The Sextuple Phenyl Embrace, a Ubiquitous Concerted Supramolecular Motif

## Ian Dance* and Marcia Scudder

School of Chemistry, University of New South Wales, Sydney 2052, Australia

The sextuple phenyl embrace, a supramolecular attraction between Ph₃P moieties due to a concert of six attractive edge-to-face interactions between phenyl groups, has frequent occurrence in crystals, is usually centrosymmetric, and contributes an attraction of 60–85 kJ mol⁻¹.

The principal objectives of research in supramolecular chemistry are to discover and understand the attractive motifs which determine the associations of molecules in condensed phases, and to develop an ability to design and fabricate total supramolecular structures and molecular crystals. The structure of a molecular solid is the net result of local intermolecular interactions in concert and competition, and one strategy in this research is to recognise concerted and elaborated supramolecular motifs.

The attractive interactions of phenyl groups, in the offset-face-to-face (**off**) and edge-to-face (**ef**) conformations, are well understood as commonly occurring supramolecular motifs.[1,2] We report here the widespread occurrence of a concerted intermolecular attraction which uses six phenyl **ef** interactions, from two triphenylphosphine moieties. As shown in Fig. 1, the two Ph₃P groups approach each other such that each phenyl ring
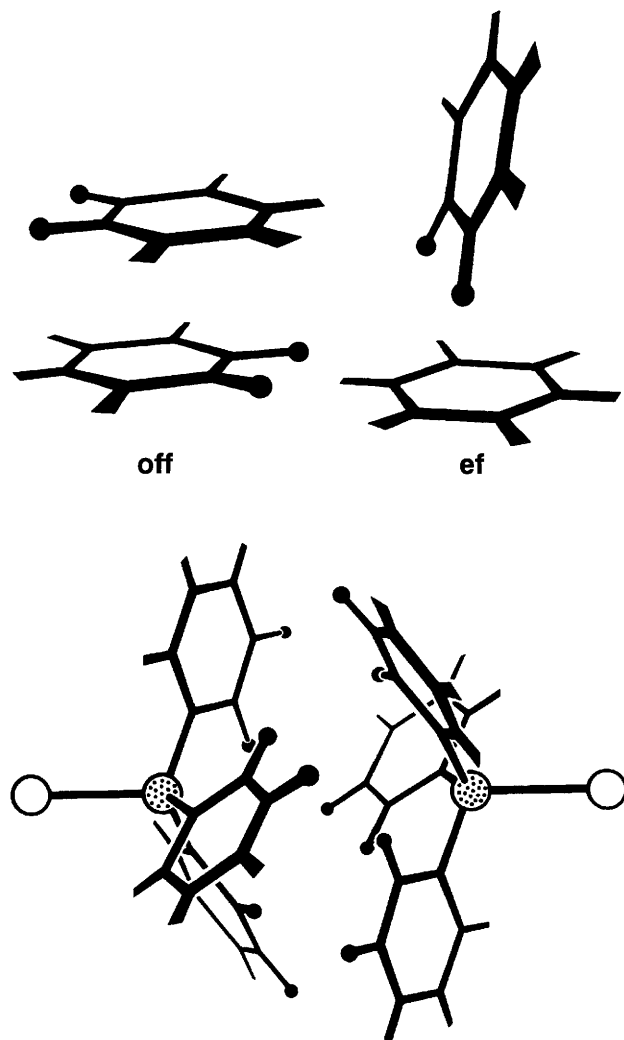
is interleaved between two rings on the other molecule, with approximate S_3 symmetry for the pair. Two hydrogen atoms on each ring are directed, with **ef** geometry, towards carbon atoms of a phenyl ring on the other molecule. This concerted motif is named the sextuple phenyl embrace (SPE).

