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Schiff Base liquid Crystals with Terminal Alkoxy Group Synthesis and Thermotropic Properties

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Abstract

A new homologous series of Schiff base esters comprising a terminal alkoxy substituent N-{(n-alkoxy-4``-bezoyloxy)-4`- benzylidene}-4-butyl aniline was studied. The alkyloxy substituent contributes to the molecular polarizability, thus, affecting intermolecular interactions, hence, resulting in nematic polymorphism. The mesomorphic properties were studied using polarizing optical microscope (POM). The lower members, n-methoxy and n-ethoxy derivatives were non-mesogens, enantiotropic nematogenic phase was observed on further lengthening of the alkyl chain from C3 to C6 and smectogenic phase was observed for compounds C7 and C8. FT-IR, ^{1}HNMR, ^{13}CNMR, EI-MS and elemental analysis were employed to elucidate the molecular structure of the title compounds whereas the liquid crystal properties were determined by POM analysis. The mesomorphic behaviors of the homologous compounds are rationalized based on the varying lengths of the alky chain.

Keywords: Schiff`s bases, nematic liquid crystals.

Introduction

Liquid crystalline materials have many practical applications in scientific and technological areas, in particular as display devices, organic light emitting diodes, anisotropic networks, photoconductors and semiconductor materials [1-3]. High demand of new liquid crystals for applications has led to the preparation and study of numerous mesogens in particular, thermotropic liquid crystals [4-5]. Most thermotropic liquid crystals are rod-like molecules having a rigid core possessed of two or more phenyl rings and one or more flexible terminal alkyl chains. Schiff base, also known as imine (CH=N), is a linking group used in connecting the rigid core groups. Though it provides a stepped core structure, yet it retains molecular linearity, hence providing higher stability and enabling formation of mesophase [6]. Comprehensive studies on Schiff base core systems have been conducted since the discovery of N-(4-Methoxybenzylidene)-4-butylaniline (MBBA) which exhibited a nematic phase at room temperature [7]. Several studies have been conducted on Schiff base esters owing to their interesting properties and substantial temperature range [8-11]. Understanding of structure-property relationship is elemental on molecular modifications for synthesis of new mesogens with desirable properties and future applications [12]. Typical terminal moieties exhibiting liquid crystal properties are those alkoxy group. Polar substituents possessing strong dipole moments, thus having the ability to promote mesomorphic properties [13]. The increased dipole moment enhances the stability of the lattice and melting temperatures[14]. As the length of the terminal substituent increases, the molecules tend to orientate in a parallel arrangement [15].

Instrumental

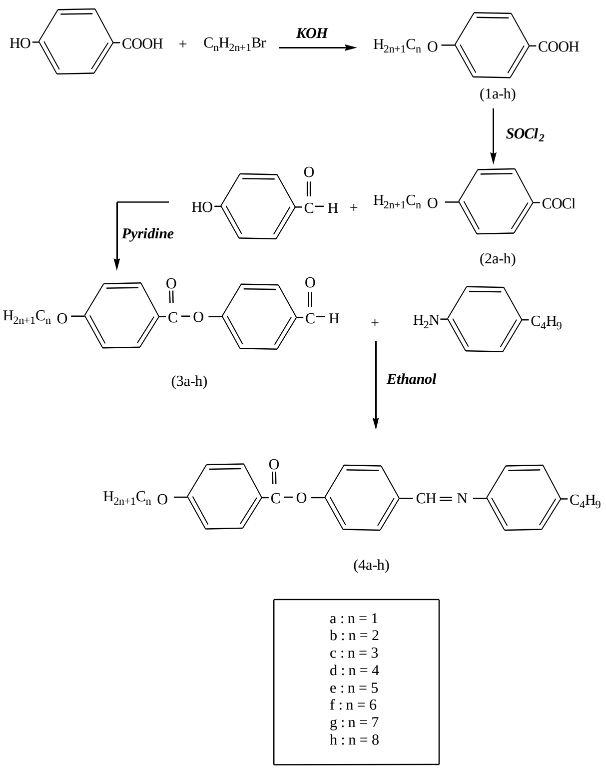
All chemicals and solvents were of analar grade and were used without further puriffcation. Electron ionization mass spectrum (EI-MS) was recorded using a Shimadzu GCMS-QP2010 Ultra/SE mass spectrometer operating at 70 eV ionizing energy. Samples were introduced using a direct inlet system with a source temperature of 200ºC. Microanalyses were carried out on Euro EA Elemental analyzer A-3000. FT-IR data were acquired with a 8300 Shimadzu Fourier Transform Infrared spectrophotometer in the frequency range of 4000 to 400 cm^{-1} with samples embedded in KBr pellets. ^{1}HNMR and ^{13}CNMR spectra were recorded in DMSO using a Bruker 300 MHz NMR

Spectrometer with Trimethylsilane (TMS) as the internal standard.

