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Liquid Crystalline Pyridine Containing 1,2,4-Oxadiazoles

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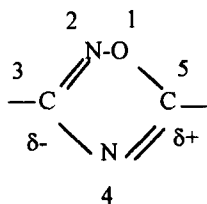
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New mesomorphic 1,2,4-oxadiazoles containing as an electron-acceptor substituent the pyridine cycle with different position of the nitrogen atom with respect to the oxadiazole cycle have been synthesized. The reaction of the isonicotinic and nicotinic amidoximes with various acid chlorides smoothly provided the corresponding mesogenic 3-(4-pyridinyl)- and 3-(3-pyridinyl)-1,2,4-oxadiazoles. On the contrary with picolinic amidoxime as a starting material mainly the uncyclized nonmesomorphic products were obtained. Temperature and dielectric characteristics of new pyridinic liquid crystals were measured and compared with analogous parameters of corresponding phenyl (cyclohexyl) substituted oxadiazoles.

Keywords: pyridine; oxadiazole; liquid crystal; dielectric anisotropy

INTRODUCTION

It is known that the 1,2,4-oxadiazoles exhibit a polarized structure with asymmetric distribution of the electron density [1]:



The electrons are located at C₃-atom of the five-membered heterocycle. There is a lack of electrons at C₅ position. It is logical to suggest that placing electron-acceptor substituents at C₃-atom increases the polarization of the whole molecule. At the same time it must lead to the increase of the dielectric anisotropy ($\Delta\epsilon$) of the compounds.

As it was shown in our previous works a strong correlation between the nature of the substituents and their positions with respect to the asymmetric oxadiazolic ring is present [2, 3]. This dependence is especially evident when one of the substituents has an electron-acceptor character.

The aim of the present investigation is the synthesis of new isomeric 2-, 3- and 4-pyridinyl-1,2,4-oxadiazoles and the study of their transition temperatures and dielectric properties depending on the position of N-atom in pyridine ring. This work is a continuation of our study in the frame of "molecular structure – mesomorphic properties" with model compounds from 1,2,4-oxadiazole series.

EXPERIMENTAL

The transition temperatures were determined using a Mettler FP-5 apparatus with a polarizing microscope.

The dielectric constants of the investigated compounds were determined in the nematic phase by an AC bridge method for layers of 60 μm thickness. A magnetic field of 7 kG was used to align the NLC's. The cell capacitance was measured at 1000 Hz; the accuracy was about $\pm 5\%$.

NMR spectra were recorded on a Bruker WM-250 spectrometer, solvent - CDCl_3 .

Satisfactory elemental analyses were obtained for all the compounds.

Synthesis of pyridinyl amidoximes

A solution of 22 g (0.55 mol) of NaOH in 100 ml of water is added dropwise under stirring to a mixture of 44 g (0.4 mol) of nitrile (2-3-, or 4-cyanopyridine) and 33.6 g (0.48 mol) oxyammonia hydrochloride in 300 ml of alcohol. The resulted mixture is stirred at the boiling point for 15 hours, then concentrated. The crystalline product is filtered, washed with water and dried. It can be used in the next stage without purification, the yield is 60-65 %.

2-Pyridine amidoxime, m.p. 114 °C (from alcohol);

3-Pyridine amidoxime, m.p. 126 °C (from alcohol);

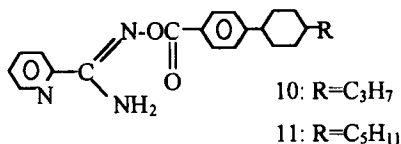
4-Pyridine amidoxime, m.p. 152 °C (from alcohol)

Synthesis of pyridinyl 1,2,4-oxadiazoles (1-7) and their carbocycle substituted analogs (8, 9)





A solution of 0.005 mol appropriated acid chloride in a small amount of toluene is added dropwise at the room temperature to the stirring mixture of 0.62 g (0.005 mol) of pyridine amidoxime in 16 ml of dry toluene and 8 ml of pyridine. Then the obtained mixture is heated and stirred at the boiling point of the solvent for 5-7 hours. After cooling the mixture is placed in water, extracted by toluene, washed and concentrated in vacuum. The products are purified by chromatography on SiO₂ in benzene, toluene and petroleum and recrystallized from appropriate solvent. The yield is 40-50 %.

Synthesis of analogs (8, 9) with carbocyclic substituents (instead of the pyridine ring) was made in the same way with phenylamidoxime (m.p. 70 °C) and cyclohexylamidoxime (m.p. 93 °C), as starting materials.

The transition temperatures and dielectric characteristics of all synthesized mesomorphic compounds (1-9) are presented in the Table. The main products from picolinic amidoxime (compound 10: R=C₃H₇ and compound 11: R=C₅H₁₁) were separated by column chromatography on SiO₂ with CHCl₃ as eluent. These products are not mesomorphic. Their structure was identified by NMR spectra:





1	2	3	4	5	6	7
6.		K 123 N 151 I				
7.		K 93 S 95 N 153 I	5.31	5.61	-0.3	96.2
8.		K 75 S 89 N 162 I	5.14	3.38	1.76	96.2
9.		K 65 S 71 N 76 I			+0.03	

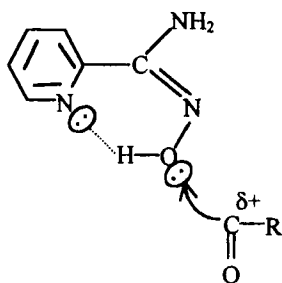
Ester (10): m.p. 210-212 °C.

