

Low Transition Temperature Liquid Crystalline Amines Incorporating the *Trans*-1,4-Substituted Cyclohexane Ring System

JOHN H. MacMILLAN and M. M. LABES

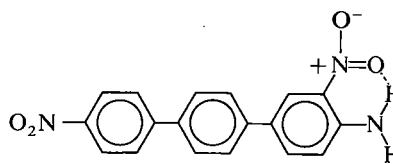
Department of Chemistry, Temple University, Philadelphia, Pennsylvania 19122

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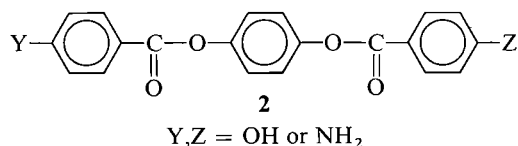
A series of para substituted *trans*-4-*n*-alkylcyclohexylbenzylamines was prepared and examined for mesomorphic properties. The *n*-pentyl derivative **5b** showed monotropic smectic behavior while the *n*-heptyl derivative **5c** was an enantiotropic smectic. **5b** and **5c** are the first examples of low temperature liquid crystals incorporating an amino functionality. While the *p*-(*trans*-4-*n*-alkylcyclohexyl)anilines were not liquid crystalline, *N*-alkyl-substituted-*p*-(*trans*-4-*n*-alkylcyclohexyl)anilines such as *N*-(*n*-butyl)-*p*-(*trans*-4-*n*-pentylcyclohexyl)aniline **12a** exhibit low temperature mesophases. A strong tendency to spontaneous homeotropic alignment was found in the nematic members of this series.

INTRODUCTION

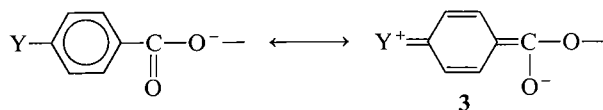
Mesomorphic compounds incorporating a primary amino functionality remain fairly scarce. Gray¹ has proposed that the paucity of mesogenic amines (and phenols) may result from intermolecular hydrogen bonding raising the melting point above the anticipated mesophase-isotropic liquid transition temperature. However, compounds such as **1**, where intramolecular hydrogen bonding may compete, often exhibit a mesophase.



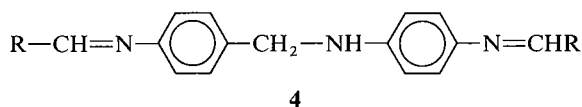
Gray¹ postulated that intermolecular hydrogen bonding may promote a nonlinear molecular array detrimental to mesophases. Whatever the causes, they may be overridden in cases where other structural factors predominate. For example Schroeder and Schroeder^{2,3} have reported a series of *p*-phenylenedibenzoates **2** to be mesomorphic.



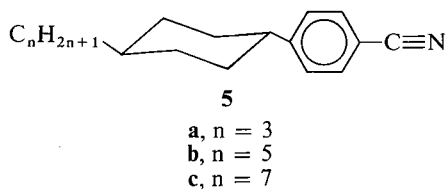
While intramolecular hydrogen bonding is not possible for this system, Dewar⁴ has postulated that electron donation by the groups *Y* and *Z* promote polar resonance contributors such as **3**. Such a polar contributor should increase intermolecular attractions, therefore promoting a liquid crystalline phase.



Liquid crystalline secondary amines are also known.⁵ They consist of largely conjugated long rodlike molecules such as **4**, again indicating that other favorable structural factors may outweigh possible deleterious effects of hydrogen bonding.

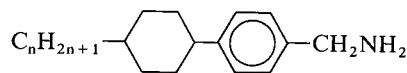


The commercial availability of a series of mesogenic *trans*-4-*n*-alkylcyclohexyl benzonitriles, **5a-c** promoted us to explore whether favorable structural factors might cause mesophases in amines synthesizable from **5a-c**, and offer low temperature liquid crystalline structures with a terminal polar electron donating group.



RESULTS AND DISCUSSION

Compounds **5a-c** were readily reduced to benzylamines **6a-c** with lithium aluminum hydride.

