SUPPLEMENTARY INFORMATION

Understanding the twist-bend nematic phase: the characterisation of 1-(4-cyanobiphenyl-4'-yloxy)-6-(4-cyanobiphenyl-4'-yl) hexane (CB6OCB) and comparison with CB7CB

Daniel A. Paterson[1], Min Gao[2], Young-Ki Kim[2], Afsoon Jamali[2], Kirsten Finley[3], Beatriz Robles-Hernández[3], Sergio Diez-Berart[3], Josep Salud[3], M. Rosario de la Fuente[4], Bakir A.Timimi[5], Herbert Zimmermann[6], Cristina Greco[7], Alberta Ferrarini[7], John M.D. Storey[1], David O. López[3], Oleg D. Lavrentovich[2], Geoffrey R. Luckhurst[5], and Corrie T. Imrie[1*]

[1]*Department of Chemistry, School of Natural and Computing Sciences, University of Aberdeen, Meston Building, Aberdeen AB24 3UE, UK*
[2]*Liquid Crystal Institute and Chemical Physics Interdisciplinary Program, Kent State University, Kent, OH 44242, USA*
[3]*Department of Physics and Nuclear Engineering, Polytechnic University of Catalonia, Barcelona, Spain*
[4]*Department of Applied Physics II, University of the Basque Country, E-48080 Bilbao, Spain*
[5]*Chemistry, University of Southampton, Highfield, Southampton SO17 1BJ, UK*
[6]*Max-Planck-Institut für Medizinische Förschung, D-69120 Heidelberg, Germany*
[7]*Dipartimento di Scienze Chimiche, Università di Padova, via Marzolo 1, 35121 Padova, Italy.*

*Author for correspondence: c.t.imrie@abdn.ac.uk

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Section 1: Materials/ General methods/ Instrumentation

Materials

All reagents and solvents were available commercially and purchased from Sigma Aldrich before being used as received unless otherwise stated. Silica gel for column chromatography, grade 60A 40-63 micron, was purchased from Flurochem. Reactions were monitored using TLC (Thin Layer Chromatography) and an appropriate solvent system. Silica gel coated aluminium plates were purchased from Merck KGaA. Spots were visualised using UV light (254 nm).

General methods and instrumentation

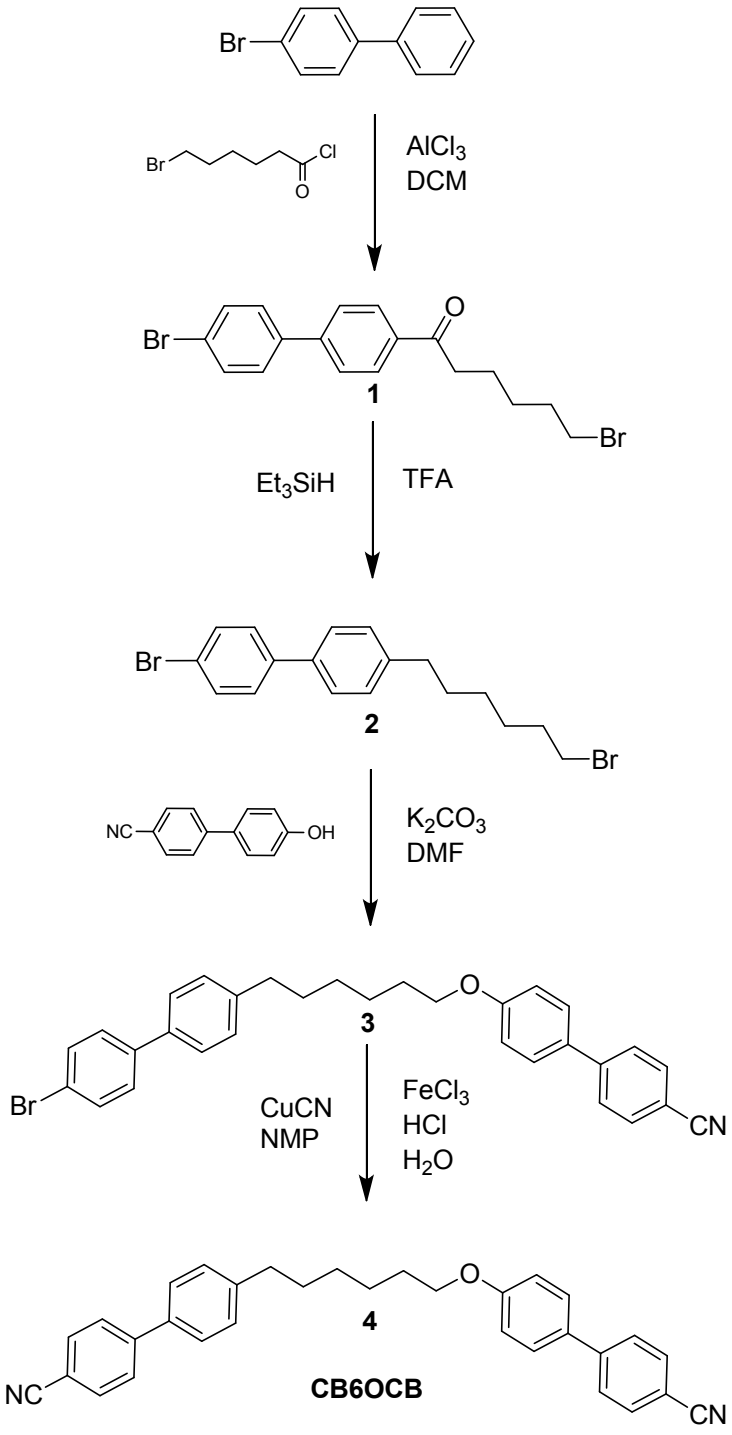
The proposed structures of CB6OCB and its intermediates were characterised using a combination of ^{1}H and ^{13}C NMR, and FTIR spectroscopies. ^{1}H and ^{13}C NMR spectra were recorded on a Varian Unity INOVA 400 MHz NMR spectrometer with pulsed field gradients and waveform generator. Infrared spectra were recorded on a Thermal Scientific Nicolet IR100 FT-IR spectrometer with an ATR diamond cell.

