Molecular Crystals and Liquid Crystals

Liquid Crystals V. Nematic Materials Derived from p-Alkylcarbonato-p'-Alkoxyphenyl Benzoates

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Version of record first published: 21 Mar 2007.

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Liquid Crystals V. Nematic Materials Derived from p-Alkylcarbonato-p'-Alkoxyphenyl Benzoates[†][‡]

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Abstract—In our continued effort to synthesize materials which exhibit nematic behavior at room temperature, homologous p-alkylcarbonato-p-' alkoxyphenyl benzoates were prepared. Of the 48 compounds that were synthesized, 27 exhibited enantiotropic and 14 monotropic nematic properties while only 7 were not liquid crystalline. One binary mixture of enantiotropic derivatives had a nematic range of 27–73 °C while a ternary mixture exhibited nematic behavior between 24 and 76 °C. In addition, seven other mixtures had crystal → nematic transition temperatures below 30 °C.

Until several years ago, very few compounds were known to exhibit crystal → nematic transition temperatures at or below room temperature. The discovery of dynamic scattering in certain classes of nematic compounds,[1] however, prompted an investigation into the preparation of such nematic materials. Our efforts during the past several years have, therefore, been directed toward the preparation of comparatively low molecular weight Schiff base materials in order to accomplish this objective.[2,3] The compounds selected for the present study were not Schiff bases but they were derived from p-alkylcarbonato-p'-alkoxyphenyl benzoates (I).

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$$R'OCO-\bigcirc-C-O-\bigcirc-OR$$

I (R, R' = n-Alkyl)
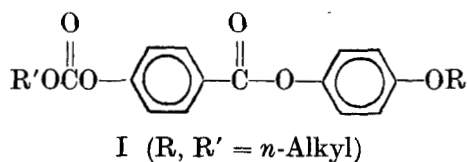
The compounds were prepared in three steps by the following synthetic route:

$$CO_2H \quad + Cl-COR' \xrightarrow{NaOH} CO_2H \xrightarrow{SOCl_2}$$

OH   II   OCOR'

II

$$C=O \quad Cl \quad + \quad OH \quad \xrightarrow{N} I$$

OCOR'   OR

III
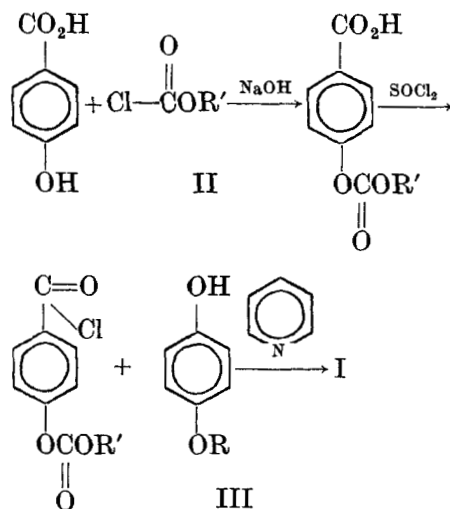
Both the alkyl chloroformates[4] (II) and alkoxyphenols[4] (III) contained from one to seven carbon atoms in a straight chain.[5] The products, which were obtained in 40 to 60% overall yield, were purified by repeated recrystallizations from hexane. Recrystallization was continued until the nematic-isotropic transition temperature was constant and reversible. This resulted in materials with resistivities of 10^9 to 10^{10} ohm-cm. The compounds were then characterized by elemental analysis.[6] The transition temperatures were measured in open capillary tubes with an Arthur H. Thomas Unimelt apparatus.[7] The results of this work are presented in Table 1.

Of the 48 compounds that were prepared, 27 exhibited enantiotropic and 14 monotropic nematic properties and only seven were not liquid crystalline.

In order to facilitate a better understanding of the effects of

TABLE 1 p-Alkylcarbonato-p'-Alkoxyphenyl Benzoates
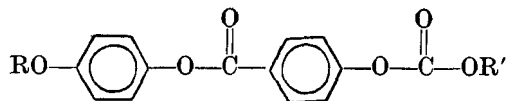
No.	R	R'	Crystal-Nematic Transition °C	Nematic-Isotropic Transition °C
1	CH_3	CH_3	—	115[a]
2	C_2H_5	CH_3	86	110
3	C_3H_7	CH_3	—	106 (83)[b]
4	C_4H_9	CH_3	91	96
5	C_5H_{11}	CH_3	—	109 (86)[b]
6	C_6H_{13}	CH_3	—	75[a]
7	C_7H_{15}	CH_3	52	66
8	C_8H_{17}	CH_3	—	80[a]
9	CH_3	C_2H_5	—	110 (82)[b]
10	C_2H_5	C_2H_5	—	104 (96)[b]
11	C_3H_7	C_2H_5	—	86[a]
12	C_4H_9	C_2H_5	—	98 (80)[b]
13	C_5H_{11}	C_2H_5	—	81 (78)[b]
14	C_6H_{13}	C_2H_5	75	91
15	C_7H_{15}	C_2H_5	70	83
16	CH_3	C_3H_7	—	78 (60)[b]
17	C_2H_5	C_3H_7	—	82 (79)[b]
18	C_3H_7	C_3H_7	—	76[a]
19	C_4H_9	C_3H_7	—	84 (71)[b]
20	C_5H_{11}	C_3H_7	—	71 (65)[b]
21	C_6H_{13}	C_3H_7	70	73
22	C_7H_{15}	C_3H_7	58	68
23	C_8H_{17}	C_3H_7	—	48[a]
24	CH_3	C_4H_9	—	70 (57)[b]
25	C_2H_5	C_4H_9	49	90
26	C_3H_7	C_4H_9	—	70 (67)[b]
27	C_4H_9	C_4H_9	74	81
28	C_5H_{11}	C_4H_9	53	69
29	C_6H_{13}	C_4H_9	44	84
30	C_7H_{15}	C_4H_9	45	74
31	C_8H_{17}	C_4H_9	—	77[a]
32	CH_3	C_5H_{11}	—	54 (53)[b]
33	C_2H_5	C_5H_{11}	59	74
34	C_3H_7	C_5H_{11}	67	72
35	C_4H_9	C_5H_{11}	53	74
36	C_5H_{11}	C_5H_{11}	45	85
37	C_6H_{13}	C_5H_{11}	42	76
38	C_7H_{15}	C_5H_{11}	47	72
39	CH_3	C_6H_{13}	—	57 (56)[b]
40	C_2H_5	C_6H_{13}	64	79
41	C_3H_7	C_6H_{13}	71	86
42	C_4H_9	C_6H_{13}	48	80
43	C_5H_{11}	C_6H_{13}	41	89
44	C_6H_{13}	C_6H_{13}	43	84
45	C_7H_{15}	C_6H_{13}	36	54
46	CH_3	C_7H_{15}	55	81
47	C_2H_5	C_7H_{15}	60	91
48	C_3H_7	C_7H_{15}	58	91

