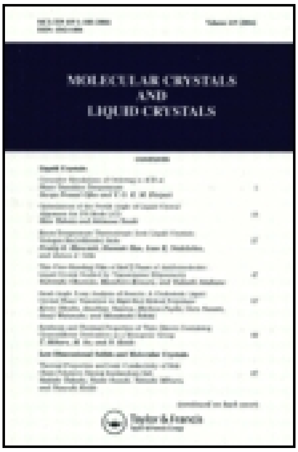

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Dielectric, Calorimetric and Optical Investigations of Pyridine Containing Oxadiazoles

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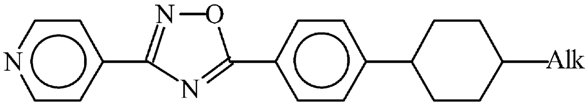
Astract: Three series of new isomeric 4-, 3- and 2-pyridine containing 1,2,4-oxadiazoles have been investigated via DSC and optical microscopy. DSC and microscopy investigations are mostly in good agreement and show that the transition temperatures and type of mesophases strictly depend on the nature and the length of the substitutent in the oxazolic part of 1,2,4-oxadiazoles and on the position of the heteroatom in the pyridine substituent. The mesomorphic properties of the compounds under study were compared with analogous 1,2,4–oxadiazoles, containing only carbocyclic units.

Keywords pyridine; oxadiazole; liquid crystal; differential scanning calorimetry; optical microscopy

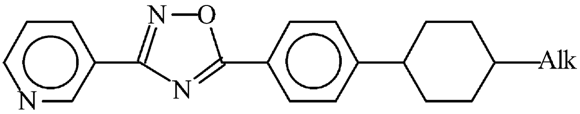
INTRODUCTION

Before works [1-4], 1,2,4-oxadiazolic cycle never was studied as fragments of possible liquid crystalline compounds. Nevertheless, this asymmetrical 5-membered heterocyclic fragment leads to mesogens with extremely interesting physico-chemical properties.

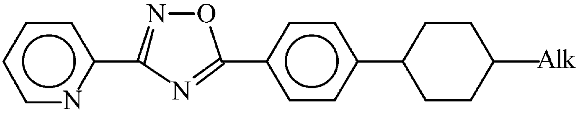
In this paper, three series of new isomeric 4-, 3- and 2-pyridine containing 1,2,4-oxadiazoles (I, II, III, respectively) have been investigated via optical microscopy and differential scanning calorimetry (DSC). The enthalpies of the phase transitions were approximately calculated.



(I)



(II)



(III)

Where Alk= C_3H_7 (a), C_5H_{11} (b)

FIGURE 1 - Chemical formulae of the pyridine containing oxadiazoles investigated.

As it was shown in our previous works, a strong correlation is present between the nature of the substituents, their positions with respect to the asymmetric oxadiazolic ring and the physico-chemical properties of new mesogens [1-4]. This dependence is especially evident when one of the substituents has an electron-acceptor character. It is due to the fact that the 1,2,4-oxadiazolic ring exhibits itself a polarized structure with asymmetric distribution of the electron density [5].

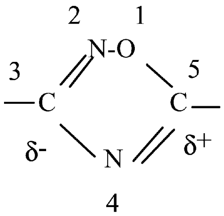


FIGURE 2 - Charge excess δ of the asymmetric oxadiazolic ring.

The electrons are in the average located at C_3–atom of the five-membered heterocycle. There is a lack of electrons at C_5 position. It is logical to suggest that placing an electron-acceptor substituent at C_3-atom, the polarization of the whole molecule will be increased.

In a recent paper [6] we have already demonstrated the influence of the position of N-atom in pyridine ring on the dielectric anisotropy of the liquid crystal compounds. The aim of the present investigation is the study of the phase transition temperatures and the correspondent enthalpies of new isomeric 2-, 3- and 4- pyridinyl-1,2,4-oxadiazoles. This work is a continuation of our previous study in the frame of the correspondence "molecular structure – mesomorphic properties" with model compounds from 1,2,4-oxadiazole series.

EXPERIMENT

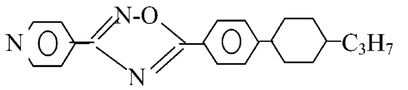
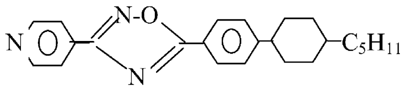
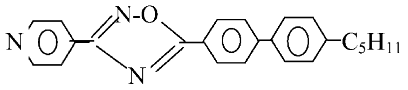
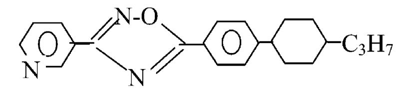
The phase transition temperatures of the compounds have been detected via optical microscopy (Leitz polarizing microscope with JVC-Grundig-Sony recording set-up, Linkam TMS-90 and Mettler FP-90 thermosystems) and DSC (Perkin-Elmer DSC-7 apparatus) techniques. The cells used for optical microscopy were made by glass plates without any treatment. The samples for DSC measurement were prepared with a mass of about 5 mg each, using a piezoelectric balance Gibertini E50S, with 10 μg sensitivity.

