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Molecular mechanics simulations of charge-transfer molecular superconductors

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We report a detailed computational lattice statics study of the organic superconducting charge-transfer BEDT-TTF salts, using molecular mechanics methods. Our calculations show that standard, transferable forcefields yield accurate crystal structures for these complex materials within the constant volume regime.

Introduction

The construction of lattices created from molecular building blocks has been the focus of considerable synthetic as well as theoretical endeavour over the last 25–30 years. The potential for the incorporation of unusual electrical, magnetic, optical and structural properties in materials that can display very different features compared to conventional continuous lattices has driven this effort. One area that has provided many examples of materials with varying physical properties are organic charge-transfer (CT) salts. They exhibit the electrical properties of metals even though they often contain no metals in the electrical conducting framework. Simulations can provide an understanding at the atomic level of the complex interactions involved in these types of systems and allow different building blocks to be tested quickly and easily.

There are many examples of the simulation of extended lattices using energy minimisation methods, but more commonly simple ionic or semi-ionic systems (zeolites *e.g.* silicates) have been considered. Atomistic calculations allow the exploration of the structure of very large systems that are beyond the capability of *ab initio* calculations. Along with structural information, the effect of bonding *versus* cohesion, lattice vibrations, phase transitions and dynamics can be extracted from molecular mechanics simulations. In this paper the applicability of molecular mechanics methods to the study of the BEDT-TTF family of charge-transfer salts will be examined.

BEDT-TTF, first synthesised by Mizuno *et al.*[1] (Fig. 1) has been extensively studied as it is the organic component of a large family of superconducting molecular charge-transfer salts. Lying on the borderline between localisation and delocalisation in their long-range order means that low dimensional molecular charge-transfer salts exhibit many more physical properties than the phenomenon of superconductivity. The materials show a large range of electronic and magnetic states; and this diversity of behaviour is one of the attractive features of these systems. It is possible to grow large single crystals with relative ease, which allows the study of many physical aspects, which are simplified, in low dimensional materials. Within the field of molecular chemistry there are many permutations of different molecular components that are used in synthesis and a great number of structures can be produced which allows systematic variation of certain characteristics by normal chemical means.

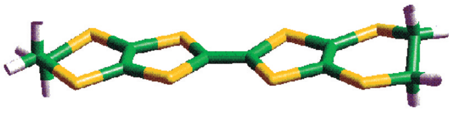

Fig. 1 BEDT-TTF [bis(ethylenedithio)tetrathiafulvalene] ($C_{10}S_8H_8$).

An important structural feature of these systems, based on the donor molecule BEDT-TTF, is the separation of the organic cations and the inorganic anions into alternating layers and stacks. As a consequence, there are many different lattice packings of BEDT-TTF, resulting in a wide range of physical properties.

The ability to predict lattice packing would clearly be of value. In view of the size and complexity of the unit cells of these systems there is a strong incentive for the application of interatomic potential (or forcefield) methods. The neutral BEDT-TTF molecular crystal has four BEDT-TTF molecules per unit cell, *i.e.* 104 atoms per unit cell and the ability of various forcefields to reproduce the experimental crystal structure is examined first in this paper. BEDT-TTF[$FeBr_4$] is the smallest salt with 62 atoms in the unit cell: next therefore, both constant volume and constant pressure energy minimisation calculations are reported on the system, before moving to constant volume calculations of larger systems, for example BEDT-TTF_2[$Cr(NCS)_4(NH_3)_2$], which has 292 atoms per unit cell. Our calculations demonstrate the viability of general purpose transferable potentials for modelling these complex materials.

Methodology

The first important issue to confront is the selection of a forcefield that will satisfy our requirements. There are many forcefields available to the computational chemist, but the majority are parameterised for application to specific systems, for example the forcefields GROMOS, AMBER for biomolecules or those of Sauer *et al.*,[2–4] which were parameterised to allow investigation of silicate fragments and silicate extended frameworks. Our interest is in molecular crystals containing many different types of anions, (*e.g.* linear I_3^-, tetrahedral $FeBr_4^-$ and octahedral metal centres and their ligands), and solvents, such as pyridine, which act as spacers between the BEDT-TTF stacks or layers. Therefore, a forcefield is required that will allow the study of systems containing different types of interatomic potentials for transition metals and heavy elements, such as bromine and iodine. We have found that the most appropriate forcefield is ESFF (extended systematic forcefield),[5] which offers a broad coverage of the periodic table, in combination with the minimisation engine Discover3,[5] which uses periodic boundary conditions to simulate an extended lattice.

