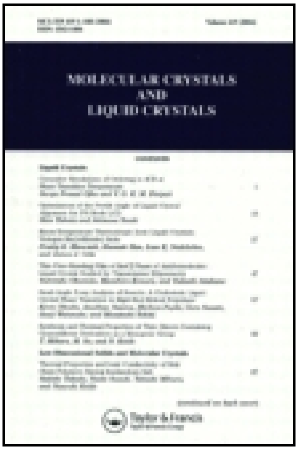

Molecular Crystals and Liquid Crystals Incorporating Nonlinear Optics

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Synthesis and Liquid Crystalline Properties of 1 -(trans-4-Alkylcyclohexylethyl)-4-Alkyl- and -4-Alkoxy-Benzenes, Their Ketone Precursors, and Some Lateral Fluoro-Derivatives

George W. Gray [a] , David Lacey [a] , Richard M. Scrowston [a] , Ibrahim G. Shenouda [a] & Kenneth J. Toyne [a]

[a] School of Chemistry, University of Hull, Hull, HU6 7RX, England

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Synthesis and Liquid Crystalline Properties of 1-(*trans*-4-Alkylcyclohexylethyl)-4-Alkyl- and -4-Alkoxy-Benzenes, Their Ketone Precursors, and Some Lateral Fluoro-Derivatives

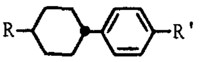
GEORGE W. GRAY, DAVID LACEY, RICHARD M. SCROWSTON, IBRAHIM G. SHENOUDA, and KENNETH J. TOYNE
School of Chemistry, University of Hull, Hull, HU6 7RX, England

(*Received: January 18, 1988*)

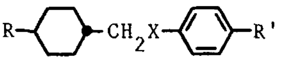
The preparation of some 1-(*trans*-4-alkylcyclohexylethyl)-4-alkyl- and -4-alkoxy-benzenes, their methylenecarbonyl linked analogues and their laterally fluoro- and bromo-substituted derivatives is reported. Twenty-four inter-related compounds have been prepared and the trends in their transition temperatures are discussed. Both the melting points and clearing points for these compounds are relatively low and, in general, S_B and S_A phases predominate. The suitability of these compounds as additives to S_C materials has been assessed using two S_C hosts.

Keywords: Mesogenic cyclohexylethanes, mesogenic ketones, fluoro-substitution of mesogens

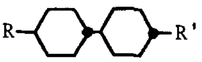
Terminally non-polar compounds with a short molecular core are useful systems for providing host materials of low viscosity and low birefringence for use in electro-optic display devices; the necessity for compounds with these properties is particularly acute in the area of host materials for ferroelectric S_C^* devices. Normally systems with at least two rings [e.g., (**1**)[1,2], (**2a**)[3,4], (**2b**)[5], (**3**)[1,2,3]] are needed to give compounds with mesophases within the temperature ranges required, but even single ring core systems have been considered.[6] Of these relatively simple structures, structure (**2a**) offers the greatest opportunity for modification of the parent system by changing the terminal groups, modifying the dimethylene linkage, and placing lateral substituents in the aromatic ring in order, to produce material of negative dielectric anisotropy.[4] We have therefore made a variety of two-ring systems related to (**2a**) in order to find out whether or not suitable mesophase types and appropriate mesophase temperature ranges could be obtained. Some results have already been reported[4] for lateral fluoro derivatives of compounds (**2a**) with shorter alkyl and alkoxy terminal chains, but these compounds have low T_{N-I} values (maximum value of 35°C for those reported) and so we have concentrated on compounds of longer terminal-chain lengths.



(**1**)



(**2**) a . . X = CH_2
b . . X = O



(**3**)

The transition temperatures for some of the compounds we have prepared are shown in Table I (the *trans*-4-heptylcyclohexyl was the longest alkylcyclohexyl unit available to us in reasonable amounts). Most of the compounds shown have 4-alkoxyphenyl units, with or without halogeno substituents (F, Br), in combination with a methylenecarbonyl or dimethylene linking group, but a few unsubstituted 4-alkylphenyl systems were also prepared.

Compound (**4a**) has a low melting point and only a monotropic phase; lengthening the alkylphenyl group to C_9H_{19} [compounds (**4b**) and (**4c**)] or $C_{11}H_{23}$ [compound (**4d**)] caused a gradual increase in clearing point and gave enantiotropic S_B phases which differed only slightly in their thermal stability for compounds with [compound (**4b**)] or without [compound (**4c**)] the carbonyl group in the link. The dipropyl analogue of compounds (**4a**) and (**4b**) has been reported[2] to have K 52.2°C I, with no mesophase down to 25°C.

