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Research

Synthesis, Characterization and Phase Behavior with Ester of Terminal Alkoxy Chains and Methoxy Substituent

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Abstract:
A series of calamitic phenyl ester-aromatic imine derived from the reaction of 4-(N'-(4-methoxyphenyl)acetimidamido)phenyl 4-alkoxybenzoate by condensing 0.1 Mole of 4- acetamidophenyl -4-*n*-alkoxy benzoates [B] with 0.1 mole of 4-anisidine exhibited mesomorphic and present series compared with other structure related series have been successfully synthesized and characterized. The general molecular structures of ultimate compounds show the central fragment made up by a hybrid core of phenyl ester-aromatic imine in which the terminal alkoxy(-OR) chains, $C_n H_{2n+1}$ in which $n = 1$ to8, 10,12,14 and 16 were connected to phenyl while the other end consists of methoxy moiety attached to a phenyl ring. All the target compounds under polarized lights exhibit enantiotropic nematic phase of which the temperature range was further supported by DSC analysis. It can be summarized that the lengthening of terminal alkoxy (-OR) chains has contributed to the lowering of melting and clearing temperatures as well as the thermal stability of nematic phase.

Keywords: Aromatic imine, central fragment, enantiotropic, polarized, nematic

Introduction

Liquid crystals (LCs) are fluid materials made of anisotropic molecules, exhibiting as an intermediary state between isotropic liquid and crystalline solid [1–3]. LCs typically have low viscosities (~0.1 P) and the ordered phase is characterized by fascinating optical properties like low-threshold laser emission, Bragg reflection and strong Rayleigh scattering [4,5]. Interestingly, they are found in everywhere and utilized in numerous appliances, display devices, manufacturing facilities, automotive and medical technology [6–10].

The orientation of LCs materials is effectively controlled by weak electric or magnetic field owing to the anisotropy of the electrical and magnetic properties [11,12]. The calamitic mesogens have commonly been associated with the rod-like (elongated) molecule. It is one of the most influential molecular types in the formation of liquid crystals. The existence of this matter can be explained based on the anisotropic interactions and steric packing of the molecules [13,14]. In general, the molecular length (l) of rod-like molecule is significantly greater than the molecular breadth (h). It has well been reported that rod-like molecules packed together in parallel to maximise the use of available volume and thus minimize the free volume [15,16]. The typical for- mulation of the calamitic mesogens can be exemplified with the presence of aromatic/nonaromatic rigid core and flexible hydrocarbon chains. The introduction of the flexible terminal chains on the rigid core is very useful to offset the molecular structure in promoting the liquid crystalline properties [17–20]. Fornasieri and co-workers reported three series of rod-shaped LCs comprising a mesogenic core (monophenyl, biphenyl or phenyl benzoate groups) bonded to a perflourinated chain through thioester linkage and a hydrocarbon chain with terminal double bond [21]. Throughout their observation, the increase of the aromatic rings in the core structure of the LCs compound as well as elongating the hydrocarbon chains gave significant

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effects on the liquid crystalline behaviour and transition temperature wherein the long hydrocarbon chains led to a reduction in the mesomorphic properties whilst increasing the number of aromatic rings in the core fragments resulted in the increase of the transition temperature [21].

Apart from behaving as liquid crystal, many researchers prompted to innovate and synthesize new materials which possess the potential to show the magnetic proper- ties. The magnetic interaction occurred when the materials exert either attractive or repulsive forces on another. These magnetic properties typically lie in the orbital and spin motions of electrons [22,23]. The magnetic properties of liquid crystalline materials can be classified into several main categories, which are diamagnetism, para- magnetism and ferromagnetism [24–26]. Many studies have claimed that the requirement of a material to possess magnetic behaviour depends on the structure of com- pound, usually associated with the rare-earth elements, metal-complexes and organic radical compounds [27,28]. One of these works focussed on the magnetic behaviour that was discovered for nitronyl nitroxide and verdazyl derivatives [29]. Besides, the magnetic behaviour of the materials had been linked to the influence brought about by the introduction of specific substituent in the compound. For instance, the influence of the different fluoro- substituted phenylacetates on co-ligands can improve the structural topologies and subsequently affect the mag- netic properties of azido-Cu(II) complexes [30]. The experimental studies have shown the unusual intermolecular magnetic interaction in the SmC phase of organic radical compound [31]. To better understand the effect of the macroscopic structures on the magnetic properties, Umeta and co-workers analyzed the magnetic properties of organic radical fibers aligned self-assembled in the LCs. The organic radicals are anticipated as organic magnetic
compounds because of the magnetic moments obtained from the odd electrons [32]. Magnetic LCs containing rare-earth complex are attracting widespread interest due to their large magnetic anisotropy, hence the external magnetic field is required to align these paramagnetic LCs [33]. Although substantial research has been conducted on metal and organic radical materials with magnetic and liquid crystal properties, but there is only minimal study on non-metal or non-radical compounds that exhibit magnetic and liquid crystal properties. Our group has recently discovered the presence of magnetism in non-radical or non-metal materials on a liquid crystal- line compound of tri-substituted phenyl derivatives [34].

