

CHAPTER 9

Host-guest Chemistry: Hirshfeld surface analysis of phosphonium salts

Treatment of (phosphoniumⁿ⁺)(Cl⁻ or Br⁻)_n and (imidazoliumⁿ⁺)(X⁻)_n, n = 1 or 2 with p-sulfonatocalix[4]arene and aquated gadolinium ions results in metathetical exchange, affording crystalline salts (phosphoniumⁿ⁺)(X⁻)_n (X⁻ = [SCN]⁻, [N(CN)₂]⁻, [C(CN)₃]⁻, [PF₆]⁻, [CF₃SO₃]⁻ or [N(CF₃SO₂)₂]⁻), with the imidazolium cation residing in the cavity of the calixarene in solution, as established from ¹H NMR studies. The structurally authenticated phosphonium salts have been examined using Hirshfeld surface analysis, revealing the domination of C-H...X non-classical hydrogen-bonding between the cations and anions.

9.1 Introduction

Supramolecular building block (tectons) bearing phenyl or aryl groups can interact with each other, and with other molecules of the same ilk through multiple phenyl (or aryl) embraces. This relates to the electronic and geometrical complementarity of the molecules ^[218-220]. The concept of embracing molecules organised on their surfaces were recognised and developed since 1995 by Dance and co-workers ^[221]. The investigations were deemed important in the development of introducing new embrace paradigm in the well-known intermolecular motif, as a tool for supramolecular chemistry by analysing the packing of molecules in crystals ^[222].

Embrace motifs can be bimolecular or multimolecular and they are described with names, in which the number refers to the number of the embracing phenyl (or aryl) groups, and with symbols giving the types and multiplicities of local interactions ^[220]. Individual phenyl groups are engaged in edge-to-face (**ef**) and offset-face-to-face (**off**) attractive phenyl...phenyl interactions, Figure 9.1.

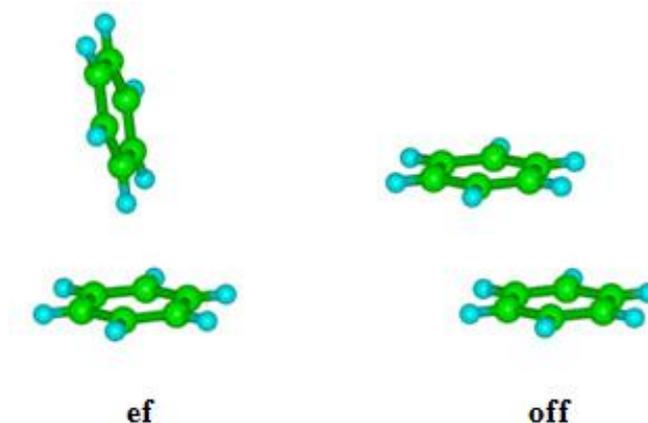


Figure 9.1. Phenyl...phenyl interactions of the multiple phenyl embraces.

The major categories of multiple phenyl embrace are the sixfold phenyl embrace (**6PE**) and two types of fourfold phenyl embrace (**4PE**) which has orthogonal and parallel variants, which are also known as **O4PE** and **P4PE** respectively [217, 218]. The simplest embrace is the **P4PE** where two phenyl groups on each molecule are engaged in one **off** interaction together with two **ef** interactions and the $C_{\text{ipso}}\text{-P-C}_{\text{ipso}}$ planes for the two molecules are exactly or approximately parallel [220-223]. In the **O4PE**, the two $C_{\text{ipso}}\text{-P-C}_{\text{ipso}}$ planes for the four phenyl rings are approximately orthogonal and are engaged in four **ef** interactions. **6PE** contains six **ef** attractions involving three phenyl rings from each molecule with net attractive energy for the phenyl rings in the range 8–11 kcal mol⁻¹ [202, 220].

This type of embraces occurs frequently in crystals of compounds having terminal Ph_3P ligands, and in crystals containing the Ph_4P^+ cation in the solid state. It is also noteworthy that the cation Ph_4P^+ can participate in more than one multiple phenyl embrace, with the crystal structures usually containing chains and networks of such arrangements of interacting phenyl rings [218]. Dance and co-workers reported the general occurrence of continuous chains of these embraces, Figure 9.2, as the zig-zag infinite chain of sixfold phenyl embraces (**ZZI6PE**) and the linear infinite chain of translational fourfold phenyl embraces (**LIT4PE**, translational repetition of Ph_4P^+ along a pseudo-twofold axis generates **O4PE** motifs) [218]. In the **LIT4PE** only two of the “edges” of the Ph_4P^+ tetrahedron are involved in **4PE**, while in the **ZZI6PE** only two “faces” of the tetrahedron are used [218]. Therefore there are additional opportunities for multiple phenyl embraces which can take place.

