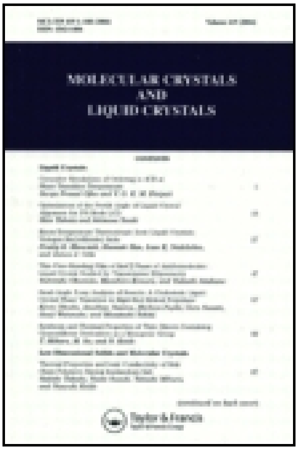

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Thermal Properties of New Homologous Series of 4-(4-Alkoxyphenoxycarbonyl)phenyl 4-(4-Nitrobenzoyl)benzoates

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Thermal Properties of New Homologous Series of 4-(4-Alkoxyphenoxycarbonyl)phenyl 4-(4-Nitrobenzoyl)benzoates

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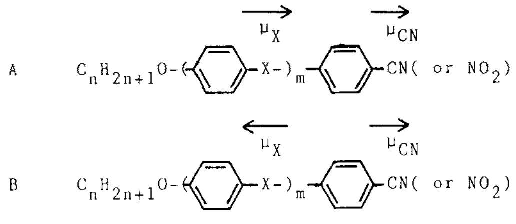
A homologous series of 4-(4-alkoxyphenoxycarbonyl)phenyl 4-(4-nitrobenzoyl) benzoates has been prepared. The octyloxy and nonyloxy homologs give rise to three kinds of smectic A phases (S_1, S_2, and S_3) and a nematic one, and the decyloxy homolog gives rise to two kinds of the smectic A phases (S_1 and S_3). The S_1 and S_3 phases are isomorphous with a partially bilayered smectic A phase (S_{Ad}) of CBOOA and a bilayered smectic A phase (S_{A2}) of 4-(4-pentylphenoxycarbonyl)phenyl 4-cyanobenzoate, respectively. The S_2 phase may correspond to the antiphase ($S_{\tilde{A}}$) of a smectic A phase. These phase transitions are observed only by the differential scanning calorimeter. Their microscope textures are quite similar to each other.

INTRODUCTION

It is well known that some mesogenic molecules having a cyano or a nitro group as the terminal function form antiparallel correlations,[1-4] and give rise to an interesting thermal behavior such as an induced smectic phase in a binary mixture or a reentrant phenomenon. Recent works have shown that an intermolecular dipole-dipole interaction plays a very important role in determining the arrangement of molecules in the mesophases. The general features of the molecules are illustrated as follows.



X = -COO-, -CH=N-, -CH=CH-, none, etc

In these systems, the dipoles arising from the linkages also play an important role in determining thermal behavior.[5-7] Therefore, the two classes are slightly different not only in their dielectric behavior but also in their thermal one.

The molecules in system A with $m = 1$ usually give rise to nematic and/or smectic properties, and frequently reveal an induced smectic phase or a large enhanced smectic phase[8-15] in nonpolar mesogenic solvents. In system A with $m = 2$, the molecules frequently reveal a reentrant phenomena.[16-18] In system B ($m = 2$), the reentrant phenomenon is relatively rare.[19] Instead the molecules give rise to multiple smectic A phases and experience smectic A–smectic A transitions.[20,21]

In the present work, we describe the thermal properties of a homologous series of 4-(4-alkoxyphenoxycarbonyl)phenyl 4-(4-nitrobenzoyl)benzoates. We have studied only a few higher homologs in the series, since our main interest was to elucidate the thermal properties of the smectic A phase.

EXPERIMENTALS

Materials

4-(4-Nitrobenzoyl)benzoic acid was obtained by a chromic acid oxidation of 4-nitro-4′-methylbenzophenone in a solvent mixture of acetic acid and sulfuric acid: mp > 280 °C, IR: $\nu(\text{—COO—}) = 1675$ and $\nu(\text{—CO—}) = 1650\ \text{cm}^{-1}$. The reaction of 4-(4-nitrobenzoyl)benzoic acid chloride and 4-(4-alkoxybenzoyloxy)phenols in a solvent mixture of benzene and pyridine (95 : 5) at 80 °C gave the corresponding esters. The esters were purified by column chromatography on silica-

