SYNTHESIS AND CYCLOADDITION REACTION OF 3-VINYLTHIENO[3,2-*b*][1]BENZOTHIOPHENE

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A new method of synthesis of 3-substituted thieno[3,2-*b*][1]benzothiophenes based on a halogen dance process was developed. The cycloaddition reaction of the title compound with dimethyl acetylenedicarboxylate leads to the formation of a complex mixture of products resulting from a series of consecutive reactions of the primary adduct.

Keywords: Fused heterocycles; 3-Vinylthieno[3,2-*b*]benzothiophene; [4+2] Cycloadditions; Diels–Alder reaction; Pericyclic reactions; Rearrangements; Ene reaction; Liquid crystals.

Liquid crystals have become most important molecular electronic materials of the current era. They found a broad application especially in various types of flat-panel displays known as the LCD's. Therefore much effort has been devoted to designing novel materials and establishing the structure–mesomorphic properties relationships. In this context, the role of various core units have been studied in the molecules of liquid crystals, many of which were derived from five- and six-membered heterocyclic systems[1–4]. Due to our interest in synthesis[5–10] and material application[11–15] of fused heterocyclic compounds, we documented the general utility of fused thiophene, thienothiophene, and thienofuran heterocycles[16–20] in the design of calamitic liquid crystals which exhibited formation of nematic and polar smectic phases. The Diels–Alder reaction[21,22] was utilized to synthesize various benzo-fused heterocycles. In the due course, cycloaddition reactions of various 2-vinylthiophenes with dimethyl acetylenedicarboxylate (DMAD) were found to be unexpectedly accompanied by an unprecedented ring expansion of thiophene to thiopyrane leading to new thialene-based heterocycles[23]. A nonconcerted reaction mechanism was suggested which involves participitation of the heterocyclic sulfur atom through a resonance-stabilized intermediate thiiranium ion in the course of the cycloaddition.

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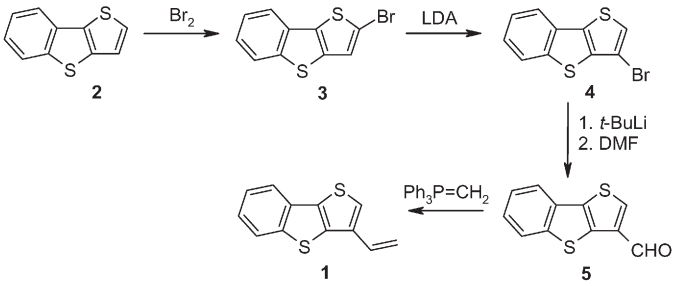
In order to further investigate this hypothesis, we shifted the vinyl moiety from position 2 of the thiophene ring to position 3 which should lead to exclusion of the sulfur atom in the transition state of the cycloaddition. In this short communication, we report results of synthesis and cycloaddition reaction of the isomeric 3-vinylthieno[3,2-*b*][1]benzothiophene (**1**) with DMAD.

Various 2-substituted thieno[3,2-*b*][1]benzothiophenes[24] are known; most of them are available either by electrophilic substitution and metallation reactions of the parent heterocycle or by condensation reactions[12]. However, only two examples of 3-substituted thieno[3,2-*b*][1]benzothiophenes were reported[25,26] and we first sought to elaborate a convenient route to the starting 3-vinyl derivative **1**.

RESULTS AND DISCUSSION

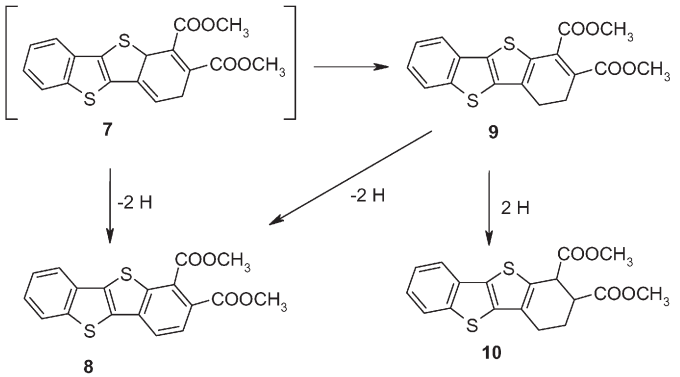
The synthesis of **1** started from the parent heterocycle **2** which was brominated[24] with bromine to afford 2-bromothieno[3,2-*b*][1]benzothiophene (**3**) in 88% yield. It has been demonstrated that various simple 2-halo-substituted thiophenes can be isomerized to the corresponding 3-halothiophenes in a halogen dance process[27,28]. For the first time, we applied this halogen dance procedure to the fused thienothiophene system and indeed the 2-bromo derivative **3** could smoothly be isomerized in the presence of LDA at –78 °C to the 3-bromo derivative **4** in almost quantitative yield. Next we intended to perform a coupling reaction of vinyl bromide with **4**. However, neither vinyl cuprate[29] nor the Kumada coupling[30] yielded the desired product. The Negishi coupling of the organozinc species, obtained by lithiation of **4** with *tert*-butyllithium and transmetallation with zinc chloride, with vinyl bromide in the presence of $[Pd(PPh_3)_4]$ afforded the vinyl derivative **1** in a low yield of 9%. In our preceding study[23], the 2-vinylthiophenes were obtained by Wittig methylidenation of thiophene-2-carbaldehydes in satisfactory yields. Therefore we tried to transform bromide **4** to the corresponding thieno[3,2-*b*][1]benzothiophene-3-carbaldehyde (**5**). Thus, lithiation of **4** with butyllithium at –78 °C and subsequent reaction with DMF afforded a mixture of the required aldehyde **5** (yield 37%) and the isomeric thieno[3,2-*b*][1]benzothiophene-2-carbaldehyde[24] (**6**, 43%). It is evident that the lithiation proceeded very slowly under these conditions and was accompanied by a series of parallel equilibrium deprotonation-protonation steps analogous to those in the halogen dance, ultimately forming the more stable 2-lithio derivative salt. When butyllithium was replaced with *tert*-butyllithium and the reaction

