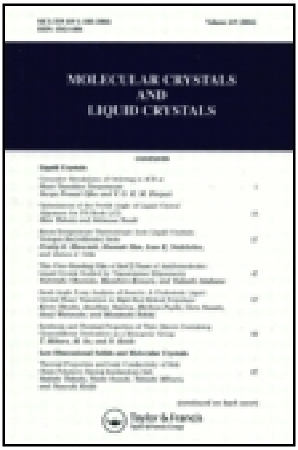

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Synthesis, X-ray structure and Molecular Orbital study of a radical cation salt of a S-position isomer of an EDT-TTF derivative: C.I$_3$ where C = 6, 7-dimethylsulfanyl-2,3-(dithiabutane-1,4-diyl)tetrathiafulvalene

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Synthesis, X-ray structure and Molecular Orbital study of a radical cation salt of a S-position isomer of an EDT-TTF derivative : $C.I_3$ where C = 6, 7-dimethylsulfanyl-2,3-(dithiabutane-1,4-diyl)tetrathiafulvalene

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The X-ray crystalline structure at 293 K and 150 K of the radical cation salt ($C_{10}H_{10}S_8I_3$) obtained from a disulfide tetrathiafulvalene (TTF) derivative, is described. The title compound crystallizes in the $P\bar{1}$ space group with the lattice constants at 293 K : $a = 9.7634(12)$ Å, $b = 9.9311(13)$ Å, $c = 12.780(2)$ Å, $\alpha = 72.94(1)°$, $\beta = 74.51(1)°$, $\gamma = 63.08(3)°$, $V = 1043.1(6)$ Å^3, $Z = 2$. The structural study at low temperature indicates a similar crystal structure without any apparent symmetry and structural modifications.

Donors are stacked in a zig-zag mode along *a*-axis with a strong dimerization, confirmed by the molecular orbital calculations. The structural particularity of the new π-donor C engaged in the described salt being the terminal disulfide bridge, we discuss here the influence of outer sulfur atoms on the structural organization.

Keywords: tetrathiafulvalene; radical cation salts; X-ray structure; molecular orbital calculations

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INTRODUCTION

Bis(ethylenedithio)tetrathiafulvalene (BEDT-TTF) (figure 1) is known to provide organic superconductors endowed with the highest Tc in the tetrathiafulvalene series,[1],[2] the Tc record being still held by the two kappa phases $(BEDT\text{-}TTF)_2CuN(CN)_2Br$ (Tc = 11.6 K, ambient pressure)[3] and $(BEDT\text{-}TTF)_2CuN(CN)_2Cl$ (Tc = 12.8 K, 0.3 kbar).[4] The prominent role of the outer sulfur atoms in BEDT-TTF and other related π-donors[5] on increasing the dimensionality of the corresponding salts is now well recognized and constitutes a requisite to stabilize the metallic state at low temperature.

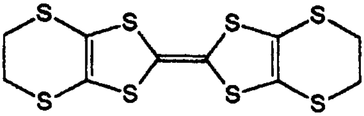
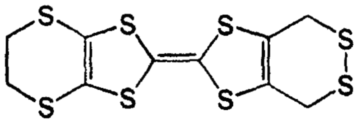


FIGURE 1 bis(ethylenedithio)tetrathiafulvalene (BEDT-TTF)

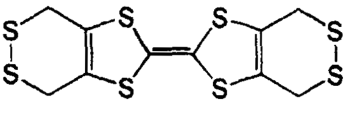
In this purpose, dissymmetrical and symmetrical sulfur-position isomers of BEDT-TTF, respectively **A**[6] and **B**, [7] and the related derivative **C**[6] have been recently synthesized (figure 2). These new π-donors are characterized by the presence of one or two disulfide bridges. Considering their structural similarities with BEDT-TTF, it appears of particular interest to study the role of their terminal sulfur atoms on the structural organization of resulting salts.

