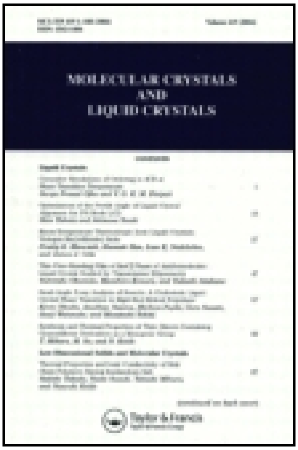

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Thermotropic Liquid Crystal Behavior in Some Aromatic Esteramides

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Thermotropic Liquid Crystal Behavior in Some Aromatic Esteramides

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Ester-amide analogs of *p*-phenylene di-*p*-substituted benzoates have been synthesized and the thermotropic liquid crystal properties of the two series are compared. The crystalline, smectic, and nematic phases are all more thermally stable in the ester-amides than in the diesters. In the corresponding series of 4-alkoxybenzoyl compounds, as the alkyl chain length increases the difference in nematic phase stability also increases, but the difference in smectic phase stability decreases. Introduction of a methyl substituent into the central ring reduces the stability of all three phases, and increases the sensitivity of smectic phase stability, but not of crystalline or nematic phase stability, to alkyl chain length.

INTRODUCTION

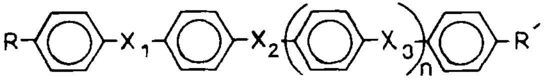
Although the amide group has been included in a list of units that may occur between aromatic rings in thermotropic liquid crystal substances of low molecular weight, and a variety of thermotropic liquid crystal compounds possessing such structures have been described, its presence is not usually considered conductive to the formation of a stable nematic phase. Probably the most important reason for this view is its ability to form hydrogen bonds between neighboring molecules, leading to a relatively high enthalpy of fusion and melting temperature such that the upper limit of thermal stability of the nematic phase, if any, often lies well below the melting point.

A comparison of known isostructural pairs of thermotropic liquid crystal amides and esters[1] (Table I) illustrates the difference in crystalline melting point, but does not permit a clear conclusion about the relative nematic phase stabilities in the two series.

Recently it has been shown that thermotropic liquid crystal polymers containing amide groups in the repeating unit can be obtained, and the structures are such that there can be no doubt that the amide group contributes to the

TABLE I

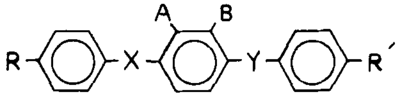
Comparison of transition data for amides and esters



						Transition temps. (amide) °C		ΔT$_1$°C (amide to ester)		
									N-I	
n	*R*	*X*$_1$	*X*$_2$	*X*$_3$	*R*^{1}	C-N	N-I	C-N	+	−
0	CH_3O	CH:N	CO.NH[a]	—	$COOCH_3$	227	dec.	10		
0	H	CH:CH.CH:N	CO.NH[a]	—	$COOCH_3$	332	336	147	111	
1	CH_3O	CO.NH[a]	direct link	NH.CO[b]	OCH_3	371	dec.	120	5	
1	H	CH:N	CO.NH[a]	N:CH	H	230	235	36		15
1	CH_3	CH:N	CO.NH[a]	N:CH	CH_3	239	>310	52		
1	CH_3O	CH:N	CO.NH[a]	N:CH	OCH_3	221	dec.	15		
1	C_2H_5O	CH:N	CO.NH[a]	N:CH	OC_2H_5	218	267	45		>63
1	O_2N	CH:N	CO.NH[b]	N:CH	NO_2	253	>300	49	>95	
1	H	CH:CH.CH:N	CO.NH[b]	N:CH.CH:CH	H	278	dec.	72	>28	

[a] CO.O in esters.
[b] O.CO in ester.

mesogenic unit. Examples include polyester-amides synthesized from 4-aminophenol and a range of aromatic dicarboxylic acids containing *p*-phenylene units[2] and co-polyester-amides containing *p*-benzamide and ethylene terephthalate repeating units.[3] In order to characterize the contribution of the amide group to mesogenic activity in such polymers, an examination has been carried out of its contribution in related compounds of low molecular weight. This examination has concentrated upon compounds of the structure (I),



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where X and Y are amide and/or ester groups. Compounds of this type where X and Y are both ester groups have been widely studied, and the relation between chemical structure and thermotropic liquid crystal behavior is rather well understood in this series; therefore a good basis for comparison of the mesogenic activity of amide and ester groups is available.

