Synthesis of the First Thieno[3,4-c]thiophene Stabilized Only by Electronic Effects

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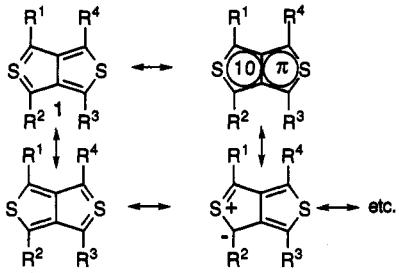
The stable, crystalline 1,3-dibromo-4,6-dicyanothieno[3,4-c]thiophene (**3a**) has been synthesized. This is the first example of a thieno[3,4-c]thiophene stabilized solely by electronic effects. The dicarbomethoxy dibromo analog **3b** and the tetrabromo analog **3c** were also generated and found to be considerably less stable.

Introduction

Thieno[3,4-c]thiophenes, the so-called nonclassical thiophenes, have been the object of chemical investigations for about two and a half decades.[1] The 10-electron system with sulfur in the formal oxidation state +4 is of interest from both the synthetic[2-7] and the theoretical[3] viewpoints.



1	R^1	R^2	R^3	R^4
a	H	H	H	H
b	H	H	Me	Me
c	H	H	COOMe	COOMe
d	Ph	Ph	Ph	Ph
e	2-Th	2-Th	2-Th	2-Th
f	S-Alkyl	S-Alkyl	S-Alkyl	S-Alkyl
g	CHO	S-*i*-Pr	CHO	S-*i*-Pr

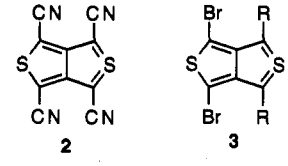
Despite this interest, only a few isolable compounds of this class have been synthesized. Unfortunately, the earliest generated members **1b,c**[2a,b] as well as the parent thienothiophene **1a**[2c] and some recently generated alkyl-substituted derivatives,[2d] were unstable and could only be detected by trapping experiments as cycloaddition products.

The tetraphenyl derivative **1d** was the first and for many years the sole stable thieno[3,4-c]thiophene described in the literature.[3]

The synthesis used for these thienothiophenes was the Pummerer dehydration of the corresponding 1*H*,3*H*-thieno[3,4-c]thiophene 2-oxide. This method was recently applied to produce the stable tetra-2-thienyl derivative **1e**.[4] A remarkable dimerization of bis(alkylthio)cyclopropenethiones in the presence of tributyl- or triphenylphosphine was found to give access to a series of alkylthio-substituted thienothiophenes **1f**.[5] Those bearing bulky substituent groups were remarkably stable to air. Some other derivatives were obtained by reaction of the tetrakis(*tert*-butylthio or *i*-propylthio) compound with the Vilsmeier reagent, followed by condensation of the resulting mono- or dialdehyde **1g** (i.e.) with malononitrile, ethyl cyanoacetate, or 1,1-dimethylhydrazine, respectively.[6] Some alkylation products of the *in situ* generated 3,4,6-tris(*tert*-butylthio)thieno[3,4-c]thiophene-1-thiolate[6c] have also been reported, as well as the oxidation of the tetrakis(*i*-propylthio) compound with *m*-chloroperbenzoic acid to furnish the corresponding sulfinate and sulfoxide.[7]

The as yet prepared stable thieno[3,4-c]thiophenes[3-7] bear four bulky substituents, or at least two bulky substituents combined with acceptor groups (i.e. **1g**), but those stabilized only by electronic effects are unknown.

We now report the synthesis and characterization of the novel stable 1,3-dibromo-4,6-dicyanothieno[3,4-c]-thiophene (**3a**) which is stabilized only by electronic effects as well as the generation of the dibromodicarbomethoxy-thienothiophene **3b** and the generation of the first tetrahalothieno[3,4-c]thiophene **3c**.



