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Synthesis and Crystal, Molecular, and Electronic Structure of the Organosulfur π-Electron-Donor 2-(Thiopyran-4′-ylidene)-1,3-dithiole[1]

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A three-step synthesis of the organosulfur π-electron-donor 2-(thiopyran-4′-ylidene)-1,3-dithiole (TPDT, **1a**), which is iso-π-electronic to tetrathiafulvalene (TTF, **2a**) and $\Delta^{4,4'}$-bithiopyran (BTP, **3a**), is detailed. A comparative study of the molecular and solid-state properties of TPDT, TTF, and BTP is reported. This study involves cyclic voltammetry, ion–radical salt formation with 7,7,8,8-tetracyanoquinodimethane (TCNQ), and gas-phase ultraviolet photoelectron spectroscopy (UPS). While TPDT and TTF have similar first redox potentials (0.28 and 0.33 V vs SCE, respectively) and vertical ionization potentials (IP; 6.68 and 6.81 eV, respectively), TTF interacts with TCNQ to give a metallic ion–radical solid, while TPDT interacts with TCNQ to give semiconducting phases of 1:1 and 2:3 stoichiometry. The dicarbomethoxy ester of TPDT (**1b**), the tetracarbomethoxy derivative of TTF (**2b**), and the tetracyano derivative of TTF (**2d**) have also been studied by UPS and exhibit first vertical IPs of 6.75, 7.00, and 8.35 eV, respectively. TPDT, $C_8H_6S_3$, crystallizes in the monoclinic space group $P2_1/c$ with a = 8.601 (1) Å, b = 7.814 (3) Å, c = 12.525 (4) Å, β = 93.09 (2)°, V = 840.5 Å^3, Z = 4. The structure, solved by direct methods, reveals, in contrast to TTF, a nonstacked array, and the molecular parameters are similar to those of other systems containing neutral 1,3-dithiole and 4-thiopyranylidene moieties. CNDO/S3 calculations are used to describe the molecular electronic structures of TPDT, TTF, and BTP, and by application of Koopmans' theorem, to interpret the UPS data. TPDT and TTF are found to have very similar ground-state orbital properties. The derivation of the sulfur parameters used in the CNDO/S3 calculations is detailed.

Introduction

Current interest in heterocyclic chalcogen compounds, iso-π-electronic to heptafulvene, includes synthesis,[1a,b,3] chemical transformations,[4] molecular electronic structure,[5] aspects of crystal and molecular structure,[1a,3c,6] the electrical and magnetic properties of charge-transfer salts of these compounds in the solid state,[3d,3e,7] and discussions of possible relationships between molecular properties and

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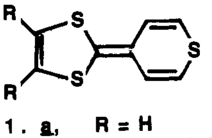
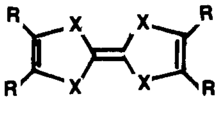
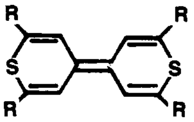
novel solid-state phenomena.[6h,7a,8] This paper details our studies of the organosulfur donor 2-(thiopyran-4-ylidene)-1,3-dithiole (TPDT, **1a**) and its characterization by cyclic voltammetry, the study of its crystal and molecular structure by single-crystal X-ray crystallography, and the characterization of its electronic structure by ultraviolet photoelectron spectroscopy (UPS) and associated CNDO/S3 molecular orbital calculations. Recently, the synthesis of the selenium and mixed sulfur–selenium analogues of TPDT,[9a] annelated analogues,[9b] and preparation of conductive TCNQ complexes of these donors have been communicated. While we find that many of the molecular properties of TPDT are readily comparable to those of the iso-π-electronic sulfur donors tetrathiafulvalene (TTF, **2**) and $\Delta^{4,4'}$-bithiopyan (BTP,**3a**), there are marked differences in the supramolecular behavior of these three sulfur donors.[8b,c] Our studies of the structural and electrical properties of ion–radical solids derived from **3a–c** have been reported.[10]



1. a, R = H
b, R = CO_2CH_3



2. a, R = H, X = S
b, R = CO_2CH_3, X = S
c, R = H, X = Se
d, R = CN, X = S



3. a, R = H
b, R = CH_3
c, R = $CO_2C_2H_5$

Experimental Section

General Techniques. Melting points are uncorrected. Elemental analysis was performed by Schwarzkopf Microanalytical Laboratory, Woodside, NY. Ultraviolet–visible spectra were obtained on a Cary 15 spectrophotometer, and the charge-transfer spectrum was obtained on a Cary 17D spectrophotometer, both in 1-cm cells. Infrared spectra were recorded on a Perkin-Elmer 283 instrument. Proton nuclear magnetic resonance spectra were recorded on a JEOL instrument at 60 MHz in carbon tetrachloride solution; chemical shifts are reported in parts per million downfield from internal tetramethylsilane. Cyclic voltammetry measurements were carried out on a Princeton Applied Research PAR 170 instrument in acetonitrile solution using a platinum electrode with 0.1 M tetraethylammonium perchlorate (TEAP) as support electrolyte; potentials reported are vs a saturated calomel electrode (SCE). Scan rates were in the range 50–200 mV/s. For **1a** the potential was scanned between −0.10 and +1.00 V, and for **1b**, the potential was scanned from −1.50 to +1.40 V. Conductivity measurements were performed on compressed pellets using a four-probe technique. UPS data were recorded on a Perkin-Elmer helium(I) instrument.