EXPERIMENTAL

Acids

4-Ethoxybenzoic acid (Aldrich) was used without further purification. 4-*n*-Propoxy- and 4-*n*-butoxybenzoic acids were prepared by the method of Jones.[4] 4-*n*-Pentyloxy-, 4-*n*-hexyloxy-, and 4-*n*-heptyloxy-benzoic acids were prepared by the method of Pierce *et al.*,[5] which gave superior yields with these higher homologues. 4-*n*-Octyloxy-, 4-*n*-nonyloxy-, 4-*n*-decyloxy-, and 4-*n*-dodecyloxy- benzoic acids were prepared by a modification of Jones's method using ethanol as solvent instead of water, which gave yields of 40–60% after purification.

Acid chlorides

The acid chlorides from the above acids were made by heating with a large excess of redistilled thionyl chloride together with 4–5 drops of dimethyl formamide as catalyst. Yields of redistilled product were 75–85%.

Other acid chlorides (Aldrich) were used without further purification, except 4-nitrobenzoyl chloride which was recrystallized from petroleum ether.

Amino phenols

4-Aminophenol (B.D.H.) and 4-N-methylaminophenol (Aldrich) were recrystallized twice from water containing 3% by weight of sodium dithionite based on the aminophenol.

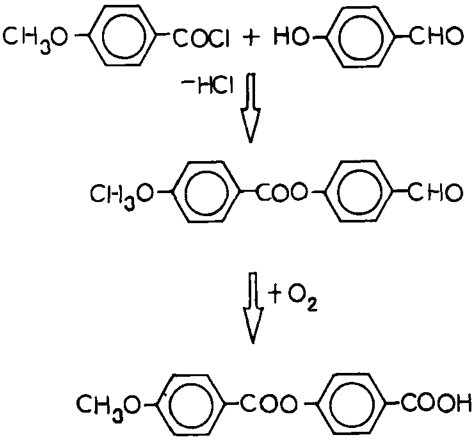
3-Methyl-4-aminophenol, m.p. 177.5–178.5°C, (lit. 179°C)[6] was prepared by hydrogenation of 3-methyl-4-nitrophenol (recrystallized from 1% aqueous HCl) in ethanol at room temperature using 5% palladium on carbon as catalyst. The yield was 82% after recrystallization from water containing sodium dithionite.

2-Chloro-4-aminophenol, m.p. 148–150°C (decomp.) (lit. 150–151°C)[7] was prepared similarly except that Adams platinum catalyst was used instead of palladium on carbon, which caused further reduction to *p*-aminophenol. The yield was 48% after recrystallization twice from water containing sodium dithionite.

Ester-containing intermediates

4-Chlorophenyl 4-aminobenzoate, m.p. 171–174°C, (lit. 176–177°C)[8] was made by hydrogenation of the corresponding nitro compound (m.p. 165.5–166°C, lit. 171°C)[9] in ethanol at room temperature using 5% palladium on carbon as catalyst. The yield was 90% after recrystallization from 70% ethanol.

4-Carboxyphenyl 4-methoxybenzoate, C 220–222° N 266° I (lit. C 223 N 272° I)[10] was made by the following route.



SCHEME 1

The first stage was conducted in chloroform as solvent at room temperature using triethylamine as acid acceptor. After 1 hour the solution was evaporated and the residue was treated with a little petroleum ether, filtered, and washed with warm water. The yield of aldehyde m.p. 89–91°C, (lit. 89°C)[1], was 86%. The aldehyde was oxidized by boiling a solution in propionic acid for 12 h in the presence of cobalt and manganese bromides as catalysts while passing in oxygen. The acid was filtered off and obtained in 57% yield after crystallization from acetic acid in the presence of decolorizing charcoal.

The corresponding acid chloride, 4-chloroformylphenyl 4-methoxybenzoate, m.p. 148–149°C was made as above. The yield after crystallization from petroleum ether was 83%.

