

The Madelung constant of organic salts

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SUPPLEMENTARY INFORMATION

General comments on the EUGEN method and program

The program numerically calculates the Madelung constant from the coordinates of cations and anions in the crystal structure. Access to the source code is described on page 5.

Describing the unit cell

A calculation cell defining the positions and charges of the anions and cations needs to be input into the program. In most cases the calculation cell is the same as the unit cell of the crystal structure which can be any parallelepiped, as shown in Figure S1, which when repeated in the directions of the cell axes reproduces the crystal structure. The cell dimensions input into the program are:

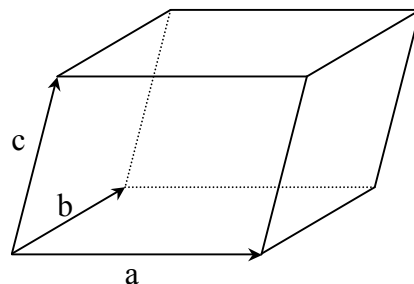


Figure S1. Example of a unit cell

- lengths a , b and c
- α = angle between b and c
- β = angle between a and c
- γ = angle between a and b

The format of the input file is as follows:

Line	Description
1	a, b, c
2	α, β, γ
3	Tolerance threshold
4	Reference ion: a_i^f, b_i^f, c_i^f , charge
5-end	Other ions in the unit cell a_i^f, b_i^f, c_i^f , charge

All angles should be in degrees and all coordinates should be input as *fractional coordinates* (a_i^f, b_i^f, c_i^f) in the lattice co-ordinate system.

Reference Ions

Since only ions within the asymmetric unit of the unit cell are unique by symmetry, their Madelung constants are also unique. The Madelung constants of the other ions comprising the unit cell will be the same as the corresponding ions in the asymmetric unit. Therefore, calculation of only the unique Madelung constants of ions of the asymmetric unit cell is required. Each of these ions is treated in turn as the reference ion in the calculation.

Note that the program is run for each reference ion in the asymmetric unit of the unit cell and then an appropriate average taken of the Madelung constants of each ion.

Conversion from non-orthogonal unit cell coordinates to orthogonal (x,y,z) coordinates where necessary

It is necessary to convert non-orthogonal coordinates, which are expressed as fractions of the non-orthogonal unit cell lengths (a, b, c), to orthogonal coordinates so that the general algorithm of the program can operate on these coordinates.

To convert non-orthogonal coordinates to orthogonal coordinates, the x axis is chosen to coincide with the a axis, the y axis is chosen so that it is in the ab plane and perpendicular to the x axis and the z axis is chosen so that it is perpendicular to both the x and y axis. The following equations can be used to convert the fractional unit cell coordinates (a_i^f, b_i^f, c_i^f) into the orthogonal coordinates (x_1^f, y_1^f, z_1^f):

$$x_i^f = a_i^f + b_{xi}^f + c_{xi}^f \quad (1)$$

$$y_i^f = b_{yi}^f + c_{yi}^f \quad (2)$$

$$z_i^f = b_{zi}^f + c_{zi}^f \quad (3)$$

where b_x and b_y , etc are the components of b along the x etc axes respectively and similarly for c .

The components b_x, b_y, c_x, c_y and c_z can be mathematically calculated as:

$$b_x = b \cos \gamma$$

$$b_y = b \sin \gamma$$

$$c_x = c \cos \beta$$

$$c_y = \frac{c(\cos \alpha - \cos \beta \cos \gamma)}{\sin \gamma}$$

$$c_z = c \sqrt{\sin^2 \beta - \left(\frac{c_y}{c}\right)^2}$$

If the cell is orthogonal, *i.e.* $\alpha = \beta = \gamma = 90^\circ$, then $b_y = b, c_z = c$ and $b_x = c_x = c_y = 0$.

