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Synthesis of Certain Mesogenic Azomethines Derived from 4-Cycloalkylanilines and from 4-Cycloalkylbenzaldehydes

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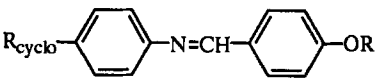
General procedures are described for the synthesis of members of five pairs of related homologous series of mesogenic azomethines differing in the mode of linkage of the CH=N group and containing a cycloalkyl group in a terminal position.

INTRODUCTION

The work described in the preceding paper[1] completed an earlier investigation[2] of the liquid crystal properties of members of homologous series of azomethines derived from 4-cycloalkylanilines and from 4-cycloalkylbenzaldehydes. The two papers discuss the properties of members of five pairs of related series of azomethines, (1) and (2), which differ in the mode of linkage of the —CH=N— group and contain either a cyclo-propyl, -pentyl, -hexyl, -heptyl or -octyl ring located in a terminal position. The work necessitated the investigation of 105 compounds and the general procedures employed to prepare these azomethines [the N-(4-alkoxybenzylidene)-4-cycloalkylanilines (1) and the 4-alkoxy-N-(4-cycloalkylbenzylidene) anilines (2)] are now reported.



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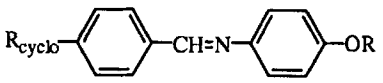

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DISCUSSION

The starting materials for the synthetic work were the appropriate cycloalkylbenzenes (phenylcycloalkanes), namely cyclopropylbenzene (which was commercially available) and cyclo-pentyl-, -hexyl-, -heptyl-, and -octyl-benzene.

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Cyclopentyl- and cyclohexyl–benzene were conveniently prepared by Friedel–Crafts alkylation of benzene using the appropriate cycloalkyl bromide and aluminium chloride as the Lewis acid catalyst. However, the syntheses of cycloheptyl- and cyclooctyl-benzene were not attempted by this method due to the likelihood of rearrangement of the seven- and eight-membered ring systems under Friedel–Crafts conditions. These compounds were therefore obtained by reaction of the Grignard reagent derived from bromobenzene with cycloheptanone and with cyclooctanone affording the appropriate 1-phenylcycloalkyl alcohol. Some dehydration of these alcohols occurred spontaneously but was completed by the action of anhydrous formic acid. The resulting 1-phenylcycloalkenes were then subjected to catalytic hydrogenation to give the required cycloheptyl- and cyclooctyl-benzenes.

Friedel–Crafts acylation of the cycloalkylbenzenes gave the corresponding 4-cycloalkylacetophenones. These were then converted into the oxime by the action of hydroxylamine hydrochloride and then into the required 4-cycloalkylaniline via a Beckmann rearrangement followed by hydrolysis of the rearranged product. Alkylation of 4-hydroxybenzaldehyde with the appropriate 1-bromoalkane in cyclohexanone gave the necessary 4-alkoxybenzaldehydes for condensation with each 4-cycloalkylaniline obtained, affording the members of the homologous series of N-(4-alkoxybenzylidene)-4-cycloalkylanilines (1).

The synthesis of the corresponding 'reversed' series of azomethines (2) required the preparation of 4-cycloalkylbenzaldehydes and three routes to these compounds were employed. A direct route employed formylation of the appropriate cycloalkylbenzene with 1, 1-dichloromethyl methyl ether in the presence of tin (IV) chloride as the Lewis acid catalyst. Yields were variable by this method. An excellent indirect route involved hypobromite oxidation of the appropriate 4-cycloalkylacetophenone followed by esterification of the resulting 4-cycloalkylbenzoic acid with methanol-boron trifluoride complex. The methyl ester was then reduced with lithium aluminium hydride and the resulting benzyl alcohol converted into the required 4-cycloalkylbenzaldehyde by oxidation with pyridinium chlorochromate.[4] Each of these stages was readily accomplished and gave excellent yields. The metal-assisted reducing medium reported by Johnstone *et al.*[3] which utilises the addition of a cadmium chloride-dimethylformamide complex to sodium borohydride in acetonitrile at $-35°C$, is a highly specific reagent which does not reduce aldehydes to a significant extent, and was used to convert 4-cyclohexylbenzoyl chloride into 4-cyclohexylbenzaldehyde in good yield. Alkylation of 4-nitrophenol with the appropriate 1-bromoalkane in the presence of anhydrous potassium carbonate followed by reduction of the nitro-group by catalytic hydrogenation gave the required 4-alkoxyanilines necessary for the preparation of members of the 'reversed' series of azomethines, the 4-alkoxy-N-(4-cycloalkylbenzylidene) anilines (2), by condensation with each 4-cycloalkylbenzaldehyde prepared.

