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# Structure and degree of charge transfer of two polymorphs of a 1:1 molecular complex: [2,2′-bis-1,3-dithiole][9-dicyanomethylene-4,5,7-trinitrofluorene-2-carboxylic acid methyl ester] (TTF-MeDC2TNF)

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A new organic charge-transfer complex, $C_{18}H_7N_5O_8{\cdot}C_6H_4S_4$, has been prepared using TTF (tetrathiafulvalene) as a donor ($D$) and MeDC2TNF (9-dicyanomethylene-4,5,7-trinitrofluorene-2-carboxylic acid methyl ester) as an acceptor ($A$). Two monoclinic polymorphs of the 1:1 salt were crystallized and characterized by X-ray diffraction. Form $\alpha$ crystallizes in space group $P2_1/n$ with $Z' = 1$, while form $\beta$ crystallizes in space group $C2/c$ with $Z' = \frac{1}{2}$ and the MeDC2TNF moiety disordered across a twofold axis. Both phases have mixed-stack crystal packings, which are characteristic of semiconducting one-dimensional organic complexes. However, the observed crystal packings are significantly different, with a single $D\cdots A$ interlayer separation of 3.452 Å for the disordered $\beta$ polymorph and interlayer separations of 3.378 and 3.483 Å in the case of the ordered $\alpha$ form. These variations are reflected in the degree of charge transfer, $\delta$, which was estimated on the basis of the $b_{2u}$ stretching-mode frequency shift observed in the IR spectra for the cyano groups of the MeDC2TNF radical anion. The fact that the charge transfer is more efficient for $\alpha$-(TTF-MeDC2TNF) than for $\beta$-(TTF-MeDC2TNF) ($\delta = 0.35$ and 0.31, respectively) is consistent with the structural features observed for each crystalline form.

## 1. Introduction

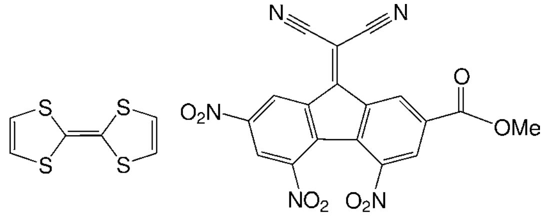
The chemistry and crystallography of organic charge-transfer complexes (CTCs) have been very active fields since the pioneering work of Melby on TCNQ salts (Melby *et al.*, 1962). This long-standing interest is mainly due to the hope of fine tuning the degree of charge transfer (DoCT) in these complexes, an ability that is essential for the design of new materials with unusual electrical and magnetic properties. Research in the 1970s was dominated by the emblematic 1:1 TTF-TCNQ salt (Pearlstein *et al.*, 1972; Heeger & Garito, 1972), which exhibits metallic behaviour (TTF is tetrathiafulvalene and TCNQ is 7,7,8,8-tetracyanoquinodimethane). The structure–property relationship has been clearly established (Conwell, 1988) for this material; the crystal packing is based on segregated stacks, *i.e.* donors ($D$) and acceptors ($A$) form separated stacks in the crystal, with close contacts within each stack. However, in this virtually one-dimensional structure, weak interactions through $\pi$-overlap occur between the stacks, thus providing partially filled electron energy bands. This arrangement results in highly anisotropic electronic transport properties, with metallic behaviour directed along the stacking directions, at least at room temperature. Numerous CTCs with segregated stack structures have been synthesized; the majority are highly conductive materials, in many cases to temperatures below 100 K, while mixed-stack CTCs, in which donors and acceptors stack alternately, are generally semiconductors or insulators (Bechgaard & Andersen, 1980) because of electron localization on the acceptor moiety.

Polymorphism is not uncommon in this class of compounds, especially for salts with a 1:1 stoichiometric composition. This phenomenon seems to influence the electronic properties of the material. For instance, in the case of the NMP-TCNQ salt (NMP is *N*-methylphenazinium), the triclinic polymorph is found to consist of ordered segregated stacks, and this structure is consistent with the high electrical conductivity measured for this solid; the monoclinic phase is characterized by an NMP radical cation that is one-dimensionally disordered along the crystallographic *c* axis and has semiconducting properties (Kobayashi, 1975). This kind of disorder was also observed for salts with 1:2 stoichiometry, such as ARD-$TCNQ_2$ (Kobayashi, 1974) and Q-$TCNQ_2$ (Kobayashi *et al.*, 1971), which complicates the interpretation of transport properties (ARD is aridinium and Q is quinolinuim).

