

Supplementary Materials

New Liquid Crystals Based on Terminal Fatty Chains and Polymorphic Phase Formation from Their Mixtures

Fowzia S. Alamro ¹, Hoda A. Ahmed ^{2,3,*}, Noha S. Bedowr ³, Magdi M. Naoum ², Ayman M. Mostafa ^{4,5} and Nada S. Al-Kadhi ¹

¹ Department of Chemistry, College of Science, Princess Nourah Bint Abdulrahman University, P.O. Box 84428, Riyadh 11671, Saudi Arabia; fsalamro@pnu.edu.sa (F.S.A.); nsalkadhi@pnu.edu.sa (N.S.A.-K.)

² Department of Chemistry, Faculty of Science, Cairo University, Giza 12613, Egypt; magdinaoum@yahoo.co.uk

³ Chemistry Department, College of Sciences, Taibah University, Yanbu 30799, Saudi Arabia; nbedowr@taibahu.edu.sa

⁴ Laser Technology Unit, Centre of Excellent for Advanced Science, National Research Centre, Giza 12622, Egypt; aymanmdarwish@gmail.com

⁵ Spectroscopy Department, Physics Research Institute, National Research Centre, Giza 12622, Egypt

* Correspondence: ahoda@sci.cu.edu.eg

S1. Materials

4-methoxybenzaldehyde, oleic acid, linoleic acid, and 4-hydroxyaniline were obtained from Sigma Aldrich (Germany). *N,N'*-dicyclohexylcarbodiimide (DCC), 4-dimethylaminopyridine (DMAP), dichloromethane, ethanol, and methanol were purchased from Aldrich (Wisconsin, USA). All chemicals were used without further purification.

S2. Synthesis of 4-methoxybenzylideneamino)phenol A

Equimolar amounts of 4-methoxybenzaldehyde and 4-aminophenol (4.1 mmol each) in ethanol (10 ml) were refluxed for 2 hours. The reaction mixture was allowed to cool, and the separated product filtered. The obtained solid was recrystallized from ethanol.

S3. Synthesis of fatty acid derivatives I–III

Equimolar equivalents of (4-methoxybenzylideneamino) phenol A (4.1 mmol) and 4-fatty acids (4.1 mmol each) were dissolved in 25 ml dry methylene chloride. *N,N'*-dicyclohexylcarbodiimide (DCC, 0.02 mole) and a few crystals of 4-dimethylaminopyridine (DMAP) as a catalyst were added. The mixture was left to stand for 72 hours at room temperature with continuous stirring. The solid residue obtained was filtered off and recrystallized twice from ethanol to give TLC pure products, indicated by TLC as one clear spot in their TLC chromatogram and sharp melting and clearing peaks in their differential scanning calorimetry (DSC) thermograms.

Derivative I:

Yield = 92.0%, m.p. = 90.0 °C, FTIR (ν' , cm^{-1}): 2924–2865 (CH_2 stretching), 1739 ($\text{C}=\text{O}$), 1613 ($\text{C}=\text{N}$), 1604 ($\text{C}=\text{C}$), 1472 ($\text{C}-\text{O}_{\text{Asym}}$), 1232 ($\text{C}-\text{O}_{\text{Sym}}$). ^1H NMR (500 MHz, $\text{DMSO}-d_6$) δ 8.63 (s, 1H, $\text{CH}=\text{N}$), 7.93 (d, 2H, Ar-H), 7.57 (d, 2H, Ar-H), 7.30 (d, 2H, Ar-H), 7.14 (d, 2H, Ar-H), 3.90–3.10 (m, 3H), 2.50 (m, 2H, CH_2), 1.68–1.59 (m, 2H, CH_2), 1.34–1.22 (m, 24H, 12 CH_2), 0.82 (t, 3H, CH_3). Anal. Calc.: C, 77.38; H, 9.31; N, 3.01. Found: C, 77.35; H, 9.30; N, 3.00.

Derivative II:

Yield = 94.7%, m.p. = 41.9 °C, ^1H NMR (600 MHz, DMSO) δ 8.37 (s, 1H), 7.85 (d, J = 8.7 Hz, 2H), 7.20 (d, J = 8.6 Hz, 2H), 7.09 (d, J = 8.6 Hz, 2H), 6.99 (d, J = 8.7 Hz, 2H), 5.98 (m, 1H), 5.36 (m, 1H), 3.87 (s, 3H), 2.55 (t, J = 7.5 Hz, 2H), 2.11–1.95 (m, 4H), 1.78–1.69 (m, 2H), 1.53–1.07 (m, 22H), 0.87 (t, J = 6.9 Hz, 3H). ^{13}C NMR (151 MHz, DMSO) δ = 169.24, 158.86, 156.44, 146.42, 145.04, 127.24, 126.76, 126.46, 125.70, 118.93, 118.35, 110.91, 52.25, 30.99, 30.56, 28.55, 26.42, 26.34, 26.18, 25.98, 25.81, 25.75, 25.72, 23.84, 22.27, 21.62, 19.38. Anal. Calc.: C, 78.17; H, 9.22; N, 2.85. Found: C, 78.16; H, 9.20; N, 2.84.

