

EFFICIENT SYNTHESIS OF 2-iodo AND 2-DICYANOMETHYL
DERIVATIVES OF THIOPHENE, SELENOPHENE, TELLUROPHENE,
AND THIENO[3,2-*b*]THIOPHENE

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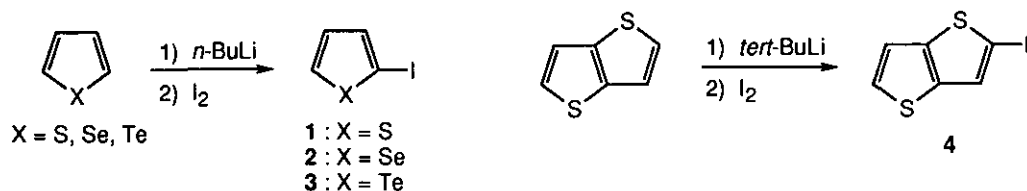
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Abstract- An effective synthesis of 2-iodothiophene, 2-iodotellurophene, and 2-iodothieno[3,2-*b*]thiophene and a Pd-catalyzed carbon-carbon coupling reaction of these iodo derivatives as well as 2-iodoselenophene with malononitrile affording novel thienyl-, tellurienyl-, thieno[3,2-*b*]thienyl-, and selenienylmalononitrile are described. These heteroarylmalononitriles are important synthons for the preparation of 2-dicyanomethylene-2,5-dihydroheterophene chromophores.

In recent years, heterocycle-incorporated conjugated molecules exhibiting interesting electrochemical and optical properties have been widely developed in the field of pure and applied chemistry.¹ The Pd- or Ni-catalyzed carbon-carbon bond formation,² a key stage in the synthesis of many currently interesting heterocycle-incorporated compounds, has proved to proceed generally and effectively by using the iodo derivatives of the corresponding heteroaromatic compounds. However, the existing methodologies for the preparation of 2-iodothiophene (**1**)³ and 2-iodothieno[3,2-*b*]thiophene (**4**)⁴ were limited to the use of toxic mercuric oxide-iodine combination and **4** was obtained in only 20% yield.⁵ Iodination of tellurophene was performed with *trans*-1-chloro-2-dichloroiodoethylene, but it was problematic in giving 2-iodotellurophene (**3**) in a very poor yield of 7%.⁶ We have now found more convenient and effective synthetic methods for 2-heteroaryl iodides (**1**), (**3**), and (**4**), without using toxic yellow mercuric oxide, which are important compounds for the preparation of heterocyclic derivatives *via* low-valent transition metal catalyzed carbon-carbon cross-coupling reactions. Heteroarylmalononitriles, capable of acting as key synthetic precursors for a building block of heterocycle-extended electron acceptors,⁷ have never been reported to date, although

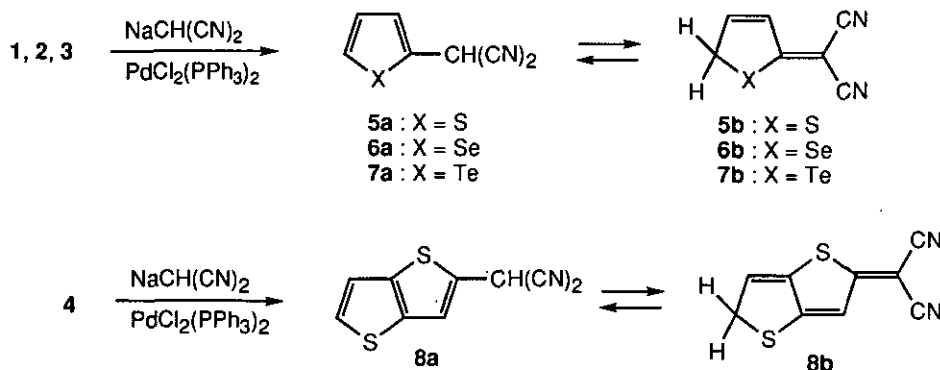
the efficient preparation of arylmalononitriles has been reported.⁸ We have now synthesized novel thienyl- (5), selenienyl- (6), tellurienyl- (7), and thieno[3,2-*b*]thienylmalononitrile (8) by a Pd-catalyzed cross-coupling reaction of these iodo derivatives (1—4) with sodium malononitrile.