The 4-alkoxyphenyl compounds, by comparison with the 4-alkylphenyl analogues [i.e., compounds (**4g**) and (**4b**), (**4h**) and (**4c**), (**4i**) and (**4d**)] have higher melting points and higher clearing points, and the presence of a carbonyl group in the linkage in conjunction with an alkoxy terminal group appears initially to favour the generation of an S_A phase [compare compounds (**4g**) with (**4b**) and (**4i**) with (**4d**)], but the more rapidly rising thermal stability of the S_B phase means that in compound (**4o**), the S_A phase has been lost. When the carbonyl group is present in alkyl compounds [(**4a**), (**4b**) and (**4d**)] or when alkoxy compounds have a dimethylene linkage [(**4h**), (**4j**) and (**4p**)], then the compounds are solely S_B.

Fluoro-substitution *ortho*- to an alkoxy group in the carbonyl containing compounds [see (**4k**) and (**4i**), (**4q**) and (**4o**)] lowers the melting point slightly, removes the S_B phase and only depresses the S_A thermal stability by 8.7°C [compound (**4k**)] or by a maximum of 11°C [compound (**4q**)]. Surprisingly, although both of these fluoro-compounds have had their S_B character suppressed, they have given rise to monotropic S_E phases. The same type of fluoro-substitution in the dimethylene linked compound [see compounds (**4l**) and (**4j**), (**4r**) and (**4p**)] *increases* the melting point, removes the S_B phase and depresses the clearing point more severely than for the ketones.

For the ketones, when the fluoro-substituent is *meta*- to the alkoxy group [see compounds (**4m**) and (**4i**), (**4s**) and (**4o**)], the melting points are still slightly depressed, but the S_B phases remain, although their thermal stabilities are decreased by 16°C and 8°C [for (**4m**) and (**4s**), respectively]. The magnitude of the depression of the S_A thermal stability in compound (**4m**) (8.7°C) is almost identical to the effect on the S_A phase caused by the fluoro-substituent *ortho*- to the alkoxy group (see above).

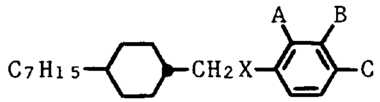
For the dimethylene linked compound with *meta*-fluoro-/alkoxy-substituents [compounds (**4n**) and (**4j**)], the melting point has again increased slightly (as noted for the *ortho*-fluoro-substituent) and the complete removal of the S_B phase has revealed a N phase and a monotropic S_A phase. Comparison of the values for compounds (**4t**) and (**4p**) shows similar changes of increased melting point and suppression of the S_B phase (but not total removal) to reveal enantiotropic S_A and N phases.

Comparison of the *ortho*-fluoro-/alkoxy- compounds (**4e**), (**4l**) and (**4r**) shows that the increasing alkoxy chain length has little effect on melting point and promotes S_A tendencies more than nematic. For the isomeric series of *meta*-fluoro compounds [(**4f**), (**4n**), (**4t**)], all the compounds remain nematic and their T_{N-I} values increase slightly, but the S_A properties become more pronounced.

Two compounds with a large lateral substituent (Br) were prepared to see whether or not the greater size of the lateral group would more efficiently suppress the ordered smectic phases. The bromo-substituent in (**4u**) did not affect the melting point [compound (**4o**)] and the S_B phase was suppressed [by at least 18°C; compound (**4u**) supercools to 60°C]. The bromo-substituted compound (**4v**) had a low melting point and, in comparison with compound (**4r**), the appearance

TABLE I.

Transition temperatures (°C) for compounds of structure (**4a–v**)



(4)

	X	A	B	C	K	S_E	S_B	S_A	N	I
a	CO	H	H	C_5H_{11}	• 33	—	(• 31)	—	—	•
b	CO	H	H	C_9H_{19}	• 38	—	• 56	—	—	•
c	CH_2	H	H	C_9H_{19}	• 33	—	• 52	—	—	•
d	CO	H	H	$C_{11}H_{23}$	• 45	—	• 62	—	—	•
e[4]	CH_2	H	F	OC_6H_{13}	• 45	—	—	—	(• 35)	•
f[4]	CH_2	F	H	OC_6H_{13}	• 29.5	—	—	—	• 35	•
g	CO	H	H	OC_8H_{17}	• 71	—	(• 58	• 70)	—	•
h	CH_2	H	H	OC_8H_{17}	• 37	—	• 61	—	—	•
i	CO	H	H	$OC_{10}H_{21}$	• 68	—	• 74	• 74.7	—	•