Reaction of Dimethyl 2-Thioxo-1,3-dithiole-4,5-dicarboxylate (4) with Thiacyclohexan-4-one in the Presence of Trimethyl Phosphite. A mixture of 4[11] (15.3 g, 68 mmol), thiacyclohexan-4-one (79.8 g, 688 mmol), and trimethyl phosphite (123 g, 740 mmol) in benzene (450 mL) solution was heated at reflux under nitrogen for at least 8 h. The benzene was removed under reduced pressure, and excess thiacyclohexan-4-one (67 g) was recovered by vacuum sublimation. The dark residue (10 g) was chromatographed in 1:1 hexane–benzene on silica gel (260 g) and eluted with 1:1 and 1:2 hexane–benzene and benzene to give **5** as an orange powder (6.5 g, 30% yield). Recrystallization of **5** from hexane gave an analytical sample, mp 124 °C. The absorption spectrum in acetonitrile exhibited the following λ_{max} (log ϵ): 407 (3.30), 327 (3.98), and 262 nm (4.08). The infrared spectrum (Nujol) exhibited the following absorption: 5.85, 6.25, 6.40, 7.85, 8.05, 9.20, 9.75, 10.25, 10.65, 11.05, 12.50, 12.95, 13.25, 14.15 μm. The ^1H NMR spectrum exhibited the following resonances: δ 3.70 (singlet, 6 H-OCH_3); 2.70–2.20 (complex, 8 H).

Use of smaller amounts of trimethyl phosphite or thiacyclohexan-4-one in this experiment resulted in incomplete reaction of 4 and reduced yields of 5.

Anal. Calcd for $C_{12}H_{14}O_4S_3$: C, 45.28; H, 4.40; S, 30.21. Found: C, 45.10; H, 4.36; S, 29.86.

Preparation of the Dicarbomethoxy Derivative of TPDT (1b). A mixture of 5 (2.4 g, 7.5 mmol) and *p*-chloranil (5.0 g, 20.3 mmol) in mixed xylenes (100 mL) was heated at reflux for 16 h. The cooled mixture was diluted with benzene (75 mL) and this mixture was washed with 5% sodium hydroxide until the extracts were colorless; then a water wash followed. The organic solution was dried over magnesium sulfate and evaporated to about half of its original volume under reduced pressure. Analytically pure **1b** (1.9 g, 80% yield), mp 146–148 °C, precipitated from this solution on cooling. The infrared spectrum (Nujol) exhibited abosorption at 5.75, 5.85, 6.35, 7.00, 7.30, 8.05, 9.15, 9.75, 10.20, 10.95, 11.05, 11.45, 12.50, 12.90, 13.35, 13.85, 14.10, and 14.25 μm. The ^1H NMR spectrum exhibited resonances at δ 3.70 (singlet, 6 H-OCH_3) and 5.83 (singlet, 4 H). The absorption spectrum in acetonitrile revealed the following λ_{max} (log ϵ): 482 (3.0), 376 sh (3.91), 352 sh (4.56), and 337 (4.44) nm.

Anal. Calcd for $C_{12}H_{10}O_4S_3$: C, 45.86; H, 3.18; S, 30.57. Found: C, 45.78; H, 3.27; S, 30.32.

Preparation of TPDT (1a). Anhydrous lithium bromide (0.21 g, 2.5 mmol) was dissolved in hexamethyl phosphoramide (4 mL) in an Erlenmeyer flask at approximately 80 °C, and two drops of water were added. This solution was heated to 150–160 °C on a hot plate, and **1b** (0.20 g, 0.64 mmol) was added. The reaction mixture was kept at 150–160 °C for 30 min when it was poured into cold 10% sodium bisulfite solution. Typically, four of these experiments were carried out simultaneously, and the products were combined. The brown precipitate of crude 1 was dissolved in benzene (30 mL). This solution was dried over magnesium sulfate and concentrated under reduced pressure to give 1, 0.45 g, mp 120 °C. Further purification was achieved by gradient sublimation[12] on Kapton film at 70 °C and 10^{-6} mmHg to give 0.37 g, mp 127 °C, 70% yield. The absorption spectrum in acetonitrile exhibited the following λ_{max} (log ϵ): 359 (4.5), 348 sh (4.4), and 2.52 (3.6) nm. The infrared spectrum (Nujol) exhibited the following absorption: 3.28, 6.20, 6.45, 6.50, 6.65, 7.38, 7.75, 7.95, 8.37, 8.75, 9.15, 10.70, 10.80, 11.10, 11.40, 12.50, 13.20, 14.10, 14.50, and 15.30 μm. The ^1H NMR spectrum showed resonances at δ 6.06 (singlet, two dithiole protons) and δ 5.77 (singlet, four thiopyranylidene protons). The mass spectrum exhibited a parent and base peak at *m/e* 198. The observed intensities at *m/e* 198–202 are 100, 11.5, 15.3, 1.5, and 0.5, while those calculated for $C_8H_6S_3$ are 100, 11.47, 13.92, 1.44, and 0.70.

Anal. Calcd for $C_8H_6S_3$: C, 48.45; H, 3.05; S, 48.50. Found: C, 48.59; H, 3.03; S, 48.30.