Our synthetic routes to the iodides are outlined in Scheme 1. Thiophene, tellurophene, and thieno[3,2-*b*]thiophene were first lithiated with *n*-BuLi or *tert*-BuLi in ether and then allowed to react with iodine to give 1 (88%), 3 (67%), and 4 (quant). 2-Iodoselenophene (2) was prepared by lithiation of selenophene and subsequent iodination of lithioselenophene with iodine in 58% yield.⁹ We have now found that 2 is obtained in 93% yield when it is purified by silica gel chromatography, not by distillation.



Scheme 1

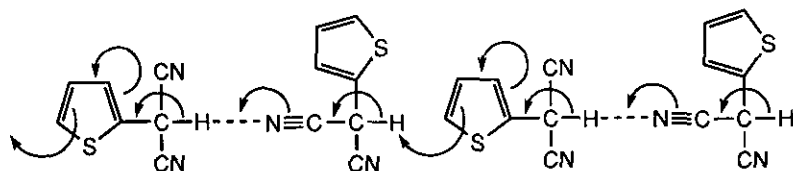
Novel heteroarylmalononitriles (5—8) were synthesized in 46—61% yields¹⁰ by the reaction of the corresponding iodides (1—4) with sodium malononitrile in the presence of PdCl₂(PPh₃)₂ in THF as shown in Scheme 2.



Scheme 2

In contrast to phenylmalononitrile, double bond isomerizations between 5a—8a and 5b—8b can occur in these compounds, since the heterocycles are less aromatic than the phenyl group. Although 2-thienylmalononitrile (5a) was stable in aprotic solvents such as benzene, ether, dichloromethane, and chloroform,¹¹ this compound isomerized in neat at room temperature affording quantitatively 2-dicyanomethylene-2,5-dihydrothiophene (5b). The negative charge of the sodium salt of 5 is largely

concentrated on the carbon atom carrying the cyano groups or on the nitrogen atoms of the cyano groups, because **5a** was predominantly obtained on quenching the aqueous alkaline solutions of **5b** or **5a** with conc. HCl at -15°C . Thus the isomerization of **5a** to **5b** appears to occur in a proton transfer mechanism through the formation of an intermolecular hydrogen bond between the basic nitrogen atom and the acidic methine hydrogen atom of the dicyanomethyl group as shown in Scheme 3.



Scheme 3

Selenienyl- (**6**) and tellurienylmalononitrile (**7**) were synthesized as 2-dicyanomethylene-2,5-dihydroheterophene type isomers (**6b**) and (**7b**), respectively, and neither isomer (**6a**) nor isomer (**7a**) was detected in the reaction products. On the other hand, **8** was obtained as thieno[3,2-*b*]thienylmalononitrile (**8a**), no isomer (**8b**) being detected in the reaction products. These results demonstrate that the 2-dicyanomethylene-2,5-dihydroheterophene type isomer predominates in the compounds incorporating a heterocycle with a decreased aromaticity. All compounds (**5a**), (**5b**), (**6b**), (**7b**), and (**8a**) reacted with cyclopropenone derivatives in the presence of β -alanine in refluxing acetic anhydride to afford 5-cyclopropenylidene-2-dicyanomethylene-2,5-dihydroheterophenes derivatives⁷ in a good yield. This fact indicates that **5**—**8** undergo nucleophilic reactions predominantly at the 5-position and therefore the utility potential of these compounds to synthetic precursors for 2-dicyanomethylene-2,5-dihydroheterophenyl chromophores is not restricted by their prototropic isomerization. The synthesis of π -electron systems incorporating these chromophores, which was not convenient so far,¹² has now become easily accessible by using these excellent synthons (**5**—**8**), so that a variety of new type of functional compounds will be created hereafter starting from these synthons.

EXPERIMENTAL PART

All melting points were uncorrected. Nmr spectra were recorded on either a Bruker AC-200p, Bruker AM-600 spectrometer. All ^1H nmr and ^{13}C nmr chemical shifts are recorded relative to TMS as internal standard. Chemical shift assignments were confirmed through spin decoupling and two-dimensional carbon-proton chemical shift correlation experiments. Ir spectra were recorded on a HORIBA FT-300

spectrophotometer. Ms spectra were recorded on a JEOL-JMS-HX110 spectrometer. Uv spectra were recorded on a Hitachi U-3210 spectrophotometer. Elemental analyses were performed at Instrumental Analysis Center for Chemistry, Tohoku University.

