The Madelung Constant of Organic Salts

Ekaterina I. Izgorodina,* Uditha L. Bernard, Pamela M. Dean, Jennifer M. Pringle, and Douglas R. MacFarlane*

School of Chemistry, Monash University, Clayton, Victoria 3800, Australia

Received June 11, 2009; Revised Manuscript Received August 18, 2009

ABSTRACT: The Madelung constant is a key feature determining the lattice energy of a crystal structure and hence its stability. However, the complexity of the calculation has meant that it has previously not been readily available for complex structures, for example for organic salts. We propose a new robust method for calculating Madelung constants of such structures based on a generalized numerical direct summation approach. The method is applied to various organic salts from the ionic liquid and pharmaceutical fields. The electrostatic energy contribution to the lattice energy derived from these Madelung constants is compared with a variety of inorganic salts and the relative importance of electrostatic interactions is discussed.

The idea of the Madelung constant as a measure of the net electrostatic interaction energy, \( E_{\text{es}} \), in ionic solids was introduced by Madelung in 1918.\(^1\) He summed all electrostatic interactions experienced by an ion in the crystal structure and then expressed the total as

\[
E_{\text{es}} = \frac{M q_{\text{cation}} q_{\text{anion}}}{4\pi\varepsilon_0 d_{\text{min}}} \tag{1}
\]

where \( d_{\text{min}} \) is the distance to the nearest counterion. If one considers the electrostatic binding energy of a single ion pair to be \( E_{\text{IP}}^{\text{IP}} \) then \( E_{\text{es}} = M E_{\text{IP}}^{\text{IP}} \) and hence \( M \) represents the degree to which the lattice of ions is more stable than the isolated collection of ion pairs would be. For stable crystal structures \( M > 1 \) and the larger \( M \) is, the more stable the crystal structure will be. For simple inorganic salts \( E_{\text{es}} \) makes up a large part of the lattice energy, \( U_L \), of the salt:

\[
U_L = E_{\text{es}} + E_{\text{SR}} \tag{2}
\]

where \( E_{\text{SR}} \) is the energy of short-range interactions including atom–atom repulsive interactions. In the case of organic salts, these short-range interactions include a number of important attractive components including, for example, \( \pi-\pi \) interactions, hydrogen bonding, and van der Waals interactions.

The Madelung constant can in principle always be calculated by choosing an ion as the origin and then summing all possible electrostatic interactions with surrounding ions at increasing distances from the origin. An (effectively) infinite series of contributions, the Madelung series, is generated in which each term represents electrostatic interactions with ions at a particular distance from the origin. Since Madelung’s original work, most of the calculations have followed the same direct summation approach aiming to generate a series expansion for the Madelung constant, which converges to a general method of calculating the Madelung constant directly from a known crystal structure. We describe here the basis of the approach we have developed and a number of example calculations for organic salts of interest in both the ionic liquid and pharmaceutical fields. The electrostatic energy contribution to the lattice energy derived from these Madelung constants is compared with a variety of inorganic salts and the relative importance of electrostatic interactions is discussed.

The much-discussed Madelung constant is an important fundamental aspect of our understanding of the solid state. It describes the total interaction energy of an ion in a crystalline lattice, with all of the other ions, and hence provides us with an understanding of the origins of the lattice energy of an ionic crystal. The Madelung constant of various simple inorganic salts has been the focus of much attention for nearly 100 years and a variety of approaches to its calculation have been developed.\(^1\)–\(^14\) However, these approaches are not easily generalized to provide a mechanism for the calculation of the Madelung constant of more complex ionic crystals, for example, organic salts, and hence the detailed understanding that it provides is largely lacking in respect of such crystals. On the other hand, complex organic salts have become a major area of interest in recent years for a variety of reasons. For example, about 50% of known pharmaceutical compounds are produced as organic salts\(^15\) and their solid-state phase behavior in terms of polymorphism is of very great concern from the point of view of stability and bioavailability.\(^16\) In a different arena, the field of ionic liquids has generated a huge range of new organic salts\(^17\)–\(^20\) and an intense interest in understanding and predicting the melting points of these salts.\(^21\)–\(^22\) As an offshoot of that field, a number of these salts exhibit plastic phases in their crystalline state and these are of growing interest as solid-state ion conductors.\(^23\)