On the basis of previous observations, the first condition for obtaining high electrical conductivity in a CTC-based material is to orient the structure towards segregated stacks rather than mixed stacks, and the second condition is to avoid polymorphism (Torrance, 1979). Obviously, both conditions are difficult to achieve during the design of a new material. On the other hand, these conditions can be relaxed for some systems. For example, in the case of DAP-BRL (DAP is 1,6-diaminopyrene and BRL is *p*-bromanil), two polymorphs have been reported, both of which have a mixed-stack arrangement but a relatively high conductivity ($s_{\rm RT} = 10^{-1}$ $W^{-1}$ $cm^{-1}$; Fujinawa *et al.*, 1999). A similar case was reported recently (Sakaue *et al.*, 2002) for the complex system (BEDT-TTF)(BrMeTCNQ) [BEDT-TTF is bis(ethylenedithio)tetrathiafulvalene], which has a mixed-stack structure with electronic properties close to the ionic neutral border.

In such efforts to characterize these materials and to understand their structure–properties relationships, it is important to estimate precisely the DoCT in the complex. Indeed, the donor–acceptor interactions in a CTC induce a redistribution of the electron density in the complex, which is directly correlated to the DoCT (expressed as $\delta$). Empirical observations determined that CTCs with a metallic character have a $\delta$ value in the range 0.4–0.7 (Kampar & Neilands, 1986). For the reference material TTF-TCNQ, $\delta = 0.59$ and $s_{\rm RT} = 500$ $W^{-1}$ $cm^{-1}$ (Chapell *et al.*, 1981; Miller, 1978). Note that a $\delta$ value in the aforementioned range is a necessary but not a sufficient condition for obtaining a metallic CTC; for the polymorphic phases of TTF-TCNE (TCNE is tetracyanoethylene), $\delta$ is 0.54 (10) e, which is very close to the $\delta$ value for TTF-TCNQ, but the one-dimensional mixed-stack arrangements for these compounds result in very high electrical resistivity (~$10^9$ Ω cm; Clemente & Marzotto, 1996).

In the present work, we report a study of polymorphism in the 1:1 TTF-MeDC2TNF salt [9-dicyanomethylene-4,5,7-trinitrofluorene-2-carboxylic acid methyl ester; (I)] and show that IR spectroscopy is a powerful tool for estimating $\delta$ values in structurally related complexes. Note that, surprisingly, few fluorene-based acceptors have been studied so far (Soriano-García *et al.*, 1989; Perepichka *et al.*, 1998), while TTF has been complexed with a wide range of other acceptors.



(I)

## 2. Experimental

TTF was purchased from Aldrich and used as received. MeDC2TNF was prepared according to a modification of the procedure of Sulzberg & Cotter (1970). Starting materials were mixed in hot acetonitrile in a 1:1 stoichiometry at a concentration of $\sim 10^{-2}$ mol $l^{-1}$. The mixture was slowly cooled and left at room temperature. Dark-brown needle-shaped crystals were collected after 24 d and were identified as the title compound, in the form of the polymorph denoted $\alpha$ below. Analysis calculated for $C_{24}H_{11}N_5O_8S_4$: C 46.08, H 1.77, N 11.19, O 20.46, S 20.50%; found: C 45.99, H 1.58, N 11.01, O 21.23, S 20.19%.

When the same procedure was carried out with a TTF/MeDC2TNF 2:1 stoichiometry, two crystal forms, which were separated by hand, were obtained, namely needle-shaped crystals, denoted form $\alpha$ (25% yield based on starting materials), and irregular block-shaped crystals, denoted form $\beta$ (11% yield).

FT–IR spectra were recorded in the range 3600–400 $cm^{-1}$ on a Nicolet Magna 750 spectrophotometer. Samples were diluted in KBr (1:65 *w*/*w*) and spectra were recorded on 3 mm-diameter pellets, with an experimental resolution of 4 $cm^{-1}$.

Selection of suitable samples for diffraction was complicated by the marked tendency of this system toward twinning. Available single crystals are systematically small and diffract poorly. Data collections were thus limited to a resolution of 0.84 Å. At such a resolution, the achieved $\langle I/\sigma(I)\rangle$ values (10.5 and 13.5 for forms $\alpha$ and $\beta$, respectively) should still ensure accurate refinements. Data were collected (Table 1) at room-temperature using routine techniques (Siemens, 1996) and were corrected for absorption effects on the basis of $\psi$ scans for crystals of form $\beta$. Structures were solved by direct methods and were refined anisotropically using standard methods (*SHELXL*97; Sheldrick, 1997). H atoms were placed at idealized positions and refined as riding on their parent atoms, with fixed $U_{\rm iso}$ values. In the case of form $\beta$, the disorder between the nitro and the methyl ester group on atom C2 was fully resolved. As a result of the position of the

