Synthesis of a new Weitz-type Organosulphur π-Donor: 1,2-Bis(thioxanthen-9-ylidene)ethene

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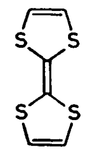
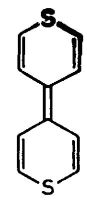
Summary The new organosulphur π-donor, 1,2-bis(thioxanthen-9-ylidene)ethene (**4**), which has high molecular symmetry, D_{2h}, a minimized Coulombic repulsion of electrons in the doubly ionized state, and a planar cross-conjugated π-system, has been synthesized by a two-step sequence in an overall yield of 70%.

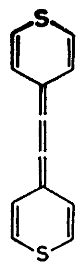
In order to design highly conducting, organic charge-transfer salts the synthesis of a new class of π-donors has been studied.[1] It is well known that tetrathiafulvalene (TTF) (**1**), $\Delta^{4,4'}$-bithiopyran (BTP) (**2**), and some of their derivatives are valuable π-donors in the preparation of organic charge-transfer salts with metallic properties.[2] The related diylidene-ethane analogues of TTF[3] and BTP[4] have also been synthesized recently. We studied the structural features of the organosulphur π-donor 1,2-bi^{5}-(4H-thiopyran-4-ylidene)ethene (**3**), which has promise as a component of conducting charge-transfer salts because of (i) the high molecular symmetry, D_{2h}, identical with TTF and BTP, (ii) a minimized Coulombic repulsion of electrons in the doubly ionized state, and (iii), in contrast with BTP, a high planarity with extended π-molecular orbitals due to the absence of steric hindrance between non-bonded hydrogens on both the heterocyclic rings.[5] Furthermore, compound (**3**) is regarded as a typical example of the Weitz-type two-stage redox system[6] in which two terminal π-systems are connected by cumulenic double bonds. We now report the synthesis of a tetrabenzo-annelated derivative of (**3**), 1,2-bis-(thioxanthen-9-ylidene)ethene (**4**).



(1)



(2)



(3)

The synthetic route is shown in the Scheme.† 9-Ethynyl-9-hydroxythioxanthene (**5**),[7] prepared in 95% yield by the reaction of thioxanthone with lithium acetylide in tetrahydrofuran (THF),[8] was converted into its lithium salt (butyl-lithium in THF and hexane at −78 °C) which was treated with thioxanthone to give the diol (**6**) as needles, m.p. 180 °C (decomp.), in 88% yield; *m/e* 450 (M^+); ν (Nujol)

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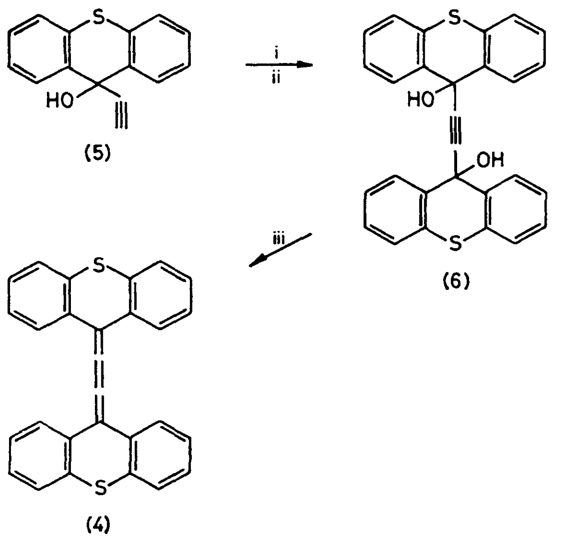
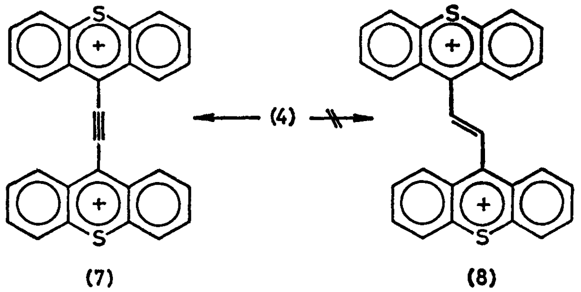
† Both compounds (**6**) and (**4**) gave satisfactory elemental analyses for C, H, and S.



SCHEME. *Reagents:* i, Bu^{n}Li, tetrahydrofuran–hexane, -78 °C; ii, thioxanthone, -40 °C; iii, SnCl$_2$, HCl–ether, -60 °C.

3350 cm^{-1} (OH). Reductive dehydroxylation of (**6**) with stannous chloride in ether saturated with hydrogen chloride gave the desired compound (**4**) as green needles with a metallic lustre, m.p. 233 °C (decomp.) from xylene, in 80% yield, *m/e* 416 (M^+); λ_{max} (CH$_2$Cl$_2$)550 (log ϵ 4·70), 376 (3·66), 318 (4·07), and 262 nm (4·88). The D_{2h} symmetrical structure of (**4**) was characterized on the basis of Raman and ^{1}H and ^{13}C n.m.r. spectroscopy: ν 2015 cm^{-1} (C=C=C=C); δ_H(100 MHz, CS$_2$ + CD$_2$Cl$_2$, Me$_4$Si as internal standard) 7·81—7·91 (4 H, m), and 7·18—7·31 (12 H, m); δ_C (22·5 MHz, CS$_2$ + CD$_2$Cl$_2$, Me$_4$Si as internal standard) 141 (C-11), 113 (C-9), 130, 131 (C-4a,-10a), and 128, 127, 126, and 125 (C-1, -2, -3, and -4) p.p.m.

Cyclic voltammetry of (**4**) at a glassy carbon electrode under nitrogen at -50 °C in dichloromethane showed two reversible one-electron oxidations at E_1 + 0·43 V (100 mV s^{-1} scan) and E_2 + 0·65 V.‡ This value of E_1 for (**4**) may be compared with those reported for HMTSF, TMTSF, and TSF (0·41, 0·44, and 0·44 V, respectively).[5] The ease of oxidation of (**4**) was shown by the reaction of (**4**) with concentrated sulphuric acid which gave the acetylenic dication (**7**) instead of the expected protonated dication (**8**). The formation of (**7**) is evident from the ^{13}C n.m.r. spectrum (in concentrated H$_2$SO$_4$) which showed an acetylenic carbon signal at δ_C 99·0 p.p.m.§ along with seven sp^2-C signals at δ_C 117·7, 120·2, 123·1, 123·3, 128·2, 134·6, and 137·8 p.p.m.



The cumulenic bond which connects the two thiopyran rings in (**3**) makes it possible to modify the structure of this unusual π-donor without producing steric hindrance, which is not the case for BTP (**2**). The synthesis of the 2,2′,6,6′-tetraphenyl derivative of (**3**) and studies of the physical properties of charge-transfer salts of (**4**) are now in progress.

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‡ Voltammograms of (4) in dichloromethane which contained Bu$^n_4$NClO$_4$ were recorded in atmospheric conditions and were irreversible. We thank Professor S. Misumi and Miss Nishikawa for their assistance in recording the cyclic voltammogram.

§ A resonance contribution, such as C=C=C$^+$–C$^+$, is a useful rationalization of the relatively low chemical shift of the acetylenic carbons.

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