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Low Transition Temperature Liquid Crystalline Amines Incorporating The Biphenyl Ring System

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LOW TRANSITION TEMPERATURE LIQUID CRYSTALLINE AMINES INCORPORATING THE BIPHENYL RING SYSTEM

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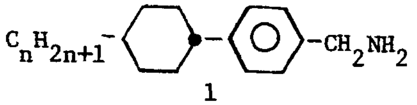
N-(n-butyl)-4-n-pentyl-4'-biphenylamine has an enantiotropic smectic A phase between 45 and 78°. 4-n-pentyl-4'-biphenylmethanamine has a monotropic smectic phase from 63-56°. These compounds, together with the previously reported phenylcyclohexane analogs, are the first examples of liquid crystalline amines not involving intramolecular hydrogen bonding or extensive conjugative interactions.

We have previously reported[1] the first examples of liquid crystalline amines not involving compounds containing intramolecular hydrogen bonds,[2] or extensive conjugative interactions.[3] Thus, p-(trans-4-n-alkylcyclohexyl)benzylamines 1 (n = 5 or 7) exhibited smectic mesophases (n = 5 monotropic, S_A 9-0°; n = 7, enantiotropic, S_A 15-26°, cooling, $S_A \rightarrow S_B$ 20°). p-(trans-4-n-alkylcyclohexyl)anilines 2 (n = 3, 5, 7) were non-mesogens, while the N-alkyl-p-(trans-4-n-alkylcyclohexyl)anilines 3 showed nematic mesophases.



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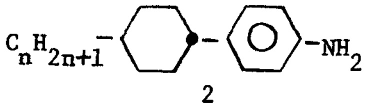

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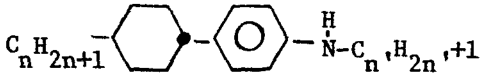
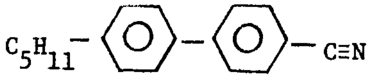


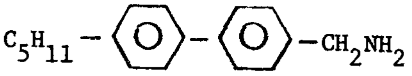
3

Since the cyclohexane ring is quite flexible, it seemed logical that replacement by the rigid planar aromatic moiety should allow mesogenic behavior. Consequently, we undertook synthesis of amines from the commercially available nematic liquid crystal 4-cyano-4'-n-pentylcyanobiphenyl (CPB) 4.



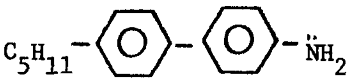
4

Reduction of CPB with lithium aluminum hydride (LAH) gave the biphenylmethanamine 5. Similarly to the cyclohexylbenzylamines, 5 proved somewhat hygroscopic, forming a solid hydrate on prolonged standing at room temperature.



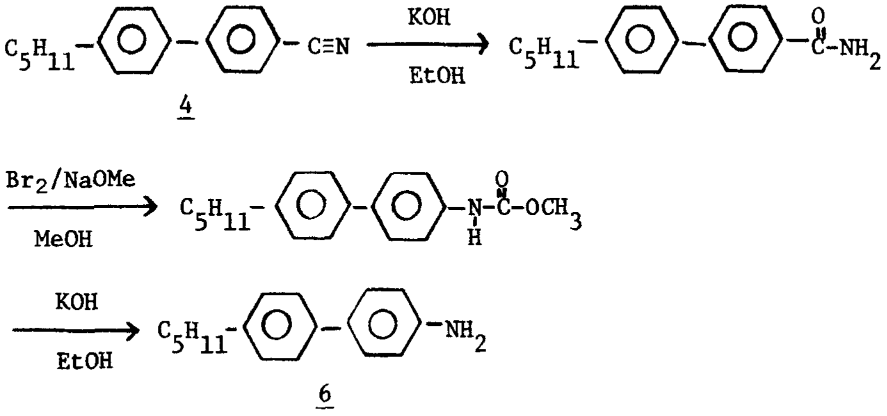
5

5 exhibited monotropic smectic behavior, the phase behaving texturally as a smectic D, on cooling from 63 to 56°. These results may be compared to compound 1 (n = 5) which also exhibited monotropic behavior but at a much lower temperature (9 to 0°). We hoped that the increased rigidity in the biphenyl series might promote mesogenic behavior in the biphenyl analog of 2, 4-n-pentyl-4'-biphenylamine 6.



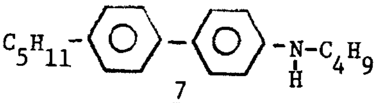
6

Therefore, 4 was converted to 6 by the previously described[1] sequence of reactions involving basic saponification to the amide, Hoffmann degradation to the carbamate and hydrolysis to the amine.