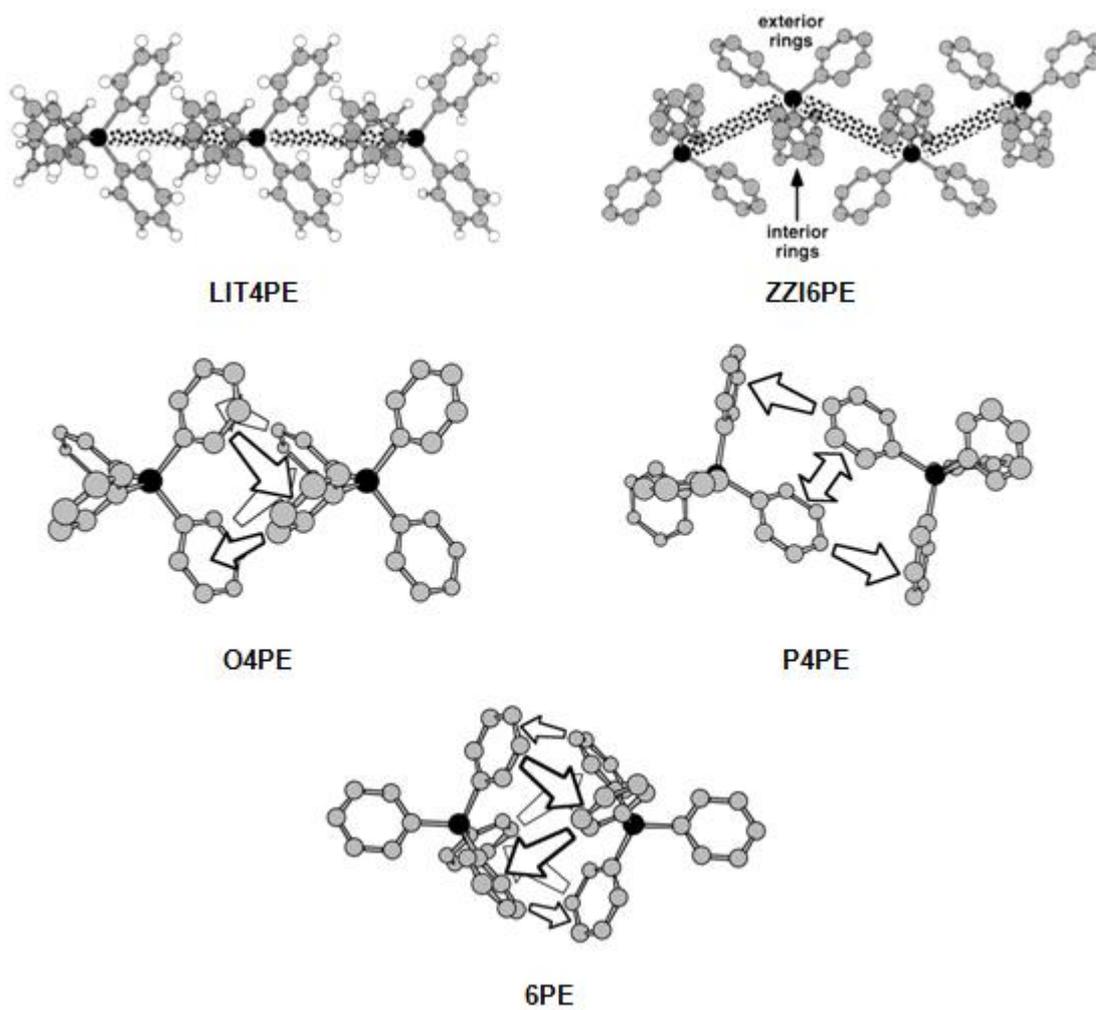
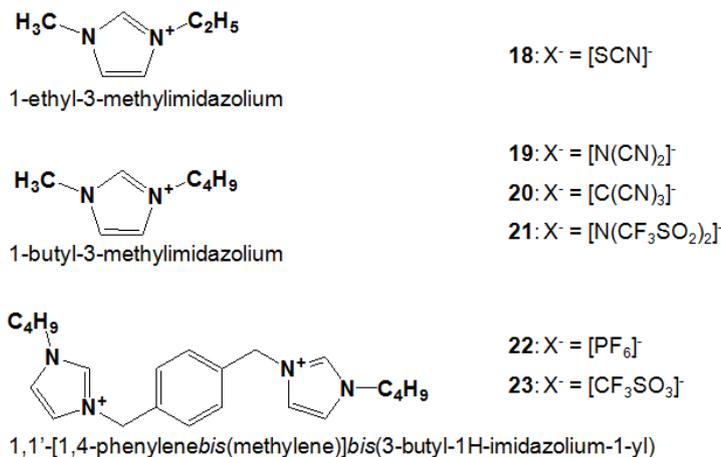


Figure 9.2. General occurrence of phenyl embraces ^[219].

9.2 Solid state structures of phosphonium salts

Molecules bearing two or more phenyl groups, as in phosphonium cations, can form multiple phenyl embraces, and these can dominate their self assembly and overall cohesion in the solid state. Eleven organic compounds containing phosphonium cations, possessing three or four phenyl rings attached to phosphorus centres, including a *bis*-phosphonium cation, and a variety of anions were successfully isolated and structurally elucidated, Table 9.1. The organisation of the large phosphonium cations in the solid state are coupled with anions based on the common species featuring in ionic liquids, specifically $[\text{SCN}]^-$, $[\text{N}(\text{CN})_2]^-$, $[\text{C}(\text{CN})_3]^-$, $[\text{PF}_6]^-$, $[\text{CF}_3\text{SO}_3]^-$ and $[\text{N}(\text{CF}_3\text{SO}_2)_2]^-$. Interestingly these compounds were essentially formed by metathetical exchange involving phosphonium halides (Cl^- or Br^-), with ionic liquid anions based on imidazolium salts of the aforementioned cations, in the presence of the sodium salt of *p*-sulfonatocalix[4]arene, crystallising the least soluble salt, and presumably this is facilitated by the binding of the imidazolium cation in the cavity of the calixarene, which have been recently established as a favoured process over binding of phenyl rings of phosphonium cations. The interaction between the cations and anions in all the compounds is dominated by $\text{CH}\cdots\text{X}$ non-classical hydrogen-bonding.

While the phosphonium cations do not favour the formation of low melting point solids, the nature of their interaction with the aforementioned anions is of interest in the overall cohesion of ‘ionic liquids’ in the solid state, as well as in their liquidous state, noting that all the anions in the present study readily form ionic liquids, depending on the nature of the cations. The high melting point solids which afforded single crystals were suitable for acquisition of X-ray diffraction data of sufficient quality to be able to study the interaction of the components using Hirshfeld surface analysis.



Scheme 9.1. Imidazolium salts featuring in ionic liquids.

The structures containing a series of different phosphonium cations and anions, Scheme 9.1, are reported in a convenient graphical presentation which illustrates different packing arrangements as well as polymorphisms for selected compounds, Figure 9.3. The Hirshfeld surfaces analyses were undertaken using Crystal Explorer, on each structure to further understand the nature of the intermolecular interactions between the phosphonium and the anion molecules, and themselves ^[194]. In doing so, the intermolecular interactions of the compounds are compared using the fingerprint plots generated by the Hirshfeld surfaces noting that the fingerprint plots have been found to be useful in comparative studies between different crystal structures of the same molecule, as well as different polymorphs ^[194]. Fingerprint plots are sensitive to the immediate environment of the molecule and indeed are unique for a given molecule in a particular polymorphic form ^[194]. The Hirshfeld surface and its corresponding fingerprint plots also provide information about the more distant contacts and areas where interactions are weakest. The fingerprint plot is constructed by a colouring scheme on a two-dimensional grid according to the fraction of the total surface area, with the smallest non-zero contribution coloured blue to red for a contribution of 0.1% or greater to the total surface area ^[191,192].

