

Electronic Supplementary Information (ESI)

**^{13}C NMR Investigations and Molecular Order of
4-(trans-4'-hexylcyclohexyl)-isothiocyanatobenzene (6CHBT)**

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PELF pulse sequence:

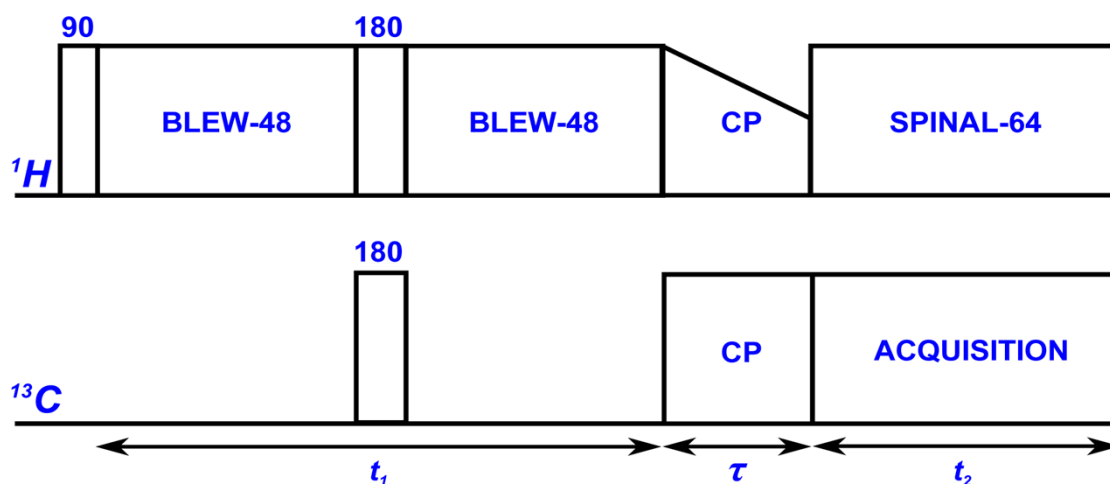


Figure S1: Pulse sequence for 2D Proton Encoded Local Field (PELF) pulse sequence a variant of Separated Local Field (SLF) experiment. To suppress the proton–proton dipolar couplings BLEW-48 homonuclear decoupling sequence employed during t_1 period and heteronuclear decoupling sequence SPINAL-64 is applied during t_2 period. The method yields a 2D spectrum with carbon chemical shifts along the F_2 dimension and the proton-carbon dipolar couplings along the F_1 dimension.

Solution 2D NMR Experimental Details:

Solution NMR experiments were made on a JEOL ECA-500 MHz high resolution FT-NMR spectrometer operating at frequencies 500.16 MHz (^1H) and 125.77 MHz (^{13}C). 25 mg of 6CHBT was dissolved in 0.7 ml of CDCl_3 . Tetramethylsilane (TMS) was used as an internal reference standard for the assignment of ^1H and ^{13}C chemical shifts. All the NMR spectra were recorded at 25°C. JEOL-Delta software package (version 5.0.3) was used for the purpose of NMR pulse sequences and data processing. The experimental parameters chosen for 1D $^1\text{H}/^{13}\text{C}$ NMR were as follows: spectral width 15/200 ppm, number of data points 16384/32768, number of scans 8/200, acquisition time 1.3/0.83s, relaxation delay 5/2s, and 90° pulse width 12.625/11 μs . Exponential multiplication was applied before Fourier-transformation in both cases. Furthermore, 2D correlation spectra were recorded in order to track ^1H - ^1H , ^1H - ^{13}C and ^{13}C - ^{13}C correlations. A relaxation delay of 1.5s was used in all the 2D experiments excluding ^{13}C - ^{13}C INADEQUATE, where 15s was used.

^1H - ^1H COSY: COSY spectra were obtained using the gradient version of dqf cosy pulse sequence of the JEOL-Delta software. The spectra resulted from 1024 (F_2) \times 256 (F_1) data matrix size with one scan per t_1 increment. A spectral width of 15 ppm was used in both F_1 and F_2 dimensions.

^1H - ^{13}C HETCOR: HETCOR spectra were recorded using the standard hector pulse program of the JEOL-Delta software. The acquisition parameters were as follows: spectra resulted from 1024 \times 128 data matrix size with eight scans per t_1 increment. A spectra width of 180 ppm in F_2 and 15 ppm in F_1 was recorded.

^1H - ^{13}C HSQC: The one-bond correlation of ^1H and ^{13}C was tracked using the phase sensitive HSQC pulse sequence of the JEOL-Delta software. The experiments were optimised for the one-bond coupling constant ($^1J_{\text{CH}}$) as 140 Hz. The spectra were obtained from 1024×256 data matrix size with four scans per t_1 increment. A spectral width of 15 ppm in F_2 and 180 ppm in F_1 was recorded.

^1H - ^{13}C HMBC: The gradient version of HMBC experiments were recorded in order to sketch the long-range (two and three bonds) ^1H - ^{13}C correlations. The long-range coupling constant ($^nJ_{\text{CH}}$) optimised was 8 Hz. The spectra resulted from 2048×256 data matrix size with eight scans per t_1 increment. A spectral width of 15 ppm in F_2 and 180 ppm in F_1 was recorded.

