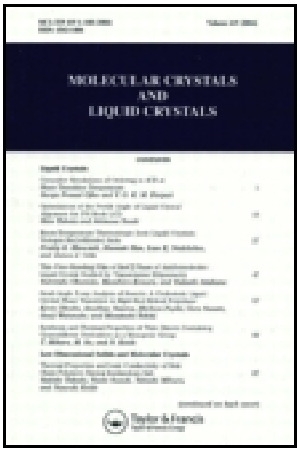

Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl16

Optical Properties, Conductivity and Structure of the DTT-TCNQ CT Complex

F. Bertinelli [a] , P. Costa Bizzarri [b] , C. Della Casa [b] , A. Marchesini [c] , G. Pelizzi [d] , R. Zamboni [e] & C. Taliani [e]

[a] Istituto di Chimica Fisica e Spettroscopia, Università, 40136, Bologna, Italy

[b] Istituto di Chimica Industriale, Università, 40136, Bologna, Italy

[c] Istituto di Chimica Industriale, Università, 20133, Milano, Italy

[d] Centro di Studio per la Strutturistica Difrattometrica del CNR, Istituto di Chimica Generale, Università, 43100, Parma, Italy

[e] Istituto di Spettroscopia Molecolare del CNR, 40126, Bologna, Italy

Version of record first published: 20 Apr 2011.

To cite this article: F. Bertinelli , P. Costa Bizzarri , C. Della Casa , A. Marchesini , G. Pelizzi , R. Zamboni & C. Taliani (1984): Optical Properties, Conductivity and Structure of the DTT-TCNQ CT Complex, Molecular Crystals and Liquid Crystals, 109:2-4, 289-302

To link to this article: http://dx.doi.org/10.1080/00268948408078714

Mol. Cryst. Liq. Cryst., 1984, Vol. 109, pp. 289–302
0026-8941/84/1094-0289/$18.50/0

Optical Properties, Conductivity and Structure of the DTT-TCNQ CT Complex

F. BERTINELLI
Istituto di Chimica Fisica e Spettroscopia, Università, 40136 Bologna, Italy

P. COSTA BIZZARRI and C. DELLA CASA
Istituto di Chimica Industriale, Università, 40136 Bologna, Italy

A. MARCHESINI
Istituto di Chimica Industriale, Università, 20133 Milano, Italy

G. PELIZZI
Centro di Studio per la Strutturistica Difrattometrica del CNR, c/o Istituto di Chimica Generale, Università, 43100 Parma, Italy

and

R. ZAMBONI and C. TALIANI
Istituto di Spettroscopia Molecolare del CNR, 40126 Bologna, Italy

(*Received February 7, 1984*)

The crystal structure, the optical spectra and electrical conductivity of dithieno(3,2-*b*; 2′,3′-*d*)thiophene-tetracyanoquinodimethane (DTT-TCNQ) charge-transfer complex have been measured. DTT-TCNQ crystallizes in the monoclinic space group $P2_1/c$ with $a = 7.206(2)$, $b = 7.574(2)$, $c = 32.324(9)$, $\beta = 92.18(4)°$, $Z = 4$, and the donor and acceptor molecules are arranged in alternated stacks.

The low conductivity ($\sigma = 10^{-12}$ S cm^{-1} for the single crystal, along the stacking axis a) is characteristic of a semiconductor with activation energy of .61–.76 eV, and is related to the alternate stack structure.

Despite the poor conductivity of the DTT-TCNQ CT complex we estimated, from structural and IR data, a low degree of ionicity (ρ = .2–.3) which characterizes the DTT molecule as an interesting donor.

The polarized IR spectra shows the effect of vibronic activation of some of the a_g modes of TCNQ.

1. INTRODUCTION

Dithieno(3,2-*b*;2′,3′-*d*)thiophene, hereafter referred to as DTT, is a novel prototype molecule which consists of three condensed thiophene rings whose electronic structure has been recently studied.[1]

Because of the large delocalized π system and the presence of the sulfur heteroatoms it appears as an interesting candidate in the formation of donor–acceptor charge transfer complexes.

We have chosen to point our attention to the charge transfer (CT) complex with TCNQ, which, among the several possible acceptor molecules, is by far the more extensively studied and characterized. The molecular structures of both molecules are shown in Figure 1.

In the present paper we investigate the optical and electrical properties as well as the structure of the DTT-TCNQ CT complex with the aim to characterize this new material by making use of the correlation among those properties. In particular we will discuss the structure in terms of electron–molecular vibration (e–mv) interactions and will make an estimate of the degree of ionicity.

