

1. The BEDT-TTF charge calculation

In 1997 Guionneau and Day found [1] that the charge q of the BEDT-TTF molecule is linearly related to δ as

$$q = 6.347 - 7.463\delta$$

where the δ is the bond length difference between the C-S and C=C bonds,

$$\delta = (r_b + r_c) - (r_a + r_d)$$

[1] P. Guionneau, C. J. Kepert, G. Bravic, D. Chasseau, M.R. Truter, M. Kurmoo, P. Day, Synth. Met., 1997, **86**, 1973.

On the basis of this relationship and the C=C and C-S bond lengths determined in the present analysis of the 300K structure of (BEDT-TTF)₄CoBr₄(C₆H₄Cl₂) we calculated the charges on BEDT-TTF molecules.

In 300K structure there are two independent radical cation layers **I** and **II**. There are three different BEDT-TTF units in each radical cation layer:

Layer I:

$$\delta_{\text{molecules denoted S(1)}} = (\text{C1S7} + \text{C7S7}) - (\text{C1C2} + \text{C7C8}) = [1.764(12) + 1.718(11)] - [1.356(15) + 1.325(15)] = 3.482(23) - 2.680(30) = 0.80(5)$$

$$q_{\text{calc S(1)}} = 6.347 - 7.463 \cdot 0.80(5) = 6.347 - 5.97(40) = +\mathbf{0.38(40)}$$

$$\delta_{\text{molecule denoted S(9)}} = (\text{S12C11} + \text{S12C13}) - (\text{C11C11} + \text{C12C13}) = [1.743(13) + 1.752(11)] - [1.345(19) + 1.339(16)] = 3.495(24) - 2.684(35) = 0.811(60)$$

$$q_{\text{calc S(9)}} = 6.347 - 7.463 \cdot 0.811(60) = 6.347 - 6.052(447) = +\mathbf{0.30(45)}$$

$$\delta_{\text{molecule denoted S(13)}} = (\text{S13C16} + \text{S13C17}) - (\text{C16C16} + \text{C17C18}) = [1.759(13) + 1.738(10)] - [(1.31(2) + 1.382(14))] = 3.497(23) - 2.692(34) = 0.805(57)$$

$$q_{\text{calc S(13)}} = 6.347 - 7.463 \cdot 0.805(57) = 6.347 - 6.012(425) = +\mathbf{0.34(40)}$$

Layer II:

$$\delta_{\text{molecules denoted S(17)}} = (\text{C24S23} + \text{S23C22}) - (\text{C21C22} + \text{C23C24}) = [1.726(11) + 1.725(11)] - [1.431(13) + 1.366(15)] = 3.451(22) - 2.797(28) = 0.65(5)$$

$$q_{\text{calc S(17)}} = 6.347 - 7.463 \cdot 0.65(5) = 6.347 - 4.85(37) = +\mathbf{1.50(40)}$$

$$\delta_{\text{molecule denoted S(29)}} = (\text{S32C31} + \text{S32C32}) - (\text{C31C31} + \text{C32C33}) = (1.751(11) + 1.793(10)) - (1.36(2) + 1.303(14)) = 3.544(21) - 2.66(3) = 0.88(5)$$

$$q_{\text{calc S(29)}} = 6.347 - 7.463 \cdot 0.88(5) = 6.347 - 6.57(37) = -\mathbf{0.22(40)}$$

$$\delta_{\text{molecule denoted S(25)}} = (\text{S28C38} + \text{S28C36}) - (\text{C36C36} + \text{C37C38}) = [1.742(11) + 1.719(12)] - [1.42(2) + 1.316(14)] = 3.461(23) - 2.736(34) = 0.725(57)$$

$$q_{\text{calc S(25)}} = 6.347 - 7.463 \cdot 0.725(57) = 6.347 - 5.41(42) = +\mathbf{0.94(42)}$$

These data indicate a significant difference in the oxidation state of the BEDT-TTF donor molecules from layers **I** and **II**.

Assuming the S(29) molecule charge to be equal to 0 (negatively charged BEDT-TTF cannot be stable in ambient conditions), we conclude on that calculated total charge is:

$$\Sigma q_{\text{calc}} = 2 \cdot 0.38 + 0.30 + 0.34 + 2 \cdot 1.50 + 0.94 = +5.34 \text{ per eight BEDT-TTF}$$

The calculated charges should be normalized in such a way that their sum would be +4.

Previously, the total charge of the BEDT-TTF units in BEDT-TTF salts comprising pentafluorothiomethylsulfonate anions calculated using the Guionneau-Day equation was also higher than the anion charge (Williams et al, Chem. Mater. **2000**, 12, 343). The charges calculated using this equation were 1.66; 1.35; and 1.18 times lowered for β'' -(BEDT-TTF)₂SF₅CH₂SO₃, β'' -(BEDT-TTF)₂SF₅CHFSO₃ and β' -(BEDT-TTF)₂SF₅CF₂SO₃, respectively, in order to the sum of the charges on different BEDT-TTF units was equal to the anion charge. Similarly to that paper, in the present paper the charge numbers are scaled to:

$$q_{S(1)} = +0.28(30)$$

$$q_{S(9)} = +0.22(34)$$

$$q_{S(13)} = +0.25(30)$$

$$q_{S(17)} = +1.12(30)$$

$$q_{S(29)} = -0.16(30) \sim 0$$

$$q_{S(25)} = +0.70(31)$$

by dividing the above calculated values by $5.34/4=1.335$.

These data show a noticeable difference in the charge state of the BEDT-TTF units from layer **I** and layer **II**. This provides for different degree of occupancy of the conduction band for each layer and correspondingly different conductivity in layers **I** and **II**. This is a new and unusual result. A relatively low accuracy of the determination of bond lengths prevents from confidently stating about absolute values of charges of layer **I**, but +1 and +0.7 charges of the BEDT-TTF units from layer **II** are essentially higher than the error and are valid.

2. Refinement special details

300K Structure:

When refining the structure at 300 K we excluded N reflections using the operation omit. The 300 K crystal structure was corrected via a new refinement by using least-squares restraints isor.

343K Structure:

When determining the structure of the tetragonal phase at 343 K we failed to localize the solvent molecule from the difference Fourier syntheses. Two peaks of electron density only are found in the difference syntheses which were identified by us as chlorine and carbon atoms bound with each other. The dichlorobenzene molecule in 343 K structure was reconstructed using the data of the structure of the triclinic phase, i.e. the dichlorobenzene molecule was transferred from the structure of the triclinic phase to the tetragonal one and corrections were made to atomic coordinates taking into account the Cl and C positions, found from the difference Fourier syntheses at 343 K. Therefore, it was possible to refine the dichlorobenzene molecule in the structure at 343 K only when imposing a great number of constraints on bond lengths (dfix) and flat constraints.

Disordering of terminal ethylene groups in the BEDT-TTF molecule lying about an inversion centre was revealed in the structure at 343 K. The atoms of this disordered group were also refined by imposing constraints.