(a) Not nematic;   (b) Monotropic.

changes in molecular structure as a function of mesomorphic behavior, the data of Table 1 have been used to construct a series of phase transition plots. These diagrams (Figs. 1 through 13) illustrate the changes in phase transition temperatures with an increase in the length of an alkyl chain attached to one of the terminal positions of the molecule. It is well-known[8] that when the nematic-isotropic transition temperatures for homologous series of compounds, e.g., in a series of n-alkyl ethers or esters, are plotted against the number of carbon atoms in the alkyl chain, a regular alternation of the nematic-isotropic transition temperature occurs. This behavior, which was found to occur with all of the series reported here has been discussed[8] in terms of the interactions between terminal groups of adjacent molecules arranged in an end-to-end manner.

Another well-known phenomenon which occurs with liquid crystalline compounds as well as with some other organic compounds is a decrease in the melting points of the members of a homologous series with increase in the length of an alkyl chain. Since the melting characteristics of a compound are largely determined by the strength of intermolecular interactions in the crystal lattice, it follows that a reduction in the strength of these interactions by separation of the active centers of charge would produce lower melting materials. Thus, as we increase the length of an alkyl chain the dipolar (alkoxy) and polarizable (ester) centers of the molecule become further separated from one another, and lower melting points are produced.

In the first series of derivatives (Fig. 1), the methyl carbonato group produces such strong terminal intermolecular attractions that extension of the chain in the alkoxy portion (OR) does not produce a dramatic reduction in melting point until the chain contains seven carbon atoms. However, as we proceeded to increase the chain in the carbonato ester portion of the molecule, these terminal inter-actions were reduced. Thus, compounds which contain from four to six carbon atoms in the carbonato chain gave a lower melting series of derivatives and as a result, a larger number of enantiotropic mesomorphic compounds (Figs. 4, 5 and 6). Similar results were obtained when the alkoxy chain was kept constant and the carbonato chain was extended as illustrated in Figs. 7 through 12. A summary
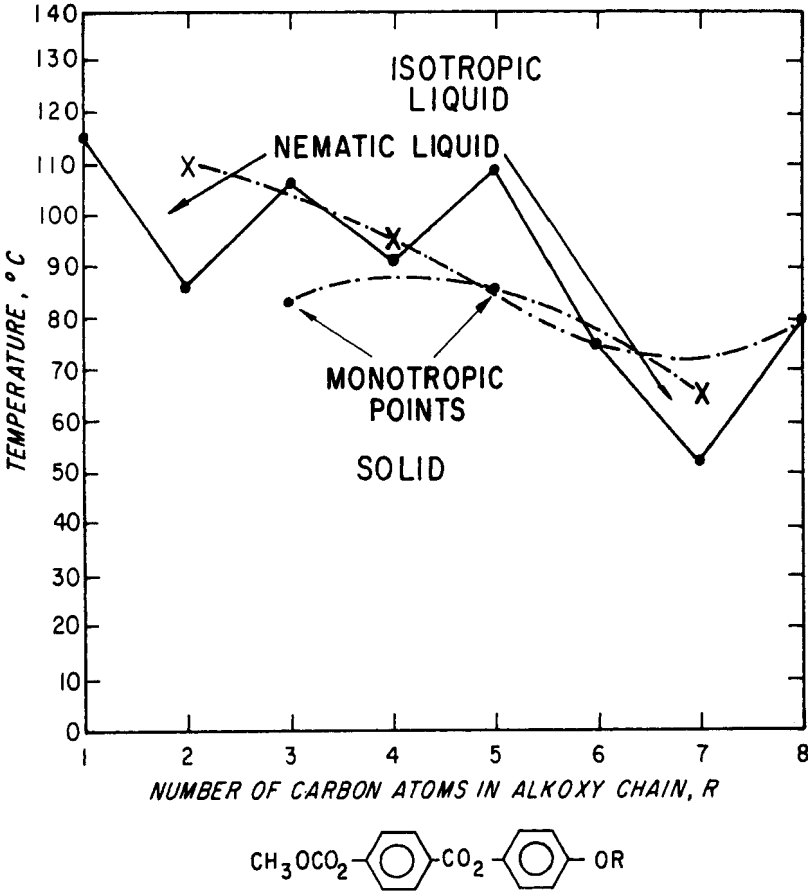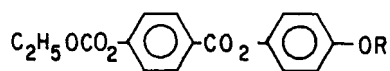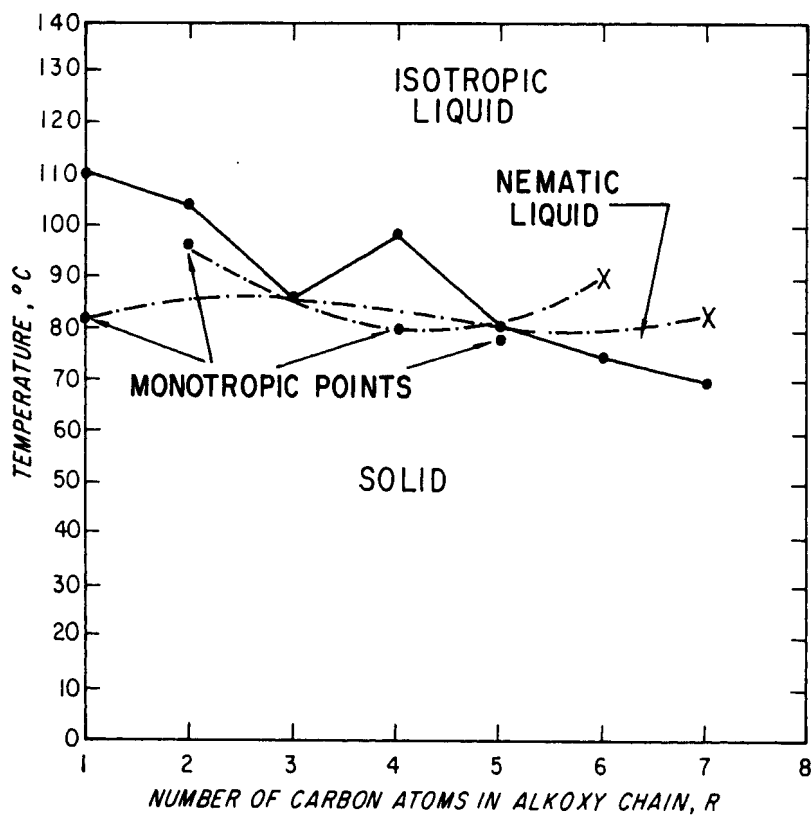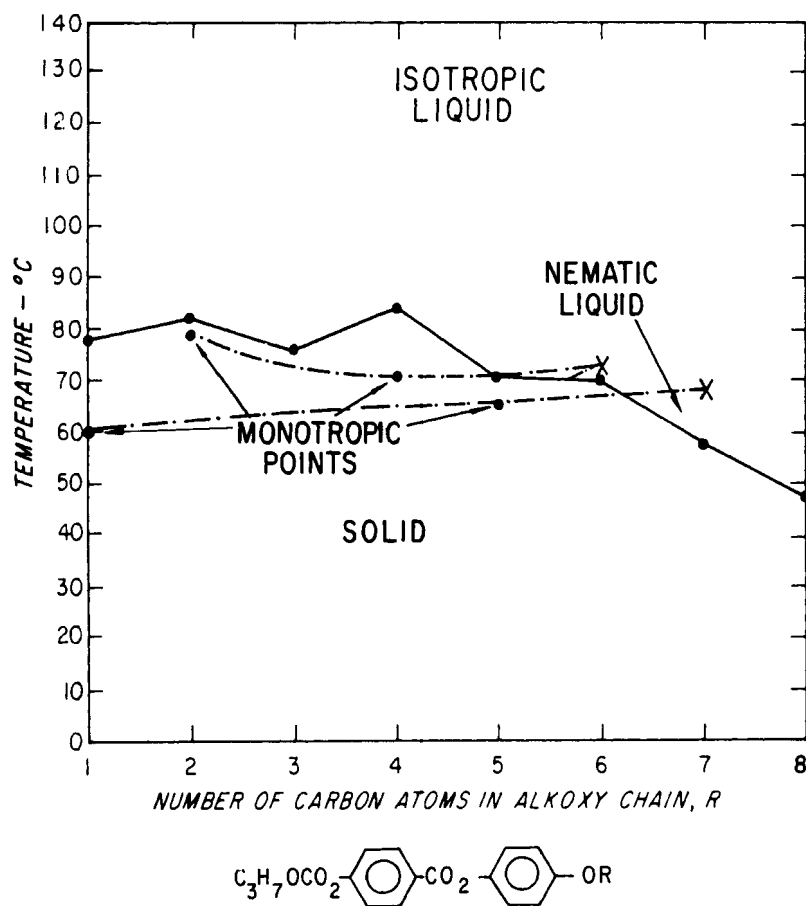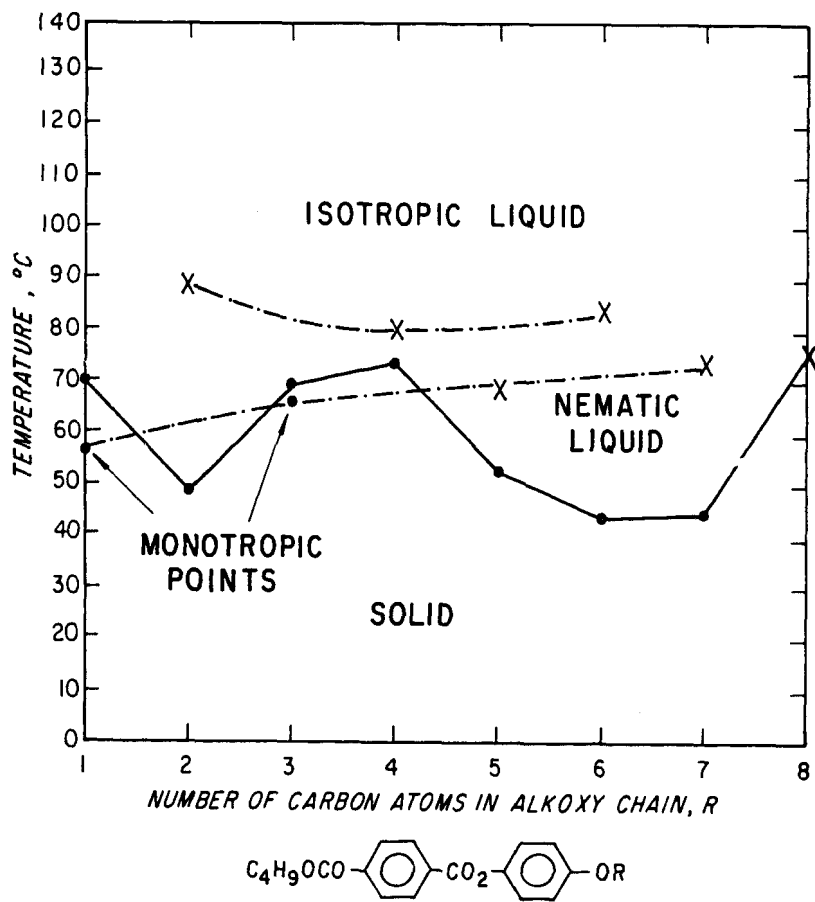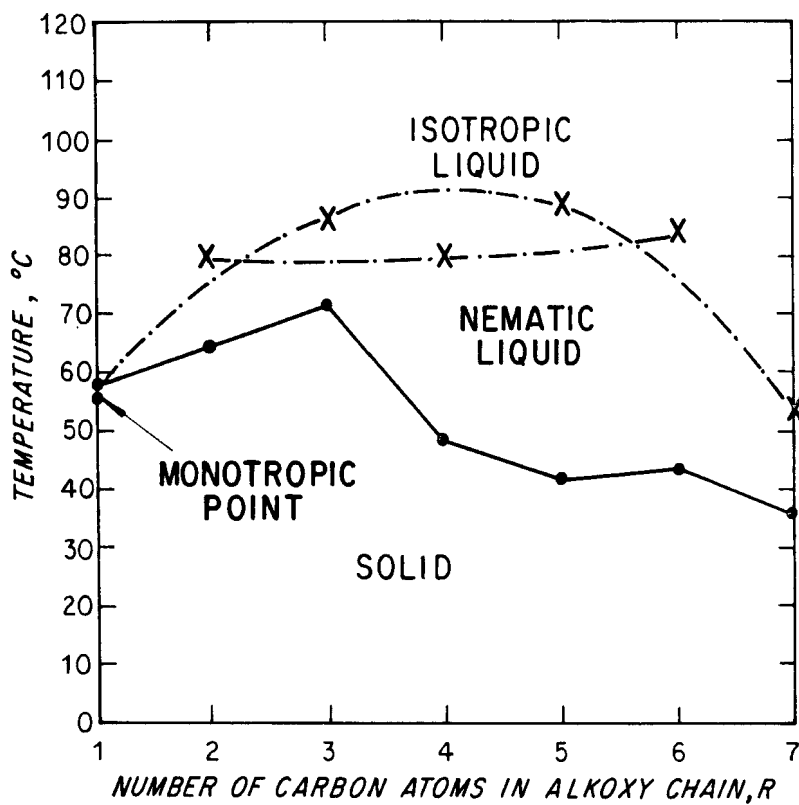
Figure 1