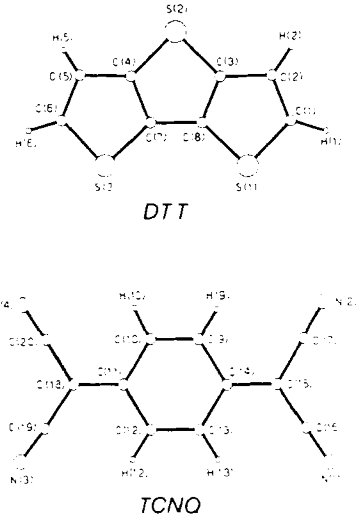

FIGURE 1 Schematic drawing illustrating the atom-numbering scheme for DTT and TCNQ.

2. EXPERIMENTAL

2.1. Preparation

DTT was synthesized and purified according to the literature.[2] Commercial TCNQ (Aldrich) and acetonitrile were purified according to the usual methods.[3]

DTT (0.5276 g, 2.69 mmol) and TCNQ (0.5488 g, 2.69 mmol) were refluxed for 30′ in 85 ml of acetonitrile. Cooling and filtration gave 1.00 g (93%) of the 1 : 1 CT complex as reflective blue-violet needles, mp 229–230 °C (uncorrected).

Anal. Calcd. for $C_{20}H_8N_4S_3$: C, 59.98; H, 2.01; N, 13.99; S, 24.02. Found: C, 58.72; H, 2.03; N, 14.07; S, 23.91.

2.2. X-ray analysis and structure determination

The automatic centering and indexing routines of a single-crystal Siemens AED diffractometer gave a monoclinic unit-cell in space group $P2_1/c$ with $a = 7.206(2)$, $b = 7.574(2)$, $c = 32.324(9)$ Å, $\beta = 92.18(4)°$, $V = 1762.9(8)$ Å^3 and $Z = 4$. Intensity data were collected by the θ–2θ scan technique, using CuK_α radiation ($\bar{\lambda} = 1.54178$ Å) and 2990 unique data were obtained ($3.0° < \theta < 65.0°$). The data

TABLE I

Fractional Atomic Coordinates ($\times 10^4$)

Atom	X/A	Y/B	Z/C	Atom	X/A	Y/B	Z/C
S1	5332(1)	6827(1)	6939(0)	C12	−237(5)	7669(5)	6437(1)
S2	5037(1)	4604(1)	5755(0)	C13	400(4)	6748(4)	6765(1)
S3	3583(1)	9821(1)	6010(0)	C14	932(4)	4925(4)	6733(1)
N1	1904(5)	5509(4)	7785(1)	C15	1600(4)	4010(4)	7072(1)
N2	2635(5)	748(4)	7034(1)	C16	1786(5)	4833(5)	7471(1)
N3	−1860(5)	11107(4)	5737(1)	C17	2178(5)	2185(5)	7051(1)
N4	−1531(5)	6511(5)	4966(1)	C18	−1045(4)	7806(4)	5696(1)
C1	6088(5)	1667(5)	6975(1)	C19	−1494(5)	9648(5)	5723(1)
C2	6068(5)	3796(5)	6612(1)	C20	−1288(5)	7048(5)	5292(1)
C3	5401(4)	4905(4)	6284(1)	H1	6492(61)	4266(54)	7246(15)
C4	4270(5)	6765(4)	5705(1)	H2	6383(50)	2749(50)	6581(11)
C5	3656(5)	7822(5)	5631(1)	H5	3519(60)	7433(60)	5083(13)
C6	3255(6)	9477(5)	5488(1)	H6	2887(57)	10536(57)	5316(14)
C7	4304(4)	7667(4)	6078(1)	H9	1069(48)	2875(50)	6310(10)
C8	4954(4)	6592(4)	6414(1)	H10	−41(57)	4483(55)	5731(14)
C9	740(5)	4109(4)	6330(1)	H12	−527(46)	8863(48)	6482(11)
C10	102(5)	5026(4)	5999(1)	H13	485(53)	7257(56)	7039(12)
C11	−412(4)	6858(4)	6035(1)				

TABLE II

Bond Distances (Å) and Angles (°)