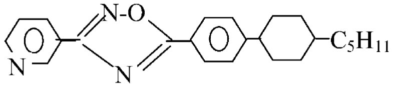
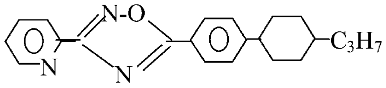
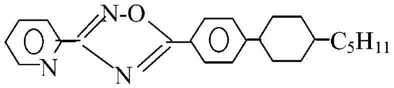
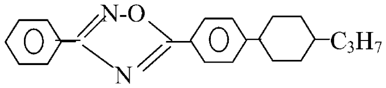
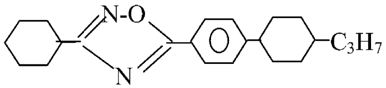
The data are presented in the Table.

DISCUSSION

The transition temperatures obtained by the two techniques are in a rather good agreement (within ± 3°C, see the Table).

By comparing different compounds it is possible to understand the role played by the various fragments of the molecules influencing the macroscopic properties of the compound, as the different types and the temperature ranges of the involved mesophases, the position of melting and clearing points. Let us start to compare compounds (1), (4), (6) with (8), (9). All of them have equal substituent in 5-position of the oxadiazolic ring, possessing as a donor the same alkyl chain -C_3H_7; they only differ due to the substituent in 3-position, i.e. para-pyridinyl (1), TABLE - Mesomorphic properties of pyridine containing 1,2,4-oxadiazoles and their analogs. The enthalpies are measured with rate = 1°C/min.

1	**2**	**3**		**4**		
No.	**Structure formula**	**Transition temperatures (°C)**		**Enthalpy (J/g)**		
		Microscopy	**DSC**	**K_1/K_2 (K/S, K/N)**	**S/N**	**N/I**
1.		K 97 N 156 I	K 94 N 157 I	69.7	-	0.6
2.		K 75 S 80 N 157 I	K 78 N 158 I	44	-	0.8
3.		K 90 S 145 N 167 I	K 90 S 142 N 165 I	56	1.9	0.8
4.		K_1 71 K_2 75 S 80 N 190 I	K_1 72 K_2 73 S 76 N 190 I	29.1 (11.8)	0.1	1.0

1	**2**	**3**		**4**		
5.		K 57 S 99 N 187 I	-	-	-	-
6.		K_1 120 K_2 126 N 151 I	K_1 120 K_2 127 N 154 I	59.4 (7.5)	-	0.5
7.		K 91 S 97 N 152 I	K 95 N 152 I	56.5	-	0.9
8.		K 91 N 167 I	K 88 N 168 I	58.4	-	0.9
9.		K 65 S 71 N 76 I	K 69 S 70 N 76 I	13.8	9.5	1.2

(meta-pyridinyl (4), ortho-pyridinyl (6), phenyl (8), and cyclohexyl (9), respectively. This determines a strong change in the thermodynamic properties. In fact, the first and the last three substances present only nematic phase, whereas (4) exhibits also smectic phase. Moreover, compounds (1) and (8) have the nematic range incomparably larger than (9), and shifted towards higher temperatures. This behavior can be explained considering the structure of cyclohexyl ring which is three-dimensional and is more flexible, not allowing the molecules to be closer to each other, as in the other three cases, where the phenyl- and pyridinyl- rings undergo stacking interactions, allowing a more ordered bulk structure, even at higher temperature. The mesophase range of compound (4) covers all the nematic ranges of the previous three compounds (1, 8, 9). When the acceptor nitrogen atom is in the meta-position to oxadiazolic heterocycle, its free electron pair takes a part in the whole conjugation chain of the molecule increasing the anisotropy of polarizability. This leads to rising of the clearing temperatures as well as the mesomorphic interval in isomer (4) and to the appearance of smectic phase.

Furthermore, meta-pyridinyl (4) possibly favors an alternate parallel piling of molecules, which turns out to be more compact, due to stronger stacking interactions. Instead orthopyridinyl, inducing an inclined dipole moment [6], favors the molecules to pack in a bidimensional lattice, enhancing the melting point (6).