Liquid crystalline properties were investigated by POM using a (Meiji MT9000) Polarizing Optical Microscope attached to an INSTEC Hot stage. The texture of the compounds were observed using polarized light with crossed polarizers, the sample being prepared as a thin film sandwiched between a glass slide and a cover. A camera (Lumenera) was installed on the polarizing microscope.

Synthesis

The intermediate and title compounds were prepared according to the following scheme:



Scheme (1) The synthetic pathway for the titled compounds.

Synthesis of 4-n-alkoxybezoic acid and 4-n-alkoxybezoyl chloride:

Were prepared according to previously reported methods [16].

Synthesis of 4-(4`-n-alkoxybezoyloxy) benzaldehyde [16]

Equal amounts of 4-hydroxybenzaldehyde and 4-n-alkoxybezoylchoride, along with 10 ml of dry pyridine were stirred for three hours in an ice bath. The mixture was poured into cold water acidified with HCl and filtered. The product was washed with cold water.

Synthesis of N-{(n-alkoxy-4``-bezoyloxy)-4`-benzylidene}-4-butyl aniline [16]:

Equal amounts of 4-[4`-n-alkoxybezoyloxy] benzaldehyde and 4-n-butylaniline, along with 30 ml of absolute ethanol were refluxed for three hours. The mixture was cooled to room temperature and filtered. The yellow product was recrystallized with ethanol until its transition temperature remained constant (Scheme (1)). The percentage yield and analytical data of the title compounds are tabulated in Table (1). EI-MS, IR, ^{1}HNMR and ^{13}CNMR data of the representative compound 4d are given as follows: EI-MS (m/z, relative intensity): 429 (20) [M+, 57 (100); IR (KBr) (cm^{-1}): 2927.3, 2845.1 (υ C-H aliphatic); 1752.7 (υ C=O ester); 1621.4 (υ CH=N), 1284.3 (υ C-O), 831.2 (γ disubstituted benzene); ^{1}HNMR: δ 0.94 (t, 6H (H1 & H8)), 2.5 (t, H4), 1.57-1.75 (q, 8H, H3 & H6), 3.94 (H5, t, 2H, $-CH_2-O-$), 6.98 – 7.42 (dd, 4H, Ar-H), 7.94 – 8.19 (dd, 4H, Ar-H), 8.66 (s, 1H, -CH^e=N-); ^{13}CNMR (100 MHz, DMSO,): δ 13.7 – 40.8 for (CH_3-) and (- CH_2 –), 63.6 ($-CH_2O-$), 113.9 – 163.1 for aromatic carbons, 163.64 (-CH=N-), 191.9 (-COO-).

Results and Discussion

Synthesis and spectral studies

Structure elucidation of compounds 4a-h was ascertained by using elemental analysis, mass spectrometry and IR and spectroscopic methods Figs. (1 to 4). The experimental and theoretical values obtained from the elemental analysis of 4a-h (Table (1)) were in good agreement.

Table (1)
Percentage yields and analytical data of compound 4a-h.

Compound	*Yield (%)*	*Formula*	*% Found (% Calcd.)*		
			C	*H*	*N*
3a	84.5	$C_{15}H_{12}O_4$	70.42(70.31)	4.51(4.68)	-
3d	88.3	$C_{18}H_{18}O_4$	72.53(72.48)	5.99(6.04)	-
3h	80.2	$C_{22}H_{26}O_4$	74.43(74.57)	7.28(7.34)	-
4a	67.9	$C_{25}H_{25}O_3N$	77.58(77.51)	6.34(6.45)	3.58(3.61)
4b	78.6	$C_{26}H_{27}O_3N$	77.89(77.80)	6.69(6.73)	3.45(3.49)
4c	77.0	$C_{27}H_{29}O_3N$	78.11(78.07)	6.88(6.98)	3.32(3.37)
4d	75.3	$C_{28}H_{31}O_3N$	78.41(78.32)	7.17(7.22)	3.29(3.26)
4e	76.9	$C_{29}H_{33}O_3N$	78.64(78.55)	7.39(7.44)	3.10(3.16)