TABLE I

Elemental analyses

n	Formula	Calcd.(%)			Found(%)		
		C	H	N	C	H	N
4	$C_{31}H_{25}O_8N$	69.01	4.67	2.60	68.84	4.64	2.59
5	$C_{32}H_{27}O_8N$	69.43	4.92	2.53	69.44	4.93	2.45
6	$C_{33}H_{29}O_8N$	69.83	5.15	2.47	69.94	5.19	2.48
7	$C_{34}H_{31}O_8N$	70.21	5.37	2.41	70.02	5.46	2.33
8	$C_{35}H_{33}O_8N$	70.57	5.58	2.35	70.45	5.67	2.27
9	$C_{36}H_{35}O_8N$	70.92	5.79	2.30	70.87	5.85	2.21
10	$C_{37}H_{37}O_8N$	71.25	5.98	2.25	71.07	6.01	2.09

gel, where a mixture of pet. ether (b.p. 30–40 °C) and ether (90 : 10–80 : 20) was used as the eluting solvent, followed by recrystallization from absolute ethanol, IR : ν(—COO—) = 1735 and ν(—CO—) = 1660 cm^{-1}. CBOOA was purchased from BDH Chemical Co, and recrystallized three times from absolute ethanol. Elemental analysis calculated for $C_{22}H_{26}N_2O$: C, 79.01; H, 7.84; N, 8.37. Found: C, 78.89; H, 7.81; N, 8.21. This compound underwent the phase transitions: C-74.6-S_A-84.9-N-109.2-I(T/ °C). 4-Pentylphenyl 4-(4-cyanobenzoyloxy)benzoate was prepared according to a literature method.[22] This compound underwent the phase transitions: C-125-S_A-139-N-256-I.

Elemental analyses for the present series are summarized in Table I.

Method

Transition temperatures were determined using a Nikon Model POH polarizing microscope fitted with a Mettler FP 52 heating stage and a FP 5 control unit, and a Daini-Seikosha SSC-560 differential scanning calorimeter (DSC). Indium (99.9%) was used as a calibration standard at a heating rate of 5 °C/min.

RESULTS

The DSC recordings for the octyloxy homolog are shown in Figure 1a.

The DSC recording on the first heating reveals three endotherms arising from the crystal–smectic A at 146.0 °C (ΔH = 54.7 kJ/mol), smectic A–nematic at 155.5 (0.7), and nematic–isotropic transitions at

198.0 (1.63) (run 1 Figure 1a). The DSC recording on the cooling stage at a cooling rate of 5 °C/min (run 2, Figure 1a) reveals three exotherms arising from the isotropic–nematic transition at 196.0, nematic–smectic A at 155.5, and recrystallization at 127.0, and additional two exotherms at 150.5 and 145.5 °C. The exothermal peaks at 155.5 °C (ΔH = 0.88 kJ/mol), 150.5 (0.61), and 145.5 (0.62) reveal complicating features compared with those of the isotropic–nematic and smectic–crystal transitions. The phase transitions in Figure 1 are