**Table 1**
Experimental table.

| | $\alpha$-(TTF-MeDC2TNF) | $\beta$-(TTF-MeDC2TNF) |
|---|---|---|
| Crystal data | | |
| Chemical formula | $C_{18}H_7N_5O_8{\cdot}C_6H_4S_4$ | $C_{18}H_7N_5O_8{\cdot}C_6H_4S_4$ |
| $M_r$ | 625.62 | 625.62 |
| Cell setting, space group | Monoclinic, $P2_1/n$ | Monoclinic, $C2/c$ |
| $a, b, c$ (Å) | 6.7816 (17), 30.572 (4), 12.4381 (13) | 15.2489 (14), 12.6920 (10), 13.7950 (13) |
| $\beta$ (°) | 94.304 (11) | 104.350 (7) |
| $V$ (Å$^3$) | 2571.5 (8) | 2586.6 (4) |
| $Z$ | 4 | 4 |
| $D_x$ (Mg m$^{-3}$) | 1.616 | 1.607 |
| Radiation type | Mo $K\alpha$ | Mo $K\alpha$ |
| No. of reflections for cell parameters | 60 | 70 |
| $\theta$ range (°) | 4.7–11.1 | 4.3–11.9 |
| $\mu$ (mm$^{-1}$) | 0.43 | 0.43 |
| Temperature (K) | 296 (1) | 296 (1) |
| Crystal form, colour | Needle, dark brown | Block, dark brown |
| Crystal size (mm) | 0.70 × 0.16 × 0.08 | 0.40 × 0.20 × 0.18 |
| | | |
| Data collection | | |
| Diffractometer | Bruker $P4$ | Bruker $P4$ |
| Data collection method | $2\theta/\omega$ scans | $2\theta/\omega$ scans |
| Absorption correction | None | $\psi$ scan |
| $T_{\min}$ | – | 0.890 |
| $T_{\max}$ | – | 0.926 |
| No. of measured, independent and observed reflections | 5958, 4503, 3133 | 3590, 2274, 1768 |
| Criterion for observed reflections | $I > 2\sigma(I)$ | $I > 2\sigma(I)$ |
| $R_{\rm int}$ | 0.041 | 0.020 |
| $\theta_{\max}$ (°) | 25.0 | 25.0 |
| Range of $h, k, l$ | $-8 \rightarrow h \rightarrow 1$<br>$-1 \rightarrow k \rightarrow 36$<br>$-14 \rightarrow l \rightarrow 14$ | $-18 \rightarrow h \rightarrow 6$<br>$-15 \rightarrow k \rightarrow 1$<br>$-16 \rightarrow l \rightarrow 16$ |
| No. and frequency of standard reflections | 2 every 48 reflections | 2 every 48 reflections |
| Intensity decay (%) | 1 | 1 |
| | | |
| Refinement | | |
| Refinement on | $F^2$ | $F^2$ |
| $R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, $S$ | 0.065, 0.169, 1.06 | 0.041, 0.098, 1.04 |
| No. of reflections | 4503 reflections | 2274 reflections |
| No. of parameters | 370 | 218 |
| H-atom treatment | Constrained to parent site | Constrained to parent site |
| Weighting scheme | $w = 1/[\sigma^2(F_o^2) + (0.0585P)^2 + 5.5383P]$ where $P = (F_o^2 + 2F_c^2)/3$ | $w = 1/[\sigma^2(F_o^2) + (0.0359P)^2 + 3.2371P]$ where $P = (F_o^2 + 2F_c^2)/3$ |
| $(\Delta/\sigma)_{\max}$ | 0.001 | <0.0001 |
| $\Delta\rho_{\max}$, $\Delta\rho_{\min}$ (e Å$^{-3}$) | 0.66, –0.35 | 0.25, –0.26 |

† Computer programs: *XSCANS* (Siemens, 1996); *SHELXTL* (Sheldrick, 1998); *SHELXL*97 (Sheldrick, 1997).

fluorene group in the asymmetric unit (see below), site-occupation factors for disordered atoms were fixed to 0.5. In order to avoid overlap in the disordered parts, distances were constrained as follows: C2—N11 = 1.48 (2) Å, N11—O12 = 1.25 (2) Å, N11—O13 = 1.25 (2) Å, C2—C14 = 1.48 (2) Å, C14—O15 = 1.21 (2) Å, C14—O16 = 1.32 (2) Å and O16—C17 = 1.47 (2) Å.

## 3. Results and discussion

### 3.1. Structures for charge-transfer polymorphs

During attempts to crystallize the TTF-MeDC2TNF CTC, we observed that two habits of the single crystals appeared (see §2), which were separated by hand and transpired to be two polymorphs of the same 1:1 salt. These forms, denoted $\alpha$ and $\beta$, both correspond to mixed-stack arrangements. The $\alpha$ form is ordered, while the $\beta$ form exhibits an orientational disorder of the acceptor moiety.

