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New liquid crystalline 3-methyl-6-(4-substituted phenyl)-4,5-dihydrobenzo[*d*]isoxazoles and 3,5-disubstituted 4,5-dihydroisoxazoles: synthesis and mesomorphic properties

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The synthesis and mesomorphic properties of new liquid crystalline 3-methyl-6-(4-substituted phenyl)-4,5-dihydrobenzo[*d*]isoxazoles and 3,5-disubstituted 4,5-dihydroisoxazoles are reported. These compounds have been synthesized by the reaction of 6-(4-substituted phenyl)-3-acetyl cyclohex-2-enones with hydroxylamine hydrochloride and of the corresponding oximes with unsaturated compounds in the presence of *N*-chlorosuccinimide and triethylamine, respectively.

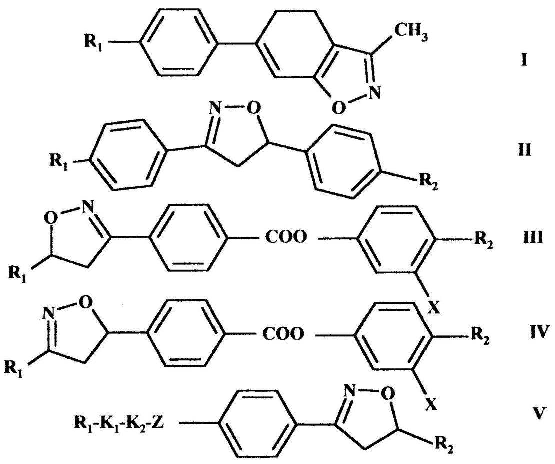
1. Introduction

There have been many reports of liquid crystalline compounds containing five-membered heterocyclic rings [1–6]. It was found that non-linear heterocyclic liquid crystals, such as pyrazole, thiophene, furan and isoxazole derivatives form smectic or nematic phases at low temperatures and over wide temperature ranges. In addition, the presence of hetero-atoms leads to an increase of the molecular dipole moment and in the dielectric anisotropy. These parameters are very important in the design of new compounds, having potential use as components in nematic or smectic C* liquid crystalline mixtures for display applications. In a previous publication we described the properties of liquid crystals containing isoxazole or isoxazoline fragments in the mesogenic core [7]. To continue this work we synthesized some novel liquid crystalline 4,5-dihydrobenzo[*d*]isoxazole and 4,5-dihydroisoxazole derivatives (**I**–**V**) see scheme 1, and investigated their mesomorphic properties with a particular interest in their structure–property relationships.

2. Results and discussion

2.1. *Synthesis*

The liquid crystalline 3-methyl-6-(4-substituted phenyl)-4,5-dihydrobenzo[*d*]isoxazoles **I** and 3,5-diaryl-4,5-dihydroisoxazoles **II** were synthesized by the reaction of 6-(4-substituted phenyl)-3-acetyl cyclohex-2-enones [8, 9] with hydroxylamine hydrochloride, and the oximes of 4-substituted benzaldehydes with 4-substituted styrenes, in the presence of *N*-chlorosuccinimide and triethylamine [10, 11], respectively. The aryl esters of 4-(5-alkyl-4,5-dihydro-3-isoxazolyl)benzoic **III** and 4-(3-alkyl-4,5-dihydro-5-isoxazolyl)benzoic **IV** acids were prepared in 70–80% yield using the same 1,3-dipolar cycloaddition of the corresponding nitrile oxides to 1-alkenes or methyl esters of 4-styrylbenzoic acids, and the subsequent base hydrolysis of the methyl esters **VI**, **VII** and esterification of the acids **VIII**, **IX** with various



Scheme 1. $R_1 = H_9C_4$, $H_{11}C_5$; $H_{21}C_{10}$, CH_3O, $H_{13}C_6O$–$H_{19}C_9O$; Z = single bond or COO; K_1 = single bond or 3-chlorobenzene ring; K_2 = benzene or cyclohexane ring; X = H or F; $R_2 = CN$, C_2H_5–C_6H_{13}, $OOCCH_3$, $COOCH_2CH(CH_3)C_2H_5$, $COOCH(CH_3)C_6H_{13}$, $C_6H_4COOCH(CH_3)C_6H_{13}$.