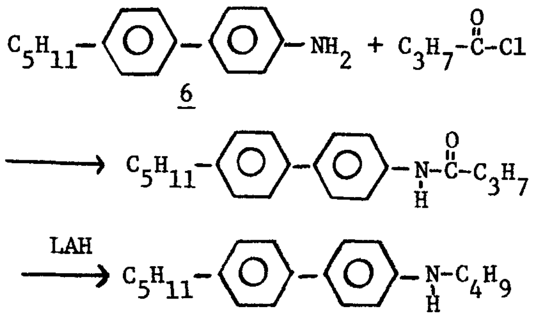
However, like 2, 6 proved non-mesogenic, exhibiting a crystal→isotropic transition at 72.7° with no evidence for monotropic behavior. Thus, all attempts to demonstrate a liquid crystal containing a primary terminal anilino group have proven futile. Gray[4] has proposed that this effect may result from the hydrogen bonded polar amino group raising the crystal→isotropic transition temperature above the mesogenic range. However, this hypothesis does not explain the lack of monotropic behavior in 2 and 6 when the melt is supercooled.

By contrast, the N-(n-butyl) derivative of 6, 7 was enantiotropic, exhibiting a smectic A phase between 45 and 78°. 7 may be compared to compound 3 (n = 5, n' = 4) which shows nematic behavior from 28 to 33°. On cooling, 7 showed a $S_A \rightarrow S_B$ transition at 46°.



7

7 was prepared as previously described[1] by treatment of 6 with butanoyl chloride followed by reduction with LAH.



6

7

Compound 7 also exhibits interesting mixed phase behavior with CPB, which will be discussed in a later publication.[5]

EXPERIMENTAL

Apparatus and procedures were identical to those previously described.[1]

4-n-Pentyl-4'-biphenylmethanamine 5

This compound was prepared via LAH reduction of CPB by the previously described[1] procedure.

CPB (0.647 g, 2.6 mmol) was stirred overnight with a large excess of LAH in ether (50 ml). Standard work-up gave 540 mg (81%) of the desired amine: B.P. $\sim$ 140° (0.1 mm); I.R. (cm^{-1}) 3400, 3300, 3050, 2950, 1960, 1610; m.p. K-I 74.6°, cooling, I-S 63.4°, S-K 56°. Anal. calc. for $C_{18}H_{23}N$: C, 85.32; H, 9.15; N, 5.53; Found: C, 85.58; H, 9.13; N, 5.13.

4-n-Pentyl-4'-biphenyl-carboxamide

This compound was prepared by basic partial hydrolysis of CPB with KOH/ethanol as previously described.[1]

CPB (1.99 g, 7.93 mmol) was heated three hours with potassium hydroxide (6.0 g, 0.105 mol) in ethanol (100 ml) and water (20 ml). Standard work-up gave 1.81 g (85%) of amide, m.p. 231-2°. I.R. (cm^{-1}) 3420, 3200, 2960, 2870, 1640, 1620.

Methyl-N-(4-n-pentyl-4'-biphenyl)carbamate

This compound was prepared by the previously described[1] Hoffmann degradation of the above amide in methanol.

The amide (1.8 g, 6.7 mmol) in methanol (400 ml) with sodium (4.0 g, 0.174 mol) and bromine (2 ml) gave 1.37 g (68%) of the carbamate, m.p. 129-30°. I.R. (cm^{-1}) 3400, 3020, 2960, 2880, 1700.

4-n-Pentyl-4'-biphenylamine 6

This compound was prepared as previously described[1] by hydrolysis of the above carbamate with KOH/ethanol.

The carbamate (1.12 g, 3.7 mmol) was refluxed overnight in ethanol (60 ml) with potassium hydroxide (10 g) and water (10 ml). Standard work-up gave 0.895 g (77%) of 6. B.P. ∿ 140° (0.1 mm), m.p. K-I 72.7°; I.R. (cm^{-1}) 3450, 3420, 3330, 3240, 3050, 2950, 2870, 1630. Anal. calc. for $C_{17}H_{21}N$: C, 85.30; H, 8.85; N, 5.85; Found: C, 85.48; H, 8.91; N, 5.85.

N-(4-n-pentyl-4'-biphenyl)butanamide

This compound was prepared as previously described[1] by reaction of 6 above with butanoyl chloride.

The amine (0.534 g, 2.2 mmol) was treated with butanoy] chloride (2 g, 18.9 mmol) in benzene (20 ml). Standard work-up gave 210 mg (62%) of the amide, m.p. 171-2°. I.R. (cm^{-1}) 3340, 2980, 2940, 2880, 1660, 1600.

N-(n-butyl)-4-n-pentyl-4'-biphenylamine 7

This compound was prepared as previously described[1] by reduction of the above amide with LAH.

The amide (0.145 g, 0.47 mmol) was stirred overnight with LAH (1.0 g, 26 mmol) in ether (20 ml). Standard work-up gave essentially quantitative yield of amine, B.P. ∿ 140° (0.1 mm), m.p. K-S_A 45°, S_A-I 77.6°. I.R. (cm^{-1}) 3430, 3040, 2950, 2860, 1610. Cooling: $S_A \rightarrow S_B$ 46°. Anal. calc. for $C_{21}H_{29}N$: C, 85.36; H, 9.89; N, 4.74; Found: C, 85.49; H, 9.75; N, 4.71.

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