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Liquid-crystalline behaviour of some bis(4-alkyloxyphenyl) thiazolo [5,4-d] dithiazoles

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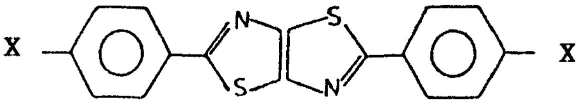
The preparation of liquid-crystalline 2,5-bis(4-alkyloxyphenyl) thiazolo [5,4-d] dithiazoles (ATT$_n$), in which the alkyl group is C_nH_{2n+1} (where $n = 1$ to 10, 12), has been described. Mesomorphic properties and phase transitions as determined by polarizing hot stage microscopy and differential scanning calorimetry are discussed as a function of the number of carbon atoms in the alkyloxy chain. The exhibition of tilted smectic phases (smectic C and smectic I) by these compounds is an interesting feature since there is no significant central dipole moment transverse to these molecules.

1. Introduction

The condensation of dithio-oxamide with aromatic aldehydes was first reported by Ephraim [1]. Johnson and Ketcham [2] later studied the reaction and identified the structure of the final product, the parent heterobicycle as thiazolo [5,4-d] dithiazole (I).



(I)

Subsequently, other workers [3–6] have reported the preparation of other simple as well as some more highly conjugated derivatives of 2,5-bisphenyl thiazolo [5,4-d] dithiazole. Fikrat and Oneto [4] have extended the scope and widened the applicability of the reaction to include systems with heterocyclic substituents such as pyridyl, quinolyl and indolyl. It has been pointed out [2, 5, 6] that some of the derivatives of (I) (X = halo, alkyl, or alkyloxy substituents) exhibit solid–liquid crystal transitions below the true melting points. Novel liquid-crystalline materials with a new type of rigid core, namely benzobisthiazole (BBT), have been recently synthesized by Kim *et al.* [7]. The purpose of our investigation has been to prepare a series of 2,5-bis(4-alkyloxyphenyl) thiazolo [5,4-d] dithiazoles (ATT$_n$) and to discuss their liquid-crystalline behaviour with respect to the alkyloxy chain length.

2. Experimental

2.1. *Synthesis of materials*

4-Alkyloxybenzaldehydes, $C_nH_{2n+1}OC_6H_4CHO$ ($n = 1$ to 10, 12) were synthesized [8] by adding a solution of 0·2 mol of 4-hydroxybenzaldehyde in 100 ml of methanol containing 0·2 mol of KOH to 0·24 mol of the appropriate alkyl bromide, $C_nH_{2n+1}Br$, in 30 ml of methanol and the mixture was heated under reflux with stirring for 20 h. The mixture was cooled, the organic layer was separated and washed successively with

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100 ml of saturated $NaHCO_3$ and 100 ml of H_2O. The organic layer was dried over anhydrous Na_2SO_4 and the solvent was removed on a rotary evaporator. The concentrate was applied to a silica gel column and the pure 4-alkyloxybenzaldehyde was eluted with diethyl ether and recovered as an oily liquid on removal of the solvent.

2,5-Bis(4-alkyloxyphenyl) thiazolo [5,4-d] dithiazoles (ATT_n) (in which the alkyl group is C_nH_{2n+1} and $n = 1$ to 10, 12) were synthesized by adding 50 mmol of the appropriate 4-alkyloxybenzaldehyde to 10 mmol of dithio-oxamide in 100 ml of *N*,*N*-dimethylformamide and the reaction mixture was heated under reflux with stirring for 3 h. The reaction mixture was cooled and the yellow crystalline product was collected by filtration. The crude product was washed with ethanol and recrystallized from chloroform. All the prepared dithiazoles (ATT_n) had satisfactory elemental analyses.

2.2. *Spectral, optical and thermal characterization*

IR spectra (KBr) were recorded on a Pye Unicam SP3-300 spectrometer. UV spectra were recorded on a Pye Unicam SP8-100 UV spectrophotometer. ^1H NMR spectra were recorded on a Bruker WH-90 spectrometer. The phase transitions were observed with a Leitz Laborlux 12 Pol in conjuction with a Leitz 350 hot stage and equipped with a Vario-Orthomat camera. Differential scanning calorimetry results were recorded at a scan rate of $10^\circ C\,min^{-1}$ with a Stanton Redcroft DSC 700 instrument.