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phenols in the presence of dicyclohexylcarbodiimide and 4-*N*,*N*-dimethylaminopyridine as catalyst, see scheme 2.

An esterification was used for the synthesis of 3-[4-(*trans*-4-pentylcyclohexanoyloxy)phenyl]-5-cyano-4,5-dihydroisoxazole and the chiral 3-[4-(4-decyl-3-chlorobiphenyl-4′-carbonyloxy)phenyl]-5-(2-octyloxycarbonyl)-4,5-dihydroisoxazole **V**. However, this synthetic pathway does not give high yields of the final products, because the 3-(4-hydroxyphenyl)-5-cyano-4,5-dihydroisoxazole **X** and 3-(4-hydroxyphenyl)-5-(2-octyloxycarbonyl)-4,5-dihydroisoxazole **XI** cannot be prepared from the oximes of 4-hydroxybenzaldehyde or 4-benzyloxybenzaldehyde in yield higher than 40–50% (see scheme 3), and are very difficult to isolate by crystallization from the reaction mixture. As our investigations have shown, the interaction of oximes of 4-(4-alkoxybenzoyloxy)benzaldehydes with acrylonitrile in the presence of *N*-chlorosuccinimide and triethylamine gives the products (**V**, $R_1 = C_8H_{17}O$, $C_9H_{19}O$; $K_1 =$ bond; $K_2 =$ Ph) in higher yields (more than 60%).

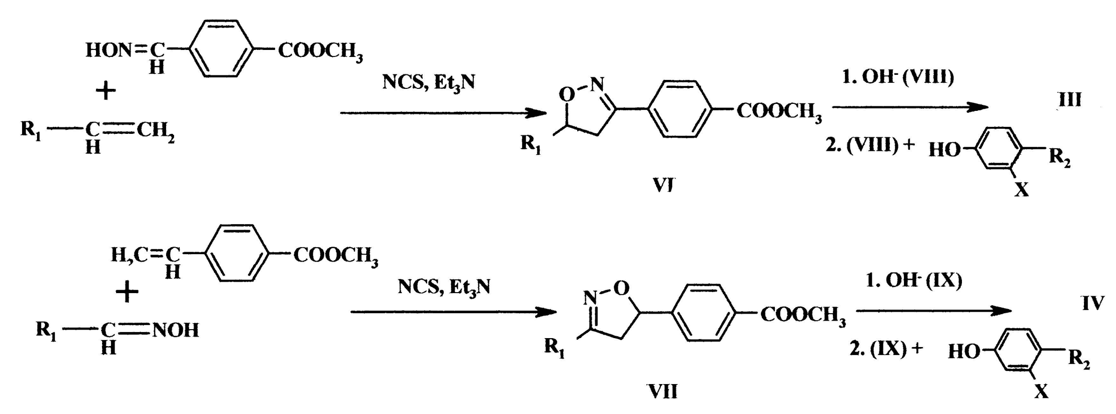
The structures of compounds **I**–**V** were confirmed by ^{1}H NMR, IR and mass spectroscopy. The proton NMR spectra (δ, ppm) of the aryl esters of 4-(5-alkyl-4,5-dihydro-3-isoxazolyl)benzoic acids **III** contained the doublet–doublet signals at 2.92 and 3.36 ppm belonging to the protons located at the fourth carbon atom of the isoxazoline fragment. The multiplet at 4.70 ppm in the spectra corresponds to the proton located at the fifth carbon atom in this fragment. The signals from the same protons of the 3,5-disubstituted 4,5-dihydroisoxazoles **V** are observed at 3.59, 3.68 and 5.32 ppm. The signals at 6.81–8.24 ppm in the NMR spectra of isoxazolines **I**–**V** belong to the aromatic protons.

The IR spectra of the esters **III**–**V** contained intense bands at 1720–1740 and 2235 cm^{-1} corresponding to the stretching vibrations of the carbonyl and cyano groups, respectively.

