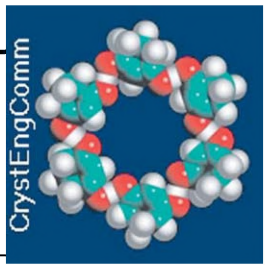
Charge transfer complexes of 2,4,6-tricyano-*s*-triazine with tetrathiafulvalene (TTF) and *N*,*N*,*N*′,*N*′-tetramethyl-*p*-phenylenediamine (TMPD)



Paper

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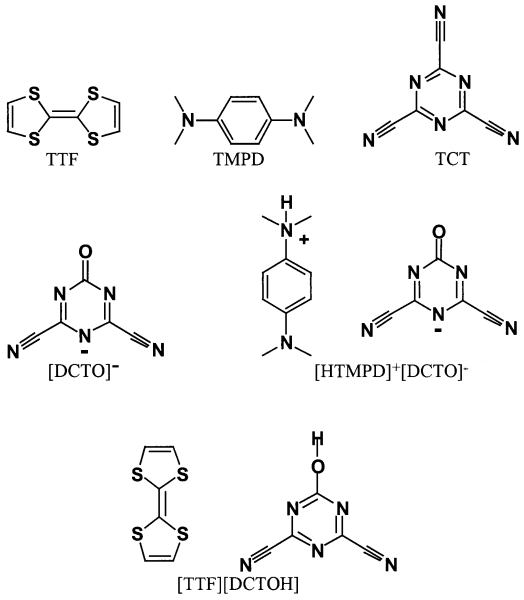
Reaction of 2,4,6-tricyano-*s*-triazine (TCT) with tetrathiafulvalene (TTF) and *N*,*N*,*N*′,*N*′-tetramethyl-*p*-phenylenediamine (TMPD) leads to 1 : 1 charge transfer complexes. The crystal structures of the TTF[TCT], as well as the decomposition product due to hydrolysis of the [TMPD][TCT], *i.e.* $[HTMPD]^+[2,4\text{-dicyano-6-oxy-}s\text{-triazine}]^-$, are reported and spectroscopically characterized.

Introduction

2,4,6-Tricyano-*s*-triazine (TCT) has been studied as an electron acceptor in the search for new stable organic radicals,[1] as well as part of charge transfer complexes,[2,3] in hopes of building 3-D polymer network materials. The synthesis of the radical anion of TCT, $[TCT]^{\bullet -}$, was previously attempted by reacting the neutral TCT with alkali metals such as sodium and potassium.[1] However, the results were not well understood and could not be explained based on common organic mechanistic chemistry. Electron transfer salts were also studied, but neither the structures nor the decomposition products following electron transfer were reported.[2,3] Herein we report the structure and spectroscopic data of [TTF][TCT] (TTF = tetrathiafulvalene), as well as the hydrolysis product of the TCT as the [TMPD][TCT] complex, *i.e.*, $[HTMPD]^+[DCTO]^-$ (TMPD = *N*,*N*,*N*′,*N*′-tetramethyl-*p*-phenylenediamine).



Experimental

Synthesis

[TTF][TCT]. A solution of TTF (200 mg, 0.98 mmol) in 10 mL MeCN was added to a solution of TCT (152 mg, 0.98 mmol) in 5 mL MeCN. The solution turned an immediate deep-green color, and was allowed to stir for 12 h. The solvent was evaporated and the residue recrystallized from hot MeCN, yielding blue-green crystals. Yield: 320 mg (91%). IR, ν/cm^{-1}: 3100 w, 3068 w, 2262 w, 2241 m, 1504 s, 1482 s, 1328 m, 1320 m, 1249 w, 1082 w, 971 w, 936 m, 796 s, 782 m, 733 w, 673 m, 659 m, 516 m. Elemental analysis, $C_{12}H_4N_6S_4$: calc.: C, 39.98%; H, 1.12%; N, 23.31%; found: C, 40.15%; H, 1.29%; N, 23.20%.