2.3. *X-ray structure determination*

The data were measured on an Enraf–Nonius CAD4 diffractometer. The structure solution and refinement were done on a PDP 11/34 computer using the Enraf–Nonius structure determination package. 991 reflections were used in the refinement, which converged at $R = 0{\cdot}042$, $R' = 0{\cdot}045$.

3. Results and discussion

All ATT_n compounds exhibited intense IR absorptions at *c.* $1605\,cm^{-1}$ (C=C stretch) [9], $1500\,cm^{-1}$ (C=N cyclic, stretch) [10], and $1250\,cm^{-1}$ (C–O–C, stretch). A medium absorption was also recorded at $3050\,cm^{-1}$ (C=C–H unsaturated, stretch), $2930\,cm^{-1}$ (C–C–H saturated, stretch), 815–$850\,cm^{-1}$ (*p*-substituted aromatic ring) and $685\,cm^{-1}$ (C–S, stretch). The UV absorption spectra in chloroform of the ATT_n compounds were identical and contained two bands with λ_{max} at 372 nm ($\log \varepsilon = 4{\cdot}93$) and 240 nm ($\log \varepsilon = 4{\cdot}45$) (here ε is the molar extinction coefficient). The ^1H NMR spectral data for the ATT_n series of compounds show broadly similar spectral characteristics and the data for ATT_7 compound is representative of the series; δ ($CDCl_3$) 0·95(t, $J = 7{\cdot}0$ Hz, 6H, CH_3), 1·36 (m, 16 H), 1·84 (m, 4 H), 4·05 (t, $J = 7{\cdot}0$ Hz, 4 H, O–CH_2), 7·0 (d, $J = 8{\cdot}8$ Hz, 4 H) and 7·97 ppm (d, $J = 8{\cdot}8$ Hz, 4 H).

The DSC scans carried out on these compounds show transitions at temperatures which are in agreement with those obtained with optical microscopy. These transition temperatures are given in table 1. Among these compounds thermal reversibility was poor for the first two members of the series as they tend to decompose on heating close to the isotropic liquid. The DSC traces for the remaining compounds revealed well-behaved phase transitions (see figure 1) which were reproducible on subsequent heatings (see figure 2).

A plot of the transition temperatures versus the number of carbon atoms, *n*, in the alkyloxy chain for the ATT_n series of compounds is shown in figure 3. The plot shows typical mesomorphic trends. The nematic–isotropic transition temperature curve is a

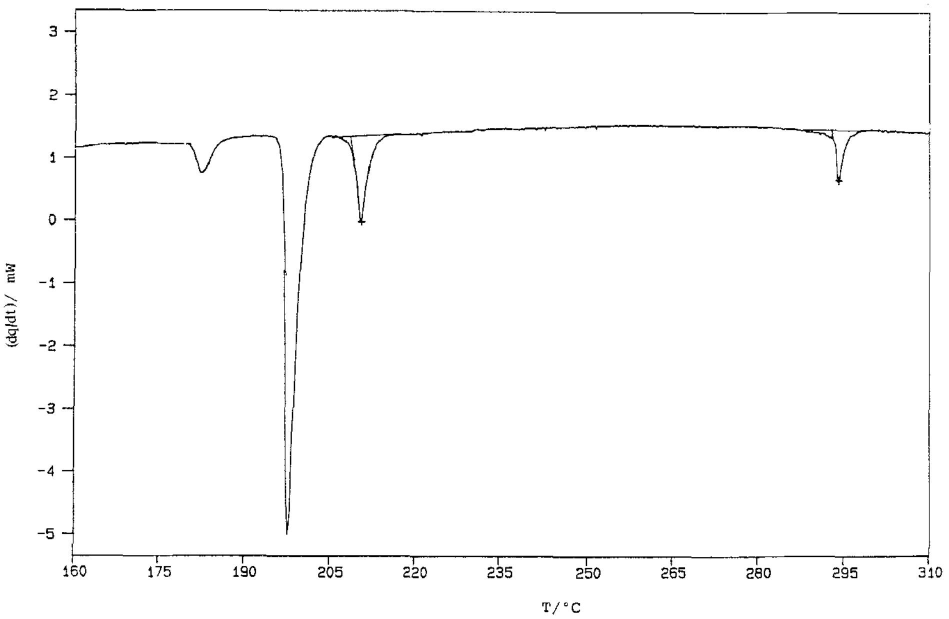

Figure 1. DSC trace for the ATT_4 compound.

