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Proton-decoupled deuterium NMR study of an asymmetric liquid crystal dimer having two nematic phases

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Proton-decoupled deuterium NMR spectra were obtained for an asymmetric liquid crystal dimer 1-(4-cyanobiphenyl-4′-yloxy)-6-(4-cyanobiphenyl-4′-yl)hexane (CB6OCB) containing a single -CD$_2$- group. The sample has two nematic liquid crystal phases: a twist-bend nematic, N_{TB}, at the lowest temperature followed by a uniaxial nematic, N_U, on increasing the temperature. Proton decoupling reduces the linewidths of the peaks in the deuterium spectrum from kHz to ∼100 Hz, enabling quadrupolar splittings, $\Delta\nu$, to be obtained with enhanced precision as well as the dipolar coupling between deuterium nuclei within the CD$_2$ group, hence enhancing the information content.

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I. INTRODUCTION

Deuterium NMR spectroscopy has often been used to study the structure, orientational order, and conformational distributions of liquid crystal molecules [1]. The natural abundance of deuterium is only 0.016% and the NMR receptivity relative to protons is 1.56×10^{-6} so that studies of liquid crystals by ^{2}H NMR typically use samples in which deuterium has been introduced by chemical synthesis. The asymmetric liquid crystal dimer 1-(4-cyanobiphenyl-4′-yloxy)-6-(4-cyanobiphenyl-4′-yl)hexane (CB6OCB), whose molecular structure is shown in Fig. 1, is used here as the isotopomer CB6OCB-d_2 with deuterium incorporated at positions 41 and 42 to illustrate the advantages of applying proton decoupling when recording deuterium spectra.

The liquid crystal CB6OCB is unusual in having two nematic phases, N_U and N_{TB}, the latter being enantiomorphic even though the constituent molecules are achiral. The phase sequence is [2]

$$\begin{aligned} \text{isotropic}(I) &\rightarrow 153\,^\circ\text{C nematic}\,(N_U)\\ &\rightarrow 109\,^\circ\text{C twist-bend nematic}\,(N_{TB})\\ &\rightarrow 100\,^\circ\text{C crystal}\,(Cr)\end{aligned}$$

The isotopomer CB6OCB-d_2 has been studied previously [2] by ^{2}H NMR without proton decoupling with the aim of determining how the molecular orientational order varies with temperature and phase. The ^{2}H NMR spectrum of CB6OCB-d_2 in the N_U phase is a doublet with a splitting $\Delta\nu(T)$:

$$\Delta\nu_i(T) = 3q_i(T)/2, \tag{1}$$

where $q_i(T)$ is the component, along the liquid crystal director, of the interaction of the deuterium electric quadrupole moment with the electric field gradient at the nucleus at site i in the molecule. The two components of the doublet are broadened by residual dipolar interactions, $D_{i,H}$, with all the protons in the molecule. On entering the N_{TB} phase the ^{2}H NMR spectrum becomes a pair of doublets with quadrupolar splittings $\Delta\nu_1(T)$ and $\Delta\nu_2(T)$, which is consistent with the loss of symmetry equivalence of the two deuterons because of the chirality of this phase. The mean of the two splittings, $\Delta\nu_{\text{mean}}(T)$ decreases as $(T_{N_{TB}N_U} - T)$ increases, while their difference, $\Delta[\Delta\nu_i(T)]$, increases. Both these observations are consistent with a model for the spatial distribution of local directors, $\boldsymbol{n}$, in the N_{TB} phase proposed by Dozov [3] as being helical as shown in Fig. 2.

The diffusion of molecules along the helix direction is sufficiently rapid to produce averaged NMR interactions and

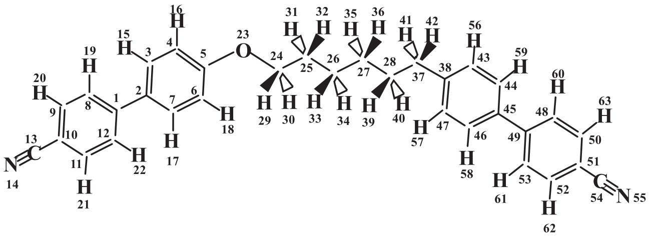

FIG. 1. Structure and atomic labeling of the asymmetric liquid crystal dimer CB6OCB.

