6390 *Inorg. Chem.* **2001,** *40,* 6390−6396

# Crossover Phase Behavior (Discotic to Calamitic) in Liquid-Crystalline Copper Complexes. Dependence on the Length and Position of Alkoxy Chains in New Polycatenar Bis[5-(dialkoxybenzylidine)aminotropololonato]copper(II) Complexes

**James M. Elliott,[†] John R. Chipperfield, and Stephen Clark**

Department of Chemistry, University of Hull, Hull HU6 7RX, U.K.

**Ekkehard Sinn***

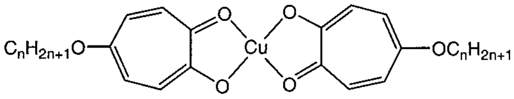
Department of Chemistry, University of Missouri—Rolla, Rolla, Missouri 65409

*Received December 29, 2000*

New polycatenar metallomesogens have been synthesized containing a tropolone core joined to benzylidine terminal rings. Variation of the position, number, and nature of alkoxy substituents on the terminal rings allows for the control of the phase behavior of the compounds. In particular, for copper complexes with 3,4-dialkoxy substitution, a change from calamitic to discotic (columnar) behavior is seen as the chain lengths are increased.

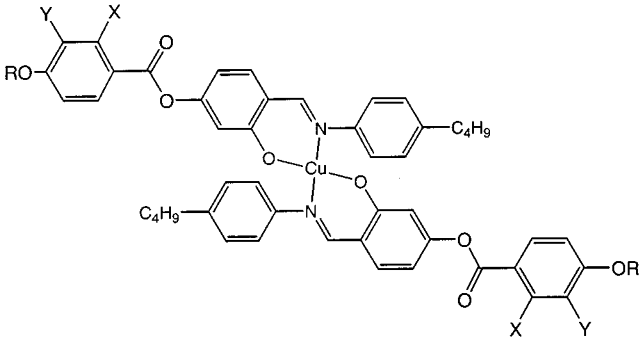
## Introduction

Calamitic liquid-crystalline molecules have rigid cores with terminal flexible alkyl groups. The majority of the rigid cores of organic liquid crystals are based upon benzene rings. In metal-based liquid crystals (metallomesogens), rigid chelate rings also form part of the rigid cores. Metallomesogens based on Schiff bases use phenyl rings as rigid cores with alkyl chains, all of which are necessarily located opposite but off-center to the metal. To place one substituent in an opposite site, we have replaced one of the benzenes by five- and seven-membered rings and have formed the first metallomesogens (**1**)[1] based on tropolone (2-hydroxycyclohepta-2,4,6-trienone). This work was subsequently confirmed by Mori et al.[2] Tropolone is a versatile chelating agent with a complexing ability akin to that of $\beta$-diketones (log $K_1$ for tropolonate−$Cu^{2+}$ is 8.35, and for acetylacetonate−$Cu^{2+}$ it is 8.16). Tropolones are also of interest as the cores of the natural products hinokitiol ($\beta$-thujaplicin and 4-isopropyltropolone), a powerful fungicide, and colchicines, which show strong antitumor and antigout activity. This high-binding constant explains why copper(II) tropolonate is a classical complex which can readily be used for the purification of tropolone by reversing complexation (e.g., with cyanide).[3] Copper complexes can also be used for the chromatographic separation of the tropolone-based compounds, colchicine and trimethylcolchicinic acid.[4]



**1**

While the tropolone core is aromatic, it is some 13% broader than benzene and is, therefore, likely to impart different packing arrangements on complexes. The tropolone complexes **1** have high transition temperatures, but for many (though not all) of the applications of metallomesogens, low transition temperatures are desirable. To reduce these temperatures, the tropolone ligands need modification. One successful way of lowering mesophase transition temperatures is by the incorporation of *m*-alkyl chain substituents on benzene rings as well as the usual *p*-alkyl chains: Berdague et al.[5] have synthesized Schiff-base complexes with both para and ortho substituents and also with both para and meta chains. Table 1 shows that the transition temperatures of both of these are reduced when lateral chains are added. The complexes **2** (X = Y = H) have extended cores, which are rodlike in character and consistent with calamitic liquid-crystal properties. However, the introduction of ortho or meta substitution in the terminal benzene rings makes the



**2**

---

[†] Present address: University of Missouri-Rolla.

(1) Chipperfield, J. R.; Clark, S.; Elliott, J. M.; Sinn, E. *Chem. Commun.* **1998**, 195.

(2) Mori, A.; Takemoto, M.; Mori, R.; Takeshita, H.; Ujiie, S.; Vill, V. *Chem. Lett.* **1998**, 601.

(3) Roberts, J. D.; Caserio, M. C. *Basic Principles of Organic Chemistry*, 2nd ed.; W. A. Benjamin, Inc.: Menlo Park, CA, 1977. Lloyd, D. *Nonbenzenoid Conjugated Carbocyclic Compounds*; Elsevier: New York, 1984.

(4) Lacey, E.; Brady, R. *J. Chromatogr.* **1984**, *315*, 233.

(5) Berdague, P.; Perez, F.; Courtieu, J.; Bayle, J. P. *Bull. Soc. Chim. Fr.* **1994**, *131*, 335.

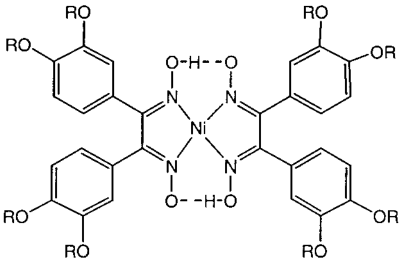
10.1021/ic001475u CCC: $20.00 © 2001 American Chemical Society
Published on Web 11/06/2001

**Table 1.** Effects of Substitution on the Phase Properties of **2**

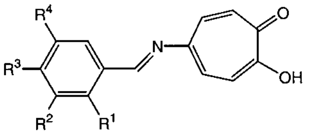
| | para chain only | ortho and para chains | meta and para chains |
|---|---|---|---|
| R | **2** (X = Y = H) | **2** (X = OR, Y = H) | **2** (X = H, Y = OR) |
| $C_4H_9$ | cryst 231 *N* 261 iso | cryst 138 iso | cryst 171.5 $S_C$ 177.5 iso |
| $C_8H_{17}$ | cryst 195 *N* 257 iso | cryst 92.8 iso | cryst 138 *S* 158.5 iso |
| $C_{12}H_{25}$ | cryst 173 *N* 248 iso | cryst 52.5 *N* 61.5 iso | cryst 115.5 *S* 141 iso |
| $C_{16}H_{33}$ | cryst 158 *N* 233 iso | cryst 75 iso | cryst 109.5 *S* 140 iso |

complexes broader and lowers mesophase transitions. In particular, alkoxy groups ortho to the ester link cause a substantial lowering of the temperature.

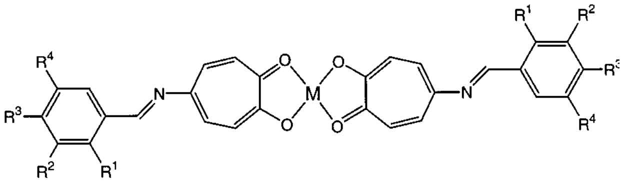
The first liquid crystals which showed a crossover from calamitic to discotic (columnar) behavior dependent on the chain length were described by Malthete and co-workers[6,7] and called phasmids (named after the stick insect, the phasma). It is of great interest to discover such crossover behavior in metallomesogens. The first biforked hybrids were described by Nguyen et al.[8] and later termed, from the number of alkyl chains present, polycatenars.[9,10] Although most polycatenars are organic liquid crystals, metal-containing polycatenars include 1,3-butadiene iron carbonyl complexes[11] and stilbazole complexes of silver(I),[12] palladium, and platinum.[13,14] Recently Ohta et al.[15] has reported a series of substituted bis(diphenylglyoximato)-nickel(II) complexes **3** where, as the alkyl chains were shortened, mesophase behavior changed from columnar to lamellar, though these materials are not polycatenar. Polycatenars are represented by compounds recently reported by Tschierske,[16,17] Ziessel,[18,19] and Swager[20,21] and their co-workers. In our work to extend the range of metallomesogen cores, we have synthesized a series of 5-(alkoxybenzylidine)tropolones (**4**) and prepared complexes **5** from them. The complexes show how the subtle interactions between the core nature and chain length affect the melting behavior and have given rise to a novel series of metallomesogens showing phase-crossover behavior.



**3**



**4**



**5**

## Experimental Section

**5-Aminotropolone.** This was prepared using a modification of Uemura's method.[22] 5-Nitrosotropolone (2.32 g, 15.36 mmol) was suspended in ethanol (100 cm$^3$). A total of 5% of palladium/charcoal (20 mg) was added as a catalyst, and the reaction was stirred under a hydrogen atmosphere at room temperature for 8 h. No further hydrogen was taken up in a further 24 h. The dark-green solution was filtered to reclaim the catalyst, and the solvent was removed to give a hard-orange powder. Sublimation (95 °C at 0.5 mmHg) and recrystallization gave 5-aminotropolone (1.96 g, 92%) as orange needles, mp 178 °C (from ethyl acetate; lit.[22] 177−178 °C. IR $\upsilon_{max}$/cm$^{-1}$ (KBr disk): 3440, 3370, 3220 br, 1675, 1540 s, 1460 vs, 1421 vs, 1220 vs, 780. $^1$H NMR $\delta$ (400 MHz, DMSO-$d_6$, $Me_4Si$): 7.09 (2H, d, $J$ = 12.0, trop), 6.70 (2H, d, $J$ = 12.0, trop), 6.25 (2H, s, trop−$NH_2$). MS $m/z$: 137 ($M^+$, 38%), 109 (100), 91 (6), 82 (21), 80 (82), 68 (7), 63 (21), 58 (9), 55 (19), 53 (54), 52 (64), 45 (6). $J$ values are given in hertz throughout.

