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A NEW ELECTRON DONOR FOR CONDUCTING LANGMUIR–BLODGETT FILMS — STEAROYLMETHYLBIS(ETHYLENEDITHIO)TETRATHIAFULVALENE

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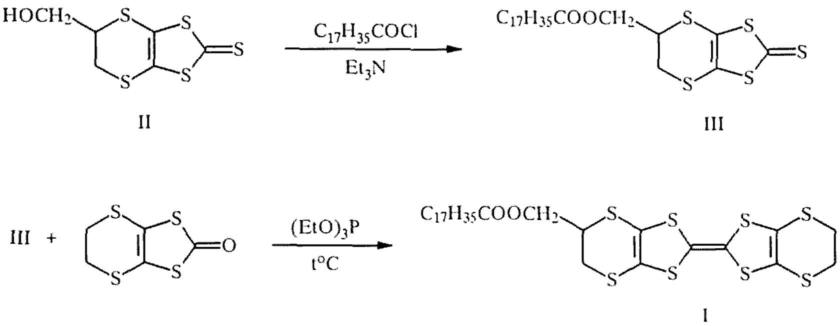
There is considerable interest in substances capable of forming electrically conducting Langmuir–Blodgett monomolecular layers. Hexadecylbis(ethylenedithio)tetrathiafulvalene [1] and other amphiphilic donors and acceptors [2] have been used successfully for this purpose. We have undertaken the synthesis of stearoylmethylbis(ethylenedithio)tetrathiafulvalene (I) as a further modification of the structure of tetrathiafulvalene derivatives.



Hydroxymethylethylenedithio-1,3-dithiol-2-thione (II) was prepared by a method we developed previously [3]. Stearoyloxymethylethylenedithio-1,3-dithiol-2-thione (III) was obtained by acylation of the hydroxymethylthione (II).

Compound I was prepared by cross-condensation of thione III and ethylenedithio-1,3-dithiol-2-one in the presence of triethyl phosphite, a method developed by Japanese workers for compounds of different structures [4]. A mixture of symmetrical derivatives of tetrathiafulvalene and I was obtained from which compound I was isolated as yellow-orange crystals by chromatography. Cyclic voltammetry in acetonitrile solution showed two reversible oxidation peaks at $E_1 = 0.7$ V and $E_2 = 0.87$ V (Ag/AgCl). Compound I formed conducting Langmuir–Blodgett films with excellent properties [5].

Hydroxymethyl-4,5-ethylenedithio-1,3-dithiol-2-thione (II, $C_6H_6OS_5$). $(C_3S_5)_x$ (11.8 g), allyl alcohol (20 ml) and benzene (30 ml) were boiled for 5 h, evaporated in vacuum, the residue extracted with boiling ethanol and recrystallised from ethanol to give 10.5 g (68%) of yellow crystals, m.p. 92-93°C. IR Spectrum: 3328 (OH), 1054, 1028, 1012 ($S_2C{=}S$), 920. ^1H NMR Spectrum (in $CDCl_3$): 1.88 (1H, t, OH), 3.32 (2H, d, CH_2S), 3.86 (3H, m. CHS, CH_2O).

Stearoyloxymethyl-4,5-ethylenedithio-1,3-dithiol-2-thione (II, $C_{24}H_{40}O_2S_5$). Stearoyl chloride, thione II and triethylamine (molar ratio 1:0.9:2) were boiled in anhydrous benzene for 4 h. After filtration and evaporation of the benzene, the residue was recrystallised from hexane to give III (80-89%), m.p. 48-50°C. IR Spectrum: 1736 (C=O), 1154, 1064 ($S_2C{=}S$), 720. ^1H NMR Spectrum (in $CDCl_3$): 0.85 (3H, t, CH_3), 1.25-1.75 (30H, m, CH_2), 2.33 (2H, t, CH_2CO), 3.25 (2H, m, CH_2S), 3.90 (1H, m, CHS), 4.32 (2H, d, CH_2O).

Stearoyloxymethylbis(ethylenedithio)tetrathiafulvalene (I, $C_{29}H_{44}O_2S_8$). Thione III (0.5 g, 0.96 mmol), ethylenedithio-1,3-dithiol-2-one (0.40 g, 1.92 mmol) and triethyl phosphite (5 ml) were heated for 2 h, at 110°C. After cooling the mixture was filtered off, dissolved in benzene (50 ml) and filtered. The solution was chromatographed on a silica gel column with 1:1 benzene–hexane as eluent. I was isolated (0.22 g, 33%), m.p. 86-88°C. ^1H NMR Spectrum (in $CDCl_3$): 0.83 (3H, t, CH_3), 1.20-1.75 (30H, m, CH_2), 2.26 (2H, t, CH_2CO), 3.14 (2H, m, CH_2S), 3.23 (4H, s, CH_2S), 3.48 (1H, m, CHS), 4.27 (2H, d, CH_2O).

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