Table 9.1 Crystallographic Details for Complexes XXIIa-XXIXb

Compound	XXIIa	XXIIb	XXIII	XXIV	XXV
Formula	$C_{19}H_{18}F_6P_2$	$C_{19}H_{18}F_6P_2$	$C_{25}H_{20}N_3P$	$C_{25}H_{22}NPS$	$C_{25}H_{22}F_6P_2$
FW (g mol ⁻¹)	422.27	422.27	405.42	411.48	498.37
Size (mm ³)	0.25 x 0.14 x 0.03	0.31 x 0.29 x 0.13	0.28 x 0.24 x 0.21	0.34 x 0.21 x 0.13	0.48 x 0.14 x 0.13
Crystal system	monoclinic	triclinic	tetragonal	monoclinic	hexagonal
Space group	$P2_1/c$ (No. 14)	$P-1$ (No. 2)	$I-4$ (No. 82)	$P2_1/n$ (No. 14)	$P6_1$ (No. 169)
<i>a</i> (Å)	21.0221(13)	10.4960(5)	16.946(2)	12.9268(1)	9.9669(2)
<i>b</i> (Å)	13.0920(6)	13.6086(6)	16.946(2)	12.2301(1)	9.9669(2)
<i>c</i> (Å)	14.5647(9)	13.6691(11)	14.303(2)	13.3369(1)	40.3361(6)
α (deg)	90.00	87.766(5)	90.00	90.00	90.00
β (deg)	109.382(7)	87.959(5)	90.00	91.491(1)	90.00
γ (deg)	90.00	74.793(4)	90.00	90.00	120.00
Vol (Å ³)	3781.3(4)	1881.99(19)	4107.3(8)	2107.80(3)	3470.12(7)
Z, <i>D_c</i> (g cm ⁻³)	8, 1.484	4, 1.490	8, 1.311	4, 1.297	6, 1.431
F(000)	1728	864	1696	864	1536
μ (mm ⁻¹)	2.638	0.289	0.152	0.242	0.247
$2\theta_{max}$ (deg)	134.4	64.9	64.7	65.2	57.6
Reflns (total)	41383	49476	54064	64934	60355
Reflns (unique)	6729	12509	7020	7451	5801
R_{int}	0.0737	0.0564	0.0634	0.0435	0.0508
Obsd data ($I > 2\sigma(I)$)	5162	9772	5879	5667	4914
R_1 (obsd data)	0.1045	0.1249	0.0381	0.0509	0.0417
ωR_2 (all data)	0.2974	0.3227	0.0793	0.1374	0.1038
$ \square _{max}$ [e Å ⁻³]	1.3(1)	2.0(1)	0.40(5)	2.58(8)	0.71(6)
T_m (°C)	190-202	190-202	205-210	178-182	189-210
CCDC no.	760636	760637	760638	760639	760640

Table 9.1 Crystallographic Details for Complexes XXIIa-XXIXb (cont.)

Compound	XXVIa	XXVIb	XXVII	XXVIII	XXIXa	XXIXb
Formula	C ₂₆ H ₂₂ F ₃ O ₃ PS	C ₂₆ H ₂₂ F ₃ O ₃ PS	C ₄₈ H ₃₈ N ₆ P ₂	C ₅₂ H ₃₈ N ₆ P ₂	C ₄₈ H ₃₈ F ₁₂ N ₂ O ₈ P ₂ S ₄	C ₄₈ H ₃₈ F ₁₂ N ₂ O ₈ P ₂ S ₄
FW (g mol ⁻¹)	502.47	502.47	760.78	808.82	1188.98	1188.98
Size (mm ³)	0.33 x 0.27 x 0.13	0.28 x 0.12 x 0.06	0.29 x 0.20 x 0.18	0.42 x 0.25 x 0.07	0.43 x 0.38 x 0.16	0.47 x 0.30 x 0.15
Crystal system	monoclinic	triclinic	monoclinic	monoclinic	triclinic	monoclinic
Space group	<i>P</i> 2 ₁ / <i>c</i> (No. 14)	<i>P</i> -1 (No. 2)	<i>P</i> 2 ₁ / <i>c</i> (No. 14)	<i>P</i> 2 ₁ / <i>c</i> (No. 14)	<i>P</i> -1 (No. 2)	<i>P</i> 2 ₁ / <i>c</i> (No. 14)
<i>a</i> (Å)	11.2246(4)	9.7892(4)	9.9176(4)	9.8685(2)	9.5923(5)	18.438(1)
<i>b</i> (Å)	19.4426(7)	11.4559(6)	13.7706(6)	14.9561(4)	11.4243(6)	14.6101(8)
<i>c</i> (Å)	11.2114(4)	21.464(1)	14.1618(6)	14.2387(4)	12.2741(6)	19.745(1)
<i>α</i> (deg)	90.00	88.629(4)	90.00	90.00	107.982(5)	90.00
<i>β</i> (deg)	105.701(4)	86.009(3)	96.951(4)	97.885(2)	90.275(4)	93.000(7)
<i>γ</i> (deg)	90.00	75.805(4)	90.00	90.00	101.322(4)	90.00
Vol (Å ³)	2355.43(15)	2327.85(19)	1919.88(14)	2081.68(9)	1251.37(11)	5311.6(5)
<i>Z</i> , <i>D</i> _c (g cm ⁻³)	4, 1.417	4, 1.434	2, 1.316	2, 1.290	1, 1.578	4, 1.487
<i>F</i> (000)	1040	1040	796	844	606,	2424
<i>μ</i> (mm ⁻¹)	0.256	0.259	0.158	0.150	0.355	0.334
2 θ _{max} (deg)	65.4	50.0	65.2	65.5	63.8	57.7
Reflns (total)	30215	15366	55499	24576	15083	101184
Reflns (unique)	8060	8178	6772	7053	7654	12955
<i>R</i> _{int}	0.0339	0.0478	0.0425	0.0387	0.0278	0.0649
Obsd data (<i>I</i> > 2 σ (<i>I</i>))	5850	4573	5191	4680	5446	6469
<i>R</i> ₁ (obsd data)	0.0363	0.0412	0.0395	0.0407	0.0401	0.0792
ωR_2 (all data)	0.0906	0.0605	0.1134	0.0841	0.1011	0.1899
$\Delta\rho$ _{max} [e Å ⁻³]	0.40(6)	0.33(6)	0.45(6)	0.41(5)	0.43(7)	1.25(9)
<i>T</i> _m (°C)	160-172	160-172	220-238	240-264	220-234	220-234
CCDC no.	760641	760642	760643	760644	760645	760646

