

Dynamics in the Isotropic Phase of Nematogens Using 2D IR Vibrational Echo Measurements on Natural Abundance ^{13}C N and Extended Lifetime Probes

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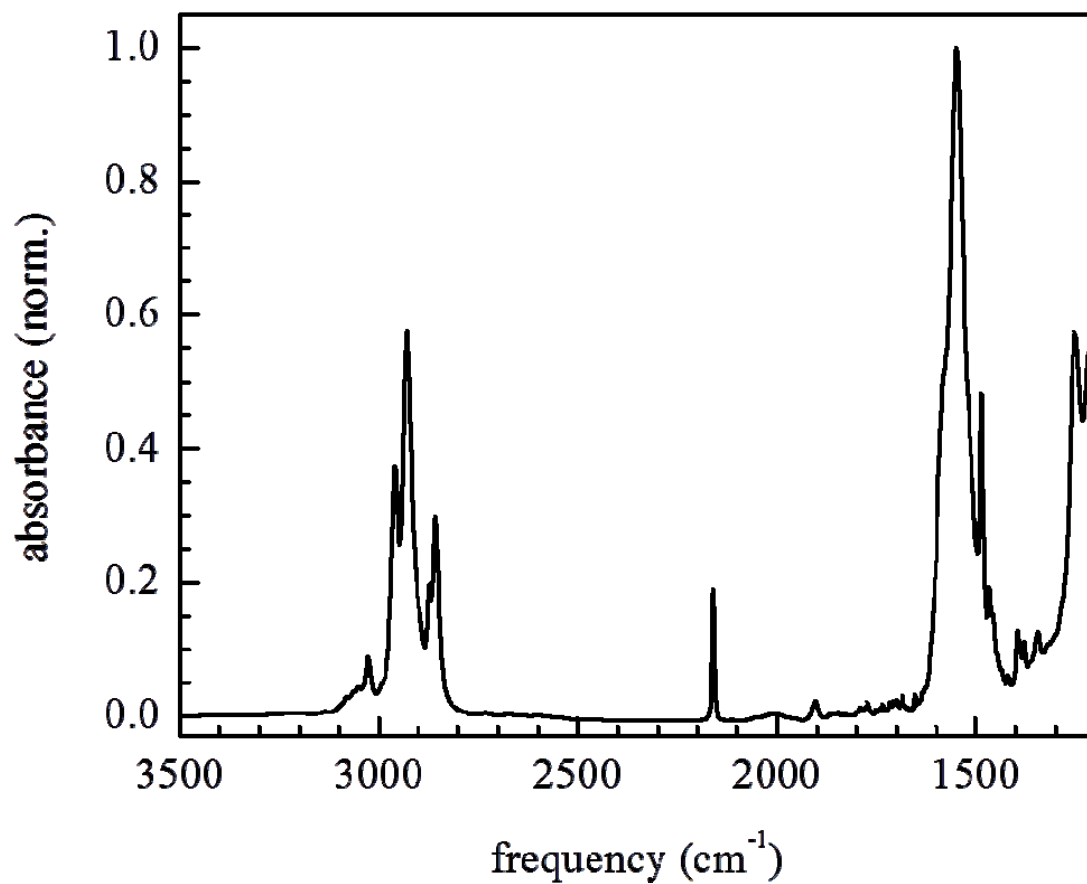
Supporting Information