Subsequent to this, they are prompted to investigate a new series of mesomorphic properties of molecules containing three phenyl rings of which the rings made up by hybrid molecular segments from phenyl ester and aromatic core where in various terminal alkoxy chains, OC_nH_{2n+1} (n = 1to8,10,12,14 and 16) connected to the phenyl but the other end of aromatic core having a *para*-methoxy group.

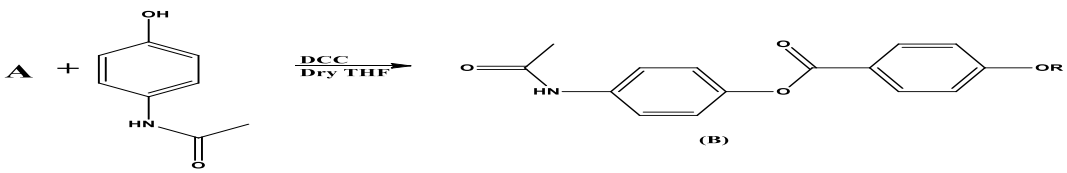
In the present study, we prepared 4-(N'-(4-methoxyphenyl) acetimidamido) phenyl 4-alkoxybenzoate by condensing 0.1 Mole of 4-acetamidophenyl -4-*n*-alkoxy benzoates [B] with 0.1 mole of 4-anisidine exhibited mesomorphism and present series compared with other structure related series.

2. Synthetic Route:

STEP 1

4-*n*-Alkoxy benzoic acids.

STEP 2



4- acetamidophenyl -4-*n*-alkoxy benzoates

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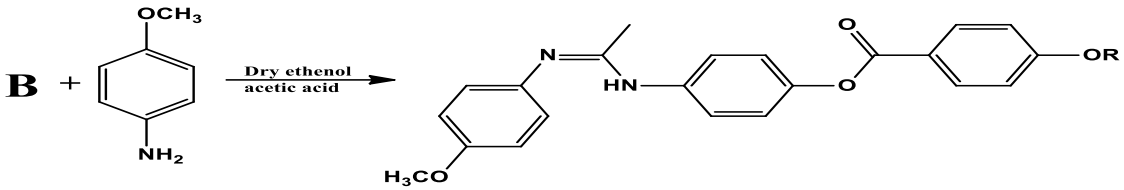
STEP 3



[4-(N'-(4-methoxyphenyl)acetimidamido)phenyl 4-alkoxybenzoate]

3. EXPERIMENTAL:

4-Hydroxybenzoic acid, the appropriate, *n*-alkyl halides, acetaminophen [Paracetamol], P-anisidine, KOH, DCC, DMAP, THF, Ethanol, Acetic acid were used as received. Solvents were dried and distilled prior to use. Microanalysis of the compounds performed on a Coleman carbon- hydrogen analyser, and IR spectra were recorded on Shimadzu lR-408. NMR spectra were recorded on a Perkin-Elmer R-32 spectrometer**.** The calorimetric studies were carried out on a Mettler TA**-**4000 DSC apparatus by adopting a scanning rate of 10^{0}c/min**.** Liquid crystalline properties were investigated on a Leitz Labour lux 12POL microscope provided with a heating stage. Fluorescent spectra were recorded on a Shimadzu Rf540spectrophotofluromete.

