Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713926090

p-Alkoxy- and *p*-alkylbenzoates of α, a'-bi-p-hydroxytoluene. New series of liquid-crystalline compounds

George M. Janini[a]; N. T. Filfil[a]; Gary M. Muschik[b]
[a] Department of Chemistry, University of Kuwait, Safat, Kuwait [b] Program Resources, Inc., Frederick, Maryland, U.S.A.

To cite this Article Janini, George M. , Filfil, N. T. and Muschik, Gary M.(1990) '*p*-Alkoxy- and *p*-alkylbenzoates of α, a'-bi-p-hydroxytoluene. New series of liquid-crystalline compounds', Liquid Crystals, 7: 4, 545 — 551

To link to this Article: DOI: 10.1080/02678299008033831

URL: http://dx.doi.org/10.1080/02678299008033831

LIQUID CRYSTALS, 1990, VOL. 7, NO. 4, 545–551

p-Alkoxy- and *p*-alkylbenzoates of α,α′-bi-*p*-hydroxytoluene

New series of liquid-crystalline compounds

by GEORGE M. JANINI and N. T. FILFIL
Department of Chemistry, University of Kuwait, 13060 Safat, Kuwait
and GARY M. MUSCHIK
Program Resources, Inc. NCI-FCRF, Box B, Frederick, Maryland 21701, U.S.A.

(*Received 4 September 1989; accepted 17 November 1989*)

Six *p*-alkoxy and eight *p*-alkylbenzoates of 1,2-(*p*-hydroxyphenyl)ethane were synthesized for potential use as stationary phases in gas–liquid chromatography. All the *p*-alkoxy derivatives were nematic. The first five members of the alkyl series were nematic and the rest exhibited both smectic and nematic character. Most possess the desired combination of a wide liquid-crystalline temperature range and a high mesomorphic–isotropic transition temperature. The nematic–isotropic transition temperatures and entropies show the usual alternations characteristic of a high-melting series.

1. Introduction

High-melting, wide range liquid crystal materials have attracted little attention because they are of small value for electron optical devices [1, 2]. They however, provide selective stationary phases for the gas-liquid chromatographic separation of rigid isomers. Several reviews deal with the use of liquid crystals in gas liquid chromatography [3, 4, 5]. The most widely used at present are the nematic Schiff's bases BMBT, BBBT and BPhBT that were introduced by Janini and his co-workers [6, 7, 8]. The nematic state is particularly favoured because of the appreciably greater column efficiency that can be achieved relative to the smectic state. Janini and co-workers further introduced two high-temperature Schiff's base series [9, 10] whereby the gas chromatographic selectivity of the nematic state is correlated with the order parameter.

This paper reports the synthesis, phase transition temperatures, enthalpies (ΔH) and entropies (ΔS) of transition for fifteen members of two series of better intrinsic stability representing *p*-alkoxy and *p*-alkylbenzoates of α,α′-bi-*p*-hydroxytoluene. To our knowledge this represents the first report whereby α,α′-bi-*p*-hydroxytoluene is used as central linkage in liquid crystal materials.

2. Experimental

2.1. *Materials*

(*a*) *Synthesis of α,α′-bi-(p-methoxytoluene).*

To 100 g amalgamated zinc, 80 ml of water, 180 ml of concentrated hydrochloric acid and 120 ml of toluene was added 50 g (0·20 moles) of desoxyanisoin. The mixture was vigorously stirred and heated under reflux for 48 hours until TLC showed the absence of starting material. Upon cooling the reaction mixture was shaken with methylene chloride, and the extract washed with water and sodium carbonate solution and dried with anhydrous magnesium sulphate. The organic solvent was removed resulting in a solid which was recrystallized from benzene to give 31 g (65 per cent yield), MP 127–128°C, of (uncorrected) product. The product gave IR, MS and ^{1}H N.M.R. spectra consistent with the structure.

(*b*) *Synthesis of α,α′-bi-(p-hydroxytoluene).*

To 9·45 g (0·04 moles) of α,α′-bi-*p*-methoxytoluene was added 150 ml of glacial acetic acid and 25 ml of 48 per cent HBr. The mixture was refluxed under nitrogen with stirring for 48 hours. The crude reaction mixture was cooled and poured into an ice–water mixture. The crude precipitate was collected, dissolved in a minimum of hot methanol and recrystallized by the addition of water until cloudy. The product was cooled, collected and dried under vacuum to yield 8·2 g (99 per cent yield) M.P. 205–206°C (uncorrected) of product. The product gave IR, MS and ^{1}H N.M.R. spectra consistent with the structure.