The EUGEN method description

The method works as follows. An ion in the asymmetric unit of the unit cell is selected as the reference ion. Generally, the unit cell is taken as it is observed in the crystal structure. First, the contributions as $\sum_{i=2}^i \pm \frac{Z_1 Z_i e^2}{d}$ are calculated from all the neighbouring ions within the original unit cell, where Z_r and Z_i are the charges of the reference ion and the neighbouring ion, respectively, and d is the distance to the reference ion. The calculation cell is expanded (translated) in space equally in the $\pm x, y$ and z direction as shown in Figure S2, thus creating $3 \times 3 \times 3, 5 \times 5 \times 5$ etc. cells. Then the electrostatic contributions from these added unit cells are calculated explicitly as $\pm \frac{Z_1 Z_i e^2}{d}$ terms. The final electrostatic lattice energy for any shape of the original unit cell can be written as:

$$E_{es} = \sum_i \sum_j \sum_k \sum_l \sqrt{(x_1 - x_i - j \cdot a - k \cdot b_x - l \cdot c_x)^2 + (y_1 - y_i - k \cdot b_y - l \cdot c_y)^2 + (z_1 - z_i - l \cdot c_z)^2} \quad (4)$$

where x_1 , y_1 , and z_1 are coordinates of the ion at the origin (*the reference ion*); x_i , y_i , and z_i are coordinates of the neighbouring ion; i is the number of neighbouring ions in the original unit cell; j , k and l are the index number of the unit cells included the current interaction and can be $-3 \leq j \leq 3$, *etc.*; a , b and c are original unit cell parameters; b_x , c_x , b_y , c_y , and c_z are unit cell parameters of the non-orthogonal cell converted to the orthogonal coordinates (if an orthogonal unit cell is given then $b_x = 0$, $b_y = b$, $c_x = c_y = 0$ and $c_z = c$). The Madelung constant is then calculated by multiplying the electrostatic lattice energy by the distance from the ion at the origin to the nearest neighbour (denoted here as r).

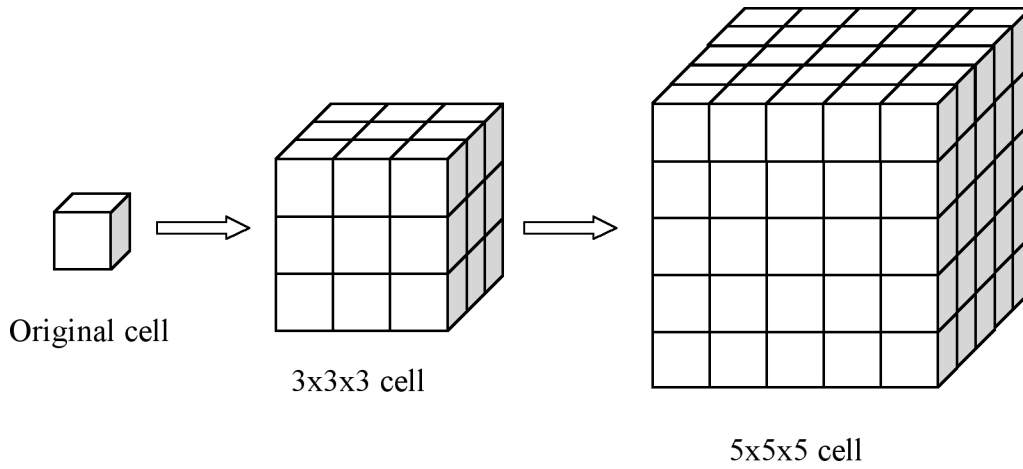


Figure S2. A schematic representation of the expansion of the original unit cell in the three dimensions (x, y and z).

The lattice is expanded out until the change in the lattice energy between successive iterations is within the tolerance threshold (e.g. 10^{-6} in $\frac{e^2}{r}$ units). Once the convergence is reached, the Madelung constant is obtained as follows:

$$M = - \frac{E_{lat}^{es} \cdot r}{|q_{cation}| \cdot |q_{anion}|} \quad (5)$$

The minus sign in equation 2 indicates that the Madelung constants are accepted to be positive (as the lattice energy is negative by default).

It should be noted that some sources report Madelung constants in other ways including either (i) with respect to the lattice parameter, a , rather than r , or (ii) as the product, $M \cdot |q_{cation}| \cdot |q_{anion}|$.

The Madelung constants are calculated for each ion in the asymmetric unit cell. The final Madelung constant of the salt is determined using a generalized expression:

$$M(\text{salt}) = \frac{1}{n+m} \left[\sum_{i=1}^n M_i^{\text{cation}} + \sum_{j=1}^m M_j^{\text{anion}} \right] \quad (6)$$

In equation 6, n is the number of cations in the asymmetric unit cell, m is the number of anions in the asymmetric unit cell, M_i^{cation} and M_j^{anion} are individual Madelung constants for each of the cations and anions, respectively.