In order to cover a broad range of atom types ESFF was

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developed in an extensible and systematic manner. To prevent the number of required parameters being too large, the forcefield employs semi-empirical rules to translate atomic based parameters to interatomic potentials. Valence bond, angle, torsion and out of plane angle energies are used to describe the internal interactions and van der Waals and electrostatic energies represent the non-bonded interactions. As a wide range of systems can be considered, large deviations in bond lengths and angles for equilibrium structures can be observed. A Morse function is used for bonding interactions and a truncated cosine series for angles.

The ESFF forcefield makes use of two sources of information to generate the atom type parameters: firstly, *ab initio* calculations and secondly, experimentally determined crystal structures. The basic *ab initio* parameters: electronegativity, hardness and ionisation potential are calculated for the elements of the first three rows of the periodic table, with information supplied about orbital hybridisation and the distribution of valence electrons in the hybridised orbitals. The atomic van der Waals parameters and field factors (required for the electronegativity equalisation method used to calculate atomic charges, described below) are determined by fitting the lattice cell vectors of the crystal structure while the internal coordinates are constrained. ESFF then employs semi-empirical rules to translate the atomic based parameters to parameters typically associated with a covalent forcefield.[6,7] Another example of a rule based forcefield, is the universal forcefield (UFF), which has atomic parameters for the whole of the periodic table.[8–12] Although UFF is similar in design to ESFF, it has more general rules and therefore less accuracy. ESFF combines rules in series rather than using a single rule, to cope with the complexity of the underlying physics. For further details of the ESFF methodology and its application see the work of Barlow *et al.*[6]

An atomic point charge model is used in ESFF. The atomic partial charges are calculated from *ab initio* computed atomic parameters, electronegativities (χ) and hardness (η), by using the rules of group and local electronegativity equalisation.[13–15] The partial charges are determined by minimising the energy with respect to the charges under the constraint that the sum of the charges is equal to the net charge on the molecule; these charges are then fixed for the calculation.

The description of the electrostatics provided by partial atomic charges is widely used but for some systems, such as those containing lone pairs or π-aromatic rings, the description is insufficient, since the partial atomic charge model constrains the charge density to be spherically symmetric, whereas valence electrons are often far from symmetric in distribution. Improvements therefore involve distributing charges, dipoles, quadrupoles and other higher multipoles at points about the molecule not just at atomic sites. For an example of the application of this method see ref. 16.

It was found that the only method of applying the non-bonding terms (electrostatic and van der Waals), that produced satisfactory results, was the Ewald summation. The other methods (atom, group or cell based) available in the Discover3 minimisation engine for the calculation of the non-bond terms lead to poor reproduction of the crystal structure.

We need to make detailed comparison of calculated and experimental crystal structures, lattice parameters, bond lengths, and, for relevant calculations, energetics; root mean square deviations have been used as a representation of the quality of reproduction of these quantities.

Results

As mentioned above, the applicability of the ESFF forcefield to reproduce accurately the BEDT-TTF neutral molecular crystal is appraised before moving to more complex systems where charge transfer occurs. Constant volume and constant pressure calculations are reported for the BEDT-TTF[FeBr$_4$] salt. An additional complexity in the modelling of these systems is introduced when there are cations with fractional charges; as examples of such materials BEDT-TTF$_2$[FeCl$_4$] and BEDT-TTF$_2$[I$_3$] are considered. Finally the BEDT-TTF$_2$[Cr(NCS)$_4$-(NH$_3$)$_2$] salt, which has 292 atoms in a unit cell, is simulated.

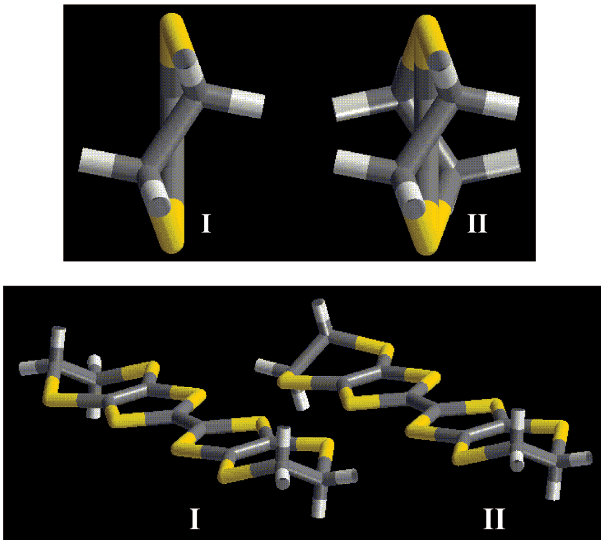

Fig. 2 Top and bottom: molecule I is in the eclipsed conformation while molecule II is in the staggered conformation.

