Supramolecular potentials and embraces for fluorous aromatic molecules

Susan Lorenzo, Gareth R. Lewis and Ian Dance*

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

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In order to understand better the supramolecular chemistry of fluorous molecules, and particularly coordination complexes and organometallic molecules with perfluoroaromatic substituents, the relevant intermolecular potentials have been parametrised. It is shown that density functional calculations using the Perdew–Wang PWC functional and numerical basis sets adequately describe weak intermolecular attractive energies [*e.g.* $(C_6H_6)_2$], but that gradient corrected BP or BLYP functionals do not. Due to a dearth of experimental data on intermolecular energies for perfluoroaromatic systems, these density functional calculations of the supramolecular isomers of $(C_6F_6)_2$ are used to parametrise the Lennard-Jones plus electrostatic potential for fluoroaromatic and derivative molecules. Intermolecular energies for local interactions in the crystal structures of C_6F_6, $C_6F_6 \cdot C_6D_6$, and octafluoronaphthalene are reported. Strong directionality is not observed in the supramolecular forces between fluoroaromatics and the electrostatic components of the intermolecular energies are small, $<15\%$ of the total; the polarisation of the C–F bond is also less than expected from electronegativity differences. Perfluorinated molecules and ions such as $[B(C_6F_5)_4]^-$ engage in multiple phenyl embrace motifs, comparable to those of phenylated molecules, despite the reversed polarity of aromatic C–F relative to C–H bonds (and the opposite quadrupole moments of C_6F_6 and C_6H_6). Examples of the sixfold perfluorophenyl embrace ($6P^FE$), the hexagonal array of sixfold perfluorophenyl embraces ($HA6P^FE$), and fourfold perfluorophenyl embraces ($4P^FE$) are described. The intermolecular attractive energies of some of these motifs comprised of concerted edge-to-face and offset-face-to-face interactions are in the range -5.5 to -11.7 kcal mol^{-1}. It is concluded that there are no major differences between the supramolecular motifs and energies of perfluorinated- and hydroaromatics.

As part of our investigations of supramolecular inorganic and organometallic chemistry we are examining interactions between molecules and ions with fluorinated peripheries, sometimes called fluorous molecules. Various qualitative experiences lead to a perception of fluorous molecules having weak intermolecular attractions: teflon doesn't stick; freons have low boiling points and low enthalpies of vapourisation; BF_4^-, PF_6^- and triflate ($CF_3SO_3^-$) are poorly coordinating and their salts are generally very soluble, implying low attractive energies in the solids; the anions $[B(C_6F_5)_4]^-$ and $[B\{3,5\text{-}(CF_3)_2C_6F_3\}_4]^-$ ($BAr^F{}_4^-$) interact very weakly with cations.[1,2] Fluorous solvents for reactions and biphasic catalyses behave as inert media,[3,4] and fluorinated reagents for these catalyses are being developed.[5,6]

Recently Dunitz and Taylor[7] presented more substantial evidence that intermolecular interactions at covalently bound fluorine atoms are weak, concluding "the experimental evidence leaves no doubt that covalently bonded F hardly ever acts as a H-bond acceptor". There is, however, evidence for O–H···F–C hydrogen bonding.[8] In contrast, the F^- ion forms very strong hydrogen bonds.

Since intermolecular forces generally appear to be minimal and uninfluential for many molecules with covalently bound fluorine, it could be asked—jocularly—whether suprafluorous chemistry is superfluous? However, perfluoroaromatic molecules are known to associate specifically with fluorine-free homologs,[9,10] and are being used for supramolecular construction.[11] Organometallic fluorides and fluoro-coordination complexes aggregated through F have been reviewed recently[12] and metal-bound fluoride ligands show evidence of strong and directional hydrogen bond acceptor behaviour.[13]

Our goal is to probe further the supramolecularity of fluorous molecules, particularly in the context of inorganic systems where fluorine can be bonded to atoms with low electronegativity, and polar bonds to peripheral fluorine atoms can be present. A fundamental question is the extent to which electrostatic forces provide directionality to the underlying isotropic van der Waals forces.[13] The large volume of precise data on crystal packing is a significant resource in this investigation, and in crystal supramolecularity the occurrence of recurring packing patterns is good evidence for specific supramolecular motifs. However, understanding of supramolecularity requires energy information as well as geometry information. In contrast to the surfeit of metrical data there is a dearth of experimental energy data relevant to supramolecular interactions. Because systems of interest are large and complex, reliable intermolecular potentials are required for the calculation of supramolecular energies. In the absence of relevant experimental data for the empirical development of potentials, *ab initio* and density functional calculations can be used to guide the parameterisation. We use validated density functional methods that can deal with large and inorganic molecular aggregates.

We focus first on fluoroaromatics, and particularly hexafluorobenzene and the pentafluorophenyl group, abbreviated Pf. The crystal structure of hexafluorobenzene at 120 K is known.[14] A supramolecular pair of hexafluorobenzene molecules in the gas phase has been observed,[15] but we can find no experimental data on the association energy for $(C_6F_6)_{2(g)}$. There are data on the dissociation of $[(C_6F_6)_2]^+$ and of $[(C_6F_6)_2]^-$,[16] and on $[(C_6F_6)(C_6H_6)]^+$.[17] There are experimental data on the dissociation of the hydrous analogues

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$[(C_6H_6)_2]^{0}$ [18,19] and $[(C_6H_6)_2]^{+\cdot}$.[17] These last data show that the charged pairs are bound more strongly than the neutral pairs, due to charge transfer stabilisation: this stabilisation of radical pairs is indirectly useful for the development of potentials that will be applied to closed shell supramolecular assembles, as shown below.

Caution is needed for density functional (DF) calculations of weak intermolecular interactions, because not all of the available functionals provide accurate results. Wesolowski *et al.* have shown that it is important to use functionals for the exchange-correlation energy that are well behaved at high values of the reduced density gradient.[20] Therefore, in this paper we report some validations and calibrations of our DF methods against intermolecular data for relevant systems, particularly $(C_6H_6)_2$, which is both closely relevant and one of the best understood supramolecular entities. The supramolecular isomers of $(C_6F_6)_2$ are then calculated and used to determine parameters for the empirical potential. We analyse the supramolecular motifs and their energies for crystalline hexafluorobenzene, the cocrystallite $C_6F_6 \cdot C_6D_6$, and crystalline octafluoronaphthalene. The analysis is extended to some perfluorophenylated molecules, specifically $Ge(C_6F_5)_4$ and some salts of the $[B(C_6F_5)_4]^-$ ion, and we describe the occurrence and energies of the multiple perfluorophenyl embraces, which are well-known as the prevalent supramolecular motif in phenylated molecules.[21–29]

Intermolecular potential

Our intermolecular potential (E^t) is the standard combination of Lennard-Jones potential (E^{vdW}) and electrostatic energies (E^e), within the summed atom approximation,[30] eqn. (1):

$$E^t = \Sigma_{ij}(E_{ij}^{vdW} + E_{ij}^{e}) \quad (1)$$

$$E_{ij}^{vdW} = e_{ij}^{a}[(d_{ij}/d_{ij}^{a})^{-12} - 2(d_{ij}/d_{ij}^{a})^{-6}] \quad (2)$$

d_{ij} is the distance between atoms i and j, for which d_{ij}^{a} is the interatomic separation at which the net van der Waals energy is a minimum with magnitude $-e_{ij}^{a}$. For mixed atom types the combinations in eqns. (3) and (4) are used: the atomic radii r_i^a represent the most stabilising distances, and are larger[29,31] than the conventional or crystallographic van der Waals radii.[32]

$$d_{ij}^{a} = r_i^a + r_j^a \quad (3)$$

$$e_{ij}^{a} = (e_i^a e_j^a)^{0.5} \quad (4)$$

The interatomic electrostatic energy is expressed as eqn. (5), in which q are the atom partial charges and ε is the permittivity of the medium.

$$E_{ij}^{e} = q_i q_j/\varepsilon d_{ij} \quad (5)$$

Thus the parametrisation of the intermolecular potential requires determination of parameters r^a and e^a for the relevant atom types, estimation of atom charges for each relevant molecule, and assignment of ε appropriate for the milieu.

