A periodic density functional study of BEDT–TTF salts†

S. A. French,* P. Day and C. R. A. Catlow

The Royal Institution of Great Britain, 21 Albemarle Street, London, UK W1X 4BS. E-mail: sam@ri.ac.uk

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We report the first *ab initio* computational study of the structural and electronic properties of BEDT–TTF charge transfer salts, which have wide ranging physical properties which are derived primarily from the packing of the donor-radical cations. The calculations accurately reproduce the observed crystal structure of the material and provide new information on the electronic structure of the (BEDT-TTF)[FeBr$_4$] salt.

BEDT–TTF [bis(ethylenedithio)tetrathiafulvalene] or 'ET', first synthesised by Mizuno *et al.*[1] has been extensively studied as it is the organic component of a family of superconducting molecular charge transfer salts. An important structural feature of these systems, based on the donor molecule ET, is the separation of the organic cations and the inorganic anion into alternating layers and stacks. As a consequence, there are many lattice packings of ET, which lead to insulating, semiconducting, metallic and superconducting phases. These physical properties result primarily from the packing of the donor-radical cations in the crystal structure. The orientation and distance between the cations has a critical influence on the electronic behaviour. The sulfur–sulfur interaction is the major influence on the intermolecular interactions owing to the larger size of these heteroatoms. However, the exact mechanistic process by which superconduction occurs below T_c, is unknown.

To investigate the structure and electronic properties of these molecular charge transfer salts we have used density functional theory (DFT); periodic boundary conditions were employed and the calculations were performed using the DMol[3] code,[2] with the local density (LD) exchange and correlation functionals of Perdew and Wang.[3] DMol[3] uses numerical basis sets where the basis functions are given as values on an atomic centred spherical polar mesh. Calculations were performed using the double numeric + polarisation (DNP) basis set. Previously it has only been possible to perform single point calculations but with the increase in computer power we can now perform a full geometry optimisation within the constraint of the observed cell dimensions on (ET)FeBr$_4$.[4] These calculations thus represent a considerable advance in the level of theory applied to these systems, and they include a detailed treatment of steric and crystal field effect; they are, however computationally expensive. We note that previous studies have used much simpler levels of theory such as extended Huckel theory[5–7] or have simply considered the isolated organic cation.[8, 9]

First let us consider the calculated structure. From Fig. 1 and Table 1 it is clear that there is excellent agreement between calculated and experimental structures. There are minor deviations in the hydrogen positions but this is consistent with the crystallographic data[4] which shows hydrogen having the largest thermal ellipsoids. Analyses of the bond lengths in Table 1 show excellent agreement with the experimental values.

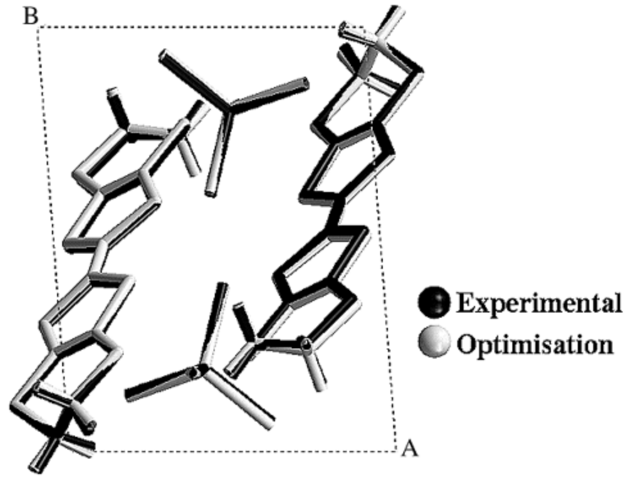
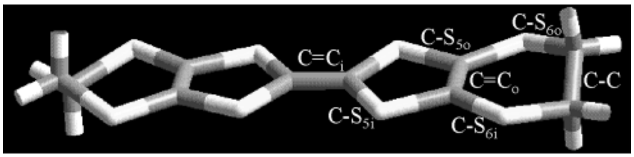


Fig. 1 Superposition of experimental (crystal structure) and calculated structure of (ET)FeBr$_4$.

Turning now to the electronic structure of the salts, we recall that the mechanism of superconductivity is unknown but clearly charge transfer is vital. The Mulliken population analysis allows examination of the charge distribution on each constituent atom; the combined value for the ET molecule is 0.784 of an electron clearly showing that charge transfer has occurred. By analysing the spin distribution we find that the calculated spin for the anion, 4.935 electrons is very close to the expected value of 5/2 electron pairs per high spin d^5 Fe^{3+}. As expected, the description of the spin on the anion shows that there is covalent bonding between iron and bromine as the spin density indicates 0.31 electrons donated from iron to each bromine. Of interest is the spin distribution over the ET molecule. The single spin left upon ET after charge transfer implies an unpaired spin on both ET molecules in the unit cell. The Mulliken population analysis shows no spin on the ET cation which suggests that a covalent bond is formed between ET molecules of opposite spin. The bonding interaction is within the combined van der Waals radius of sulfur at *ca.* 3.5 Å.

In the superconducting phases of ET salts, the formation of stacks leads to holes being present at an intermolecular distance of *ca.* 3.6 Å which has led to the hypothesis that the intermolecular sulfur–sulfur interactions are an important component of the interstack transfer integrals and hence the electronic band structure. (ET)FeBr$_4$ has been experimentally categorised as an insulator, owing to the formation of dimers. The calculated band gap of −0.265 eV agrees with the experimental observation. Analysis of the highest occupied

Table 1 Comparison of experimental (crystal structure) and calculated bond lengths (Å) for (ET)FeBr$_4$.



	Exptl.	Calc.		Exptl.	Calc.
Fe–Br	2.337	2.327	C–S$_{6i}$	1.741	1.741
C=C$_i$	1.383	1.383	C–S$_{60}$	1.818	1.810
C=C$_o$	1.371	1.388	C–C	1.497	1.448
C–S$_{5i}$	1.733	1.723	C–H	1.105	0.95
C–S$_{5o}$	1.742	1.730			

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† Electronic supplementary information (ESI) available: colour versions of the Figures. See http://www.rsc.org/suppdata/cc/1999/2015/

molecular orbital (HOMO) of (ET)$FeBr_4$ agrees with previous experimental studies[10–12] and calculations using extended Huckel theory (EHT) and tight binding schemes,[5–7] that the orbital is situated on the ET molecules and in particular on sulfur. For (ET)$FeBr_4$ there are clearly no pathways for the hopping of conduction electrons owing to the barrier of the anions.

Our calculations show that, using DFT methods, it is possible to model accurately the structures and electronic properties of these important materials and it is clear that QM calculations provide a tool for further insight into the electronic properties both of the constituent molecules and their salts.

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