The molecular ion peak at m/z = 429 in the mass spectrum of the representative compound 4d (Fig. (1)) suggested that 4d with a molecular formula of ($C_{28}H_{31}NO_3$) was successfully synthesized, the other peaks are shown in the fragmentation pattern (Scheme (2)). Fourier transform infrared (FTIR) spectrum (Fig. (2)) show that the diagnostic bands assignable to the stretching of representative compound 4d were observed at the respective frequencies 2927.3, 2845.1 and 1752.7 cm^{-1}. The absorption band assignable to the stretching of CH=N bond was observed at frequency of 1621.4 cm^{-1}, and these values conform with those reported in the Infrared (IR) spectra for various substituted aromatic Schiff bases[17]. The ^{1}HNMR spectrum of 4d (Fig. (3)) further supported its structure. The two triplets at $\delta = 0.94$ ppm and $\delta = 3.94$ ppm, were, respectively ascribed to the methyl and methylene protons ($-CH_2O-Ar$), while the multiplet at $\delta = 1.57$ ppm was assigned to the methylene protons of the long alkyl chain $\{CH_3(CH_2)_2\}$. The four distinct doublets between $\delta = 6.98-7.90$ ppm were indicative of the aromatic C-H and carbonyl (C=O of ester) of protons. The singlet observed at the most downfield region, $\delta = 8.66$ ppm, supported the presence of the imine linking group [11]. The molecular structure of 4d was further verified by using ^{13}CNMR spectroscopy (Fig. (4)). The peak at $\delta = 13.5$ ppm was attributed to the methyl carbon while the peaks between $\delta = 18.8 – 31.1$ ppm represented the methylene carbons of the long alkyl chain. The 18 carbons of the aromatic ring in 4d resonated between $\delta = 113.9$ to 163.1 ppm. The peak at $\delta= 163.6$ ppm and $\delta= 191.9$ ppm confirmed the presence of the azomethine carbon and the carbonyl group in the molecule.

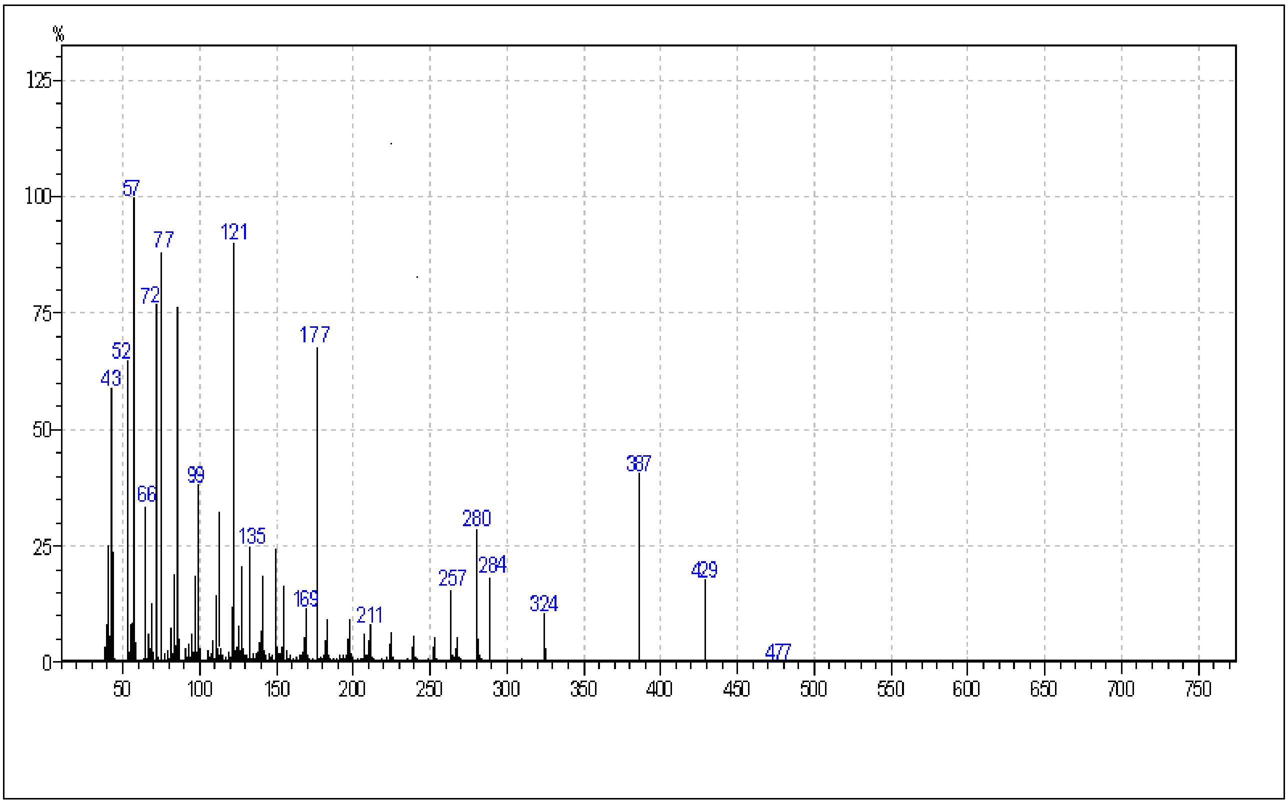


Fig.(1) EI-MS Spectrum of compound 4d.