Results

Density functional calculations

Our DF methodology uses double numerical basis sets, calculated with the relevant density functional, as implemented in the program DMol.[33–35] The advantage of these atomic basis sets is the avoidance of basis set superposition errors.[33]

A vital consideration in the calculation of weak intermolecular energies is the validity of the density functional, which we first test with calculations on the well-known benzene pair, $(C_6H_6)_2$. Calculations with the gradient-corrected functionals BLYP (Becke–Lee–Yang–Parr)[36,37] and BP (Becke–Perdew),[36,38] which are accurate for strong intramolecular bonding properties, did not show the known weak intermolecular attraction within the benzene pair. However, the VWN (Vosko–Wilk–Nusair)[39] functional and (in DMol[3]) the PWC (Perdew–Wang)[38] functional do yield an attractive potential. This is the conclusion from the more fundamental investigation of DF calculations for weak intermolecular interactions made by Wesolowski *et al.*,[20] who showed also that the PW91 functional[40] gave good agreement with experimental data and with *ab initio* calculations (MP2, corrected for basis set superposition) of weak intermolecular energies. In our investigation we also evaluated the effect in DMol of expanding the real space cutoffs in the calculation of the numerical basis sets, because intermolecular interactions occur over larger distances than does intramolecular bonding.

Fig. 1 shows the four supramolecular isomers for the benzene pair $(C_6H_6)_2$, three of which (**ef**, **vf** and **off**) are observed in phenyl···phenyl interactions in crystals; the face-to-face (**ff**) isomer is rarely observed, except when enforced by stronger intra- or intermolecular interactions. Table 1 contains the optimised energies for these four useful reference points on the geometry–energy surface. The intermolecular distances (see Fig. 1) for the gas phase are generally less than those observed in crystals, because the attractive surroundings of the pair are absent in the gas phase.

Experimental information on the benzene pair gives the association energy as -2.4 ± 0.4 kcal mol^{-1} [per $(C_6H_6)_2$].[18,19,41,42] This is supported by other *ab initio* calculations on the pair and higher associates of benzene.[41–49]

The results in Table 1 (excepting the **ff** isomer, which is not observed) indicate that our DF methods overestimate slightly the intermolecular attractive energy for the benzene pair, and

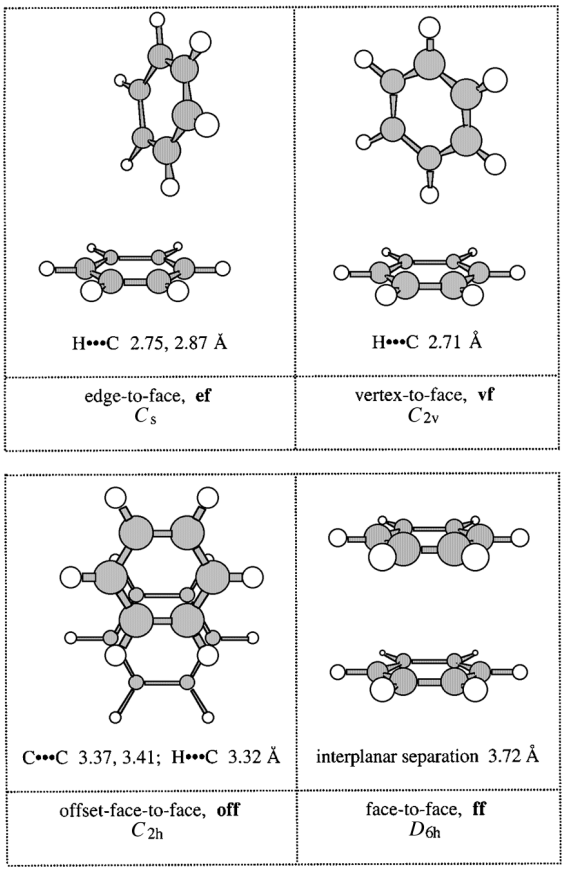


Fig. 1 Four supra-isomers for $(C_6H_6)_2$, optimised by density functional calculations under imposition of the symmetries specified. The shortest intermolecular distances are provided.

Table 1 Optimised structures and energies for the benzene pair $(C_6H_6)_2$ using the Perdew–Wang functional PWC

Isomer (see Fig. 1) and imposed symmetry	Functional	Pair binding energy /kcal mol^{-1}
ef, C_s	PWC	−2.93
	PWC7	−3.19
vf, C_{2v}	PWC	−3.28
	PWC7	−3.55
off, C_{2h}	PWC	−3.19
	PWC7	−3.54
ff, D_{6h}	PWC	−1.51
	PWC7	−1.85

[a] In DMol, PWC and PWC7 use cutoffs of 10.4 and 16.0 au, respectively, for calculation of the numerical basis sets

yield scaling factors of 0.81 for PWC calculations and 0.70 for PWC7 calculations of intermolecular energy. The accuracy of our scaled PWC7-DF calculation is supported by other similar calculations of the energies of weak supramolecular aggregates to be reported separately,[50] but several relevant results are presented here (all energies are PWC7 × 0.7, literature data in brackets): for Ar···Ar, ΔE − 0.43 [−0.29[51]] kcal mol^{-1}; for C_6H_6···Ar, ΔE − 1.3 [−0.97[52,53]] kcal mol^{-1}.

There are experimental data on the dissociation energies of the charged dimers $(C_6H_6)_2^+$, $(C_6F_6)_2^+$ and $(C_6F_6)_2^-$. Therefore, we have investigated these related but odd-electron species, using spin unrestricted calculations. The results are collected in Table 2, as PWC7 energies scaled by 0.7. For $(C_6H_6)_2^+$ Moet-Ner *et al.*[17] report an experimental dissociation enthalpy of 17.0 kcal mol^{-1}, and cite prior measurements of 15, 8, >10 and 14.8 kcal mol^{-1}. We note that the calculated energy for the **off** isomer of $(C_6H_6)_2^+$ is 16.7 kcal mol^{-1}, in excellent agreement with the latest experimental value, while the **ff** isomer (which may occur for the charged pair) is within 1.6 kcal mol^{-1}. The other isomers with less overlap of the rings are less stable and less likely. Hiraoka *et al.*[16] report association enthalpies of -7.2 ± 1 kcal mol^{-1} for $(C_6F_6)_2^+$ and -10.4 ± 1 kcal mol^{-1} for $(C_6F_6)_2^-$. In comparison of these data and the calculations in Table 2 it is evident that despite the spread over the different calculated geometrical isomers (the geometries of the gas phase species are not known), the calculated energies (PWC7 scaled by 0.7) reflect the enhanced stabilities of charged pairs over neutral pairs. The calculated intermolecular distances for both cationic and anionic pairs are shorter than those of the neutral pairs. Apart from the **off** isomer of $(C_6F_6)_2^-$, which is calculated to be unusually strongly bound, there is general agreement between the experimental and calculated energies. Because the charged pairs with open-shell electronic states are less relevant to the neutral molecules for which the potential is to be developed, no adjustment to the scaling factor of 0.7 was made.

