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Four unit linking groups IV. Liquid crystals of positive dielectric anisotropy

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Four unit linking groups

IV. Liquid crystals of positive dielectric anisotropy

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Three separate series of new materials of weak to strongly positive dielectric anisotropy have been prepared. Each series contains four sub-sets of materials each incorporating a different four unit linking group (i.e., C_4H_8, C_4H_6, C_3H_6O and C_3H_4O) and the same series of end groups (i.e. F, CN and OCF_3) in various substitution patterns. The synthesis and liquid crystal transition temperatures of these novel substances are described and compared with those of the corresponding materials incorporating standard central linkages (i.e. —, C_2H_4, CH_2O, COO). The effect of an additional *trans* carbon–carbon double bond in the terminal alkyl chain and in the central linking unit has also been studied.

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1. Introduction

Compounds of high positive dielectric anisotropy ($\Delta\varepsilon \approx +10$) and low viscosity in the nematic phase are required for most types of twisted nematic [1] and supertwisted nematic displays (SBE, STN, OMI, etc.) [2–5]. Such materials are normally benzonitriles (for high $\Delta\varepsilon$) incorporating a *trans* 1,4-disubstituted cyclohexane ring joined to the benzene ring by a short linking unit (e.g. —, C_2H_4) for low viscosity [6, 7]. A *trans* carbon–carbon double bond can often be incorporated into such structures to improve the nematic temperature range or elastic constant ratios for superior display performance [8–11].

Materials which exhibit nematic phases of very high positive dielectric anisotropy ($\Delta\varepsilon \leqslant +50$) are used in normal twisted nematic displays where a low threshold voltage is required (e.g. for outdoor applications) [12, 13]. Such compounds are 4-cyano-3-fluorophenyl ester derivatives of variously substituted benzoic acids [14, 15]. It is postulated that the fluorine atom in this position next to the terminal cyano group prevents the formation of molecular dimers and thus the full effect of the nitrile dipole moment is reflected in the threshold voltage response curve [12–15].

Much more recently, substances of only moderately strong dielectric anisotropy ($\Delta\varepsilon \geqslant +5$) in the nematic mesophase have been desired for high information content display devices of fast response and high contrast (i.e. TFT and MIM) especially for television and computer applications [16, 17]. These compounds may *not* possess substituents with large dipole moments (e.g. CN = 4·0 D) due to their tendency to dissolve and solvate ionic materials especially from the alignment layer. This has a detrimental effect on display device performance [18–20]. Therefore such substances often contain one, or more, lateral and/or terminal substituents (e.g. F, OCF_3, etc.) with small dipole moments [18–20]. The presence of *trans* 1,4-disubstituted cyclohexane rings is essential to yield nematic phases of low viscosity. A *trans* carbon–carbon double bond in the terminal alkyl chain of such systems is of special value for these applications [21].

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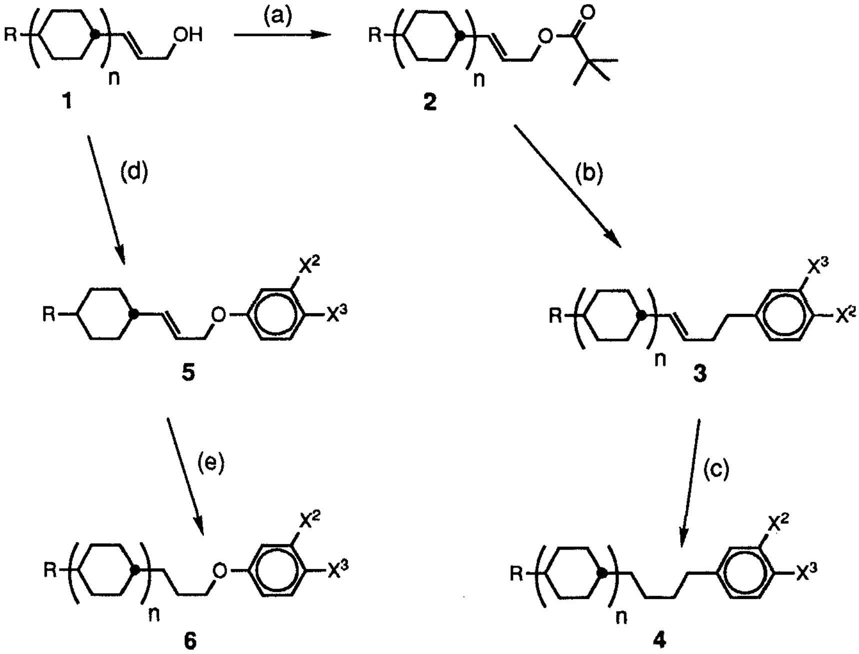
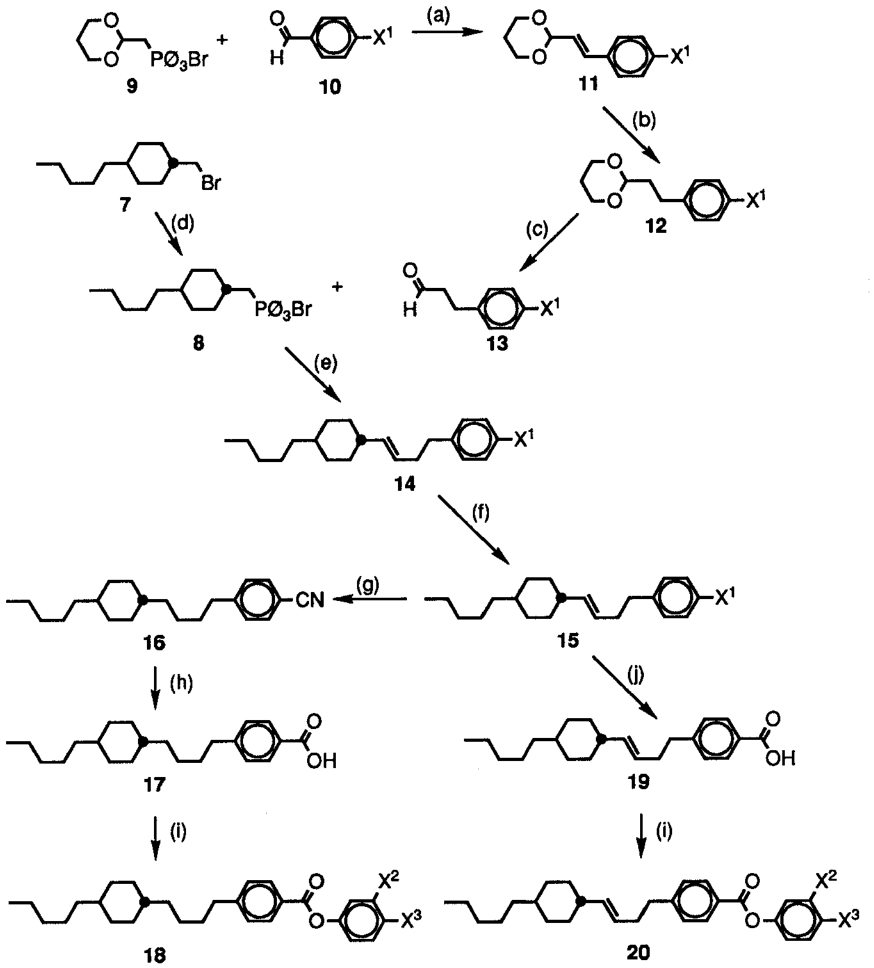
The synthesis and liquid crystal transition temperatures of three separate series of new nematogens incorporating four unit linking groups (C_4H_8, C_4H_6, C_3H_6O and C_3H_4O) and the lateral and/or terminal substituents (F, CN, OCF_3) for the corresponding electrooptic applications are now reported. The new four unit linking groups have recently been shown to be suitable central linkages for incorporation in potential mesogenic structures [22, 23]. Their suitability for nematogens of positive dielectric anisotropy is demonstrated, especially by comparison with the corresponding compounds incorporating standard central linking units (i.e. —, C_2H_4, CH_2O, and COO).