The association of BEDT-TTF to the I_3^- anion upon electrochemical or chemical oxidation led to a great number of materials (at least 12 polymorphic phases), exhibiting semi-conducting, metallic or superconducting behaviors. For instance, β-$(BEDT\text{-}TTF)_2.I_3$,[8] θ-$(BEDT\text{-}TTF)_2.I_3$,[9] κ-$(BEDT\text{-}TTF)_2.I_3$[10] and γ-$(BEDT\text{-}TTF)_3.(I_3)_{2.5}$,[11] whose structures consist of layers of donors separated by anions, present superconducting properties at ambient pressure with transition temperatures Tc of 1.4K, 3.6K, 3.6K and 2.5K respectively. The interest of I_3^- anion was also confirmed with the 2,5-bis[4,5-bis(methylthio)-1,3-dithiol-2-ylidene]- 1,3,4,6-tetrathiapentalene (TTM-TTP) as the π-donor (figure 3). Although corresponding radical cation salts are generally electrically insulating,[12] the two salts, $(TTM\text{-}TTP).I_3$[13] and β-$(TTM\text{-}TTP)_2.I_3$,[14] present a metallic behavior and for the last one down to low temperatures.

On these grounds, we have focused on the preparation of salts from **A, B** and **C** using I_3^- as the anion. As expected, the new π-donors display very similar electrochemical properties (E^1_{ox} and E^2_{ox}) as compared to BEDT-TTF,[6],[7] which make them good candidates for preparation of new radical cation salts. We report



A



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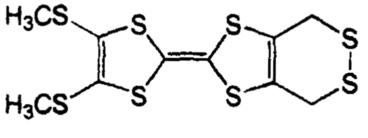

C

FIGURE 2 dissymmetrical and symmetrical S-position isomers of BEDT-TTF **A** and **B**, the bis(methylsulfanyl) derivative **C**

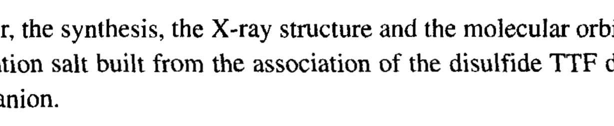

FIGURE 3 2,5-bis[4,5-bis(methylthio)-1,3-dithiol-2-ylidene]-1,3,4,6-tetrathiapentalene (TTM- TTP)

in this paper, the synthesis, the X-ray structure and the molecular orbital study of a radical cation salt built from the association of the disulfide TTF derivative **C** to the I_3^- anion.

EXPERIMENTAL

Synthesis

Black needle-like crystals were grown by oxidation with iodine vapor of donor **C** dissolved in a CH_2Cl_2/EtOH medium (4/1 *v/v ratio)* in the dark.

Structure Determination

A single crystal was used for investigations on a Stoe ϕ-axis diffractometer equipped with a 2D area detector based on imaging plate technology and with a graphite-monochromatized Mo Kα radiation. Corrections were made for absorption [μ(Mo-Kα)= 5.18 mm^{-1}] by empirical methods. Crystallographic data and the refinement procedure are reported in table I. The Patterson analysis was therefore used to localize the four independent iodine atoms. Sulfur and carbon atomic positions were then determined by Fourier difference synthesis. Calculations were performed using the XTAL 3.4 package programs.[15] Results are given in tables II and III.

