Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl16

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Version of record first published: 13 Dec 2006.

To cite this article: J. M. Lohar & Jayrang S. Dave Jr. (1983): Effect of Nitro Terminal Substituent on the Liquid Crystalline Characteristics of Ester Mesogens: p-Nitrophenyl-p'-n-Alkoxycinnamates, Molecular Crystals and Liquid Crystals, 103:1-4, 143-153

To link to this article: http://dx.doi.org/10.1080/00268948308071046

Mol. Cryst. Liq. Cryst., 1983, Vol. 103, pp. 143–153
0026-8941/83/1034–0143/$18.50/0

Printed in the United States of America

Effect of Nitro Terminal Substituent on the Liquid Crystalline Characteristics of Ester Mesogens: *p*-Nitrophenyl-*p'*-*n*-Alkoxycinnamates

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(*Received February 7, 1983; in final form June 1, 1983*)

The homologous series *p*-nitrophenyl-*p'*-*n*-alkoxycinnamates is a medium melting homologous series; the first two members are non-mesogens and do not exhibit even monotropy. The nematic phase begins from the third derivative in monotropic condition; from the fourth member enantiotropic mesomorphism commences. Polymesomorphism begins from the sixth member with the appearance of smectic mesophase and ends at the seventh member. The rest of the homologues up to the octadecyl are purely smectogens. Thus the homologous series is predominantly smectogenic even though $-NO_2$ group is reported to be enhancing nematic character.[1] Within the polymesomorphic region the nematic mesophase is homeotropic; however, it shows a clear threaded texture where it is the only mesophase shown. The N-I transitions do not exhibit the usual alternation in transitions which is a rare phenomenon. The N–I transition curve is unusually neither rising nor falling though a slight curve is seen; it merges with the S–I curve which shows a slight rising tendency as the alkyl chain length is increased. The S–N transition curve steeply rises and seems to be merging with the S–I curve. The mesomorphic range is good; the nature of the curve can predict the latent N–S or I–N transitions. All smectic orientations are of focal conic smectic A texture except in the case of sixth and seventh homologues where homeotropic nature prevails.

INTRODUCTION

The occurrence of liquid crystallinity is directly related to the molecular forces which are dependent upon the molecular geometry, the terminally and laterally attached groups in addition to the connecting

groups of the moieties, if any.[2-7] With the structural modifications brought in, the mesomorphic characteristics also undergo a change inclusive of the possibility, though rare, of elimination of the property altogether. Not only the transitions and their range but also the textures of the orientations can differ by varying the constitutional characteristics. These possibilities have provided the means by which desired alterations may be attempted to suit the requirements. It is reported that benzoate ester linkage[5] lends greater stability than that of the azomethine bridge between the rings. The effect of para substituted nitro terminal groups is also quite significant in terms of stability of mesophase and its texture. In this investigation therefore a para substituted nitro ester mesogen homologous series was synthesized and studied in the hope of getting interesting results.

EXPERIMENTAL

Synthesis

1. *p-n*-Alkoxy benzaldehydes where alkoxy group varied from $-OCH_3$ to $-OC_8H_{17}$ and $-OC_{10}H_{21}$, $-OC_{12}H_{25}$, $-OC_{14}H_{29}$, $-OC_{16}H_{33}$ and $-OC_{18}H_{37}$, were synthesized from *p*-hydroxy benzaldehyde.[8]

TABLE I

Transitions: *p*-nitrophenyl-*p'*-*n*-alkoxycinnamates

n-Alkyl group	Transition Temperatures °C		
	Smectic	Nematic	Isotropic
$-CH_3$	—	—	188.5
$-C_2H_5$	—	—	168.0
$-C_3H_7$	—	(121.5)	122.5
$-C_4H_9$	—	116.0	120.5
$-C_5H_{11}$	—	90.5	120.5
$-C_6H_{13}$	97.5	100.5	122.5
$-C_7H_{15}$	100.0	114.0	121.0
$-C_8H_{17}$	89.5	—	124.0
$-C_{10}H_{21}$	75.0	—	128.0
$-C_{12}H_{25}$	85.5	—	132.5
$-C_{14}H_{29}$	83.5	—	134.0
$-C_{16}H_{33}$	80.5	—	136.5
$-C_{18}H_{37}$	102.5	—	141.0

Value in parenthesis indicates monotropy.

