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Liquid Crystals

Publication details, including instructions for authors and subscription information:

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New liquid crystalline 3,4-disubstituted furoxanes

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Online publication date: 19 May 2010

To cite this Article Bezborodov Corresponding author, V. S. , Kauhanka, M. M. and Lapanik, V. I.(2004) 'New liquid crystalline 3,4-disubstituted furoxanes', *Liquid Crystals*, 31: 2, 295 – 297

To link to this Article: DOI: 10.1080/02678290410001670665

URL: <http://dx.doi.org/10.1080/02678290410001670665>

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Preliminary communication

New liquid crystalline 3,4-disubstituted furoxanes

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(Received 2 June 2003; in final form 1 October 2003; accepted 10 October 2003)

The synthesis and characterization of six new liquid crystalline 3,4-disubstituted furoxanes is reported. These show enantiotropic nematic phases over wide temperature ranges. This is surprising given the highly bent structure of these compounds.

It is known that non-linear five-membered heterocyclic-based liquid crystals such as pyrazole, thiophene, furane and isoxazole derivatives, form smectic or nematic phases at low temperatures and over wide temperature ranges. [1–3]. To continue this work we have synthesized novel liquid crystalline 3,4-disubstituted furoxanes [4] and investigated their mesomorphic properties.

The 3,4-disubstituted furoxanes **1a–f** have been prepared by the dimerization of 4-acetoxybenzoxazole **3**, base hydrolysis of the resulting 3,4-di-(4-acetoxyphenyl)furoxane **4** and subsequent esterification of 3,4-bis-(4-hydroxyphenyl)furoxane **5** using various acids in the presence of dicyclohexylcarbodiimide (DCC) and 4-*N,N*-dimethylaminopyridine (DMAP) as catalyst (see the scheme). A similar nitrile oxide dimerization has been widely used for the preparation of other furoxanes [5–7], whose chemical structures were confirmed by X-ray analysis [8–10].

The structures of the prepared compounds **1–5** were confirmed by NMR, IR and UV spectroscopy. The ¹H NMR spectrum (δ , ppm) of the diacetate **4** showed that two singlets at 2.33 and 2.34 belong to the protons of the acetoxy groups. The different positions of these signals in the spectrum is caused by the asymmetrical structure of the furoxane ring and the unequal interaction of the extracyclic N–O bond with the benzene rings located at the C-3 and C-4 atoms of the heterocyclic fragment [5]. In the spectrum of the bisphenol **5** broad singlets of the phenolic protons are observed at 9.08 and 9.27. The signals at 114.8 and 155.1 in the ¹³C NMR spectra of the compound **1c** correspond to C-3 and C-4 of the furoxane ring [5]. It should be noted that the chemical structure of

compounds **1a–f** as furoxanes was additionally confirmed by the chemical transformation of compound **1a** to the dioxime **7** [11].

The purity of the compounds was checked using a HP 5890 capillary gas chromatograph fitted with a H1 column. Phase transition temperatures were measured using a Linkam heating stage in conjunction with a PZO polarizing microscope, and also by using a Setaram DSC 92.

