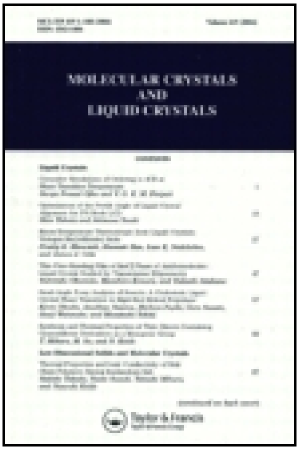

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Synthesis and Mesomorphic Properties of the 3,5-Bis-Alkoxyphenyl-Pyrazoles and-Isoxazoles

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Synthesis and Mesomorphic Properties of the 3,5-Bis-Alkoxyphenyl-Pyrazoles and -Isoxazoles

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The synthesis and measurement of physical properties using DSC, X-ray and optical methods are described for the 3,5-bis-(*p*-*n*-alkoxyphenyl)-pyrazole and 3,5-bis-(*p*-*n*-alkoxyphenyl)-isoxazole series with the carbon number of the *n*-alkylgroup from three to eight. The pyrazole series with longer *n*-alkylgroups ($n = 6$, 7, and 8) show the smectic A (*SmA*) as well as smectic C (*SmC*) phases. The corresponding isoxazole compounds show nematic (*N*) and also *SmA* phases. The compounds with shorter *n*-alkylgroups ($n = 3$, 4 and 5) show either nematic or *SmA* phases for both series respectively.

INTRODUCTION

β-diketones are suitable precursors for the formation of heteroaromatic systems. The introduction of an azole ring between two phenyl rings opens the possibility of generating new mesogenic units. Besides, the heteroatoms can cause considerable changes of polarity, polarisability and geometry of the molecules and influence the type and the phase transition temperature of the mesophases.

Recently, the X-ray investigation on 3,5-bis-(*p*-5-hexenyl-1-oxyphenyl)-isoxazole is performed. It is found that a *SmA* structure is formed probably due to the overlapping of the end C=C bonds and in nematic phase, the longitudinal correlation length is approximately two-times of the molecular length within four to five Kelvin above *SmA*-*N* phase transition.[1] So we have interest in the liquid crystal properties of new synthesized isoxazole and pyrazole series but without end C=C bonding.

SYNTHESIS

One well known synthetic way for the pyrazoles and isoxazoles is the reaction of β-diketones with hydrazine and hydroxylamine,[2,3] e.g., using 1,3-bis-(*p*-*n*-alkoxyphenyl)-propane-1,3-diones to obtain the corresponding compounds. The β-diketones were prepared according to Ohta et al.[4] by reacting methyl-*p*-*n*-alkoxybenzoates and *p*-*n*-alkoxyacetophenones in dimethyloxyethane with NaH as base.

The synthesis of pyrazoles and isoxazoles is carried out by refluxing the β-diketones with hydrazine hydrate and hydroxylamine hydrochloride respectively. This is illustrated in Figure 1.

The compounds were synthesized through the detailed procedures described below. The structural analysis of the compounds was confirmed by IR (Perkin-Elmer 237 and 577), ^{1}H-NMR (Varian T-60A), and ^{13}C-NMR (Varian CFT-20) spectra. As standard tetramethylsilane (TMS) is used by NMR. In Table I, the synthetic yields and the data of the elemental analysis are given for two series.

- 3,5-bis-(*p*-*n*-alkoxyphenyl)-pyrazoles (I)

  A mixture of 0.015 mol of 1,3-bis-(*p*-*n*-alkoxyphenyl)-propane-1,3-dione and 0.030 mol hydrazine hydrate (96%) in methanol (200 ml) was refluxed for 5 hours under stirring. The mixture was then cooled to room temperature, and the solid obtained was filtered and recrystallized from methanol.

  Spectroscopic Characterization:

  I.R. (KBr disk): cm^{-1}: 3230 (N—H), 1610 (C=N), 1580 (C=C).