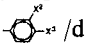
2. Synthesis

The reaction pathway leading to the two ring ($n = 1$) and three ring (*E*)-butenyl, butyl, allyloxy and propyloxy substituted benzenes **3**, **4**, **5** and **6**, respectively is shown in scheme 1. The pure (*E*)-allylalcohol **1** [23] was converted using pivaloyl chloride to the (*E*/*Z*) pivalate ester **2**. The amount of the *cis* isomer is small (*c*. 8–12 per cent) and can be removed by recrystallization of the butene compound **3** formed via a Grignard reaction with the appropriate benzyl bromide, catalysed using copper (I) chloride to suppress addition at the carbon–carbon double bond [24]. Hydrogenation of the butene compounds **3** over a palladium catalyst on charcoal give the corresponding butanes **4** in quantitative yield. Alkylation of the allylalcohol **1** with the desired phenols in a Mitsunobu reaction [25] led to the (*E*)-allyloxy materials **5**, which, in turn, could be hydrogenated as previously described to yield the propyloxy derivatives **6**. Alternatively a normal Williamson ether synthesis involving the same commercially available phenols and 3-(*trans*-4-pentyl)-1-bromopropane [23] could be used to prepare the ethers **6**.



Scheme 1. (*a*) $(CH_3)_3CCOCl$/pyridine, (*b*) BrMgCH_2 /CuCl/ether, (*c*) Pd/C/ethyl acetate, (*d*) DEAD/TPP/HO (*e*) Pd/C/ethyl acetate.



Scheme 2. (*a*) KOC$(CH_3)_3$/tetrahydrofuran, (*b*) Pd/C/ethyl acetate, (*c*) HCO_2H/toluene, (*d*) TPP/dimethylformamide, (*e*) KOC$(CH_3)_3$/tetrahydrofuran, (*f*) $C_6H_5SO_2H$/ethanol, (*g*) Pd/C/ethyl acetate, (*h*) $H_2SO_4/CH_3CO_2H/H_2O$, (*i*) DCC/DMAP/HO/dichloromethane, (*j*) KOH/ethanol.

The method of synthesis of the butenyl and butyl benzonitriles **15** (X^1 = CN) and **16**, respectively, as well as the corresponding phenyl benzoates **18** and **20**, respectively, is depicted in scheme 2. The aldehyde **13** was prepared by a C-2 elongation reaction *via* a Wittig reaction involving the commercially available dioxolane Wittig salt **9** and 4-cyanobenzaldehyde **10**, yielding the alkene **11**, which was subsequently hydrogenated over a palladium catalyst, followed by ring opening using formic acid. A further Wittig reaction using the Wittig salt **8** [26] and the aldehyde **13** yielded primarily the *cis* isomer of the butenyl-substituted benzonitrile **14** (X^1 = CN) which was then isomerized [27] to the predominantly *trans* isomer, which could be purified by recrystallization to pure (*E*) **15** (X^1 = CN). Subsequent hydrogenation of the butenyl benzonitrile **15** gave the butyl benzonitrile **16**, which was saponified under acid conditions to yield the

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corresponding benzoic acid **17**. Esterification of the acid **17** with the appropriate commercially available phenols using the DCC method [28] gave the desired butyl-substituted phenyl benzoates **18**.

The reaction sequence leading to the butenyl-substituted phenyl benzoate esters **20** is also shown in scheme 2 and is similar in most respects to the butyl method. A Wittig reaction involving the commercially available dioxolane salt **9** and methyl 4-carboxybenzaldehyde **10** ($X^1 = CO_2CH_3$) yielded the ethene **11**. Hydrogenation gave the ethane **12**, which yielded the aldehyde **13** with formic acid. A second Wittig reaction with the salt **8** led to the *cis* butene **14**, isomerization of which yielded the *trans* butene **15**. Saponification of the methyl ester **15** ($X^1 = CO_2CH_3$) with potassium hydroxide and subsequent acidification gave the benzoic acid **19**, esterification of which in the normal way [28] with the required commercially available phenols yielded the desired (*E*)-butenyl-substituted phenyl benzoates **20**.

The preparation of the propyloxy-substituted phenyl benzoates **24**, *via* alkylation of commercially available 4-hydroxybenzaldehyde with 3-(*trans*-4-pentylcyclohexyl)-1-bromopropane [23] to form the aldehyde **22**, subsequently oxidized to the benzoic acid **23** with Jones reagent [29] followed by esterification in the normal way [28] is described in the experimental section.

