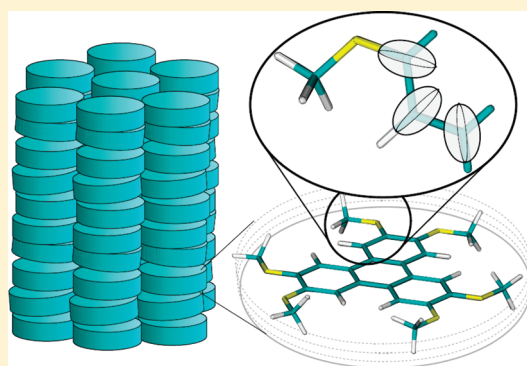


Carbon-13 NMR Chemical Shifts in Columnar Liquid Crystals

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ABSTRACT: In this article, we present quantum chemical density functional theory (DFT) calculations of the NMR ¹³C chemical shift (CS) tensors in 2,3,6,7,10,11-hexahexylthiotriphenylene (HHTT). The DFT calculations are performed on a smaller model molecule where the hexyl chains were reduced to methyl groups (HMTT). These tensors are compared with our previously reported experimental results carried out under magic-angle spinning (MAS) conditions. The phase diagram of HHTT is K ↔ H ↔ D_{hd} ↔ I, where H is a helical phase and D_{hd} is a columnar liquid crystal. The motivation for the present study was to explain experimentally observed and puzzling thermal history effects, which resulted in different behavior in the helical phase upon cooling and heating. In particular, the CS tensors for the aromatic carbons measured in the helical phase upon heating from the solid phase were essentially unaffected, while the cooling from the columnar liquid crystal resulted in a significant averaging. We investigate the effect on the CS tensors of (i) conformational transitions, and (ii) relative molecular orientations within the columns for dimer and trimer configurations. Finally a motional wobbling (PIZZA) model for the dynamic averaging of the CS tensor in the helical phase is suggested.

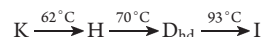


■ INTRODUCTION

Typical discotic molecules have a flat or nearly flat, often aromatic, core with six or more flexible side chains covalently linked to it. The molecular symmetry of these compounds is usually trigonal although some molecules with lower symmetry also form discotic liquid crystals. Columnar liquid crystals have some unique properties, which are beginning to be exploited for commercial use. For technical applications, the most important aspect is the geometry of the mesophase that enables one-dimensional charge transport within the columns.^{1–6} There is a very large anisotropy in the conductivity between the direction parallel to the column axis and those perpendicular to it, caused by the insulating effect of the side chains. The ratio of the conductivity values in these two directions is typically about 1000:1, but with special design this value can be increased by several orders of magnitude.^{1,7,8} Some of the compounds exhibit extremely high charge mobility, in fact higher than that in any other organic material.^{1,8}

In this article we present carbon-13 NMR chemical shift quantum chemical density functional theory (DFT) calculations in 2,3,6,7,10,11-hexahexylthiotriphenylene (HHTT) where the hexyl chains have been replaced by methyl groups HMTT, Figure 1a. The combination of NMR measurements and DFT calculations of chemical shift (CS) tensors constitutes a powerful tool for investigations of liquid crystalline systems at the molecular level.^{9–15} The phase diagram of HHTT was determined

using X-ray and differential-scanning-calorimetry (DSC) techniques,^{7,16–18}



where K and I are the solid and isotropic phases respectively, and D_{hd} is a hexagonal (h), disordered (d) columnar liquid crystal. The helical (H) phase has also been identified as a columnar D_{ho} liquid crystal,^{17,19} where the subscript “o” denotes ordered phase, and refers to the intracolumnar order of the mesophase. The D_{ho}–D_{hd} transition has been claimed to be unique for HHTT.^{16,17,19} Furthermore, it has been suggested that the D_{ho} phase exhibits solid crystalline structure, rather than liquid crystalline, with the helical molecular orientational order within the columns.^{17,19,20} The molecular description of D_{ho} and D_{hd} phases has been addressed in several theoretical investigations of HHTT.^{21–26}

In a previous article we have shown, using various solid-state NMR techniques,²⁷ that there is no fast (on the NMR time scale) molecular motion in the H phase. Such motion is considered to be characteristic for a liquid crystalline phase.

