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New Synthesis of Phenyl-substituted 2,3-Dihydro-1,3-Dithiolo[4,5-e][1,4]Dithiin-6-Thione

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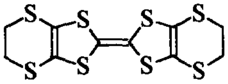
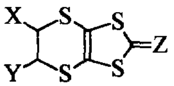
Abstract: The facile synthesis of **4** and (±)-**6** was carried out *via* a Diels-Alder type [2+4] cycloaddition reaction of oligomeric dien **8** with styrene or *t*-stilbene, respectively, as a dienophile by a thermal reaction and/or photoreaction. (±)-**6** crystallized as a racemic compound composed of **(2R,3R)** and **(2S,3S)** enantiomers. Copyright © 1996 Elsevier Science Ltd

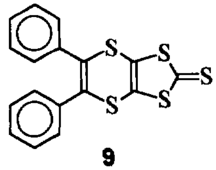
BEDT-TTF **1** is the most widely used electron-donor molecule for the synthesis of new organic metals and superconductors.[1] It can be synthesized by several methods, one of which is by self-coupling reaction of 2,3-dihydro-1,3-dithiolo[4,5-e][1,4]dithiin-6-thione **2** or 6-one **3**. To strengthen the interactions between the anions and the cations in radical salts of **1**, continuous efforts have been devoted to synthesize many derivatives of **1** and its precursors containing various peripheral groups.[1-11] As an example of the modification of **2**, an unsymmetrically substituted compound containing a phenyl group was reported,[2] and which was made by the well-known salt-elimination method using moisture sensitive Na_2dmit (dmit^{2-}: 4,5-dimercapto-1,3-dithiole-2-thione) and (±)-1,2-dibromoethylbenzene. This method has also been used to prepare derivatives of **2** which contain mono- or di-substituents on the ethylene moiety such as $-CH_3$,[3] $-COOCH_3$,[4] and -Ph.[2, 5-7] We use, however, a completely different synthetic pathway for **4** and **6**: a Diels-Alder type [2+4] cycloaddition of oligomeric dien, oligo(1,3-dithiol-2,4,5-trithione) **8**, with reactive dienophiles such as styrene and *t*-stilbene. This method is known to be an efficient synthetic pathway for new multisulfur precursors and a number of reports have recently appeared concerning derivatives of **2** and their corresponding self-coupled products which were prepared from dienophiles such as TTF[8-9], dimethyl acetylenedicarboxylate[10] and 1,4-dioxene.[11] Here, we report the facile syntheses of cycloadducts (**4** and **6**) and their oxo-compounds (**5** and **7**) along with the x-ray structure of **4** and **6**.



1

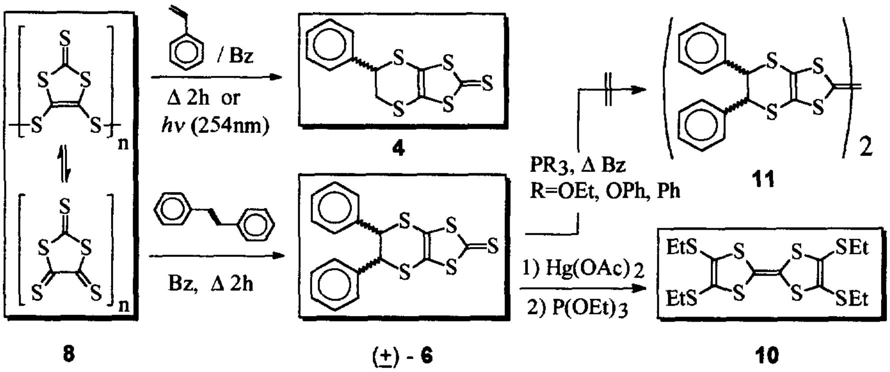


2 X = Y = H, Z = S
3 X = Y = H, Z = O
4 X = H, Y = Ph, Z = S
5 X = H, Y = Ph, Z = O
6 X = Y = Ph, Z = S
7 X = Y = Ph, Z = O



9

Oligomeric dien **8** was readily prepared by iodine oxidation of $[(n\text{-}C_4H_9)_4N]_2[Zn(dmit)_2]$ at room temperature.[8,12] **8** is believed to generate an active monomer by thermal depolymerization.(Scheme 1) Reaction of **8** with styrene or *t*-stilbene was also readily achieved by direct thermal reaction (refluxing) in benzene for 2h. After recrystallization from CH_2Cl_2/CH_3OH (1:1), products **4** and **6** were isolated as shiny yellow and orange crystals of plate form, respectively. They were identified by high- / low-resolution electron impact mass spectra (HR-/ LR-EIMS) and x-ray crystal structure analysis as well as other spectroscopic methods.[13-14] **4** could also be synthesized by photoreaction: Exposure of a benzene solution of **8** with excess styrene to UV light (254nm) affords **4** in very low yield (5% and 9% after 3h and 5h's exposure, respectively). It was confirmed by FT-IR and UV spectroscopic measurements that this product was identical with the compound made by the direct thermal method. As far as we are aware, it is the first cycloadduct synthesized by a photoreaction of **8**. This reaction opens up new possibilities of preparing various derivatives of **4** bearing functional groups on the phenyl substituent.



