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Thermodynamic Properties and X-ray Studies of the Homologous Series Arylthiophene Azoles

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In this work is described the thermodynamic properties and structural data of the homologous series 3–5 (4-alkoxyphenyl)5(2-propylthienyl) and 3–5(4-alkoxyphenyl)5(2-hexylthienyl) -pyrazoles and -isoxazoles. The series isoxazoles exhibit nematic phases and compounds with greater number of carbon atoms in the alkoxy chains also exhibit the smectic C phase. In contrast, the pyrazoles series exhibit only the smectic A phase.

Keywords: Thermodynamic properties, X-ray studies, arylthiophene azoles, smectic C.

INTRODUCTION

A relatively large number of mesomorphic compounds containing heterocyclic units have been synthesized and interest in such structures is constantly growing.[1,2] The introduction of an azole ring as a link between two phenyl groups and now between one phenyl and one thienyl ring, opens the possibility of generating new mesogenic units. 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 also the geometry of a molecule in relation to the geometry with phenyl rings.[3] These can greatly influence the types of mesophases which occur, the phase transition temperatures, and the electro-optic properties of the mesogenic. Continuing our investigations of compounds with heterocyclic rings,[4–6] we have presented the new compounds: 3-5(4-alkoxyphenyl)5(2-hexylthienyl) isoxazol, series RnN0R6; 3-5(4-alkoxyphenyl)5(2-hexylthienyl) pyrazol, series RnN2R6; 3-5(4-alkoxyphenyl)5(2-propylthienyl) isoxazol, series RnN0R3 and 3-5(4-alkoxyphenyl)5(2-propylthienyl) pyrazol, series RnN2R3. The synthesis was previously described.[7]

PHYSICAL INVESTIGATION METHODS

The thermal behaviour of the compounds was identified using DSC equipment (Perkin-Elmer DSC-2) calibrated with pure Indium and using a 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 sample was enclosed in a 0.7 mm Lindemann capillar with one oven with the temperature accuracy ± 0.5 K. The exact data analysis along (001) direction or aligned compounds were performed by a focusing horizontal two-circle X-ray tube (Siemens FK). The CuKα radiation $\lambda = 1.54056$ Å is focused by a curved Ge (111)-monochomator. The mechanical and electrical controlled smallest stepwidth of the diffractometer in 2θ and ω circle is 0.001°. For the fast diffractometry a detector is used with a resolution of the stepwidth 0.01 in 2θ. The temperature stability at the location sample in the range of 30°C to 250°C is 0.01 K during the measurements. The detailed description of the X-ray set-up and the oven is given in another paper.[8,9]

RESULTS AND DISCUSSION

The phase transition temperatures for the two series isoxazoles RnN0R6 and RnN0R3 and the two series pyrazoles RnN2R6 and RnN2R3 are plotted as a function of the number of carbon atoms in the alkoxy chains in Figure 1 and in Figure 2. The thermal properties are summarized in Tables I, II, III and IV. For the isoxazole compounds with longer n-alkyl groups ($n = 5$ to 9 for RnNOR6 and $n = 8$ and 9 for RnN0R3) the SmC phase is observed for both series at low temperature while at high temperature the

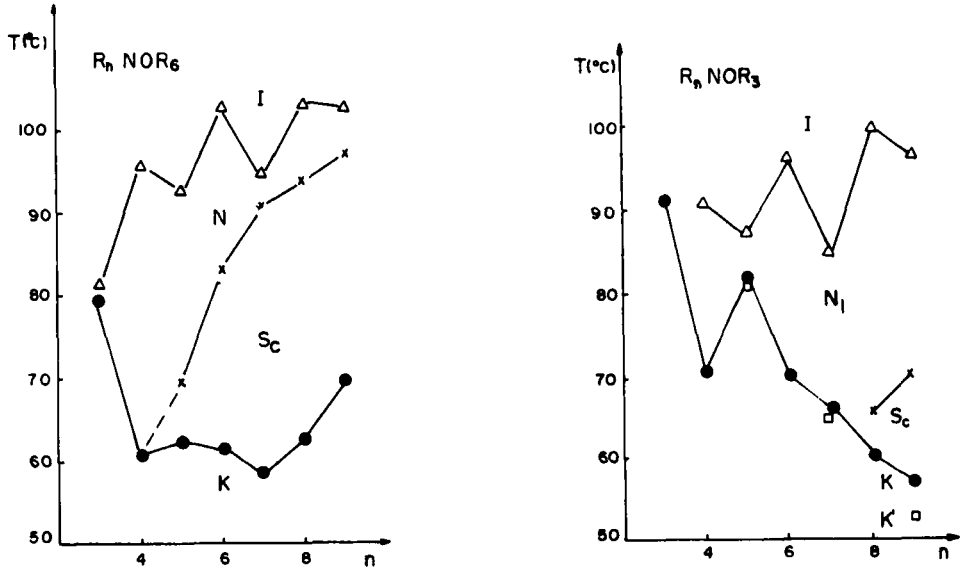


FIGURE 1 The phase transition temperature for isoxazol series. a) Series RnN0R6; b) Series RnN0R3.