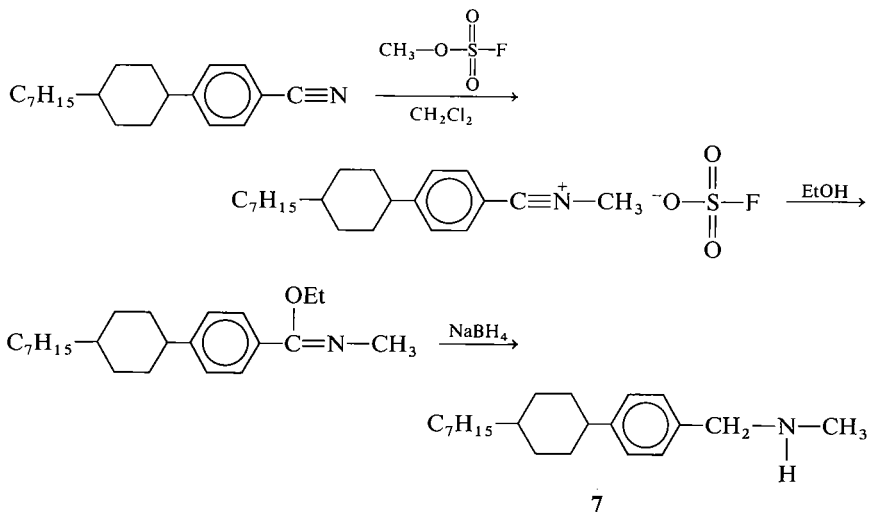
**6a-c**

a, n = 3

b, n = 5

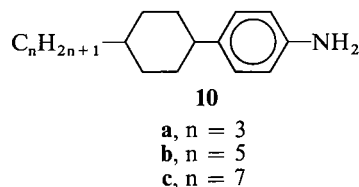
c, n = 7

The materials proved surprisingly hygroscopic; however, they could be conveniently stored as their non-hygroscopic hydrochloride salts. Compound **6a** showed a simple solid \rightarrow isotropic transition, whereas **6b** exhibited monotropic behavior with a smectic A phase between 9° and 0° on cooling. **6c** had an enantiotropic smectic A range between 15° and 26° . On cooling **6a** showed a $S_A \rightarrow S_B$ transition at 20° . This series of materials constitutes the first reported examples of low temperature liquid crystals incorporating the amino functionality. In order to explore whether N-alkylation would expand the mesophase range by diminution of hydrogen bonding, the N-methyl derivative of **6c**, **7** was prepared. The procedure of Borch⁶ was employed.

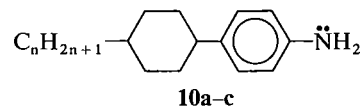
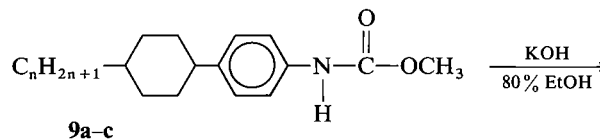
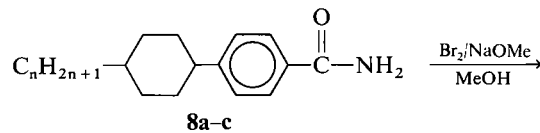
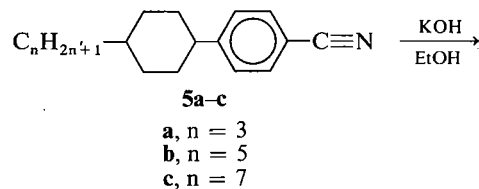


Compound **7** had a 3° enantiotropic nematic range from -1° to $+2^\circ$. Preparation of other N-alkyl derivatives is necessary in order to determine the structural requirements for low temperature nematic behavior in this series.

We next investigated a series of *trans*-4-*n*-alkylcyclohexylanilines.



