nitrogen is notably missing in the list; there is no published crystal structure with an –NPh_3 group, and the N atom geometry in triphenylamine, NPh_3,[12] is close to planar.

Colinearity and distances

Scatterplots of A–P···P–A collinearities against P···P distances have been published for Ph_4P^+ cations and metal-bound –PPh_3 ligands.[1] These plots are essentially reproduced in this study, and need not be shown again. To give a couple of different examples, the scatterplots for Ph_4As^+ cations and C–CPh_3 groups are shown in Fig. 3. The plot for Ph_4As^+, Fig. 3(*a*), is very similar to that of Ph_4P^+.[1] There is a very distinct and densely populated cluster of data points at high colinearities and short As···As separations, and these points all correspond to 6PEs. The average As···As separation in the cluster is 6.31 Å and the shortest distances are around 5.7 Å. The relatively large size of the cluster shows that the 6PE allows considerable geometrical distortions. At C–As···As–C colinearities close to 125°, there is a different cluster of data points with short As···As distances down to about 6.3 Å. This cluster represents a different kind of multiple phenyl interaction, called the 'orthogonal four-fold phenyl embrace' (O4PE),[2,4] a typical example of which is shown in Fig. 4. In the O4PE, there are four edge-to-face interactions between phenyl groups and the C–As–C planes of the contacting groups are orthogonal with respect to each other. The O4PE obviously occurs (at least for Ph_4As^+) far less frequently than the 6PE. The cation can also form a number of other multiple phenyl embraces,[4] but these have longer As···As distances, are less distinct in their geometries and do not lead to clustering in Fig. 3(*a*).

To give an example for uncharged triphenyl groups, the corresponding scatterplot for C–CPh_3 is shown in Fig. 3(*b*). There is also a distinct cluster representing 6PEs and, as for the Ph_4As^+ cations, the broad scatter indicates that the 6PE allows large distortions. Also the distance range of the 6PEs is very similar as for Ph_4As^+ ions (mean value 6.37 Å). The figure is qualitatively similar for all other R–XPh_3 groups (R ≠ Ph), irrespective of the nature of X, R, and the charge situation. Nevertheless, there are variations in the details of

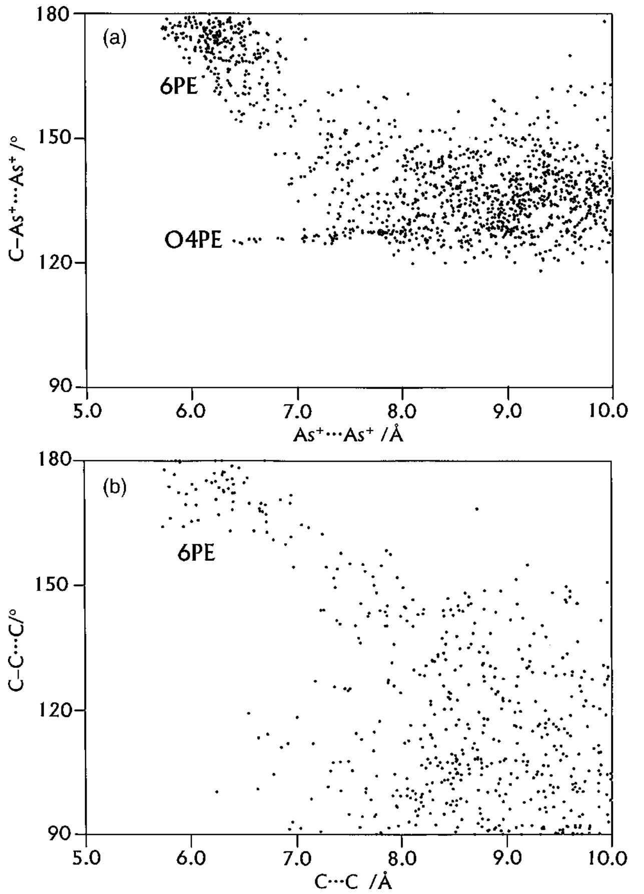

Fig. 3 Scatterplots of C–X···X–C collinearities against X···X separations in contacts between –XPh$_3$ groups. The C–X···X–C colinearity is the mean of the largest C–X···X and X···X–C angles in the contact.[1] (*a*) In contacts between Ph$_4$As$^+$ cations, (*b*) in contacts between C–CPh$_3$ groups.