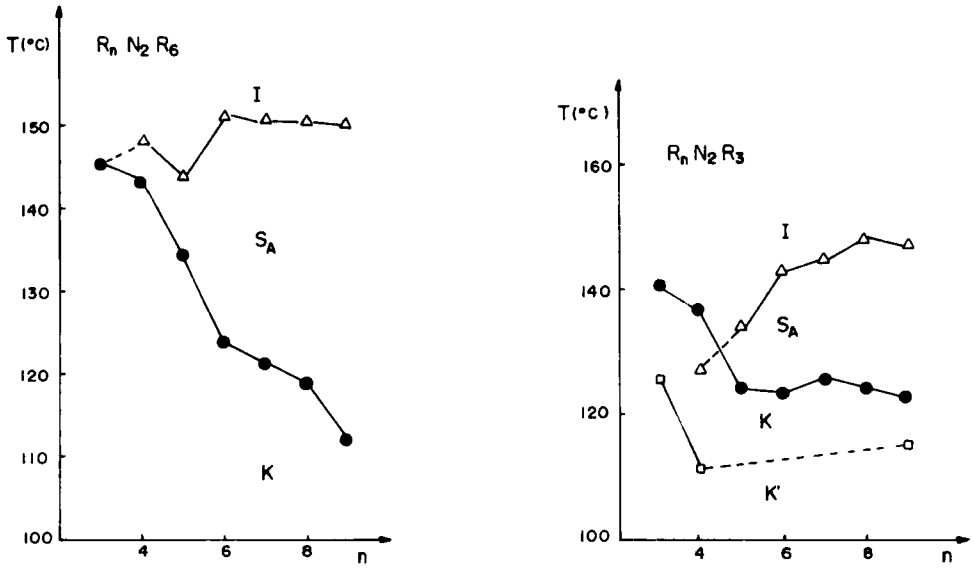
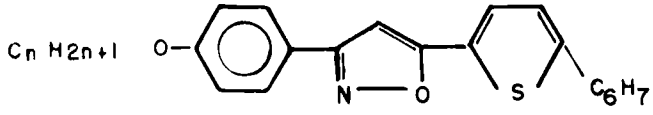


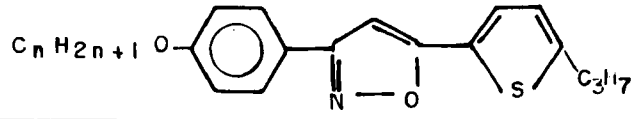
FIGURE 2 The phase transition temperature for pyrazol series. a) Series RnN2R6; b) Series RnN2R3.

TABLE I
Transition Temperatures (°C) (a) and (b) enthalpies (kJ/mole) of 3–5 (4-alkoxyphenyl)5(2-hexylthienyl) isoxazol, series RnN0R6



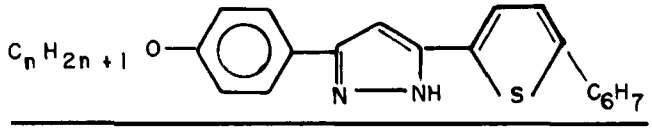
n		*K*		*Sc*		*N*		*I*
3	a)	–	79,5	–		–	81,0	–
	b)		44,6					
4	a)	–	60,5	–		–	95,5	–
	b)		68,4				1,7	
5	a)	–	62,2	–	69,5	–	92,7	–
	b)		53,5		2,3		1,3	
6	a)	–	61,0	–	83,2	–	102,3	–
	b)		50,1		3,6		2,9	
7	a)	–	58,7	–	91,0	–	94,6	–
	b)		74,7		6,1		2,5	
8	a)	–	62,7	–	94,1	–	103,0	–
	b)		69,6		4,2		3,3	
9	a)	–	69,5	–	97,4	–	102,7	–
	b)		74,7		4,9		2,5	

TABLE II
Transition Temperatures (°C) (a) and (b) enthalpies (kJ/moles) of 3–5 (4-alkoxyphenyl) 5(2-propylthienyl) isoxazol, series RnN0R3