**2-Hydroxy-4-dodecyloxybenzaldehyde.** This was prepared in butanone from 2,4-dihydroxybenzaldehyde and bromododecane in the presence of potassium bicarbonate in a manner similar to that reported.[23,24] The change in the solvent from acetone[24] to butanone increased the yield. 2-Hydroxy-4-dodecyloxybenzaldehyde was obtained (overall yield 75%) as white needles, mp 40 °C (from ethyl acetate; lit.[24] 39 °C), with $^1$H NMR agreeing with the reports.[23,24]

**2-Hydroxy-4-hexadecyloxybenzaldehyde.** This was made similarly in 60% yield as pale-yellow needles, mp 51 °C (from ethyl acetate). IR $\upsilon_{max}$/cm$^{-1}$ (KBr disk): 3201−3000, 2923, 2855, 1681, 1578, 1508, 1395, 1355, 1321, 1298, 820. $^1$H NMR $\delta$ (400 MHz, $CD_2Cl_2$, $Me_4Si$): 0.87 (3H, t, $J$ = 7.0, $-CH_3$), 1.20−1.48 (26H, m, $(CH_2)_{13}$), 1.75−1.88 (2H, m, Ar−O−$CH_2$−C$H_2$−R), 4.01 (2H, t, $J$ = 6.6, Ar−O−$CH_2$−R), 6.40 (1H, s, Ar), 6.53 (1H, d, $J$ = 8.6, Ar), 7.44 (1H, d, $J$ = 8.6, Ar), 9.70 (1H, s, O=CH−Ar), 11.46 (1H, s, HO−Ar). MS $m/z$: 362 ($M^+$, 36%), 245 (18), 333 (14), 277 (16), 207 (15), 179 (12), 151 (22), 138 (100), 123 (16), 69 (35). Although previously reported,[25] there are no data in the literature.

---

(6) Malthete, J.; Levelut, A. M.; Nguyen, H. T. *J. Phys., Lett.* **1985**, *46*, L875.

(7) Malthete, J.; Nguyen, H. T.; Destrade, C. *Liq. Cryst.* **1993**, *13*, 171.

(8) Nguyen, H. T.; Destrade, C.; Levelut, A. M.; Malthete, J. *J. Phys. (Paris)* **1986**, *47*, 553.

(9) Gasparoux, H.; Hardouin, F.; Destrade, C.; Nguyen, H. T. *New J. Chem.* **1992**, *16*, 295.

(10) Nguyen, H. T.; Destrade, C.; Malthete, J. *Adv. Mater.* **1997**, *9*, 375.

(11) Jacq, P.; Malthete, J. *Liq. Cryst.* **1996**, *21*, 291.

(12) Donnio, B.; Heinrich, B.; Gulik Krzywicki, T.; Delacroix, H.; Guillon, D.; Bruce, D. W. *Chem. Mater.* **1997**, *9*, 2951.

(13) Donnio, B.; Bruce, D. W. *J. Chem. Soc., Dalton Trans.* **1997**, 2745.

(14) Neve, F.; Ghedini, M.; Francescangeli, O. *Liq. Cryst.* **1996**, *21*, 625−630.

(15) Ohta, K.; Higashi, R.; Ikejima, M.; Yamamoto, I.; Kobayashi, N. *J. Mater. Chem.* **1998**, *8*, 1979.

(16) Hegmann, T.; Peidis, F.; Diele, S.; Tschierske, C. *Liq. Cryst.* **2000**, *27*, 1261.

(17) Hegmann, T.; Neumann, B.; Kain, J.; Diele, S.; Tschierske, C. *J. Mater. Chem.* **2000**, *10*, 2244.

(18) El-ghayoury, A.; Douce, L.; Skoulios, A.; Ziessel, R. *Angew. Chem., Int. Ed. Engl.* **1988**, *37*, 2205.

(19) Ziessel, R.; Douce, L.; El-ghayoury, A.; Harriman, A.; Skoulios, A. *Angew. Chem., Int. Ed.* **2000**, *39*, 1489.

(20) Trzaska, S. T.; Zheng, H. X.; Swager, T. M. *Chem. Mater.* **1999**, *11*, 130.

(21) Levitsky, I. A.; Kishikawa, K.; Eichhorn, S. H.; Swager, T. M. *J. Am. Chem. Soc.* **2000**, *122*, 2474.

(22) Uemura, T.; Takenaka, S.; Kusabayashi, S.; Seto, S. *Mol. Cryst. Liq. Cryst.* **1983**, *95*, 287.

(23) Binnemans, K.; Galyametdinov, Y. G.; Collinson, S. R.; Bruce, D. W. *J. Mater. Chem.* **1998**, *8*, 1551.

(24) Lai, C. K.; Chang, C.-H.; Tsai, C.-H. *J. Mater. Chem.* **1998**, *8*, 599.

(25) Cerrada, P.; Marcos, M.; Serrano, J. L. *Mol. Cryst. Liq. Cryst.* **1989**, *170*, 79.

**2-Hexyloxy-4-dodecyloxybenzaldehyde (6a).** 2-Hydroxy-4-dodecyloxybenzaldehyde (2.00 g, 6.53 mmol), potassium carbonate (0.91 g, 6.60 mmol), and 1-bromohexane (1.15 cm$^3$, 7 mmol) were added to DMF (100 cm$^3$) and refluxed for 4 h. The solvent was removed using a rotary evaporator, and the brown residue was extracted into diethyl ether (100 cm$^3$) and then filtered before being washed with water (3 × 100 cm$^3$) and a saturated sodium chloride solution (2 × 100 cm$^3$). The diethyl ether layer was then dried with calcium chloride before removing the solvent and washing the solid with cold light petroleum (bp 40−60 °C, 2 × 10 cm$^3$) to yield **6a** (2.38 g, 93%) as a white powder, mp 50 °C (from hexane). IR $\upsilon_{max}$/cm$^{-1}$ (KBr disk): 2915 vs, 2840 vs, 1670 s, 1601 vs, 1462 s, 1293 s, 1260 s, 1190 s, 1110 s. $^1$H NMR $\delta$ (400 MHz, CD$_2$Cl$_2$, Me$_4$Si): 0.88 (3H, t, *J* = 7.0, −CH$_3$), 0.91 (3H, t, *J* = 7.0, −CH$_3$), 1.20−1.52 (24H, m, (CH$_2$)$_3$ + (CH$_2$)$_9$), 1.75−1.88 (2H, m, Ar−O−CH$_2$−C*H*$_2$−R), 1.87 (2H, m, Ar−O−CH$_2$−C*H*$_2$−R), 3.99 (2H, t, *J* = 6.4, Ar−O−CH$_2$−R), 4.02 (2H, t, *J* = 6.3, Ar−O−CH$_2$−R), 6.42 (1H, s, Ar), 6.49 (1H, d, *J* = 8.6, Ar), 7.71 (1H, d, *J* = 8.6, Ar), 10.28 (1H, s, O═CH−Ar).

Aldehydes **6b−g** were made similarly. Their characterization follows.

**2-Decyloxy-4-dodecyloxybenzaldehyde (6b)** was prepared in an 85% yield as a light-brown powder, mp 55 °C (from hexane). IR $\upsilon_{max}$/cm$^{-1}$ (KBr disk): 2922 vs, 2840 vs, 1670 s, 1601 vs, 1462 s, 1293 s, 1260 s, 1190 s, 1110 s. $^1$H NMR $\delta$ (400 MHz, CD$_2$Cl$_2$, Me$_4$Si): 0.89 (6H, t, *J* = 7.0, 2 × −CH$_3$), 1.20−1.52 (32H, m, (CH$_2$)$_7$ + (CH$_2$)$_9$), 1.80 (2H, m, Ar−O−CH$_2$−C*H*$_2$−R), 1.75−1.88 (2H, m, Ar−O−CH$_2$−C*H*$_2$−R), 3.99 (2H, t, *J* = 6.4, Ar−O−CH$_2$−R), 4.04 (2H, t, *J* = 6.3, Ar−O−CH$_2$−R), 6.42 (1H, s, Ar), 6.49 (1H, d, *J* = 8.6, Ar), 7.71 (1H, d, *J* = 8.6, Ar), 10.23 (1H, s, O═CH−Ar).