The motivation for the present study was to investigate the molecular background to the thermal history effects, which

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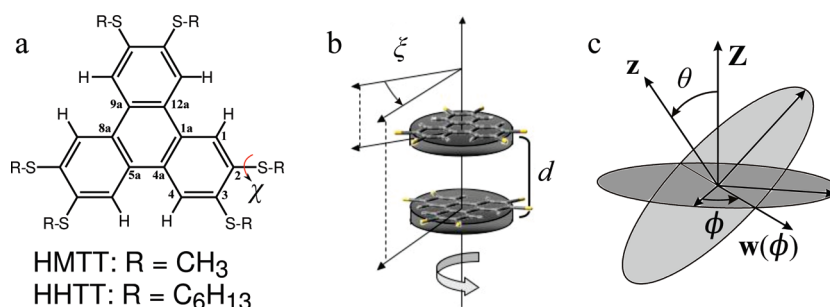


Figure 1. Schematic of hexaalkylthiotriphenylenes (a), molecular arrangement of the dimer (b), and the frames relevant for the motional averaging of the chemical shift tensor (c).

Table 1. Conformational Dependence (Torsion Angle χ Defined in Figure 1a) of the Relative Energy (in kJ mol^{−1}) and Chemical Shift Tensors (in ppm) Calculated for the Aromatic Carbons in the HMTT Molecule

torsion angle, χ (deg)	relative energy	C1a			C1			C2		
		$\delta_{xx}^{\text{calc}}$	$\delta_{yy}^{\text{calc}}$	$\delta_{zz}^{\text{calc}}$	$\delta_{xx}^{\text{calc}}$	$\delta_{yy}^{\text{calc}}$	$\delta_{zz}^{\text{calc}}$	$\delta_{xx}^{\text{calc}}$	$\delta_{yy}^{\text{calc}}$	$\delta_{zz}^{\text{calc}}$
0	0	203.45	165.19	5.01	206.86	124.82	8.07	218.24	160.89	38.68
45	58.2	204.36	165.98	5.27	222.37	136.95	17.47	233.73	163.37	42.65
90	28.6	211.47	170.74	5.99	231.49	138.44	33.57	233.94	162.79	43.67
110	7.0	210.58	171.07	5.62	228.84	134.39	34.03	232.70	161.33	44.09

resulted in different chemical shift tensors in H[↑] and H[↓], which denote the helical phase formed upon heating the solid phase and cooling the columnar liquid crystalline phase, respectively. In the helical (H[↑]) phase the core, similarly to the solid phase, is essentially rigid. The difference between the solid and H[↑] phases is mainly manifested in an increased mobility of the aliphatic chains observed in the latter phase. In the H[↓] phase, on the other hand, there exists an overall dynamical process that averages significantly the aromatic carbon-13 CS tensors.

METHODS

The computational study was carried out using Gaussian 03 software²⁸ employing Gauss View 3.0 for building of the molecules. The DFT methods were used following the recommendations for chemical shielding calculations on large molecules.²⁹ It is well-known that the calculated shielding tensors are very sensitive to the basis set size effects and to the molecular geometry. To account for these requirements, we decided to retain the 6-31+G(d) basis set throughout our geometry optimizations at the B3LYP³⁰ level of theory.

Following ref 31 the chemical shielding calculations were carried out using the modified Perdew–Wang³² exchange–correlation functional, denoted MPW1PW91.³³ Because the NMR chemical shielding is a very small effect, its calculation requires accurate determination of the wave functions. Most of the calculations were performed using the 6-311+G(d,p) basis set (one polarization function and one diffuse function), which increases the quality of the calculation and is the best compromise between accuracy and CPU time. It has to be noted that the approach adopted in this work was previously tested and found to be generally satisfactory for ¹³C NMR shielding calculation of several different medium–large size organic compounds.³¹ Furthermore the integrated computational and solid-state NMR approach has been recently successfully applied to the study of magnetic properties of a

ferroelectric liquid crystal.⁹ Two methods were considered: (i) the gauge including atomic orbital (GIAO)³⁴ for the numerous advantages it presents³⁵ and (ii) a method developed by Keith and Bader, based on the continuous set of gauge transformations (CSGT).³⁶

