crystals

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Supplementary Data

Characterization of new H-bonded liquid crystalline complexes based on iminophenyl nicotinate

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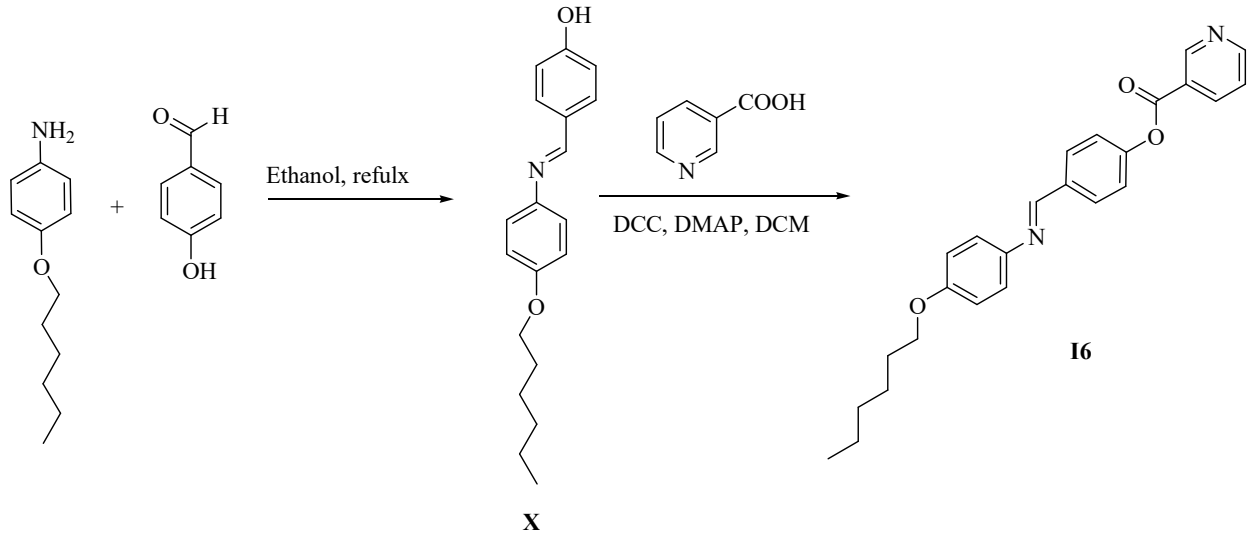
1. Materials

4-Hexyloxyaniline, 4-hydroxybenzaldehyde were purchased from Sigma Aldrich (Germany). Nicotinic acid, *N,N'*-dicyclohexylcarbodiimide (DCC), dichloromethane, ethanol were purchased from Aldrich (Wisconsin, USA).

1.1. Synthesis

Compounds were prepared according to the following scheme:



Scheme 1.Preparation of 4-(4-(hexyloxy)phenylimino)methyl)phenyl nicotinate (**I6**).

Synthesis of 4-((4-hexyloxyphenylimino))methyl)phenol (X) [1]

Mixture 4-hexyloxyaniline 4.1 mmol) and 4–hydroxybenzaldehyde (4.1 mmol) were dissolved in ethanol (10 ml). The solution was heated under reflux for two hours, and then allowed to cool at

room temperature for complete precipitation. The obtained precipitate was filtered and washed was cold ethanol and recrystallized from hot ethanol.

Synthesis of 4-(4-(hexyloxy)phenylimino)methyl)phenyl nicotinate (I6) [1]

A mixture of 4–dimethylaminopyridine (DMAP) (catalytic amount) and *N*, *N'*–dicyclohexylcarbodiimide (DCC, 0.02 mole) was added to a solution of 0.01 mole *4-((4-hexyloxyphenylimino))methyl)phenol* (**X**) and nicotinic acid (1.23 g, 0.01 mole) in 25 ml dry methylene chloride. The reaction mixture was kept under stirring at room temperature for 72 hours. Separated byproduct, *N,N*-dicyclohexylurea, was filtered off. The filtrate was then evaporated till dryness. The obtained solid product was purified by recrystallization for twice from ethanol (**Scheme 1**).

