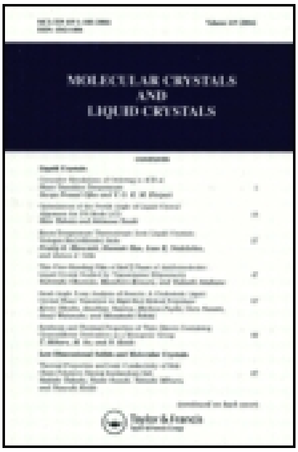

Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl16

Effect of Molecular Structure on Mesomorphism. 18.[1] Twin Dimers Having Methylene, Ethylene Oxide and Siloxane Spacers

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Version of record first published: 28 Mar 2007.

To cite this article: David Creed, John R. D. Gross, Sarah L. Sullivan, Anselm C. Griffin & Charles E. Hoyle (1987): Effect of Molecular Structure on Mesomorphism. 18.[1] Twin Dimers Having Methylene, Ethylene Oxide and Siloxane Spacers, Molecular Crystals and Liquid Crystals, 149:1, 185-193

To link to this article: http://dx.doi.org/10.1080/00268948708082979

Mol. Cryst. Liq. Cryst., 1987, Vol. 149, pp. 185–193
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Printed in the United States of America

Effect of Molecular Structure on Mesomorphism. 18.[1] Twin Dimers Having Methylene, Ethylene Oxide and Siloxane Spacers

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(*Received December 10, 1986*)

Six Twin dimeric compounds having two rigid cores connected by a central spacer group are described. Two types of rigid units, 4-pentyloxyphenyl cinnamates and 4-cyano-4′-oxybiphenyl, were employed. The spacer groups were pentamethylene (PM), diethylene oxide (EO) and disiloxane (DS). For each rigid core the nematic–isotropic temperature followed the order PM > EO > DS. Investigation of the ΔH and ΔS parameters for the nematic–isotropic (clearing) transition revealed that for these compounds the clearing transition was driven by ΔS. The EO mesogens have larger ΔS values than for the PM mesogens, which result in lowered clearing temperatures due to relatively constant ΔH values. The conformational preference for gauche isomers in the spacer of the EO compounds is seen as conducive to proper orientational alignment of the rigid cores in the nematic phase, better so than for the PM and DS spacers.

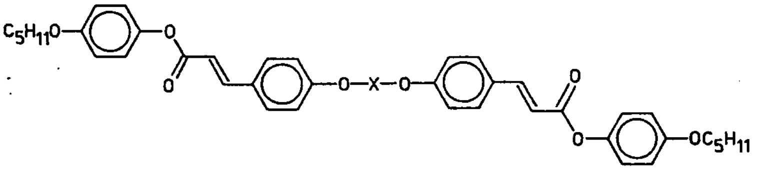
INTRODUCTION

Polymeric mesogens having a regularly alternating rigid-flexible repeating structure in the polymer main chain are reported to exhibit significant variations in liquid crystalline properties depending on the nature of the flexible spacer connecting the rigid groups.[2] The majority of studies on (rigid-flexible)$_n$ mesogenic polymers have focused on homologous series containing flexible polymethylene chains of various lengths. In these polymers, alternation in liquid crystalline properties depends on the number of methylene groups in the spacer (odd or even).[3] There have also been reports of oligooxyethylene[2,4] spacers and of siloxane-containing[5] spacers in such liquid crystalline polymers. The oligooxyethylene spacers are stereochemically similar in some respects to their all-carbon methylene counterparts, i.e., bond lengths and bond angles, but are nonetheless different in that there is an energetic preference for *gauche* rather than *trans* conformations for the carbon-carbon bond in —OCH_2CH_2O— segments.[6] Siloxane spacers are considerably different from methylene spacers in virtually all aspects including bond lengths, bond angles, and conformational preferences.[7] This combination of large alternations in bond lengths and bond angles for siloxane spacers is expected to produce a poor orientational alignment of the major axes of the rigid cores. Thus it can be safely concluded that for (rigid-flexible)$_n$ polymers the spacer group can and in fact does play a significant role in determining the liquid crystalline properties of the polymer. In order to provide a sound basis for interpretation of the effect of various spacer groups on the liquid crystalline properties of such (rigid-flexible)$_n$ polymers, it is necessary to study carefully designed small molecule model systems. Recently, liquid crystalline compounds having a rigid-flexible-rigid structure have been studied as models for liquid crystalline polymers.[8] These Twinned dimeric liquid crystals (DLC) retain the crucial structural component of many main chain thermotropic polymers, a flexible segment between rigid cores, shown below, yet are amenable to a more straightforward interpretation since they are monodisperse and as such are not complicated by a molecular weight distribution. The lack of functionalized end groups in these dimers renders them better models than actual oligomers in that they are structually more similar to a high polymer than are actual oligomers which have end groups, such as COOH and OH, which can alter or even dominate the liquid crystallinity of the material. In this paper, we report the thermodynamic parameters of Twinned liquid crystalline dimers with methylene, ethylene oxide and siloxane spacers. Two rigid cores, a phenyl cinnamate ester and a cyanobiphenyl, are in-