TABLE I Crystallographic data of C.I_3 at ambient temperature and at 150 K

Compound	**D1**.I_3	**D1**.I_3
Formula	$C_{10}H_8S_8I_3$	$C_{10}H_8S_8I_3$
Formula weight, (g.mol^{-1})	767.42	767.42
Space group	$P\bar{1}$	$P\bar{1}$
Temp (K)	**298**	**150**
a, Å	9.7634(12)	9.6536(12)
b, Å	9.9311(13)	9.8709(13)
c, Å	12.780(2)	12.711(2)
α, deg	72.94(1)	72.77(1)
β, deg	74.51(1)	74.42(1)
γ, deg	63.08(1)	63.07(1)
Cell volume, Å^3	1043.1(6)	1019.6(6)
Z	2	2
Density, g.cm^{-3}	2.444	2.500
Crystal dimensions, mm	0.5 * 0.06 * 0.01	0.5 * 0.06 * 0.01
Reflections measured	4559	4457
$I>3\sigma(I)$	2194	3087
Variables number	193	193
Linear absorption coefficient (mm^{-1})	5.18	5.18
R	0.045	0.041
Rw	0.052	0.049
G.O.F	1.380	1.122

TABLE II Atomic Coordinates and Equivalent Isotropic Thermal Parameters for $C.I_3$ at 298 K

Atom	*X*	*y*	*z*	*Beq*
I1	0.000	0.000	0.0000	3.43(6)
I2	0.500	0.000	0.5000	4.10(6)
I3	0.8119(2)	−0.1258(1)	0.3728(1)	5.18(5)
I4	0.7973(1)	0.2288(1)	0.84459(9)	4.77(5)
S1	1.2101(6)	0.1503(6)	0.2212(5)	6.4 (2)
S2	1.1353(6)	0.3795(6)	0.1654(4)	6.1(2)
S3	0.7831(4)	0.2088(4)	0.4592(3)	3.2(2)
S4	0.8179(5)	0.4799(5)	0.4666(3)	3.4(2)
S5	0.4909(5)	0.2848(4)	0.6641(3)	3.5(2)
S6	0.5369(4)	0.5539(4)	0.6643(3)	3.2(2)
S7	0.2569(5)	0.3136(6)	0.8726(4)	5.1(2)
S8	0.3113(5)	0.6155(5)	0.8753(4)	5.2(2)
C1	1.024(2)	0.137(2)	0.286(2)	4.5(7)
C2	1.063(2)	0.441(2)	0.298(2)	4.0(7)
C3	0.932(2)	0.249(2)	0.364(2)	3.4(7)
C4	0.946(2)	0.376(2)	0.368(2)	4.3(7)
C5	0.721(2)	0.360 (2)	0.522(1)	3.2(6)
C6	0.594(2)	0.398(2)	0.606(1)	3.1(6)
C7	0.385(2)	0.380(2)	0.774(1)	3.0(6)
C8	0.407(2)	0.504(2)	0.774(2)	3.3(6)
C9	0.371(2)	0.110(3)	0.894(2)	6.0(9)
C10	0.438(2)	0.712(2)	0.860(2)	7.3(8)

TABLE III Donor bond lengths in $C.I_3$ at 298 K and 150 K

Distances	*T = 298 K*	*T = 150 K*
I1-I4	2.899(1)	2.9010(7)
I2-I3	2.929(1)	2.9279(8)
S1-S2	2.011(8)	2.036(4)
S1-C1	1.83(2)	1.81(1)
S2-C2	1.82(2)	1.81(1)
S3-C3	1.74(2)	1.75(1)
S3-C5	1.70(2)	1.73(1)
S4-C4	1.72(1)	1.73(1)
S4-C5	1.72(2)	1.71(1)
S5-C6	1.72(2)	1.71(1)
S5-C7	1.74(2)	1.77(1)

Distances	*T = 298 K*	*T = 150 K*
S6-C6	1.71(2)	1.71(2)
S6-C8	1.74(2)	1.74(1)
S7-C7	1.73(2)	1.74(1)
S7-C9	1.79(2)	1.81(1)
S8-C8	1.74(2)	1.73(1)
S8-C10	1.82(3)	1.82(2)
C1-C3	1.52(2)	1.51(1)
C2-C4	1.52(3)	1.51(2)
C3-C4	1.35(3)	1.35(2)
C5-C6	1.39(2)	1.39(1)
C7-C8	1.35(3)	1.35(2)