EXPERIMENTAL

Physical Measurements

Structural confirmation of the identity of intermediates (where necessary) and final products was obtained by standard techniques. I. r. spectra were recorded as KBr discs

with a Perkin–Elmer 157 grating spectrophotometer, and ^1H n.m.r. spectra were measured as solutions in $CDCl_3$ with tetramethylsilane as internal standard with a JEOL FX60Q Fourier transform spectrometer. Mass spectra were determined with an A.E.I. MS 902S spectrometer equipped with a Mass Spectrometry Services 200 console and an INCOS 2300 data system.

Materials

1-Phenylcycloalkenes

1-Phenylcyclooctene. Cyclooctanone (55 g, 0.44 mol) was added dropwise, under reflux, over 15 min. to an ethereal solution of phenyl magnesium bromide prepared from magnesium turning (10 g, 0.425 mol) and bromobenzene (70 g, 0.45 mol) in diethyl ether (300 cm^3) by the usual procedure for Grignard reagents. The reaction mixture was heated under reflux for a further 30 min., then poured into a cold solution of sulphuric acid (concentrated, 25 cm^3) and ammonium chloride (25 g) in water (750 cm^3) and stirred for 30 min. After separation of the two layers, the aqueous phase was extracted with dichloromethane and the extracts were then combined with the organic phase, washed with water, dried ($MgSO_4$), and the solvent removed. The light brown residue was stirred with anhydrous formic acid (250 cm^3, 6.6 mol) for 30 min. The resulting colourless oil was extracted with diethyl ether, dried, and distilled under reduced pressure to give the *1-phenylcyclooctene*, 61.5 g (93%), as a colourless oil, b.p. 89°C/0.1 mmHg; $\delta_H(CDCl_3)$, 1.4 (8H, br, CH_2), 2.3 (4H, m, CH_2), 5.9 (1H, t, CH), 7.3 (5H, m, C_6H_5-).

1-Phenylcycloheptene, 23 g (60%), was prepared in a similar manner by the reaction between cycloheptanone (25 g, 0.23 mol) and an ethereal solution of the Grignard reagent derived from magnesium turnings (0.25 mol) and bromobenzene (0.25 mol), and was obtained as a colourless oil, b. p. 98–100°C/0.8 mmHg; δ_H ($CDCl_3$) 1.4 (6H, br, CH_2), 2.3 (4H, m, CH_2), 6.0 (1H, t, CH), 7.0 (5H, m, C_6H_5-).

Phenylcycloalkanes [cycloalkylbenzenes] (method 1)

Phenylcyclooctane. A suspension of 1-phenylcyclooctene (40 g, 0.217 mol) and palladium on charcoal (5%, 4.0 g) in ethanol (300 cm^3) was hydrogenated at 90°C under a pressure of 200 psi for 90 min. The catalyst was filtered off, the solvent removed, and the residue then distilled under reduced pressure affording the *phenylcyclooctane*, 36.7 g (92%), as a colourless oil, b.p. 98°C/0.02 mmHg; δ_H ($CDCl_3$) 1.65 (14H, br, CH_2), 2.6 (1H, s, CH), 7.1 (5H, s, C_6H_5-).

Phenylcycloheptane, 17.2 g (90%), prepared in a similar manner by catalytic hydrogenation of phenylcycloheptene (19 g, 0.11 mol) in the presence of palladium on charcoal (5% 1.9 g), was obtained as a colourless oil, b.p. 78°C/0.4 mmHg; δ_H ($CDCl_3$) 1.65 (12H, br, CH_2), 2.6 (1H, m, CH), 7.1 (5H, s, C_6H_5-).