The synthesis of the analogous (*E*)-allyloxy-substituted phenyl benzoates **27** by a similar reaction pathway, but using the *trans* allylalcohol **1** in a Mitsunobu reaction to yield the aldehyde **25** and subsequent oxidation to the acid **26** followed by esterification as usual, is also described in the experimental section.

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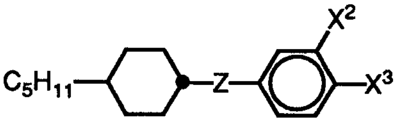
3. Results

The liquid crystal transition temperatures and some enthalpies of fusion of the two ring substituted benzenes **3–6** ($n = 1$) are collated in table 1. The four series **3–6** differ only in the nature of the central linkage ($Z = C_4H_6$, C_4H_8, C_3H_4O and C_3H_6O, respectively). In each of the four series the same lateral substituents ($X^2 = H$ or F; $X^3 = F$, CN or OCF_3) are varied. All four series are characterized by low, mostly monotropic nematic mesophases. Only one compound **6** ($n = 1$, $Z = C_3H_6O$; $X^2 = H$; $X^3 = CN$) exhibits even a very narrow range, enantiotropic nematic phase (1°C). Comparing only those compounds where a nematic phase could be observed, it is found that the clearing points (T_{NI}) of all four series ($Z = C_4H_8$, C_4H_6, C_3H_6O and C_3H_4O) are basically similar in magnitude (3°C, 3°C, 21°C and 10°C, on average, respectively). This is also true for the melting points (T_{CN} and T_{CI}) of all four series (27°C, 13°C, 27°C and 33°C, on average, respectively). The 3-propyloxy series **6** ($Z = C_3H_6O$) exhibits the greatest tendency to nematic mesophase formation. Such low transition temperatures are common for such structures (see the Discussion). That the four nitriles ($X^2 = H$, $X^3 = CN$) possess substantially higher clearing points than the other materials bearing less polar terminal substituents (F and OCF_3) and disubstituted compounds ($X^2 = X^3 = F$) can be explained by their relative tendencies for molecular dimer formation.

The liquid crystal transition temperatures and some enthalpies of fusion for the three ring materials ($n = 2$) **3**, **4**, **5** and **6** containing the four unit linking groups under investigation, (*E*)-3-butenyl, butyl, (*E*)-allyloxy, and propyloxy ($Z = C_4H_6$, C_4H_8, C_3H_4O, and C_3H_6O, respectively) and one or two substituents (X^2, $X^3 = H$, F and/or OCF_3) are collated in table 2. The butyl compounds **4** ($Z = C_4H_8$) exhibit a low melting point (34°C, on average), an enantiotropic smectic B–nematic transition (69°C, on average) and a relatively high clearing point (127°C, on average). The incorporation of

Table 1. Liquid crystal transition temperatures and some enthalpies of fusion for the compounds of the structure below.



Z	*X*^{2}	*X*^{3}	$T_{CN/I}$/°C	T_{NI}/°C	ΔH/kJ mol^{-1}
	H	F	13	(−17)	
	F	F	6	—	20·3
	H	CN	51	(39)	—
	H	OCF$_3$	18	(−12)	27·6
	H	F	−5	(−11)	18·0
	F	F	−11	(−33)	21·8
	H	CN	40	(39)	22·1
	H	OCF$_3$	5	(−17)	22·1
	H	F	17	(11)	27·2
	F	F	4	—	18·8
	H	CN	45	46	26·3
	H	OCF$_3$	20	(5)	26·3
	H	F	23	(−12)	13·2
	F	F	11	—	20·1
	H	CN	64	(43)	—
	H	OCF$_3$	13	(−2)	19·4

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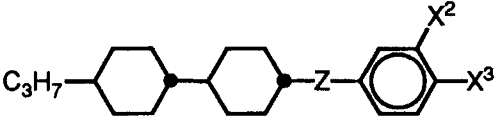
a *trans* carbon–carbon bond in compounds **4** to yield compounds **3** results in an increase (+29°C) in the nematic range by decreasing both the melting point (−13°C, on average) and the smectic B–nematic transition temperature (−12°C), while, at the same time, increasing the clearing point (+17°C). The introduction of an oxygen atom in the butyl materials **4** to give the propyloxy substances **6** ($Z = C_3H_6O$) increases both the melting and clearing points (+20°C and +16°C, on average, respectively) while decreasing the smectic B–nematic transition temperature significantly, so that only one homologue ($X^2 = H$; $X^3 = OCF_3$) exhibits a smectic B mesophase. The consequence of these changes is an increase in the nematic range (+20°C, on average) due to the suppression of the enantiotropic smectic B mesophase. The incorporation of a *trans* carbon–carbon double bond in the propyloxy compounds **6** to yield the (*E*)-allyloxy materials **5** ($Z = C_3H_4O$) results in a melting point decrease (−12°C, on average), the disappearance of the smectic B phase, while the clearing point remains unchanged (116°C, on average). Thus the nematic range is increased further (+12°C, on average). Therefore the allyloxy compounds **5** exhibit the widest nematic range of all four series investigated.

The liquid crystal transition temperatures and some enthalpies of fusion of three very similar series of three ring materials **3** and **4** ($n = 2$) differing in the nature of the substituents ($X^2 = H$ and F; $X^3 = F$ and OCF_3) and the number of *trans* carbon–carbon double bonds in the central linkage ($Z = C_4H_8$ and C_4H_6) or the terminal alkyl chain ($R = C_3H_7$ and C_3H_5) are recorded in table 3. The thermal data listed in the table allow an insight into the effect of additional *trans* olefinic bonds first in the central linking unit and then also in the terminal alkyl chain. The three butyl compounds **4** ($R = C_3H_7$; $n = 2$) all exhibit an enantiotropic smectic B and nematic mesophase. The introduction of an additional *trans* carbon–carbon double bond in the central linkage to yield the

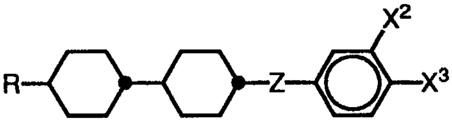
Table 2. Liquid crystal transition temperatures and some enthalpies of fusion for the compounds of the structure below.