Ester-amides

The following general procedure was used:

The aminophenol (0.01 mole) and triethylamine (0.022 mole) were dissolved in dichloromethane (60–120 ml.). The acid chloride (0.02 mole) was added to the stirred solution as rapidly as possible. After stirring for 1 h at room temperature, the precipitated product was filtered off, washed with warm aqueous potassium carbonate then distilled water, and crystallized from an appropriate solvent until the D.S.C. melting point was sharp and constant. Further details are given in Tables II, III, IV, and V.

Characterization of products

Transition temperatures were measured using (a) a hot stage Reichert polarizing microscope, and (b) a duPont DSC 990/910 differential scanning calorimeter at a heating rate of 10°C/min. Compounds were judged to be adequately pure when the melting point (taken as the temperature of the endothermal peak) was constant and the melting range was 2°C or less. The type of phase was assigned on the basis of microscopic observations.

Infra-red spectra were obtained as KBr discs using a Unicam SP1025 spectrometer.

RESULTS AND DISCUSSION

The simplest ester-amide of the series examined, N,O-dibenzoyl 4-aminophenol, did not exhibit nematic or smectic behavior down to a supercooled melt temperature of 185°C. The analogous diester, *p*-phenylene dibenzoate,

TABLE II

Thermal transitions for ester-amides (structure I, X = COO—, Y = —NHCO—, $A = B = H$).

Compound No.	$R = R^1$	DSC transition temperatures, °C			Notes
		C-N	N-I	C-I	
1	H	—	—	234	$T_{NI} < 185$°C
2	CH_3	—	235[a]	251	
3	Cl	—	271[a]	273	
4	NO_2	273	283.5	—	m.p. 264°C[11]
5	NH_2	304	>360[b]	—	
6	CH_3CONH	358	>358[b]	—	
7	CH_3O	255	303	—	m.p. 249-251°C[12]

[a] monotropic.

[b] decomposes before transition.

TABLE III

Thermal transitions for ester-amides (structure I, X = —COO—, Y = —NHCO—, $R = C_nH_{2n+1}O$, A = H)

Compound			DSC transition temperatures, °C				
No.	*B*	*n*	C-S	C-N	S-N	S-I	N-I
7	H	1	—	255	—	—	303
8		2	—	257	—	—	297
9		3	—	247.5	—	—	260.5
10		4	—	228.5	—	—	254
11		5	—	204	—	—	234
12		6	190	—	197.5	—	230
13		7	191	—	212	—	225
14		8	185	—	219.5	—	222
15		9	181	—	—	220	—
16		10	174.5	—	—	220	—
17		12	168	—	—	215.5	—
18	CH_3	1	—	213	—	—	261
19		2	—	212	—	—	261
20		3	—	197.5	—	—	224
21		5	—	162.5	—	—	196.5
22		6	—	149.5	—	—	193.5
23		7	—	143	123[a]	—	185
24		8	—	139	139[a]	—	182
25		9	133	—	153.5	—	176
26		10	129	—	162.5	—	173
27		12	126	—	—	169	—

[a] monotropic.

TABLE IV

Thermal transitions for other ester-amides (structure I)

Compound							DSC transition temperatures, °C		
No.	*X*	*Y*	*R*	*R*^{1}	*A*	*B*	C-N	N-I	C-I
28	—OOC—	—NHCO—	Cl	Cl	H	H	229	247	—
29	—OOC—	—NHCO—	Cl	OCH_3	H	H	252.5	277.5	—
30	—COO—	—CONH—	CH_3O	OCH_3	H	H	224.5	284	—
31	—COO—	—N(CH_3)CO—	CH_3O	OCH_3	H	H	—	—	104
32	—COO—	—NHCO—	NO_2	NO_2	H	CH_3	—	255[a]	262
33	—COO—	—NHCO—	CH_3O	OCH_3	Cl	H	231.5	240	—

[a] monotropic.

