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Structural and electrical properties of bis(ethylenedithio)tetrathiafulvalenium hydrogen fumarate (2/1): a BEDT-TTF mixed-valency salt with a hydrogen-bonding organic anion

Michel Giffard,*[a] Amédée Riou,[a] Gilles Mabon,[a] Nicolas Mercier,[a] Philippe Molinié[b] and Thien Phap Nguyen[b]

[a] *Laboratoire d'Ingénierie Moléculaire et Matériaux Organiques, UMR CNRS 6501, Université d'Angers, 2 Bd Lavoisier, F-49045 Angers, France. E-mail: giffard@univ-angers.fr*
[b] *Institut des Matériaux de Nantes, UMR CNRS 6510, Université de Nantes, 2 rue de la Houssinière, F-44072 Nantes, France*

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Electro-oxidation of BEDT-TTF in the presence of tetrabutylammonium hydrogen fumarate affords the salt (BEDT-TTF)$_2$[(*E*)-HO$_2$C-CH=CH-CO$_2$], in which the BEDT-TTF units adopt a β-type packing and the organic anions form infinite chains by hydrogen-bonding; this salt is a semiconductor and its room-temperature conductivity is *ca.* 3 S cm^{-1}.

The synthesis, structure and properties of cation radical salts derived from bis(ethylenedithio)tetrathiafulvalene (BEDT-TTF) are of considerable interest.[1–10] Nevertheless, to the best of our knowledge, there is no report of such salts with simple organic counteranions derived from carboxylic acids (R-CO$_2$H) and, *a fortiori*, from di- and polycarboxylic acids.

The anions derived from this kind of acid (*e.g.* oxalic, maleic, fumaric acids) display a variety of shapes and symmetries, likely to influence the crystal packing of their salts and, consequently, their electrical properties.

Furthermore, it can be seen that, in the BEDT-TTF salts series, the higher-T_c superconductors, such as κ-(BEDT-TTF)$_2$Cu(NCS)$_2$, possess a polymeric network of coordination-bonded anions; vibrations of this anion sublattice are thought to be involved in the process of superconductivity.[1,2] By using organic hydrogeno-anions, *i.e.* partially neutralized di- or polyacids, one can expect to build new BEDT-TTF salts with polymeric networks of anions which will be, in this case, linked by hydrogen bonds.[10–16] The *E* configuration of the hydrogen fumarate anion appears to be very favourable to the formation of intermolecular hydrogen bonds and we have chosen to prepare, initially, the title compound (BEDT-TTF)$_2$ [(*E*)-HO$_2$C-CH=CH-CO$_2$] (**1**) by electro-oxidation of BEDT-TTF, in the presence of tetrabutylammonium hydrogen fumarate (**2**) as supporting electrolyte.†

From X-ray diffraction data‡, the centrosymmetric unit cell of **1** contains one hydrogen fumarate anion C$_4$H$_3$O$_4$$^-$ and two equivalent BEDT-TTF. Thus, each donor molecule is in a mixed-valency state and carries a fractional charge of $+\frac{1}{2}$. The BEDT-TTF moieties are planar with the exception of their terminal -CH$_2$-CH$_2$- groups, which adopt an eclipsed relative arrangement and are not subject to conformational disorder; the various internal bond lengths in these BEDT-TTF units (see Fig. 1a) are in agreement, through empirical relations, with the fractional charge of $+\frac{1}{2}$.[3]

The planar anions are linked by hydrogen bonds occurring between oxygen atoms (labelled as O(1) in Fig. 1b) which are formally singly bonded to carbon[12,13] (C(12)–O(1) = 1.301(3) Å, to be compared to C(12)–O(2) = 1.219(4) Å), thus these anions do form infinite chains directed along the *b*-axis of the cell (Fig. 2a). The short O(1)···O(1) distance (2.48 Å) is indicative of a strong hydrogen bond.[10–14] We did not succeed in precisely locating the shared hydrogen by means of difference-Fourier techniques, so the question remains whether this hydrogen bond is symmetrical (single-well potential) or unsymmetrical (double-well potential); strong hydrogen bonds are often symmetrical and, furthermore, the O$_2$C-CH=CH-CO$_2$ moiety appears to be centrosymmetric, thus the former hypothesis is probable, however doubt still exists since a proton disorder between the two minima of a hypothetical double-well potential would also make the anion crystallographically centrosymmetric.[10–16]