3	R
a	CN
b	COOMe
c	Br

Results and Discussion

Our renewed interest in thieno[3,4-c]thiophenes was aimed at preparing derivatives bearing small substituents

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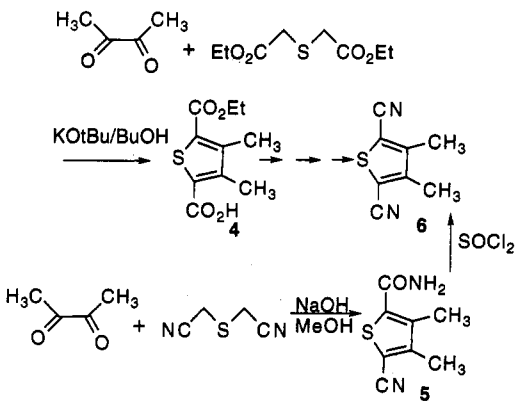
with acceptor properties. Our initial goal was the synthesis of 1,3,4,6-tetracyanothieno[3,4-*c*]thiophene (**2**), which we believe should be highly stabilized by resonance and quite stable to air and oligomerization.

The unknown 2,5-dicyano-3,4-dimethylthiophene (**6**) appeared to be the best synthon for the synthesis of tetracyanothienothiophene **3a**. In our initial approach, we repeated the condensation of biacetyl with thiodiglycolic acid diethyl ester in the presence of potassium *tert*-butoxide,[8] but we experienced irreproducible yields. Also, the resulting monoester **4** was difficult to purify in view of the tarry byproducts formed from biacetyl under the drastic cyclization conditions. However, it was found that



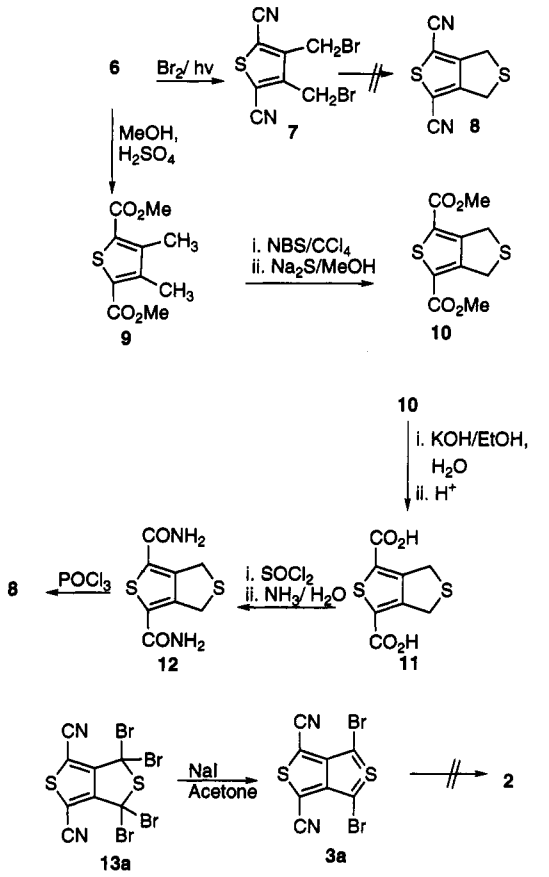
when the thiodiglycolic acid ester was replaced by the readily accessible bis(cyanomethyl) sulfide, the condensation with biacetyl in the presence of sodium methoxide furnished 5-cyano-3,4-dimethylthiophene-2-carboxamide (**5**) in excellent yield. Subsequent dehydration of the amido group of **5** cleanly led to the dinitrile **6**. The conditions used here are much milder than those employed with the diester in view of the higher acidity of the dinitrile. Consequently, little self-condensation of the biacetyl takes place.

Following the general literature approach[8] to the 1*H*,3*H*-thieno[3,4-*c*]thiophene system, the dicyano compound **6** was brominated, but the subsequent desired closure reaction of the dibromide **7** with sodium sulfide under various conditions failed. It was therefore decided first to prepare the known 4,6-dicarbomethoxy-1*H*,3*H*-thieno-[3,4-*c*]thiophene (**10**)[8] and to convert it into the corresponding dicyano compound.

Dicyanothiophene **6** was methanolized using a modified procedure by Adams[9] to furnish in high yield the corresponding dimethyl ester **9**, which was then transformed into the 1*H*,3*H*-thieno[3,4-*c*]thiophene **10**.