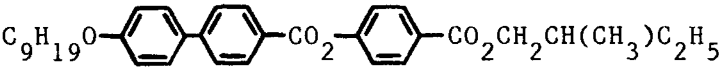
j	CH_2	H	H	$OC_{10}H_{21}$	• 27	——	• 64	——	——	•
k	CO	H	F	$OC_{10}H_{21}$	• 60	(• 39)	——	• 66	——	•
l	CH_2	H	F	$OC_{10}H_{21}$	• 42	——	——	(• 34)	——	•
m	CO	F	H	$OC_{10}H_{21}$	• 65	——	(• 58)	• 66	——	•
n	CH_2	F	H	$OC_{10}H_{21}$	• 36	——	——	(• 32)	• 40	•
o	CO	H	H	$OC_{12}H_{25}$	• 70	——	• 78	——	——	•
p	CH_2	H	H	$OC_{12}H_{25}$	• 34	——	• 65	——	——	•
q	CO	H	F	$OC_{12}H_{25}$	• 63	(• 53)	——	• 67	——	•
r	CH_2	H	F	$OC_{12}H_{25}$	• 47	——	——	(• 40)	——	•
s	CO	F	H	$OC_{12}H_{25}$	• 64	——	• 70	——	——	•
t	CH_2	F	H	$OC_{12}H_{25}$	• 40.5	——	(• 22)	• 40.7	• 42.5	•
u	CO	H	Br	$OC_{12}H_{25}$	• 70	——	——	——	——	•
v	CH_2	H	Br	$OC_{12}H_{25}$	• 31	——	——	(• 11.3	• 19.5)	•

K, crystal; S, smectic; N, nematic; I, isotropic liquid

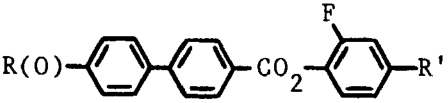
( ) signifies a monotropic transition

of a monotropic nematic phase shows that the bromo-substituent causes a greater depression of the S_A thermal stability than of the nematic.

All of these compounds were therefore found to be of quite low melting points, of low clearing points and, in general, somewhat dominated by their tendencies to produce S_B phases. Although, in several instances fluoro- or bromo-substitution had removed the S_B phase and in three examples S_A and N phases had been obtained, in none of the compounds had monotropic or enantiotropic S_C phases been detected. In order to assess the compatibility of some of these compounds with S_C host material, and so obtain an indication of their virtual S_C–S_A transition temperatures, selected compounds were mixed with PG495 [see (**5**)[7]] and with another standard S_C mixture (M609; from BDH Limited), based on compounds of structure (**6**); the transition temperatures for these mixtures are shown in Table II.



(**5**)



(**6**)

The compounds used had a methylenecarbonyl and dimethylene system [(**4i**) and (**4j**) respectively], with a fluoro-substituent *ortho-* to the alkoxy- group [(**4k**) and (**4l**) respectively] and with a fluoro-substituent *meta-* to the alkoxy- group [(**4m**) and (**4n**) respectively]. The results from these mixtures are not entirely consistent between the two hosts, but it appears that the unsubstituted methylenecarbonyl linked compound (**4i**) has the greatest S_C tendencies, whereas the laterally fluoro-substituted dimethylene compound (**4n**) has the lowest. However, even for compound (**4i**), the S_C tendencies are not sufficiently pronounced to offer promise of any of these two-ring systems providing suitable S_C hosts for use in ferroelectric devices.

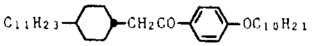
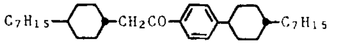
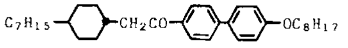
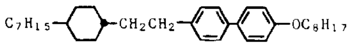
Four further compounds [(**7**)–(**10**)] were prepared to determine whether increasing the alkylcyclohexyl chain length or having a third ring present improved the properties of these compounds; the tran-

TABLE II.

Transition temperatures (°C) for mixtures of some of the Cyclohexyl-dimethylene- and methylenecarbonyl-phenyls [Compounds (**4i**)–(**4n**)] in two S_C hosts and the derived virtual S_C–S_A transition temperatures (°C)

Compound No		**PG495 Host**					**M609 Host**				
	w/w %	K-S_C	S_C-S_A	S_A-I	[S_C-S_A] of solute	w/w %	S_I-S_C	S_C-S_A	S_A-N	N-I	[S_C-S_A] of solute
		58	142	185			28	104	113	154	
(4i)	11.2	-	130	174	[35]	8.1	-	95	112	145	[-7]
(4j)	10.8	-	122	176	[-43]	9.2	-	87	112	144	[-81]
(4k)	10.9	59	115	169	[-106]	11.6	-	88	113	138	[-34]
(4l)	11.1	57	120	173	[-56]	10.4	-	86	112	143	[-69]
(4m)	10.5	60	120	170	[-67]	9.5	-	90	110	144	[-43]
(4n)	9.8	-	112	170	[-164]	9.4	-	83	103	141	[-119]

sition temperatures for these compounds are shown below. Increasing the alkyl chain length from C_7H_{15} [compound (**4i**)] to $C_{11}H_{23}$ [compound (**7**)] gave compounds of similar mp and of enhanced S_B character, so that the short-range S_A phase in compound (**4i**) was eliminated. The presence of a cyclohexyl ring as a third ring in compound (**8**) gave a compound which still had a reasonably low mp, but the S_B thermal stability had increased quite markedly. Compounds (**9**) and (**10**) are directly comparable with compounds (**4g**) and (**4h**) respectively and these comparisons illustrate the change caused by introducing a phenyl ring as the third ring. For compound (**9**), the melting point has increased, an S_G phase has appeared and the S_A thermal stability has increased by approximately 100°C. For compound (**10**), the melting point has also increased and the S_B phase persists to a temperature approximately 100°C higher than for compound (**4h**) and the S_A thermal stability has been increased by even more than this.