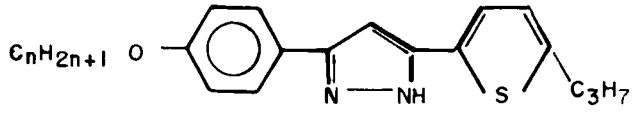
n		k'		k		Sc		N		I
3	a)	–		–	91,3	–		–		–
	b)				36,2					
4	a)	–		–	70,2	–		–	91,0	–
	b)				21,5				0,3	
5	a)	–	81,0	–	82,0	–		–	87,5	–
	b)				27,9				0,6	
6	a)	–		–	69,9	–		–	96,5	–
	b)				23,6				1,2	
7	a)	–	64,7	–	65,5	–		–	94,8	–
	b)				31,3				1,3	
8	a)	–		–	60,0	–	65,5	–	100,0	–
	b)				13,4		0,6		0,9	
9	a)	–	52,7	–	57,0	–	70,0	–	96,8	–
	b)		3,4		29,1		1,7		2,1	

TABLE III
Transition Temperatures (°C) (a) and (b) enthalpies (kJ/moles) of 3–5 (4-alkoxyphenyl)5(2-hexylthienyl) pyrazol, series RnN2R6



n		k		SA		I
3	a)	–	145,6	–		–
	b)		41,2			
4	a)	–	143,5	–	148,5	–
	b)		34,1		7,2	
5	a)	–	134,3	–	144,2	–
	b)		31,1		7,3	
6	a)	–	124,0	–	151,7	–
	b)		62,2		9,5	
7	a)	–	121,5	–	151,3	–
	b)		61,3		9,7	
8	a)	–	118,8	–	151,0	–
	b)		64,9		9,8	
9	a)	–	112,2	–	150,7	–
	b)		68,7		12,1	

TABLE IV
Transition Temperatures (°C) (a) and (b) enthalpies (kJ/moles) of 3-5 (4-alkoxyphenyl)5 (2-propylthienyl) pyrazol, series RnN2R3



n		*k'*		*k*		*SA*		*I*
3	a)	–	126,0	–	140,5	–		–
	b)		12,3		22,9			
4	a)	–	111,3	–	137,3	–	(127,5)	–
	b)		19,1		25,3		2,5	
5	a)	–		–	124,0	–	133,5	–
	b)				33,8		4,3	
6	a)	–		–	123,5	–	143,0	–
	b)				34,9		5,1	
7	a)	–		–	125,5	–	144,8	–
	b)				44,7		9,7	
8	a)	–		–	124,2	–	148,0	–
	b)				43,1		5,5	
9	a)	–	115,0	–	122,5	–	147,3	–
	b)		1,2		37,8		2,6	

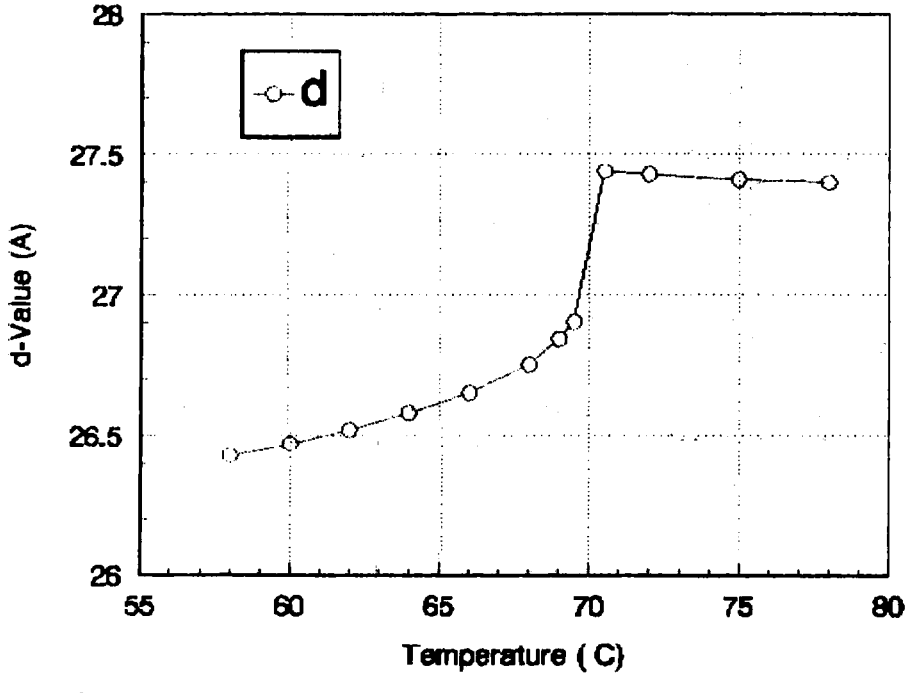


FIGURE 3 The d-value vs temperature for R9N0R3 with smectic C and nematic phases.