corporated as the mesogenic moieties. Results for the Twin cinnamate esters are of particular interest as models for photoreactive liquid crystalline polymers recently developed in our laboratory.

EXPERIMENTAL

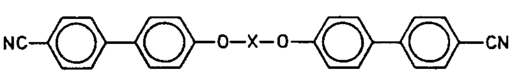
Two series of Siamese Twin dimeric mesogens each separately having pentamethylene, diethylene oxide, or symmetrical bis methylene tetramethyldisiloxane spacers were prepared. In each series an ether linkage connects the spacer to the rigid cores. One series, *1–3*, incorporates 4-pentyloxyphenyl 4′-oxycinnamate groups as the terminal mesogenic units. The second series, *4–6*, has terminal 4-cyano-4′-oxybiphenyl rigid groups. Chemical structures for these two series are shown below.



X = $—CH_2CH_2CH_2CH_2CH_2—$ 1

$—CH_2CH_2OCH_2CH_2—$ 2

$—CH_2\overset{CH_3}{\underset{CH_3}{Si}}—O—\overset{CH_3}{\underset{CH_3}{Si}}CH_2—$ 3



X = $—CH_2CH_2CH_2CH_2CH_2—$ 4

$—CH_2CH_2OCH_2CH_2—$ 5

$—CH_2\overset{CH_3}{\underset{CH_3}{Si}}—O—\overset{CH_3}{\underset{CH_3}{Si}}CH_2—$ 6

The bis cinnamate intermediates were prepared by reacting the methyl ester of 4-hydroxycinnamic acid with the appropriate spacer precursor 1,5-dibromopentane; bis 2-chloroethyl ether; or 1,3-bis (bromomethyl)-1,1,3,3-tetramethyldisiloxane in DMF at 120°C for 8 hours using sodium carbonate as base according to standard procedures.[9] The mixture was then poured into a large quantity of ice-water and the resulting solid collected by filtration, dried, and crystallized from methanol. The product bis cinnamates were then hydrolyzed to the bis cinnamic acids by refluxing in aqueous ethanol in the presence of excess potassium hydroxide. The bis acids were then precipitated by acidification of the solution with 30% HCl, collected by filtration, washed well with water, dried under vacuum, and then recrystallized from DMF/ethanol.[9]

The bis cinnamoyl chlorides were then prepared by refluxing the bis acids with thionyl chloride for 4 hours. The thionyl chloride was evaporated under reduced pressure and the bis acid chlorides crystallized from hexane or hexane/chloroform. The bis phenyl cinnamate esters were prepared by the room temperature reaction between 4-pentyloxyphenol and the appropriate bis cinnamoyl chloride (2:1 ratio) in chloroform with pyridine as acid scavenger. The solutions were stirred for 24 hours, washed with sodium carbonate solution and water, dried and evaporated. The crude product was crystallized from ethanol and then chromatographed on preparative scale thin layer chromatography plates of silica gel using chloroform as elutant. The desired bands were collected, the product extracted with ethyl acetate, and the solvent evaporated. The Siamese Twin products were then crystallized from aqueous ethanol.

The bis cyanobiphenoxy compounds with ethylene oxide and methylene spacers were obtained by reaction of 4-hydroxy-4′-cyanobiphenyl with the appropriate spacer precursor (2-iodoethyl ether or 1,5-dibromopentane) in DMF under reflux for 4 hours, using sodium carbonate as base. The mixture was then poured into ice-water and the solid material collected by filtration. The siloxane compound was obtained by reaction of 4-hydroxy-4′-cyanobiphenyl with 1,3-bis (bromomethyl)-1,1,3,3-tetramethyldisiloxane in acetonitrile under reflux for 12 hours, the solution filtered, and the solvent evaporated. The compounds were recrystallized from ethanol, purified by preparative tlc as described above, and recrystallized from ethyl acetate (methylene spacer) or ethanol (ethylene oxide spacer and siloxane spacer).