		K		S_G[a]		S_B		S_A		I (°C)
(**7**)		•	69	—		•	76	—		•
(**8**)		•	72	—		•	152	—		•
(**9**)		•	116	•	129	—		•	171	•
(**10**)		•	55	—		•	157	•	163	•

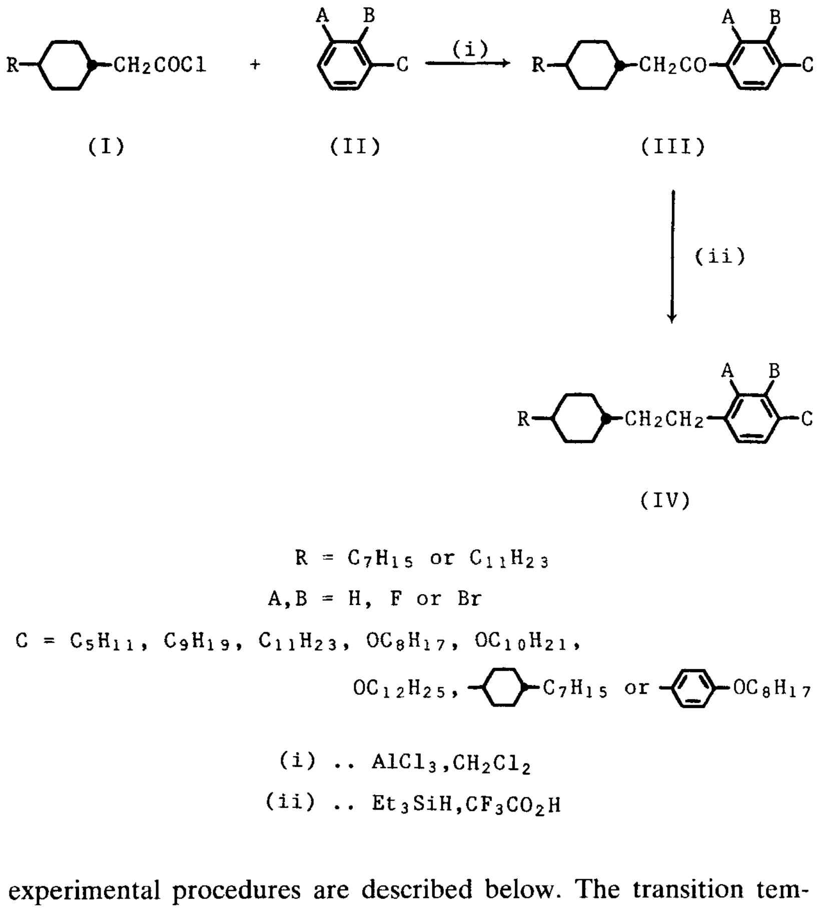
a .. the S_G phase has not yet been confirmed by X-ray crystallography

EXPERIMENTAL

All final products were shown to be pure by tlc, glc or hplc analysis. Structural confirmation of final products and intermediates was obtained by ^1H nmr spectroscopy (solvent $CDCl_3$, standard Me_4Si; JEOL JNM-PMX60 and JEOL JNM-GX270 FT spectrometers), infrared spectroscopy (Perkin-Elmer 457 grating spectrometer) and mass spectrometry (AEI MS 902 and Finnigan MAT 1020 GC/MS spectrometers). Transition temperatures were measured using a Mettler FP5 hot stage and control unit in conjunction with an Olympus BDSP 753 polarising microscope. In all cases calorimetry was used to confirm transition temperatures (Perkin-Elmer DSC-2C with data station).

The route for the preparation of the methylenecarbonyl and dimethylene compounds is shown in the Scheme and representative

SCHEME



$R = C_7H_{15}$ or $C_{11}H_{23}$

A,B = H, F or Br

$C = C_5H_{11}$, C_9H_{19}, $C_{11}H_{23}$, OC_8H_{17}, $OC_{10}H_{21}$,

(i) .. $AlCl_3, CH_2Cl_2$

(ii) .. Et_3SiH, CF_3CO_2H

experimental procedures are described below. The transition temperatures of the final products are given in Table I and are not repeated in the Experimental Section.