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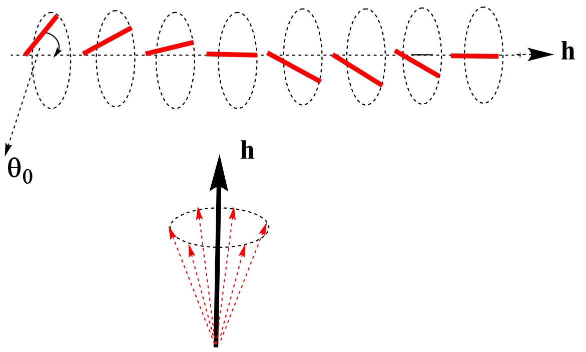

FIG. 2. Helical twist of local directors, **n** (red) about the helix axis **h** in N_{TB} phase. Local directors lie on the surface of a cone and make a constant angle, θ_0,with **h**.

the helix axis becomes the effective director for the N_{TB} phase and has uniaxial symmetry [4]. The axis **h** is aligned along the direction of the applied magnetic field throughout the N_{TB} phase. The Dozov model predicts that the cone angle, θ_0, increases on reducing the temperature in the N_{TB} phase producing a reduction in $\Delta\nu_{\text{mean}}(T)$ by a factor $R[\Delta(T)]$ given by

$$R[\Delta(T)] = \{3\cos^2\theta_0[\Delta(T)] - 1\}/2, \tag{2}$$

which increases as the cone angle, θ_0, increases on reducing the temperature in the N_{TB} phase.

The difference $\Delta[\Delta\nu_i(T)]$ is predicted by the Dozov model to be zero at $T_{N_{TB}N_U}$ and to increase as $(T_{N_{TB}N_U} - T)$ increases, as observed.

The temperature profile observed for $\Delta\nu(T)$ in the N_U phase of CB6OCB-d_2 has a shallow maximum value, T_{max}, approximately 10 °C before $T_{N_{TB}N_U}$ is reached and then decreases until the transition to the chiral phase occurs. This unusual temperature profile has also been found [5] for the order parameter, S_{zz}, for the z axis of the biphenyl-CH$_2$ group of CB6OCB (see Fig. 3) from measurements of the ^{13}C chemical-shift anisotropy of C45 (see Fig. 1).

This behavior has been interpreted [5] as indicating that there is a tilting of the director away from the direction of the applied magnetic field in the N_U phase by an angle, θ_{tilt}, which is equal to the cone angle, θ_0, at $T_{N_{TB}N_U}$ and decreases with increasing temperature in the N_U phase. One explanation for finite values of θ_{tilt} above $T_{N_{TB}N_U}$ is that the phase sequence in CB6OCB is

$$I \rightarrow N_U \rightarrow N_{SB} \rightarrow N_{TB} \rightarrow \text{crys},$$

where N_{SB} is a splay-bend nematic phase; another attributes finite values of θ_{tilt} above $T_{N_{TB}N_U}$ as being a pretransitional effect [5].

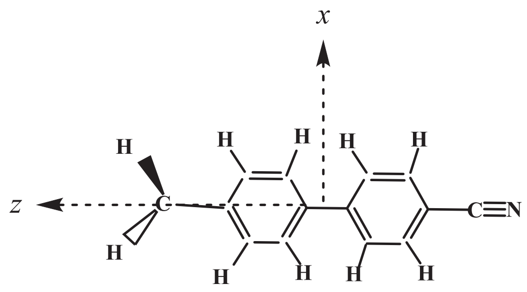

FIG. 3. Location of axes (xyz) in the biphenyl-CH$_2$ fragment of CB6OCB. Axis y is normal to xz plane.

We show here how proton decoupling on a sample of CB6OCB-d_2 dramatically reduces the widths of the peaks in the deuterium spectrum, increasing the precision with which $\Delta\nu$ is obtained and enables the residual dipolar coupling, D, between the two deuterium nuclei to be measured. The extra information obtained allows a more critical examination to be made of the models used to interpret the behavior of molecules in liquid crystals having both N_U and N_{TB} phases.

The sample of CB6OCB-d_2 that was investigated in these studies was prepared in the Max-Planck-Institut für Medizinische Forschung, Heidelberg, Germany using the synthetic procedure described in the Supplemental Material associated with Ref. [2].

The layout of our paper is as follows.

Section II describes how the ^{2}H–{^{1}H} spectra were obtained while maintaining a constant temperature of the sample. Section III shows the effect proton decoupling has on deuterium spectra obtained when the sample is in the N_U phase, and Sec. IV gives simulations of the spectra expected from a pair of symmetry-equivalent ^{2}H nuclei together with expressions relating the line positions with values of q and D. Section V shows ^{2}H–{^{1}H} spectra obtained when the sample is in the N_{TB} and these are compared in Sec. VI with simulated spectra for two nonequivalent ^{2}H nuclei, again with expressions relating the line positions with two values, q_1 and q_2, of the quadrupolar interaction and a single value of D. Section VII shows the experimentally obtained temperature dependences of the quadrupolar and dipolar interactions throughout both N_U and N_{NB} phases, while Sec. VIII gives values of molecular orientational order parameters derived from them. These order parameters are used in Sec. IX to derive values of θ_{tilt}, the angle the directors of these phases make with the direction of the applied magnetic field. In Sec. X the advantages of obtaining values of both the quadrupolar interaction and the dipolar coupling from proton-decoupled deuterium spectra are summarized.