The SPE is prevalent where the stereochemistry at P is tetrahedral, and is characterised by approximate colinearity of the two P atoms and the atoms X which complete their tetrahedral geometry (Fig. 1). In the Cambridge Structural Database (CSD, 1994)[3] there are about 3800 compounds containing at least one Ph₃P bonded to a transition metal M. Fig. 2 shows a scatterplot of the intermolecular interactions where the P⋯P separation is in the range 5.5–8.0 Å, and the M–P⋯P–M colinearity (half the sum of the M–P⋯P and P⋯P–M angles) ranges from 120 to 180°. The preponderance of instances in the range 6.4–7.4 Å and 160–180° is clearly evident; these are all sextuple phenyl embraces. The interpenetration of the two PPh₃ moieties in the SPE is apparent from the fact that the P⋯P separations are very much less than 13.6 Å, which is twice the van der Waals radius of PPh₃ regarded as a hemisphere. There are 3165 compounds containing M–PPh₃ with coordinates available from the CSD, and 965 (30%) of these lead to points in the SPE domain (colinearity ⩾160°) of Fig. 2.

A cation popular with synthetic chemists for the crystallisation of anions is Ph₄P⁺, and there are approximately 875 compounds in the CSD containing one or more Ph₄P⁺ ions. The comparable scatterplot for these compounds (Fig. 3) shows that this SPE is characterised by an even shorter P⋯P separation in the range 5.8–6.8 Å.† The proportion of Ph₄P⁺-containing compounds which are involved in SPEs (colinearity ⩾160° in Fig. 3) is 60%, namely 438 compounds out of 733 for which details are available.

The essence of the SPE resides in the intermolecular **ef** interactions of the phenyl rings.‡ Using the CSD, statistical examination of details of the SPE geometry (*via* the intermolecular separations of the phenyl ring centroids and the angles
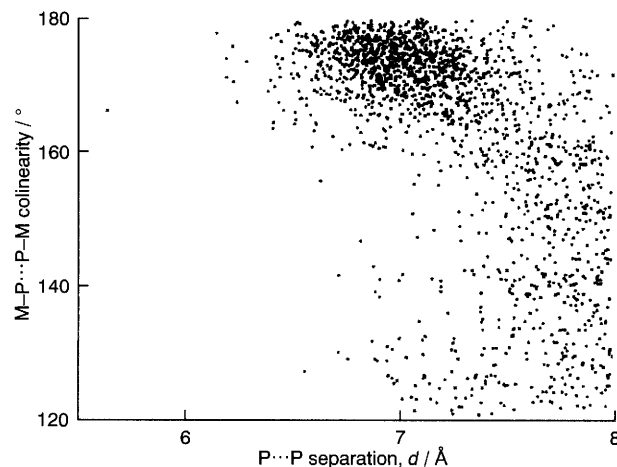

Fig. 1 The intermolecular sextuple phenyl embrace of two X-PPh₃ moieties. Hydrogen atoms at the 2 and 3 positions of each ring (filled circles) are directed towards carbon atoms at the 2, 3, 4 and 5 positions of an opposite ring. The approximate colinearity of the two X–P groups is evident.

Fig. 2 Scatterplot of the geometry of the shorter intermolecular contacts for transition metal (M) compounds with PPh₃ ligands. The M–P⋯P–M colinearity is half the sum of the M–P⋯P and P⋯P–M angles; 1498 of the 1987 points occur in the domain 160–180° for the M–P⋯P–M colinearity.

between the normals to the phenyl ring planes) shows that the geometry of the SPE is remarkably consistent, and its conformation invariant. There is close (but rarely exact) approach to C_3 symmetry for the pair of Ph_3P moieties, while a most significant result is that more than 95% of the SPE interactions we have examined occur across a crystallographic centre of symmetry. Clearly Ph_3P ligands should not be used in attempts to synthesise metal compounds with non-centric lattices for application in non-linear optics.