2-Iodothiophene (1). To a solution of thiophene (1.00 g., 11.9 mmol) in anhydrous ether (20 ml) was added dropwise a hexane solution of *n*-BuLi (1.57 M solution, 7.57 ml, 11.9 mmol) with stirring at 0 °C under argon atmosphere, and the reaction mixture was stirred for 1 h at room temperature. To this was added dropwise at 0 °C a solution of iodine (3.02 g, 11.9 mmol) in anhydrous ether (40 ml) over a period of 10 min and the reaction mixture was stirred for 1 h at room temperature. The reaction mixture was then poured into ice water and extracted with ether. The combined ether extracts were washed successively with saturated aqueous NaHSO₃ and brine, and dried over Na₂SO₄. Solvent evaporation afforded an oily product (2.43 g) which was chromatographed on silica gel by eluting with pentane to give 2-iodothiophene (1) as a colorless oil (2.20 g, 88%). ¹H Nmr (200 MHz, CDCl₃) δ 6.81 (1H, dd, *J*_{4,5} = 5.41 Hz, *J*_{4,3} = 3.62 Hz, H-4), 7.25 (1H, dd, *J*_{3,4} = 3.62 Hz, *J*_{3,5} = 1.84 Hz, H-3), 7.37 (1H, dd, *J*_{5,4} = 5.41 Hz, *J*_{5,3} = 1.84 Hz, H-5). lit.^{13,14} ¹H Nmr (40 MHz, cyclohexane) δ 6.60 (1H, dd, *J*_{4,5} = 5.0 Hz, *J*_{4,3} = 3.8 Hz, H-4), 7.09 (1H, dd, *J*_{3,4} = 3.8 Hz, *J*_{3,5} = 1.3 Hz, H-3), 7.21 (1H, dd, *J*_{5,4} = 5.0 Hz, *J*_{5,3} = 1.3 Hz, H-5). Anal. Calcd for C₄H₃IS: C, 22.87; H, 1.44; S, 15.27; I, 60.42. Found: C, 22.59; H, 1.64; S, 14.98; I, 60.63.

2-Iodoselenophene (2). To a solution of selenophene (1.00 g, 7.63 mmol) in anhydrous ether (20 ml) was added dropwise a hexane solution of *n*-BuLi (1.61 M solution, 4.74 ml, 7.63 mmol) with stirring at room temperature under argon atmosphere, and then the reaction mixture was refluxed for 10 min. After being cooled to -78 °C, to this was added dropwise a solution of iodine (1.94 g, 7.63 mmol) in anhydrous ether (40 ml) over a period of 20 min. The solution was allowed to warm to 0 °C and stirred for 1 h. After being warmed to room temperature, the reaction mixture was worked up in a manner similar to **1** and an oily product (2.33 g) was chromatographed on silica gel by eluting with pentane to give 2-iodoselenophene (2) as a colorless oil (1.82 g, 93%). ¹H Nmr (200 MHz, CDCl₃) δ 6.96 (1H, dd, *J*_{4,5} = 5.94 Hz, *J*_{4,3} = 3.80 Hz, H-4), 7.56 (1H, dd, *J*_{3,4} = 3.80 Hz, *J*_{3,5} = 1.17 Hz, H-3), 8.24 (1H, dd, *J*_{5,4} = 5.94 Hz, *J*_{5,3} = 1.17 Hz, H-5). lit.⁹ ¹H Nmr (100 MHz, acetone-*d*₆) δ 6.99 (1H, dd, *J*_{4,5} = 5.88 Hz, *J*_{4,3} = 3.76 Hz, H-4), 7.56 (1H, dd, *J*_{3,4} = 3.76 Hz, *J*_{3,5} = 1.20 Hz, H-3), 8.24 (1H, dd, *J*_{5,4} = 5.88 Hz, *J*_{5,3} = 1.20 Hz, H-5). Anal. Calcd for C₄H₃ISe: C, 18.70; H, 1.18; I, 49.39. Found: C, 18.88; H, 1.30; I, 49.24.