Z	X^2	X^3	$T_{CS_B/N}$/°C	T_{S_BN}/°C	T_{NI}/°C	ΔH/kJ mol^{-1}
	H	F	56	87	116	29·6
	F	F	39	69	103	30·5
	H	OCF_3	47	86	111	27·2
	H	F	33	74	135	27·9
	F	F	27	50	119	20·4
	H	OCF_3	41	83	128	3·1
	H	F	78	—	124	35·8
	F	F	79	—	107	35·1
	H	OCF_3	44	62	117	25·5
	H	F	75	—	127	29·9
	F	F	48	—	101	27·0
	H	OCF_3	43	—	120	

butenyl compounds **3** ($R = C_3H_7$; $n = 2$) leads to a decrease (−13°C and −12°C, on average, respectively) in the melting point (T_{CS_B}) and the smectic B–nematic transition temperature (T_{S_BN}) and to an increase (+17°C, on average) in the clearing point (T_{NI}). This produces a doubling in the nematic range (+29°C). The incorporation of a second *trans* carbon–carbon double bond in the butenyl materials ($Z = C_4H_6$), this time in the terminal alkyl chain ($R = C_3H_5$) leads to an almost equal increase (+24°C and +22°C, on average, respectively) in the melting point (T_{CN}) and the clearing point (T_{NI}). However, the absence of a smectic modification for the materials incorporating two olefinic bonds ($R = C_3H_5$ and $Z = C_4H_6$) results in a further broadening (+23°C, on average) in the nematic range (91°C, on average). Some of the enthalpies of fusion for these substances are very low, especially for purely nematic materials (e.g. $X^2 = H$; $X^3 = F$; $R = C_3H_5$ and $Z = C_4H_6$).

Table 3. Liquid crystal transition temperatures and some enthalpies of fusion for the compounds of the structure below.



R	Z	X^2	X^3	$T_{CS_B/N}$/°C	T_{S_BN}/°C	T_{NI}/°C	ΔH/kJ mol^{-1}
		H	F	56	87	116	29·6
		F	F	39	69	103	30·5
		H	OCF_3	47	86	111	27·2
		H	F	33	74	135	27·9
		F	F	27	50	119	20·4
		H	OCF_3	41	83	128	3·1
		H	F	52	—	159	9·9
		F	F	60	—	140	13·6
		H	OCF_3	63	—	149	—

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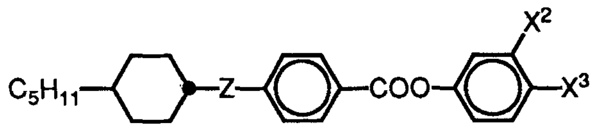
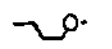
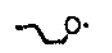
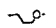
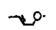
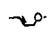
In table 4 are collated the liquid crystal transition temperatures and most enthalpies of fusion of the esters **18**, **20**, **24** and **27** incorporating the four central linkages ($Z = C_4H_8$, C_4H_6, C_3H_6O and C_3H_4O, respectively). The five esters containing a butyl central linkage **18** ($Z = C_4H_8$) all exhibit an enantiotropic nematic mesophase over an extended temperature range. The addition of a second fluorine atom to the monofluoro-substituted ester ($X^2 = H$; $X^3 = F$) and the mono-substituted nitrile ($X^2 = H$; $X^3 = CN$) to yield the difluoro-substituted ester ($X^2 = X^3 = F$) and the fluoro-substituted nitrile ($X^2 = F$; $X^3 = CN$) leads in both cases to decreases in the melting point (−13°C and −19°C, respectively) and the clearing point (−16°C and −19°C, respectively) to more or less the same degree. This has a minimal effect (−3°C and 0°C, respectively) on the nematic range of both systems, which then exists at lower temperatures. The transition temperatures of the trifluoromethoxy-substituted ester ($X^2 = H$; $X^3 = OCF_3$) resemble those of the monofluoro-substituted ester ($X^2 = H$, $X^3 = F$) as is often the case.

The introduction of the additional *trans* carbon–carbon double bond into the butyl-substituted esters **18** ($Z = C_4H_8$) to create the butenyl-substituted esters **20** ($Z = C_4H_6$) leads to a marginal decrease (−1°C, on average) in the melting point (T_{CN}), but a substantial increase (+19°C, on average) in the clearing point (T_{NI}). This results in a significant increase (+20°C, on average) in the nematic range. No smectic modifications could be observed. The difluoro-substituted ester ($X^2 = X^3 = F$) exhibits the lowest melting point ($T_{CN} = 40$°C) of all the variously substituted esters **18**, **20**, **24** and **27**.

Table 4. Liquid crystal transition temperatures and some enthalpies of fusion for the compounds of the structure below.



Z	X^2	X^3	$T_{CS_A/N}$/°C	T_{S_AN}/°C	T_{NI}/°C	ΔH/kJ mol^{-1}
	H	F	63	—	104	28·0
	F	F	50	—	88	33·6
	H	CN	78	—	151	29·0
	F	CN	59	—	132	17·9
	H	OCF_3	71	—	109	
	H	F	65	—	123	
	F	F	40	—	104	20·8
	H	CN	76	—	171	18·5
	F	CN	63	—	149	18·9
	H	OCF_3	70	—	128	20·4
	H	F	90	(73)	127	18·3
	F	F	75	(65)	110	29·1
	H	CN	82	117	168	23·3
	F	CN	75	—	146	29·4
	H	OCF_3	74	110	132	27·6
	H	F	105	(102)	132	27·4
	F	F	93	(88)	111	23·9
	H	CN	79	—	170	21·5
	F	CN	54	68	145	
	H	OCF_3	88	128	136	23·7

If, instead of the double bond an oxygen atom is incorporated into the butyl-substituted esters **18** ($Z=C_4H_8$) to produce the propyloxy-substituted esters **24** ($Z=C_3H_6O$) then both the melting point (T_{CS_A} and T_{CN}) and the clearing point (T_{NI}) are increased substantially (+13°C and +20°C, on average, respectively). An enantiotropic or monotropic smectic A mesophase is observed for most of the esters prepared. The effects of all these changes is to decrease (−5°C, on average) the range of the enantiotropic nematic mesophase.

The presence of an additional *trans* carbon–carbon double bond in the allyloxy esters **27** ($Z=C_3H_4O$) with respect to the propyloxy esters **24** ($Z=C_3H_6O$) induces small increases (+5°C, +6°C and +2°C, on average, respectively) in the melting point (T_{CS_A} and T_{CN}), the smectic A–nematic transition temperature and the clearing point (T_{NI}). A small decrease (−4°C, on average) is observed in the nematic range.