[TTF][DCTOH]. The above procedure was followed exactly, with 0.5 mL H_2O added to the TCT solution before addition of the TMPD, resulting in an immediate red precipitate. Yield: 295 mg (83.8%). IR, ν/cm^{-1}: 3405 s, 3082 m, 2247 w, 1438 m, 1340 s, 1269 m, 1145 w, 1022 m, 930 w, 812 m, 700 m.

[TMPD][TCT]. A solution of TMPD (100 mg, 0.61 mmol) in 5 mL MeCN was added to a solution of TCT (95 mg, 0.61 mmol) in 5 mL MeCN. An immediate blue powder precipitated, which was recrystallized from hot MeCN. Yield: 115 mg (58.9%). IR, ν/cm^{-1}: 2957 m, 2891 m, 2851 m, 2806 m, 2256 m, 2246 m, 2235 m, 1610 m, 1521 s, 1497 s, 1479 s, 1330 m, 1317 m, 1213 m, 1178 w, 1130 w, 1056 w, 970 w, 946 m, 829 m, 807 w, 796 s, 660 m, 542 w. Elemental analysis, $C_{16}H_{16}N_8$: calc.: C, 59.99%; H, 5.03%; N, 34.98%; found: C, 59.97%; H, 5.08%; N, 34.90%.

[TMPD][DCTOH]. The above procedure was followed exactly, with 0.5 mL H_2O added to the TCT solution before addition of the TMPD, resulting in an immediate yellow precipitate. Crystals were grown by reacting TMPD with TCT under dry conditions, then adding water after 5 min and allowing the solvent to slowly evaporate. Yield: 186 mg (95.3%). IR, ν/cm^{-1}: 2960 w, 2904 w, 2860 w, 2819 w, 2249 w,

Table 1 Crystallographic data for [TTF][TCT] and [TMPD][DCTOH]''

Parameter	[TTF][TCT]	[TMPD][DCTOH]
Empirical formula	$C_{12}H_4N_6S_4$	$C_{15}H_{17}N_7O$
M	360.45	311.36
Crystal system	orthorhombic	monoclinic
Space group	$Pbca$	$P2_1/m$
a/Å	7.1430(1)	10.641(3)
b/Å	16.5138(5)	6.614(3)
c/Å	25.4640(7)	11.793(5)
β/°		90.07(3)
V/Å^3	3003.68(13)	830.0(2)
Z	8	2
T/K	200	293
ρ_{calc}/Mg m^{-3}	1.594	1.246
F(000)	1456	328
M/mm^{-1}	0.636	0.085
Reflections collected	6305	6184
Independent reflections	3416 [R(int) = 0.0378]	2210 [R(int) = 0.0660]
GOF	1.038	0.873
R_1 ($I > 2\sigma(I)$)	0.0378	0.0431
wR_2 ($I > 2\sigma(I)$)	0.0861	0.1054

''Click here for full crystallographic data (CCDC 172417 and 172418).

2224 w, 1580 s, 1540 s, 1523 s, 1446 s, 1361 m, 1309 s, 1235 w, 1186 s, 1055 m, 997 w, 934 m, 910 w, 815 s, 668 w, 547 m. Elemental analysis, $C_{15}H_{17}N_7O$: calc.: C, 57.87%; H, 5.50%; N, 31.49%; found: C, 57.86%; H, 5.44%; N, 31.56%.

Crystal structure determination

A single crystal of each of the compounds was covered with a drop of vacuum grease, and mounted on a Nonius KapaCCD diffractometer. Data were collected for the green [TTF][TCT] crystals at 200 K, and the [HTMPD][DCTO] data were collected at ambient temperature (293 K). The crystal structures were determined with SHELXS-97 and refined with SHELXL-97 computer programs.[4] Crsytallographic information is summarised in Table 1.

Spectroscopic studies

Infrared spectra were taken using a Bio-Rad FTS-40 FTIR spectrophotometer with ± 1 cm^{-1} resolution, and scanned in the range of 400–4000 cm^{-1}. UV/Visible spectroscopy was carried out on a Hewlett Packard 8452A Diode Array Spectrophotometer, scanning from 190–800 nm. Samples were prepared as KBr pressed pellets (~5% w/w) for both experiments.

