Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Supplementary Information for the paper:

Molecular biaxiality determines the helical structure - Infrared measurements of the molecular order in the N_{TB} phase of difluoro terphenyl dimers

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In order to establish the geometric parameters of the dimers and other IR spectroscopic properties, quantum mechanical density functional theory (DFT) was used [25]. All calculations were performed using the Gaussian 09 program, version E.01 [29]. Molecular structures, harmonic vibrational force constants, and absolute IR intensities were calculated using DFT theory with the Becke's three-parameter exchange functional in combination with the Lee, Yang, and Parr correlation functional the B3-LYP method with the diffusion basis set: 6-311+G [25,26]. In order to find the most stable conformation of the dimer the optimization of the geometry were performed in a few steps (see information in the SM). All possible conformation of dimers we have considered is defined by the values of dihedral angles φ_1 - φ_8 (Fig 1a). In the first stage the energy barriers for the internal rotation of the terphenyl (torsional angles φ_2 and φ_3) have been determined. In a further step, energy barriers for the rotation around the dihedral angle (φ_1, φ_4) between terphenyl and the linker / tail in the MTC5 monomer were determined. The approximate potential energy functions have been calculated at intervals of 10. In the calculations, the torsional angles (φ_1-φ_4, each in turn) fixed at arbitrary selected values while the other geometrical parameters were optimized; relaxed potential energy scans were performed. This procedure allowed determining the values of torsion angles for which the minimum energy was obtained. As the energy barrier for the internal rotation in the alkyl chain is very small (approx. 1 kJ/mol), therefore, we did not consider any other spacer and tail conformations than the all-trans. In the next step, taking into account the determined values of torsion angles, full optimization of the geometry was performed for the DTC5C5. All DFT optimization were carried out with the following convergence criteria used with Berny algorithm: the maximum component of the force was set to 0.00045, the root-mean square (RMS) of the forces calculated for the next step—smaller then 0.0003—the computed displacement for the next step—smaller than 0.0018—and the RMS of the displacement below 0.0012. These criteria restrict the dependence of the final geometry parameters on the initial starting geometry. Therefore, the vibrational calculations were done for the most probable conformers with the lowest energy for the MTC, the DTC5C5. For B3LYP frequency calculations, a pruned 99,590 grid was used to obtain a more accurate numerical integration; it is important for computing low frequency modes. Maximal force (in atomic units) that was lower than $3.6x\ 10^{-5}$ after geometry optimization. The rotational frequencies were very close to zero, the translational frequencies smaller than $7.5\ cm^{-1}$. The theoretical vibrational frequencies were scaled by one coefficient equal 0.98 in order to simplify the comparison with experiment.

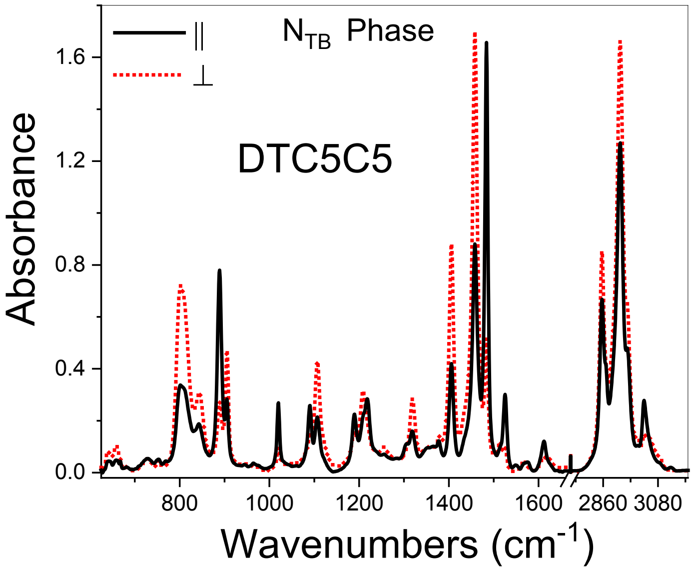


Fig.1S. Infrared spectra of DTC5C5 dimer of the planar sample for parallel - *solid black line* and perpendicular – *short dot red line,* orientation of the polarizer with respect to the alignment axis, in the twist-bend phase given as an example.