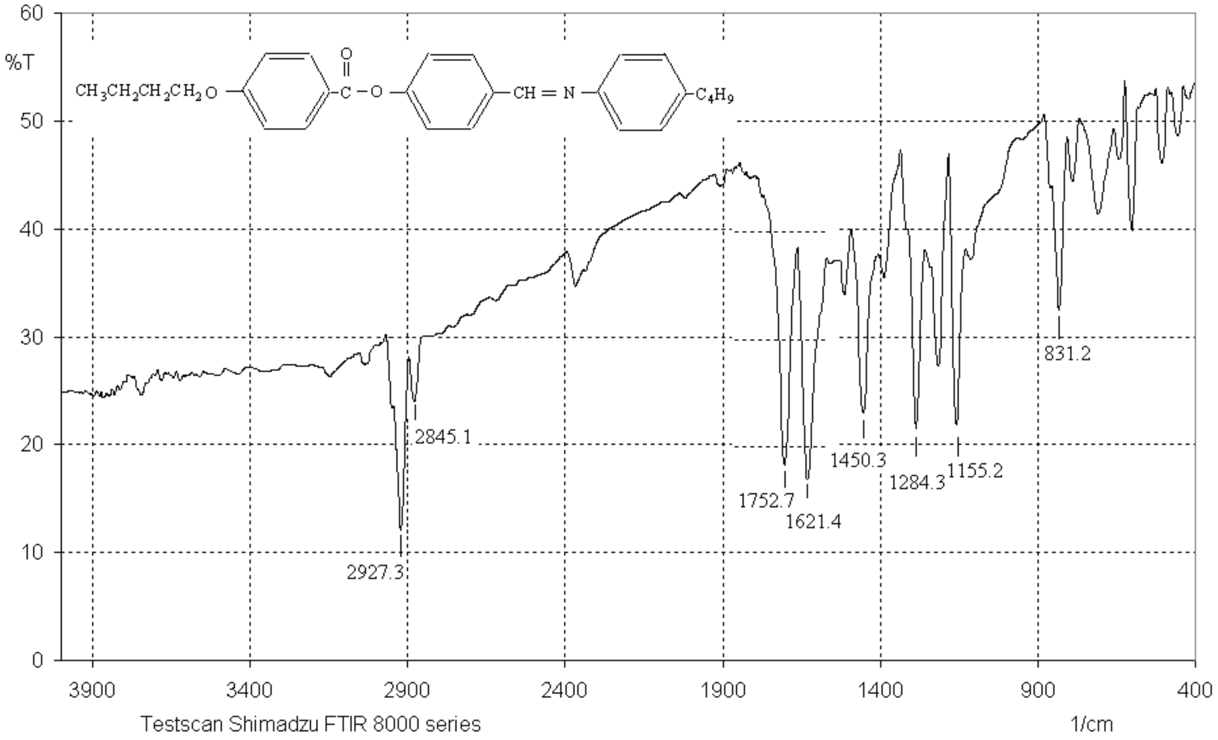
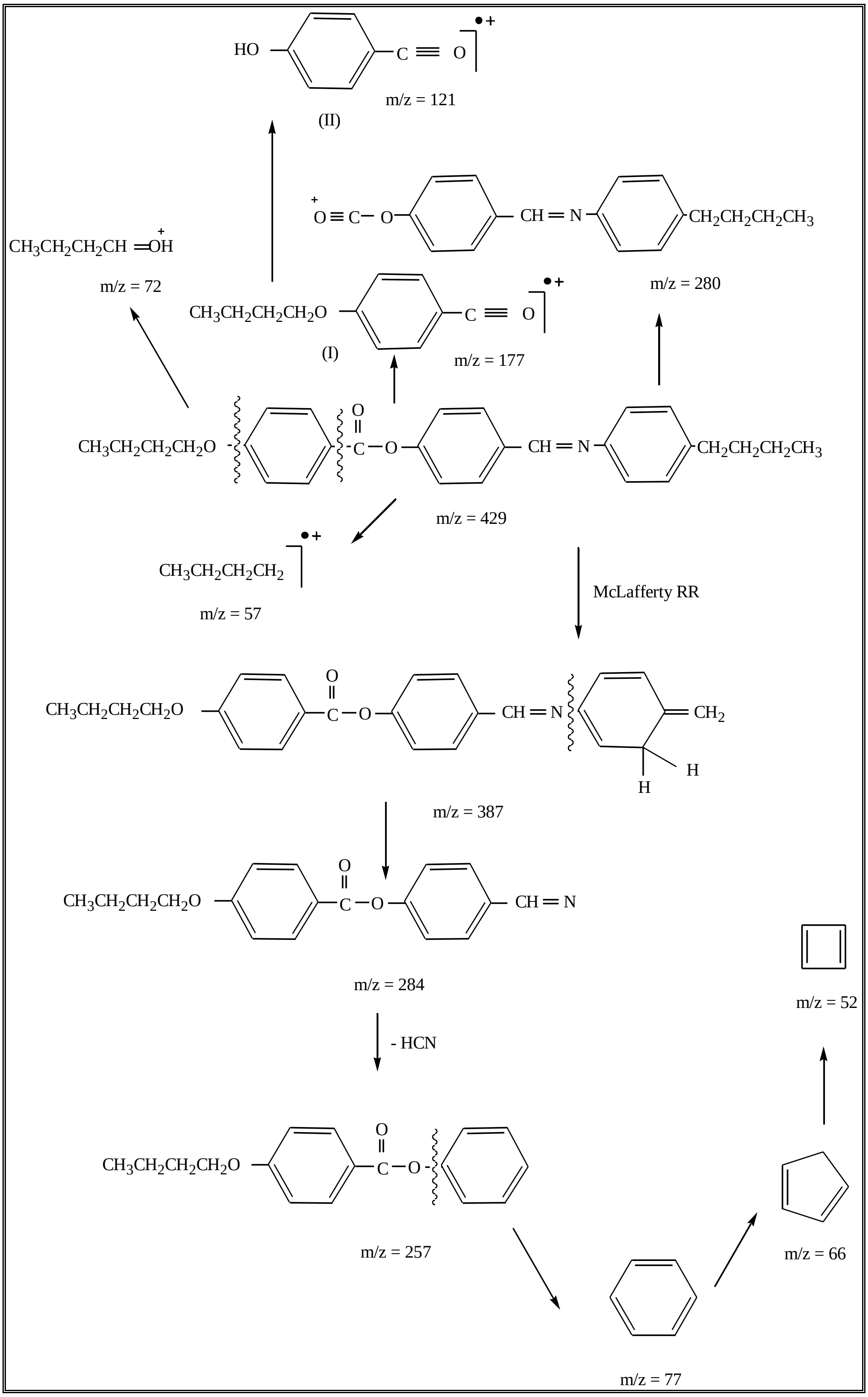