All compounds were characterized by infrared and proton nmr spectroscopy and gave results consistent with the proposed structures. Elemental analysis gave results in agreement (±0.40%) with the theoretical values for all compounds (1–6). Transition temperatures were obtained by both polarized light microscopy and differential scanning calorimetry. Agreement between the two methods was excellent. Quantitative enthalpic measurement was made using computer-integrated peak areas, on a Du Pont 9900 DSC, with indium as standard.

RESULTS AND DISCUSSION

Figure 1 shows a typical DSC scan for a representative compound, 2, with characteristic endotherms at 113.2°C and 163.9°C. The lower temperature is the crystalline melting point representing a crystal → nematic transition. The upper temperature is a typical nematic → isotropic (clearing) transition. Identical results were obtained for transition temperatures for compound 2 using polarized light microscopy. The mesophase was identified as nematic by optical microscopy (droplets which coalesced to a Schlieren texture). Similar analysis of the other compounds yielded the results in Table I. Compounds 1, 2, 4 and 5 are enantiotropic nematics. Compound 3 was nematic, yet monotropic, with a nematic–isotropic (N–I) temperature of ~70°C measured by rapidly cooling the sample into the mesophase and then reheating the monotropic nematic phase through the N–I transition. Finally, compound 6 showed no liquid crystalline behavior either by DSC or by optical microscopy.

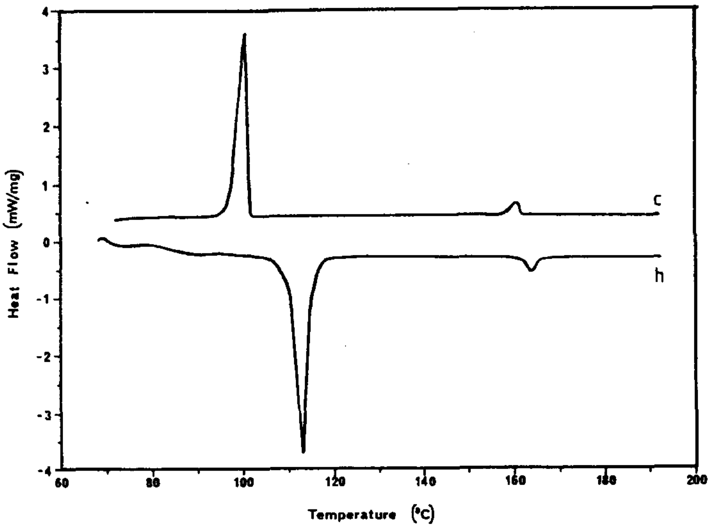


FIGURE 1 DSC scan of compound 2, bis cinnamate with ethylene oxide spacer.

Upon closer examination of the data in Table I, it is readily seen that the clearing temperatures (N–I) for both series show the same general trend—an increase from disiloxane spacer to diethylene oxide to pentamethylene. This trend parallels the barriers to rotation of the relevant bonds in the spacer, Si—O < C—O < C—C, and it is tempting to rationalize the T_{NI} data simply on this basis, i.e., the more flexible the spacer, the more easily disordered are the core groups. In order to provide additional insight, however, into the effect of the spacer group structure on the liquid crystalline properties of the model systems; it is necessary to evaluate the enthalpies (ΔH) and entropies (ΔS) associated with the *nematic–isotropic* transition. The ΔH and ΔS values for these transitions of the six model compounds (1–6) are also listed in Table I. These results can be interpreted by careful consideration of the conformational structure of each of the spacer groups.

For the pentamethylene spacer, the lowest energy all *trans* conformation allows neither collinearity nor parallelism of the rigid core groups, important factors in stability of the nematic phase. For the

TABLE I

Thermal (DSC) data for Twin compounds 1–6; 1–3 are phenyl cinnamates, 4–6 are cyanobiphenyls

Compound	Spacer	K–N			N–I		
		T[a]	ΔH[b]	ΔS[c]	T[a]	ΔH[b]	ΔS[c]
1	PM	130.4	38.52	95.50	178.3	1.78	3.94
2	EO	113.2[d]	73.32	189.85	163.9	2.19	5.01
3	DS	122.6	65.83	166.39	~70[e]	—	—
4[f]	PM	138.3[g]	22.69	55.15	184.1	1.89	4.13
5	EO	146.5	44.88	106.94	153.5	2.08	4.88
6	DS	138.9[h]	40.52	98.34	—	—	—

[a] in °C

[b] in kJ/mole

[c] in J/mol·K

[d] On some runs a small exotherm appears at 81.5°C with a corresponding reduction in the magnitude of ΔH and ΔS at K–N

