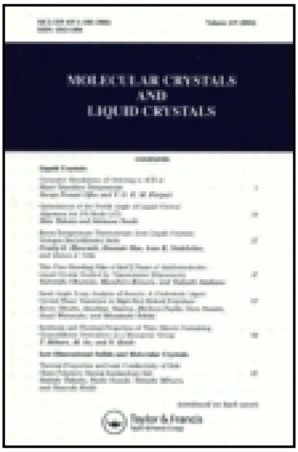


Molecular Crystals and Liquid Crystals Incorporating Nonlinear Optics
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl17

Effect of Molecular Structure on Mesomorphism 22.[1] Liquid Crystalline1-Alkanol Derivatives

A. C. Griffin [a] & S. R. Vaidya [a]
[a] Departments of Chemistry and Polymer Science, University of Southern Mississippi, Hattiesburg, MS, 39406, USA

Version of record first published: 22 Sep 2006.

To cite this article: A. C. Griffin & S. R. Vaidya (1989): Effect of Molecular Structure on Mesomorphism 22.[1] Liquid Crystalline1-Alkanol Derivatives, Molecular Crystals and Liquid Crystals Incorporating Nonlinear Optics, 173:1, 85-88

To link to this article: http://dx.doi.org/10.1080/00268948908033369

Mol. Cryst. Liq. Cryst., 1989, Vol. 173, pp. 85–88
Reprints available directly from the publisher
Photocopying permitted by license only

Printed in the United States of America

Effect of Molecular Structure on Mesomorphism.22.[1] Liquid Crystalline 1-Alkanol Derivatives

A. C. GRIFFIN and S. R. VAIDYA[2]

Departments of Chemistry and Polymer Science, University of Southern Mississippi, Hattiesburg, MS 39406 USA

(*Received February 2, 1989*)

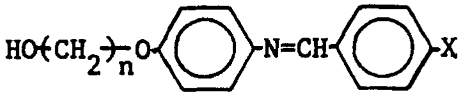
Several 1-alkanols having a mesogenic unit attached to the omega-carbon have been prepared. Many of these are liquid crystalline. The nematic mesophase is predominant for these materials. This is presumably due to intermolecular hydrogen-bonding between polar terminal groups such as cyano or nitro and the primary hydroxyl functionality of a proximal molecule. The resulting end-to-end association favors a nematic mesophase.

In the course of synthesis of unsymmetrical dimeric mesogens,[3] several 1-alkanols were prepared in which a mesogenic moiety was attached to the ω-carbon of the alkanol. These compounds are structurally analogous to classical *n*-alkoxy terminated mesogens, except that the terminus of the chain is polar(OH) and capable of associative behavior. The hydrogen bonding ability of hydroxyl offers an interesting perturbation on a classical mesogenic structure. An additional feature of the compounds studied here is the presence of a polar hydrogen bond proton-acceptor: cyano, nitro or trifluoromethyl, at the end of the mesogenic moiety.

It is known that cyano[4] and nitro[5] can participate in intermolecular hydrogen bonding with hydroxyl groups; cyano being the more effective. Trifluoromethyl should likewise be capable of some degree of association with hydroxyl. In this paper are reported synthesis and characterization of twelve 1-alkanols having a mesogenic unit attached to the ω-carbon of the alcohol. The general structure is shown below.

Series I

n = 6, 11, 12



Series II

$X = CN, NO_2, CF_3$

$n = 6, 11, 12$

The three members of series I were prepared by an alkylation reaction involving 4-cyano-4′-hydroxybiphenyl and an equimolar amount of the corresponding ω-halo-1-alkanol in refluxing DMF using potassium carbonate as base and a water work-up. The products were recrystallized from ethyl acetate. Approximate yields of 75–80% were obtained. Chloro and bromo were employed in the haloalkanols.

The nine members of series II were synthesized in three steps. Initially, 0.1 mole of ω-halo-1-alkanol was coupled with 0.1 mole of 4-hydroxyacetanilide in DMF as described above. The crude amide was then dissolved in 50 ml of absolute ethanol. To this solution 50 ml of concentrated hydrochloric acid was added and the reaction mixture was refluxed for three hours and then allowed to cool overnight. The precipitated salt (anilinium chloride) was filtered and then recrystallized from absolute ethanol. Approximately 55–60% yields were obtained. The salts were then slurried with an excess of saturated sodium bicarbonate solution for an hour and the precipitate was filtered and then recrystallized from absolute ethanol. Yields of the amines were about 75–80% from the salts. Finally, equimolar amounts of the appropriate amine and the desired aldehyde (4-substituted benzaldehyde) were separately dissolved in the minimum quantities of absolute ethanol and the solutions were mixed at room temperature and stirred overnight. The excess ethanol was removed by rotary evaporation and the product was recrystallized from a mixed solvent system consisting of water and ethanol.