2-Iidotellurophene (3). To a solution of tellurophene (1.29 g, 7.20 mmol) in anhydrous ether (40 ml)

was added dropwise a hexane solution of *n*-BuLi (1.60 M solution, 4.50 ml, 7.20 mmol) with stirring at 0 °C under argon atmosphere and the reaction mixture was stirred for 45 min at room temperature. After being cooled to -78 °C, to this was added dropwise a solution of iodine (1.83 g, 7.20 mmol) in anhydrous ether (15 ml) over a period of 30 min, and then the reaction mixture was stirred for 30 min at room temperature. The reaction mixture was worked up in a manner similar to **1** and an oily product (1.65 g) was chromatographed on silica gel by eluting with pentane to give 2-iodotellurophene (**3**) as a colorless oil (1.47 g, 67%). ¹H Nmr (200 MHz, CDCl₃) δ 7.30 (1H, dd, *J*_{4,5} = 7.18 Hz, *J*_{4,3} = 4.09 Hz, H-4), 8.08 (1H, dd, *J*_{3,4} = 4.09 Hz, *J*_{3,5} = 1.25 Hz, H-3), 9.02 (1H, dd, *J*_{5,4} = 7.18 Hz, *J*_{5,3} = 1.25 Hz, H-5). lit.⁶ ¹H Nmr (60 MHz, acetone-*d*₆) δ 7.32 (1H, dd, *J*_{4,5} = 7.10 Hz, *J*_{4,3} = 4.06 Hz, H-4), 8.11 (1H, dd, *J*_{3,4} = 4.06 Hz, *J*_{3,5} = 1.54 Hz, H-3), 9.13 (1H, dd, *J*_{5,4} = 7.10 Hz, *J*_{5,3} = 1.54 Hz, H-5). Anal. Calcd for C₄H₃ITe: C, 15.72; H, 0.99; I, 41.53. Found: C, 15.48; H, 1.25; I, 41.38.

2-Iodothieno[3,2-*b*]thiophene (4). To a solution of thieno[3,2-*b*]thiophene (1.00 g, 7.13 mmol) in anhydrous ether (20 ml) was added dropwise a pentane solution of *tert*-BuLi (1.60 M solution, 4.68 ml, 7.49 mmol) with stirring at 0 °C under argon atmosphere, and the reaction mixture was stirred for 1 h at room temperature. After being cooled to 0 °C, to this was added dropwise a solution of iodine (1.99 g, 7.84 mmol) in anhydrous ether (40 ml) over a period of 10 min, and then the resulting solution was stirred for 1 h at room temperature. The reaction mixture was worked up in a manner similar to **1** and a solid reaction product (2.07 g) was chromatographed on silica gel by eluting with hexane to give pure 2-iodothieno[3,2-*b*]thiophene (**4**) (1.90 g, 7.13 mmol, quant). Colorless crystals, mp 48.8—49.2 °C. (lit.,⁴ 49 °C). ¹H Nmr (200 MHz, CDCl₃) δ 7.19 (1H, d, *J*_{6,5} = 5.26 Hz, H-6), 7.40 (1H, d, *J*_{5,6} = 5.26 Hz, H-5), 7.43 (1H, s, H-3); ¹³C nmr (50 MHz, CDCl₃) δ 74.69 (C-2), 118.58 (C-6), 126.99 (C-5), 128.30 (C-3), 139.40 (C-3a), 143.88 (C-6a); LRms (70 eV, EI) *m/z* (rel. int. %) 268 (M⁺+2, 9.21), 267 (M⁺+1, 9.16), 266 (M⁺, 100), 139 (M⁺-1, 47.23). Anal. Calcd for C₆H₃IS₂: C, 27.08; H, 1.14; S, 24.10; I, 47.69. Found: C, 26.97; H, 1.20; S, 23.89; I, 47.43.