Phenylcycloalkanes [cycloalkylbenzenes] (method 2)

Phenylcyclopentane. To anhydrous aluminium chloride (10 g, 0.075 mol) in dry benzene (350 g, 4.5 mol), cyclopentyl bromide (90 g, 0.6 mol) in dry benzene (150 g) was added,

with stirring, maintaining the temperature of the reaction mixture below 25°C throughout. Stirring was continued overnight, and the mixture was then poured into ice-water (1.5 dm^3) and stirred vigorously for 30 min. The layers were separated and the aqueous phase extracted with diethyl ether (2 × 400 cm^3) and the extracts and the organic phase then combined, washed with water, dried, and the solvent removed. Distillation of the residue under reduced pressure gave the phenylcyclopentane, 81 g, (92%), as a clear oil, b.p. 98–100°C/13 mmHg (lit[5]. b.p. 215–217°C).

Phenylcyclohexane was either prepared in a similar manner from cyclohexyl bromide or was obtained commercially.

Phenylcyclopropane was obtained commercially.

4-Cycloalkylacetophenones

4-Cyclohexylacetophenone. Friedel–Crafts acylation of phenylcyclohexane (60 g, 0.35 mol) was carried out by dropwise addition over 2 min., to a mixture of aluminium chloride (51.3 g, 0.39 mol) in dry dichloromethane (250 cm^3) to which acetyl chloride (28 g, 0.35 mol) had previously been added, dropwise, over 30 min. The reaction mixture was stirred and maintained at room temperature throughout and for a further 24 h, whereafter it was poured into a mixture of ice-cold water (400 cm^3) and hydrochloric acid (concentrated, 400 cm^3), with stirring. The layers were separated and the aqueous phase was extracted with dichloromethane (2 × 200 cm^3). The extracts and the organic phase were then combined, dried, and the solvent removed. The resulting crude ketone was purified by crystallisation from methanol. The 4-cyclohexylacetophenone, 76 g (85%), was obtained as a white crystalline solid, m.p. 68–69°C (lit[6]. m.p. 68–69°C).

Other ketones were prepared in a similar manner but were purified by distillation under reduced pressure, affording pale yellow oils: *4-cyclopropylacetophenone* (58%), b.p. 101–103°C/0.4 mmHg; *m/z* 160 (M^+); $\nu_{max.}$ (oil film) 1680 s (C = Ostr) cm^{-1}; δ_H ($CDCl_3$) 0.9 (4H, m, CH_2), 1.8 (1H, m, CH), 2.5 (3H, s, CH_3), 7.25 and 7.85 (each 2H, AA′XX′ system, $|J_{AX} + J_{AX'}| = 8$Hz, —C_6H_4—); 4-cyclopentylacetophenone (91%), b.p. 104–106°C/0.2 mmHg (lit.[7] b.p. 140–145°C/2.5 mmHg); *4-cycloheptylacetophenone* (83%), b.p. 117–119°C/0.1 mmHg; $\nu_{max.}$ (oil film) 1680 s (C=Ostr) cm^{-1}; δ_H ($CDCl_3$) 1.6 (12H, br, CH_2), 2.4 (3H, s, CH_3), 2.7 (1H, m, CH), 7.1 and 7.7 (each 2H, AA′XX′ system $|J_{AX} + J_{AX'}| = 8$Hz, —C_6H_4—); and *4-cyclooctylacetophenone* (82%), 150–151°C/0.2 mmHg; $\nu_{max.}$ (oil film) 1690 s (C = Ostr) cm^{-1}; δ_H($CDCl_3$) 1.7 (14H, br, CH_2) 2.6 (3H, s, CH_3), 2.8 (1H, m, CH), 7.25 and 7.9 (each 2H, AA′XX′ system, $|J_{AX} + J_{AX'}| = 8$Hz, —C_6H_4—).

4-Cycloalkylacetophenone oximes

4-Cyclohexylacetophenone oxime. 4-Cyclohexylacetophenone (26.5 g, 0.13 mol) and hydroxylamine hydrochloride (24.8 g, 0.36 mol) in a mixture of ethanol (60 cm^3) and pyridine (180 cm^3) were heated under reflux for 3 h. Most of the solvent was then removed under reduced pressure, and the residue poured into water, (1.8 dm^3). The precipitated oxime was filtered off, washed with water, dried under vacuum, and crystallised from ethanol. The 4-cyclohexylacetophenone oxime, 23.4 g (82%), was

obtained as pale yellow needles, m.p. 116–117°C (lit.[8] m.p. 117°C). The oxime was stored under nitrogen to prevent decomposition.