temperature was decreased to –120 °C, lithiation proceeded selectively and the desired aldehyde **5** was isolated in 85% yield. Aldehyde **6**, which was formed in trace amount (approx. 0.5%), was easily removed by crystallization. Finally, the Wittig reaction of **5** with methylidenetriphenylphosphorane afforded the key 3-vinyl derivative **1** in 93% yield (Scheme 1).



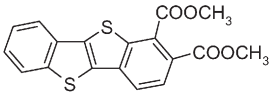
SCHEME 1

The cycloaddition reaction of **1** with DMAD was performed by heating both components in toluene at 110 °C for an extended time in accord with the previous study[23]. A complex mixture of products formed was separated by multiple column chromatography. Structures of individual compounds were unambiguously assigned by ^{1}H NMR, APT, ^{1}H-^{1}H COSY, HMBC, HMQC, and NOE experiments. From the structures of products it can be deduced, that contrary to the cycloaddition of 2-vinylthiophenes[23], the reaction followed a standard course of a [4+2] cycloaddition. The primary adduct **7** of a 1:1 reaction was not detected, but isolation of products **8**–**10** indirectly confirmed its formation. Adduct **7** evidently followed several further transformations (Scheme 2). Rearrangement of **7** by a double bond

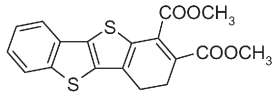


SCHEME 2

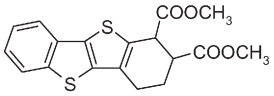
shift formed **9** and spontaneous aromatization of which led to **8** accompanied by a partial hydrogen transfer yielding tetrahydro derivative **10** and 3-ethylthieno[3,2-*b*][1]benzothiophene (**17**) in trace amounts. In addition, products of the successive transformations of **8**–**10**, i.e. **11**–**15** and **16**, were also obtained. The absence of any product containing the thiopyran ring suggests that the shift of the vinyl group from position 2 to 3 in **1** excludes the thiophene sulfur participation in the cycloaddition of **1**.