The purity of the final product was verified using C,H,N microanalysis performed by the Micro Analytical Laboratory in the School of Chemistry at the University of Manchester.

Section 2: Synthetic procedures

Synthesis of 1-(4-cyanobiphenyl-4'-yloxy)-6-(4-cyanobiphenyl-4'-yl) hexane, CB6OCB

The synthetic route used to obtain 1-(4-cyanobiphenyl-4'-yloxy)-6-(4-cyanobiphenyl-4'-yl) hexane, CB6OCB, is shown in scheme 1;



Scheme 1.

2.1.1. 4-Bromo-4'-(6-bromohexanoyl)biphenyl, *1*

A solution of 6-bromohexanoyl chloride (24.18 g, 0.11 mol) and 4-bromobiphenyl (25.05 g, 0.11 mol) in dichloromethane (50 ml) was added dropwise to a stirred suspension of aluminium chloride (14.68 g, 0.11 mol) in dichloromethane (50 ml) cooled to 0 °C in an ice bath. This mixture was warmed to room temperature and stirred overnight. The reaction mixture was added to H_2O (250 ml) and extracted using dichloromethane (2 x 80 ml). The organic fractions were combined and dried over anhydrous magnesium sulphate before the solvent was removed under vacuum. The crude product was purified using silica gel chromatography with a petroleum ether (B.p. 40–60 °C) and dichloromethane, 50:50 mixture as eluent, R.f. 0.45. The crude product thus obtained was recrystallised from ethanol to give the title compound as a white solid. Yield: 22.70 g, 50%. T_{CrI} 77 °C. Infrared *v* cm^{-1}: 2925 (C-H), 1679 (C=O), 1603, 1258, 1184, 971, 807, 665. ^{1}H NMR (400 MHz $CDCl_3$)δ: 7.96 (2H, d, *J* 8.7 Hz, Ar), 7.57 (2H, d, *J* 8.7 Hz, Ar), 7.52 (2H, d, *J* 8.7 Hz, Ar), 7.42 (2H, d, *J* 8.7 Hz, Ar), 3.37 (2H, t, *J* 6.7 Hz, Br$\underline{CH_2}CH_2$), 2.95 (2H, t, *J* 7.40 Hz, CO$\underline{CH_2}CH_2$), 1.87 (2H, quin, *J* 6.70 Hz, $CH_2CH_2\underline{CH_2}CH_2$), 1.73 (2H, quin, *J* 7.40 Hz, $CH_2\underline{CH_2}CH_2CH_2$), 1.49 (2H, m, $CH_2CH_2\underline{CH_2}CH_2CH_2$). ^{13}C NMR (100 MHz $CDCl_3$)δ: 199.45, 144.39, 138.78, 135.94, 132.10, 128.81, 128.72, 127.06, 122.64, 38.35, 33.61, 32.62, 27.87, 23.35.

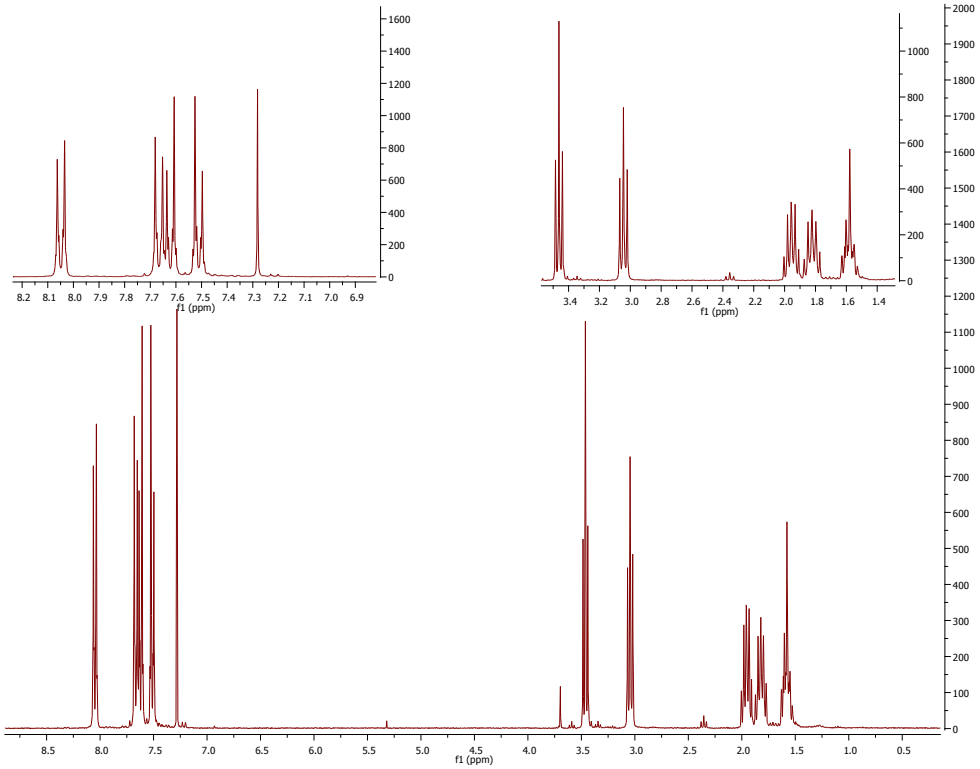


Figure 1. ^{1}H NMR (400 MHz $CDCl_3$) spectra of **1**, insets show expansions of the aromatic region (top left) and aliphatic region (top right).

