J Chem Crystallogr (2011) 41:936–943
DOI 10.1007/s10870-011-0021-y

ORIGINAL PAPER

Layered, Two-Dimensional Hydrogen Bonding Nets in the Structure of the 1:1 Encounter Complex TMTTF–TCNB: Combined Structural and Spectroscopic Study

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Received: 28 December 2010 / Accepted: 1 February 2011 / Published online: 19 February 2011

Abstract The synthesis, crystal structure and spectroscopic properties as determined by infrared spectroscopy of the 1:1 encounter complex TMTTF–TCNB are reported. The complex crystallizes with each of the constituent molecules on an inversion center in the triclinic space group $P-1$ with $a = 6.7953(16)$ Å, $b = 7.9141(16)$ Å, $c = 9.775(2)$ Å, $\alpha = 98.63(3)°$, $\beta = 105.27(3)°$, and $\gamma = 94.49(3)°$. The determination of this crystal structure provided cyanide bond distances which when compared to the reported literature values for free TCNB suggest the presence of the neutral acceptor. The central C=C bond and four ancillary C–S bonds in TMTTF provide structural evidence that the donor, like the acceptor, also exists in its neutral state. These crystallographic observations and conclusions were confirmed by infrared spectroscopic analysis. Of particular interest is a two dimensional hydrogen bonding net which occurs within the $(13\bar{1})$ plane. When stacked as repeat units along the a axis, this net is reminiscent of stacked graphene layers in graphite.

Keywords TMTTF · Tetracyanobenzene · TTF

Introduction

The field of organic materials that display charge transfer properties has been a research topic of considerable interest since the discovery of metallic conductivity in the charge transfer salt TTF–TCNQ. In this material, partial chemical oxidation of tetrathiafulvalene (TTF) by TCNQ (TCNQ = 7,7,8,8-tetracyanoquinodimethane) results in the formation of a charge transfer salt with metallic conductivity that reaches a maximum of 10^4 S cm^{-1} at 66 K prior to undergoing a metal-to-insulator transition [1–3]. Concomitant with the partial charge transfer is the solid state organization of the donor and acceptor molecules into segregated stacks. This packing orientation maximizes molecular orbital overlap among molecules of similar symmetry thus creating a more facile pathway for the transfer of itinerant electron density. Although the purely organic material TTF–TCNQ is considered a seminal discovery in the realm of TTF-based complexes, a considerably larger number of charge transfer salts have been prepared electrochemically via slow galvanostatic oxidation at the surface of platinum electrodes in the presence of inorganic anions of various charges and geometries [4]. Central to this field of research is the preparation of multifunctional hybrid materials exhibiting physical properties once considered inimical in a continuous crystalline lattice [5–14].

Various novel materials have also been obtained using substituted TTF derivatives. Among those derivatives is the permethylated-TTF 2,3,6,7-tetramethyl-1,4,5,8-tetrathiafulvalene (TMTTF) which has seen widespread use throughout the field of organic materials. For example, salts have been prepared electrochemically between TMTTF and

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the Lindqvist polyoxometallate clusters $W_6O_{19}{}^{2-}$ and $Mo_6O_{19}{}^{2-}$, the hexanuclear niobium cluster $Nb_6Cl_{18}{}^{3-}$, the dirhenium anion $Re_2Cl_8{}^{2-}$ which contains a quadruple bond between the rhenium atoms, Br^- and $PF_6{}^-$ [15–19]. Among these salts, the latter two possessed the most interesting transport properties and had a solid state packing which mirrored those of the classic Bechgaard salts, known in the solid state physics community to be the first examples of organic superconductors [20–23]. Researchers in 1994 were successful in observing the entrance of $(TMTTF)_2[Br]$ into the superconducting state under the application of ~26 kbar of pressure [18]. Later in 2000, $(TMTTF)_2[PF_6]$ was found also to become a superconductor after the application of more than 50 kbar of external pressure [19]. The $(TMTTF)_2[X]$ family of salts, where "X" represents any monovalent anion, were later christened the Fabre salts after Jean-Marc Fabre, who launched the first systematic study into the synthesis and properties of salts prepared electrochemically with TMTTF [24].