Other oximes were prepared by similar procedures: *4-cyclopropylacetophenone oxime* (53%), m.p. 96.5°C; $\nu_{max.}$ (KBr) 3250 vbr (O—Hstr), 1605w (C=Nstr) cm^{-1}; δ_H ($CDCl_3$) 0.9 (4H, m, CH_2), 1.8 (1H, m, CH), 2.3 (3H, s, CH_3), 7.3 and 7.7 (each AA'XX' system, $|J_{AX} + J_{AX'}| = 8$ H, —C_6H_4—), 8.9 (1H, s, OH). 4-cyclopentylacetophenone oxime (71%), m.p. 105–106°C (lit.[9] m.p. 104°C); *4-cycloheptylacetophenone oxime* (66%), m.p. 112.5–114.5°C; $\nu_{max.}$ (KBr) 3250vbr (O—Hstr), 1610 w (C=Nstr) cm^{-1}; δ_H ($CDCl_3$) 1.6 (12H, br, CH_2), 3.3 (3H, s, CH_3), 2.5 (1H, m, CH), 7.2 and 7.6 (each 2H, AA'XX' system, $|J_{AX} + J_{AX'}| = 8$Hz, —C_6H_4—), 9.2 (1H, s, OH); *4-cyclooctylacetophenone oxime* (80%), m.p. 67–69°C; $\nu_{max.}$ (KBr) 3300vbr (O—Hstr), 1610w (C=Nstr) cm^{-1}; δ_H ($CDCl_3$) 1.6 (14H, br, CH_2), 2.2 (3H, s, CH_3), 2.7 (1H, m, CH), 7.3 and 7.7 (each 2H, AA'XX' system, $|J_{AX} + J_{AX'}| = 8$Hz, —C_6H_4—), 9.05 (1H, s, OH).

4-cycloalkylanilines

4-Cyclohexylaniline. A Beckmann rearrangement of 4-cyclohexylacetophenone oxime (22 g, 0.1 mol) suspended in dry toluene (550 cm^3) was carried out by the addition of phosphorus pentachloride (28.4 g, 0.14 mol). The mixture was heated under reflux for 15 min., then cooled and added to a mixture of hydrochloric acid (concentrated, 40 cm^3) and ethanol (200 cm^3) and heated under reflux for 4 h. in order to hydrolyse the product of the rearrangement. The reaction mixture was cooled and most of the solvent was removed under reduced pressure, whereafter the residue was made alkaline with aqueous sodium hydroxide (2 mol dm^{-3}) and extracted with diethyl ether. The extract was dried, the diethyl ether removed, and the residue distilled under reduced pressure to give the 4-cyclohexylaniline, 10.2 g (54%), as the main fraction, b.p. 166°C/13 mmHg, m.p. 57°C (lit.[6] m.p. 57°C).

Other amines were prepared in an analogous manner: *4-cyclopropylaniline* (64%), b.p. 84°C/0.1 mmHg; $^m/_z$ 133 (M^+); $\nu_{max.}$ (oil film) 3400m (N—Hstr), 3200m (N—Hstr), 3000s (C—Hstr), 1620s (N—Hdef), 1520s (C=Cstr) cm^{-1}; δ_H ($CDCl_3$) 0.7 (4H, m, CH_2), 1.7 (1H, m, CH), 3.2 (2H, s, NH_2), 6.55 and 6.95 (each 2H, AA'XX' system, $|J_{AX} + J_{AX'}| = 8$Hz, —C_6H_4—); 4-cyclopentylaniline (90%), b.p. 95°C/0.1 mmHg (lit.[9] b.p. 165–167°C/22 mmHg); *4-cycloheptylaniline* (69%), b.p. 128–130°C/0.1 mmHg; $\nu_{max.}$ (oil film) 3450m (N—Hstr), 3380m (N—Hstr), 2950s (C—Hstr), 1610s (N—Hdef), 1500s (C—Cstr) cm^{-1}; δ_H ($CDCl_3$) 0.7 (12H, m, CH_2), 1.7 (1H, m, CH), 3.4 (2H, s, NH_2), 6.6 and 7.0 (each 2H, AA'XX' system, $|J_{AX} + J_{AX'}| = 8$Hz, —C_6H_4—); *4-cyclooctylaniline* (58%), b.p. 130°C/0.1 mmHg; $\nu_{max.}$ (oil film) 3500m (N—Hstr), 3400m (N—Hstr), 2950s (C—Hstr), 1630s (N—Hdef), 1510s (C=Cstr) cm^{-1}; δ_H ($CDCl_3$) 1.6 (14H, m, CH_2), 2.7 (1H, m, CH), 3.75 (2H, s, NH_2), 6.65 and 7.05 (each 2H, AA'XX' system, $|J_{AX} + J_{AX'}| = 8$Hz, —C_6H_4—).

