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Synthesis and Mesomorphic Properties of 3,5-bis-(p-n-Alkoxyphenyl)Isoxazole and 3,5-bis-(p-n-Alkoxyphenyl)Pyrazole

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Synthesis and Mesomorphic Properties of 3,5-bis-(*p-n*-Alkoxyphenyl)Isoxazole and 3,5-bis-(*p-n*-Alkoxyphenyl)Pyrazole

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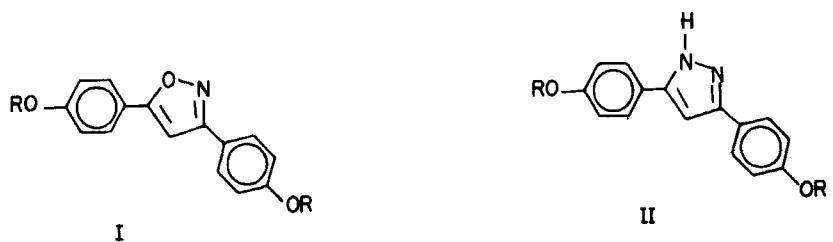
The synthesis and mesomorphic behavior of 3,5-bis-(*p-n*-alkoxyphenyl)isoxazole (series I) and 3,5-bis-(*p-n*-alkoxyphenyl)pyrazole (series II) are reported for the number of carbon atoms (*n*) in the alkoxy chains varying from three to eight. Series I shows an enantiotropic nematic phase for all *n* and an enantiotropic smectic phase for *n* ≥ 6. Series II shows one smectic phase SI for all *n* and an additional smectic phase SII for *n* ≥ 6. From optical and X-ray data, the smectic phase of series I is identified as smectic C and in series II the SI phase is classified as smectic A and SII as a smectic C with a temperature dependent tilt angle. The 1-methyl substituted pyrazole was prepared and did not show mesophases.

INTRODUCTION

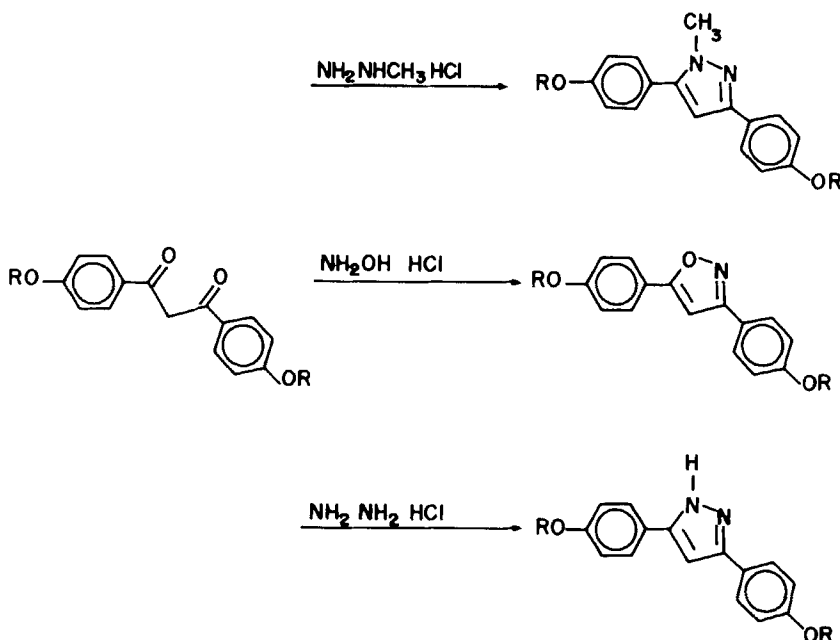
A relatively large number of mesomorphic compounds containing heterocyclic units have been synthesized and interest in such structures constantly grows.^{1,2} This is not only because of the greater possibilities with heterocyclic rings for the design of new mesogenic molecules, but also because the introduction of heteroatoms can cause considerable changes in polarity, polarizability and at times, the geometry of a molecule in relation to the geometry with phenyl rings.^{3,4} These can, greatly influence the types of mesophases which occur, the phase transition temperatures, and the dielectric and other properties of the mesogens. Continuing our investigations of compounds with heterocyclic rings,^{5,6} we have synthesized new, potentially mesogenic heterocyclic compounds derivatives of 3,5-bis-(*p-n*-alkoxyphenyl)isoxazole and 3,5-bis-(*p-n*-alkoxyphenyl)pyrazole, series I and II respectively.