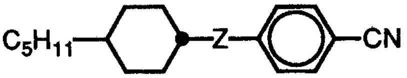
The enthalpies of fusion of the esters **18**, **20**, **24** and **27** are very similar (24·6 kJ mol^{-1}, on average) in most cases and are of a moderately high value.

4. Discussion

The relative merits of the new four unit linking groups (C_4H_8, C_4H_6, C_3H_6O, and C_3H_4O) and the standard central linkages (C_2H_4, CH_2O, —, and COO) in two ring, polar systems is clearly demonstrated by the thermal data shown in table 5. Whereas each of the known materials ($Z=C_2H_4$, CH_2O, —, and COO) exhibits an enantiotropic nematic mesophase between the melting point ($T_{CN}=44$°C, on average) and the clearing point ($T_{NI}=62$°C, on average), the compounds **3–6** ($n=1$) ($Z=C_4H_8$, C_4H_6, C_3H_6O, and C_3H_4O) possess only a monotropic nematic mesophase of low clearing point ($T_{NI}=44$°C, on average) below the relatively high melting point ($T_{CI}=54$°C, on average). The same clearing point ($T_{NI}=39$°C) for the butyl ($Z=C_4H_8$ and the (*E*-3-butenyl ($Z=C_4H_6$) substituted benzonitriles is most unusual (see tables 1–4).

The liquid crystal transition temperatures of variously substituted three ring structures differing only in the nature of the central linkage ($Z=C_2H_4$, CH_2O, —, COO, C_4H_8, C_4H_6, C_3H_6O, and C_3H_4O) are collated in the tables 6–8. A salient feature of all three tables is the similarity of the transition temperatures of the ethyl-substituted ($Z=C_2H_4$) and the (*E*)-3-butenyl-substituted (C_4H_6) compounds (e.g. $Z=C_2H_4$; $T_{CS_B}=18$°C; $T_{S_BN}=50$°C; $T_{NI}=118$°C and $Z=C_4H_6$; $T_{CS_B}=27$°C;

Table 5. Liquid crystal transition temperatures for compounds of the structure below differing only in the nature of the central linking unit *Z*.



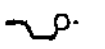
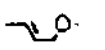
Z	$T_{CN/I}$/°C	T_{NI}/°C	Reference
	45	55	[7]
	48	54	[7]
—	30	59	[6]
	55	81	[30]
	51	(39)	
	40	(39)	
	63	(54)	
	64	(43)	

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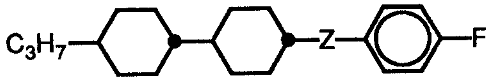
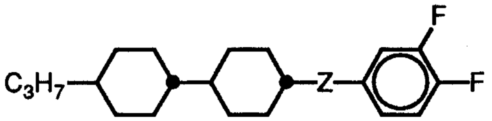
Table 6. Liquid crystal transition temperatures for compounds of the structure below differing only in the nature of the central linking unit Z.



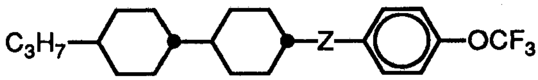
Z	$T_{CS_B/N}$/°C	T_{S_BN}/°C	T_{NI}/°C	Reference
	45	—	134	[19]
	92	—	133	[19]
—	90	—	158	[19]
	71	—	183	
	56	87	116	
	33	74	135	
	78	—	124	
	75	—	127	

Table 7. Liquid crystal transition temperatures for compounds of the structure below differing only in the nature of the central linking unit Z.



Z	$T_{CS_B/N}$/°C	T_{S_BN}/°C	T_{NI}/°C	Reference
	18	50	118	[19]
	80	—	103	[19]
—	46	—	124	[19]
	57	—	153	[31]
	39	69	103	
	27	50	119	
	79	—	107	
	48	—	101	

Table 8. Liquid crystal transition temperatures for compounds of the structure below differing only in the nature of the central linking unit Z.



Z	$T_{CS_B/N}$/°C	T_{S_BN}/°C	T_{NI}/°C	Reference
	44	108	139	[19]
	85	—	126	[19]
—	39	68	149	[19]
	52	127	186	[32]
	47	86	111	
	41	83	128	
	44	62	117	
	43	—	120	

$T_{S_BN} = 50°C$; $T_{NI} = 119°C$; see table 7). Otherwise, both the melting point (T_{CS_B} and T_{CN}) and the clearing point (T_{NI}) of the compounds containing the usual central linking units are higher (+9°C and +25°C, on average, respectively) than those of the corresponding materials incorporating the new four unit linking groups. However, this results in only a moderate increase (+16°C, on average) in the nematic range, when the smectic transition temperatures (T_{S_BN}), which are difficult to compare, are neglected, see tables 6–8.

5. Conclusions

The three separate series of new compounds containing four unit linking groups (i.e. C_4H_8, C_4H_6, C_3H_6O, and C_3H_4O) and various lateral and terminal substituents (F, OCF_3, and CN) designed to exhibit moderately high, high and very high positive dielectric anisotropy for a variety of twisted nematic applications (e.g. TN, SBE, STN, OMI, TFT, MIM, etc.) generally possess monotropic nematic mesophases for two ring systems and enantiotropic, wide range nematic mesophases, sometimes accompanied by enantiotropic smectic B mesophases, at elevated temperatures for three ring substances. For three ring systems, there exists a high degree of similarity between the liquid crystal transition temperatures of the ethyl (C_2H_4) and the (*E*)-3-butenyl-substituted materials.

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6. Experimental

The liquid crystal transition temperatures of the compounds prepared listed in tables 1–4 were determined by optical microscopy using a Leitz Ortholux II POL-BK microscope in conjunction with a Mettler FP 82 heating stage and FP 80 control unit. All of the monotropic liquid crystal phases could be observed using a microscope and no virtual values (extrapolated) had to be determined. When necessary the Mettler stage could be cooled ($< -20°C$) by allowing nitrogen gas, cooled by liquid nitrogen, to pass through the stage at a controlled rate. The liquid crystal transition temperatures and enthalpies were also determined using a Mettler DTA TA 2000.

The purity of the compounds was determined by thin layer chromatography, gas chromatography and DTA analysis. A Perkin–Elmer 8310 gas chromatograph and GP-100 graphics printer were used. 4 × 8 cm precoated TLC plates, SiO_2 SIL G/UV_{254}, layer thickness 0·25 mm (Macheray-Nagel, Düren, Germany) were utilized.