S4. Characterization

TLC was performed with TLC sheets coated with silica gel (E. Merck, Darmstadt, Germany); spots were detected by UV irradiation.

Varian EM 350L 500 MHz spectrometer (Oxford, UK) was used for recording ^1H NMR spectra, using tetramethyl silane as an internal standard in CDCl_3 ; the chemical shift values were recorded as δ (in ppm units). Thermo Scientific Flash 2000 CHS/O Elemental Analyzer (Milan, Italy) was used for elemental analyses.

TA Instruments Co. (Q20 Differential Scanning Calorimeter, DSC; New Castle, DE, USA) was used for recording phase transitions. DSC calibration was carried out using lead and indium to calibrate the melting temperatures and enthalpies. Samples of 2–3 mg were used in aluminum pans for DSC investigation. The heating rate was 10 °C/min in nitrogen gas as an inert atmosphere (30 ml/min). All transitions temperatures were measured from the second heating scan from room temperature to 300 °C on heating and then cooled to 0 °C.

Transition temperatures for the prepared compounds were checked and phases identified by Polarized optical microscope (POM, Wild, Germany) attached with Mettler FP82HT hot stage (Greifensee, Switzerland).

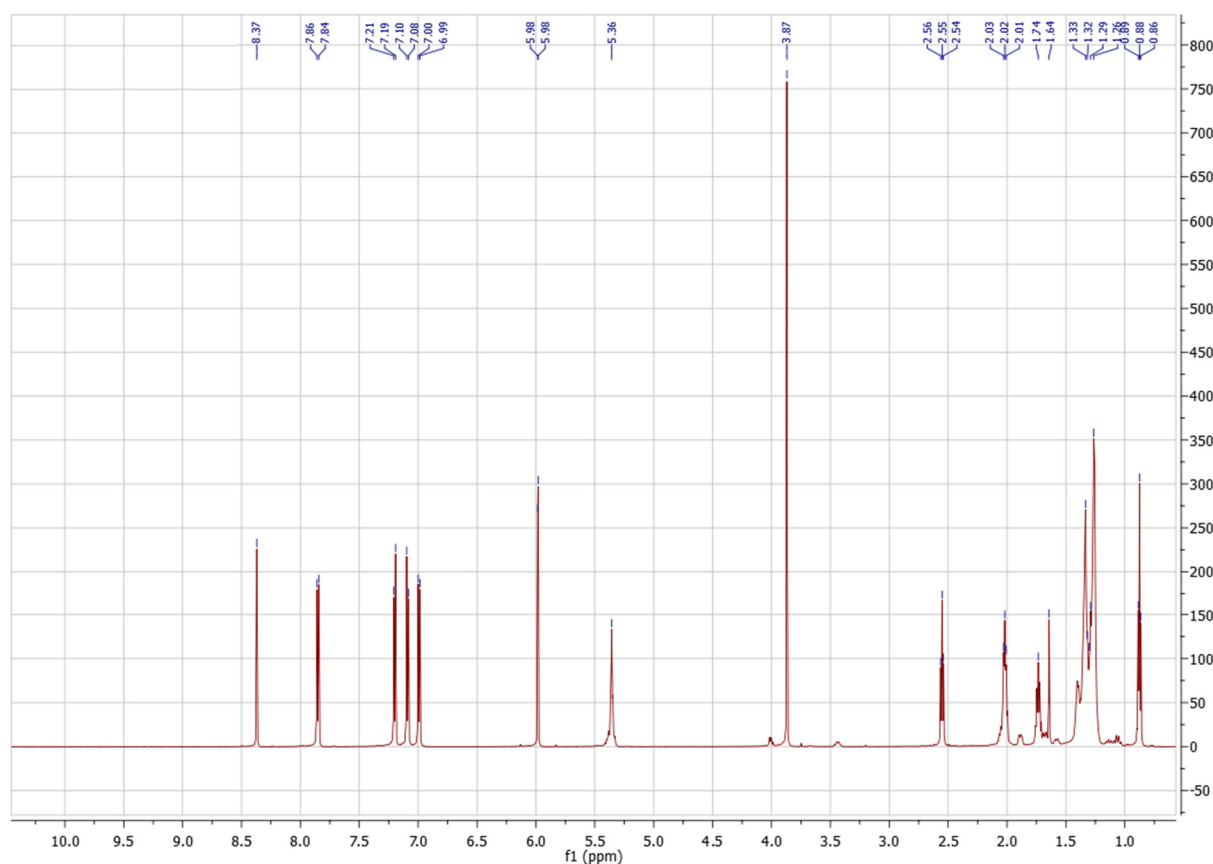


Figure S1. ^1H -NMR of derivative **II**, as an example.