Salts containing TMTTF have also been successfully prepared using chemical methods. Among this group are those salts prepared with TCNQ and the quinone derivative bromanil, both of which contain partially oxidized TMTTF, a significant electronic feature necessary for the observation of non-activated conductivity levels [25, 26]. A soluble salt with the formula $(TMTTF)[BF_4]$ was also prepared by reacting equimolar amounts of TMTTF and the strong oxidizer tris(*p*-bromophenyl)amminium tetrafluoroborate in CH_2Cl_2 [27]. This salt appears quite soluble and could allow for hybrid materials to be prepared by metathesis techniques.

The organocyanide acceptor tetracyanobenzene (TCNB), whose X-ray crystallographic structure was first reported in 1973, is known to form charge transfer complexes with other organic donors and aromatic solvents [28–53]. Among some of the most fascinating discoveries with TCNB include those with anthracene, naphthalene and phenanthrene which show levels of orientational disorder in the donor sublattice [37, 54]. Other donors studied for complex formation with TCNB include benzanthracene, *p*-phenylenediamine, pyrene, *N*,*N*-dimethyl-*p*-phenylenediamine, bis(2-methylbenzyl-cyanide), chiral 1,1′-bis-2-naphthol derivatives, TTF and *o*-Me_2TTF (*o*-Me_2TTF = *o*-3,4-dimethyltetrathiafulvalene) [38, 48, 49, 55–59].

In order to expand the database of TMTTF complexes with organocyanide acceptors, we report herein the 1:1 encounter complex which forms between TMTTF and TCNB. An encounter complex can be described as a complex which forms between a donor and acceptor in the absence of dipolar interactions facilitated by charge transfer. The resulting crystallographic data reveal integrated stacks of TMTTF donors and TCNB acceptors, which when combined with the analyses of critical bond distances and stretching frequencies, suggest that the constituent molecules co-crystallize in their neutral forms.

Experimental Section

Preparation of Compounds

The donor TMTTF was prepared by the group of Prof. Marc Fourmigué and used without additional purification. The organic acceptor TCNB was purchased from Sigma–Aldrich and used without additional purification. The solvent acetonitrile, utilized in the preparation of the title encounter complex, was not dried prior to its use. For the complex's preparation, crystals were grown by slow evaporation of combined acetonitrile solutions of the donor and acceptor. Single crystals of TCNB, used to prepare IR samples for the cyanide stretching frequency analyses, were prepared by slow evaporation of a clear, homogeneous solution of the acceptor dissolved in hot acetonitrile.

TMTTF–TCNB

A CH_3CN solution of TMTTF (0.026 g, 1.00×10^{-4} mol) was combined with a solution of TCNB (0.024 g, 1.01×10^{-4} mol) dissolved in a minimum of warm CH_3CN. The solution was concentrated via slow evaporation in air over the period of 1 month and placed in a freezer at −10 °C. This process resulted in the formation of black needle-like crystals; yield 0.031 g (70%) (Fig. 1).

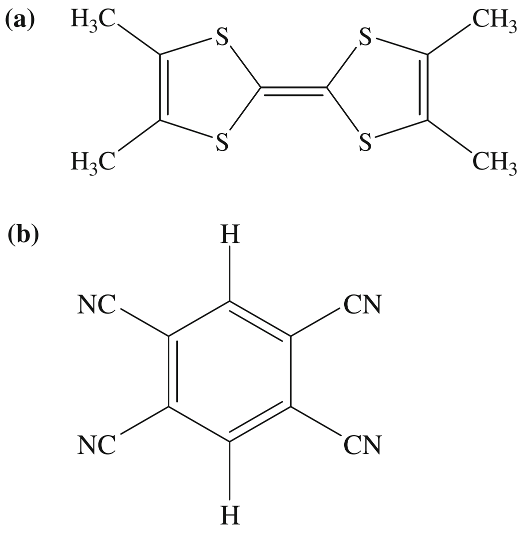

Fig. 1 TMTTF (**a**) and TCNB (**b**)