2-Dicyanomethylthiophene (5a). To a suspension of sodium hydride (55—65 wt %, 2.86 g, about 71 mmol) in anhydrous THF (20 ml) was added dropwise a solution of malononitrile (3.15 g, 47.6 mmol) in anhydrous THF (20 ml) with stirring at 0 °C over a period of 10 min under argon atmosphere. After being allowed to warm to room temperature, to this were added successively 2-iodothiophene (**1**) (5.00 g, 23.8 mmol) and PdCl₂(PPh₃)₂ (1.67 g, 2.38 mmol), and the reaction mixture was refluxed for 42 h. The reaction mixture was cooled to room temperature, poured into 1 N HCl at 0 °C, and extracted with

dichloromethane. The combined dichloromethane extracts were washed with water and then brine, and dried over Na_2SO_4 . Solvent evaporation afforded a residue (6.58 g) which was dissolved in 2N NaOH (60 ml). After being washed with benzene, the aqueous alkaline solution was poured into conc. HCl (300 ml) at around -15°C over a period of 1 h, and extracted with benzene. The combined benzene extracts were washed with water and then brine, and dried over Na_2SO_4 . Solvent evaporation gave 2-dicyanomethylthiophene (**5a**) containing 10% of 2-dicyanomethylene-2,5-dihydrothiophene (**5b**) as a pale yellow oil (1.87 g, 53%). ^1H Nmr (CDCl_3 , 200 MHz) of **5a** δ 5.30 (1H, d, $J_{3,6} = 0.93$ Hz, $\text{CH}(\text{CN})_2$), 7.09 (1H, dd, $J_{4,5} = 5.20$, $J_{3,4} = 3.68$ Hz, H-4), 7.40 (1H, ddd, $J_{3,4} = 3.68$, $J_{3,5} = 1.27$ Hz, $J_{3,6} = 0.93$ Hz, H-3), 7.55 (1H, dd, $J_{4,5} = 5.20$, $J_{5,3} = 1.27$ Hz, H-5); ^{13}C nmr (CDCl_3 , 50 MHz) of **5a** δ 23.7 ($\text{CH}(\text{CN})_2$), 111.1, (CN), 126.5 (C-2), 127.8 (C-4), 128.7 (C-5), 129.1 (C-3); ir (KBr) 3114, 2897, 2258, 2222, 1589, 1512 1429, 1360, 1267, 1236, 1196, 1169, 1119, 1082, 1043, 1001, 972, 921, 897, 847, 783, 750, 714 cm^{-1} ; uv (MeCN) λ_{max} nm (log ϵ) 328 (3.48), 232 (3.82).

For the synthetic purpose, the aqueous alkaline solution was acidified by adding 1 N HCl at 0°C , extracted with benzene, and then worked up in a manner described above to give a mixture of **5a** and **5b** comprising in a ratio of 10:4.5, which can be submitted directly to subsequent reactions.

2-Dicyanomethylene-2,5-dihydrothiophene (5b). The oily mixture of **5a** and **5b** (28:1) (1.20 g, 8.10 mmol) was allowed to stand at room temperature for 3 days to afford pale brown crystals. The crystals were washed with ether to give **5b** as colorless needles (1.15 g, 96%). Pure **5b** was isolated after recrystallization. Colorless fine needles (from CH_2Cl_2 -hexane), mp 75.5 — 76.0°C . ^1H Nmr (CDCl_3 , 200 MHz) δ 4.40 (2H, dd, $J_{5,4} = 2.74$, $J_{5,3} = 1.96$ Hz, H-5), 7.05 (1H, dt, $J_{3,4} = 5.98$, $J_{3,5} = 1.96$ Hz, H-3), 7.17 (1H, dt, $J_{4,3} = 5.98$, $J_{4,5} = 2.74$ Hz, H-4); ^{13}C nmr (CDCl_3 , 50 MHz) δ 45.8 (C-5), 68.6 ($\text{C}(\text{CN})_2$), 111.1 (CN), 112.7 (CN), 131.6 (C-3), 149.9 (C-4), 185.2 (C-2); ir (KBr) 3068, 2952, 2922, 2227, 1583, 1550, 1522, 1390, 1344, 1228, 1099, 968, 906, 879, 782, 752 cm^{-1} ; uv (MeCN) λ_{max} nm (log ϵ) 333 sh (3.51), 303 (4.06), 242 sh (3.74), 234 sh (3.79), 217 (3.82); LRms (DEI, 70 eV) m/z (rel. int. %) 149 ($\text{M}^+ + 1$, 9.0), 148 (M^+ , 66.9), 147 ($\text{M}^+ - 1$, 17.2), 123 ($\text{M}^+ - \text{CN} + 1$, 5.4), 122 ($\text{M}^+ - \text{CN}$, 17.9), 121 ($\text{M}^+ - \text{CN} - 1$, 100). HRms (DEI, 70 eV) Found: m/z , 148.0092. Calcd for $\text{C}_7\text{H}_4\text{N}_2\text{S}$: M, 148.0095. Anal. Calcd for $\text{C}_7\text{H}_4\text{N}_2\text{S}$: C, 56.74; H, 2.72; N, 18.90; S, 21.64. Found: C, 56.88; H, 2.92; N, 18.95; S, 21.52.