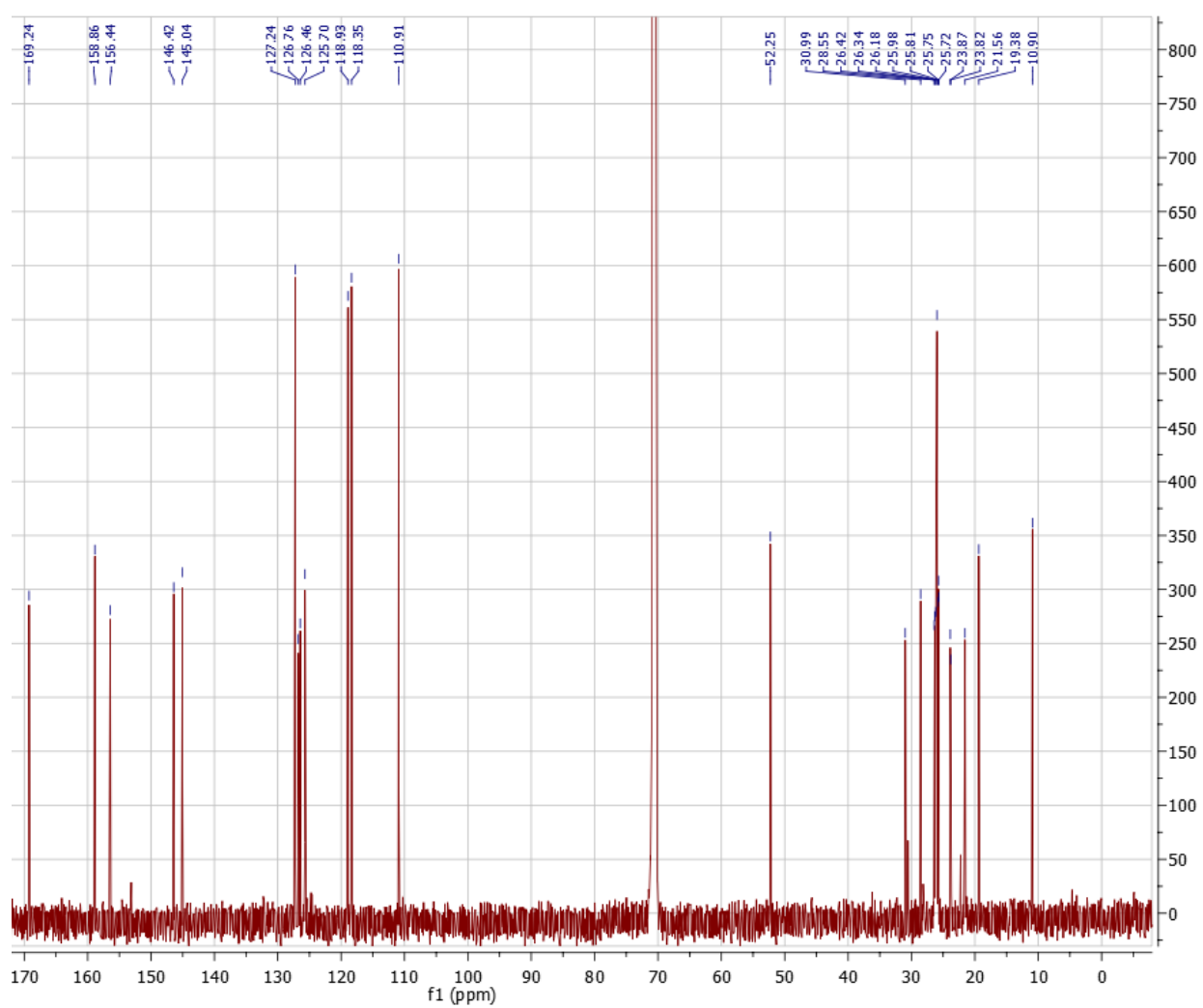


Figure S2. ^{13}C -NMR of derivative II, as an example.