Ion–Radical Solids from 1a and TCNQ. (a) 1:1 Stoichiometry. To a solution of **1a** (248 mg, 1.25 mmol) in acetonitrile was added a saturated acetonitrile solution of gradient-sublimed TCNQ (204 mg, 1 mmol). The solution turned green, and a black solid precipitated immediately. This solid was isolated by suction filtration and vacuum dried to give 300 mg (75% yield). X-ray

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Scheme I

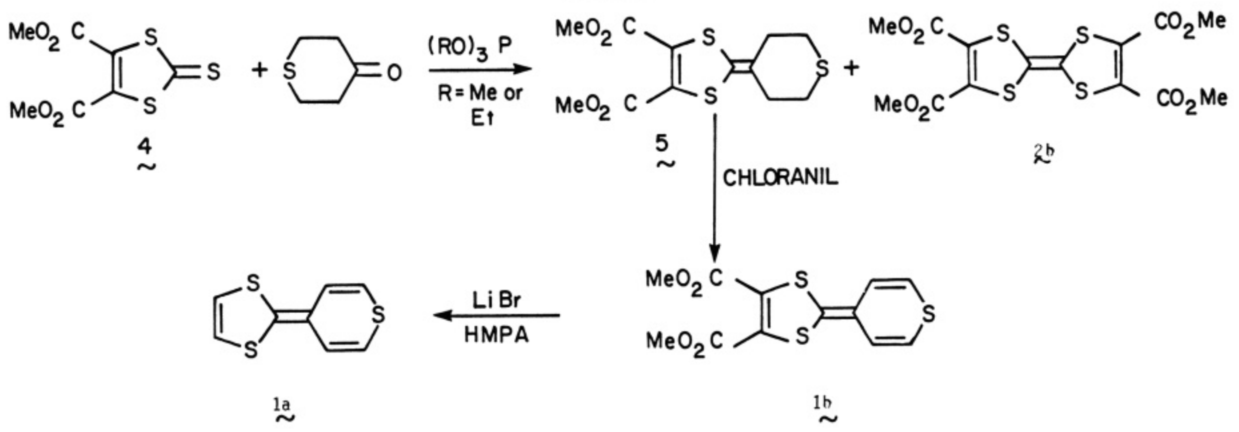

Table I. Crystal Data and Experimental Conditions

$a = 8.601$ (1) Å	$\alpha = 90°$
$b = 7.814$ (3) Å	$\beta = 93.09(2)°$
$c = 12.525$ (4) Å	$\gamma = 90°$
$V = 840.5$ Å^3	$D_c = 1.56$ g/cm^3
MW = 198.33	$D_m = 1.56$ g/cm^3
space group $P2_1/c$	$Z = 4$
μ (Mo Kα radiation), 7.725 cm^{-1}	
scan rate 4–20°/min (depending on intensity)	
scan range 2θ (Mo Kα_1) −0.5° to 2θ (Mo Kα_2) +0.5°	
range of data $0° < 2\theta$ (MoKα) $< 50°$	
total ind rflctns, 1700	
rflctns with $F_o > 3\sigma(F_o)$, 959	

Table II. Positional and Isotropic Thermal Parameters[a]

	x	y	z	U_{eq}/U
S(1)	1.3054 (1)	0.2383 (1)	0.6338 (1)	0.0525 (6)
S(2)	1.1687 (1)	0.4866 (1)	0.7777 (1)	0.0540 (6)
S(3)	0.6701 (1)	0.2944 (2)	0.4853 (1)	0.0650 (7)
C(1)	1.4163 (5)	0.2986 (6)	0.7464 (3)	0.0607 (28)
C(2)	1.3531 (5)	0.4081 (6)	0.8114 (4)	0.0626 (30)
C(3)	1.1385 (4)	0.3567 (4)	0.6636 (3)	0.0378 (19)
C(4)	0.3475 (4)	0.6058 (3)	0.0109 (5)	0.0370 (20)
C(5)	0.9823 (5)	0.2405 (4)	0.5116 (3)	0.0435 (21)
C(6)	0.8507 (5)	0.2112 (5)	0.4563 (3)	0.0514 (25)
C(7)	0.7255 (5)	0.4309 (5)	0.5897 (3)	0.0565 (27)
C(8)	0.8666 (4)	0.4457 (5)	0.6349 (3)	0.0451 (22)
H(1)	1.5180 (55)	0.2431 (54)	0.7576 (36)	0.0788 (148)
H(2)	1.3997 (45)	0.4378 (52)	0.8698 (30)	0.0580 (126)
H(5)	1.0724 (38)	0.1850 (44)	0.4858 (25)	0.0383 (98)
H(6)	0.8462 (43)	0.1394 (47)	0.3904 (29)	0.0561 (115)
H(7)	0.6438 (45)	0.5019 (46)	0.6130 (30)	0.0633 (123)
H(8)	0.8805 (37)	0.5254 (43)	0.6989 (25)	0.0387 (98)

[a] Estimated standard deviations are in parentheses. For atoms refined anisotropically, $U_{eq} = (^1/_6\pi^2)\sum_i\sum_j\beta_{ij}\mathbf{a}_i\cdot\mathbf{a}_j$.

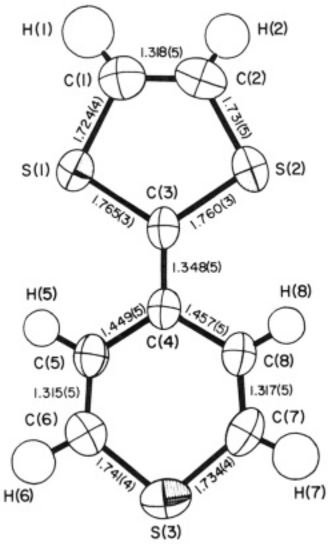

Figure 1. Molecular structure of TPDT showing atomic notation and all non-hydrogen bond lengths.

powder diffraction of this solid exhibited the following: 7.3 Å, 6.3 (s = strong), 5.4, 5.15, 4.10, 4.00, 3.70, 3.60, 3.50, 3.35, 3.30, 3.18 (s), 3.08. A compressed pellet of this solid had a dc conductivity of 10^{-2} (Ω cm)$^{-1}$.