  ^{1}H-NMR ($CDCl_3$, TMS): δppm = 6.56 (s, 1H, —CH= of pyrazole ring), 7.16 (AB quartet, 8H aromatic), 11.60 (s, 1H, N—H).

  ^{13}C-NMR ($CDCl_3$, TMS): δppm = 158.94 (s, C_3 and C_5 of pyrazole ring), 98.50 (d, —CH= of pyrazole ring).
- 3,5-bis-(*p*-*n*-alkoxyphenyl)-isoxazoles (II)

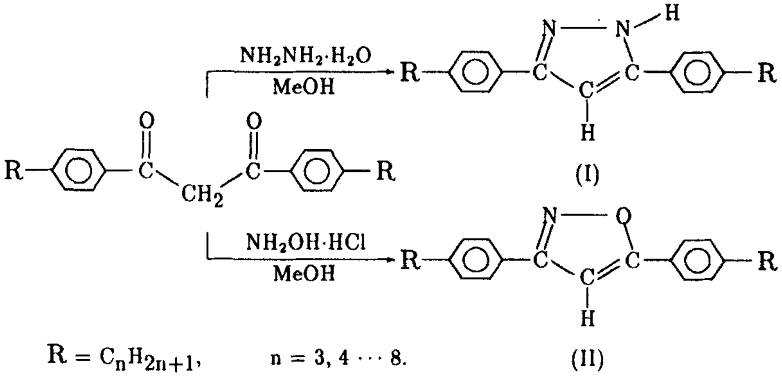

FIGURE 1 Synthetic scheme for pyrazoles and isoxazoles.

TABLE I

Synthesis yield and elemental analysis

Compound	Yield	C (%)		H(%)	
No.	%	Theor.	Exp.	Theor.	Exp.
I_3	82.0	74.97	74.84	7.19	7.56
I_4	94.5	75.59	75.81	7.74	7.83
I_5	89.0	76.49	76.24	8.22	8.42
I_6	92.5	77.10	76.75	8.63	9.00
I_7	91.5	77.63	77.44	8.99	9.30
I_8	94.3	78.10	77.81	9.30	9.38
II_3	76.1	74.75	74.89	6.87	7.12
II_4	96.0	75.59	75.08	7.45	7.39
II_5	87.5	76.30	76.18	7.94	7.49
II_6	90.5	76.92	76.81	8.37	7.97
II_7	84.3	77.46	77.84	8.74	9.03
II_8	94.0	77.94	78.05	9.07	9.22

I_3–I_8: pyrazoles with n-alkylgroup (n = 3, 4 ··· 8)

II_3–II_8: isoxazoles with n-alkylgroup (n = 3, 4 ··· 8)

A mixture of 0.015 mol of 1,3-di-(*p*-*n*-alkoxyphenyl)-propane-1,3-dione and 0.030 mol hydroxylamine hydrochloride in methanol (200 ml) was refluxed for 6 hours under stirring. The mixture was then cooled to room temperature. The solid obtained was filtered and recrystallized from methanol.

Spectroscopic Characterization:

I.R. (KBr disk): $\mathrm{cm^{-1}}$: 3120 (C—H of =CH—), 1620 (C=N), 1570 (C=C).
^{1}H-NMR ($CDCl_3$, TMS): δppm = 6.60 (s, 1H, —CH= of isoxazole ring).
^{13}C-NMR ($CDCl_3$, TMS): δppm = 170.10 (s. =C—O of isoxazole ring), 162.48 (d, —CH=N of isoxazole ring), 95.76 (d, —CH= of isoxazole ring).

PHYSICAL INVESTIGATION METHODS

The thermal behaviours of the compounds were identified using a DSC equipment (Perkin-Elmer DSC-2) calibrated with pure Indium (99.9%) and using polarizing microscope (Leitz Ortholux) in conjunction with a Mettler FP-52 hot stage.