TABLE V

Analytical data for ester-amides
For key to compound nos. see Tables II-IV

Compound No.	Crystallization solvent	Required, %			Found, % (±0.05)		
		C	H	N	C	H	N
2	Benzene/acetone	76.50	5.55	4.06	76.2	5.55	4.0
3	Dioxan/water	62.18	3.37	3.63	62.25	3.55	3.55
4[a]	Ethoxyethanol	58.97	3.22	10.32	58.9	3.1	10.3
5	Dimethylacetamide/water	69.15	4.93	12.10	69.2	4.8	11.7
6	Dimethylacetamide/water	66.82	4.87	9.74	66.65	5.0	9.7
7	Ethoxyethanol	70.02	5.07	3.71	69.9	5.05	3.75
8	Butanone	71.09	5.72	3.46	71.2	5.7	3.4
9	Butanone	72.04	6.28	3.23	71.6	6.15	3.15
10	Acetone	72.86	6.77	3.04	72.6	6.8	2.7
11	Butanone	73.59	7.21	2.86	73.75	7.0	2.8
12	Butanone	74.24	7.59	2.71	74.2	7.5	2.6
13	Butanone	74.83	7.94	2.57	74.55	7.9	2.4
14	Acetone	75.36	8.26	2.44	75.15	8.2	2.2
15	Butanone	75.84	8.54	2.33	75.9	8.5	2.4
16	Acetone/butanone	76.25	8.80	2.22	76.3	8.9	2.0
17	Butanone	77.04	9.26	2.04	77.45	9.55	2.1
18	Butanone	70.57	5.41	3.58	70.45	5.5	3.45
19	Dioxan/water	71.58	6.01	3.34	71.45	6.05	3.45
20	Ethanol	72.46	6.53	3.13	72.75	6.55	3.25
21	Methanol	73.93	7.41	2.78	73.85	7.35	2.65
22	Ethanol	74.54	7.77	2.63	74.5	7.8	2.4
23	Acetone	75.10	8.10	2.50	74.85	8.15	2.5
24	Acetone	75.60	8.40	2.38	75.75	8.35	2.1
25	Acetone	76.06	8.68	2.27	76.1	9.0	2.25
26	Acetone	76.48	8.92	2.17	76.65	8.85	2.05
27	Butanone	77.21	9.36	2.00	77.55	9.2	2.3
28[a]	Ethanol/acetone	62.18	3.37	3.62	62.45	3.35	3.45
29[a]	Butanone	66.05	4.19	3.67	66.2	4.4	3.95
30	Butanone	70.02	5.04	3.71	69.9	5.05	3.75
31	Methanol/water	70.57	5.41	3.58	70.35	5.1	3.45
32	Butanone	59.85	3.56	9.98	60.1	3.75	10.15
33[a]	Acetone	64.15	4.37	3.40	64.0	4.4	3.4

[a] Compound 4: Cl required 18.4%, found 18.7%
28: Cl required 18.4%, found 18.1%
29: Cl required 9.3%, found 9.4%
33: Cl required 8.6%, found 8.75%

although lower-melting, has also failed to exhibit liquid crystal behavior. Introduction of various substituents into the *para*-positions of the benzoyl groups gave ester-amides that did exhibit nematic mesophases, either enantiotropic or monotropic. The data in Table II show that the thermal stabilities of the nematic phases lie in the following order for different substituents (*I*, $R = R^1$):

$$CH_3CONH,\ NH_2 > CH_3O > NO_2 > Cl > CH_3$$

TABLE VI

Difference in crystal and nematic thermal stabilities between ester-amides and diesters (structure I, *X* = —COO—, *Y* = —NHOC— or OOC, *A* = *B* = *H*)

$R = R^1$	ΔT_N (amide-ester)	ΔT_C (amide-ester)
CH_3	−1[17]	19.5[17]
Cl	25[14]	47[14]
NO_2	2.5[17],17.5[14]	11[17],13[14]
CH_3O	3[16],6[14],2[18],4[20]	33[16],42[14],38[18],37.5[20]

