

Orientational Order of Two Fluoro- and Isothiocyanate-Substituted Nematogens by Combination of ^{13}C NMR Spectroscopy and DFT Calculations

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1. Comparison of NMR data calculated by M06-2X and B3LYP functionals

We performed in vacuo NMR calculations using B3LYP and M06-2X functionals and 6-311+G(d,p) basis set (Figure S1). Both sets of calculations satisfactorily reproduce the experimental ^{13}C isotropic chemical shifts. The root mean square deviation (RMS) between experimental and computed data is 5.7 and 6.7 ppm for B3LYP and M06-2X functional, respectively; the B3LYP functional was selected for all the following NMR calculations.

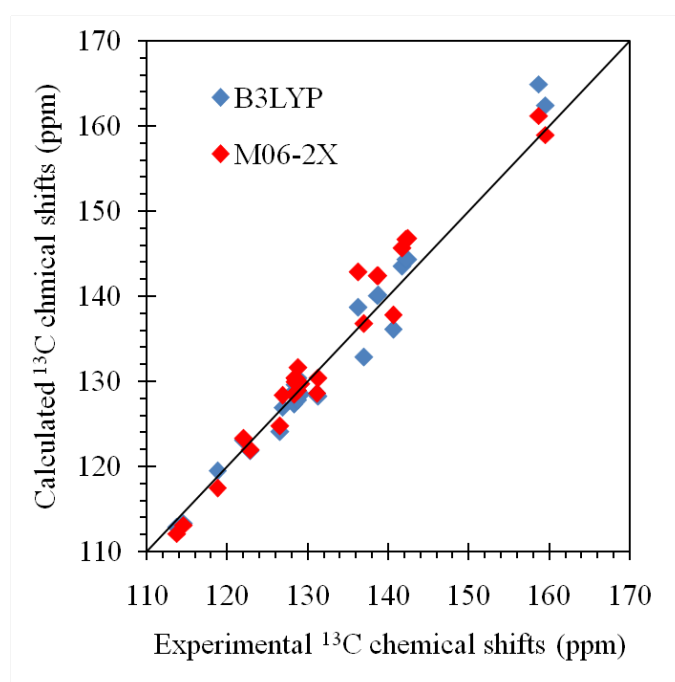


Figure S1. Correlation of experimental and calculated ^{13}C NMR chemical shifts (ppm) at B3LYP and M06-2X levels of theory for the two mesogens.

2. Conformational analysis by Potential Energy Surface scan

In order to evaluate the conformational effects on NMR parameters we performed a relaxed Potential Energy Surface (PES) scan along the $\tau(\text{C4-C5-C8-C9})$ dihedral angle (Figure S2) for both the molecules in the gas-phase.

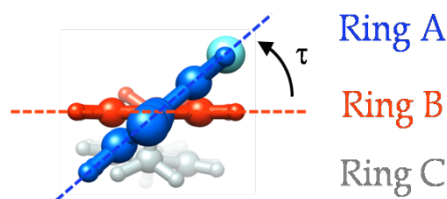


Figure S2. Schematic representation of $\tau(\text{C4-C5-C8-C9})$ angle.

For this purpose we used M06-2X functional and 6-31G(d) basis set, and we varied the τ angle between 0 and 360 degrees with steps of 10 degrees. Figures S3 and S4 show the energy profiles for **ORTHO** and **META**, respectively. We found four minima differing by less than 0.04 and 0.06 Kcal/mol for **ORTHO** and **META**, respectively. ^{13}C isotropic chemical shifts calculated for the different conformers differed by less than 1.3 ppm and 1 ppm for **ORTHO** and **META**, respectively, with respect to the absolute minimum (minimum number 4 in figures S3 and S4).