2-Dicyanomethylene-2,5-dihydroselenophene (6b). To a suspension of sodium hydride (55—65 wt%, 848 mg, about 21 mmol) in anhydrous THF (5 ml) was added dropwise a solution of malononitrile

(938 mg, 14.2 mmol) in anhydrous THF (5 ml) with stirring at 0 °C over a period of 15 min under argon atmosphere. After being warmed to room temperature, to this were added successively 2-iodoselenophene (**2**) (1.82 g, 7.08 mmol) and PdCl₂(PPh₃)₂ (477 mg, 0.708 mmol). The reaction mixture was refluxed for 40 h, cooled to room temperature, poured into 1 N HCl at 0 °C, and extracted with dichloromethane. The combined dichloromethane extracts were washed with water and then brine, and dried over Na₂SO₄. Solvent evaporation gave a residue (1.67 g) which was chromatographed on silica gel by eluting with dichloromethane to give pure 2-dicyanomethylene-2,5-dihydroselenophene (**6b**) (847 mg, 61%). Colorless needles (from CH₂Cl₂-hexane), mp 119–123 °C (decomp.). ¹H Nmr (CDCl₃, 200 MHz) δ 4.55 (2H, dd, *J*_{5,4} = 2.87 Hz, *J*_{5,3} = 1.90 Hz, H-5), 7.12 (1H, dt, *J*_{3,4} = 6.29 Hz, *J*_{3,5} = 1.90 Hz, H-3), 7.21 (1H, dt, *J*_{4,3} = 6.29 Hz, *J*_{4,5} = 2.87 Hz, H-4); ¹³C nmr (CDCl₃, 50 MHz) δ 39.6 (C-5), 73.1 (C(CN)₂), 112.9, 114.7 (CN), 133.6 (C-3), 151.7 (C-4), 186.5 (C-2); ir (KBr) 3053, 2962, 2924, 2212, 1851, 1518, 1387, 1346, 1248, 1140, 1045, 955, 879, 744 cm⁻¹; uv (MeCN) λ_{max} nm (log ε) 352 (4.19), 269 (4.13), 233 sh (3.64), 225 sh (3.72); LRms (DEI, 70 eV) *m/z* (rel. int. %) 198 (M⁺+2, 12.9), 197 (M⁺+1, 11.3), 196 (M⁺, 72.3), 195 (M⁺-1, 24.2), 194 (M⁺-2, 34.7), 193 (M⁺-3, 22.6), 192 (M⁺-4, 16.8), 191 (M⁺-5, 4.64), 171 (M⁺+1-CN, 17.7), 170 (M⁺-CN, 13.1), 169 (M⁺-1-CN, 100), 168 (M⁺-2-CN, 12.9), 167 (M⁺-3-CN, 49.3), 166 (M⁺-4-CN, 20.6), 165 (M⁺-5-CN, 20.3); HRms (DEI, 70 eV) Found: *m/z*, 195.9538. Calcd for C₇H₄N₂Se : M, 195.9540. Anal. Calcd for C₇H₄N₂Se : C, 43.10; H, 2.07; N, 14.36. Found : C, 43.32; H, 2.18; N, 14.56.