The phase behavior of these organic compounds is often a subtle combination of long-range and short-range interactions. The short-range interactions are relatively easy to identify and understand when a crystal structure is available. Tools such as the Hirshfeld surface have been of great assistance in this respect.\(^24\) However, the long-range interactions are electrostatic and to understand their relative importance one effectively needs to be able to obtain the Madelung constant for the crystal structure.\(^25\) Hence, as part of our effort in designing and understanding the properties of organic salts for a variety of applications, we sought to develop a

*Corresponding authors. E-mail: katya.izgorodina@sci.monash.edu.au (E.I.I.) d.macfarlane@sci.monahs.edu.au (D.R.M.). Tel.: +61-3-9905-8639 (E.I.I.), +61-3-9905-4540 (D.R.M.). Fax: +61-3-9905-4597.
Article

Crystal Growth & Design, Vol. 9, No. 11, 2009 4835

Table 1. Melting Points (T_m), Number of Ions, Calculated and Literature Madelung Constants (M) and Electrostatic Energy Densities (EED) of Traditional Crystals Together with Number of Ion Pairs in the Unit Cell (N), Crystal Structure Type and Space Group

<table>
<thead>
<tr>
<th>salt</th>
<th>T_m</th>
<th>N</th>
<th>crystal type</th>
<th>space group</th>
<th>number of ions</th>
<th>M</th>
<th>M (literature)</th>
<th>EED × 10^3 J/m^3</th>
<th>source of crystal structure</th>
</tr>
</thead>
<tbody>
<tr>
<td>ZnS</td>
<td>1700</td>
<td>4</td>
<td>cubic</td>
<td>P3m1</td>
<td>1.4 x 10^4</td>
<td>1.640 ± 0.006</td>
<td>1.638 ± 0.002</td>
<td>-3899.2 ± 1633</td>
<td>38</td>
</tr>
<tr>
<td>CaF_2</td>
<td>1418</td>
<td>4</td>
<td>cubic</td>
<td>Fm3m</td>
<td>2.1 x 10^4</td>
<td>2.524 ± 0.010</td>
<td>2.519 ± 0.010</td>
<td>-2974.1 ± 1213</td>
<td>38</td>
</tr>
<tr>
<td>CsCl</td>
<td>877</td>
<td>2</td>
<td>orthorhombic</td>
<td>Fm3m</td>
<td>1.1 x 10^4</td>
<td>2.364 ± 0.005</td>
<td>2.365 ± 0.005</td>
<td>-2432.6 ± 477</td>
<td>40</td>
</tr>
<tr>
<td>NaCl</td>
<td>801</td>
<td>4</td>
<td>cubic</td>
<td>Fm3m</td>
<td>1.8 x 10^4</td>
<td>1.7467 ± 0.010</td>
<td>1.7467 ± 0.010</td>
<td>-586.2 ± 318</td>
<td>38</td>
</tr>
<tr>
<td>CsCl</td>
<td>645</td>
<td>1</td>
<td>cubic</td>
<td>Pmn2_1</td>
<td>3.5 x 10^4</td>
<td>1.768 ± 0.007</td>
<td>1.7627 ± 0.007</td>
<td>-690.0 ± 136</td>
<td>38</td>
</tr>
<tr>
<td>[NMEm][BF_4]</td>
<td>443</td>
<td>2</td>
<td>tetragonal</td>
<td>P4/nmm</td>
<td>8.0 x 10^4</td>
<td>1.6859 n/a</td>
<td>1.6859 n/a</td>
<td>-489.6 ± 40.8</td>
<td>42</td>
</tr>
<tr>
<td>[Cmpyr][Cl]</td>
<td>245</td>
<td>8</td>
<td>orthorhombic</td>
<td>Pbcn</td>
<td>1.7 x 10^4</td>
<td>1.5358 n/a</td>
<td>1.5358 n/a</td>
<td>-549.9 ± 38.0</td>
<td>44</td>
</tr>
<tr>
<td>[Mep][Sac]</td>
<td>188</td>
<td>4</td>
<td>orthorhombic</td>
<td>P2_1_2_1_1</td>
<td>2.0 x 10^4</td>
<td>1.8141 n/a</td>
<td>1.8141 n/a</td>
<td>-406.0 ± 10.9</td>
<td>45</td>
</tr>
<tr>
<td>[Prop][Br]</td>
<td>167</td>
<td>8</td>
<td>tetragonal</td>
<td>P4/n</td>
<td>5.4 x 10^4</td>
<td>1.4857 n/a</td>
<td>1.4857 n/a</td>
<td>-451.7 ± 13.2</td>
<td>45</td>
</tr>
<tr>
<td>[Cmpyr][NTf_2]</td>
<td>132</td>
<td>4</td>
<td>monoclinic</td>
<td>P2_1_1</td>
<td>8.9 x 10^4</td>
<td>1.3583 n/a</td>
<td>1.3583 n/a</td>
<td>-416.6 ± 18.6</td>
<td>47</td>
</tr>
<tr>
<td>[Cmpyr][tos]</td>
<td>120</td>
<td>2</td>
<td>monoclinic</td>
<td>Pn</td>
<td>2.4 x 10^4</td>
<td>1.408 ± 0.004</td>
<td>1.408 ± 0.004</td>
<td>-519.5 ± 22.4</td>
<td>49</td>
</tr>
<tr>
<td>[Cmpyr][tos]</td>
<td>115</td>
<td>4</td>
<td>triclinic</td>
<td>P</td>
<td>1.0 x 10^3</td>
<td>1.2963 n/a</td>
<td>1.2963 n/a</td>
<td>-504.1 ± 19.1</td>
<td>49</td>
</tr>
<tr>
<td>[Ccamim][Cl]</td>
<td>65</td>
<td>4</td>
<td>orthorhombic</td>
<td>Pna2_1</td>
<td>4.7 x 10^4</td>
<td>1.379 ± 0.004</td>
<td>1.379 ± 0.004</td>
<td>-474.2 ± 32.8</td>
<td>50</td>
</tr>
<tr>
<td>[Ccamim][Cl]</td>
<td>41</td>
<td>4</td>
<td>monoclinic</td>
<td>P2_1_1</td>
<td>2.4 x 10^4</td>
<td>1.3447 n/a</td>
<td>1.3447 n/a</td>
<td>-450.3 ± 31.0</td>
<td>50</td>
</tr>
<tr>
<td>[Cmpyr][NMe_3]</td>
<td>40</td>
<td>4</td>
<td>monoclinic</td>
<td>P2_1_1</td>
<td>3.4 x 10^4</td>
<td>1.1932 n/a</td>
<td>1.1932 n/a</td>
<td>-413.5 ± 21.7</td>
<td>52</td>
</tr>
<tr>
<td>[Cmpyr][NMe_3]</td>
<td>36</td>
<td>8</td>
<td>orthorhombic</td>
<td>Pbcn</td>
<td>3.5 x 10^4</td>
<td>1.1639 n/a</td>
<td>1.1639 n/a</td>
<td>-424.9 ± 17.9</td>
<td>52</td>
</tr>
<tr>
<td>[Cmpyr][NTf_2]</td>
<td>-18</td>
<td>4</td>
<td>orthorhombic</td>
<td>P2_1_2_1_1</td>
<td>5.6 x 10^4</td>
<td>1.2854 n/a</td>
<td>1.2854 n/a</td>
<td>-423.1 ± 15.5</td>
<td>53</td>
</tr>
</tbody>
</table>