STEP 1

Process:

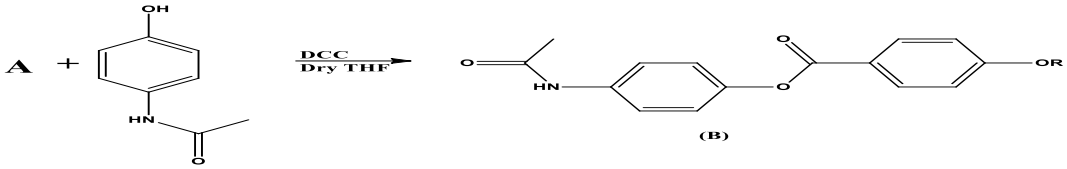
Preparation of 4-*n*-Alkoxybenzoic acid: [**A**]:

4-*n*-Alkoxy benzoic acids.

4-*n*-Alkoxybenzoic acid were synthesized by the method of Dave and Vora. Commercially available 4-methoxybenzoic acid (*p*-anisic acid, B. D. H) was used. Numbers of methods [35,36] are known for alkylation of 4-hydroxybenzoic acid. However, in the present study, the method developed by Dave and Vora [37] was followed. 0.1 Mole of the 4-hydroxybenzoic acid, 0.12 mole of appropriate 1-bromoalkane and 0.25 mole of the potassium hydroxide were dissolved in 100 ml ethanol and refluxed for seven to eight hours. 25 ml of 10% percent aqueous potassium hydroxide solution was added and reflux was continued for two hours to hydrolyse any ester formed. The solution was cooled and acidified with 1:1 cold aqueous hydrochloric acid to precipitate the acid. The alkoxy [-OR] acids were crystallized several times from ethanol or acetic acid until constant transition temperature was obtained. The transition temperatures are in good accordance with the literature [37].

Preparation of [4- acetamidophenyl -4-*n*-alkoxy benzoates] [**B**]:

STEP 2



4- acetamidophenyl -4-*n*-alkoxy benzoates

0.1 Mole of 4-(4'-*n*-Alkoxybenzoic acids) **[A],** 0.1 mole acetaminophen[Paracetamol], 0.1 mole of DCC [38] and 0.1 mole of DMAP were dissolved in dry THF and stirred at room temperature for overnight. The insoluble solid was removed through filtration. The crude product was repeatedly crystallized from the methanol. All the compounds of the present series were synthesized with the same method. Yield in general is 60-65%. The elemental analysis of all the compounds was found to be satisfactory and all are listed in table.

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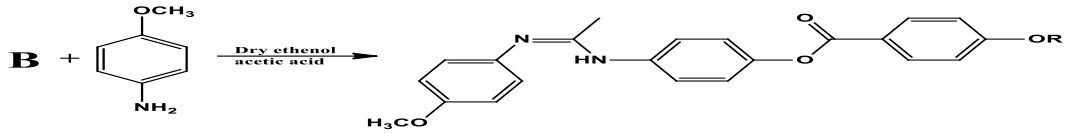
Preparation of (Z)-4-(N'-(4-methoxyphenyl)acetimidamido)phenyl 4-alkoxybenzoate

STEP 3



[4-(N'-(4-methoxyphenyl)acetimidamido)phenyl 4-alkoxybenzoate]

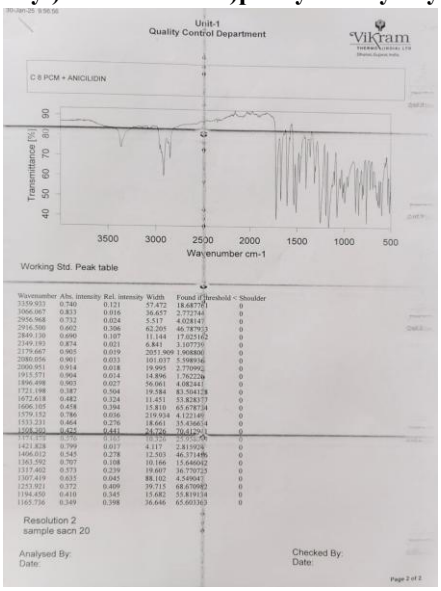
The corresponding 0.1 Mole of 4- acetamidophenyl -4-*n*-alkoxy benzoates [B] was dissolved in dry ethanol. The solution was added drop wise to the round bottom flask containing 0.1 mole of 4-anisidine, which was previously dissolved in dry ethanol and few drops of acetic acid. After mixing them the content of the flask heated under reflux for four hours. The crude product was repeatedly crystallized from the ethanol. All the compounds of the present series were synthesized with the same method. Yield in general is 80-85%. The transition temperatures agree well with the reported value [39].

