On the rôle of the charge distribution in the crystal packing of charge-transfer salts

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Molecular modelling techniques are applied to the structures of organic charge-transfer salts; accurate crystal structures are calculated provided atomic charges are allowed to vary during the course of the energy minimisation.

Computer modelling techniques have been applied in recent years to increasingly complex problems in solid-state chemistry, for example the chemistry of microporous materials[1] and of organometallic intercalates.[2] Modelling of such systems still relies mainly on 'force-field' techniques which employ interatomic potentials in minimisation or dynamical simulations. The charges assigned to the atoms are crucial parameters in such force fields; they are normally treated as independent of the interatomic spacings. In this communication we show how, by relaxing this constraint and allowing charges to vary in a systematic manner during the simulation, we are able to extend the applicability of these methods to a new class of material. Using this approach, we are able accurately to model the structures of several charge-transfer salts of BEDT-TTF [*i.e.* bis(ethylenedithio)tetrathiofulvalene]. Members of this family have been intensively studied since it was first shown that these organic metals showed the phenomenon of superconductivity.[3,4]

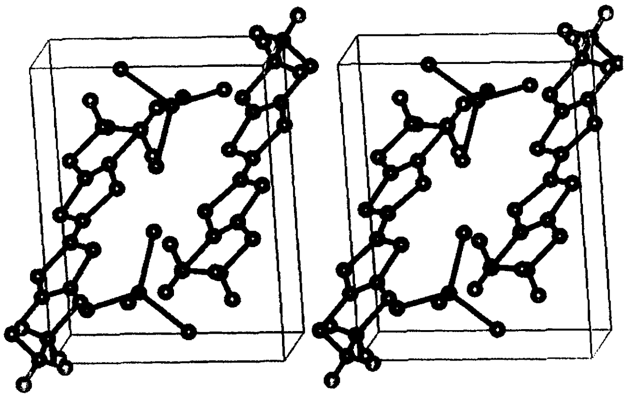
To model the structures of these systems we have used energy minimisation procedures employing a valence force field comprising both *intra-* and *inter*-molecular terms. A flexible and widely applicable force field of this type is provided by the ESFF parameterisation of MSI[5] which proves particularly suitable for the present study. The force field has the standard molecular mechanics components—bonding, bond angle, torsional, out-of-plane and non-bonding energies—which have been parameterised from a combination of empirical and theoretical sources. Crucially, however, in the present study the atomic charges are determined *during* the calculation using a standard extended Hückel theory (EHT) calculation on the crystal structure at each point during the minimisation.

Our procedure is therefore to calculate the lattice energy using standard simulation procedures (with non-bonded and Coulomb contributions being summed[6] directly over all atoms in the 26 neighbouring unit cells). A steepest descent minimisation method is used with charges being recalculated by the EHT method every *n* iterations, where *n* varies during the course of the minimisation in a manner that minimises the computational cost. To test the accuracy of the final structures, we define a *discrepancy index* $\Delta = 1/N \sum_{i}^{N} \Delta r_i$ where Δr_i is the difference between the calculated and experimental position of the atom in the unit cell and the summation extends over all the atoms in the unit cell. Table 1 lists the calculated values for the compounds investigated.

We first tested the method with the (BEDT-TTF)$FeBr_4$ salt.[7] The minimisation was started from the crystallographic data by calculating the charge distribution inside the cell. The resulting minimum energy structure is very close to the crystallographic structure (see Fig. 1 and the Δ value in Table 1). The charges change appreciably (by up to 30% during the course of the minimisation) and inclusion of the variation in charge is essential in obtaining an accurate energy-minimised structure. For example, the discrepancies index, Δ, is increased by a factor of 6 for the case of $(BEDT\text{-}TTF)_2InBr_4$ if the charge variation is not included. Next, we investigated the effect of changing the anion, by performing calculations on $(BEDT\text{-}TTF)_2InBr_4$.[7] Our procedure again generates a structure similar to that observed

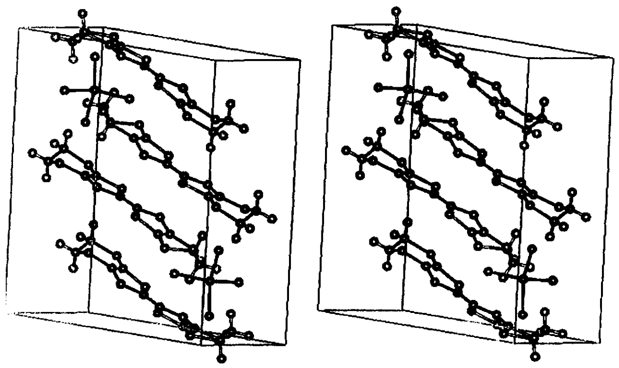
Table 1 Calculated Δ values for the studied crystals