X-ray Crystallography

A black, needle-like crystal of dimensions 0.29 × 0.06 × 0.01 mm^3 was secured to a cryoloop using Dow Corning grease and placed into the liquid nitrogen stream of a Bruker APEXII diffractometer where data was collected using Mo-Kα radiation ($\lambda = 0.71073$ Å) at 110 K. A hemisphere of data was collected in multi-run mode using ω as the rotation axis. Data collection and initial indexing were handled using SMART [60]. Frame integration, Lorentz-polarization corrections, and final cell parameter calculations were carried out using SAINT [61]. Multi-scan absorption corrections were performed using SADABS [62]. The structure was solved using direct methods and difference Fourier techniques. All hydrogen atoms were attached via the riding model. The final structural refinement included anisotropic temperature factors on all non-hydrogen atoms. Structure solution, refinement, graphics, and creation of publication material were performed using SHELXTL and XSEED [63–66]. The solid state structure with anisotropic displacement ellipsoids at 50% probability is shown in Fig. 2. Projections for TMTTF–TCNB in the *ac* and *bc* planes are presented in Fig. 3a and b. Additional information regarding refinement details and bond distances for the 1:1 encounter complex are listed in Tables 1 and 2. CCDC file 787194 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Results and Discussion

X-Ray Crystallographic Analysis

It has been well established by our group and others that when organic chalcofulvalene donors form integrated stacks with organic acceptors of non-equivalent redox potentials, intermolecular forces such as π–π or S···S interactions become the dominant feature in facilitating

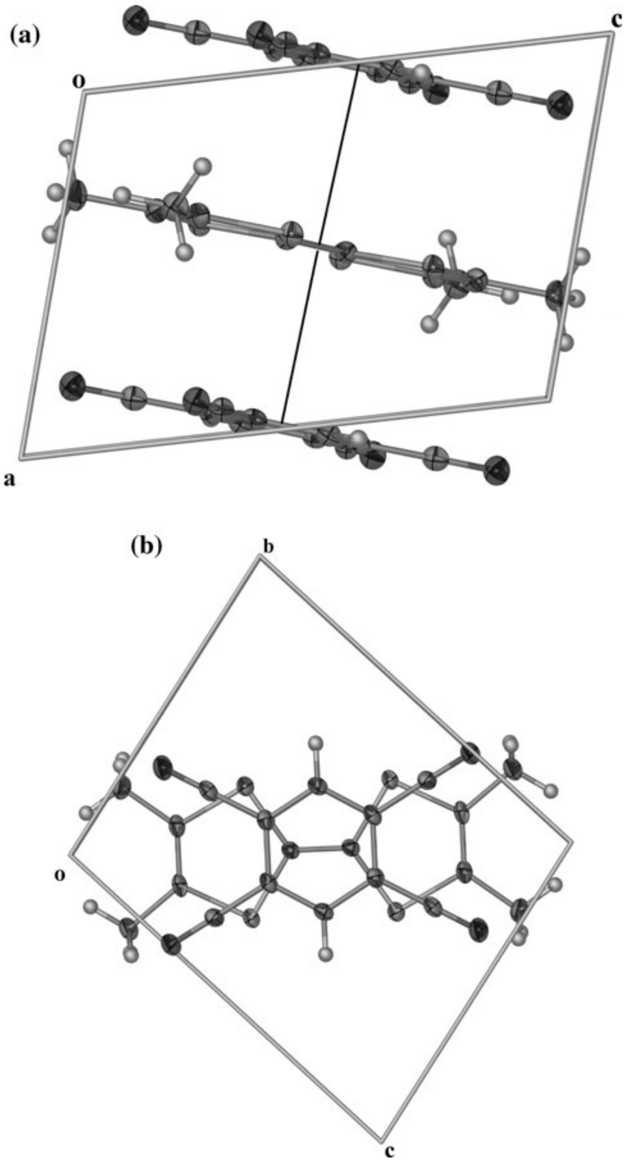

Fig. 3 Projection of the crystal structure of TMTTF–TCNB in the *ac* (**a**) and *bc* (**b**) planes illustrating the formation of integrated stacks of donors and acceptors. The equivalent centroid-to-centroid distances of 3.398 Å between the constituent molecules is highlighted (**a**)

Fig. 2 X-ray crystal structure of TMTTF–TCNB with anisotropic displacement ellipsoids at 50% probability