Table 1: Transition temperatures (ºC) of the series I compound

Compound No.	R= -C_nH_{2n+1} *n* =	Cr		N		I
1	*1*	•	171	•	195	•
2	*2*	•	165	•	188	•
3	*3*	•	160	•	178	•
4	*4*	•	158	•	177	•
5	*5*	•	149	•	171	•
6	*6*	•	125	•	175	•
7	*7*	•	114	•	179	•
8	*8*	•	106	•	202	•
9	*10*	•	101	•	193	•
10	*12*	•	98	•	188	•
11	*14*	•	94	•	181	•
12	*16*	•	91	•	175	•

()=monotropic value; Cr=crystalline solid; Sm A=smectic A phase; N=nematic phase; I=isotropic liquid phase; •=phase exists.

IR graph of 4-(N'-(4-methoxyphenyl)acetimidamido)phenyl 4-octyloxybenzoate



IR Spectrum (KBr) $V_{max/Cm-1}$: 3359(-NH), 2956, 2916,2349, 2179 (-C=N), 1721 (-COO-), 1606, 1508, 1253(C-N), 1165, 1042, 885, 753.

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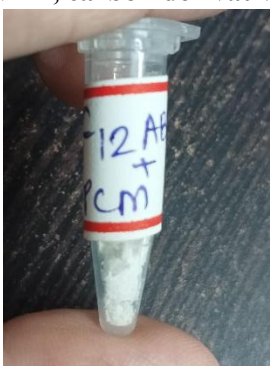
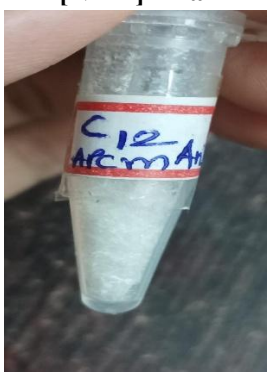
IR graph of 4-(N'-(4-methoxyphenyl)acetimidamido)phenyl 4-octyloxybenzoate [N=8] final

Preparation of [4- acetamidophenyl -4-*n*-butoxy benzoates] [B]: N=4, carbon derivative

Preparation of [4- acetamidophenyl -4-*n*-dodecyloxy benzoates] [B]: N=12, carbon derivative



Preparation of (Z)-4-(N'-(4-methoxyphenyl)acetimidamido)phenyl 4-dodecyloxybenzoate [N=12]-final



Preparation of (Z)-4-(N'-(4-methoxyphenyl)acetimidamido)phenyl 4-butyloxybenzoate [N=4]-final

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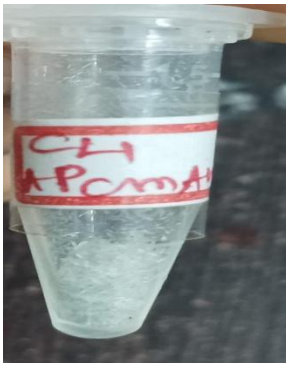

5. Mesophase behavior:

The mesomorphic phase exhibited by the octyloxy homologues of the series, were examined by POM [Polarising optical microscope]. Thin film of the sample was prepared by sandwiching samples of both the series between a glass slide and a cover slip.

Butyl oxy homologues of derivatives show Nematic liquid crystalline properties. On cooling from the isotropic liquid, *n*-Butoxy homologue of series showed to exhibit Nematic at 152°C . Octyloxy homologues of derivatives show Nematic liquid crystalline properties. On cooling from the isotropic liquid, *n*-Octyloxy homologue of series showed to exhibit Smectic A at 152°C. Dodecyl homologues of derivatives show Nematic liquid crystalline properties. On cooling from the isotropic liquid, *n*-Dodecyl homologue of series showed to exhibit Smectic A at 152°C .