Table 2 Optimised structures and energies for $(C_6H_6)_2^+$, $(C_6F_6)_2^+$ and $(C_6F_6)_2^-$ using the Perdew–Wang functional PWC7, spin unrestricted

Structure	Isomer	0.7 × Pair binding energy kcal mol^{-1}
$(C_6H_6)_2^+$	**ef**, C_s	−13.0
	vf, C_{2v}	−12.0
	off, C_{2h}	−16.7
	ff, D_{6h}	−18.6
$(C_6F_6)_2^+$	**off**, C_{2h}	−8.9
	ff, D_{6h}	−10.6
$(C_6F_6)_2^-$	**ef**, C_s	−13.2
	vf, C_{2v}	−11.9
	off, C_{2h}	−19.2
	ff, D_{6h}	−13.6

[a] The **ef** and **off** isomers $(C_6F_6)_2^+$ are calculated to have complex electronic structures with close-lying electronic states.

These calibrated DF methods were then applied to pairs of hexafluorobenzene, $(C_6F_6)_2$. It was evident from the gradients during the DF optimisations that the energy surface is rather flat and that there is not a strong directionality in the intermolecular forces. As an illustration of this, the oblique **ef** isomer is not an energy minimum and on minimisation the rings become parallel, forming the **off** isomer. Similarly, the **vf** isomer is very slippery. Therefore, in order to provide reference points in the subsequent development of the potential, the **ef** and **vf** isomers were constrained to C_{2v} symmetry. The optimised geometries are presented in Fig. 2. Even though the eclipsed face-to-face isomer **ff** is not observed and the **ef** isomer is not a minimum, the four geometries in Fig. 2 are valuable for the calibration of the relatively flat intermolecular potential. The calculations also revealed a second **off** isomer (not shown), in which the rings are parallel but the offset is unusually large such that only F atoms overlap the other ring.

The reversion of the **ef** isomer to **off** geometry, and the relatively close separation of the rings in the **ff** isomer, indicate that there is not a strongly electrostatic contribution to the intermolecular energy.

Parametrisation of the empirical potential

For each of these four isomers of $(C_6F_6)_2$ we calculated the intermolecular energy potential [eqns (1)–(5)] for variable separation of the two molecules. These potentials were then used to optimise the parameters r^a, e^a and $q_F = -q_H$, as well as ε.

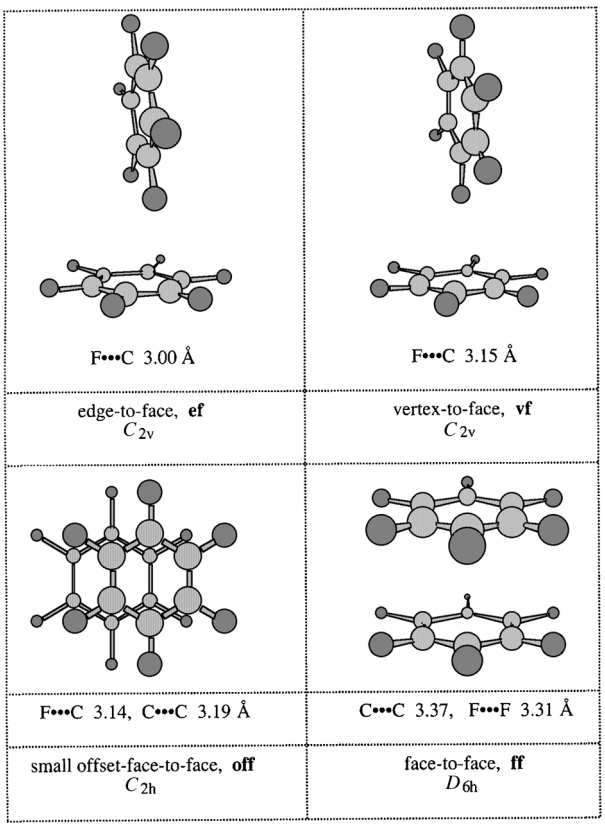


Fig. 2 Optimised structures for $(C_6F_6)_2$, with symmetries imposed, and key intermolecular distances. The **ef** isomer is not an energy minimum.

In estimating atom partial charges q for C_6F_6 for use in eqn. (5) we have been guided by five sources of information: the (*a*) Mulliken and (*b*) Hirshfeld apportioned charges from the DF calculation; (*c*) the ESP charges, which are fitted to the electrostatic potential from the DF calculation; (*d*) the charge equilibration method (QEq) of Rappe and Goddard;[54] and (*e*) the different consequences of electrostatic energy in the four different isomers of $(C_6F_6)_2$. From a DF calculation of C_6F_6 the Mulliken charges are ± 0.24, the Hirshfeld charges are ± 0.05, and the ESP charges are ± 0.09 (polarity $C^{\delta+}F^{\delta-}$ in all cases). General experience with the calculation of atom partial charges by our DF methods indicates that the Mulliken method over-polarises bonds and Hirshfeld under-polarises bonds, with the ESP charges intermediate and often most accurate. The QEq method uses the conventional electronegativities explicitly, leading to increased polarisation of the C–F bond as $C^{+0.45}$–$F^{-0.45}$. These are excessive and inconsistent with all other results, particularly the conclusion from the DF calculations of the energy surface of $(C_6F_6)_2$, and were thus rejected. Therefore, we started with atom charges in the vicinity of 0.10 to 0.15 and tested these values in the fitting of the intermolecular potentials.

There is good separability of variables in the parametrisation of the intermolecular potential: in the **off** and **ff** isomers the electrostatic contribution is repulsive, but it is attractive in the **ef** and **vf** isomers. This permits reliable balancing of the van der Waals and electrostatic contributions, which indicated that the electrostatic contributions should be relatively small and confirmed our view that the QEq-derived atom charges are excessive. The permittivity was set as $\varepsilon = 2d_{ij}$, consistent with Warshel and Papazyan's comprehensive review of the probable magnitudes of the dielectric in and around proteins and other macromolecules.[55] The parameters resulting from this analysis are presented in Tables 3 and 4, together with extensions to related molecules described below, and parameters from evaluations of intermolecular potentials for other atom types,[56] used in energy calculations below. Fig. 3 displays the intermolecular potentials for the four isomers, as calculated by DF methods and by the parametrised potential. The agreement is better than 0.5 kcal mol^{-1} over the distance ranges that occur in crystals, and is adequate for our purposes. The discrepancies are more likely to be due to the models than to the parameters. These parameters have not been tested for fluoroalkyl systems.

