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Polymorphism in the [(TTF)₂(TCNE)₂] Charge-Transfer Complex

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Abstract. — The reaction between tetrathiafulvalene (TTF) and tetracyanoethylene (TCNE) yields two polymorphs (α and β) both having formula [(TTF)₂^{2δ+}(TCNE)₂^{2δ-}] with similar molecular structure. Both polymorphs display a stack structure of the type ···(TTF-TTF)(TCNE-TCNE)(TTF-TTF)(TCNE-TCNE)··· but they differ in crystal structure for hydrogen bonding system and lamellar sheets. These two CT complexes possess an high resistivity ($\cong 10^9 \Omega \cdot \text{cm}$) and a degree of charge-transfer of $\delta = 0.54e$ estimated through the C-S bond length.

1. Introduction

Most organic charge-transfer (CT) salts display unusual solid state properties like metallic conductivity up to $5 \times 10^5 \text{ Scm}^{-1}$ at 3.5 K for Cu(2,5-DMDCNQI)₂ [1], molecular based magnetism and superconductivity. In particular, one-dimensional charge-transfer complexes (1-D CT) containing the *donor* tetrathiafulvalene (TTF) or substituted TTF have attracted and still attract great interest after the discovery of electrical conductivity, comparable with that of metals, for the compound TTF-TCNQ (TCNQ=tetracyano-*p*-quinodimethane) [2], and the discovery of the first sulfur-based organic superconductor, (BEDT-TTF)₂ReO₄ [3], [BEDT=bis(ethylene-dithiolo); $T_c = 1.4 \text{ K}$ at 4 kbar]. Moreover, some CT complexes, as B-TCNB [4] (B=biphenyl, TCNB acceptor=1, 2, 4, 5-tetracyanobenzene), DPA-TCNB [5] (DPA = diphenylacetylene), BP-TCNB [6] (BP=biphenylene), TSB-TCNB [7] (TSB=*trans*-stilbene), $2[(\text{C}_3\text{H}_7)_4\text{N}^+](\text{DDQ})_2^{2-}$ [2-8] (DDQ = 2, 3-dichoro-5, 6-dicyano-*p*-benzoquinone) and TTF-TCNB [9] were also synthesized and studied by us in order to verify the level of oxidation of the *donor* and the level of reduction of the *acceptor* which are a necessary requirement to obtain highly conducting organic metals.

So we have investigated the TTF-TCNE system (TCNE=tetracyanoethylene) since it was reported [10] that this compound possesses at room temperature a resistivity of nearly $10^9 \Omega \cdot \text{cm}$. In order to verify whether such behaviour is due to a crystal packing different from that of TTF-TCNQ, we have prepared and studied by X-ray diffraction the TTF-TCNE CT complex.

2. Experimental Section

Two different polymorphs of TTF-TCNE were prepared by mixing at room temperature equimolar amounts (0.489 mmol) of TTF and TCNE respectively in tetrahydrofuran (α -phase) or acetonitrile (β -phase). An analogous synthesis of this complex has been described by Wudl and Southwick [11]. Red-brown crystals of each phase, suitable for X-ray structure determination, were obtained by slow evaporation of solvents.

Intensity data, collected with a Philips PW-1100 diffractometer ($\text{MoK}\alpha$, $\lambda = 0.7107 \text{ \AA}$), were corrected for Lorentz and polarization effects. Absorption correction (empirical ψ -scan) and secondary isotropic extinction effects were considered only for the α -polymorph since the low μ value (6.5 cm^{-1}) and the small size of specimen of the β -polymorph. The structures were solved by direct and difference Fourier methods and were refined anisotropically for non-hydrogen atoms and isotropically for the hydrogen atoms using full-matrix least-squares techniques. The final

Table I. — Bond lengths (\AA) in TTF-TCNE.