2. trans *p-n*-Alkoxy cinnamic acids were synthesized from *p-n*-alkoxy benzaldehydes.[9]

3. trans *p-n*-Alkoxy cinnamoyl chlorides were synthesized from trans *p-n*-alkoxy cinnamic acids.[10]

4. *p*-nitrophenyl-*p'*-*n*-alkoxycinnamates: *p*-Nitrophenol (0.01 mole) was dissolved in dry pyridine (10 ml) and was added slowly to the trans *p-n*-alkoxy cinnamoyl chloride (0.015 mole). The mixture was warmed while shaking for an hour and was allowed to stand overnight. It was acidified with cold hydrochloric acid and the precipitates were collected by filtration and were washed with water. The precipitates were further washed with cold dilute sodium hydroxide solution followed by water. The esters viz. *p*-nitrophenyl-*p'*-*n*-alkoxycinnamates obtained were crystallized from ethyl acetate: ethyl alcohol (20 : 80) mixture. The elemental analysis conforms with the calculated ones.

STUDY

The mesomorphic characteristics were studied by optical microscopy and the transitions are recorded in Table I.

RESULTS AND DISCUSSION

This ester mesogens homologous series *p*-nitrophenyl-*p'*-*n*-alkoxycinnamates presents a characteristic difference when the very first two homologues turn out to be non-mesogens though in an overall sense the series is not much different from a low melting type (Figure 1). Both terminals of the linear molecules of these homologues (Figure 2) are equipped with sufficiently polar groups viz. methoxy and ethoxy on the left side and nitro on the right, which should ensure sufficient terminal attractions for the nematic orientation to show up. In a striking contrast, both these homologues exhibit high thermal stability and absence of a gradual breakdown first into an oriented fluid followed by isotropic transition. The third homologue of the series *p*-nitrophenyl-*p'*-*n*-alkoxycinnamates (I) (Figure 2) has an alkyl chain at the left end which has greater length by one more methylene unit than the second one; it seems that this change is sufficient to weaken the thermal resistance offered by the molecule to the extent of about 70° as compared to the first homologue and about 50° to the second, with the result that the (third) homologue exhibits nematic property