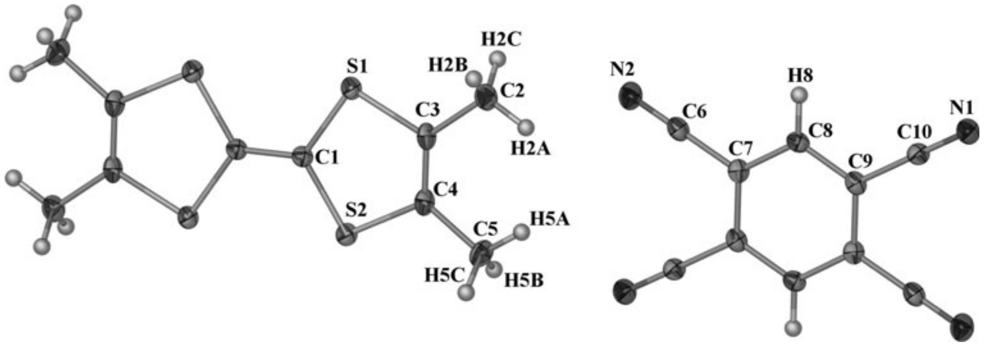

Table 1 X-ray crystallographic and refinement data for TMTTF–TCNB

Compound	TMTTF–TCNB
CCDC code	787194
Formula	$C_{20}H_{14}N_4S_4$
Formula weight	438.59
Temp.	110(2)
Space group	P − 1
a (Å)	6.7953(14)
b (Å)	7.9141(16)
c (Å)	9.775(2)
α (°)	98.63(3)
β (°)	105.27(3)
γ (°)	94.49(3)
Volume (Å^3)	497.6(2)
Z	1
Density (calculated) (mg/m^3)	1.464
μ (mm^{-1})	0.491
Scan	ω scan
θ range for data collection (°)	2.42–28.72
Reflections measured	5592
Independent observed reflns.	2467
Independent reflns. [$I > 2\sigma$]	1792
Data/restraints/parameters	2467/0/129
R_{int}	0.0425
Final *R* indices [$I > 2\sigma$]	$R_1 = 0.0437$, $wR2 = 0.1069$
R indices (all data)	$R_1 = 0.0594$, $wR2 = 0.1147$
Goodness-of-fit on F^2	0.986

Table 2 Bond distances for TMTTF–TCNB in Å

S(1)–C(1)	1.749(2)
S(1)–C(3)	1.757(2)
S(2)–C(1)	1.748(2)
S(2)–C(4)	1.761(2)
N(1)–C(10)	1.139(3)
N(2)–C(6)	1.140(3)
C(1)–C(1a)	1.343(4)
C(2)–C(3)	1.497(3)
C(3)–C(4)	1.324(3)
C(4)–C(5)	1.495(3)
C(6)–C(7)	1.439(3)
C(7)–C(8)	1.384(3)
C(7)–C(9)	1.397(3)
C(8)–C(9)	1.384(3)
C(9)–C(10)	1.439(3)

their adoption of a planar conformation [67–74]. In the absence of these forces, neutral chalcofulvalene donors are non-planar, often exhibiting significant bends of up to 30° along dithiole or diseleno bridges [75]. Upon oxidation of any tetrathiafulvalene donor, structural changes in the molecule occur, including the adoption of a planar conformation followed by a lengthening of the central C=C bond and a shortening of the C–S bonds in the central TTF core [12, 13, 76–85]. These bond distances are the most susceptible to the oxidation state of the donor and have been used by Coppens and coworkers to develop an empirical relationship that can be used to calculate the overall oxidation state of the TTF derivative [86]. Upon inspection of these bond distances and application of the formula from Coppens, it can be calculated that the TMTTF donor molecule in the title complex remains neutral. The conclusion that TMTTF exists in its neutral state is further supported by its central C=C bond occurring between atom C1 and its symmetry generated congener C1′ at a distance of 1.343(6) Å. This bond distance is nearly equivalent to analogous C=C bonds in other neutral chalcofulvalene derivatives and provides further evidence for the donor's neutrality [87]. Table 3 contains a summary of the calculated charges for TMTTF in the title 1:1 complex as well as other salts synthesized by both chemical and electrochemical methods [15, 17, 19, 25–27, 88].

The terminal cyanide ligands on the TCNB acceptor also provide a qualitative indication of charge transfer. Much like the scenario encountered with the organocyanide acceptors TCNQ and $TCNQF_4$ ($TCNQF_4$ = 2,3,5,6-tetrafluoro-7,7,8,8-tetracyanoquinodiimine), any spontaneous electron transfer from TMTTF to TCNB would be accompanied by a lengthening of the cyanide bond distances as electrons are donated into their antibonding π^*-orbitals [89–92]. According to the X-ray crystallographic structure for TMTTF–TCNB, the bond distances for the cyanide ligands of TCNB have values of 1.139(3) and 1.140(3) Å, values comparable to those reported in the literature for free TCNB providing structural evidence that the acceptor in the 1:1 encounter complex also appears to be neutral [28].