The overall crystal arrangement of **1** consists of slabs of

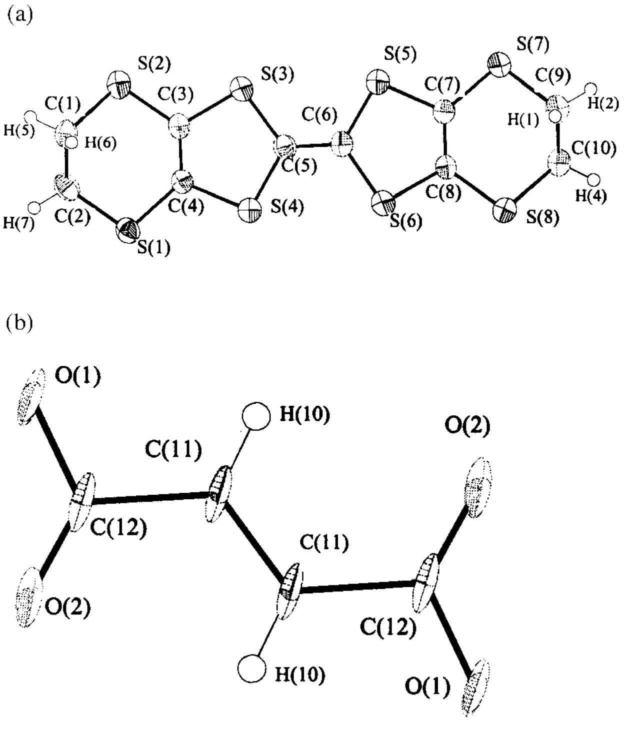

Fig. 1 Drawings of (a) a BEDT-TTF unit (b) a hydrogen fumarate anion, showing the atomic labelling. Selected bond lengths (Å): in the BEDT-TTF unit: C(6)–C(5) 1.363(5), C(5)–S(4) 1.742(3), S(4)–C(4) 1.752(3), C(4)–C(3) 1.344(4), C(3)–S(3) 1.743(3), S(3)–C(5) 1.739(3), C(6)–S(5) 1.732(3), S(5)–C(7) 1.747(3), C(7)–C(8) 1.354(4), C(8)–S(6) 1.740(3), S(6)–C(6) 1.743(3); in the anion: C(11)–C(11) 1.347(4), C(11)–C(12) 1.510(4), C(12)–O(1) 1.301(3), C(12)–O(2) 1.219(4).