Molecular Orbital Calculations

In order to get a better insight into the electronic structure of $C.I_3$, molecular and tight-binding[16] extended Hückel calculations were carried out using the packages YAeHMOP 2.0 [17] and CACAO 4.0.[18],[19] Standard atomic parameters were used for H,[20] C,[19] S[21]and I.[22] The exponent (ξ) and the valence shell ionization potential (H_{ii} in eV) were respectively 1.3, −13.6 for H 1s; 1.625, −21.4 for C 2s; 1.625, −11.4 for C 2p; 2.122, -20.0 for S 3s; 1.817, -11.0 for S 3p; 2.679, -18 for I 5s; 2.322, -12.7 for I 5p. Tight-binding calculations were carried out on the one-dimensional $(C_2)^{2+}$ stack running along the [100] direction. 40 k-points were used for computations.

DISCUSSION

The described salt crystallizes in the $P\bar{1}$ space group and is characterized by an [1:1] stoichiometry. Four iodide atoms are independent : I_1 and I_2 atoms are located on the (0,0,0) and (1/2, 0, 1/2) symmetry centers whereas I_3 and I_4 are in general position. Thus, the centrosymmetrical anions I_4-I_1-I_4' and I_3-I_2-I_3' are found at the origin of the unit cell and in the middle of the **ac** faces respectively (figure 4). Intramolecular iodide-iodide bond lengths are 2.905(1) Å and 2.933(1) Å for both I_3^- anions at room temperature and are in good agreement with usual values.[9]

The unit cell contains two donor molecules (noted **1** and **2**) in general position, which are centrosymmetrically related (one independent molecule). The [1:1]

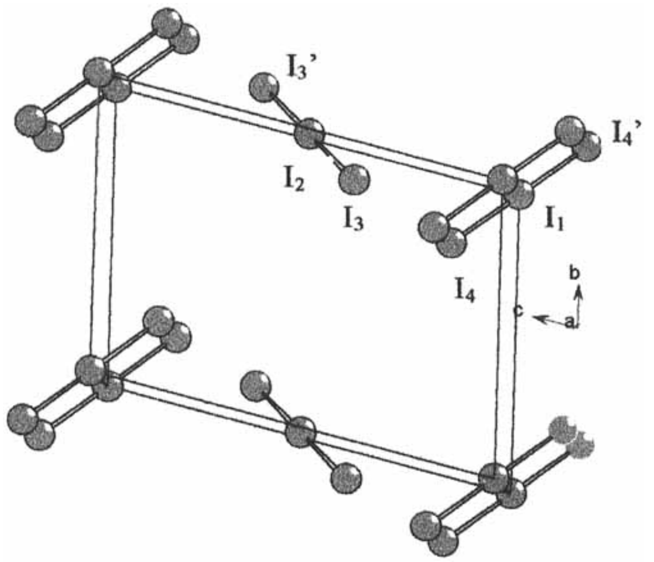

FIGURE 4 Projection on the **bc** plane : anions positions in lattice

stoichiometry of the salt indicates that donors are carrying a charge +I. It is well known that the geometry of TTF derivatives vary with the oxidation state of engaged donors. As expected, a decrease of C-S bond lengths and an increase of the C = C bond lengths of the TTF core is observed in $C.I_3$ salt in comparison with the geometry of the neutral molecule.[6] Moreover, from the structure established at room temperature, the S-S and S-C distances of the π-donor in this salt could be well compared with those found in other **C** salts and are in good agreement with those observed for TTF and BEDT-TTF radical cations (table IV).[23],[24] We should also note that bond lengths of molecule **C** are quite similar at 150 K. Relationship between charge transfer and geometry of the TTF core has recently been established for BEDT-TTF salts.[25] When applied to the case of $C.I_3$ salt (table V), this relation shows a rather good convergence to a [1:1] stoichiometry, with a calculated charge for the donor of +1.1 and + 0.97 at 293 K and 150 K respectively.