Nonanoylbenzene

A solution of nonanoyl chloride (17.7 g, 0.10 mol) in sodium-dried benzene (10 ml) was added dropwise under anhydrous conditions to a mixture of anhydrous aluminium trichloride (16.0 g, 0.12 mol) and sodium-dried benzene (30 ml) at 0°C. The reaction mixture was then heated under reflux for 2 h, cooled and poured into a mixture of water (100 ml) and concentrated hydrochloric acid (15 ml). The benzene layer was separated and the aqueous phase was washed with benzene (2 × 50 ml). The combined benzene solutions were washed with water (100 ml) and dried ($MgSO_4$). The solvent was removed under reduced pressure and the crude product was distilled at 104–108°C/0.4–0.5 mm Hg to give the ketone; yield 20.2 g, 93%. ^1H nmr δ 0.90 (3H, t), 1.10–2.00 (12H, m), 3.00 (2H, t), 7.40–8.20 (5H, m); m/z 218 (M^+), 133, 120, 105; ν_{max} (film) 3100–2800, 1690, 1600, 1450, 690 cm^{-1}.

Undecanoylbenzene was prepared similarly; bp 138–140°C/0.7 mm Hg, yield 89%. ^1H nmr δ 0.90 (3H, t), 1.10–2.00 (16H, m), 2.95 (2H, t), 7.40–8.20 (5H, m).

Nonylbenzene

A stirred mixture of nonanoylbenzene (19.6 g, 0.09 mol), hydrazine hydrate (12 ml), potassium hydroxide (16.0 g) and diethylene glycol (70 ml) was heated under reflux at 130°C for 2 h. Volatiles were then distilled off as the internal temperature was slowly raised to 200°C and kept at this temperature for 4 h. The reaction mixture was cooled, diluted with water (500 ml) and the crude product was extracted into ether (2 × 50 ml). The combined ether extracts were washed with water (100 ml) and dried ($MgSO_4$). The solvent was removed under reduced pressure and the crude product was distilled at 90–94°C/0.8 mm Hg; yield 12.7 g, 69%. ^1H nmr δ 0.90 (3H, t), 1.10–2.00 (14H, m), 2.60 (2H, t), 7.20 (5H, m); m/z 204 (M^+), 203, 105, 91; ν_{max} (film) 3100–2860, 1605, 1495, 1455, 700 cm^{-1}.

Undecylbenzene was prepared similarly; bp 112–114°C/0.45 mm Hg, yield 60%. ^1H nmr δ 0.90 (3H, t), 1.10–2.00 (18H, m), 2.60 (2H, t), 7.20 (5H, m).

Octoxybenzene

Phenol (9.4 g, 0.10 mol) was added to a stirred solution of sodium hydroxide (4.0 g, 0.10 mol), water (8 ml) and ethanol (30 ml). 1-Bromo-octane (21.2 g, 0.11 mol) was then added and the mixture was heated under reflux for 20 h. The ethanol was removed under reduced pressure and replaced by an equal volume of water. The cold mixture was washed with ether (2 × 100 ml) and the combined ether extracts were washed with water (100 ml) and dried ($MgSO_4$). The solvent was removed under reduced pressure and the crude product was distilled at 97–99°C/0.45 mm Hg; yield 17.4 g, 84%. ^1H nmr δ 0.90 (3H, t), 1.10–2.00 (12H, m), 3.90 (2H, t), 6.60–7.40 (5H, m); m/z 206 (M^+), 205, 93; ν_{max} (film) 3100–2800, 1605, 1500, 1250, 755, 690 cm^{-1}

The following ethers were prepared similarly using the appropriate phenols and halo-alkanes.

Decoxybenzene; bp 105–110°C/0.3 mm Hg, yield 75%. ^{1}H nmr δ 0.90 (3H, t), 1.10–2.00 (16H, m), 3.95 (2H, t), 6.80–7.50 (5H, m).

Dodecoxybenzene; bp 122–130°C/0.3 mm Hg, yield 94%. ^{1}H nmr δ 0.90 (3H, t), 1.10–2.00 (20H, m), 3.95 (2H, t), 6.80–7.50 (5H, m).

1-Decoxy-2-fluorobenzene; bp 100–112°C/0.15–0.25 mm Hg, yield 91%. ^{1}H nmr δ 0.90 (3H, t), 1.10–2.00 (16H, m), 4.05 (2H, t), 6.80–7.40 (4H, m).

1-Decoxy-3-fluorobenzene; bp 113–114°C/0.45 mm Hg, yield 87%. ^{1}H nmr δ 0.90 (3H, t), 1.10–2.00 (16H, m), 3.90 (2H, t), 6.40–6.90 (3H, m), 6.95–7.45 (1H, m).

1-Dodecoxy-2-fluorobenzene; bp 120–126°C/0.25 mm Hg, yield 73%. ^{1}H nmr δ 0.90 (3H, t), 1.10–2.00 (20H, m), 4.05 (2H, t), 6.80–7.30 (4H, m).

