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New synthesis of 2-[1,3-dithiol-2-ylidene]-5,6-dihydro-1,3-dithiolo[4,5-*b*][1,4]dithiins with formyl group on fused benzene, [1,4]dithiin, or thiophene ring

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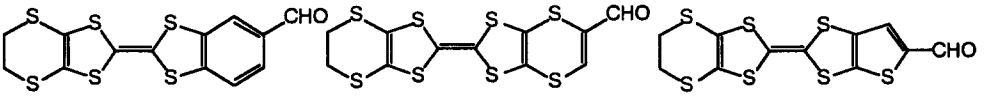
Abstract

As novel TTF-based annelated donors, 2-[1,3-dithiol-2-ylidene]-5,6-dihydro-1,3-dithiolo[4,5-*b*][1,4]dithiins with a formyl group on fused benzene, [1,4]-dithiin, or thiophene ring, respectively, were prepared using Diels–Alder or an intramolecular aldol reaction.

Keywords: thiafulvalenes; aldehydes; benzenes; thiophenes.

Preparation of periphery-modified TTF derivatives has been actively explored because they are indispensable constituents in developing new functional organic solids.[1] Among such modifications, annelation of the TTF skeleton[2] may be especially effective in changing redox potentials, augmenting intermolecular interactions, or adding extra functionalities. However, annelated donors carrying a certain functional group which can be derivatized responding to the various requirements have been scarcely developed. Annelated donors with a formyl group can be regarded as a prototype of such derivatizable donors. In this paper we report a new straightforward synthesis of 2-[1,3-dithiol-2-ylidene]-5,6-dihydro-1,3-dithiolo[4,5-*b*][1,4]dithiin with a formyl group on fused benzene, [1,4]dithiin, or thiophene ring (**5**, **10**, **15**), respectively. For instance, the formyl group of these donors can react with amines to be converted to a mesogenic group. It can also be condensed with *N,N′*-bishydroxyldiamine to afford a cyclic bishydroxyldiamine, which is oxidized to a stable nitronyl nitroxide radical group.



5 **10** **15**

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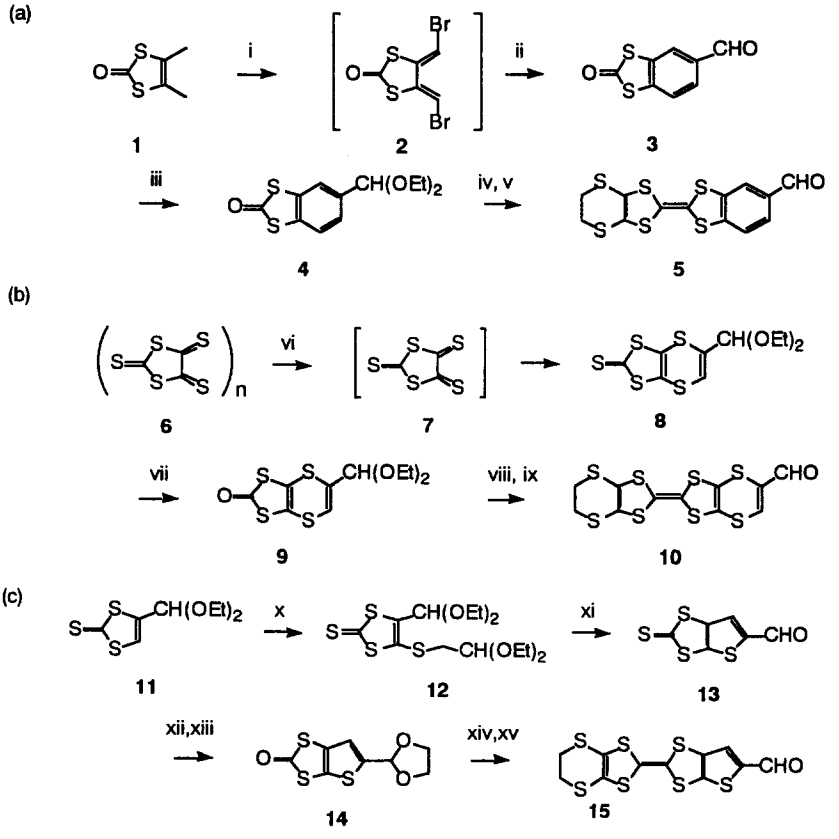
Usually benzo-annelated TTFs are prepared using anthranilic acid or benzene-1,2-dithiol derivative[3] as a starting material. The main drawback of this method lies in a limited availability of substituted anthranilic acids or benzene-1,2-dithiols. In our synthetic strategy, a Diels–Alder approach was adapted utilizing acrolein as a dienophile and 4,5-bis(bromomethylene)-1,3-dithiol-2-one as a diene as shown in Scheme 1(a). The key diene was easily obtained from 4,5-dimethyl-1,3-dithiol-2-one[4] through successive treatments with 4 molar NBS and with iodide ion.[5] Twofold dehydrobromination occurred smoothly in refluxing acetonitrile to afford the β-formylated benzo-derivative (**3**) in 75% yield. Reaction of the diene with ethyl acrylate gave an equally excellent result.