The chemical shift tensors were obtained by referring chemical shielding tensors obtained by the DFT and other ab initio methods (Hartree–Fock (HF) and Møller–Plesset second order perturbation theory (MP2)) to the absolute shielding of tetramethylsilane (TMS), 185.97, 195.10, and 197.04 ppm for DFT, HF and MP2, respectively, which was calculated at the same level of theory as the models.

RESULTS AND DISCUSSION

We start the analysis by considering the geometry optimization of the HMTT molecule, Figure 1a. The conformational variable is the torsion angle defined by C1–C2–S–C α , Figure 1a, and denoted χ . The calculated relative energies for the conformational dependence are included in Table 1. The reason for the nonsymmetric set of conformations is that the $\chi = 135^\circ$ state results in a strong steric repulsion between the chains. The conformations of the two adjacent chains were assumed to be correlated. Clearly, the torsion angle $\chi = 0^\circ$ corresponds to the lowest energy state, which is consistent with previous experimental observations using deuterium NMR³⁷ on hexaalkyloxytriphenylenes and carbon-13 investigations of THES.³⁸ In addition quantum chemical calculations using semiempirical methods predict the same conformational behavior.³⁹

The analysis of the chemical shift tensors included all phases (K, H[↑], D_{hd}, and H[↓]) and were carried out for several values of the torsion angle χ . The elements of the calculated CS tensors can be compared with the experimental counterparts on HHTT derived from the slow magic angle spinning (MAS) experiments where the 2D PASS technique was employed.^{27,40} The calculated (HMTT) and experimental (HHTT) CS tensors for aromatic

Table 2. Temperature Dependence of the Experimental²⁷ Chemical Shift Tensors^a (in ppm) Determined for the Aromatic Carbons in the HHTT Molecule in Different Phases:
 $\delta_{\text{iso}}^{\text{exp}} = (\delta_{xx} + \delta_{yy} + \delta_{zz})/3$, $\delta_{\text{aniso}}^{\text{exp}} = \delta_{zz} - \delta_{\text{iso}}$, $\eta^{\text{exp}} = (\delta_{yy} - \delta_{xx})/\delta_{\text{aniso}}$

temp (°C), phase	C1a			C1			C2		
	$\delta_{\text{iso}}^{\text{exp}}$	$\delta_{\text{aniso}}^{\text{exp}}$	η^{exp}	$\delta_{\text{iso}}^{\text{exp}}$	$\delta_{\text{aniso}}^{\text{exp}}$	η^{exp}	$\delta_{\text{iso}}^{\text{exp}}$	$\delta_{\text{aniso}}^{\text{exp}}$	η^{exp}
25, K	124.0	-123.0	0.45	114.8	-99.0	0.83	131.8	-93.0	0.72
60, K	124.3	-128.0	0.42	115.1	-100.0	0.76	132.1	-95.0	0.73
68, H [†]	123.8	-126.0	0.42	115.9	-90.0	0.85	131.9	-91.0	0.77
68, H [‡]	123.8	-41.0	0.92	115.9	42.0	0.84	131.9	39.0	0.94
76, D _{hd}	124.6	-120.0	0.00	118.3	-101.0	0.00	133.7	-100.0	0.00

^a Note that a factor of 2/3 is missing in eq 3 of ref 27.