Absolute vs. Harrison convergence

The dipole moment of the initial unit cell is computed at the beginning of the calculation. If the total dipole moment is zero, the program proceeds in the way described above, thus reaching absolute convergence. If the total dipole moment of the initial unit cell is non-zero (*e.g.* in the unit cells of ZnS, CaF₂ *etc.*), a well-known issue of conditional convergence arises (different limits depending on approach taken to summation in the calculation). The program then switches to the Harrison convergence method (for more detail see ref. 26 in the paper). The initial unit cell is still expanded the same way as shown in Figure S2 but with a new boundary condition, a sphere of radius R ; *i.e.* the program will exclude any electrostatic contribution from the ions that are found to be outside the selected sphere. This way it is ensured that the result will not suffer from conditional convergence. The summation of electrostatic interactions within a sphere leads to a net charge fluctuation that can be either positive or negative. The magnitude of the charge fluctuation also increases with increasing R . To compensate for this charge imbalance a thin shell of counter-charge Q at radius R is added in the calculation and the electrostatic contribution from this shell is computed as $-Q/R$. The calculation is performed iteratively, with the radius R changing by the step of r , the distance from the ion at the origin to the nearest neighbour. Since the result in this case tends to produce a slow oscillation towards convergence, the software calculates a moving average (and standard deviation) of the 5 most recent iterations and reports this value when the convergence condition is reached. If the convergence is not reached after 60 iterations, the calculation stops and the final Madelung constant is calculated as an average of the 5 last iterations.

Program Code

The program code for the EUGEN method is available for download from:

<http://www.chem.monash.edu/ionicliquids>

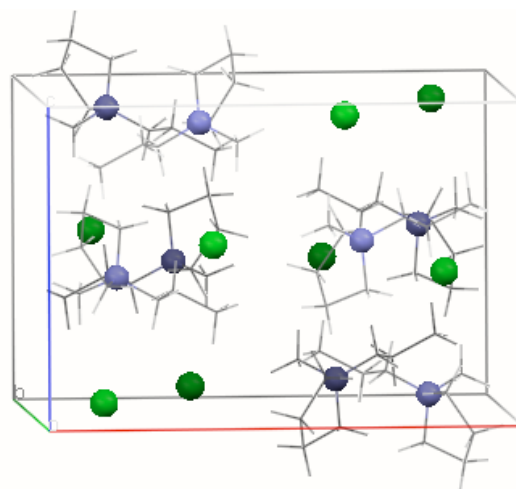
Worked Example [C₃mpyr][Cl]

Fractional coordinates of N and Cl atoms in the unit cell were obtained. Any program that allows extraction of fractional coordinates from the crystal structure can be used for this purpose. In this case, *Mercury* (the graphical user interface of the CCDC) was used. The positions of the N atoms in the C_nmpyr cations were taken as the +1 sites and the positions of the Cl atoms were taken as the -1 sites.

There were 8 anions and 8 cations within the unit cell, with only *two* ions comprising the asymmetric unit cell. Therefore, 2 input files were created, with either the anion or the cation as the reference ion. Note that the ion at the origin is the ion whose coordinates are in the fourth line of the input file. Sample input and output files are given below:

Input file - anion

```
14.5863, 13.219, 9.9779
90.,90.,90.
0.000001
0.3602, 0.8244, 0.0522, -1 (The reference ion)
0.3291, 0.8692, 0.435, 1
0.1709, 0.6308, 0.935, 1
0.8291, 0.6308, 0.565, 1
0.6709, 0.8692, 0.065, 1
0.6709, 0.1308, 0.565, 1
0.8291, 0.3692, 0.065, 1
0.1709, 0.3692, 0.435, 1
0.3291, 0.1308, 0.935, 1
0.1398, 0.6756, 0.5522, -1
0.8602, 0.6756, 0.9478, -1
0.6398, 0.8244, 0.4478, -1
0.6398, 0.1756, 0.9478, -1
0.8602, 0.3244, 0.4478, -1
0.1398, 0.3244, 0.0522, -1
0.3602, 0.1756, 0.5522, -1
```



$$a = 14.5863 \text{ \AA}, b = 13.2196 \text{ \AA}, c = 9.9779 \text{ \AA}$$

$$\alpha = \beta = \gamma = 90^\circ Z = 8$$

Output file - anion

```
Convergence criterion = 0.000001
Centre ion: 0.3602 0.8244 0.0522 -1.0
Distance to the nearest neighbour = 3.8917
Total Dipole moment of the unit cell = 0.00
ABSOLUTE convergence
```