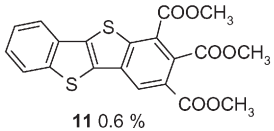
8 28 %



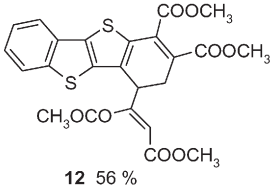
9 12 %



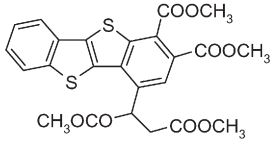
10 0.8 %



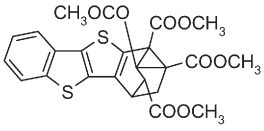
11 0.6 %



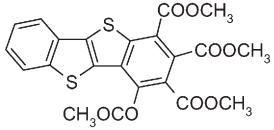
12 56 %



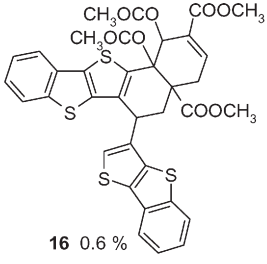
13 0.9 %



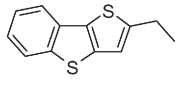
14 0.7 %



15 0.9 %

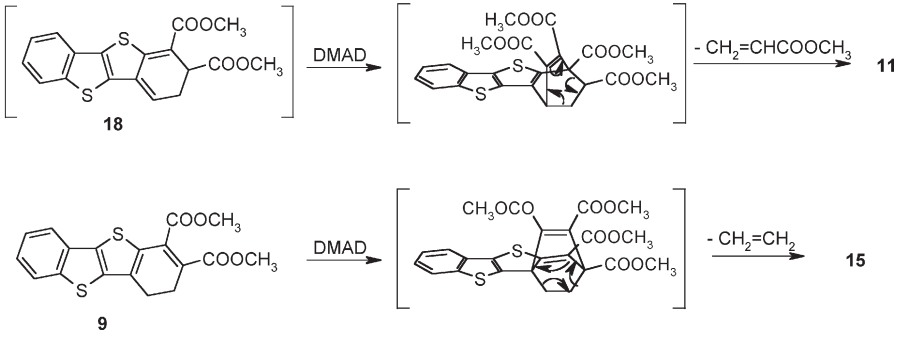


16 0.6 %



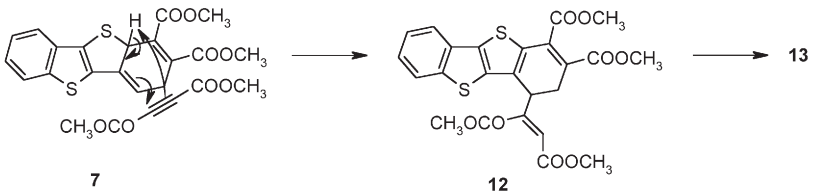
17 0.7 %

The second possible double bond shift in **7** may be represented by the intermediate **18** (Scheme 3). Although **18** also was not isolated in the product mixture, it plays a key role in the formation of triester **11**. The same holds true for ester **9**, the intermediate in the formation of tetraester **15**. Both **18** and **9** possess a new diene system and undergo a consecutive cycloaddition with DMAD. The bridged intermediates are subsequently subjected to a *retro*-Diels–Alder transformation. Release of methyl acrylate[22] and ethene[31] leads to formation of **11** and **15**, respectively.



SCHEME 3

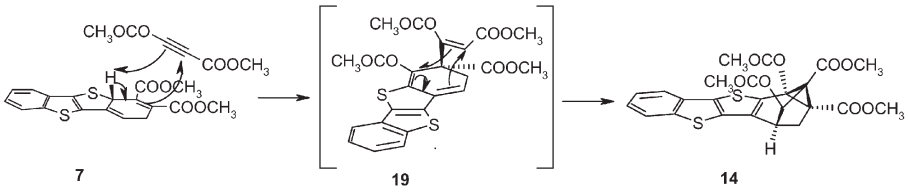
The major product of the studied cycloaddition reaction is the tetraester **12** isolated in 56% yield. It was presumably formed by an ene reaction of the primary adduct **7** and another molecule of DMAD (Scheme 4). Formation of structurally related tetraester was previously observed in the cycloaddition reaction of 2-vinylthiophenes[23,32]. Tetraester **12** partly rearranged during chromatographic separation of the product mixture to the more stable, fully aromatized tetraester **13** (0.9% yield).



SCHEME 4

Another minor product **14** (0.7% yield) possesses a bridged structure of a tricyclo[2.2.2.0^{2,6}]octane (Scheme 5). Formation of **14** may be explained by a series of pericyclic reactions starting with adduct **7**, which entered another and less populated ene reaction with DMAD. The intermediate **19**

subsequently underwent an additional intramolecular [4+2] cycloaddition resulting in the formation of **14**. Only one example of such a ring system, formed by cycloaddition of DMAD and an azulene derivative, has been described in the literature[33].



SCHEME 5

The last isolated product was tetraester **16** which resulted from a 2:2 reaction of the starting components. Fortunately, its structure could be confirmed by the single-crystal X-ray structure analysis (Fig. 1). Its formation can be again explained by a series of consecutive pericyclic reactions. In the first step the major product **12** reacts with **1** in a [4+2] cycloaddition proceeding with *endo* selectivity (Scheme 6). The formed bridged system of **20** releases its ring strain by a [3,3] sigmatropic rearrangement, which can be evidenced by the fact that the ester grouping ($COOCH_3$) is located above the cyclohexane ring (*endo*). Formation of a single stereoisomer is a conse-

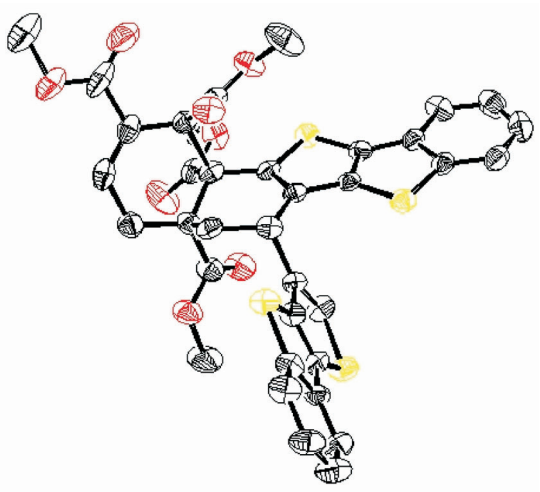
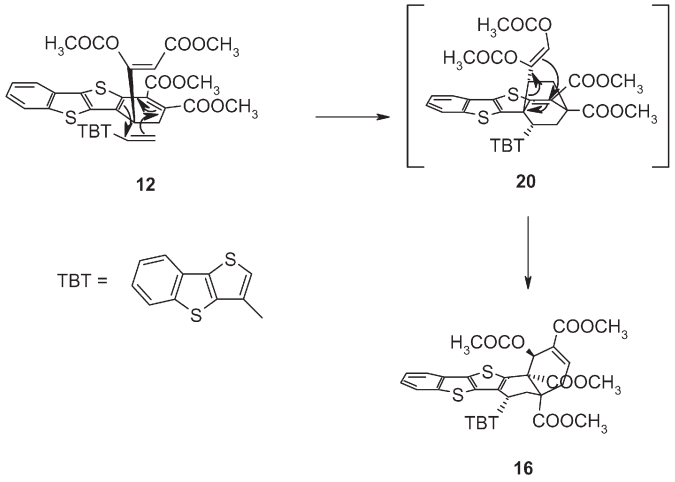


FIG. 1
Stereoscopic view of the X-ray crystal structure of **16** (thermal ellipsoids are shown with 50% probability)

quence of the pericyclic reaction stereospecificity and *Z* configuration of the maleate fragment in **12**.