The diester **10** was converted to the diamide **12** by standard procedures, and dehydration of **12** with phosphorus oxychloride gave 4,6-dicyano-1*H*,3*H*-thienothiophene (**8**) in 72% yield overall.

The 1*H*,3*H*-thienothiophene **8** was tetrabrominated photochemically, leading to 4,6-dicyano-1,1,3,3-tetrabromo-1*H*,3*H*-thieno[3,4-*c*]thiophene (**13a**) which lost bromine readily upon heating in DMF to give a purple-red solution of 1,3-dibromo-4,6-dicyanothieno[3,4-*c*]thiophene (**3a**). Thienothiophene **3a** was best prepared from **13a** by dehalogenation with sodium iodide in acetone and purified by chromatography (silica, methylene chloride); it formed



dark purple crystals which were remarkably stable in air.

To our knowledge this synthesis represents the first preparation of a thienothiophene in which elimination of halogen is involved in the formation of the final aromatic system. Unfortunately, replacement of the two remaining bromine atoms of **3a** by CN groups did not succeed, although various methods such as substitution with sodium cyanide[10] in aprotic media, copper cyanide in DMF,[11] or tetrabutylammonium cyanide in methylene chloride[12] were attempted. Under all conditions tried, only unidentified dark water or methanol-soluble materials were formed.

In order to study the stability of some related thienothiophenes we then focused upon the synthesis of tetrabromothieno[3,4-*c*]thiophene **3c** and 1,3-dibromo-4,6-dicarbomethoxythieno[3,4-*c*]thiophene (**3b**). Both thienothiophenes were prepared by procedures analogous to those outlined for **3a**. Bromination of 4,6-dibromo-1*H*,3*H*-thienothiophene (**15**), obtained from thiophene **6** by a modified literature procedure,[13] and also the 4,6-dicarbomethoxy-1*H*,3*H*-thienothiophene (**10**), furnished the corresponding hexabromo and tetrabromo compounds **13c** and **13b**, respectively. Elimination of bromine using tetrabutylammonium iodide in methylene chloride or sodium iodide in acetone led to the generation of tetra-

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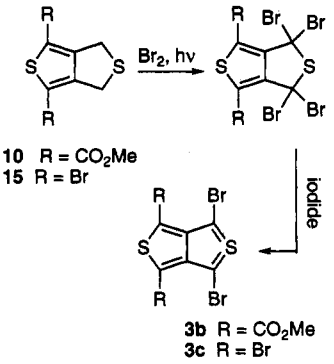
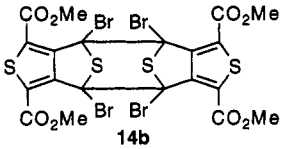
bromothienothiophene **3c** and the dibromo diester **3b**, respectively.



Although both thienothiophenes were detectable as highly colored species in solution, neither one could be isolated. The tetrabromo compound **3c** was apparently oxidized to a complex mixture, while the dibromo diester readily afforded a crystalline dimer.

A comparison of the three thienothiophenes **3a–c** clearly shows that the degree of stabilization of the bicyclic nucleus parallels the electron-withdrawing nature of the substituents. Thus, the dibromo dinitrile **3a** is very stable both in solution and in crystalline form, while the dibromo diester **3b** is stable for only a few hours in solution and the tetrabromide **3c** is stable for only a short time in solution.

Evaporation of a solution of **3b** gave a purple solid which transformed into pink crystals assigned the gross dimeric structure **14b**. The NMR spectra of this dimer were consistent with its formulation as a mixture of *syn* and *anti* isomers. Thus, the ^{1}H NMR spectrum showed two distinct methyl ester signals at 4.04 and 3.98 ppm. The ^{13}CMR showed, in addition to the two slightly different carbomethoxys (53.7, 53.2, 156.1, and 158.6), the bridge carbons as a single peak at 34.1 and the aromatic thiophene signals at 133.1, 130.5, and 138.3. Its mass spectrum showed only a molecular ion for the monomer **3b**.