4-Cycloaklylbenzaldehydes (method 1)

4-Cyclopropylbenzaldehyde. Formylation of cyclopropylbenzene (5 g, 0.64 mol) in dry 1,2-dichloroethane (250 cm^3) was carried out by the addition of 1,1-dichloromethyl methyl ether (24.3 g, 0.27 mol) followed by dropwise addition of anhydrous tin (IV)

chloride (75 cm^3, 0.64 mol). The reaction mixture was stirred for 24 h., then poured into hydrochloric acid (4 mol dm^{-3}, 500 cm^3) and stirred for 45 min. The aldehyde was extracted from the aqueous solution with dichloromethane and the extract was dried, the solvent removed, and the residue distilled under vacuum to give the *4-cyclopropylbenzaldehyde*, 3.7 g, (60%), as a yellow oil, b.p. 75–77°C/0.5 mmHg; *m/z* 146 (M^+); $\nu_{max.}$ (oil film) 3050w (C—Hstr), 2840s (C—Hstr), 2740m (C—Hstr), 1700s (C=Ostr), 1610s (C=Cstr) cm^{-1}; δ_H ($CDCl_3$) 1.2 (4H, m, CH_2), 2.2 (1H, m, CH), 7.5 and 7.95 (each 2H, AA'XX' system, $|J_{AX} + J_{AX'}| = 8$Hz, —C_6H_4—), 10.1 (1H, s, CH=O). Other aldehydes were prepared by a similar procedure: 4-cyclohexylbenzaldehyde (75%), b.p. 131–133°C/0.6 mmHg (lit.[10] b.p. 159°C/10 mmHg); *4-cycloheptylbenzaldehyde* (87%), 120°C/0.2 mmHg; $\nu_{max.}$ (oil film) 3040 w (C—Hstr), 2995s (C—Hstr), 2910s (C—Hstr), 1700s (C=Ostr), 1610s (C=Cstr) cm^{-1}; δ_H ($CDCl_3$) 1.6 (12H, br, CH_2) 2.7 (1H, m, CH), 7.4 and 7.85 (each 2H, AA'XX' system, $|J_{AX} + J_{AX'}| = 8$Hz, —C_6H_4—), 9.8 (1H, s, CH=O); *4-cyclooctylbenzaldehyde* (89%), b.p. 172°C/0.1 mmHg; $\nu_{max.}$ (oil film) 3050w (C—Hstr), 2995s (C—Hstr), 2885m (C—Hstr), 1700s (C=Ostr), 1610s (C=Cstr) cm^{-1}; δ_H ($CDCl_3$) 1.4 (14H, br, CH_2), 2.6 (1H, m, CH), 7.4 and 7.85 (each 2H, AA'XX' system, $|J_{AX} + J_{AX'}| = 8$Hz, —C_6H_4—), 9.8 (1H, s, CH=O).

The aldehydes were prone to oxidation on storage and were used without substantial delay.

4-Cycloalkylbenzaldehydes (method 2)

4-Cyclopentylbenzaldehyde

4-Cyclopentylbenzoic acid (95%), prepared by hypobromite oxidation[11] of 4-cyclopentylacetophenone, was recrystallised from glacial acetic acid as colourless plates, m.p. 203–204°C (lit.[7] m.p. 196–198°C).

Methy 4-cyclopentylbenzoate was obtained by esterification of 4-cyclopentylbenzoic acid (10 g, 0.053 mol) with boron trifluoride-methanol complex (12% w/v, 60 cm^3) in dry methanol (120 cm^3). The mixture was stirred and heated under reflux for 6 h, then cooled and poured into ice-cold saturated aqueous sodium bicarbonate (250 cm^3) and stirred for 5 min. The product was isolated and distilled under vacuum to give the ester, 9.9 g (92%), as a clear oil, b.p. 80°C/0.22 mmHg, which solidified on cooling. Crystallisation from light petroleum (b.p. 40–60°C) gave the *methyl 4-cyclopentylbenzoate* as colourless flakes, m.p. 37–39°C (Found C, 76.2; H, 7.6. $C_{13}H_{16}O_2$ requires C, 76.4; H, 7.9%); $\nu_{max.}$ (oil film) 1730 (C=Ostr) cm^{-1}; δ_H ($CDCl_3$) 1.8 (8H, m, CH_2), 2.95 (1H, m, CH), 3.85 (3H, s, CH_3), 7.2 and 7.85 (each 2H, AA'XX' system, $|J_{AX} + J_{AX'}| = 8$Hz, —C_6H_4—).