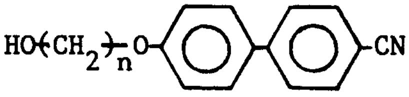
Structures for all members of the two series were determined by FT infrared and proton nuclear magnetic resonance spectroscopy. Elemental analysis also gave results consistent with the proposed structures. Differential scanning calorimetry (DuPont 9900; 910 DSC) and optical microscopy (Reichert/Mettler FP5/52) were used to examine mesophase properties.

In Table I thermal properties of the two series of mesogenic alcohols are given. For series I, the cyanobiphenyl series, only a nematic phase is seen for all three compounds. This is in contrast to the corresponding methyl terminated chains (OH replaced by CH_3) for which compounds having the longer alkoxy tails exhibit only smectic A mesophases. For example, 4-cyano-4′-dodecyloxybiphenyl, comparable to $n = 11$ in series I, shows the phase sequence $K69S_A89I$.[6] It is obvious from both the clearing temperatures and from the phase behavior that the nematic phase is strongly promoted by the hydroxy terminus for this series.

Series II mesogens likewise exhibit a pronounced tendency toward nematic behavior in comparison to their methyl analogues. In each case the cyano group is most effective at nematic phase stabilization compared to nitro which itself exhibits an increased nematic stability though less than that for cyano. The trifluoromethyl

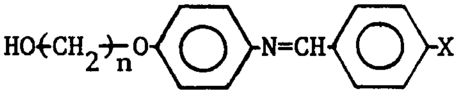
TABLE I

Thermal properties for two series of mesogens having hydroxy terminated alkoxy chains



Series I

n	Thermal Properties
6	K91.9N109.8I
11	K92.0N(91.2)I
12	K90.3N99.4I



Series II

n	X	Thermal Properties
6	CN	K117.5N132.3I
6	NO_2	K125.7I
6	CF_3	K117.5I
11	CN	K103.1N109.5I
11	NO_2	K78.8S_A89.0N95.1I
11	CF_3	K111.0I
12	CN	K111.2N(105.6)I
12	NO_2	K94.9S_A(87.0)N(93.1)I
12	CF_3	K111.0I

compounds are not mesogenic. This is at first somewhat surprising since trifluoromethyl as a para-substituted aromatic terminal group is effective at producing mesomorphic materials.[7]

However, trifluoromethyl in this position produces exclusively smectic phases due, presumably, to the extreme tendency toward segregation of fluorocarbon and hydrocarbon molecular components, leading to layered (segregated) structures. In the case here (hydrogen-bonding of OH and CF_3) nematic phases, not smectic, would be stabilized. As a result of these competing factors, the trifluoromethyl members of series II are not mesogenic. The tendency toward segregation is sufficiently strong to prevent nematic phase formation. Another interesting feature of series II is the formation of smectic A phases for the longer nitro members, but not for the cyano members. Perhaps this is reflective of the greater tendency of cyano toward hydrogen bonding leading thereby to more end-to-end string-like (nematic) association for cyano precluding smectic formation, but producing higher N-I temperatures than for the analogous nitro members.

Although it is risky to relate melting points *per se* to molecular structure, the melting temperatures of the hydroxy-terminated chains are, for each compound in the two series, elevated relative to their methyl analogues. Solid-state hydrogen bonding (OH to OH or OH to X) can reasonably be inferred from this observation.

Preliminary x-ray powder diffraction data was obtained for the $n = 11$ hydroxy-terminated nitro compound in series II. The sample was cooled from the isotropic phase through its nematic and smectic A phases to room temperature. The room temperature xrd pattern is simple with only two low angle maxima. The most intense ring corresponded to 36.4Å and the weaker ring had an associated distance of 21.0Å. From space filling molecular models it appears that the 36.4Å may arise from an A_d bilayer smectic A phase (pi-overlap between rings) of the mesogen. Molecular origins of the 21.0Å ring are less clear. It would appear that for the cyano and nitro mesogens in this study the hydroxy group can disrupt (unpair) the "normal" bilayer smectic A organization promoting a head-to-tail nematic string of mesogens instead. In the case of the longer nitro mesogens of series II, their weaker (than cyano) tendency to hydrogen-bond permits formation of a bilayer smectic A phase below the enhanced nematic.

Acknowledgment

We wish to thank the National Science Foundation (DMR-8417834) for support of this work.

References

1. For part 21 in this series see A. C. Griffin, S. L. Sullivan and W. E. Hughes, *Liquid Crystals*, in press.
2. Present address: Polymer Products Department, E. I. du Pont de Nemours & Company, Parkersburg, WV 26102.
3. A. C. Griffin and S. R. Vaidya, *Liquid Crystals*, **3**, 1275 (1988).
4. A. Allerhand and P. V. R. Schleyer, *J. Am. Chem. Soc.*, **85**, 866 (1963).
5. W. F. Baitinger, P. V. R. Schleyer, T. S. S. R. Murty and L. Robinson, *Tetrahedron*, **20**, 1635 (1964).
6. G. W. Gray, J. Phys. [Paris], Coll. C1 **36**, 337 (1975).
7. See for example A. C. Griffin and N. W. Buckley, *Mol. Cryst. Liq. Cryst. (Lett.)*, **41**, 141 (1978).