Anal. Calcd for $C_{20}H_{10}N_4S_3$: C, 59.66; H, 2.50; N, 13.92; S, 23.92. Found: C, 60.15; H, 2.41; N, 13.71; S, 22.93.

(b) 2:3 Stoichiometry. To an acetonitrile solution of TCNQ (408 mg, 2 mmol) was added an acetonitrile solution of **1a** (198 mg, 1 mmol). The reaction solution turned green, and a black precipitate formed immediately. This solid was isolated by suction filtration and vacuum dried to give 302 mg (60% yield). X-ray powder diffraction of this solid exhibited the following: 7.8 Å, 6.9, 6.3 (s), 4.5, 4.35, 4.2, 3.95, 3.65, 3.35, 3.25, 3.13 (s). A compressed pellet of this solid had a dc conductivity of 10^{-1} (Ω cm)$^{-1}$.

Anal. Calcd for $C_{52}H_{24}N_{12}S_6$: C, 61.83f H, 2.39; N, 16.71; S, 19.06. Found: C, 61.69; H, 2.65; N, 15.47; S, 19.73.

Complex of 1b with TCNQ. To a hot saturated acetonitrile solution of gradient-sublimed TCNQ (35.6 mg, 0.17 mmol) was added a hot saturated acetonitrile solution of **1b** (50.0 mg, 0.16 mmol). The hot solution was allowed to cool to room temperature, and a greenish-brown precipitate was isolated by suction filtration, mp 208–211 °C (dec), 50 mg, 61% yield. A compressed pellet of this solid had a dc conductivity less than 10^{-10} (Ω cm)$^{-1}$. In dichloromethane solution at a concentration of 10^{-2} M in both **1b** and TCNQ, an absorption maximum assigned to a charge-transfer transition was observed at 1360 nm.

Anal. Calcd for $C_{24}H_{14}N_4O_4S_3$: C, 55.59; H, 2.72; N, 10.80; S, 18.55. Found: C, 55.87; H, 2.81; N, 10.67; S, 18.75.

Collection and Reduction of X-ray Data for 1a. A summary of the experimental details is given in Table I. The crystal chosen for data collection was an ochre plate 0.15 × 0.20 × 0.08 mm obtained by hexane solution crystallization of gradient-sublimed material. The reflection width at half-height from ω scans was 0.2°. Intensities were collected at ambient temperature on an Enraf-Nonius CAD4 diffractometer, θ–2θ scan mode, with a scan rate of 4–20°/min^{-1}. Graphite-monochromated Mo Kα radiation; 1739 reflections measured ($0 \le 2\theta \le 50°$), 1700 independent, 1162 with $F_o > \sigma(F_o)$. No crystal decay was observed during data collection. The data were corrected for Lorentz and polarization effects but not for absorption.

Structure Analysis and Refinement. Carbon and sulfur atoms were located by direct methods. Full-matrix least-squares refinement was performed with C and S anisotropic, H isotropic. The final R and R_w values (based upon the 1162 reflections greater than $\sigma(F_o)$) are 0.045 and 0.047. Programs, sources of scattering factor data, and details of the weighting scheme are those previously used.[10] Final positional and thermal parameters are given in Table II. In the figures, vibration ellipsoids are drawn at the 50% probability level. The list of observed and calculated structure factors is contained in the supplementary material (see the paragraph at the end of the paper). The atomic notation used in the tables and discussion is given in Figure 1.

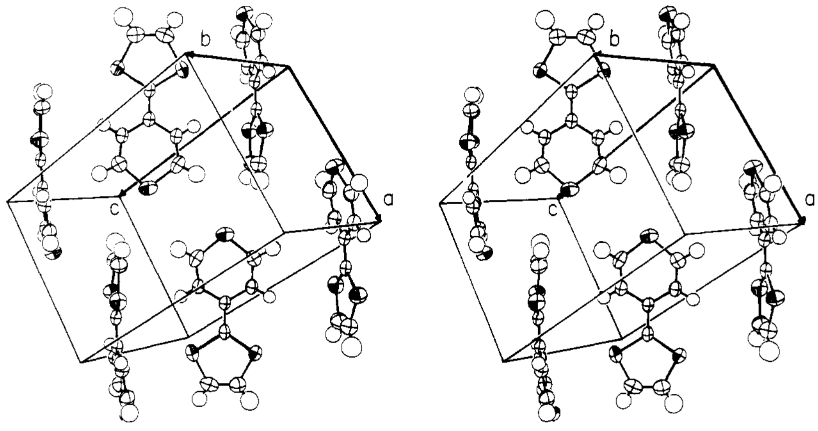

Figure 2. Stereoscopic view of the TPDT unit cell.

Results and Discussion

Synthesis. Our synthetic route to TPDT is summarized in Scheme I. Dimethyl 2-thioxo-1,3-dithiole-4,5-dicarboxylate (4)[11] reacts with a trialkyl phosphite, preferably trimethyl phosphite, to give a Wittig-like intermediate that reacts with thiacyclohexan-4-one to give the cross-coupled product 5 in yields up to 30%. The tetracarbomethoxy derivative of TTF (**2b**) also forms in this reaction, and 5 is isolated by column chromatography. Sato, Gonnella, and Cava[13] have described a versatile alternative to cross-coupled procedures that involves in situ generation of a phosphorane intermediate. They were able to prepare 5 in 84% yield by their procedure.