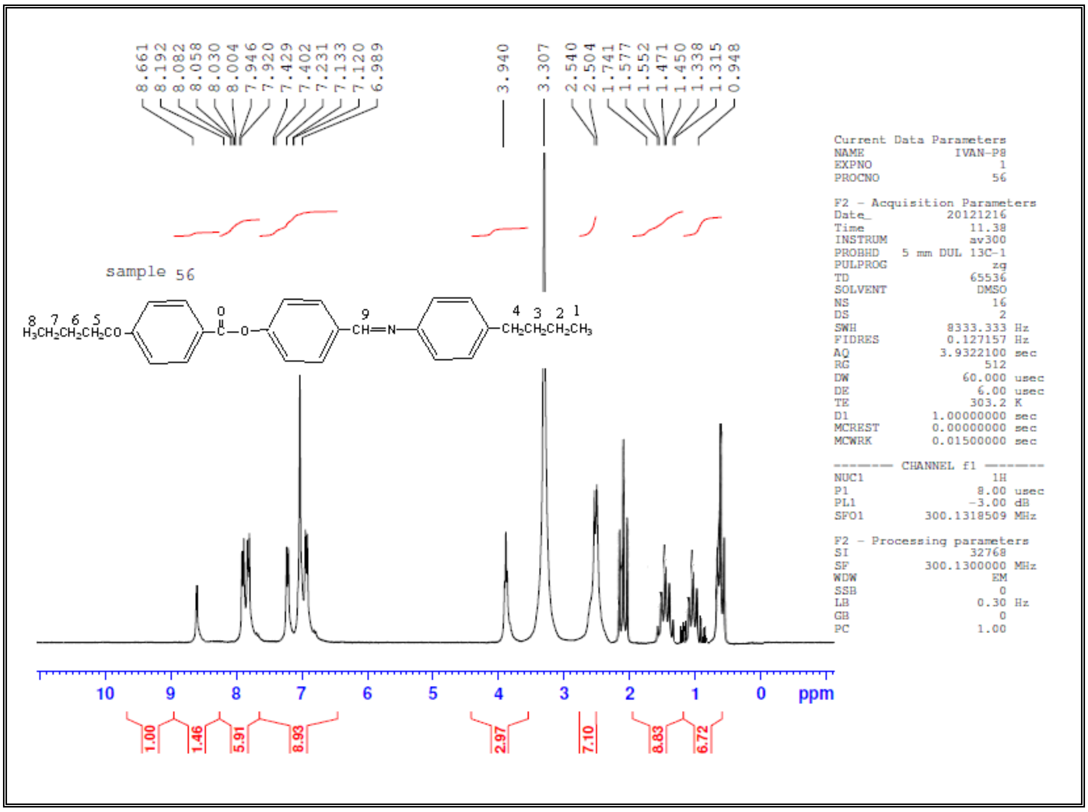


