

## Neutral bis(ethylenedithio)tetrathiafulvalene at 100 K

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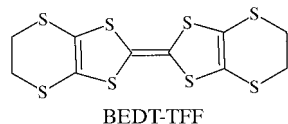
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The low-temperature crystal structure of bis(ethylenedithio)tetrathiafulvalene (BEDT-TTF), C<sub>10</sub>H<sub>8</sub>S<sub>8</sub>, is similar to its high-temperature structure. The room-temperature central bond lengths of this molecule are often used as reference in empirical methods to estimate the charge carried by the (BEDT-TTF)<sub>x</sub><sup>n+</sup> cations in the BEDT-TTF molecule-based organic conductors. We show that the method we previously reported can still be used with low-temperature BEDT-TTF salts data. Moreover, we confirm the purely thermal origin of the ordering of the ethylene group.

## Comment

The BEDT-TTF molecule is used to build the very well known (BEDT-TTF)<sub>x</sub><sup>n+</sup>X<sup>n-</sup> salts which exhibit such a diversity of physical and structural properties (Williams *et al.*, 1992). In our aim to correlate structural and conducting properties in this series we assume that knowledge of the low-temperature structural properties of the neutral molecule will be important. Indeed, the room-temperature intramolecular structural parameters of this molecule are used as a reference to analyse the intramolecular structural parameters of the corresponding cation in the corresponding family salts.



In particular we developed a statistical method to give an estimation of the charge carried by the BEDT-TTF cation in such salts (Guionneau *et al.*, 1997) from a combination of the averaged values of the four central bond lengths. This method shows the linear variation of the charge with the distance  $\delta = (b + c) - (a + d)$  where  $b$  and  $c$  are the averaged values of the

central S—S bond lengths while  $a$  and  $d$  are the averaged values of the central C—C bond lengths (Fig. 1). The estimation of the charge carried,  $Q$ , in such a way was obtained with an accuracy of 10%, the equation of linear variation was found to be  $Q = 6.347 - 7.463\delta$ . The central bond lengths of the neutral BEDT-TTF molecule were used as a reference point to obtain this equation. In order to know if we could use this method with low-temperature data of BEDT-TTF salts we needed to compare the values of  $\delta$  at room temperature and a temperature of around 100 K for which a lot of structural data are available in the studied series. The averaged central bond length values are close at room temperature and 100 K:  $a = 1.343$  (4),  $b = 1.756$  (3),  $c = 1.760$  (3),  $d = 1.333$  (4) Å (Guionneau *et al.*, 1997) and  $a = 1.352$  (4),  $b = 1.763$  (3),  $c = 1.771$  (3) and  $d = 1.349$  (4) Å, respectively. The associated  $\delta$  values are extremely close at room temperature [0.840 (15) Å] and 100 K [0.834 (15) Å]. The small difference between these two values (−0.006 Å) corresponds to a difference in the charge estimation (+0.04 e<sup>−</sup>) which appears lower than the accuracy of the method (0.10 e<sup>−</sup>). It also shows that the charge calculated with this method from low-temperature data could be slightly overestimated as suspected in Gaultier *et al.* (1999). Thus, these results seem to confirm the validity of the  $\delta$  method as a rough but quick and easy tool to estimate the charge partition in BEDT-TTF salts. Such a partition has been calculated using this method and successfully explains the conducting properties of some organic conductors (Martin *et al.*, 1999; Coronado *et al.*, 1998). It has also been used to show the change in the degree of ionicity that can occur when cooling (Gaultier *et al.*, 1999; Guionneau *et al.*, 1998).