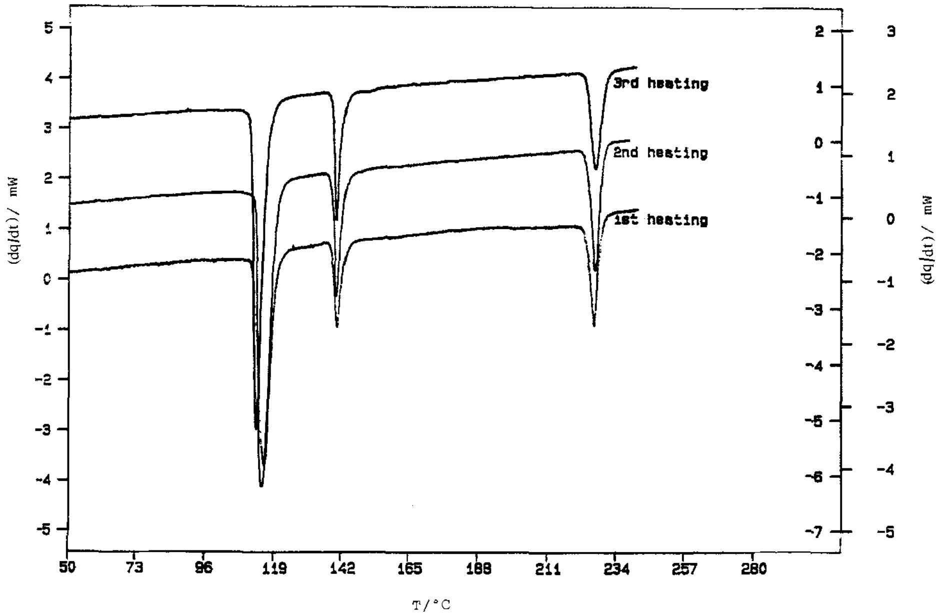

Figure 2. DSC traces showing the effect of subsequent heating operations on the same sample of the ATT_{10} compound.

Table 1. Transition temperatures (°C) for the ATT$_n$ series.

Compound	C_2	C_1	S_I	S_C	N	I
ATT$_1$					273·9	349·3
ATT$_2$					238·4	328·2
ATT$_3$					213·4	305·9
ATT$_4$		182·6		197·7	210·6	294·2
ATT$_5$	89·7	119·1	179·8	224·1		270·7
ATT$_6$		119·2	167·4	232·6		262·7
ATT$_7$		113·4	160·7	236·1		250·3
ATT$_8$		110·3	153·1	237·1		244·0
ATT$_9$		120·9	147·6			233·7
ATT$_{10}$		115·8	140·6			226·8
ATT$_{12}$		122·5	129·0			221·1

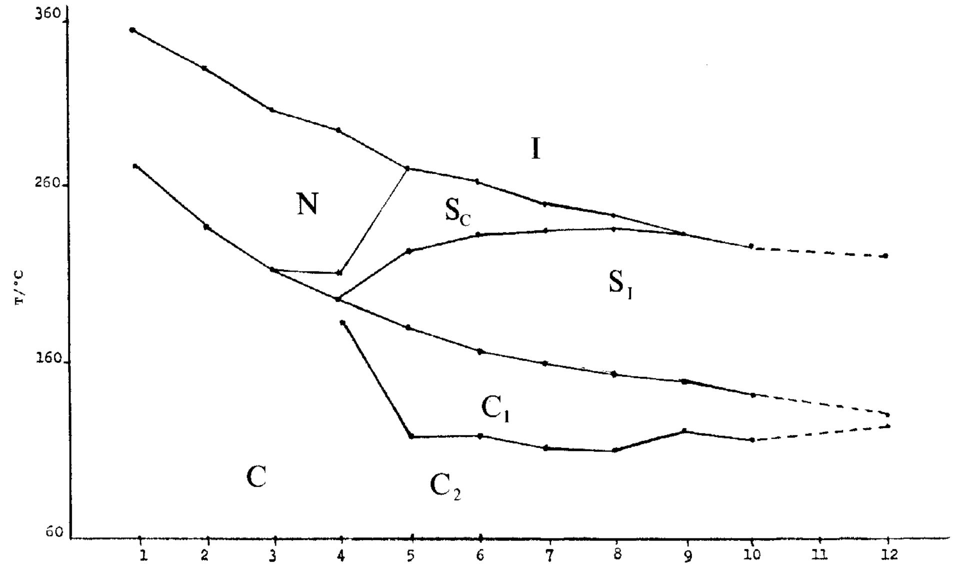

Figure 3. Transition temperatures as a function of alkyloxy chain length for the ATT$_n$ series.