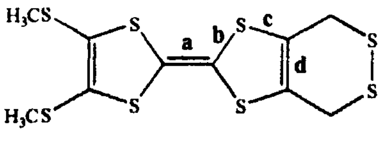

TABLE IV comparison of TTF core bond lengths in [1:1] salts of BEDT-TTF, TTF and in $C.I_3$

Composé	*Charge*	*a(Å)*	*b(Å)*	*c(Å)*	*d(Å)*
(BEDT-TTF).PF_6, ½ THF[23]	+1	1.379(6)	1.722(4)	1.737(5)	1.353(6)
TTF.ClO_4[22]	+1	1.404(13)	1.713(9)	1.725(12)	1.306(13)
$C.I_3$	+1	1.39(2)	1.71(2)	1.73(2)	1.35(3)

TABLE V calculation* of donor charge in $C.I_3$. C_{2v} symmetry has been imposed

T(K)	***a (Å)***	***b (Å)***	***c (Å)***	***d (Å)***	***Qcalc***
298 K	1.39(2)	1.71(2)	1.73(2)	1.35(3)	+1.12
150 K	1.39(1)	1.71(1)	1.75(1)	1.35(2)	+0.97

* Using the relation $Qcalc = 6.347-7.463\,\delta$ ***with*** $\delta = (b + c)-(a+d)$

As shown on figure 5, the central TTF core of donor **C** is roughly planar and the terminal S-CH_3 bonds extend out of the molecular plane of **C** with dihedral angles of 40.4° and 19.30° for (C_{10}-S_8-C_8-S_6) and (C_9-S_7-C_7-S_5), respectively. This observation is in contrast with previous results on $C.PF_6$,[6] $C.ClO_4$[6] and $C_2.CuCl_4$[26] salts, for which the methyl groups of the methylsulfanyl fragments approximately lie in the donor plane. Similarly to the peripheral ethylene groups in BEDT-TTF, the outer disulfide bridge in **C** adopts a twist conformation relative to the molecular plane. Contrary to $C.ClO_4$ or $C.PF_6$ salts, for which the terminal disulfide bridge adopts two symmetrical twisted conformation in a 60/40 relative ratio,[6] both sulfur atoms S_1 and S_2 in $C.I_3$ are found in only one position with however some position disorder as evidenced by large thermal parameters for those two sulfur atoms.

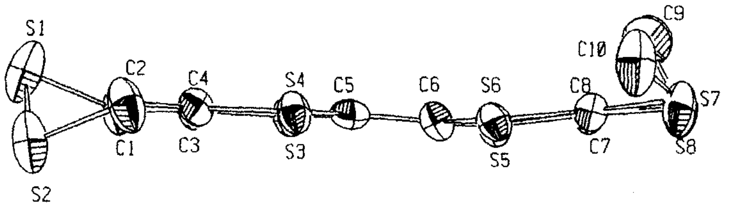

FIGURE 5 Ortep view of the crystal structure of **C** in $C.I_3$

Organic array is organized in zig-zag columns along *a*-axis (figure 6) and molecules are stacking in a head-to-tail manner. The strongly dimerized structure is characterized by some short contacts ($d(S_4\text{-}S_5') = d(S_5\text{-}S_4') = 3.39(2)$ Å,

$d(S_3\text{-}S_6') = d(S_6\text{-}S_3') = 3.43(2)$ Å) and the important overlap observed inside a dimer, given evidence of strong interactions between donors (figure 7). However, interactions between dimers along the ***a*** axis are obviously very weak.