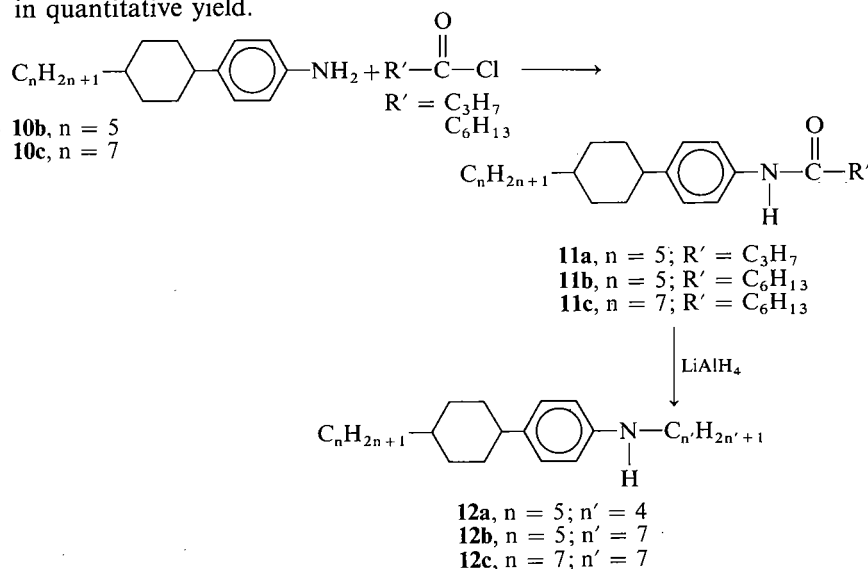
10a-c were prepared by a three step sequence involving basic hydrolysis of **5a-c** to the amides **8a-c**. Standard Hoffman degradation of **8a-c** failed due to insolubility in aqueous media. However, degradation in methanol went smoothly giving carbamates **9a-c** in good yield. Saponification in basic aqueous ethanol gave **10a-c** in 70-80% yields.



In light of the mesomorphic behavior of the benzylamines, we were somewhat surprised to observe that **10a-c** are not mesogenic, but show sharp solid \rightarrow isotropic transitions at approximately 58° with no evidence for monotropic behavior. **10a-c** have proved to exhibit interesting mixed phase behavior with **5a-c**, which has been published elsewhere.⁷

On the other hand, the *N*-alkylated derivatives of **10a-c** show potential as low temperature nematic materials. Three members of the series have been prepared by treatment of **10a-c** with the appropriate acid chloride,

yielding the amides **11a-c**. Reduction of **11a-c** gave N-alkylated amines **12a-c** in quantitative yield.



Compound **12c** showed a solid \rightarrow isotropic transition, while **12b** exhibited a transient nematic texture on cooling, indicating that suitable manipulation of the alkyl groups should yield nematic materials. This behavior was realized with **12a**, which gives enantiotropic behavior, showing a birefringent homeotropically aligned nematic phase between 28° and 33° . The phase shows a transient thread-like texture approximately one degree before the isotropic point.

Compounds **12b** and **12c** also were effective spontaneous homeotropically aligning agents for nematics such as **5a-c**. Schroeder and Schroeder² observed a similar homeotropically aligned phase with $2/Y, Z = \text{NH}_2$). The powerfully basic amino functionality seems to be an effective group for binding to glass surfaces resulting in the promotion of bulk homeotropy.

Since **both** low temperature nematic behavior and spontaneous alignment are possible in this class of compounds, further manipulation of the structural aspects of these compounds is expected to result in interesting mesogens of possible utilization in aligned liquid crystalline devices.

EXPERIMENTAL

Physical measurements and purity of materials

Transition temperatures were measured utilizing a Perkin-Elmer DSC 1-B, or via polarized optical microscopy on a Mettler FP-2 hot stage. The

structures of all materials were confirmed by infrared spectroscopy and satisfactory microanalyses (Galbraith Laboratories, Knoxville, Tenn.). Vacuum distillations of liquid amines were conveniently accomplished using an Aldrich "Kugelrohr" apparatus.

Preparation of materials

p - (4 - *n* - Alkylcyclohexyl)benzylamines (**6a-c**) These materials were prepared by lithium aluminum hydride (LAH) reduction of commercially available *p*-(4-*n*-alkylcyclohexyl)benzonnitriles (EM Laboratories). The benzylamines proved quite hygroscopic, necessitating manipulations under dry nitrogen and storage as hydrochloride salts. A representative procedure follows.

p-(*trans*-4-*m*-Pentylcyclohexyl)benzylamine (**6b**) A 100 ml oven dried three neck flask was charged under nitrogen with 1.0 g (4 mmol) of the nitrile precursor, 50 ml of dry diethyl ether and 1.0 g (26 mmol) of LAH. The solution was stirred overnight under nitrogen, after which the excess LAH was decomposed by cautious addition of water until a white precipitate formed. The precipitate was filtered off and the filtrate dried over sodium sulfate. The ether was distilled off and the liquid residue vacuum distilled yielding ~800 mg (80%) of the benzylamine, B.P. ~135° (0.1 mm), m.p. crystal-isotropic (K-I) 27°, cooling: *I* → *S_A* 9°, *S_A* → *K* 0°, I.R. (cm⁻¹) 3300, 3250, 3010, 2900, 1600. *Anal.* Calc. for C₁₈H₂₉N: C, 83.32; H, 11.27; N, 5.40. Found: C, 83.22; H, 11.40; N, 5.46. *Hydrochloride Salt*, Calc. for C₁₈H₃₀NCl: C, 73.06; H, 10.22; N, 4.73. Found: C, 73.18; H, 10.20; N, 4.76.