(a) in the DTT molecule					
S(1)—C(1)	1.727(4)	S(2)—C(3)	1.735(3)	S(3)—C(7)	1.724(3)
S(1)—C(8)	1.718(3)	S(2)—C(4)	1.733(3)	S(3)—C(6)	1.715(3)
C(1)—C(2)	1.346(5)	C(7)—C(8)	1.422(4)	C(6)—C(5)	1.354(5)
C(2)—C(3)	1.422(5)	C(7)—C(4)	1.385(4)	C(5)—C(4)	1.427(5)
C(3)—C(8)	1.387(4)				
C(1)—S(1)—C(8)	90.3(2)	C(3)—S(2)—C(4)	90.2(1)	C(7)—S(3)—C(6)	90.6(2)
S(1)—C(1)—C(2)	114.4(3)	C(8)—C(3)—S(2)	113.0(2)	S(3)—C(7)—C(4)	111.1(2)
C(1)—C(2)—C(3)	110.6(3)	C(3)—C(8)—C(7)	111.7(3)	C(7)—C(4)—C(5)	113.3(3)
C(2)—C(3)—C(8)	113.2(3)	C(8)—C(7)—C(4)	112.1(3)	S(2)—C(4)—C(5)	133.7(3)
C(2)—C(3)—S(2)	133.7(3)	C(8)—C(7)—S(3)	136.7(3)	C(4)—C(5)—C(6)	110.3(3)
C(3)—C(8)—S(1)	111.4(2)	C(7)—C(4)—S(2)	112.9(2)	C(5)—C(6)—S(3)	114.6(3)
S(1)—C(8)—C(7)	136.9(2)				
(b) in the TCNQ molecule					
N(1)—C(16)	1.137(5)	C(9)—C(10)	1.342(4)	N(3)—C(19)	1.137(5)
C(16)—C(15)	1.434(5)	C(10)—C(11)	1.442(4)	C(19)—C(18)	1.436(5)
N(2)—C(17)	1.139(5)	C(11)—C(12)	1.438(5)	N(4)—C(20)	1.137(5)
C(17)—C(15)	1.446(5)	C(12)—C(13)	1.336(5)	C(20)—C(18)	1.431(5)
C(15)—C(14)	1.368(4)	C(13)—C(14)	1.438(4)	C(18)—C(11)	1.373(4)
		C(14)—C(9)	1.444(4)		
N(1)—C(16)—C(15)	178.6(4)	C(10)—C(9)—C(14)	121.1(3)	N(3)—C(19)—C(18)	178.8(4)
N(2)—C(17)—C(15)	180.0(4)	C(9)—C(10)—C(11)	121.0(3)	N(4)—C(20)—C(18)	176.8(4)
C(16)—C(15)—C(17)	116.1(3)	C(10)—C(11)—C(12)	118.0(3)	C(19)—C(18)—C(20)	115.2(3)
C(16)—C(15)—C(14)	121.2(3)	C(11)—C(12)—C(13)	120.6(3)	C(19)—C(18)—C(11)	121.9(3)
C(17)—C(15)—C(14)	122.7(3)	C(12)—C(13)—C(14)	121.9(3)	C(20)—C(18)—C(11)	122.9(3)
C(15)—C(14)—C(9)	121.6(3)	C(13)—C(14)—C(9)	117.3(3)	C(18)—C(11)—C(10)	121.1(3)
C(15)—C(14)—C(13)	121.0(3)			C(18)—C(11)—C(12)	120.8(3)

processing included corrections for background, Lorentz and polarization effects, but not for absorption.

The structure was solved by direct methods using MULTAN,[4] which yielded all non-hydrogen atoms in the E-map based on the phase set with highest figure of merit. Full-matrix least squares refinement based on 1835 reflections with $I > 2\sigma(I)$ and using anisotropic thermal parameters for non-hydrogen atoms and isotropic for hydrogens gave $R = 0.0348$.

Calculations were carried out with the SHELX-76 system of computer programs.[5] The final atomic coordinates together with their standard deviations are given in Table I, bond distances and angles involving non-hydrogen atoms are collected in Table II. Figure 1 gives schematic drawings which define the atom-numbering scheme employed for the two molecules. The molecular arrangements in the crystal viewed along the [010] and [100] axes are illustrated in Figures 2 and 3.