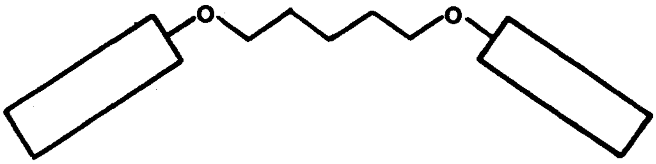
[e] observed on rapid cooling

[f] This compound has been reported previously.[1,10] Transition temperatures are in excellent agreement with those reported here. Quantitative enthalpic (and entropic) data are in general agreement with literature values. The values for 4 in this table were taken under the same conditions as the other tabular data and are therefore internally self-consistent.

[g] a K–K transition occurs at 121.0°C

[h] K–I

pentamethylene spacer in the all *trans* conformation the rigid cores are tilted by about 30° with respect to the spacer axis. The schematic below depicts this molecular geometry. Even allowing for some gauche conformers the major axes of the rigid cores are not expected to be collinear or parallel and the molecule is, on the average, bent. Since order in the liquid crystalline phase is favored by the ability of the component molecules to pack efficiently (usually at the expense of conformational freedom), the pentamethylene spacer in the angular all *trans* conformation prevents formation of an extended, rod-like structure with favorable steric packing of these rods.



The ethylene oxide spacer, on the other hand, has a preference for the *gauche* conformation.[6] This allows a larger fraction of conformers with the proper core-core orientational alignment as this more flexible and conformationally mobile spacer more easily accommodates the orientational order requirement of the rigid cores in the mesophase. As a result of the ethylene oxide mesogen's natural preference for *gauche* conformers of the —OCH_2CH_2O— carbon-carbon bond which place the cores in a more orientationally ordered alignment, compounds (2 and 5) with the ethylene oxide spacer have larger values of ΔS for the N–I transition than the compounds with the pentamethylene spacer. It is interesting that the pentamethylene spacer in both series has the larger T_{NI} yet the smaller ΔS as compared with their ethylene oxide counterparts. That is, the nematic phase is more ordered in the ethylene oxides, yet the T_{NI} is lower. These interpretations (and predictions) of relative order in the methylene and ethylene oxide spacers are subject to testing by examining order parameters for these systems, by such methods as nmr spectroscopy. Since the N–I transition enthalpies of compounds 1 and 2 and compounds 4 and 5, are relatively constant, it is the entropy which controls the transition temperature. This accounts for the elevated T_{NI} values for compounds 1 and 4 compared with 2 and 5, respectively.

Finally, it is well known that the siloxane spacer group present in compounds 3 and 6 prefers the *trans* geometry, but due to the alternating bond lengths and bond angles[8] along the chain, it has difficulty adopting a collinear core arrangement. Consequently, for compound

3 only a low temperature (~70°C) transition from the isotropic to the nematic phase is observed upon rapid cooling far below the K–I temperature. In addition, compound 6 which also has the siloxane spacer does not exhibit even a monotropic mesophase. Apparently, the greater axial ratio of the longer rigid core of the bis cinnamate offsets the deleterious effect of the siloxane space better than does the biphenyl species thus accounting for the monotropic behavior of compound 3 compared to compound 6 which cannot form a mesophase at all.

CONCLUSIONS

In this report the liquid crystalline properties of several Twinned dimeric compounds have been reported. Three types of spacer groups (methylene, siloxane, and ethylene oxide) and two rigid core groups (cyanobiphenyl and phenyl cinnamate) have been combined to produce the six compounds investigated. Specific conclusions are:

1. Ethylene oxide spacers provide better packing than pentamethylene spacers resulting in larger entropies for nematic–isotropic transitions and lower transition temperatures for the ethylene oxide spacer.
2. Nematic–isotropic transitions for the Twinned dimers investigated are entropically driven.
3. Siloxane spacers prevent Twinned dimers from adopting the collinear core arrangement required for liquid crystalline behavior.
4. The greater axial ratio in the phenyl cinnamate ester core groups are able to compensate, to a limited degree, for the detrimental effects of siloxane spacers thereby generating a monotropic nematic phase whereas the compound having the cyanobiphenyl rigid cores with a smaller axial ratio, is not liquid crystalline.

Work is in progress on phenyl cinnamate containing polymers, which also incorporate the spacer groups described here, as photoreactive crosslinkable liquid crystalline polymers.

Acknowledgment

The authors wish to thank Armstrong World Industries for partial support of this work. ACG and SLS also wish to thank the National Science Foundation for partial support of this project (DMR-8417834).

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