By an entirely analogous procedure the following benzylamines were prepared.

p-(*trans*-4-*n*-Propylcyclohexyl)benzylamine (**6a**) 1.0 g (4.4 mmol) of the nitrile precursor in 40 ml diethyl ether with 1.0 g (26 mmol) LAH gave ~700 mg (70%) of the benzylamine, B.P. ~130° (0.1 mm), K-I 20°, I.R. (cm⁻¹) 3300, 3250, 3010, 2900, 1600. *Hydrochloride Salt*, Calc. for C₁₆H₂₆NCl: C, 71.74; H, 9.79; N, 5.23. Found: C, 71.82; H, 9.90; N, 5.42.

p-(*trans*-4-*n*-Heptylcyclohexyl)benzylamine (**6c**) 1.0 g (3.6 mmol) of the nitrile precursor in 50 ml diethyl ether with 1.0 g (26 mmol) LAH gave ~800 mg (80%) of the benzylamine, B.P. ~140° (0.1 mm), m.p. crystal-smectic A (*K-S_A*) 15°; smectic A-isotropic (*S_A-I*) 26°; cooling: *S_A* → *S_B* 20°; I.R. (cm⁻¹) 3300, 3250, 3010, 2900, 1600. *Hydrochloride Salt*, Calc. for C₂₀H₃₄NCl: C, 74.15; H, 10.57; N, 4.32. Found: C, 74.11; H, 10.66; N, 4.34.

N-Methyl-*p*-(*trans*-4-*n*-heptylcyclohexyl)benzylamine (7) This compound was prepared, albeit in a low yield, by the procedure of Borch⁶ for the direct conversion of a nitrile to a secondary amine.

A flame dried 50 ml three neck flask equipped with condenser, calcium chloride drying tube, and septum cap was charged under nitrogen with 1.16 g (4.2 mmol) of the nitrile precursor and ~2 ml of "Magic Methyl" (Aldrich). The reaction was heated at 100° under nitrogen overnight, at which time I.R. analysis indicated all nitrile to have reacted. 5 ml dichloromethane was syringed into the solution and the reaction cooled to 0°. 2 ml absolute ethanol was then added, the solution stirred for 2.5 hr, and decomposed at 0° with 10 ml of 6 N NaOH. The solution was extracted three times with 5 ml ether portions, the combined extracts shaken with water until neutral, then dried over sodium sulfate. The ether was removed and the residue taken up in 20 ml absolute ethanol with 1.5 g sodium borohydride. After stirring 48 hrs. under nitrogen the ethanol was removed, the residue taken up in 50 ml H₂O and the solution extracted three times with ~20 ml ether portions. The combined extracts were dried over sodium sulfate and the ether evaporated. The residue was vacuum distilled giving ~400 mg. (~30%) of the secondary amine, B.P. ~130° (0.1 mm), m.p. K-N -1°; N-I 2°; I.R. (cm⁻¹) 3300, 3010, 2900, 1620. *Hydrochloride*, Calc. for C₂₁H₃₅NCl: C, 74.84; H, 10.47; N, 4.15. Found: C, 75.06; H, 10.52; N, 4.19.

p-(*trans*-4-*n*-Alkylcyclohexyl)benzamides (8a-c) These compounds were easily prepared from their nitrile precursors by refluxing with aqueous potassium hydroxide/ethanol. A representative procedure follows.

p-(*trans*-4-*n*-Pentylcyclohexyl)benzamide (8b) A 3.09 g (12 mmol) sample of the nitrile precursor was refluxed overnight with 4.0 g (70 mmol) of potassium hydroxide in 60 ml ethanol with 20 ml water. The copious white precipitate was suction collected and air dried. Yield, 2.9 g (88%); m.p. 234-5°; I.R. (cm⁻¹) 3300, 3010, 2970, 2950, 1640. *Anal.* Calc. for C₁₈H₂₇NO: C, 79.06; H, 9.96; N, 5.12. Found: C, 79.36; H, 10.04; N, 5.07. By an entirely analogous procedure and in similar yields were prepared:

p-(*trans*-4-*n*-Propylcyclohexyl)benzamide (8a), m.p. 256-7°.

p-(*trans*-4-*n*-Heptylcyclohexyl)benzamide (8c), m.p. 218-19°.