2-Dicyanomethylene-2,5-dihydrotellurophene (7b). To a suspension of sodium hydride (55–65 wt%, 426 mg, about 11 mmol) in anhydrous THF (43 ml) was added dropwise a solution of malononitrile (469 mg, 7.10 mmol) in anhydrous THF (43 ml) with stirring at 0 °C over a period of 15 min under argon atmosphere. After being warmed to room temperature, to this were added successively a solution of 2-iodotellurophene (**3**) (1.08 g, 3.55 mmol) in anhydrous THF (43 ml) and PdCl₂(PPh₃)₂ (249 mg, 0.355 mmol). The reaction mixture was refluxed for 16.5 h and worked up in a manner similar to **6b** and crude products (1.22 g) were chromatographed on silica gel by eluting with dichloromethane to give pure 2-dicyanomethylene-2,5-dihydrotellurophene (**7b**) (398 mg, 46%). Pale yellow crystals, mp 99–101 °C. ¹H Nmr (CDCl₃, 200 MHz) δ 4.78 (2H, dd, *J*_{5,4} = 3.28 Hz, *J*_{5,3} = 1.79 Hz, H-5), 7.16 (1H, dt, *J*_{3,4} = 6.58 Hz, *J*_{3,5} = 1.79 Hz, H-3), 7.26 (1H, dt, *J*_{4,3} = 6.58 Hz, *J*_{4,5} = 3.28 Hz, H-4); ¹³C nmr (CDCl₃, 50 MHz) δ 22.0 (C-5), 80.6 (C(CN)₂), 113.1, 116.5 (CN), 138.9 (C-3), 154.1 (C-4), 179.5 (C-2); ir (KBr) 3037, 2916, 2210, 1577, 1504, 1375, 1356, 1192, 1142, 1080, 943, 874, 808, 723 cm⁻¹; uv (MeCN)

λ_{\max} nm (log ϵ) 400 (3.88), 361 (3.88), 280 (4.00), 244 (3.99); LRms (DEI, 70 eV) m/z (rel. int. %) 247 ($M^+ + 1$, 7.9), 246 (M^+ , 100), 245 ($M^+ - 1$, 11.1), 244 ($M^+ - 2$, 90.7), 243 ($M^+ - 3$, 6.7), 242 ($M^+ - 4$, 56.5), 241 ($M^+ - 5$, 22.5), 240 ($M^+ - 6$, 15.8), 239 ($M^+ - 7$, 73.3), 238 ($M^+ - 8$, 7.2), 219 ($M^+ - \text{CN} - 1$, 27.7); HRms (DEI, 70 eV) Found: m/z , 245.9434. Calcd for $C_7H_4N_2Te$: M, 245.9437. Anal. Calcd for $C_7H_4N_2Te$: C, 34.50; H, 1.77; N, 11.56. Found: C, 34.63; H, 1.86; N, 11.62.

2-Dicyanomethylthieno[3,2-*b*]thiophene (8a). To a suspension of sodium hydride (55–65 wt %, 934 mg, about 21 mmol) in anhydrous THF (5 ml) was added dropwise a solution of malononitrile (945 mg, 14.3 mmol) in anhydrous THF (5 ml) with stirring at 0 °C over a period of 10 min under argon atmosphere. After being warmed to room temperature, to this were added successively 2-iodothieno[3,2-*b*]thiophene (**4**) (1.90 g, 7.14 mmol) and $PdCl_2(PPh_3)_2$ (501 mg, 0.714 mmol). The reaction mixture was refluxed for 24 h and worked up in a manner similar to **6b** and crude products (1.97 g) were chromatographed on silica gel by eluting with dichloromethane and recrystallized to give pure 2-dicyanomethylthieno[3,2-*b*]thiophene (**8a**) (818 mg, 56%). Pale yellow prisms (from MeCN), mp 138–139 °C. 1H Nmr ($CDCl_3$, 600 MHz) δ 5.35 (1H, s, $CH(CN)_2$), 7.28 (1H, d, $J_{6,5} = 5.29$ Hz, H-6), 7.52 (1H, s, H-3), 7.53 (1H, d, $J_{5,6} = 5.29$ Hz, H-5); ^{13}C nmr ($CDCl_3$, 150 MHz) δ 24.6 ($CH(CN)_2$), 110.7 (CN), 119.4 (C-6), 121.5 (C-3), 127.5 (C-2), 130.0 (C-5), 138.3 (C-3a), 140.3 (C-6a); ir (KBr) 3113, 3086, 2873, 2254, 1736, 1711, 1680, 1655, 1631, 1581, 1543, 1504, 1454, 1435, 1348, 1271, 1219, 1194, 1124, 1084, 1012, 926, 876, 843, 823, 766, 711 cm^{-1} ; uv (MeCN) λ_{\max} nm (log ϵ) 355 (3.71), 280 (sh, 4.10), 272 (4.20), 265 (4.20); LRms (DEI, 70 eV) m/z (rel. int. %) 205 ($M^+ + 1$, 11.23), 204 (M^+ , 51.00), 203 ($M^+ - 1$, 100), 177 ($M^+ + 1 - \text{CN}$, 20.73), 176 ($M^+ - \text{CN}$, 52.61); HRms (DEI, 70 eV) Found: m/z , 203.9809. Calcd for $C_9H_4N_2S_2$: M, 203.9816. Anal. Calcd for $C_9H_4N_2S_2$: C, 52.92; H, 1.97; N, 13.71; S, 31.39. Found: C, 53.04; H, 2.17; N, 13.88; S, 31.69.