Abbreviations have the following meanings: C_aMpyr = (C_4-alkyl)methylpyrrolidinium, C_aMmim = butylmethylimidazolium, Mep = mepenzolate, Prop = propanethiolate, Sac = succinate, Sac = tosylate, Mes = CH_3SO_3, TF = CF_3SO_3. Structures of the propylthiole and mepenzolate ions are shown in Figures 2 and 3. Number of ions needed in the calculation to reach convergence of the lattice energy using the EUGEN method. Cases where the unit cell has a nonzero dipole moment and therefore convergence reached using the Harrison method. DSC measurements carried out from −150 to 150 °C at a scan rate of 10 °C min^-1. Onset temperatures are reported in all cases. A broad peak characteristic of plastic crystal transitions.

Limit. Emersleben developed two approaches to these direct summation calculations: (1) by considering ever expanding cubes and (2) by considering ever expanding spheres with respect to the ion at the origin. However, the direct summation approach becomes intractable for all but the simplest of inorganic salt structures. There are two ways to overcome this problem: the Ewald method and the Evjen method. However, in both methods the sum representing the net electrostatic interactions is conditionally convergent, which means that the result depends on the order of summation if the unit cell possesses a nonzero dipole moment. A discussion of such calculations and the various corrections required can be found in the work of Wood. Neither of these methods has made the evaluation of the Madelung constant straightforward and able to be carried out in a generic way, with a number of factors affecting the outcome of the calculations. To improve convergence, modifications to both methods have been thoroughly studied and introduced. Among the simplest and easily achievable technique is the method introduced by Harrison. Importantly, this method does not suffer from conditional convergence like the Ewald and Evjen methods; that is, it always converges to the correct Madelung constant.