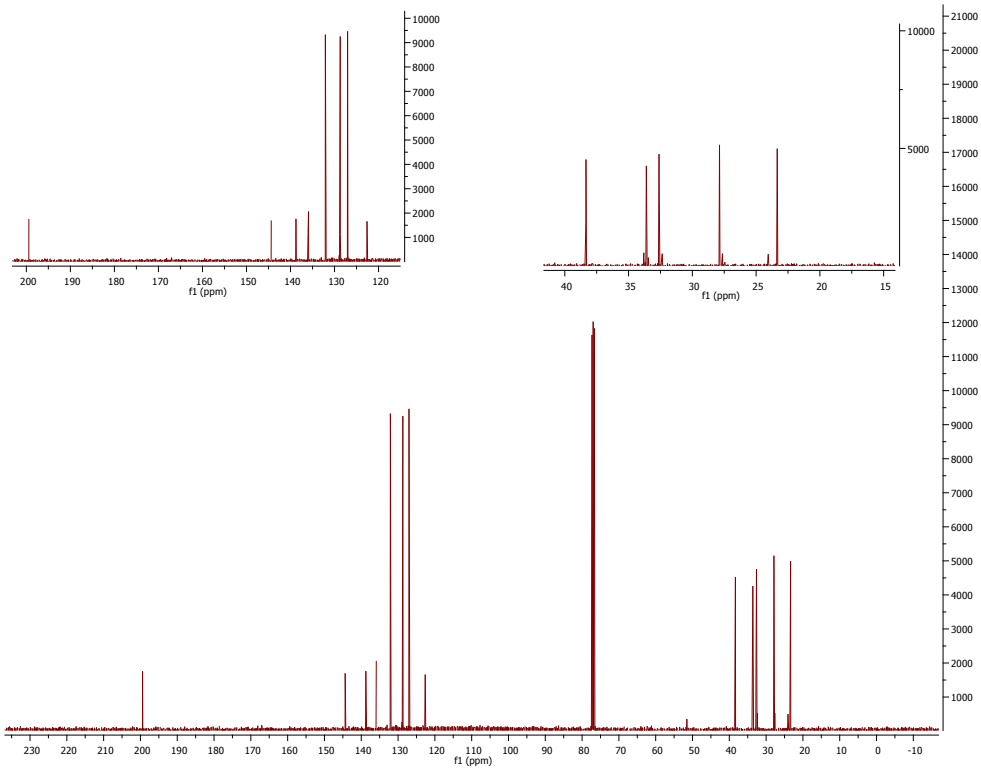


Figure 2. ^{13}C NMR (100 MHz $CDCl_3$) spectra of **1**, insets show expansions of the aromatic region (top left) and aliphatic region (top right).

2.1.2. 1-Bromo-6-(4'-bromobiphenyl-4-yl)hexane, *2*

Compound **2** was prepared by reduction of the carbonyl group on **1** using triethylsilane in trifluoroacetic acid[1]. Triethylsilane (22 ml, 0.14 mol) was added dropwise to a stirred solution of **1** (22.70 g, 0.057 mol) in trifluoroacetic acid (33.5 ml, 0.44 mol) cooled in an ice bath, maintaining the temperature below 20 °C. The reaction mixture was stirred overnight at room temperature before being added to a mixture of dichloromethane (100 ml) and H_2O (300 ml). The layers were separated and the aqueous layer was washed with dichloromethane (2 x 100 ml). The organic layers were combined and dried over anhydrous magnesium sulphate before removing the solvent under vacuum. The crude product thus obtained was recrystallised from ethanol to give the title compound as a white solid. Yield: 11.13 g, 51%. T_{Crl} 77 °C. Infrared *v* cm^{-1}: 2928 (C-H), 2854 (C-H), 1479, 1077, 1000, 804, 646, 503. ^1H NMR (400 MHz $CDCl_3$)δ: 7.54 (2H, d, *J* 8.5 Hz, Ar), 7.47 (2H, d, *J* 8.5 Hz, Ar), 7.44 (2H, d, *J* 8.5 Hz, Ar), 7.25 (2H, d, *J* 8.5 Hz, Ar), 3.41 (2H, t, *J* 6.6 Hz, $BrCH_2CH_2$), 2.65 (2H, t, *J* 7.3 Hz, $ArCH_2CH_2$), 1.87 (2H, quin, *J* 7.8 Hz, $BrCH_2CH_2CH_2$), 1.67 (2H, quin, *J* 7.4 Hz, $ArCH_2CH_2CH_2$), 1.48 (2H, m, $CH_2CH_2CH_2CH_2$), 1.39 (2H, m, $CH_2CH_2CH_2CH_2$). ^{13}C NMR (100 MHz $CDCl_3$)δ: 142.18, 140.02, 137.41, 131.79, 128.94, 128.55, 126.81, 121.20, 35.41, 33.93, 32.71, 31.18, 28.28, 28.01.