Table 3 Parameters for the Lennard-Jones intermolecular potential, eqn. (2)

Atom type	r^a/Å	e^a/kcal mol^{-1}	Ref.
C in C_6F_6 and C_6F_5	1.8	0.063	This work
F in C_6F_6 and C_6F_5	1.6	0.10	This work
C in C_6H_6 and hydroaromatics	1.94	0.093	56
H in all systems	1.62	0.02	56
B in $[B(C_6F_5)_4]^-$	1.98	0.06	56
Ge in $Ge(C_6F_5)_4$	2.03	0.20	56
Al in $(THF)Al(C_6F_5)_3$	1.95	0.06	This work
C in THF	2.18	0.039	56
O in THF	1.805	0.08	56
P in $H_3PB(C_6F_5)_3$	2.3	0.26	56

Crystal structure of hexafluorobenzene

The crystal structure of hexafluorobenzene at 120 K has been reported [Cambridge Structural Database (CSD) refcode HFBENZ].[14] There are 1.5 molecules per asymmetric unit in space group $P2_1/c$ and the structure is not isomorphous with benzene or with hexachlorobenzene. Fig. 4 shows the crystal structure of hexafluorobenzene, in comparison with the structure of benzene, and shows that the general herringbone motif is present in both. However, the strands of the herringbone are tilted differently in C_6F_6 than in C_6H_6, relative to the strand axis (vertical in Fig. 4): in C_6F_6 the rings are inclined at *ca.* 22 and 30° to the strand axis, while in C_6H_6 the inclination is *ca.* 45°. Also, there is an alternation of the ring tilt directions in C_6F_6 that does not occur in C_6H_6. Further, there is larger separation of the strands in C_6F_6, but even so there is a larger density of closer F···F proximities than of H···H proximities, as shown in the space-filling representations (Fig. 4). Dunitz has discussed differences between these two structures.[57]

The variety of local pairwise interactions between C_6F_6 rings in HFBENZ are shown in Fig. 5, together with their van

Table 4 Atom partial charges used in eqn. (5)

Atom type	q	Ref.
C in C_6F_6	+0.15	This work
F in C_6F_6 and C_6F_5	−0.15	This work
F in octafluoronaphthalene	−0.15	This work
C in octafluoronaphthalene	+0.15 except C2, 3, 6, 7 +0.1	This work
C in C_6H_6	−0.10	56
C_{ipso} in C_6H_5	−0.02	56
Other C in C_6H_5	−0.08	56
H in C_6H_6, C_6H_5, D in C_6D_6	+0.10	56
B in $[B(C_6F_5)_4]^-$	+0.16	56
C_{ipso} in $[B(C_6F_5)_4]^-$	−0.04	This work
Other C in $[B(C_6F_5)_4]^-$	+0.10	This work
Ge in $Ge(C_6F_5)_4$	+0.20	56
C_{ipso} in $Ge(C_6F_5)_4$	0.0	This work
Other C in $Ge(C_6F_5)_4$	+0.14	This work
Al in $(THF)Al(C_6F_5)_3$	0.20	56
C in THF	0.02 (bonded to O) −0.2 (other)	56
O in THF	−0.25	56
H in THF	0.1	56
C_{ipso} in C_6F_5 in $(THF)Al(C_6F_5)_3$	−0.08	This work
Other C in C_6F_5 in $(THF)Al(C_6F_5)_3$	0.14	This work
C_{ipso} in $H_3PB(C_6F_5)_3$	−0.06	This work
Other C in $H_3PB(C_6F_5)_3$	0.15	This work
P in $H_3PB(C_6F_5)_3$	0.07	56
B in $H_3PB(C_6F_5)_3$	0.08	56
H in $H_3PB(C_6F_5)_3$	0.01	56

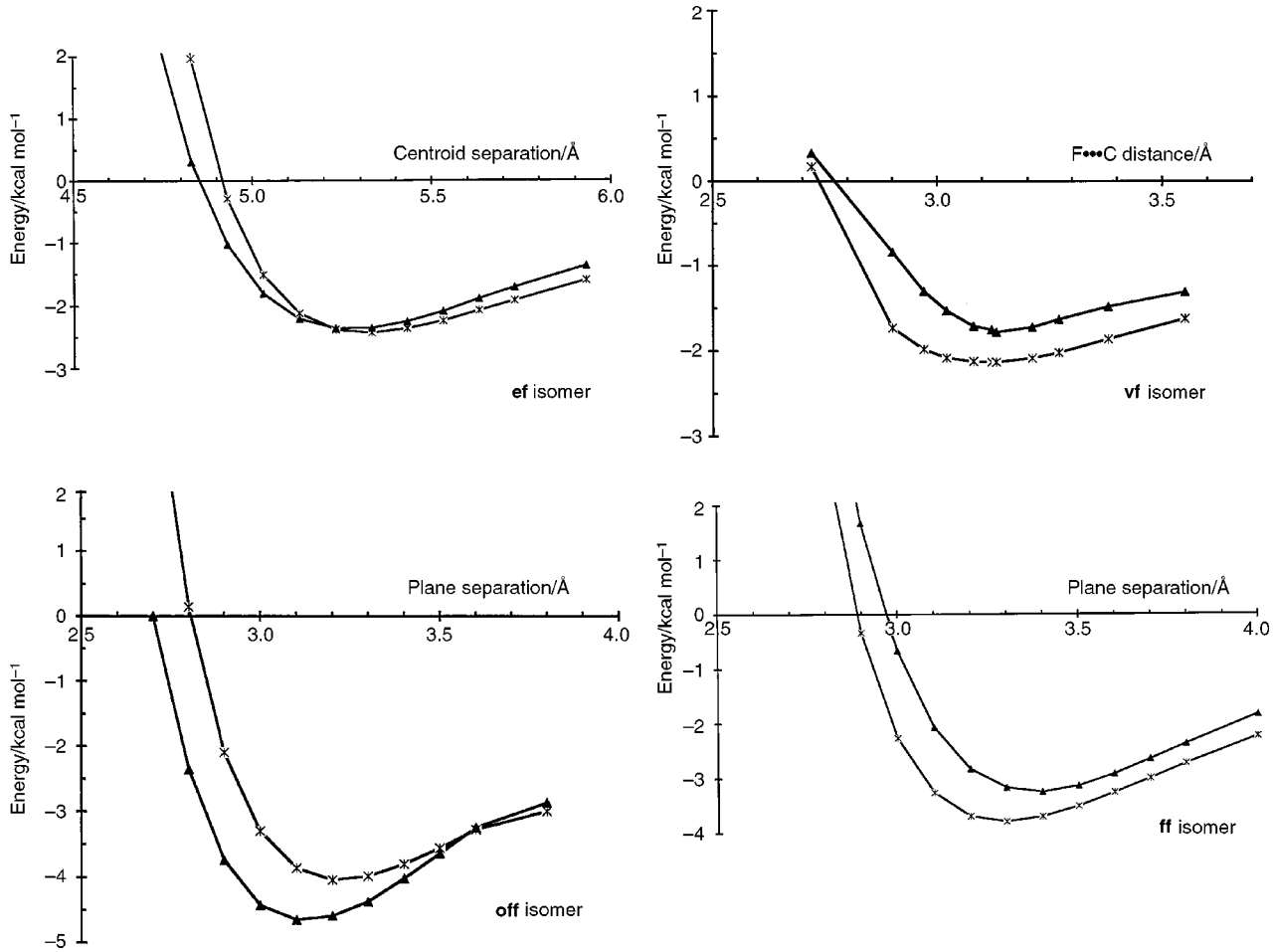


Fig. 3 Intermolecular potentials for the four supramolecular isomers of $(C_6F_6)_2$ pictured in Fig. 2, as a function of the appropriate intermolecular separation: ▲ are the density functional energies, scaled as described in the text; ✳ are from eqn. (1) with the parameters of Tables 3 and 4.

der Waals and electrostatic energies computed with the empirical potential. The total energies range from 1.3 to 2.4 kcal mol^{-1} attraction, and in each case the electrostatic component is small (*ca.* 10% of the total) and attractive.