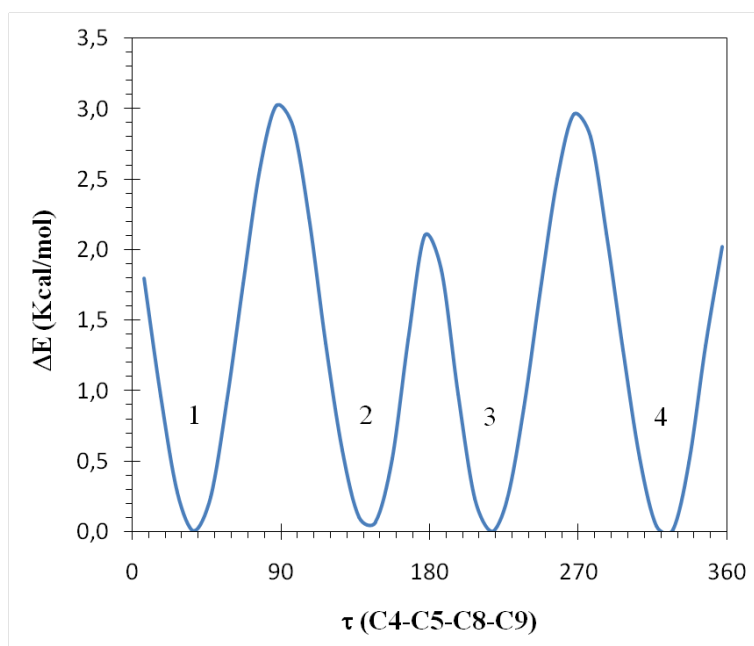


Figure S3. Potential Energy Surface (PES) scan along the $\tau(\text{C4-C5-C8-C9})$ dihedral angle for **ORTHO** molecule. On y axis the differences of energy are represented with respect to the energy of the absolute minimum conformation (minimum number 4).

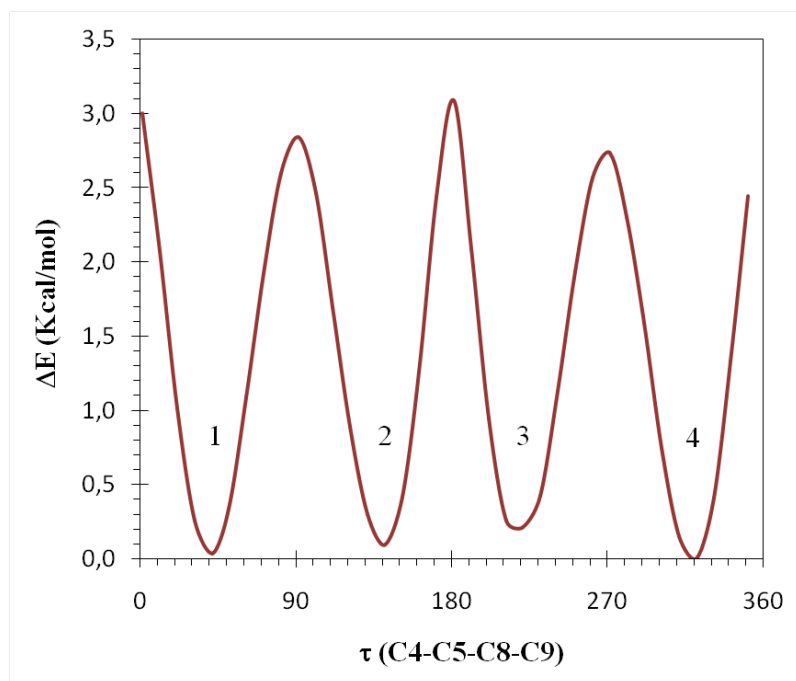


Figure S4. Potential Energy Surface (PES) scan along the τ (C4-C5-C8-C9) dihedral angle for **META** molecule. On y axis the differences of energy are represented with respect to the energy of the absolute minimum conformation (minimum number 4).