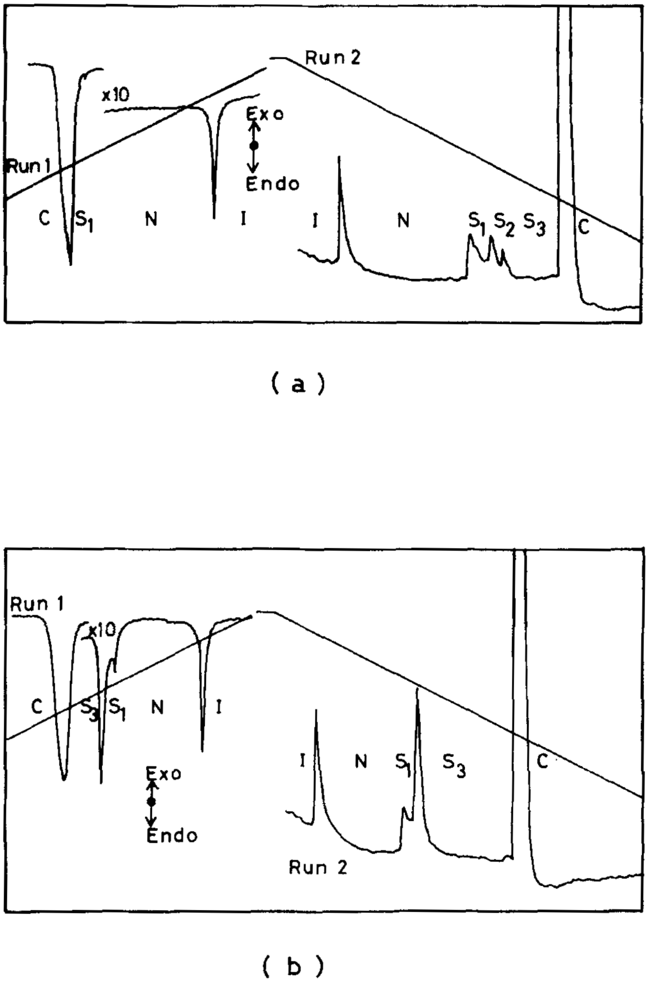


FIGURE 1 DSC thermograms for (a) the octyloxy and (b) decyloxy homologs.

almost independent of the cooling rate between 1 and 10 °C/min. As will be assigned later, these phases are smectic A phases, namely, S_1, S_2, and S_3, respectively. On the other hand, the classical microscopic observations between glass plate and cover slip reveal only two mesophases: the nematic and only one smectic A phases. The S_2–S_3 phase transition could not be detected because these phases reveal very similar textures which are shown in Figure 2.

The highest smectic A phase (S_1) shows a typical fan-shaped texture, and the other phases, S_2 and S_3 show somewhat broken fan-shaped textures which are very similar to each other. The microscopic observation of the S_2–S_3 phase transition was very difficult, since both smectic phases had similar textures. The DSC thermograms for the decyloxy homolog are shown in Figure 1b. The DSC recordings reveal four endotherms arising from crystal–smectic (S_3) at 144.0 °C (ΔH = 45.2 kJ/mol), smectic (S_3)–smectic (S_1) at 160.5 (1.76), smectic (S_1)–nematic at 164.0 (0.57), and nematic–isotropic transitions at 192.0 (1.76) on the first heating, and four enantiotropic exotherms on the cooling stage (run 2). An interesting fact in this case is that the latent heat for the S_3–S_1 transition is 1.76 kJ/mol which is comparable with that (1.76 kJ/mol) for the nematic–isotropic one. The textures of the S_1 and S_3 phases are very similar to those in Figures 2a and 2c, respectively.

In order to identify these smectic phases, the isobaric diagrams for the mixtures of the octyloxy and nonyloxy homologs, and the octyloxy and decyloxy homologs were examined. The results are shown in Figure 3, in which all data were taken on the cooling stage at a cooling rate of 5 °C/min. In Figure 3a, the isotropic–nematic, nematic–S_1, S_1–S_2, and S_2–S_3 transitions show almost linear correlation with composition indicating that both compounds have a very similar thermal behavior. In Figure 3b, the S_1 and S_3 phases of the decyloxy homolog are isomorphous with the S_1 and S_3 phases of the octyloxy one. On the other hand, the S_2 phase of the octyloxy homolog disappears in the middle region of the diagram.

In order to characterize these smectic phases, the isobaric diagrams for the mixtures of CBOOA and the nonyloxy homolog, and 4-pentylphenyl 4-(4-cyanobenzoyloxy)benzoate and the decyloxy homolog were examined. The results are shown in Figure 4.

Although smectic A–nematic transition temperatures show a positive deviation from the additivity in Figure 4a, the S_1 phase of the nonyloxy homolog is isomorphous with the smectic A phase of CBOOA. On the other hand, the thermal stabilities of both S_2 and S_3 phases rapidly decrease with increasing a composition of CBOOA, and