The diesters liquid crystals were synthesized as follows: To a mixture of 0·01 moles of diol (4,4′-bi-phenol or α,α′-bi-(*p*-hydroxy-toluene) in a 50 ml of pyridine at room temperature was added 0·02 moles of the appropriate acid chloride. The mixture was allowed to stir at room temperature for 24 hours. The reaction mixture was poured into 200–300 ml of water and extracted several times with diethyl ether. The ether extracts were washed with 5 per cent HCl to remove the pyridine and with water and dried over anhydrous magnesium sulphate. The organic solvent was removed and the esters were recrystallized from suitable solvents. The IR, MS, and ^{1}H NMR spectra were consistent with the structure of each product.

The mesophase types were identified by optical microscopy using Bausch and Lomb Stereozoom 7 microscope coupled to a Mettler PF 52 heating stage and PF 5 temperature control unit.

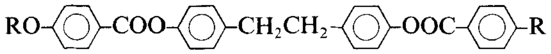
2.2. *Differential scanning calorimetry*

A Du pont Model 1999 was used for the calorimetric determination, after calibration with pure indium (m.p. 156·60°C), tin (m.p. 231·88°C) and lead (m.p. 327·47°C). The enthalpies of transitions were determined by comparing the chart peak areas per milligram of sample with that of a known weight of indium (ΔH 28·32 Joule/g). A heating rate of 10°/min. was used for all determinations and the instrument sensitivity settings were adjusted to maximize the areas under the small peaks. Under these conditions, multiple ΔH measurements on aliquots of individual liquid crystals were reproducible to within ± 5 per cent. Transition temperatures were reproducible to within ± 1°C. The purity of these compounds was not determined; however, all compounds were purified by recrystallization to constant mesophase to isotropic transition temperatures. The sharp DSC transition peaks are indicative of highly pure products.

3. Results and discussion

Table 1 lists the *N*,*N*′-bis[*p*-alkoxybenzoate]-α,α′-bi-*p*-hydroxyphenols, together with their respective melting points, mesomorphic transition temperatures, and the thermodynamic properties of the N–I transition. All members, (methoxy through hexyloxy) are pure nematogens. The melting points increase from CO1 to CO3 then fall gradually, while the N–I transition temperature decrease with increasing carbon number in the terminal substituent. Odd–even alternations are slightly evident and the trend is similar to the majority of over 70 homologous series examined by Gray [11, 12]. The ethoxy homologue in this series has a lower N–I transition temperature than the methoxy homologue, which is the reverse of the order observed for the first members of the series, *N*,*N′*-bis[*p*-alkoxybenzylidene]-α-α′-bi-*p*-toluidine (figure 1 [9]).

Table 1. Phase transition temperatures and thermodynamic properties for the nematic–isotropic transition for the series:



		C–N	N–I		
Compound	*R*	*T*/°C	*T*/°C	ΔH/kJ mol^{-1} ± 5 per cent	ΔS/J mol^{-1} K^{-1} ± 5 per cent
CO1	CH_3O–	167·5	305	6·64	11·48
CO2	C_2H_5O–	174·0	301·2	7·55	13·15
CO3	C_3H_7O–	175·2	272·5	6·07	11·12
CO4	C_4H_9O–	158·9	254·1	6·36	12·06
CO5	$C_5H_{11}O$–	158·4	247·4	5·59	10·75
CO6	$C_6H_{13}O$–	147·8	228·8	5·19	10·33

C, crystalline; N, nematic; I, isotropic

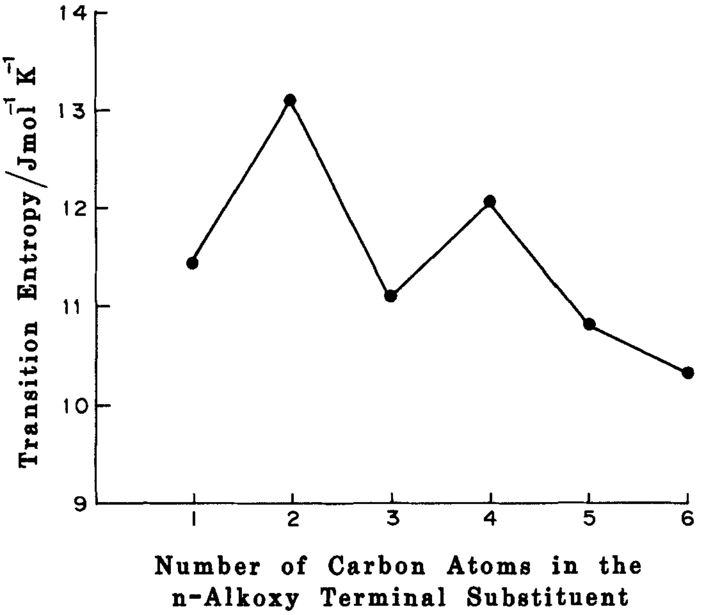
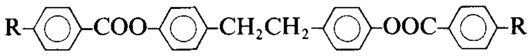