Methyl - p - (trans - 4 - n - alkylcyclohexyl)phenylcarbamates (9a-c) These materials were prepared from the above amides by a Hoffman degradation in methanol using a modified organic reactions⁸ procedure. A representative procedure follows.

Methyl - p - (trans - 4 - n - pentylcyclohexyl)phenylcarbamate (9b) A 1 liter flask with condenser and drying tube was charged with 400 ml. dry methanol. Sodium chunks (~4g, 0.16 mol.) were added and the solution stirred until the sodium had dissolved. The solution was cooled to room temperature and 1.5 g (5.5 mmol) of amide was added. To the resulting slurry bromine (~2 ml) was added with rapid stirring. The bromine instantly decolorized, the amide dissolved, and a mild exotherm ensued. The solution was gently warmed for 4 hrs. and the methanol removed. The residue was stirred with 200 ml. of water and the precipitated solid suction collected. Yield, crude carbamate 1.6 g (94%), m.p. 105–10°. Recrystallization from methanol gave 1.3 g of pure material, m.p. 111–112°; I.R. (cm^{-1}) 3250, 2950, 1700, 1590. *Anal.* Calc. for $\text{C}_{19}\text{H}_{29}\text{NO}_2$: C, 75.20; H, 9.63; N, 4.62. Found: C, 75.15; H, 9.83; N, 4.67. By an entirely analogous procedure the following methyl-carbamates were prepared:

Methyl - p - (trans - 4 - n - propylcyclohexyl)phenylcarbamate (9a), m.p. 127–8°.

Methyl - p - (trans - 4 - n - heptylcyclohexyl)phenylcarbamate (9c), m.p. 100–101°.

p-(trans-4-n-Alkylcyclohexyl)anilines (10a-c) These materials were synthesized in good yield by basic hydrolysis of the above carbamates in aqueous ethanol. A representative synthesis follows.

p-(trans-4-n-Heptylcyclohexyl)aniline (10c) A 0.512 g (1.55 mmol) sample of the carbamate was refluxed in 20% aqueous ethanol (40 ml) with potassium hydroxide (10 g) under nitrogen. After 24 hrs. the ethanol was removed and the residue taken up in 50 ml. of water. The solution was extracted with three 10 ml. ether portions and the combined extracts dried over sodium sulfate. The ether was removed and the residue vacuum distilled yielding 0.348 g (82%) of liquid which solidified on standing. B.P. ~140° (0.1 mm), m.p. K-I 55.8°; I.R. (cm^{-1}) 3420, 3350, 3250, 3050, 2950, 1630. *Anal.* Calc. for $\text{C}_{19}\text{H}_{31}\text{N}$: C, 83.45; H, 11.43; N, 5.12. Found: C, 83.76; H, 11.18; N, 5.09. By a similar procedure the following alkylcyclohexylanilines were synthesized in good yields.

p-(trans-4-n-Propylcyclohexyl)aniline (10a) B.P. ~130° (0.1 mm), m.p. K-I 58.6°; I.R. (cm^{-1}) 3420, 3350, 3250, 3050, 2950, 1620. *Anal.* Calc. for $\text{C}_{15}\text{H}_{23}\text{N}$: C, 82.89; H, 10.67; N, 6.45. Found: C, 83.01; H, 10.78; N, 6.33.

p-(trans-4-n-Pentylcyclohexyl)aniline (10b) B.P. ~135° (0.1 mm), m.p. K-I 56.7°; I.R. (cm^{-1}) 3500, 3420, 3350, 3250, 3050, 2950, 1620. *Anal.* Calc.

for $C_{17}H_{27}N$: C, 83.20; H, 11.09; N, 5.71. Found: C, 83.19; H, 11.22; N, 5.57.

N-(*trans*-4-*n*-Alkylcyclohexyl)phenylalkanoamides (**11a-c**) These intermediates were prepared by treatment of the previously described anilines with the appropriate acid chloride in dry benzene. In all cases a precipitate resulted which consisted of the desired amide and the hydrochloride salt of the amine. The amides were obtained by fractional crystallization from ethanol. A representative procedure follows.

