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Improvement of Thermotropic Liquid Crystallinity by Incorporation of Unsaturated Fatty Alcohol Tail Units

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Directed "synthesis" of organic crystals with desirable supermolecular structure is currently an active and exciting research field.[1] In applications where thin films are required, however, crystals often present difficult processing problems. In this context thermotropic liquid crystals (LCs) provide a very rich and promising approach for the creation of organic thin films with desirable properties and unique processibility.[2] In addition, many of the important structural features necessary for thin film applications may be achieved in LCs. Thus, ferroelectric liquid crystals (FLCs)[3] possess thermodynamically stable polar order, which affords properties making them the basis of potentially revolutionary devices ranging from VLSI silicon/FLC spatial light modulators[4] and ultrafast electrooptic modulators[5] to large-area flat-panel displays.[6]

While the origins of some important LC properties, for example the ferroelectric polarization of FLCs, are now grossly understood at the molecular level,[3] the most fundamental LC property of all—liquid crystallinity (or mesogenicity) itself—is understood only in the most general terms. Design of new LCs is thus a highly empirical undertaking which is often frustrated by the fact that seemingly small changes in molecular structure can dramatically change, or even destroy, mesogenicity.

This problem is typically solved by the creation of complex LC mixtures with desired phases and transition temperatures, an approach guided chiefly by intuition. When new materials are characterized for development of structure/activity relationships, however, it is often preferable to have a single component with the desired combination of molecular structural elements and LC phase sequence. In addition, some measurements are most conveniently accomplished at room temperature. Finally, pure LC components with broad LC phase ranges and low melting points could serve as excellent components of LC mixtures.

In particular, we have been seeking *o*-nitro-1-[(methylheptyl)oxy]phenyl biphenylcarboxylates of general structure shown in Table 3, possessing room-temperature smectic C* or A* phases for evaluation of electronic second-order nonlinear optical[5] and electroclinic susceptibilities,[7,8] respectively. In this system, however, while excellent mesogenicity abounds (quite consistent with the properties of many other LCs possessing the biphenylbenzoate core[9]), none of the standard *n*-alkoxy tails produced a material with an enantiotropic LC phase below about 45 °C (the C_{10} homolog exhibits the enantiotropic phase sequence $\mathrm{X}\ \text{–}63.5 \rightarrow \mathrm{C}^* \leftarrow 93.7 \rightarrow \mathrm{A}^* \rightarrow 116.0 \rightarrow \mathrm{I}$ where X is crystalline solid, C* is the chiral smectic C phase, A* is the chiral smectic A phase, and I is isotropic liquid), and to date it has proven impossible in our hands to obtain an enantiotropic room-temperature LC of this type by mixing simple homologs.

An approach for achieving room-temperature LCs in this system was suggested by a fact which has become part of the lore of organic chemistry: The melting points of long-chain alkanoic acids of even carbon number (the naturally occurring fatty acids) are dramatically depressed by incorporation of *cis*-alkenyl units.[10] This observation extends to the corresponding fatty alcohols and, of course, to the triacyl glyercols and lyotropic liquid crystals derived therefrom. In the prototypical case, octadecanoic acid (stearic acid) has a melting point of 69.6 °C while *Z*-9-octadecenoic acid (oleic acid) melts at 16.3 °C (a depression of 53.3 °C), octadecan-1-ol has a melting point of 59.6 °C, while Z-9-octadecen-1-ol melts at 16 °C (a depression of 43.6 °C), and tristearoylglycerol has a melting point of 73.0 °C while trioleylglycerol melts at 5.5 °C (a depression of 67.5 °C).[11]

Surprisingly, this natural approach to the lowering of melting points in mesogens has not been exploited in thermotropic LCs. Thus, we are aware of only one study,

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[1] Professor Etter, to whom this special issue of *Chemistry of Materials* is dedicated, was a pioneer in this field and published one of her earliest papers on the subject in the first issue of the first volume of this journal (Etter, M. C.; Frankenbach, G. M. *Chem. Mater.* **1989**, *1*, 10–12). For a more recent leading reference see: Russell, V. A.; Etter, M.; Ward, M. D. *J. Am. Chem. Soc.* **1994**, *116*, 1941–1952. Mr. Daniel Dyer, who accomplished the bulk of the work reported herein, was influenced directly by Professor Etter, having taken her introductory organic chemistry course at the University of Minnesota.

[2] de Gennes, P.-G. *The Physics of Liquid Crystals*; Oxford University Press: London, 1974.