Figure 2

$$C_3H_7OCO_2 \bigcirc CO_2 \bigcirc - OR$$

Figure 3

Figure 4

Figure 5

$C_6H_{13}OCO_2$ —⟨O⟩— CO_2 —⟨O⟩— OR

Figure 6

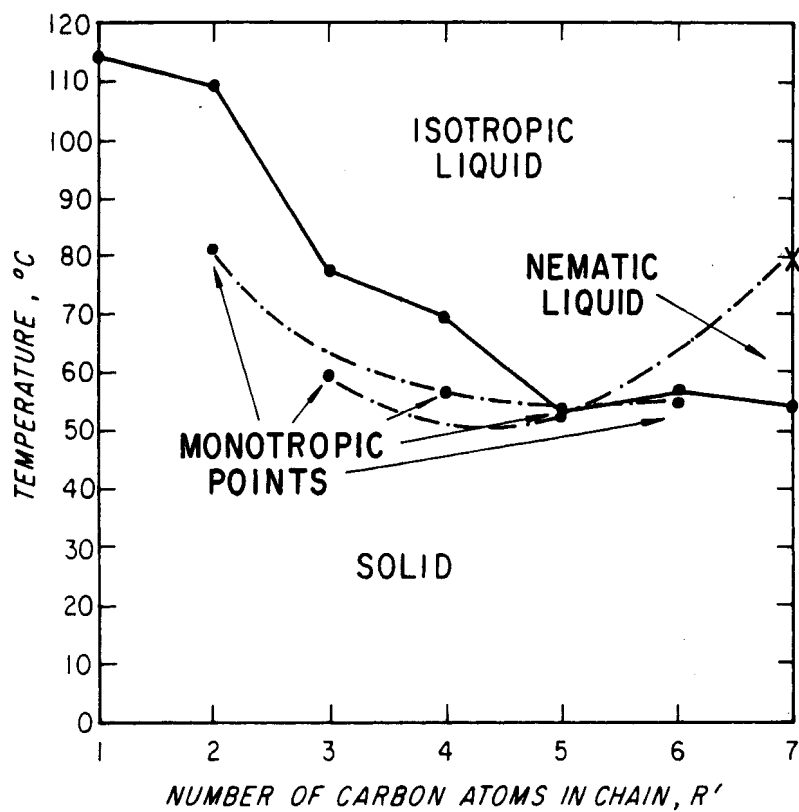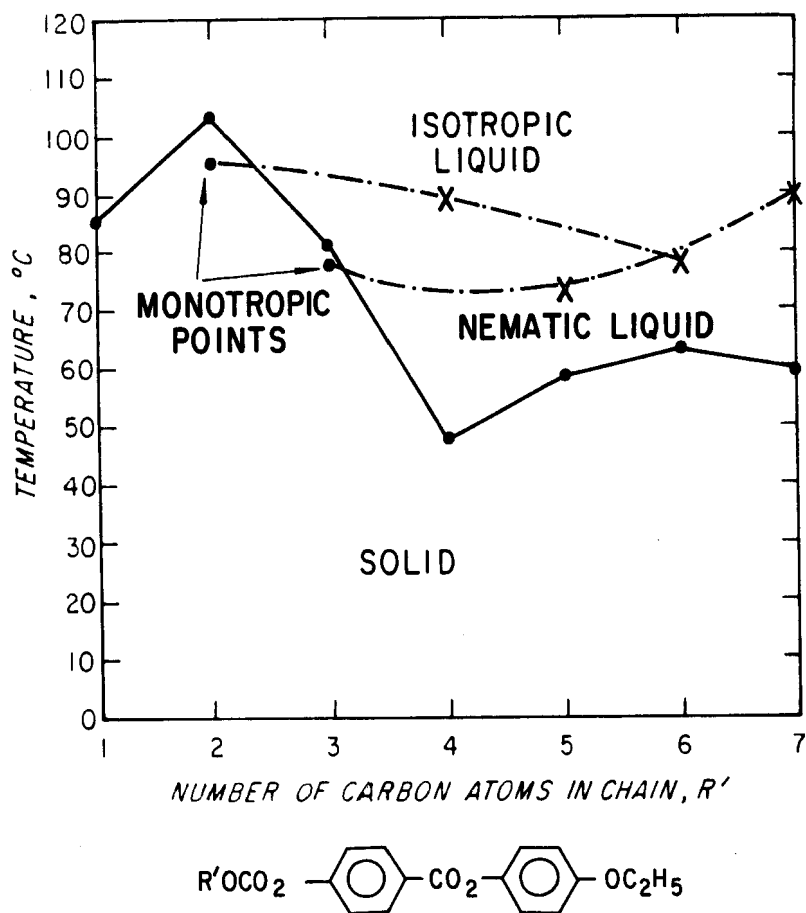$$R'OCO_2 -\!\!\langle\!\bigcirc\!\rangle\!- CO_2 -\!\!\langle\!\bigcirc\!\rangle\!- OCH_3$$
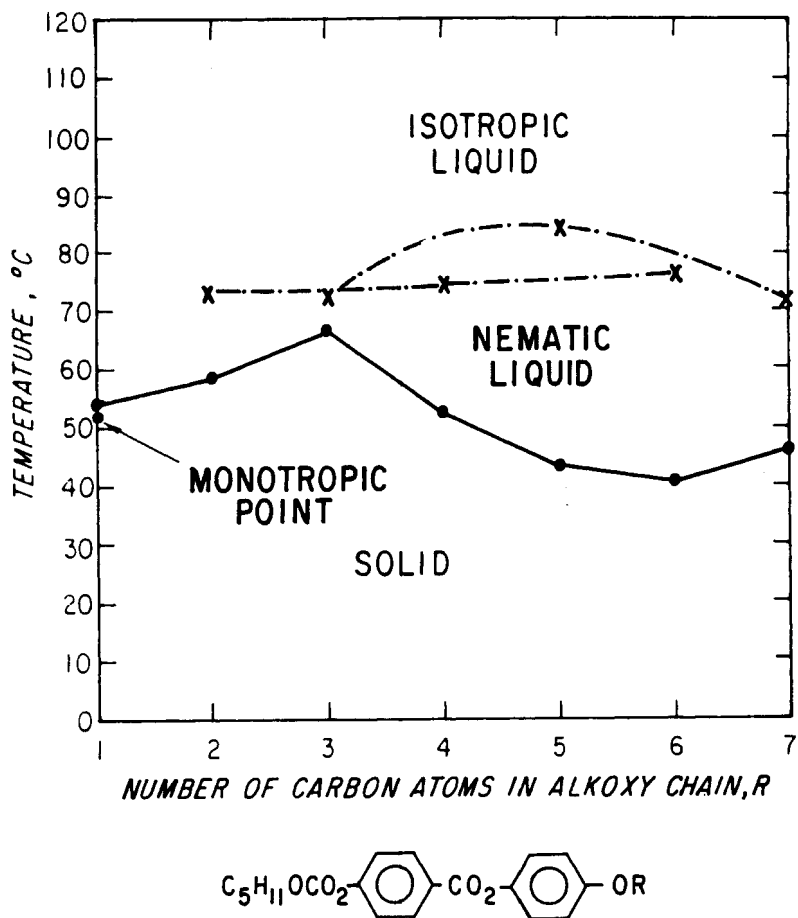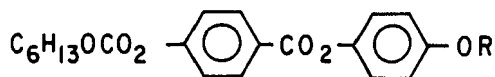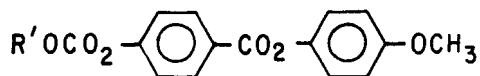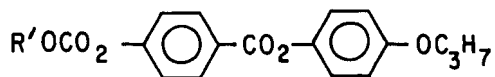
Figure 7