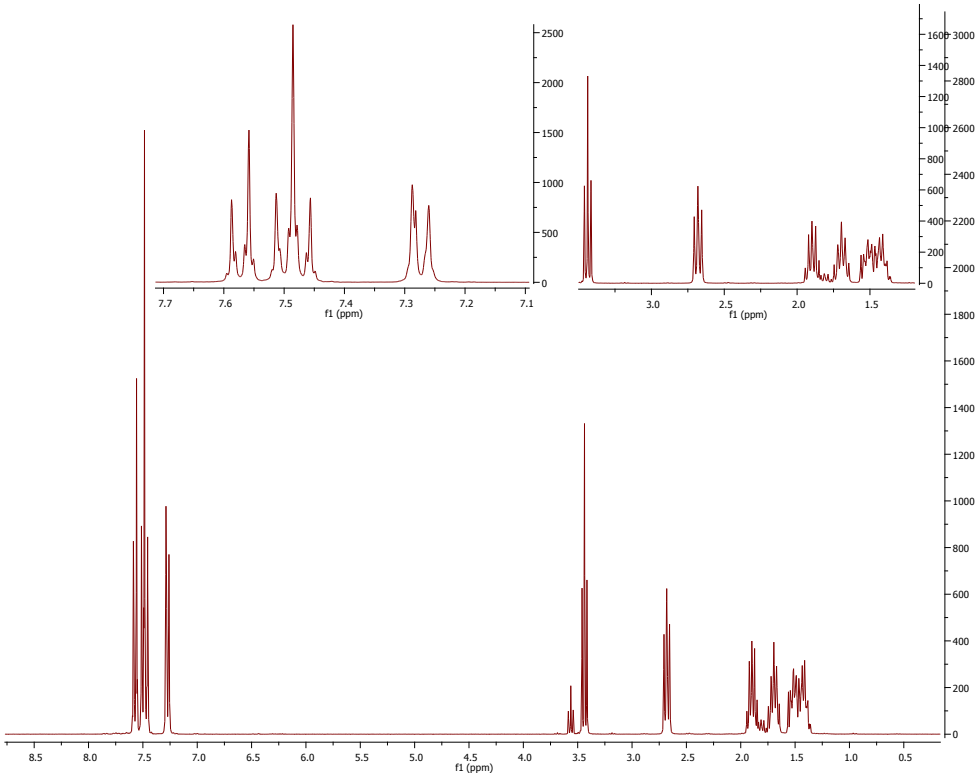


Figure 3. ^{1}H NMR (400 MHz $CDCl_3$) spectra of **2**, insets show expansions of the aromatic region (top left) and aliphatic region (top right).

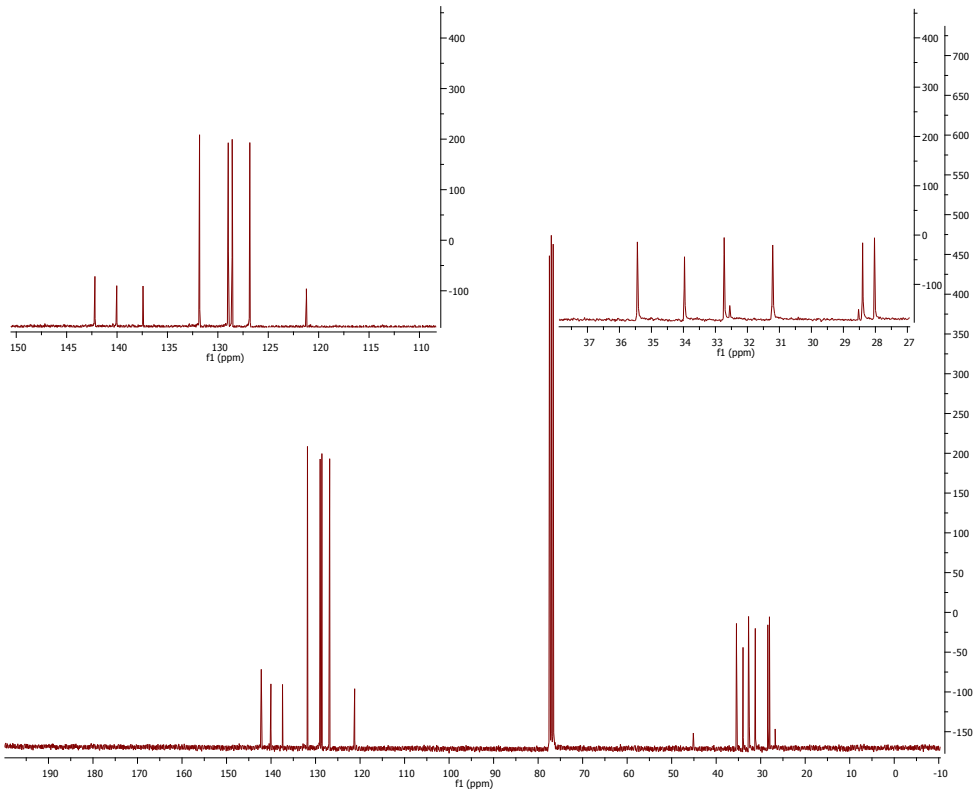


Figure 4. ^{13}C NMR (100 MHz $CDCl_3$) spectra of **2**, insets show expansions of the aromatic region (top left) and aliphatic region (top right).