[3] Walba, D. M. Ferroelectric Liquid Crystals: A Unique State of Matter. In *Advances in the Synthesis and Reactivity of Solids*; Mallouk, T. E., Ed.; JAI Press Ltd.; Greenwich, Connecticut, 1991; Vol. 1, pp 173–235.

[4] (a) Drabik, T. J.; Handschy, M. A. *Appl. Opt.* **1990**, *29*, 5220–5222. (b) Handschy, M. A.; Drabik, T. J.; Cotter, L. K.; Gaalema, S. D. Fast ferroelectric-liquid-crystal spatial light modulator with silicon-integrated-circuit active backplane. *Optical Digital GaAs Technology, Signal-Processing Applications*; *Proc. SPIE* **1990**, *1291*, 158–164.

[5] (a) Walba, D. M.; Ros, M. B.; Clark, N. A.; Shao, R.; Robinson, M. G.; Liu, J.-Y.; Johnson, K. M.; Doroski, D. *J. Am. Chem. Soc.* **1991**, *113*, 5471–5474. (b) Walba, D. M.; Rego, J. A.; Clark, N. A.; Shao, R. Studies on Ferroelectric Liquid Crystal Tolan Derivatives Designed for Nonlinear Optical Applications. In *Macromolecular Host–Guest Complexes: Optical and Optoelectronic Properties and Applications*; Jenekhe, S. A., Ed.; Materials Research Society: Pittsburgh, PA, 1992; Vol. 277, pp 205–216. (c) Walba, D. M.; Zummach, D. A.; Wand, M. D.; Thurmes, W. N.; Moray, K. M.; Arnett, K. E. Synthesis of Ferroelectric Liquid Crystal Oligomer Glasses for Second Order Nonlinear Optics. *Liquid Crystal Materials, Devices, and Applications II*, Wand, M. D., Efron, U., Eds.; *Proc. SPIE* **1993**, *1911*, 21–28.

[6] Kanbe, J.; Inoue, H.; Mizutome, A.; Hanyuu, Y.; Katagiri, K.; Yoshihara, S. *Ferroelectrics* **1991**, *114*, 3–26.

[7] Andersson, G.; Dahl, I.; Keller, P.; Kuczynski, W.; Lagerwall, S. T.; Skarp, K.; Stebler, B. *Appl. Phys. Lett.* **1987**, *51*, 640.

[8] Williams, P. A.; Ros, M. B.; Clark, N. A.; Walba, D. M.; Wand, M. D. *Ferroelectrics* **1991**, *121*, 143–146.

[9] Goodby, J. W.; Gray, G. W.; McDonnel, D. G. *Mol. Cryst. Liq. Cryst.* **1977**, *34*, 183–188.

[10] This observation seems so old that it is apparently not attributed to an individual. Perhaps this is not surprising given that the first chemist to isolate glycerol from hydrolysis of fat (Scheele in about 1779) thought that fats and oils were composed of phlogiston, fire, and earth (from the introduction to: Mead, J. F.; Alfin-Slater, R. B.; Howton, D. R.; Popák, G. *Lipids; Chemistry, Biochemistry, and Nutrition*; Plenum Press: New York, 1986). The latter reference states simply that "The striking depression of melting points effected by substitution of a *cis*-olefinic center for a pair of methylene groups in a normal fatty acid ... has been known for a long time" (page 51). A rather interesting rationale for the observation is then given based upon the observed crystal structure of the low melting form of oleic acid.

[11] Data on the fatty acids and triacylglycerols were taken from: Davenport, J. B. 3. Physical Chemistry of Lipids. In *Biochemistry and Methodology of Lipids*; Johnson, A. R., Davenport, J. B., Eds.; Wiley-Interscience: New York, 1971; pp 47–83. The melting points of the fatty alcohols were taken from: *The Merck Index, Ninth Edition*; Windholz, M., Ed.; Merck & Co., Inc.: Rahway, NJ, 1976.