falling one showing that at longer alkyloxy chain lengths, the nematic phase stability decreases with an increase in the smectic phase stability range. The smectic C phase appeared at $n=4$ while the nematic phase disappeared at $n=5$. The smectic C–isotopic transition curve is met at $n=9$ by a rising smectic I–smectic C curve at $n=5$ with elimination of the smectic C phase at $n=9$. The melting curve is a falling one with no indication through $n=12$ of a minimum or as to when the phase length of the smectic I would start to decrease. This is to be expected since longer flexible chains are needed to compensate for the long and rigid central core in this four ring system.

Microscopic studies of the textures exhibited by these materials show that schlieren and focal conic textures are displayed by these smectics. Schlieren textures are first observed when a smectic C or I phase is formed directly from cooling the isotropic liquid. These are sometimes followed by focal conic textures (see figures 4 and 5).

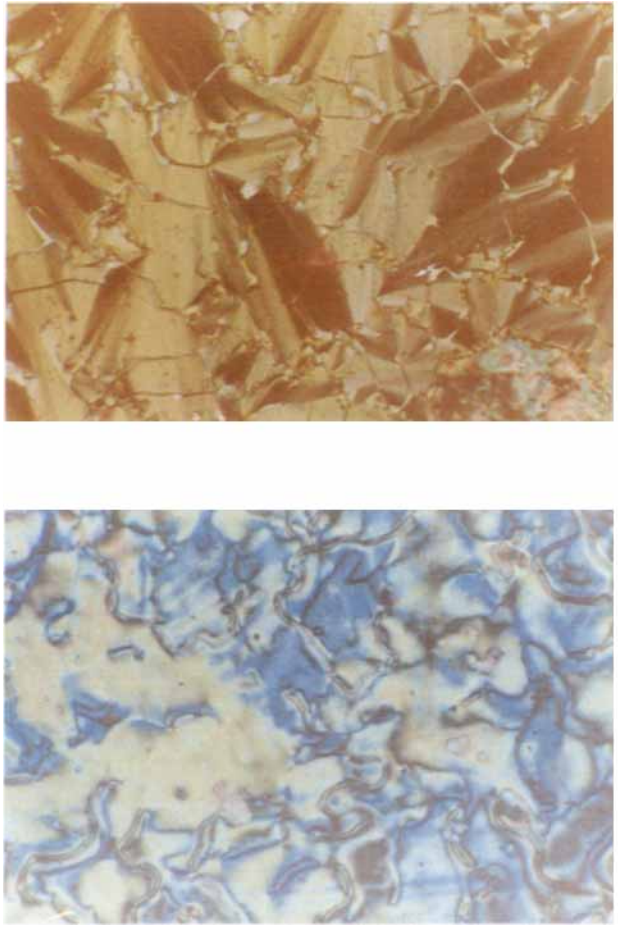

Figure 4. Top: fan texture of the smectic C phase of ATT_4 at 202°C (× 162). Bottom: smectic C schlieren texture for ATT_8 at 240°C (× 162).