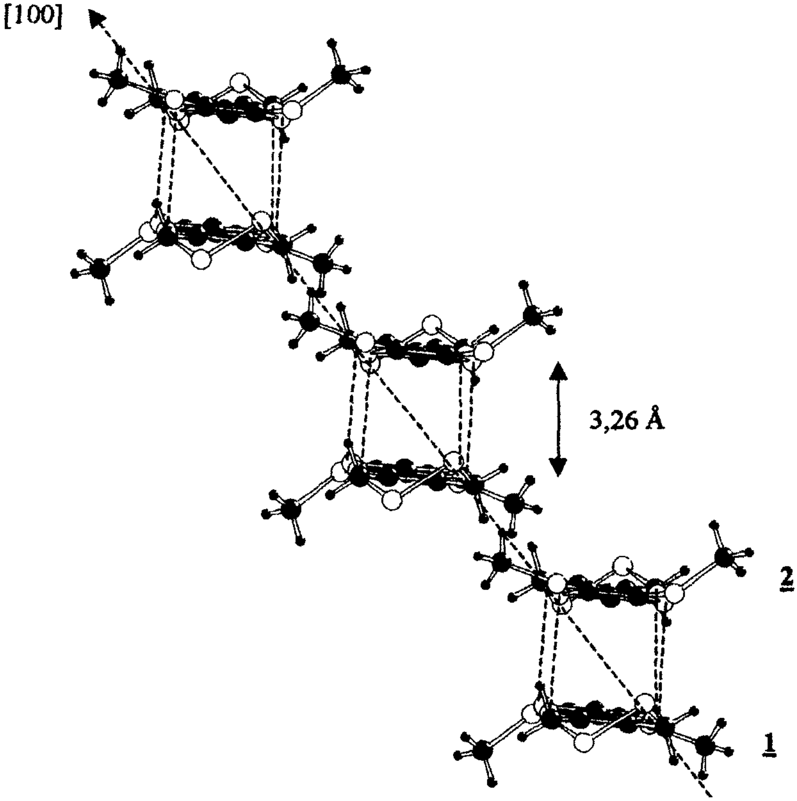

FIGURE 6 Zig-zag columnar stacking of donors along *a*-axis

In opposition to observations previously made on various **C** salts,[6],[26] it appears that peripheral S atoms are not involved in the structural organization of dimerized columns and that could be related to the linear geometry of the anion. Thus, columns of donors are separated by anions layers along ***b*** as well as ***c*** axis and therefore, no interstack contact is possible. Only some short S...I distances ($d(I_3\text{-}S_3) = 3.668(7)$ Å and $d(I_3\text{-}S_4) = 3.753(6)$ Å) between organic and anions arrays are also formed along the *b*-axis (figure 8).

As in the neutral molecule C,[5] the HOMO is mainly localized on the TTF framework and the sulfur atoms of the methylsulfanyl groups, while the outer

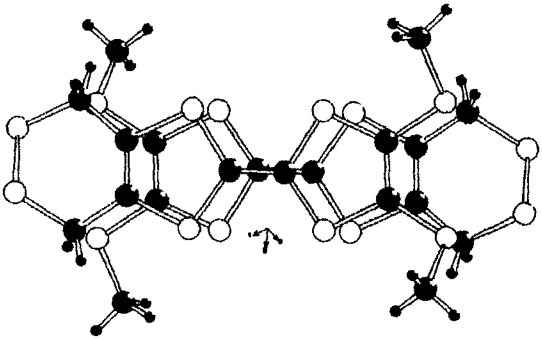

FIGURE 7 overlap of donors inside a dimer

sulfur atoms of the disulfide bridge have a weak contribution (figure 9). In the radical cation salt $[C_{10}H_{10}S_8]^+ I_3^-$, the I_3^- anion presents no contribution in the calculated HOMO.