X-ray diffraction patterns were recorded using a flatfilm camera with CuKα radiation. The samples were enclosed in 0.7 mm Lindemann capillaries within one oven with the temperature accuracy ± 0.5K. The exact data analysis along [001] direction for aligned compounds were performed by a focusing horizontal two-circle X-ray diffractometer (STOE STADI 2). The X-ray source is a long fine focus X-ray tube (SIEMENS FK) with a line focus of $0.4 \times 12\ \mathrm{mm}^2$. The CuK$\alpha$ radiation $\lambda = 1.54056$ Å is focused by a curved Ge(111)-monochromator. The mechanical and electrical controlled smallest stepwidth of the diffractometer in the 2θ and ω

circle is 0.001°. For the fast diffractometry a linear position sensitive detector (STOE Mini PSD) is used with a resolution of the stepwidth 0.01° in 2θ. By means of one differential temperature controller (Thor-PID) the temperature stability at the location of the sample in the range of 30°C to 250°C is better than 0.01K during the measurements. The detailed description of the X-ray set-up and the oven is given in our previous paper.[5,6]

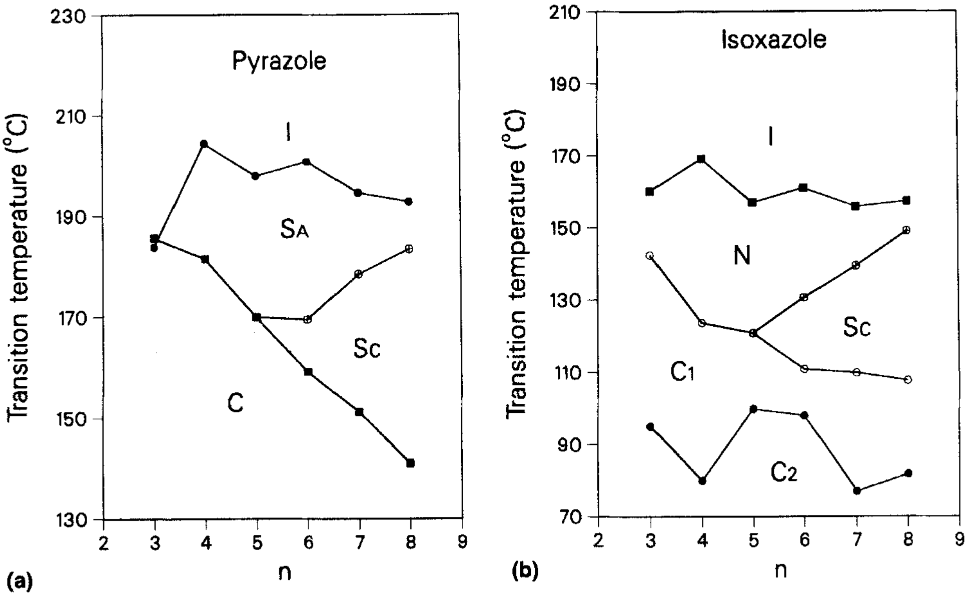

FIGURE 2 The phase transition temperature for a) pyrazole-series; b) isoxazole-series.

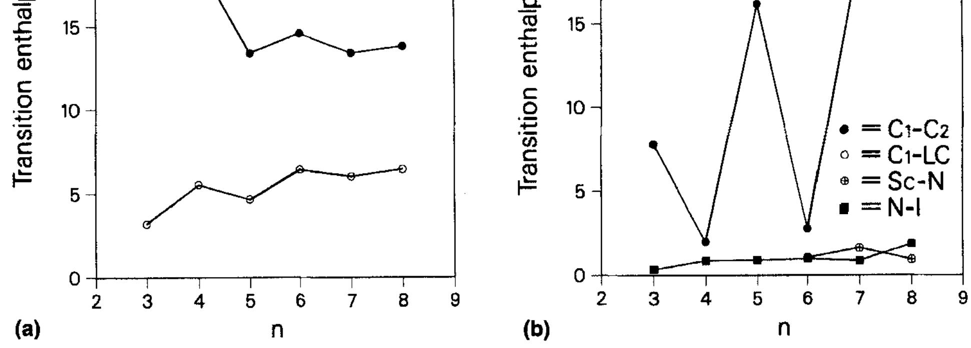

FIGURE 3 The phase transition enthalpies for a) pyrazole-series; b) isoxazole-series.