The $\alpha$ polymorph crystallizes in space group $P2_1/n$, and the asymmetric unit contains one TTF moiety and one MeDC2TNF moiety, both in general positions (Fig. 1). The geometry of the TTF moiety is consistent with that of a radical cation, when compared with the geometry of neutral TTF (Ellern *et al.*, 1994). For instance, the central double bond is characterized by a bond length of 1.356 (6) Å, which is intermediate between that observed in neutral TTF [1.337(4) Å] and that observed for TTF-TCNQ [1.369 (4) Å] (Kistenmacher *et al.*, 1974). The ten non-H atoms forming the TTF moiety are almost coplanar, the r.m.s. deviation from the calculated mean plane being 0.023 Å. In contrast, the fluorene core of the MeDC2TNF molecule exhibits a severe out-of-plane distortion. The r.m.s. deviation from the mean plane calculated through the 13 C atoms of the ring system is 0.072 Å. Each ring is almost planar, but a significant dihedral angle of 8.09 (4)° is observed between the planes of the six-membered rings, thus giving the acceptor a twisted geometry. This deformation mainly arises from steric hindrance and electrostatic repulsion between the two adjacent nitro groups on atoms C4 and C5. The corresponding $NO_2$ planes form dihedral angles with the planes of the six-membered rings to which they are bonded of 33.2 (3) and 36.9 (3)° for the nitro groups on atoms C4 and C5, respectively. These rotation angles are typical of 4,5-dinitrosubstituted fluorenes. The non-hindered substituents on atoms C2 (a methyl ester function) and C7 (a nitro group) are approximately conjugated with

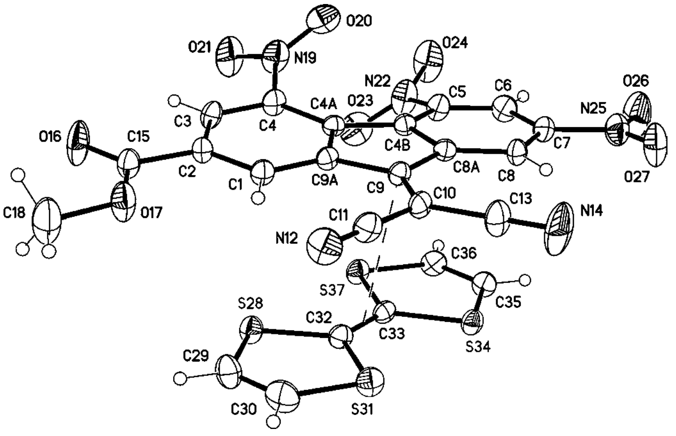


**Figure 1**
Molecular structure of $\alpha$-(TTF-MeDC2TNF), with displacements ellipsoids shown at the 30% probability level. The dotted line joining atom C9 and the centroid between atoms C32 and C33 represents the $D{\cdots}A$ separation.

their respective benzene rings, with dihedral angles of 1.65 (6) and 3.90 (6)°, respectively. Finally, a dicyanomethylene fragment is substituted at the 9-position of the fluorene group, and this substituent deviates slightly from the plane of the cyclopentadiene central ring by a dihedral angle of 5.5 (1)°. The exocyclic C9═C10 double bond of 1.371 (6) Å is consistent with a slight decrease of bond order with respect to a pure $\pi$ bond; this behaviour is expected because of the partial anionic character of the molecule in the CTC.

Polymorph $\beta$ (Fig. 2) crystallizes in space group *C*2/*c*, with one-half of the CTC in the asymmetric unit ($Z' = \frac{1}{2}$). The TTF molecule lies on an inversion centre (Wyckoff site symmetry *a*), *i.e.* with a crystallographic symmetry compatible with the point symmetry, $D_{2h}$. The dimensions for this radical cation are similar, within the s.u. values, to those observed for the ordered $\alpha$ phase.

For example, the r.m.s. deviation from the mean plane through the ten non-H atoms is small (0.017 Å), and the central C25═C25$^{i}$ double bond [1.356 (5) Å; symmetry code: (i) $1 - x, 1 - y, 1 - z$] is identical in the two polymorphs. The special position of the MeDC2TNF radical anion is determined by the exocyclic C7═C8 double bond, which is located on a twofold axis at ($\frac{1}{2}$, $y$, $\frac{3}{4}$) (Wyckoff site symmetry *e*). As a result of this local symmetry, disorder is observed for the substituents at the 2- and 7-positions of the fluorene system; the two crystallographically equivalent sites are occupied by a nitro group and a carboxylic acid methyl ester group, with symmetry-imposed site-occupation factors of 0.5. In other words, the point-group symmetry for the MeDC2TNF molecule increases from $C_1$ in the ordered $\alpha$ phase (actual point symmetry) to a pseudo-$C_2$ symmetry in the $\beta$ phase as a consequence of the local disorder.