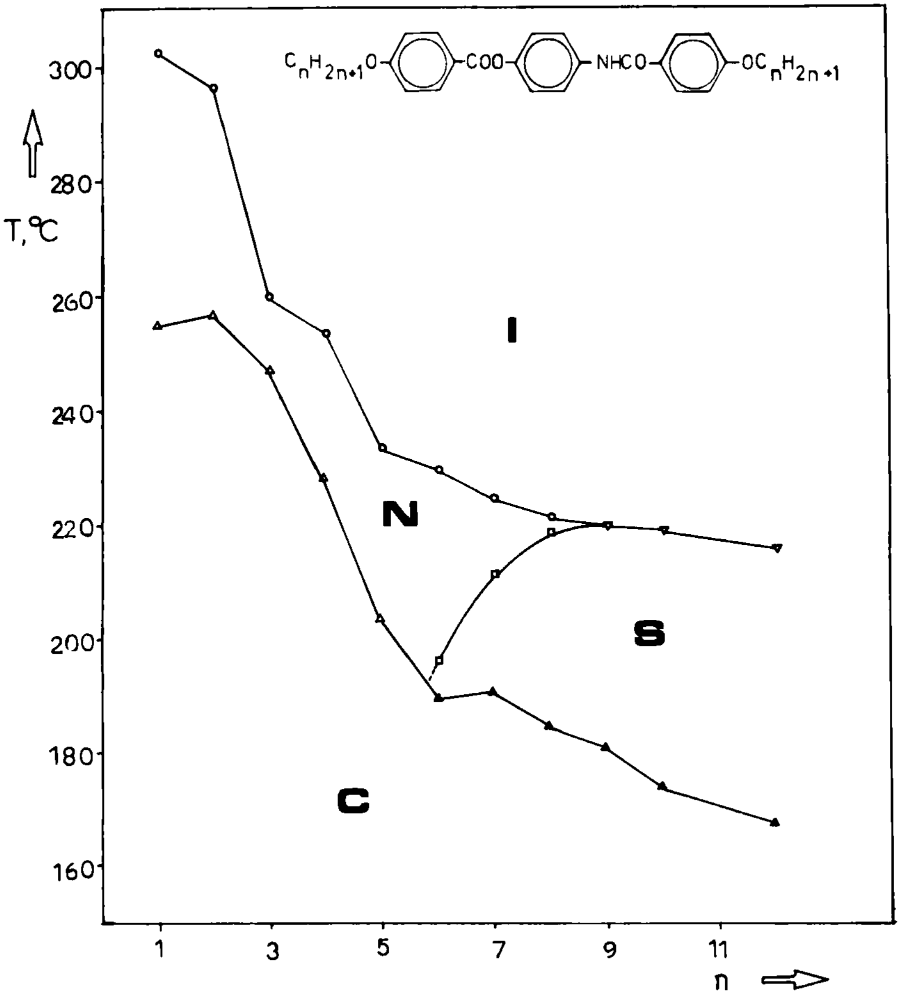


FIGURE 1 Phase transition data for ester-amides derived from 4-aminophenol and alkoxybenzoic acids.

This is a similar sequence to that found for the diester series and is explained in terms of (a) a contribution by the substituents to axial polarizability, (b) conjugative interaction with the carbonyl oxygen, and (c) size and dipolar orientation of the substituents;[13,14] the sequence is similar to the average terminal group efficiencies quoted by Gray.[15] Comparison with the nematic thermal stabilities of the diesters (Table VI) shows a slight tendency for the ester-amides to be more stable than the diesters.

Two series of di-4-alkoxybenzoyl compounds, those derived from 4-aminophenol and from 3-methyl-4-aminophenol, were synthesized. Phase transition data from Table III are plotted in Figures 1 and 2 for the two series. The