14b

In the case of the tetrabromide **3c**, no crystalline dimer was isolated when solutions were evaporated. The mass spectrum of the resulting brown gum did, however, show a peak corresponding to monomer **3c**.

The UV-visible spectra of the three thienothiophenes all show an intense visible band with maxima at 552 (**3a**), 543 (**3b**) and 528 nm (**3c**). Electron-withdrawing substituents clearly produce a bathochromic effect on the absorption of the bicyclic nucleus.

The ^{13}C NMR of the dibromodicyanothienothiophene **3a** shows the ring junction carbons at 95.9 ppm, while the carbons bearing a cyano group appear at 111.5, and those bearing a bromine appear at 144.6. It is interesting to note that the two latter values are almost identical to the CCN value (111.1) and the CBr value (143.3) observed for the *dihydro*thienothiophenes 8 and 13c, respectively.

Experimental Section

All ^{1}H and ^{13}C NMR spectra are reported in ppm.

Bis(cyanomethyl) Sulfide. To a solution of sodium sulfide nonahydrate (240 g, 1 mol) and benzyltrimethylammonium chloride (10 g) in water (500 mL) and methylene chloride (500 mL) was added with cooling (0–5 °C) and stirring, chloroacetonitrile (140 mL, 2.2 mol). After 15 min the cooling bath was removed and stirring was continued for 30 min. The organic layer was separated and dried over sodium sulfate. Evaporation of the solvent and recrystallization from methanol gave 60 g (54%) of the sulfide as colorless crystals, mp 45–47 °C (lit.[14] 45–47 °C).

5-Cyano-3,4-dimethylthiophene-2-carboxamide (5). To a solution of bis(cyanomethyl) sulfide (35 g, 0.312 mol) and biacetyl (32.9 mL, 0.375 mol) in methanol (700 mL), cooled with an ice-water bath, was added rapidly with stirring a 1 M solution of sodium methoxide (312 mL, 0.312 mol). The color of the reaction mixture changed from yellow to colorless and finally to gray-brown while the product precipitated partially. After 15 min of stirring with cooling, the solvent was removed *in vacuo* and the remaining dark crystalline product was washed with water till the solid was white. Recrystallization from methanol furnished 52.8 g (94%) of **5** as colorless crystals: mp 192–193 °C; ^{1}H NMR 2.25 (s, 3H), 2.31 (s, 3H), 6.49 (broad, 2H); ^{13}C NMR ($CDCl_3$/DMSO-d_6 = 9:1) 13.6, 14.6, 106.2, 113.6, 136.6, 139.9, 149.9, 163.1; IR (KBr) 2230 cm^{-1} (CN), 3480 (m) 3150 (m) 1675 (s) 1610 (m) cm^{-1} ($CONH_2$); UV (MeCN) λ_{max} (nm) (log e) 271 (4.28) MS m/z (relative intensity) 180 (M^+, 69), 164 ($M^+ - NH_2$, 100). Anal. Calcd for $C_8H_8N_2OS$: C, 53.31; H, 4.47; N, 15.55; S, 17.79. Found: C, 53.33; H, 4.45; N, 15.54; S, 17.75.

2,5-Dicyano-3,4-dimethylthiophene (6). Thiophene **5** (52 g, 0.289 mol) was refluxed in thionyl chloride (150 mL) for 2.5 h. The excess thionyl chloride was distilled off and the residue was treated with ice-water. After filtering, washing with water, and drying, the material was dissolved in CH_2Cl_2 (400 mL) and chromatographed over silica to give after evaporation 42.8 g (91%) of compound **6** as colorless crystals: mp 122–123 °C (methanol); ^{1}H NMR 2.31; ^{13}C NMR 14.4, 111.0, 112.3, 148.3; IR (KBr) 2240 cm^{-1} (CN); UV (MeCN) λ_{max} (nm) (log e) 271 (4.25), 285 sh (4.1); MS m/z (relative intensity) 162 (M^+, 100). Anal. Calcd for $C_8H_6N_2S$: C, 59.23; H, 3.73; N, 17.27; S, 19.77. Found: C, 59.28; H, 3.74; N, 17.20; S, 19.68.