Figure 8

Figure 9
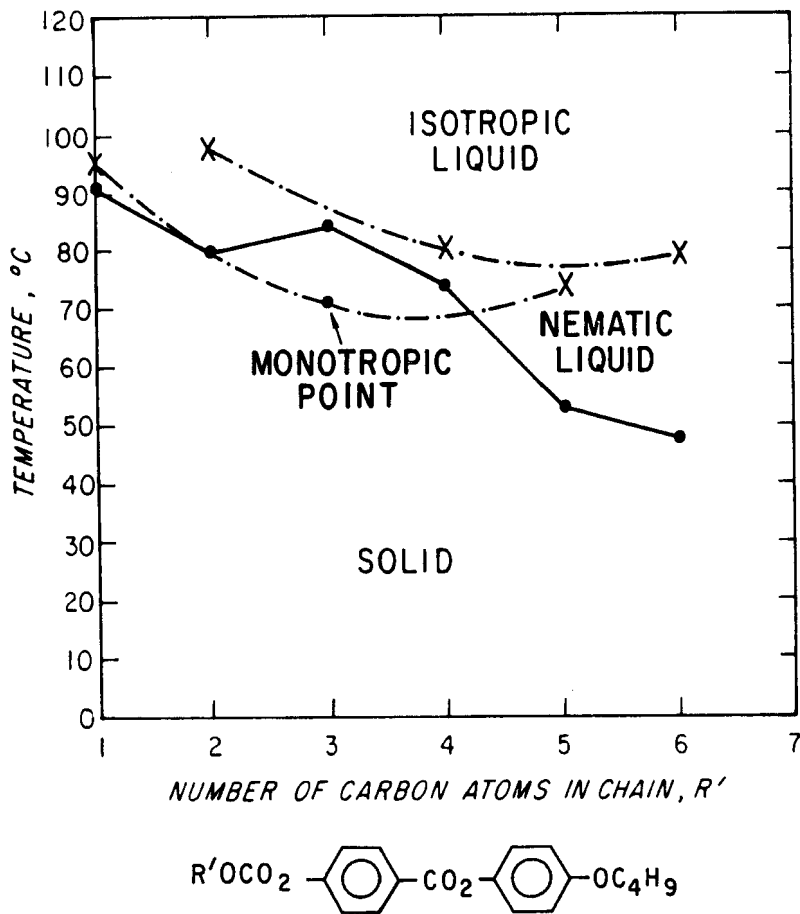
Figure 10
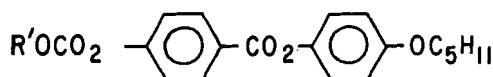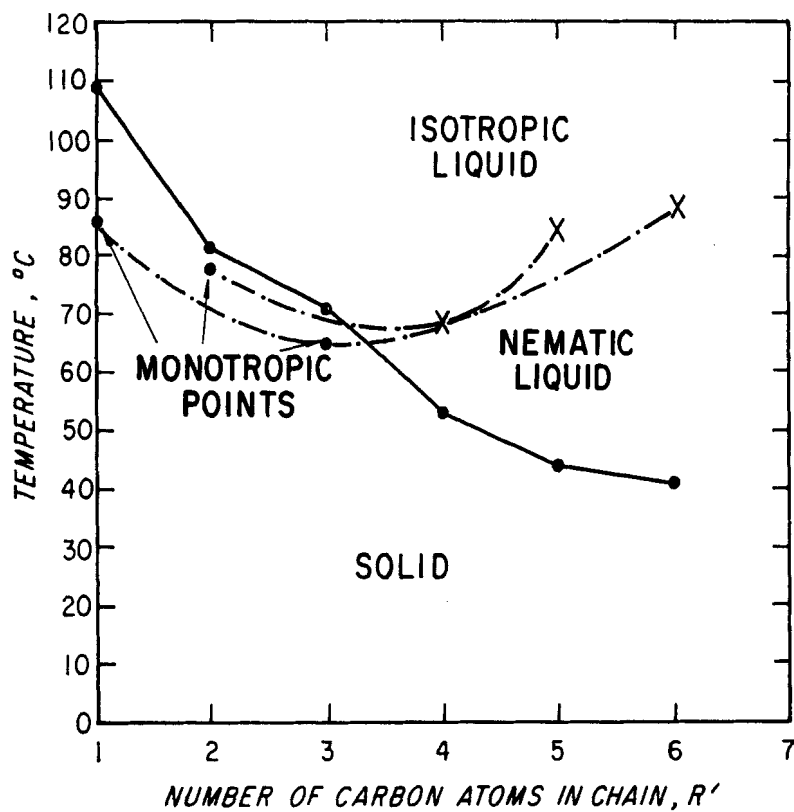
Figure 11