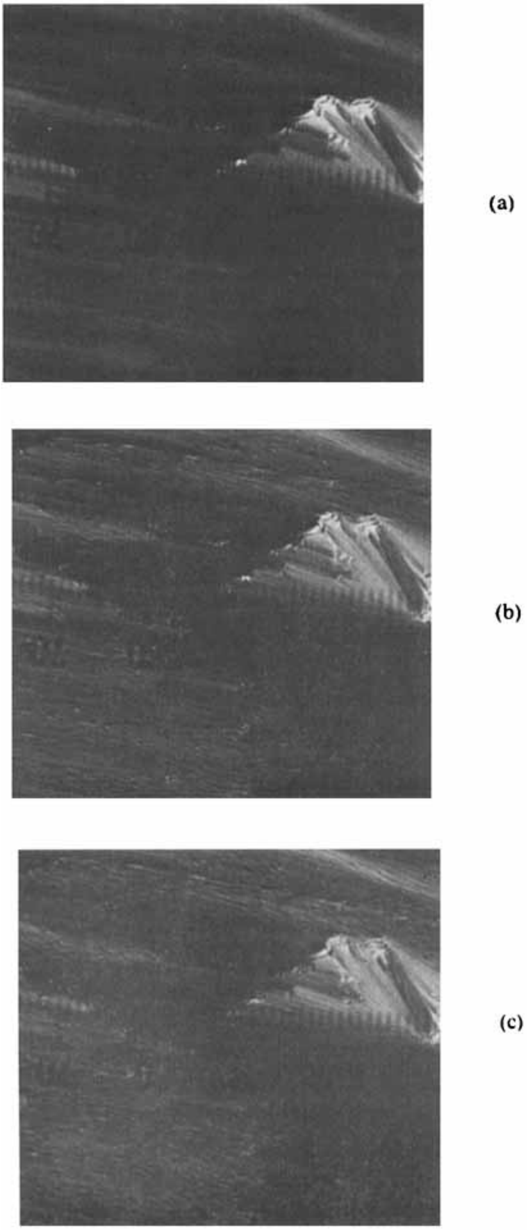
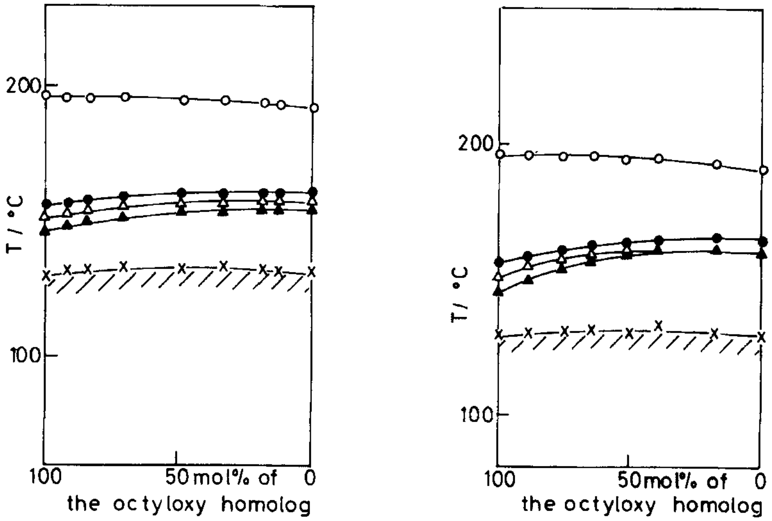


FIGURE 2 Micrographs (100X) for the octyloxy homolog: (a) S_1 (at 152.0 °C), (b) S_2 (at 148.0 °C), and (c) S_3 phases (at 142.0 °C).

both phases disappear in the middle region of the diagram. Although the S_3–S_1 or –nematic transition temperatures in Figure 4b show considerable non-ideal solution behavior, the S_3 phase of the decyloxy homolog is isomorphous with the smectic A phase of 4-pentylphenyl 4-(4-cyanobenzoyloxy)benzoate. On the other hand, the S_2 phase disappears in the middle region of the diagram. The thermal data are summarized in Table II, and the transition temperatures are plotted against *n* in Figure 5.

The virtual transition temperatures in Table II were evaluated from an extrapolation of the isobaric diagram for a mixture of the octyloxy and heptyloxy homologs. The nematic–isotropic transition temperatures gradually decrease and reveal a typical even–odd effect, with increasing the carbon number, *n* in the alkoxy chain. The nematic–isotropic transition temperatures for this series are lower than those for a homologous series of 4-alkoxyphenyl 4-(4-cyanobenzoyloxy)benzoates, whereas the formers have larger cores than the



(a)

(b)

FIGURE 3 Isobaric diagrams: (a) a mixture of the octyloxy and nonyloxy homologs. (b) a mixture of the octyloxy and decyloxy homologs. The horizontal lines represent a transition to a metastable crystalline forms. The diagrams were obtained from DSC thermograms on a cooling stage. ○; isotropic–nematic, ●; nematic–S_1, △; S_1–S_2, and ▲; S_1– or S_2–S_3 transitions.