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REFERENCES AND NOTES

1. K. Takahashi, *Pure and Appl. Chem.*, 1993, **65**, 127; S. H. Kawai, S. L. Gilat, and J. -M. Lehn, *J. Chem. Soc., Chem. Comm.*, 1994, 1011; T. Saika, T. Iyoda, K. Honda, and T. Shimidzu, *J. Chem.*

- Soc., Chem. Comm.*, **1992**, 591; K. Yui, Y. Aso, T. Otsubo, and F. Ogura, *Bull. Chem. Soc. Jpn.*, **1989**, **62**, 1539; K. Takahashi, T. Suzuki, K. Akiyama, Y. Ikegami, and Y. Fukazawa, *J. Am. Chem. Soc.*, **1991**, **113**, 4576.
2. V. N. Kalinin, *Synthesis*, **1992**, 413; R. D. McCullough, R. D. Lowe, M. Jayaraman, and D. L. Anderson, *J. Org. Chem.*, **1993**, **58**, 904.
 3. W. Minns, *Org. Synth. Coll. Vol. II*, **1950**, 357.
 4. F. Challenger and R. Emmott, *J. Inst. Petrol., London*, **1951**, **37**, 396.
 5. After the completion of our present study, a new iodinating reagent of thiophene derivatives was published: M. D'Auria and G. Mauriello, *Tetrahedron Lett.*, **1995**, **36**, 4883.
 6. F. Fringuelli, S. Gronowitz, A. -B. Hörnfeldt, I. Johnson, and A. Taticchi, *Acta Chemica Scand.*, **1976**, **B 30**, 605.
 7. K. Takahashi and S. Tarutani, *J. Chem. Soc., Chem. Comm.*, **1994**, 519; K. Takahashi and S. Tarutani, *Adv. Mater.*, **1995**, 639; K. Takahashi and S. Tarutani, *Synth. Metals*, **1995**, **70**, 1165; K. Takahashi, S. Tarutani, and M. Yoshifuji, The 69th Annual Meeting of the Chemical Society of Japan, Kyoto, March, **1995**, Abstr. I, p. 437.
 8. M. Uno, K. Seto, and S. Takahashi, *J. Chem. Soc., Chem. Comm.*, **1984**, 932.
 9. S. Gronowitz, I. Johnson, and A. -B. Hörnfeldt, *Chemica Scripta*, **1975**, **7**, 111.
 10. The yield of **7 (7b)** becomes much lower by using a less amount of THF (see experimental part).
 11. Compound (**5a**) destroyed gradually in methanol at room temperature.
 12. Inconvenient stepwise synthesis of a π -electron system with 2-dicyanomethylene-2,5-dihydrothiophene moiety was reported: K. Takahashi, K. Takase, and T. Sakae, *Chem. Lett.*, **1980**, 1485.
 13. R. A. Hoffman and S. Gronowitz, *Arkiv Kemi.*, **1960**, **16**, 515.
 14. S. Gronowitz and R. A. Hoffman, *Arkiv Kemi.*, **1960**, **16**, 539.

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