4-Cyclopentylbenzyl alcohol was prepared by the slow addition of methyl 4-cyclopentylbenzoate (8 g, 0.039 mol) in dry diethyl ether (100 cm^3) to lithium aluminium hydride (3 g, 0.08 mol) in dry diethyl ether (100 cm^3), under reflux. The reaction mixture was stirred and an atmosphere of nitrogen was maintained throughout. Heating was continued for a further 30 min. and the reaction mixture was then cooled and water added, dropwise, to destroy the excess of the reducing agent, followed by hydrochloric acid (4 mol dm^{-3}) to break down the complex. The aqueous layer was separated, extracted with diethyl ether (3 × 150 cm^3), and the extracts and organic layer then

combined, dried, and the solvent removed. The residue was distilled under reduced pressure to give the *4-cyclopentylbenzyl alcohol*, 6.1 g (89%), as a clear oil, b.p. 97–98°C/0.1 mmHg (Found C, 81.5; H, 9.0 $C_{12}H_{16}O$ requires C, 81.8; H, 9.2%); $\nu_{max.}$ (oil film) 3310vbr (O—Hstr) cm^{-1}; δ_H ($CDCl_3$) 2.05 (8H, m, CH_2), 2.35 (1H, s, OH; dissapears on D_2O exchange), 3.15 (1H, m, CH), 4.50 (2H, s, CH_2O), 7.15 (4H, —C_6H_4—). *4-Cyclopentylbenzaldehyde* was obtained by the partial oxidation of 4-cyclopentylbenzyl alcohol (5 g, 0.0284 mol) in dry dichloromethane (30 cm^3) by addition to a stirred suspension of pyridinium chlorochromate[4] (9.5 g, 0.044 mol) in dry dichloromethane (50 cm^3). After 2 h at room temperature, dry diethyl ether (250 cm^3) was added and the solvent then decanted off. The residue was washed with diethyl ether (2 × 150 cm^3), the washings and the decanted solvent combined, and the solvent removed. The residue was distilled under reduced pressure giving the 4-cyclopentylbenzaldehyde, (82%), as a clear oil, b.p. 78°C/0.1 mmHg (lit.[12] b.p. 149–150°C). *4-cyclohexylbenzaldehyde* was also prepared by an analogous procedure.

4-cycloalkylbenzaldehydes (method 3)

4-Cyclohexylbenzaldehyde was also obtained by the metal assisted reduction[3] of 4-cyclohexylbenzoyl chloride [prepared by heating 4-cyclohexylbenzoic acid (11 g, 0.055 mol) with thionyl chloride (32 g, 0.28 mol), under reflux]. The acid chloride (10.5 g, 0.05 mol) in acetonitrile (50 cm^3) and dry diethyl ether (80 cm^3) was added at −35°C, over 15 min., to a stirred suspension of the $CdCl_2$. $1\frac{1}{2}$ DMF salt [obtained by crystallisation of cadmium chloride from dimethylformamide] (18.6 g, 0.063 mol) in acetonitrile (60 cm^3) to which sodium borohydride (1.9 g, 0.05 mol) in diemethylformamide (15 cm^3) and acetonitrile (100 cm^3) had been added at 0–5°C, over 10 min. After a further 15 min. the solid was filtered off, washed with diethyl ether, and the filtrate and washings then combined and the solvent removed. The residue was distilled under reduced pressure affording the 4-cyclohexylbenzaldehyde, 7.1 g, (75%), as a clear oil.