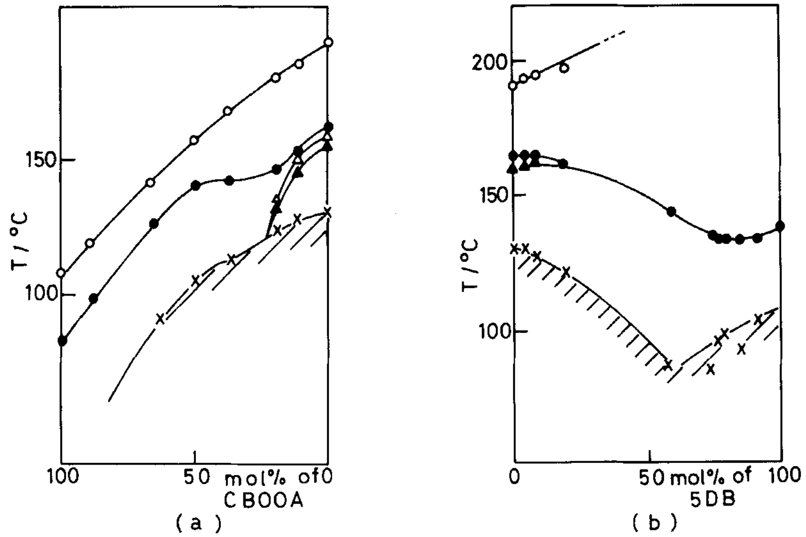


FIGURE 4 Isobaric diagrams: (a) a mixture of CBOOA and the nonyloxy homolog. (b) a mixture of the decyloxy homolog and 4-pentylphenyl 4-(4-cyanobenzoyloxy)benzoate (5DB). The horizontal lines represent a transition to a metastable crystalline forms. The diagrams were obtained from DSC thermograms on a cooling stage. ○; isotropic–nematic, ●; nematic–S_1 or $-S_3$, △; S_1–S_2, and ▲; S_1– or S_2–S_3 transitions.

TABLE II

Transition temperatures of the homologous series

(a) All data were taken from microscopic observation ($T/$ °C)

n	C		S_A		N		I
4	·	181.5	—		·	208.5	·
5	·	145.0	(·	123.0)	·	210.0	·
6	·	170.9	(·	136.0)	·	204.7	·
7	·	148.3	(·	148.2)	·	199.7	·
8	·	147.6	·	156.8	·	197.5	·
9	·	146.8	·	162.2	·	194.8	·
10	·	146.0	·	165.0	·	193.5	·

The values in parentheses indicate monotropic transitions.

(b) All data were taken from DSC thermograms (on the cooling stage at a cooling rate of 5 °C/min: $T/$ °C)

n	S_3		S_2		S_1		N		I
7	—	[110]	—	[137]	—	145.5	·	198.0	·
8	·	145.5	·	150.5	·	155.5	·	196.0	·
9	·	155.5	·	157.8	·	160.5	·	192.0	·
10	·	160.5	—		·	164.0	·	192.0	·

The values in brackets indicate virtual transitions.

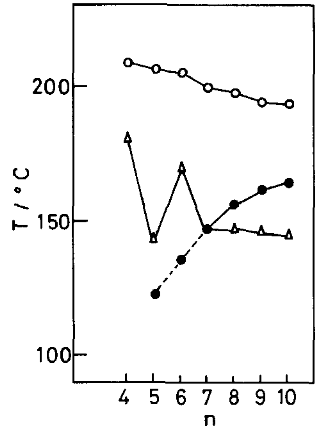


FIGURE 5 Plots of transition temperatures against carbon number *n*. ○; nematic–isotropic, ●; smectic A–nematic, and △; crystal–nematic or –smectic A transitions.

latters. The smectic phase (S_1) commences from the pentyloxy homolog and S_2 and S_3 commence from the octyloxy homolog. The thermal stabilities of the smectic phases increase with increasing *n*.