1-Dodecoxy-3-fluorobenzene; bp 134–138°C/0.5–0.6 mm Hg, yield 84%. ^{1}H nmr δ 0.90 (3H, t), 1.10–2.00 (20H, m), 3.95 (2H, t), 6.50–6.90 (3H, m), 6.95–7.50 (1H, m).

2-Bromo-1-dodecoxybenzene; bp 172–173°C/0.85 mm Hg, yield 78%. ^{1}H nmr δ 0.90 (3H, t), 1.10–1.60 (18H, m), 1.75–1.95 (2H, m), 4.00 (2H, t), 6.75–6.95 (2H, m), 7.20–7.30 (1H, m), 7.50–7.60 (1H, m).

4-Octoxybiphenyl; bp 176–179°C/0.15–0.2 mm Hg, yield 92%. ^{1}H nmr δ 0.90 (3H, t), 1.10–2.00 (12H, m), 3.95 (2H, t), 6.70–7.10 (2H, d), 7.10–7.80 (7H, m).

trans-1-Heptyl-4-phenylcyclohexane

A mixture of 4-(*trans*-4-heptylcyclohexyl)benzoic acid (15.0 g, 0.050 mol), basic copper carbonate [$CuCO_3.Cu(OH)_2.H_2O$] (0.5 g) and quinoline (50 ml) was heated at 160°C and the water present was removed by reducing the pressure (water pump). The temperature was raised to 250°C and the progress of the reaction was monitored by glc analysis. After being heated for 2.5 h, the reaction mixture was cooled and the crude product was extracted into ether (2 × 200 ml). The combined ether extracts were washed successively with 10% hydrochloric acid (200 ml), water (100 ml), aqueous sodium carbonate (100 ml), and water (100 ml), then dried ($MgSO_4$). The solvent was removed under reduced pressure and the main product was distilled at 144–146°C/0.8 mm Hg; yield 10.7 g, 83%. ^{1}H nmr δ 0.90 (3H, t), 1.00–2.70 (21H, m), 3.30–3.50 (1H, m), 7.10 (5H, m); *m/z* 258 (M^+), 117, 104, 91; ν_{max} (film) 3100–2760, 1605, 1495, 1450, 755, 700 cm^{-1}.

2-(*trans*-4-Heptylcyclohexyl)-1-(4-pentylphenyl)ethanone (4a)

A solution of pentylbenzene (1.48 g, 0.01 mol) in molecular sieve-dried dichloromethane (10 ml) was added dropwise at 0°C under anhydrous conditions to a stirred mixture of *trans*-4-heptylcyclohexylacetyl chloride (2.58 g, 0.01 mol) and anhydrous aluminium trichloride (1.47 g, 0.011 mol) in molecular sieve-dried dichloromethane (10 ml). The reaction mixture was stirred overnight at room temperature and then poured onto a mixture of ice (20 g) and concentrated hydrochloric acid (10 ml). The organic layer was separated and the aqueous layer was washed with dichloromethane (20 ml). The combined organic layers were washed with water (2 × 20 ml) and dried ($MgSO_4$). The solvent was removed under reduced pressure and the crude product was purified by column chromatography on silica gel, with petroleum fraction (bp 40–60°C)-chloroform (10:1) as eluent and then recrystallised (ethanol); yield 2.70 g, 73%. ^1H nmr δ 0.90 (6H, t), 1.10–2.20 (28H, m), 2.40–2.90 (4H, m), 7.20–7.50 (2H, d), 7.80–8.10 (2H, d); *m/z* 371, 370 (M^+), 369, 299, 298; ν_{max} (film) 3100–2760, 1770, 1610.

The following compounds were prepared similarly using the appropriate acid chloride and benzene derivative. All the crude products were purified by column chromatography on silica gel (mesh 60–120; the eluents used are given) followed by recrystallisation (the solvents used are in parentheses).

*2-(*trans*-4-Heptylcyclohexyl)-1-(4-nonylphenyl)ethanone* (**4b**); petroleum fraction (bp 40–60°C)-chloroform (2:1), (hexane); yield 70%. ^1H nmr δ 0.90 (6H, t), 1.10–2.20 (36H, m), 2.50–3.00 (4H, m), 7.30–7.60 (2H, d), 7.90–8.20 (2H, d).

*2-(*trans*-4-Heptylcyclohexyl)-1-(4-undecylphenyl)ethanone* (**4d**); petroleum fraction (bp 40–60°C)-chloroform (2:1), (petroleum fraction [bp below 40°C]); yield 57%. ^1H nmr δ 0.90 (6H, t), 1.10–2.00 (40H, m), 2.65 (2H, t), 2.80 (2H, d), 7.25 (2H, d), 7.85 (2H, d).