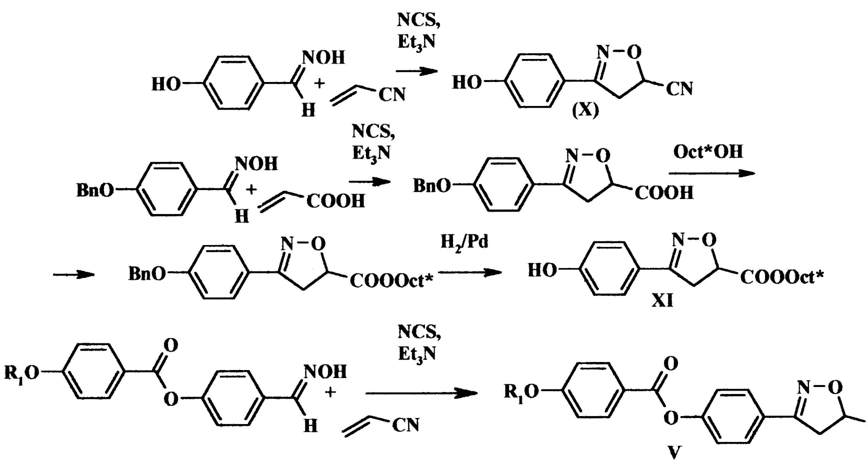
2.2 *Mesomorphic properties*

The phase transition temperatures of the 3-methyl-6-(4-substituted phenyl)-4,5-dihydrobenzo[*d*]isoxazoles **I** and 3,5-disubstituted 4,5-dihydroisoxazoles **II**–**V** are listed in tables 1–5.

As can be seen from tables 1 and 2, the 3,5-diaryl-4,5-dihydroisoxazoles **IIa**–**c** are not mesomorphic, while the 3-methyl-6-(4-substituted phenyl)-4,5-dihydrobenzo-[*d*]isoxazoles **Ia**–**d** form only a monotropic smectic A

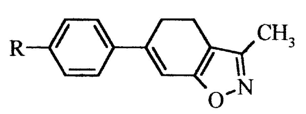


Scheme 2.



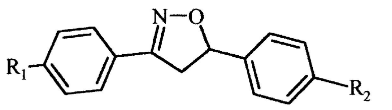
Scheme 3.

Table 1. Transition temperatures (°C) of 3-methyl-6-(4-substituted phenyl)-4,5-dihydrobenzo[*d*]isoxazoles **I**.



Compound	*R*	Cr		SmA		I
Ia	C_2H_5	•		—	105	•
Ib	C_6H_{13}	•		—	84	•
Ic	C_2H_5O	•	(75)	•	148	•
Id	C_4H_9O	•	(86)	•	94	•

Table 2. Transition temperatures (°C) of 3,5-diaryl-4,5-dihydroisoxazoles **II**.



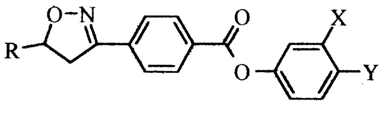
Compound	*R*		Cr		I
IIa	$C_6H_{13}O$	OCH_3	•	141	•
IIb	CH_3O	C_6H_{13}	•	136	•
IIc	$C_6H_{13}O$	$OOCCH_3$	•	153	•

phase. By comparison, the 3-aryl-5-alkyl-4,5-dihydroisoxazoles **IIIa**–**f** exhibit nematic or smectic A or B phases in the temperature range 85–154°C. In particular, the ethyl and chiral carboxyalkyl derivatives **IIIa**,**b**,**e**,**f** form a smectic phase, whereas only a nematic phase is observed for the corresponding fluorocyano derivatives **IIIc**,**d**. The rearrangement of the substituents in the heterocyclic fragment leads to the disappearance of the mesomorphic properties and a reduction of the melting point as seen for the 3-alkyl-5-aryl-4,5-dihydroisoxazoles **IV**–**a**,**b** (see table 4). This may be explained by a weakening of the intermolecular interactions going from the 3-aryl-5-alkyl to the 3-alkyl-5-aryl derivatives resulting from the reduced electronic conjugation and the increase in the non-linearity of the molecule (see the figure).

The data presented in table 5 reveal that 3-(4′-pentylbiphenyl-4-yl)-5-pentyl-4,5-dihydroisoxazole **Va**, like the 3-aryl-5-alkyl-4,5-dihydroisoxazoles **IIIa**,**b** (see table 3), forms a smectic A phase over the temperature range 142–179°C. The replacement of the benzene ring by a cyclohexane fragment and the addition of an extra methylene unit in the chain of **Vb**, however, lead to a sharp decrease in the temperature range of the smectic A phase.