2.1.3. 1-(4-Cyanobiphenyl-4'-yloxy)-6-(4-bromobiphenyl-4'-yl)hexane, 3

A mixture of **2** (5.21 g, 0.013 mol), 4-cyano-4'-hydroxybiphenyl (2.51 g, 0.013 mol), potassium carbonate (3.67 g, 0.027 mol) and dimethylformamide (50 ml) was heated at reflux overnight. The reaction mixture was cooled to room temperature, poured into H_2O (150 ml), and the white precipitate was collected by vacuum filtration. The crude product thus obtained was recrystallised from ethyl acetate to give the title compound as a white solid. Yield: 2.19 g, 33%. T_{NI} 120 °C, T_{CrI} 142 °C. Infrared v cm^{-1}: 2922 (C-H), 2222 (C≡N), 1602, 1493, 1481, 1249, 1001, 823, 805, 535, 506. ^{1}H NMR (400 MHz $CDCl_3$)δ: 7.68 (2H, d, *J* 8.5 Hz, Ar), 7.62 (2H, d, *J* 8.5 Hz, Ar), 7.53 (2H, d, *J* 8.5 Hz, Ar), 7.51 (2H, d, *J* 8.5 Hz, Ar), 7.46 (2H, d, *J* 8.5 Hz, Ar), 7.43 (2H, d, *J* 8.5 Hz, Ar), 7.25 (2H, d, *J* 8.5 Hz, Ar), 6.97 (2H, d, *J* 8.5 Hz, Ar), 4.00 (2H, t, *J* 6.3 Hz, O$\underline{CH_2}CH_2$), 2.67 (2H, t, *J* 7.8 Hz, Ar$\underline{CH_2}CH_2$), 1.82 (2H, quin, *J* 7.8 Hz, $OCH_2\underline{CH_2}CH_2$), 1.69 (2H, quin, *J* 7.5 Hz, $ArCH_2\underline{CH_2}CH_2$), 1.53 (2H, m, $CH_2\underline{CH_2}CH_2CH_2$), 1.45 (2H, m, $CH_2CH_2\underline{CH_2}CH_2$). ^{13}C NMR (100 MHz $CDCl_3$)δ: 159.76, 145.24, 142.27, 140.00, 137.37, 132.57, 131.80, 131.28, 128.98, 128.53, 128.34, 127.06, 126.79, 121.20, 119.12, 115.08, 110.05, 68.04, 35.46, 31.29, 29.11, 28.92, 25.90.

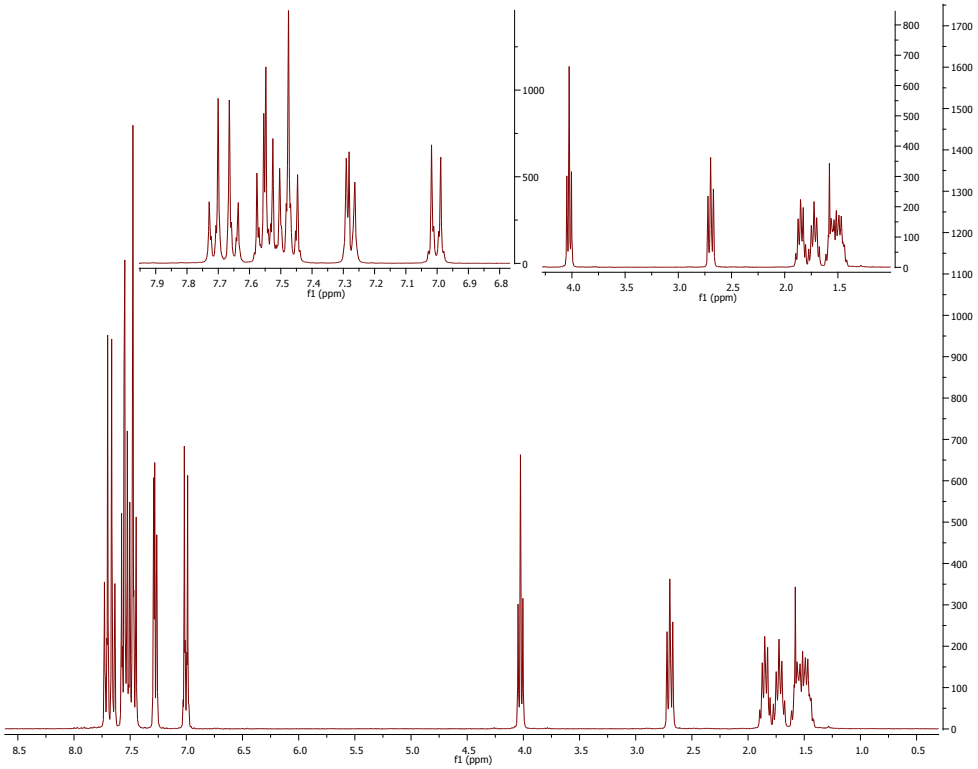


Figure 5. ^{1}H NMR (400 MHz $CDCl_3$) spectra of **3**, insets show expansions of the aromatic region (top left) and aliphatic region (top right).