Figure 1. Plot of liquid crystal transition entropies vs. *n*-alkoxy chain length for *N*,*N′*-bis-[*p*-alkoxybenzoate]-α,α′-bi-*p*-hydroxyphenol.

Figure 1 presents a plot of N–I transition entropies vs. *n*-alkoxy chain length for this series from data reported in table 1. It is observed that ΔS values for the compounds with even carbon number are appreciably higher than those with odd carbon numbers. Low molar mass nematogens have low ΔH values ranging from 0·4–4 kJ mol^{-1} [13]. In contrast ΔH values for this series are considerably higher indicating stronger mesophase stabilizing forces.

Table 2 lists the *N*,*N'*-bis[*p*-alkylbenzoate]α,α'-bi-*p*-hydroxytoluenes, together with their respective melting points, mesomorphic transition temperatures and the thermodynamic properties of the N–I transitions. In this series smectic B and A phases appear starting with the *n*-hexyl derivative. The first five members of the series are nematogens. Figure 2 shows the phase diagram with data from table 2 and figure 3 shows the DSC scan of the *n*-hexyl derivative.

Table 2. Phase transition temperatures and theromodynamic properties for the nematic–isotropic transition for the series:



						N–I		
Compound	*R*	C–S_B T/°C	C–N T/°C	S_B–S_A T/°C	S_A–N T/°C	T/°C	ΔH/kJ mol^{-1} ± 5 per cent	ΔS/J mol^{-1} K^{-1} ± 5 per cent
C1	CH_3–		190·5			273·5	5·47	10·0
C2	C_2H_5–		174·2			246·8	5·02	9·66
C3	C_3H_7–		175·0			255·2	5·50	10·41
C4	C_4H_9–		161·7			236·5	5·28	10·36
C5	C_5H_{11}–		160·9			236·0	6·09	11·96
C6	C_6H_{13}–	139·0		165·8	168·4	219·1	5·89	11·97
C7	C_7H_{15}–	128·9		162·0	174·1	208·5	5·25	11·13
C8	C_8H_{17}–	120·3		164·3	183·3	199·5	4·82	10·59

As expected the N–I transition temperature for each member is lower than that of the corresponding *n*-alkoxy derivative with the same carbon number in the terminal chain. Odd–even alternation in the clearing points is more evident here for the lower member of the series and becomes less marked as the series is ascended. The trend in the solid–mesomorphic transition temperatures is strikingly similar to that of the N–I transitions. Unlike the *n*-alkoxy series all members of this series beyond C3 exhibit multiple solid–solid transition as illustrated in figure 3.

Figure 4 shows a plot of N–I transition entropies versus *n*-alkyl chain length. Here again we note the relatively high entropy values, however, no odd–even alterations are apparent as in the case with the *n*-alkoxy series.

Comparing the two diester series presented here with the analogous di Schiff's base series presented in [8] and [9], we note that the smectic mesophase is more favored in the di Schiff's series as it appears in members with shorter carbon chain in the *n*-alkoxy and *n*-alkyl terminal groups.

