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Concerted supramolecular motifs: inverted sextuple aryl embraces in crystalline tris(9-anthracenyl)phosphine

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Abstract—Crystalline tris(9-anthracenyl)phosphine **1** contains an unusual supramolecular motif, an inverted sextuple aryl embrace (ISAE) of a pair of phosphines. This embrace, which is maintained by six intermolecular edge-to-face interactions between anthracenyl groups, differs from the normal sextuple phenyl embraces (SPE) of Ph_3P in that the phosphines are inverted relative to each other. The P–C vectors are directed away from the interaction zone in the ISAE, rather than into the interaction zone as in the SPE. The ISAE has $\bar{3}$ symmetry. The net attractive energy of this concerted supramolecular motif is calculated to be 165 kJ mol^{-1} for the ISAE pair. Each molecule of **1** is also involved in three quadruple anthracenyl embraces with three other neighbouring molecules, in geometry comparable with the parallel quadruple phenyl embraces of Ph_3P and Ph_4P^+. © 1997 Elsevier Science Ltd

Keywords: supramolecular; multiple phenyl embrace; aryl interactions.

The attractive interactions between phenyl and aryl groups are well-established, and are fundamental to many supramolecular phenomena [1]. We are investigating instances of concerted phenyl–phenyl interactions, and have identified the multiple phenyl embraces which occur between XPh_3 groups. A prevalent multiple phenyl embrace is the sextuple phenyl embrace (SPE) which occurs for compounds containing Ph_3P or Ph_4P^+, and is a dominant factor in their crystal packing [2–4]. The six phenyl rings of the sextuple phenyl embrace, shown in Fig. 1, engage six edge-to-face phenyl–phenyl interactions in the interaction domain. The net attractive energy of an SPE is calculated to be in the range 60–85 kJ mol^{-1} [2,3].

A characteristic of all of these SPEs is that the P—C bonds for the phenyl rings are directed into the interaction zone between the P atoms, as shown in Fig. 2(a). In this paper we identify an unusual sextuple embrace in which the P–C vectors are directed *away* from the interaction zone, as shown in Fig. 2(b). This occurs in the compound tris(9-anthracenyl) phosphine, **1** [5], (Cambridge structural database [6] reference code PAMWAB) and is drawn in Fig. 3. One ring of each anthracenyl group is positioned in

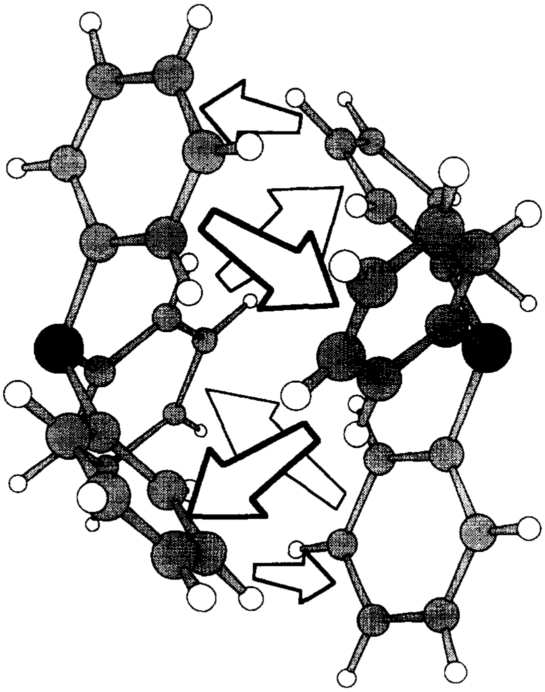

Fig. 1. A typical sextuple phenyl embrace. The arrows mark the edge-to-face phenyl–phenyl interactions, being directed from H to C.

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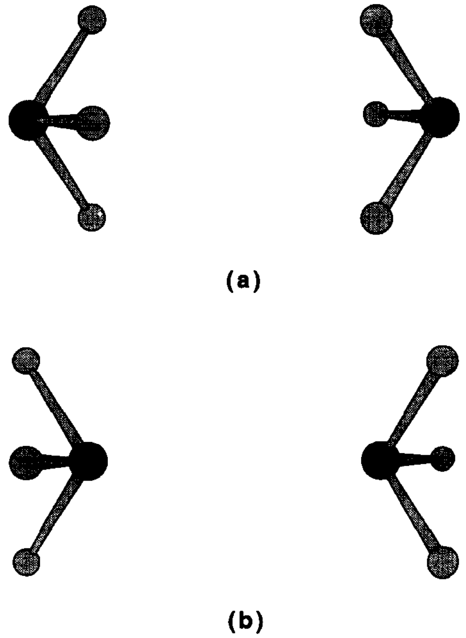