Yield: 94.3 %; mp 131.0 ˚C, FTIR (ύ, cm^{-1}): 2959-2833 (CH_2 stretching), 1743 (C=O), 1581 (C=C), 1473 (C–O_{Asym}), 1242 (C-O $_{Sym}$). ^1H NMR (400 MHz, $CDCl_3$) δ 10.08 (s, 1H, CH=N), 9.59 (s, 1H, pyr), 9.11-9.04 (m, 2H, pyr), 8.10-8.05 (m, 3H, pyr, ArH), 7.43 (d, *J* = 8.5 Hz, 2H, ArH), 7.01 (d, *J* = 8.1 Hz, 2H, ArH), 6.83 (d, *J* = 8.1 Hz, 2H, ArH), 9.93 (t, *J* = 6.2 Hz, 2H, $CH_3(CH_2)_3CH_2\underline{CH_2}$), 1.92 –1.75 (m, 2H,$CH_3(CH_2)_3\underline{CH_2}CH_2$), 1.56 – 1.51 (m, 6H, $CH_3\underline{(CH_2)_3}CH_2CH_2$), 0.92 (t, *J* = 6.3 Hz, 3H, $\underline{CH_3}(CH_2)_3CH_2CH_2$).

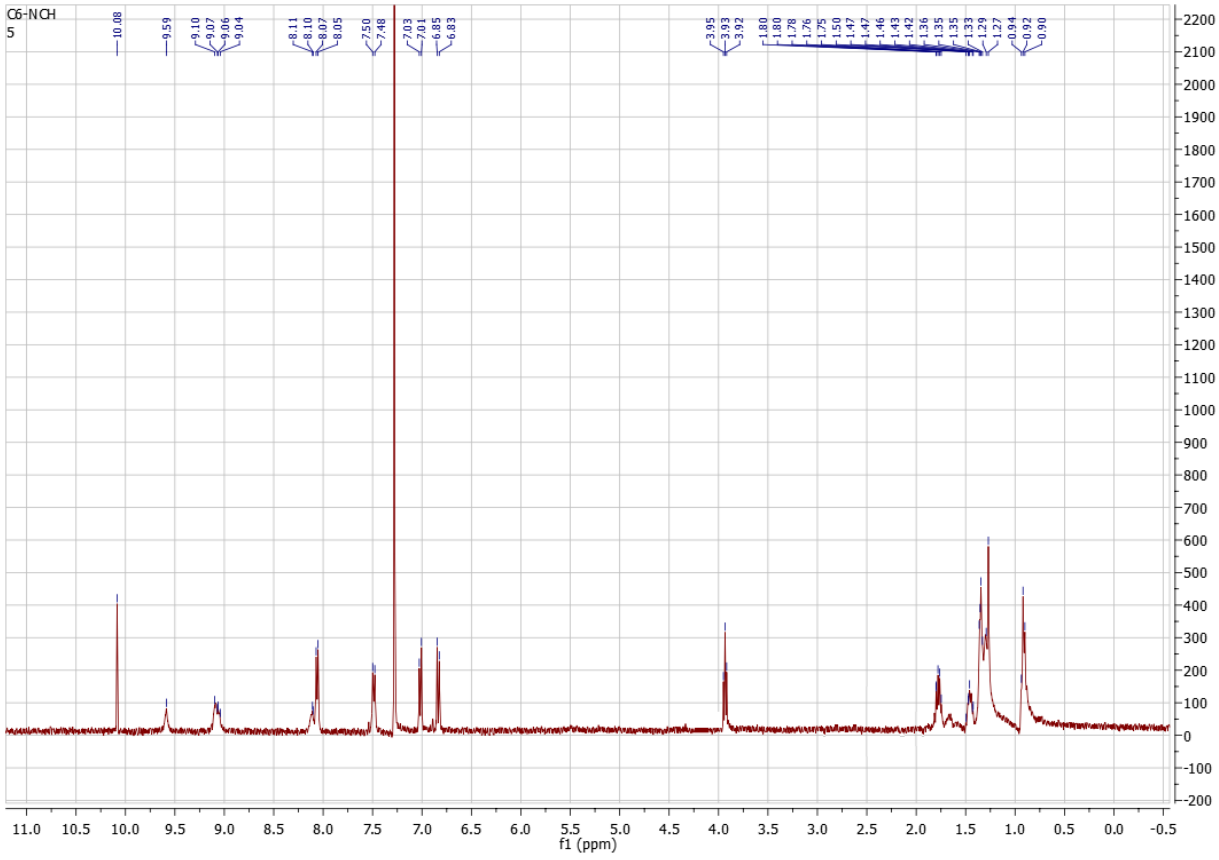


Figure S1. ^1H-NMR if 4-(4-(hexyloxy)phenylimino)methyl)phenyl nicotinate (**I6**).