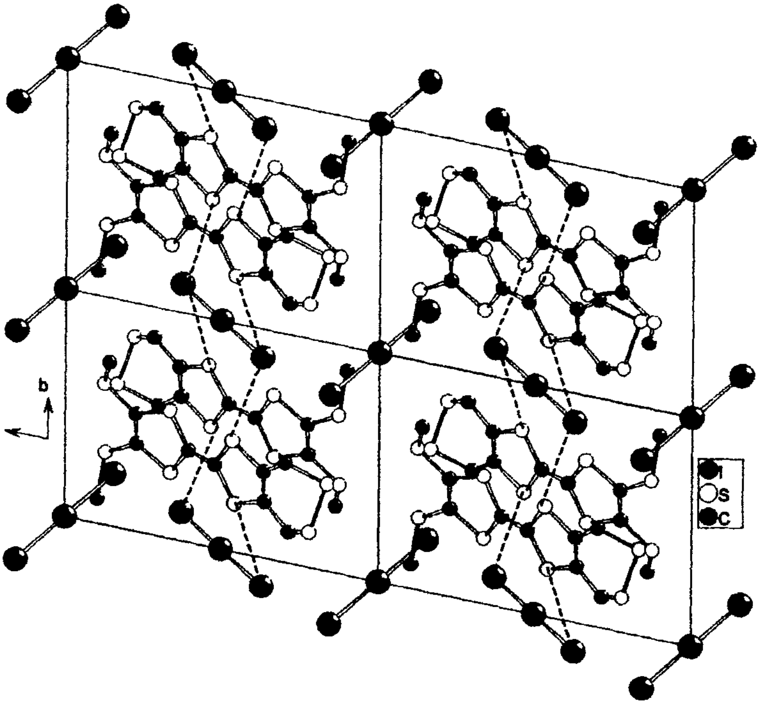

FIGURE 8 projection onto the bc plane. Shorter S… I contacts are represented by dotted lines

As clearly shown in figure 10, the HOMO of molecules 1 and 2 forming a dimer interacts to give an in-phase and an out-of-phase combination separated by roughly 0.6 eV. Assuming a charge distribution $C^+(I_3)^-$, the lowest MO is occupied and the highest MO is vacant. Band structure calculations carried out on the one-dimensional chain of $(C_2)^{2+}$ (figure 11) indicate that dimers hardly interact together. Indeed, bands deriving from the HOMOs of the molecules forming dimers are nearly flat along the direction in the reciprocal space corresponding to the stacking *a* axis. This is in agreement with the long S...S inter-dimer separations. As above mentioned, there are no S...S distances lower than the sum of Van der Waals radii : the lowest distance S...S between two dimers is 4.07 Å. The 0.6 eV band gap, is comparable to the HOMO-LUMO gap computed in the dimer.

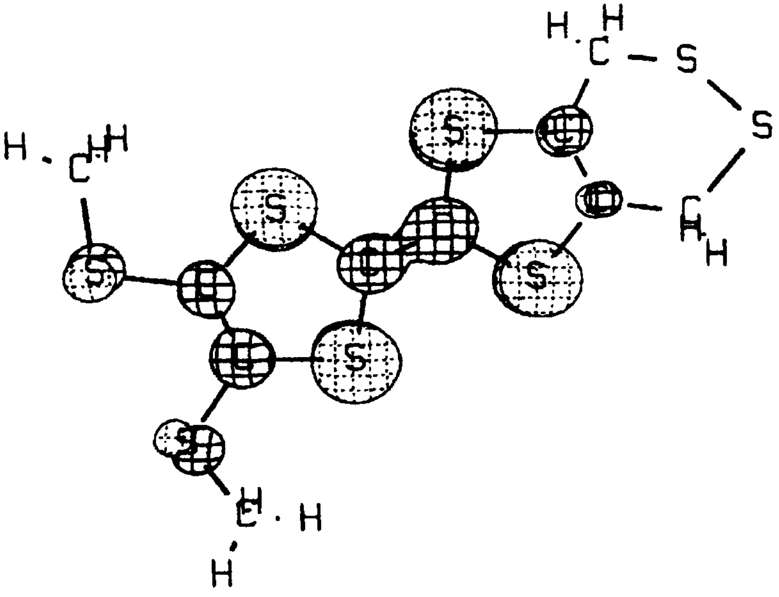

FIGURE 9 the Highest Occupied Molecular Orbital (HOMO) of the salt $C.I_3$

As expected from the charge distribution $(C_2)^{2+}.2(I_3)^-$, measurements carried out on a single crystal using the two probe technique show a conductivity lower than 10^{-5} S.cm^{-1} at room temperature.