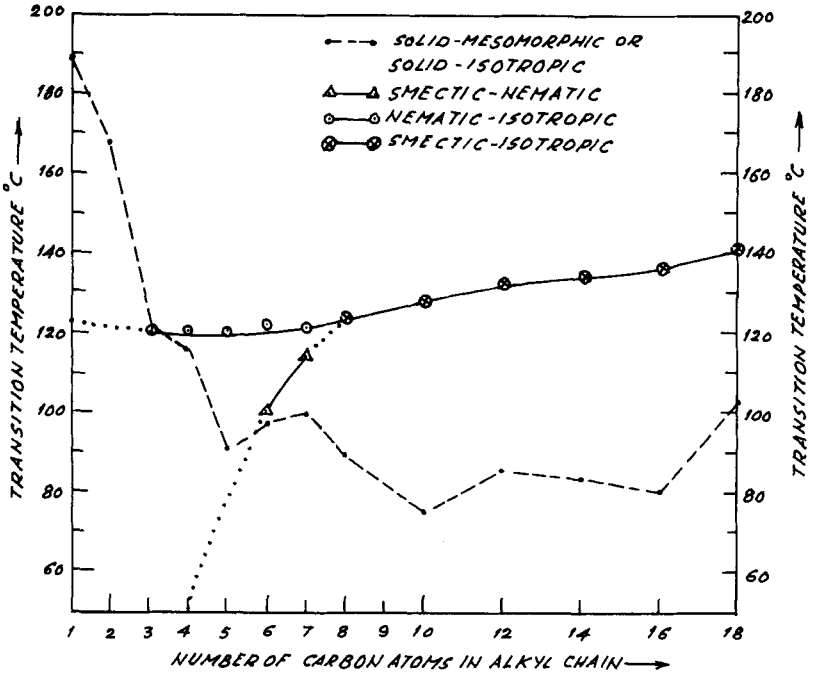

FIGURE 1 *p*-nitrophenyl-*p'*-*n*-alkoxycinnamates

though of hardly 1° range in the monotropic condition. The homologues thereafter up to the seventh exhibit nematic mesophase of reasonable phase length. Here again, a characteristic difference of unusual nature is well marked in the absence of the usual odd-even effect in the nematic–isotropic transitions. The plot of the transitions versus the number of carbon atoms in the alkyl chain at the left end, for this series (Figure 1) does not leave any iota of doubt about the absence of the alternation effect, though surprising. While such instances are rare, an explanation on the basis of the existing theories[12] is not easily coming forth.

I. $C_nH_{2n+1}O-C_6H_4-CH=CH-COO-C_6H_4-NO_2$

II. $NO_2-C_6H_4-CH=CH-COO-C_6H_4-OC_nH_{2n+1}$[11]

FIGURE 2 Homologous series

An isomeric homologous series[11] *p*-*n*-alkoxyphenyl-*p*-nitrocinnamates (II) (Figure 2) offers an interesting comparison though the data available is from the fourth to the eighth homologues only. A plot of the transitions for the homologous series (II) versus the number of carbon atoms of the alkyl chain at the right end (Figure 3) has been reconstructed, which clearly indicates an alternating effect for the nematic-isotropic transitions. Apparently, though perhaps not studied by the original authors and therefore not reported,[11] the first three homologues of this isomeric homologous series may also, presumably be non-mesogens since the fourth homologue itself is only a monotropic nematogen like the third one of the series *p*-nitrophenyl-*p'*-*n*-alkoxycinnamates. The definite indication for the odd-even effect in the N–I transitions is given by the N–I transition for the fifth homologue of the isomeric series (II) which differs by about 1.5° from the preceding and about 4.0° from the immediately next homologues, thereby giving rise to two N–I transition curves. This isomeric homologous series (II) as discerned by the rising nature of the N–I transition curves as the alkyl chain length increases, is a low melting series; thus the present homologous series *p*-nitrophenyl-*p'*-*n*-alkoxycinnamates, despite a plateau type nature of its N–I curve, is to be taken as a low melting series because they form isomeric pair.

Besides the absence of odd-even effect in the nematic-isotropic transitions of the homologous series (I), there are other significant differences in the isomeric pair of homologous series under comparison. While the present series (I) exhibits polymesomorphism at the hexyl and heptyl homologues with smectic and nematic mesophases, the series (II) is devoid of polymesomorphism up to the eighth member as reported.[11] From the octyl homologue onwards, the members of the series (I) exhibit smectic property only. While smectic property cannot be ruled out for the members nonyl and beyond in the case of the isomeric homologous series (II), though not reported, the commencement of smectic mesophase is from the sixth member in the present series versus a probability for the series (II) from the nonyl member. Thus the present homologous series (I) *p*-nitrophenyl-*p'*-*n*-alkoxycinnamates is more smectogenic than the isomeric series (II) under comparison with the absence of polymesomorphism in its case. Where almost an identical, if not perfectly identical, behaviour is expected in the case of isomeric pairs of homologous series[13] a sizeable contrast is noted in these two isomeric series. And since, there is no other effective change in the molecular geometry, other than the exchange of places for the nitro terminal group, the contrast presented should logically be due to the changed disposition of the nitro group.

