UNIVERSITI PUTRA MALAYSIA

MESOGENIC PROPERTIES OF A SERIES OF SYNTHESIZED CALAMITIC LIQUID CRYSTALS CONTAINING 1,2,4,5-TETRAZINE MOIETIES

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By

NOOR HAFIZAH ABDUL HALIM

Thesis Submitted to the School of Graduate Studies, Universiti Putra Malaysia, in Fulfilment of the Requirements for the Degree of Master of Science

June 2009

Abstract of thesis presented to the senate of Universiti Putra Malaysia in fulfilment of requirement for the degree of Master of Science

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Chairman : Associate Professor Dr. Sidik Silong

Faculty : Science

In this research, a series of calamitic liquid crystal containing 1,2,4,5-tetrazine moieties have been synthesized. 1,2,4,5-tetrazine is a mesomorphic compound containing heterocyclic units and such structures have greater possibilities to obtain mesogenic molecules. All compounds were synthesized by esterication of $HOC_6H_4C_2N_4C_6H_4OH$ with carboxylic acids that vary in substituents chain lengths. The structures of the liquid crystal compounds were elucidated based on FT-IR, mass spectroscopy, CHN and NMR analyses. The infrared spectra of the compounds showed the characteristic of the tetrazine and ester functional group for νC=O, νC=C, νC=N, νN-N and νC-O at (1750-1758 cm^{-1}), (1602-1604 cm^{-1}), (1318-1396 cm^{-1}), (1142-1168 cm^{-1}) and (1016-1102 cm^{-1}). The elemental analyses agree with the expected formula $R-C_6H_4C_2N_4C_6H_4-R$ where R = C_2H_5 (FZ-4), C_4H_9(Isobutyl) (FZ-49E), C_5H_{11} (FZ-37B), $C_{11}H_{23}$ (FZ-53), $C_{15}H_{31}$ (FZ-34A) and $C_{17}H_{35}$ (FZ-35A). The ^1H NMR spectra reflected the high symmetry of the molecules

with the benzene protons appeared as a doublet at δ(8.69–8.67ppm) and δ(7.36-7.34ppm), respectively. The ^{13}C signals for the 1,2,4,5-tetrazine, C=O and C-O appeared at δ(163.30-163.25), δ(171.82-171.02ppm) and δ(154.48-154.40ppm), respectively. Differential scanning calorimetry (DSC) and polarizing optical microscopy (POM) analyses of FZ-37B, FZ-53, FZ-34A and FZ-35A revealed the existence of smectic and schlieren smectic mesophases.

Abstrak tesis yang dikemukakan kepada Senat Universiti Putra Malaysia sebagai memenuhi keperluan untuk Ijazah Master Sains

SIFAT-SIFAT MESOGENIK SATU SIRI CECAIR HABLUR KALAMITIK TERSINTESIS MENGANDUNGI BAHAGIAN 1,2,4,5-TETRAZINE

Oleh

NOOR HAFIZAH ABDUL HALIM

Jun 2009

Pengerusi : Profesor Madya Dr. Sidik Silong

Fakulti : Sains

Dalam kajian ini, satu siri cecair hablur kalamitik mengandungi bahagian 1,2,4,5-tetrazine telah disintesis. 1,2,4,5-tetrazine adalah satu sebatian mesomorfik yang mengandungi unit-unit heterosiklik dan struktur seperti itu berkemungkinan besar untuk membentuk molekul mesogenik. Semua sebatian telah disintesis melalui pengesteran $HOC_6H_4C_2N_4C_6H_4OH$ dengan asid karboksilik yang berbeza dalam penukarganti rantai panjang. Struktur sebatian cecair hablur ini dijelaskan berasaskan kepada FT-IR, spektroskopi jisim (MS) dan analisis CHN serta NMR. Spektrum infra-merah bagi sebatian menunjukkan ciri-ciri kumpulan berfungsi tetrazin dan ester bagi νC=O, νC=C, νC=N, νN-N dan νC-O pada (1750-1758 cm^{-1}), (1602-1604 cm^{-1}), (1318-1396 cm^{-1}), (1142-1168 cm^{-1}) dan (1016-1102 cm^{-1}). Analisis unsur bersetuju dengan formula yang dicadangkan $R-C_6H_4C_2N_4C_6H_4-R$ di mana R = C_2H_5 (FZ-4), C_4H_9(Isobutyl) (FZ-49E), C_5H_{11} (FZ-37B), $C_{11}H_{23}$ (FZ-53), $C_{15}H_{31}$ (FZ-34A) and $C_{17}H_{35}$ (FZ-35A). Spektrum ^1H

NMR menggambarkan ketinggian simetri sebatian dengan proton-proton benzena muncul sebagai dublet pada δ(8.69–8.67ppm) dan δ(7.36-7.34ppm). Puncak ^{13}C bagi 1,2,4,5-tetrazine, C=O dan C-O muncul di δ(163.30-163.25), δ(171.82-171.02ppm) dan δ(154.48-154.40ppm). Analisis teknik kalorimeter imbasan keberdaan (DSC) dan mikroskopi berkutub optik (OPM) bagi FZ-37B, FZ-53, FZ-34A dan FZ-35A mendedahkan kehadiran mesofasa-mesofasa smektik dan smektik yang memancar.

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I certify that a Thesis Examination Committee has met on 23 June 2009 to conduct the final examination of Noor Hafizah binti Abdul Halim on her thesis entitled "Mesogenic Properties of a Series of Synthesized Calamitic Liquid Crystals Containing 1,2,4,5-Tetrazine Moieties" in accordance with the Universities and University Colleges Act 1971 and the Constitution of the Universiti putra Malaysia [P.U.(A) 106] 15 March 1998. The committee recommends that the student be awarded the Master of Science.

Members of the Thesis Examination Committee were as follows:

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This thesis was submitted to the Senate of Universiti Putra Malaysia has been accepted as fulfilment of the requirement for the degree of Master of Science. The members of the Supervisory Committee were as follows:

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Date : 16 November 2009

DECLARATION

I hereby declare that the thesis is based on my original work except for quotations and citations, which have been duly acknowledged. I also declare that it has not been previously or concurrently submitted for any other degree at UPM or other institutions.

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NOOR HAFIZAH ABDUL HALIM

Date : 4 January 2010

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LIST OF ABBREVIATIONS

LCs	Liquid Crystals
S	Smectic
N	Nematic
DSC	Differential Scanning Calorimetry
OPM	Optical Polarize Microscope
DCC	1,3-dicyclohexylcarbodiimide
DMAP	4-(N,N-dimethylamino)pyridine
POMBOH	2-(prenyloxymethyl)benzoic acid
POMB	2-(prenyloxymethyl)benzoyl
CH_2Cl_2	dichloromethane
NaOH	Natrium hydroxide
^{1}H	proton
^{13}C	Carbon 13
NMR	Nuclear Magnetic Resonance
DEPT	Distortionless Enhancement by Polarisation Transfer
IR	Infra red
EIMS	Electron Impact Mass Spectrometry
$CDCl_3$	chloroform
DMSO-d_6	dimethyl sulfoxide
cm^{-1}	per centimeter
ºC	degree in Celcius

δ	delta (chemical shift in ppm)
g	gram
m.p.	melting point
R	Alkyl group
I	Isotropic
Cr	Crystalline
d	doublet
dd	doublet of doublet
t	triplet
s	singlet
m	multiplet