TABLE II

Phase transition temperatures (°C) and phase transition enthalpies (kJ · mol^{-1}) for pyrazole series

Compound		C		*SmC*		*SmA*		I
I_3	T/°C	·	185.6	–		·	(183.8)	·
	ΔH		25.1				3.22	
I_4	T/°C	·	181.5	–		·	204.0	·
	ΔH		18.9				5.55	
I_5	T/°C	·	170.0	–		·	198.0	·
	ΔH		13.4				4.68	
I_6	T/°C	·	159.2	·	169.5	·	200.8	·
	ΔH		14.6				6.44	
I_7	T/°C	·	151.2	·	178.5	·	194.6	·
	ΔH		13.4				6.02	
I_8	T/°C	·	141.0	·	183.4	·	192.8	·
	ΔH		13.8				6.44	

–: the phase is not observed.

TABLE III

Phase transition temperatures (°C) and phase transition enthalpies (kJ · mol^{-1}) for isoxazole series

Compound		C_1		C_2		*SmC*		*N*		I
II_3	T/°C	·	95.0	·	142.4	–		·	160.2	·
	ΔH		7.8		26.5				0.34	
II_4	T/°C	·	80.0	·	123.7	–		·	169.2	·
	ΔH		2.0		19.5				0.87	
II_5	T/°C	·	99.8	·	120.8	–		·	157.0	·
	ΔH		16.2		22.8				0.90	
II_6	T/°C	·	98.0	·	110.8	·	130.6	·	161.0	·
	ΔH		2.8		21.5		1.04		0.98	
II_7	T/°C	·	77.0	·	109.8	·	139.4	·	155.8	·
	ΔH		18.9		23.1		1.62		0.86	
II_8	T/°C	·	81.8	·	107.3	·	149.0	·	157.3	·
	ΔH		24.1		25.1		0.93		1.86	

–: the phase is not observed.

RESULTS AND DISCUSSIONS

The phase transition temperatures for the two series are plotted in Figure 2. For the compounds with longer *n*-alkylgroups (n = 6, 7 and 8), the *SmC* phase is

