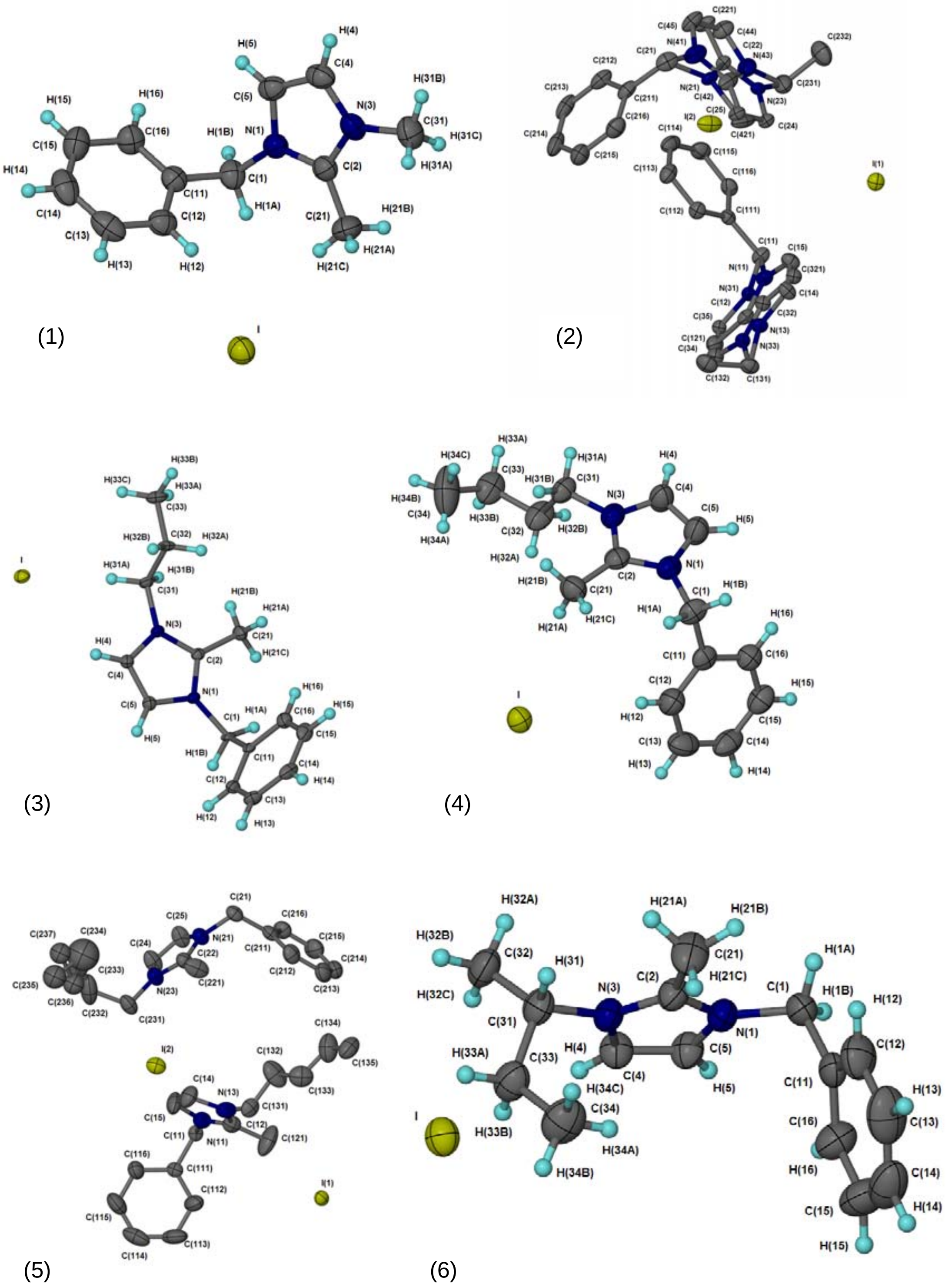
Electronic Supplementary Information



(1)

(2)

(3)

(4)

(5)

(6)

Fig. S1. The asymmetric units of (**1**), (**2**), (**3**), (**4**), (**5**) and (**6**) shown with with 50% probability amplitude displacement ellipsoids and hydrogen atoms as spheres of arbitrary radius. Hydrogen atoms are omitted on (**2**) and (**5**) due to disorder obstructing clarity.