*2-(*trans*-4-Heptylcyclohexyl)-1-(4-octoxyphenyl)ethanone* (**4g**); petroleum fraction (bp 40–60°C)-chloroform (2:1), (ethanol); yield 75%. ^1H nmr δ 0.90 (6H, t), 1.10–2.20 (34H, m), 2.60–2.90 (2H, d), 4.00 (2H, t), 6.70–7.00 (2H, d), 7.80–8.10 (2H, d).

*1-(4-Decoxyphenyl)-2-(*trans*-4-heptylcyclohexyl)ethanone* (**4i**); petroleum fraction (bp 40–60°C)-chloroform (5:1), (petroleum fraction [bp below 40°C]); yield 85%. ^1H nmr δ 0.90 (6H, t), 1.10–2.20 (38H, m), 2.60–2.90 (2H, d), 4.10 (2H, t), 6.80–7.10 (2H, d), 7.90–8.20 (2H, d).

*1-(4-Decoxy-3-fluorophenyl)-2-(*trans*-4-heptylcyclohexyl)ethanone*

(**4k**); petroleum fraction (bp 40–60°C)-chloroform (1:1), (petroleum fraction [bp below 40°C]); yield 63%. ^{1}H nmr δ 0.90 (6H, t), 1.10–2.20 (38H, m), 2.60–2.90 (2H, d), 4.10 (2H, t), 6.80–7.20 (1H, m), 7.50–7.90 (2H, m).

*1-(4-Decoxy-2-fluorophenyl)-2-(*trans*-4-heptylcyclohexyl)ethanone* (**4m**); petroleum fraction (bp 40–60°C)-chloroform (5:1), (petroleum fraction [bp below 40°C]); yield 66%. ^{1}H nmr δ 0.90 (6H, t), 1.10–2.20 (38H, m), 2.70–3.00 (2H, m), 4.10 (2H, t), 6.60–7.20 (2H, m), 8.10 (1H, t).

*1-(4-Dodecoxyphenyl)-2-(*trans*-4-heptylcyclohexyl)ethanone* (**4o**); petroleum fraction (bp 40–60°C)-chloroform (5:1), (petroleum fraction [bp below 40°C]); yield 79%. ^{1}H nmr δ 0.90 (6H, t), 1.10–2.20 (42H, m), 2.70–3.00 (2H, d), 4.10 (2H, t), 6.90–7.20 (2H, d), 7.90–8.20 (2H, d).

*1-(4-Dodecoxy-3-fluorophenyl)-2-(*trans*-4-heptylcyclohexyl)ethanone* (**4q**); petroleum fraction (bp 40–60°C)-chloroform (1:1), (petroleum fraction [bp below 40°C]); yield 61%. ^{1}H nmr δ 0.90 (6H, t), 1.10–2.20 (42H, m), 2.60–2.80 (2H, d), 4.10 (2H, t), 6.80–7.20 (1H, m), 7.50–7.90 (2H, m).

*1-(4-Dodecoxy-2-fluorophenyl)-2-(*trans*-4-heptylcyclohexyl)ethanone* (**4s**); petroleum fraction (bp 40–60°C)-chloroform (5:1), (petroleum fraction [bp below 40°C]); yield 64%. ^{1}H nmr δ 0.90 (6H, t), 1.10–2.20 (42H, m), 2.70–3.00 (2H, m), 4.10 (2H, t), 6.50–7.00 (2H, m), 8.10 (1H, t).

*1-(3-Bromo-4-dodecoxyphenyl)-2-(*trans*-4-heptylcyclohexyl)ethanone* (**4u**); petroleum fraction (bp 40–60°C)-chloroform (1:1), (ethanol); yield 60%. ^{1}H nmr δ 0.90 (6H, t), 1.10–2.00 (42H, m), 2.75 (2H, d), 4.10 (2H, t), 6.90 (1H, d), 7.90 (1H, q), 8.15 (1H, d).

*1-(4-Decoxyphenyl)-2-(*trans*-4-undecylcyclohexyl)ethanone* (**7**); petroleum fraction (bp 40–60°C)-chloroform (2:1), (ethanol); yield 31%. ^{1}H nmr δ 0.90 (6H, t), 1.10–2.20 (46H, m), 2.80–2.90 (2H, d), 4.10 (2H, t), 7.10 (2H, d), 8.10 (2H, d).

*2-(*trans*-4-Heptylcyclohexyl)-1-(4-*[trans*-4-heptylcyclohexyl*]*phenyl)ethanone* (**8**); petroleum fraction (bp 40–60°C)-chloroform (2:1), (ethanol); yield 69%. ^{1}H nmr δ 0.90 (6H, t), 1.00–2.00 (43H, m), 2.45–2.60 (1H, m), 2.80 (2H, d), 7.30 (2H, d), 7.90 (2H, d).