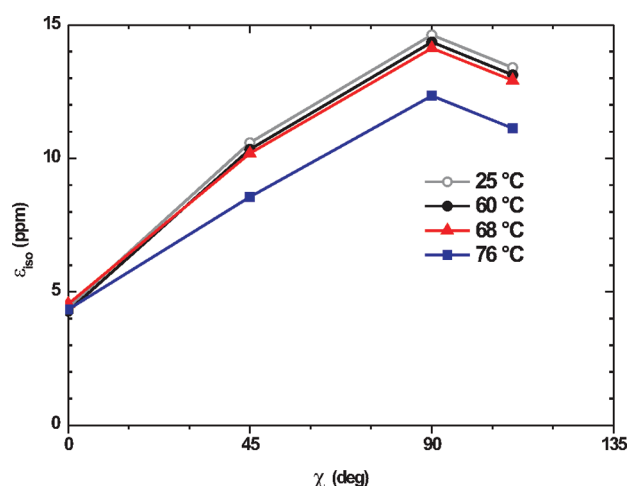


Figure 2. Conformational dependence of the error function, ϵ_{iso} , defined in eq 1, in the solid phase (K) at 25 and 60 °C (open and filled circles, respectively), helical (H[†]) at 68 °C (triangles), and columnar (D_{hd}) at 76 °C (squares). The calculated and experimental values of the chemical shift tensors used for calculations of ϵ_{iso} were taken from Tables 1 and 2, respectively.

carbons are collected in Tables 1 and 2, respectively. These CS tensors are compared by defining an error function

$$\epsilon_{\text{iso}} = \left(\frac{1}{N} \sum_{j=1}^N (\delta_{\text{iso}}^{j,\text{exp}} - \delta_{\text{iso}}^{j,\text{calc}})^2 \right)^{1/2} \quad (1)$$

where N is the number of carbon atoms and $\delta_{\text{iso}}^{j,\text{exp}}$ and $\delta_{\text{iso}}^{j,\text{calc}}$ are the experimental and calculated isotropic chemical shifts, respectively, with the latter defined by $\delta_{\text{iso}}^j = (1/3)(\delta_{xx}^j + \delta_{yy}^j + \delta_{zz}^j)$ where $\delta_{\alpha\alpha}^j$ are the principal elements of the CS tensor for the j th carbon-13 nucleus.

The ϵ_{iso} dependence on the torsion angle χ , defined in Figure 1a, was evaluated for all three aromatic carbons in the triphenylene fragment at 25, 60, 68, and 76 °C. The ϵ_{iso} displayed in Figure 2 clearly indicates the best agreement, smallest ϵ_{iso} value, for the $\chi = 0^\circ$ conformation. This observation is consistent with the energy values indicated above and with previously reported experimental results.^{37,38}