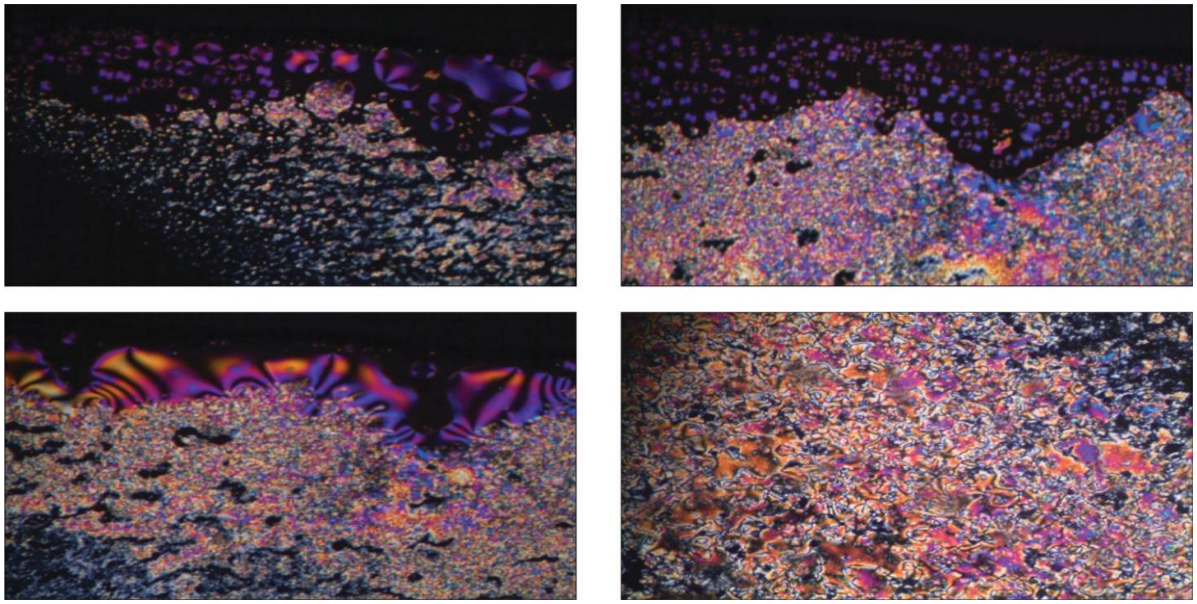

figure 1. Microphotograph nematic mesophase (Series **I**; *n*=4) at 172 ºC on cooling.

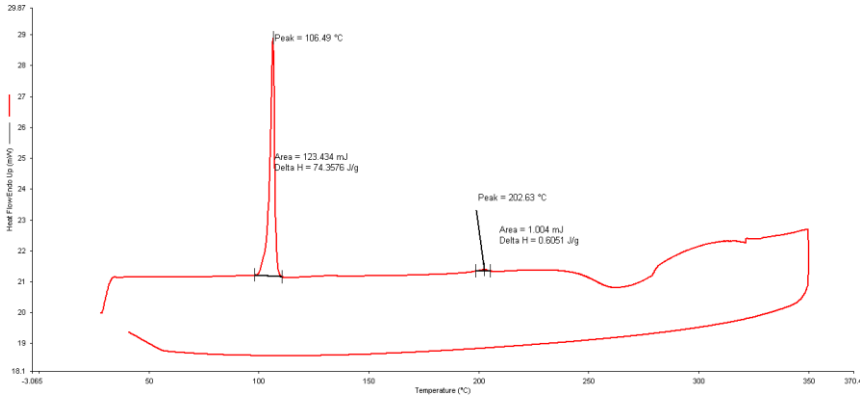

Figure 2. DSC Thermogram of (Series **I**; *n*=8) derivatives.

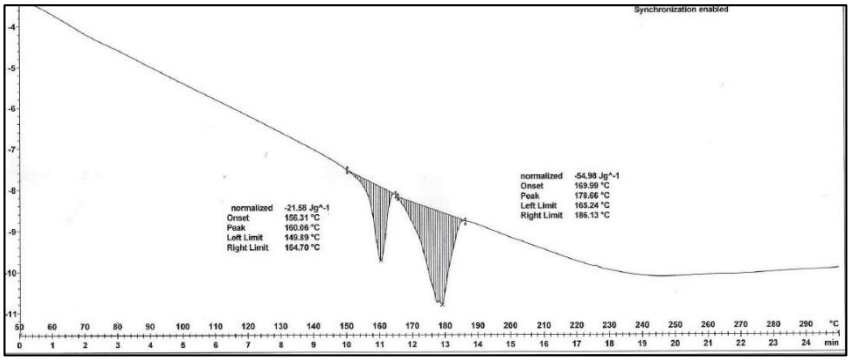

Figure 3. DSC Thermogram of (Series **I**; *n*=3) derivatives.

