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MESOMORPHIC PROPERTIES OF DI- (4 - ALKOXYPHENYL) AND DI- (4 - ALKANOYLOXYPHENYL) TETRATHIAFULVALENES

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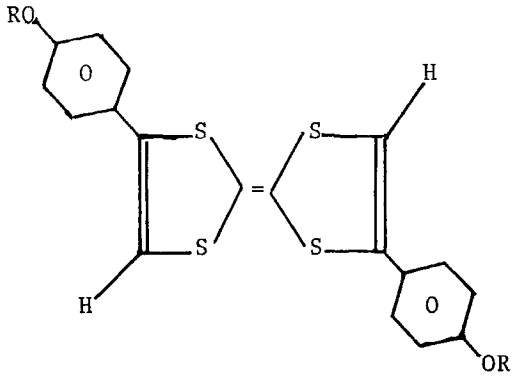
Abstract

The polymorphism of the di- (4 - alkoxyphenyl) and di- (4 - alkanoyloxyphenyl) tetrathiafulvalenes (TTF) is investigated. In the dialkoxy series, the short chain derivative exhibits a smectic G phase and a nematic phase. The latter phase disappears in the long chain derivative. The dialkanoyloxy derivatives exhibit a smectic G phase (for short chains) and a smectic C phase (for long chains). A plot of the mesormorphic-isotropic transition temperatures against the number of carbon atoms of the substituent shows the usual odd-even effect. Some tetra (alkoxyphenyl) tetrathiafulvalenes are described, unfortunately they have no mesomorphic properties.

Introduction

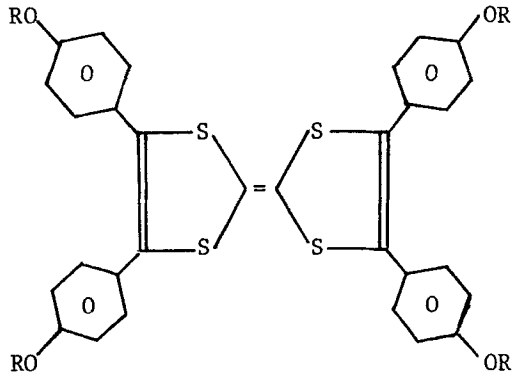
Recently Mueller-Westerhoff et al.[1] have reported that strong electron-donors such as di- (4 - alkylphenyl) tetrathiafulvalenes are mesomorphic. Moreover these substances can form mixed crystals with the bis-styryl dithiolato metal complexes[2]. On the other hand, Fugnitto et al.[3] have reported that the plate-like molecules of the 2,2',6,6'tetraaryl-bipyran - 4 - ylidenes exhibit a mesophase. This motivated us to synthesize the diaryl and tetraaryl tetrathiafulvalenes.

We have synthesized three homologues of the di- (4 - alkoxyphenyl) TTF (series 1), eight homologues of the di- (4 - alkanoyloxyphenyl) TTF (series 2) and three homologues of the tetra- (4 - alkoxyphenyl) TTF (series 3)



Series 1 : R = C_nH_{2n+1}

2 : R = C_nH_{2n+1} - CO -



Series 3 : R = C_nH_{2n+1}

Results and discussion

The polymorphism and transition temperatures of these compounds were determined by means of a polarizing microscope equipped with a heating and cooling stage (Mettler FP5) and a differential scanning calorimeter (Dupont 990). The results are listed in Table 1.

Table 1 : Transition temperatures (°C) of the compounds of the series 1 and 2.

R	K	S_G	S_C	N	I
C_4H_9	. 171	. 186	-	.	210 .
C_8H_{17}	. 146	. 156	. 172	-	.
$C_{10}H_{21}$	. 157	-	. 207	-	.
C_5H_{11} - CO -	. 186	. 195	-	-	.
C_6H_{13} - CO -	. 175	. 187	. 192	-	.
C_7H_{15} - CO -	. 174	. 182	. 214	-	.
C_8H_{17} - CO -	. 171	. 174	. 207	-	.
C_9H_{19} - CO -	. 165	. 169	. 205	-	.
$C_{10}H_{21}$ - CO -	. 162	-	. 198	-	.
$C_{11}H_{23}$ - CO -	. 160.5	-	. 200	-	.
$C_{12}H_{25}$ - CO -	. 157	-	. 194	-	.

K : crystal phase ; S_G, S_C : smectic G.C phases ; N : nematic phase ; I : isotropic phase ; . = the phase is observed ; - : the phase is not observed.

