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C. G. Seguel^a; B. Borchers^a; W. Haase^{ab}; C. Aguilera^a

^a Departamento de Química, Facultad de Ciencias, Universidad de Concepción, Concepción, Chile ^b Institut für Physikalische Chemie, Technische Hochschule Darmstadt, Darmstadt, Germany

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Synthesis and thermotropic properties of new mesogenic pyrazole and isoxazole derivatives

by C. G. SEGUEL†, B. BORCHERS†, W. HAASE‡
and C. AGUILERA*†

† Departamento de Química, Facultad de Ciencias, Universidad de Concepción,
Casilla 3-C, Concepción, Chile

‡ Institut für Physikalische Chemie, Technische Hochschule Darmstadt,
Petersenstr. 20, D-6100 Darmstadt, Germany

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The synthesis of new mesogenic alkyloxy pyrazole and isoxazole derivatives is reported. The mesogenic properties of these compounds were investigated by differential scanning calorimetry, polarizing microscopy and X-ray diffraction. Almost all compounds show preferred orientation in a magnetic field of about 1.5 T. Pyrazole derivatives show higher transition temperatures than the corresponding isoxazole derivatives. Small differences (1–3 Å) between the molecular lengths (as determined from models and the smectic layer thickness indicated by X-rays) are explained in terms of interdigitation or skewing of the alkyloxy chains.

1. Introduction

Various mesomorphic heterocyclic compounds have been reported [1–6] but none with five membered rings of the pyrazole and isoxazole type. These groups have aromatic character [7], planar conformation and high dipole moments perpendicular to the principal molecular axis. It was, of interest therefore, to investigate their mesogenic properties.

2. Results and discussion

The transition temperatures, enthalpies and phase of behaviour of the two series of compounds investigated are given in tables 1 (isoxazole) and 2 (pyrazole).

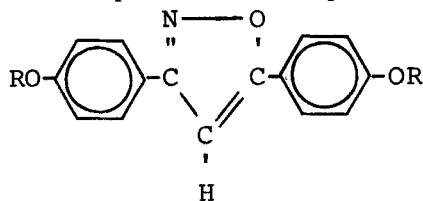
Compound **1a** formed a nematic homeotropic phase; compound **1b** formed a smectic A phase with a classical fan texture which becomes homeotropic near the S_A-N transition. Compound **1c**, in addition to the S_A phase, forms two crystalline phases. These isoxazole derivatives showed behaviour typical of compounds which *n*-alkyl or *n*-alkoxide terminal groups: nematic phases for short chains, both smectic and nematic phases for chains of intermediate length and only smectic phase for long chains [8].

Of the pyrazole derivatives studied, only compounds **2b** and **2c** give mesophases and these are of a smectic type. Like compounds **1c**, compound **2c** also formed two crystalline phases. These compounds have transition temperatures higher than those of the isoxazole derivatives. We take the presence of only smectic phases to indicate that pyrazolic compounds tend towards higher levels of structural order, perhaps due to the higher molecular symmetry, and the increased level of hydrogen bonding.

The mesophase stability range of the compounds in series **1** is practically the same for three and six carbon atom chains; it increases by 10°C when the hydrocarbon chain

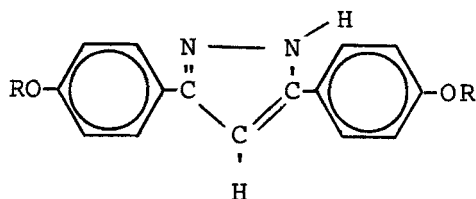
* Author for correspondence.

Table 1. Phase transition temperatures and enthalpies of isoxazole derivatives.



R: CH ₂ -CH-(CH ₂) _{-n}	Phase transitions °C	ΔHkJ mol ⁻¹
a: 1	C 135 N 178 I	C 20.65 N 0.6 I
b: 4	C 99 S _A 114 N 144 I	C 22.17 S _A 0.32 N 1.0 I
c: 9	C 88 K ₁ 92 S _A 145 I	C 22.79 C 33.14 S _A 6.90 I

Table 2. Phase transition temperatures and enthalpies of pyrazole derivatives.



R: CH ₂ =CH-(CH ₂) _{-n}	Phase transitions °C	ΔHkJ mol ⁻¹
a: 1	C 160 I	C 28 I
b: 4	C 154 S _A 178 I	C 30.97 S _A d I
c: 9	C 68 C ₁ 80 S _x 114 S _c 164 S _A 169 I	C 16.52 C ₁ 23.03 S _x * S _c 6.20 S _A * I

S_x, undetermined smectic phase; d, decomposition; *, not detectable by DSC.

is increased to eleven. The mesogenic ranges for pyrazole derivatives ranged from 29 to 89°C.

From X-ray diffraction studies (with samples aligned using an external magnetic field of about 1.5 T) the phase assignments were confirmed and the mesophases were observed by polarizing microscopy. Diffraction patterns are shown in figure 1, for a smectic A phase and a nematic phase with preferred alignment for compound **1B**.