3-[4-(4-*trans*-4-Pentylcyclohexyl)phenyl]-5-hexyl-4,5-dihydroisoxazole **Vb** is not mesomorphic and

Table 3. Transition temperatures (°C) of 3-aryl-5-alkyl-4,5-dihydroisoxazoles **III**.

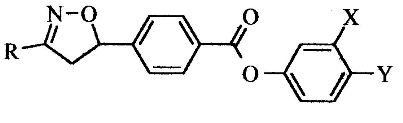


Compound	*R*	*X*	*Y*	Cr		SmA		N		I
IIIa	C_4H_9	H	Et	•		•		—	145	•
IIIb	C_5H_{11}	H	Et	•	132	•		—	154	•
IIIc	C_4H_9	F	CN	•	128	—	107	•	138	•
IIId	C_5H_{11}	F	CN	•	92.5	—		•	129	•
IIIe[b]	C_5H_{11}	H	C_6H_4COOAm[a]	•		—		—	220–224	•
IIIf[b]	C_5H_{11}	H	COOOct[a]	•	85	• (SmB)		—	126	•

[a] Am = $CH_2CH(CH_3)C_2H_5$, Oct = $CH(CH_3)C_6H_{13}$.

[b] These compounds have been obtained after crystallization as mixture of the epimers on C-5 atom of isoxazole ring (^{1}H NMR data).

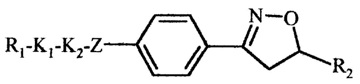
Table 4. Transition temperatures of 3-alkyl-5-aryl-4,5-dihydroisoxazoles **IV**.



Compound	*R*	*X*	*Y*	Cr		SmA		I
IVa	C_5H_{11}	H	$C_6H_4COOOct$[a]	•	(127)	•	136	•
IVb	C_5H_{11}	F	CN	•		—	53	•

[a] Oct = $CH(CH_3)C_6H_{13}$.

Table 5. Transition temperatures of 3-aryl-5-substituted 4,5-dihydroisoxazoles **V**.



Compound	R_1	K_1[a]	K_2	Z	R_2	Cr		SmA		N		I
Va	C_5H_{11}	B	—	—	C_5H_{11}	•	142	•		—	179	•
Vb	C_5H_{11}	C	—	—	C_6H_{13}	•		—		—	148	•
Vc	C_5H_{11}	C	—	—	CN	•	(76)	•		—	123	•
Vd	$C_8H_{17}O$	B	—	COO	C_3H_7	•	120	•	152	•	162	•
Ve	$C_8H_{17}O$	B	—	COO	CN	•	(86)	•		—	132	•
Vf	$C_9H_{19}O$	B	—	COO	CN	•	(87)	•		—	137	•
Vg	C_5H_{11}	C	—	COO	CN	•	107	•		—	121	•
Vh	$C_{10}H_{21}$	3-CIB	B	COO	COOOct[b]	•	(84)	•		—	124	

[a] B = 1,4-phenylene; C = *trans*-1,4-cyclohexenylene; 3-CIB = 3-Cl-1,4-phenylene.
[b] Oct = $CH(CH_3)C_6H_{13}$.

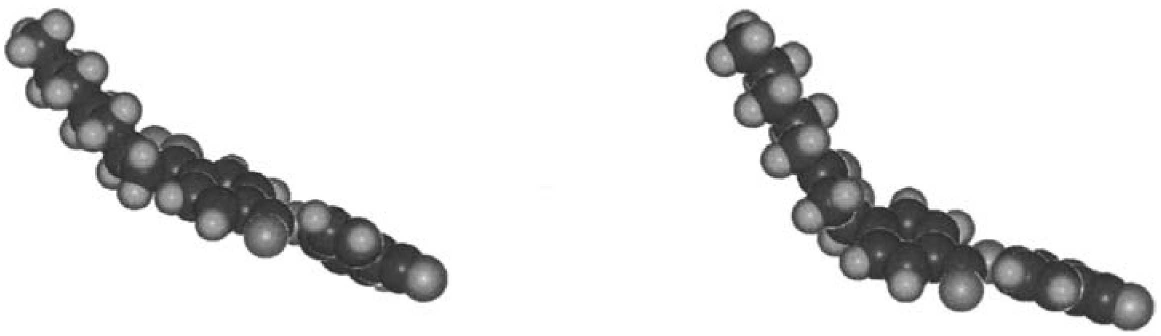


Figure. Molecular models of 3-aryl-5-alkyl-4,5-dihydroisoxazole **IIId** and 3-alkyl-5-aryl-4,5-dihydroisoxazole **IVb**.