We found that the dehydrogenation of 5 is conveniently accomplished by *p*-chloranil in refluxing xylenes to give the diester of TPDT (**1b**) in 80% yield. Our attempts to effect this dehydrogenation with 2,3-dichloro-5,6-dicyano-*p*-benzoquinone (DDQ) in reluxing benzene led to **1b** in yields under 10%.

Lithium bromide in hexamethylphosphoric triamide[14] conveniently converted **1b** to TPDT in 60–70% yield. We prefer the simplicity of this method to the use of the diacid of TPDT with pyridine in a sealed tube.[11] The details of our preferred procedures are given in the Experimental Section, and the overall yield of our three-step synthesis is 15%.

Cyclic Voltammetry (CV) and Complex Formation. CV studies of **1a** and **1b** in acetonitrile solution 0.10 M in TEAP reveal two reversible one-electron transfers at a platinum electrode. For **1a**, the values of E_1 and E_2 are 0.28 and 0.64 V vs SCE, while the corresponding values for **1b** are 0.47 and 0.80 V. The increase in E_1 and E_2 on introduction of the electron-attracting ester groups in **1b** has also been noted for TTF and BTP derivatives.[3a] Not surprisingly in view of the structural parts, E_1 and E_2 for TPDT lie between the values of TTF and BTP, and E_1–E_2 for TPDT (0.36 V) is similar to the value for TTF (0.37 V).[3a] Additionally, **1b** exhibits an irreversible reduction at −1.37 V.

TPDT interacts with TCNQ in acetonitrile solution to form ion–radical solids of 1:1 and 2:3 stoichiometry which have polycrystalline conductivities of 10^{-2} and 10^{-1} $(\Omega\ \text{cm})^{-1}$, respectively. The latter value is similar to that observed for $(\text{BTP})_2(\text{TCNQ})_3$.[10b] The X-ray powder pattern of $(\text{TPDT})_2(\text{TCNQ})_3$ is very similar to that of $(\text{BTP})_2(\text{TCNQ})_3$,[10b] suggesting isomorphous crystal structures. Indeed, a mixed phase with similar powder pattern is readily formed by adding a solution of a mixture of BTP and TPDT to TCNQ in acetonitrile.

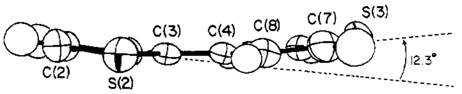

Figure 3. Side view of TPDT revealing molecular nonplanarity.

TCNQ and **1b** interact in hot acetonitrile to give a 1:1 greenish-brown solid complex which is an electrical insulator with a compaction conductivity less than 10^{-10} $(\Omega\ \text{cm})^{-1}$. The infrared spectrum of this complex exhibits the absorptions of **1b** and neutral TCNQ with $\nu_{\text{CN}} = 2211\ \text{cm}^{-1}$, indicating the lack of significant ground-state electron transfer.[15-17] This spectrum may be contrasted with that of the 1:1 solid from **1a** and TCNQ, which lacks the features of the neutral components and exhibits $\nu_{\text{CN}} = 2194$, $2178\ \text{cm}^{-1}$, indicating significant ionic character. The formation of a weak complex between TCNQ and **1b** is noteworthy, as **1b** has the same E_1 value as tetraselenafulvalene (TSeF, **2c**), $E_1 = 0.48$ V, which forms a metallic ion radical solid with TCNQ. For π-electron-donors with E_1 values comparable to **1b** and **2c**, the first redox potential is not a good predictor of electron transfer with TCNQ.[8b]

Crystal and Molecular Structure of TPDT. The structural and molecular dimensions of a donor such as TPDT are clearly of interest for purposes of comparison to TTF and BTP derivatives and also for electronic structure calculations. A stereoscopic drawing of the monoclinic unit cell is given in Figure 2. In contrast to TTF,[6b,18] the molecules do not form chains in the solid state although molecules related by inversion centers at 0,0,0 and 0,$^1/_2$,$^1/_2$ form *short stacks*. There are no indications of any unusual intermolecular contacts between atoms, in contrast to TTF.[6b,18]

The individual rings are nearly planar, with the greatest deviations from the least-squares planes being 0.065 (3) Å in the six-membered ring and 0.075 (3) Å in the five-membered ring. As can be seen from Figure 3, however, the two rings are clearly not coplanar but tilted by about 12° with respect to each other. In the absence of any short intermolecular contacts, it seems likely that the tilting is due to an intramolecular effect. The nonplanarity of TPDT may be compared with the planar **3c**[10a] and

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Table III. Selected Bond Angles (Degrees)[a]

S(1)-C(3)-S(2)	112.8 (2)°	C(6)-C(5)-C(4)	126.0 (4)
S(1)-C(1)-C(2)	117.0 (4)	C(7)-C(8)-C(4)	125.2 (4)
S(2)-C(2)-C(1)	118.8 (4)	S(3)-C(6)-C(5)	125.3 (3)
C(1)-S(1)-C(3)	96.0 (2)	S(3)-C(7)-C(8)	126.0 (3)
C(2)-S(2)-C(3)	95.3 (2)	C(6)-S(3)-C(7)	100.0 (2)
C(5)-C(4)-C(8)	116.7 (3)		

[a] Estimated standard deviations in parentheses.

