Smectic and Nematic Derivatives of Tetrathiafulvalene (TTF) and their Charge Transfer Complexes with Mesomorphic Dithienes

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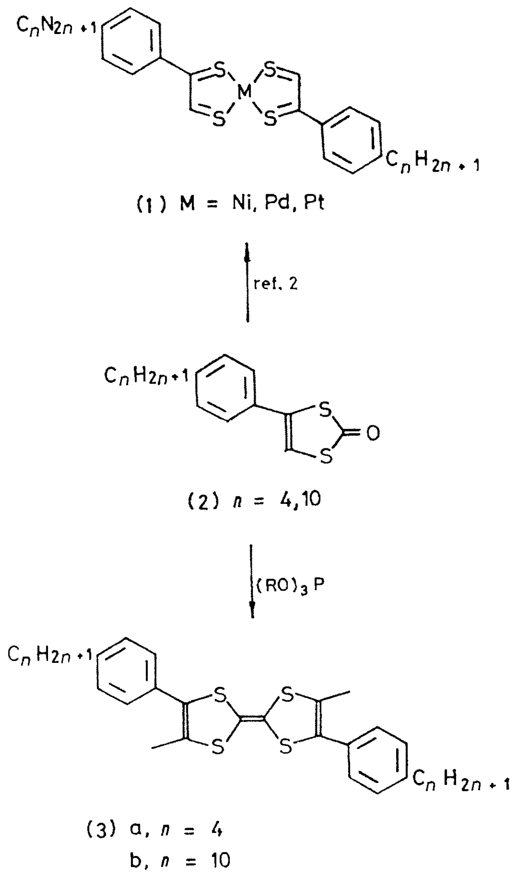
Summary The synthesis and characterization of a smectic and a nematic derivative of the strong electron donor tetrathiafulvalene are described which were found to form mixed crystals with the bis-styryl dithiolato metal complexes, which by themselves are smectic or nematic.

In the course of our investigations of mesomorphic transition metal complexes[1,2] of type (**1**), we have developed[2] a synthesis of these materials using the *p*-alkyl styryldithiocarbonates (**2**) as intermediates. Various ethylene dithiocarbonates have been used in previous syntheses of the strong electron donor tetrathiafulvalene (TTF) and of some of its derivatives.[3] This motivated us to attempt the synthesis of the substituted TTF derivatives (**3**), because we suspected that they might be mesomorphic. Such materials could be of interest in the design of mesomorphic charge transfer systems.

The simplest and most direct reaction to produce TTF derivatives from dithiocarbonates is the coupling by trialkyl phosphites, but this reaction seems to be ineffective in many cases.[4] The reaction of the dithiocarbonates (**2**) with triethyl phosphite in boiling toluene is indeed slow, but after reflux for 48 h the substituted TTF derivatives (**3**) can be isolated in modest yields (25—30%). After evaporation of the solvent and the excess of triethyl phosphite, the remaining oil can be brought to partial crystallization by the addition of methanol. The crude product is then purified by column chromatography (Al_2O_3 basic III with ether–hexane as the eluent) and recrystallization from hexane or acetone–methanol. From the Bu^n- and the n-$C_{10}H_{21}$-substituted styryl dithiocarbonates (**2**) we have obtained in this way the TTF derivatives (**3a**) and (**3b**) as orange crystals which were identified by their elemental analyses and ^{1}H n.m.r. spectra.

Although, in principle, both the *cis*- and the *trans*-isomers of (3) should be formed, we have not observed both isomers. In both the C_4 and the C_{10} case, we obtained products which appeared homogeneous. Of course, the conditions of the synthesis could well allow for isomerization to the thermodynamically more stable product to occur, which we assume to be the *trans*-isomer shown in formula (3).

The mesomorphic properties of the TTF derivatives (**3a**) and (**3b**) were investigated by hot stage polarized light microscopy. The compound (**3b**) with a C_{10} chain shows a transition at 102 °C to a smectic phase. Further heating produces no additional transitions, but at temperatures of 180 °C and above, the compound decomposes rapidly. The behaviour of the C_4–TTF (**3a**) is more complex: at 104 and 126 °C, there are transitions to uncharacterized phases, at 134 °C the material becomes nematic, and there is no further change up to 200 °C. It could be possible that *cis–trans* isomerizations play a role in the two undefined phase transitions.



(1) M = Ni, Pd, Pt

(2) *n* = 4,10

(3) a, *n* = 4
b, *n* = 10

The electron donor properties of the C_4– and C_{10}-TTF derivatives (**3a**) and (**3b**) are comparable with those of TTF itself. The oxidation potentials, determined by cyclic voltammetry,† are E_2° + 0·43 V and E_2° + 0·88 V for the C_4–TTF (**3a**) and E_1° + 0·43 V and E_2° + 0·89 V for the C_{10}-derivative (**3b**). The unsubstituted TTF has E_1° + 0·35 V and E_2° + 0·73 V. Knowing that the mesomorphic dithiene complexes (**1**) are weak electron acceptors [(**1**; *n* = 5, M = Ni) has E_1° = + 0·06 V, E_2° = − 0·76 V]† we have investigated the formation of charge transfer complexes between the donors (**3**) and the acceptors (**1**). Mixtures of the smectic C_{10}–Ni complex (**1**; *n* = 10, M = Ni) with the smectic TTF derivative (**3b**) were obtained in a variety of stoicheiometries. All these materials are smectic. We have looked especially at the mixture of the two nematic partners C_4–TTF (**3a**) and C_4–Ni (**1**; *n* = 4, M = Ni), because we supposed that the combination of nematic donors and nematic acceptors could lead, through enhanced intermolecular interactions, to smectic complexes. This we

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† Determined by Dr. A. Diaz of this laboratory. Potential E_1° and E_2° (on Pt *vs.* standard calomel electrode) are for CH_2Cl_2 solutions of compounds (**1**) and (**3**) and for a methanol solution of TTF.

have been unable to show, because the charge transfer interactions appear to be too weak to lead to stoicheiometric complexes. Depending upon the conditions of crystallization, mixtures of different composition were obtained, all of which were nematic. The ratio of C_4–TTF to C_4–Ni was determined by integration of the n.m.r. signals of solutions of these materials in $CDCl_3$ and varied between 0·5 and 0·9. The fact that we were able to obtain well resolved n.m.r. spectra of these complexes indicated that, at least in solution, the amount of charge transfer between (**1**) and (**3**) is negligible.

The reaction of the electron donor (**3b**) with the acceptor tetracyanoquinodimethane (TCNQ) offers an unusual example for the dominance of molecular shape over donor–acceptor interactions. Many cases are known, in which a donor–acceptor system shows less charge transfer in solution (where it is determined by the relative donor and acceptor strength of the solvated components) than in the solid. The TTF–TCNQ system itself has a strongly solvent-dependent charge transfer, which is always far less in solution than in the solid.[5] This situation is the norm, from which the pair (**3b**)–TCNQ deviates. In solution containing equimolar amounts of (**3b**) and TCNQ the deep green colour of the TCNQ radical anion indicates a considerable degree of charge transfer. However, from the green solution the orange-yellow donor and the yellow acceptor precipitate in separate crystals. Evidently, the extreme dissimilarity in shapes of the donor [(**3b**) has a length of over 40 Å] and the acceptor TCNQ does not allow the formation of mixed or charge transfer crystals with either a mixed stack or segregated stack arrangement.

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