**2-Propyloxy-4-hexadecyloxybenzaldehyde (6c)** was prepared in a 77% yield as a white powder, mp 44 °C (from hexane). IR $\upsilon_{max}$/cm$^{-1}$ (KBr disk): 2922 vs, 2840 vs, 1670 s, 1601 vs, 1462 s, 1290 s, 1260 s, 1200 s, 1110 s. $^1$H NMR $\delta$ (400 MHz, CD$_2$Cl$_2$, Me$_4$Si): 0.88 (3H, t, *J* = 7.0, −CH$_3$), 1.20−1.52 (29H, m, −CH$_3$ + (CH$_2$)$_{13}$), 1.80 (2H, m, Ar−O−CH$_2$−C*H*$_2$−R), 1.71−1.88 (2H, m, Ar−O−CH$_2$−C*H*$_2$−R), 3.97 (2H, t, *J* = 6.4, Ar−O−CH$_2$−R), 4.03 (2H, t, *J* = 6.3, Ar−O−CH$_2$−R), 6.42 (1H, s, Ar), 6.48 (1H, d, *J* = 8.6, Ar), 7.71 (1H, d, *J* = 8.6, Ar), 10.23 (1H, s, O═CH−Ar).

**2-Hexyloxy-4-hexadecyloxybenzaldehyde (6d)** was prepared in a 77% yield as a white powder, mp 42 °C (from ethyl acetate). IR $\upsilon_{max}$/cm$^{-1}$ (KBr disk): 2920 vs, 2835 vs, 1670 s, 1602 vs, 1462 s, 1290, 1260 s, 1200 s, 1110 s. $^1$H NMR $\delta$ (400 MHz, CD$_2$Cl$_2$, Me$_4$Si): 0.88 (3H, t, *J* = 7.0, −CH$_3$), 0.92 (3H, t, *J* = 7.0, −CH$_3$), 1.24−1.47 (32H, m, (CH$_2$)$_3$ + (CH$_2$)$_{13}$), 1.75−1.88 (2H, m, Ar−O−CH$_2$−C*H*$_2$−R), 1.85 (2H, m, Ar−O−CH$_2$−C*H*$_2$−R), 3.97 (2H, t, *J* = 6.4, Ar−O−CH$_2$−R), 4.03 (2H, t, *J* = 6.3, Ar−O−CH$_2$−R), 6.44 (1H, s, Ar), 6.52 (1H, d, *J* = 8.6, Ar), 7.71 (1H, d, *J* = 8.6, Ar), 10.23 (1H, s, O═CH−Ar).

**2-Decyloxy-4-hexadecyloxybenzaldehyde (6e)** was prepared in a 78% yield as a white powder, mp 40 °C (from ethyl acetate). IR $\upsilon_{max}$/cm$^{-1}$ (KBr disk): 2915 vs, 2835 vs, 1671 s, 1603 vs, 1462 s, 1290, 1260 s, 1200 s, 1108 s. $^1$H NMR $\delta$ (400 MHz, CD$_2$Cl$_2$, Me$_4$Si): 0.87 (6H, t, *J* = 7.0, 2 × −CH$_3$), 1.22−1.51 (40H, m, (CH$_2$)$_9$ + (CH$_2$)$_{13}$), 1.78−1.88 (2H, m, *J* = 6.8, Ar−O−CH$_2$−C*H*$_2$−R), 1.85 (2H, m, Ar−O−CH$_2$−C*H*$_2$−R), 4.01 (2H, t, *J* = 6.4, Ar−O−CH$_2$−R), 4.06 (2H, t, *J* = 6.4, Ar−O−CH$_2$−R), 6.44 (1H, s, Ar), 6.53 (1H, d, *J* = 8.6, Ar), 7.71 (1H, d, *J* = 8.6, Ar), 10.23 (1H, s, O═CH−Ar).

**2,4-Dihexadecyloxybenzaldehyde (6f)** was prepared in an 82% yield as a white powder, mp 58 °C (from ethyl acetate). IR $\upsilon_{max}$/cm$^{-1}$ (KBr disk): 2920 vs, 2835 vs, 1671 s, 1603 vs, 1462 s, 1290, 1260 s, 1195 s, 1108 s. $^1$H NMR $\delta$ (400 MHz, CD$_2$Cl$_2$, Me$_4$Si): 0.87 (6H, t, *J* = 7.0, 2 × −CH$_3$), 1.21−1.49 (52H, m, 2 × (CH$_2$)$_{13}$), 1.78−1.89 (4H, m, 2 × Ar−O−CH$_2$−C*H*$_2$−R), 3.96 (2H, t, *J* = 6.4, Ar−O−CH$_2$−R), 4.06 (2H, t, *J* = 6.4, Ar−O−CH$_2$−R), 6.44 (1H, s, Ar), 6.53 (1H, d, *J* = 8.6, Ar), 7.71 (1H, d, *J* = 8.6, Ar), 10.21 (1H, s, O═CH−Ar).

**2,4-Dipropyloxybenzaldehyde (6g)** was prepared in 94% yield as white crystals, mp 52 °C (from ethanol). IR $\upsilon_{max}$/cm$^{-1}$ (KBr disk): 2921 vs, 2835 vs, 1670 s, 1603 vs, 1462 s, 1290, 1260 s, 1195 s, 1108 s. $^1$H NMR $\delta$ (400 MHz, CD$_2$Cl$_2$, Me$_4$Si): 1.04 (6H, m, 2 × −CH$_3$), 1.79 (2H, m, 2 × Ar−O−CH$_2$−C*H*$_2$−CH$_3$), 1.85 (2H, t, *J* = 6.8, Ar−O−CH$_2$−C*H*$_2$−CH$_3$), 3.99 (2H, t, *J* = 6.4, Ar−O−CH$_2$−R), 4.02 (2H, t, *J* = 6.4, Ar−O−CH$_2$−R), 6.45 (1H, s, Ar), 6.54 (1H, d, *J* = 8.6, Ar), 7.73 (1H, d, *J* = 8.6, Ar), 10.21 (1H, s, O═CH−Ar).

**3,4-Dioctyloxybenzaldehyde (6h).** 3,4-Dihydroxybenzaldehyde (3.00 g, 21.74 mmol), potassium bicarbonate (4.45 g, 44.00 mmol), potassium iodide (0.10 g), and 1-bromooctane (8.49 cm$^3$, 44.00 mmol) were suspended in butanone (120 cm$^3$) and refluxed for 18 h under a nitrogen atmosphere. The suspension was cooled, and the solvent was removed to give a yellow solid, which was extracted into dichloromethane (100 cm$^3$). The extract was washed with 1 M hydrochloric acid (2 × 100 cm$^3$) and water (100 cm$^3$) and then dried with magnesium sulfate, and the solvent was removed. The solid residue was washed with ethanol (2 × 10 cm$^3$) to yield **6h** (5.43 g, 69%) as white prisms, mp 51 °C (from hexane/methanol, 4:1). IR $\upsilon_{max}$/cm$^{-1}$ (KBr disk): 2925 vs, 2854 s, 1680, 1608 s, 1516 s, 1467 s, 1433 vs, 1356 s, 1266 s, 1179 w. $^1$H NMR $\delta$ (400 MHz, CD$_2$Cl$_2$, Me$_4$Si): 0.89 (3H, m, 2 × −CH$_3$), 1.21−1.56 (20H, m, 2 × (CH$_2$)$_5$), 1.83−1.94 (4H, m, 2 × Ar−O−CH$_2$−C*H*$_2$−R), 4.03 (2H, t, *J* = 6.6, Ar−O−CH$_2$−R), 4.07 (2H, t, *J* = 6.6, Ar−O−CH$_2$−R), 6.97 (1H, d, *J* = 8.3, Ar), 7.37 (1H, s, Ar), 7.42 (1H, d, *J* = 8.3, Ar), 9.81 (1H, s, O═CH−Ar).

Aldehydes **6i−m** were made similarly. Their characterization follows.

**3,4-Didecyloxybenzaldehyde (6i)** was prepared in a 72% yield as white prisms, mp 64 °C (from hexane/methanol, 4:1). IR $\upsilon_{max}$/cm$^{-1}$ (KBr disk): 2925 vs, 2854 s, 1680, 1608 s, 1516 s, 1467 s, 1433 vs, 1356 s, 1266 s, 1179 w. $^1$H NMR $\delta$ (400 MHz, CD$_2$Cl$_2$, Me$_4$Si): 0.88 (6H, m, 2 × −CH$_3$), 1.18−1.53 (28H, m, 2 × (CH$_2$)$_7$), 1.82 (2H, m, Ar−O−CH$_2$−C*H*$_2$−R), 1.85−1.94 (2H, m, Ar−O−CH$_2$−C*H*$_2$−R), 4.03 (2H, t, *J* = 6.6, Ar−O−CH$_2$−R), 6.97 (1H, d, *J* = 8.3, Ar), 7.36 (1H, s, Ar), 7.41 (1H, d, *J* = 8.3, Ar), 9.80 (1H, s, O═CH−Ar).

**3,4-Didodecyloxybenzaldehyde (6j)** was prepared in a 67% yield as a white powder, mp 70 °C (from hexane/ethanol, 4:1). IR $\upsilon_{max}$/cm$^{-1}$ (KBr disk): 3432 w, 2930 vs, 2858 s, 1705 s, 1680, 1601 s, 1465 s, 1300, 1170 s, 1059, 721. $^1$H NMR $\delta$ (400 MHz, CD$_2$Cl$_2$, Me$_4$Si): 0.88 (6H, t, 2 × −CH$_3$), 1.14−1.60 (36H, m, 2 × (CH$_2$)$_9$), 1.82−1.92 (4H, m, 2 × Ar−O−CH$_2$−C*H*$_2$−R), 4.03 (2H, t, *J* = 6.6, Ar−O−CH$_2$−R), 4.06 (2H, t, *J* = 6.6, Ar−O−CH$_2$−R), 6.97 (1H, d, *J* = 8.0, Ar), 7.36 (1H, s, Ar), 7.42 (1H, d, *J* = 8.0, Ar), 9.80 (1H, s, O═CH−Ar).