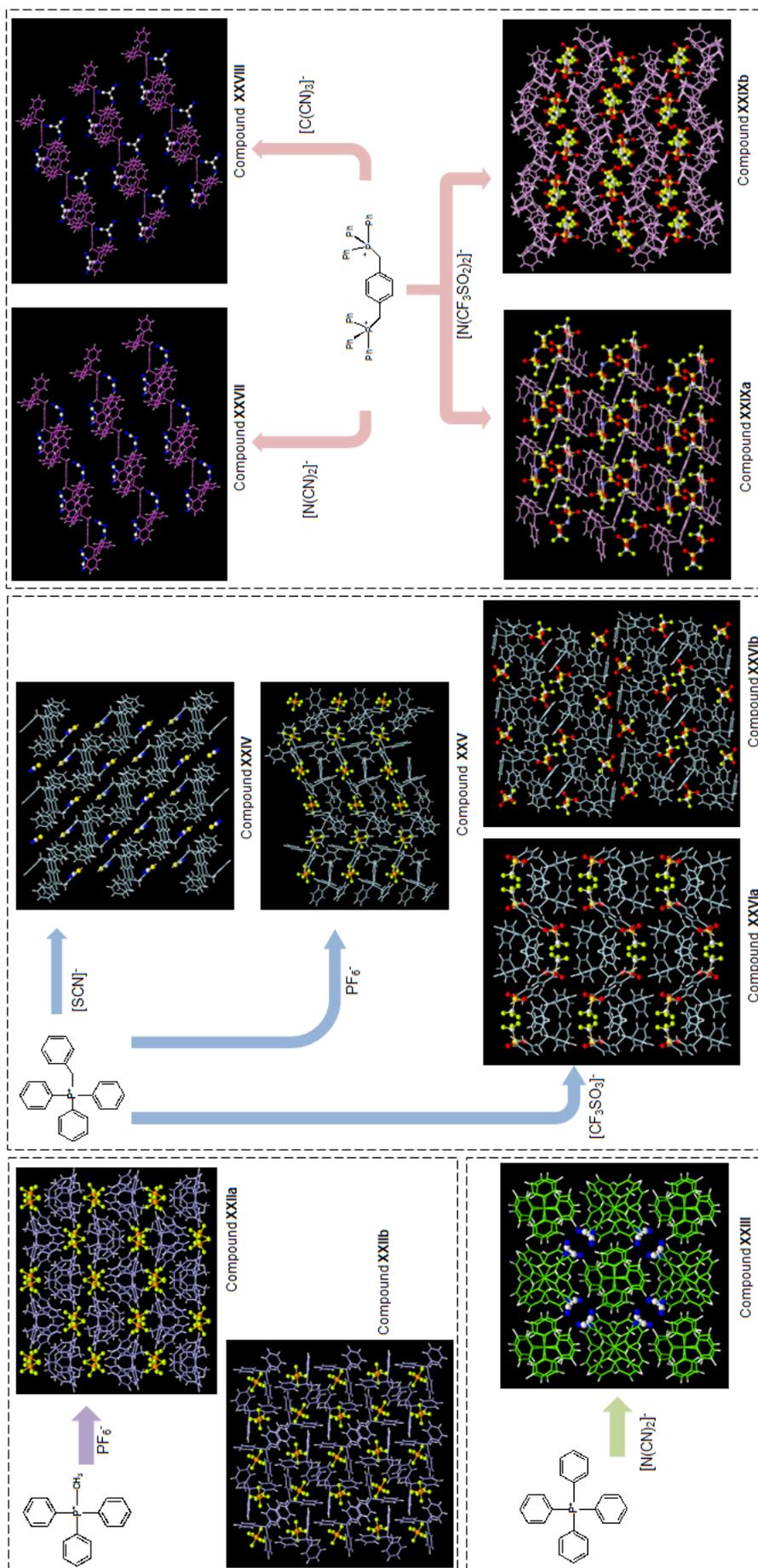


Figure 9.3. Crystal packing in the structures of compounds XXIIIa – XXIXb.

The crystals containing triphenylmethyl phosphonium cations and hexafluorophosphate in compounds **XXIIa** and **XXIIb** appear as polymorphs, crystallising in monoclinic and triclinic space groups respectively. In compound **XXIIa**, the phosphonium cations are embraced in two different pairs, one pair with one **of** and two **ef** interactions, the other pair having three **ef** interactions between the cations with P...P separations at 7.4 and 7.5 Å respectively, and these pairs of phosphonium cations are propagated by translation operation resulting in infinite chains forming columns in zigzag sequence running parallel to the *c*-axis. The polymorph of the same compound, compound **XXIIb**, has shorter P...P separation at 6.0 Å with the associated embrace having the methyl groups directed towards the phenyl rings with C... π_{centroid} close distances at 3.45 Å. The pairs of cations form a rectangular array with **off** interactions between the nearest phosphonium cations in both directions.

Compound **XXIII** crystallises in the tetragonal system having four independent tetraphenyl phosphonium cations with each P atom lying on a site with crystallographically imposed -4 symmetry. The phosphonium cations are in the common multiple embrace motifs with one pair of phosphonium cations is engaged in the established orthogonal fourfold phenyl embrace consisting of four **ef** interactions, and another pair has 2 **off** interactions, forming stacks of columns effectively arranged in an alternate linear translation manner along the *c*-axis, having a P...P separation of 7.2 Å for the embrace pairing, and a P...P separation of 9.2 Å between columns. The **ef** and **off** interactions have close C... π_{centroid} and $\pi_{\text{centroid}}...$ π_{centroid} distances ranging from 3.51 to 3.60 Å and at 3.92 Å respectively between each neighbouring pair of phenyl rings. It is noteworthy that $[\text{Ph}_4\text{P}]^+$ cations often coordinate into chains and networks of the dominant multiple phenyl embrace *i.e.* sixfold and fourfold phenyl embraces (zigzag infinite and linear infinite)^[218]. In addition, $[\text{Ph}_4\text{P}]^+$ cations can also pack into tetragonal

lattices, with C_{60}^- and I^- occupying the tetragonal prismatic cavities formed by eight cations [219, 220].

Crystal structures of compound **XXIV** to **XXVI** are comprised of triphenylbenzyl phosphonium cations with different anions, namely thiocyanide, hexafluorophosphate and trifluoromethanesulfonate respectively. The phosphonium cation bearing a benzyl arm forms infinite zigzag chain, and they associate through slightly different phenyl embraces for each compound. In compound **XXIV** the cations are engaged in the parallel fourfold phenyl embraces where the motif comprises of one **off** ($\pi_{\text{centroid}} \cdots \pi_{\text{centroid}}$ distance at 4.19 Å) and two **ef** ($C \cdots \pi_{\text{centroid}}$ distance at 3.69 and 3.95 Å) interactions between each neighbouring pair of phenyl rings with a $P \cdots P$ separation at 7.4 Å and $P \cdots P \cdots P$ angle at 110.9°. Compound **XXV** crystallises in a hexagonal space group and the arrangement of phosphonium cations is unusual compared to other compounds with the same cation. They are not organized in the common embrace fashion but rather they are connected with one **ef** interaction between one another forming continuous zigzag chains, with $P \cdots P$ separations at 8.5 to 9.8 Å, and with $P \cdots P \cdots P$ angles at 96.2 to 107.3°. Compound **XXVIa** and **XXVIb** are polymorphs of the same compound, crystallising in monoclinic and triclinic space groups respectively, and both the polymorphs have fourfold phenyl embraces with four **ef** interactions ($C \cdots \pi_{\text{centroid}}$ distances ranging from 3.56 to 4.41 Å) between neighbouring phenyl rings, except for the interaction between the phosphonium cation pairs; in compound **XXVIa** the phosphonium cations are linked through **ef** interactions with distance at $C \cdots \pi_{\text{centroid}}$ 3.85 Å, while in compound **XXVIb** they are linked through **ef** and **off** interactions ($C \cdots \pi_{\text{centroid}}$ distance at 3.99 and $\pi_{\text{centroid}} \cdots \pi_{\text{centroid}}$ distance at 3.95 Å respectively). The embraced phosphonium cations have $P \cdots P$ separations at 7.2 and 7.6 Å for compound **XXVIa** and compound **XXVIb** respectively.