The role of the different types of pyridinyl, according to the positions of the heteroatom (N), can be stressed considering other cases too, where the substituent in 5-position of oxadiazolic ring is the same as in the previous mentioned situation, except for the presence of longer alkyl chain (-C_5H_{11}), whereas in 3-position there is para-, meta-, and ortho-pyridinyl substituent, respectively (2, 5, 7). All these compounds exhibit both smectic- and nematic phase, but their temperature ranges are different. In particular, meta-pyridinyl (5) has the largest mesophase interval, and para- pyridinyl (2) has an intermediate mesophase range, as compared with ortho-pyridinyl (7), probably due to the stacking interaction which favors the 3-pyridinyl-substituent with asymmetric structure, enhancing the packing of the molecules, provided that the dipole is almost parallel to the molecular long axis, whereas if the dipole is deeply inclined, then the molecular ordering at higher temperature is frustrated, and at lower temperature the crystallinity is favored.

On the other hand, the alkyl chains are electronic donors and their lengthening can enlarge the mesophase range of the compounds having as acceptors the same pyridinyl, and even cause the appearance of smectic phase - as it is shown comparing (1) with (2) - para-pyridinyl and (4) with (5) - meta-pyridinyl.

The phenyl ring does not interrupt the conjugation chain, then allows the molecular dipole to be larger, thus favoring the ordering at higher temperatures, increasing the clearing point, and the packing at lower temperatures due to stacking interactions, thus dramatically increasing the width of the smectic region - compare (3) with (2).

It is very interesting to analyse the degree of order of the phase transitions in all compounds investigated. In fact, usually the transition enthalpies are approximately evaluated dividing the peak areas in the DSC-thermograms by the heating (or cooling) rate and by the sample mass. But Ratna and Chandrasekhar [7] showed that DSC peak areas are not only affected by the transition enthalpies, since they take into account also the heat capacities of the two phases surrounding the transition together with the dispersion due to the thermal contact between the holder and the sample and the external heat losses. As a conclusion, the DSC calculated enthalpies are actually dependent on the rate, and are only an estimate of the transition enthalpies. Choosing the rate equal to 1°C/min, a good compromise has been reached between the necessity of not being too far from the thermodynamic equilibrium and the opportunity to have high sensitivity in detecting the differential power supplied to the sample. The estimated enthalpies range between 10 and 70 J/g in the case of K-K or K-S or K-N transitions, 0.1-5 J/g for S-N and 0.6-1 J/g for N-I transitions, respectively. According to Navard-Haudin theory [8], by comparing two heating runs (the second run at double rate than the other), the ratio r of the heights of the transition peaks (second- to first run) can discriminate, in the case of pure substances, between first - and second order transition. Namely, when r = 1.0 - 1.4, the transition is first order, whereas r = 2 implies a second order transition.

This theory is powerful and easy to be used. By applying it to liquid crystal field, Hassel and van Hecke [9] demonstrated that in T8 only the N phase is re-entrant.

From our data, measured with heating rates 1 to 0.5, 2 to 1 and 4 to 2, we have found that the melting points of para-, meta-, and ortho-pyridinyl compounds (1), (4), and (6) with alkyl chain C_3H_7 are characterized by: 1st-order (K to N), 2nd-order (K_2 to S) and 1st-order (K_2 to N), respectively. The clearing points of the same compounds turn out to be weak-1st-order (1), and 1st-order (4), (6), as generally predicted for a N-I transition [10-12].

It is interesting that also the S/N transitions appear to be either 1st order - as for compound (4) with meta-pyridinyl - or 2nd order - as for compounds (3, 9) with para-pyridinyl and cyclohexyl as substituent in 3rd-position. This can be interpreted in the sense that in the first case the nematic director fluctuations play an important role in the S/N transition, whereas in the other two cases they are suppressed [13].

Systematic work devoted to the reliable determination of the transition enthalpy and of the phase transition order of 1,2,4-oxadiazoles will be the subject of our further investigation.

CONCLUSION

1. Three series of new isomeric 4-, 3- and 2-pyridine containing 1,2,4-oxadiazoles have been investigated by optical microscopy and DSC. The data obtained by both techniques were in rather good agreement.
2. It was shown that the transition temperatures and the type of mesophase strictly depend on the nature and length of the substituent in oxazolic part of 1,2,4-oxadiazoles and on the position of heteroatom in the pyridine substituent.
3. The enthalpies (i.e. peak areas) are in the range 10 - 70 J/g in the case of K-K or K-S or K-N transitions, 0.1-5 J/g for S-N and 0.6-1 J/g for N-I transitions, respectively.
4. The melting points turn out to be either 1st-order or 2nd-order transitions, as well as the S/N transitions, whereas the clearing points are either weak-1st-order or 1st-order transitions.

Acknowledgments

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