**3,4-Ditridecyloxybenzaldehyde (6k)** was prepared in a 65% yield as a yellow powder, mp 73 °C (from chloroform/methanol, 2:1). IR $\upsilon_{max}$/cm$^{-1}$ (KBr disk): 2930 vs, 2851 s, 1706, 1680 s, 1601 s, 1465 s, 1300, 1170 s, 1059, 721, 710 w. $^1$H NMR $\delta$ (400 MHz, CD$_2$Cl$_2$, Me$_4$Si): 0.88 (6H, t, 2 × −CH$_3$), 1.20−1.58 (40H, m, 2 × (CH$_2$)$_{10}$), 1.81−1.94 (4H, m, Ar−O−CH$_2$−C*H*$_2$−R), 4.03 (2H, t, *J* = 6.6, Ar−O−CH$_2$−R), 4.06 (2H, t, *J* = 6.6, Ar−O−CH$_2$−R), 6.97 (1H, d, *J* = 8.0, Ar), 7.37 (1H, s, Ar), 7.42 (1H, d, *J* = 8.0, Ar), 9.81 (1H, s, O═CH−Ar).

**3,4-Ditetradecyloxybenzaldehyde (6l)** was prepared in a 62% yield as a yellow powder, mp 74 °C (from chloroform/methanol, 2:1). IR $\upsilon_{max}$/cm$^{-1}$ (KBr disk): 2930 vs, 2851 s, 1706 s, 1680, 1601 s, 1465 s, 1300, 1170 s, 1059, 721, 712 w. $^1$H NMR $\delta$ (400 MHz, CD$_2$Cl$_2$, Me$_4$Si): 0.87 (6H, t, 2 × CH$_3$), 1.20−1.58 (44H, m, 2 × (CH$_2$)$_{11}$), 1.82−1.94 (4H, m, 2 × Ar−O−CH$_2$−C*H*$_2$−R), 4.03 (2H, t, *J* = 6.6, Ar−O−CH$_2$−R), 4.06 (2H, t, *J* = 6.6, Ar−O−CH$_2$−R), 6.97 (1H, d, *J* = 8.0, Ar), 7.36 (1H, s, Ar), 7.41 (1H, d, *J* = 8.0, Ar), 9.80 (1H, s, O═CH−Ar).

**3,4-Dihexadecyloxybenzaldehyde (6m)** was prepared in a 69% yield as a white powder, mp 81 °C (from chloroform/ethanol, 1:1). IR $\upsilon_{max}$/cm$^{-1}$ (KBr disk): 2920 vs, 2851 s, 1680, 1617 s, 1516 s, 1467 s, 1433 vs, 1356 vs, 1266 s, 1170 w. $^1$H NMR $\delta$ (400 MHz, CD$_2$Cl$_2$, Me$_4$Si): 0.87 (6H, t, 2 × CH$_3$), 1.20−1.55 (52H, m, 2 × (CH$_2$)$_{13}$), 1.82−1.94 (4H, m, 2 × Ar−O−CH$_2$−C*H*$_2$−R), 4.03 (2H, t, *J* = 6.6, Ar−O−CH$_2$−R), 4.06 (2H, t, *J* = 6.6, Ar−O−CH$_2$−R), 6.96 (1H, d, *J* = 8.0, Ar), 7.36 (1H, s, Ar), 7.41 (1H, d, *J* = 8.0, Ar), 9.80 (1H, s, O═CH−Ar).

**3,5-Dihexadecyloxybenzaldehyde (6n).** 3,5-Dihydroxybenzaldehyde (1.00 g, 7.25 mmol), potassium bicarbonate (1.50 g, 15.00 mmol), potassium iodide (ca. 0.10 g), and 1-bromohexadecane (4.58 cm$^3$, 15.00 mmol), were suspended in butanone (120 cm$^3$), and the mixture was refluxed for 4 h before being cooled to room temperature and water was added (200 cm$^3$). The crude product was extracted from the aqueous solution with dichloromethane (8 × 20 cm$^3$) and washed with 1 M hydrochloric acid (10 × 50 cm$^3$), a saturated sodium bicarbonate solution (4 × 100 cm$^3$), and water (2 × 100 cm$^3$). The dichloromethane layer was dried with calcium chloride, and the solvent was removed. The crude product was washed with ethanol (2 × 10 cm$^3$) and light petroleum (bp 40−60 °C, 10 cm$^3$) to yield **6n** (3.18 g, 75%) as a white powder, mp 59 °C (from chloroform/ethanol, 2:1). IR $\upsilon_{max}$/cm$^{-1}$ (KBr disk): 2927 vs, 2857 s, 1701, 1604, 1471 s, 1358, 1301, 1190, 1067 w, 720. $^1$H NMR $\delta$ (400 MHz, $CD_2Cl_2$, $Me_4Si$): 0.87 (6H, t, 2 × $-CH_3$), 1.18−1.50 (52H, m, 2 × $(CH_2)_{13}$), 1.78−1.90 (4H, m, 2 × Ar−O−$CH_2$−$C\mathit{H}_2$−R), 3.98 (4H, t, *J* = 6.6, 2 × Ar−O−$CH_2$−R), 6.69 (1H, s, Ar), 6.96 (2H, s, Ar), 9.87 (1H, s, O═CH−Ar).

**5-(2-Hexyloxy-4-dodecyloxybenzylidine)aminotropolone (4a).** Compound **6a** (1.00 g, 2.57 mmol), acetic acid (5 drops), and 5-aminotropolone (0.33 g, 2.40 mmol) were suspended in toluene (60 cm$^3$). A Dean−Stark trap was fitted to the reaction vessel, and the reaction mixture was refluxed under a nitrogen atmosphere for 4 days before the removal of the solvent by rotary evaporation. The yellow solid produced was washed with ethanol (2 × 10 cm$^3$) and cold diethyl ether (10 cm$^3$) and dried under vacuum for 2 h to yield **4a** (1.03 g, 84%) as a yellow solid, mp 71 °C (from ethanol). IR $\upsilon_{max}$/cm$^{-1}$ (KBr disk): 3300−3100 br, 2920 vs, 2850 s, 1660, 1620, 1540 vs, 1515 s, 1450 vs, 1431 s, 1379 s, 1362 vs, 1144. $^1$H NMR $\delta$ (400 MHz, $CD_2Cl_2$, $Me_4Si$): 0.86 (3H, t, $-CH_3$), 0.87 (3H, t, $-CH_3$), 1.20−1.50 (24H, m, $(CH_2)_3 + (CH_2)_9$), 1.81−1.93 (4H, m, 2 × Ar−O−$CH_2$−$C\mathit{H}_2$−R), 4.02 (2H, t, *J* = 6.6, Ar−O−$C\mathit{H}_2$−R), 4.04 (2H, t, *J* = 6.6, Ar−O−$CH_2$−R), 6.46 (1H, s, Ar), 6.56 (1H, d, *J* = 8.8, Ar), 7.22 (2H, d, *J* = 12.0, trop), 7.33 (2H, d, *J* = 12.0, trop), 8.00 (1H, d, *J* = 8.8, Ar), 8.73 (1H, s, N═CH).

Schiff bases **4b**−**n** were made similarly. Their characterization follows.

**5-(2-Decyloxy-4-dodecyloxybenzylidine)aminotropolone (4b)** was prepared in an 81% yield as a yellow powder, mp 75 °C (from ethanol). IR $\upsilon_{max}$/cm$^{-1}$ (KBr disk): 3300−3100 br, 2921 vs, 2850 s, 1660, 1620, 1540 vs, 1515 s, 1450 vs, 1430 s, 1379 s, 1362 vs, 1145. $^1$H NMR $\delta$ (400 MHz, $CD_2Cl_2$, $Me_4Si$): 0.86 (3H, t, $-CH_3$), 0.87 (3H, t, $-CH_3$), 1.20−1.50 (32H, m, $(CH_2)_7 + (CH_2)_9$), 1.81−1.93 (4H, m, 2 × Ar−O−$CH_2$−$C\mathit{H}_2$−R), 4.02 (2H, t, *J* = 6.6, Ar−O−$C\mathit{H}_2$−R), 4.04 (2H, t, *J* = 6.6, Ar−O−$CH_2$−R), 6.46 (1H, s, Ar), 6.56 (1H, d, *J* = 8.8, Ar), 7.22 (2H, d, *J* = 12.0, trop), 7.33 (2H, d, *J* = 12.0, trop), 8.00 (1H, d, *J* = 8.8, Ar), 8.73 (1H, s, N═CH).