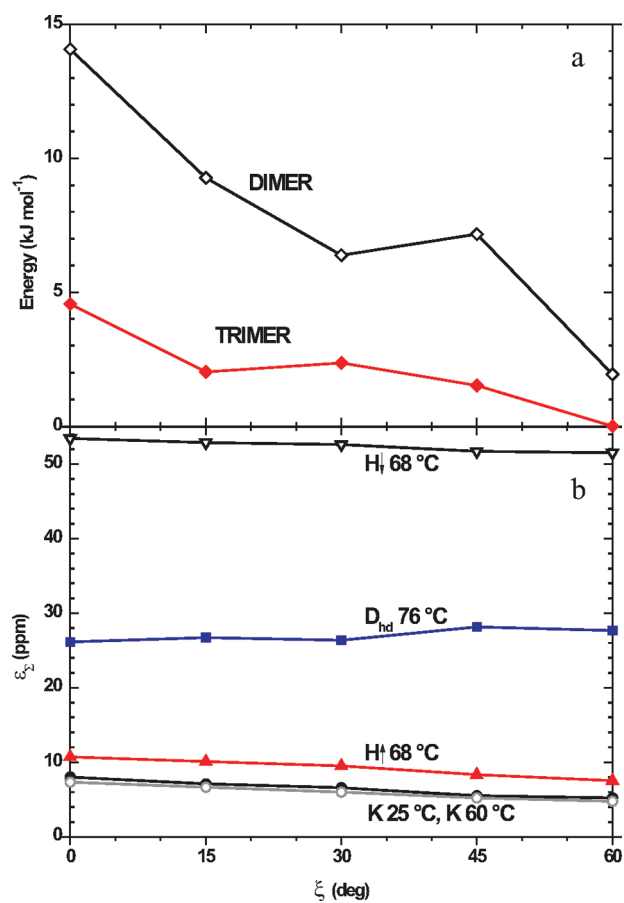


Figure 3. Dependence on the relative molecular orientation (defined by the twist angle ξ , Figure 1b) of (a) normalized energy (kJ mol^{-1}) calculated using the DFT method for dimer and trimer configurations of HMTT and (b) the error function ϵ_{Σ} between the experimental (Table 2) and calculated for the trimer configuration (Table 3) chemical shift tensors in the solid phase (K) at 25 °C, and 60 °C (open and filled circles, respectively), helical (H[†] and H[‡]) phases at 68 °C (open and filled triangles, respectively) and the columnar (D_{hd}) phase at 76 °C (squares).

In order to model the relative arrangement of the molecules in the different phases, dimers and trimers with different twist angles ξ , defined in Figure 1b, were constructed. The normalized energy profiles for this angle are displayed in Figure 3a. Clearly, the configuration corresponding to $\xi = 60^\circ$ is the energy minimum for both dimer and trimer configurations. The same relative orientation of the triphenylene cores was derived from quantum chemical calculations^{39,41} and ascribed to the p orbital interactions. Similar orientation of adjacent molecules was observed in an X-ray investigation of the solid phase of HHTT.¹⁹ The trimer arrangement is a better representation of the columnar phase, which indeed is manifested in a lower energy.

We now investigate the effect of the relative orientations of adjacent molecules on the chemical shifts of the aromatic carbons. These tensors were calculated for both dimer and trimer configurations. For the dimer an average value of the two molecules was considered, whereas the trimer CS tensors for the central molecule are reported. The principal components of the CS tensors are averaged over the six equivalent nuclei for carbons C1a, C1 and C2 and are collected in Table 3. The difference between dimer and trimer configurations is small, and in the following we will only consider the CS tensors derived

Table 3. Twist Angle (ξ , Defined in Figure 1b) Dependence of the Chemical Shift Tensors (in ppm) Calculated Using the DFT Method for the Aromatic Carbons in the HMTT Molecule for Dimer and Trimer Configurations

twist angle, ξ (deg)	C1a			C1			C2		
	$\delta_{xx}^{\text{calc}}$	$\delta_{yy}^{\text{calc}}$	$\delta_{zz}^{\text{calc}}$	$\delta_{xx}^{\text{calc}}$	$\delta_{yy}^{\text{calc}}$	$\delta_{zz}^{\text{calc}}$	$\delta_{xx}^{\text{calc}}$	$\delta_{yy}^{\text{calc}}$	$\delta_{zz}^{\text{calc}}$
Dimer									
0	205.97	167.36	−0.73	210.20	127.98	5.32	217.64	160.05	31.50
15	205.67	167.30	0.23	210.53	127.39	6.79	216.98	155.26	33.36
30	205.69	167.17	0.04	210.94	129.22	6.64	214.55	155.05	30.90
45	208.03	166.78	−0.10	211.03	127.92	9.65	214.72	150.18	33.50
60	209.16	163.54	1.40	208.39	127.39	8.03	214.50	151.66	33.44
Trimer									
0	206.09	167.38	−0.57	209.96	129.17	6.46	219.34	157.39	30.07
15	206.44	167.20	0.13	211.42	128.05	5.83	217.63	154.31	32.77
30	207.21	166.92	−0.32	209.79	128.31	6.63	215.90	153.21	31.70
45	207.36	164.95	1.79	209.35	125.92	9.43	219.97	146.87	31.55
60	206.08	164.33	−2.30	208.62	124.78	12.20	219.81	150.36	34.53

from the trimer configuration. In the crystalline phase (monoclinic structure) the distance between the aromatic core planes is $d = 3.938 \text{ \AA}$ ^{17,19} whereas three column superlattice structure was observed in the helical phase, probably arising from the frustration imposed by molecular interdigitation in triangular symmetry. The intracolumnar molecular spacing $d = 3.638 \text{ \AA}$ was determined in the helical phase.^{17,19} In our preliminary tests the CS tensors were only weakly dependent on the intermolecular distance and therefore we used a constant separation $d = 3.9 \text{ \AA}$ for the dimers and trimers.