Compound	Δ/Å
(BEDT-TTF)$FeBr_4$	0.08350
$(BEDT\text{-}TTF)_2InBr_4$	0.01477
β″-$(BEDT\text{-}TTF)_2AuBr_2$	0.09442
α′-$(BEDT\text{-}TTF)_2I_3$	0.04624
β-$(BEDT\text{-}TTF)_2I_3$	0.02705



Calculated Structure   Crystallographic Structure

Fig. 1 Comparison of calculated and crystallographic structures for (BEDT-TTF)$FeBr_4$



Calculated Structure   Crystallographic Structure

Fig. 2 Comparison of calculated and crystallographic structures for (BEDT-TTF)$InBr_4$

experimentally (see Fig. 2 and Table 1). Changes in the geometry and nature of the anion were then examined. We chose the β″-(BEDT-TTF)$_2$AuBr$_4$[8] which has a linear anion. Once more, our minimisation procedure generated a structure in good agreement with experiment.

Finally, we focused the study on two phases of (BEDT-TTF)$_2$I$_3$, namely the α and α′ structures. Crystals of α′-(BEDT-TTF)$_2$I$_3$ are quasi-two-dimensional organic metals which have a stable superconducting state at 8 K and ambient pressure.[9] They can be prepared by tempering crystals of the α phase above 70 °C for several days, resulting in a structural phase transition.[10] The structure of α′-(BEDT-TTF)$_2$I$_3$ is very similar to that of β-(BEDT-TTF)$_2$I$_3$, as was shown by several spectroscopic methods.[11] Nevertheless, its exact structure is not yet known. Optimised structures using our techniques are shown in Figs. 3 and 4;again they compare well with available experimental data.

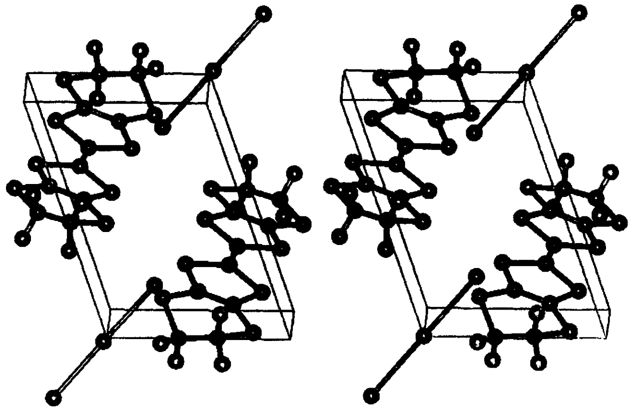

Calculated Structure Crystallographic Structure

Fig. 3 Comparison of calculated and crystallographic structures for α′-(BEDT-TTF)$_2$I$_3$

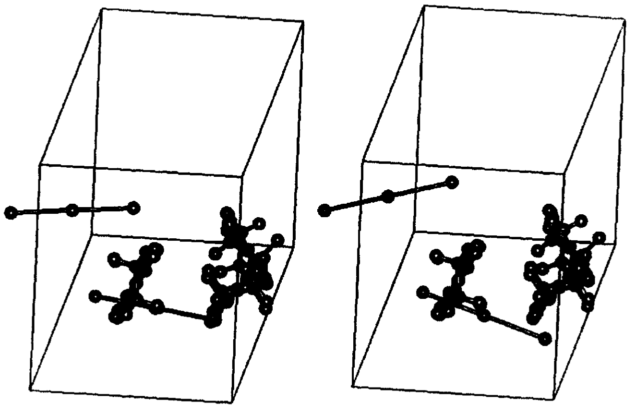

Calculated Structure Crystallographic Structure

Fig. 4 Comparison of calculated and crystallographic structures for β-(BEDT-TTF)$_2$I$_3$

In summary, our new procedure works well on modelling structural properties of organic charge-transfer salts. Preliminary calculations suggest that the approach may also be successfully implemented in dynamical simulations. The methods offer the opportunities of guiding future synthetic and crystallographic studies of these materials.

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Footnote

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