In general, one of the features of BEDT-TTF entities is the disorder that can affect the ethylene extremities. At room temperature such a disorder often appears in BEDT-TTF molecule-based salts. It was also found in neutral BEDT-TTF (Kobayashi *et al.*, 1986; Guionneau *et al.*, 1997). One of the commonly used estimates of the disordering is the deviation from the normal corresponding C—C bond lengths (around 1.53 Å). In the title molecule, ethylene-group bond lengths (C13—C14 and C18—C19) are much closer from the normal values at 100 K [1.518 (3) and 1.517 (3) Å, respectively] than at room temperature [1.467 (3) and 1.421 Å]. Moreover, at

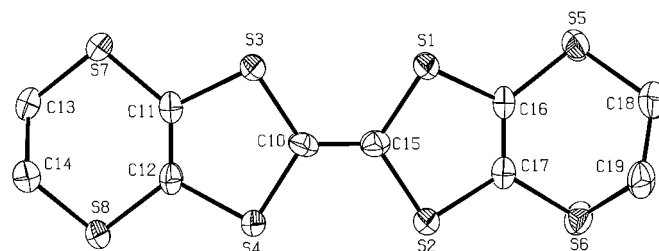


Figure 1

Displacement ellipsoid view (90% probability) of the BEDT-TTF molecule at 110 K. The distances discussed in the text are as follows:  $a$  is C10—C15,  $b$  is the average value of C10—S4, C10—S3, C15—S2 and C15—S1,  $c$  is the average value of C12—S4, C11—S3, C16—S1 and C17—S2,  $d$  is the average value of C11—C12 and C16—C17.

100 K, the displacement parameters of the ethylene-C atoms appear to be of the same order of magnitude as those of the other C atoms of the molecule at room temperature while they are three times higher at room temperature. Such a thermal ordering of neutral BEDT-TTF should be kept in mind when trying to understand BEDT-TTF entities intramolecular changes that may occur by cooling in the corresponding salts.

The molecular packing of BEDT-TTF at room temperature, described as based on dimers (Kobayashi *et al.*, 1986), remains identical at 100 K. It is worth noting that this behaviour is different from that of the TTF crystals, where TTF or tetra-thiofulvalene corresponds to the core of the BEDT-TTF molecule, which undergo a structural transition at low temperature (Batsanov, 1998).

## Experimental

Crystals were prepared according to Mizuno *et al.* (1978).

### Crystal data

$C_{10}H_8S_8$	$D_x = 1.794 \text{ Mg m}^{-3}$
$M_r = 384.64$	Mo $K\alpha$ radiation
Monoclinic, $P2_1/c$	Cell parameters from 425 reflections
$a = 6.6583 (1) \text{ \AA}$	$\theta = 20.48\text{--}34.05^\circ$
$b = 13.733 (2) \text{ \AA}$	$\mu = 1.229 \text{ mm}^{-1}$
$c = 17.414 (1) \text{ \AA}$	$T = 100 (2) \text{ K}$
$\beta = 116.57 (1)^\circ$	Needle, orange
$V = 1424.1 (1) \text{ \AA}^3$	$0.20 \times 0.15 \times 0.10 \text{ mm}$
$Z = 4$	

### Data collection

SMART Siemens CCD diffractometer	3251 independent reflections
$\omega$ scans	2714 reflections with $I > 2\sigma(I)$
Absorption correction: empirical (SADABS; Sheldrick, 1996)	$R_{\text{int}} = 0.037$
$T_{\text{min}} = 0.768$ , $T_{\text{max}} = 0.915$	$\theta_{\text{max}} = 27.43^\circ$
12398 measured reflections	$h = -8 \rightarrow 8$
	$k = -17 \rightarrow 17$
	$l = -22 \rightarrow 22$

### Refinement

Refinement on $F^2$	$w = 1/[\sigma^2(F_o^2) + (0.0191P)^2 + 1.0583P]$
$R(F) = 0.027$	where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.061$	$(\Delta/\sigma)_{\text{max}} = 0.001$
$S = 1.086$	$\Delta\rho_{\text{max}} = 0.35 \text{ e \AA}^{-3}$
3251 reflections	$\Delta\rho_{\text{min}} = -0.36 \text{ e \AA}^{-3}$
163 parameters	
H-atom parameters constrained	

Data collection: SMART (Siemens, 1996); cell refinement: SMART; data reduction: SAINT (Siemens, 1996); program(s) used to solve structure: SHELXS97 (Sheldrick, 1997); program(s) used to refine structure: SHELXL97 (Sheldrick, 1997); molecular graphics: PLATON (Spek, 1999).

Supplementary data for this paper are available from the IUCr electronic archives (Reference: SK1337). Services for accessing these data are described at the back of the journal.

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