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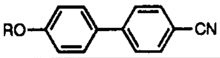
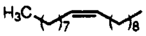
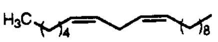
Table 1. Effect of Unsaturated Tails on Phase Transitions in the Cyanobiphenyl System

compound	 R	phase transitions	change in mp relative to 1, °C	change in range of enantiotropic LC phases, °C
1	$C_{18}H_{37}$—	$X \underset{76}{\overset{87}{\rightleftarrows}} A \underset{89}{\overset{93}{\rightleftarrows}} I$		
2		$X \underset{25}{\overset{34}{\rightleftarrows}} A \underset{58}{\overset{64}{\rightleftarrows}} I$	−53	+24
3		$X \underset{-5}{\overset{15}{\rightleftarrows}} A \underset{45}{\overset{49}{\rightleftarrows}} I$	−72	+28

which was only very recently published, explicitly addressing the effect of double bonds on phase sequences in thermotropic LC tails.[12] This work shows that cis double bonds can lower the melting points of LCs possessing the phenylpyrimidine core, but they are limited to tails of conventional length (C4 to C12). And while the liquid crystallinity of cholesteryl oleate was first reported in 1912,[13] there has been very little work on LCs possessing naturally occurring unsaturated tails, and no systematic investigation of the efficacy of this approach to LC phase engineering.[14,15] Herein we report for the first time LCs with 18-carbon natural unsaturated fatty acid-derived tails possessing useful properties.

While our initial work was with ferroelectrics of the type shown in Table 3, two very common LC structural systems, *p*′-alkoxycyanobiphenyls and 5-nonyl-2-[4′-alkoxyphenyl]pyrimidines, were also examined. As shown in Table 1, in the cyanobiphenyl system the oleyl ether (*p*′-(*Z*-9′-octadecenyloxy)cyanobiphenyl, **2**) and the linoleyl ether (*p*′-(Z,Z-9′,12′-(octadecadienyloxy))cyanobiphenyl, **3**) exhibited dramatically reduced melting points relative to the stearyl ether (*p*′-(octadecyloxy)cyanobiphenyl, **1**). Interestingly, the depression of melting point obtained with the monounsaturated oleyloxy tail relative to the saturated stearyl alcohol derivative is the same as that observed for oleic acid relative to stearic acid (53 °C), while the depression obtained for the doubly unsaturated linoleyloxy tail is within 4 °C of that observed for linoleic acid relative to stearic acid (76.1 °C)!

More importantly, the enantiotropic LC phase ranges of the compounds possessing the unsaturated tails are also extended relative to the saturated analog, as shown in Table 1. Of the simple *p*′-(alkyloxy)cyanobiphenyls reported in the literature (alkoxy tails from C5 to C12), the pentyloxy homolog (phase sequence: X ← 48 → N ← 68 → I, where N is the nematic LC phase) has the lowest melting point, while the octyloxy homolog (phase sequence: X ← 54.5 → A ← 67.5 → N ← 80 → I) has the broadest enantiotropic LC range (25.5 °C).[16] Both compounds **2** and **3** exhibit broader phase ranges (30 and 35 °C respectively).

The 5-nonyl-2-[4-alkoxyphenyl]pyrimidine system behaved similarly, as indicated in Table 2. In this case replacement of the stearyloxy tail of compound **4** with oleyloxy (compound **5**) depresses the melting point 57 °C and broadens the LC phase range 28 °C, and the (linoleyloxy)phenylpyrimidine **6** exhibits even larger numbers in both columns and possesses an enantiotropic LC phase range of 47 °C.

The lowest melting of the simple 5-alkyl-2-[4-alkoxyphenyl]pyrimidines is 5-nonyl-2-[4-(hexyloxy)phenyl]pyrimidine, which also has the broadest phase range = 46.5 °C (phase sequence: X ← 24 → C ← 43 → A ← 69.5 → N ← 70.5 → I).[17] In the study of [(alkenyloxy)phenyl]pyrimidines mentioned earlier,[12] eleven different 5-nonyl-2-[4-*Z*-(alkenyloxy)phenyl]pyrimidines were examined. The lowest melting (by a large margin) was the *Z*-3-nonenyloxy compound (phase sequence: X ← 6 → C ← 38 → A ← 51 → I), which also exhibited the broadest LC phase range (45 °C). In comparison with these optimized structures the oleyloxy and linoleyloxy compounds **5** and **6** show similar melting points and phase ranges. However, they are clearly superior to the saturated C_{18} analog **4**.

As expected based upon the fatty acid precedent, a trans diene tail (compound **7**) did not depress the melting point as much as the cis alkene units and, perhaps more interestingly, did not increase the enantiotropic phase range at all. Finally, as shown in Table 2, the oleic and linoleic ester tails derived from the fatty acids themselves (compounds **8** and **9**), were also not as effective as the ethers in lowering melting point or enhancing mesogenicity.