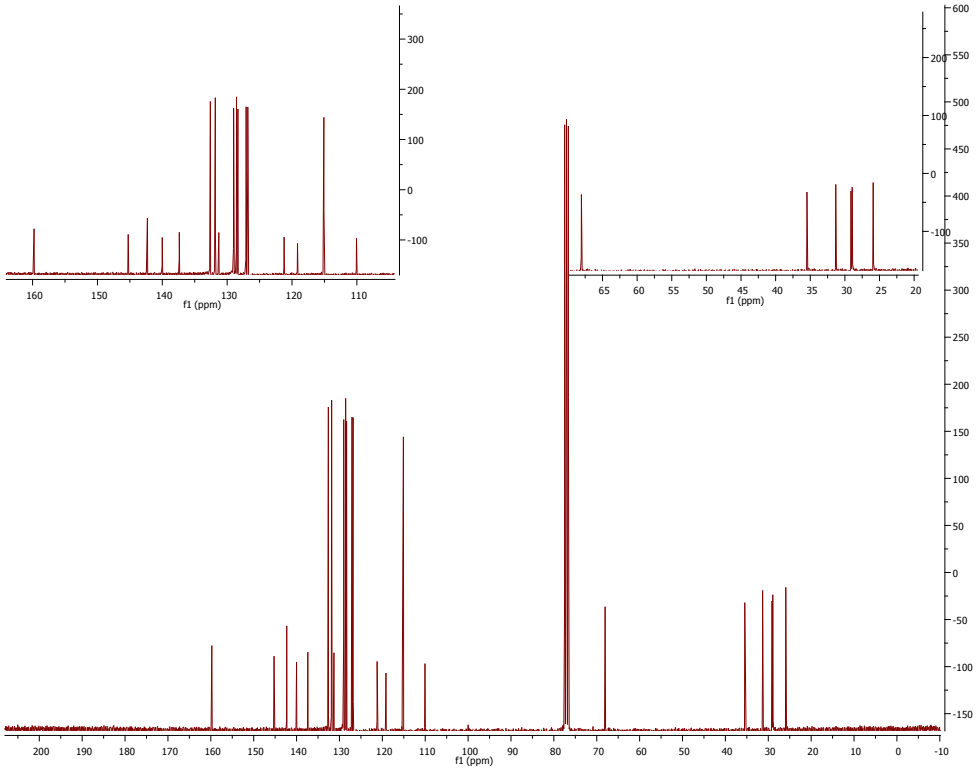


Figure 6. ^{13}C NMR (100 MHz $CDCl_3$) spectra of **3**, insets show expansions of the aromatic region (top left) and aliphatic region (top right).

2.1.4. 1-(4-Cyanobiphenyl-4'-yloxy)-6-(4-cyanobiphenyl-4'-yl)hexane, 4, CB6OCB

The cyanation of **3** was achieved using a modified Rosenmund-von Braun reaction as described by Coates and Gray[2]. A mixture of **3** (4.12 g, 0.008 mol), copper cyanide (1.88 g, 0.021 mol) and dry N-methyl-2-pyrrolidone (50 ml) was heated to 200 °C for 4 h. The reaction mixture was cooled to 80 °C and to this was added a solution of iron chloride (6.90 g, 0.05 mol), H_2O (15 ml) and 32 % hydrochloric acid (6 ml) at 60 °C. This was allowed to cool slowly to room temperature and stirred overnight, then added to a dichloromethane (200 ml) and H_2O (200 ml) mix. The aqueous layer was washed with dichloromethane (100 ml). All organic fractions were combined and washed with H_2O (3 x 100 ml) before drying over anhydrous magnesium sulphate. Solvent was removed under vacuum to yield a brown liquid which was added to H_2O (200 ml). The brown precipitate was collected by vacuum filtration and washed with H_2O (400 ml). The crude product was purified by silica gel chromatography using dichloromethane as eluent, R.f. 0.54. The crude product thus obtained was recrystallised from ethanol to give the title compound as a white solid. Yield: 1.98 g, 43%. $T_{CrN_{TB}}$ 100 °C, $T_{N_{TB}N}$ 109 °C, T_{NI} 155.2 °C. Elemental analysis: Calculated for $C_{32}H_{28}N_2O$: C, 84.14%, H, 6.18%, N, 6.14%. Found: C, 84.41%, H, 6.21%, N, 6.17%. Infrared v cm^{-1}: 2925 (C-H), 2219 (C≡N), 1601, 1493, 1471, 1250, 1174, 817, 807, 563, 525. ^{1}H NMR (400 MHz $CDCl_3$)δ: 7.70 (2H, d, *J* 8.3 Hz, Ar), 7.67 (2H, d, *J* 8.3 Hz, Ar), 7.65 (2H, d, *J* 8.3 Hz, Ar), 7.63 (2H, d, *J* 8.3 Hz, Ar), 7.52 (2H, d, *J* 8.3 Hz, Ar), 7.51 (2H, d, *J* 8.3 Hz, Ar), 7.29 (2H, d, *J* 8.3 Hz, Ar), 6.98 (2H, d, *J* 8.3 Hz, Ar), 4.01 (2H, t, *J* 6.3 Hz, O$\underline{CH_2}CH_2$), 2.69 (2H, t, *J* 7.8 Hz, Ar$\underline{CH_2}CH_2$), 1.83 (2H, quin, *J* 7.8 Hz, OCH$_2\underline{CH_2}CH_2$), 1.70 (2H, quin, *J* 7.4 Hz, ArCH$_2\underline{CH_2}CH_2$), 1.53 (2H, m, CH$_2\underline{CH_2}CH_2CH_2$), 1.45 (2H, m, CH$_2CH_2\underline{CH_2}CH_2$). ^{13}C NMR (100 MHz $CDCl_3$)δ: 159.76, 145.89, 145.53, 143.38, 137.37, 133.27, 133.23, 131.81, 129.56, 128.67, 127.98, 127.77, 119.12, 119.09, 117.05, 110.44, 110.21, 68.05, 35.64, 31.27, 29.11, 28.99, 25.91.