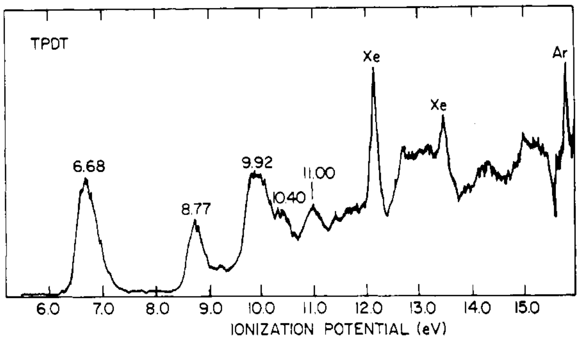

Figure 4. Gas-phase UPS of TPDT showing Xe and Ar calibration lines.

TTF,[6h,18] which is slightly distorted into a chair.

The bond lengths between non-hydrogen atoms are summarized in Figure 1. The average C–H bond distance is 0.94 (1) Å. The inter-ring double bond, found to be especially long in **3c**,[10a] seems normal in the present example. The remaining bond lengths are similar to those of analogous bonds found in TTF[6h,18] and in neutral BTP derivatives,[10a,19] with the possible exception of the double bonds in the six-membered ring, which are slightly shorter than those previously reported[10a,19] but similar to those found in 2,6-dimethyl-4*H*-1-thiapyran-4-one.[20]

Selected bond angles are listed in Table III. They do not vary significantly from the corresponding values found in TTF[6h,18] and the tetraphenyl derivative of BTP.[19]

Gas-Phase Ultraviolet Photoelectron Spectra. Gas-phase ultraviolet photoelectron spectroscopy (UPS) has been used to measure vertical ionization potentials (IP) of several classes of chalcogen π-electron donors: tetrachalcogenofulvalenes,[5,21] naphthalene-*peri*-dichalcogenides,[8d,22] and tetrathiabutadienes.[23] When combined with solid-state ionization potentials from photoemission studies, this information has been used to estimate polarization energies of these donor solids.[21,22,24] In this section, we report gas-phase UPS of TPDT and **1b**, as well as two TTF derivatives with electron-attracting substituents: the tetraester **2b** and the tetracyano compound **2d**.[25]

The UPS of TPDT, taken with He(I) radiation, is shown in Figure 4 and summarized in the section below on CNDO/S3 calculations for the higher ionizations. The first vertical ionization is at 6.68 eV; this value may be compared with the range reported for TTF (6.70–6.92 eV).[8b,21] Taken under analogous conditions, the UPS of **1b** is exhibited in Figure 5. The presence of the electron-attracting carbomethoxy groups results in a slight shift to higher ionization energies with the first vertical IP being observed at 6.75 eV.

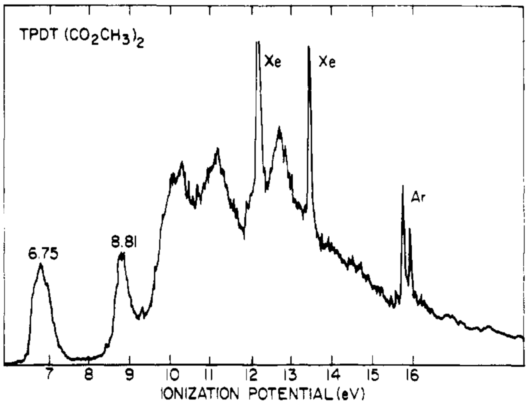

Figure 5. Gas-phase UPS of **1b** showing Xe and Ar calibration lines.

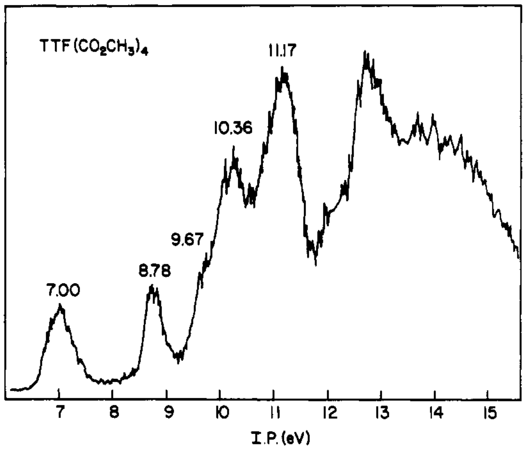

Figure 6. Gas-phase UPS of **2b**.

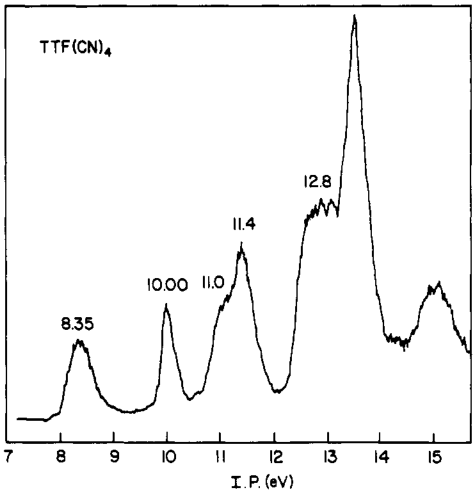

Figure 7. Gas-phase UPS of **2d**.