Table 3 shows the interlamellar distances, molecular lengths (*d*) and the inphase intermolecular spacings (*D*). Comparing *d* with the molecular length (*l*) of each compound estimated from Dreiding stereomodels, we observe that there is a good correlation between *d* and *l* for compound **1a**. A dispersion angle of 21° would explain the differences between *l* and *d* for the smectic A phase of compound **1b**. This calculated angle is consistent with the order parameters *P*₂ and *P*₄ determined by X-rays for these phases [9]. The differences (*l*-*d*) found for the nematic phase are included in the periodic alignment characteristics of this mesophase which has implicitly a disorientation angle with respect to the director [10]. For compound **1c** the difference is 3 Å, and can be explained in terms of an angular spread of alignment smectic A phase [11] as well as by twisting of the chains [12]. It was not possible to obtain samples with a preferential orientation by cooling from the isotropic state for compound **2b** since this compound is unstable at these temperatures. Compound **2c** showed some preferential orientation in

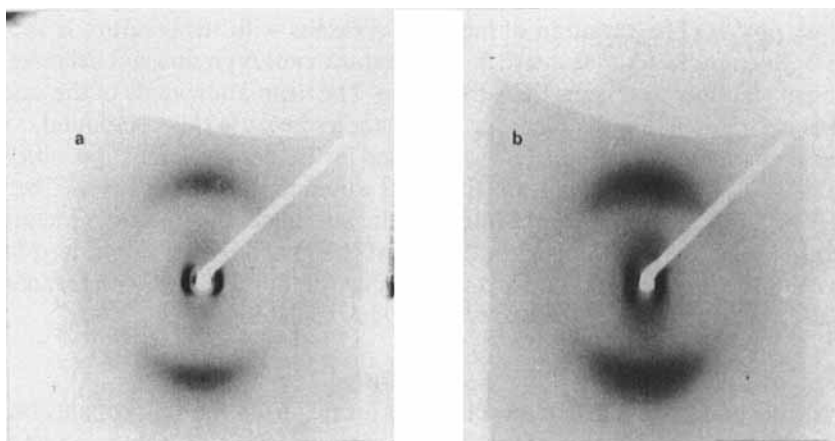


Figure 1. The X-ray diffraction patterns of (a) smectic A phase (102°C), (b) nematic phase (123°C) with preferred alignment.

Table 3. The interlamellar distances, molecular lengths and the in-phase intermolecular springs of each compound.

Compound	Mesophase	$d/\text{Å}$	$D/\text{Å}$	$l-d/\text{Å}$
1a	N	20.34	4.5	0.5
1b	N	28.55	4.9	1.8
	S_A	28.03		2.3
1c	S_A	36.0	5.1	3.0
2b	S_A	27.80	4.9	2.3
2c	S_A	29.0	5.0	10.0
	S_C	33.50	5.0	5.5

d : interlamellar distance or molecular length for nematic phase; D , in-plane intermolecular distance; l , molecular length determined by Dreiding Stereomodel.

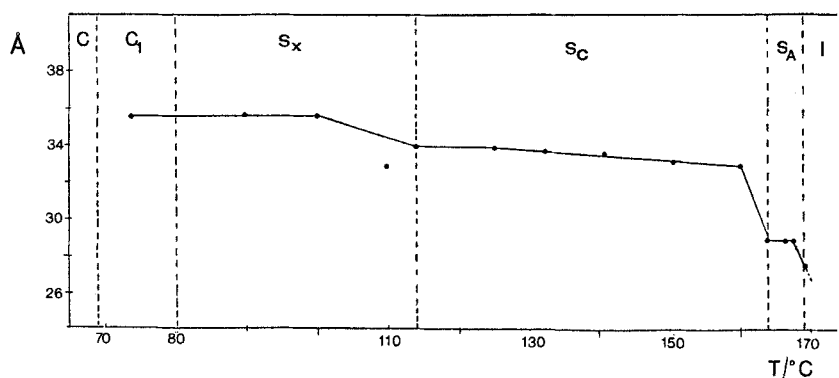


Figure 2. The space variation versus temperature for the crystal (C and C_1), S_x , S_C , S_A and I phases of compound **1b**.

the mass phases. The variation of lamellar thickness with temperature is shown by figure 2 which indicates a decrease in temperature, causes an unusual decrease of the spacing at the smectic C–smectic A transition. The inclination angle of the smectic C phase is not directly obtainable from X-ray studies because this compound does not present preferential orientation, but a calculated inclination angle ($\cos^{-1} \alpha = d/l$) of 31° , which is typical of this kind of transition [13] would explain the differences between l and d . The unusual decrease of the interlamellar spacing of the smectic A phase can be explained by an interdigitation of the long alkyl chains of adjacent sheets in addition to the twisting chains or to a certain inclination angle of the molecules with regards to the normal layer, a product of smectic C–smectic A transition.