This dimorphism for TTF-MeDC2TNF appears to be achievable because the nitro group and the COO moiety of the ester group have very similar dimensions. However, it should be mentioned that, in the present study, the diffraction data are good enough to resolve precisely the atomic sites of chemically non-equivalent fragments (see §2). On the other hand, the space groups are consistent with point symmetries, namely $P2_1/n$ for a $C_1$ MeDC2TNF molecule and *C*2/*c* for a $C_2$-MeDC2TNF molecule. A noteworthy corroboration of the symmetry increase, $C_1 \rightarrow C_2$, induced by disordering the acceptor moiety in TTF-MeDC2TNF is found in the IR spectra (Fig. 3); the stretching vibration for the cyano functional group, which appears in a range free of other signals, has a shape related to the crystallographic symmetry of the MeDC2TNF molecule. In the case of the $C_2$-MeDC2TNF form found in the disordered $\beta$ phase, a single vibration is observed (at 2214 cm$^{-1}$), which indicates the presence of two symmetry-equivalent cyano groups. In the case of the $C_1$ MeDC2TNF form found in the ordered $\alpha$ phase, this signal is clearly split into two unresolved bands, namely one at 2212 and one at 2202 cm$^{-1}$, which correspond to two non-symmetry-equivalent cyano groups. As expected, neutral MeDC2TNF (actual $C_1$ point group) exhibits a band shape that is very similar to that observed for $\alpha$-TTF-MeDC2TNF but is shifted to higher wavenumbers; this behaviour is expected on the basis of the relative oxidation states.

The geometry of the MeDC2TNF moiety in polymorph $\beta$ is close to that observed in phase $\alpha$. The 13 C atoms of the fluorene core exhibit an r.m.s. deviation from the corresponding mean plane of 0.088 Å, and the twist distortion is characterized by the dihedral angle between the benzene rings [9.43 (9)°]. The hindered nitro groups on atoms C4 and C4$^{ii}$ [symmetry code: (ii) $-x + 1$, $y$, $-z + \frac{3}{2}$] are rotated from the plane of the benzene rings by 33.6 (2)°, while the remaining non-hindered substituents are almost conjugated with the fluorene group; the dihedral angles are 13 (1) (NO$_2$ on atom C2), 8(3) (methyl ester on atom C2) and 6.60 (11)° (dicyanomethylene on atom C7).

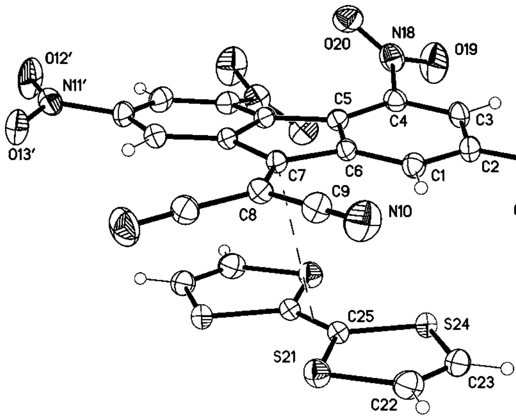


**Figure 2**
Molecular structure of $\beta$-(TTF-MeDC2TNF), with displacements ellipsoids shown at the 30% probability level. For clarity, the disorder of the substituents on atom C2 has been omitted; the methyl ester component is shown on atom C2, while the nitro component is shown on atom C2$^{ii}$ [symmetry code: (ii) $-x + 1$, $y$, $-z + \frac{3}{2}$], both components having a site-occupation factor of 0.5. The dotted line joining atom C7 and the centroid between atoms C25 and C25$^{i}$ [symmetry code: (i) $1 - x$, $1 - y$, $1 - z$] represents the $D\cdots A$ separation.

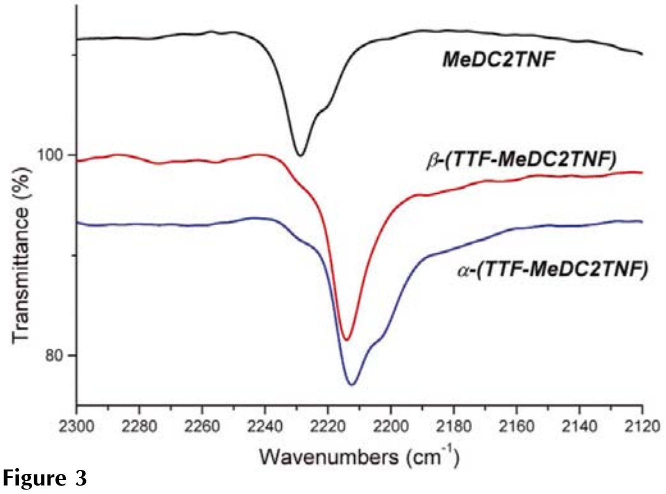


**Figure 3**
FT–IR spectra for the neutral acceptor MeDC2TNF and the $\alpha$ and $\beta$ forms of its TTF salts, in the range 2300–2100 cm$^{-1}$. The transmittance scale matches the actual measurements for the two polymorphs, but the MeDC2TNF spectrum was shifted arbitrarily to higher transmittance values in order to clarify the figure.