Constant volume calculations of neutral BEDT-TTF

Before examining the charge-transfer salts of BEDT-TTF, the ability of ESFF to model the neutral BEDT-TTF crystal has been compared with three of the popular organic materials forcefields, namely CVFF,[17] CFF91[18,19] and PCFF,[2,20–22] although we would be unable to use them for calculations on BEDT-TTF salts as they do not have atom types for the inorganic anions.

The neutral BEDT-TTF molecular crystal contains four BEDT-TTF molecules in a conventional unit cell, with a single molecule per asymmetric unit, see Fig. 3 below. The structure of neutral BEDT-TTF is unlike other BEDT-TTF salts: as no charge transfer occurs, the molecules are warped, with one of the terminal ethylene groups having the boat conformation, rather than the two possible twist conformations, see Fig. 2, (which have been shown to be of lower energy when molecular

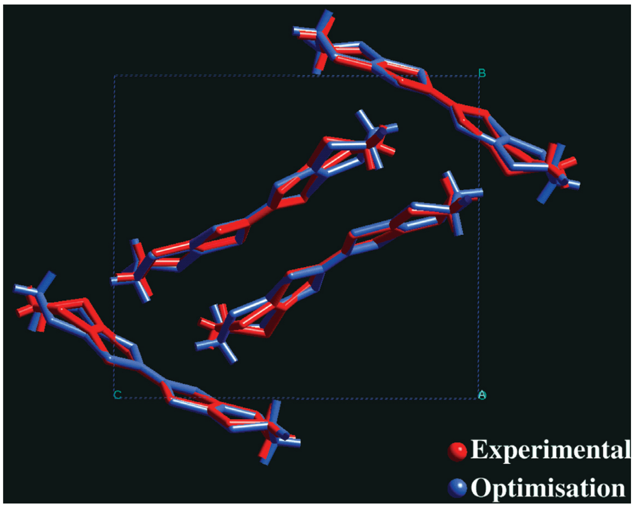

Fig. 3 A comparison of the BEDT-TTF neutral structure before and after geometry optimisation when using the ESFF forcefield.

Table 1 RMS deviations for exploratory calculations on the neutral BEDT-TTF salt. Constant volume calculations have been performed with all optimisation criteria and cut-off properties remaining consistent between forcefields

Forcefields[5]	Root mean square deviation/Å
ESFF	0.277
CFF91	0.366
CVFF	0.987
PCFF	0.359

DFT calculations are applied[23,24]). The crystal structure of Guionneau[25] has been used in this work as a starting geometry.

The reduced electrostatic contributions of the neutral BEDT-TTF molecular crystal, as there is no charge transfer, will provide a stringent test of the ability of the interatomic potentials to model the organic component of the family of charge-transfer salts. Constant volume geometry minimisation calculations have been applied and the RMS values are reported in Table 1. The results show that the ESFF is the best choice of forcefield (of those considered) for the modelling of the BEDT-TTF charge-transfer molecular crystals. The RMS values are only an indication of the quality of the representation of the system, but it is important and significant that the correct structural geometry of the molecule is reproduced.

As mentioned above, there is a boat conformation for one of the terminal ethylene groups which is not a characteristic feature of the salts where partial ionisation of the BEDT-TTF molecule occurs which leads to the twist conformations being adopted by both terminal ethylenes of the outer six-membered rings. For the neutral BEDT-TTF molecular crystal, none of the forcefields tested reproduce this subtle feature of the structure but they do reproduce the structure of the rest of the BEDT-TTF molecule extremely well. The thermal isotropic disorder parameters of the sp^3 carbon atoms of the outer six-membered rings are always higher than the ring sp^2 carbons and sulfurs. There are many cases where libration is obviously important. In this case it seems more likely that, owing to the lower electrostatic energies in the neutral BEDT-TTF molecular crystal there is a lower barrier to rotation, therefore allowing the boat conformation.