**5-(2-Propyloxy-4-hexadecyloxybenzylidine)aminotropolone (4c)** was prepared in a 75% yield as a yellow powder, mp 54 °C (from ethanol). IR $\upsilon_{max}$/cm$^{-1}$ (KBr disk): 3300−3100 br, 2920 vs, 2850 s, 1660, 1620, 1541 vs, 1515 s, 1450 vs, 1430 s, 1379 s, 1362 vs, 1143. $^1$H NMR $\delta$ (400 MHz, $CD_2Cl_2$, $Me_4Si$): 0.86 (3H, t, $-CH_3$), 1.04 (3H, t, $-CH_3$), 1.20−1.50 (26H, m, $(CH_2)_{13}$), 1.81−1.93 (4H, m, 2 × Ar−O−$CH_2$−$C\mathit{H}_2$−R), 4.02 (4H, m, 2 × Ar−O−$C\mathit{H}_2$−R), 6.46 (1H, s, Ar), 6.56 (1H, d, *J* = 8.8, Ar), 7.22 (2H, d, *J* = 12.0, trop), 7.33 (2H, d, *J* = 12.0, trop), 8.00 (1H, d, *J* = 8.8, Ar), 8.73 (1H, s, N═CH).

**5-(2-Hexyloxy-4-hexadecyloxybenzylidine)aminotropolone (4d)** was prepared in a 83% yield as a yellow powder, mp 60 °C (from methanol/chloroform, 4:1). IR $\upsilon_{max}$/cm$^{-1}$ (KBr disk): 3300−3100 br, 2920 vs, 2850 s, 1660, 1620, 1539 vs, 1510 s, 1450 vs, 1425 s, 1372 s, 1362 vs, 1144. $^1$H NMR $\delta$ (400 MHz, $CD_2Cl_2$, $Me_4Si$): 0.86 (3H, t, $-CH_3$), 0.87 (3H, t, $-CH_3$), 1.20−1.50 (32H, m, $(CH_2)_3 + (CH_2)_{13}$), 1.81−1.93 (4H, m, 2 × Ar−O−$CH_2$−$C\mathit{H}_2$−R), 4.02 (2H, t, *J* = 6.6, Ar−O−$C\mathit{H}_2$−R), 4.04 (2H, t, *J* = 6.6, Ar−O−$CH_2$−R), 6.46 (1H, s, Ar), 6.56 (1H, d, *J* = 8.8, Ar), 7.22 (2H, d, *J* = 12.0, trop), 7.33 (2H, d, *J* = 12.0, trop), 8.00 (1H, d, *J* = 8.8, Ar), 8.73 (1H, s, N═CH).

**5-(2-Decyloxy-4-hexadecyloxybenzylidine)aminotropolone (4e)** was prepared in a 72% yield as a yellow powder, mp 63 °C (from ethanol/chloroform, 4:1). IR $\upsilon_{max}$/cm$^{-1}$ (KBr disk): 3300−3100 br, 2918 vs, 2861 s, 1660, 1620, 1540 vs, 1515 s, 1449 vs, 1430 s, 1382 s, 1362 vs, 1145. $^1$H NMR $\delta$ (400 MHz, $CD_2Cl_2$, $Me_4Si$): 0.86 (6H, t, 2 × $-CH_3$), 1.20−1.50 (40H, m, $(CH_2)_7 + (CH_2)_{13}$), 1.81−1.93 (4H, m, 2 × Ar−O−$CH_2$−$C\mathit{H}_2$−R), 4.02 (2H, t, *J* = 6.6, Ar−O−$C\mathit{H}_2$−R), 4.04 (2H, t, *J* = 6.6, Ar−O−$CH_2$−R), 6.46 (1 H, s, Ar), 6.56 (1H, d, *J* = 8.8, Ar), 7.22 (2H, d, *J* = 12.0, trop), 7.33 (2H, d, *J* = 12.0, trop), 8.00 (1H, d, *J* = 8.8, Ar), 8.73 (1H, s, N═CH).

**5-(2,4-Dihexadecyloxybenzylidine)aminotropolone (4f)** was prepared in a 67% yield as a yellow powder, mp 65 °C (from ethanol/chloroform, 3:1). IR $\upsilon_{max}$/cm$^{-1}$ (KBr disk): 3300−3100 br, 2924 vs, 2851 s, 1660, 1620, 1533 vs, 1515 s, 1450 vs, 1431 s, 1380 s, 1362 vs, 1145. $^1$H NMR $\delta$ (400 MHz, $CD_2Cl_2$, $Me_4Si$): 0.87 (6H, t, 2 × $-CH_3$), 1.18−1.50 (52H, m, 2 × $(CH_2)_{13}$), 1.80−1.92 (4H, m, Ar−O−$CH_2$−$C\mathit{H}_2$−R), 4.01 (2H, t, *J* = 6.6, Ar−O−$C\mathit{H}_2$−R), 4.03 (2H, t, *J* = 6.6, Ar−O−$C\mathit{H}_2$−R), 6.47 (1H, s, Ar), 6.55 (1H, d, *J* = 8.8, Ar), 7.23 (2H, d, *J* = 12.0, trop), 7.33 (2H, d, *J* = 12.0, trop), 8.00 (1H, d, *J* = 8.8, Ar), 8.73 (1H, s, N═CH).

**5-(2,4-Dipropyloxybenzylidine)aminotropolone (4g)** was prepared in a 92% yield as yellow needles, mp 46 °C (from ethanol). IR $\upsilon_{max}$/cm$^{-1}$ (KBr disk): 3300−3100 br, 2924 vs, 2850 s, 1660, 1620, 1541 vs, 1518 s, 1429 vs, 1433 s, 1383 s, 1361 vs, 1144. $^1$H NMR $\delta$ (400 MHz, $CD_2Cl_2$, $Me_4Si$): 1.03 (6H, m, 2 × $-CH_3$), 1.82−1.94 (4H, m, 2 × Ar−O−$CH_2$−$C\mathit{H}_2$−$CH_3$), 3.94 (2H, t, Ar−O−$CH_2$−Et), 3.97 (2H, t, Ar−O−$CH_2$−Et), 6.47 (1H, s, Ar), 6.55 (1H, d, *J* = 8.8, Ar), 7.23 (2H, d, *J* = 12.0, trop), 7.33 (2H, d, *J* = 12.0, trop), 8.00 (1H, d, *J* = 8.8, Ar), 8.73 (1H, s, N═CH).

**5-(3,4-Dioctyloxybenzylidine)aminotropolone (4h)** was prepared in a 90% yield as a yellow powder, mp 115 °C (from ethanol). IR $\upsilon_{max}$/cm$^{-1}$ (KBr disk): 3300−3100 br, 2921 vs, 2850 s, 1660, 1622, 1540 vs, 1515 s, 1450 vs, 1430 s, 1379 s, 1362 vs, 1145. $^1$H NMR $\delta$ (400 MHz, $CD_2Cl_2$, $Me_4Si$): 0.86 (6H, t, *J* = 7.0, 2 × $-CH_3$), 1.22−1.51 (20H, m, 2 × $(CH_2)_5$), 1.81−1.88 (4H, m, 2 × Ar−O−$CH_2$−$C\mathit{H}_2$−R), 4.03 (4H, t, *J* = 6.6, 2 × Ar−O−$CH_2$−R), 6.92 (1H, d, *J* = 8.3, Ar), 7.23−7.32 (3H, m, 2 trop + 1 Ar), 7.38 (2H, d, *J* = 12.0, trop), 7.52 (1H, s, Ar), 8.25 (1H, s, N═CH).

**5-(3,4-Didecyloxybenzylidine)aminotropolone (4i)** was prepared in an 86% yield as a yellow powder, mp 112 °C (from ethanol). IR $\upsilon_{max}$/cm$^{-1}$ (KBr disk): 3300−3100 br, 2920 vs, 2852 s, 1660, 1620, 1541 vs, 1510 s, 1450 vs, 1425 s, 1372 s, 1362 vs, 1144. $^1$H NMR $\delta$ (400 MHz, $CD_2Cl_2$, $Me_4Si$): 0.86 (6H, t, *J* = 7.0, 2 × $-CH_3$), 1.21−1.51 (28H, m, 2 × $(CH_2)_7$), 1.81−1.88 (4H, m, 2 × Ar−O−$CH_2$−$C\mathit{H}_2$−R), 4.03 (4H, t, *J* = 6.6, 2 × Ar−O−$CH_2$−R), 6.92 (1H, d, *J* = 8.3, Ar), 7.23−7.32 (3H, m, 2 trop + 1 Ar), 7.38 (2H, d, *J* = 12.0, trop), 7.52 (1H, s, Ar), 8.25 (1H, s, N═CH).

**5-(3,4-Didodecyloxybenzylidine)aminotropolone (4j)** was prepared in an 82% yield as a yellow powder, mp 110 °C (from ethanol/chloroform, 5:1). IR $\upsilon_{max}$/cm$^{-1}$ (KBr disk): 3300−3100 br, 2924 vs, 2850 s, 1660, 1620, 1541 vs, 1520 s, 1429 vs, 1433 s, 1383 s, 1366 vs, 1144. $^1$H NMR $\delta$ (400 MHz, $CD_2Cl_2$, $Me_4Si$): 0.86 (6H, t, *J* = 7.0, 2 × $-CH_3$), 1.21−1.51 (36H, m, 2 × $(CH_2)_9$), 1.82−1.92 (4H, m, 2 × Ar−O−$CH_2$−$C\mathit{H}_2$−R), 4.03 (4H, t, *J* = 6.6, 2 × Ar−O−$CH_2$−R), 6.92 (1H, d, *J* = 8.3, Ar), 7.23−7.32 (3H, m, 2 trop + 1 Ar), 7.38 (2H, d, *J* = 12.0, trop), 7.52 (1H, s, Ar), 8.25 (1H, s, N═CH).