N-(*trans*-4-*n*-Heptylcyclohexyl)phenylheptanoamide (**11c**) A 0.196 g (0.72 mmol) sample of the amine was dissolved in 10 ml benzene. The solution was treated under nitrogen with 1 ml heptanoyl chloride. After cooling to room temperature the precipitate was suction collected and taken up in 10 ml boiling 95% ethanol. Cooling gave 95 mg. (66%) of the desired amide. m.p. 135-6°; I.R. (cm^{-1}) 3350, 2950, 2850, 1660, 1600. *Anal.* Calc. for $C_{26}H_{43}NO$: C, 80.98; H, 11.24; N, 3.63. Found: C, 81.20; H, 11.42; N, 3.43. By a similar procedure the following amides were prepared.

N-(*trans*-4-*n*-Pentylcyclohexyl)phenylheptanoamide (**11b**), m.p. 144-5°.

N-(*trans*-4-*n*-Pentylcyclohexyl)phenylbutanoamide (**11a**), m.p. 142°.

N-alkyl-*p*-(*trans*-4-*n*-Alkylcyclohexyl)anilines (**12a-c**) These compounds were easily prepared in essentially quantitative yield by reduction of the previously described amides with LAH in dry ether. A representative preparation follows.

N-(*n*-Butyl)-*p*-(*trans*-4-*n*-pentylcyclohexyl)aniline (**12a**) A 0.127 g (0.4 mmol) sample of the amide precursor was dissolved under nitrogen in dry ether (25 ml) LAH (1.0 g, 26 mmol) was added and the reaction stirred overnight under nitrogen. The excess hydride was decomposed by careful addition of water until a white precipitate formed. The precipitate was suction filtered and the filtrate dried over sodium sulfate. The ether was removed and the residue vacuum distilled giving essentially quantitative yield of secondary amine, B.P. ~140° (0.1 mm), m.p. K-N 28°; N-I 33.5°; I.R. (cm^{-1}) 3350, 3050, 2950, 1620. *Anal.* Calc. for $C_{21}H_{35}N$: C, 83.65; H, 11.70; N, 4.65. Found: C, 83.73; H, 11.75; N, 4.77. By an analogous procedure the following amines were synthesized.

N-(*n*-Heptyl)-*p*-(*trans*-4-*n*-pentylcyclohexyl)aniline (**12b**), B.P. ~145° (0.1 mm), K-I 46.4°; I.R. (cm^{-1}) 3450, 3050, 2950, 1620, 1580. *Anal.* Calc.

for $C_{24}H_{41}N$: C, 83.89; H, 12.03; N, 4.08. Found: C, 83.91; H, 12.26; N, 3.96.

N-(*n*-Heptyl)-*p*-(*trans*-4-*n*-heptylcyclohexyl)aniline (**12c**) B.P. $\sim 145^\circ$ (0.1 mm), m.p. K-I 51.0° ; I.R. (cm^{-1}) 3430, 3050, 2950, 1620, 1590. *Anal.* Calc. for $C_{26}H_{45}N$: C, 84.02; H, 12.21; N, 3.77. Found: C, 83.91; H, 12.42; N, 3.72.

CONCLUSIONS

Liquid crystalline behaviour can be obtained in structures bearing terminal *N*-alkylanilino or benzylamino moieties attached to the *p*-(*trans*-4-*n*-alkylcyclohexane) ring system. Both low temperature nematic or smectic properties and spontaneous homeotropic alignment are observed in these compounds.

Although previous work suggested that either intramolecular hydrogen bonding or extensive conjugative interactions must be present in order to incorporate the amino group in liquid crystalline structures, it is clear from this work that neither factor is a necessary condition for observing mesophase behavior.

Acknowledgment

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References

1. P. Culling, G. W. Gray, and D. Lewis, *J. Chem. Soc.*, 2699 (1960).
2. D. C. Schroeder and J. P. Schroeder, *J. Am. Chem. Soc.*, **96**, 4347 (1974).
3. D. C. Schroeder and J. P. Schroeder, *J. Org. Chem.*, **41**, 2566 (1976).
4. M. J. S. Dewar and R. S. Goldberg, *J. Org. Chem.*, **35**, 2711 (1970).
5. *Flüssige Kristalle in Tabellen*, VEB Deutscher Verlag für Grundstoffindustrie, Leipzig, 1974, pp. 88-89.
6. R. F. Borch, *J. Org. Chem.*, **34**, 627 (1969).
7. J. H. MacMillan and M. M. Labes, *Mol. Cryst. Liq. Cryst. Lett.*, **56**, 7 (1979).
8. *Organic Reactions*, edited by Roger Adams (John Wiley and Sons Inc., New York, 1946), Chap. 7, p. 282.