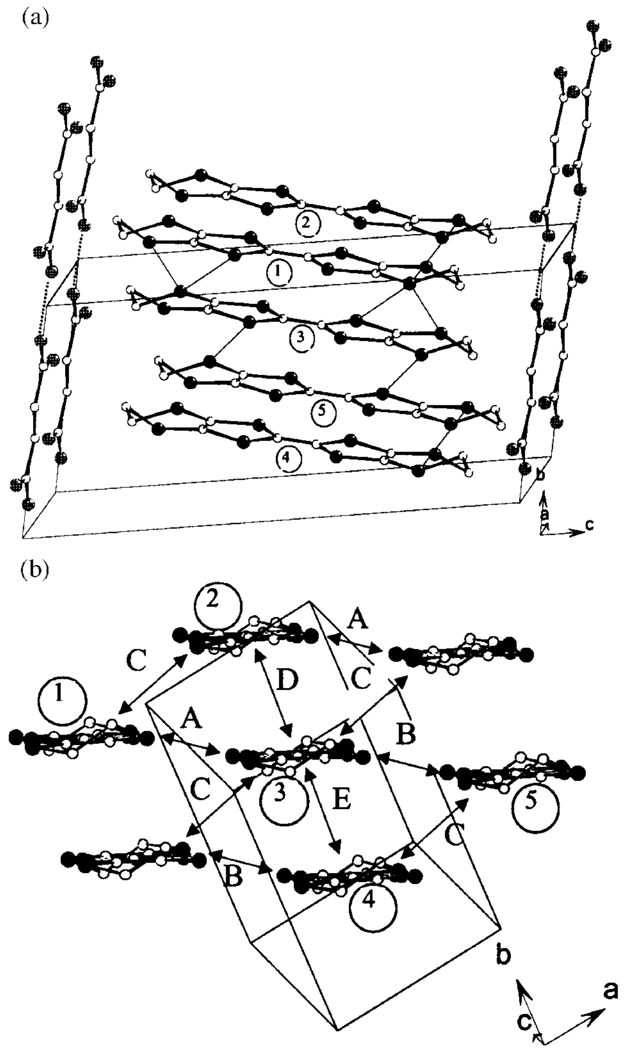

Fig. 2 Crystal packing of **1**. (a) View along the *a*-axis; the short (<3.7 Å) S···S contacts between the BEDT-TTF units are denoted by thin lines and the hydrogen bonds between the hydrogen fumarate anions by dotted lines. (b) View of a sheet of BEDT-TTF along the *c*-axis showing the different possible relative situations (A, B, C, D and E) of these donor molecules. *N.B.* the numbers (1–5) allow the reader to make a connection between the a) and b) views but all BEDT-TTF units are equivalent.

Table 1 Short (<3.7 Å) intermolecular S···S distances (Å) in **1**

A[a]	B[a]	C[a]
3.581 (*i-o*)[b]	3.478 (*i-o*)[b]	3.629 (*o-o*)[b]
3.581 (*o-i*)[b]	3.478 (*o-i*)[b]	
3.583 (*o-o*)[b]		
3.583 (*o-o*)[b]		

[a] Entries A, B and C relate to the three kinds of interstack interactions depicted in Fig. 2b. There are no intrastack (D and E situations in Fig. 2b) distances shorter than 3.7 Å. [b] Interacting atoms: *i* denotes an inner sulfur atom of the BEDT-TTF unit (labelled as S3, S4, S5 or S6 in Fig. 1a), *o* denotes an outer sulfur atom (S1, S2, S7 or S8).

cations, separated by thin walls of anions[4,17] (Fig. 2a). The BEDT-TTF units are piled up in stacks parallel to the *b*-axis and the stacking axis forms an angle $\varphi = 69°$ with the BEDT-TTF mean plane. Intrastack distances are not especially short (the distance between the mean planes of two adjacent BEDT-TTF is 3.74 Å if they are in the D relative situation and 3.87 Å in the case of the E situation, see Fig. 2b), but close S···S contacts (*i.e.* shorter or slightly longer than a distance of 3.6–3.7 Å, which can be regarded, somewhat arbitrarily, as twice the value of the sulfur van der Waals radius[1,18]) appear between the stacks (A, B and C situations), connecting the BEDT-TTF molecules through a two-dimensional zig-zag array of short non-bonded contacts (Fig. 2a and Table 1). This type of packing indicates that **1** belongs to the β family of BEDT-TTF salts whose several members, such as β-(BEDT-TTF)$_2$I$_3$, are low temperature superconductors;[1] more precisely, the details of the structure of **1**, especially the value of the stacking angle φ defined above, allow this compound to be placed in the so-called β″ subgroup, such as β″-(BEDT-TTF)$_2$ AuBr$_2$ or the superconducting β″-(BEDT-TTF)$_2$ Fe(C$_2$O$_4$)$_3$, H$_2$O, C$_6$H$_5$CN.[1,8,9] A closer examination of Table 1 indicates that the C interstack interaction (one short S···S contact) appears to be weaker than the A and B ones (respectively four and two short S···S contacts), the D and E intrastack interactions being, in any case, still weaker; this suggests that **1** may, in fact, possess a pronounced monodimensional character along the line of the A and B interactions (see Fig. 2b). On the other hand, these room-temperature structural features of **1** do not clearly prove the occurrence of either intra- or interstack definite dimers (BEDT-TTF)$_2$$^{+}$. Finally, proximity interactions between the anions and the hydrogen atoms of BEDT-TTF[2,4] also appear, involving especially the carbonyl oxygen atoms of the anion (H(2)···O(2)=2.45 Å).