TTF unit	α -phase		β -phase	
	a	b	a	b
S(1)-C(3)	1.739 (3)	1.740 (2)	1.74 (1)	1.73 (1)
S(2)-C(3)	1.733 (5)	1.736 (4)	1.73 (1)	1.74 (1)
S(1)-C(1)	1.713 (3)	1.730 (4)	1.73 (1)	1.73 (1)
S(2)-C(2)	1.728 (2)	1.733 (2)	1.72 (1)	1.75 (1)
C(1)-C(2)	1.320 (5)	1.311 (4)	1.33 (1)	1.32 (1)
C(3)-C(3)'	1.378 (2)		1.38 (1)	
TCNE unit				
C(6)-C(4)	1.434 (2)	1.432 (2)	1.43 (1)	1.43 (1)
C(6)-C(5)	1.413 (2)	1.426 (3)	1.43 (1)	1.41 (1)
C(4)-N(1)	1.137 (2)	1.143 (2)	1.15 (1)	1.15 (1)
C(5)-N(2)	1.146 (3)	1.142 (3)	1.13 (1)	1.15 (1)
C(6)-C(6)'	1.397 (4)		1.40 (1)	

a and b refer to the two pentatomic rings of TTF or to the two equivalent TCNE halves. The same specification is indicated in Figure 1 by apostrophes.

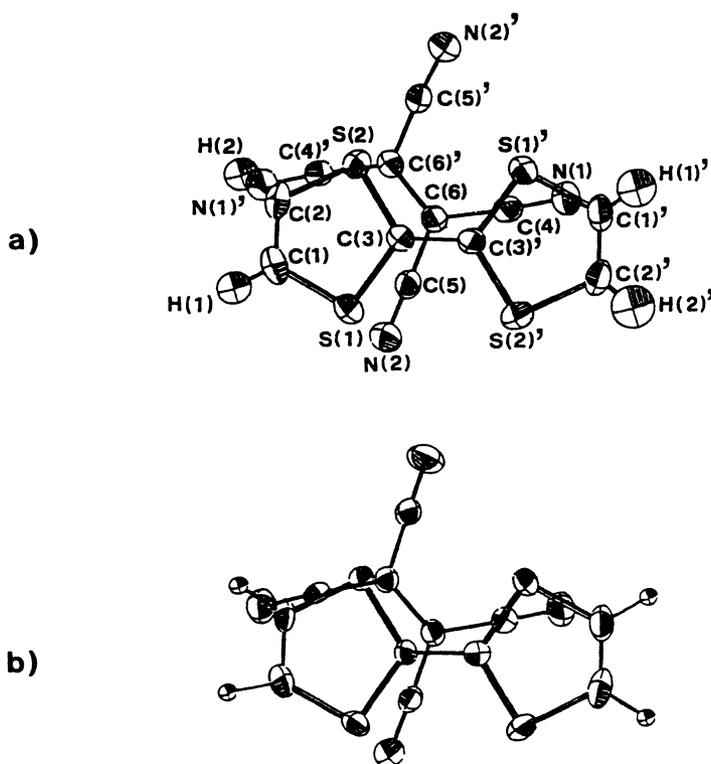


Fig. 1. — Molecular overlapping of (TTF)⁶⁺ and (TCNE)⁶⁻ projected on the (TTF)⁶⁺ plane for α -form (a) and β -form (b) that has the same atom numbering as (a). Atoms related by the *pseudo*-molecular center of symmetry are distinguished by an apostrophe.

discrepancy factors were, for the α -phase: $R = 0.034$, $R_w = 0.030$ for 2484 observed reflections and for the β -phase: $R = 0.058$, $R_w = 0.056$ for 2160 observed reflections. Scattering factors are taken from the *International Tables for X-ray Crystallography* and the computer programs used are those written by us or by Becker and Coppens, as reported in reference [5]. Listing of fractional atomic coordinates and structure factors are available from author D. A. Clemente.

3. Results and Discussion

Both the α - and β -polymorphs are monoclinic with space group $P2_1/n$ and $Z = 4$ (α -polymorph: $a = 13.310$ (6), $b = 15.475$ (5), $c = 6.864$ (3) Å, $\beta = 101.18$ (2)°, $V = 1387.0$ (1.0) Å³; β -polymorph, $a = 15.429$ (6), $b = 6.632$ (4), $c = 14.165$ (6) Å, $\beta = 104.32$ (3)°, $V = 1404.4$ (1.2) Å³). Table I reports bond lengths of α - and β -phases and Figure 1 (a and b) show their molecular structures respectively. The crystal structure consists of integrated stacks of $\cdots(\text{TTF-TTF})(\text{TCNE-TCNE})(\text{TTF-TTF})(\text{TCNE-TCNE})\cdots$ running nearly parallel to the a axis for the α -phase and to the c axis for the β -phase. The two polymorphs differ mainly for the hydrogen bonding system while the dihedral angles between TTF and TCNE mean planes are 1.26° (for α -phase) and 2.20° (for β -phase).