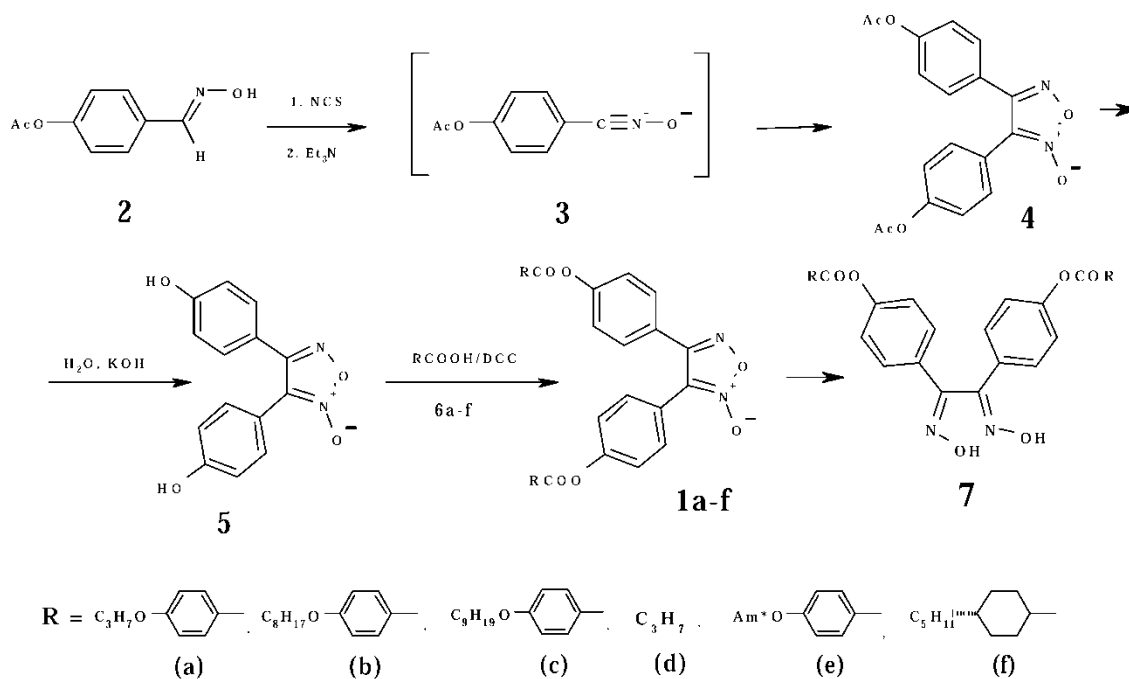
For the synthesis of 3,4-bis-(4-acetoxyphenyl)furoxane (**4**), to a stirred solution of 5.0 g of oxime **2** in 80 ml of chloroform three drops of pyridine (catalyst) and then 4.1 g of *N*-chlorosuccinimide were added. The mixture was stirred for about 1 h at r.t., was cooled to -5°C ; 4.3 ml of triethylamine in 70 ml chloroform was then added. After stirring the reaction mixture for 12 h at r.t., 10% aqueous hydrochloric acid was added; the organic layer was separated, washed with water and then dried over anhydrous sodium sulphate. The residue obtained after removing the solvent was crystallized from 2-propanol; yield 0.92 g (9.5%).

For the synthesis of 3,4-bis-(4-hydroxyphenyl)furoxane **5**, a mixture of 0.38 g of diacetate **4** and 0.15 g of potassium hydroxide in 12 ml of 80% aqueous methanol was heated under reflux for 1 h. After cooling the reaction mixture to r.t., 15 ml of 10% aqueous hydrochloric acid was added and the product filtered off, washed with water and used, after drying in air, in the next stage; yield 0.26 g (89.7%).

The furoxanes **1a–f** (see the table) were synthesized by the esterification of bisphenol **5** with acids **6a–f** in the presence of DCC and DMAP as catalyst [12].

As can be seen from the table, the furoxanes **1a–f** are enantiotropic mesogenic compounds showing nematic behaviour over a very wide temperature range, greater than 100°C . These results are not in accordance with the properties of the corresponding liquid crystalline

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five-membered heterocyclic compounds. The similar bent-core compounds [1–3], in general, do not form the nematic phase but instead form a smectic phase over a narrow temperature range. This surprising behaviour of

Table. Transition temperatures of 3,4-disubstituted furoxanes **1a–f**.

Furoxane	Transition temperatures/°C			
	Cr	Sm	N	I
1a	• 187.5	—	—	• 309 •
1b	• 107	—	—	• 262 •
1c	• 108	—	—	• 253 •
1d	• 114	—	—	• 126 •
1e	• 161	—	—	• 269 •
1f	• 110	• SmB	124.5	• 280 •

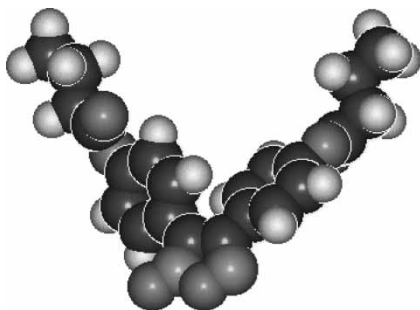


Figure. Molecular model of the furoxane **1d**.

the bent shaped furoxanes **1a–f** (see the figure) may be explained by a strong polar interaction of the furoxane fragments, leading to anti-parallel correlations or other stable arrangements of the molecules in the mesophase, for example, the type of ordering, theoretically predicted for ‘biaxial nematics’ [13, 14].

We are now going to synthesize other structurally similar LC compounds to assess their ability to generate the nematic phase. We hope that this information will allow us to better understand the nature of these liquid crystals and their properties.

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