Analysis of the Structures

1,2-dimethyl-3-benzylimidazolium iodide, (1). The asymmetric unit consists of a single 1,2-dimethyl-3-benzylimidazolium cation and a single iodide anion disposed in general positions (Fig. S1). The imidazolium ring of the cation is planar ($\chi^2(C_3N_2)$ 2.8), with geometries (Table 3) typical of an aromatic imidazolium ring.· The benzyl substituent ($\chi^2(C_6)$ 52) lies to one side of the mean plane of the five-membered imidazolium ring with bond lengths and angles within normal ranges (Allen *et al.*,1987).· The extended structure (Fig. S2) consists of layers of cations and anions lying parallel to (001). Several interionic C-H···I close contacts (Table 5), occur which results in a chain of alternating cations and anions. Additionally inter-ring π···π and C-H···π interactions (Fig. S3, Tables 6,7) occur between cations of parallel chains, thus resulting in a three-dimensional lattice.

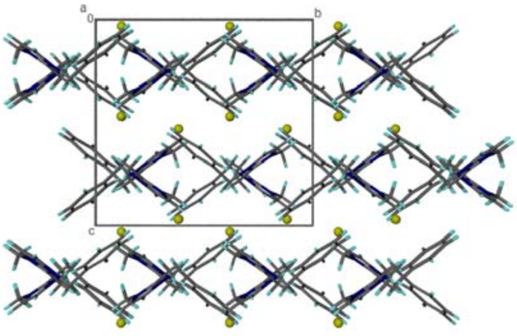


Fig. S2. Unit cell contents of 1,2-dimethyl-3-benzylimidazolium iodide (**1**), projected down *a*.

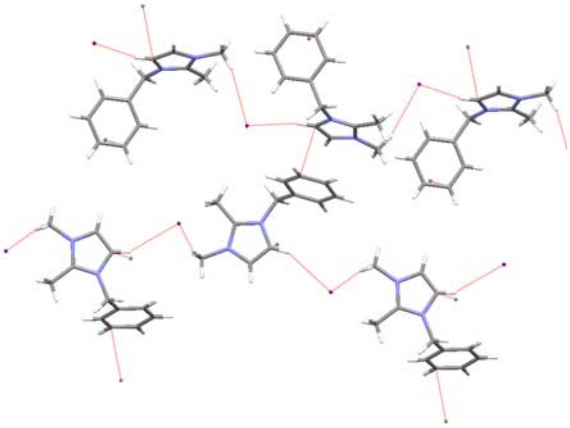


Fig. S3. Schematic displaying selected intermolecular interactions within 1,2-dimethyl-3-benzylimidazolium iodide (**1**)

1-ethyl-2-methyl-3-benzylimidazolium iodide, (2). The asymmetric unit consists of two 1-ethyl-2-methyl-3-benzylimidazolium iodide cations and two iodide anions disposed in general positions. The imidazolium ring of the cation was modelled as disordered over two sites with population 0.5 (Fig. S1). The imidazolium and benzyl rings of the cation are planar (χ^2(C_3N_2, $C'_3N'_2$; the benzyl C_6) 3.8, 0.6; 14.6) displaying bond distances and angles (Table 3, main text) within the normal range (Allen *et al*., 1987). Within the first cation the benzyl and ethyl substituent both lie to the same site of the mean plane of the five-membered imidazolium ring; the second cation displays one substituent 'above' the ring and the other 'below'.

The extended structure (Fig. S4) consists of a zigzag-like arrangement consisting of clusters of cations and anions. The clusters are arranged in an interesting jigsaw type arrangements with the cations held together in a cluster of three with inter-ring π···π interactions between the benzyl ring of cation 1 inbetween the imidazolium aromatic rings of two cation 2's. Additionally a C-H···π interaction occurs between the benzyl substituents of the two cations (Table 7). This arrangement creates channels wherein the anions are located. Several interionic C-H···I close contacts (Table 5) thus result and a three-dimensional lattice eventuates.

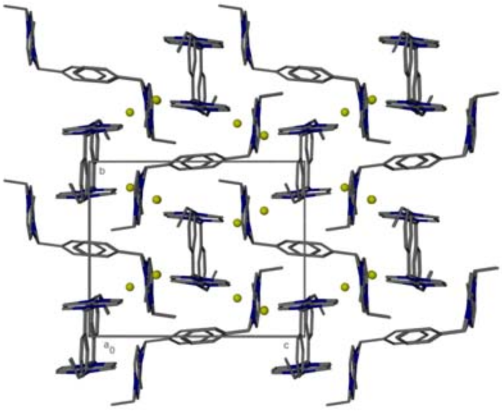


Fig. S4. Unit cell contents of 1-ethyl-2-methyl-3-benzylimidazolium iodide (**2**) projected down *a*.