Table II. — Correlation between [C-S] *b* distances and degree of charge-transfer in TTF^{δ+} cations.

Formula	TTF ^{δ+} charge	<i>b</i> distance (Å)	Numbering and Ref.
TTF ⁰	δ+ =0.00	1.757(2)	1 → Ref.14
(TTF)(SCN) _{0.57}	δ+ =0.57	1.739(17)	2 → Ref.15
(TTF) ₃ (SCN) ₂	δ+ =0.66	1.731(2)	3 → Ref.16
(TTF) ₃ (SnCl ₆)	δ+ =0.66	1.736(10)	4 → Ref.17
(TTF) ₇ I ₅	δ+ =0.71	1.732 §	5 → Ref.18
(TTF)(HgCl ₃)	δ+ =1.00	1.720(10)	6 → Ref.19
(TTF)I ₃	δ+ =1.00	1.719(8)	7 → Ref.20
(TTF)(SnMe ₂ Cl ₃)	δ+ =1.00	1.718(4)	8 → Ref.21
(TTF)(ClO ₄)	δ+ =1.00	1.713(9)	9 → Ref.22
(BEDT-TTF)(ClO ₄) ₂ *	δ+ =2.00	1.683(3)	10 → Ref.23

* (BEDT-TTF)(ClO₄)₂ was used because bond lengths for (TTF)Cl₂ so far are not available.

§ E.s.d. not directly reported in ref.18.

We have estimated the degree of charge-transfer (from TTF to TCNE) by using the values of bond lengths reported in Table I. In fact, it is known that the distances indicated in the molecular scheme of Figure 2 with a, b, c, d are very sensitive to the effective charge present in the TTF moiety. TTF⁰ is able to lose one electron, becoming a TTF⁺ radical cation like in the (TTF)(ClO₄) salt, or two electrons becoming a TTF²⁺ cation like in (TTF)Cl₂. Since these two electrons are contained in the highest occupied molecular orbital (HOMO of *b_{1u}* symmetry in point group *D_{2h}*), the bond lengths variation due to TTF oxidation can be easily explained by the HOMO nodal properties [12]. As nodes are present in b and c bonds but not in a and d, an increase of the δ+ charge induces in TTF^{δ+} shorter b and c but longer a and d bonds. Although this situation was clear from the beginning, several authors pointed out that further factors, like hydrogen bonding, short intermolecular contacts (especially S··S), solvent effects, stacking geometry and molecular dimerization or overlapping, may be responsible for the amount of charge-transfer. Taking into account such limitations and considering that the nodal properties of the HOMO orbital are the dominant factors, we have attempted to correlate the *b* distances [C(3)-S(2)], which appear to be the most sensitive, with the charge of the TTF^{δ+} cation. In this analysis we have considered TTF⁰ and nine TTF salts (Tab. II) having anions (Cl⁻, ClO₄⁻, SCN⁻, I₃⁻..) with perfectly defined charge so that, for the electro-neutrality principle, also the TTF^{δ+} cation possesses a perfectly defined charge. The linear equation resulting from the diagram of Figure 2 is: $b = 1.757 - 0.0385 \cdot (\delta+)$. Thus, the *b* distance of 1.736 Å (mean of eight distances) found in the two polymorphs corresponds to a charge of 0.54*e*, in good agreement with 0.5 ± 0.1*e* obtained from infrared and Raman measurements [9, 13].