Figure 6 displays the UPS of **2b**. When compared to the UPS of TTF,[21] the presence of the electron-attracting carbomethoxy groups results in the first two IPs appearing at slightly higher energy, 7.00 and 8.78 eV. The more strongly electron-attracting cyano groups in **2d** have an

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Table IV. Parameters Used in the CNDO/S3 Model for π Organosulfur Donor Molecules

atom	I_s, eV	I_p, eV	I_d, eV	β_s, eV	β_p, eV	β_d, eV	γ, eV	ζ, Å^{-1}
H*	13.60			10			12.85	2.33
C(sp^2)^a	21.34	11.54		20	17		10.63	3.78
C(sp^3)^a	21.34	11.54		20	17		10.63	3.07
S	21.02	10.97	2.0	18	15	3	9.67	4.37 (s) 3.80 (p) 3.00 (d)

[a] Reference 30.

even larger effect. Shown in Figure 7, the first two IPs are observed at 8.35 and 10.00 eV. As judged by either gas-phase IP or solution redox potentials.[8b] **2b** and **2d** are poorer donors than TTF, and complex formation with these compounds has not been reported.

Further discussion of the assignments of the UPS spectra in Figures 4–7 is given in the next section, which is a CNDO/S3 treatment of the electronic structure of organosulfur donors.

CNDO/S3 Calculations. Parameters used in these calculations are summarized in Table IV. Those used for carbon and hydrogen are identical with those in the original CNDO/S3 model.[26] Sulfur parameters were developed in the following fashion. Sulfur valence-shell ionization potentials (VSIP) for 3s and 3p orbitals were taken from prescriptions of Oleari et al.;[27] VSIP for sulfur 3d levels was estimated from atomic spectroscopic data.[28] Resonance integrals β for sulfur 3s orbital were taken directly from the original CNDO model,[29] whereas those for the 3p level were scaled from the β_s/β_p ratio used for carbon, fluorine, oxygen, and nitrogen, i.e., $\beta_s/\beta_p \approx 1.2$.[30] From the Wolfsberg–Helmholz relation, $\beta\mu = kI\mu$, and the 3p and 3d VSIP, it was possible to estimate β_d. Sulfur Coulomb integrals γ_{AA} were chosen to be consistent with the CNDO/S3 formalism.[26] As found by Lipari and Duke,[26] the orbital exponents were found to have a significant effect on the calculations. The values for sulfur were obtained by systematically varying the Clementi–Raimondi sulfur exponents[31] so as to give the best fit to the UPS spectra for a model compound, thiophene. This quantum chemical methodology has been previously applied to naphthalene 1,8-disulfide[8d] and tetrathiabutadiene.[23a]

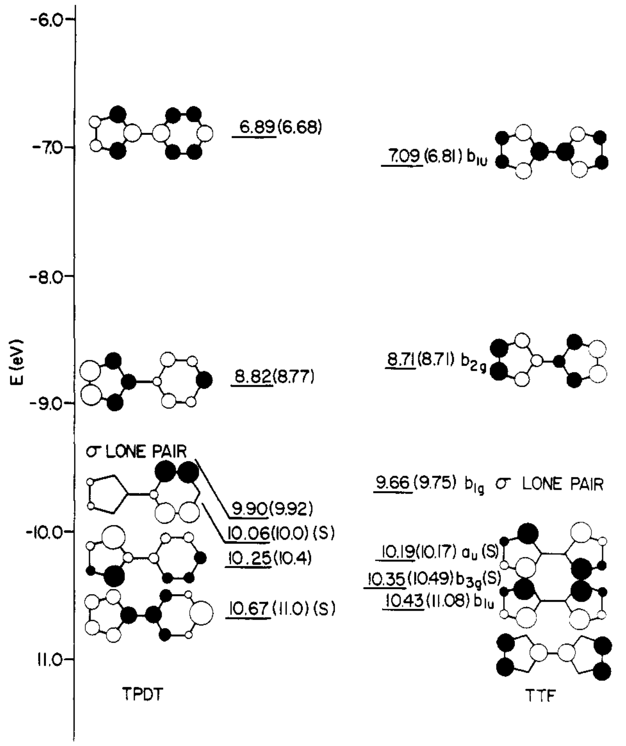

Figure 8. Results of CNDO/S3 calculation for TPDT and TTF. Experimentally determined ionization energies are shown in brackets.

With the parameters shown in Table IV and experimental molecular geometries, CNDO/S3 calculations were done for TPDT, TTF, and BTP. In all of these calculations the x and y axes were chosen to be along the long and short molecular axes, respectively. As shown in Figure 8, there is a good numerical agreement between calculated Koopmans' orbital energies and experimental ionization potentials for TPDT and TTF. As expected, the highest occupied valence structure is clearly dominated by π levels. As shown in Figure 8, the orbital character of these levels fall into four distinct categories. *Mixed antibonding* levels, which result from a carbon–sulfur antibonding interaction, make up the HOMO levels (ionization potentials from 6.0 to 9.0 eV). Intermediate in energy are the *sulfur lone-pair* levels, in which sulfur character predominates, and *nonsulfur* orbitals such as the b_{1u} level in TTF, which have little or no sulfur participation and are essentially carbon based in orbital character. Still lower in energy (and not shown in Figure 8) are carbon–sulfur *bonding* orbitals.