SYNTHESIS

The β-diketones are suitable precursors for the formation of hetero-aromatic systems. The introduction of an azole ring as a link between two phenyl groups opens



Schematic 1



SCHEME I

the possibility of generating new mesogenic units. Thus, derivatives of isoxazole and pyrazole were obtained by reacting 1,3-di-(*p-n*-alkoxyphenyl)-propane-1,3-diones with hydrazine hydrate and hydroxylamine hydrochloride using standard methods.⁷ The synthesis of 3,5-bis-(*p-n*-alkoxyphenyl)isoxazole (series I) and 3,5-bis-(*p-n*-alkoxyphenyl)pyrazole (series II) was carried out according to Scheme I.

The β -diketones were prepared by using methyl *p-n*-alkoxybenzoates and *p-n*-alkoxyacetophenones in dimethoxyethane and NaH as base.⁸

All compounds were characterized by NMR ¹H, NMR ¹³C and IR (see experimental part). The yields and elemental analysis data for series I and II are given in Table III.

The one methyl substituted derivative of pyrazole, 3,5-di-(*p-n*-pentyloxyphenyl)-1-methylpyrazole, was also synthesized but did not show mesophases. However, the melting point was 39.5°C; considerably lower than the 170°C of the non-substituted pyrazole (Table III).

RESULTS AND DISCUSSION

The transition temperatures and transition heats were determined using a Perkin-Elmer DSC-2 calibrated with Indium and the transition temperatures checked using a Leitz Ortholux polarizing microscope with a Mettler FP 52 hot stage. The transition temperatures in all tables are those determined using the DSC. X-ray diffraction patterns using nickel filtered CuK_α radiation were recorded using a flat plate camera with the sample in 0.7 mm Lindemann capillaries in a oven controlled to within 1°C .

The thermal properties for series I and II are summarized in Tables I and II and the transition temperatures as a function of the number of carbon atoms in the alkoxy chains are shown in Figures 1 and 2. The melting points of the pyrazole compounds are quite different from those of the analogous isoxazole compounds, being on the order of 40 to 50 degrees higher. Also the mesophases shown by the two series are quite different. The derivatives of isoxazole have only an enantiotropic nematic phases up to $n = 5$ and starting at $n = 6$, an enantiotropic smectic phase also appears. The derivatives of pyrazole exhibit only one smectic phase SI up to $n = 5$ and at $n = 6$ a second smectic phase SII appears.

The textures occurring in the higher temperature phase of the isoxazole derivatives are Schlieren, threaded or homeotropic and the behavior at the transition to the isotropic phase is characteristic of the nematic phase. The SI phase presents a focal-conic or Schlieren texture and the transition texture at the smectic-nematic transition is that characteristic of a nematic-smectic C transition. The X-ray dif-

TABLE I
Transition Temperatures ($^\circ\text{C}$) (a) and (b) enthalpies ($J \text{ mole}^{-1}$) of
3,5-bis-(*p*-*n*-alkoxyphenyl)isoxazole, Series I

<i>n</i>	K	K'	SI	N	I
3I a)	95.0	142.4	-	160.2	.
b)	7.8	26.5		0.34	
4I a)	80.0	123.7	-	169.2	.
b)	2.0	19.5		0.9	
5I a)	99.8	120.8	-	157.0	.
b)	16.2	22.8		0.9	
6I a)	98.0	110.8	134.6	161.0	.
b)	2.8	21.5	1.0	0.98	
7I a)	77.0	109.8	139.4	155.8	.
b)	18.9	23.1	1.6	0.86	
8I a)	81.8	107.3	149.0	157.3	.
b)	24.1	25.1	0.9	1.9	

K and K' are crystalline phases.