In this work, we describe a generic approach to calculating the Madelung constant that involves a direct numerical summation, and which can therefore be used even with the complex crystal structures that occur with organic salts. In principle, it can be used to obtain the Madelung constant for any known crystal structure including nonorthogonal unit cell structures and those containing more than one ion pair in the asymmetric unit, all very common circumstances. The approach could be integrated into standard crystallography or crystal structure display software. The unit cells can be of any shape: cubic, orthorhombic, monoclinic, etc., and contain an unlimited number of ion pairs. In this sense, the proposed method can be considered as an expanding unit-cells generalized numerical method, which we refer to as the EUGEN method. We demonstrate the convergence and accuracy of the EUGEN calculation for known crystal structures such as NaCl, body-centered cubic CsCl, CaF_2, ZnS, and CaCl_2 and also calculate, for the first time, Madelung constants of selected examples of organic salts of interest in the ionic liquid/plastic crystal field and the pharmaceutical salt field.

Results

Accuracy and Convergence. The Madelung constants calculated for a number of simple inorganic and organic salts are compared in Table 1. The crystal structures of the two tosylate salts are described here for the first time (CCDC Refcodes: 713020 for [C_mpyr][tos] and 713021 for [C_mpyr][tos]). The comparison in Table 1 shows that the values calculated for the Madelung constants of ZnS, CaF_2, CaCl_2, NaCl, and CsCl using the EUGEN method are in excellent agreement with values reported in the literature. In the case of the organic salts convergence typically requires 24 iterations on average. The selected convergence threshold corresponds to only 1 x 10^-3 J mol^-1 in the lattice energy. Loosening the threshold to 1 kcal mol^-1 (traditionally considered to be “chemical accuracy”) further shortens the calculation time. Nonetheless, the calculation for even the most complex crystal structures in Table 1 still only requires a few minutes on a laptop computer.

Organic Salt Madelung Constants. The organic salts studied here are comprised of singly charged ions and, therefore, a direct comparison with the Madelung constants of NaCl and CsCl can be made. The Madelung constants of all of the organic salts studied here are lower, in some cases considerably so, than those of NaCl and CsCl, which is in accord with their much lower melting points. For example, salts such as [C_mpyr][NMe_3], [C_mpyr][NMe_3], and [C_mpyr][NTf_2], with melting points below 100 °C, have Madelung constants at least 25% lower than that of NaCl. The arrangement of ions in the unit cell with respect to one another is a major factor in determining the Madelung constant of the organic salts, much more so than is the case for the inorganic salts. For example, [NMMe][BF_4], Figure 1, crystallizes in a cubic system with very uniformly arranged positions of the ions with respect to all of their neighbors. To simplify inspection of the structure, we show in Figure 1 a version in which only the
As a result of the highly symmetrical packing the Madelung constant, at 1.69, is only very slightly lower than that of NaCl ($M = 1.7476$) or CsCl ($M = 1.7627$). On the other hand, Figure 2 shows the structure of propantheline bromide ([Prop][Br]); this compound is a muscarinic acetylcholine receptor antagonist sold under the trade name Pro-Banthine. Figure 2b shows that the charged atoms are positioned in clusters in the unit cell, with distinct ion-pairing also present (i.e., one counterion in much closer proximity than any other). This lowers the Madelung constant considerably, to 1.49. To put this effect in context, a tight ion pair that is well isolated in a large neutral species from neighboring ion pairs could have a Madelung constant approaching 1.0. This situation is illustrated to an extent by mepenzolate saccharinate ([Mep][Sacc]) in Figure 3; the mepenzolate cation is a skeletal muscle relaxant sold commercially as the Br$^-$ salt under the trade name Cantil. In this structure, we see more distinct ion pairs and a correspondingly lower Madelung constant of 1.18. The fact that this compound has a melting point as high as 188°C, despite this very low Madelung constant, is a clear sign of the strong anion–cation $\pi-\pi$ stacking that is present in this salt.