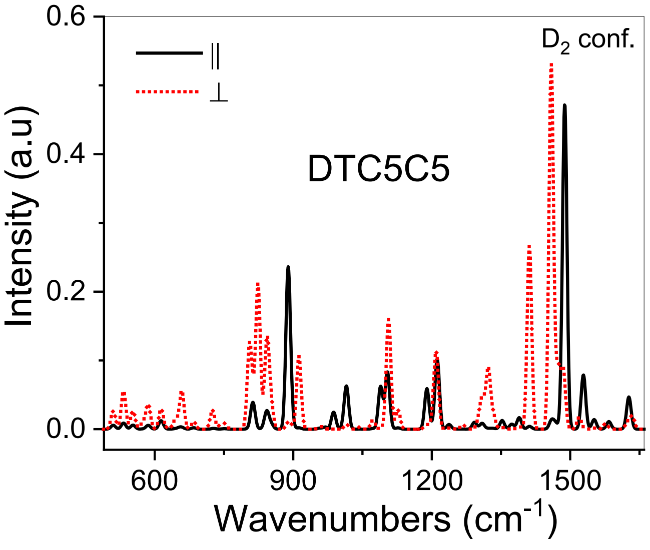


Fig2S. Theoretical spectra of the DTC5C5 dimer for the helical conformation of the terphenyl (*φ_1=-43.5, φ_2=-43.2*) using DFT method (B3LYP/6-311+G). Longitudinal transition dipole moment – *solid black line* and transverse transition dipole moment – short dot red line.

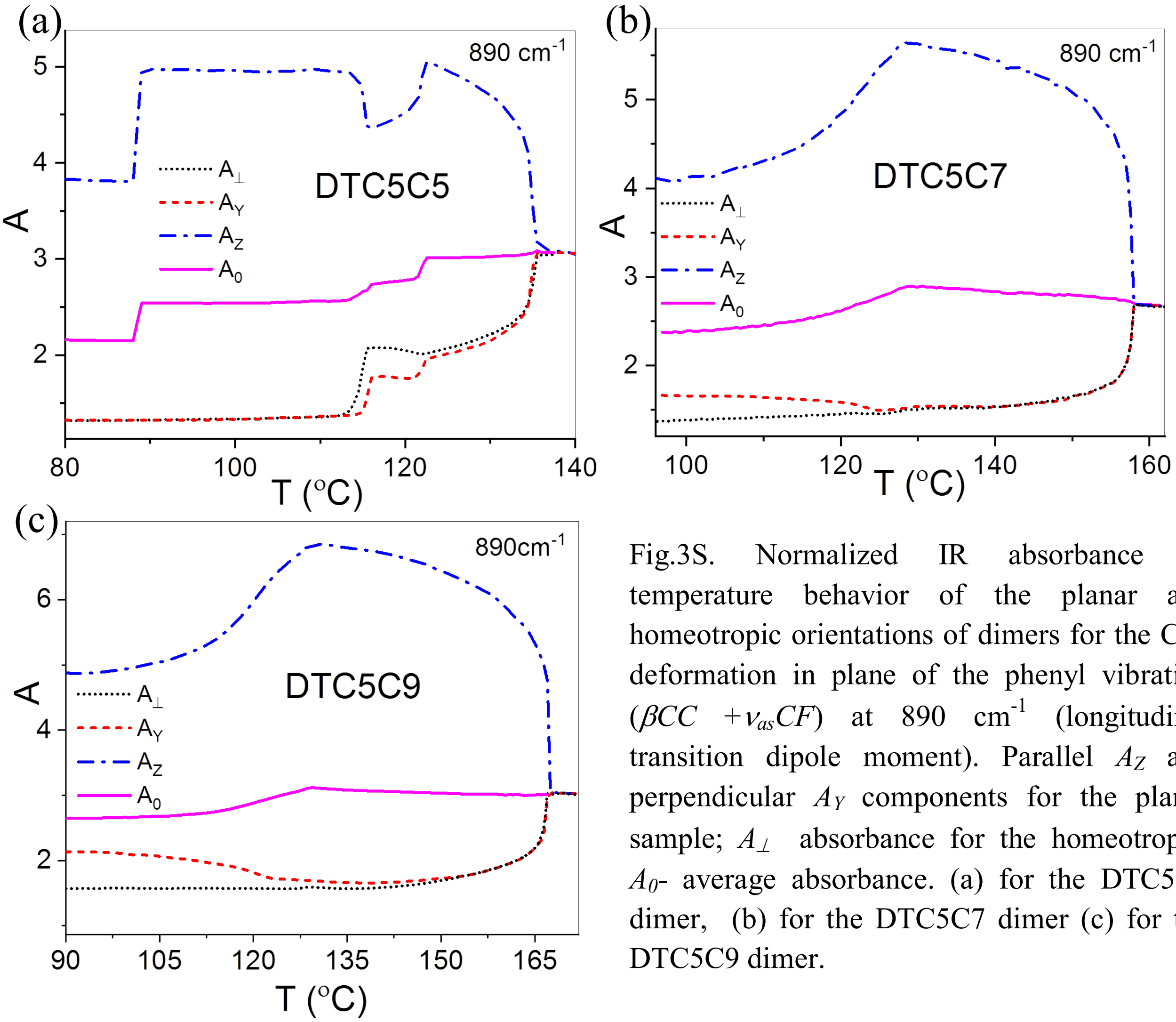


Fig.3S. Normalized IR absorbance vs temperature behavior of the planar and homeotropic orientations of dimers for the C-C deformation in plane of the phenyl vibration ($\beta CC\ + \nu_{as} CF$) at 890 cm^{-1} (longitudinal transition dipole moment). Parallel A_Z and perpendicular A_Y components for the planar sample; $A_\perp$ absorbance for the homeotropic. A_0- average absorbance. (a) for the DTC5C5 dimer, (b) for the DTC5C7 dimer (c) for the DTC5C9 dimer.