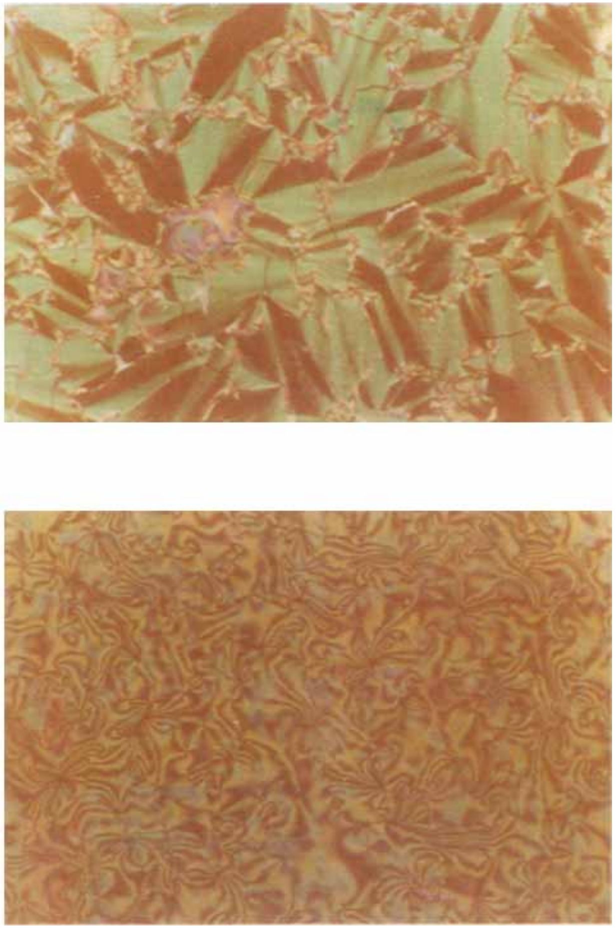

Figure 5. Top: fan texture of the smectic I phase of ATT_{10} at 145°C (× 162). Bottom: smectic I schlieren texture of ATT_{12} at 139°C (× 162).

Several crystal–crystal transformations appear on DSC traces but they were not observed by optical microscopy. Each of the compounds ($n = 4$–10, 12) exhibited one crystal–crystal transition with the exception of one homologue, $n = 5$, which displayed two crystal–crystal transformations. No such transformations were observed for the first three members, $n = 1$ to 3, of the series. Subsequent cooling and reheating cycles carried out on the same sample revealed slightly lower temperatures for these transitions (see figure 2). These transitions were not investigated further since we were primarily interested in mesomorphic transitions. The enthalpy and entropy values associated with these crystal-crystal transitions are presented in table 2. The enthalpy and entropy changes for the transitions in the ATT$_n$ series (see table 2) are plotted as a function of the carbon chain length in figures 6 and 7, respectively. When plotting the crystal–mesophase transition enthalpy and entropy of these compounds, the value used is the summed enthalpy and entropy of transition for all crystal forms detected. Previous workers [11–13] have cited the importance in using the summed entropy of transition for all the crystal forms which are stable between 0 K and the transition temperature when considering the entropy of the solid–mesophase transition. This point has been demonstrated for other transitions in organic compounds and is probably necessary in order to observe regular trends [14].

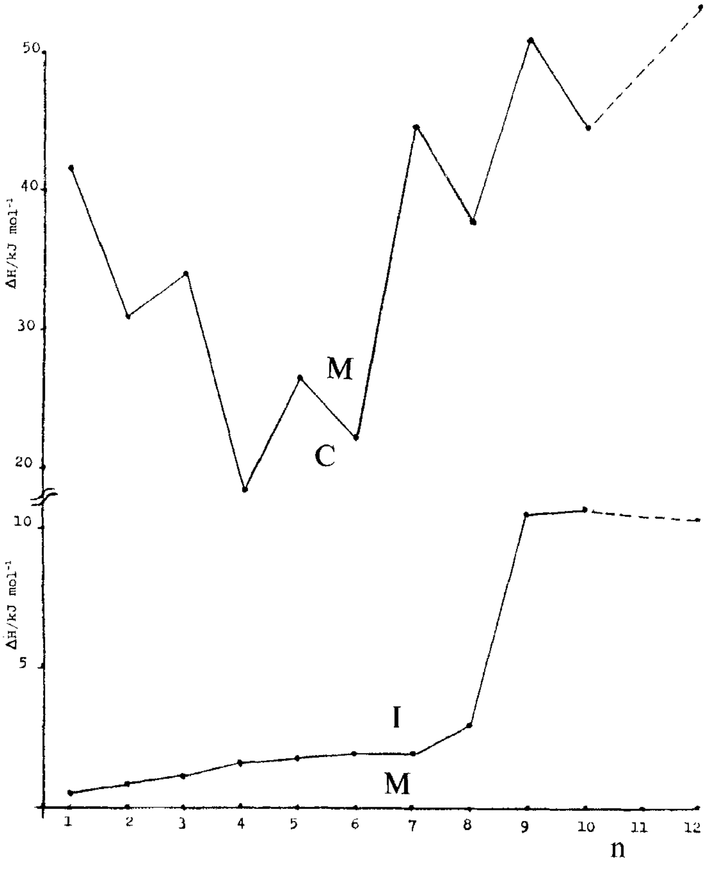

Figure 6. Enthalpy change for mesophase transitions as a function of alkyloxy chain length for the ATT$_n$ series.

