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Tetrathiafulvalene-thioindigo annelated donor–acceptor system with intramolecular charge transfer

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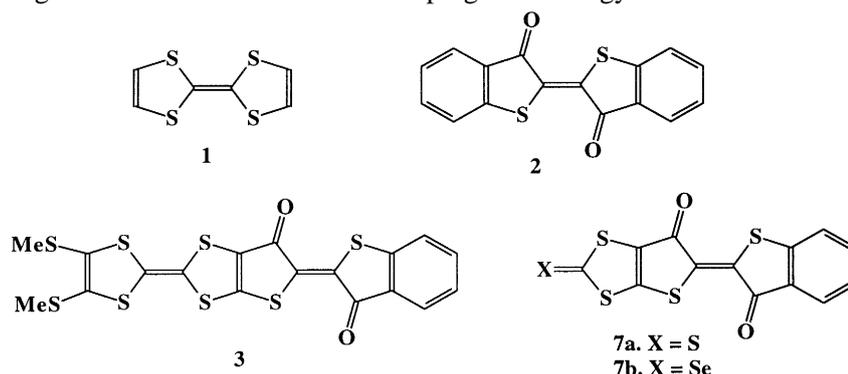
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Abstract

The synthesis, UV–vis spectra, X-ray structure and redox properties of novel models for intramolecular D–A interaction, which incorporate tetrathiafulvalene and a thioindigo basic chromophoric system, are described. © 2000 Elsevier Science Ltd. All rights reserved.

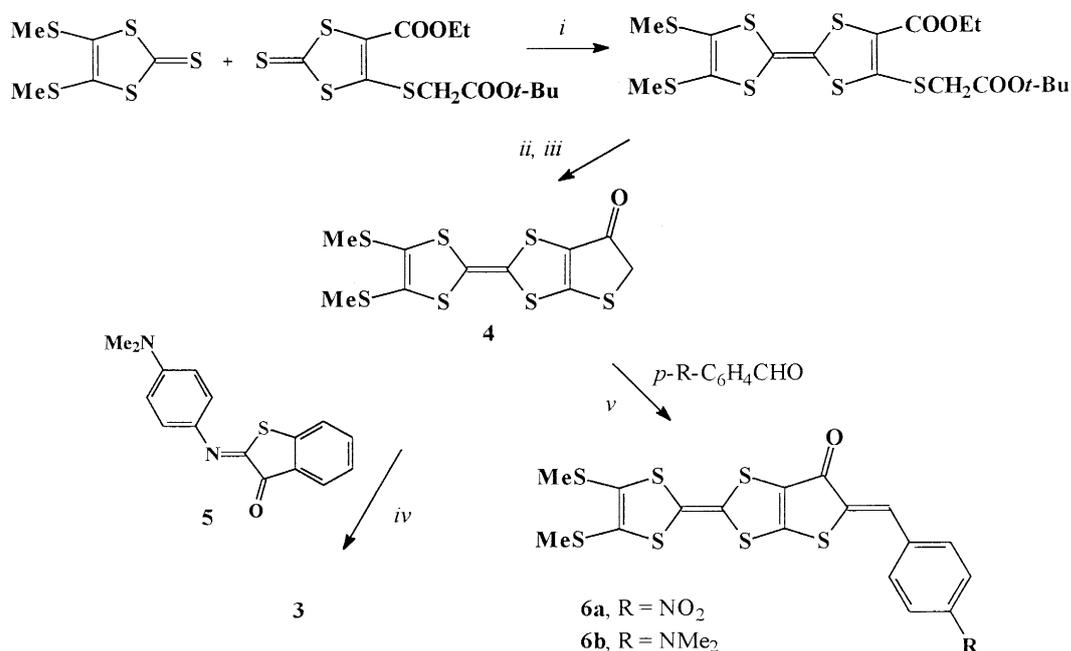
Keywords: thiafulvalene; benzothiopenes; donors; acceptors.

Tetrathiafulvalene (TTF, **1**) derivatives belong to one of the most investigated to-date organic electron donors which are widely employed as components for both inter- and intramolecular charge transfer materials.¹ Recently, the interest in thioindigo (TI, **2**) derivatives has been renewed and focused on examining the possibility of using their photochromic properties for elaboration of photoinduced molecular switches.² TI itself exhibits two-stage one-electron reduction steps similar to 1,4-benzoquinone and redox properties of thioindigoid dyes in both ground and excited states is another aspect that has been intensively investigated with the final aim of developing solar energy conservation technologies.³



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Here we report on the synthesis and crystal structure of a hybrid molecule involving both TTF and TI moieties. The synthetic strategy is outlined in Scheme 1.