3-[4-(4-*trans*-4-pentylcyclohexyl)phenyl]-5-cyano-4,5-dihydroisoxazole **Vc** exhibits only a monotropic smectic A phase. The insertion of the COO linking group into the molecular core increases the temperature range of the smectic A phase and leads to the appearance of a nematic phase. The 4-(5-Cyano-4,5-dihydro-isoxazol-3-yl)phenyl and 4-(5-propyl-4,5-dihydroisoxazol-3-yl)phenyl esters of 4-alkoxybenzoic and *trans*-4-pentylcyclohexane carboxylic acids **Vd–g** form these phases in the temperature range 120–162°C.

Investigations of the electro-optical and dynamic properties of LC mixtures containing the cyanoderivatives **IIId**, **IVb**, **Vg**, have shown that these compounds can be successfully used as components of liquid crystalline mixtures which are characterized by low threshold and saturation voltages in the twisted nematic effect, by step voltage–contrast characteristics and by low values of switch-on and switch-off times (table 6).

3. Experimental

3.1. *Characterization*

Confirmation of the structures of all intermediates and final products was obtained using a GC/MS mass spectrometer (HP 5972) and ^1H NMR spectroscopy. Phase transition temperatures were measured using a Linkam heating stage in conjunction with a polarizing PZO microscope and also by differential scanning calorimetry (Setaram DSC 92). The measurements of the electro-optical parameters of the mixtures were performed at room temperature in twisted nematic cells with 6 µm spacers; a polyamide layer was used to obtain homogeneous oriented samples.

3.2. *4-(5-Cyano-4,5-dihydroisoxazole-3-yl)-phenyl 4-nonyloxybenzoate **Vf***

To a cooled (−5°C) and stirred solution of an appropriate oxime (2.0 g), acrylonitrile (5 ml) and *N*-chlorosuccinimide (0.8 g) in 35 ml chloroform and 10 ml *N*,*N*-dimethylformamide, was added 0.85 ml triethylamine during 2 h. The reaction mixture was additionally stirred for 2 h at 0°C and for 18 h at room temperature; it was then acidified with 10% aqueous hydrochloric acid and the organic layer shaken with ether. The ethereal extract was washed with water and dried over anhydrous magnesium sulphate. The solvent was removed under vacuum and the product crystallized from isopropanol; yield 54.7%.

Table 6. Physical and electro-optical parameters of the nematic compositions[a].

Composition[b]	V_{10}/V	V_{90}/V	$P_{10\text{-}90}$	$N_{10\text{-}90}$	$\tau_{\text{on (ms)}}$	$\tau_{\text{off (ms)}}$
IIId in mixture **A**	2.7	3.6	0.333	12	78	48
IIId in mixture **B**	1.46	1.99	0.363	11	29	96
IVb in mixture **A**	2.04	2.80	0.373	11	34	72
IVb in mixture **B**	1.28	1.78	0.390	10	23	78
Vg in mixture **B**	1.67	2.46	0.471	7	36	88

[a] LC mixtures consist of 80% of the base mixture and 20% of the compound.

[b] Base mixtures: **A**—4-ethoxyphenylester of *trans*-4-butylcyclohexane carboxylic acid 35%; 4-butoxyphenylester of *trans*-4-butylcyclohexane carboxylic acid 35%; *trans* 4-(4-ethoxypheny)-1-propylcyclohexane 30%. **B**—4-pentyl-4-cyanobiphenyl 35%; 4-octyl-4-cyanobiphenyl 15%; 4-propoxy-4-cyanobiphenyl 25%; 4-ethoxyphenylester of *trans*-4-butylcyclohexane carboxylic acid 20%; 4-cyanobiphenyl ester of *trans*-4-butylcyclohexane carboxylic acid 5%.

Similar methods gave the other compounds **I**–**V** presented in tables 1–5.

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