In analogy with eq 1 we define an error function $\varepsilon_{\Sigma} = [(3N)^{-1} \sum_{\alpha \in \{x,y,z\}} \sum_j^N (\delta_{\alpha\alpha}^{j,\text{exp}} - \delta_{\alpha\alpha}^{j,\text{calc}})^2]^{1/2}$ which is determined for several relative orientations of adjacent molecules in the trimer configuration and displayed in Figure 3b. In the columnar phase the molecules rotate rapidly around the columnar axis, and therefore the concept of a static twist angle is not relevant. In the crystal (25 and 60 °C) and helical, H \uparrow (68 °C), phases, the ε_{Σ} values indicate that the twist angle ξ of 45 or 60° constitutes a reasonable model for the molecular arrangements of the HHTT. In fact, these results are in reasonable agreement with previous X-ray diffraction data reported for HHTT where the relative molecular orientations corresponding to $\xi = 60^\circ$ and $\xi = 45.5^\circ$ were determined in the solid and helical phases, respectively.^{17,19} In analogy with the discussion on relative stability (see above) we assume that the p orbital interaction^{39,41} is the main effect of the variation of the chemical shift with the relative molecular orientations of the triphenylene cores. The ε_{Σ} values in the H \downarrow phase are very large compared to the solid and H \uparrow phases. Obviously, the assumption of static molecular arrangements is not relevant in the H \downarrow phase and we need to consider a motional model that would correctly explain the averaging of the CS tensor in this phase.

We start by describing the averaging of the columnar liquid crystal D_{hd} which is experimentally obtained by heating the H \uparrow phase. In contrast to the two phases (solid and H \uparrow) considered before, the columnar phase is characterized by fast molecular reorientation of the aromatic core around the columnar axis. Thus, this motion results in an averaging of the two in plane components (a uniaxial tensor) of the aromatic carbon-13 CS tensors, while the last component is essentially unaffected.

In general, a rotation with angle θ around a vector $\mathbf{v} = \{v_x, v_y, v_z\}^T$, where T indicates the transpose, may be carried out by using the three Euler angles (α, β, γ) .⁴² Here we use another approach and construct the rotational matrix $\mathbf{R}_{\mathbf{v}}(\theta)$ by employing the quaternions^{43,44}

$$q(\theta, \mathbf{v}^T) = \left\{ \cos\left(\frac{\theta}{2}\right), \sin\left(\frac{\theta}{2}\right) \mathbf{v}^T \right\} = \{q_1, q_2, q_3, q_4\} \quad (2)$$

where q_i are the quaternion elements. The rotation matrix $\mathbf{R}_{\mathbf{v}}(\theta)$ associated with the quaternion is given by⁴³

$$\mathbf{R}_{\mathbf{v}}(\theta) = \begin{bmatrix} q_1^2 + q_2^2 - q_3^2 - q_4^2 & 2(q_2q_3 - q_1q_4) & 2(q_2q_4 + q_1q_3) \\ 2(q_2q_3 + q_1q_4) & q_1^2 - q_2^2 + q_3^2 - q_4^2 & 2(q_3q_4 - q_1q_2) \\ 2(q_2q_4 - q_1q_3) & 2(q_3q_4 + q_1q_2) & q_1^2 - q_2^2 - q_3^2 + q_4^2 \end{bmatrix} \quad (3)$$

In the columnar liquid crystal two dynamic processes can be identified: a molecular rotation about the normal axis to the aromatic plane, defined by the angle ψ , and a wobbling of this axis, that is reflected in the molecular order parameter. The rotation ψ around the columnar axis $\mathbf{Z} = \{0, 0, 1\}^T$ is defined by the quaternion $q(\psi, \{0, 0, 1\})$ and the wobbling is defined by a rotation θ around all possible vectors perpendicular to the columnar axis, thus the quaternion becomes $q(\theta, \{\cos \phi, \sin \phi, 0\})$ where $0 \leq \phi < 2\pi$ represents the azimuthal angle of the rotation axis.