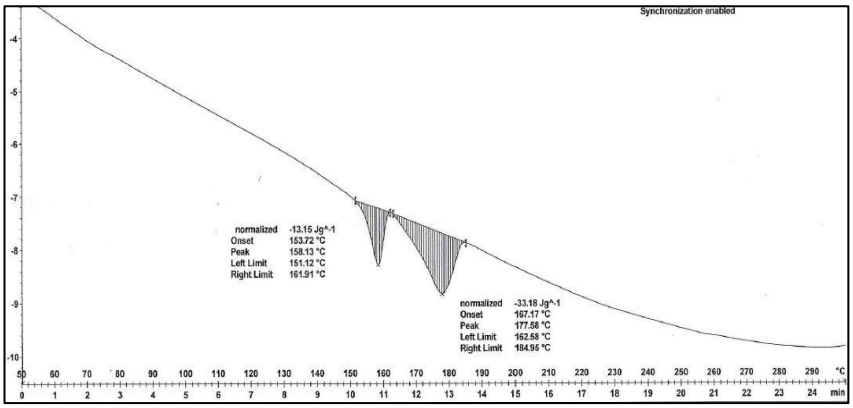

Figure 4. DSC Thermogram of (Series **I**; *n*=4) derivatives

References.

[1] Rajak P, Nath LK, Bhuyan B. Liquid crystals: an approach in drug delivery. Indian J Pharm Sci. 2019;81(1):11–21. doi: 10.4172/pharmaceutical- sciences.1000474

[2] Collings PJ, Goodby JW. Introduction to liquid crystals: chemistry and physics. Boca Raton (FL): CRC Press; 2019.

[3] Kim YK, Noh J, Nayani K, et al. Soft matter from liquid crystals. Soft Matter. 2019;15(35):6913–6929. doi: 10. 1039/C9SM01424A

[4] Pincus P. Magnetic properties of liquid crystals. J Appl Phys. 1970;41(3):974–979. doi: 10.1063/1.1659047

[5] Carlescu I, editor. Liquid crystals: self-organized soft functional materials for advanced applications. London (UK): BoD–Books on Demand; 2019.

[6] Khoo IC. Liquid crystals. Hoboken (NJ): John Wiley and Sons; 2022.

[7] Choudhury PK, M A Ibrahim A-B, editors. Liquid crystals. London (UK): IntechOpen. 2022.

[8] Lueder E, Knoll P, Lee SH. Liquid crystal displays: addressing schemes and electro-optical effects. Hoboken (NJ): John Wiley and Sons; 2022.

[9] Wang D, Park SY, Kang IK. Liquid crystals: emerging materials for use in real-time detection applications. J Mater Chem C. 2015;3(35):9038–9047. doi: 10.1039/ C5TC01321F

[10] Palffy-Muhoray P. Orientationally ordered soft matter: the diverse world of liquid crystals. Electronic-Liquid Crystal Communications (E-LC). 2007;60(9):54–60. doi: 10.1063/1.2784685

[11] Bury P, Veveričík M, Černobila F, et al. Study of structural changes in nematic liquid crystals doped with magnetic nanoparticles using surface acoustic waves. Crystals. 2020;10(11):1023. doi: 10.3390/ cryst10111023

[12] Ghamsari MS, Carlescu I, editors. Liquid crystals and display technology. London (UK): BoD–Books on Demand; 2020.

[13] Ha ST, Koh TM, Lee SL, et al. Synthesis of new schiff base ester liquid crystals with a benzothiazole core. Liq Cryst. 2010;37(5):547–554. doi: 10.1080/02678291003710425

[14] Zafiropoulos NA, Choi EJ, Dingemans T, et al. New all-aromatic liquid crystal architectures. Chem Mater. 2008;20(12):3821–3831. doi: 10.1021/cm701862w

[15] Goodby JW, Collings PJ, Kato T, et al., editors. Handbook of liquid crystals. Vol. 7. Weinheim (Germany):Wiley-VCH; 2014

[16] Demus D, Goodby JW, Gray GW, et al., editors. Handbook of liquid crystals, volume 2A: low molecular weight liquid crystals I: calamitic liquid crystals. Weinheim (Germany): John Wiley and Sons; 2011.