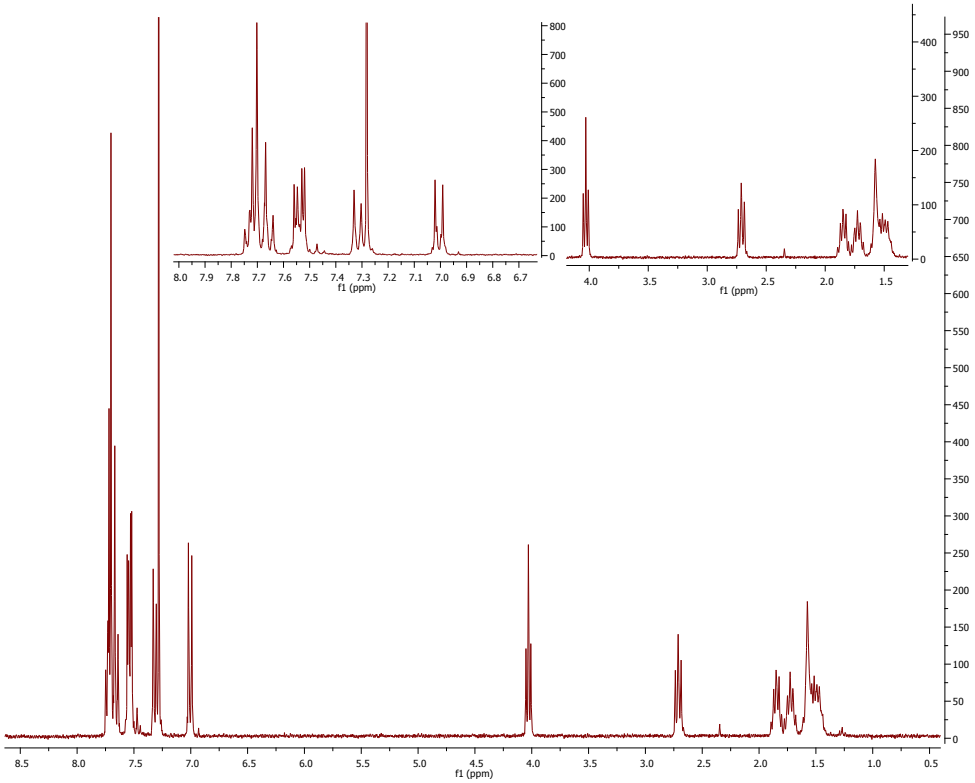


Figure 7. ^{1}H NMR (400 MHz $CDCl_3$) spectra of CB6OCB, insets show expansions of the aromatic region (top left) and aliphatic region (top right).

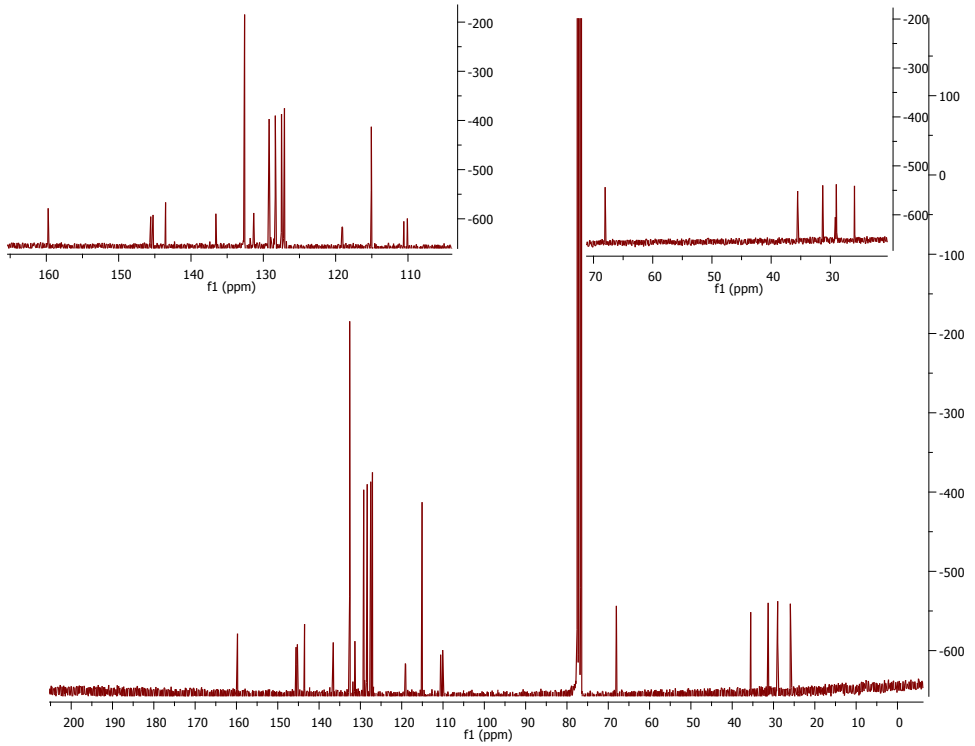


Figure 8. ^{13}C NMR (100 MHz $CDCl_3$) spectra of CB6OCB, insets show expansions of the aromatic region (top left) and aliphatic region (top right).

2.2. Synthesis of CB6OCB–d_2

CB6OCB–d_2 was synthesized from deuteriated triethylsilane, Et_3SiD; this was first prepared from chlorotriethylsilane and $LiAlD_4$ as described elsewhere [3]. The synthesis was identical to that described earlier for CB6OCB. The structure and purity of the final product was confirmed using NMR and mass spectroscopy, see Figures 9 and 10, respectively.