Fig.(2) FTIR spectrum of compound 4d.



Scheme (2) The fragmentation modes for compound 4d.



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PROCNO                 56

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PULPROG                zg
TD                  65536
SOLVENT              DMSO
NS                     16
DS                      2
SWH              8333.333 Hz
FIDRES           0.127157 Hz
AQ              3.9322100 sec
RG                    512
DW                 60.000 usec
DE                   6.00 usec
TE                  303.2 K
D1             1.00000000 sec
MCREST         0.00000000 sec
MCWRK          0.01500000 sec

======== CHANNEL f1 ========
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P1                   8.00 usec
PL1                 -3.00 dB
SFO1          300.1318509 MHz

F2 - Processing parameters
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GB                      0
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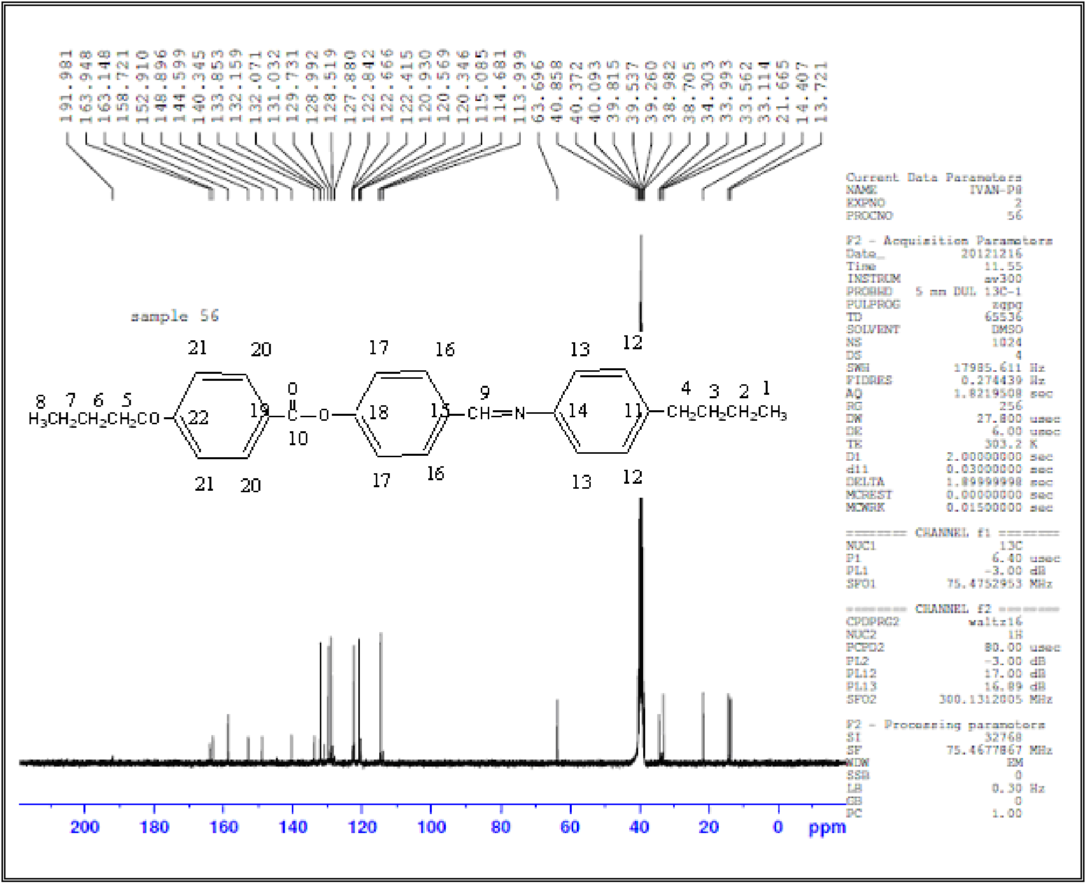
Fig.(3) ^{1}HNMR spectrum for compound 4d.