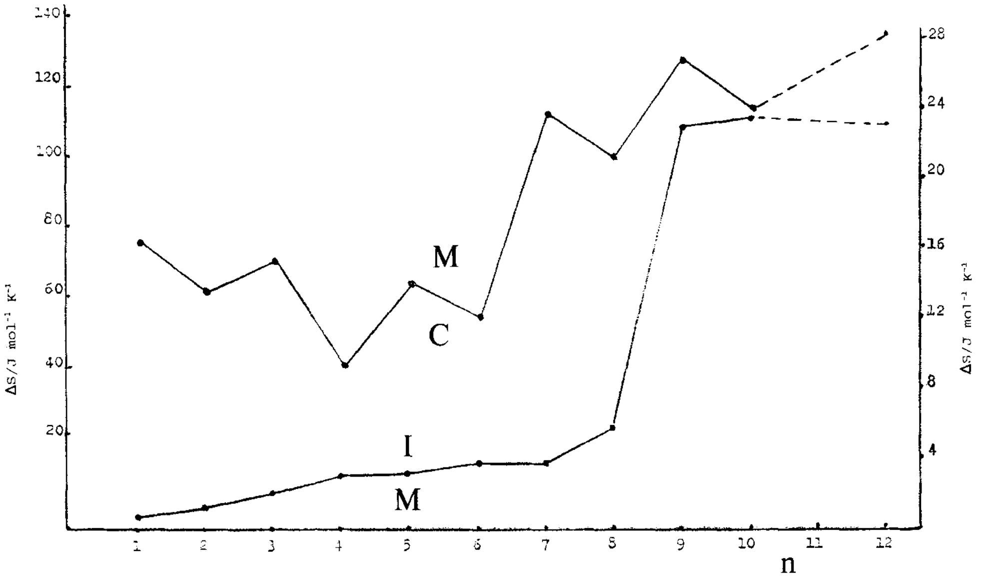

Figure 7. Entropy change for mesophase transitions as a function of alkyloxy chain length for the ATT$_n$ series.

Figures 6 and 7 show that there is an odd/even alternation in the total crystal–mesophase transition enthalpies and entropies when plotted as a function of the alkyloxy chain length. It has also been shown [15] that transition temperatures and, in some cases, heats of transition may lack correlation and demonstrate the importance in considering the change in entropy. However both ΔH and ΔS follow quite similar patterns in this series. For the crystal–nematic transitions, $n = 1$ to 3 only, the odd/even alternating behaviour has been explained by the increasing flexibility of the terminal chains found in mesophases with increasing chain length over that found in the crystalline phase. For the crystal–smectic transitions both enthalpy and entropy changes (starting at $n = 4$) increase considerably, with an odd/even alternation, as the alkyloxy chain increases. This implies that the intermolecular forces between the alkyloxy chains become increasingly important and that the chains play a more important role in the crystalline packing of the solid phase [16].

Plots of enthalpy changes (see figure 6) and entropy changes (see figure 7) for the mesophase to isotropic transitions as a function of alkyloxy chain length show relatively low values (the first two points are unreliable due to thermal decomposition) for the transitions to the isotropic liquid from the nematic phase, followed by a continuous increase when the transition occurs from the S_C phase and finally a sharp increase (at $n = 9$) when the transition occurs from a S_I phase at which point the curves then level off.

The assignment of the smectic I phase was based purely on optical microscopy study. Attempts to obtain suitable standards for miscibility studies to substantiate the assignment of the smectic I phase proved unsuccessful due to the particular chemical nature of the compounds.

The crystal and molecular structures, at room temperature, were solved for a single crystal (see figure 8) of the dimethyl derivative. Crystal data: $C_{18}H_{14}N_2S_2$, $M = 322{\cdot}6$, monoclinic space group $P2_1/c$, $a = 0{\cdot}9328(2)$, $b = 0{\cdot}6143(2)$, $c = 1{\cdot}3157(2)\,\mathrm{nm}$,

Table 2. Thermodynamic data for phase transitions in the ATT$_n$ series.