Optical texture observations

On cooling the isotropic phase of the butoxy derivative (1, R = C_4H_9) the nematic phase appears with a classical schlieren texture. One can observe the smectic C phase of the other derivatives either with a schlieren or a broken fan-shaped texture. The smectic G phase often occurs as a mosaic texture. The identification of the smectic phases S_G and S_C was carried out by the miscibility method.

Figure 1 shows that the two smectic phases of the di-(4 - octylphenyl) TTF, 4 (K 102 S_G 124 S_C 172 I) are completely miscible with the S_G and S_C phases of a reference substance : 4 - pentylbenzoyloxy - 4' - pentylstilbene 5 (K 100 S_G 118 S_F 120 S_C 136 N 228 I). These two smectic phases of 4 are miscible with those of 1 (R = C_8H_{17}) (Fig. 2). Finally figure 3 shows that the two smectic phases of 2 (R = C_9H_{19}- CO-) are also S_G and S_C phases.

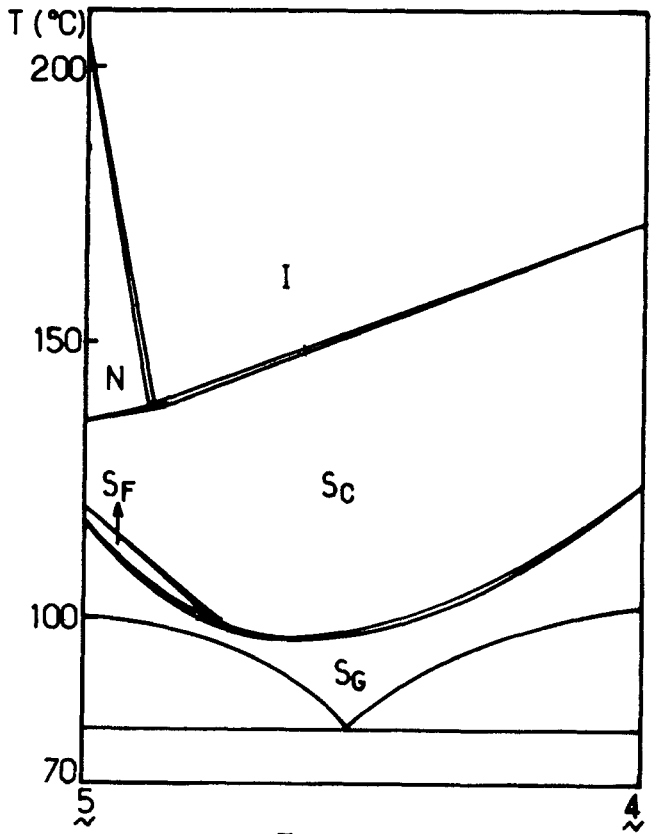


Fig 1

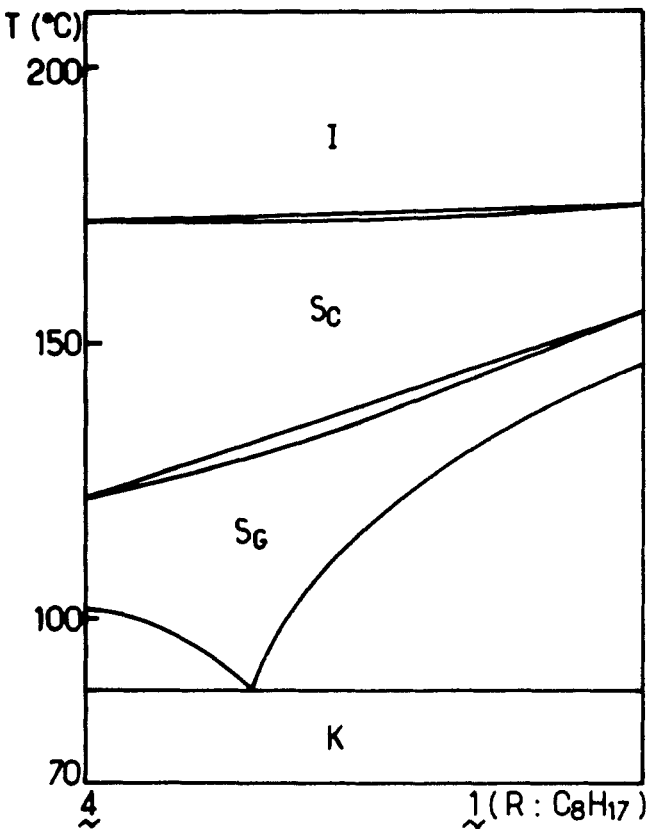


Fig 2

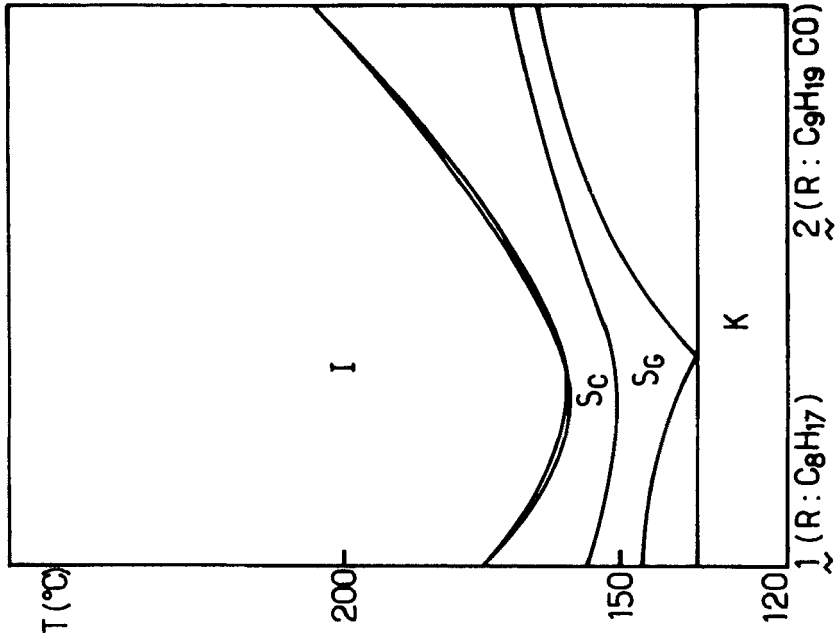


Fig 3

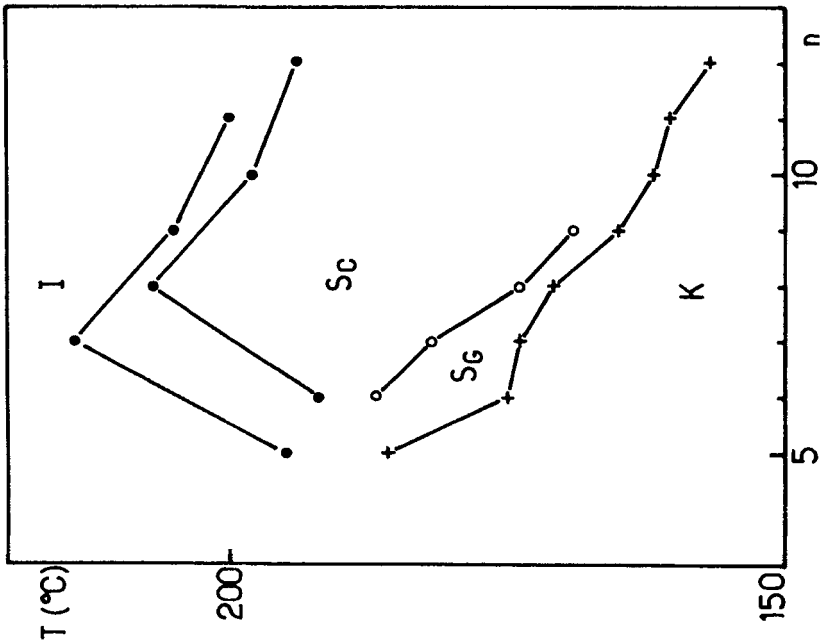


Fig 4

As seen from Table 1, the first derivative (1, R = C_4H_9) shows a nematic phase. This nematic phase is also observed with short chains in the two series of di- (4 - alkylphenyl) TTF[1] and of bis-styryldithiolato-metal complexes[2]. It is not observed with series 2 derivatives. In this series, one can observe the S_G phase for the short chains and S_C for the long chains. Elsewhere the odd-even effect in the clearing temperatures has also been observed (Fig. 4).

Three homologues of the series 3 have no mesomorphic properties and the transition temperatures are given below.

R	K		I
C_4H_9	.	172	.
C_8H_{17}	.	121	.
$C_{10}H_{21}$	.	127	.

We must point out that the striking mesomorphic character of this new central rigid core gives rise to the presence of very ordered mesomorphic phases. There seems to be a relation between this behaviour and the flat and rigid structure of the core. This consideration will stimulate the synthesis of other series with very flexible substituents in order to inhance the mesomorphic polymorphism.

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