Synthesis of 4-pentyl-4'-thiocyanobiphenyl

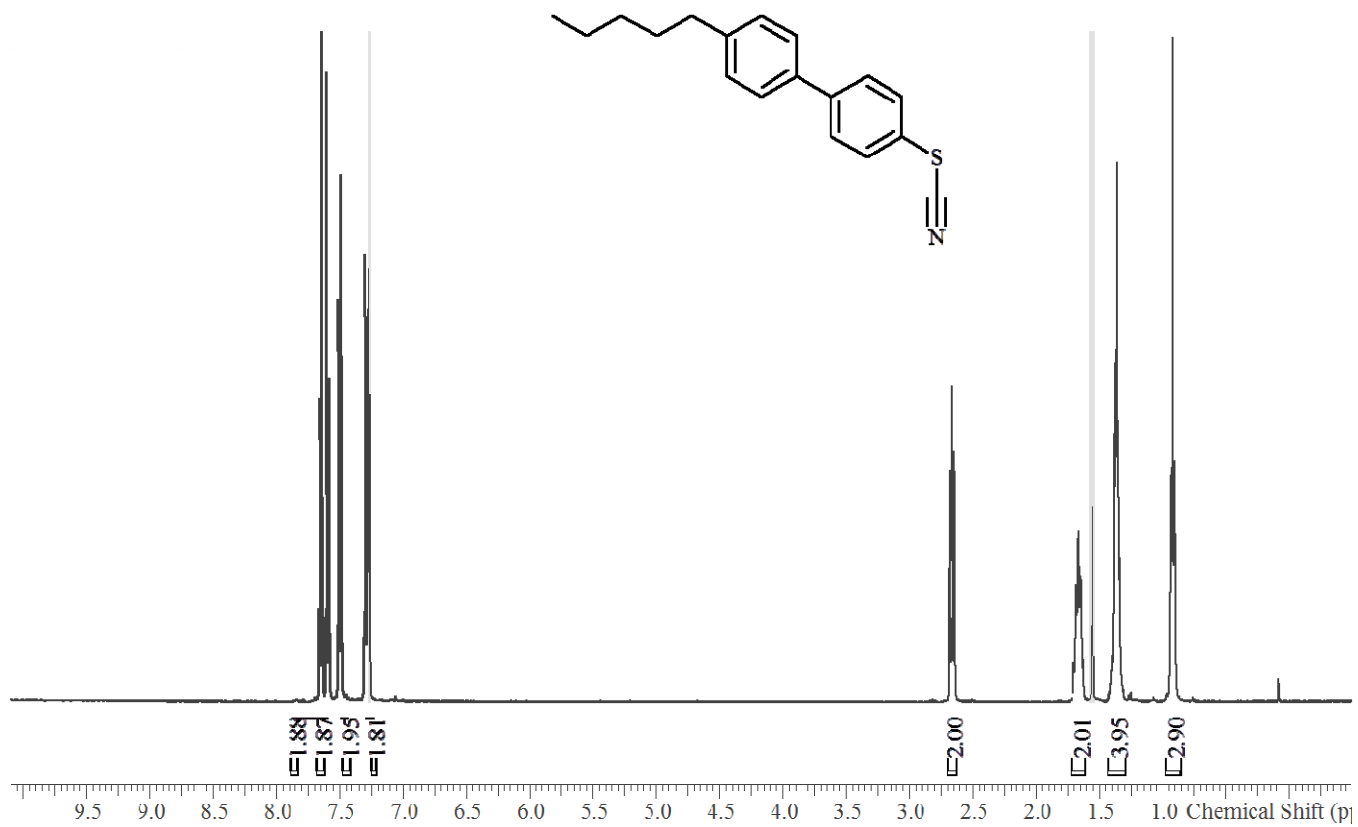
Solvents and chemicals with the exception of 4-bromo-4'-pentylbiphenyl were purchased and used as is from Sigma Aldrich. 4-bromo-4'-pentylbiphenyl was purchased from TCI America and used as received. Chromatography was carried out with silica gel (Aldrich, 70-230 mesh). Proton chemical shifts are reported as ppm downfield from tetramethylsilane (TMS).

The conversion of the aryl bromide to aryl amine is based on a procedure outlined by Lee.¹ 4-bromo-4'-pentylbiphenyl (1.566 g, 5.22 mmol) and a catalytic amount of tris(dibenzylideneacetone)dipalladium(0) (0.024 g, 0.03 mmol) were placed in a round bottom flask which was then evacuated and back-filled with nitrogen (2x). In a glove box, lithium bis(trimethylsilyl)amide (0.945 g, 5.65 mmol), catalytic amounts tri-tertbutyl phosphine (0.015 g, 0.07 mmol), and dry toluene (15 mL) were added to the same flask. The flask was stoppered with a septum and removed from the glove box. The reaction was allowed to stir overnight (~14 h) while immersed in an oil bath at 70 °C. Over the course of the reaction, the flask contents became significantly lighter. The product, 4-amino-4'-pentylbiphenyl (0.92 g, 3.85 mmol), was isolated in 74% yield according to Work-up Procedure 2 outlined in the Supporting Information of Lee et al.¹ Synthesis of the aryl amine was confirmed by comparison of the ^1H NMR (400 MHz, d_3 -acetonitrile) chemical shifts to known values.²