### 3.2. Packing structures

Polymorphs $\alpha$ and $\beta$ therefore exhibit very similar dimensions for donor and acceptor molecules, but the two polymorphs are differentiated by their intermolecular dimensions and crystal packings. In a $D\cdots A$ pair, charge transfer is indicated by the presence of short contacts. For the CTC under consideration, the shortest interatomic contacts for non-H atoms within the asymmetric units are S37—O20 = 3.279 (4) Å for form $\alpha$ and S24—C1 = 3.321 (3) Å for form $\beta$ [the corresponding van der Waals distances (Bondi, 1964) are 3.32 and 3.50 Å, respectively]. However, these contacts involving atoms at the periphery of the MeDC2TNF molecules probably arise from the out-of-plane deformation of these moieties rather than the charge transfer. A close approach of $D$ and $A$ molecules is best described using the separation between the centre of the central double bond of the TTF molecule and atom C9 of the exocyclic double bond of the fluorene molecule (C7 in form $\beta$). These separations are 3.378 and 3.452 Å for forms $\alpha$ and $\beta$, respectively, and the vectors defining these distances deviate from the normal vectors of the mean TTF planes by 8.9 and 12.1°, respectively. These last deviations are important parameters for defining the DoCT, because they indicate the relative alignment of the $D$ and $A$ molecules in the asymmetric units. The best structural descriptor, including estimated s.u. values, is the dihedral angle between the least-squares mean planes of the TTF (ten atoms) and the MeDC2TNF (13 atoms) molecules; these tilting angles are 2.50 (2) and 2.91 (4)° for forms $\alpha$ and $\beta$, respectively. Considering that the molecules have very similar dimensions in the two polymorphs, the difference between tilting angles, at the 10 s.u. level, is significant.

Finally, the crystal packings consist of $DA$ units stacked along the $a$ axis in form $\alpha$ (Fig. 4) and along the $c$ axis in form $\beta$ (Fig. 5), and these stacks are arranged within the crystalline lattice in a manner typical of this class of 1:1 CTC. However, as a consequence of distinct crystallographic symmetries, a key feature differentiates these crystal packings. The $\alpha$ polymorph, with molecules lying in general positions, exhibits an interunit $DA$ separation that differs from the intraunit $DA$ contact. If these separations are calculated on the basis of $X$—C9 distances (where $X$ is the centroid of the central double bond of the TTF molecule; see §3.1), the $D$ and $A$ molecules are separated by 3.378 Å within a $DA$ unit (asymmetric unit), while the $D\cdots A$ separations for symmetry-related units is larger (3.483 Å; Fig. 4 inset). A totally different geometry is observed in the case of the $\beta$ polymorph, in which the $D$ and $A$ molecules are spaced regularly in a stack, with a unique distance contact of 3.452 Å (Fig. 5 inset). Although both phases were crystallized at the same temperature, the observed distortion from a uniform stack (form $\beta$) to a stack of alternate short–long spacings is reminiscent of the Peierls distortion reported for a number of one-dimensional and quasi-one-dimensional systems, including CTCs (McCall *et al.*, 1985).

For the present system, the best description for the solid state is a quasi-one-dimensional system of mixed stacks, rather than an actual one-dimensional solid, because there are numerous interstack contacts. Potential hydrogen bonds are present in both polymorphs but are very weak, *i.e.* electrostatic interactions between neighbouring stacks in the cell should be very low compared with charge delocalizations along the stacks.

### 3.3. Degree of charge transfer

An obvious concern is to establish how the disorder observed in polymorph $\beta$ could affect the degree of charge transfer (DoCT) with respect to the ordered polymorph $\alpha$. Numerous techniques are available for estimating $\delta$, the parameter that measures the DoCT, in anisotropic CTCs. A classic method consists of correlating $\delta$ with frequency shifts of the IR-active fundamental modes of the $D$ or $A$ molecules (Chapell *et al.*, 1981):

$$\delta = (2\Delta\nu/\nu_0)(1 - \nu_1^2/\nu_0^2)^{-1},$$

where $\Delta\nu = \nu_0 - \nu_{\rm CTC}$.

Here, $\nu_0$ is the observed frequency for neutral MeDC2TNF, $\nu_{\rm CTC}$ is the frequency for the same vibration mode observed in the CTC, and $\nu_1$ is the frequency corresponding to a totally ionized MeDC2TNF molecule, for example, in the potassium salt $K^+\cdot$MeDC2TNF$^-$. In the present study, we use the $b_{2u}$

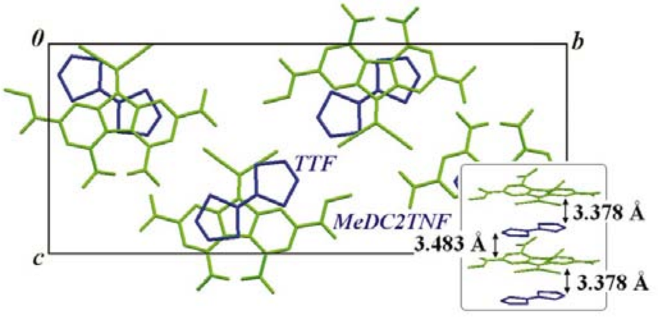


**Figure 4**
Packing structure of $\alpha$-(TTF-MeDC2TNF), viewed along the short $a$ axis. H atoms have been omitted for clarity. The inset shows one stack with two pairs of $DA$ subunits rotated by ~90° with respect to the main figure.