3. Temperature dependence of ^{13}C NMR spectra of ORTHO and META in the N phase

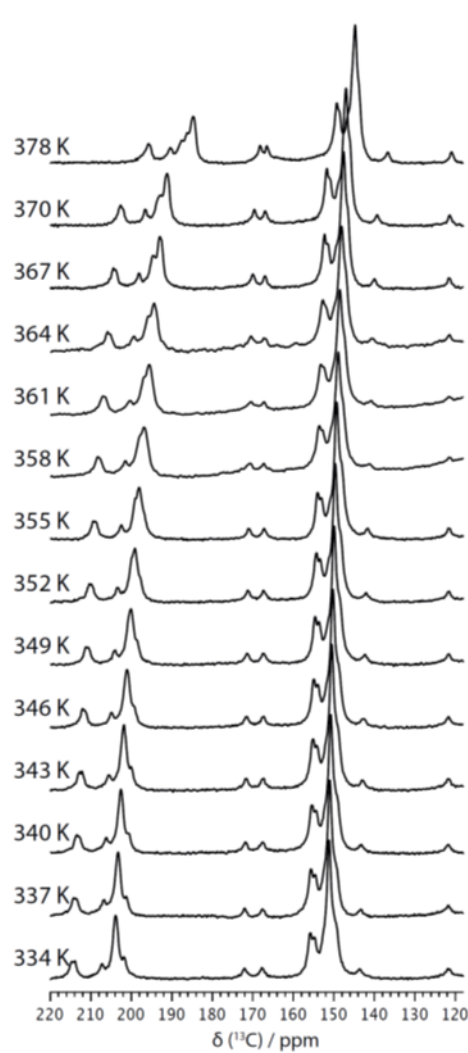


Figure S5. Temperature dependence of the aromatic region of the ^{13}C DE NMR spectra of **ORTHO** within the N phase.

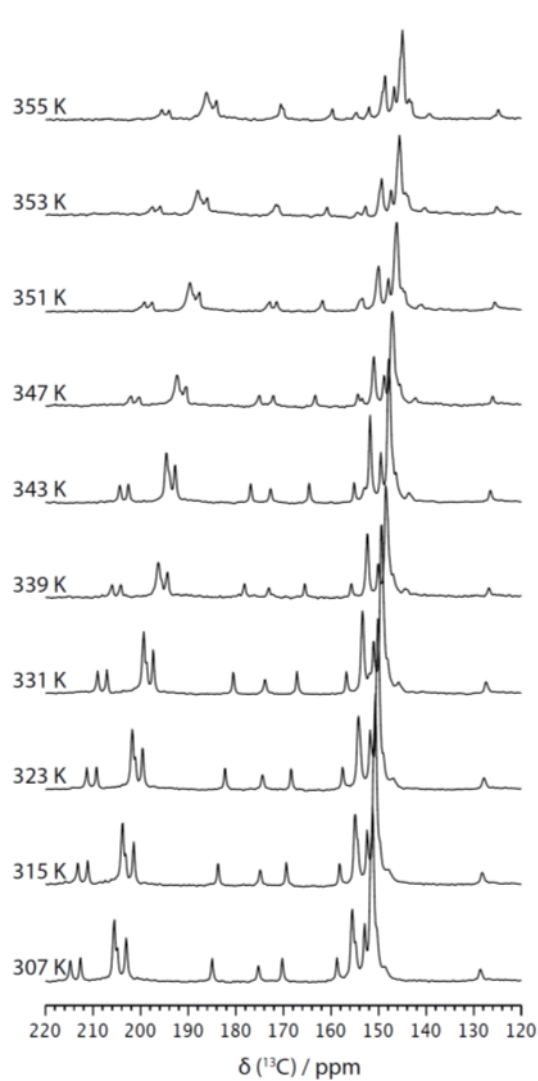


Figure S6. Temperature dependence of the aromatic region of the ^{13}C DE NMR spectra of **META** within the N phase.