Scheme 1

Treatment of **8** with *t*-stilbene gives more interesting results on the stereospecific synthesis of (±)-**6**: Depending on the orientation of approach of **8** to planar *t*-stilbene (*exo* and *endo* approaches), two distinct products denoted as **(2R,3R)-6** and **(2S,3S)-6** could be expected with equal probability.[15] Actually, we obtained the racemic compound (±)-**6** in which equal amounts of enantiomers, **(2R,3R)-6** and **(2S,3S)-6**, crystallized together in a crystal. The packing diagram of the racemic compound (±)-**6** determined by x-ray analysis is shown in Fig. 1-b and compared with that of **4** (Fig. 1-a).[16] As shown in Fig.1-a, all the 2,3-dihydro-1,3-dithiolo[4,5-e][1,4]dithiin-6-thione moieties in **4** lie on the same plane and show a head-to-tail overlap with the neighboring molecule. As for (±)-**6** in Fig. 1-b, however, it has a completely different crystal packing from **4**. One **(2S,3S)** enantiomer is coupled and overlaps with a neighbor **(2R,3R)** and is mutually perpendicular to the other neighbor **(2R,3R)**, and *vice versa*. It is comparable to the recent report[6] where only the **(2R,3R)** enantiomer of **6** was synthesized by a salt-elimination method. Reactions of this type could provide a facile way to preparing various derivatives of **2** with a remarkable control of stereospecificity.

When **6** was refluxed with DDQ in benzene for 2 hours with the objective of preparing a totally unsaturated compound **9**, we observed no reaction to occur.

This Diels-Alder type cycloaddition is considered to be reversible because in the low-resolution mass spectra of **4** ~ **7**, the maximum peak(100%) appears at m/z=180 (**6** and **7**) and at m/z=104 (**4** and **5**) which can be attributted to *t*-stilbene (exact mass: 180.09) and styrene (exact mass: 104.06), respectively, produced by the reverse reaction. A similar reverse reaction was observed in the case of the reaction of TTF.[8] The oxo-compounds **5**[17] and **7**[18] were prepared according to the standard procedure[2] using $Hg(OAc)_2$ in $CHCl_3$.

Reactions of **6** or **7** with PR_3 (R = OEt, OPh, Ph) in benzene, toluene or xylene afford stilbene and unidentified low-molecular weight solid (probably the decomposition products) instead of the self-coupled product **11**. However, the reaction of **7** in neat refluxing $P(OEt)_3$ unexpectedly yields the TTF-derivative **10**[10,19]. Other methods to the self-coupled product **11** are currently under investigation.

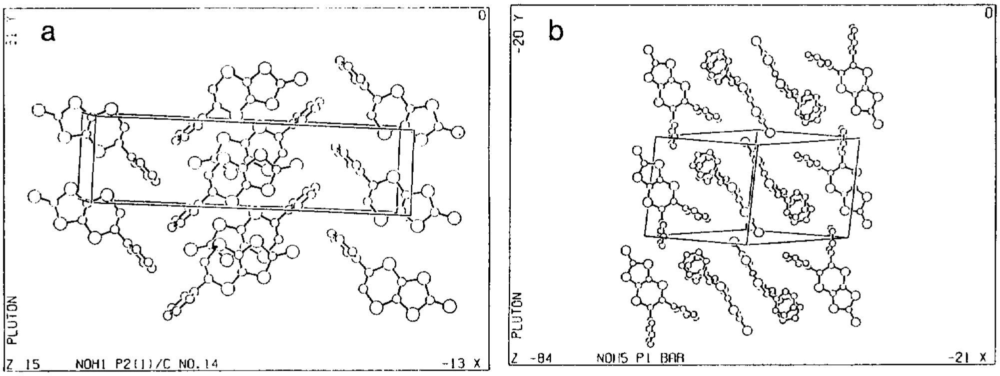


Fig.1. Crystal packing diagrams of (a) **4** and (b) (±)-**6**.