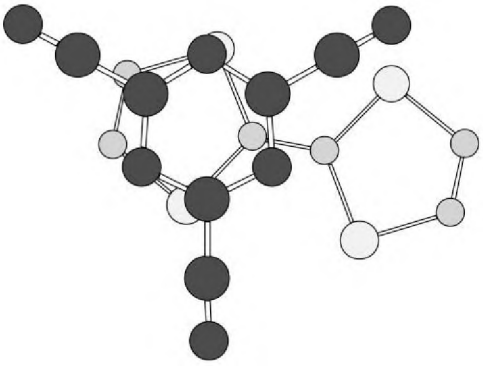


Fig. 2 Overlap of TCT (filled circles) and TTF (open circles) viewed down the axis perpendicular to the plane of the TCT ring.

Results and discussion

TCT has the irreversible reduction potential of −0.39 V *vs.* SCE,[5] making it difficult to reduce to the radical anion, and thus requires a strong electron donor to effect electron transfer. [TTF][TCT] has been reported to result in a charge transfer complex, but only ν_{CN} and elemental analyses were included for the pure and decomposition materials.[2a]

Reaction of TTF ($E_{1/2}^{o}$ = +0.30 V *vs.* SCE in MeCN)[6] with TCT in acetonitrile results in the precipitation of deep green crystals of [TTF][TCT] composition. The structure of [TTF][TCT] was determined and is comprised of stacks of alternating TTF and TCT in a ···DADA··· (D = TTF; A = TCT) motif (Fig. 1). The bulk of the TCT ring overlaps with one ring of the TTF (Fig. 2). The closest contact is 3.17 Å, which is the S3–C9 distance. The planar TTF and TCT are not coplanar within a stack, deviating by ~8° from each other. The angle between the TTF in one stack and the TCT in an adjacent stack is ~45°.

The UV/Visible/NIR spectrum for the [TTF][TCT] complex in MeCN is the sum of the solution spectra for TTF and TCT. In the solid state, as pressed KBr pellets, a new absorption appears at 10000 cm^{-1} (1000 nm), assigned to be the TTF → TCT charge transfer (CT) band (Fig. 3). The IR spectrum also shows peaks predominantly from the two independent neutral species, with slight shifts in the nitrile region of the TCT, as well as the $\nu_{C\equiv N}$ (TCT) and ν_{C-S} regions. Hence, electron transfer does not occur in either solution or the solid state, as expected due to the reduction potential of TCT

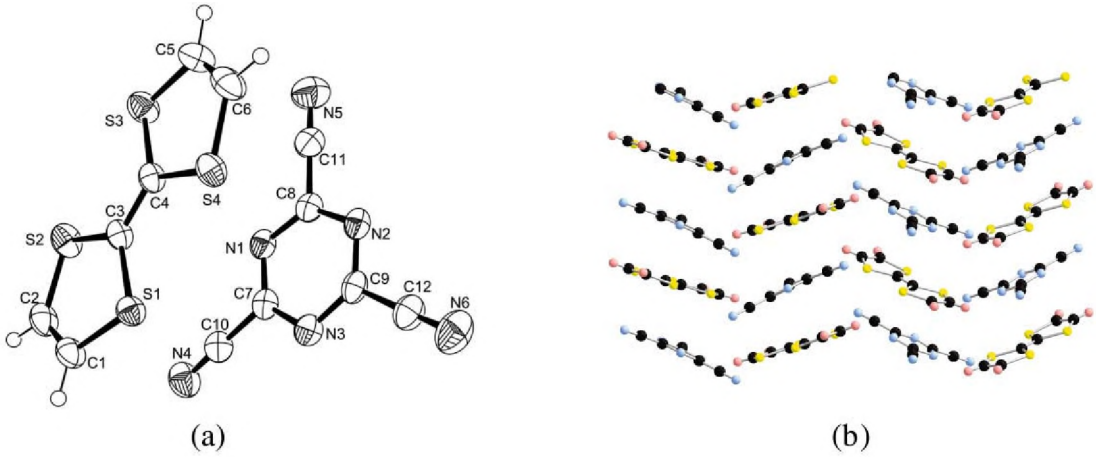


Fig. 1 (a) ORTEP of [TTF][TCT] (50% probability). (b) Stacking arrangement of [TTF][TCT] as seen down the crystallographic b-axis. Click image or here to access a 3D representation.