1-**propyl-2-methyl-3-benzylimidazolium iodide, (3).** The asymmetric unit consists of a single 1-propyl-2-methyl-3-benzylimidazolium cation and a single iodide anion disposed in general positions (Fig. S1). The imidazolium and benzyl rings of the cation are planar ($\chi^2(C_3N_2,C_6)$ 0.3, 5.8) displaying bond distances and angles (Table 3) within the normal range (Allen *et al.*,1987). The benzyl and propyl substituents lie to the same side of the mean plane of the five-membered imidazolium ring. The propyl substituent adopts the energetically preferred *trans* conformation with an N-C-C-C torsion angle of 175.8(3)º. The extended structure (Fig. S5) consists of layers of anions and cations where dimers of cations (associated *via* an inversion centre) are arranged so that the alkyl chains are intercalated inbetween the benzyl substituents, resulting in several π···π and C-H···π interactions (Table 6,7). The cationic dimers are linked to the next dimeric pair *via* C-H···π interactions (Table 7) in one direction (parallel to (100)). Parallel to (001) the dimers are associated *via* the benzyl substituents, resulting in cationic layers (see Fig. S5). The anions are sequestered in-between these layers and form several C-H···I close contacts (Table 5), the most polarized of which involves CH(21). The combination of these interactions (see Fig. S6) results in a three-dimensional lattice.

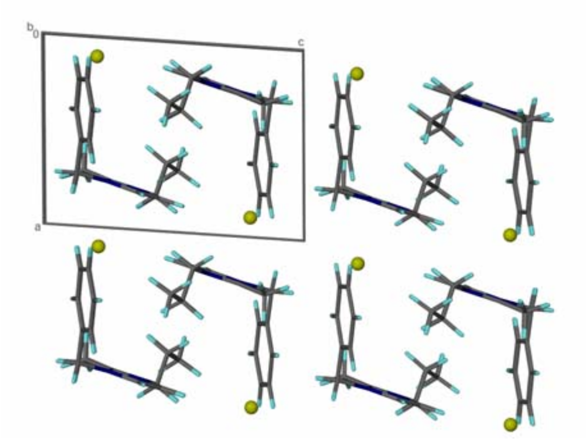


Fig. S5. Unit cell contents of 1-propyl-2-methyl-3-benzylimidazolium iodide (**3**), projected down *b*.

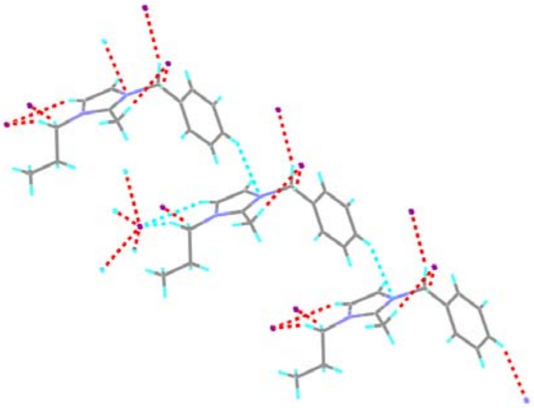


Fig S6. Schematic displaying selected intermolecular interactions within 1-propyl-2-methyl-3-benzylimidazolium iodide (**3**)

1-(*n*-)butyl-2-methyl-3-benzylimidazolium iodide (4). The asymmetric unit consists of a single 1-(*n*-)butyl-2-methyl-3-benzylimidazolium cation and a single iodide anion disposed in general positions (Fig. S1). The imidazolium ring of the cation is planar ($\chi^2(C_3N_2)$ 17) with the benzyl and butyl substituents to the same side of the mean plane (Table 3). The bond lengths and angles are within normal ranges (Allen *et al.*, 1987).

The butyl substituent adopts a *cis*-oid conformation with a C-C-C-C torsional angle of –65.2(1)°. The extended structure (Fig. S7) consists of layers of cations and anions lying parallel to (001). The predominant interactions are C-H···I close contacts which link the cation and anion *via* C(21)-H(21A)···I···H(4)-C(4) into a two-dimensional chain (Table 5, Fig. S8). Several chains of this type stack next to each other in a zigzag array (as viewed down *a*) with the array of cations and anions aligned togther but sufficiently far from each other to prevent any significant π···π and C-H···π interactions (Tables 6,7). No alkyl chain intercalation is seen.