Constant volume calculations of BEDT-TTF[$FeBr_4$]

The first charge-transfer salt to be investigated is BEDT-TTF[$FeBr_4$], which was first synthesised by Mallah *et al.*[26] Although the anion has a transition metal centre, BEDT-TTF[$FeBr_4$] is one of the simplest salts containing only sixty-two atoms in the unit cell. There is a 1 : 1 ratio between anions and cations in the triclinic cell containing two BEDT-TTF cations and two tetrahedral $FeBr_4$ anions, meaning that, formally, the anion can be considered to have a charge of -1 and each cation a charge of $+1$, leading to a greater degree of planarity of the BEDT-TTF cation compared with BEDT-TTF in the neutral molecular crystal, due to population of the delocalised LUMO. The tendency of the BEDT-TTF family of molecular crystals is to form salts with cation : anion ratios of 2 : 1 or 3 : 2, as will be described later. There are no stacks or planes of closely spaced BEDT-TTF molecules in the structure of BEDT-TTF[$FeBr_4$], which are known to lead to the interesting physical properties of these systems. The only cation–cation (specifically sulfur–sulfur) short-range interactions are between dimeric molecules of BEDT-TTF; the $FeBr_4$ anions act as spacers and block further cation–cation interactions. As there are no stacks or sheets of cations in the material, there is no conduction pathway and the material is experimentally classified as an insulator.[26]

The three different carbon potentials and two different iron potentials, parameterised in ESFF, have been compared for BEDT-TTF[$FeBr_4$] as the more planar cation, particularly for the five-membered ring, will be a good test of the ability of the carbon potentials to represent BEDT-TTF.

The atom type equivalence tables[5] show that the potentials have identical parameters for the equilibrium bond length, r_0 and the ε^0 values and only differ in partial charges. The same is true for the iron parameter sets, with both potentials being parameterised for tetrahedral iron centres with the formal charges being two and three, which means only a small difference in the partial charges. The best parameter set, which has the combination with the lowest partial charges, has proved to provide the best description for BEDT-TTF[$FeBr_4$] with a RMS value of 0.284 Å. A comparison of the experimental crystal and calculated structure is shown in Fig. 4 and bond lengths are compared in Fig. 5.

Particularly good agreement is seen for the description of the anion, with a relatively small discrepancy of 0.05 Å for the Fe–Br bond length. The topology of the outer six-membered rings is not reproduced as well as for the rest of the system but experimental crystal diffraction data show large *R* values for these atomic sites.

Constant pressure calculations of BEDT-TTF[$FeBr_4$]

When modelling molecular crystals using forcefield methods, the intermolecular electrostatics are far weaker than in metal oxide or zeolite systems, and it is the latter interactions that affect the internal structure of the molecules and determine the intermolecular distances. If no constraints are placed on the lattice parameters, the accurate calculation of crystal structure can be a challenging task, as the cell volume strongly depends upon all the intermolecular interactions.

By first minimising the molecular components and keeping

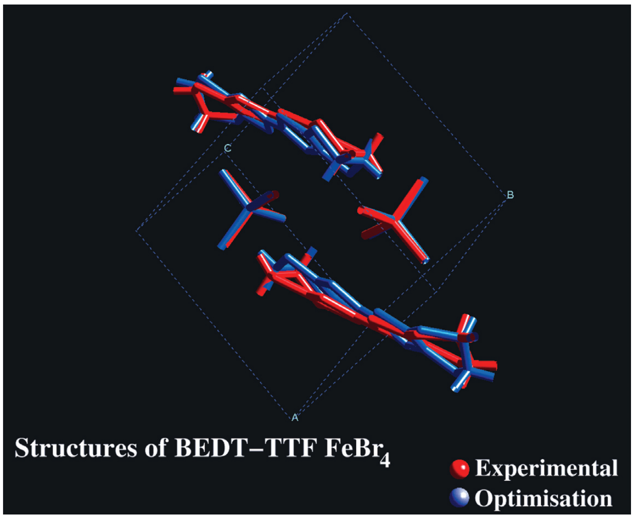

Fig. 4 Comparison between the experimental crystal structure and the calculated structure; note the excellent agreement.