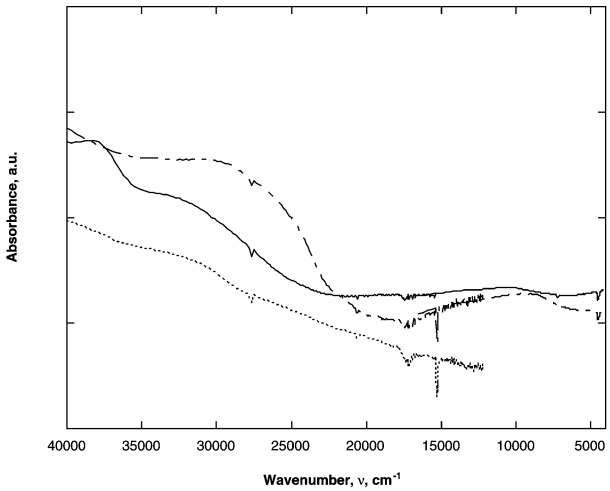


Fig. 3 Solid state spectra of TTF^0 (dotted line), [TTF][TCT] (dashed line) and [TMPD][TCT] (solid line) as pressed KBr pellets.

being much more negative than that of TTF. This is consistent with the reported low dc electrical conductivity for [TTF][TCT].[2a]

The reaction of TMPD ($E_{1/2}^{o}$ = +0.10 and 0.72 V),[7] and TCT in MeCN leads to the isolation of [TMPD][TCT], which did not yield crystals suitable for its single crystal structural determination. The electronic absorption spectrum of [TMPD][TCT] is similar to that of [TTF][TCT], with an absorption at ~10000 cm^{-1} assigned to the TMPD → TCT CT band (Fig. 3). Likewise, the IR spectrum shows peaks predominantly from the two independent neutral species. Hence, electron transfer does not occur in either solution or the solid state, again as expected.

It was reported that the blue-green [TTF][TCT] decomposes when exposed to aqueous conditions, either as water in solution/solvents, or when the solid is exposed to water vapor in the air, the latter being a much slower process.[2] Based upon the IR spectral changes, it was proposed that a nitrile on the TCT is hydrolyzed and replaced by –OH from the water, with the loss of HCN, forming deep red and moderately conductive [TTF][DCTOH].[2] It is expected that only one nitrile group is substituted, as the addition of one OH most likely deactivates the ring to further nucleophilic substitution.[8]

As part of our studies of TCT, TMPD was reacted TCT in MeCN containing ~5% water, which yielded a yellow precipitate. The crystal structure of the yellow solid was determined and revealed the composition of [TMPD][DCTOH]. Hence, the nucleophilic displacement of one of the nitriles by water followed by a proton transfer (acid–base reaction) from the newly formed 2,4-dicyano-6-hydroxy-*s*-triazine to one of the TMPD nitrogens occurred. Hence, the solid is best described as $[HTMPD]^+[DCTO]^-$, Fig. 4.

$[HTMPD]^+$ is clearly present based on the amine group on N7 being rotated 90° out of the expected coplanarity with the benzene ring due to the nitrogen being protonated. The average bond angle around the N7 is 109.4°, indicating sp^3 hybridization. Though the proton position was refined as an sp^3 nitrogen, it is expected that the 2,4-dicyano-6-hydroxy-*s*-triazine would be fairly acidic considering the electronegativity of the triazine ring.[9] In the $[DCTO]^-$ fragment, it appears that the anion is located within the ring, and the result is a ketone, with the C1–O1 bond 1.242 Å and the angles around C1 averaging 120°, which is H-bonded to the $[HTMPD]^+$.