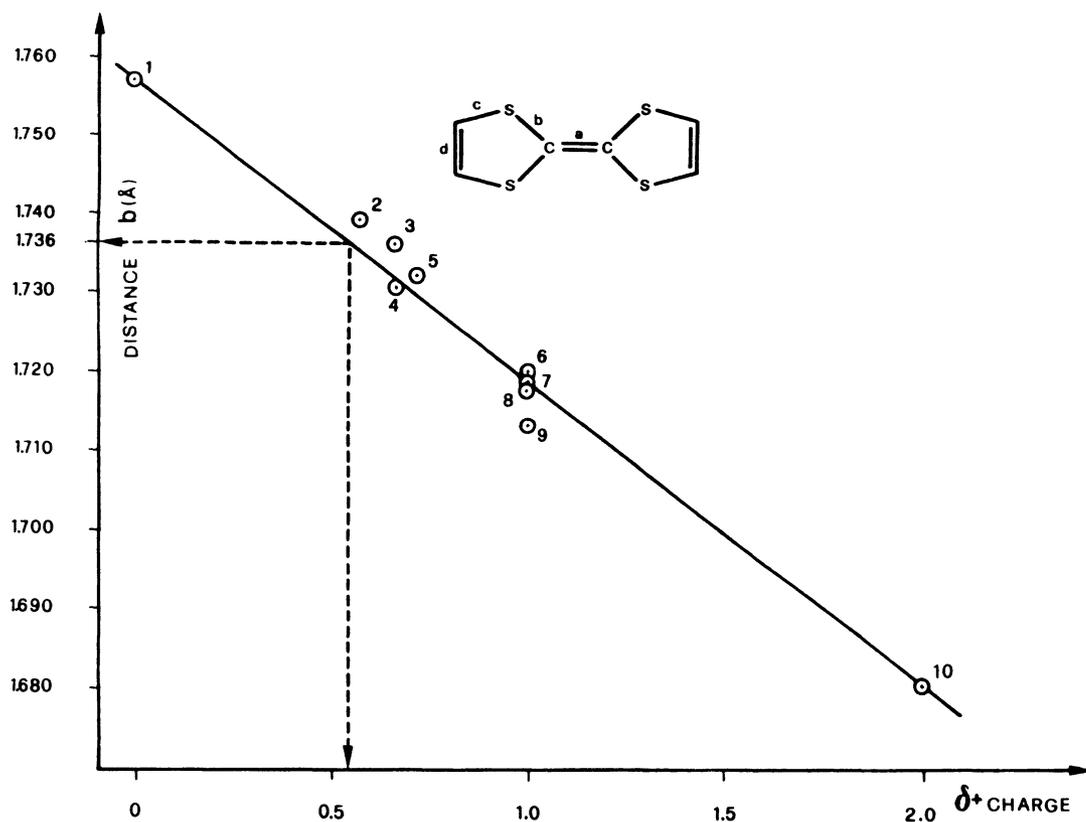


Fig. 2. — Linear correlation between b (mean C-S bond distance) and $\delta+$ (TTF charge) in ten TTF molecules numbered as indicated in Table II. The linear equation resulting from this diagram is: $b = 1.757 - 0.0385.(\delta+)$.

The nodal properties of the LUMO orbital (b_{2g} symmetry in point group D_{2h}) of neutral TCNE give a π -bonding character to the C-CN bond and an antibonding character to C=C and C \equiv N bonds. Consistent with this view, the present value of the C=C bond of 1.397 Å is higher than that found for cubic [1.344(3) Å] [24] and monoclinic [1.348(2) Å] [25] neutral TCNE, indicating a partial negative charge on TCNE.

In conclusion, the present results show that two different polymorphs of TTF-TCNE are obtained by using as solvent tetrahydrofuran or acetonitrile. Although the charge-transfer between the electron donor and the acceptor molecules is nearly equal to that of TTF-TCNQ, the TTF-TCNE system exhibits a resistivity much higher (10^9 against 0.10 Ω .cm [10]). This behaviour is due to the formation in the TTF-TCNE complex of mixed stacks such as $\cdots(A^{\delta-} A^{\delta-})(D^{\delta+} D^{\delta+})(A^{\delta-} A^{\delta-})(D^{\delta+} D^{\delta+})\cdots$ indicating that segregate stacks of TTF cation radicals and TCNQ represent a necessary requirement for this class of CT complexes to obtain a very high conductivity.

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