**5-(3,4-Ditridecyloxybenzylidine)aminotropolone (4k)** was prepared in a 73% yield as a yellow powder, mp 108 °C (from ethanol/chloroform, 4:1). IR $\upsilon_{max}$/cm$^{-1}$ (KBr disk): 3300−3100 br, 2918 vs, 2850 s, 1660, 1620, 1539 vs, 1510 s, 1450 vs, 1425 s, 1372 s, 1362 vs, 1144. $^1$H NMR $\delta$ (400 MHz, $CD_2Cl_2$, $Me_4Si$): 0.86 (6H, t, *J* = 7.0, 2 × $-CH_3$), 1.21−1.50 (40H, m, 2 × $(CH_2)_{10}$), 1.82−1.92 (4H, m, 2 × Ar−O−$CH_2$−$C\mathit{H}_2$−R), 4.03 (4H, t, *J* = 6.6, 2 × Ar−O−$CH_2$−R), 6.92 (1H, d, *J* = 8.3, Ar), 7.23−7.32 (3H, m, 2 trop + 1 Ar), 7.38 (2H, d, *J* = 12.0, trop), 7.52 (1H, s, Ar), 8.25 (1H, s, N═CH).

**5-(3,4-Ditetradecyloxybenzylidine)aminotropolone (4l)** was prepared in a 68% yield as a yellow powder, mp 107 °C (from ethanol/chloroform, 4:1). IR $\upsilon_{max}$/cm$^{-1}$ (KBr disk): 3300−3100 br, 2917 vs, 2849 s, 1660, 1620, 1540 vs, 1515 s, 1454 vs, 1425 s, 1372 s, 1362 vs, 1141. $^1$H NMR $\delta$ (400 MHz, $CD_2Cl_2$, $Me_4Si$): 0.86 (6H, t, *J* = 7.0, 2 × $-CH_3$), 1.21−1.50 (44H, m, 2 × $(CH_2)_{11}$), 1.82−1.94 (4H, m, 2 × Ar−O−$CH_2$−$C\mathit{H}_2$−R), 4.03 (4H, t, *J* = 6.6, 2 × Ar−O−$CH_2$−R), 6.92 (1H, d, *J* = 8.3, Ar), 7.23−7.33 (3H, m, 2 trop + 1 Ar), 7.38 (2H, d, *J* = 12.0, trop), 7.52 (1H, s, Ar), 8.25 (1H, s, N═CH).

**5-(3,4-Dihexadecyloxybenzylidine)aminotropolone (4m)** was prepared in a 64% yield as a yellow powder, mp 105 °C (from ethanol/cloroform, 3:1). IR $\upsilon_{max}$/cm$^{-1}$ (KBr disk): 3300−3100 br, 2924 vs, 2850 s, 1660, 1620, 1541 vs, 1520 s, 1429 vs, 1433 s, 1383 s, 1366 vs, 1144. $^1$H NMR $\delta$ (400 MHz, $CD_2Cl_2$, $Me_4Si$): 0.86 (6H, t, *J* = 7.0, 2 × $-CH_3$), 1.21−1.51 (52H, m, 2 × $(CH_2)_{13}$), 1.82−1.90 (4H, m, 2 × Ar−O−$CH_2$−$C\mathit{H}_2$−R), 4.03 (4H, t, *J* = 6.6, 2 × Ar−O−$CH_2$−R), 6.92 (1H, d, *J* = 8.3, Ar), 7.23−7.33 (3H, m, 2 trop + 1 Ar), 7.38 (2H, d, *J* = 12.0, trop), 7.52 (1H, s, Ar), 8.25 (1H, s, N═CH).

**5-(3,5-Dihexadecyloxybenzylidine)aminotropolone (4n)** was prepared in a 34% yield as a yellow powder, mp 47 °C (from butanol/

**Table 2.** Synthesis of 5-(Dialkoxybenzylidine)aminotropolones

| aromatic ring substituents | | | | | | | |
|---|---|---|---|---|---|---|---|
| 2-R$^1$ | 3-R$^2$ | 4-R$^3$ | 5-R$^4$ | aldehyde no. | Schiff base no. | mp Schiff base/°C | Cu complex no. |
| $C_6H_{13}O$ | H | $C_{12}H_{25}O$ | H | **6a** | **4a** | 71 | **5a** |
| $C_{10}H_{21}O$ | H | $C_{12}H_{25}O$ | H | **6b** | **4b** | 75 | **5b** |
| $C_3H_7O$ | H | $C_{16}H_{33}O$ | H | **6c** | **4c** | 54 | **5c** |
| $C_6H_{13}O$ | H | $C_{16}H_{33}O$ | H | **6d** | **4d** | 60 | **5d** |
| $C_{10}H_{21}O$ | H | $C_{16}H_{33}O$ | H | **6e** | **4e** | 63 | **5e** |
| $C_{16}H_{33}O$ | H | $C_{16}H_{33}O$ | H | **6f** | **4f** | 65 | **5f** |
| $C_3H_7O$ | H | $C_3H_7O$ | H | **6g** | **4g** | 46 | **5g** |
| H | $C_8H_{17}O$ | $C_8H_{17}O$ | H | **6h** | **4h** | 115 | **5h** |
| H | $C_{10}H_{21}O$ | $C_{10}H_{21}O$ | H | **6i** | **4i** | 112 | **5i** |
| H | $C_{12}H_{25}O$ | $C_{12}H_{25}O$ | H | **6j** | **4j** | 110 | **5j** |
| H | $C_{13}H_{27}O$ | $C_{13}H_{27}O$ | H | **6k** | **4k** | 108 | **5k** |
| H | $C_{14}H_{29}O$ | $C_{14}H_{29}O$ | H | **6l** | **4l** | 107 | **5l** |
| H | $C_{16}H_{33}O$ | $C_{16}H_{33}O$ | H | **6m** | **4m** | 105 | **5m** |
| H | $C_{16}H_{33}O$ | H | $C_{16}H_{33}O$ | **6n** | **4n** | 47 | **5n** |

choroform, 4:1). IR $\upsilon_{max}$/cm$^{-1}$ (KBr disk): 3300−3100 br, 2924 vs, 2850 s, 1660, 1620, 1541 vs, 1520 s, 1429 vs, 1433 s, 1383 s, 1366 vs, 1144. $^1$H NMR $\delta$ (400 MHz, $CD_2Cl_2$, $Me_4Si$): 0.87 (6H, t, $J = 7.0$, 2 × $-CH_3$), 1.18−1.50 (52H, m, 2 × $(CH_2)_{13}$), 1.78−1.90 (4H, m, 2 × Ar−O−$CH_2$−C$H_2$−R), 3.99 (4H, t, $J = 6.6$, 2 × Ar−O−$CH_2$−R), 6.59 (1H, t, $J = 2.4$, Ar), 7.01 (2H, d, $J = 2.4$, Ar), 7.26 (2H, d, $J = 11.9$, trop), 7.35 (2H, d, $J = 11.9$, trop), 8.30 (1H, s, N=CH).

**Bis[5-(2-hexyloxy-4-dodecyloxybenzylidine)aminotropolonato]-copper(II) (5a).** Compound **4a** (0.30 g, 0.59 mmol) was added to a solution of anhydrous NaOAc (82 mg, 1.00 mmol) in ethanol (40 cm$^3$) and stirred for 10 min. A solution of $Cu(OAc)_2 \cdot H_2O$ (60 mg, 0.30 mmol) in ethanol (20 cm$^3$) was added to the reaction mixture, and the mixture was refluxed for 2 h. The mixture was cooled in an ice bath, and the yellow solid was filtered off. The solid was washed in diethyl ether (10 cm$^3$) and cold tetrahydrofuran (2 × 10 cm$^3$) before being dried under vacuum (0.5 mmHg) for 4 h. The crude product was purified twice by a Soxhlet extraction with hexane to yield **5a** (0.27 g, 84%) as a yellow powder, mp 152 °C (from toluene). Anal. Calcd for $CuC_{64}H_{92}N_2O_8$: C, 71.11; H, 8.58; N, 2.59. Found: C, 71.32; H, 8.47; N, 2.51. IR $\upsilon_{max}$/cm$^{-1}$ (KBr disk): 3600−3350, 2925 s, 2855 s, 1655, 1605 s, 1515 s, 1471 s, 1433 vs, 1364 s, 1312 s, 1181 w.

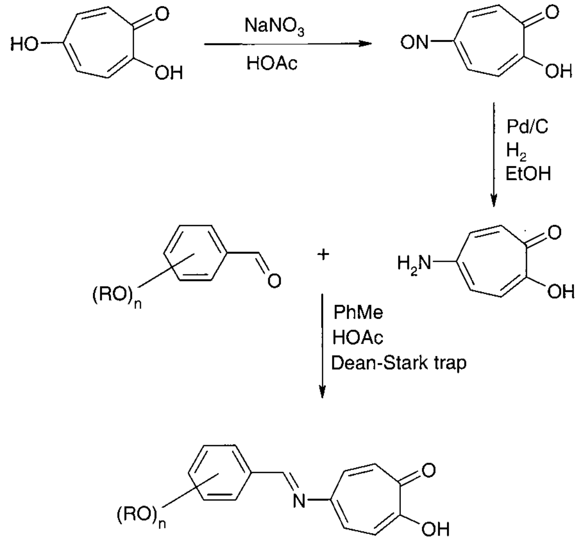
Copper complexes **5b**−**n** were prepared similarly. As is common with copper(II) chelate complexes, traces of water were very hard to remove. Complex **5o** was made from **4m** and $NiCl_2 \cdot 6H_2O$, and **5p** was prepared from **4m** and $ZnCl_2 \cdot 2H_2O$, similarly.