SCHEME 6

In conclusion, a new synthetic route leading to various 3-substituted thieno[3,2-*b*][1]benzothiophene derivatives was explored. Cycloaddition of 3-vinyl derivative **1** shows a complex course and proceeds without participation of sulfur in the transition state. The primary products undergo a series of consecutive transformations and various products of 1:1, 1:2 and 2:2 reactions were isolated and identified. Unlike the earlier studied cycloaddition of the corresponding 2-vinylthiophenes[23], the primary cycloadduct preferentially enters the ene reaction with DMAD to form the tetraester **12**.

EXPERIMENTAL

Melting points were determined on a Leica VM TG block and are uncorrected. Elemental analyses were carried out on a Perkin–Elmer 2400 instrument. IR spectra (ν, cm^{-1}) were recorded on a Nicolet 740 FTIR spectrometer in chloroform. NMR spectra (δ, ppm; *J*, Hz) were measured on a Varian Gemini 300 HC (300 MHz for ^{1}H and 75 MHz for ^{13}C) and Bruker DRX 500 (500 MHz for ^{1}H and 125 MHz for ^{13}C). Deuteriochloroform was used as solvent and the signals of the solvent served as internal standards. The 2D experiments, COSY, HMBC, HMQC, were carried out using pulse sequence and program provided by the manufacturer.

X-ray data for **16**: $C_{36}H_{28}O_8S_4$, M = 716.88, monoclinic system, space group $C2/c$, a = 28.46(2) Å, b = 24.08(2) Å, c = 12.011(6) Å, β = 104.00(5)°, Z = 8, V = 7986(8) Å^3, D_c = 1.192 g cm^{-3}, μ(CuKα) = 2.561 mm^{-1}, crystal dimensions 0.04 × 0.12 × 0.20 mm. Data were col-

lected at room temperature on an Xcalibur PX diffractometer with graphite-monochromatized CuKα radiation. The structure was solved by direct methods[34] and anisotropically refined by full-matrix least-squares on F [35] to final R = 0.0598 and R_w = 0.0642 using 2269 independent reflections (θ_{max} = 76.442°). Hydrogen atoms were placed into calculated positions and not refined. Very large solvent-accessible voids can be found in the crystal structure. Crystals were obtained from a mixture of toluene and *tert*-butyl methyl ether. Unfortunately, the solvent was highly disordered and therefore, cannot be identified precisely. During the refinement the program Platon Squeeze[36] was used to reduce the residual density found in these voids. The crystal was very small and diffracted weakly; therefore, the R_{int} is 0.156. CCDC 629393 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge, CB2 1EZ, UK; fax: +44 1223 336033; or deposit@ccdc.cam.ac.uk).

2-Bromothieno[3,2-*b*][1]benzothiophene (**3**)

A solution of bromine (1.47 g, 9.2 mmol) in dichloromethane (5 ml) was added dropwise to a vigorously stirred solution of thieno[3,2-*b*][1]benzothiophene[12] (1.75 g, 9.2 mmol) in dichloromethane (20 ml) at –30 °C. The mixture was stirred at 0 °C for 4 h and stirrring was continued at room temperature overnight. Water (20 ml) was added and the mixture was extracted with toluene (2 × 10 ml). The combined organic layers were washed with aqueous solution of sodium hydrogencarbonate (20 ml), brine (2 × 20 ml), and dried with anhydrous magnesium sulfate. After evaporation of the solvent, the residue (2.4 g) was chromatographed on silica gel (hexane). Yield 2.18 g (88%) of white crystals, m.p. 98.6–100.2 °C, m.p.[24] 98 °C. For $C_{10}H_5BrS_2$ (269.2) calculated: 44.62% C, 1.87% H, 29.68% Br; found: 44.58% C, 1.85% H, 29.70% Br. ^{1}H NMR: 7.32 s, 1 H (H-3); 7.38 m, 2 H (H-5 and H-8); 7.77 d, 1 H, J = 7.6; 7.84 d, 1 H, J = 7.3. ^{13}C NMR: 114.15; 120.76 (CH); 123.03 (CH); 123.75 (CH); 124.61 (CH); 124.85 (CH); 132.18; 134.85; 136.65; 141.43. IR: 3024, 2924, 2853, 1941, 1741, 1603, 1472, 1439, 1412, 1016, 979, 932.

3-Bromothieno[3,2-*b*][1]benzothiophene (**4**)

Butyllithium (6.0 ml of a 2 M solution in hexane, 12 mmol) was added to a mixture of diisopropylamine (1.20 g, 12 mmol, 1.7 ml) in THF (10 ml) at –78 °C in argon atmosphere. The mixture was allowed to reach room temperature and then cooled back to –78 °C. A solution of **3** (2.46 g, 9.1 mmol) in THF (20 ml) was added and then stirred at –78 °C for 20 h. The reaction was quenched with water (20 ml) and the mixture was extracted with ethyl acetate (2 × 20 ml), washed with brine (20 ml), and dried with anhydrous magnesium sulfate. The residue after evaporation was purified by column chromatography (silica gel, hexane). 2.21 g (90%) of **4** was obtained as white crystals, m.p. 108.6–108.9 °C. For $C_{10}H_5BrS_2$ (269.2) calculated: 44.62% C, 1.87% H, 29.68% Br; found: 44.52% C, 1.92% H, 29.55% Br. ^{1}H NMR: 7.39 s, 1 H (H-2); 7.41 m, 2 H (H-5 and H-8); 7.83 d, 1 H, J = 7.3; 7.88 d, 1 H, J = 7.9. ^{13}C NMR: 103.47; 121.00 (CH); 124.10 (CH); 124.33 (CH); 124.92 (CH); 125.02 (CH); 133.08; 134.23; 139.39; 142.26. IR: 3115, 3063, 2923, 2853, 1940, 1740, 1603, 1508, 1467, 1438, 1411, 1353, 1323, 1067, 1018, 987, 935.