Column chromatography was carried out using silica gel 60 (230–400 mesh ASTM). Reaction solvents and liquid reagents were purified by distillation or drying shortly before use. Reactions were carried out under nitrogen unless water was present as solvent or reagent. All temperatures were measured externally unless otherwise stated. The ^1H NMR spectra were recorded at 60 MHz (Varian T-60), 80 MHz (Bruker WP-80) or 270 MHz (Bruker HX-270). Mass spectra were recorded on a MS9 (AEZ, Manchester) spectrometer.

(E/Z)-[trans-4-(trans-4-[(E)-propenyl]cyclohexyl)cyclohexyl]allyl pivalate 2 ($R = C_3H_5$; $n = 2$). A solution of pivaloyl chloride (4·1 g, 0·0340 mol) and toluene (50 ml) was added dropwise to a solution of (*E*)-[*trans*-4-(*trans*-4-[(*E*)-propenyl]cyclohexyl)cyclohexyl]allylalcohol [23] (7·5 g, 0·0284 mol) and pyridine (3·4 g, 0·0425 mol) in toluene (50 ml) at 0°C. The reaction mixture was stirred at room temperature overnight and then poured into water (100 ml). The organic layer was separated off and the aqueous layer extracted with toluene (2 × 50 ml). The combined organic layers were washed with dilute hydrochloric acid (2 × 50 ml), with water (2 × 50 ml), dried ($MgSO_4$), filtered and evaporated down. The residue was purified by column chromatography on

silica gel with toluene as eluent to give pure (*E*/*Z*)-[*trans*-4-(*trans*-4-[(*E*)-propenyl]cyclohexyl)cyclohexyl]allyl pivalate (yield 7·5 g, 76 per cent; 85/15: *trans*/*cis*). IR (film): 2920, 2851, 1791, 1668, 1447, 1151, 967 cm^{-1}. MS: 346 (M^{+}), 244 ($C_{18}H_{28}$).

The following pivalate esters were prepared using the same procedure:

(E/Z)-(trans-4-Pentylcyclohexyl)allyl pivalate **2** ($R = C_5H_{11}$, $n = 1$) (yield 99 per cent). IR (film): 2929, 2852, 1790, 1651, 1450, 1282, 1151, 968 cm^{-1}. MS: 252 ($C_{16}H_{28}O_2$), 192 ($C_{14}H_{24}$).

(E/Z)-[trans-4-(trans-4-propylcyclohexyl)cyclohexyl]allyl pivalate **2** ($R = C_3H_7$; $n = 2$) (yield 61 per cent). IR (film): 2919, 2850, 1731, 1230, 1151, 969 cm^{-1}. MS: 246 ($C_{18}H_{30}^{+}$).

*1-Fluoro-4-[(E)-4-[*trans*-4-(trans-4-[(E)-propenyl]cyclohexyl)cyclohexyl]-3-butenyl]benzene* **3** ($R = C_3H_5$; $n = 2$; $X^2 = H$; $X^3 = F$). A solution of Grignard reagent (produced as usual from 4-fluorobenzylbromide (2·2 g, 0·0115 mol), magnesium turnings (0·3 g, 0·0115 mol) and ether (25 ml)) was added dropwise to a mixture of (*E*/*Z*)-[*trans*-4-(*trans*-4-[(*E*)-propenyl]cyclohexyl)cyclohexyl]allyl pivalate (2·0 g, 0·0058 mol) and copper (I) chloride (0·06 g, 0·0006 mol) in ether (25 ml) at 0°C and under an atmosphere of nitrogen. The reaction mixture was stirred at room temperature for a further 30 min and then poured into 25 per cent hydrochloric acid (50 ml). The organic layer was separated off and the aqueous layer extracted with ether (3 x 100 ml). The combined organic layers were washed with brine (100 ml), concentrated potassium carbonate solution (100 ml, brine (100 ml), dried ($MgSO_4$), filtered and evaporated down under slightly reduced pressure. Purification of the residue of silica gel using hexane as eluent followed by recrystallization from acetone gave pure product (1·9 g, 91 per cent), see tables 1–3 for the liquid crystal transition temperatures and enthalpy of fusion for this final product and other homologues prepared using this general method. IR (KBr): 2914, 2848, 1601, 1508, 1218, 964, 831 cm^{-1}. MS: 354 (M^{+}), 109 (C_7H_6F).

1-Fluoro-4-[4-trans-4-pentylcyclohexyl)-1-butyl]benzene **4** ($R = C_5H_{11}$; $n = 1$; $X^2 = H$; $X^3 = F$). A solution of 1-fluoro-4-[4-(*trans*-4-pentylcyclohexyl)-3-butenyl]-benzene (2·0 g, 0·007 mol), 10 per cent palladium on active charcoal (0·2 g) and ethyl acetate was hydrogenated until no more hydrogen was taken up. The catalyst was removed by filtration and the filtrate evaporated down. The residue was purified by recrystallization from acetone at −78°C to give pure (99·8 per cent) product. The liquid crystal transition temperatures of this compound and others prepared by this general procedure are recorded in tables 1–2 and 4–8. IR (KRr): 2930, 2845, 1599, 1509, 1221, 828 cm^{-1}. MS: 358 (M^{+}), 109 (C_7H_6F).

1-Fluoro-4-[3-(trans-4-pentylcyclohexyl)propyloxy]benzene **6** ($R = C_5H_{11}$; $n = 1$; $X^2 = H$; $X^3 = F$). A mixture of 4-fluorophenol (0·25 g, 0·0022 mol), 3-(*trans*-4-pentylcyclohexyl)-1-bromopropane (0·68 g, 0·0025 mol), potassium carbonate (1·2 g, 0·0089 mol) and butanone (25 ml) was heated under gentle reflux overnight. The inorganic material was removed by filtration and the filtrate evaporated down. The residue was purified by column chromatography on silica gel using toluene as eluent followed by recrystallization from alcohol at −25°C to give pure product. The liquid crystal transition temperatures of this ether and other ethers prepared using this general method are recorded in tables 1–2 and 4–8. IR (KBr): 2920, 2849, 1607, 1507, 1249, 1219, 1029, 826 cm^{-1}. MS: 306 (M^{+}), 112 (C_6H_5FO).