Compounds **XXVII** to **XXIX** contain larger phosphonium moieties which lie about inversion centres in *trans*-conformation, except for a polymorph in compound **XXIXb**. The crystal packing for compounds **XXVII** and **XXVIII** are similar where the phenyl rings of the *bis*-phosphonium cation are involved in two **ef** interactions ($C\cdots\pi$ distances ranging from 3.70 to 3.73 Å) between three neighbouring *bis*-phosphonium cations, forming infinite zigzag chains in ladder-like layers arranged in alternating two dimensional arrays, with a slightly shorter P \cdots P separation at 8.5 Å in compound **XXVII** relative to that in compound **XXVIII**, at 8.7 Å. Compounds **XXIXa** and **XXIXb** with the same *bis*-phosphonium cation crystallised as polymorphs, in triclinic and monoclinic space groups respectively. The significant difference between these polymorphs is the conformation of the *bis*-phosphonium cation, where the cations are in the *trans* and *cis*-conformations respectively.

The cations in compound **XXIXa** form continuous zigzag arrangement but with more **ef** interactions between the phenyl rings ($C\cdots\pi$ distances ranging from 3.59 to 3.89 Å), having a shorter P \cdots P separation at 5.7 Å. The cations in compound **XXIXb** are arranged in an up-down fashion alternately with the multiple phenyl embrace comprised of two **ef** interactions ($C\cdots\pi$ distances ranging from 3.87 to 4.28 Å), with a P \cdots P separation at 8.2 Å. The higher positive charges of these *bis*-phosphonium cations with a two fold increase in the number of univalent anions results in an expansion of the lattice are different packing arrangements of the ions.

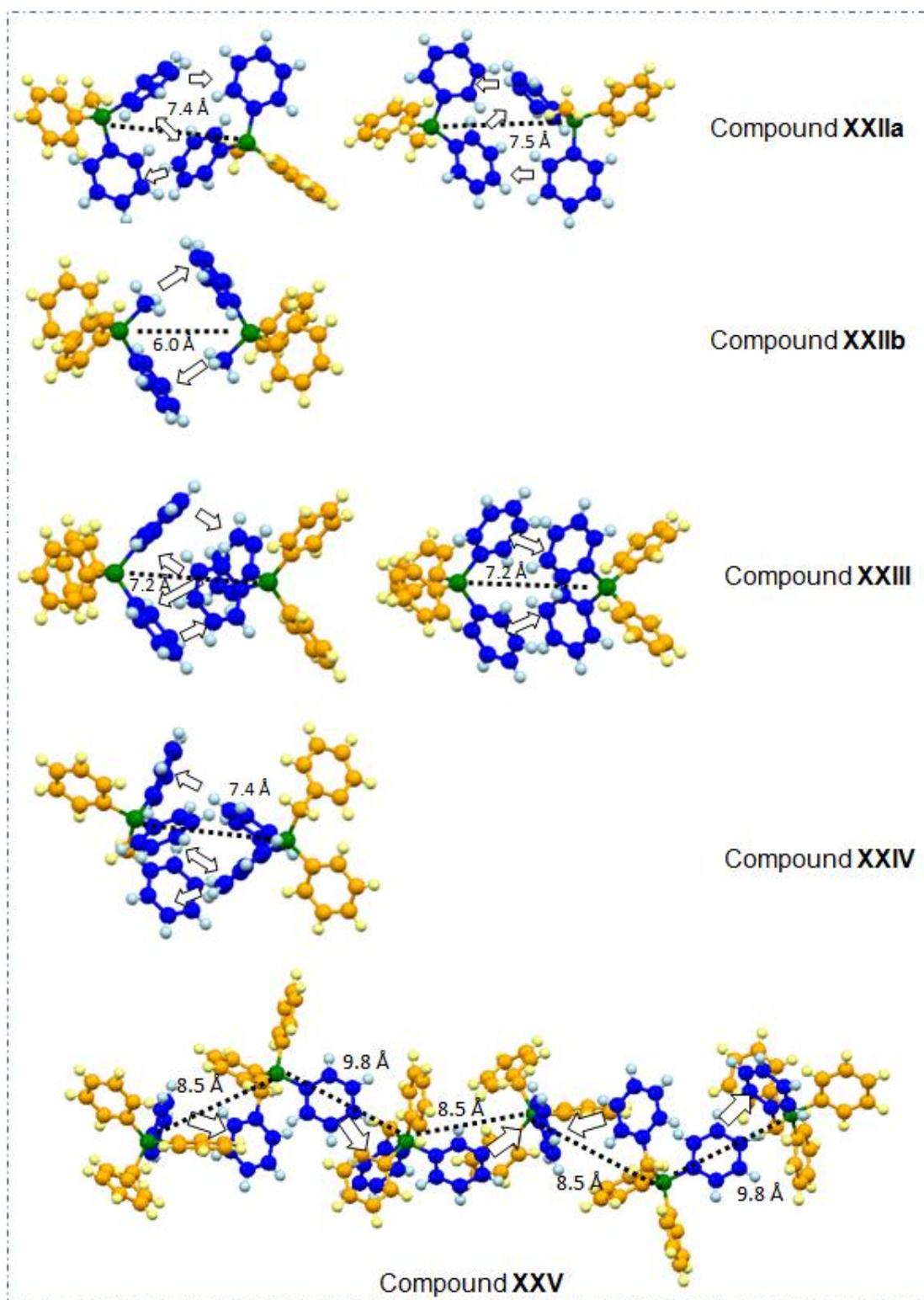


Figure 9.4(a). Phenyl embraces of the phosphonium cations in **off** (double arrow) and **ef** (single arrow) with the interacting phenyl rings in blue and the non-interacting in orange.