**Phase Studies**. The phase behavior of the complexes was examined by using an Olympus BH2 polarizing microscope in conjunction with a Mettler FP5 hot stage and controller. Phase-transition enthalpies were measured using a Perkin-Elmer DSC-2C with a PC 3600 thermal analysis data station. The heating rates used were normally 10 °C min$^{-1}$, and the measured onset of the indium standard was 156.66 °C, $\Delta H = 28.50$ J g$^{-1}$ (standard[2626] value is 156.60 °C, $\Delta H = 28.45$ J g$^{-1}$).

## Results and Discussion

**Synthesis.** Scheme 1 shows the synthesis of 5-(alkoxybenzylidine)tropolones. A supply of 5-aminotropolone is readily synthesized. Tropolone is first treated with sodium nitrite to form 5-nitrosotropolone,[22] which is then reduced with hydrogen over 5% palladium/charcoal in ethanol to yield 5-aminotropolone. The alkoxylated benzaldehydes **6** were prepared from the appropriate hydroxybenzaldehyde.[27−32] Details of preparation and identification of the substituted benzaldehydes not in the literature are given in the Experimental Section. The alkoxylated benzaldehydes and 5-aminotropolone were then condensed to give the Schiff bases.[22] Two copper complexes were readily prepared from the 5-(alkoxybenzylidine)tropolones by reaction with copper(II) acetate in the presence of sodium acetate. The compounds synthesized are given in Table 2. The identity and purity of all of the ligands was assessed by NMR, MS, and TLC. Elemental analyses were satisfactory for all of the copper complexes (Table 3).

**Scheme 1.** Synthesis of Ligands



**Melting Behavior of Complexes. (a) 2,4-Substituted Complexes.** For copper complexes **5a**−**g** with substituents in the 2 and 4 positions of the benzylidine ring, there are no mesophases, but melting points are much lower than the clearing temperatures of the 5-alkoxytropolone derivatives previously reported[1] (Table 4and Figure 1).

As expected, the length of the alkoxy chains, whether at the 2 or the 4 position, affects the melting points, which are the lowest when both of the chains are the longest.

Changing the metal atom from copper to nickel to zinc produced little change in the melting point (Table 5).

**(b) 3,5-Substituted Complexes.** Scheme 2 shows the melting behavior of bis[5-(3,5-dialkoxybenzylidine)tropolonato]copper (**5n**; R$^1$ = R$^3$ = H and R$^2$ = R$^4$ = $OC_{16}H_{33}$).

The spread-out chains confer a disklike structure, and microscopy confirmed a columnar-hexagonal disordered phase. This agrees with the columnar phases identified in 3,4-substituted polycatenar silver(I) complexes.[33]

---

(26) *CRC Handbook of Physics and Chemistry*, 68th ed.; Weast, R. C., Ed.; CRC Press: Boca Raton, FL.

(27) Donnio, B.; Bruce, D. W. *J. Chem. Soc., Dalton Trans.* **1997**, 2745.

(28) Destrade, C.; Nguyen, H. T.; Alstermark, C.; Lindsten, G.; Nilsson, M. *Mol. Cryst. Liq. Cryst.* **1990**, *180*, 265.

(29) Hoshino, N.; Takahashi, H.; Matsunaga, Y.; Okamoto, H.; Mitani, T. *Mol. Cryst. Liq. Cryst.* **1992**, *216*, 265.

(30) Kosteyn, F.; Zerban, G.; Meier, H. *Chem. Ber.* **1992**, *125*, 893.

(31) Zerban, G.; Meier, H. *Z. Naturforsch., B: Chem. Sci.* **1993**, *48*, 171.

(32) Kretzschmann, H.; Muller, K.; Kolshorn, H.; Schollmeyer, D.; Meier, H. *Chem. Ber.* **1994**, *127*, 1735.

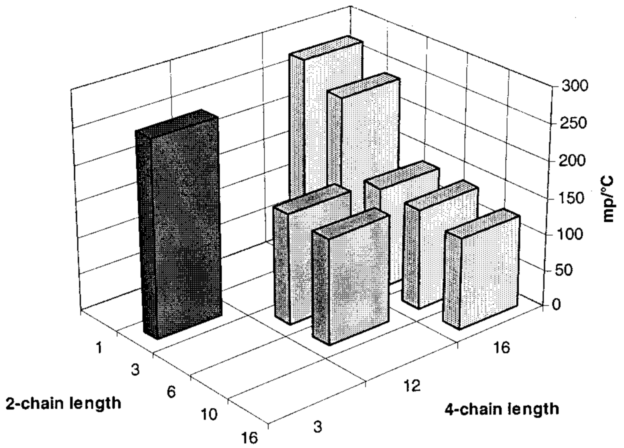


**Figure 1.** Melting behavior of 2,4-substituted copper complexes **5a**–**g**. The length of the 2 chain is much more important than that of the 4 chain in influencing the melting point (detailed data is in Table 4).

**Table 3.** Elemental Analysis of Complexes

| no. | formula | %C exptl | %C calcd | %H exptl | %H calcd | %N exptl | %N calcd |
|---|---|---|---|---|---|---|---|
| **5a** | $C_{64}H_{92}CuN_2O_8$ | 71.32 | 71.11 | 8.47 | 8.58 | 2.51 | 2.59 |
| **5b** | $C_{72}H_{108}CuN_2O_8$ | 72.55 | 72.48 | 9.20 | 9.12 | 2.14 | 2.34 |
| **5c** | $C_{66}H_{96}CuN_2O_8{\cdot}0.5H_2O$ | 70.95 | 70.90 | 8.72 | 8.74 | 2.61 | 2.51 |
| **5d** | $C_{72}H_{108}CuN_2O_8$ | 72.93 | 72.47 | 9.45 | 9.12 | 2.36 | 2.35 |
| **5e** | $C_{80}H_{124}CuN_2O_8$ | 73.26 | 73.60 | 9.85 | 9.42 | 2.22 | 2.15 |
| **5f** | $C_{92}H_{148}CuN_2O_8$ | 74.87 | 74.98 | 9.95 | 10.12 | 1.98 | 1.90 |
| **5g** | $C_{40}H_{44}CuN_2O_8$ | 64.69 | 64.55 | 5.95 | 5.96 | 3.91 | 3.76 |
| **5h** | $C_{60}H_{84}CuN_2O_8$ | 70.88 | 70.31 | 8.55 | 8.26 | 2.80 | 2.73 |
| **5i** | $C_{68}H_{100}CuN_2O_8$ | 71.88 | 71.82 | 8.96 | 8.87 | 2.50 | 2.46 |
| **5j** | $C_{76}H_{116}CuN_2O_8$ | 73.23 | 73.07 | 9.60 | 9.36 | 2.25 | 2.24 |
| **5k** | $C_{80}H_{124}CuN_2O_8$ | 73.44 | 73.60 | 9.95 | 9.77 | 2.08 | 2.06 |
| **5l** | $C_{84}H_{132}CuN_2O_8{\cdot}0.5H_2$ | 73.51 | 73.61 | 9.95 | 9.78 | 2.08 | 2.04 |
| **5m** | $C_{92}H_{148}CuN_2O_8{\cdot}0.5H_2O$ | 74.49 | 74.52 | 10.61 | 10.13 | 1.88 | 1.89 |
| **5n** | $C_{92}H_{148}CuN_2O_8{\cdot}0.5H_2O$ | 74.52 | 74.52 | 10.05 | 10.13 | 1.82 | 1.89 |
| **5o** | $C_{92}H_{148}N_2NiO_8{\cdot}0.5H_2O$ | 74.55 | 74.77 | 10.21 | 10.16 | 1.80 | 1.90 |
| **5p** | $C_{92}H_{148}N_2O_8Zn{\cdot}H_2O$ | 73.81 | 73.98 | 10.24 | 10.12 | 1.60 | 1.88 |

**Table 4.** Melting Behavior of Bis[5-(2,4-dialkoxybenzylidine)-tropolonato]copper Complexes **5a**–**g**

| compd no. | $R^1 = OC_nH_{2n+1}$ *n* | $R^3 = OC_mH_{2m+1}$ *m* | temp of cryst–iso transition (°C) |
|---|---|---|---|
| **5a** | 12 | 6 | 152 |
| **5b** | 12 | 10 | 146 |
| **5c** | 16 | 3 | 241 |
| **5d** | 16 | 6 | 141 |
| **5e** | 16 | 10 | 138 |
| **5f** | 16 | 16 | 126 |
| **5g** | 3 | 3 | 270 (dec) |