2.3. Electric Measurements

Electrical dc conductivity measurements were carried out in flowing anhydrous nitrogen on single crystals obtained by slow evaporation at room temperature of an acetonitrile solution of the complex, as well as

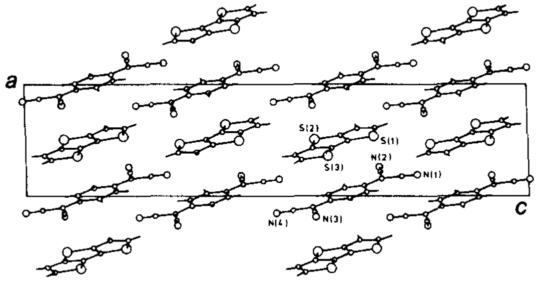

FIGURE 2 Projection of the structure along [010].

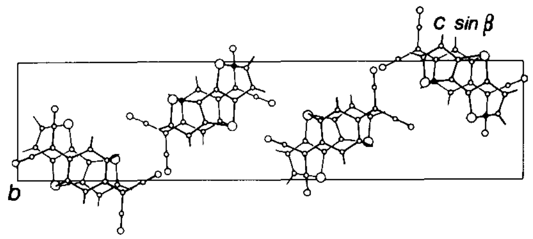

FIGURE 3 Projection of the structure along [100].

on pellets of powders compressed under a pressure of 6000 kg · cm^{-2}. Contacts were made of silver paste; for crystals, the electric field was applied along the stacking axis *a*.

The conductivity was studied as function of temperature in the 25–85 °C range.

2.4. Optical measurements

Infrared spectra of KBr pellets and isooriented monocrystals were performed on a Bruker Fourier Transform Interferometer model IFS 113.

3. RESULTS AND DISCUSSION

3.1. Crystal structure

The title compound has a *mixed stack* crystal structure which alternates DTT and TCNQ molecules along the *a* axis. These molecules are nearly parallel with a dihedral angle between their best planes by only 3.2(1)°. Since both donor and acceptor molecules lie at general positions in the space group $P2_1/c$, the relationship between any particular molecule and the two adjacent ones in the stack are not necessarily equivalent. Thus the distances of the atoms of TCNQ at x, y, z and at $1 + x, y, z$ to the least-squares plane of DTT range from 3.13 to 3.59 Å (av. 3.32 Å) and from 3.22 to 3.68 Å (av. 3.49 Å), respectively, and in this way a *partial dimerization* along the stack is obtained. The shortest intermolecular contact in the stack is 3.299(5) Å from C(1) to C(15). There are also two short contacts between TCNQ molecules in adjacent stacks (*N*(4)...*N*(4) $(\bar{x}, 1 - y, 1 - z)$ 3.181(5) Å; *N*(1)...*C*(17) $(\bar{x}, 1/2 + y, 3/2 - z)$ 3.265(5) Å).

The molecule of DTT is nearly planar, with the deviation of any contributing atom from the least squares plane being only 0.02 Å. The molecular dimensions in it appear to be normal, with both distances equal to or, but only slightly, longer than the corresponding ones in DTT itself.[1] With regards to the S—C bonds, all of which show some double bond character, those involving the central sulfur (1.733(3), 1.735(3) Å) are significantly longer than the other ones, which average 1.721(3) Å. Although the quinoid ring and the two dicyanomethylene groups are individually planar to within experimental error, the TCNQ molecule as a whole is not, the two $C(CN)_2$ planes being bent 1.2(1)° and 2.3(1)° out of the ring plane. The C—C—N groups are all very nearly linear; the C—C double bond connecting the cyano groups with the rings has been measured to be 1.383 Å. The structural parameters found for TCNQ in the present investigation are in good agreement with those found in the free compound[6] and in a number of mixed stack charge transfer complexes with planar aromatic compounds.[7]

3.2. Electrical conductivity

Current-voltage measurements were carried out by the two probe method on both single crystals, up to a field of 17,600 V cm^{-1}, and pellets, up to a field of 25,400 V cm^{-1}.

The single crystal conductivity behaviour varies with the applied field and temperature, and appears to be ohmic below 4900 V cm^{-1} except for high temperatures (> 55 °C), while pellets exhibit an ohmic behaviour all over the range of fields and temperatures used. Typical results for the conductivity temperature dependence of DTT-TCNQ are shown in Figure 4.