TABLE II
Transition Temperatures (°C) (a) and (b) enthalpies (*J mole*⁻¹) of
3,5-bis-(*p-n*-alkoxyphenyl)pyrazole, Series II

n		K	SII	SI	I
3II	a)	. 185.6	-	. (183.8)	.
	b)	25.1		3.2	
4II	a)	. 181.5	-	. 204.0	.
	b)	18.9		5.6	
5II	a)	. 170.0	-	. 198.0	.
	b)	13.4		4.7	
6II	a)	. 159.2	. 169.5	. 200.8	.
	b)	14.6	*	6.4	
7II	a)	. 151.2	. 177.7	. 194.6	.
	b)	13.4	*	6.0	
8II	a)	. 141.0	. 183.4	. 192.8	.
	b)	13.8	*	6.4	

Values in parenthesis indicate monotropic transitions *, enthalpies too small to measure.

TABLE III
Yields and elemental analyses of series I, 3,5-bis-(*p-n*-alkoxyphenyl)isoxazole. and series II,
3,5-bis-(*p-n*-alkoxyphenyl)pyrazole

Compound.	Yield	C(%)		H(%)	
		Required	Found	Required	Found
3I	76.1	74.75	74.89	6.87	7.12
4I	96.0	75.59	75.08	7.45	7.39
5I	87.5	76.30	76.18	7.94	7.49
6I	90.5	76.92	76.81	8.37	7.97
7I	84.3	77.46	77.84	8.74	9.03
8I	94.0	77.94	78.05	9.07	9.22
3II	82.0	74.97	74.84	7.19	7.56
4II	94.5	75.59	75.81	7.74	7.83
5II	89.0	76.49	76.24	8.22	8.42
6II	92.5	77.10	76.75	8.63	9.00
7II	91.5	77.63	77.44	8.99	9.30
8II	94.2	78.10	77.81	9.30	9.38

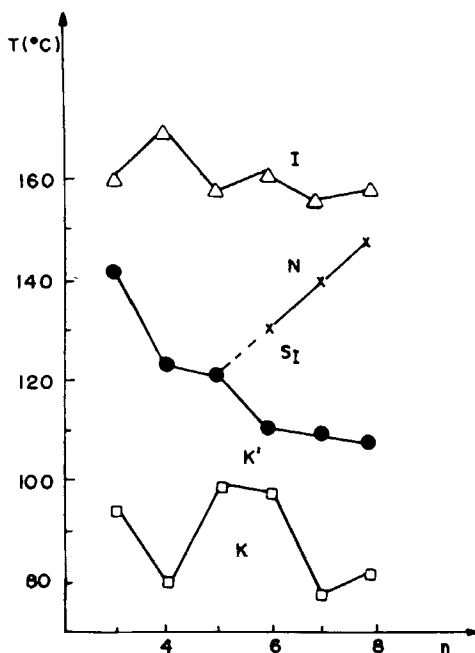


FIGURE 1 Transition temperatures for 3,5-bis-(*p*-*n*-alkoxyphenyl)isoxazole as a function of (n) the number of carbon atoms in the alkoxy chain.

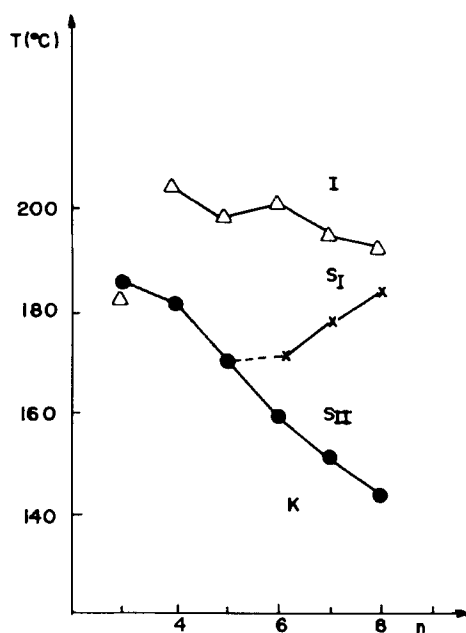


FIGURE 2 Transition temperatures of 3,5-bis-(*p*-*n*-alkoxyphenyl)pyrazole as a function of (n) the number of carbon atoms in the alkoxy chain.