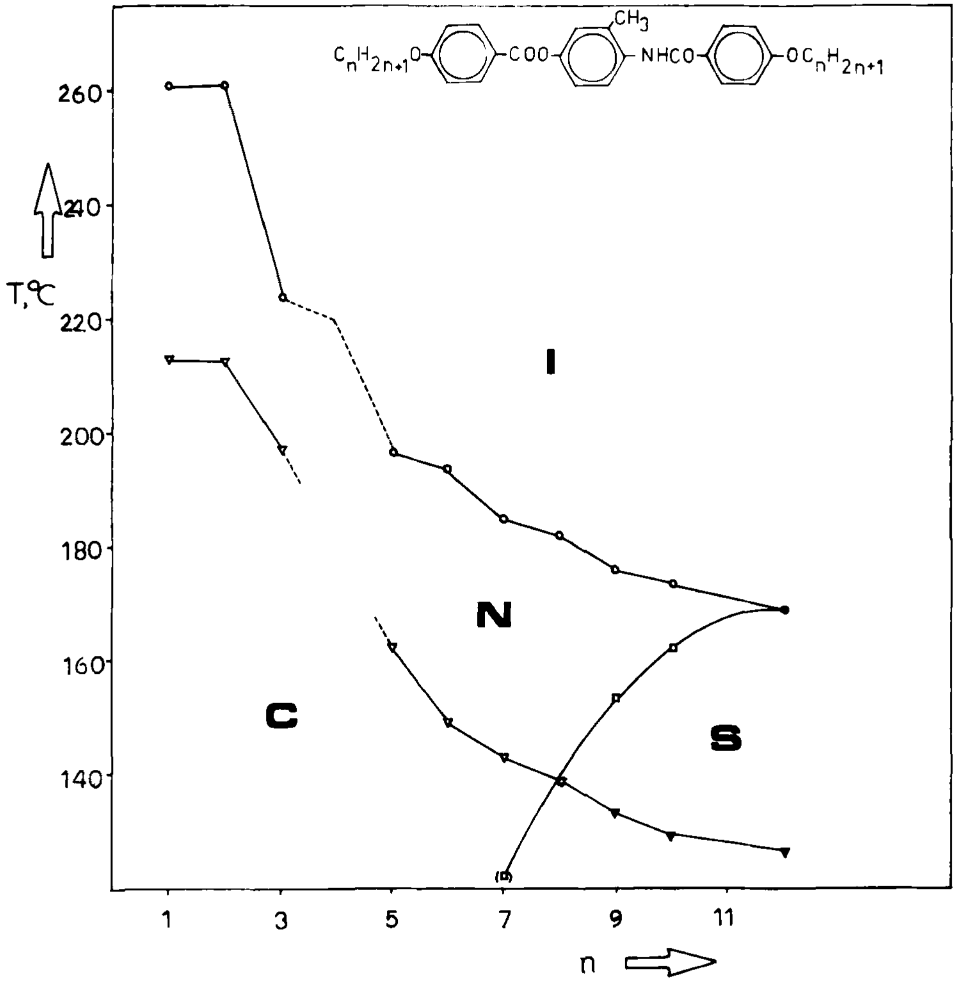


FIGURE 2 Phase transition data for ester-amides derived from 3-methyl-4-aminophenol and alkoxybenzoic acids.

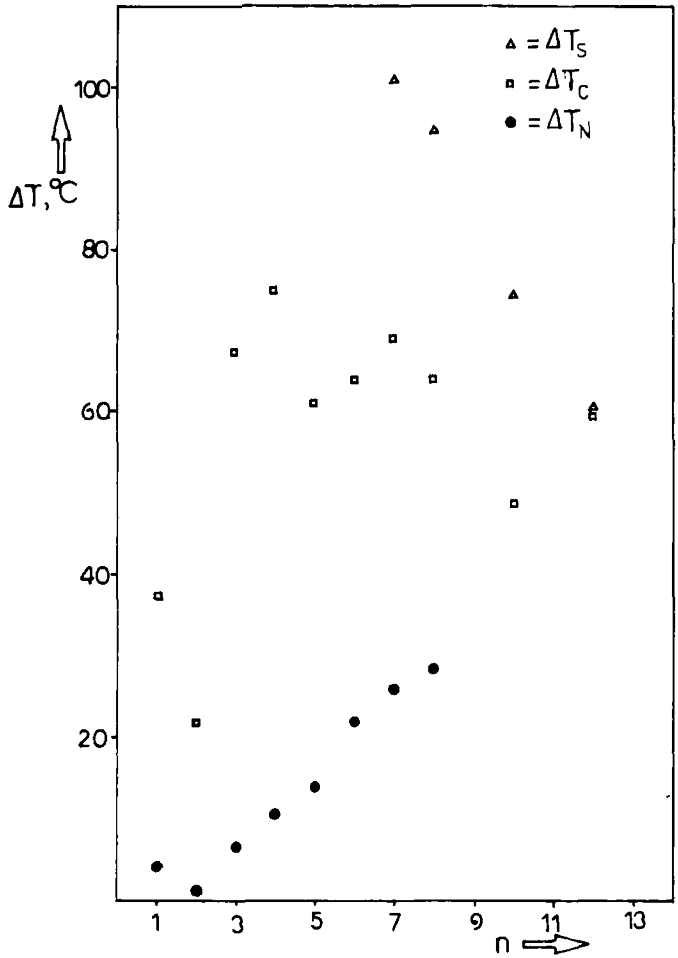


FIGURE 3 Differences in phase stability between ester-amides and diesters from alkoxybenzoic acids: no substituent in central ring.