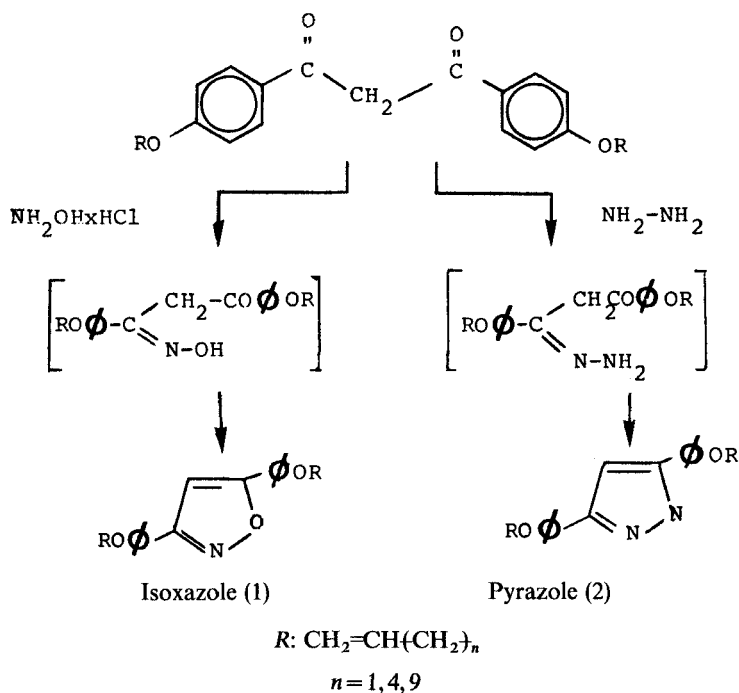
3. Conclusion

Pyrazole and isoxazole heterocyclic rings formed from the 1,3-propanedione unit appear to increase molecular rigidity. The presence of lone pairs of electrons on the two nitrogen atoms of the pyrazole ring and on the oxygen and nitrogen atoms of the isoxazole ring enhance the polarization of the molecules giving dipolar moments of 21.64 D and 2.83 D, respectively [14]. These facts would explain the high fusion and transition temperatures.

4. Experimental

The route adopted for the synthesis of the isoxazole and pyrazole derivatives is shown in the scheme. IR spectra were recorded on a Perkin–Elmer IR, 300 MHz ^1H NMR and 60 MHz ^{13}C NMR were recorded on Bruker instruments. Optical tax lines were investigated with an Ortho-Lux Pol Bk II polarizing microscope provided with a Mettler FP84 heating stage. X-ray diffraction (Philips PW 1140) was used to confirm the classification of the mesophases.

The compounds were synthesized by the following steps:



Methods previously described were used to synthesize the bis-(4-*n*-alkenyloxyphenyl)-1,3-propanediones [15] and the cyclisations to the respective isoxazole and pyrazole derivatives were carried out using hydroxylamine hydrochloride or hydrazine hydrate [16, 17].

4.1. Synthesis of 3,5-bis-(4-*n*-alkenyloxyphenyl)-isoxazole or pyrazole

20 mol of chlorhydrate-hydroxylamine or hydrazine hydrate 96 per cent were added to 1.0 mol of bis-(4-*n*-alkenyloxyphenyl)-1,3-propanedione in 30 ml of methanol in a 100 ml round bottom flask. The solution was refluxed with constant stirring for about 3 h. After the reaction period, the separated solid was filtered and recrystallized from methanol.

4.2. Some spectroscopic data of the 3,5-bis-(4-*n*-alkenyloxyphenyl)-isoxazole (I)

IR(KBr): $\gamma = 1620 \text{ cm}^{-1}$ (C=C conjugated and C-N), 1528 cm^{-1} (N-O). ^1H NMR (300 MHz, CDCl_3) of the compound 1a in table 1: $\delta = 4.59$ ppm (d, 4 H, OCH_2), 4.91 and 5.03 ppm (4 H vinylic geminal), 6.01 (m, 2 H, vinylic), 6.64 ppm (s, 1 H olefinic isoxazole ring), 6.94 (2 d, 4 H meta), 7.69 (2 d, 4 H ortho). ^{13}C NMR (60 MHz, CDCl_3): $\delta = 170.07$ ppm (C-O), 162.44 ppm (C-N), 96.00 ppm (CH = isoxazole ring).

4.3. Some spectroscopic data of the 3,5-bis-(4-*n*-alkenyloxyphenyl)-pyrazole (II)

IR(KBr): $\gamma = 1255 \text{ cm}^{-1}$ (N-H), 1500 cm^{-1} (C-N), 3410 cm^{-1} (C-H). ^1H NMR (300 MHz, CDCl_3) of the compound 2a table 2: $\delta = 6.10$ ppm (m, 2 H vinylic), 6.49 ppm (s, 1 H olefinic pyrazole ring), 7.00 ppm (d, 4 H aromatic), 7.85 ppm (d, 4 H aromatic).

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