*2-(*trans*-4-Heptylcyclohexyl)-1-(4'-octoxybiphenyl-4-yl)ethanone* (**9**); petroleum fraction (bp 40–60°C)-chloroform (2:1), (ethanol); yield 32%. ^{1}H nmr δ 0.90 (6H, t), 1.10–2.20 (34H, m), 2.80 (2H, d), 3.90 (2H, t), 6.80–7.00 (2H, d), 7.40–7.70 (4H, m), 7.80–8.00 (2H, d).

1-(*trans*-4-Heptylcyclohexyl)-2-(4-nonylphenyl)ethane (4c)

Triethylsilane (0.35 g, 0.48 ml, 3.0 mmol) was added dropwise under anhydrous conditions at room temperature to a stirred solution of 2-(*trans*-4-heptylcyclohexyl)-1-(4-nonylphenyl)ethanone (0.43 g, 1.0 mmol) in trifluoroacetic acid (10 ml). The reaction mixture was stirred for 3 h and then poured onto ice. The crude product was extracted into petroleum fraction (bp 40–60°C) (2 × 10 ml) and the combined organic phases were washed with water (2 × 10 ml), aqueous sodium carbonate (2 × 10 ml) and dried ($MgSO_4$). The solvent was removed under reduced pressure (crude yield 0.40 g, 97%) and the product was recrystallised (ethanol). ^{1}H nmr δ 0.90 (6H, t), 1.10–2.00 (38H, m), 2.50–2.60 (4H, m), 7.10 (4H, s); *m/z* 412 (M^+), 218, 105; ν_{max} (KCl) 3100–2760, 1515, 1455, 720 cm^{-1}.

The following compounds were prepared similarly in approximately 90% crude yield using the appropriate ketone; the solvents used for recrystallisation are given in parentheses.

*1-(*trans*-4-Heptylcyclohexyl)-2-(4-octoxyphenyl)ethane* (**4h**); (ethanol). ^{1}H nmr δ 0.90 (6H, t), 1.10–2.00 (36H, m), 2.50 (2H, t), 3.90 (2H, t), 6.75 (2H, d), 7.05 (2H, d).

*1-(4-Decoxyphenyl)-2-(*trans*-4-heptylcyclohexyl)ethane* (**4j**); (petroleum fraction [bp below 40°C]). ^{1}H nmr δ 0.90 (6H, t), 1.10–2.00 (40H, m), 2.50 (2H, t), 4.00 (2H, t), 6.90 (2H, d), 7.20 (2H, d).

*1-(4-Decoxy-3-fluorophenyl)-2-(*trans*-4-heptylcyclohexyl)ethane* (**4l**); (hexane). ^{1}H nmr δ 0.90 (6H, t), 1.10–2.00 (40H, m), 2.55 (2H, t), 4.00 (2H, t), 6.80–6.95 (3H, m).

*1-(4-Decoxy-2-fluorophenyl)-2-(*trans*-4-heptylcyclohexyl)ethane* (**4n**); (ethanol). ^{1}H nmr δ 0.90 (6H, t), 1.10–2.00 (40H, m), 2.50 (2H, t), 3.90 (2H, t), 6.40–7.20 (3H, m).

*1-(4-Dodecoxyphenyl)-2-(*trans*-4-heptylcyclohexyl)ethane* (**4p**); (petroleum fraction [bp below 40°C]). ^{1}H nmr δ 0.90 (6H, t), 1.10–2.00 (44H, m), 2.55 (2H, t), 3.95 (2H, t), 6.80 (2H, d), 7.05 (2H, d).

*1-(4-Dodecoxy-3-fluorophenyl)-2-(*trans*-4-heptylcyclohexyl)ethane* (**4r**); (petroleum fraction [bp below 40°C]). ^{1}H nmr δ 0.90 (6H, t), 1.10–2.00 (44H, m), 2.55 (2H, t), 4.00 (2H, t), 6.80–6.95 (3H, m).

*1-(4-Dodecoxy-2-fluorophenyl)-2-(*trans*-4-heptylcyclohexyl)ethane* (**4t**); (ethanol). ^{1}H nmr δ 0.90 (6H, t), 1.10–2.00 (44H, m), 2.50 (2H, t), 3.90 (2H, t), 6.40–7.20 (3H, m).

*1-(3-Bromo-4-dodecoxyphenyl)-2-(*trans*-4-heptylcyclohexyl)ethane* (**4v**); (ethanol). ^{1}H nmr δ 0.90 (6H, t), 1.10–2.00 (44H, m), 2.50 (2H, t), 3.95 (2H, t), 6.60–7.40 (3H, m).

*1-(*trans*-4-Heptylcyclohexyl)-2-(4'-octoxybiphenyl-4-yl)ethane* **(10)**; (ethanol). ^{1}H nmr δ 0.90 (6H, t), 1.10–2.00 (36H, m), 2.50 (2H, t), 3.95 (2H, t), 6.70–7.60 (8H, m).

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