In the columnar phase the averaging of the chemical shift tensor, δ , is therefore given by

$$\langle \delta \rangle = \int_0^{2\pi} \int_0^\pi \int_0^{2\pi} P(\theta) \cdot \mathbf{R}_{\mathbf{p}} \cdot \delta \cdot \mathbf{R}_{\mathbf{p}}^T d\phi \sin \theta d\theta d\psi \quad (4)$$

where $P(\theta)$ is the normalized distribution function and $\mathbf{R}_{\mathbf{p}}$ is a rotation around the normal of the aromatic plane and the wobbling, thus $\mathbf{R}_{\mathbf{p}} = \mathbf{R}_{\mathbf{w}(\phi)}(\theta) \cdot \mathbf{R}_{\mathbf{Z}}(\psi)$ with the wobbling vector $\mathbf{w}(\phi) = \{\cos \phi, \sin \phi, 0\}^T$. In fact, it is tempting to call this a PIZZA-model because the motion resembles the rotation of a pizza when tossed away just before the baking!

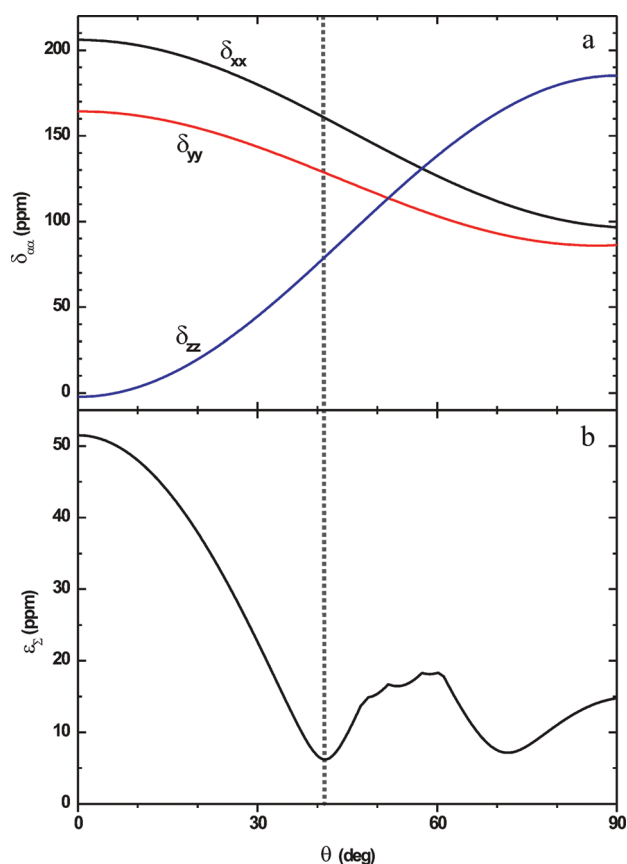


Figure 4. The wobbling angle, θ , dependence of (a) the chemical shift tensor components $\delta_{\alpha\alpha}$ where $\alpha \in \{x, y, z\}$ for the C1a carbon, and (b) the error function ε_Σ for the three aromatic carbons C1a, C1 and C2 calculated for the H \downarrow phase at 68 °C. The global minimum of the error function is indicated by the vertical dotted line.

We will now consider the helical phase H \downarrow obtained upon cooling from the columnar phase. The molecular dynamics in this phase is different from the columnar liquid crystal. In the previous investigation of HHTT²⁷ we observed a remarkable averaging of the chemical shift tensor in H \downarrow shown in Table 2. In addition, the dipolar splittings (in ^{13}C – ^1H FSLG-CP experiments^{27,45}) were absent for the C1 and C α carbons in the aromatic core and chains. These observations were attributed to dynamic processes on the time scale of 10^{-3} – 10^{-4} s which is comparable to the spinning speed in a MAS experiment and the reciprocal values of the dipolar coupling and CSA interaction. The dynamical model we suggest here for the H \downarrow phase rests therefore on the following restrictions compared to the dynamics in the columnar phase: (i) the fast molecular rotation described by the angle ψ is absent, and (ii) the distribution function, $P(\theta)$, becomes a delta function where only one wobbling angle θ is present. Thus the averaged CS tensor becomes a function of θ

$$\langle \delta \rangle(\theta) = \frac{1}{2\pi} \int_0^{2\pi} \mathbf{R}_{\mathbf{w}(\phi)}(\theta) \cdot \boldsymbol{\delta} \cdot \mathbf{R}_{\mathbf{w}(\phi)}^T(\theta) d\phi \quad (5)$$