Iteration	Number of ions	Ees	Madlung
1	144	-0.392900	-1.529052
2	666	-0.397752	-1.547934
3	1829	-0.398381	-1.550383
4	3888	-0.398631	-1.551355
5	7098	-0.398759	-1.551852
6	11717	-0.398833	-1.552139
7	18000	-0.398879	-1.552320
8	26202	-0.398910	-1.552441
9	36581	-0.398932	-1.552526
10	49392	-0.398948	-1.552588
11	64890	-0.398960	-1.552635
12	83333	-0.398969	-1.552671
13	104976	-0.398976	-1.552699
14	130074	-0.398982	-1.552722
15	158885	-0.398987	-1.552740
16	191664	-0.398991	-1.552755
17	228666	-0.398994	-1.552768
18	270149	-0.398997	-1.552779
19	316368	-0.398999	-1.552788
20	367578	-0.399001	-1.552795
21	424037	-0.399003	-1.552802

Figure S3. Orthogonal unit cell of [C₃mpyr][Cl]. One ion pair comprises the asymmetric unit.

22	486000	-0.399004	-1.552808
23	553722	-0.399006	-1.552813
24	627461	-0.399007	-1.552817
25	707472	-0.399008	-1.552821
26	794010	-0.399009	-1.552825

Madelung constant = 1.5528
Number of ions = 794010

End of the program

Hence, the Madelung constant of the anion is 1.552825.

Input file - cation

```
14.5863, 13.219, 9.9779
90.,90.,90.
0.000001
0.3291, 0.8692, 0.435, 1 (The reference cation)
0.3602, 0.8244, 0.0522, -1
0.1709, 0.6308, 0.935, 1
0.8291, 0.6308, 0.565, 1
0.6709, 0.8692, 0.065, 1
0.6709, 0.1308, 0.565, 1
0.8291, 0.3692, 0.065, 1
0.1709, 0.3692, 0.435, 1
0.3291, 0.1308, 0.935, 1
0.1398, 0.6756, 0.5522, -1
0.8602, 0.6756, 0.9478, -1
0.6398, 0.8244, 0.4478, -1
0.6398, 0.1756, 0.9478, -1
0.8602, 0.3244, 0.4478, -1
0.1398, 0.3244, 0.0522, -1
0.3602, 0.1756, 0.5522, -1
```

Output file - cation

```
Convergence criterion = 0.000001
Centre ion: 0.3291 0.8692 0.4350 1.0
Distance to the nearest neighbour = 3.8917
Total Dipole moment of the unit cell = 0.00
ABSOLUTE convergence
```

Iteration	Number of ions	Ees	Madelung
1	144	-0.391874	-1.525060
2	666	-0.390742	-1.520655
3	1829	-0.390497	-1.519701
4	3888	-0.390397	-1.519311
5	7098	-0.390346	-1.519113
6	11717	-0.390317	-1.518999
7	18000	-0.390298	-1.518927
8	26202	-0.390286	-1.518879
9	36581	-0.390277	-1.518846
10	49392	-0.390271	-1.518821
11	64890	-0.390266	-1.518803
12	83333	-0.390263	-1.518789
13	104976	-0.390260	-1.518777
14	130074	-0.390258	-1.518768
15	158885	-0.390256	-1.518761
16	191664	-0.390254	-1.518755
17	228666	-0.390253	-1.518750
18	270149	-0.390252	-1.518746
19	316368	-0.390251	-1.518743

Madelung constant = 1.5187
Number of ions = 316368

End of the program

Hence, the Madelung constant of the cation is 1.518743.

In the end the Madelung constant of the organic salt is the average of the Madelung constants of the ions in the asymmetric unit cell.

$$M(\text{salt}) = \frac{1}{2} [M^{\text{cation}} + M^{\text{anion}}] = \frac{1}{2} [1.518743 + 1.552825] = 1.5358$$

Details of crystal structures: [C₂mpyr][tos] and [C₄mpyr][tos]