fraction pattern in the smectic phase shows only one sharp peak at small angles. For example, compound 7I shows a peak that corresponds to a distance of 24.7 ± 2.0 Å, using Bragg's Law. The length of the molecule was calculated to be 29.5 Å for the most extended conformation using standard bond lengths. This clearly indicates that the smectic phase is non-orthogonal and that the molecular axis is inclined to the smectic layers by an angle of the order of 30 degrees. Considering the optical and X-ray results, we feel there is little doubt that the smectic phase of the isoxazole derivatives is a smectic C phase.

The texture of phase SI of the pyrazole derivatives is focal-conic or homeotropic with a very strong tendency for the occurrence of the homeotropic texture. The texture of phase SII was Schlieren or focal-conic and it was possible to obtain areas of uniform alignment sufficiently large for conoscopic observations in the SII phase. SI gives a centered positive uniaxial cross and at the transition to the SII, the phase becomes biaxial with the acute bisectrix of the interference figure inclining rapidly with respect to the microscope axis with decrease of temperature. The X-ray diffraction pattern in both phases shows only one sharp peak at small angles. The angular position of the peak is constant in SI and varies with temperature in SII. Figure 3 shows the variation of the layer thickness as a function of temperature, using Bragg's Law, for compound 7II. The length of the fully extended molecule was calculated to be 29.5 Å. The transition enthalpy at the SI-SII transition was too small to be accurately determined using the DSC. The optical and X-ray data clearly indicate that SI should be classified as a smectic A and SII as a smectic C phase with a temperature dependent tilt angle.

As can be seen from Schematic 1, apparently, the molecular structures of Series I and II are far from being those of a linear rod and one can ask why these compounds are mesomorphic. The Chem3D program was used on a Macintosh Classic to minimize the conformation energy of 3,5-bis-(*p*-*n*-pentyoxyphenyl)pyrazole and the result is shown in Figure 4. The geometry is much more linear than one would be lead to believe by Schematic 1. The 2,5-diaril substitution in the isoxazole and pyrazole compounds introduces a small deviation from linearity and does not inhibit the formation of mesophases. On the other hand, the deriv-

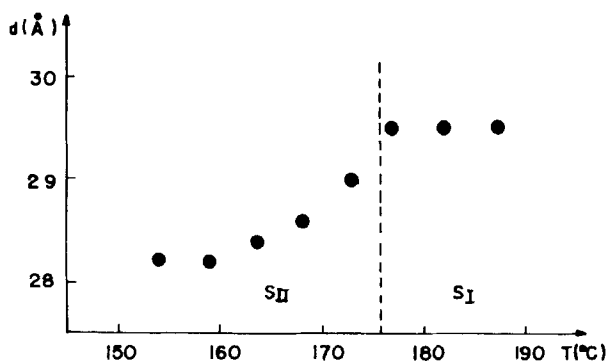


FIGURE 3 Smectic layer thickness, measured using X-rays, for 3,5-bis-(*p*-*n*-heptoxyphenyl)pyrazole as a function of temperature.



FIGURE 4 Molecular structure for the minimum energy conformation of 3,5-bis-(*p-n*-pentyloxyphenyl)pyrazole.

atives of 2,5-diaryl-1,3,4-oxadiazol¹⁰ are not mesogenic; probably, because the deviation from a linear molecule is larger than in Series I and II.