The three diagonal components of the motionally averaged CS tensor $\langle \delta \rangle$ depend on the wobbling angle θ , and this dependence is displayed in Figure 4a. Clearly, the values for the static ($\theta = 0$) CS tensor for C1a correspond to the calculated values $\delta_{xx} = 206.08$, $\delta_{yy} = 164.33$ and $\delta_{zz} = -2.30$ ppm, obtained for the lowest energy trimer configuration ($\xi = 60^\circ$), see Table 3.

The wobbling dependence for sites C1 and C2 (not shown) is similar to that for C1a. The x directions of the CS tensors are along the C1a–C12a, C1–H1, and C2–S2 bonds for the C1a, C1 and C2 carbons, respectively. The z direction for all carbons is the normal to the aromatic plane. Furthermore, we follow the convention where $\delta_{xx} \geq \delta_{yy} \geq \delta_{zz}$. The motional averaging changes the values and leads to an increased asymmetry of the CS tensor.

In Figure 4b the error function, ε_Σ , for all carbons and tensor components between experimental (Table 2) and motionally averaged tensors (Figure 4a) is displayed. All three carbon atoms in the aromatic core are averaged by the same dynamic process, and therefore the total error ε_Σ is considered. The global minimum is indicated by the vertical dashed line in Figure 4, thus the experimental results reported in ref 27 are consistent with the wobbling model using a single wobbling angle of around 40° . We note that the second (local) minimum also corresponds to a CS tensor with high asymmetry where the wobbling angle is about 70° .

CONCLUSIONS

The present study is motivated by our experimental NMR investigations²⁷ of the mesomorphism in columnar phases of 2,3,6,7,10,11-hexahexylthiotriphenylene (HHTT). In particular, we observed significant differences between the spectral characteristics in the helical phase obtained by heating the solid sample (denoted H \uparrow) and cooling the columnar liquid crystal (H \downarrow). In an attempt to understand the experimental observations we here perform quantum chemical DFT calculations on a model molecule: hexamethylthiotriphenylene (HMTT). We have investigated the conformational behavior of the aliphatic chains in a single molecule and the relative orientations of dimer and trimer configurations. The energy profiles indicated that the chains prefer the orientation in the plane of the aromatic core, which is in good agreement with previously reported studies on similar compounds where NMR experiments and molecular modeling was employed.^{37–39} The relative orientations of the aromatic cores indicated a twist of the order of 45 to 60° , which is also in agreement with earlier X-ray studies.^{16,17} The main focus of the DFT study was the calculation of the chemical shift (CS) tensors of the aromatic carbons. In fact, the chemical shifts turned out to be sensitive to both conformational changes and the configurations of the molecules (the twist). Here again we obtained the best agreement with the experiments for the in-plane conformation and for the relative twist angle of 60° . Finally, in order to explain the remarkable averaging of the chemical shift tensor in the H \downarrow phase we invoked a dynamic (PIZZA) model where the HHTT molecules wobble slowly in the columns. This motion can be characterized by using the wobbling angle θ and the azimuthal angle ϕ , defined in Figure 1c. The best agreement between the calculated averaged tensors and the experimental results in the H \downarrow phase was found for $\theta = 40^\circ$. Finally, we can comment on the rates of the wobbling motion in the H \downarrow phase. Based on the dipolar spectra obtained from the ^{13}C – ^1H FSLG-CP experiments²⁷ we concluded that the time scale of the wobbling process is on the order of 10^{-3} – 10^{-4} s, which in principle can be investigated using 2D MAS exchange experiment.⁴⁶

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Notes

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