CONCLUSION

Dimerized stacks of C molecule are found in the new $C.I_3$ salt as shown by X-ray study (at room temperature and at 150 K) and confirmed by band structure

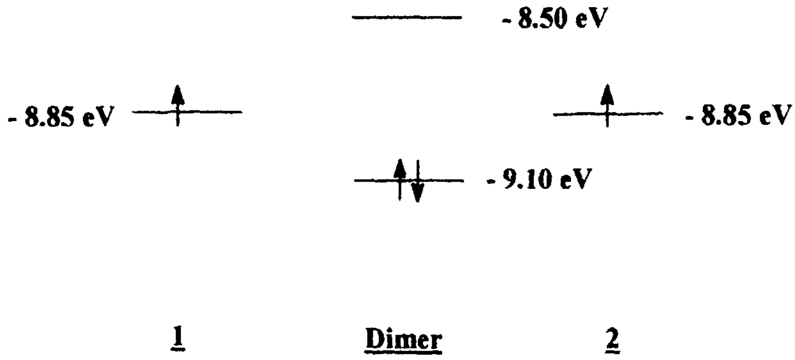

FIGURE 10 Interaction diagram of the HOMOs of the two C^+ molecules to form the dimer $(C_2)^{2+}$

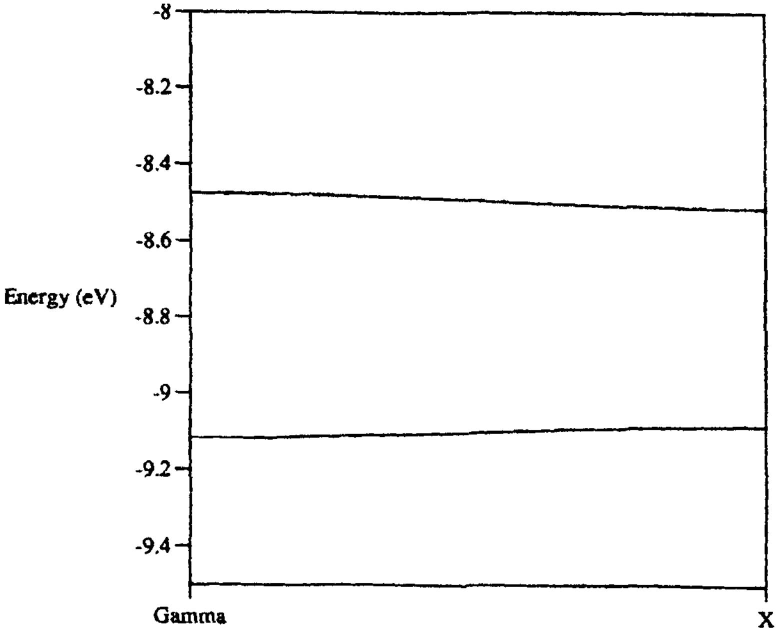

FIGURE 11 Band dispersion for the $(C_2)^{2+}$ stack in $C.I_3$

calculations. Unexpectedly, the disulfide bridge of C does not have any effect on the structural organization of the organic array. Work is in progress to prepare other radical cation salts in order to confirm the influence of outer sulfur atoms in the association mode of the network as previously observed for other C salts.

Attempts are also currently underway to associate this new donor to other linear anions in order to study if the structural arrangement of the donor array found for $C.I_3$ could be really related to the anion geometry.

Moreover, we have clearly demonstrated that the relationship established to determine the charge carried by BEDT-TTF in its different salts could be applied to C, probably thanks to their structural similarities.

Supplementary material available : bond angles at 293 K and 150 K and atomic displacement parameters.

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