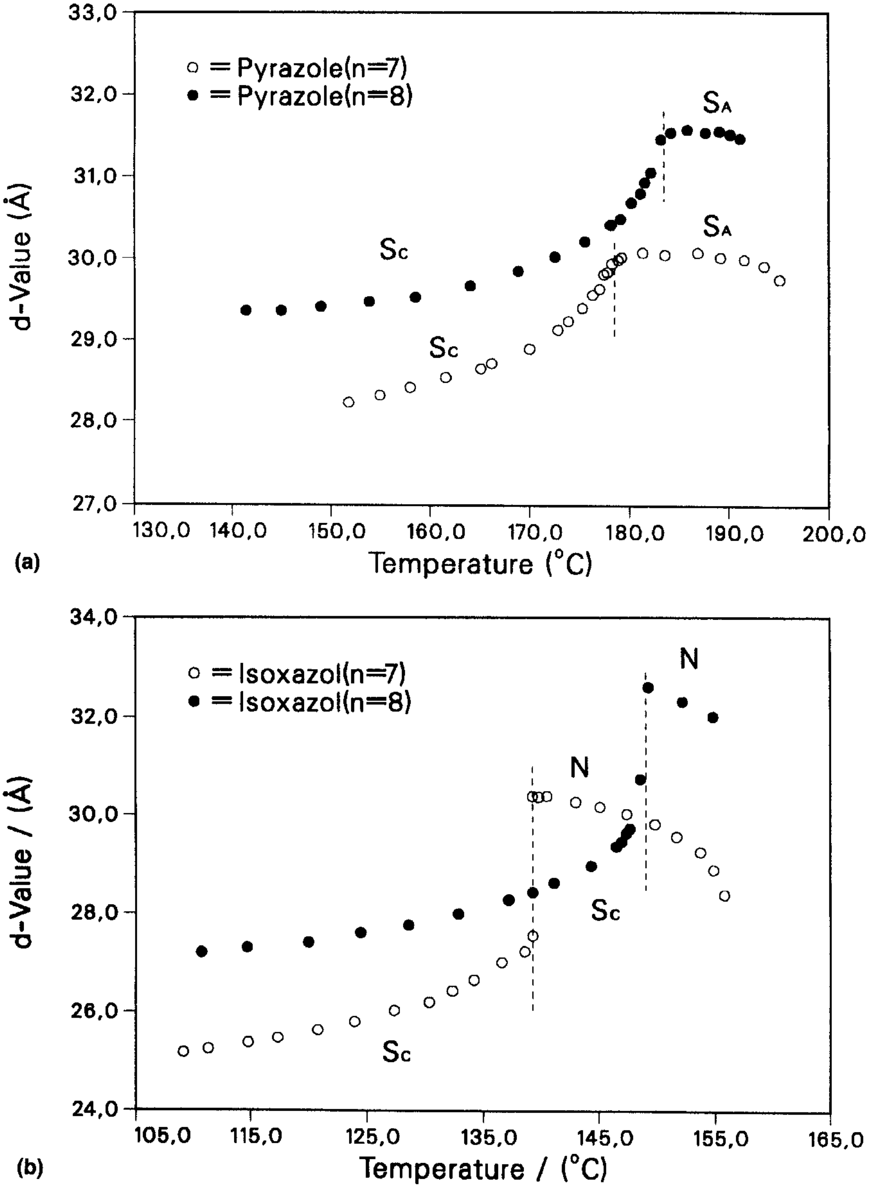

FIGURE 4 The *d*-value vs temperature for a) pyrazole series with $n = 7$ and 8 wing groups; b) isoxazole series with $n = 7$ and 8 wing groups.

observed for both series at low temperature while at high temperature the *SmA* phase for pyrazoles and the nematic phase for isoxazoles. The isoxazole series shows the focal conic textures in *SmA* phase and the typical schlieren texture in nematic phase by polarizing microscope. The pyrazole series shows the fan-shaped texture in *SmC* phase and the *SmC-SmA* phase transition can only be seen with careful microscopic observation. For the compounds with shorter *n*-alkyl groups