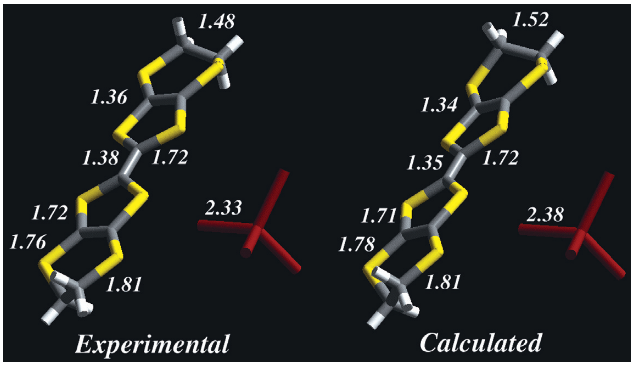

Fig. 5 Bond lengths (Å) for BEDT-TTF[$FeBr_4$].

Table 2 Cell parameters before and after minimisation for BEDT-TTF[FeBr$_4$]

Lattice parameter	Experimental data	Calculated data
a/Å	8.634	8.066
b/Å	10.980	11.165
c/Å	11.773	12.748
α/°	91.92	93.44
β/°	102.84	106.43
γ/°	93.73	96.03
Cell volume/Å^3	1084.56	1089.23

the lattice parameters fixed (*i.e.* a constant volume calculation) and then performing a full minimisation including relaxation of the lattice parameters, a reasonable cell volume is obtained (Table 2). The *a* and *c* lattice vectors show an error of up to 10%, but the molecular geometry is virtually unchanged. To improve correspondence between lattice parameters it would be necessary to extend the method to include the distributed multipole analysis.[16]

The results of the constant volume calculations for both the neutral BEDT-TTF molecular crystal structure and the BEDT-TTF[FeBr$_4$] salt show that ESFF is capable of modelling the structure of this family of molecular crystals to an acceptable level of accuracy. The constant pressure calculations for BEDT-TTF[FeBr$_4$] show an increase in the cell volume but within an acceptable level of error.

Constant volume calculations of larger systems with fractional cation charges

The BEDT-TTF family of molecular crystals contains many large low symmetry systems showing a wide range of physical properties. Here we report investigations of some of the more interesting larger systems.

The charge assignment routine of Discover3 was altered to allow the use of partial charges, obtained from Mulliken population analyses of molecular electronic structure calculations. (The alteration overrides the charges calculated by the electronegativity equalisation method and fixes them for the duration of the calculation.) Further details of the molecular electronic structure calculations are given in ref. 24.

In the following sections use will be made of ESFF to model large molecular charge-transfer salts.

BEDT-TTF$_2$[FeCl$_4$]

As an example of a system with a fractional formal charge of +½ on each BEDT-TTF cation BEDT-TTF$_2$[FeCl$_4$][26] has been selected. The asymmetric unit of the triclinic BEDT-TTF$_2$[FeCl$_4$] crystal contains two BEDT-TTF cations and one FeCl$_4^-$ anion. The lattice of BEDT-TTF$_2$[FeCl$_4$] consists of dimerised stacks of BEDT-TTF molecules separated by a sheet of anions, which are situated in the cavity formed by the ethylene groups of BEDT-TTF. There are 114 atoms in the unit cell, four BEDT-TTF cations and two anions. The formal charge of each BEDT-TTF molecule is +½. By performing electronic structure calculations on BEDT-TTF^0 and BEDT-TTF^{+1} [24] and averaging the Mulliken charges the partial charges can be obtained. The comparison of experimental and calculated structure, shown in Fig. 6, clearly shows that this method works well.

α-BEDT-TTF$_2$[I$_3$]

BEDT-TTF$_2$[I$_3$] has been synthesised in many phases, which show different physical properties. α-BEDT-TTF$_2$[I$_3$] synthesised by Bender *et al.*[27] has been used in this study, as the structure has small thermal ellipsoids. The BEDT-TTF molecules form stacks, when viewed along the *a* plane, which are connected *via* intermolecular sulfur–sulfur contacts into sheets, parallel to the *ab* plane, of alternating cations and anions. The most prominent sulfur–sulfur contacts are found between neighbouring stacks of BEDT-TTF molecules rather than the interstack distance, which gives BEDT-TTF$_2$[I$_3$] a two dimensional metallic Fermi surface as shown by conductivity measurements.[27]