Single crystals show a room temperature conductivity on the order of magnitude of 10^{-12} S cm^{-1}, and we observe that a discontinuity appears in the high temperature region with a transition occurring at about 55 °C. Pressed pellets show a conductivity of three orders of

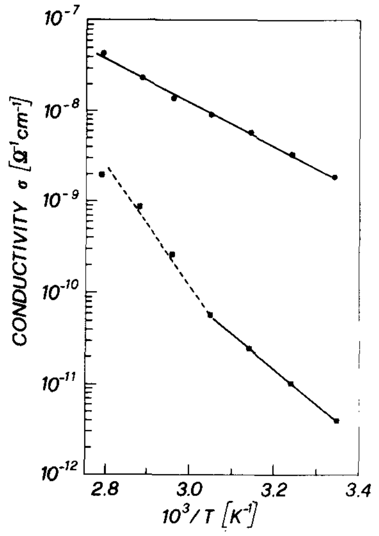

FIGURE 4 Electrical conductivity versus temperature at an electric field of 2100 V cm^{-1} for pressed pellets (squares) and single crystals of DTT-TCNQ (circles). The broken line is referred to non-ohmic behaviour.

magnitude higher, i.e. 10^{-9} S cm^{-1}. These values are typical of poorly conducting CT complexes.

Semiconduction activation energies E, determined in the ohmic regions using the standard expression $\sigma = \sigma_0 \exp(-E/kT)$, are in the range 0.61 to 0.76 eV for crystals and 0.45 eV for pellets. These activation energies, together with the conductivity data, are in agreement with the values found for TCNQ weak complexes[8] and for TCNQ itself,[9] and suggest an extrinsic semiconduction due to ionic impurities, particularly sodium.[8,9]

A decrease in the activation energy to about 0.45 eV is observed for crystals submitted to repeated thermal cycles over the range 25 to 85 °C. At the same time the crystal surface show a partial decomposition of the complex (yellow spots), caused by the thermal cycling, probably due to DTT sublimation. This observation may be an evidence of a predominant surface conduction with an activation energy of 0.45 eV.

3.3. Optical spectra

The FTIR transmission spectrum of a KBr pellet of DTT-TCNQ CT complex in the spectral range of 8500-450 cm^{-1} is shown in Figure 5. A new broad (fwhm $\cong$ 2000 cm^{-1}) absorption which does not belong either to TCNQ nor to DTT, but which is characteristic of the D-A complex, appears in the near IR at about 6200 cm^{-1} (0.77 eV) and is assigned to the CT transition from the highest occupied molecular orbital of DTT to the lowest unoccupied molecular orbital of TCNQ.

The FTIR transmission spectrum of a KBr pellet in the spectral range of the mid-IR (2300-450 cm^{-1}) is shown in Figure 6. The majority of the weak features appears at the same frequency as in the

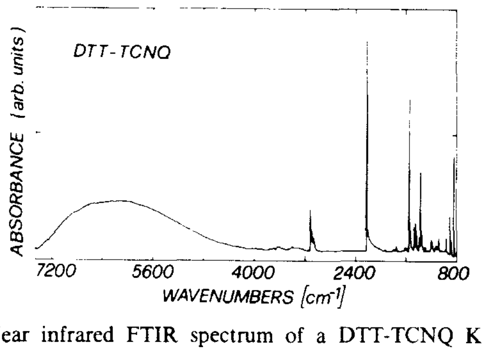

FIGURE 5 Near infrared FTIR spectrum of a DTT-TCNQ KBr pellet at room temperature.

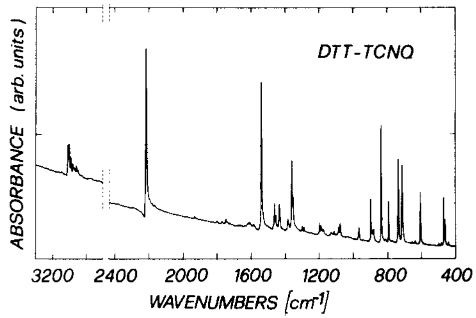

FIGURE 6 Mid-IR FTIR spectrum of a DTT-TCNQ KBr pellet at room temperature.

IR spectra of the isolated molecular species; a complete vibrational analysis of the DTT molecule is under study and will be reported elsewhere. The most prominent bands are located at 2217, 1541, 836 and 735 cm^{-1} and their intensity is from twice to three times stronger than the C—H stretching vibration at about 3060 cm^{-1}.