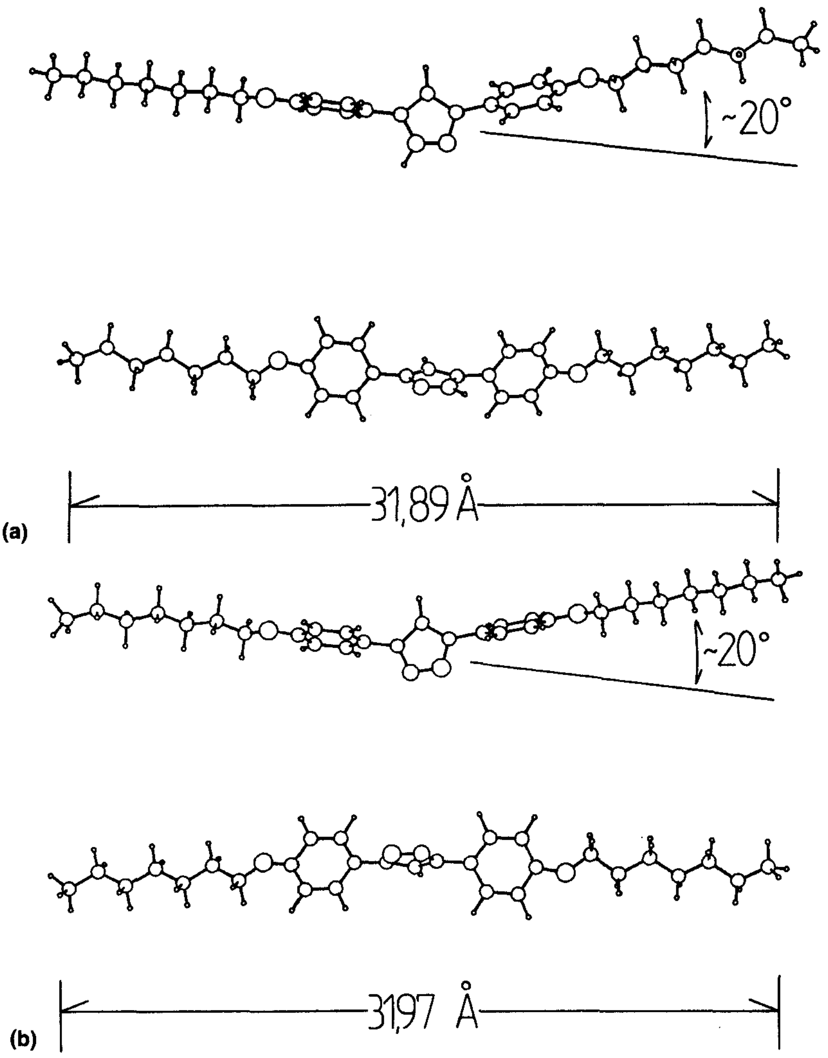

FIGURE 5 Simulated molecular configuration for a) pyrazole with heptyl wing group; b) isoxazole with heptyl wing group.

(*n* = 3, 4 and 5) only *SmA* or nematic phases are observed for pyrazole and isoxazole series respectively. The pyrazole with propyl group represents even a very short supercooled *SmA* phase. The odd-even effect is obviously observed for all two series at liquid crystal-isotropic phase transition.

The phase transition enthalpies for both series are given in Figure 3. In contrast to the *SmA-N* phase transition for isoxazole series, the *SmC-SmA* phase transition for pyrazole series can not be found by DSC measurements. It may concern a second order phase transition with small geometric change through the phase transition.

The exact data of the transition temperatures and the phase transition enthalpies are listed in Tables II and III.

The X-ray diffraction photography and diffractometry measurements confirm the results obtained by DSC and microscopic observation. For all compounds in smectic phases, the FWHM (Full Width at Half Maximum) varied from 0.02° to 0.06° in 2θ and in the nematic phase from 0.11° to 1.1° in 2θ. As examples, the d-values for both series with heptyl and octyl groups are plotted in Figure 4. In *SmC* phase, the *d*-value increases along the increasing temperature for both series. A discontinuity can be seen through the *SmC-N* phase transition by the isoxazole compounds. This characteristic behaviours can be certified by DSC measurements. By isoxazole with heptyl group, the coexistence of the *SmC* and nematic fluctuation of the microdomains is observed at the point of the *SmC-N* phase transition.

In contrast, the *SmC-SmA* phase transition for pyrazole series occurs as the phase transition temperature is approached and the structural change seems to be continuous (Figure 4a). This process has been reported by de Vries for the compound trans-1,4-cyclohexane-di-*n*-octyloxybenzoate.[7] It may also be the reason why the phase transition enthalpies can not be measured as mentioned above. In comparison with the longest *d*-value in *SmA*, the tilt angle in *SmC* phase, deviated from average director direction, amounts as a maximum near 20° for pyrazole.

We have simulated the molecular configuration using MNDO program.[8] Two examples are given in Figure 5, in which the molecules are plotted in view of the one phenyl ring or the middle ring with heteroatoms respectively. In comparison with the simulated molecular data, the thickness of the *SmA* layers or the *d*-values in the nematic phase are a little shorter. Looking at the molecular structure, the smectic phase may be stabilized by the mutual effect of the middle rings between the neighbouring molecules. As shown in Figure 2, by the homologous pyrazole series the temperatures of the mesophases are higher and narrower than the isoxazole series. It may have resulted from the H-atom of the middle azole ring attached to the N-atom which causes hydrogen bonding between the neighbouring molecules.

Acknowledgment

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