Figure 12
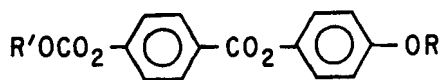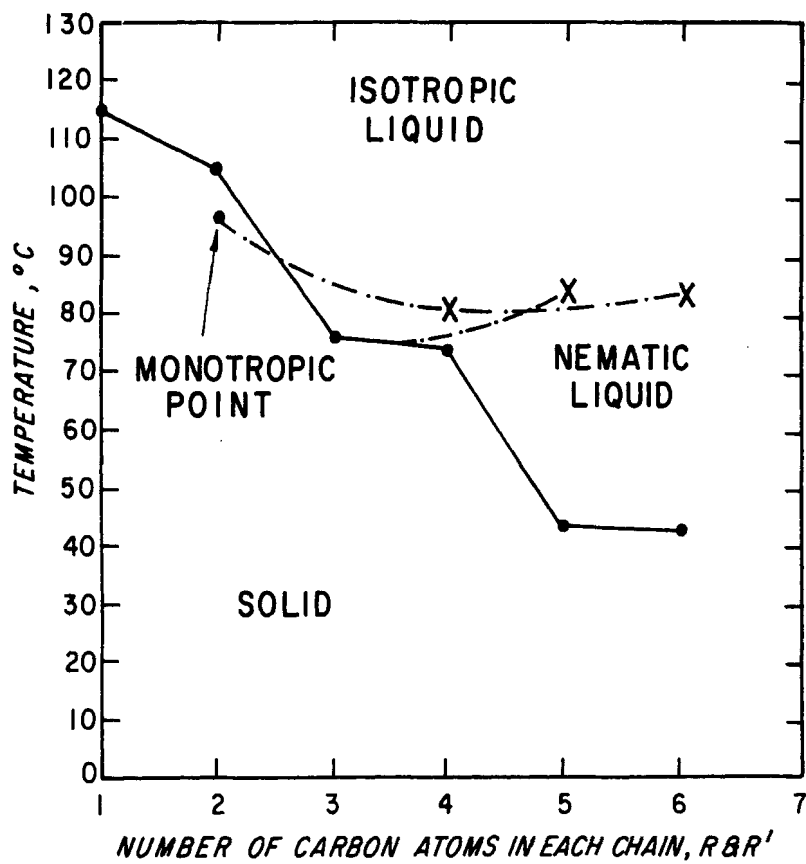
Figure 13

