

New Esters Liquid-crystalline 3,5-disubstituted (4,5-dihidroisoxazol-5-yl)alkyl Benzoates.

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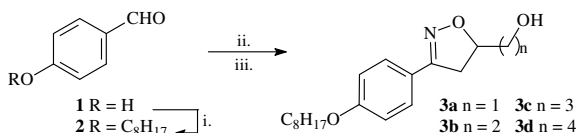
INTRODUCTION

The incorporation of isoxazolinic ring into the mesogenic core is the great opportunity to evaluate the influence of some parameters related with liquid crystal (LC) properties.¹ Due to the deviation from linearity, the use of these rings contributes to the studies of the understanding of steric and electronic influence related to molecular structure that will influence the mesomorphic properties. In this communication we are reporting the preparation and thermal analysis of three series of LC based on 3,5-disubstituted isoxazolines with different numbers of methylene carbons between the heterocyclic ring and the ester group.

RESULTS AND DISCUSSION

The synthetic route used for synthesis of isoxazoline **3a-d** is described in Scheme 1. The aldehyde **2** was synthesized by alkylation of **1** with bromooctane.² To prepare the isoxazolines **3a-d** a [3+2] cycloaddition between a nitrile oxide (*in situ* oxidation) and four different allylic alcohol homologs as dipolarophiles were performed. The compounds **3a-d** showed no liquid-crystalline properties.

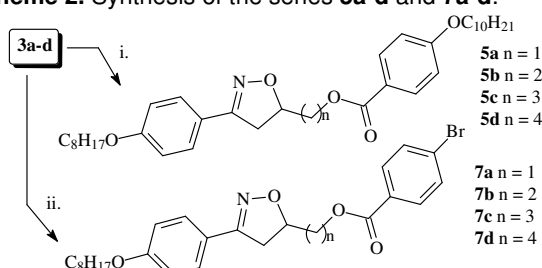
Scheme 1. Synthesis of compounds **3a-d**.



Reaction conditions: (i) RBr, KOH, CH₃CN, reflux, 4h (72%); (ii) HONH₂.HCl, AcONa, EtOH/H₂O, reflux, 1h (73-93%); (iii) CH₂=CH(CH₂)_nOH, NCS, pyridine, CHCl₃, r.t., 4h (33-36%).

Scheme 2 describes the preparation of **5a-d** and **7a-d** which were prepared by esterification reaction between *p*-*n*-decyloxybenzoic acid (**4**) or *p*-bromobenzoic acid (**6**) and isoxazolines **3a-d**. Smectic C monotropic phase (broken fan texture) was observed for the compounds **5a,b**. The compounds **5c,d** showed mesomorphic behavior (SmC) only in the fast cooling during the crystallization process. The compounds **7a-d** showed no liquid crystalline properties.

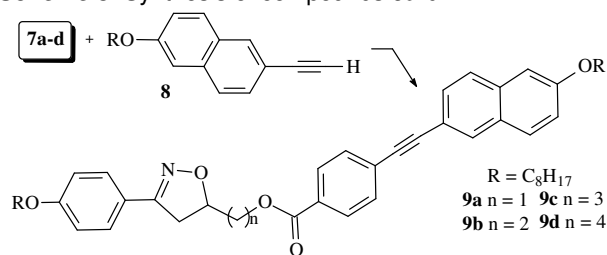
Scheme 2. Synthesis of the series **5a-d** and **7a-d**.



Reaction conditions: (i) **4**, DCC/DMAP, THF, r.t., 24h (30-81%); (ii) **6**, DCC/DMAP, THF, r.t., 24h (44-57%).

The route used for synthesis of the materials LC **9a-d** is outlined in Scheme 3. The reactions were carried out through Sonogashira cross-coupling between the intermediates **7a-d** and the terminal alkyne **8** in the presence of palladium catalyst.² **9a-d** exhibited enantiotropic nematic mesophase.

Scheme 3. Synthesis of compounds **9a-d**.



Reaction conditions: [PdCl₂(PPh₃)₂], CuI, PPh₃, Et₃N, reflux, 48h.

CONCLUSION

The compounds of the series **9a-d** have molecular structure rod-shaped more pronounced than the series of compounds **5a-d** and **7a-d** and showed more stable mesophase (enantiotropic). The effect even-odd in this series was observed using the transition temperatures and enthalpy values.

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