The direct reaction of TTF with TCT in similar "wet" conditions results in an immediate red-brown precipitate, which as suggested earlier[2] is believed to be [TTF][DCTOH]. In the IR spectrum of [TTF][DCTOH], the ν_{OH} at ~3300 cm^{-1} was present, which was absent in [TMPD][DCTOH]. The remaining IR peaks are consistent with the previously reported isolation of this compound.[2] It is expected that TTF is not a good proton acceptor and is much less basic than TMPD,[10] and thus no proton transfer takes place from the hydroxy-triazine to TTF. As there is no proton transfer, this could also explain why there is no shift in the peaks of the IR of the TTF fragment, as well as no shift in absorptions in the UV/Visible experiments.

In summary, charge transfer complexes of TCT with TMPD and TTF were synthesized and characterized, in addition to the decomposition products due to hydrolysis of the TCT to form DCTOH. Due to the basicity of the TMPD nitrogens, proton transfer occurs following the hydrolysis of [TMPD][TCT], whereas no proton transfer is observed for [TTF][DCTOH]. Spectroscopic studies show that solutions of the complexes contain only the neutral species, and that upon precipitation

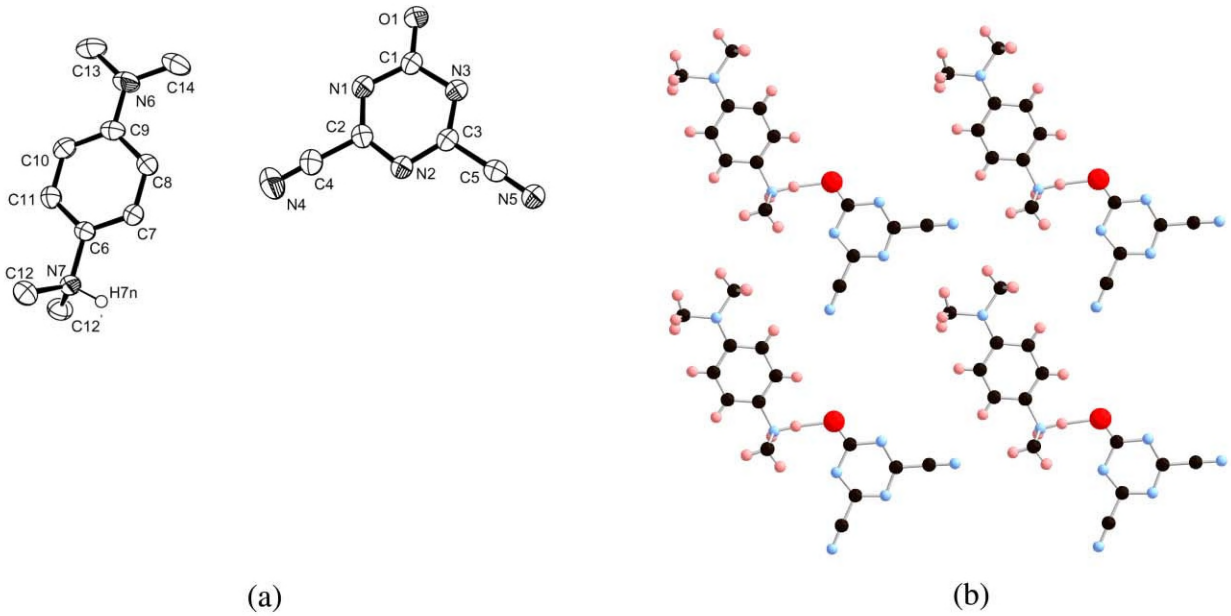


Fig. 4 (a) ORTEP of $[HTMPD]^+[DCTO]^-$ (50% probability), and (b) hydrogen bonding in $[HTMPD]^+[DCTO]^-$.

donor–acceptor stacks form, resulting in charge transfer as seen by a band at $\sim 10000\ cm^{-1}$ in the near-IR region.

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