(trans-4-Pentylcyclohexyl)methyltriphenylphosphonium bromide **8**. A solution of (*trans*-4-pentylcyclohexyl)bromomethane **7** [33] (25 g, 0·1 mol), triphenylphosphine (32 g, 0·12 mol) and *N*,*N*′-dimethylformamide (10 ml) was heated at 100°C for 48 hours. Ethyl acetate (200 ml) was added dropwise with stirring to the cooled reaction mixture,

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which was then maintained at 0°C for 24 hours. The white precipitate was filtered off, washed with portions of cold ethyl acetate and then dried at 50°C to give the desired Wittig reagent (yield 39 g, 77 per cent).

(E/Z)-1-(4-Cyanophenyl)-2-(1,3-dioxolan-2-yl)ethene **11** (X^1 = CN). Potassium *tert*.-butylate (9·4 g, 0·0840 mol) was added portionwise to a mixture of 4-cyanobenzaldehyde **10** (X^1 = CN) (10·0 g, 0·0763 mol), (1,3-dioxolan-2-yl)methyl-triphenylphosphonium bromide (39·3 g, 0·0916 mol) and tetrahydrofuran (500 ml). After completion of the addition the reaction mixture was stirred for 2 hours at room temperature and then added to water (1000 ml). The organic layer was separated off and the aqueous layer extracted with ether (3 x 100 ml). The combined organic layers were washed with brine (2 x 500 ml), dried ($MgSO_4$), filtered and evaporated down under slightly reduced pressure. The residue was purified on silica gel using a 4:1 hexane/ethyl acetate mixture as eluent to give pure (99·0 per cent) ethene (yield 10·2 g, 66 per cent). IR (film): 2959, 2227, 1608, 1505, 1122, 975, 860 cm^{-1}. MS: 201 (M^+), 129 (C_9H_7N).

(E/Z)-1-(4-[Methylcarboxy]phenyl)-2-(1,3-dioxolan-2-yl)ethene **11** (X^1 = CO_2CH_3) (yield 72 per cent). MS: 234 (M^+) was prepared using the same procedure.

1-(4-Cyanophenyl)-2-(1,3-dioxolan-2-yl)ethane **12** (X^1 = CN). A mixture of (*E*/*Z*)-1-(4-cyanophenyl)-2-(1,3-dioxolan-2-yl) ethene (40 g), 10 per cent palladium on charcoal (0·5 g), triethylamine (5 ml) and ethyl acetate (50 ml) was hydrogenated until no more hydrogen was taken up. The catalyst was removed by filtration and the filtrate evaporated down. The residue was purified by column chromatography on silica gel using a 9:1 hexane/ethyl acetate mixture as eluent followed by crystallization from a 9:1 hexane/ethanol mixture at −25°C to give pure (99·8 per cent) ethane (yield 35 g, 88 per cent); mp 64–65°C. IR (KBr): 2959, 2855, 2227, 1608, 1506, 1123, 846, 821 cm^{-1}. MS: 203 (M^+), 202 ($C_{12}H_{12}NO_2^+$), 143 ($C_{10}H_9N^+$), 117 (C_8H_7N).

1-(4-[Methylcarboxy]phenyl)-2-(1,3-dioxolan-2-yl)ethane **12** (X^1 = CO_2CH_3) (yield 83 per cent); mp 47–48°C. IR (KBr): 2952, 1715, 1611, 1575, 1510, 1282, 1110, 898 cm^{-1}. MS: 235 (M^+), 205 ($C_{12}H_{13}O_3$) was prepared using the same procedure.

3-(4-Cyanophenyl)propionaldehyde **13** (X^1 = CN). A mixture of (4-cyanophenyl)-2-(1,3-dioxolan-2-yl)ethane (25 g), formic acid (12 ml) and toluene (25 ml) was stirred vigorously at room temperature overnight and then added to water (500 ml). The organic layer was separated off and the aqueous layer extracted with toluene (2 x 50 ml). The combined organic layers were washed with water (500 ml), dilute potassium carbonate solution (200 ml) and again with water (500 ml), dried ($MgSO_4$), filtered and evaporated. This gave pure (95 per cent) aldehyde (18 g, 92 per cent); mp 106–107°C. IR (film): 2730, 2227, 1722, 1607, 1505, 819 cm^{-1}. MS: 159 (M^+), 130 (C_9H_8N), 116 (C_8H_6N).

3-(4-Methylcarboxyphenyl)propionaldehyde **13** (X^1 = CO_2CH_3) (yield 36 per cent). IR (film): 2952, 2842, 2710, 1721, 1611, 1575, 1282, 863 cm^{-1}. MS: 192 (M^+), 161 ($C_{10}H_9O_2$), 150 ($C_9H_{10}O_2$) was prepared using the same procedure.

4-[(E/Z)-4-(trans-4-Pentylcyclohexyl)-3-butenyl]benzonitrile **14** (X^1 = CN). Potassium *tert*.- butylate (2·9 g, 0·02 mol) was added portionwise to a mixture of 3-(4-cyanophenyl)propionaldehyde (3·1 g, 0·02 mol), (*trans*-4-pentylcyclohexyl) methylphosphoniumbromide (10·0 g, 0·02 mol) and tetrahydrofuran (200 ml) at 0°C. The reaction mixture was stirred for a further 2 hours at room temperature and then poured into water (500 ml). The organic layer was separated off and the aqueous layer extracted with ether (4 x 100 ml). The combined organic layers were washed with brine (2 x 500 ml), dried ($MgSO_4$), filtered and then evaporated down under slightly reduced

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pressure. The residue was purified by column chromatography on silica gel using a 9 : 1 hexane/ethyl acetate mixture as eluent to give pure (98 per cent) product (yield 1·8 g, 30 per cent). MS: 309 (M^+).

Methyl-4-[(E/Z)-4-(trans-4-pentylcyclohexyl)-3-butenyl]benzoate **14** ($X^1 = CO_2CH_3$) (yield 36 per cent). MS: 342 (M^+) was prepared using the same procedure.