The d.c. conductivity in the larger plane of single platelets of **1** (crystallographic $\bar{1}1\bar{1}$ plane) was measured by the four probe method. The salt **1** is reasonably conducting at room temperature ($\sigma \sim 3$ S cm^{-1}) but the temperature dependence of its electrical resistivity denotes a semiconducting behaviour (Fig. 3). The magnetic susceptibility of **1** was also measured, as a function of temperature, by the means of SQUID experiments: it does not obey the Curie–Weiss law but its shape suggests a low dimensional behaviour.

In conclusion, it may be underlined that the synthesis of the salt **1** examplifies the possibility of building TTF based materials with organic carboxylate counteranions, which, as conjugates of Brønsted weak acids (reported pK_a values for fumaric acid: pK_{a_1}=3.03, pK_{a_2}=4.44[19]) possess some basic character.§ The electrical properties of **1** appear somewhat disappointing considering its apparently promising structural characteristics. Anyway, the electrical properties of such materials obviously depend upon small structural details which are *a priori* difficult to predict, thus we shall pursue this work by making new cation radical salts using other organic acid derived anions.

Notes and references

† *Synthesis of tetrabutylammonium hydrogen fumarate* (**2**): Fumaric acid (25 mmol) was dissolved in a solution consisting of 25 ml of 1.0 mol l^{-1} methanolic tetrabutylammonium hydroxide (Aldrich), diluted with 50 ml of methanol. The solvent was evaporated under reduced pressure with gentle heating, then the remaining material was redissolved in acetonitrile. The acetonitrile solution was filtered to

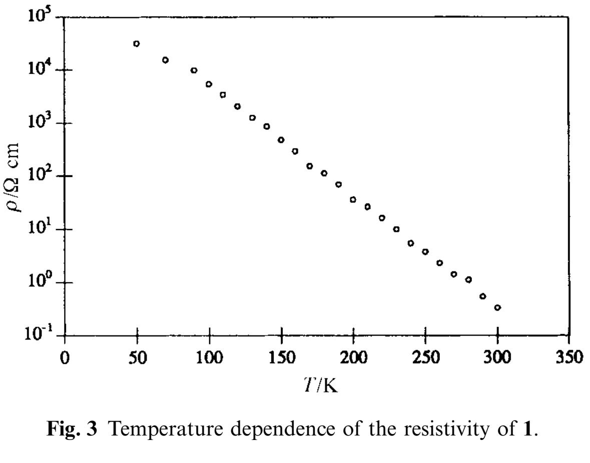

Fig. 3 Temperature dependence of the resistivity of **1**.

remove a small amount of insoluble impurities. Evaporation of acetonitrile left a colorless oil which crystallized after addition of ethyl acetate. The hygroscopic salt **2** was then filtered under nitrogen. Yield: 8.46 g (95%). Mp 92 °C. Elemental analysis: found: C 67.10, H 11.02, N 4.05, O 18.13; calcd. for $C_{20}H_{39}NO_4$: C 67.19, H 10.99, N 3.92, O 17.90%. ^{1}H NMR, 500 MHz (CD_3CN) δ: 12–17 (concentration dependent, broad s, 1H), 6.53 (s, 2H), 3.12 (m, 8H), 1.59 (m, 8H), 1.32 (sextet, 8H) and 0.93 (t, 12H). ^{13}C NMR, 125.77 MHz (CD_3CN) δ: 170.2, 136.5, 59.1, 24.2, 20.2 and 13.8.