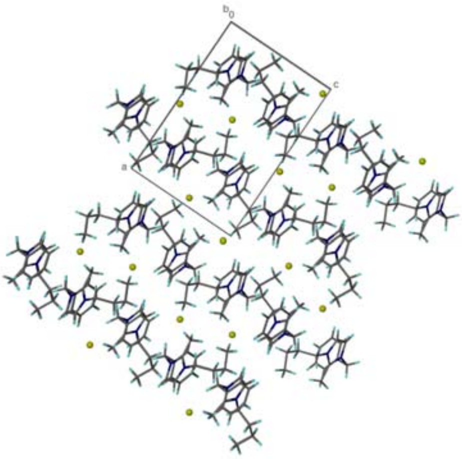


Fig. S7. Unit cell contents of 1-(*n*-)butyl-2-methyl-3-benzylimidazolium iodide (**4**) viewed down *b*.

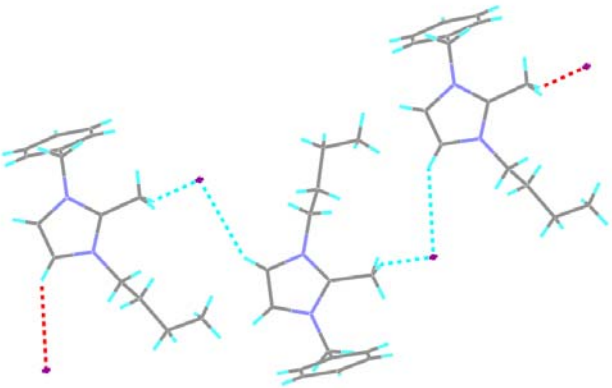


Fig. S8. Schematic displaying selected intermolecular interactions within 1-(*n*-)butyl-2-methyl-3-benzylimidazolium iodide (**4**).

1-pentyl-2-methyl-3-benzylimidazolium iodide (5). The asymmetric unit consists of two 1-pentyl-2-methyl-3-benzylimidazolium cations and two iodide anions (Fig. S1). Two sites were identified for C(233) and C(234) for the disordered alkyl chain for cation (2). The imidazolium rings of both cations are planar, displaying the benzyl and pentyl substituents to opposite sides of the mean plane of each ring (Table 3). The bond lengths and angles are within normal ranges (Allen *et al*., 1987). The pentyl substituent adopts a *trans*-oid conformation for cation (1) with a C(131)-C(132)-C(133)-C(134) torsional angle of 175.0(6)°. A *cis*-oid conformation is shown for both disordered conformations for cation (2) with a C(231)-C(232)-C(233)-C(234) torsional angle of –79.1(8)°, and C(231)-C(232)-C(233)-C(236) torsional angle of –50(2)°.

The extended structure (Fig. S9) consists of clusters of cations and anions within a brickwork-type array. Two dimers exist for the cations, both related *via* an inversion centre. Their alkyl chains are stretched away from the central aromatic association. The second dimer for cation (2) shows the *cis*-oid alkyl substituents 'curled' in-between the aromatic rings of the cations. Weak C-H···H interactions link the dimer, whilst the benzyl substituents point directly away and are not involved in any significant interaction. These two dimers pack in a complicated extended structure related by glide planes and screw axes, which results in voids wherein the iodine atoms are located. This arrangement allows for a series of C-H···I close contacts which results in a three-dimensional lattice (Table 5). Some alkyl chain intercalation is seen between the disordered alkyl chain between cation (2), but, once again, the distances are too far to allow for any significant interactions.

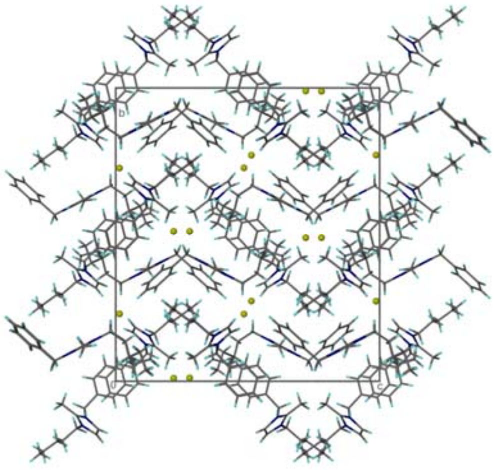


Fig. S9. Unit cell contents of 1-pentyl-2-methyl-3-benzylimidazolium iodide (**5**) viewed down *a*.