The conclusion from examination of the geometries in this one structure is that the directional local interactions are not as influential as they are in benzene. The energy calculations support this, because the dominant component is the non-directional van der Waals attraction.

The cocrystallite of C_6F_6 and C_6D_6

The crystal structure[58] of the low temperature phase of $C_6D_6 \cdot C_6F_6$ [BICVUE01] is shown in Fig. 6, from which it is evident that there are no **ef** interactions. The crystal is comprised of extremely offset homo-ring stacks, but the most significant attractive interaction occurs in the slightly offset stacks of alternating rings, for which details are shown in Fig. 7. The contrast between the parallel packing of $C_6D_6 \cdot C_6F_6$ and the herringbone packing of C_6H_6 and of C_6F_6 is attributable to the oppositely signed quadrupole moments of C_6H_6 and C_6F_6,[9,57] and has been deployed in crystal design.[11] While this qualitative difference between the hetero-ring and homo-ring structures has an electrostatic origin, the magnitude of the electrostatic (ES) energies relative to the van der Waals (vdW) energies has been questioned.[57] Our potentials yield energies of −4.7 (vdW −4.3, ES −0.4) kcal mol^{-1} for each of the local **off** interactions between C_6F_6 and C_6D_6 shown in Fig. 7. An SCF-MP2 calculation of $C_6H_6 \cdot C_6F_6$ in face-to-face geometry yielded a similar energy of −4.3 kcal mol^{-1}.[59] The best **off** interactions involving homo-ring pairs, being severely offset, have lesser calculated energies: $(C_6F_6)_2$ −2.0 (vdW −1.75, ES −0.22) kcal mol^{-1}; $(C_6D_6)_2$ −1.3 (vdW −1.25, ES −0.04) kcal mol^{-1}.

It is significant that the separation of the planes of the hetero-rings in the **off** motif is considerably less—it is *ca.* 3.35 Å in BICVUE01—than the separation of planes in homo-**off** motifs involving C_6H_5 rings (*ca.* 3.5 Å).

The structure just described is the lowest temperature (30 K) phase of $C_6D_6 \cdot C_6F_6$. Three higher temperature phases have been identified, with some structural information available, and there is speculation about the increasing rotational motion of the molecules at the higher temperatures.[58] At room temperature the molecules rotate about the axis of each stack of alternating molecules.[60] These thermal motions are consistent with the relatively isotropic character of the potentials for C_6F_6 and C_6D_6 and the dominance of the **off** $C_6D_6 \cdots C_6F_6$ energy.

Octafluoronaphthalene crystallises with the standard herringbone pattern, in space group $P2_1/c$.[61] The local **off** and **ef** interactions are shown in Fig. 8, together with their calculated energies. In the **ef** interaction two F atoms are directed towards a C1–C2 bond of the other molecule, and the angle between the ring planes is *ca.* 80°.

Multiple perfluorophenyl embraces

There is now in the CSD a collection of crystal structures of compounds containing the moieties $E(C_6F_5)_3$ and $E(C_6F_5)_4$ (E from periodic groups 13, 14, 15). We have examined all of these and investigated the occurrence of the various multiple phenyl embraces, which occur widely for EPh_3 and

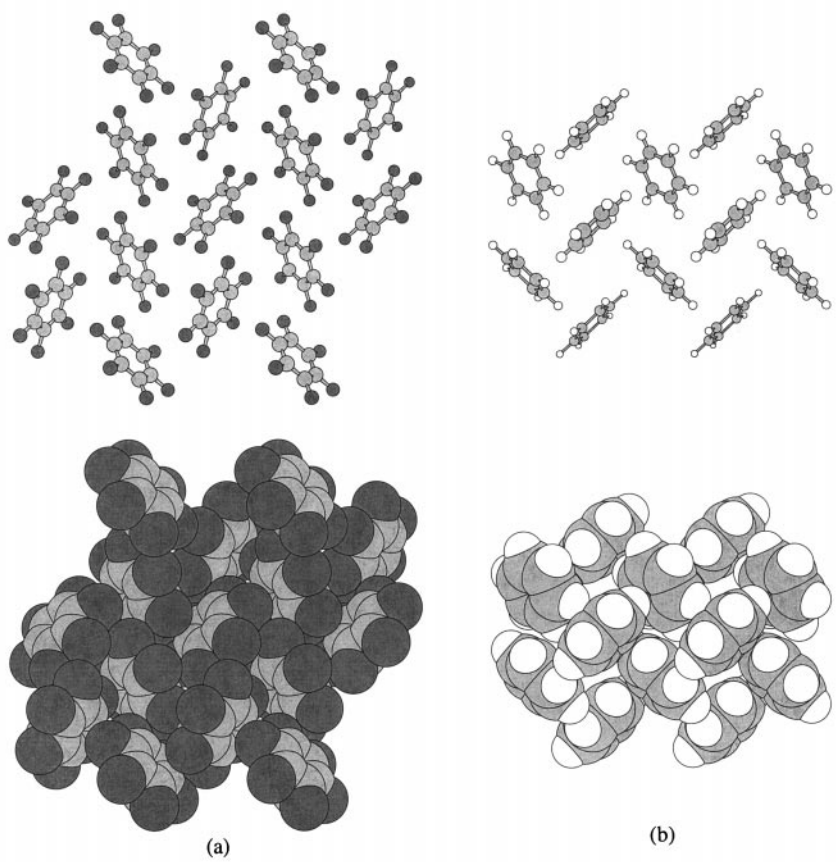


Fig. 4 The crystal structures of (*a*) hexafluorobenzene [HFBENZ] and (*b*) benzene [BENZEN], oriented to emphasise the similarities and the differences.

EPh_4.[21–29] Comprehensive analyses of the geometrical properties of these fluorophenyl embraces will be published separately, but here we investigate the energies of representative examples and the balance of van der Waals and electrostatic components. Multiple phenyl embrace motifs are comprised of concerted **ef**, **off** and **vf** local interactions. The abbreviation P^FE is used in the symbols for perfluorinated phenyl embraces.