We have evaluated the attractive energies of representative sextuple phenyl embraces, $\{Ph_4P^+\}_2$ and $\{[CuPPh_3]^+\}_2$, using atom–atom potential calculations.§ For both examples the total intermolecular energies range from -60 to -85 kJ mol^{-1}, with the tighter embraces being the more attractive. It is informative to examine some of the component energies: each phenyl ring is attracted by 10 to 14 kJ mol^{-1} to each of its opposite neighbours; each H⋯C interaction in the ef conformations contributes ca. 2.1 kJ mol^{-1} attraction, mostly coulombic in origin. The intermolecular repulsion between the pair of $P^{0.4+}$ or the pair of $Cu^{0.5+}$ in the SPE is negligible. It is incorrect to regard Ph_4P^+ cations as being repulsive in crystal packing: they are demonstrably attractive.
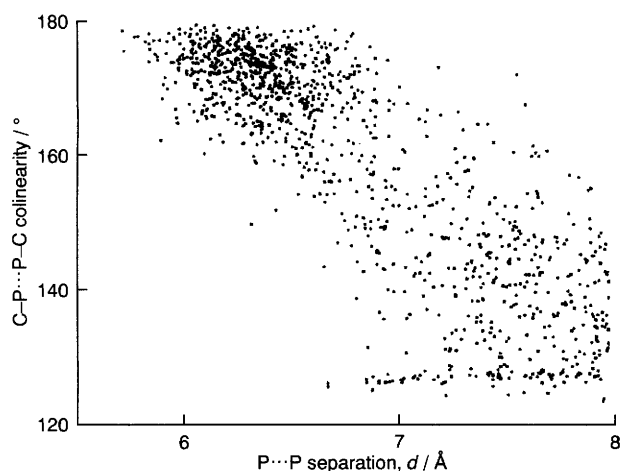
Fig. 3 Scatterplot of the geometry of the shorter intermolecular contacts between Ph_4P^+ ions. The C–P⋯P–C colinearity is half the sum of the pertinent C–P⋯P and P⋯P–C angles (X = C in Fig. 1): 845 of the 1239 points occur in the domain 160–180° for C–P⋯P–C colinearity.

The Ph_4P^+ cation has four PPh_3 sets, and is able to engage in more than one SPE. In a separate paper[4] we will describe the extended networks of embracing Ph_4P^+ cations which commonly occur in crystals, and the consequences of these multiple SPEs for the associated anions which were usually the focus of interest in each compound. The SPE is not the only mode of attractive association for XPh_3 moieties, and there are other motifs which also occur commonly in crystals.[4]

We have exposed a supramolecular motif which is ubiquitous, directional and strong. The SPE underlies the pragmatic wisdom of synthetic chemists who know that PPh_3 and related ligands, and Ph_4P^+ cations, frequently yield quality crystals. We are exploring the deployment of the SPE for purposes of crystal engineering.

Footnotes

† The geometrical difference between the sextuple phenyl embraces for $MPPh_3$ and Ph_4P^+ is a consequence of the fact that M–P–C angles in $MPPh_3$ compounds are consistently larger (mean 114°) than the tetrahedral C–P–C angles in Ph_4P^+ compounds. The pattern for crystals containing Ph_4As^+ is very similar to that for Ph_4P^+.

‡ The H⋯C distances in the intermolecular ef interactions range from 2.8 to 3.2 Å, comparable with those established for benzene and other aromatic compounds.

§ Parameters: van der Waals parameter sets r*/Å, ε/kJ mol^{-1} for H, C, P, Cu, are respectively (1.50, 0.17), (2.00, 0.21), (2.07, 0.84) and (2.20, 0.63); partial charges are $H^{0.15+}$, $C^{0.1-}$, $P^{0.4+}$ in Ph_4P^+, $P^{0.05+}$ in PPh_3, $Cu^{0.5+}$.

References

1 G. R. Desiraju, Crystal Engineering: The Design of Organic Solids, Elsevier, Amsterdam, 1989.
2 D. E. Williams, Acta Crystallogr., Sect. A, 1980, 36, 715; J. H. Lii and N. L. Allinger, J. Am. Chem. Soc., 1989, 111, 8576; A. Gavezzotti, Chem. Phys. Lett., 1989, 161, 67; W. L. Jorgensen and D. L. Severance, J. Am. Chem. Soc., 1990, 112, 4768; C. A. Hunter and J. K. M. Sanders, J. Am. Chem. Soc., 1990, 112, 5525; C. A. Hunter, Philos. Trans. R. Soc. London, Ser. A, 1993, 345, 77.
3 F. H. Allen, J. E. Davies, J. J. Galloy, O. Johnson, O. Kennard, C. F. Macrae and E. M. Mitchell, J. Chem. Inf. Comp. Sci., 1991, 31, 187.
4 I. G. Dance and M. L. Scudder, in preparation.