The observation of "new" absorption bands in the IR spectra of intermolecular CT complexes has been originally observed in alkali metal salts of TCNE[10] and later in TCNQ salts.[11] An interpretation was based on the Ferguson-Matsen mechanism[12] in which a variation in the D-A wavefunction overlap modulated by a molecular vibration could cause a charge density oscillation which can in turn couple with certain normal modes, making them acquire intensity in the IR spectrum. A more formal theory[13] was later formulated for CT complexes like benzene-I_2, assuming the radical-radical dimer model, and was successfully applied to the interpretation of the activation of several a_g modes in the IR spectra of TCNQ ion-radical salts,[11c,14] where the presence of a segregated stacks structure would make possible the dimerization of TCNQ. The mixed stack structure, as it has been shown recently in the case of TTF-chloranil CT complexes,[15] could as well show the IR activation of totally symmetric modes by the effect of charge oscillation between D and A molecules, modulated by the molecular vibration within the mixed stack. The resulting coupling of a number of "gerade" molecular vibrations with the electronic CT absorption would result into an intensity transfer from the electronic to the coupled vibrational mode.

In order to assign the vibrational spectrum and in particular to ascertain the nature of the most prominent bands we have measured the FTIR polarized spectra of an iso-oriented polycrystal of DTT-

TCNQ, as well as the KBr pellet spectra of the separate DTT and TCNQ molecules. A summary of the results is given in Table III.

All the low frequency bands below 881 cm^{-1} have a polarization which is mainly parallel to the stacking axis and hence perpendicular to the molecular planes of both the DTT and TCNQ molecules. In particular the 606, 715 and 794 cm^{-1} bands belong to vibrational

TABLE III

Polarized FTIR Spectra of DTT-TCNQ Iso-oriented Polycrystal at Room Temperature. The polarization ratio $I \perp a/I \parallel a$ is given in column 3, where a is the stacking axis.

ν (cm^{-1})	Intensity	Pol. ratio	Remarks[a,b]
459	w	—	D 460 cm^{-1}
467	mw	.6	T 476 cm^{-1}, $b_{3u}\nu_{52}$ out of plane
606	m	.4	D 601 cm^{-1}
715	m	.6	D 700 cm^{-1}
735	m	.7	—
794	m	.6	D 792 cm^{-1}
836	s	.6	T 859, $b_{3u}\nu_{50}$ out of plane
881	w		
898	m	1.5	D 898 cm^{-1}
970	w	3.	D 968 cm^{-1}
1078	w	~ 1.	D 1084 cm^{-1}
1085	w		1088 cm^{-1}
1113	vw	~ 1.7	T 1114 cm^{-1}, b_{2u}
1129	vw	~ 3.	T 1125 cm^{-1}, $b_{1u}\nu_{37}$
1175	vw	~ 1.	D 1176 cm^{-1}
1188	vw		—
1197	w		1194 cm^{-1}
1290	vw	~ .8	T 1287 cm^{-1}, b_{2u}
1300	vw	~ 2.5	D 1302 cm^{-1}
1355	mw	—	D 1359 cm^{-1}
1362	m	2.5	T 1354 cm^{-1}, $b_{2u}\nu_{35}$
1385	w	~ 4.	—
1434	w	~ 1.	D 1437 cm^{-1}
1462	w	~ 1.	D 1465 cm^{-1}
1541	s	1.2	T 1602 cm^{-1}, $a_g\nu_3$
1770	vw	~ 3.3	T 1770 cm^{-1}, b_{2u}
1801	vw	~ 2.8	T 1804 cm^{-1}, b_{1u}
2217	vs	1.3	T 2229 cm^{-1}, $a_g\nu_2$
3059	w	3.	T 3059 cm^{-1}, $b_{2u}\nu_{32}$
3080	w	1.5	D 3079 cm^{-1}
3109	m	1.2	D 3096 cm^{-1}
3143	m	5.	T 3135 cm^{-1}, b_{2u}

[a] The TCNQ axis labelling follows the Mulliken suggestions (i.e. z parallel to the long molecular axis and x perpendicular to the molecular plane).

[b] Frequencies in cm^{-1} refer to the measured bands of the separate molecular species, D refers to DTT and T refers to TCNQ.

modes of DTT while the 836 cm^{-1} is assigned to the slightly perturbed ν_{50} out of plane vibration of TCNQ.

At higher frequencies the weak bands at 1113, and 1129 cm^{-1} are dominantly polarized in the plane of the molecule and are assigned to the 1114 cm^{-1} b_{2u} and 1125 cm^{-1} b_{1u} (ν_{37}) in plane vibration of TCNQ, as well as the strong band at 1362 cm^{-1} ($R = 2.5$) which we assign to the in plane mode $b_{2u}(\nu_{35})$ at 1354 cm^{-1}.