1-(*s*-)butyl-2-methyl-3-benzylimidazolium iodide (6). The asymmetric unit consists of a single 1-(*s*-)butyl-2-methyl-3-benzylimidazolium cation and a single iodide anion lying in general positions (Fig. S1). The imidazolium ring of the cation is planar ($\chi^2(C_3N_2)$ 3.2) displaying the benzyl and propyl unit of the (*s*-)butyl substituent above the mean plane (Table 3); the ethyl unit of the (*s*-)butyl lies below the ring. The bond lengths and angles are within normal ranges (Allen *et al*., 1987). In relation to the imidazolium ring, the propyl unit of the (*s*-)butyl, adopts a *cis*-oid conformation with the N-C-C-C torsional angle of 59.4(1)°. The (*s*)-butyl unit adopts the energetically favoured tetrahedral arrangement. The extended structure (Fig. S10) consists of layers of overlapping cations and anions lying parallel to (100). The predominant interaction is a C-H···I close contact which links the cation and anion *via* C(4)-H(4)···I (Table 5). A cluster of four cations with their benzyl substituents forms a cube-like structure as shown. Two of the (*s*)-butyl substituents are enclosed within this cube, thus resulting in C-H···π interactions (Table 7). The aromatic rings are too canted with each other to permit any strong π···π interactions (Table 6). This complex repeats and packs out into an extended two-dimensional array

(Fig. S10) resulting in voids wherein the iodine atoms are located, allowing for the C-H···I interactions.

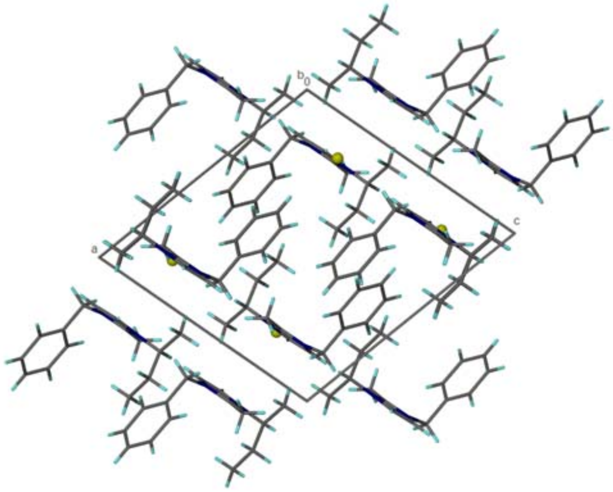


Fig. S10. Unit cell contents of 1-(*s*-)butyl-2-methyl-3-benzylimidazolium iodide (**6**), viewed down *b*.

References

1 F. H. Allen, O. Kennard, D. G. Watson, L. Brammer, A. G. Orpen and R. Taylor, *J. Chem. Soc. Perkin Trans.2*, 1957, 1.

Hirshfeld Surface Analyses

Legend: Close Contacts X···Y, where: X = atom inside the surface, Y = atom outside the surface. The diagonal lines shown on the Fingerprint Plots represent those combinations of d_i and d_e that sum to the van der Waals radii. Contacts (regions of the plot) to the left of this line can be considered to be 'close-contacts'.

1,2-dimethyl-3-benzylimidazolium iodide (1)

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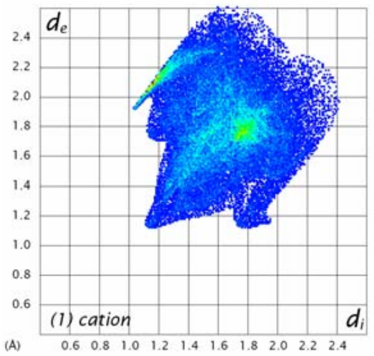
<tr><td colspan="3">
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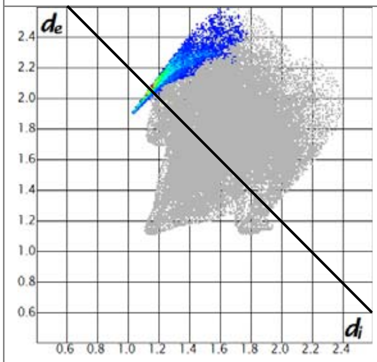
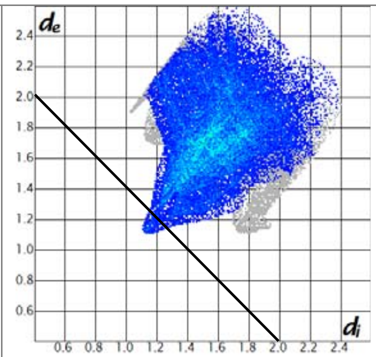
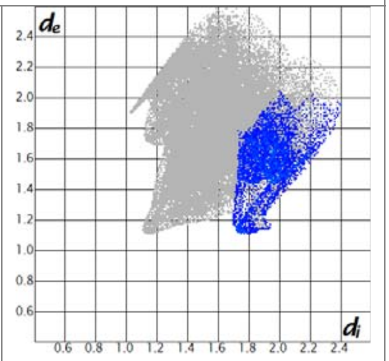
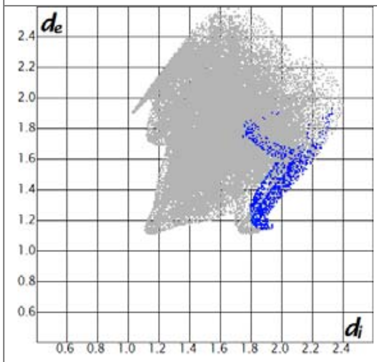
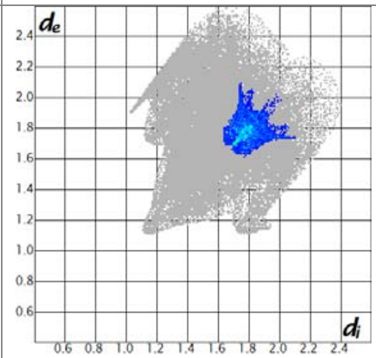
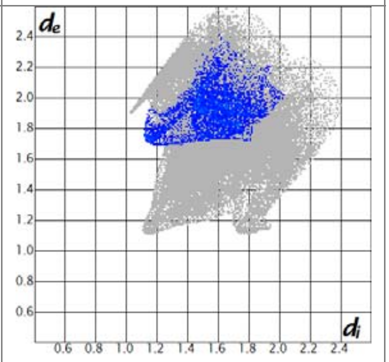
<tr><td>