4-[(E)-4-(trans-4-Pentylcyclohexyl)-3-butenyl]benzonitrile **15** ($X^1 = CN$). A solution of 4-[(*E*/*Z*)-4-(*trans*-4-pentylcyclohexyl)-3-butenyl]benzonitrile (1·8 g, 0·0058 mol), freshly prepared benzene sulphinic acid 2·0 g, 0·0058 mol), water (1 ml) and ethanol (50 ml) was heated at 65°C for 48 hours. The reaction mixture was added to brine (250 ml) and extracted with ether (3 × 50 ml). The combined organic layers were washed with concentrated potassium carbonate solution (2 × 50 ml) and brine (50 ml), dried ($MgSO_4$), filtered and evaporated under slightly reduced pressure. The residue was purified by column chromatography on silica gel using a 9 : 1 hexane/ethyl acetate mixture as eluent and recrystallization from alcohol to give pure (99·9 per cent) product (0·6 g, 33 per cent). The liquid crystal transition temperatures of this nitrile are recorded in table 1. IR (KBr): 2919, 2849, 2226, 1607, 1507, 1447, 1178, 967, 823 cm^{-1}. MS: 309 (M^+), 253 ($C_{18}H_{23}N$), 238 ($C_{17}H_{20}N$), 116 (C_8H_6N).

Methyl 4-[(E)-4-(trans-4-pentylcyclohexyl)-3-butenyl]benzoate **15** ($X^1 = CO_2CH_3$) (yield 87 per cent). MS: 342 (M^+) was prepared using this procedure.

4-[4-(trans-4-Pentylcyclohexyl)-1-butyl]benzoic acid **17.** A solution of 4-[4-*trans*-4-pentylcyclohexyl)-1-butyl]benzonitrile (36 g, 0·1158 mol), concentrated sulphuric acid (300 ml), water (300 ml) and glacial acetic acid (300 ml) was heated at 120°C overnight. The cooled reaction solution was poured into an ice/water mixture (2000 ml). The resultant precipitate was filtered off, washed with small amounts of water, pressed dry and then recrystallized from ethanol to give the pure acid (yield 28 g, 73 per cent), $T_{CN} = 195°C$; $T_{NI} = 199°C$.

4-Fluorophenyl 4-[4-trans-4-pentylcyclohexyl)-1-butyl]benzoate **18** ($X^2 = H$; $X^3 = F$). A solution of 4-[*trans*-4-pentylcyclohexyl)-1-butyl]benzoic acid (2·0 g, 0·0061 mol), 4-fluorophenol (0·7 g, 0·0061 mol), 4-(dimethylamino)pyridine (0·04 g), *N*,*N*′-dicyclohexylcarbodiimide (1·5 g, 0·0073 mol) and dichloromethane (100 ml) was stirred at room temperature overnight, filtered to remove precipitated material and then evaporated. The residue was purified by column chromatography on silica gel using toluene as eluent followed by recrystallization from alcohol until the transition temperatures remained constant. Table 4 gives the liquid crystal transition temperatures and enthalpies of fusion for this ester and the other esters prepared using this general procedure. IR (KRr): 2916, 2846, 1735, 1611, 1502, 1267, 827 cm^{-1}. MS: 313 ($C_{22}H_{33}O^+$).

4-[(E)-4-(trans-4-Pentylcyclohexyl)-3-butenyl]benzoic acid **19**. A solution of methyl-4-[(*E*)-4-*trans*-4-pentylcyclohexyl)-3-butenyl]benzoate (1·3 g), potassium hydroxide (1·3 g), water (2 ml) and ethanol (20 ml was heated at 75°C for 1 hour. 25 per cent hydrochloric acid (50 ml) was added to the cooled reaction solution (ice-bath). The reaction mixture was stirred for 15 min at room temperature and then the white precipitate was filtered off, washed with portions of water, pressed dry and then recrystallized from acetone to give pure acid (yield 64 per cent); mp 214–215°C. IR (KBr): 2921, 2850, 2666, 2594, 2547, 1677, 1608, 1573, 1319, 1290, 965, 858 cm^{-1}. MS: 328 (M^+).

4-[3-(trans-4-Pentylcyclohexyl)propyloxy]benzaldehyde **22**. A mixture of 3-(*trans*-4-pentylcyclohexyl)-1-bromopropane [23] (5·0 g, 0·018 mol), 4-hydroxybenzaldehyde

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(1·9 g, 0·015 mol), anhydrous potassium carbonate (8·3 g, 0·060 mol) and butanone (50 ml) were heated under reflux overnight. The cooled reaction mixture was poured into water (500 ml) and then extracted with ether (3 x 50 ml). The combined organic layers were washed with water (2 x 500 ml), dried ($MgSO_4$), filtered and then evaporated. The residue was purified by column chromatography on silica gel using toluene as eluent (yield 5·0 g, 88 per cent). IR (KBr): 2920, 2848, 2740, 1691, 1595, 1506, 1256, 1153, 968, 831 cm^{-1}. MS: 315 (M^+ H^+), 192 ($C_{16}H_{24}$).

4-([(E)-3-(trans-4-Pentylcyclohexyl)allyl]benzaldehyde **25** (yield 60 per cent); mp 54–55°C. IR (film): 2921, 2848, 1690, 1601, 1509, 1256, 1158, 1045, 862 cm^{-1}. MS: 316 (M^+) was prepared using the same procedure.

4-[3-(trans-4-Pentylcyclohexyl)propyloxy]benzoic acid **23.** A solution of Jones reagent [29] (10 ml) was added dropwise to a solution of 4-[3-(*trans*-4-pentylcyclohexyl)propyloxy]benzaldehyde (5 g, 0·016 mol) and acetone (100 ml) at room temperature. The reaction mixture was stirred for 1 hour and then poured into water (100 ml). The resultant precipitate was filtered off, washed with small portions of water, pressed dry and finally recrystallized from alcohol to give the pure acid (yield 2·2 g, 42 per cent). $T_{CN} = 204°C$, $T_{NI} = 215°C$. IR (KBr): 2660, 2542, 1669, 1604, 1519, 1257, 1173, 1025 cm^{-1}. MS: 332 (M^+).

4-([(E)-3-(trans-4-Pentylcyclohexyl)allyl]oxy)benzoic acid **26** (yield 62 per cent); mp 214–215°C was prepared using the method described for 4-(3-*trans*-4-pentylcyclohexyl)propyloxy]benzoic acid. IR (KBr): 2922, 2849, 2608, 2548, 1669, 1602, 1575, 1512, 1247, 1175, 966 cm^{-1}. MS: 331 (M^+ H^+).

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