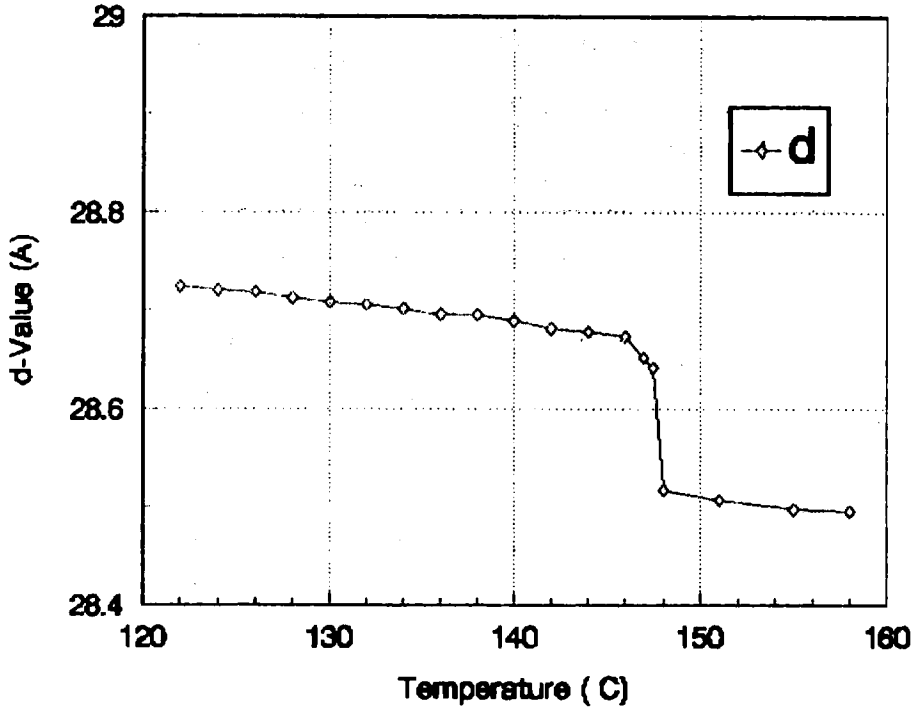


FIGURE 4 The d-value vs temperature for R9N2R3 with smectic A and isotropic phases.

nematic phase is present for all compounds except for $n = 3$ in the series RnN0R3, that also present some crystal-crystal transitions (K'-K).

The textures occurring in the higher temperature phase of the isoxazole derivatives are Schlieren and the behaviour at the transition to the isotropic phase is characteristic of the nematic phase. The transition texture at the smectic-nematic transition is that characteristic of a nematic-smectic C transition.

The melting points of the pyrazole compounds are quite different from those of the analogous isoxazole compounds, being on the order of 50 degrees higher. Also the mesophases shown by the two series are quite different. The derivatives of pyrazole exhibit only one smectic phase up to $n = 4$, with fanshape texture or homeotropic texture.

The X-ray diffraction photography and diffractometry measurements confirm the results obtained by DSC and microscope observation. The diffraction pattern in the smectic phase shows only one sharp peak at small angles. The d-values for R9N0R3 and for R9N2R3 are plotted in Figure 3 and in Figure 4. In SmC phase, the d-value increases along the increasing temperature. A discontinuity can be seen through the SmC-N phase transition by the isoxazole compounds. This characteristic behaviour can be certified by DSC measurements. For example, the compound R9N0R3 shows a peak that corresponds to a distance of $26.43 + 0.01$ Å at 58°C, by diffractometry measurements and the length of the molecule was calculated to be 28.2 A, for the most extended conformation using standard bond lengths. This indicates that the smectic

phase is non-orthogonal and that the molecular axis is inclined to the smectic layers, typical of the SmC phase.

In contrast, the compounds R9N2R3 have a length approximately constant, with a distance of 28.70 Å at 134°C, with a discontinuity through the SmA-N transition.

In both series isoxazol and pyrazol, the increasing number of carbon atoms in the alkoxy chains favours a greater number of mesophases. This is because the pyrazol series have mesophases at higher temperatures as explained previously[6] for the series 3,5-Bis-alkoxyphenyl-Pyrazoles and -Isoxazoles. In those works, one phenyl group was substituted for a Thienyl group and the consequence was a decrease in temperature of about 50 degree of the mesophases.

We tried to measure the dielectric constants of these series with an Impedence Analyzer HP4192A. But these compounds, after long contact with the glass cell, corroded the Indium Tin Oxide (ITO), destroying the condenser and making the measurements impossible.

Acknowledgments

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