two diagrams exhibit characteristics very similar to those for the corresponding diesters,[19,20] including alternation of nematic stability with odd and even values of *n*. The stabilization of smectic thermal stability for the unsubstituted series from octyloxy to decyloxy, and the subsequent decline to dodecyloxy, are not observed in the diester series (up to $n = 16$) but conform with the expectation that a maximum in smectic thermal stability will be reached before *n* becomes so large that the compound attains the character of a polymethylene. Comparison of the various transition temperatures for the two diester series and the two ester-amide series (Figures 3 and 4) shows: (i) the nematic phase is

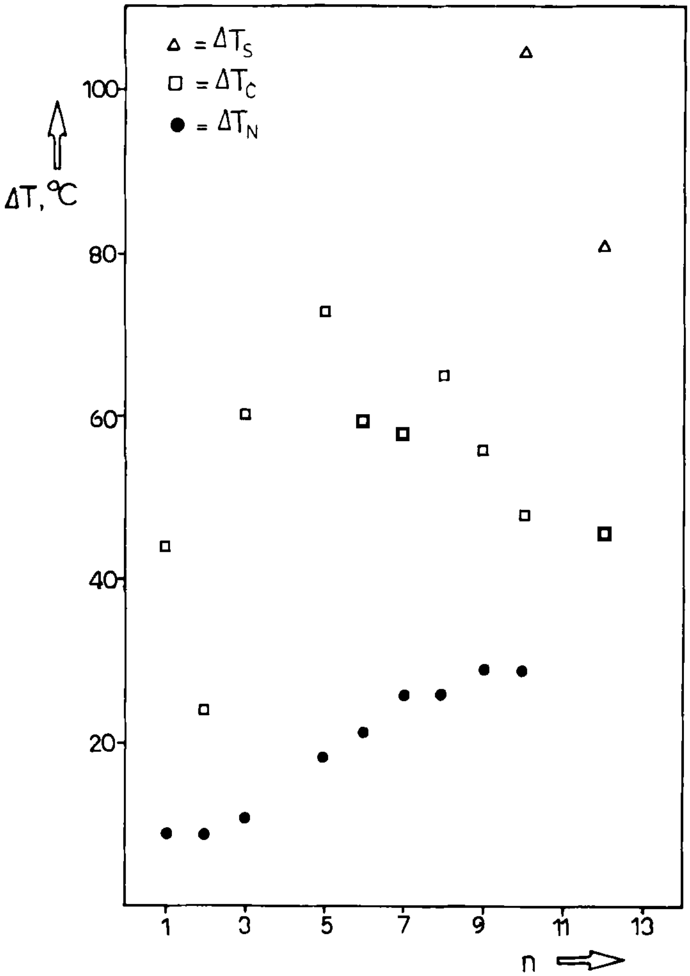


FIGURE 4 Differences in phase stability between ester-amides and diesters from alkoxybenzoic acids: methyl substituent in central ring.

more thermally stable in the ester-amide than in the diester series; (ii) the difference in stability of the nematic phase in the ester-amide series becomes greater as *n* increases; (iii) the smectic phase is more thermally stable in the ester-amide series than in the diester series; (iv) the difference in stability of the smectic phase in the ester-amide and diester series becomes less as *n* increases; (v) the crystalline phase is more thermally stable in the ester-amide series than in the diester series; (iv) the difference in stability of the crystalline phase in the ester-amide and diester series exhibits a maximum at about C_4–C_5.