Scheme 1. Reagents and conditions: (i) $\text{P}(\text{OEt})_3$, reflux, 15 min, 26%; (ii) $t\text{-BuOK}/t\text{-BuOH}$, 45 min; (iii) $\text{CF}_3\text{COOH}/\text{AcOH}$, 70°C , 30 min, 39%; (iv) AcOH , reflux, 45 min, 86%; (v) AcOH , 30 min, **6a**: 82%, **6b**: 84%

The condensation of **4** with the anil of benzo[*b*]thiophene-3(2*H*)-one **5**, or substituted benzaldehydes, afforded **3** and **6a,b** in high yields. It is noteworthy that the reaction of **4** with *N,N*-dimethyl-*p*-nitrosoaniline led to the 2,1-benzisothiazole derivative as a result of a recently described rearrangement reaction.⁴

Derivative **3** is moderately soluble in methylene chloride and benzene and crystallizes from toluene or pyridine as black crystals with a green luster. The X-ray crystal structure determination⁵ showed that the molecule is almost planar (the rms from the plane of all non-hydrogen atoms excluding Me groups is 0.019(4) Å). The bond lengths in TTF and *trans*-TI moieties of **3** (Fig. 1) are very close to those found in the known polymorphic modifications of TTF⁶ and TI,⁷ except the double bond C11=C18, which is somewhat longer than the bond C14=C16, and the bond C11-S3, which is considerably shorter than the corresponding bonds of the TTF fragment.

The electronic absorption spectra of **3** confirm the existence of the electronic interaction between the D and A moieties and exhibit, in addition to the typical band of thioindigo at 510 nm, a charge transfer (CT) band ($\epsilon \sim 3000$), the intramolecular nature of which is proven by measurements at different concentrations. This band exhibits strong positive solvatochromism and its position varies from 520 nm in carbon disulfide to 730 nm in toluene and 760 nm in benzonitrile. The photochemical behavior of **3** is unusual. Whereas derivatives **7a** and **7b**, synthesized by the analogous methodology, undergo *E/Z* photoisomerization similar to TI, irradiation of **3** at any wavelength between 500 and 700 nm gives rise to the disappearance of the CT band and appearance of poorly resolved ESR signals, as a result of photoinduced electron transfer. The cyclic voltammogram⁸ of **3** shows three reversible redox peaks at -0.52 , 0.73 and 0.98 V corresponding to one-electron reduction and a two-step one-electron oxidation

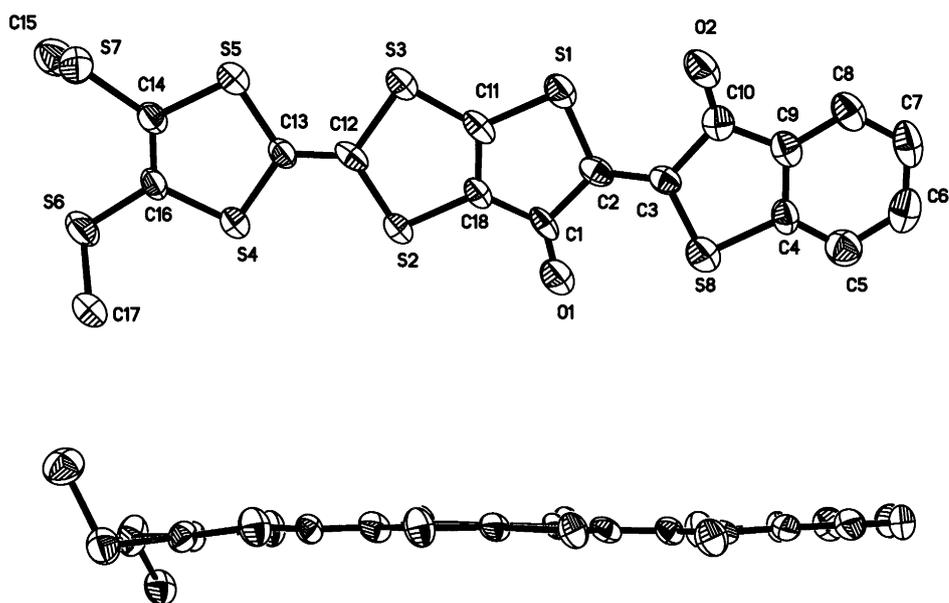


Fig. 1. ORTEP picture of **3** at the 50% probability level. C11–S3 1.715(6), C10–O2 1.165(7), C4–C9 1.400(7), C11–C18 1.360(7), C1–O1 1.168(7), C12–C13 1.342(7), C14–C16 1.339(7) Å. Intramolecular distances are S8···O1 2.917(7), S1···O2 2.72 Å