For ionic liquids containing the same anion and the cation with the alkyl chains of different length we can easily discern that the melting point decreases in accord with the Madelung constant decrease. For example, this trend is observed for the following pairs of ILs: (1) [C$_1$mpyr][NMes$_2$] and [C$_4$mpyr][NMes$_2$] and (2) [C$_1$mpyr][NTf$_2$] and [C$_4$mpyr][NTf$_2$]. However, comparison of the two pairs with each other shows that the Madelung constant of [C$_4$mpyr][NTf$_2$] is larger than...
that of \([C_{4}mpyr][NMe_3]_2\) and yet the melting point of the former is lower by about 50 degrees. This finding further reinforces the importance of additional specific interactions (such as hydrogen bonding, van der Waals interactions, \(\pi-\pi\) stacking interactions etc.) in the lattice energy, \(U_L\), of the salt. Therefore, accurate estimation of these interactions is needed before a correlation between \(U_L\) and the melting point can be established.

Also listed in Table 1 is the electrostatic contribution, \(E_{es}\), to the lattice energy calculated from the Madelung constant using eq 1. The values for the inorganic structures range from more than 1000 kJ/mol for the divalent metal salts, to values around 800 kJ/mol for NaCl. The values for the organic salts are typically much lower than these, reflecting the lower electrostatic interaction involved.

**Charge Delocalization.** Charge delocalization in molecular ions potentially places fractional charges on several atoms. This effect is relatively easy to deal within the EUGEN method if the details of the charge delocalization are known, or can be estimated. The case of the tosylate anion illustrates the simplest approach; the value listed in Table 1 is the average of the Madelung constants calculated by assuming that the unit negative charge is present on each of the oxygens in turn, producing values: 1.387, 1.500, and 1.338. A more sophisticated approach would place partial charges on the three oxygens simultaneously and we will address this approach in a future paper. The fact that the effective Madelung constants of the three oxygens in the lattice are so different indicates that they experience quite different electrostatic environments and one of the oxygens in particular (O3 in Figure S3, Supporting Information) experiences more attraction than the others. This may itself have an impact on the actual electron distribution in the ion within the crystal and the electric field vector, which is implicitly obtainable from the EUGEN method, could be used in an advanced quantum chemical calculation to further investigate this effect.

**Polymorphism.** The Madelung constant itself is effectively a geometric parameter. While each space group will have a unique Madelung constant associated with it when the structure involves close packed ions, this will not necessarily be true where the ions are molecular species. Two salts crystallizing in the same space group may have different Madelung constants if the charged atoms have different locations in the molecular ions. For organic salts, then, the Madelung constant is very much a unique feature of each individual compound. Where polymorphism exists for an organic salt, each polymorph will also very likely have a different Madelung constant. The change in lattice energy that the change in Madelung constant describes therefore becomes an important aspect of understanding the phase

---

**Figure 3.** Packing diagrams for [Mep][Sac] as viewed down the \(a\)-axis showing (a) full unit cell contents and (b) charged atoms only (the negatively charged center is shown as a larger symbol to indicate the fact that the charge is likely to be delocalized to some extent in this anion).
whereas for magnitude lower than those of the inorganic salts, falling in the range of 1.16 to 1.69. Organic salts with highly symmetrical packing, such as [NMMe][BF4], can display Madelung constants almost as high as that of NaCl. On the other hand, distinct ion pairing in a crystal, as observed in the crystal structure of [Mep][Sac], results in a considerable decrease of the Madelung constant, approaching 1.0. The Madelung constants calculated are currently only a first approximation, however the EUGEN approach paves the way for more advanced calculations, which might properly account for any charge delocalization in the ions or the effective screening of electrostatic interaction by other regions of the molecule.

Discussion

The Madelung constant allows us to calculate an electrostatic energy density (EED) for the structure:

$$EED = \frac{E_{\text{es}} N}{V} \ (J/m^3)$$

where $V$ is the unit cell volume and $N$ is the number of ion pairs in the unit cell. The EED values are also reported in Table 1. For most salts the EED makes up a large part of the lattice energy (expressed in unit volume terms) of the structure, and therefore it is a useful quantity for direct comparison of different compounds or different polymorphs of the same compound. This quantity is a more comprehensive measure of electrostatic interactions in a material, because it takes account of the very different concentrations of charged species (i.e., number of ions per unit volume) that can occur when comparing inorganic and various, much larger, organic ions. The EED values of the organic salts in Table 1 are as much as 2 orders of magnitude lower than those of the inorganic salts, whereas $E_{\text{es}}$, which is a molar quantity, varies by only about 1 order of magnitude. In general, the EED trend also shows a fairly good correlation with melting point until it drops to around $20 \times 10^3 \ J/m^3$, where undoubtedly short-range interactions begin to make an important contribution to the lattice energy.