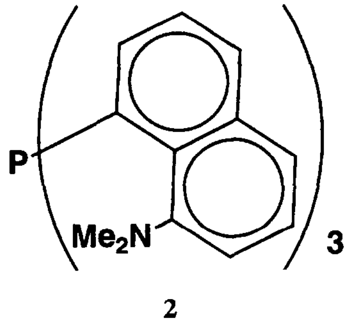
Fig. 2. (a) The P–C vectors for $(PPh_3)_2$ in a normal sextuple phenyl embrace. (b) The P–C vectors for an inverted SPE.

the interaction zone between the two P atoms, and these six rings are well placed to form the six edge-to-face interactions characteristic of the sextuple embrace. Note that the six inner phenyl rings in Fig. 3 are positioned similarly to the phenyl groups of the SPE in Fig. 1. Because each tertiary phosphine in this embrace is inverted relative to that in the regular SPE, we name the concerted supramolecular motif in Fig. 3 an inverted sextuple aryl embrace (ISAE). The inverted sextuple embrace uses the convex hemispheres of the tertiary phosphine, while the normal sextuple embrace uses the concave hemispheres. This ISAE has high point group symmetry, $\bar{3}$, and like many SPE has a crystallographic centre of inversion at its mid-point (note that the adjective 'inverted' in the name describes the characteristic configuration of each tertiary phosphine relative to its partner, not the crystallographic symmetry).

As a consequence of the inversion in the ISAE, the $P \cdots P$ distance is reduced to only 5.05 Å, substantially shorter than the range 6.4–7.4 Å found for the normal SPE in PPh_3 compounds [2]. Using the atom–atom based procedure previously described, the attractive energy of the ISAE is calculated to be 165 kcal mol^{-1}. This calculation used the atom partial charges: $P^{-0.27}$; $C_{ipso}^{0.00}$; $C^{-0.05}$ for the anthracene central ring; $C^{-0.07}$ for the eight C atoms of the outer rings; and $H^{+0.10}$. The strong net attraction in the ISAE, more than double that of the normal SPE, is at least partly due to the larger number of atoms involved.

The crystal structure of **1** has further significance. The lattice has rhombohedral symmetry, space group $R\bar{3}$, with the ISAEs aligned along the threefold axes and generating a larger high symmetry lattice of significant supramolecular interactions in which the molecules of **1** are arranged in networks of puckered six-rings. This type of lattice of multiple phenyl/aryl embraces occurs also in a set of other more diverse compounds, and we describe and analyse this general lattice type in a separate paper [7]. However there is another significant multiple aryl embrace in crystalline **1** which deserves description here, in comparison with the ISAE. Figure 4 shows and embrace of two molecules of **1** involving two anthracenyl groups from each molecule: the plane formed by the two P–C vectors on one molecule is approximately parallel to the corresponding plane on the other molecule, and so this is the anthracenyl homolog of the parallel quadruple phenyl embrace (PQPE) [3]. The embrace, here named the parallel quadruple aryl embrace (PQAE), is comprised of one offset-face-to-face attractive interaction and two edge-to-face attractive interactions. The $P \cdots P$ separation in this PQAE is 10.25 Å, and the attractive energy for the pair of molecules in this embrace is calculated to be 94 kJ mol^{-1}. Again this is substantially larger than the energy of the PQPE involving phenyl groups [3]. In crystalline **1**, the PQAEs occur along the connections which comprise the puckered hexagonal nets, while the ISAEs are the connections between these puckered hexagonal nets. Each molecule of **1** is engaged in one ISAE and three PQAEs, and so the total attractive energy between a molecule of **1** and four immediately surrounding molecules is estimated to be $(165+3\times94)/2 = 223$ kJ mol^{-1}. The lattice also contains toluene (the solvent for crystallisation), which is disordered in a cavity in the lattice and is a consequence, not cause, of the crystal packing [5].