The orbital ordering predicted by the TTF calculations, b_{1u} (π), b_{2g} (π), b_{1g} (σ) lone pair, a_u (π) lone pair, b_{3g} (π) lone pair, b_{1u} (π) olefin is in close agreement with assignments made by the ab initio calculations of Trsic and Laidlaw[32] as to the relative position of mixed, sulfur lone-pair and carbon-based π levels. The exceptions occur in the ordering of sulfur lone-pair levels, where Trsic and Laidlaw predict that the π lone pairs are less stable than σ level, i.e., their orbital sequence is a_u (π), b_{3g} (π), b_{1g} (σ). To examine this point further, the UPS spectrum of tetracyano TTF (**2d**) was investigated (Figure 7). Since inductive effects predominate in the interaction of cyano groups with π olefin systems,[33] the spectrum is interpreted as indicating a significant stabilization of the b_{1u} (π) olefin based level (IP > 12.0 eV). The sulfur lone-pair levels (11.0–11.4 eV) are stabilized to a lesser extent and become much more like the sulfur lone pair due to the withdrawal of charge on the substituted olefin positions. In particular, it would be expected that the sulfur π levels would become degenerate. Cyano substitution, therefore, would result in a distinct lone-pair region in the UPS spectra (11.0–11.4 eV) in which the ratio of intensities of the b_{1g} (σ) level to degenerate a_u (π) and b_{3g} (π) levels would be 1:2. The UPS

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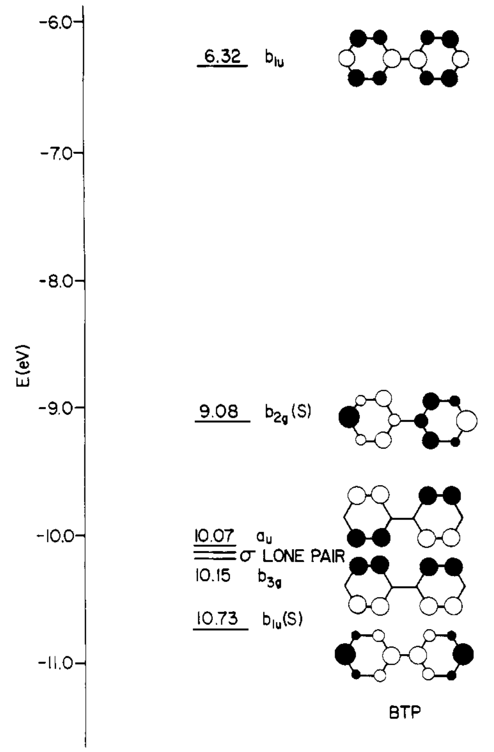

Figure 9. Results of CNDO/S3 calculation for BTP.

spectra of TTF(CN)$_4$ shows a single level at 11.0 eV followed by a doubly degenerate level at 11.4 eV and suggests that the ordering of the lone pairs is b_{1g} (σ), a_1 (π), b_{3g} (π) as given by the CNDO/S3 calculations.

The UPS spectra and CNDO/S3 calculations for TTF and TPDT are noteworthy in that the sequence of ionization potentials for TTF (6.81, 8.71, 9.75, 10.17, 10.49, and 11.08 eV) is within experimental error virtually identical with that for TPDT (6.68, 8.77, 9.92, 9.92, 10.40, and 11.00 eV). This indicates that within the Koopmans' theorem limit, the ground-state orbital properties of the two molecules are very similar. The donor–acceptor complexes formed with TCNQ in the solid state by these two species, however, are completely different, with TTF forming a metallic salt while TPDT forms semiconducting salts. The first ionization potential, redox potential, and ground-state valence structure are clearly necessary conditions for electron transfer in donor–acceptor interactions with acceptors, such as TCNQ.[8b] They are also necessary, but clearly not sufficient, conditions in determining solid-state properties of the resultant ion–radical solids.[8b] Here other factors (e.g., kinetic control of solid-phase formation,[8c,34] solid-state structure and packing,[10b] charge stabilization) are at least equally as important.

The CNDO/S3 calculations for BTP are interesting in that the first IP of this species is predicted to occur at 6.3 eV, significantly lower than that of TPDT and TTF. While the UPS of a BTP derivative has not been measured, cyclic voltammetry shows $E_{1/2}$ for BTP at 0.20 V vs SCE.[35] This should be compared to the $E_{1/2}$ values for TTF[3a,8b] and TPDT: 0.33 and 0.28 V, respectively. BTP is a stronger reducing agent as predicted by CNDO/S3 calculations, which are summarized in Figure 9. While there is a broad correlation between gas-phase IP and $E_{1/2}$, the limitations of such correlations have been discussed by the present authors.[8b,d,23a]

Acknowledgment. We thank T. J. Holmes and D. E. Warner for technical assistance and M. J. Downey for furnishing X-ray powder diffraction data.

Supplementary Material Available: Tables listing least-squares planes (1 page) and observed and calculated structure factors (8 pages). Ordering information is given on any current masthead page.

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X-Ray Photoelectron Spectroscopic Studies of Carbon Fiber Surfaces. 10. Valence-Band Studies Interpreted by X-α Calculations and the Differences between Poly(acrylonitrile)- and Pitch-Based Fibers

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X-ray photoelectron spectroscopy has been used to monitor the surface chemistry of untreated carbon fibers based on poly(acrylonitrile) and pitch. Differences were found in the core and valence-band region indicating a highly graphitic and an almost unoxidized nature for pitch-based fibers. The valence-band region of the most graphitic fiber compares well with a spectrum obtained from orbital energies and atomic contributions from an X-α calculation on coronene ($C_{24}H_{12}$).

Introduction

Carbon fibers are widely used in composite materials, especially in the aircraft industry, where the high stiffness-to-weight ratio of such composites is important. Commercially available carbon fibers are obtained either from heat treatments of polymeric materials such as poly(acrylonitrile) (PAN) or from carbon sources such as pitch from petroleum or coal tar.

The surface structure of carbon fibers is an important factor in the effective adhesion between the fiber and the composite matrix. We have carried out a series of studies[1–9] of the surface of carbon fibers based upon PAN using

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