	C_1,	C_2	Total C–M		S_I–S_C		S_C–N		M–I	
Compound	Δ*H*/kJ mol^{-1}	Δ*S*/JK^{-1} mol^{-1}	Δ*H*/kJ mol^{-1}	Δ*S*/JK^{-1} mol^{-1}	Δ*H*/kJ mol^{-1}	Δ*S*/JK^{-1} mol^{-1}	Δ*H*/kJ mol^{-1}	Δ*S*/JK^{-1} mol^{-1}	Δ*H*/kJ mol^{-1}	Δ*S*/JK^{-1} mol^{-1}
ATT_1			41·77	76·3					0·36	0·59
ATT_2			30·86	60·4					0·76	1·28
ATT_3			33·97	69·9					1·15	1·99
ATT_4	1·75	3·83	19·15	40·8			3·45	7·12	1·62	2·86
ATT_5	4·98 4·69	12·91 12·91	26·52	63·0	5·43	10·93			1·74	3·19
ATT_6	8·60	21·93	22·27	53·0	4·83	9·54			2·09	3·89
ATT_7	32·52	84·02	44·68	112·1	6·24	12·27			2·05	3·85
ATT_8	29·26	76·38	37·88	98·9	8·47	16·60			3·01	5·83
ATT_9	41·43	105·15	51·19	128·3					11·64	22·95
ATT_{10}	35·62	91·55	44·68	113·5					11·88	23·77
ATT_{12}	46·60	117·67	53·56	135·0					11·49	23·25

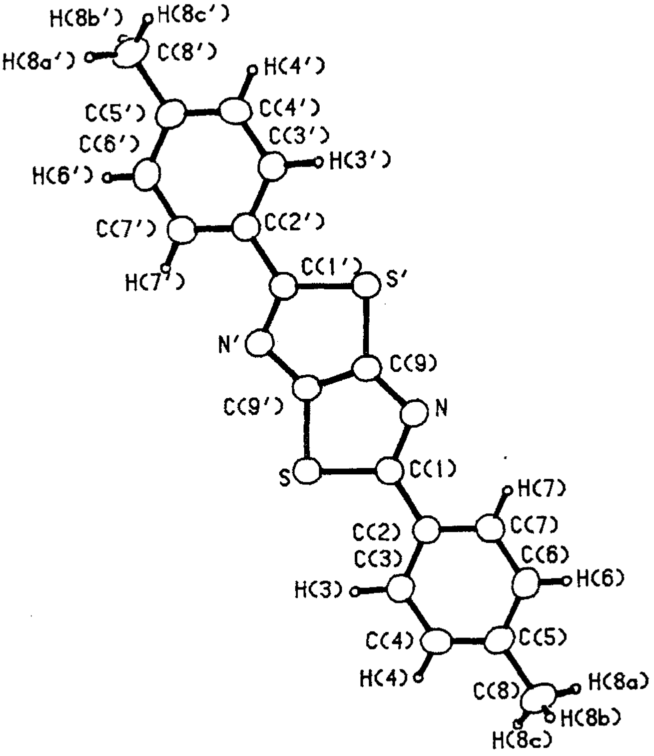

Figure 8. The molecular structure of 2,5-bis(4-methylphenyl) thiazolo [5, 4-d] dithiazole.

$\beta = 90{\cdot}5(2)^\circ$, $U = 0{\cdot}7539\,\mathrm{nm}^3$, $Z = 2$, $D_C = 1{\cdot}42\,\mathrm{g\,cm}^{-3}$, $\mu(\mathrm{Mo{-}K}_\alpha) = 3{\cdot}35\,\mathrm{cm}^{-1}$, crystal dimensions $= 0{\cdot}30 \times 0{\cdot}15 \times 0{\cdot}10\,\mathrm{mm}$.

The occurrence of the smectic C phase has been attributed to dipolar forces [17] or to molecular packing driven by zig-zag shaped molecules with a rigid core [18]. Recent work [7] on a system which incorporated a novel type of mesogenic core, BBT (a planar rigid core free of steric hindrance), was reported to exhibit the smectic C phase. It was argued [7] that compounds comprising the BBT core, which have no significant transverse central dipole moment, are reminiscent of square planar metal complexes as mesogenic cores in which bidentate coordination of ligands to a metal ion produces an anti-symmetry and leads to cancellation of the dipole moment. Compounds having such a metal complex in the rigid core and flexible alkoxy terminal groups have been recently reported [19, 20] to exhibit smectic C phases that are sensitive to the steric hindrance in the core. It seems, therefore, that the exhibition of tilted smectic phases by the ATT_n compounds (with a planar rigid core, free of steric hindrance and has no significant transverse central dipole moment), like the BBT system, is dictated by molecular geometry.

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