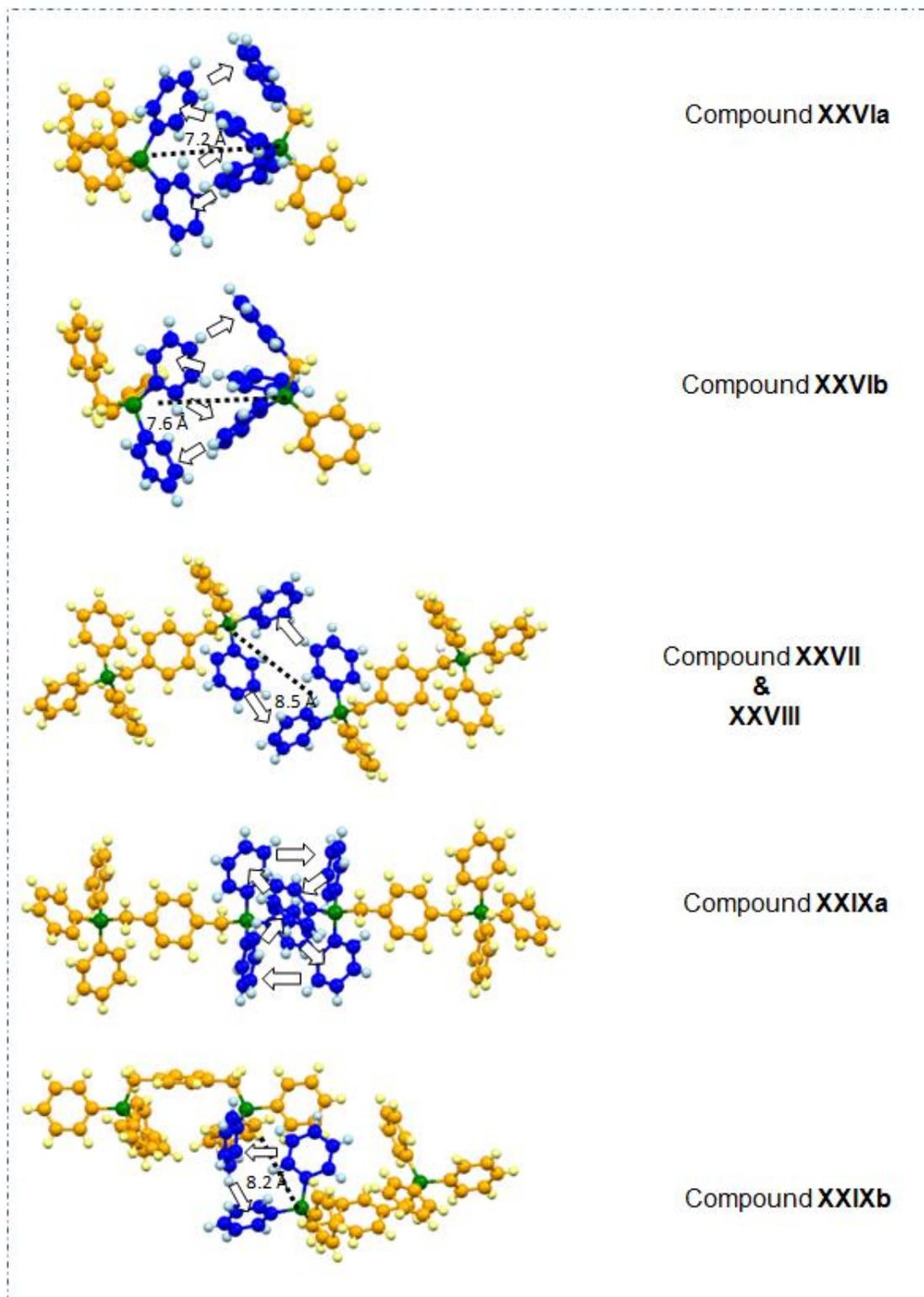


Figure 9.4(b). Phenyl embraces of the phosphonium cations in **off** (double arrow) and **ef** (single arrow) with the interacting phenyl rings in blue and the non-interacting in orange.

9.3 Hirshfeld surface analysis of phosphonium salts

Phosphonium cations

Two-dimensional fingerprint plots from Hirshfeld surface analyses, Figure 9.5, illustrate the difference between the intermolecular interaction patterns and the relative contributions to the Hirshfeld surface (in percentage) for the major intermolecular contacts associated with the phosphonium cations. Importantly, in all compounds intermolecular H···H bonding appears to be a major contributor in the crystal packing. Several herringbone arrangements can be identified, notably for compounds **XXIII**, **XXIV**, **XXVII**, **XXVIII** and **XXIXa**, where the dominant motif involves C–H··· π contacts which appear as ‘wings’. Compound **XXIII** has the shortest C–H··· π contact with $d_{\text{C}\cdots\text{H}} \approx 2.7 \text{ \AA}$, where the characteristic wings are more pronounced compared to other compounds.

In each of the structures the interaction of the cations and the anions is dominated by C–H···X (X = N, O, F) non-classical hydrogen-bonding, with a donor spike in the upper part of the fingerprint plot and some red streaking. O-atom containing anions in compounds **XXVIa**, **XXVIb**, **XXIXa** and **XXIXb** show strong C–H···O contact with a sharp donor spike relative to C–H···F contacts. There is a sharp spike indicative of strong C···C contacts involving the cyano moieties in $\text{N}(\text{CN})_2^-$ and $\text{C}(\text{CN})_3^-$ for compounds **XXVII** and **XXVIII**. However, this feature is absent in compound **XXIV** which also have cyano moieties, in SCN^- . Among all the compounds, **XXIIb**, **XXIV**, **XXVIa**, **XXVIb**, **XXVII** and **XXIXa** have poor packing efficiency with the contact distances in the fingerprint plot extended further, with regions of intermolecular voids. Interestingly this correlates with the lower melting points for these compounds.