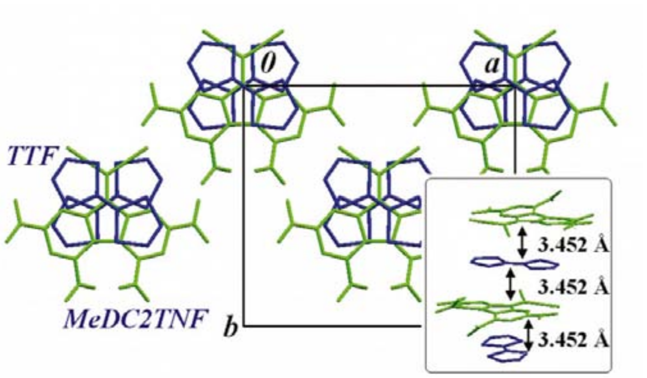


**Figure 5**
Packing structure of $\beta$-(TTF-MeDC2TNF), viewed along the short $c$ axis. H atoms have been omitted for clarity. The inset shows one stack with two pairs of $DA$ subunits rotated by ~90° with respect to the main figure. Note the symmetry-imposed rotation of $D$ and $A$ molecules for two neighbouring $DA$ subunits in the stack.

stretching mode of the cyano groups of the MeDC2TNF molecule, since this mode has the advantage of being unambiguously located at $\sim$2227 cm$^{-1}$ where there is no overlap of other vibration modes. For this mode, $\nu_0$ = 2229 cm$^{-1}$ and $\nu_1$ = 2180 cm$^{-1}$. The observed shifts are $\Delta\nu$ = 17 cm$^{-1}$ for polymorph $\alpha$ and $\Delta\nu$ = 15 cm$^{-1}$ for polymorph $\beta$ (Fig. 3). The corresponding DoCTs calculated using the Chapell approach are then

$$\delta_\alpha = 0.35 \quad \text{and} \quad \delta_\beta = 0.31.$$

The $\delta_\alpha$ value is probably underestimated because, as mentioned above, the absorption band for this phase appears with a shoulder at a lower wavenumber; the $\delta_\alpha$ value reported here is computed on the basis of a maximum absorption at 2212 cm$^{-1}$, while the shoulder at 2202 cm$^{-1}$ ($\Delta\nu$ = 27 cm$^{-1}$) would give a contribution at $\delta$ = 0.56. However, although the separation between the two contributions in the IR spectrum is larger than the experimental resolution (4 cm$^{-1}$), we were unable to deconvolute these bands in order to obtain actual $\nu_{\rm CTC}$ values for this polymorph. On the other hand, the accepted accuracy of the estimation of $\delta$ using this method is low ($\sim$0.1 e). Taking into account these observations, the numerical $\delta$ values calculated above should be considered as approximate estimates of the DoCT rather than exact values. For the present study, we conclude that, within the experimental errors, we have

$$\delta_\alpha > \delta_\beta.$$

This qualitative conclusion agrees with the observed structures. The ordered $\alpha$ phase, with the higher $\delta$ value, exhibits a shorter $D\cdots A$ separation (3.378 Å) than the disordered $\beta$ phase (3.452 Å). Charge transfer is also favoured in the first phase because of the small tilt angle between the $D$ and $A$ moieties [2.50 (2) *versus* 2.91 (4)° for the disordered case].

It should be emphasized that the correlation between the X-ray structure and the DoCT is intrinsically limited both by the uncertainties of the geometric parameters and by the fact that the $\delta$ values span a very small range. For instance, since the central C═C bond in the TTF molecule is also sensitive to the charge transfer, a comparison of this bond length could confirm the difference in the DoCT. Unfortunately, these distances are identical within the s.u. values, namely 1.356 (6) for $\alpha$-(TTF-MeDC2TNF) *versus* 1.356 (5) Å for $\beta$-(TTF-MeDC2TNF). In other words, for the achieved experimental resolution, a difference of 0.04 for $\delta$ is not reflected in the length of the central C═C bond in TTF at a two-significant-figure level, but is reflected in structural features involving the whole CTC, such as the $D\cdots A$ separation.

In spite of these limitations, the main conclusion agrees with previously reported Raman data for $\alpha$-(TTF-MeDC2TNF) ($\delta_\alpha$ = 0.32; Salmerón-Valverde *et al.*, 1999). This value was obtained using the active Raman stretching mode of the central C═C bond in TTF. Although the earlier result deviates from the value obtained in the present work, the $\delta_\alpha > \delta_\beta$ relationship still holds. The difference between Raman (0.32) and IR (0.35) $\delta_\alpha$ values should probably be attributed to the fact that distinct vibration modes are used for each spectroscopy (that is, a TTF vibration in the case of the Raman-based DoCT estimation and an acceptor vibration in the case of the IR-based DoCT estimation); moreover, different reference materials correspond to $\delta$ = 0 and $\delta$ = 1 for each technique.