3,4-Bis(bromomethyl)-2,5-dicyanothiophene (7). 2,5-Dicyano-3,4-dimethylthiophene (**6**) (10 g, 0.62 mol) in carbon tetrachloride (380 mL) was photobrominated by dropwise addition of bromine (20.09 g, 0.126 mol) in CCl_4 (10 mL) during 3 h while refluxing and irradiating with light from a 500-W sun lamp . Irradiation and refluxing was continued for 9 h. The workup was carried out by washing the organic solution with cold water, sodium bicarbonate solution, and again with water. The organic layer was dried with sodium sulfate and the carbon tetrachloride was evaporated. The residue was washed with a small amount of ether and then recrystallized to yield 10.6 g (53%) of the dibromide **7** as colorless crystals: mp 127–129 °C (methanol); ^{1}H NMR 4.64 (s); IR (KBr) 2240 cm^{-1}; UV (MeCN) λ_{max} (nm) (log e) 279 (4.09), 227 (4.25); MS m/z (relative intensity) 318 (M^+, 5), 239 ($M^+ - Br$, 73), 160 ($M^+ - 2Br$, 100). Anal. Calcd for $C_8H_4Br_2N_2S$: C, 30.03; H, 1.26; Br, 49.94; N, 8.76; S, 10.02. Found: C, 30.13; H, 1.29; Br, 49.82; N, 8.71; S, 9.96.

2,5-Dicarbomethoxy-3,4-dimethylthiophene (9). To 2,5-dicyano-3,4-dimethylhiophene (**6**) (5 g, 0.031 mol) in refluxing methanol (220 mL) was added concd sulfuric acid (100 mL) within 5 min. After refluxing for 2.25 h, the reaction mixture was cooled to 0 °C and the colorless needles were collected, washed with water until neutral, and dried to yield 6 g (85%) of **9** as colorless needles, mp 166–168 °C (lit.[8] 170–171 °C).

4,6-Dicarboxy-1*H*,3*H*-thieno[3,4-*c*]thiophene (11)[8]. The free carboxylic acid **11** was obtained as a slightly pink solid upon hydrolysis of the corresponding dimethyl ester (2.5 g, 9.7 mmol) by refluxing for 5 h with a potassium hydroxide solution (34.8 mmol) in water/ethanol (20 mL/40 mL), followed by acidification. yield 2.2 g (98%).

4,6-Dicyano-1*H*,3*H*-thieno[3,4-*c*]thiophene (8). A mixture of the carboxylic acid **11** (2.15 g, 9.34 mmol) and thionyl chloride (16 mL) was refluxed for 1 h, and the excess thionyl chloride was then removed by distillation. The solid residue was cooled to ice temperature and treated with concd aqueous ammonia and ice and stirred for 2 h. The diamide **12** was washed with water and dried to yield 1.92 g (90%) of **12** as slightly pink micro crystals

mp > 250 °C; IR (KBr) 3450 (m), 3210 (m), 1675 (s), 1615 (m) ($CONH_2$). Without further purification, diamide **12** (1.9 g, 8.3 mmol) was dehydrated in boiling phosphorus oxychloride (38 mL) during 1 h. Excess $POCl_3$ was distilled off under reduced pressure and the remaining crystalline dicyano compound was washed with ice–water and then dried. The crude product was dissolved in methylene chloride and subjected to flash chromatography (silica). After evaporation of the solvent and crystallization of the residue from CH_2Cl_2–petroleum ether, thiophene **8** was obtained in 82% (1.31 g) yield as colorless needles: mp 180–182 °C; ^1H NMR 4.09 (s); ^{13}C NMR 31.1, 105.9, 111.1, 156.3; IR (KBr) 2230 cm^{-1} (CN); UV (MeCN) λ_{max} (nm) (log *e*) 272 (4.27), 282 sh (4.2); MS *m/z* (relative intensity) 192 (M^+, 100); Anal. Calcd for $C_8H_4N_2S_2$: C, 49.98; H, 2.10; N, 14.57; S, 33.35. Found: C, 49.92; H, 2.12; N, 14.54; S, 33.32.