As previously mentioned, in spite of the geometric similarity between the isoxazole and pyrazole compounds, the melting points of the pyrazole derivatives are 40 to 50 degrees higher and they also do not present a nematic phase. There are two possible explanations for this behavior. One would be the formation of dimers by hydrogen bonding between the pyrazole rings or following Brown, *et al.*,¹¹ we could attribute this behavior to intermolecular hydrogen bonding between the hydrogen atom of the pyrazole ring and the oxygen atom of the terminal alkoxy chain. The fact that liquid crystalline phases do not occur in the 1-methylpyrazoles and N-methylpyrroles¹¹ lend support to these explanations since in the cited compounds it is not possible for hydrogen bonding to take place.^{9,11}

EXPERIMENTAL

3,5-di-(*p-n*-alkoxyphenyl)isoxazole (I): A mixture of 0.015 mole of 1,3-di-(*p-n*-alkoxyphenyl)propane-1,3-dione and 0.030 mole of hydroxylamine hydrochloride in methanol (200 ml) was refluxed for 6 hours with stirring. The mixture was then cooled, the solid obtained was filtered and recrystallized from methanol; (5I) I.R. (KBr disk): ν cm⁻¹; 3120 (C—H of =CH—), 1620 (C=N), 1570 (C=C). ¹H-NMR (CDCl₃, TMS): δ ppm = 0.93 (*t*, *J* = 6.5 Hz, 6 H, 2-CH₃); 1.30–1.87 (m, 12 H, 6-CH₂); 3.97 (*t*, *J* = 6.5 Hz, 4 H, 2-OCH₂); 6.60 (*s*, 1 H, —CH= of isoxazole ring); 6.94 (*d*, *J* = 8.5 Hz, 4 H, arom); 7.67 (*d*, *J* = 8.5 Hz, 2 H arom) and 7.79 (*d*, *J* = 8.5 Hz, 2 H arom); ¹³C-NMR (CDCl₃, TMS): δ ppm = 170.10 (*s*, =C—O of isoxazole ring), 162.48 (*s*, —C=N of isoxazole ring), 95.76 (*d*, —CH= of isoxazole ring).

3,5-di-(*p-n*-alkoxyphenyl)pyrazole(II): A mixture of 0.015 mole of 1,3-di-(*p-n*-alkoxyphenyl)propane-1,3-dione and 0.030 mole of hydrazine hydrate (96%) in methanol (200 ml), was refluxed for 5 hours with stirring. The mixture was then cooled and the solid obtained filtered and recrystallized from methanol; (5II): I.R. (KBr disk) ν cm⁻¹; 3230 (N—H), 1610 (C=N), 1580 (C=C). ¹H-NMR (CDCl₃, TMS): δ ppm = 0.92 (*t*, *J* = 6.7 Hz, 6 H, 2-CH₃); 1.33–1.76 (m, 12 H, 6-CH₂); 3.88 (*t*, *J* = 6.6 Hz, 4 H, 2-OCH₂); 6.55 (*s*, 1H, —CH= of pyrazole ring), 7.15 (AB quartet, *J* = 8.7 Hz, 8 H arom syst.), 11.6 (*s*, 1 H, N—H). ¹³C-NMR (CDCl₃, TMS): δ ppm = 158.94 (*s*, C₃ and C₅ of pyrazole ring).

3,5-di-(*p-n*-pentyloxyphenyl)-1-methyl pyrazole: To a mixture of 0.01 mole of

1,3-di-(pentyloxyphenyl)propane-1,3-dione in methanol, 0.02 mole of methyl hydrazine is added and the mixture refluxed for 5 hours with stirring. After removal of the solvent, a viscous liquid was obtained that crystallizes at sub-ambient temperatures. The product was recrystallized from ethyl alcohol. mp 39–40°C, showed no mesophases; I.R. (KBr disk) ν cm⁻¹; 2940–2860, 2870 (CH₃), 1610 (C=N). ¹H-NMR (CDCl₃, TMS): δ ppm = 1.1 (*t*, 6 H, 2-CH₃), 1.5–2.0 (*m*, 12 H, 6-CH₂), 4.1 (*t*, 7 H, 2-OCH₂ and N-CH₃, superimposed peaks), 6.7 (*s*, 1 H, —CH= of methyl pyrazole ring), 7.15 (*d*, *J* = 8.4 Hz, 4 H, arom syst), 7.6 (*d*, *J* = 8.5 Hz, 2 H, arom syst), 7.95 (*d*, *J* = 8.4 Hz, 2 H, arom syst).

Acknowledgments

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