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RG                    256
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DE                   6.00 usec
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D1             2.00000000 sec
d11            0.03000000 sec
DELTA          1.89999998 sec
MCREST         0.00000000 sec
MCWRK          0.01500000 sec

======== CHANNEL f1 ========
NUC1                  13C
P1                   6.40 usec
PL1                 -3.00 dB
SFO1           75.4752953 MHz

======== CHANNEL f2 ========
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NUC2                   1H
PCPD2               80.00 usec
PL2                 -3.00 dB
PL12                17.00 dB
PL13                16.89 dB
SFO2          300.1312005 MHz

F2 - Processing parameters
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SF             75.4677867 MHz
WDW                    EM
SSB                     0
LB                   0.30 Hz
GB                      0
PC                   1.00
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Fig.(4) ^{13}CNMR spectrum for compound 4d.

Table (2)
FTIR spectral data for synthesized compounds.

Comp No.	RO - group	υ C-H Aro. cm^{-1}	υ C-H Aliph. cm^{-1}	υ C=O cm^{-1} Ald.	υ C=N cm^{-1}	υ C=C cm^{-1}	υ C=O cm^{-1} Ester
3a	$-OCH_3$	3078.9	2904.5-2856.3	1722	-	1560.9	1741
3d	$-OC_4H_9$	3080.1	2981.7-2829.4	1738	-	1534.1	1747
3h	$-OC_8H_{17}$	3064.4	2920.2-2854.4	1724	-	1602.7	1749
4a	$-OCH_3$	3025.3	2953.8-2839.0	-	1618	1572.9	1742
4b	$-OC_2H_5$	3076.5	2974.0-2864.1	-	1620	1551.8	1735
4c	$-OC_3H_7$	3035.0	2943.7-2863.1	-	1623	1534.6	1747
4d	$-OC_4H_9$	3085.6	2959.4-2886.0	-	1625	1583.2	1752
4e	$-OC_5H_{11}$	3077.1	2935.7-2848.7	-	1621	1581.5	1744
4f	$-OC_6H_{13}$	3081.3	2968.1-2852.4	-	1628	1562.3	1738
4g	$-OC_7H_{15}$	3046.9	2942.5-2876.2	-	1622	1549.6	1743
4h	$-OC_8H_{17}$	3062.1	2984.3-2861.4	-	1626	1575.2	1744

Mesomorphic properties

The synthesized compounds exhibited interesting thermotropic properties and its melting behavior was carefully monitored by POM during both heating and cooling scans. The results from the POM observation were verified by the DSC measurements. The transition temperatures and phase sequences are summarize in Table 3. Phase identification was based on the optical textures, and the magnitude of isotropization on enthalpies is consistent with the assignment of each mesophase type, using the classification systems reported by Sackmann and Demus (1966) and Gray and Goodby (1984) [18-19]. Under POM, nematic texture was observed (Fig.(5)). Out of the eight compounds, the first two members (C1 and C2) did not possess mesomorphic properties. These molecules with short alkyloxy chains are too rigid, therefore have high melting points, thus impeding their liquid crystal properties [20]. Once the length of the terminal chain is increased, the molecule becomes more flexible, hence promoting a single mesophase in a particular compound. Therefore, the C3 – C8 members exhibited nematic mesophase. All compounds, from C3 and C8 are enantiotropic liquid crystals because the stable mesophases were observed during both heating and cooling processes. From the graph, the lower member of the homologous series, C3, possessed the highest melting temperature (Tm = 166°C). The melting point decreased as the length of the chain increased to the C8 member (Tm = 110C). This resulted from the increase in the flexibility of the molecule owing to the longer alkyl chain. It is also common that the melting temperature increases from the medium chain member onwards following a decrease from the short to the medium chain members [21]. This ascending trend could have been attributed to the increase in the Van der Waals attractive forces between the molecules [22]. As the series ascends from the C1 to the C2 member, the C -to- I transition temperatures attenuates consistently. The even members possessed high clearing temperatures compared to their odd member counterparts. Such attenuation of the melting temperatures has been observed in various homologous systems of liquid crystals [23]. While the C3 to C6 members exhibited an increase in their transition temperatures during the N-to-I transition, C7 and C8 exhibited smectic mesophase, the terminal intermolecular attractions play a role in determining the N-I transition temperatures, that is, the destruction of the nematic molecular order is determined by the fact that the terminal attractions become weaker, allowing partial interpenetration of the layers to occur more easily as the alkoxy chains grow longer, in turn depressing the S-to-I transition temperatures [24].

Table (3)
Melting points and type of transition for compounds 4a-h.

