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# Molecular Crystals and Liquid Crystals Incorporating Nonlinear Optics

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## Liquid Crystalline Benzo/1,2-d:5,4-d'/ Bisoxazoles

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LIQUID CRYSTALLINE BENZO/1,2-d:5,4-d'/BISOXAZOLES

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Abstract A number of benzo/1,2-d:5,4-d'/bisoxa-zoles have been synthesized. Only derivatives containing a cyclohexane ring exhibit liquid crystalline phases.

#### INTRODUCTION

In search of new nematic liquid crystals, we have synthesized a number of benzobisoxazole derivatives. We proceeded from the fact that the rigid rod polymers containing benzobisthiazolic<sup>1</sup>,<sup>2</sup> or benzobisoxazolic fragments<sup>3</sup> exhibit liquid crystalline properties.

#### DISCUSSION

Benzobisoxazoles (1-10) were obtained via condensation of 4,6-diaminoresorcinol dihydrochloride with appropriate acids in polyphosphoric acid by a general method<sup>4</sup>.

Symmetric benzobisoxazoles (1-3,7,10) were purified by column chromatography on silica with CHCl<sub>3</sub> as eluent. Asymmetric compounds (4-6,8,9) were isolated from the corresponding symmetric homologues by

recrystallization from hexane, purified by column chromatography and finally refined by vacuum sublimation.

The structure of the compounds was confirmed by mass- and UV-spectroscopy data.

TABLE 1 Phase transition temperatures

No	R	R'	Phase	transition (°C)	temperature
1	<sup>C</sup> 3 <sup>H</sup> 7	<sup>C</sup> 3 <sup>H</sup> 7			C- 89-I
2	<sup>C</sup> 5 <sup>H</sup> 11	<sup>C</sup> 5 <sup>H</sup> 11			C- 61-I
3	<sup>C</sup> 6 <sup>H</sup> 13	<sup>C</sup> 6 <sup>H</sup> 13			C- 58-I
4	H	<sup>C</sup> 6 <sup>H</sup> 13 <sup>-</sup>			C-191-I
5	<sup>C</sup> 5 <sup>H</sup> 11	<sup>C</sup> 6 <sup>H</sup> 13-€			C-142-I
6	<sup>C</sup> 6 <sup>H</sup> 13	°6 <sup>H</sup> 13-€			C-144-I
7	C6H13-	<sup>C</sup> 6 <sup>H</sup> 13-€			C-291-I
8	<sup>C</sup> 3 <sup>H</sup> 7	$^{\mathrm{C}}4^{\mathrm{H}}9^{-\mathrm{H}}$		C .	- 99- <b>N-1</b> 18-I
9	<sup>C</sup> 6 <sup>H</sup> 13	C4H9-(H)	(	C - 90 -S <sub>A</sub> -	- 96-N-106-I
10	C4H9-(H)	с <sub>4</sub> н <sub>9</sub> -(н)		C -	237-N-264-I

Thus, dialkylbenzobisoxazoles (1-3) exhibit no liquid crystalline properties.

Increasing geometric anisotropy of molecules by inserting aryl substituents leads to no mesophase. Only introduction of a cyclohexane ring results in liquid crystalline state. Actually, benzobisoxazoles (8,9) containing one cyclohexane fragment show mesophases at much lower temperatures as compared to the symmetrical dialkylcyclohexylbenzobisoxazole (10).

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