^{13}C - ^{13}C INADEQUATE: The gradient version of INADEQUATE experiment was performed in order to track one bond ^{13}C - ^{13}C correlations. The ^{13}C - ^{13}C coupling constant ($^1J_{\text{CC}}$) was optimised to be 40 Hz. The spectra resulted from 2048×128 data matrix size with 192 scans per t_1 increment. A spectral width of 200 ppm in F_2 was recorded. .

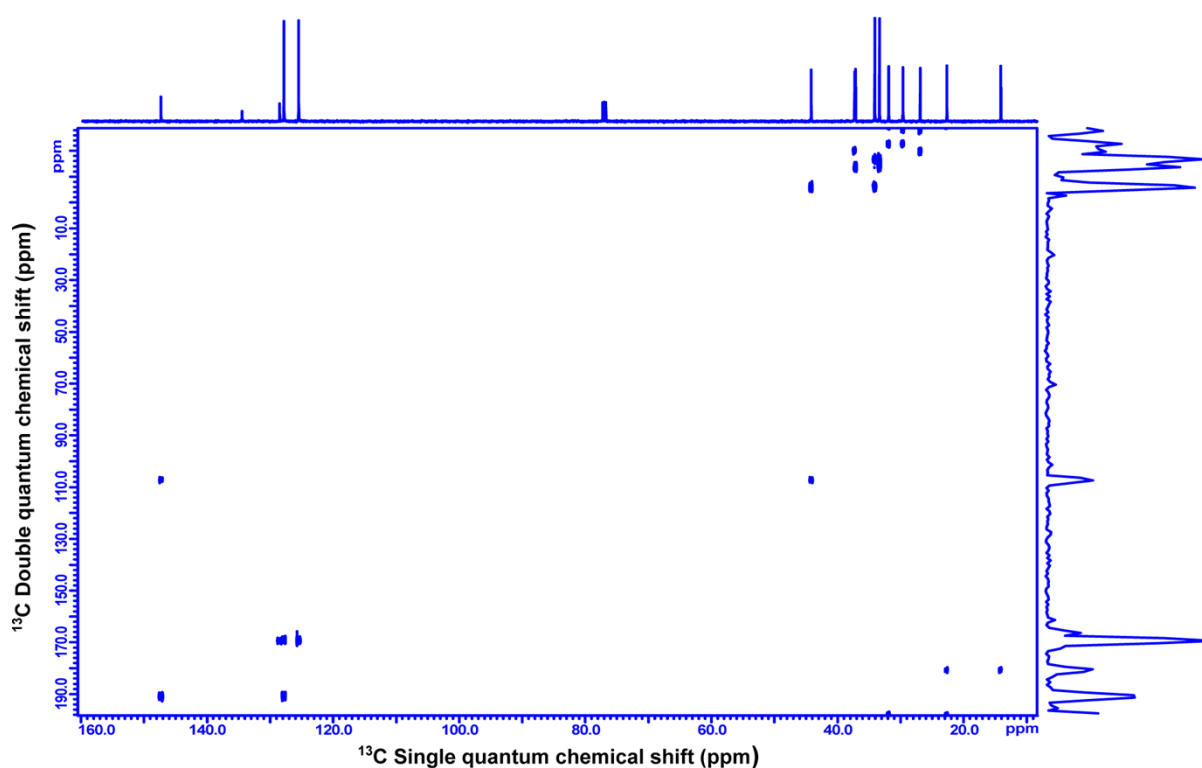


Figure S2: 2D ^{13}C - ^{13}C INADEQUATE spectrum of 6CHBT dissolved in CDCl_3

The assignment of 6CHBT in the solution state:

The ^1H NMR spectrum of the mesogen in CDCl_3 (figure not shown) shows a multiplet at 7.15 ppm for four protons which is attributed to phenyl ring protons. Among the peaks appeared for hexyl chain as well as cyclohexane ring, the assignment of methyl proton is straight forward, which exhibits a triplet at 0.88 ppm. The other methylene carbons of the hexyl chain are noticed at 1.29 ppm as a broad peak. The cyclohexyl ring protons showed long range coupling and as a result multiplicity is clearly noticed for all the protons. The equatorial (e) and axial (a) protons of 2,6 and 3,5 carbons are noticed at 1.84 ppm (e), 1.38 ppm (a) and 1.86 ppm (e), 1.04 ppm (a), respectively. The ^1H chemical shift values along with the proton numbers are listed in Table 1 of main text.

The ^{13}C NMR spectrum is depicted in Figure 2A (main text), which clearly shows sharp lines in the range 125-147.5 ppm. Of them, more intense lines appeared at 125.5 and 127.8 ppm are assigned to phenyl ring methine carbons, while the quaternary carbons showed low intense lines at 128.5 and 147.3 ppm. The terminal NCS carbon shows a line at 134.4 ppm. For the cyclohexyl ring and hexyl chain, lines in the range 14-44.5 ppm are noticed. Among them, two lines with equal intensities centred at 34.1 and 33.4 ppm are assigned to cyclohexyl ring methylene carbons 2,6 and 3,5 respectively, while the methine carbons 1 and 4 of the ring are observed at 44.2 and 37.1 ppm, respectively. The appearance of one line for 2,6 and 3,5 suggests that the carbon chemical shift values are same even though the protons are not chemically equivalent owing to equatorial and axial orientation. The hexyl chain showed well resolved lines in which methyl is distinctly seen at 14.1 ppm. The other methylene carbons exhibited similar intensity pattern and their chemical shift values are shown in Table 1 of main text.