Thieno[3,2-*b*][1]benzothiophene-3-carbaldehyde (**5**)

Method A. To a solution of **4** (0.1 g, 0.37 mmol) in THF (40 ml) at –78 °C in argon atmosphere, butyllithium (0.19 ml of a 2 M solution in hexane, 0.38 mmol) was slowly added and then stirred at –78 °C for 0.8 h. To the reaction mixture, DMF (0.11 g, 1.48 mmol, 0.12 ml) was added, and stirring was continued at –78 °C for 3 h, and finally the mixture was allowed to warm to room temperature. After decomposition with water (4 ml) and 3 M hydrochloric acid (5 ml), the product was extracted with ethyl acetate (3 × 10 ml). The combined organic layers were washed with brine (20 ml), dried with anhydrous magnesium sulfate and evaporated. Column chromatography separation (silica gel, toluene) afforded the carbaldehydes **5** (0.03 g, 37%) and **6** (0.035 g, 43%).

Method B. To a solution of **4** (2.46 g, 9.1 mmol) in THF (120 ml) at –120 °C in argon atmosphere, *tert*-butyllithium (10.8 ml of a 1.7 M solution in hexane, 18.3 mmol) was slowly added and then stirred at –120 °C for 0.5 h. To the formed lithium salt, DMF was added (2.67 g, 36.6 mmol, 2.83 ml) and the resulting mixture was allowed to warm to room temperature. The mixture was decomposed with a saturated solution of NH_4Cl (10 ml), and the aqueous layer was extracted with diethyl ether (2 × 20 ml). The combined organic layers were washed with brine (20 ml), dried with anhydrous magnesium sulfate and evaporated. The crude product was crystallized from toluene to afford 1.7 g (85%) of **5**, yellowish crystals, m.p. 151.7–152.5 °C (toluene). For $C_{11}H_6OS_2$ (218.3) calculated: 60.52% C, 2.77% H; found: 60.25% C, 2.71% H. ^{1}H NMR: 7.78 m, 2 H (H-5 and H-8); 7.92 m, 2 H (H-6 and H-7); 8.30 s, 1 H (H-2); 10.05 s, 1 H (CHO). ^{13}C NMR: 120.85 (CH); 124.23 (CH); 124.87 (CH); 125.17 (CH); 131.02; 134.79; 135.33; 135.55; 139.34 (CH); 143.27; 183.55 (C=O). IR: 3096, 2870, 2821, 2715, 1678 (C=O), 1495, 1472, 1444, 1431, 1383, 1368, 1326, 1301, 1257, 1155, 1109, 1062, 1018, 975, 851.

Thieno[3,2-b][1]benzothiophene-2-carbaldehyde (**6**). By column chromatography of the mother liquor (silica gel, toluene), yield 10 mg (0.5%). Yellowish crystals, m.p. 99.5–100.6 °C, m.p.[24] 101 °C. For $C_{11}H_6OS_2$ (218.3) calculated: 60.52% C, 2.77% H; found: 60.41% C, 2.80% H. ^{1}H NMR: 7.40 m, 2 H; 7.79 m, 1 H; 7.86 m, 1 H; 7.89 s, 1 H (H-3); 9.92 s, 1 H (CHO). ^{13}C NMR: 122.43 (CH); 124.04 (CH); 125.25 (C-H); 126.76 (C-H); 129.47 (C-H); 131.74; 137.83; 142.16; 144.54; 145.40; 183.06 (C=O). IR: 3021, 2820, 1667 (C=O), 1502, 1443, 1407, 1312, 1299, 1258, 1140, 1126, 1068, 1022, 841.

3-Vinylthieno[3,2-*b*][1]benzothiophene (**1**)

A solution of butyllithium (8.8 ml, 17.6 mmol) in hexanes was added dropwise to a mixture of methyltriphenylphosphonium bromide (6.28 g, 17.6 mmol) in THF (300 ml) at –30 °C. The resulting pale yellow mixture was then stirred without cooling for 35 min. Then it was cooled to –35 °C and a solution of **5** (1.28 g, 5.9 mmol) in THF (10 ml) was added. The cooling bath was removed and the mixture was stirred for 3 h. The work-up was accomplished by addition of water (20 ml) and extraction of the aqueous layer with diethyl ether (2 × 20 ml). The combined organic layers were washed with brine (20 ml), and dried with anhydrous magnesium sulfate. After removal of the solvent, the residue was subjected to column chromatography (silica gel, hexane), which afforded 1.18 g (93%) of **1** as a colorless oil. For $C_{12}H_8S_2$ (216.3) calculated: 66.63% C, 3.73% H; found: 66.48% C, 3.52% H. ^{1}H NMR: 5.47 d, 1 H, J(1′,2′a) = 11.4 (H-2′a); 5.74 d, 1 H, J(1′,2′b) = 17.6 (H-2′b); 6.87 dd, 1 H, J(1′,2′b) = 17.6, J(1′,2′a) = 11.4 (H-1′); 7.37 s, 1 H (H-2); 7.41 m, 1 H; 7.44 m, 1 H; 7.89 m, 2 H, J = 7.9. ^{13}C NMR: 115.33 (CH_2); 120.63 (CH); 123.70 (CH); 124.41 (CH); 124.64 (CH); 125.64 (CH); 129.66