of this effect is presented in Fig. 13 which illustrates a dramatic reduction in melting point when both chains are increased simultaneously. This plot also shows a systematic increase in nematic thermal stability with increasing chain length.
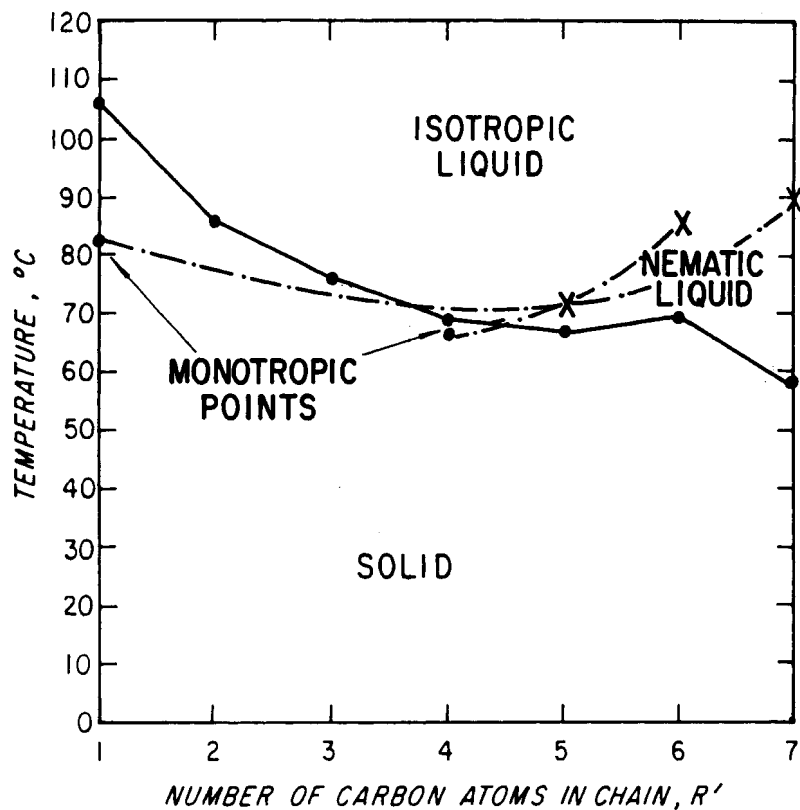
The nematic-isotropic transition temperatures for many homologous series of liquid crystalline compounds alternate regularly as the series[1] are ascended and smooth curves may be drawn through the transition temperatures for odd and even numbers as illustrated in Figs. 1–13. The shapes of the curves vary substantially from series to series.[10] In the present case, the situation is complicated by the fact that the series are quite short and that some involve non-liquid crystalline comp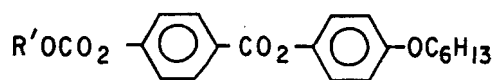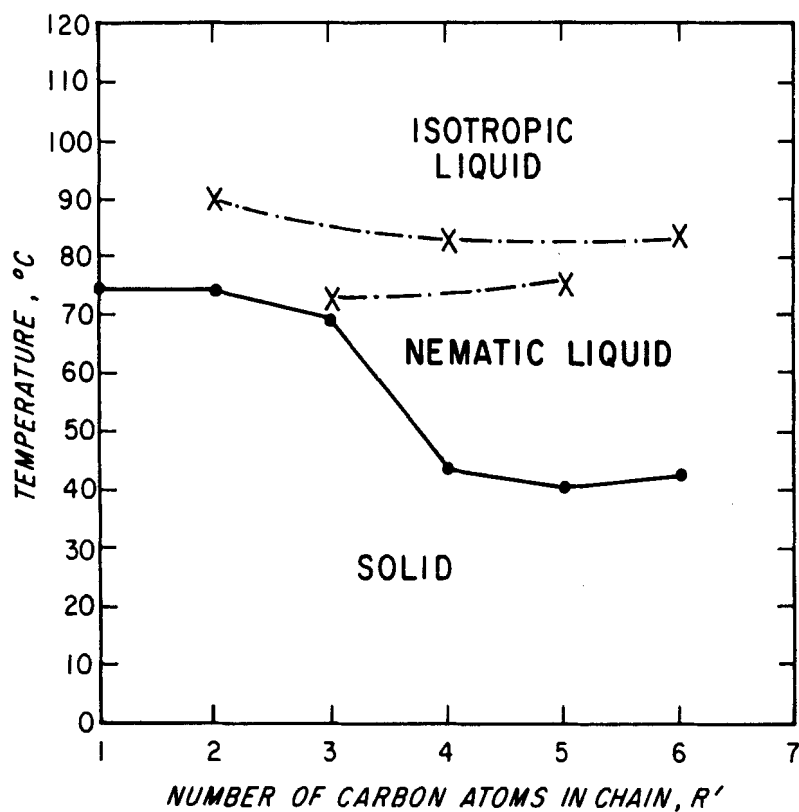ounds and also monotropic transitions. Broadly speaking, however, the transition temperatures change in a fairly regular manner as the series are ascended. In certain cases (e.g., Figs. 6 and 8), the transition lines for odd and even homologues cross. It will be interesting to see if this latter trend is observed in more extended series of esters of this kind.

In several cases (e.g., the n-propoxy derivatives shown in Figs. 2 and 3) monotropic transitions were not observed. In these and other cases where monotropic transitions might have been expected, supercooling of the melt apparently did not occur to an adequate extent to observe the change.

The above results might lead to the conclusion that a further increase in the lengths of the chains in both the alkyl carbonato and alkoxy groups would produce compounds with lower melting points and even wider nematic changes. Past experience,[8,12,13] however, has shown that chain lengths of eight or more carbon atoms produce such weak terminal interactions that the critical balance of lateral-to-terminal attractive forces is upset, and the lateral interactions become important. An increase in the ratio of lateral-to-terminal cohesions always results[8] in the appearance of smectic behavior. Further increases in the chain length then result in increased smectic thermal stability and shorter nematic ranges. In order to produce materials with lower melting points and wide nematic ranges, it was therefore necessary to use a mixture of nematic compounds.

Mixtures of non-mesomorphic compounds with nematic compounds have been investigated previously. These systems are always

characterized by a sharp decrease in both the nematic → liquid and crystal → nematic transition temperature with increasing concentration of non-mesomorphic component. An example of this type of system has recently been reported.[11]

Mixtures of two or more nematic compounds which possess subtle differences in molecular structure do not exhibit well-defined minima in their nematic → liquid transition temperatures with molar composition although eutectic points for the crystal → nematic transition temperatures are obtained. An example of this phenomenon was first reported by Demus.[10] Thus, the nematic → isotropic liquid transition temperatures form a smooth curve over the entire range of molar composition.

These effects have been explained[11] by postulating the existence of a " nematic secondary structure " which consists of freely inter-mobile molecular strands having a head-to-tail sequence. Binary and ternary mixtures of several of the carbonato derivatives in Table I showed similar results. Thus, a series of binary mixtures of compounds *44* and *45* was prepared and the transition temperatures measured. The results are presented in Table 2 and Fig. 14.