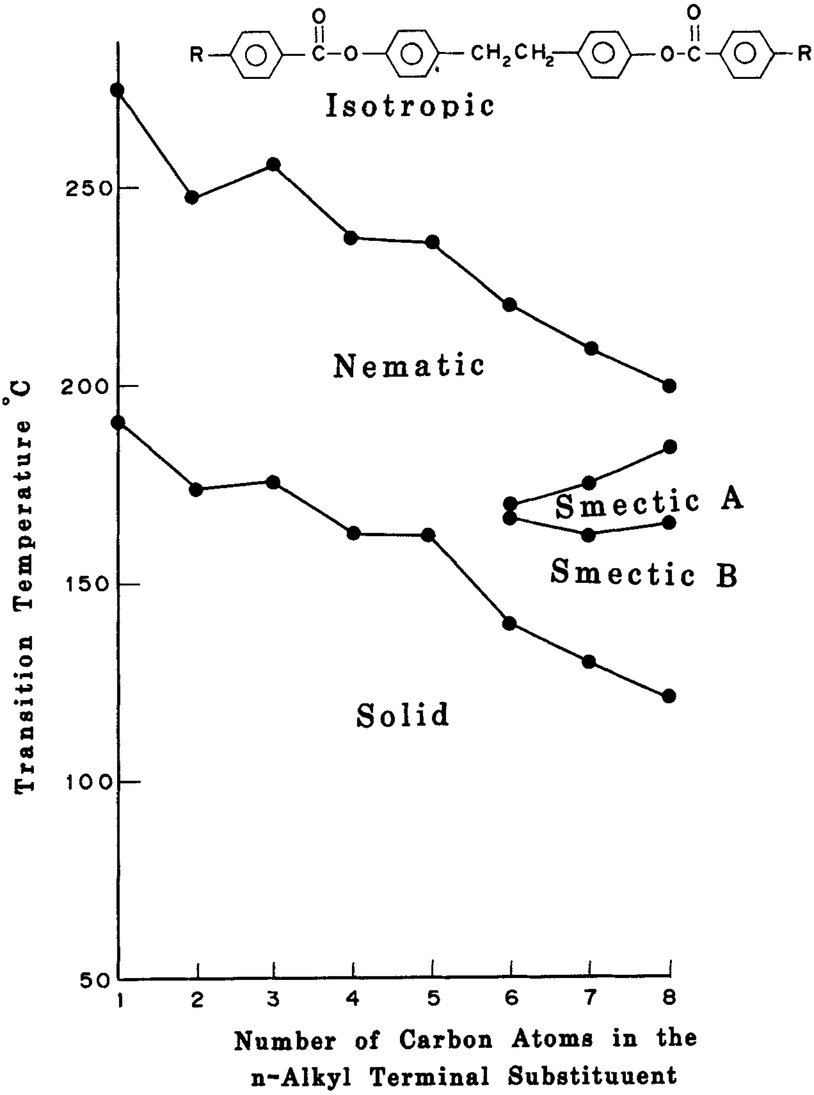


Figure 2. Plot of liquid crystal transition temperatures vs. *n*-alkyl chain length for the series *N*,*N*′-bis[*p*-alkybenzoate]-α,α′-bi-*p*-hydroxytoluene.

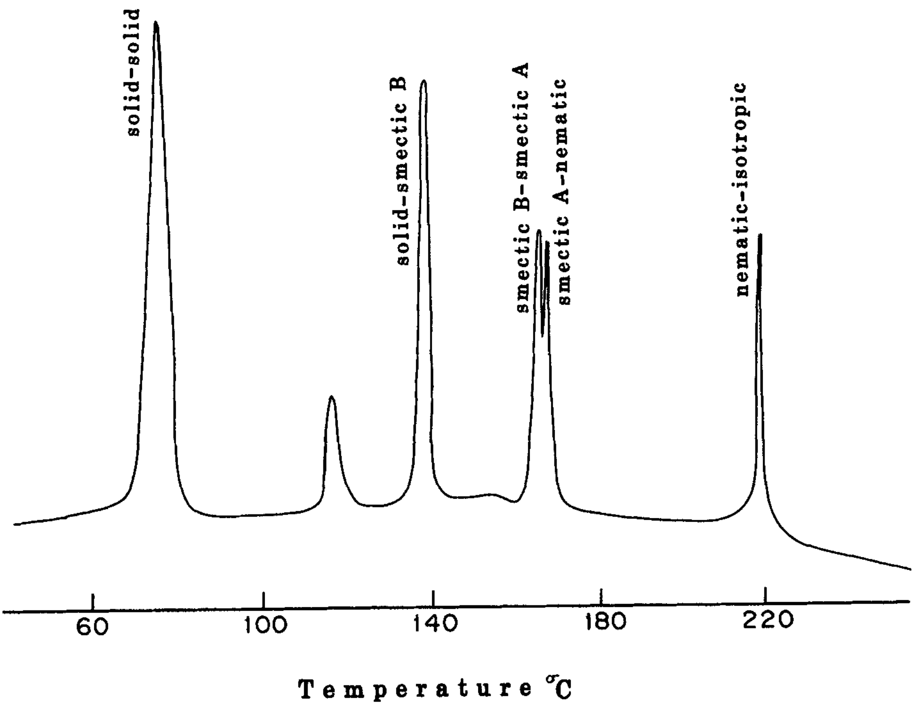


Figure 3. DSC scan of *N*,*N*′-bis[*p*-hexylbenzoate]-α,α′-bi-*p*-hydroxytoluene. Scan rate 10°C/min.