DISCUSSION

It is well known that mesogens having a cyano or a nitro group as the terminal function which results in strong antiparallel correlations, form a bilayer structure in which the molecules are interdigited.[1-4] An extent of overlap is strongly dependent on temperature. This leads to a variety of arrangement of the molecules in the anisotropic phases. The following arrangements of the molecules have been observed in a smectic A phase:

		D/l
monolayer	(S_{A1})	~ 1
partially bilayer	(S_{Ad})	~ 1.3
bilayer	(S_{A2})	~ 2
antiphase	($S_{\tilde{A}}$)	~ 2

where D and l are a layer thickness in the smectic phases and a molecular length, respectively.[23] The monolayer arrangement (S_{A1}) is observed in an induced smectic phase in binary mixtures and in a smectic phase of nonpolar mesogens. Usually, a smectic A phase of polar mesogens has a partially bilayer (S_{Ad}) or a bilayer (S_{A2}) arrangement in the high temperature region. The antiphase ($S_{\tilde{A}}$) has been found in a smectic A phase of 4-(4-heptylphenoxycarbonyl)phenyl 4-nitrobenzoate[20] and in a smectic A phase in a binary mixture of 4-cyanobenzoyloxy 4′-pentylstilbene and 4-(4-pentylphenoxycarbonyl)phenyl 4-cyanobenzoate,[24] and also in a smectic B phase of certain cyano compounds.[25] Generally, the thermal stability order is $S_{Ad} > S_{\tilde{A}} > S_{A2}$.

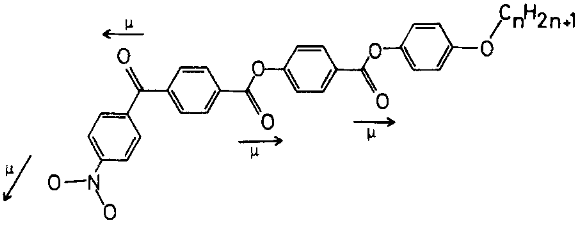
The S_A–S_A transitions have been predicted from a theoretical consideration for a binary mixture.[26] Indeed, certain binary mixtures experience the S_A–S_A transitions.[27–31] More recent works have shown that 4-(4-heptylphenoxycarbonyl)phenyl 4-nitrobenzoate[20] 4-(4-decylphenoxycarbonyl)-3-methylphenyl 4-cyanobenzoate,[21] and 4-(4-pentylphenoxycarbonyl)phenyl 4-cyanobenzoate[32] experience $S_{\tilde{A}}$–S_A, S_{A2}–S_{Ad}, and S_{A2}–S_{Ad} transitions, respectively.

The octyloxy and nonyloxy homologs in this series give rise to three kinds of smectic A phases, and experience two types of S_A–S_A transitions. The decyloxy homolog gives rise to two kinds of smectic A phases, and also experiences the S_A–S_A transition. It has been known that 4-pentylphenyl 4-(4-cyanobenzoyloxy) benzoate and CBOOA give rise to smectic A phases having bilayer (S_{A2})[22] and partially bilayer (S_{Ad})[10] arrangements of the molecules, respectively. Considering the miscible relation of the isobaric diagrams in Figures 4a and 4b, following correlations are proposed:

$$\begin{aligned} S_1 &— S_{Ad} \\ S_2 &— (S_{\tilde{A}}) \\ S_3 &— S_{A2} \end{aligned}$$

The S_2 phase may correspond to the antiphase ($S_{\tilde{A}}$) arrangement, though we have no information about the S_2 phase. The thermal stabilities of these phases are dependent on the chain length of the alkoxy group. The S_1 phase commences from the pentyl homolog and the S_3 phase commences from the octyloxy homolog. Both thermal stabilities increase with increasing n. On the other hand, the S_2 phase is formed only by the octyloxy and nonyloxy homologs. A noteworthy fact is that depression in the S_3–S_2 and S_2–S_1 transition temperatures for the heptyloxy homolog is more remarkable than that in the S_1–N transition temperature, as shown in Table IIb.

This interesting behavior should be related to their molecular structures. Although the homologous series has four aromatic rings and five polar groups, the geometrical and electronic circumstances are essentially similar to those of 4-(4-heptylphenoxycarbonyl)phenyl 4-nitrobenzoate[20] and its methyl homolog.[21] The molecular structure is shown below.



The terminal nitrophenyl group occurs at an angle with respect to the rotational axis of the entire molecule because of the bent —CO— linkage, and increases the molecular breadth. The increased molecular breadth could be responsible for the low nematic stability. The longitudinal components of the dipole moments of both ester groups are aligned antiparallel to those of the nitro and carbonyl groups. The mutual interaction of the dipoles parallel to the long molecular axis is assumed to play an important role in producing the complicated phase transitions, as mentioned by Madhusudana *et al.*[7] X-ray studies are now underway to learn more about the structures of these phases.

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