Are there other molecules which engage in inverted sextuple aryl embraces? In the Cambridge Crystallographic Database [6] (October 1996) there are no compounds X (anthracenyl)$_3$ for X other than P. As is evident from Fig. 3, a 2-naphthyl group on phosphorus would be sufficient to form an ISAE: we can find only one such compound, **2** (reference code PEXHAB) [8] but the crystal structure contains no sextuple aryl embraces. There are three crystal structures of compounds where a P atom is bound to a combination of anthracenyl (An) and phenyl (Ph) groups, namely $AnPh_2PW(CO)_5 \cdot CH_2Cl_2$ (ref. code PAMWEF) [5], $(AnPh_2PAuC)_2 \cdot (CHCl_3)_2$ (ref. code WICXUB10) [9] and $(An_2PhPAuC)_2 \cdot (CHCl_3)_6$ (ref. code WICYAI10) [9]. In none of these is there a sextuple aryl embrace, although there are other aryl–aryl interactions.



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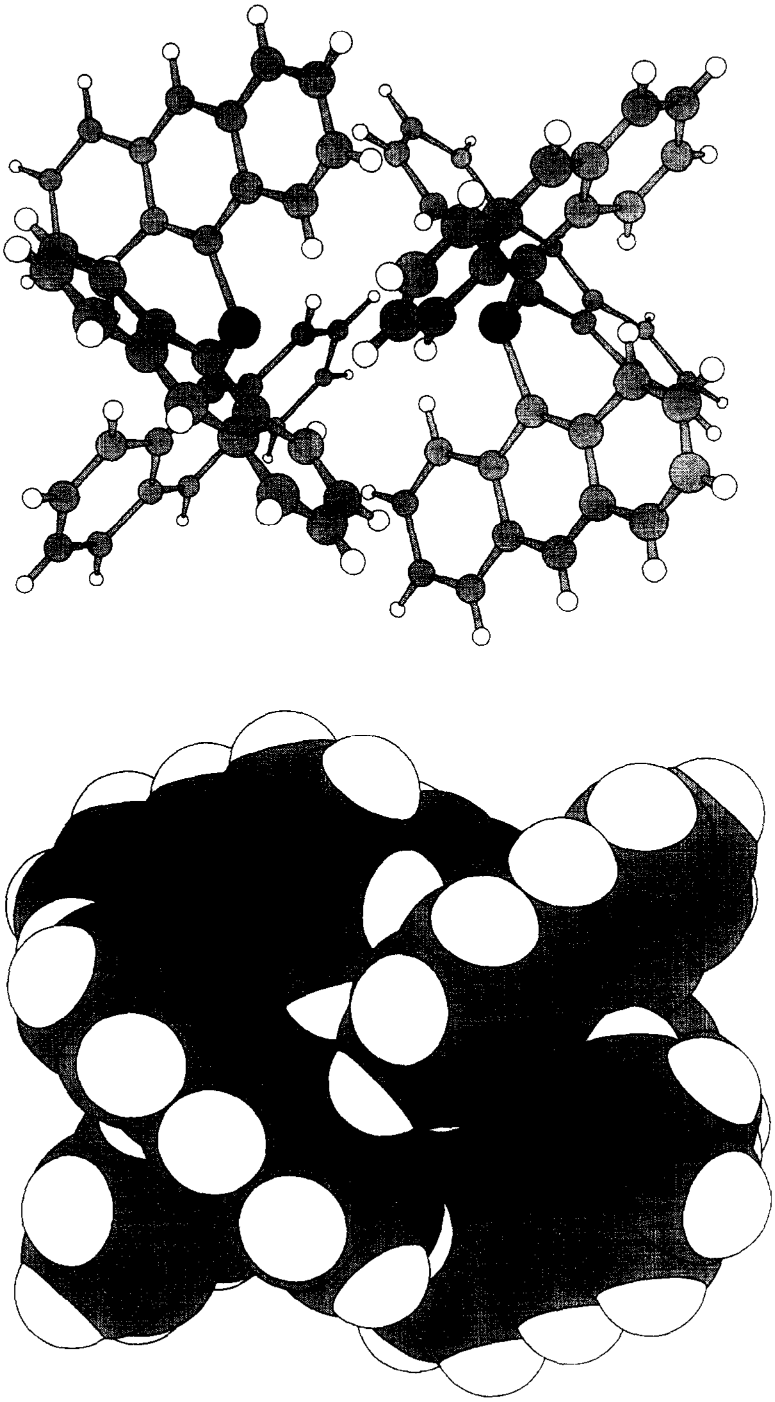

Fig. 3. (a) The inverted sextuple aryl embrace of two molecules of tris(9-anthracenyl)phosphine, **1**, as they occur in the crystal. There is a centre of inversion at the mid-point of the pair of molecules, and overall symmetry of the pair is $\bar{3}$. (b) Space-filling representation, showing clearly three of the edge-to-face interactions between the two molecules.