1-ethyl-1-methylpyrrolidinium p-toluenesulfonate

CCDC 713020

The asymmetric unit consists of a single 1-ethyl-1-methylpyrrolidinium cation and a single *p*-toluenesulfonate anion, which lie in general positions (Figure S3). [C₂mpyr][Tos] crystallizes in a monoclinic lattice with two pairs of ions occupying the unit cell. The pyrrolidinium cation in [C₂mpyr][Tos] adopts the half-chair conformation, with bond lengths and angles within normal ranges (Allen *et al.*, 1987). Likewise for the anion all angles and bond lengths are in standard ranges with a planar aromatic ring and a distorted tetrahedral arrangement of the sulfonate group. The extended structure shows distinct zigzag-type layers of alternating anions and cations which lie in the direction of the *b* axis (Figure S4). The packed out structure consists of distinct ion pairs which interact in a parallel ring-to-ring arrangement *via* C—H \cdots π ring interactions and C—H \cdots O hydrogen bonds (Figure S5, Tables S1–S3). Furthermore to this ion pair, the sulfonate O atoms interact with five other ion-paired cations (C—H \cdots O hydrogen bonds) which results in a three dimensional lattice. Finally, an intramolecular C—H \cdots O interaction (C₂A—H₂AA \cdots O₁A, D \cdots A 2.936 (3) Å, 102 °) is seen within the anion. Several weak C—H \cdots H contacts are observed.

Experimental

Silver hydroxide was synthesized by the addition of sodium hydroxide (*ca* 2.35 g) in water (40 ml) to silver nitrate (10 g, 0.0589 g) in water (40 ml), followed by filtration and washing of the precipitated silver hydroxide with water. 1-ethyl-1-methylpyrrolidinium bromide (11.36 g, 0.0589 moles) in water (20 ml) was combined with the silver hydroxide (7.35 g, 0.0589 moles) in water (20 ml) and the precipitated silver bromide removed by filtration to yield an aqueous solution of 1-ethyl-1-methylpyrrolidinium hydroxide. An aqueous solution of 1-ethyl-1-methylpyrrolidinium hydroxide (*ca* 0.0294 moles) was combined with *p*-toluenesulfonic acid (*ca* 5.6 g, 0.0294 moles) in water (20 ml) until pH7 was obtained. The resultant 1-ethyl-1-methylpyrrolidinium *p*-toluenesulfonate was dried under vacuum and crystallized at low temperatures from an acetone solution.

Refinement

The structure was solved by direct methods and refined by full matrix least squares with anisotropic thermal parameters for all non-hydrogen atoms. The hydrogen atom positions were located in the difference Fourier map but were placed in calculated positions with isotropic temperature factors assigned at $U_{\text{iso}}(\text{H}) = xU_{\text{eq}}(\text{C})$, where $x = 1.5$ for methyl and 1.2 for all other C atoms. Refinement in a standard setting of spacegroup *Pc* was found to be unsatisfactory.

References

Allen, F. H., Kennard, O., Watson, D. G., Brammer, L., Orpen, A. G. & Taylor, R. (1987). *J.Chem.Soc.PerkinTrans.2*, pp.S1-19.

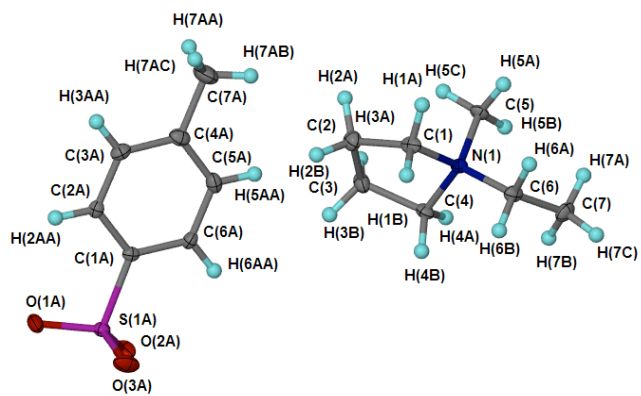


Figure S3. The asymmetric unit of $[C_2\text{mpyr}][\text{Tos}]$ shown with 50 % thermal ellipsoids, hydrogen atoms as spheres of arbitrary size and numbering scheme.

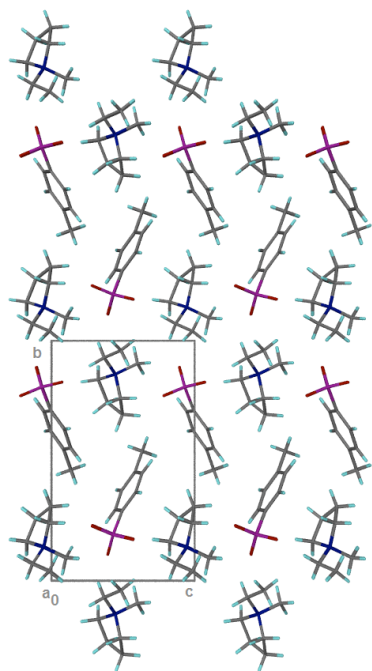


Figure S4. Stick representation of the unit cell contents of $[C_2\text{mpyr}][\text{Tos}]$ viewed down the a - axes.