The strong bands at 1541 ($R = 1.2$) and 2217 cm^{-1} ($R = 1.3$) have a considerable out of plane polarization which cannot be accounted for solely by the in plane IR active components of the C=C stretching and CN stretching respectively. On the contrary, the considerable out of plane component, together with the peculiar high intensity, which is an order of magnitude more than that expected for the ordinary IR active components, lead us to assign these modes to the 1602 cm^{-1} $a_g(\nu_3)$ and 2229 cm^{-1} $a_g(\nu_2)$ modes of TCNQ which acquire IR intensity by vibronic mixing with the CT electronic transition polarized parallel to the stack axis *a*, and whose frequencies are accordingly shifted from the unperturbed Raman frequency of the pristine TCNQ molecule.

To the high frequency side we observed that, in the C-H stretching vibrations spectral range, the 3059 cm^{-1} band ($R = 3$) conserve the in-plane character and the same frequency of the $(\nu_{32})b_{2u}$ mode of TCNQ confirming the theoretical expectation[16] that the CH a_g stretching mode is inactive in the vibronic activation mechanism.

3.4. Degree of ionicity

A quantitative measurement of the degree of ionicity (ρ) may be derived from the dependence of the vibrational frequency versus the charge density.[11c] Among the selected frequencies are the a_g fundamentals of TCNQ which suffer the highest ionization shift. We make a tentative estimate of ρ by selecting the $(\nu_2)a_g$ (TCNQ) which is the strongest band in the spectrum and whose assignment is based on the polarization measurements. In a completely ionized CT complex like Rb-TCNQ,[11c] this mode is observed in the IR at 2187 cm^{-1} while it is found at 2229 cm^{-1} in the neutral TCNQ.[17] If we assume a linear dependence of the frequency versus ρ we obtain a value of the degree of the ionicity of $\rho = 0.28$. A rudimentary independent estimate of the mean charge residing in the TCNQ molecule may be obtained from the known dependence on charge of the length of the bridging carbon double bonds (C(18)-C(11) and C(14)-C(15) in Figure 1. The length of this bond has been linearly related to ρ for a number of known CT complexes (see reference 14 and references therein). From the X-ray structure we have determined $l_{(C-C)} = 1.383$ Å which yields the estimate of $\rho = .2$ which correlates quite well with the degree of ionicity estimated from the vibrational shift.

3.5. Vibronic activation

An independent check of this estimate could be made by comparing the calculated e–mv coupling constants[16] with the experimental ones by using the theory developed for the mixed stack model[15] which extends the theory of the segregated stack models.[18] The dimensionless coupling constant for a particular a_g mode of the D and A molecules is related to the frequency of the unperturbed molecule ω_i and to the frequency of the perturbed molecule $\bar{\omega}_i$ by the equation:

$$\lambda_i = \frac{\omega_i^2 - \bar{\omega}_i^2}{\omega_i^2}\left(2 - \sum_{j \neq i} \frac{\lambda_j \omega_j^2}{\omega_j^2 - \bar{\omega}_i^2}\right) \tag{1}$$

where the summation extends over all the totally symmetric modes of both the D and the A except for $j = i$. The data used in the calculations are reported in the first two columns of Table IV: the analysis is limited to the a_g modes of TCNQ. In the first approximation we derive the dimensionless coupling constants by neglecting the summation, (i.e. $\lambda_i = 2(\omega_i^2 - \bar{\omega}_i^2)/\omega_i^2)$). These zero order values are then introduced in equation 1 and the procedure is iterated until self-consistency. The linear e–mv coupling constants is related to λ_i by:

$$g_i = \sqrt{\frac{\lambda_i \omega_i}{\chi(0)}}$$

TABLE IV

Calculated and Experimental Coupling Constants of Some a_g Modes of TCNQ Assuming a Degree of Ionicity of 0.22.

Mode	TCNQ^0 ω_i	TCNQ-DTT $\bar{\omega}_i$	λ_i^0	λ_i	g_i	g_i[b] (calc.)
ν_2	2229	2217	.021	.024	.061	.052
ν_3	1602	1541	.149	.164	.135	.131
ν_6	948	836[a]	.444	.388	.160	.029

[a] The correct assignment of this line is evidently not $\nu_6 a_g$ but $\nu_{50} b_{3u}$ as reported in Table III.

[b] Reference 16.

where the zero frequency *CT* polarizability is given *b*: $\chi(0) = 8\rho(1 - \rho)/\omega_{CT}$ and *CT* is the frequency of the *CT* electronic transition. The resulting g_i values are listed in column 5 and the calculated values obtained by CNDO molecular orbital methods[15] are in column 6.