Closer analysis of the structure for TMTTF–TCNB, which crystallizes in the triclinic space group $P - 1$ with halves of a TMTTF donor and TCNB acceptor forming the contents of the asymmetric unit within the $(13\bar{1})$ plane, reveals that the neutral donor and acceptor molecules stack in an integrated fashion parallel to the *a* axis. Within these stacks, uniform intramolecular separations with centroid-to-centroid distances of 3.398 Å exist between TMTTF and TCNB (Fig. 3a). Despite being neutral, TMTTF is planar, showing no bends along either dithiole bridge. Such a structural observation is reminiscent of that seen previously

Table 3 Estimated degree of ionicity for the TMTTF donor molecule in the title compound and its comparison to other calculated valences for published TMTTF-containing materials

Salt	Molecule	A (Å)[a]	B (Å)[b]	Q[c]	Reference
$(TMTTF)_2Br$	A	1.349(8)	1.739(8)	+0.26	[19]
	A	1.349(8)	1.739(8)	+0.26	
TMTTF–Bromanil	A	1.356(8)	1.737(5)	+0.37	[26]
TMTTF–TCNQ	A	1.368(8)	1.739(3)	+0.51	[26]
$(TMTTF)BF_4$	A	1.403(3)	1.717(5)	+1.22	[27]
$(TMTTF)_3[Re_2Cl_8]\cdot 2CH_3CN$	A	1.392(8)	1.728(4)	+0.95	[17]
	B	1.399(3)	1.717(5)	+1.17	
	C	1.357(5)	1.750(3)	+0.25	
$(TMTTF)_2[W_6O_{19}]$	A	1.370(2)	1.720(2)	+0.75	[15]
	B	1.390(2)	1.720(2)	+1.01	
$(TMTTF)[ClO_4]_2$	A	1.452(3)	1.681(4)	+2.32	[88]
TMTTF–TCNB	A	1.343(4)	1.749(3)	+0.07	This work

[a] Central C=C bond distance

[b] Mean central C–S bond distance

[c] Q = charge estimated with the formula $Q = -17.92 + 23.43 \times (A/B)$ from [86]

in the 1:1 adduct *o*-Me_2TTF–TCNB, where π–π interactions between neutral donor and acceptor molecules at distances <3.5 Å resulted in donor planarity [59]. Within the structure of the title compound, TMTTF molecules within the $(13\bar{1})$ plane are related to one another through glide planes parallel to the *b* axis. When one considers this symmetry element, the closest interatomic distances between neighboring sulfur atoms occur at distances near 3.8 Å. Despite being longer than the sum of the van der Waals radii for two sulfur atoms in close proximity (3.6 Å), these interactions form a novel repeat pattern in the solid state; formed by the offset of TMTTF donors at an approximate distance of 6 Å, a stair-step pattern within the $(13\bar{1})$ plane results. Other sets of stairs repeat ad infinitum through translations along the *c* axis (Fig. 4).

Along with this novel repeat pattern among the TMTTF donors, a two-dimensional net of hydrogen bonding interactions was found to exist encompassing interactions between donor and acceptor moieties and among neighboring acceptor molecules. Inspection of the solid state structure revealed that two categories of hydrogen bonding interactions occur: first, $C_{sp}{}^3$–H···N interactions exist between TMTTF and TCNB, while a second hydrogen bonding $C_{sp}{}^2$–H···N interaction occurs between TCNB acceptors. Previously, in the structure for TTF–TCNB, Bandoli and coworkers suggested that should interatomic distances between nitrogen and hydrogen atoms be <2.70 Å, the sum of their corresponding van der Waals radii, a hydrogen bonding interaction between the atoms can exist [58]. Within the $(13\bar{1})$ plane, a $C_{sp}{}^3$–H···N interaction between TMTTF and TCNB exists laterally (parallel to the c axis) between atoms H2A and N2 at a distance of 2.641(4) Å. Concurrently, $C_{sp}{}^2$–H···N interactions were also observed within the $(13\bar{1})$ plane between TCNB moieties related to one another by translations along the b axis at a distance of 2.445(3) Å forming infinite ribbons of hydrogen bonding interactions parallel to this axis. The unification of these two independent sets of interactions defines a two dimensional net of hydrogen bonding which lies within extensions of the $(13\bar{1})$ plane and stack atop other nets along *a* in a manner akin to the stacking of layers of graphene in graphite (Fig. 5). The distances for the hydrogen bonds reported also provide further structural evidence in support of the hypothesis that $C_{sp}{}^2$–H···N interactions are stronger than their $C_{sp}{}^3$–H···N counterparts as the distances for the former are shorter than the latter [93].