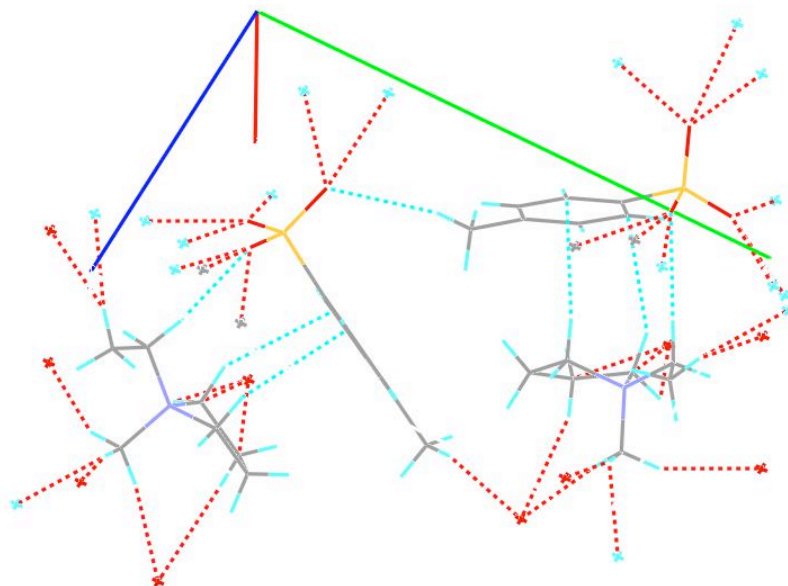


Figure S5. Schematic displaying selected intermolecular interactions within the unit cell of [C₂mpyr][Tos].

Table S1. Hydrogen-bond geometry (Å, °)

D—H \cdots A D—H H \cdots A D \cdots A D—H \cdots A

C5—H5A \cdots O1A_i 0.98 2.50 3.410 (3) 155

C5—H5B \cdots O1A_{ii} 0.98 2.42 3.393 (2) 171

C5—H5C \cdots O3A_{iii} 0.98 2.43 3.400 (2) 170

C6—H6B \cdots O2A_{iv} 0.99 2.59 3.537 (2) 160

Symmetry codes: (i) $x, y+1, z$; (ii) $x-1/2, -y+1, z+1/2$; (iii) $x+1/2, -y+1, z+1/2$; (iv) $x-1/2, -y+1, z-1/2$.

Table S2. Geometrical parameters (Å) of selected C—H \cdots O interactions.

C—H \cdots O C—H \cdots O Symmetry position of O

C7—H7C \cdots O1A 2.6035 $-1 + x, 1 + y, z$

Table S3. Geometrical parameters (Å, °) of selected inter-ring C—H \cdots π interactions. The CgJ refer to the Ring Centre-of-Gravity

X—H CgJ H \cdots Cg X—H \cdots Cg X \cdots Cg Symmetry position of CgJ

C4—H4B Cg2 3.2727 130.81 3.991 (3) $-1/2+X, 1-Y, -1/2+Z$

C7A—H7AA Cg2 3.0239 131.24 3.743 (3) $1/2+X, 1-Y, 1/2+Z$

Notes: Cg1 is the centroid of ring C1A/C2A/C3A/C4A/C5A/C6A.

1-butyl-1-methylpyrrolidinium p-toluenesulfonate

CCDC Refcode 713021

The asymmetric unit consists of a single 1-butyl-1-methylpyrrolidinium cation and a single p-toluenesulfonate anion which lie in general positions (Figure S6). [C₄mpyr][Tos] crystallizes in a triclinic lattice with two pairs of ions occupying the unit cell. The pyrrolidinium cation in [C₄mpyr][Tos] adopts the half-chair conformation, with the alkyl substituent adopting the trans configuration with a C6—C7—C8—C9 torsion angle of -171.0° . The bond lengths and angles of the cation lie within normal ranges (Allen et al., 1987), likewise for the anion all angles and bond lengths are in standard ranges with a

planar aromatic ring and a distorted tetrahedral arrangement of the sulfonate group. The extended structure show distinct zigzag-type layers of cations, alternating with linear layers of anions which lie perpendicular to the ab plane (Figure S7).