<i>H···I 9.9 %</i></td><td>

<i>H···H 65.7 %</i></td><td>

<i>C···H 6.7 %</i></td></tr>
<tr><td>

<i>N···H 1.3 %</i></td><td>

<i>C···C 6.5 %</i></td><td>

<i>H···C 6.4 %</i></td></tr>
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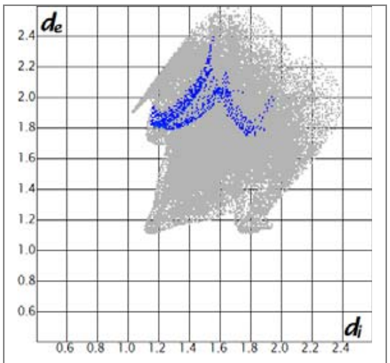
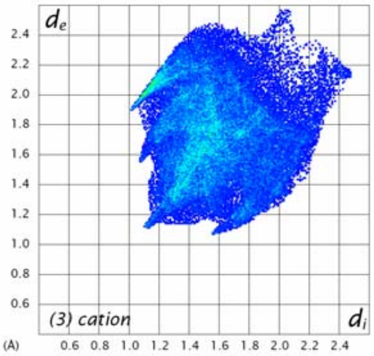


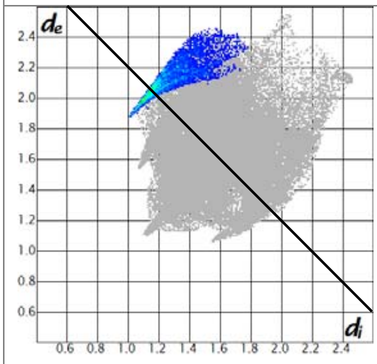
H···N 1.3 %

1-propyl-2-methyl-3-benzylimidazolium iodide (3)

Cation: Full Plot



Close contacts



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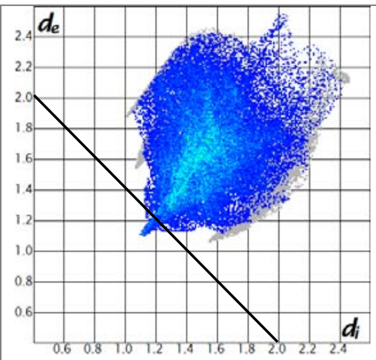
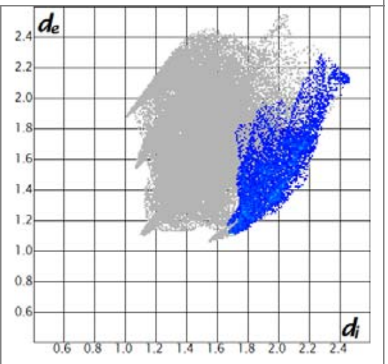


H···H 66.5 %



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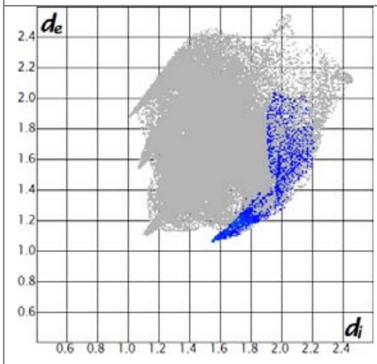