the scatterplots when varying X and R. For example, the cluster of 6PEs has appreciably different widths for different central atoms. This can be seen in the variation of the X···X distance ranges given in Table 2 (second column from the right) and deserves a closer look. The trends can be best followed with group IV central atoms. For these, the range of X···X distances widens systematically when going down the group from C to Sn (for Pb, there are too few examples to be statistically representative) and the observed minimum distance *falls*. In particular, the minimum X···X distance is 0.5 Å shorter for X = Sn than for X = C, although the mean Sn–C(Ph) bond length is over 0.6 Å longer than that of C–C(Ph) (Table 1) and the global size of the –SnPh$_3$ group is correspondingly larger. This phenomenon can be understood from the relation of the Sn···Sn distance with the geometry of the –SnPh$_3$ groups. In Fig. 5, the (Ph)C–Sn–C(Ph) angles are plotted against the Sn···Sn distance in 6PEs, showing a clear negative correlation. For the shortest contacts, the C–Sn–C angles are substantially widened from the tetrahedral value (109.5°), whereas for truly tetrahedral angles at Sn, the Sn···Sn approach in 6PEs is limited to values >6 Å. The increasing width of the 6PE distance range when moving the central atom down the periodic table is, therefore, a consequence of the well-known increasing softness of valence angles.

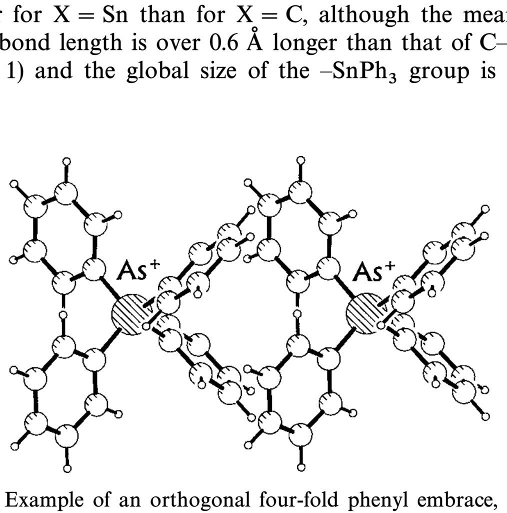

Fig. 4 Example of an orthogonal four-fold phenyl embrace, O4PE, formed between two Ph$_4$As$^+$ ions (in Ph$_4$As$^+$ClO$_4$$^-$, As···As = 6.86 Å, C–As···As–C collinearity = 125.7°; crystal structure determined by Couldwell,[13] CSD code TPASPC).

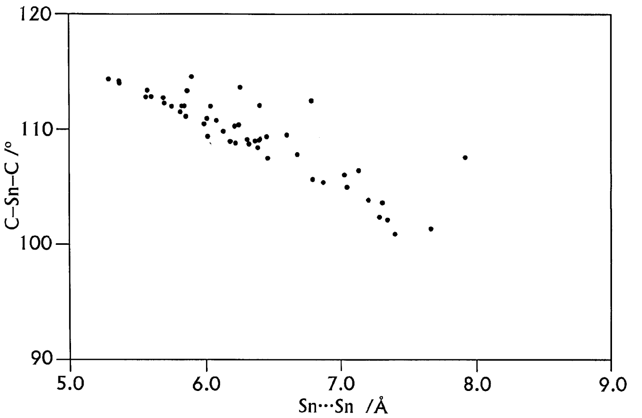

Fig. 5 Relation between Sn···Sn contact distance and mean (Ph)C–Sn–C(Ph) angle in 6PEs formed between –SnPh$_3$ groups.