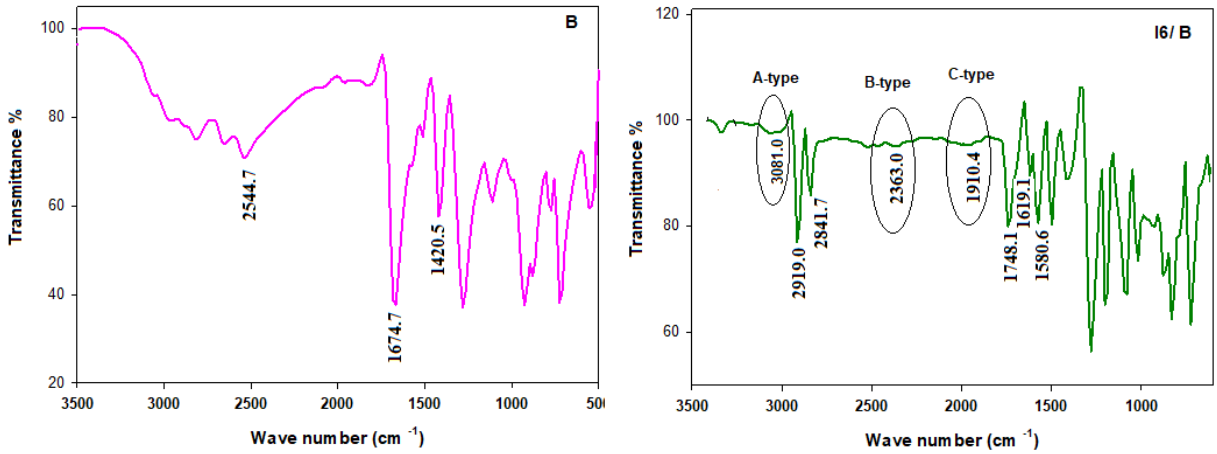


Figure S2. FT-IR spectra of the terphthalic acid (**B)** and its SMHBCs **I6/B**.

2. Instruments

TA Instruments Co. Q20 Differential Scanning Calorimeter (DSC; USA) were using for calorimetric measurements. The DSC was calibrated using the melting temperature and enthalpy of indium and lead. DSC investigation was carried out for small samples (2–3 mg) placed in aluminum pans. All measurements were achieved at a heating rate of 10°C/min in inert atmosphere of nitrogen gas (30 ml/min) and all transition recorded from the second heating scan.

Transition temperatures for the individual components and their 2:1 associated complexes, were determined by DSC, and the types of the mesophase identified by a standard polarized optical microscope (POM, Wild, Germany) attached with Mettler FP82HT hot stage. The temperature is measured by thermocouple attached to the temperature controller. Measurements were made twice and the results have accuracy in transition temperature within ± 0.2°C.

3. Characterizations

FT-IR spectra for structural characterization in the solid phases were recorded by using a diamond tip Perkin Elmer ATR spectrometer. All spectra ranging between wave numbers 4000 and 400 cm^{-1} were recorded with Fourier transform infrared spectroscopy. All spectra were collected at room temperature and the base line corrected and vector normalized. Number of scan and spectral resolution were 32 scan and 4 cm^{-1}; respectively.

The spectrophotometer technique (UV-1800 SHIMADZU, Japan) connected to hot stage of a wavelength ranging from 200–800 nm with normal incidence of light was used for all compounds.

4. Computational Method and calculations

The theoretical calculations for the investigated compounds were carried out by Gaussian 09 software [2]. DFT methods using B3LYP 6-311G basis set was selected for the calculations. The geometries were optimized by minimizing the energies with respect to all geometrical parameters without imposing any molecular symmetry constraints. The structures of the optimized geometries had been drawn with Gauss View [3]. Moreover, the calculated frequencies were carried out using the same level of theory. The frequency calculations showed that all structures were stationary points in the geometry optimization method with none imaginary frequency.

References

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