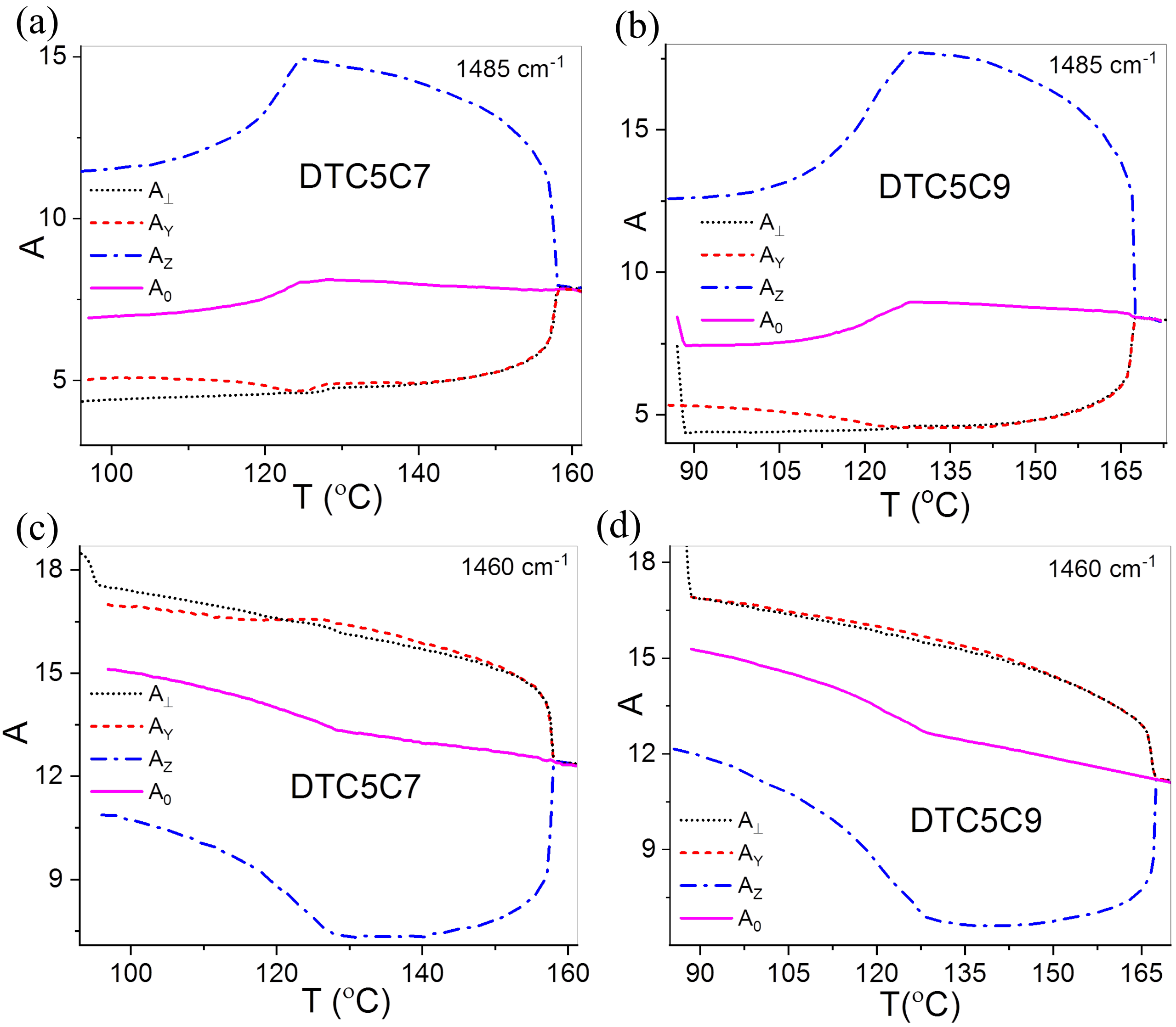
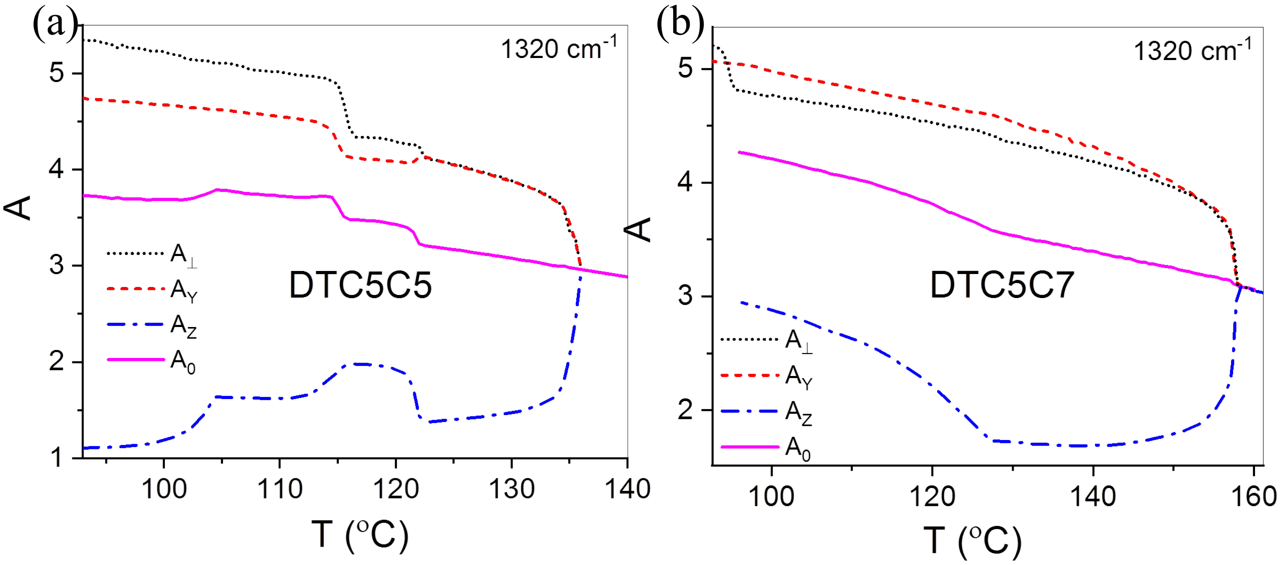