Apart from the cluster of 6PEs, there are also other differences in scatterplots like Fig. 3(*b*) when varying X and R of the R–XPh$_3$ groups involved. For example, a cluster representing O4PEs is missing in Fig. 3(*b*), but is present for some other triphenyl groups such as R=PPh$_3$ and –SnPh$_3$. Clusters representing specific interactions between phenyl rings and atoms of R are present for certain R, and absent for others. All these differences, however, are not directly connected with the 6PEs, and are not the subject of the present study.

Frequencies of 6PEs between like XPh$_4$ units

The frequencies of 6PEs formed between like tetraphenyl units are listed in Table 2. The frequencies are remarkably high for the cations Ph$_4$P$^+$ and Ph$_4$As$^+$ (0.62 and 0.52 6PE, respectively, formed per cation). It must be noted that the relative values give the average number of symmetry-independent 6PEs formed per ion. Because one ion can form more than one 6PE at a time, this is not equal to the relative frequency of ions forming 6PEs. Nevertheless, according to Dance and Scudder, 60% of the Ph$_4$P$^+$ containing compounds are involved in 6PEs,[1] which is so close to the value in Table 2 that it does not seem to be worthwhile to differentiate between different ways of counting frequencies.

For the anionic counterpart of Ph$_4$P$^+$, that is Ph$_4$B$^-$, the scatterplot of C–B···B–C colinearities against B···B separations is shown in Fig. 6. The overall appearance is quite different from that for Ph$_4$X$^+$ cations [Fig. 3(*a*)]. There is also a cluster representing 6PEs, but this cluster is only weakly populated and is shifted to longer distances. In the set of 1336 structures containing Ph$_4$B$^-$ anions, only 24 form inter-anion 6PEs. This is slightly less than 2%. The B···B distance range of the 6PEs is 6.2–7.4 Å, with a mean value of 6.85 Å. Because occurrence of the 6PE in Ph$_4$B$^-$ salts has not been noticed before, an example is shown in Fig. 7. There are no data points in Fig. 6 representing the O4PE or any other multiple phenyl embrace that would allow a very short B···B approach. The vast majority of data is found at B···B distances >8.0 Å, with a maximum density of points at B···B

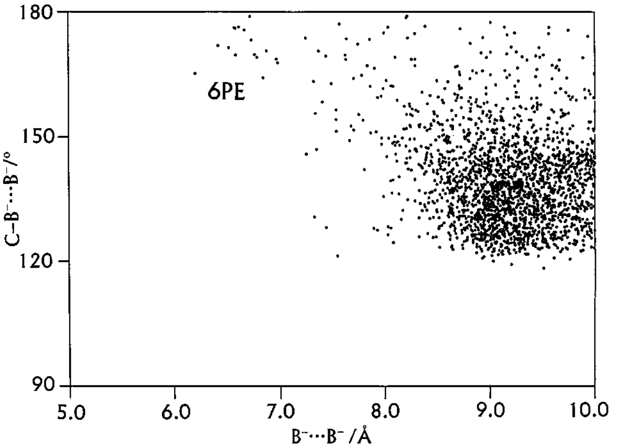

Fig. 6 Scatterplot of C–B···B–C colinearities against B···B separations in contacts between Ph_4B^- anions. Only a few 6PEs are formed.

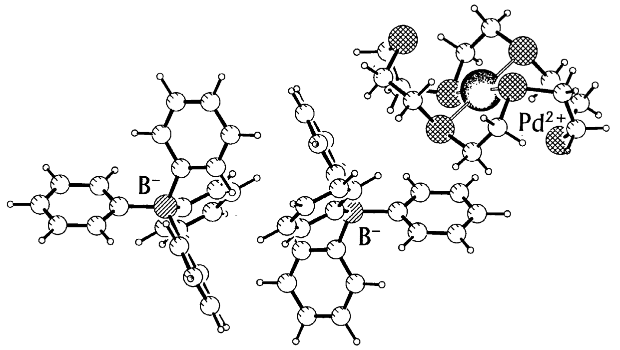

Fig. 7 Example of a 6PE formed between Ph_4B^- anions. (Ph_4B^- salt of the thio-crown ether complex $(SC_2H_4)_6Pd^{2+}$, B···B = 6.57 Å, C–B···B–C collinearity = 176.2°, crystal structure determined by Schröder and coworkers,[14] CSD code DOFSAS).