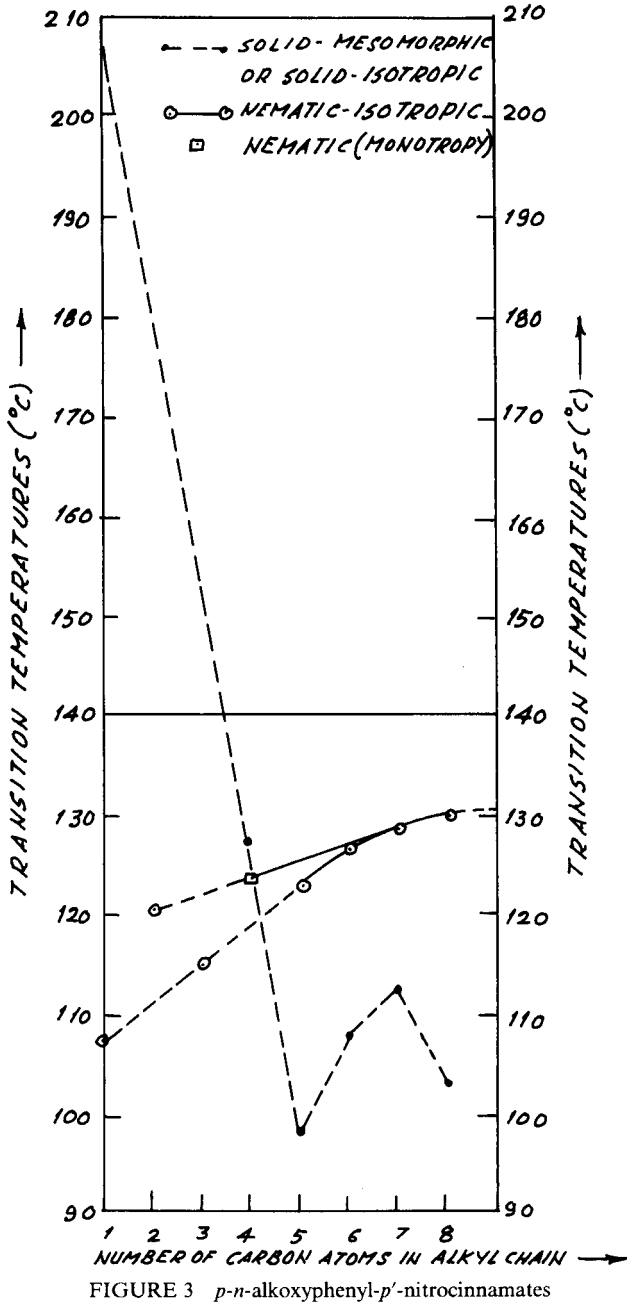

FIGURE 3 *p-n*-alkoxyphenyl-*p'*-nitrocinnamates

The nature of the solid–mesomorphic curve in the case of series (II) indicates very high solid–isotropic liquid transitions for its first three homologues like the first two of the series (I).

As a result of the terminal nitro group attached to the ring which is linked with the ester oxygen, there would be a strong conjugative interaction between them in the case of the homologous series (I). This kind of strong conjugative interactions between the bonded ester oxygen and end nitro group will not be effective when the nitro group is located at the left end as is the case in series (II) due to a distance caused by $-CH{=}CH-\overset{\overset{O}{\|}}{C}-$ link space (Figure 4). Le Fevres' data show for para nitroanisole that directed polarizability exaltations due to conjugative interactions along the 1, 4-axis in the aromatic ring are quite large.[14] It appears that the cause for alternation effect in the N–I transitions due to the spatial disposition of the alkyl chain of the alkoxy group in nematic condition as explained by Gray[15] or Marcelja[12] is well balanced by the strong conjugative interactions resulting into its absence in the case of series (I); this milieu being absent in the case of series (II), the alternating effect persists. Another homologous series *p*-(*p'-n*-alkoxy cinnamoyloxy) benzylidene anilines[16] forming an isomeric pair with the series *p*(cinnamoyloxy) benzylidene *p'-n*-alkoxy anilines[17] presents a striking contrast in terms of polymesomorphism exhibited by the first and only nematic property exhibited by the latter. This only lends support to the emerging contention that isomeric pairs may offer contrasting characteristics depending upon the