TABLE 2   Binary Mixtures of Carbonato Esters

$$H_{13}C_6OCO\langle\bigcirc\rangle CO\langle\bigcirc\rangle OR$$

A (R = C$_6$H$_{13}$),   B (R = C$_7$H$_{15}$)
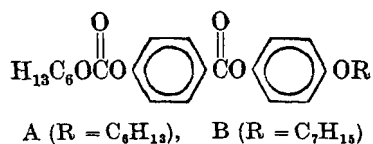
| Mole % | | Transition Temperatures, °C | |
A	B	Crystal → Nematic	Nematic → Isotropic
100	—	44	84
90	10	41	84
80	20	38	82
70	30	37	79
60	40	35	77
50	50	33	74
40	60	27	73
30	70	28	71
20	80	34	68
10	90	35	67
—	100	36	54
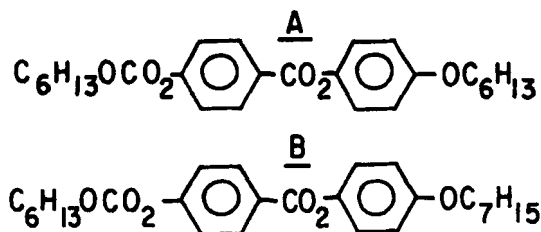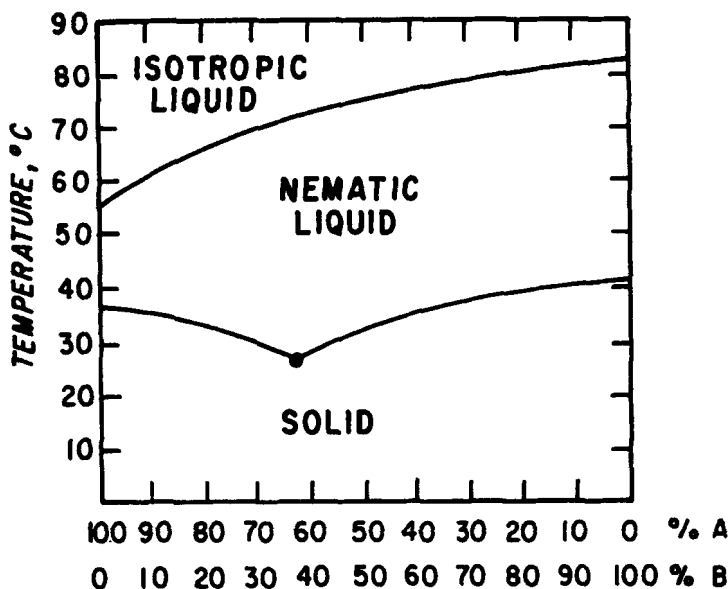
Figure 14.   Binary phase diagram of mixtures taken from the series:
$C_6H_{13}OCO_2C_6H_4CO_2C_6H_4$ OR where R = C_6H_{13} (A) and C_7H_{15} (B).

The eutectic mixture (40% A, 60% B) had a crystal → nematic transition temperature at 27 °C and a nematic isotropic transition at 73 °C.   The eutectic composition represents an approximate 2:1 mole ratio of the low melting to the high melting component in accordance with the requirements for secondary structure formation as proposed by Pohl.[11]   It was possible to obtain materials with even lower crystal → nematic transition temperatures by preparing ternary mixtures containing compounds 36, 37 and 38.   These results are shown in Table 3 and a ternary phase diagram is presented in Fig. 15.   The eutectic mixture (20% A, 40% B and 40% C) had

a crystal → nematic transition temperature at 24 °C and a nematic → isotropic transition at 76 °C. In addition, seven other mixtures which had crystal → nematic transition temperatures below 30 °C were prepared by this technique.

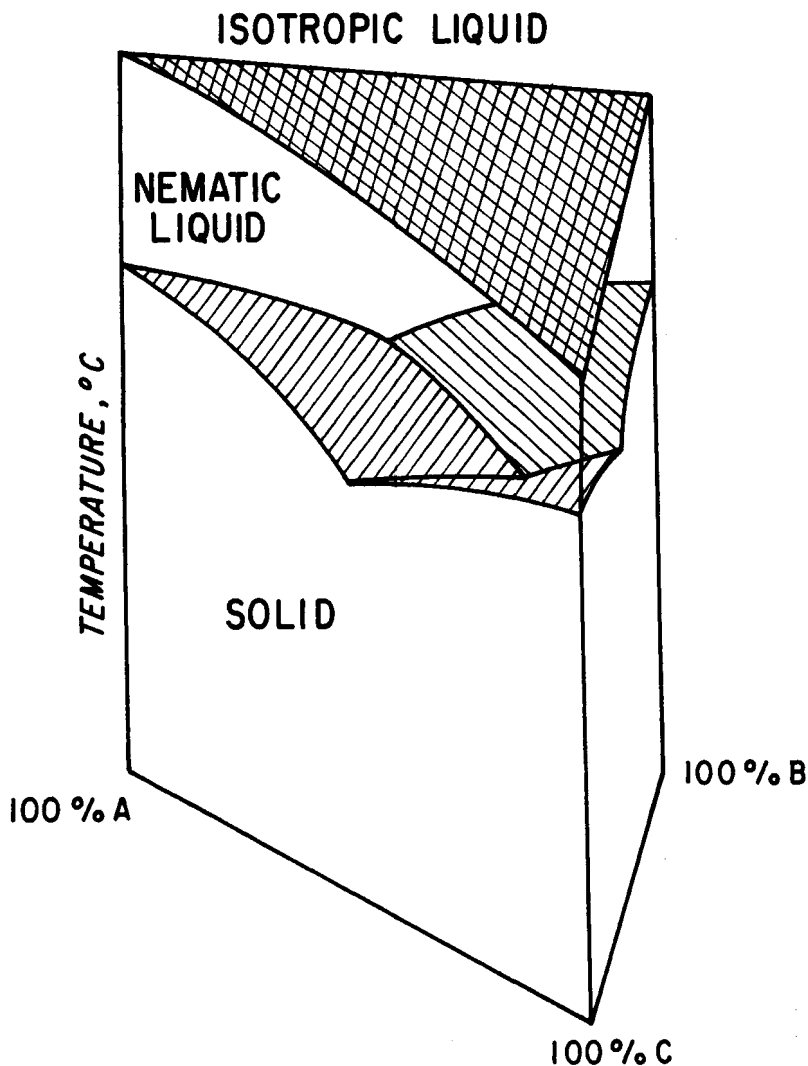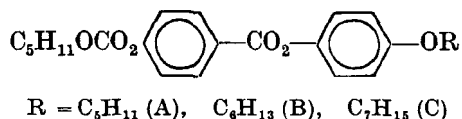Figure 15. Ternary phase diagram of compounds *36*(A), *37*(B), and *38*(C).

TABLE 3   Ternary Mixtures of Compounds taken from the Series:

$$C_5H_{11}OCO_2 \langle\bigcirc\rangle - CO_2 - \langle\bigcirc\rangle - OR$$

R $= C_5H_{11}$ (A), C_6H_{13} (B), C_7H_{15} (C)

| | Mole % | | Transition Temperatures, °C | |
A	B	C	Crystal → Nematic	Nematic → Isotropic
50	50	0	30	80
0	50	50	35	74
50	0	50	28	83
33	33	33	27	79
10	15	75	38	74
15	75	10	29	76
75	10	15	30	82
40	40	20	31	78
40	20	40	26	79
20	40	40	24	76
50	25	25	27	78
25	25	50	26	74
25	50	25	31	77

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7. We have found no significant difference between the transition temperatures obtained with this apparatus and that obtained by the differential scanning calorimetric technique.
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13. Unpublished results.