distances around 9 Å and C–B···B–C colinearities around 130°. These points typically represent contacts of neighbouring anions that involve only one phenyl–phenyl interaction. An example has recently been discussed for ammonium tetraphenylborate.[15]

Apart from the ionic species, there are also uncharged molecules Ph_4X with group IV elements as the central atom (C to Pb), and also with Os. They all crystallize isostructurally without formation of 6PEs (space group tetragonal $P\bar{4}2_1c$, No. 114). The crystal structures are characterized by molecular columns linked by O4PEs, similar to the Ph_4As^+ cations shown in Fig. 4. The interesting salts of Ph_4B^- with the cations Ph_4X^+ (X = P, As, Sb) also crystallize in this way, without formation of 6PEs.[16]

Frequencies of 6PEs between like $R–XPh_3$ units ($R \neq Ph$)

For $R–XPh_3$ units other than Ph_4X, the frequencies of 6PEs between two like groups are given in Table 2. For the group IV central atoms, the relative frequencies of 6PE formation are about 17%, a factor of 3.6 lower than the value for Ph_4P^+. For group V central atoms, the frequencies of 6PEs appear to be slightly higher and there are significent differences between different chemical systems. For example, 19% of all $C–PPh_3{}^+$ groups are involved in 6PEs, for metal bound $–PPh_3$, the frequency is 23%, and for the particular molecule triphenylphosphinoxide, $O{=}PPh_3$, the frequency is even 28%. For organic $X{=}PPh_3$ groups in general (including $O{=}PPh_3$), however, the frequency of 6PE formation is only 13%.

For $–XPh_3$ with group III central atoms, the frequency of 6PEs is much lower. Of the 53 $–XPh_3$ groups in the CSD with X = B, Al or Ga, only a single one forms a 6PE (it is of the type $N^+–BPh_3{}^-$ and occurs in the compound with the CSD identifier RAXXOD). This parallels the behaviour of Ph_4B^- anions, which also form 6PEs only very rarely.