As shown in Table 3, this strategy for achieving room-temperature C* phases in the *o*-nitro-1-[(methylheptyl)oxy]phenyl biphenylcarboxylate FLC system proved very successful. Again, the melting point of the oleyloxy compound **11** is depressed relative to the stearyloxy compound **10** by almost the same amount as oleic acid is depressed relative to stearic acid! The diene and triene tails derived from linoleic and linolenic acids (compounds **12** and **13**, respectively) behave remarkably similarly, both improved in melting point and phase range relative to the oleyl derivative.

The isomeric triene **14**, however, derived from γ-linolenic acid, while exhibiting a considerably lower clearing point, has not yet been induced to crystallize in our hands, even though DSC scans down to −40 °C have been accomplished. This behavior is quite rare in pure LC components. The apparently very large difference in transition temperatures for trienes **13** and **14** is also noteworthy. Thus, for this system placement of the olefinic units closer to the core

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(12) Kelly, S. M. *Liq. Cryst.* **1993**, *14*, 675–698.

(13) Cholesteryl oleate (the oleic acid ester of cholesterol) liquid crystallinity is reported in a dissertation from the famous liquid crystal school at Halle (Däumer, O., Dissertation, Halle 1912). The first description of LC unsaturated fatty acid esters of cholesterol in the refereed literature is apparently a mention of cholesteryl linoleate which appeared in: Page, I. H.; Rudy, H. *Biochem. Z.*, **1930**, *220*, 304. We thank Dr. Volkmar Vill for providing this difficult to access information.

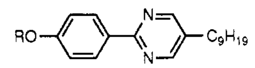
(14) Some comparisons of cholesteryl esters and ethers of unsaturated and unsaturated fatty acids and alcohols appear in the following papers: (a) Deckelbaum, R. J.; Halperin, G.; Atkinson, D. *J. Lipid Res.* **1983**, *24*, 657–661. (b) Croll, D. H.; Sripada, P. K.; Hamilton, J. A. *J. Lipid Res.* **1987**, *28*, 1444–1454. (c) Vill, V.; Weber, N. *Chemistry and Physics of Lipids* **1991**, *58*, 105–110. Interestingly, while cholesteryl stearyl ether possesses enantiotropic smectic A* and N* phases, the LC phases of cholesteryl oleyl ether and cholesteryl linoleyl ether are only monotropic (i.e., the clearing temperatures are reduced more than the melting temperatures relative to the saturated analog).

(15) The LC phase sequence and transition temperatures *p*-oleyloxybenzoic acid (*p*-Z-(9′-octadecenoxy)benzoic acid) were reported by Vill in 1990 (Vill, V.; Thiem, J. *Z. Naturforsch.* **1990**, *45a*, 1205–1210). The LC properties of *p*-(octadecyloxy)benzoic acid have also been reported in the literature (Demus, D.; Demus, H.; Zasche, H. *Flüssige Kristalle in Tabellen*; VEB Deutscher Verlag für Grundstoffindustrie: Leipzig, 1974, compound 386). In this case the unsaturated C18 tail lowers the melting point (58.3 °C) and expands the enantiotropic LC range (+37.7 °C) relative to the saturated analog, presaging the results of the present study.

(16) (a) Gray, G. W.; Harrison, K. J.; Nash, J. A.; Constant J.; Hulme, D. S.; Kirton, J.; Raynes, E. P. *Liq. Cryst. Ordered Fluids* **1973**, *2*, 617–643. (b) Gray, G. W.; Harrison, K. J.; Nash, J. A. *Electron. Lett.* **1973**, *9*, 130–131.

(17) Demus, D.; Demus, H.; Zasche, H. *Flüssige Kristalle in Tabellen*; VEB Deutscher Verlag für Grundstoffindustrie: Leipzig, 1974.

Table 2. Effect of Unsaturated Tails on Phase Transitions in a Phenylpyrimidine System