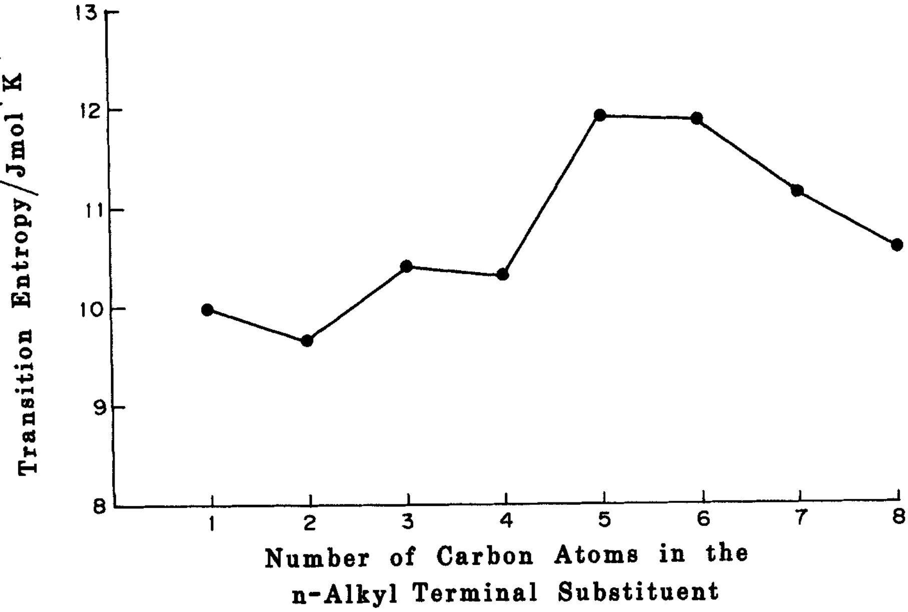


Figure 4. Plot of liquid crystal transition entropies vs. *n*-alkyl chain length for *N*,*N*′-bis-[*p*-alkylbenzoate]-α,α′-bi-*p*-hydroxytoluene.

This work was funded in part by the University of Kuwait and the Kuwait Foundation for the advancement of Science, project number SC 035/86-13/03. It was also funded in part with Federal funds from the U.S. Department of Health and Human Services under Contract Number No1-CO-74102.

References

[1] DEMUS, D., and ZASCHKE, H., 1904, *Flussige Kristalle in Tabellen II* (VEB Deutscher Verlag, F. Grundstoffindustrie, Leipzig).
[2] KELKER, H., and HATZ, R., 1980, *Handbook of Liquid Crystals* (Verlag Chemie, Weinheim).
[3] KELKER, H., 1978, *Adv. Liq. Crystals*, **3**, 237.
[4] JANINI, G. M., 1979, *Adv. Chromat.*, **17**, 231.
[5] WITKIEWICZ, Z., 1982, *J. Chromat.*, **251**, 311.
[6] JANINI, G. M., JOHNSTON, and K., ZIELINKSI, W. L., JR., 1975, *Analyt. Chem.*, **47**, 670.
[7] JANINI, G. M., MUSCHIK, G. M., and ZIELINSKI, W. L., JR., 1976, *Analyt. Chem.*, **48**, 809.
[8] JANINI, G. M., MUSCHIK, G. M., SCHROER, J. A., and ZIELINSKI, W. L., JR., 1976, *Analyt. Chem.*, **48**, 1879.
[9] JANINI, G. M., MUSCHIK, G. M., and HANLON, C. M., 1979, *Molec. Crystal liq. Crystals.*, **53**, 15.
[10] JANINI, G. M., and MUSCHIK, G. M., 1982, *Molec. Crystals liq. Crystals*, **87**, 281.
[11] GRAY, G. W., 1962, *Molecular Structure and the Properties of Liquid Crystals* (Academic Press).
[12] GRAY, G. W., 1976, *Molecular Geometry and the Properties of Nonamphiphilic Liquid Crystals*, Vol. 2, edited by G. H. Brown (Academic Press), p.1.
[13] BARRALL II, N., and JOHNSON, J., 1974, *Liquid Crystals and Plastic Crystals*, Vol. 2, edited by G. W. Gray and P. A. Winsor (Ellis Harwood Ltd.), p. 225.