NMR (DMSO, ppm): 8.65 (1H, d, Py); 8.10-8.05 (3H, 2d, Py); 7.85-7.5 (2H, 2d, Ar); 7.32 (2H, d, Ar); 6.75 (2H, broad singlet, NH₂); 2.52 (1H, t, CHCy); 1.9 (4H, d, CH₂Cy); 1.5-1.0 (9H, m, CH₂Cy and aliphatic); 0.9 (3H, t, CH₃).

Ester (11): m.p. 213-215 °C. NMR is analogous to the previous one.

RESULTS AND DISCUSSION

The reaction of cyclohexylbenzoic and biphenylcarbonic acid chlorides with isonicotinic and nicotinic amidoximes smoothly provides the cyclic products – isomeric pyridine-1,2,4-oxadiazoles (1-5) exhibiting LC properties. Moreover, C₃H₇-homolog is usually characterized by nematic or monotropic smectic phase, C₅H₁₁-homolog – by enantiotropic smectic and nematic phases. On the contrary the synthesis of the isomeric 2-pyridine-1,2,4-oxadiazoles had some difficulties. In this case, the main product (compounds 10, 11) had a noncyclic structure of the ester character, which was confirmed by the NMR spectra (see experimental part). Compounds 10 and 11 are not mesomorphic and have high melting temperatures, as it is usual for polar substances. The probable reason of this behavior can be due to the short distance between the pyridinic nitrogen and the hydroxylic group in the picolinic amidoxyme that promotes arising of the hydrogen bond and the formation of the intermediate stable cycle with fixed position of the amino-group.



Therefore, the electrophilic attack of the last one by the acid chloride could lead to the amino-esters (10, 11). We succeed to obtain the mesogenic products – 2-pyridinyl-1,2,4-oxadiazoles only with very small yields.

The new isomeric LC oxadiazoles with pyridine and phenylcyclohexane substituents (1,2,4-7) have the similar geometric anisotropy but essentially differ from each other by their melting and clearing temperatures. It is probably connected to the electronic factors.

For instance: in the pyridines (4, 5) the acceptor nitrogen atom is in the meta-position to oxadiazolic heterocycle and 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 in isomers (4, 5) comparing with p-pyridine containing LC's (1, 2). On the contrary the melting temperatures in the last ones are higher than in the m-isomeric pyridines which may be connected with more strong dipole-dipole-interactions. The dipole moment directed along the molecule axis in the pyridines (1, 2) causes also the increase of the parallel component of the macroscopic dielectric permittivity (ϵ_{\parallel}) and

consequently of the value of the positive dielectric anisotropy ($\Delta\epsilon$). In the meta-isomers (4, 5) these parameters are significantly smaller but the value of ϵ_{\perp} is bigger than the one, containing p-pyridine ring (Table).

This fact could be explained by summing up the permanent dipole moments of all polar parts of the molecule. Pyridines with o-position of N-atom with respect to oxadiazolic ring (6, 7) demonstrate also a strong difference in the dielectric characteristics. Due to the practically perpendicular strong permanent dipole moment, caused by the o-N-atom, the absolute value of the ϵ_{\perp} strongly increases, and the value of $\Delta\epsilon$ accordingly decreases even changing it's sign. The increasing of the melting temperatures of compounds (6, 7) with respect to isomers (1-5) is given by stronger dipole-dipole interactions. In order to compare with pyridine containing LC's, the dielectric and temperature characteristics of the analogous compounds with the carbocyclic substituents (8, 9) were also investigated. The oxadiazole (9) with nonpolarizable cyclohexyl substituent has a low clearing point, a narrow temperature interval of the mesophase and also $\Delta\epsilon$ is close to 0. This could be expected from the analysis of its structure. The replacement of the cyclohexane ring on the more polarizable phenyl one (10) leads to the increase of ϵ_{\parallel} and accordingly of $\Delta\epsilon$ (Table). The clearing point of LC (10) also increases (Table).

CONCLUSION

The new mesogens – 1,2,4-oxadiazoles containing two polar asymmetric heterocyclic units: pyridinic- and five membered 1,2,4-oxadiazolic one have been chosen as LC model compounds. They demonstrate the influence of the electronic factors on the mesomorphic and dielectric properties of the isomeric pyridinyl oxadiazoles. *o*-Pyridinyl-1,2,4-oxadiazoles take a particular place in these series due to the position of N-atom of pyridine close to the oxadiazolic cycle:

There are some difficulties in the synthesis of this material due to electronic and steric factors.

They demonstrate an abrupt increase of the melting points as well as decrease of the dielectric anisotropy comparing with *p*- and *m*- analogs.

Acknowledgments

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