**Table 5.** Melting Behavior of Bis[5-(2,4-dihexadecyloxy-benzylidine)tropolonato] Derivatives of Metals

| compd no. | | cryst–iso (°C) | compd no. | | cryst–iso (°C) |
|---|---|---|---|---|---|
| **5o** | Ni | 135 | **5f** | Cu | 126 |
| **5p** | Zn | 138 | | | |

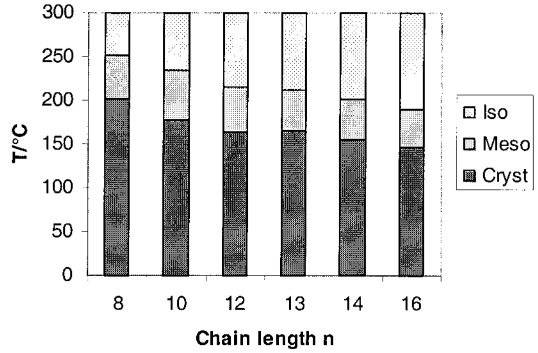
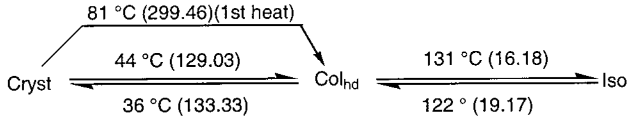
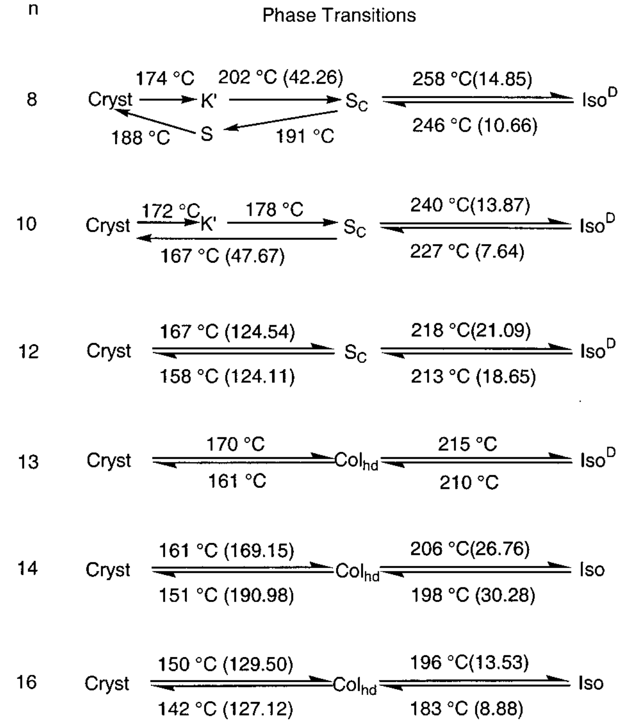


**Figure 2.** Melting behavior of 3,4-substituted copper complexes **5h**–**m**. There is a general decrease in the melting point/clearing point with the chain length irrespective of the nature of the mesophase (the nature of the mesophases is in Scheme 3).

**Scheme 2.** Mesomorphism of Bis[5-(3,5-dihexadecyloxy-benzylidine)tropolonato]copper (**5n**)



**Scheme 3.** Mesomorphism of Bis[5-(3,4-dialkoxybenzylidine)aminotropolonatocopper(II) [Enthalpies (kJ mol−$^1$) in Parentheses]



**(c) 3,4-Substituted Complexes.** The melting behavior of the copper complexes **5h**–**m** is given in Scheme 3. The bar chart (Figure 2) shows that mesophase transition temperatures decrease fairly uniformly with an increase in the chain lengths. With a chain length below 13, the transition is to a smectic *C* phase. With a chain length of 13 or greater, the mesophase is a columnar-hexagonal disordered phase. These complexes provide a fine example of polycatenar molecules with a phase changeover from lamellar to columnar. There is a competition in these complexes between the columnar behavior expected for complexes with lateral alkoxy chains and the lamellar behavior expected for the rodlike molecules containing 4-alkoxy substitutents. This phase changeover fits in well with previous considerations on the significance of the curvature of the interface between the rigid core and the alkyl chains.[34–38] With short chains, there is no imbalance between the volumes of the

---

(33) Donnio, B.; Bruce, D. W. *New J. Chem.* **1999**, *23*, 275.

(34) Charvolin, W. *J. Chim. Phys. Phys.-Chim. Biol.* **1983**, *80*, 15.

(35) Hendrikx, Y.; Levelut, A.-M. *Mol. Cryst. Liq. Cryst.* **1988**, *165*, 233.

(36) Skoulis, A.; Guillon, D. *Mol. Cryst. Liq. Cryst.* **1988**, *165*, 317.

(37) Tschierske, C. *J. Mater. Chem.* **1998**, *8*, 1551.

**Table 6.** Variation of Melting Behavior with the Substitution Pattern

| compd | positions of $C_{16}H_{33}O$ | transition | $\theta$ (°C) | transition | $\theta$ (°C) |
|---|---|---|---|---|---|
| **5f** | 2,4 | | | cryst−iso | 126 |
| **5n** | 3,5 | cryst−$col_{hd}$ | 40 | $col_{hd}$−iso | 127 |
| **5m** | 3,4 | cryst−$col_{hd}$ | 146 | $col_{hd}$−iso | 190 |

rigid core and the alkyl chains, and lamellar phases are found. With longer alkyl chains, the volume required by the chains becomes much greater than that required by the core, and columnar phases result. It is noteworthy that the analogous nickel and zinc complexes, although melting at lower temperatures, do not give rise to mesophases. This indicates that the molecular environment required for mesophases is very demanding. 3,4-Substituted polycatenar silver complexes showed cubic and columnar phases but no calamitic $N$ or $S_C$ phases.[33]

The 2,4-substituted series gave no mesophases but had lower melting points than those of the analogous 3,4-substituted complexes (Table 6).

From Table 6, it can be seen that the 3,5-dialkoxy ring produces the lowest melting point. The two lateral long alkoxy chains destabilize packing well.

## Conclusions

This new series of metallomesogens provides further evidence for the subtle balance between the chain length and molecule breadth required to give mesophases. Our results can be summarized in terms of terminal chains (alkoxy substitution at the 4 position) and lateral chains (substitution at the 3 and 5 positions). When there are no terminal chains (3,5 substitution), only columnar behavior is seen. With both terminal and lateral chains, mixed behavior is seen, depending upon the chain length. Substitution at the 2 position so disrupts packing that no mesophases are seen, even with long terminal chains. The bis(tropolonato)copper(II) core is a good base on which to graft further ring systems where molecule length and breadth can be varied. Copper complexes of alkoxy-substituted ligands often show alkoxy oxygen−copper interactions perpendicular to the chelate plane, which partly determine the three-dimensional packing.[1]

Ziessel et al.[19] reported metallomesogens based around a polypyridine core. Copper complexes synthesized with a bipyridine core have exhibited columnar mesophases. They have extended this core, using a further bipyridine ring to form a new series of dinuclear copper bis(terpyridine) complexes, which are mesogenic, and the first example of a metallomesogen with a terpyridine core. Observation of these terpyridine complexes with optical microscopy showed a schlieren texture that was indicative of a biaxial smectic phase. Crystallographic data for the core structure has shown the molecules to be aligned in parallel rows, indicative of a lamellar packing of molecules. Further characterization with XRD studies show the organization of the individual molecules into a columnar stack with lamellar morphology. The change in the design of the core, from a bipyridine to a terpyridine structure, has resulted in crossover phase behavior in the molecules from discotic to calamitic mesophases.

Tschierske et al.[16] have utilized two molecular subunits, the calamitic disubstituted 2-phenylpyrimidine core and the half-disk shape of a 1,3-diketonate with alkyl chains, to give palladium complexes of an intermediate shape between a rod and a disk. These novel palladium complexes are mesogenic, and a sequential increase in the number of alkyl chains has led to a discontinuous crossover in phase behavior from lamellar (4 or 5 chains) to columnar (7 or 8 chains). These mononuclear ortho-palladated phenylpyrimidine-1,3-diketonato organyls are the first to show thermotropic columnar mesophase behavior. Further work by Tschierske et al.[17] has again utilized the idea of fusing two submolecular units via ortho palladation to create metallomesogens which exhibit a crossover phase behavior between lamellar and columnar. Using a rodlike *p*-cyclophane core with 1,3-diketonates, the subsequent palladium complexes again show a discontinuous crossover phase behavior between lamellar (4 chains) and columnar (8 chains). Moreover, these *p*-cyclophane derivatives are the first to show thermotropic, columnar mesophase behavior.

Although these are fine examples of compounds that show crossover phase behavior, they all involve a change in the core design of the complexes to get the *jump*. Our complexes are an example of the crossover phase behavior of a more fundamental sense, with crossover seen within a single series of compounds and with no change to the core. The design of our complexes fits the model laid down for polycatenars by Malthete et al.[10] and is a true example of copper-complex tetracatenars.

**Acknowledgment.** Financial support from the EPSRC is gratefully acknowledged.

**Supporting Information Available:** Micrographs of the various phases, labeled according to chain lengths and phases. This material is available free of charge via the Internet at http://pubs.acs.org.

IC001475U

---

(38) Roll, C. P.; Donnio, B.; Weigand, W.; Bruce, D. W. *Chem. Commun.* **2000**, 709.