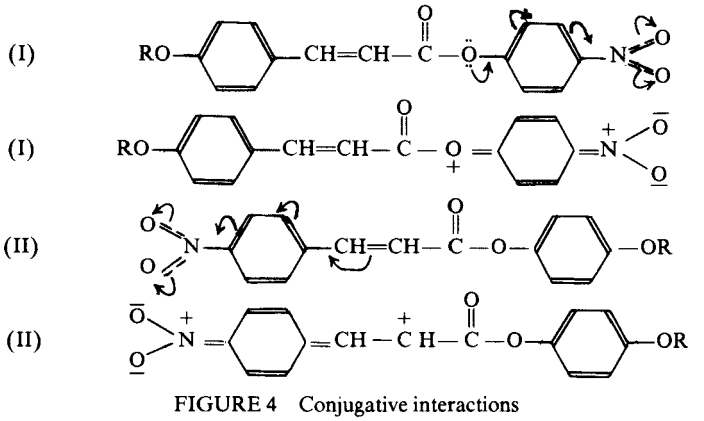

FIGURE 4 Conjugative interactions

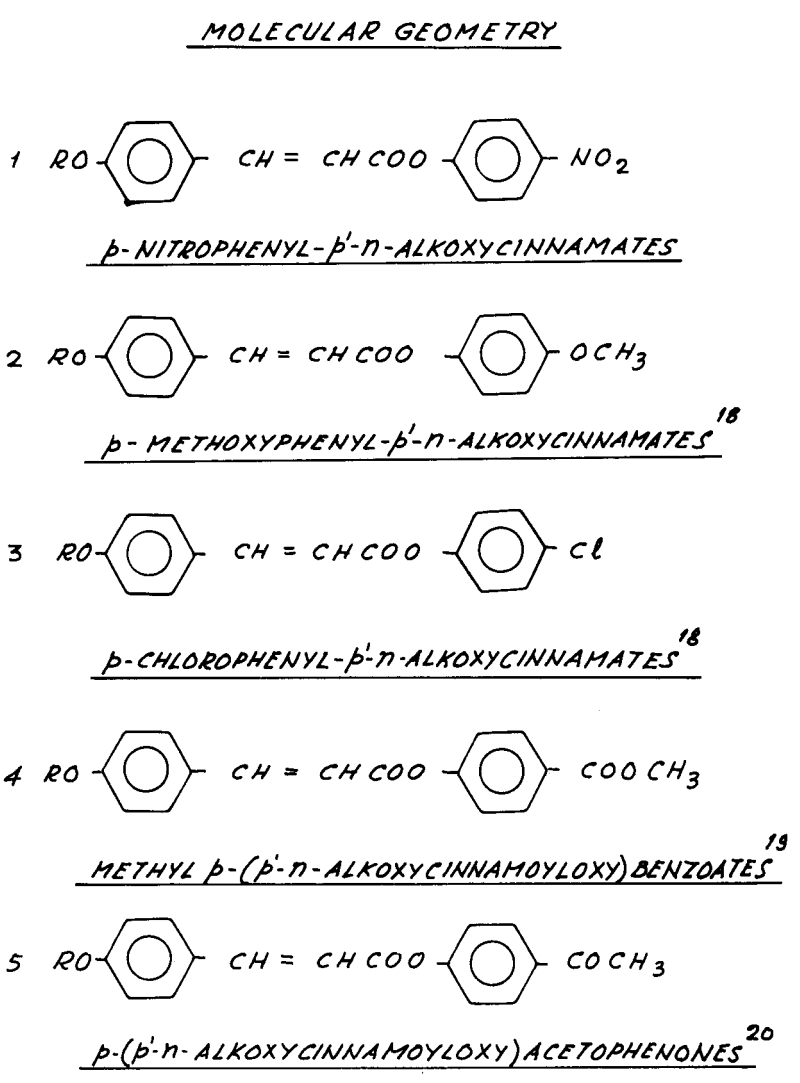

FIGURE 5 Homologous series: thermal stability comparison

variations caused in the display of molecular forces due to changed dispositions of the terminal substituents.

The homologous series *p*-nitrophenyl-*p'*-*n*-alkoxycinnamates can be compared with other structurally related homologous series for its average thermal stabilities. In Figure 5 are given the structures of the series compared and in Table II their thermal stabilities.