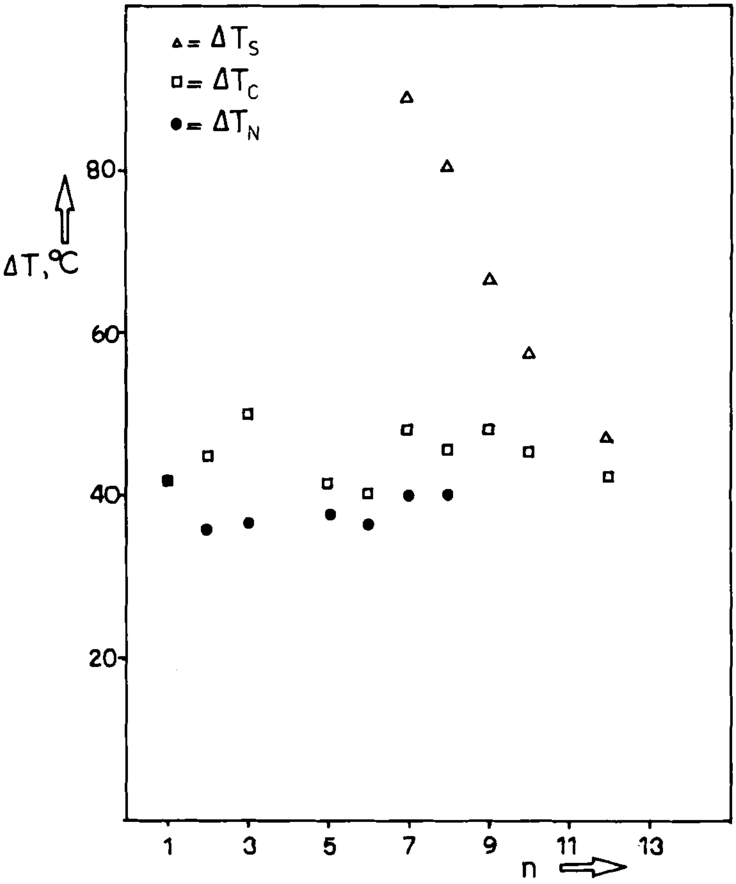


FIGURE 5 Differences in phase stability between ester-amides from alkoxybenzoic acids with and without substituent in central ring.

Comparison of the various transition temperatures for the ester-amide series and the methyl-substituted ester-amide series (Figure 5) shows that all three phases, nematic, smectic, and crystalline, are rendered less thermally stable by the methyl substituent in the central aromatic nucleus for reasons well developed by Gray.[21]

A small number of related compounds were also synthesized to test specific points. Inverting the ester group (compound 28) or the amide group (compound 30) so that the polarities of the two central linking groups were oriented in the same direction instead of in opposition and the conjugative interactions between the terminal groups and the carbonyl oxygen were altered,[14] lowered both the crystalline and nematic thermal stability. Compound 29, which differs from compound 28 in that the end substituents are unlike, rather unexpectedly had the higher crystalline thermal stability. Introducing a methyl substituent into the central ring of an ester-amide of type I where the end substituents were nitro (compound 32) gave reductions in both crystalline and nematic thermal stabilities, but the reductions were less than with any of the corresponding alkoxy end-substituted compounds. Introducing a substituent in the central ring *ortho* to the amide instead of to the ester group (compound 33) appeared to reduce the range of nematic stability, but a direct comparison of isomers is required to assess this point.

In view of the fact that certain polyester-amides containing *N*-methylated amide groups have been reported to exhibit limited thermotropic behavior,[2] the *N*-methylated analog of compound 7 was synthesized (compound 31). Despite its very low melting point, it showed no sign of either nematic or smectic behavior.

The effect of the amide group on ordered phase stability appears consistent with its rigidity and ability to form hydrogen bonds. Like the ester group, its preferred conformation is the *trans*-form. The degree of double bond character is reported to be higher for the amide than for the ester group,[22] and this is consistent with the somewhat higher nematic stability. Intermolecular hydrogen bonding, high polarity and polarizability are expected to lead to higher crystal and smectic phase thermal stability, as observed. Probably only the fact that the ester-amides examined are unsymmetrical about the plane normal to the main axis prevents them from exhibiting still higher crystal and smectic stability. Tertiary amide groups, which lack the capacity for hydrogen bond formation between each other and are relatively flexible, clearly possess little or no mesogenic activity in compounds of low molecular weight.

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