The packed out structure consists of distinct ion pairs, which interact via C—H \cdots π ring interactions and C—H \cdots O hydrogen bonds (Figure S8, Tables S4-S7). The ion pairs interacts via the anions with a direct $\pi\cdots\pi$ ring interaction and the sulfonate O atoms interact with four other ion-paired cations (C—H \cdots O hydrogen bonds) which effectively surrounds the anionic dimer with cations and thus results in a three dimensional lattice. Finally, a intramolecular C—H \cdots O interaction (C₂A—H₂AA \cdots O₃A, D \cdots A 2.917 (5) Å, 104°) is seen within the anion. Several weak C—H \cdots H contacts are observed.

Experimental

Silver hydroxide was synthesized by the addition of sodium hydroxide (ca 2.35 g) in water (40 ml) to silver nitrate (10 g, 0.0589 g) in water (40 ml), followed by filtration and washing of the precipitated silver hydroxide with water. 1-butyl-1-methylpyrrolidinium bromide (11.83 g, 0.0535 moles) in water (20 ml) was combined with the silver hydroxide (7.35 g, 0.0589 moles) in water (20 ml) and the precipitated silver bromide removed by filtration to yield an aqueous solution of 1-ethyl-1-methylpyrrolidinium hydroxide. An aqueous solution of 1-butyl-1-methylpyrrolidinium hydroxide (ca 0.02675

moles) was combined with p-toluenesulfonic acid (ca 5.08 g, 0.02675 moles) in water (20 ml) until pH7 was obtained. The resultant 1-butyl-1-methylpyrrolidinium p toluenesulfonate was dried under vacuum and crystallized at low temperatures from an acetone solution.

Refinement

The structure was solved by direct methods and refined by full matrix least squares with anisotropic thermal parameters for all non-hydrogen atoms. The hydrogen atom positions were located in the difference Fourier map but were placed in calculated positions with isotropic temperature factors assigned at $U_{iso}(H) = xU_{eq}(C)$, where $x = 1.5$ for methyl and 1.2 for all other C atoms.

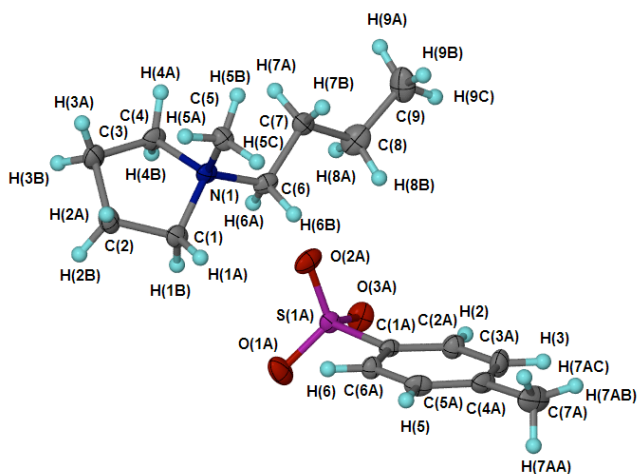


Figure S6. The asymmetric unit of [C₄mpyr][Tos] shown with 50 % thermal ellipsoids, hydrogen atoms as spheres of arbitrary size and numbering scheme.