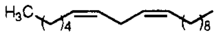
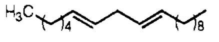
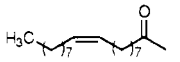
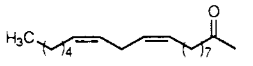
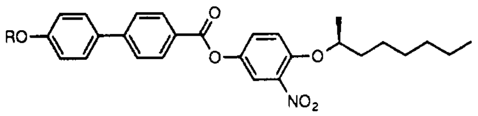
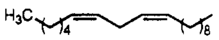
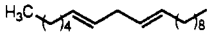
compound	R	phase transitions	change in mp relative to **4**, °C	change in range of enantiotropic LC phases, °C
4	$C_{18}H_{37}$—	$X \xrightarrow{68} A \underset{70}{\overset{77}{\rightleftarrows}} I$; $A \xrightarrow{59} C \xrightarrow{57} X$		
5		$X \underset{-15}{\overset{11}{\rightleftarrows}} C \underset{13}{\overset{14}{\rightleftarrows}} A \underset{44}{\overset{48}{\rightleftarrows}} I$	−57	+28
6		$X \underset{<-20}{\overset{0}{\rightleftarrows}} C \underset{11}{\overset{17}{\rightleftarrows}} A \underset{43}{\overset{47}{\rightleftarrows}} I$	−68	+38
7		$X \xrightarrow{43} A \underset{45}{\overset{52}{\rightleftarrows}} I$; $A \xrightarrow{25} C \xrightarrow{22} X$	−25	0
8		$X \xrightarrow{37} A \underset{42}{\overset{48}{\rightleftarrows}} I$; $A \xrightarrow{33} C \xrightarrow{3} X$	−31	+2
9		$X \xrightarrow{26} A \underset{36}{\overset{43}{\rightleftarrows}} I$; $A \xrightarrow{9} C \xrightarrow{-25} X$	−42	+8

Table 3. Effect of Unsaturated Tails on Phase Transitions in the *o*-Nitro-1-[(methylheptyl)oxy]phenyl Biphenylcarboxylate System



compound	R	phase transitions	change in mp relative to **10**, °C	change in range of enantiotropic LC phases, °C
10	$C_{18}H_{37}$—	$X \underset{56}{\overset{80}{\rightleftarrows}} C^* \underset{78}{\overset{85}{\rightleftarrows}} A^* \underset{111}{\overset{115}{\rightleftarrows}} I$		
11		$X \underset{9}{\overset{28}{\rightleftarrows}} C^* \underset{52}{\overset{58}{\rightleftarrows}} A^* \underset{89}{\overset{90}{\rightleftarrows}} I$	−52	+27
12		$X \underset{-12}{\overset{11}{\rightleftarrows}} C^* \underset{43}{\overset{52}{\rightleftarrows}} A^* \underset{78}{\overset{80}{\rightleftarrows}} I$	−69	+34
13		$X \underset{-9}{\overset{11}{\rightleftarrows}} C^* \underset{42}{\overset{45}{\rightleftarrows}} A^* \underset{70}{\overset{81}{\rightleftarrows}} I$	−69	+35
14		$X \underset{<-40}{\overset{?}{\rightleftarrows}} C^* \underset{22}{\overset{25}{\rightleftarrows}} A^* \underset{52}{\overset{55}{\rightleftarrows}} I$	*a*	*a*
15		$X \xrightarrow{37} A^* \underset{63}{\overset{74}{\rightleftarrows}} I$; $A^* \xrightarrow{34} C^* \xrightarrow{16} X$	−43	+2

[a] Crystallization has not been observed at temperatures as low as −40 °C.

provided additional depression of the melting point and clearing point. Further experiments to determine the generality of this effect are in progress. Finally, it should be noted here that o-nitro-1-[(methylheptyl)oxy]phenyl 4′-(linoleyloxy)biphenylcarboxylate (**12**) in the A* phase exhibits one of the largest electroclinic coefficients known, suggesting important applications for these materials.[18]

Finally, a brief discussion of the syntheses of the subject materials is useful. Thus, an advantage to this approach to mesogenicity enhancement is the ready availability of naturally occurring fatty acids for synthetic manipulation. In the case of esters **8** and **9**, the fatty acids were simply coupled to the core via the well-known DCC/DMAP protocol.[19] The ether linkages were easily created via the Mitsunobu coupling[20] of a phenol moiety to the fatty alcohol obtained from reduction of the fatty acid with $LiAlH_4$.

In conclusion, the incorporation of unsaturated fatty alcohol tails into LC structures is an effective approach for reducing melting points and broadening LC phases. This strategy proved effective in the development of useful FLCs with broad enantiotropic LC ranges including room temperature.

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Supplementary Material Available: Full descriptions of experimental procedures and spectral data (14 pages). Ordering information is available on any current masthead page.

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(18) Walba, D. M.; Dyer, D. J.; Shao, R.; Clark, N. A.; Vohra, R. T.; More, K.; Thurmes, W. N.; Wand, M. D. *Ferroelectrics*, in press.

(19) Neises, B.; Steglich, W. *Angew. Chem.* **1978**, *90*, 556–557.

(20) Hughes, D. L. The Mitsunobu Reaction. In *Organic Reactions*; Paquette, L. A., et al., Eds.; John Wiley & Sons, Inc.: 1992; Vol. 42, pp 335–656.