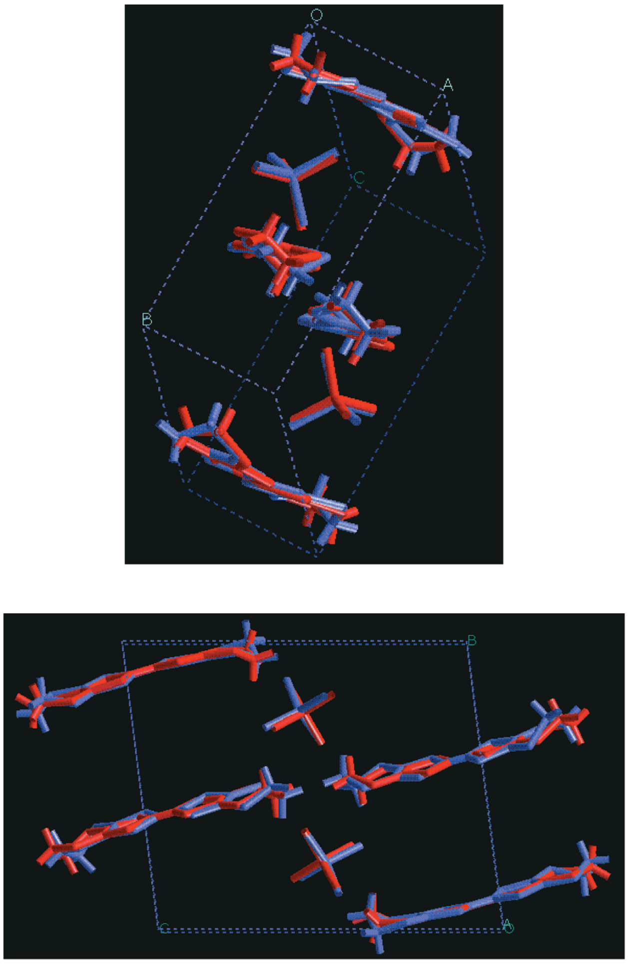

Fig. 6 Comparison of experimental and crystal structure for BEDT-TTF$_2$[FeCl$_4$]. Experimental crystal structure (red); calculated structure (blue).

The RMS value is low for the size of system at ~0.2, while the reproduction of the conformations of the molecular components, when compared to the experimental crystal structure, is excellent as shown in Fig. 7.

BEDT-TTF$_2$[Cr(NCS)$_4$(NH$_3$)$_2$]

The salt, BEDT-TTF$_2$[Cr(NCS)$_4$(NH$_3$)$_2$][28] shown in Fig. 8, is a good example of a recently discovered BEDT-TTF salt.

BEDT-TTF$_2$[Cr(NCS)$_4$(NH$_3$)$_2$] contains 292 atoms per unit cell, with each BEDT-TTF having a formal charge of +½. A very good agreement between the experimental and calculated structure is obtained by using the modified ESFF forcefield, shown in Fig. 9, with partial charges derived by molecular DFT calculations, given in Table 3.

Fig. 10 shows an analysis of bond lengths, which are in good agreement with experiment. The ability of ESFF to model this complex molecular crystal so effectively is both interesting and encouraging.

Conclusions

Forcefield methods are a proven technique for the study of many types of system, such as metal oxides and organic

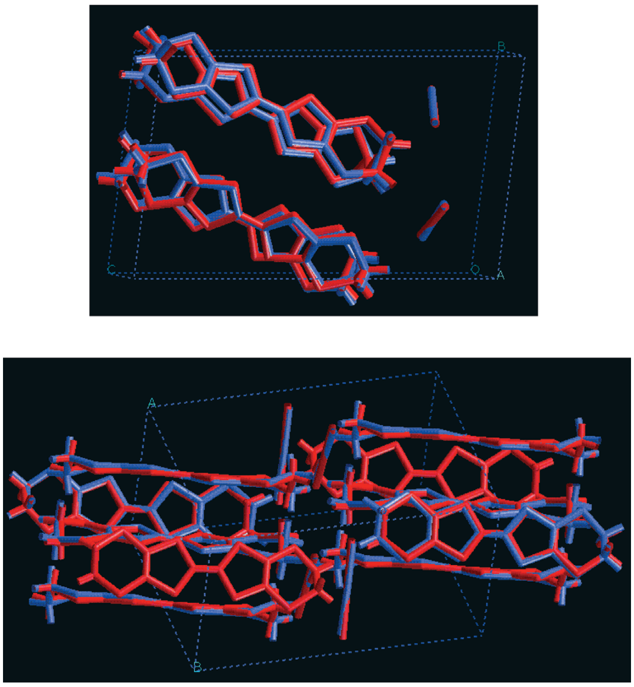

Fig. 7 Comparison of experimental and crystal structure for BEDT-TTF$_2$[I$_3$]. Experimental crystal structure (red); calculated structure (blue).

