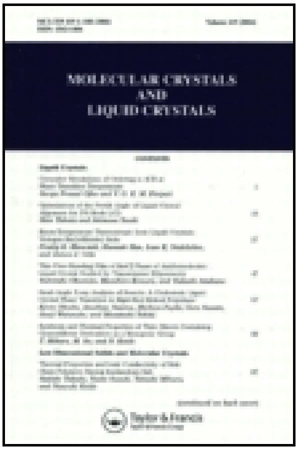

Molecular Crystals and Liquid Crystals Incorporating Nonlinear Optics

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl17

Mesomorphic Twistane Derivatives: A New Class of Chiral Nematogens

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To cite this article: R. Ch. Geivandov , I. V. Goncharova & V. V. Titov (1989): Mesomorphic Twistane Derivatives: A New Class of Chiral Nematogens, Molecular Crystals and Liquid Crystals Incorporating Nonlinear Optics, 166:1, 101-103

To link to this article: http://dx.doi.org/10.1080/00268948908037141

Mol. Cryst. Liq. Cryst., 1989, Vol. 166, pp. 101–103
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Printed in the United States of America

Mesomorphic Twistane Derivatives: A New Class of Chiral Nematogens

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(Received June 1, 1987; in final form February 5, 1988)

We present a new class of chiral nematogens, non-sterol cholesterogens, in which the optical activity is provided by asymmetry of the twistane molecule as a whole.

Keywords: twistane, chiral nematogens, tricyclo(4.4.0.$0^{3,8}$*)decane, chiral axial disymmetry, optical activity, cholesteric phase*

In the last few years, many reported materials exhibiting cholesteric phases have been sterol derivatives or non-sterol systems in which the optical activity is provided by terminal chiral alkyl or alkoxy groups.[1,2]

Recently we reported the synthesis and properties of a number of new liquid crystal compounds containing the twistane system.[3]

Here we report for the first time the properties of esters containing the optically active twistane ring system.

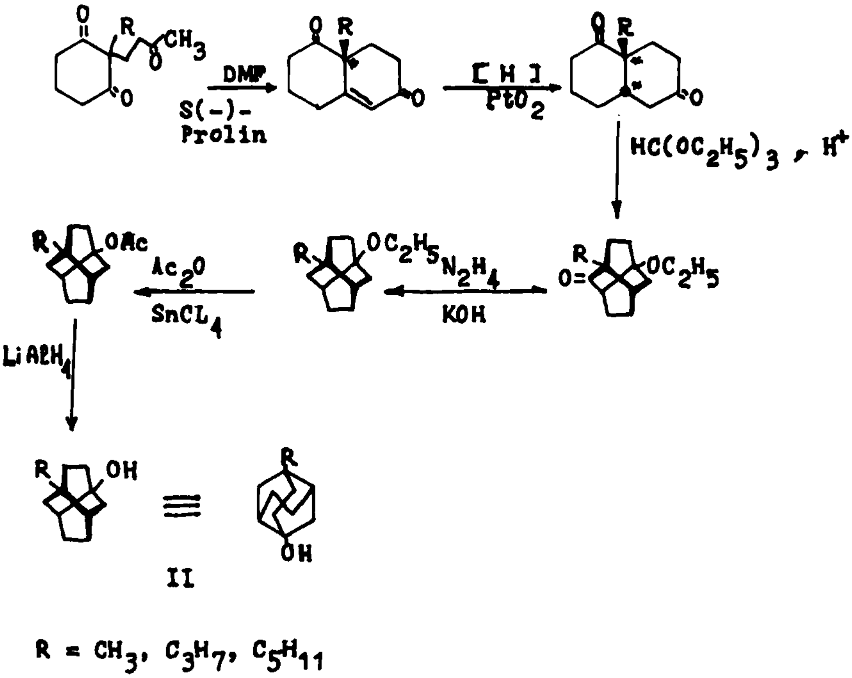
Twistane [tricyclo(4.4.0.$0^{3,8}$)decane] has a unique symmetry (D_2) and is chiral, being composed of five boat-form cyclohexane rings which are all twisted in the same sense, and existing in two enantiomeric forms Ia and Ib (cf. Figure 1).[4] According to the Cahn-Ingold-Prelog nomenclature the enantiomer Ia has P-helicity, whereas the other, Ib, has M-helicity. The chirality of twistane is due to the asymmetry of the molecule as a whole *i.e.* it is not caused by asymmetric atoms (so-called permolecular chirality).

Using optically active 8-alkyltwistanols, some liquid-crystal esters have been obtained; their melting points and transition temperatures are shown in Table I.

Ia Ib

FIGURE 1

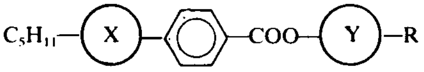
The R-(+)-8-alkyltwistanols were prepared according to the following scheme:

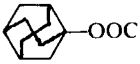


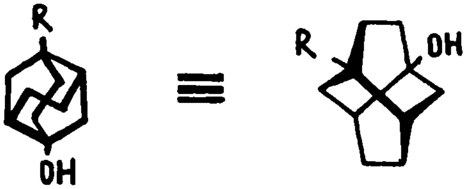
SCHEME 1

TABLE I

Transition temperatures (°C) of twistane derivatives.



Compound	X	Y	R	K		Ch		I
III			C_3H_7	·	94.2	·	119.7	·
IV			C_5H_{11}	·	71.8	·	126.4	·
V			CH_3	·	106.5	–		·
VI			C_5H_{11}	·	65.0	·	124.7	·
VII			C_5H_{11}	·	180.9	–		·



R = CH_3, C_3H_7, C_5H_{11}

FIGURE 2

The esters were prepared by acylation of the 8-alkyltwistanols with the acids chlorides in pyridine solution by the usual method.

The twistane esters III, IV, and VI exhibit cholesteric phases. The compounds IV and VI show anomalous temperature effects on the pitch which increases from 1.1 μ to 1.6 μ with increasing temperature.

We are at present investigating this problem more closely and shall publish the results elsewhere.

Details of these experimental procedures will be published later. All materials prepared were checked for purity by the usual methods (t.l.c., g.l.c., h.p.l.c.) and the structures of all final products (and where necessary those of the synthetic intermediates) were confirmed by mass spectrometry, and n.m.r. and infrared spectroscopy. Transition temperatures were determined using a Mettler-FP-5 apparatus with a polarising microscope, MIN-8.

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