N-(4-Alkoxybenzylidene)-4-cycloalkylanilines (1) and 4-Alkoxy-N-(4-cycloalkylbenzylidene) anilines (2)

The azomethines were prepared from the appropriate 4-cycloalkylaniline and 4-alkoxybenzaldehyde,[13,14] or from the appropriate 4-cycloalkylbenzaldehyde and 4-alkoxyaniline.[15]

4-Alkoxybenzaldehydes were obtained[13,14] by heating 4-hydroxybenzaldehyde (6.1 g, 0.05 mol), anhydrous potassium carbonate (30 g, 0.22 mol) and the appropriate 1-bromoalkane (0.08 mol) under reflux in cyclohexanone (50 cm^3). After work-up, the aldehydes (75–85%) were purified by vacuum distillation. B.p.s. and m.p.s. were in good agreement with reported[13] values.

4-Alkoxynitrobenzenes were similarly prepared[15] by heating 4-nitrophenol (7 g, 0.05 mol), anhydrous potassium carbonate (30 g, 0.22 mol) and the appropriate 1-bromoalkane (0.1 mol) under reflux in cyclohexanone (80 cm^3). The nitro-ethers (62–75%) were purified either by vacuum distillation or, for higher members, by crystallisation from light petroleum (b. p. 40–60°C) or from 1-propanol. Boiling and melting points agreed with those in the literature.[16,17]

4-Alkoxyanilines were obtained by atmospheric pressure reduction of the appropriate 4-alkoxynitrobenzene (0.05 mol) by stirring vigorously in ethanol (100 cm^3) in the presence of palladium on charcoal (10%, 0.05 g) until the theoretical amount of hydrogen had been taken up (2–3 h.). After filtering off the catalyst, the solvent was removed and the residue either distilled under reduced pressure or, for higher members, crystallised from light petroleum (b.p.40–60°C or 60–80°C) or hexane. In some instances the amine was isolated as the hydrochloride which was purified by crystallisation before release of the free base. Yields were in excess of 95%. Boiling points and melting points agreed with those in the literature.[17,18]

N-(4-Alkoxybenzylidene)-4-cycloalkylanilines were obtained by the addition of the appropriate 4-alkoxybenzaldehyde (0.002 mol) in ethanol (15 cm^3) to the appropriate 4-cycloalkylaniline (0.002 mol) in ethanol (15 cm^3). The mixture was then heated to boiling, glacial acetic acid (4 drops) added and, after 15 min., any precipitated solid redissolved by the addition of ethanol. On cooling, the product was filtered off and purified by recrystallisation several times, in turn, from different solvents [ethanol, light petroleum (b.p.60–80°C), acetone, or toluene: light petroleum (b. p. 60–80°C)].

4-Alkoxy-N-(4-cycloalkylbenzylidene) anilines were similarly prepared from the appropriate 4-alkoxyaniline (0.002 mol) and 4-cycloalkylbenzaldehyde (0.002 mol).

For the members of each homologous series of azomethines, (1) and (2), the mesomorphic transition temperatures are listed elsewhere[1,2] in various tables, and typical spectroscopic data, which are broadly similar in each case, are as follows:

N-(4-n-Alkoxybenzylidene)-4-cyclooctylanilines; hexyloxy homologue: $^m/_z$ 391 (M^+); $\nu_{max.}$ (KBr) 3050w (C—Hstr), 2950s (C—Hstr), 1618s (C=Nstr), 1605s (C=Cstr) cm^{-1}; δ_H ($CDCl_3$) 1.4 (25H, m, CH_2, CH_3), 2.7 (1 H, m, CH), 4.0 (2H, t, OCH_2), 6.95 and 7.85 (each 2H, AA′XX′ system, $|J_{AX} + J_{AX'}| = 8Hz$, $—C_6H_4—$), 7.15 (4H, $—C_6H_4—$), 8.4 (1H, s, N=CH).

4-Alkoxy-N-(4-cyclopropylbenzylidene) anilines; decyloxy homologue: $^m/_z$ 377 (M^+); $\nu_{max.}$ (KBr) 3050w (C—Hstr), 2950s (C—Hstr), 1615s (C=Nstr), 1605s (C=Cstr) cm^{-1}; δ_H ($CDCl_3$) 1.3 (24H, m, CH_2, CH_3), 3.95 (2H, t, OCH_2), 7.2 and 8.1 (each 2H, AA′XX′ system, $|J_{AX} + J_{AX'}| = 8Hz$, $—C_6H_4—$), 7.5 and 7.6 (each 2H, AA′XX′ system, $|J_{AX} + J_{AX'}| = 8Hz$, $—C_6H_4—$), 8.4 (1H, s, CH=N).

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