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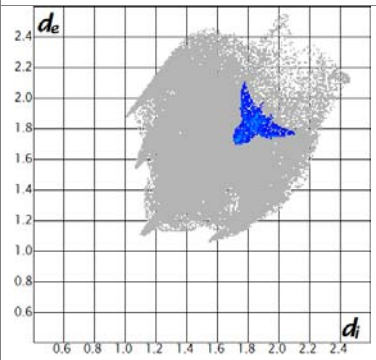
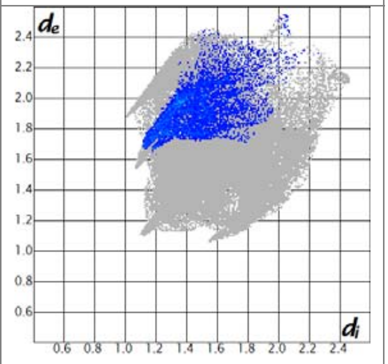


C···C 2.5 %



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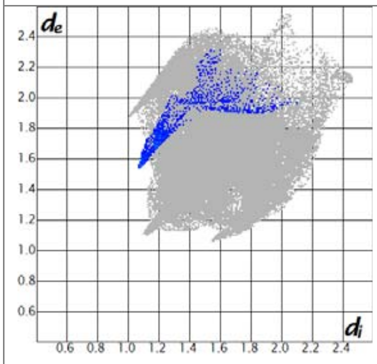

H···N 1.8 %

1-(*n*-)butyl-2-methyl-3-benzylimidazolium iodide (4)

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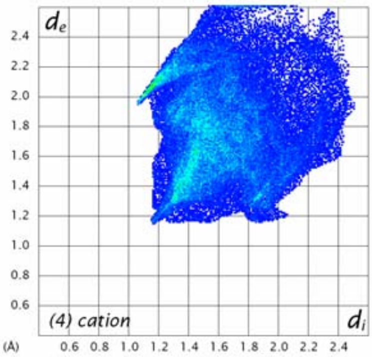

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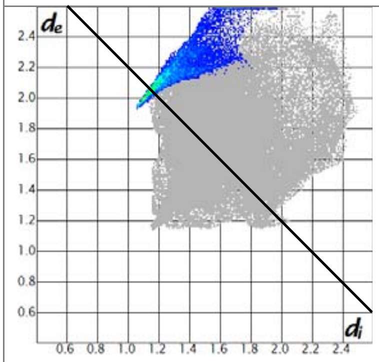

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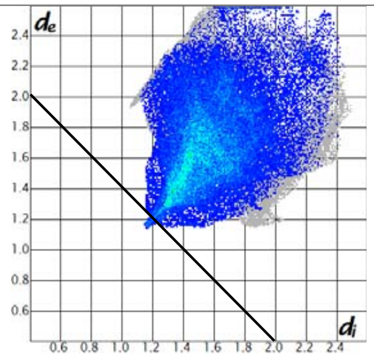
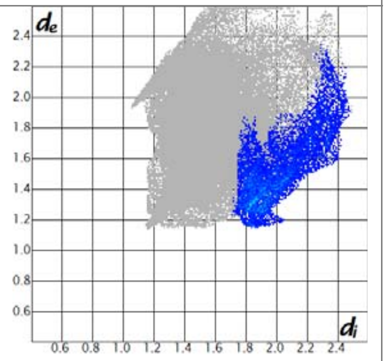


H···H 66.8 %



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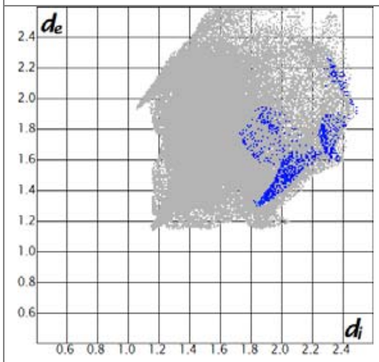

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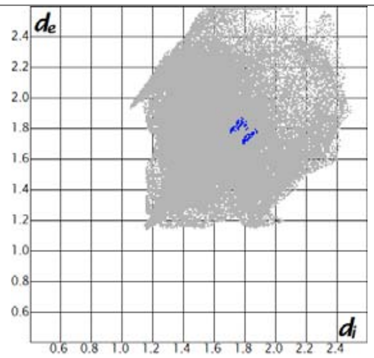