4,6-Dibromo-1*H*,3*H*-thieno[3,4-*c*]thiophene (15). This compound was prepared according to the method of Wynberg[13] from 2,5-dibromo-3,4-dimethylthiophene. Instead of starting with the hydrolysis of compound **9**, the dicyanodimethylthiophene **6** was directly hydrolyzed with aqueous sodium hydroxide by refluxing for 15 h and then the literature procedure[13] was followed to give **15** as colorless needles, mp 65–66 °C (methanol) (lit.[13b] 67–68 °C).

4,6-Dicyano-1,1,3,3-tetrabromo-1*H*,3*H*-thieno[3,4-*c*]thiophene (13a). To a boiling suspension of 4,6-dicyano-1*H*,3*H*-thieno[3,4-*c*]thiophene (**8**) (50 mg, 0.26 mmol) in carbon tetrachloride (2 mL) was added a 1 M solution (1.1 mL, 1.1 mmol) of bromine in carbon tetrachloride. After exposing the reaction mixture to light from a 500-W sun lamp and refluxing for 90 min, the solvent was distilled off under reduced pressure. Chromatography (CH_2Cl_2) of the residue on silica, followed by reprecipitation with petroleum ether from methylene chloride gave compound **13a** in 45% (60 mg) yield as colorless crystals: IR (KBr) 2240 cm^{-1}; UV (MeCN) λ_{max} (nm) (log *e*) 295 (4.06), 222 (4.25). Solutions of **13a** decomposed at a moderate rate even in the cold with the generation of thienothiophene **3a** (purple color), precluding the recording of its CMR spectrum. On heating, it darkened (mp > 360 °C), generating **3a**. It was not further characterized, but used directly to prepare **3a**, as described below.

4,6-Dicarbomethoxy-1,1,3,3-tetrabromo-1*H*,3*H*-thieno[3,4-*c*]thiophene (13b). Compound **13b** was prepared by the procedure described for **13a** starting from the dimethyl ester **10**[8] (100 mg, 0.39 mmol) in carbon tetrachloride (3 mL) and bromine (1.6 mmol); reaction time 3 h, yield 160 mg (71%): light pink crystals, 158–160 °C dec; ^1H NMR 4.02; ^{13}C NMR 39.4, 53.1, 127.9, 149.9, 158.8; IR (KBr) 1740 (s) (CO), 1240 (m) (OCH_3) cm^{-1}; UV (MeCN) λ_{max} (nm) (log *e*) 290 (4.13), 233 (4.46); MS *m/z* (relative intensity) 491 (M^+ – Br, 2.5), 414 (M^+ – 2Br + 2, 100), 412 (M^+ – 2Br, 70), 334 (M^+ – 3Br + 1, 25), 254 (M^+ – 4Br + 2, 15). The compound was not sufficiently stable for an elemental analysis.

1,1,3,3,4,6-Hexabromo-1*H*,3*H*-thieno[3,4-*c*]thiophene (13c). This compound was obtained as for **13a** using dibromide **15** (1 g, 3.3 mmol) in CCl_4 (30 mL) and a 1 M solution of bromine in CCl_4 (13.5 mL, 13.5 mmol); reaction time 1 h, yield 1.5 g (73%): colorless crystals, mp > 360 °C dec (1,2-dichloroethane); ^{13}C NMR 40.3, 109.0, 143.3; UV (MeCN λ_{max} (nm) (log *e*) 269 sh (3.7), 224 (4.02); MS *m/z* (relative intensity) 531 (M^+ – Br, 1), 456 (M^+ – 2Br + 4, 100), 452 (M^+ – 2Br, 25), 375 (M^+ – 3Br + 2, 65), 373 (M^+ – 3Br, 25), 296 (M^+ – 4Br + 2, 33), 294 (M^+ – 4Br, 15), 215 (M^+ – 5Br, 8.5); Anal. Calcd for $C_6Br_6S_2$: C, 11.71; Br, 77.88; S, 10.42. Found: C, 11.82; Br, 77.63; S, 10.32.