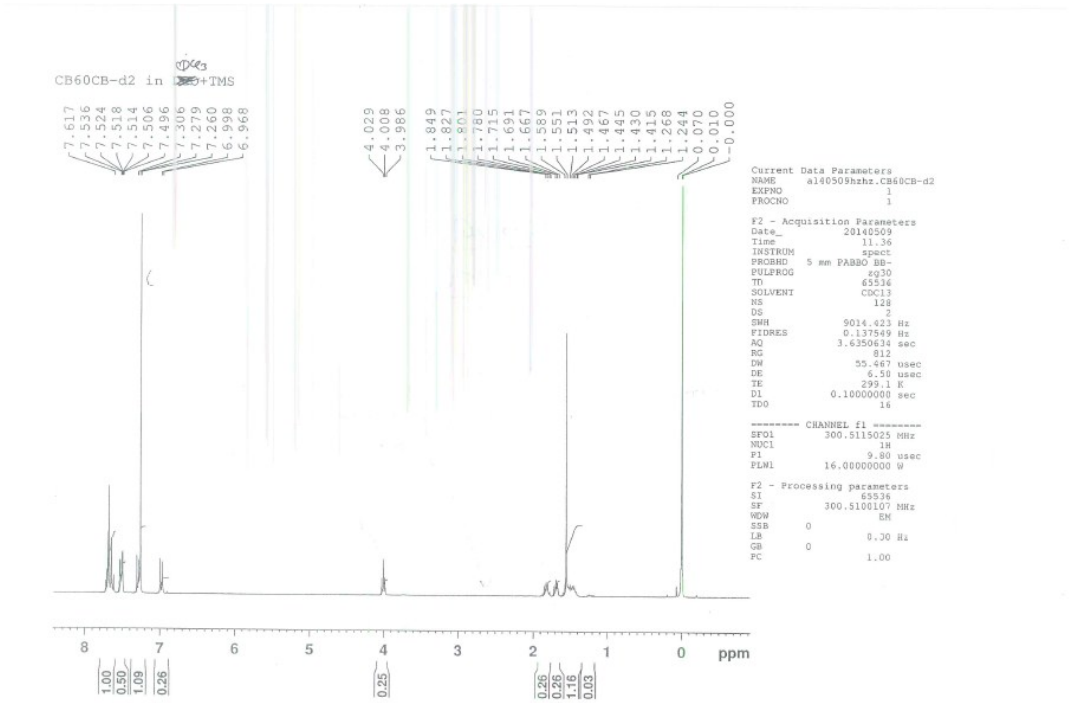


Figure 9. ^{1}H NMR (400 MHz $CDCl_3$) spectrum of CB6OCB-**–d_2**, note the absence of the peak centred at 2.69 in the spectrum of CB6OCB associated with Ar$\underline{CH_2}CH_2$, see Figure 7.

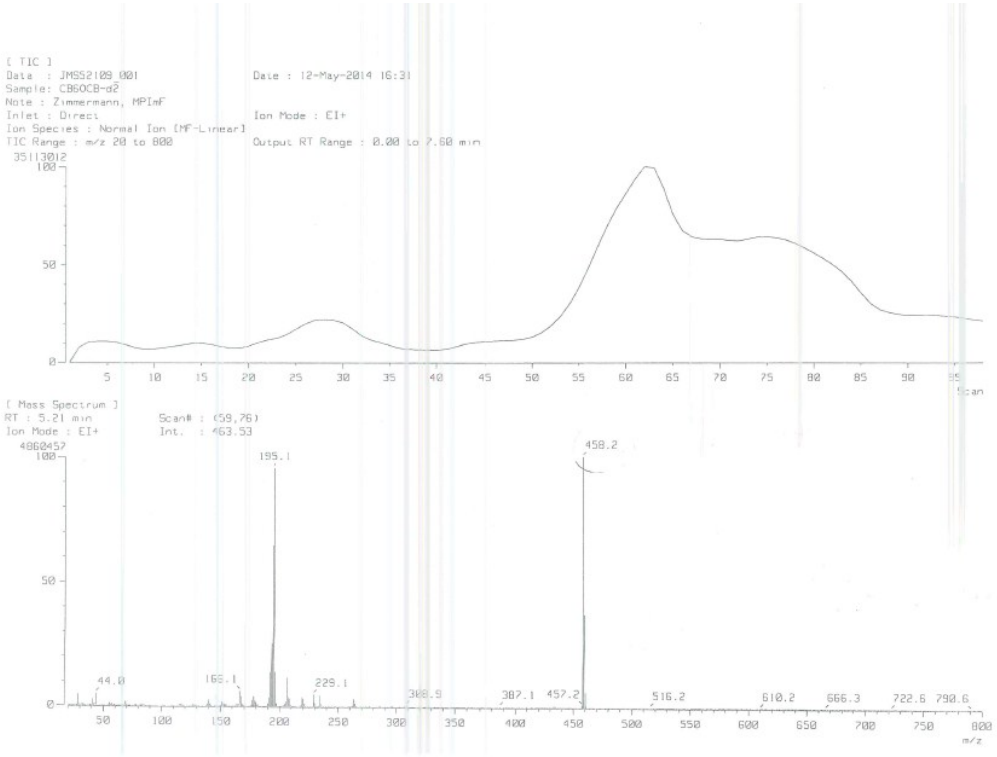


Figure 10. Mass spectrum spectrum of CB6OCB-–d_2.

Section 3: References

1. D. N. Kursanov, Z. N. Parnes and N. M. Loim, *Synthesis-Stuttgart*, 1974, 633-651.
2. D. Coates and G. W. Gray, *J. Chem. Soc.-Perkin Trans. 2*, 1976, 863-868.
3. W. Caseri and P. S. Pregosin, *J. Organometallic Chem.*, 1988, **356**, 259-269.