IR Spectroscopy

The infrared (IR) spectra for TMTTF–TCNB and free TCNB were measured as Nujol mulls placed between KBr plates on a Nicolet 740 FT-IR spectrometer. Closer inspection of the terminal cyanide stretches for these systems supports the conclusion obtained through crystal structure determination: primarily, that the TMTTF donor and TCNB acceptor co-crystallize as neutral molecules without simultaneous charge transfer. Infrared spectra obtained for TMTTF–TCNB and TCNB show cyanide stretching frequencies around 2244 cm^{-1} suggesting that no charge transfer has occurred between the donor and acceptor. When one considers the large library of infrared data available for the organocyanide family of acceptors, electron donation into the antibonding π*-orbital of the

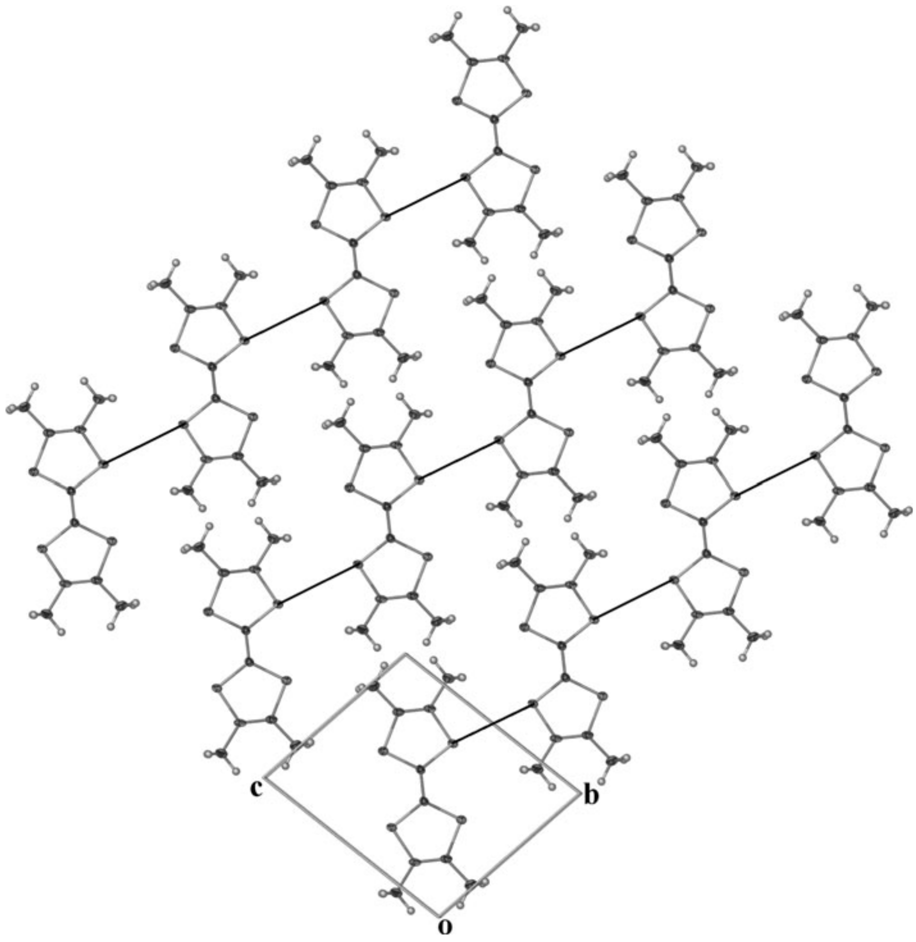

Fig. 4 Stair-step orientations of the closest interatomic interactions between neighboring sulfur atoms parallel to the *b* axis