Phosphonium cation

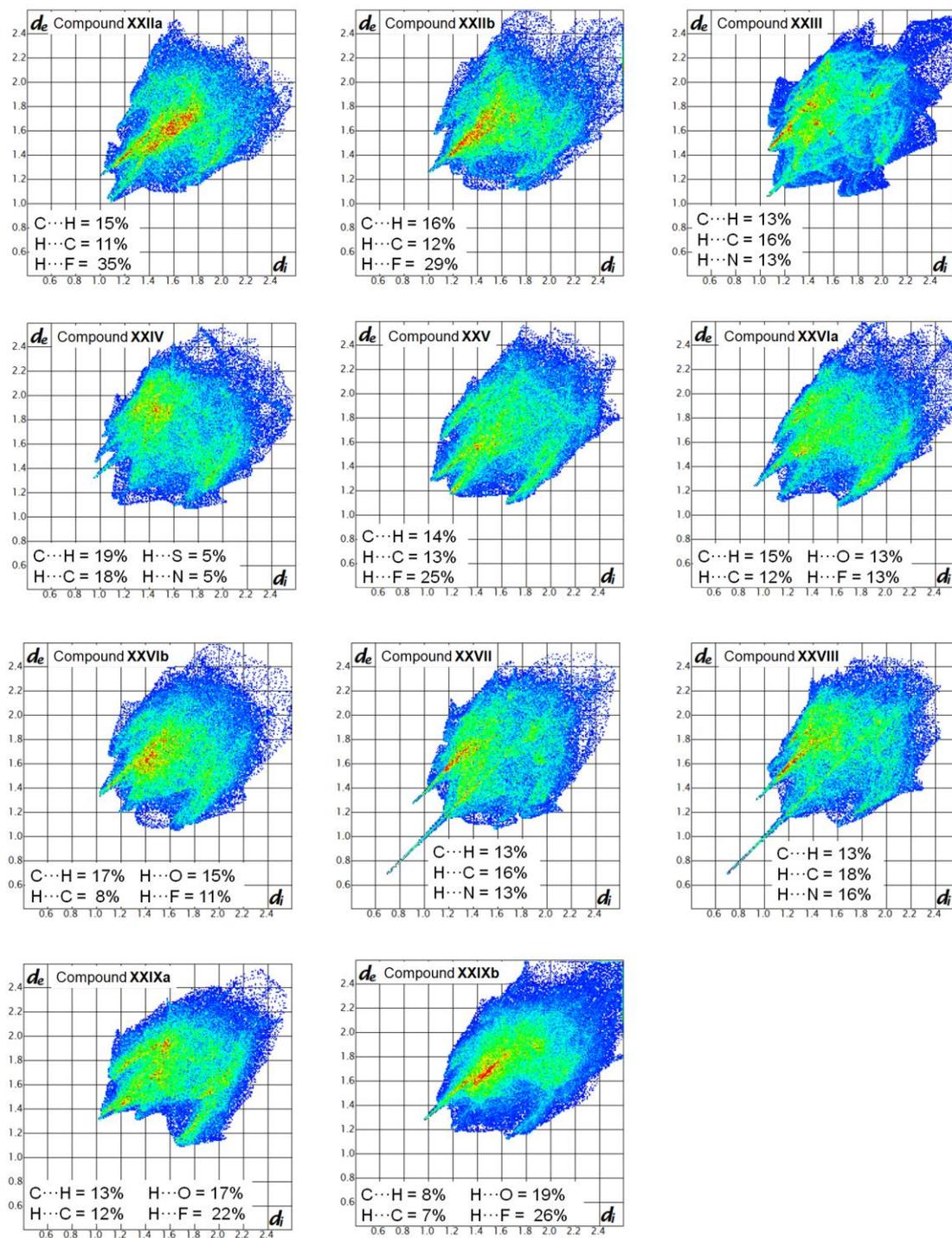


Figure 9.5. Fingerprint plots for phosphonium cations in compound XXIIa – XXIXb.

Anions

The symmetrical and non-symmetrical homo-charged anions PF_6^- , $\text{N}(\text{CN})_2^-$, $\text{C}(\text{CN})_3^-$, SCN^- , CF_3SO_3^- and $\text{N}(\text{CF}_3\text{SO}_2)_2^-$ are surrounded by the phosphonium cations which pack in different arrays through $\text{C-H}\cdots\text{X}$ non-classical hydrogen-bonding where the basis of the molecular electrostatic potential is consistent to previous studies, involving both charged fragments having close contacts for C–H and N, O or F groups. The two-dimensional fingerprint plots from Hirshfeld surface analyses for the anions are shown in Figure 9.7. Anions containing F-atoms, except for compounds **XXIII**, **XXIV**, **XXVII** and **XXVIII**, show $\text{C-H}\cdots\text{F}$ interactions, with $\text{H}\cdots\text{F}$ distances ranging from 2.66 to 2.99 Å. Compound **XXIIa** contains disordered PF_6^- anions which is related to a symmetrical spinning motion and lack preferential directionality in the solid state ^[224]. The $\text{C-H}\cdots\text{F}$ interactions between the cations and anions for compound **XXIIa**, **XXIIb** and **XXV** is dominant, while in compound **XXVIa**, **XXVIb**, **XXIXa** and **XXIXb** there is a $\text{C-H}\cdots\text{O}$ hydrogen bonding (from CF_3SO_3^- and $\text{N}(\text{CF}_3\text{SO}_2)_2^-$), with $\text{H}\cdots\text{O}$ distances ranging from 2.60 to 2.98 Å. In compound **XXIXa** and **XXIXb** there are different conformations of $[\text{N}(\text{CF}_3\text{SO}_2)_2]^-$ anions; compound **XXIXa** has $[\text{N}(\text{CF}_3\text{SO}_2)_2]^-$ anions interlocked in the trans-conformation (Figure 9.6(a)) while compound **XXIXb** has *cis*- and *trans*-conformers which are arranged in between the phosphonium cations forming narrow channels across the structure (Figure 9.6(b)).

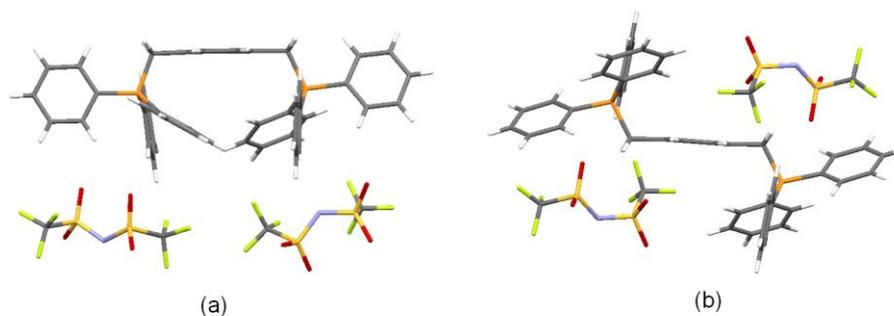


Figure 9.6. Bis-phosphonium cation and trifluoromethylsufonylamide anion in compound **XXIXb**.

For compounds containing SCN^- , $\text{N}(\text{CN})_2^-$ and $\text{C}(\text{CN})_3^-$ the anions are surrounded by oppositely charged phosphonium cations with $\text{N}\cdots\text{H}$ hydrogen bonds between N-atoms of cyano moieties and the phenyl H-atoms from the phosphonium cations, with short $\text{N}\cdots\text{H}$ distances ranging from 2.69 to 2.95 Å. The anions also have close $\text{C}-\text{N}\cdots\text{C}$ contacts from the C-atoms of the cyano groups and the phosphonium phenyl H-atoms, with distances ranging from 2.55 to 2.97 Å. The terminal S-atom in thiocyanate in compound **XXIV** has additional $\text{C}-\text{H}\cdots\text{S}$ interaction, with shortest $\text{H}\cdots\text{S}$ distances at 2.89 Å.

The green colouring towards the spikes in the fingerprint plots represent a greater relative contribution of hydrogen bonding on the surface, involving N, O, F and S atoms. There is a larger number of $\text{C}-\text{H}\cdots\text{N}$ interactions between cations and anions for compounds **XXIII**, **XXIV**, **XXVII** and **XXVIII**. For compounds containing PF_6^- anion, the prevailing $\text{F}\cdots\text{H}$ interactions have relative contribution fractions of more than 90 %. The CF_3SO_3^- and $\text{N}(\text{CF}_3\text{SO}_2)_2^-$ anions with the $\text{C}-\text{H}\cdots\text{F}$ and $\text{C}-\text{H}\cdots\text{O}$ interactions have similar contributions to the overall surface. Compounds **XXIIb**, **XXV**, **XXVIa**, and **XXIXa** have considerably less efficient close packing in the crystal as compared to the other structures.

