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WEITZ-TYPE ORGANOSULFUR π-DONORS WITH A CUMULENIC BOND. VARIATION OF TERMINAL GROUPS AND CUMULENIC BOND IN BIS(THIOPYRANYLIDENE)ETHENE SYSTEM

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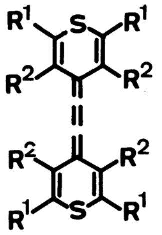
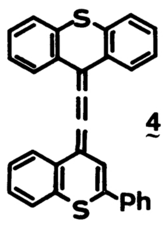
Unsymmetrical bis(thiopyranylidene)ethene (BTPE) derivatives (**4**) and (**5**) and an extended analogue of BTPE (**6**) have been prepared and their electrochemical properties are compared with those reported for the related compounds.

Recent synthetic efforts for Weitz-type[1] organosulfur π-donors such as tetrathiafulvalene (TTF) and $\Delta^{4,4'}$-bithiopyran (BTP) have provided various basic types of modifications on these π-donors. Symmetrical-,[2] unsymmetrical-,[3] condensed-,[4] and inserted-type[5] analogs have actually been investigated in order to modify the electron-donating properties of such systems. We have recently reported the preparation and the redox properties of the tetrabenzo **2**[6] and tetraphenyl derivatives **3**[5] of bis(thiopyranylidene)ethene (BTPE) (**1**) as a novel inserted type BTP by the versatile carbon-carbon bond formation using acetylide ions. The feature of the synthetic procedure makes it possible to prepare various derivatives of BTPE not only have symmetrical structure but also have unsymmetrical structure. We now describe the synthesis and redox properties of the hitherto unknown organosulfur π-donors, namely unsymmetrical BTPE derivatives, **4** and **5**, together with an extended analog **6** of BTPE.



1: $R^1=R^2=H$
2: R^1-$R^2=(CH)_4$
3: $R^1=Ph$, $R^2=H$



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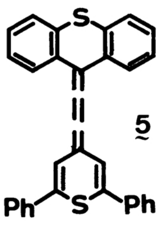

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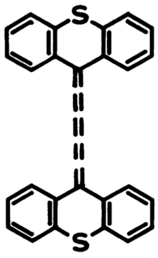

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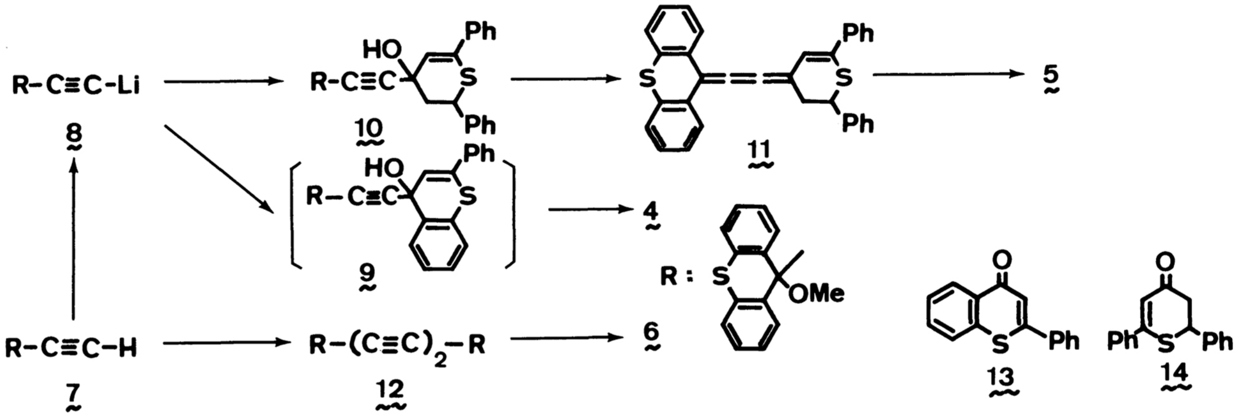
The tribenzo-phenyl-BTPE **4** was prepared in 13% yield based on **7**.[6] Thus, **7** was converted into its lithium salt **8** with butyllithium in THF, which was treated with 2-phenylthiochromanone (**13**)[7] to give the acetylene glycol monomethyl ether **9**. Treatment of the ethereal extract of **9**, without evaporation of the solvent, with tin(II) chloride dihydrate and hydrogen chloride saturated in ether at -70 °C provided **4** as green needles, m.p. 215 °C (dec.).

For the preparation of the dibenzo-diphenyl-BTPE **5**, the dihydrothiopyranone **14**[8] had to be used as a ketonic partner instead of 2,6-diphenylthiopyran-4-one due to the lack of its reactivity. Thus, **8** was treated with **14** to give the glycol **10** in 65% yield as a pale yellow solid, m.p. 64 °C (dec.). Reductive dehydroxylation of **10** into the cumulene **11**, green needles, m.p. 183 °C (dec.), was effected by tin(II) chloride/HCl in 96% yield, which was converted into **5**, green needles, m.p. 160 °C (dec.), with *p*-chloranil in refluxing dioxane for 20 min in 31% yield.

The oxidative coupling of **7** by cupric acetate in pyridine afforded the diyne glycol dimethyl ether **12** as faintly green needles in 81% yield. The conversion of **12** into the hexapentaene **6** was also achieved by the method used for the preparation of **4** and **11**, in 41% yield, m.p. 130 °C (dec.).[9]



The first and second oxidation potentials (E_1^{ox} and E_2^{ox}) and electronic spectral data of **4**, **5**, and **6** are summarized in Table 1 in which the corresponding data reported for **2**[6] and **3**[5] are also tabulated for ready comparison. In a series of organosulfur π-donors described in this paper, the effectiveness of these compounds as donor increases in the order **2** < **4** < **5** < **3**, which parallels the number of the annelated benzene rings, though qualitative as far as taking E_1^{ox} values into consideration. The feature clearly reflects the fact that the benz-annelation reduces the aromatic stability of the thiopyrylium ion moiety which is created in the oxidized forms of these donors.

Since a variety of thiopyranones are available and the ethynyl ethers are also readily prepared from either thiopyranones or dihydrothiopyranones, the method can be used to prepare many cumulene inserted-type BTP's.

Table 1. 1st and 2nd oxidation potentials (V vs. SCE)[a] and UV/VIS data of various BTPE's

Compound	E_1^{ox}	E_2^{ox}	UV/VIS (in CH_2Cl_2) λ_{max} nm (log ε)
(**2**)	0.65[b]	0.81[b]	262(4.88), 318(4.07),376(3.66), 550(4.70)
(**3**)	0.14	0.49	242(4.69), 258(s, 4.58), 284(s, 4.36), 553(4.99)
(**4**)	0.54	0.84	267(4.82), 326(4.16), 340(4.10), 380(3.73), 428(3.53), 566(4.79)
(**5**)	0.37	0.72	266(4.80), 324(4.15), 420(3.80), 564(4.78)
(**6**)	0.54	0.77	256(s, 4.72), 269(4,90), 320(s, 3.99), 334(4.11), 398(3.88) 452(s, 3.67), 580(s, 4.62), 630(5.06)

a) Measured by cyclic voltammetry in dichloromethane at -40 ~ -78 °C under nitrogen with added $(n\text{-}Bu)_4NClO_4$ (0.1 M) vs. SCE with a glassy carbon electrode as the working electrode. b) The first and second oxidation potentials for **2** are somewhat greater than those (0.4 and 0.6 V, respectively) previously reported in our paper, see ref. 6. This is mainly due to the difference in glassy carbon electrode used in this study which was deviced for the low temperature measurements.

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