Fig.4S. Normalized IR absorbance vs temperature behavior of the planar and homeotropic orientations of dimers for the phenyl stretching band (*νCC*) at wavenumbers: 1485 and 1460cm^{-1}. (a) and (b) concern the phenyl stretching band with longitudinal transition dipole moment at 1485cm^{-1} wavenumber for the DTC5C7 and the DTC5C9 dimers, respectively. (c) and (d) concern the phenyl stretching band with transverse transition dipole moment at 1460cm^{-1} for the DTC5C7 and the DTC5C9 dimers, as an example. Parallel A_Z and perpendicular A_Y components for the planar sample; $A_\perp$ absorbance for the homeotropic. A_0- average absorbance.



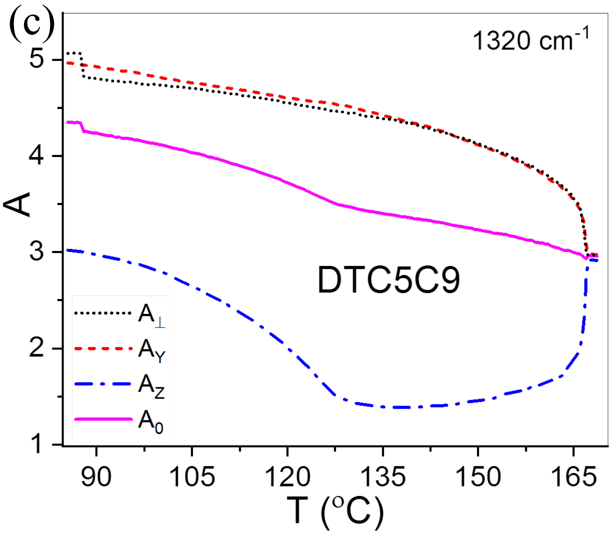


Fig.5S. Normalized IR absorbance vs temperature behavior of the planar and homeotropic orientations of dimers for asymmetric deformation of the methylene groups called twisting vibration mixed with the phenyl in plane deformation vibration ($\gamma_{as}CH2$ + βCH in plane of the terphenyl) at the 1320 cm^{-1} wavenumber. The transition dipole of this band is perpendicular to the long axis of the linker, i.e. $\theta = 90°$ (in *all trans* conformation of the linker) and its azimuthal angle is $\phi \cong 45$. Parallel A_Z and perpendicular A_Y components for the planar sample; $A_\perp$ absorbance for the homeotropic. A_0 - average absorbance. (a) for the DTC5C5 dimer, (b) for the DTC5C7 dimer (c) for the DTC5C9 dimer.