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12. Svenstrup, N.; Becher, J. *Synthesis*, **1995**, 215.
13. 2,3-dihydro-2-phenyl-1,3-dithiolo[4,5-e][1,4]dithiin-6-thione **4:** yield 57%; mp. 146 ~ 148°C; ^{1}H NMR (250MHz, $CDCl_3$) δ 7.4(5H, m), 4.7(1H, m), 3.55(2H, m); ^{13}C NMR(62.9MHz, $CDCl_3$) δ 208.210, 137.603, 129.314, 129.143, 127.618, 124.990, 121.784, 48.362, 35.725; FT-IR(KBr, cm^{-1}) 1063(C=S); UV(CH_3CN, nm) 216(st), 278(w), 410(m); HR-EIMS calc. for $C_{11}H_8S_5$ 299.9230, found 299.9251; LR-EIMS (m/z, %) 300(M^+, 100) 196(M^+-C_8H_8, 51),104(M^+-C_3S_5, 100).
14. (±)-2,3-dihydro-2,3-diphenyl-1,3-dithiolo[4,5-e][1,4]dithiin-6-thione (±)-**6:** yield 48%; mp. >180°C(dec.); ^{1}H NMR (250MHz, $CDCl_3$) δ 7.2(10H, m) 4.85(2H, m); ^{13}C NMR(62.9MHz, $CDCl_3$) δ 208.568, 135.916, 128.906, 128.712, 128.302, 125.920, 54.480; FT-IR(KBr, cm^{-1}) 1069(C=S); UV(CH_3CN, nm) 218(st) 276(w) 408(m); HR-EIMS calc. for $C_{17}H_{12}S_5$ 375.9543 found 375.9550; LR-EIMS (m/z, %) 376(M^+, 18) 180(M^+-C_3S_5, 100).
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16. Crystal data for **4**: $C_{11}H_8S_5$, FW = 300.47, monoclinic, space group P2(1)/c (No.14); a = 7.358(2)Å, b = 6.845(3)Å, c = 25.060(7)Å, β = 91.78(2)°, V = 1261.5(7)Å^3, Z = 4, D_c = 1.582g/cm^3.
    Full matrix least-squares refinement yields the final R value of 0.0739 (wR = 0.1874) for 1292 independent reflections [3.26°≤ 2θ ≤ 49.9°, I 〉 2σ(I)].
    Crystal data for (±)-**6**: $C_{34}H_{24}S_{10}$, FW = 753.13, triclinic, space group P$\bar{1}$ (No.2); a = 11.694(3)Å, b = 12.117(3)Å, c = 14.688(3)Å, α = 113.12(2)°, β = 102.23(2)°, γ = 107.02(2)°, V = 1699.1(7)Å^3, Z = 2, D_c = 1.472g/cm^3. Full matrix least-squares refinement yields the final R value of 0.0664 (wR = 0.1696) for 5963 independent reflections [3.24°≤ 2θ ≤ 50.02°, I 〉 2σ(I)].
    The crystal structures were determined by the direct method using SHELXS-86 and SHELXL-93, and measured on an Enraf-Nonius CAD-4 diffractometer at 293(2)K using graphite-monochromated molybdenum radiation (λ = 0.71073Å) and ω-2θ scan mode. Atomic coordinates and e.s.d.'s have been deposited at the Cambridge Crystallographic Data Center.
17. 2,3-dihydro-2-phenyl-1,3-dithiolo[4,5-e][1,4]dithiin-6-one **5:** yield 51%; mp. 104 ~ 105°C ^{1}H NMR(250 MHz, $CDCl_3$) δ 7.5(5H, m) 4.75(1H, m) 3.6(2H, m); ^{13}C NMR(62.9MHz, $CDCl_3$) δ 138.106, 129.237, 129.016, 127.578, 115.205, 112.192, 49.759, 37.043; FT-IR(KBr, cm^{-1}) 1624(C=O); UV(CH_3CN, nm) 218(st) 294(w); HR-EIMS calc. for $C_{11}H_8OS_4$ 283.9458 found 283.9500; LR-EIMS (m/z, %) 284(M^+, 46) 104(M^+-C_3S_5, 100).
18. 2,3-dihydro-2,3-diphenyl-1,3-dithiolo[4,5-e][1,4]dithiin-6-one **7:** yield 85%; mp. >190°C(dec.); ^{1}H NMR(250 MHz, $CDCl_3$) δ 7.2(10H, m) 4.8(2H, m); ^{13}C NMR(62.9MHz, $CDCl_3$) δ 136.399, 128.821, 128.578, 128.232, 116.398, 56.012; FT-IR(KBr, cm^{-1}) 1632(C=O); UV(CH_3CN, nm) 224(st) 294(w); HR-EIMS calc. for $C_{17}H_{12}OS_4$ 359.9771 found 359.9764; LR-EIMS (m/z, %) 360(M^+, 24) 180(M^+-C_3OS_4, 100).
19. Tetrathioethoxytetrathiafulvalene **10 :** yield 35%; ^{1}H NMR(250 MHz, $CDCl_3$) δ 2.9(8H, qr) 1.35(12H, t); HR-EIMS calc. for $C_{14}H_{20}S_8$ 443.9331 found 443.9337; LR-EIMS (m/z, %) 444(M^+, 100) 415(M^+-C_2H_5, 18) 382(M^+-SC_2H_5, 36).

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