Anions

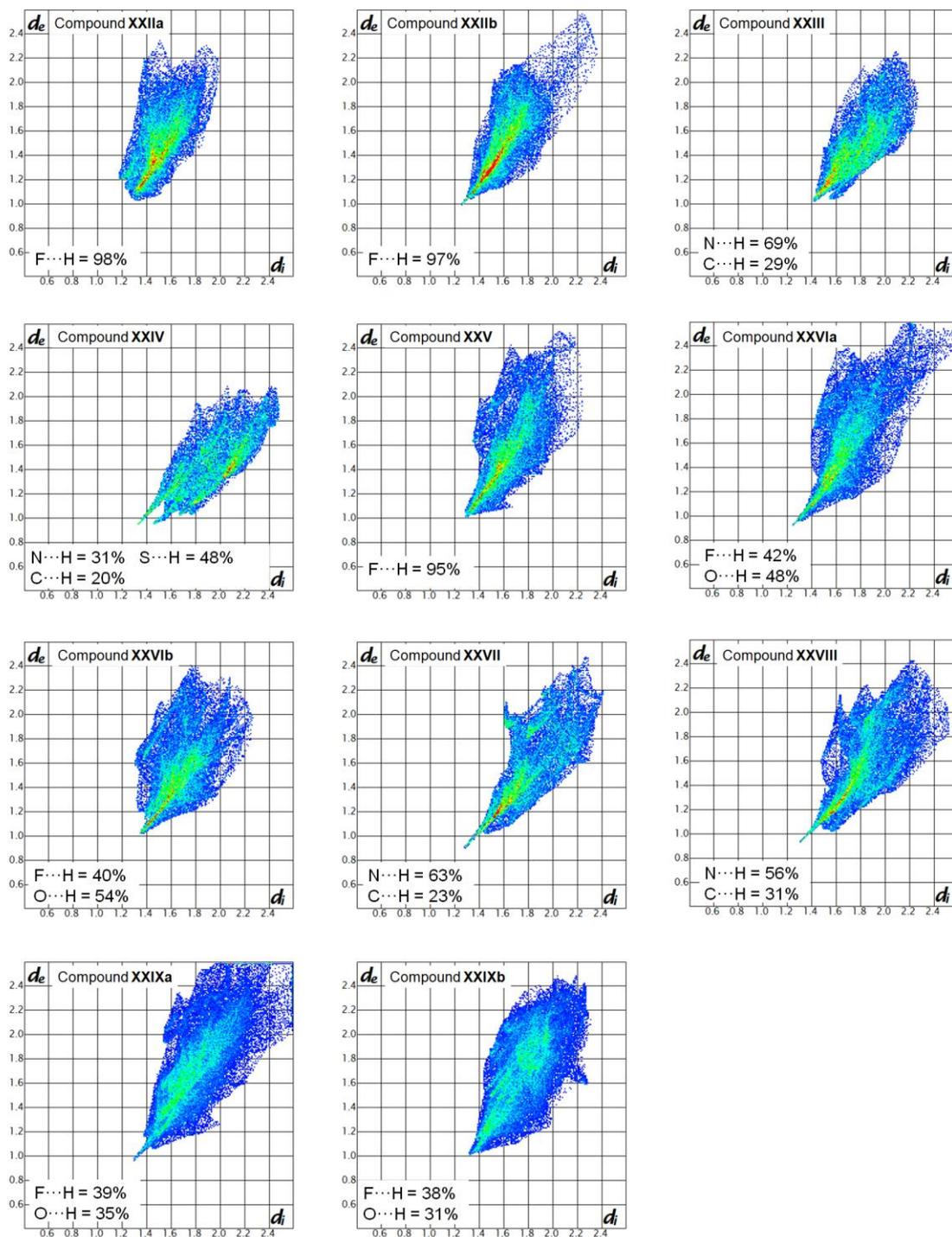


Figure 9.7. Fingerprint plots for anions in compound XXIIa – XXIXb.

9.4 Conclusions

In structurally authenticating a series of compounds based on various phosphonium cations and anions which are intrinsically important in ionic liquids, a greater understanding has been established, on how the anions, which avoid each other in the structures, interact with phosphonium cations, at the same time how the more charge diffuse cations interact with each through phenyl embraces. This dominance of the interactions of the cations with themselves and of these cations with the anions is readily identified through Hirshfeld surface analyses. Of particular interest is identifying the different contacts for polymorph pairs, *i.e.* compounds **XXIIa** and **XXIIb**, **XXVIa** and **XXVIb**, and **XXIXa** and **XXIXb**, and compounds that differ in the anion, which have similar or different three dimensional connections, *i.e.* compounds **XXIII**, **XXIV**, **XXV**, **XXVII** and **XXVIII**. The phosphonium cations usually associate through phenyl...phenyl interactions either in the **off** or **ef** types, and that these motifs can form multiple phenyl embraces which can further correlate in the formation of chains and nets. The interplay of the anions with the cations is dominated through non-classical C-H...X hydrogen bonds.

9.5 Experimental Section

A. General remarks on crystal growth

Suitable crystals of compounds **XXIIa–XXIXb** (Figure 9.3 and Table 9.1), for X-ray diffraction studies formed on slow evaporation of a solution of an equimolar mixture of *p*-sulfonatocalix[4]arene and imidazolium (1-ethyl-3methylimidazolium, 1-butyl-3methylimidazolium and 1,1'-[1,4-phenylenebis(methylene)]bis(3-butyl-1H-imidazolium-1-yl)) salts, in the presence of phosphonium salts (halides) and a threefold excess of gadolinium(III) chloride, in a mixture of THF and water (1:1, 2 mL, pH 2.5-5.4), affording colourless crystals of complexes which were suitable for X-ray diffraction studies after several days. The compounds can also be prepared directly in the presence of sodium *p*-sulfonatocalix[4]arene and gadolinium(III) chloride, in yields from 20 to 60%, albeit without forming crystals suitable for single crystal diffraction studies. Imidazolium salts containing [SCN]⁻, [N(CN)₂]⁻, [C(CN)₃]⁻, [PF₆]⁻, [CF₃SO₃]⁻ and [N(CF₃SO₂)₂]⁻ anions were synthesized as described in Section 3.4 and 6.4. Phosphonium salts were purchased from Sigma Aldrich and were used without purification.

Controlling the growth of single crystals in the presence of the calixarene is interesting given that the imidazolium charged head group is selectively drawn into the cavity of the calixarene, rather than binding of phenyl rings of phosphonium cations, both in solid and solution state, which have been discussed in Chapters 3 to 8.