(CH); 131.99; 133.28; 134.70; 134.96; 142.10. IR: 3100, 1942, 1903, 1870, 1730, 1680, 1628, 1527, 1472, 1445, 1416, 1378, 1325, 1114, 1052, 1016, 983, 906.

Reaction of **1** with Dimethyl Acetylenedicarboxylate

A solution of **1** (1.60 g, 7.40 mmol), DMAD (1.83 g, 12.9 mmol, 1.60 ml) in toluene (30 ml) was refluxed for 90 h in argon atmosphere. The solvent was evaporated and the residue chromatographed on a silica gel column; elution started with 1,2-dichloroethane and continued with a mixture 1,2-dichloroethane–methanol 95:5 v/v. The collected fractions containing a mixture of products were rechromatographed (elution with toluene–*tert*-butyl methyl ether and hexane–ethyl acetate). Products were eluted in the following order:

3-Ethylthieno[3,2-b][1]benzothiophene (**17**). Yield 10 mg (0.7%), oil. ^{1}H NMR: 1.38 t, 3 H, *J*(1′,2′) = 7.3 (CH_3); 2.80 q, 2 H, *J*(1′,2′) = 7.3 (CH_2); 7.11 s, 1 H (H-2); 7.35 m, 2 H (H-6 and H-7); 7.84 m, 2 H (H-5 and H-8).

Dimethyl [1]benzothieno[3,2-b][1]benzothiophene-1,2-dicarboxylate (**8**). Yield 730 mg (28.0%), m.p. 214–215 °C. For $C_{18}H_{12}O_4S_2$ (356.4) calculated: 60.66% C, 3.39% H; found: 60.58% C, 3.43% H. ^{1}H NMR: 3.97 s, 3 H (OCH_3); 4.06 s, 3 H (OCH_3); 7.48 m, 2 H (H-7 and H-8); 7.80 d, 1 H, *J*(3,4) = 8.0; 7.93 m, 2 H (H-6 and H-9); 8.02 d, 1 H, *J*(3,4) = 8.0. ^{13}C NMR: 52.82 (OCH_3); 53.01 (OCH_3); 122.04 (CH); 123.72 (CH); 124.03 (CH); 125.14 (CH); 125.24 (CH); 125.88 (CH); 126.73; 129.07; 132.46; 132.59; 135.68; 137.75; 142.27; 142.75; 166.69 (C=O); 168.18 (C=O). IR: 3067, 2917, 2845, 1723 (C=O), 1584, 1526, 1455, 1435, 1330, 1292, 1198, 1159, 1138, 1104, 1074, 1054, 951, 930, 909.

Dimethyl 3,4-dihydro[1]benzothieno[3,2-b][1]benzothiophene-1,2-dicarboxylate (**9**). Yield 315 mg (12.0%), m.p. 158.3–159.5 °C. For $C_{18}H_{14}O_4S_2$ (358.4) calculated: 60.32% C, 3.94% H; found: 60.25% C, 3.85% H. ^{1}H NMR: 2.87 m, 2 H; 2.98 m, 2 H; 3.83 s, 3 H (OCH_3); 3.95 s, 3 H (OCH_3); 7.40 m, 2 H; 7.82 m, 2 H. ^{13}C NMR: 22.43 (CH_2); 24.05 (CH_2); 52.40 (OCH_3); 52.80 (OCH_3); 121.25 (CH); 124.02 (CH); 125.01 (CH); 125.19 (CH); 126.17; 131.49; 132.41; 132.52; 133.62; 136.51; 137.35; 142.25; 167.02 (2 × C=O). IR: 2954, 2847, 1728 (C=O), 1708 (C=O), 1594, 1525, 1506, 1477, 1436, 1352, 1279, 1115, 1068, 1019, 993, 930, 851.