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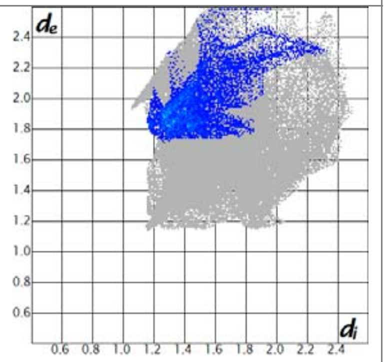
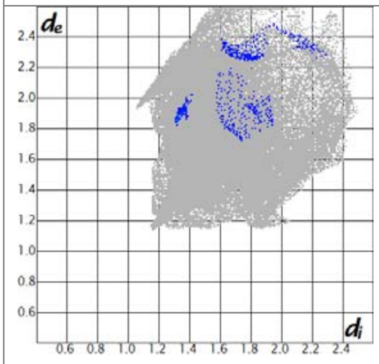


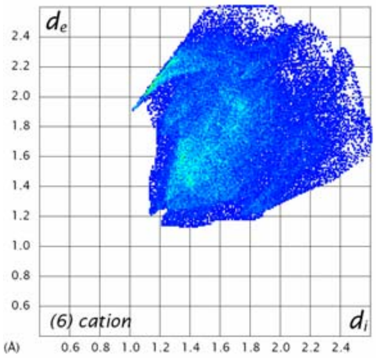
H···C 9.7 %



H···N 0.8 %

1-(*s*-)butyl-2-methyl-3-benzylimidazolium iodide (6)

Cation: Full Plot



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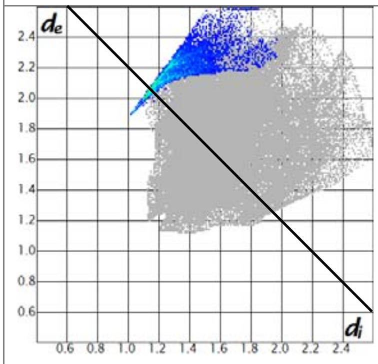
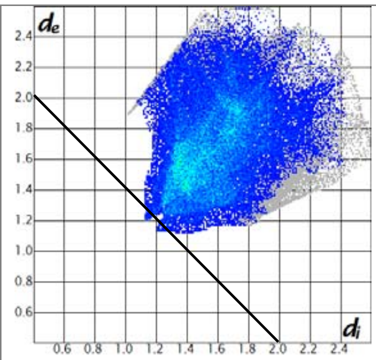
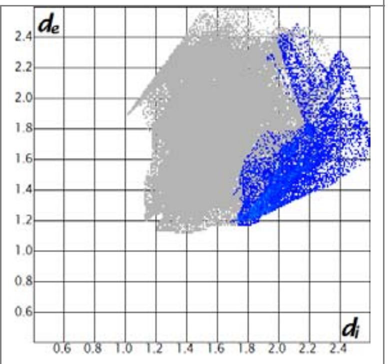


H···I 8.6 %



H···H 73.9 %



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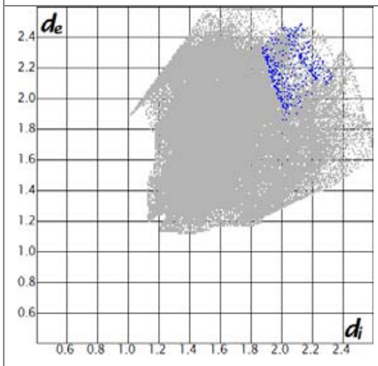

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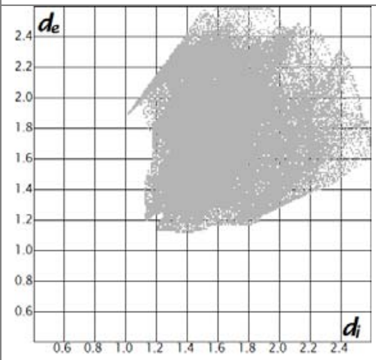

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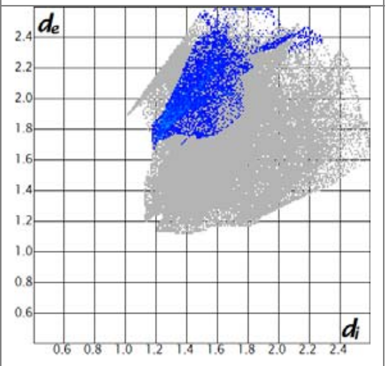
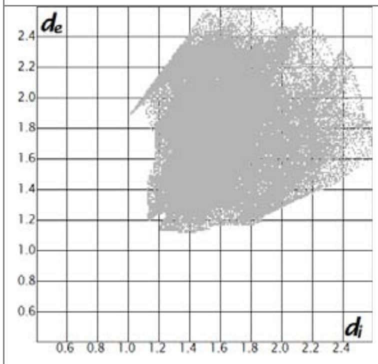


H···C 6.7 %



H···N 0.0 %