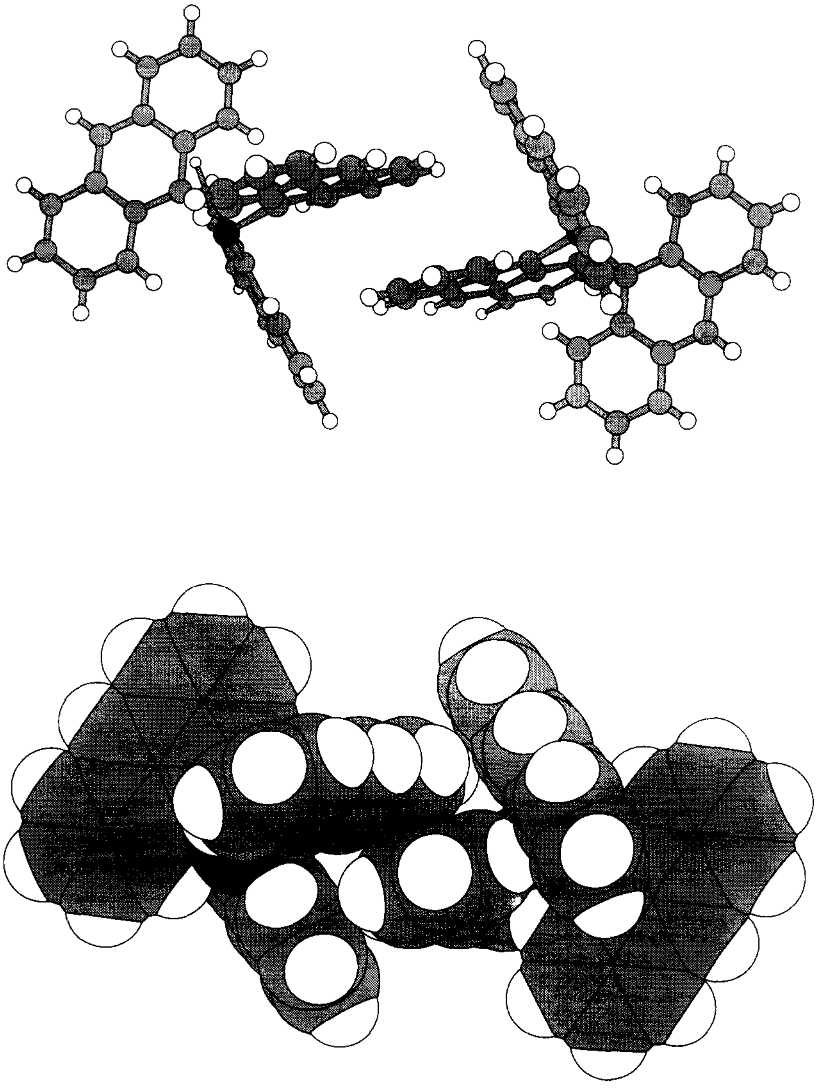

Fig. 4. The parallel quadruple aryl embrace which occurs in crystalline **1**.

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REFERENCES

1. Dance, I. G., in *The Crystal as a Supramolecular Entity*, p. 137 eds. G. R. Desiraju, John Wiley, Chichester, 1996.
2. Dance, I. G. and Scudder, M. L., *J. Chem. Soc., Chem. Comm.*, 1995, 1039.
3. Dance, I. G. and Scudder, M. L., *Chem. Eur. J.*, 1996, **2**, 481.
4. Dance, I. G. and Scudder, M. L., *J. Chem. Soc., Dalton Trans.*, 1996, 3755.
5. Wesemann, J., Jones, P. G., Schomburg, D., Heuer, L. and Schmutzler, R., *Chem. Ber.*, 1992, **125**, 2187.
6. Allen, F. H., Davies, J. E., Galloy, J. J., Johnson, O., Kennard, O., Macrae, C. F. and Watson, D. G., *Chem. Inf. Comput. Sci.*, 1991, **31**, 204.
7. Dance, I. G. and Scudder, M. L., *J. Chem. Soc., Dalton Trans.*, 1997, in preparation.
8. Chuit, C., Corriu, R. J. P., Monforte, P., Reye, C., Declercq, J.-P. and Dubourg, A., *Angew. Chem. Int. Ed. Engl.*, 1993, **32**, 1430.
9. Muller, T. E., Wing-Kin, S., Mingos, D. M. P., Murphy, D., Williams, D. J. and Yam, V. W. W., *J. Organomet. Chem.*, 1994, **484**, 209.