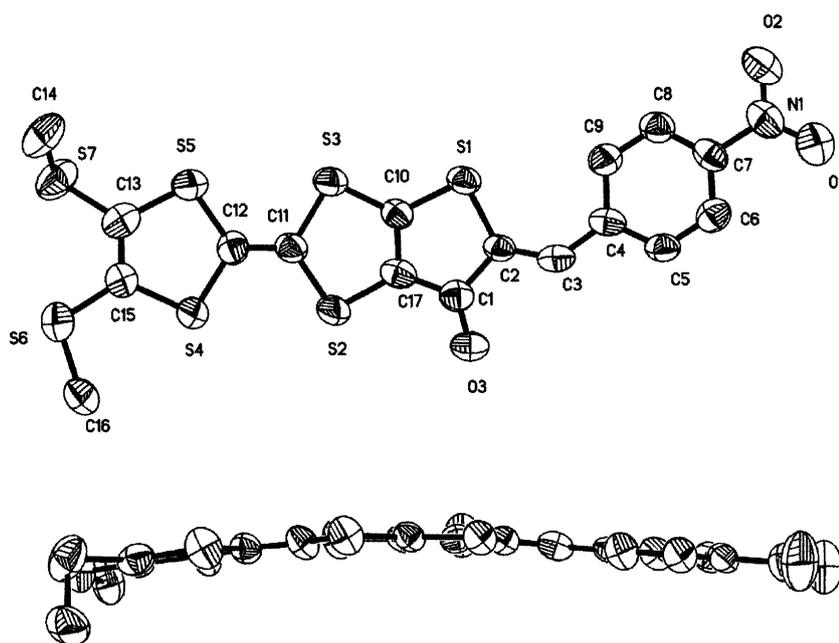


Fig. 2. ORTEP picture of **6a** at the 50% probability level. C2–C3 1.324(7), C1–O3 1.229(6), C1–C2 1.438(7), C1–C17 1.491(7), C10–C17 1.381(7), C13–C15 1.352(7), S3–C10 1.698(5), S2–C17 1.730(6) Å

process (cf. with -0.66 V for TI and with 0.46 , 0.91 V for TTF at the same experimental conditions). An irreversible reduction peak at -1.07 V is also observed.

The reaction of **4** with *p*-nitrobenzaldehyde affords derivative **6a** which crystallizes from methylene chloride as dark green crystals with a metallic luster. This molecule is slightly distorted from a plane to a boat conformation with methyl groups displaced from this plane to the same side (Fig. 2). A broad CT band with the maximum at 610 nm ($\epsilon=2700$) was observed for this compound in methylene chloride solution.

The presence of the strong electronic interaction via dihydrothienon bridge is also confirmed by electrochemical behavior of **6b**. Thus, three reversible one-electron oxidation waves at 0.69 , 0.94 and 1.20 V were observed.⁸

Acknowledgements

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5. A shiny black plate ($0.6 \times 0.3 \times 0.1$ mm) of **3** is monoclinic: $C_{18}H_{10}O_2S_8$, space group $P2_1/n$, $Z=4$, at 25°C , $a=7.657(1)$, $b=10.660(1)$, $c=24.363(3)$ Å, $\beta=90.54(1)^\circ$, $V=1988.6(4)$ Å³, $\rho_{\text{calcd}}=1.719$ Mg/m³, $F(000)=1048$. A total of 1080 frames were collected and integrated with a Bruker SAINT software package using a wide-frame integration algorithm. 20315 reflections were collected ($\theta < 21.98^\circ$), of which 2423 reflections were independent ($R_{\text{int}}=20.44\%$) and 1578 with $F_o > 4\sigma(F_o)$. The structure was refined (255 parameters) to $R1=4.61\%$, $wR2=10.58\%$, $GOF=0.939$. A dark green plate ($0.8 \times 0.4 \times 0.05$ mm) of **6a** is orthorhombic: $C_{17}H_{11}NO_3S_7$, space group $P2_12_12_1$, $Z=4$, at 25°C , $a=4.302(3)$, $b=12.037(7)$, $c=38.11(2)$ Å, $V=1974(2)$ Å³, $\rho_{\text{calcd}}=1.688$ Mg/m³, $F(000)=1024$. A total of 1080 frames were collected and integrated with Bruker SAINT software package using a wide-frame integration algorithm. 10151 reflections were collected ($\theta < 24.93^\circ$), of which 3384 reflections were independent ($R_{\text{int}}=11.11\%$) and 1985 with $F_o > 4\sigma(F_o)$. The structure was refined (255 parameters) to $R1=5.43\%$, $wR2=9.34\%$, $GOF=0.881$. Atomic coordinates, bond lengths and angles and thermal parameters have been deposited at the Cambridge Crystallographic Data Center.
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8. In benzonitrile/ 0.1 M Bu_4NClO_4 on Pt working electrode. Potentials are quoted versus SCE reference electrode at 100 mV s⁻¹ scan rate.