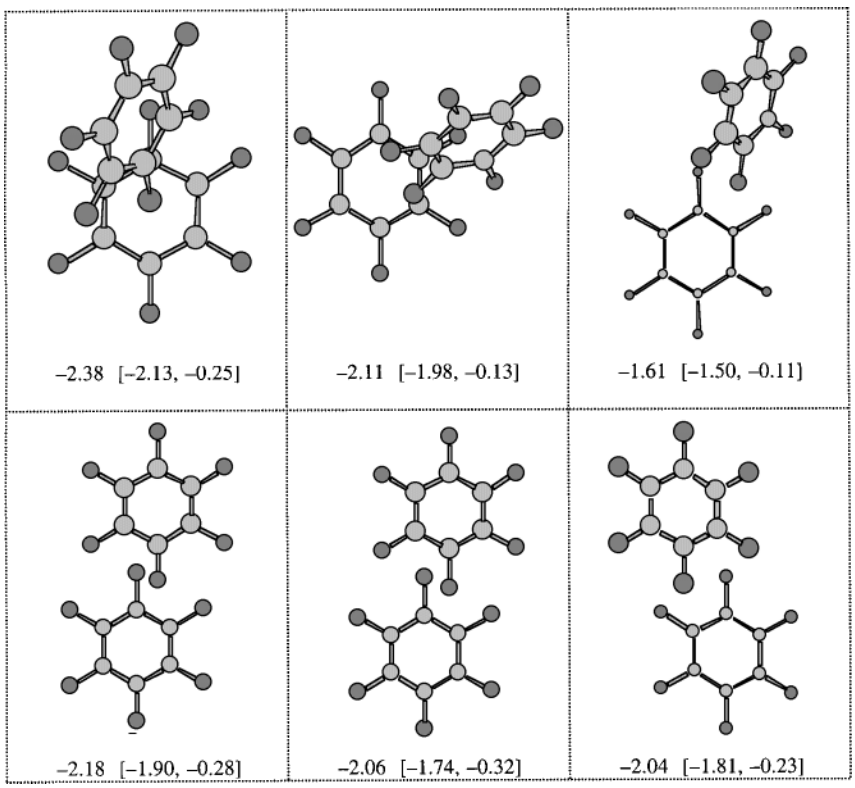


Fig. 5 The more attractive local interactions between C_6F_6 rings in crystalline C_6F_6[HFBENZ], with the calculated energies as total [vdW, electrostatic] in kcal mol^{-1}. Each representation is projected onto the plane of one ring.

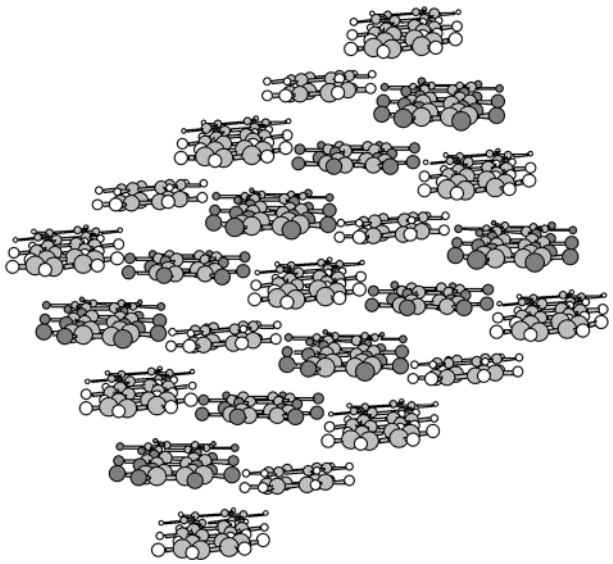


Fig. 6 The lamellar crystal structure of the low temperature phase of $C_6D_6 \cdot C_6F_6$ [BICVUE01]: F is dark, D is white.

Sixfold perfluorophenyl embraces, 6P^{F}E

The compound (THF)Al(C_6F_5)$_3$ in crystal structure ZALPUX[62] contains a sixfold perfluorophenyl embrace, abbreviated as 6P^{F}E, with six concerted **ef** interactions

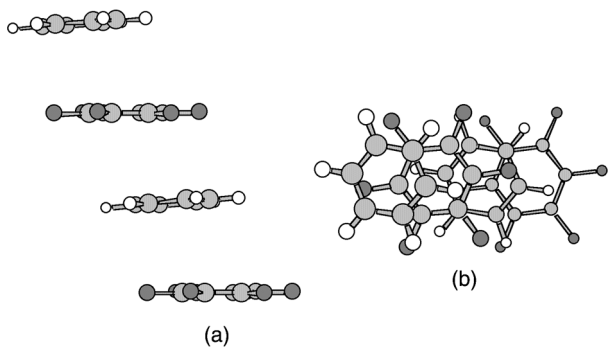


Fig. 7 Side (*a*) and top (*b*) views of the stack of alternating C_6F_6 and C_6D_6 rings in crystalline $C_6D_6 \cdot C_6F_6$: atom shading as for Fig. 6.

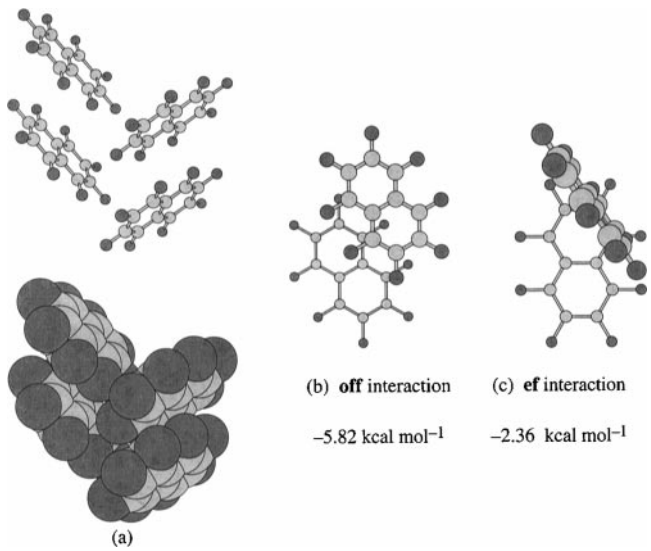


Fig. 8 The herringbone packing in crystalline octafluoronaphthalene (*a*), and the local **off** (*b*) and **ef** (*c*) interactions with their calculated energies.

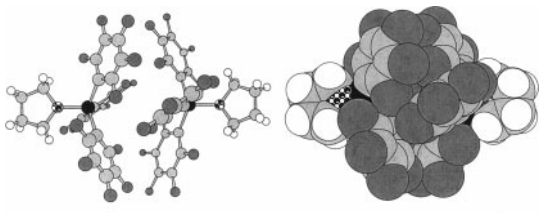


Fig. 9 The centrosymmetric 6P^{F}E in (THF)Al(C_6F_5)$_3$ [ZALPUX]. The Al···Al distance is 6.17 Å.