Tetramethyl 6-(thieno[3,2-b][1]benzothiophen-3-yl)-1,4,4a,5,6,12b-hexahydronaphtho[2′,1′:4,5]thieno-[3,2-b][1]benzothiophene-1,2,4a,12b-tetracarboxylate (**16**). Yield 60 mg (0.6%), m.p. 299–300 °C. For $C_{36}H_{28}O_8S_4$ (716.9) calculated: 60.32% C, 3.94% H; found: 60.11% C, 3.62% H. ^{1}H NMR: 2.54 d, 1 H, *J*(5a,6) = 15.0 (H-5a); 2.71 dd, 1 H, *J*(4a,4b) = 20.5, *J*(3,4a) = 4.5 (H-4a); 3.08 s, 3 H (OCH_3); 3.09 s, 3 H (OCH_3); 3.38 d, 1 H, *J*(4a,4b) = 20.5 (H-4b); 3.59 dd, 1 H, *J*(5a,6) = 15.0, *J*(5b,6) = 8.0 (H-6); 3.76 s, 3 H (OCH_3); 3.90 s, 3 H (OCH_3); 4.26 bs, 1 H (H-1); 4.35 d, 1 H, *J*(5b,6) = 8.0 (H-5b); 7.29 m, 1 H (H-3); 7.31 m, 1 H; 7.41 m, 2 H; 7.43 m, 2 H; 7.71 d, 1 H, *J* = 8.0; 7.83 d, 1 H, *J* = 8.0; 7.94 m, 2 H. ^{13}C NMR: 34.63 (C-6); 34.77 (C-5); 36.69 (C-4); 45.68 (C-4a); 51.89 (OCH_3); 52.04 (C-1); 52.12 (OCH_3); 52.57 (OCH_3); 52.94 (OCH_3); 120.78 (2 × CH); 120.98 (CH); 123.73 (CH); 124.06 (CH); 124.34 (CH); 124.44 (CH); 124.56 (CH); 124.75 (CH); 128.20; 132.76; 132.96; 134.25; 134.58; 135.08; 136.64; 137.28; 140.00 (C-3); 140.20; 142.15; 142.33; 165.85 (C=O); 171.20 (C=O); 172.54 (C=O); 174.02 (C=O). IR: 2954, 2922, 2850, 1732 (C=O), 1446, 1436, 1300, 1265, 1238, 1098, 1019.

Dimethyl 1,2,3,4-tetrahydro[1]benzothieno[3,2-b][1]benzothiophene-1,2-dicarboxylate (**10**). Yield 20 mg (0.8%), m.p. 178.4–179.3 °C. For $C_{18}H_{16}O_4S_2$ (360.5) calculated: 59.98% C, 4.47% H; found: 59.80% C, 4.35% H. ^{1}H NMR: 2.49 m, 2 H (H-3a and H-3b); 2.75 m, 1 H (H-4a); 2.90 m, 1 H (H-4b); 3.05 m, 1 H (H-2); 3.76 s, 6 H (2 × OCH_3); 4.41 d, 1 H, *J*(1,2) = 4.8 (H-1); 7.33 m, 1 H; 7.40 m, 1 H; 7.79 d, 1 H, *J* = 7.9; 7.84 d, 1 H, *J* = 8.0. ^{13}C NMR:

21.25 (C-3); 24.08 (C-4); 42.54 (C-2); 43.25 (C-1); 52.17 (OCH_3); 52.14 (OCH_3); 120.78 (CH); 123.97 (CH); 124.23 (CH); 124.71 (CH); 130.15; 132.71; 132.96; 133.10; 136.89; 141.60; 171.41 (C=O); 172.95 (C=O). IR: 2955, 2929, 2847, 1739 (C=O), 1594, 1476, 1447, 1437, 1355, 1297, 1276, 1258, 1161, 1067, 1054, 1017, 908.

Trimethyl [1]benzothieno[3,2-b][1]benzothiophene-1,2,3-tricarboxylate (**11**). Yield 20 mg (0.6%), m.p. 202–204 °C. For $C_{20}H_{14}O_6S_2$ (414.5) calculated: 57.96% C, 3.40% H; found: 57.81% C, 3.35% H. ^{1}H NMR: 4.02 s, 3 H (OCH_3); 4.06 s, 3 H (OCH_3); 4.09 s, 3 H (OCH_3); 7.50 m, 2 H (H-7 and H-8); 7.96 m, 2 H (H-6 and H-9); 8.72 s, 1 H (H-4). ^{13}C NMR: 52.85 (OCH_3); 52.97 (OCH_3); 53.21 (OCH_3); 121.09 (CH); 123.29; 124.09 (CH); 125.27 (CH); 126.06 (CH); 127.13 (CH); 138.71; 142.84; 143.07; 147.35; 164.92 (C=O); 168.63 (C=O); 171.42 (C=O). IR: 2955, 2849, 1734 (C=O), 1580, 1536, 1490, 1451, 1438, 1385, 1362, 1278, 1250, 1156, 1108, 1076, 1014, 977, 953.

Dimethyl 4-[1,2-bis(methoxycarbonyl)ethyl][1]benzothieno[3,2-b][1]benzothiophene-1,2-dicarboxylate (**13**). Yield 35 mg (0.9%), m.p. 158.6–159.7 °C. For $C_{24}H_{20}O_8S_2$ (500.6) calculated: 57.59% C, 4.03% H; found: 57.44% C, 3.90% H. ^{1}H NMR: 2.86 dd, 1 H, J(2′a,2′b) = 17.3, J(1′,2′a) = 4.7 (H-2′a); 3.38 dd, 1 H, J(2′a,2′b) = 17.3, J(1′,2′b) = 10.0 (H-2′b); 3.72 s, 3 H (OCH_3); 3.73 s, 3 H (OCH_3); 3.96 s, 3 H (OCH_3); 4.05 s, 3 H (OCH_3); 5.00 dd, 1 H, J(1′,2′b) = 10.0, J(1′,2′a) = 4.7 (H-1′); 7.50 m, 2 H (H-7 and H-8); 7.64 s, 1 H (H-3); 7.96 m, 2 H (H-6 and H-9). ^{13}C NMR: 37.24 (CH_2); 42.23 (CH); 52.18 (OCH_3); 52.88 (OCH_3); 52.92 (OCH_3); 53.11 (OCH_3); 122.02 (CH); 123.75 (2 × CH); 125.35 (CH); 126.21 (CH); 129.26; 130.70; 131.97; 134.70; 138.37; 141.51; 143.07; 143.21; 166.58 (C=O); 167.68 (C=O); 171.43 (C=O); 172.08 (C=O). IR: 2956, 2850, 1734 (C=O), 1579, 1557, 1454, 1437, 1328, 1280, 1161, 1076, 1017, 987, 950, 895.