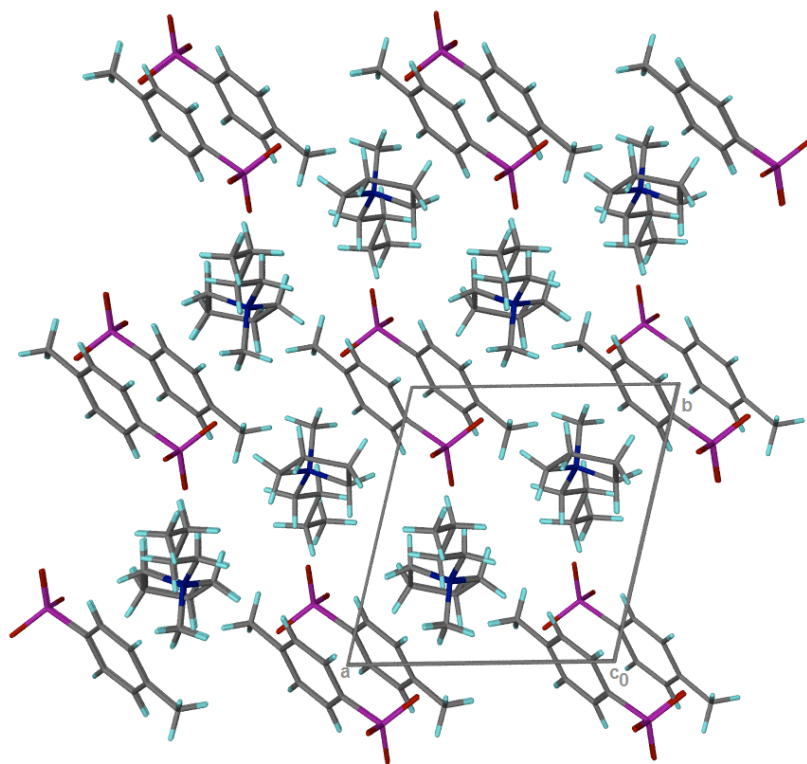


Figure S7. Stick representation of the unit cell contents of [C₄mpyr][Tos] viewed down the c- axes.

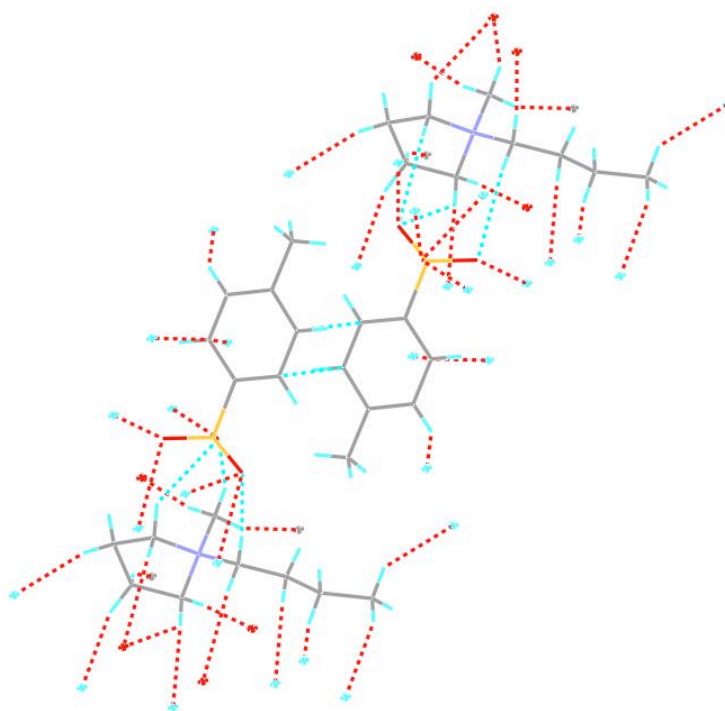


Figure S8. Schematic displaying selected intermolecular interactions for [C₄mpyr][Tos]

Table S4. Hydrogen-bond geometry (Å, °)

D—H \cdots A D—H H \cdots A D \cdots A D—H \cdots A

C1—H1A \cdots O2A 0.99 2.54 3.376 (4) 142

C4—H4A \cdots O1Ai 0.99 2.36 3.351 (5) 176

C5—H5A \cdots O2Aii 0.98 2.38 3.327 (5) 163

C5—H5C \cdots O2A 0.98 2.39 3.267 (5) 149

Symmetry codes: (i) $x+1, y, z$; (ii) $-x+1, -y, -z+2$.

Table S5. Geometrical parameters (Å) of selected C—H \cdots O interactions.

C—H \cdots O C—H \cdots O Symmetry position of O

C1—H1B \cdots O3A 2.6127 $1-x, 1-y, 2-z$

Table S6. Geometrical parameters (Å, °) of selected inter-ring C—H \cdots π interactions. The CgJ refer to the Ring Centre-of-Gravity

X—H CgJ H \cdots Cg X—H \cdots Cg X \cdots Cg Symmetry position of CgJ

C7—H7B Cg2 3.1718 136.07 3.945 (4) $1+X, Y, Z$

Notes: Cg2 is the centroid of ring C1A/C2A/C3A/C4A/C5A/C6A.

Table S7. Geometrical parameters (Å, °) of selected inter-ring π — π interactions. α is the dihedral angle between planes I and J, CgI

is the centroid of plane I and CgJ the centroid of plane J.

CgI CgJ Cg \cdots Cg α Symmetry position of CgJ

Cg2 Cg2 4.239 (2) 0.00 $-X, -Y, 1-Z$

Notes: Cg2 is the centroid of ring C1A/C2A/C3A/C4A/C5A/C6A.