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*NEW OPTICALLY ACTIVE DOPANTS FOR LIQUID CRYSTAL
MIXTURES - (S)-1-PHENYLETHYLAMINE DERIVATIVES**

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Abstract: Several new optically active dopants for liquid crystal mixtures - (S)-1-phenylethylamines - and their helical twisting powers are reported.

Chiral nematics or mixtures of nematic liquid crystals with optically active additives (mesogenic or non-mesogenic) are potentially useful for application in electro-optical devices or in surface thermography.¹ They are of higher chemical and photochemical stability than cholesterol derivatives and they exhibit similar pitch values. Nematic esters,² cyanobiphenyls³ or Schiff-bases⁴ incorporating the (S)-2-methylbutyl group (or its homologues) and some non-mesogenic compounds, eg, derivatives of 2-naphthoxy- α -substituted acetic acids, derivatives of menthol or dibenzodiazocines¹ are of greatest interest.

In this paper several new derivatives of (S)-(-)-1-phenylethylamine such as amides, Schiff-bases and benzyl derivatives are reported which are very effective optically active dopants in nematic liquid crystals. The synthesized compounds, their melting (or boiling) points, specific

* Part of this work was presented at IV International Conference on Liquid Crystals for Socialist Countries, Tbilisi, 5th-8th October 1981.

rotations α_D^{20} and helical twisting powers A_m are listed in the Table. Schiff-bases (compounds 5-9) and some amides (2-4) have relatively high helical twisting powers - about four times higher than cholesteryl nonanoate ($0.13 \mu\text{m}^{-1}\text{mol \%}^{-1}$).⁵ Amines (10, 11) and *N*-(S)-1-phenylethyl 4-decylbenzamide (1) are somewhat less effective. Some of these compounds (for example 6) can be used in mixtures with 4-cyano-4'-n-pentylbiphenyl (CB5) (2-10%) to give selective light reflection. It should be noticed that 4-(4'-octylphenylbenzoyloxy)benzylidene-(S)-1-phenylethylamine (9) gives a monotropic smectic phase.

EXPERIMENTAL

All the compounds were prepared by standard procedures from (S)-(-)-1-phenylethylamine (Fluka AG, $\alpha_D^{20} = 40 \pm 5^\circ$, $c = 10$ in ethanol) and the appropriate acyl chloride (compounds 1-4) or 4-substituted benzaldehyde⁶ (compounds 5-9). Amines 10 and 11 were obtained from appropriate anils by reduction with sodium borohydride in methanol. They solidified at room temperature after standing.

4-Alkoxybenzaldehydes were prepared by catalytic alkylation in a two phase system from the alkyl bromide and 4-hydroxybenzaldehyde in chlorobenzene in the presence of 20% aqueous KOH and a catalytic amount of tetrabutylammonium bromide; the average yield was about 80%.⁷








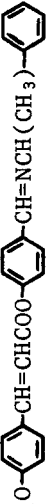



The purity of all the final products was checked by tlc; their structures were confirmed by elemental analysis and by IR spectroscopy.

Pitch measurements of the compounds under investigation in mixtures with CB5 were made by the Grandjean-Cano method. Helical twisting power A_m was calculated from the formula $1/P = A_m c_m$ where P is pitch (μm) and c_m is molar concentration (%) of optically active compound (0.5-3 mol %) in CB5. Specific rotations were measured using chloroform solutions.

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TABLE

No	Formula	mp (°C)	α_D^{20} (°C)	$A_m \left[\frac{1}{\mu\text{m mol } \%} \right]$
1		74-75	+0.9	0.32
2		102-103	+1.3	0.42
3		159.5	+1.5	0.49
4		162-163	+3.4	0.56
5		41	+6.7	0.45
6		94-95	+9.8	0.53
7		82	+10.0	0.52
8		78-79	+6.0	0.53
9		K 110 I (84) S	+5.7	0.66
10		185/1 mm Hg*	-4.2	0.26
11		170/0.1 mm Hg*	-4.3	0.36

* boiling point

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