In general, due to the nature of most organic salts, such short-range interactions make a more significant contribution to the total lattice energy than in inorganic salts. For example, the attraction due to electron correlation between imidazolium rings is about 28 kJ mol$^{-1}$ (as estimated at the CCSD(T) level of theory), which is a non-negligible contribution to the total lattice energy of salts based on this cation, for example, the C$_2$mpyr salts in Table 1. Since the type of interactions present in a particular organic salt depends very much on the nature of the constituting ions, approaches to their quantification, of the type being intensely investigated in the computational chemistry field, are needed if a complete picture of the lattice energy is to be achieved.

A “second order” issue that exists in all approaches to calculating long-range electrostatic interactions can also be dealt with by an appropriate expansion of the EUGEN code presented here. The Madelung constant is normally calculated on the basis that the electrostatic interaction between two ions occurs through a medium of dielectric constant equal to 1. In a real ionic material, including NaCl, this is plainly not the case, since ions/atoms of varying polarizability may lie between the interacting ions. In the classical Madelung analysis and all of the more modern approaches to the calculation, including the Ewald summation, this is ignored, partly on the basis that the attractive and repulsive interactions are equally affected. In a material consisting of mainly organic cations and anions this issue becomes more acute since some of the interactions may take place through regions of, for example, hydrocarbon chains; the assumption that the material is isotropic also does not necessary hold. Measurements and investigations of the components of dielectric constants in organic liquids and solids are ongoing in several groups and will assist in exploring this issue further. However, the EUGEN approach allows this issue to be explicitly accounted for in the calculation by inclusion of different values for the average dielectric constant, or potentially a spatially varying dielectric constant.

Conclusions

In this paper, we have introduced an expanding unit-cells generalized numerical (EUGEN) method for the calculation of the Madelung constants of salts with a known crystal structure. The approach has been validated against Madelung constants available in the literature for inorganic salts. Madelung constants of a number of organic salts of interest in the ionic liquid/plastic crystal and pharmaceutical fields are reported here for the first time and it was shown that the values were lower than those of the inorganic salts, falling in the range of 1.16 to 1.69. Organic salts with highly symmetrical packing, such as [NMMe][BF4], can display Madelung constants almost as high as that of NaCl. On the other hand, distinct ion pairing in a crystal, as observed in the crystal structure of [Mep][Sac], results in a considerable decrease of the Madelung constant, approaching 1.0. The Madelung constants calculated are currently only a first approximation, however the EUGEN approach paves the way for more advanced calculations, which might properly account for any charge delocalization in the ions or the effective screening of electrostatic interaction by other regions of the molecule.

Methods

Expanding Unit-Cells Generalized Numerical (EUGEN) Method.

A detailed discussion of the method and the implemented code are provided in the Supporting Information. The method requires a fully solved crystal structure as input data, from which a list of the fractional coordinates of all of the charged atoms in the unit cell has been produced. The calculation then proceeds in a series of iterations involving a larger number of ions at each step. At the $n$th iteration, the calculation constructs an expanded cell containing $n$ replicates of the unit cell along each of the unit cell directions. It then sums all of the pairwise interactions between each ion in the expanded cell and the central ion. It continues expanding the calculation cell until convergence is reached. As is well-known, such a calculation is conditionally convergent if the unit cell possesses a nonzero dipole moment, this occurs occasionally in organic salt crystal structures. The calculation checks for this property and, when present, adopts the Harrison approach to achieving convergence. Since the result in this case tends to produce a slow oscillation toward convergence, the software calculates a moving average (and standard deviation) of the five 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.

Acknowledgment. We gratefully acknowledge generous allocations of computing time from the National Facility of the National Computational Infrastructure. E.I.I. gratefully acknowledges the support of the Australian Research Council for her postdoctoral fellowship, as does D.R.M. for his Federation Fellowship.

Supporting Information Available: The supporting information contains a thorough description of the EUGEN method as well as the program that implements this method. Examples of the input files needed to run the program are also given. In addition, the supporting information provides details of the crystal structures, [C$_4$mpyr][ilos] and [C$_4$mpyr][ilos], reported here for the first time.
The program code (written in Fortran 95) for the EUGEN method is available for download from http://www.chem.monash.edu/ionicliquids. This material is available free of charge via the Internet at http://pubs.acs.org.

References

(3) Emersleben, O. Naturwissenschaften 1959, 46, 64–65.
(49) Dean, P. M.; Pringle, J. M.; MacFarlane, D. R. Both tosylate-based ionic liquids were deposited at the Cambridge Crystallographic Data Centre, the reference codes are CCDC 713020 & 713021, 2008.