Comp. No.	*Melting point°C*	*Transition*
4a	176 – 179	C → I
4b	168 – 170	C → I
4c	154 – 166	C → N
4d	115- 155	C → N
4e	120 – 140	C → N
4f	121 – 130	C → N
4g	117– 125	C → Sm
4h	110– 119	C → Sm

C = Crystal; Sm = Smectic ; N = Nematic; I = Isotropic liquid.

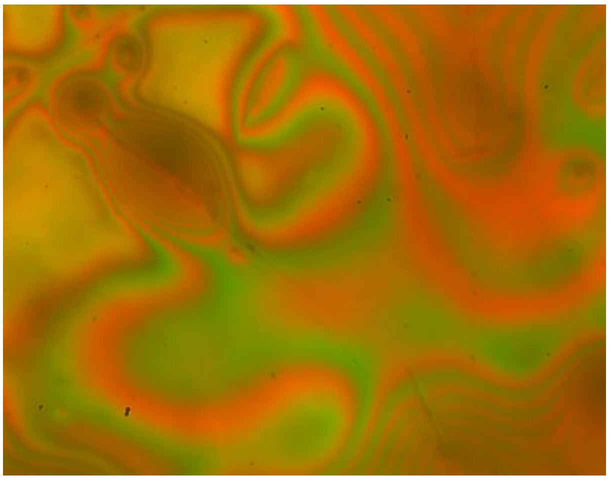

Fig.(5) Nematic texture of compound 4d.

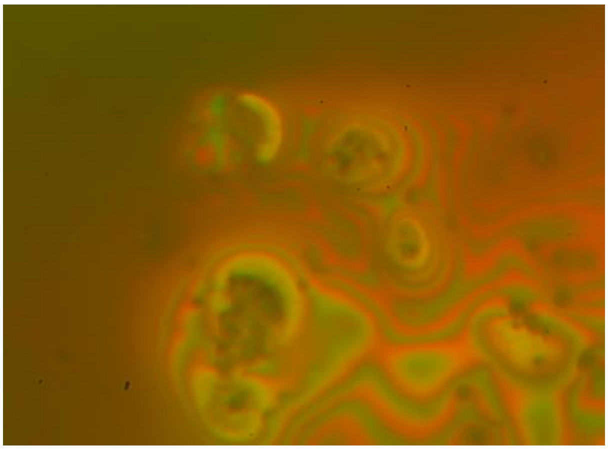

Fig.(6) Nematic texture of compound 4f.

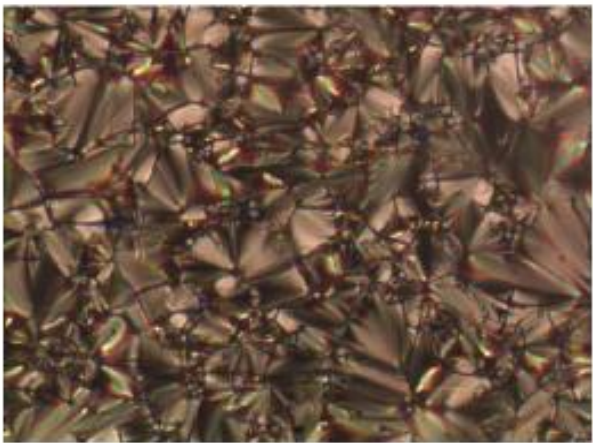

Fig.(7) Smectic texture of compound 4h.

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الخلاصة

تم دراسة سلاسل متماثلة جديدة لقواعد شف الحاوية على مجموعة استر N-[4`-{(4``-n-alkoxybezoyloxy) benzylidene} -4-butyl- aniline. تم ملاحظة تأثير تعويض مجموعة الالكوكسي على الاستقطاب الجزيئي والذي يؤثر على التآثر البيني للجزيئات والذي ادى الى ظهور اطوار متعددة نيماتي وسمكتي. تم تشخيص الصفات البلورية السائلة بأستخدام مجهر الضوء المستقطب. لم تُظهر مشتقات الميثوكسي والايثوكسي اي صفات بلورية سائلة، بينما اظهرت المشتقات C3 – C6 طور نيماتي والمركبات C7و C8 طور سمكتي. تم استخدام مطيافية الاشعة تحت الحمراء والرنين النووي المغناطيسي للبروتون والكاربون وطيف الكتلة وتحليل العناصر لتوضيح التركيب الجزيئي للمركبات المحضرة، في حين تم استخدام مجهر الضوء المستقطب

مجموعة الالكيل على ظهور الصفات البلورية السائلة. لتعيين الصفات البلورية السائلة. لوحظ تأثير زيادة طول