[17] Ting TX, Sarjadi MS, Rahman ML. Influences of central units and terminal chains on the banana-shaped liquid crystals. Crystals. 2020;10(10):857. doi: 10.3390/cryst10100857

[18] Paterson DA, Crawford CA, Pociecha D, et al. The role of a terminal chain in promoting the twist-bend nematic phase: the synthesis and characterisation of the 1-(4-cyanobiphenyl-4′-yl)-6-(4-alkyloxyanilineben- zylidene-4′-oxy) hexanes. Liq Cryst. 2018;45(13–15):2341–2351. doi: 10.1080/02678292.2018.1525503

[19] Jamain Z, Khairuddean M, Zulbaharen NN, et al. Synthesis, characterization and determination of meso- phase transition of azo-azomethine derivatives with different terminal chain lengths. Malays J Chem. 2019;22:73–85.

[20] Kumar S. Chemistry of discotic liquid crystals: from monomers to polymers. Boca Raton (FL): CRC press; 2016.

[21] Fornasieri G, Guittard F, G Ribaldi S. Influence of the structure of the mesogenic core on the thermotropic properties of ω-unsaturated fluorinated liquid crystals. Liq Cryst. 2003;30(2):251–257. doi: 10.1080/0267829031000065155

[22] Prasad R. Physics and technology for engineers: under- standing materials and sustainability. Germany: Springer Nature Switzerland; 2023.

[23] Fulay P, Lee J. Electronic, magnetic, and optical materi- als. United States: CRC Press; 2016.

[24] Coey JMD. Magnetism and magnetic materials. India: Cambridge University Press; 2010.

[25] Wagner D. Introduction to the theory of magnetism: international series of monographs in natural philoso- phy. Vol. 48. Netherlands: Elsevier Science; 2013.

[26] Selwood PW. Magnetochemistry. Redditch (UK): Read Books Limited; 2013.

[27] Coronado E, Delhaès P, Gatteschi D, et al. Molecular magnetism: from molecular assemblies to the devices. Dordrecht(Netherlands): Springer Science and Business Media; 2013.

[28] Miller JS. Organic-and molecule-based magnets. Mater Today. 2014;17(5):224–235. doi: 10.1016/j.mattod. 2014.04.023

[29] Miyashiro S, Ishii T, Miura Y, et al. Synthesis and magnetic properties of stable radical derivatives carry- ing a phenylacetylene unit. Molecules. 2018;23(2):371. doi: 10.3390/molecules23020371

[30] Liu X, Ma X, Cen P, et al. A substituent effect of phenylacetic acid coligand perturbed structures and magnetic properties observed in two triple-bridged azido-cu (II) chain compounds with ferromagnetic ordering and slow magnetic relaxation. Dalton Trans. 2017;46(23):7556–7566. doi: 10.1039/C7DT01338H

[31] Uchida Y, Ikuma N, Tamura R, et al. Unusual inter- molecular magnetic interaction observed in an all-organic radical liquid crystal. J Mater Chem. 2008;18(25):2950–2952. doi: 10.1039/b801704b

[32] Umeta Y, Eimura H. Magnetic properties of organic radical fibers aligned in liquid crystals. Tokyo (Japan): MERIT Self-directed Joint Research; 2015.

[33] Binnemans K, Galyametdinov YG, Van Deun R, et al. Rare-earth-containing magnetic liquid crystals. J Am Chem Soc. 2000;122(18):4335–4344. doi: 10.1021/ja993351q

[34] Iskandar NAJTN, Yeap GY, Maeta N, et al. Anisotropic and magnetic properties in non-metal and non-radical organic aggregates of tri-substituted phenyl derivatives. New J Chem. 2020;44(1):210–217. doi: 10.1039/C9NJ02730K

[35] Gray, G.W. and Jones, B., J. Chem. Soc., 4179 (1953); 678, 683, 1467 (1954); 236 (1955).

[36] Jones, B., J. Chem. Soc., 1874 (1935).

[37] Dave, J. S. and Vora, R. A., Liquid Crystals and Ordered Fluids, Edited by Johonson, J. F., and Porter, R. S., Plenum Press, New York, 477 (1970).

[38] Hassen, A. and Alexanian, V., Tetra. Lett., 4475 (1978).

[39] Dave, J. S. and Patel, P. R., Mol. Cryst., **2**, 115 (1966).