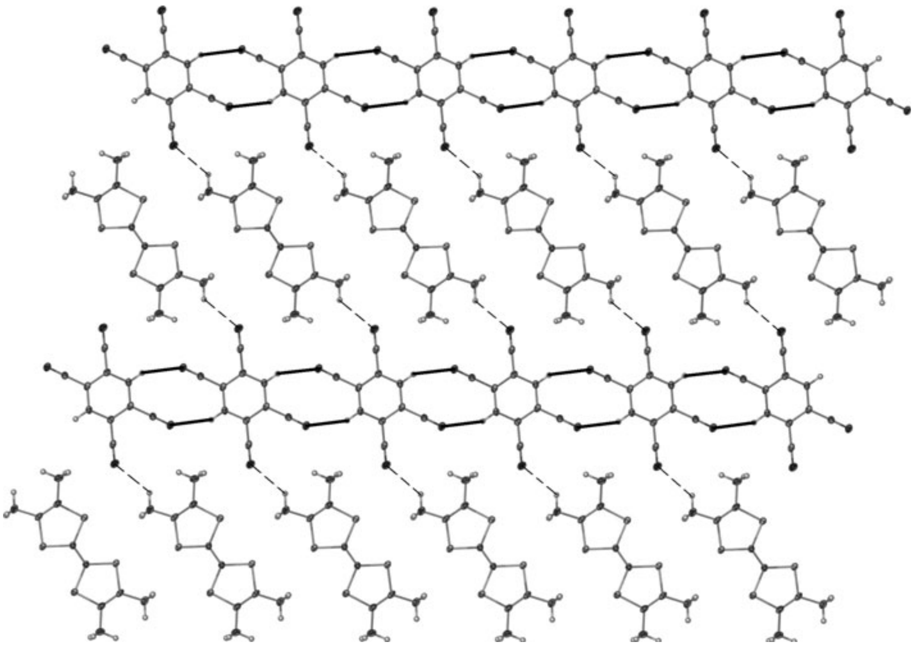

Fig. 5 Two-dimensional hydrogen bonding net within projections of the $(13\bar{1})$ plane containing $C_{sp}{}^{2}$–H···N interactions between TCNB acceptors (*continuous line*) and $C_{sp}{}^{3}$–H···N interactions between TMTTF and TCNB (*dashed line*)

terminal cyanide ligand leads to a lengthening of the triple bond and a lowering in its corresponding stretching frequency upon reduction. For example, when TCNQ is reduced in the presence of reducing agents such as $(Cp^*)_2M$ (M = Fe or Co), the cyanide stretching frequency reduces from 2222 cm^{-1} in its neutral form to a multiplet and singlet at 2153 and 2179 cm^{-1} respectively in the radical anionic ($TCNQ^{\bullet -}$) state. Concurrently, the length of the cyanide triple bond increases upon reduction of TCNQ° to its radical anion, lengthening from 1.140(1) to 1.153(7) Å [89–92]. Since the cyanide stretching frequencies for TMTTF–TCNB are nearly equivalent to those for free TCNB, the conclusions reached through structure solution are confirmed spectroscopically.

Conclusion

In this manuscript, we present the structure of the 1:1 encounter complex containing the chalcofulvalene donor TMTTF and the organocyanide acceptor TCNB. This complex contains integrated stacks of donor and acceptor molecules that stack parallel to the *a* axis at uniform distances. Hydrogen bonding interactions were found to occur between the donor and acceptor molecules and among dyads of TCNB acceptors related by translation along the *b* axis forming a two dimensional net within the $(13\bar{1})$ plane. The presence of black crystals in this system is cryptic, suggesting the presence of charge transfer; however, no charge transfer was observed as determined by X-ray crystallography and infrared spectroscopy. Further analyses, such as single crystal IR and Raman studies, will be done on crystals of this adduct and the results will be reported in due course.

Acknowledgments This work was supported by The Welch Foundation (Grant A-1449) and the U.S. Department of Energy (Grant DE-FG01-05ER05-01). We also acknowledge the National Science Foundation (Grant 9807975) for the funds to purchase the X-ray diffractometer. EWR would like to sincerely thank Nancy Erskine for additional editorial assistance.

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