Electrocrystallization of 1: A conventional H-shaped cell[1] was charged with 20 ml of a 0.1 mol l^{-1} solution of **2** in a 97.5/2.5 (v/v) dichloromethane–ethanol mixture, degassed with nitrogen. BEDT-TTF (30.8 mg) was introduced in the anodic arm and was then electro-oxidised, at room temperature, under galvanostatic conditions with stepwise increases of the applied current:[5] 1 μA for one week, then 2 μA for another week and finally 3 μA for five days. 25.6 mg of **1**, deposited at the platinum wire anode (diameter: 1 mm, length: 15 mm) as black platelets of typical dimensions 4 × 2 × 0.1 mm, were then harvested. Several other experiments, performed under slightly varying conditions (noticeably: omission of ethanol as cosolvent) afforded smaller crystals which were shown, through X-ray determination of their unit cell, to be chemically and crystallographically identical to those described above.

‡ *Crystal data for 1*: $C_{24}H_{19}O_4S_{16}$ ($M_W = 884.37$), triclinic $P\bar{1}$, $Z = 1$, cell measured with MoKα radiation ($\lambda_{MoK\alpha} = 0.71069$). $a = 6.135(4)$ Å, $b = 8.107(4)$ Å, $c = 16.981(9)$ Å, $\alpha = 79.98(3)°$, $\beta = 79.68(3)°$, $\gamma = 81.88(4)°$, $V = 812.9(6)$ Å^3, D_c 1.806 g cm^{-3}.

Data collection was carried at room temperature by the ω scan technique in the 2–30° θ range on an Enraf Nonius MACH3 four circle diffractometer. Conditions of measurements were $t_{max} = 40$ s, range hkl (h 0,8; k −11,11; l −23,23). Intensity control reflections were measured every 2 hours without appreciable decay (0.15%). A total of 4725 independent reflections from which 3358 were observed with $I/\sigma(I) > 3$. After Lorentz and polarisation corrections, the structure was solved by direct methods (SIR), which revealed all non-hydrogen atoms. After anisotropic refinements of all non-H atoms, the coordinates of H atoms were determined both from Fourier difference synthesis and the Hydro program of MolEN package. The whole structure was refined by full-matrix least-squares techniques (refinement on F; x,y,z, U_{ij} for S, O and C atoms; x,y,z and U fixed for H atoms; 199 variables for 3358 observations, weighting scheme: non-Poisson contribution with $\omega = 1/\sigma(F_o)^2 = 4F_o{}^2/[\sigma(I)^2 + (0.04F_o{}^2)^2]$; $R = 0.064$, $R_W = 0.090$, GOF = 1.86.

Full crystallographic details, excluding structure factor tables, have been deposited at the Cambridge Crystallographic Data Centre (CCDC). For details of the deposition scheme, see 'Information for Authors', *J. Mater. Chem.*, available *via* the RSC web page (http://www.rsc.org/authors). Any request to the CCDC for this material should quote the full literature citation and the reference number 1145/145. See http://www.rsc.org/suppdata/jm/1999/851/ for crystallographic files in .cif format.

§ This result was not *a priori* ensured. There is a relationship between acido-basicity and the redox behaviour of TTF derivatives. We have previously shown that strong enough protic acids can induce the formation of radical cations TTF$^{\bullet+}$ from TTF although the mechanism of this oxidation is not fully understood.[20] Conversely, strong enough bases may induce a reduction of TTF$^{\bullet+}$ ions: for example we have observed that the addition of triethylamine to a $(CD_3)_2SO$ solution of TTF$^{\bullet+}$, Cl$^-$ leads to the formation of TTF, detected by NMR (see also ref. 21). In fact, one can wonder what level of basicity a TTF derived radical cation is able to tolerate. The obtention of the monofumarate salt **1** indicates, in any case, that the p$K_a = 0$ value has no particular critical meaning in this matter.

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Communication 8/10002K