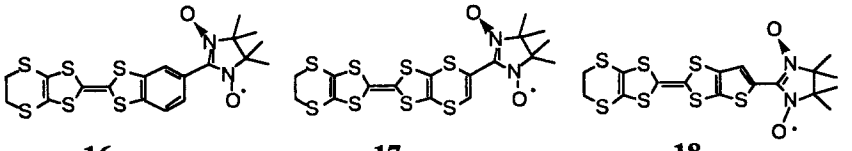


Scheme 1. *Reagents and conditions (yield)*: (i) (1) 4 equiv. NBS, CCl_4, reflux; (2) Et_4NI, CH_3CN, reflux; (ii) excess acrolein, CH_3CN, reflux (75%); (iii) $HC(OEt)_3$, Amberlyst (quant.); (iv) 5,6-dihydro-1,3-dithiolo[4,5-*b*][1,4]dithiin-2-thione, $P(OEt)_3$, 120°C (20%); (v) acetone, Amberlyst, $CHCl_3$ (81%); (vi) propargyl aldehyde diethyl ketal, toluene, reflux (12%); (vii) $Hg(OAc)_2$, Na_2CO_3, CH_3CN (95%); (viii) 5,6-dihydro-1,3-dithiolo[4,5-*b*][1,4]dithiin-2-thione, $P(OEt)_3$, PhH, reflux (45%); (ix) acetone, *p*-TsOH, CH_2Cl_2 (70%); (x) (1) LDA, THF, −78°C; (2) $(SCH_2CH(OEt)_2)_2$ (85%); (xi) (1) acetone, Amberlyst; (2) silica gel, CH_2Cl_2 (75%); (xii) $HOCH_2CH_2OH$, Amberlyst, PhH, reflux (90%); (xiii) $Hg(OAc)_2$, CH_3CN (95%); (xiv) 5,6-dihydro-1,3-dithiolo[4,5-*b*][1,4]dithiin-2-thione, $P(OEt)_3$ PhH, reflux (25%); (xv) acetone, *p*-TsOH, CH_2Cl_2 (88%)

1,3-Dithiole-2,4,5-trithione (**7**), which is also known to be a good enophile in Diels–Alder reactions,[6] is applied to the preparation of a dithiin-fused 1,3-dithiole-2-thione derivative carrying a protected formyl group (**8**). The enophile **7**, which was generated from its oligomer (**6**) according to the literature,[6,7] was reacted with an excess amount of propargyl aldehyde diethyl ketal to give rise to a protected 5-formyl-1,3-dithiolo[4,5-*b*][1,4]dithiin-2-thione (**8**) (Scheme 1(b)). Although the yield of **8** is moderate (12%), the one-step preparation from readily available starting materials is advantageous over the formylation of 1,3-dithiolo[4,5-*b*][1,4]dithiin-2-thione.[8]

5-Formylthieno[2,3-*d*]-1,3-dithiole-2-thione (**13**) was prepared using aldol condensation as a key reaction (Scheme 1(c)). The presence of a formyl group enables a totally different synthetic strategy (C_5–C_6 bond formation starting from a 1,3-dithiole-2-thione derivative) from the preceding syntheses (S_1–C_{6a}/S_3–C_{3a} bond formation starting from thiacyclopentane derivatives[9]). The requisite dialdehyde for the aldol reaction was generated from the bisketal **12**, which was, in turn, prepared from protected 4-formyl-1,3-dithiole-2-thione **11**.[10] One of the possible synthetic routes from **11** to **12** is to utilize the electrophilic reaction of bromoacetaldehyde diethyl ketal with a thiolate which was generated by sulfurization of a metallated **11**. This route, however, failed to afford **12** due to the poor reactivity of bromoacetaldehyde diethyl ketal towards the thiolate.[11] The desired product **12**, however, turned out to be obtained through the reaction of bis(2,2-diethoxyethyl)disulfide[12] with the metallated **11** in 85% yield. The intramolecular aldol condensation of deprotected **12** proceeded smoothly in the presence of silica gel to give **13** in 75% yield.