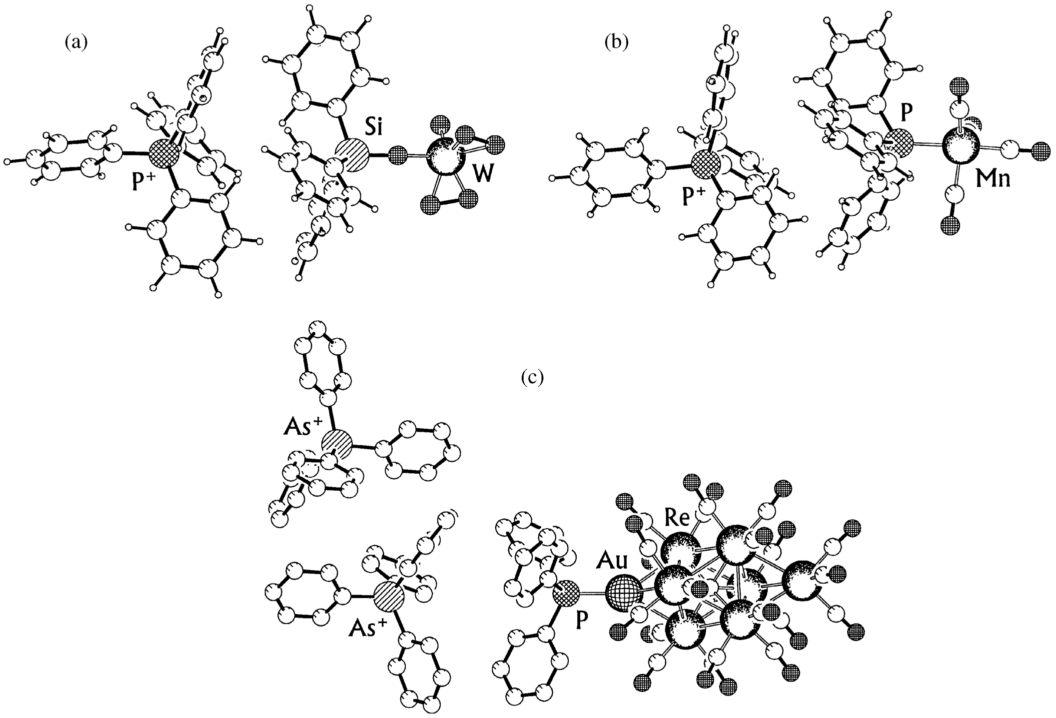

Fig. 8 Examples of 6PEs between unlike $–XPh_3$ groups: (*a*) between a $–SiPh_3$ group and a Ph_4P^+ cation in tetraphenylphosphonium oxodiperoxo(triphenylsilanolato)tungsten, Si···P = 6.61 Å, O–Si···P–C collinearity = 175.4°, crystal structure determined by Brégault and coworkers,[17] CSD code NOFGOE; (*b*) between a $–PPh_3$ group and a Ph_4P^+ cation in $Ph_4P^+[Ph_3P(CO)_4Mn]^-$, P···P = 6.94 Å, Mn–P···P–C collinearity = 173.1°, crystal structure determined by Riley and Davis,[18] CSD code PHPCMN; (*c*) between a $–PPh_3$ group and a Ph_4As^+ cation in $(Ph_4As^+)_2[Re_7C(CO)_{21}Au(PPh_3)]^{2-}$, P···As = 7.02 Å, Au–P···As–C collinearity = 174.6°, note also the 6PE formed between the two symmetry-independent Ph_4As^+ cations; crystal structure determined by Henly *et al.*,[19] CSD code DUKBOA.

Frequencies of 6PEs between unlike Ph_4X and/or $-XPh_3$ units

If there are different kinds of triphenyl groups present in a solid state system, there is a certain chance that they will associate by forming a 6PE, *i.e.*, form a hetero-pair $R_1-XPh_3\cdots Ph_3Y-R_2$. Unfortunately, the CSD contains only very few relevant crystal structures, as is shown in the second half of Table 2. For group IV and V central atoms, there is a total of 51 relevant fragment pairs, and these form a total of nine hetero-6PEs. This is a relative frequency of 18%, which is similar to the values for many kinds of homo-pairs (see above). Although the statistical significance of this result is poor, it seems that the chance of 6PE formation between hetero-pairs in general is neither strongly favoured nor strongly disfavoured compared to the formation of homo-pairs.

There are 42 fragment pairs with one group III central atom (Ph_4B^- in all cases). No 6PE is formed between any of these pairs.

Since there is so little literature on 6PEs between unlike $R-XPh_3$ groups, examples are shown in Fig. 8 for all fragment pairs where the 6PE has not been mentioned in a previous publication. These are the combinations $-SiPh_3\cdots Ph_4P^+$, $M-PPh_3\cdots Ph_4P^+$ and $M-PPh_3\cdots Ph_4As^+$ (for the pairs $-CPh_3\cdots Ph_3P{=}$ and $-SiPh_3\cdots Ph_3P{=}$, see refs. 8 and 9, respectively). Substance names, interaction geometries and literature references are given in the figure legend. It is expected that many other combinations of $-XPh_3$ groups can make the 6PE, but further experimental work is clearly needed before more statistically sound conclusions can be drawn.