Tetramethyl [1]benzothieno[3,2-b][1]benzothiophene-1,2,3,4-tetracarboxylate (**15**). Yield 40 mg (0.6%), m.p. 194.1–195.8 °C. For $C_{22}H_{16}O_8S_2$ (472.5) calculated: 55.93% C, 3.41% H; found: 55.70% C, 3.35% H. ^{1}H NMR: 3.94 s, 3 H (OCH_3); 3.97 s, 3 H (OCH_3); 4.07 s, 3 H (OCH_3); 4.13 s, 3 H (OCH_3); 7.48 m, 2 H (H-7 and H-8); 7.91 m, 1 H; 7.96 m, 1 H. ^{13}C NMR: 53.17 (OCH_3); 53.31 (OCH_3); 53.43 (2 × OCH_3); 122.10 (CH); 123.61 (CH); 125.19 (CH); 126.62 (CH); 127.30; 129.49; 131.08; 131.20; 131.73; 132.40; 140.17; 143.68; 143.70; 146.33; 164.90 (C=O); 166.06 (C=O); 166.80 (C=O); 167.49 (C=O). IR: 2956, 2926, 2852, 1735 (C=O), 1566, 1522, 1485, 1443, 1408, 1387, 1355, 1308, 1259, 1184, 1134, 1094, 1017, 1001, 965, 889.

Dimethyl 4-[1,2-bis(methoxycarbonyl)vinyl]-3,4-dihydro[1]benzothieno[3,2-b][1]benzothiophene-1,2-dicarboxylate (**12**). Yield 2.07 g (56%), m.p. 143.9–145.8 °C. For $C_{24}H_{20}O_8S_2$ (500.55) calculated: 57.59% C, 4.03% H; found: 57.44% C, 3.93% H. ^{1}H NMR: 3.06 dd, 1 H, J(3a,3b) = 17.9, J(3a,4) = 8.5 (H-3a); 3.16 dd, 1 H, J(3a,3b) = 17.9, J(3b,4) = 5.3 (H-3b); 3.67 s, 3 H (OCH_3); 3.83 s, 6 H (2 × OCH_3); 3.95 s, 3 H (OCH_3); 4.15 dd, 1 H, J(3a,4) = 8.5 (H-3a), J(3b,4) = 5.3 (H-4); 5.67 s, 1 H (H-2′); 7.40 m, 2 H (H-7 and H-8); 7.83 m, 2 H. ^{13}C NMR: 29.14 (CH_2); 37.46 (CH); 52.02 (OCH_3); 52.57 (OCH_3); 52.74 (OCH_3); 52.92 (OCH_3); 121.27 (CH); 121.89 (CH); 124.01 (CH); 124.47; 125.15 (CH); 125.61 (CH); 129.11; 132.20; 133.23; 134.02; 137.02; 137.30; 142.57; 147.23; 165.00 (C=O); 166.25 (C=O); 166.52 (C=O); 167.81 (C=O). IR: 2953, 1728 (C=O), 1599, 1521, 1436, 1275, 1174, 1118, 1055, 1024, 929.

Trimethyl [1-(methoxycarbonyl)ethane[1,1,2]triyl]-1,2,3,4-tetrahydro[1]benzothieno[3,2-b][1]benzothiophene-1,2,3-tricarboxylate (**14**). Yield 25 mg (0.7%). For $C_{24}H_{20}O_8S_2$ (500.6) calculated: 57.59% C, 4.03% H; found: 57.33% C, 3.91% H. ^{1}H NMR: 2.43 d, 1 H, J = 10.5; 3,00 dd, 1 H, J = 10.5, J = 4.6; 3.77 s, 6 H (2 × OCH_3); 3.81 s, 3 H (OCH_3); 3.88 s, 3 H (OCH_3); 4.03 d, 1 H, J = 4.6; 4.77 bs, 1 H; 7.35 m, 1 H; 7.41 m, 1 H; 7.79 d, 1 H, J = 7.7; 7.85 d, 1 H, J = 7.8. ^{13}C NMR: 41.60 (CH); 41.95; 47.22 (CH_2); 48.27 (CH); 52.17 (OCH_3); 52.32 (OCH_3); 52.53 (OCH_3);

52.89 (OCH_3); 59.31; 120.72 (CH); 123.89 (CH); 124.42 (CH); 124.73 (CH); 132.24; 132.74; 133.29; 138.02; 141.64; 150.08; 163.76 (C=O); 163.81 (C=O); 169.80 (C=O); 171.82 (C=O). IR: 2955, 2 848, 1737 (C=O), 1634, 1604, 1445, 1437, 1381, 1285, 1266, 1178, 1111, 1092, 1068, 1020, 945, 848.

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