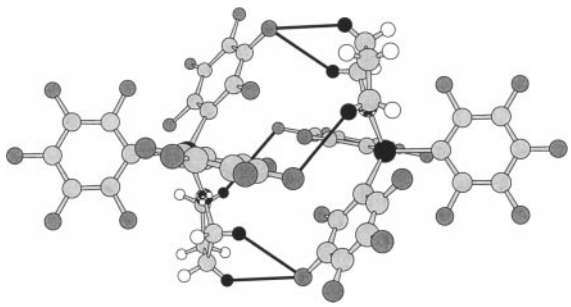


Fig. 10 The centrosymmetric pseudo-6P^{F}E in (THF)Al(C_6F_5)$_3$ [ZALPUX]. The Al···Al distance is 7.06 Å. There are two Pf···Pf edge-to-face interactions and three H atoms (emphasised in black) on each THF molecule form C–H···F interactions (2.8–3.2 Å), which are drawn as flat connectors.

between Pf rings. This motif, shown in Fig. 9, is centrosymmetric, as is usual for the analogous 6PE, and the three Pf rings on each molecule have approximate threefold rotor conformations. The calculated energy is −11.7 (vdW −11.1, ES −0.6) kcal mol^{-1}. In crystalline ZALPUX there occurs also a centrosymmetric pseudo-6P^{F}E (see Fig. 10) in which the THF ring takes the place of one Pf ring on each molecule. In the pseudo-6P^{F}E there are only two **ef** interactions between Pf rings, but the coordinated THF molecules are oriented to form weak C–H···F interactions, which are marked on Fig. 10. This is the analog of the pseudo-6PE, which is known but not common. There are two crystallographically independent pseudo-6P^{F}E motifs in ZALPUX, for which the calculated energies are −9.1 (vdW −8.3, ES −0.8) kcal mol^{-1} (Al···Al 7.06 Å) and −9.8 (vdW −9.7, ES −0.1) kcal mol^{-1} (Al···Al 7.23 Å).

Hexagonal array of sixfold perfluorophenyl embraces, HA6P^{F}E

Molecules of the type Ph_3XZ, with threefold symmetry, and salts of the type $(MePh_3P^+)_2A^{2-}$, crystallise in trigonal or rhombohedral lattices in which there are hexagonal arrays of sixfold phenyl embraces: the Z groups of one array usually occupy the centres of the hexagons of molecules and in $(MePh_3P^+)_2A^{2-}$ there are cavities formed by 12 cations constraining the anions to sites of D_3 symmetry and dinegative charge.[24,25,63] We have identified one instance of a similar lattice formed by $H_3PB(C_6F_5)_3$ [JICWUN].[64] The two crystallographically independent 6P^{F}E motifs in this crystal have geometrically good **ef** interactions and favourable energies of −11.5 (vdW −10.7, ES −0.8) kcal mol^{-1} (at B···B = 6.19 Å), and −11.0 (vdW −10.2, ES −0.8) kcal mol^{-1} (at B···B = 6.40 Å.). Two representations of this lattice are provided in Fig. 11.

Fourfold perfluorophenyl embraces, 4P^{F}E

There are two main classes of fourfold phenyl embraces involving XPh_2 moieties on adjacent molecules. In the parallel supra-isomer, P4PE, the X(C_{ipso})$_2$ planes on the two molecules are exactly or approximately parallel, while in the orthogonal isomer, O4PE, the X(C_{ipso})$_2$ planes are approximately orthogonal.[26]

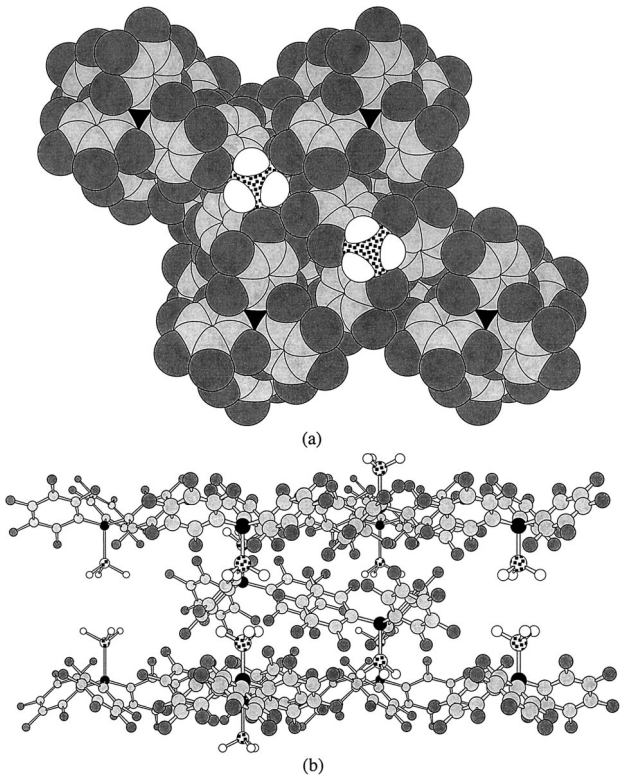
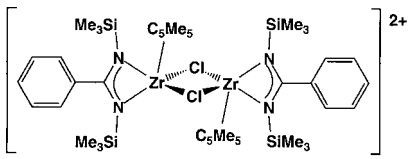


Fig. 11 Representations of the HA6P^{F}E lattice formed by $H_3PB(C_6F_5)_3$ in JICWUN, space group $P\bar{3}$: B black, P speckled, H white. (*a*) Space-filling view along the trigonal axis. (*b*) Side view of the same molecules drawn in (*a*), showing parts of three of the layers.

The relationship between the two molecules involved in an O4PE is frequently translation, and so crystals usually contain infinite linear chains of these O4PE.[23,27] This occurs also in $E(C_6F_5)_4$, E = Si [PFPSIL],[65] Ge [PFPHGE10][66] and Sn [TFUPSN].[66] Fig. 12 shows that the *orthogonal* fourfold perfluorophenyl embrace—O4P^{F}E—is very well formed in PFPHGE10. The four C_6F_5 rings involved make a very good concerted cycle of edge-to-face interactions with a Ge···Ge distance of 8.12 Å. The energy of this O4P^{F}E in $Ge(C_6F_5)_4$ is calculated to be −9.55 (vdW −8.93, ES −0.62) kcal mol^{-1}. The tetragonal lattice (space group $I4_1/a$) contains parallel infinite chains of these embraces and is isostructural with the lattice of the EPh_4 compounds.

The perfluorinated *parallel* fourfold phenyl embrace—P4P^{F}E—occurs also, but with a difference from the unfluorinated versions. Fig. 13 shows two views of the P4P^{F}E between $[B(C_6F_5)_4]^-$ ions in crystals POPXOH10 of the compound $[(\mu\text{-}Cl)_2\{Cp^*Zr[Me_3SiNC(Ph)NSiMe_3]\}_2]^{2+}[B(C_6F_5)_4]^-\}_2 \cdot CH_2Cl_2$.[67] The normal, hydro-P4PE is comprised of two **ef** interactions and one **off** interaction.[26] In the P4P^{F}E there are well-developed **ef** interactions, as shown in Fig. 13(a), but the face-to-face interaction between rings in the centre of the motif is abnormally offset, to the extent that there is minimal overlap of the rings [see Fig. 13(b)]. Nevertheless, the calculated attractive energy is still appreciable, at −5.45 kcal mol^{-1}, and the motif is centrosymmetric.



cation in POPXOH10

Another example of the P4P^{F}E is found in crystals of the compound *trans*-$[(C_6F_5)_3P]_2PtCl_2$ [VUBRIT].[68] Here the embrace is between two PPf_3 ligands, which is unusual because coordinated PPh_3 ligands normally form 6PEs and rarely form the P4PE, as a consequence of steric interference