## 4. Conclusions

We have established that dimorphism in the solid state of TTF-MeDC2TNF produces small variations in the structural features of the CTC; as reported for numerous related CTCs, these variations could dramatically affect transport properties. Although it remains very difficult to predict changes in electrical conductivity induced by polymorphism for the system under study, the estimation of the DoCT correlates well with the X-ray structures. This kind of study can be considered a good first approach for selecting materials prior to electrical conductivity measurements at variable temperature, taking into account that these are often tedious and difficult experiments that are not easily reproducible . In some cases, serious limitations occur, for instance, for 100 µm-sized single crystals and/or for single crystals without well shaped faces. Both limitations occur in the case of $\beta$-(TTF-MeDC2TNF).

## References

Bechgaard, K. & Andersen, J. R. (1980). *Physics and Chemistry of Low-Dimensional Solids*, edited by L. Alacacer, p. 247. Dordrecht: Reidel.

Bondi, A. (1964). *J. Phys. Chem.* **68**, 441–451.

Chapell, J. S., Bloch, A. N., Bryden, W. A., Maxfield, M., Poheler, T. O. & Cowan, D. O. (1981). *J. Am. Chem. Soc.* **103**, 2442–2443.

Clemente, D. A. & Marzotto, A. (1996). *J. Mater. Chem.* **6**, 941–946.

Conwell, E. (1988). *Semiconductors and Semimetals*, Vol. 27, *Highly Conducting Quasi-One-Dimensional Organic Crystals*, p. 3. San Diego, CA: Academic Press.

Ellern, A., Bernstein, J., Becker, J. Y., Zamir, Sh., Shahal, L. & Cohen, S. (1994). *Chem. Mater.* **6**, 1378–1385.

Fujinawa, T., Goto, H., Naito, T., Inabe, T., Akutagawa, T. & Nakamura, T. (1999). *Bull. Chem. Soc. Jpn*, **72**, 21–26.

Heeger, A. J. & Garito, A. F. (1972). *AIP Conf. Proc.* **10**, 1476.

Kampar, E. & Neilands, O. (1986). *Russ. Chem. Rev.* **55**, 334–341.

Kistenmacher, T. J., Phillips, T. E. & Cowan, D. O. (1974). *Acta Cryst.* B**30**, 763–768.

Kobayashi, H. (1974). *Bull. Chem. Soc. Jpn*, **47**, 1346–1352.

Kobayashi, H. (1975). *Bull. Chem. Soc. Jpn*, **48**, 1373–1377.

Kobayashi, H., Marumo, F. & Saito, Y. (1971). *Acta Cryst.* B**27**, 373–378.

McCall, R. P., Tanner, D. B., Miller, J. S., Epstein, A. J., Howard, I. A. & Conwell, E. M. (1985). *Synth. Met.* **11**, 231–237.

Melby, L. R., Harder, R. J., Hertler, W. R., Mahler, W., Benson, R. E. & Mochel, W. E. (1962). *J. Am. Chem. Soc.* **84**, 3374–3387.

Miller, J. S. (1978). *Ann. N. Y. Acad. Sci.* **313**, 25–60.

Pearlstein, J. H., Ferraris, J. P., Walatka, V. V. & Cowan, D. O. (1972). *AIP Conf. Proc.* **10**, 1494.

Perepichka, I. F., Kuz'mina, L. G., Perepichka, D. F., Bryce, M. R., Goldenberg, L. M., Popov, A. F. & Howard, J. A. K. (1998). *J. Org. Chem.* **63**, 6484–6493.

Sakaue, M., Hasegawa, T., Akutagawa, T. & Nakamura, T. (2002). *Nippon Kagakkai Koen Yokoshu*, **81**, 337.

Salmerón-Valverde, A., Robles-Martínez, J. G., García-Serrano, J., Gómez, R., Ridaura, R. M., Quintana, M. & Zehe, A. (1999). *Mol. Eng.* **8**, 419–426.

Sheldrick, G. M. (1997). *SHELXL*97. University of Göttingen, Germany.

Sheldrick, G. M. (1997). *SHELXTL*. Version 5.10. Bruker AXS Inc., Madison, Wisconsin, USA.

Siemens (1996). *XSCANS*. Version 2.21. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.

Soriano-García, M., Toscano, R. A., Robles Martínez, J. G., Salmerón, A. & Lezama R. (1989). *Acta Cryst.* C**45**, 1442–1444.

Sulzberg, T. & Cotter, R. J. (1970). *J. Org. Chem.* **35**, 2762–2769.

Torrance, J. B. (1979). *Molecular Metals*, edited by W. E. Hatfield, pp. 7–14. New York: Plenum.