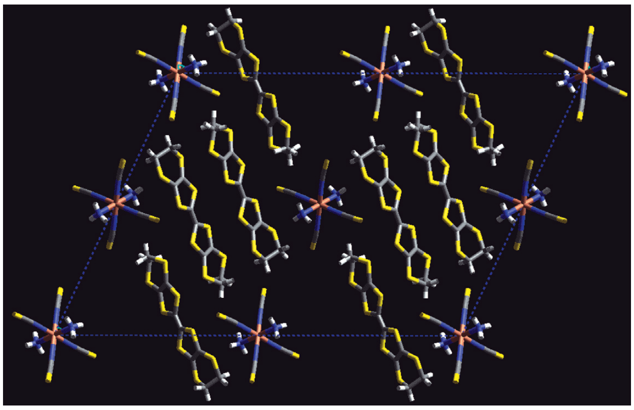

Fig. 8 The unit cell of BEDT-TTF$_2$[Cr(NCS)$_4$(NH$_3$)$_2$], which contains 292 atoms per unit cell.

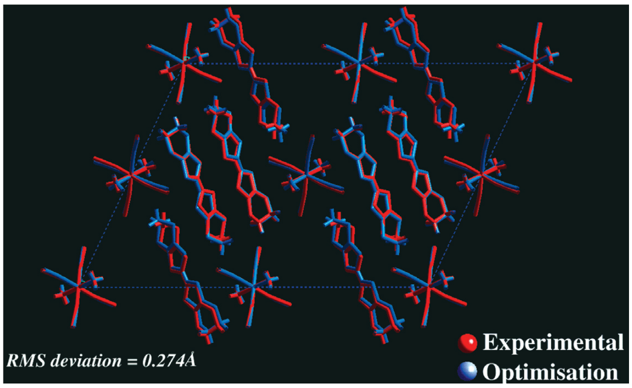

Fig. 9 Comparison of the experimental crystal data and calculated structure for BEDT-TTF$_2$[Cr(NCS)$_4$(NH$_3$)$_2$]. Experimental crystal structure (red); calculated structure (blue).

Table 3 The Mulliken charges of [Cr^{3+}(NCS)$_4$(NH$_3$)$_2$]$^-$ calculated using DMol^3, with the bp[29,30] functional and DN basis set.[31]

Atom	Mulliken charge	Mulliken spin
Cr	0.473	2.685
N	−0.160	−0.033
N	−0.155	−0.032
N	−0.416	−0.038
C	0.198	0.029
C	0.198	0.025
S	−0.559	0.099
S	−0.567	0.095
H	0.240	0.004
H	0.241	0.003
H	0.243	0.004

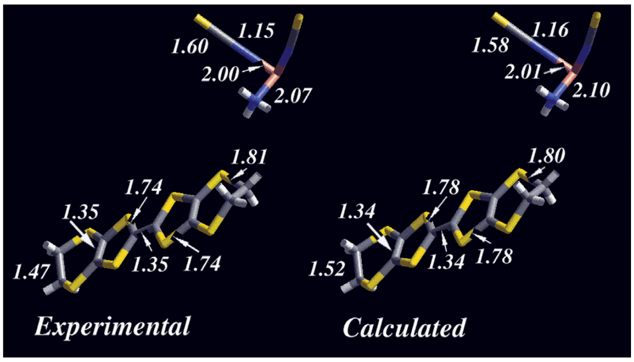

Fig. 10 Bond lengths (Å) of BEDT-TTF$_2$[Cr(NCS)$_4$(NH$_3$)$_2$].

molecules, but the use of molecular mechanics to calculate the structure of complex molecular crystals is growing.[32–35] The intermolecular interactions in molecular crystals are a much severer test of the quality of forcefield and parameter set. The ESFF forcefield in combination with the Discover3 minimisation engine has been shown to reproduce the structure of BEDT-TTF salts after modification of the code even for large and complex systems. Extension of the methodology to permit the studying of a wider range of extended lattices would be desirable.

The use of the methods reported in this paper will significantly enhance our ability to predict and design new crystal structures and aid the refinement of crystal structures from diffraction data.

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