1,3-Dibromo-4,6-dicyanothieno[3,4-*c*]thiophene (3a). The crude tetrabromo compound **13a** from **8** (50 mg) was treated with a solution of sodium iodide (150 mg, 1 mmol) in acetone (20 mL) for 5 min to eliminate bromine and to form the thieno-[3,4-*c*]thiophene **3a**. Following evaporation of the acetone, extraction of the remaining solid with CH_2Cl_2 (100 mL) and subsequent washing with saturated sodium thiosulfate solution gave an intense purple CH_2Cl_2 layer with a strong fluorescence. The organic layer was separated and dried and the solvent removed *in vacuo*. The purple residue was subjected to dry column chromatography (silica, methylene chloride) and the fast-running purple band was collected to yield compound **3a** (40 mg, 44%), after evaporation of the solvent as dark purple crystals: mp > 360 °C dec; ^{13}C NMR 95.9, 111.5, 144.6, 152.1; IR (KBr) 2200 cm^{-1}; UV-vis (CH_2Cl_2) λ_{max} (nm) (log *e*) 552 (3.96), 308 (4.07), 260 (sh) (3.96); MS *m/z* (relative intensity) 348 (M^+ + 2, 100), 346 (M^+, 53), 267 (M^+ – Br, 30), 188 (M^+ – 2Br, 35); HRMS calcd for $C_8Br_2N_2S_2$ *m/z* 345.7869, found 345.7848. Elemental analysis gave only fair values: Anal. Calcd for $C_8Br_2N_2S_2$: C, 27.61; N, 8.05; S, 18.42. Found: C, 28.57; N, 7.80; S, 18.01.

Generation of 1,3-Dibromo-4,6-dicarbomethoxythieno[3,4-*c*]thiophene (3b) and Isolation of Dimer 14b. The crude tetrabromo compound **13b** from **10** (100 mg) was mixed with sodium iodide (250 mg, 1.66 mmol) in acetone (20 mL) and stirred for 5 min to eliminate bromine, producing thienothiophene **3b**. Following evaporation of the acetone, extraction of the remaining solid with CH_2Cl_2 (100 mL) and subsequent washing with saturated sodium thiosulfate solution afforded an intense purple CH_2Cl_2 layer with a strong fluorescence. The organic layer was separated and dried, and the solvent was removed *in vacuo*. The purple residue was quickly redissolved and subjected to dry column chromatography (silica, methylene chloride) and the front-running purple band collected to yield a solution of compound **3b**: UV-vis (methylene chloride) λ_{max} (nm) 543, 296. Removal of the solvent gave dimer **14b**, which was reprecipitated from 1,2-dichloroethane with petroleum ether to give slightly pink crystals, mp 135–137 °C; ^1H NMR 4.04 (s), 3.98 (s). The mass spectrum of **14b** was that of monomer **3b**: MS *m/z* (relative intensity) 414 (M^+, 100), 412 (61) 334 (46); HRMS calcd for $C_{10}H_6Br_2O_4S_2$ *m/z* 411.8074; Found: 411.8057. Elemental analysis gave only fair values: Anal. Calcd for $C_{20}H_{12}Br_4O_8S_4$: C, 28.84; H, 1.45; S, 15.30; Br, 37.50. Found: C, 28.00; H, 1.50; S, 14.74; Br, 37.31. Solutions of **14b** became bright purple on warming, indicating its ease of dissociation to **3b**.

Generation of 1,3,4,6-Tetrabromothieno[3,4-*c*]thiophene (3c). Compound **3c** was generated by treatment of the hexabromide **13c** (50 mg, 0.08 mmol) in methylene chloride (2 mL) with tetrabutylammonium iodide (75 mg, 0.2 mmol) in methylene chloride (2 mL). Immediately the color of the mixture turned to purple indicating the formation of thienothiophene **3c**. Removal of the iodine present was carried out by extraction with sodium thiosulfate solution. UV-vis (methylene chloride) λ_{max} (nm) 528, 286. The purple color of the solution soon vanished, and evaporation gave a brownish gum. This gum presumably contains a dimer of **3c**, which cracks to **3c** in the mass spectrometer: MS *m/z* (relative intensity) 456 (M^+, 100), 452 (25), 375 (65), 373 (25), 296 (33), 294 (15), 215 (8.5).

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