Protected 1,3-dithiol-2-ones **4**, **9**, and **14** were coupled with 5,6-dihydro-1,3-dithiolo[4,5-*b*][1,4]-dithiin-2-thione by triethyl phosphite, and deprotection of the coupling products gave the desired donors **5**, **10**, and **15**, respectively.[13] Among them, thiophen-fused donor **15**, in particular, is interesting because the functional group can be introduced along the long axis of the donor molecule. Such a type of substitution pattern cannot be achieved even by periphery-modified TTF-based donors, excepting the pyrrolo-annelated donor prepared by Cava et al.[2]



16 **17** **18**

These formylated TTF-based donors can be converted into nitronyl nitroxide radicals which are considered as building blocks of organic conducting magnets.[14] While the target donor radicals **16**, **17**, and **18** were obtained by an ordinary method,[15] dithiin-type derivative **17** could not be isolated due to the kinetic instability.[16] Among these donor radicals, benzo-annelated derivative **16** was most processorable and it afforded a 1:1 charge transfer complex with F_4TCNQ. The IR spectrum of the complex showed a broad absorption band, which is assignable to a CT transition, in a higher wavenumber range than 1800 cm^{-1}. The CN stretching absorption of the complex was observed at 2194 cm^{-1}, indicating that F_4TCNQ exists as an anion radical. The complex is basically a paramagnet with a small negative Weiss temperature (θ=−1 K).[17] Judging from Curie constant of 0.375 for **16**·F_4TCNQ, all spins on radical sites are considered to be preserved. Such a stable CT complex is preferable for further studies.

Other chemical modifications using these donors are also in progress in these laboratories.

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2. Examples of the fused rings include benzene, 1,2,5-thiadiazole, [1,4]dithiin, benzo[1,4]dithiin, naphtho[1,4]dithiin, furan, thiophene, selenophene, pyrrole, and pyrazine. About recent studies, see for example: (a) Jigami, T.; Takimiya, K.; Aso, Y.; Otsubo, T. *Chem. Lett.* **1997**, 1091; (b) Zong, K.; Cava, M. P. *J. Org. Chem.* **1997**, *62*, 1903; (c) Zong, K.; Chen, W.; Cava, M. P.; Rogers, R. D. *J. Org. Chem.* **1996**, *61*, 8117.
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11. Even the selenolate which was obtained in a similar manner hardly afforded the desired selenide (3% yield). In contrast, the reaction of the thiolate with ethyl bromoacetate was found to give the corresponding sulfide in 90% yield. Thus, the low yield in the case of bromoacetaldehyde diethyl ketal can be ascribed to the low reactivity of the substrate.
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13. Compound **5**: ^{1}H NMR ($CDCl_3$, δ) 9.89 (s, 1H), 7.73 (d, *J*=1.5 Hz, 1H), 7.60 (dd, *J*=8.1, 1.5 Hz, 1H), 7.39 (d, *J*=8.1 Hz, 1H), 3.31 (s, 4H). IR (KBr, cm^{-1}) 1680 (vs), 1574 (s), 1199 (s). Mass calcd for $C_{13}H_8OS_6$: 371.8900; found: 371.8914. Compound **10**: ^{1}H NMR ($CDCl_3$, δ) 9.53 (s, 1H), 7.45 (s, 1H), 3.30 (s, 4H). IR (KBr, cm^{-1}) 1665 (vs), 1134 (s). Mass 410 (M^+, 6%), 322 (60%); calcd for $C_9H_6OS_6$ ($M-C_2S_2$): 321.8742; found: 321.8731. Compound **15**: ^{1}H NMR ($CDCl_3$, δ) 9.72 (s, 1H), 7.46 (s, 1H), 3.32 (s, 4H). IR (KBr, cm^{-1}) 1656 (vs), 1373 (s). Mass calcd for $C_{11}H_6OS_7$: 377.8464; found: 377.8473.
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16. Compound **16**: ESR (benzene) *g*=2.006, a_N=0.75 mT (2N). IR (KBr, cm^{-1}) 1451 (w), 1415 (m), 1383 (w), 1366 (w), 1348 (s), 1285 (w), 1263 (w), 1216 (m), 1166 (m), 1136 (m), 885 (w), 865 (w), 817 (m), 774 (m), 629 (w), 549 (w), 540 (w), 448 (w), 410 (w). $E_{1/2}$=0.62, 0.89, 1.04 V (versus Ag/AgCl, in 0.1 M $Bu_4N{\cdot}ClO_4$–PhCN solution, scanned 200 mV/s). Compound **18**: ESR (benzene) *g*=2.006, a_N=0.75 mT (2N). IR (KBr, cm^{-1}) 1548 (m), 1446 (w), 1419 (m), 1387 (s), 1367 (s), 1313 (m), 1216 (w), 1187 (m), 1134 (m), 768 (m), 617 (w), 540 (w), 448 (w). $E_{1/2}$=0.58, 0.89, 1.10 V (versus Ag/AgCl, in 0.1 M $Bu_4N{\cdot}ClO_4$–PhCN solution, scanned 200 mV/s).
17. As to the preparation of charge transfer complexes with amine-based radical donors, see: Sakurai, H.; Izuoka, A.; Sugawara, T. *Mol. Cryst. Liq. Cryst.* **1997**, *306*, 879, and references cited therein.