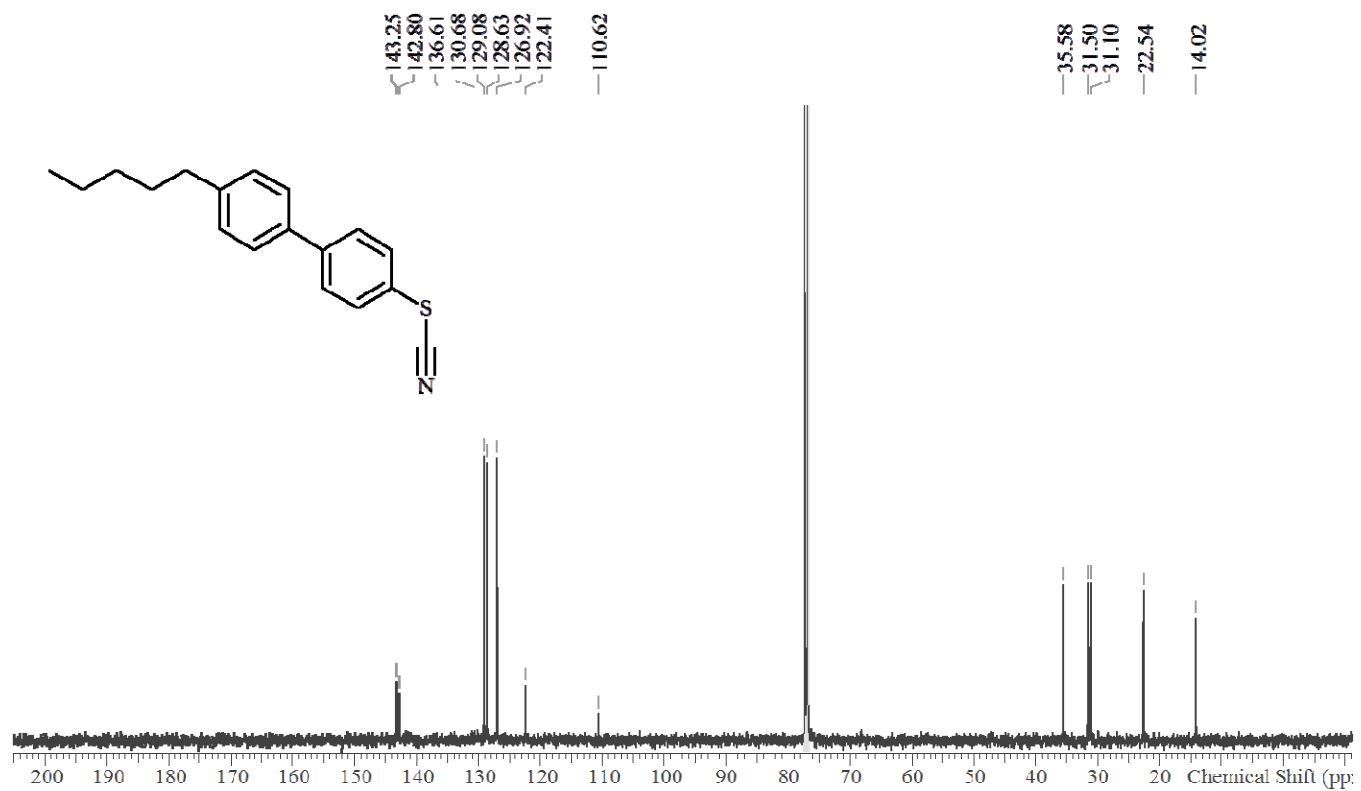
A portion of the 4-bromo-4'-pentylbiphenyl product (0.707 g, 2.96 mmol) was diazotized with 30% sulfuric acid (4.5 mL) and sodium nitrite (0.266 g, 3.13 mmol) at 0 °C in a large flask. The reaction temperature was achieved with an ice/NaCl slurry bath. Acetonitrile (250 mL) was added to the flask and allowed to reach 0 °C. Once the reaction had cooled sufficiently, KSCN (0.774 g, 7.96 mmol) and CuSCN (1.340 g, 11.02 mmol) were added to the flask. At this point, gas was seen evolving, and the reaction became reddish in color. The reaction was removed from the slurry bath and allowed to stir at room temperature for 24 h. The reaction mixture was placed in a large separatory funnel with CH₂Cl₂ (100 mL) and water (100 mL). The aqueous layer was removed and extracted with CH₂Cl₂ (2x 100 mL). The organic layers were combined and washed with water (2x 100 mL). The resulting organic solution was dried with MgSO₄ which was then removed by gravity filtration. Solvent was removed under reduced pressure to yield ~500 mg of crude brown solid. The crude product was purified on a silica column with 1:1 CH₂Cl₂:hexanes as an eluent. Two species were separated by the column; after concentration, the more polar species was identified to be 4-pentyl-4'-thiocyanobiphenyl (5SCB, 0.146 g, 0.52 mmol) at 18% yield from the aryl amine. FT-IR of 5SCB in CCl₄ shows a narrow peak at 2161 cm⁻¹, indicative of a thiocyanate as opposed to isothiocyanate (generally broader).²⁻⁶ ¹H NMR (Varian Mercury 400 MHz, chloroform-*d*) δ ppm 7.66 (d, *J* = 8.5 Hz, 2 H) 7.59 (d, *J* = 8.5 Hz, 2 H) 7.50 (d, *J* = 7.3 Hz, 2 H) 7.29 (d, *J* = 6.9 Hz, 2 H) 2.66 (t, *J* = 7.8 Hz, 2 H) 1.66 (quin, *J* = 7.9 Hz, 2 H) 1.36 (m, 4 H) 0.92 (t, *J* = 6.7 Hz, 3 H). ¹³C NMR (Varian Inova 500 MHz, chloroform-*d*) δ ppm 143.6, 142.8, 136.6, 130.7, 129.1, 128.6, 126.9, 122.4, 110.6, 35.6, 31.5, 31.1, 22.5, 14.0. GCMS with electron ionization (solvent: acetonitrile) showed the molecular ion peak at 281 m/z in agreement with calculated mass of ¹H₁₉¹²C₁₈¹⁴N³²S.