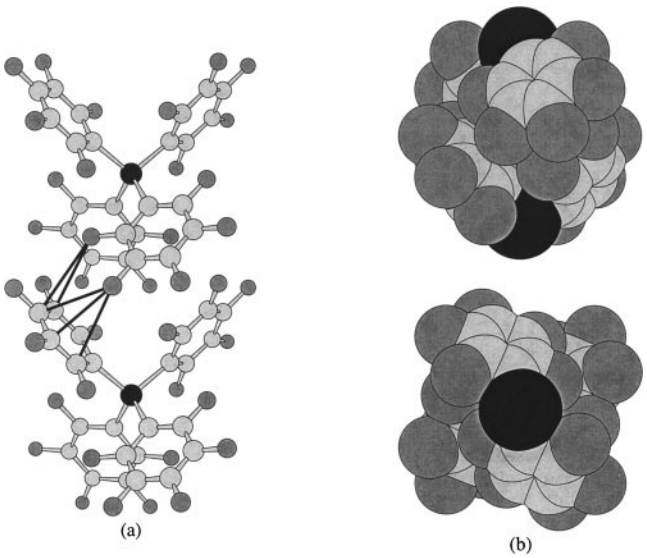


Fig. 12 The O4P^{F}E in crystalline $Ge(C_6F_5)_4$, [PFPHGE10]: Ge is black. (*a*) The five intermolecular connectors marked are the F···C distances of 3.15–3.35 Å in one of the four symmetrically equivalent edge-to-face interactions. (*b*) Side and top views of the four C_6F_5 rings engaged in the O4P^{F}E, emphasising the concerted cycle of four edge-to-face interactions.

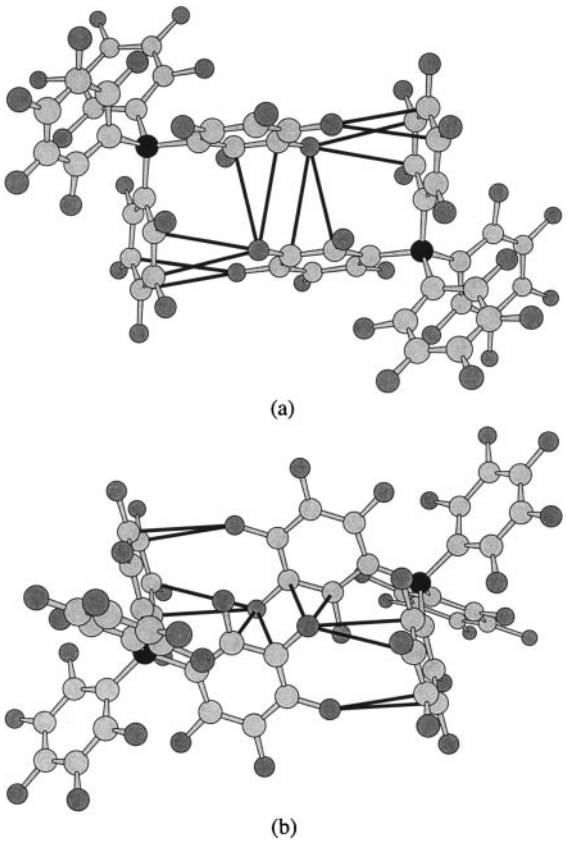


Fig. 13 The perfluorinated parallel fourfold phenyl embrace, P4P^{F}E, between two $[B(C_6F_5)_4]^-$ ions in POPXOH10: B is black and the B···B separation is 8.84 Å. The most significant F···C interactions are marked. (*a*) Side view. (*b*) Projection onto the planes of the central C_6F_5 rings to show the pronounced offset of the central off interaction.

from other ligands in the complex.[69] The pronounced offset of the central rings, noted for POPXOH10, occurs also in VUBRIT.

Discussion and conclusions

1. Intermolecular energies within $(C_6H_6)_2$ and $(C_6F_6)_2$ can be calculated by our density functional procedures, using the Perdew–Wang PWC functional, but not with gradient corrected BP or BLYP functionals. The factors that scale these DF energies to experimental data have been evaluated.

2. The intermolecular potential energy surface for a pair of C_6F_6 molecules, investigated by DF calculations, is found to be relatively flat and the supramolecular isomers have been characterised. These results are consistent with relatively small electrostatic contributions to the intermolecular energies.

3. Parameters for a Lennard-Jones plus electrostatic intermolecular potential for C_6F_6 have been derived by fitting to the calculated DF energies. Unfortunately, there are no data (such as crystal sublimation enthalpies) against which the accuracy of these potentials can assessed directly. The potentials are consistent with indirect data and with DF calculations to better than 0.5 kcal mol^{-1}.

4. It is evident that the C–F bond cannot be polarised to the extent implied by the conventional electronegativies: the atom charges derived in this analysis are $C^{+0.15}$–$F^{-0.15}$. The high density of contiguous F atoms in the crystal structures analysed is also evidence that F···F electrostatic repulsion is not a large or influential contribution to total energies.

5. These intermolecular potentials should be transferable as such to other fluoro- and perfluoroaromatic systems and to molecules with C_6F_5 substituents: atom charges require small adjustments according to the identity of the remainder of the molecule or ion.

6. Intermolecular attractions between fluoroaromatics are slightly more attractive than those of the hydro analogs. This is due mainly to the increased van der Waals component. It has been pointed out[14] that many of the thermodynamic properties of benzene and hexafluorobenzene are almost identical: the triple points differ by 0.4°, the boiling points differ by 0.2°, and the enthalpies of fusion are 12.66 and 11.58 kJ mol^{-1}, respectively. This similarity is qualitatively consistent with our calculated energies.

7. From the calculations reported here, and others,[56] we note that in both fluoroaromatics and hydroaromatics, and in molecules with Pf substituents and in molecules with Ph substituents, the proportion of electrostatic energy in the total intermolecular energy between these groups is less than 15%. This conclusion extends also to ions with Pf or Ph substituents, such as Pf_4B^-, Ph_4B^-, Ph_4P^+: the redistribution of charge to the Pf and Ph groups in such ions is relatively small and the changed electrostatic contribution to the total energy is still small. Small electrostatic energies are the result of the cancellation of opposing contributions. Electrostatic forces in perfluoroaromatics provide no more directionality than they do in hydroaromatics.

8. Slightly offset face-to-face $C_6H_6\cdots C_6F_6$ interactions are approximately twice as attractive as analogous homoaromatic interactions and by extension similar enhanced attraction is expected between Pf and Ph.

9. Molecules and ions containing XPf_4 and XPf_3 form (in crystals) the multiple phenyl embraces that are well known for analogous XPh_4 and XPh_3 systems. The energy of the sixfold perfluorophenyl embrace between $(THF)AlPf_3$ molecules is calculated to be -11.7 kcal mol^{-1} and the energies of the other types of embraces involving Pf are calculated to be similar to those with Ph.

Finally, our investigations show that suprafluorous chemistry is not superfluous, but is similar to the corresponding suprahydrous chemistry, at least within the scope of the compounds we have considered. We are now extending this analysis to the crystal packing of a wider range of fluorous compounds.

Acknowledgements

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