Discussion

The global abundancies of 6PEs, that is the average over all competitive situations, are high only for the family of cations Ph_4X^+ and highest for Ph_4P^+ (0.62 6PEs formed per ion). For $R-XPh_3$ groups ($R \neq Ph$, $X =$ group IV or V atom), the relative frequencies are lower, ranging between 13 and 28% depending on R–X. They are very low, about 2%, for the Ph_4B^- anion and for $R-XPh_3$ groups with X being a group III atom. These probabilities of formation do not seem to make the 6PE between $-XPh_3$ groups a supramolecular synthon[20] that is particularly attractive for crystal engineering purposes. It is hardly worthwhile designing and producing a crystal structure if the success rate of a given construction element is only 17% or so. However, one must consider that the values in Table 2 represent averages over all occurring molecular compositions and shapes, and all competitive situations. At least in principle, it might be possible to design molecules or supermolecules in such a way that upon crystallization, 6PEs are formed with much a higher (or lower, if desired) probability than found in the corresponding line of Table 2.

Acknowledgements

Part of this study has been performed in the Weizmann Institute of Science, Department of Structural Biology, Rehovot 76100, Israel, in the laboratory of Professor Joel L. Sussman, and was supported by the Minerva-Foundation (Munich). The study was completed in the laboratory of Professor Wolfram Saenger (Berlin), who is thanked for giving the opportunity to carry out this work.

References

1 I. Dance and M. Scudder, *J. Chem. Soc., Chem. Commun.*, 1995, 1039.

2 I. Dance and M. Scudder, *New J. Chem.*, 1998, **22**, 481.

3 G. E. Bacon, N. A. Curry and S. A. Wilson, *Proc. R. Soc. London, Ser. A*, 1964, **279**, 98.

4 I. Dance and M. Scudder, *Chem. Eur. J.*, 1996, **2**, 481.

5 I. Dance and M. Scudder, *J. Chem. Soc., Dalton Trans.*, 1996, 3755.

6 M. Scudder and I. Dance, *J. Chem. Soc., Dalton Trans.*, 1998, 329.

7 M. L. Scudder, H. A. Goodwin and I. G. Dance, *New J. Chem.*, 1999, **23**, 695.

8 T. Steiner, J. van der Maas and B. Lutz, *J. Chem. Soc., Perkin Trans. 2*, 1997, 1287.

9 T. Steiner, *Trans. Am. Crystallogr. Assoc.*, 1998, **33**, 165; *Acta Crystallogr., Sect. C*, submitted (MS DE 1126).

10 F. H. Allen and O. Kennard, *Chem. Des. Automat. News*, 1993, **8**, 1.

11 F. H. Allen, W. D. S. Motherwell, P. R. Raithby, G. P. Shields and R. Taylor, *New J. Chem.*, 1999, **23**, 25.

12 A. N. Sobolev, V. K. Belsky, I. P. Romm, N. Y. Chernikova and E. N. Guryanova, *Acta Crystallogr., Sect. C*, 1985, **41**, 967.

13 M. C. Couldwell, *Cryst. Struct. Commun.*, 1979, **8**, 469.

14 A. J. Blake, R. O. Gould, A. J. Lavery and M. Schröder, *Angew. Chem., Int. Ed. Engl.*, 1986, **25**, 274.

15 T. Steiner and S. A. Mason, *Acta Crystallogr., Sect. B*, in press (paper KA0046).

16 M. A. Lloyd and C. P. Brock, *Acta Crystallogr., Sect. B*, 1997, **53**, 773.

17 J.-Y. Piquemal, S. Halut and J.-M. Brégeault, *Angew. Chem., Int. Ed. Engl.*, 1998, **37**, 1146.

18 P. E. Riley and R. E. Davis, *Inorg. Chem.*, 1980, **19**, 159.

19 T. J. Henly, J. R. Shapley and A. L. Rheingold, *J. Organomet. Chem.*, 1986, **310**, 55.

20 G. R. Desiraju, *Angew. Chem., Int. Ed. Engl.*, 1995, **34**, 2311.

Paper a909054a