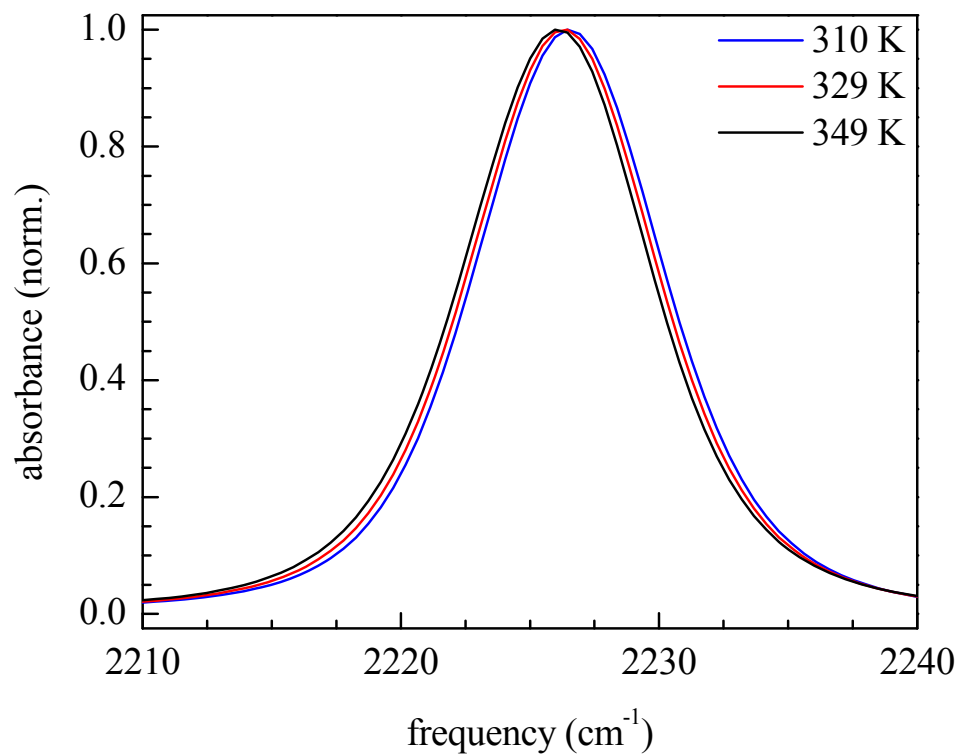
S1: FT-IR spectrum of 5SCB in CCl₄. The sharp peak at 2160 cm⁻¹ is further evidence that the thiocyno derivative was produced, as the CN stretch in an isothiocyno compound is much broader.



S2: ^1H NMR spectrum of 5SCB in CDCl_3 .



S3: Carbon NMR spectrum of 5SCB in CDCl₃. The peak at ~ 110 ppm is indicative of an SCN carbon attached to a phenyl ring.



S4: Normalized temperature dependent FT-IR spectrum of neat 5CB. The sample was prepared as described in the main text.

References

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