There is good agreement between the experimental and calculated e–mv coupling constants for the first two modes which confirms the assignment of the 2217 cm^{-1} band as $(\nu_2)a_g$ and the 1541 band as the $(\nu_3)a_g$ of TCNQ, while the 836 cm^{-1} band cannot be regarded as the $(\nu_6)a_g$ vibronically activated TCNQ mode but rather as out of plane vibration, namely $(\nu_{50})b_{3u}$ as it is confirmed by polarization measurement (vide supra).

CONCLUSIONS

The poor conductivity of the DTT-TCNQ CT complex is related to the mixed stack structure. The optical absorption shows the activation of some a_g modes of TCNQ which is in agreement with the partial dimerization along the stack. The moderate ionicity of the complex makes the DTT entity as a potentially promising donor as well as an interesting monomer unit along the line of electrocrystallization of doped polymers.

Acknowledgment

This work has been made possible by support from the Consiglio Nazionale delle Ricerche (C.N.R.), Progetto Finalizzato "Chimica Fine e Secondaria". We thank Mr. A. Martiniello, Mr. L. Minghetti and Mr. R. Pezzoli for technical assistance. Supplementary material available: Tables of observed and calculated structure factors and of thermal parameters.

References

1. F. Bertinelli, P. Palmieri, C. Stremmenos, G. Pelizzi and C. Taliani, *J. Phys. Chem.*, **87**, 2317 (1983).
2. F. De Jong and M. J. Janssen, *J. Org. Chem.*, **36**, 1645, 1988 (1971).
3. See for example: R. V. Gemmer, D. O. Cowan, T. O. Poehler, A. N. Bloch, R.E. Pyle and R. H. Banks, *J. Org. Chem.*, **40**, 3544 (1975).
4. P. Main, M. M. Woolfson, L. Lessinger, G. Germain, J. P. Declerq, MULTAN 74. A System of Computer Programs for the Automatic Solutions of Crystal Structures. Univs. of York, England and Louvain, Belgium, 1974.
5. G. M. Sheldrick, SHELX-76. Program for Crystal Structure Determination. Univ. of Cambridge, England, 1976.
6. R. E. Long, R. A. Sparks and K. N. Trueblood, *Acta Cryst.*, **18**, 932 (1965).

7. G. C. Lisensky, C. K. Johnson and H. A. Levy, *Acta Cryst.*, **B32**, 2188 (1976) and refs therein.
8. V. M. Vincent and J. D. Wright, *J. Chem. Soc. Faraday Trans. I*, **70**, 58 (1974).
9. J. Hurditch, V. M. Vincent and J. D. Wright, *J. Chem. Soc. Faraday Trans. I*, **68**, 465 (1972).
10. (a) J. Stanley, D. Smith, B. Latimer and J. P. Devlin, *J. Phys. Chem.*, **70**, 2011 (1966); (b) J. C. Moore, D. Smith, Y. Youhne and J. P. Devlin, *J. Phys. Chem.*, **75**, 325 (1971).
11. (a) G. R. Anderson and J. P. Devlin, *J. Phys. Chem.*, **79**, 1100 (1975); (b) R. Bozio, I. Zanon, A. Girlando and C. Pecile, *J. Chem. Soc. Faraday II*, **74**, 235 (1978); (c) R. Bozio and C. Pecile, in Physics and Chemistry of Low Dimensional Solids, edited by L. Alcacer (Reidel, Dordrecht), (1980), p. 165.
12. E. E. Ferguson and F. A. Matsen, *J. Am. Chem. Soc.*, **82**, 3268 (1960).
13. H. B. Friedrich and W. B. Person, *J. Chem. Phys.*, **44**, 2161, (1966).
14. M. J. Rice, V. M. Yartsev and C. S. Jacobsen, *Phys. Rev.*, **21B**, 3437 (1980).
15. A. Girlando, R. Bozio, C. Pecile and J. B. Torrance, *Phys. Rev.*, **26B**, 2306 (1982).
16. N. O. Lipari, C. B. Duke, R. Bozio, A. Girlando, C. Pecile and A. Padua, *Chem. Phys. Lett.*, **44**, 236 (1976); M. J. Rice and N. O. Lipari, *Phys. Rev. Lett.*, **38**, 437 (1977).
17. A. Girlando and C. Pecile, *Spectrochim. Acta*, **29A**, 1859 (1973).
18. M. J. Rice, *Solid State Commun.*, **31**, 93 (1979).