1. *p*-Nitrophenyl-*p'*-*n*-alkoxycinnamates
2. *p*-Methoxyphenyl-*p'*-*n*-alkoxycinnamates[18]
3. *p*-Chlorophenyl-*p'*-*n*-alkoxycinnamates[18]
4. Methyl-*p*-(*p'*-*n*-Alkoxy cinnamoyloxy) benzoates[19]
5. *p*-(*p'*-*n*-Alkoxy cinnamoyloxy) acetophenones.[20]

All the homologous series selected for comparative study resemble very much (Figure 5) i.e. the alkoxy terminal substituents at the left end, two benzene rings and the central bridge viz. vinyl carboxy, —CH=CHCOO—, are the same in each. These differ only in one respect, that is the other terminal substituent which is $-NO_2$, $-OCH_3$, —Cl, $-COOCH_3$, $-COCH_3$ respectively for the series 1, 2, 3, 4 and 5. Thus the relative thermal stabilities of these series have a direct bearing with these differing terminal substituents. It can be seen from Table II that the N–I thermal stabilities for the series 1 and 3 are the lowest but equal. The two terminal groups concerned are $-NO_2$ and —Cl respectively. While the dipolar nature of NO_2 group far outweighs that of the —Cl group, the —Cl group is sufficiently broad and polarizable. It appears that these two forces match well in the case of these two series. The series 2 with $-OCH_3$ terminal group is having higher N–I thermal stability as expected due to high polar $-OCH_3$ group which is responsible for high terminal attractions. The series 4 and 5 have the highest N–I thermal stability; the reason could

TABLE II

Average Thermal Stabilities (°C)

Series	1	2	3	4	5
Nematic–Isotropic	121.2 (C_4—C_6)	126.0 (C_4—C_6)	121.2 (C_4—C_6)	138.3 (C_4—C_6)	136.8 (C_4—C_6)
Smectic–Nematic or Smectic–Isotropic	136.0 (C_{12}—C_{18})	95.1 (C_{12}—C_{18})	114.5 (C_{12}—C_{18})	131.7 (C_{12}—C_{18})	139.7 (C_{12}—C_{18})
Commencement of Smectic mesophase.	C_6	C_8	C_4	C_4	C_5

be found in the longer $-COOCH_3$ and $-COCH_3$ terminal groups respectively. The polarizability of the molecules is thus greatly enhanced which in turn enhances the N–I thermal stability.[21]

Regarding the S–N or S–I thermal stability it may be mentioned at the out set that the series 1 is having sufficiently higher S–N or S–I thermal stability which fact too is somewhat in contravention to the normally accepted generalization regarding the $-NO_2$ group.[1] The S–N or S–I thermal stability for the homologues of series 2 is the lowest due to their high polar $-OCH_3$ terminal group which weakens the lateral attractions. A little bit higher S–N or S–I thermal stability for the series 3 is due to tilting effect of the C–Cl dipole.[22] The overall polarizability of the molecules as well as the ratio of lateral to terminal attractions for the series 4 and 5 due to the $-COOCH_3$ and $-COCH_3$ groups respectively speak for their higher S–N or S–I thermal stability. It is also known that the ring $-COOCH_3$ linkage having dipole moment acting across the long molecular axis attributes to the smectogenic characteristics.[23]

The early commencement of the smectic mesophase in series 3 is due to the terminal —Cl group where as the very late commencement of the smectic phase in series 2 is on account of the terminal polar $-OCH_3$ group. The greater overall polarizability of the homologues of the series 4 and 5 due to —CH=CHCOO— central bridge and longer terminal groups $-COOCH_3$ and $COCH_3$ speaks for the early commencement of the smectic phase in their cases. The predominance of smectogenic characteristics in series 1 with $-NO_2$ terminal substituent is surprising which has already been mentioned in earlier discussion. The thermal stability orders as emerging from this study are:

$$\text{N–I} \quad -COOCH_3 > -COCH_3 > -OCH_3 > -Cl{=}NO_2$$

$$\text{S–N or S–I} \quad -COCH_3 > -NO_2 > -COOCH_3 > -Cl > -OCH_3$$

Extrapolation of the smectic-nematic transition curve (Figure 1) to the left yields values for the latent transition temperatures for the smectic mesophase for the fifth and fourth homologues which are 79.0 and 51.0 °C respectively. Similarly, extrapolation of the nematic-isotropic transition curve to the left indicates 121.0° and 122.0 °C as latent transition temperatures of nematic mesophase for the second and first homologues. A mixture of these two homologues, however, fails to give rise to mixed nematic property quite contrary to the

expectations[24] the details of which along with those of other binary systems will be discussed elsewhere.

One of us (JSD) thanks the M.S. University of Baroda for award of a fellowship during which time the present investigation was carried out.

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