II. NMR EXPERIMENTS

All of the spectra were recorded on a Bruker spectrometer at the High Field Laboratory in Lyon, France designed primarily to obtain spectra of solid samples. The field strength was 11.7 T corresponding to Larmor frequencies of 500 MHz for protons and 76.77 MHz for deuterium. The sample was contained in an "L"-shaped glass tube as described previously [5] with an internal diameter of ∼ 2 mm, and ∼ 10 mm in length. Heating was by a stream of N$_2$ gas, with the temperature monitored by a thermocouple located close to but outside of the sample and maintained constant at the set temperature by a Bruker Extreme controller. It has been established recently [6] for the liquid crystal CB9CB, which also displays both N_U and N_{TB} phases, that the transition temperatures T_{NI} and $T_{N_{TB}N_U}$ are independent of the strength of an applied magnetic field of

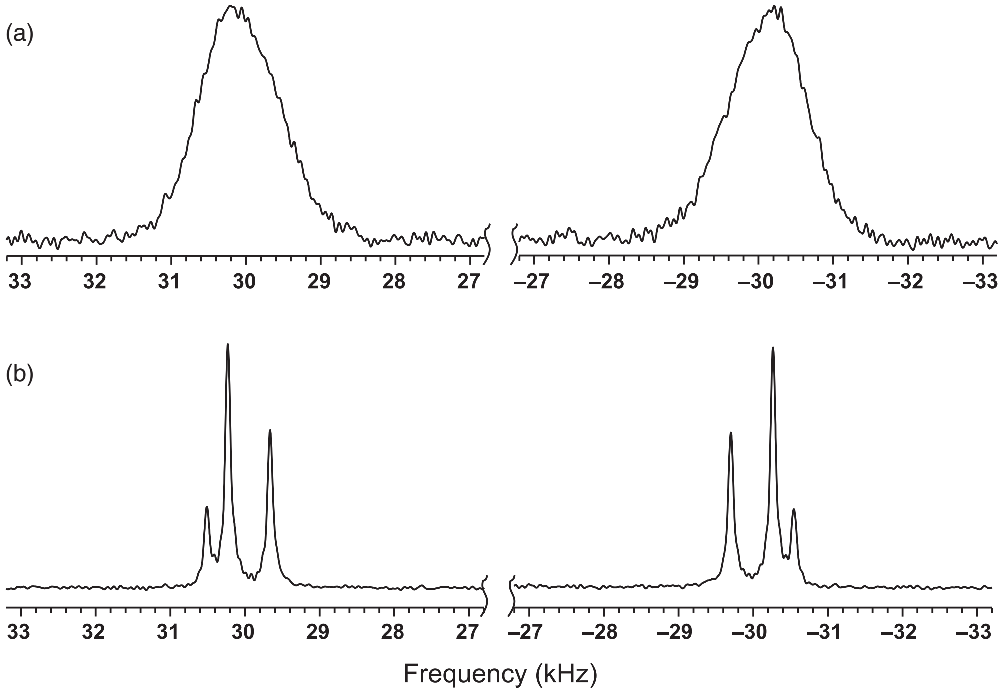

FIG. 4. The 76.77-MHz spectra of deuterium in CB6OCB-d$_2$ in N_U phase at 385 K: (a) without and (b) with proton decoupling at 25 kHz of rf power.

$\leqslant$23.5 T, so that for the present NMR experiments, recorded in a magnetic field of 11.7 T, the transition temperatures can be taken to be equal to those measured outside the magnet [2]. Consequently, the changes in the NMR spectra observed in a particular set of experiments as the temperature passes through a phase transition can be used to calibrate the difference between the temperature set by the controller and that inside the sample. Note that the sample temperature depends strongly on the flow of the N_2 gas, which must be maintained constant throughout a particular set of NMR experiments. The precision of obtaining the temperature at the sample over time and the set temperature is estimated to be <2 K.

The 1D ^{2}H spectra were obtained with a single, repeated $\pi/2$ pulse of duration 4.625 μs and either with or without ^{1}H decoupling during the acquisition time. A SPINAL-64 sequence [7] was applied for ^{1}H decoupling with 25 kHz of power for the whole acquisition time of 13.95 ms.

III. DEUTERIUM SPECTRA IN THE N_U PHASE

The ^{2}H spectra of CB6OCB-d_2 in the N_U phase consist of a pair of broad resonances separated by $\Delta\nu$. The peaks are broad and featureless as a result of dipolar coupling with all the protons in the molecule and so the fine structure from dipolar coupling within the CD$_2$ group is obscured. The dipolar couplings to the protons can be removed by irradiating the protons while acquiring the deuterium spectrum, as illustrated in Fig. 4. There is a significant reduction in the widths of the resolved lines in Fig. 4 from ∼ 1200 to ∼ 100 Hz.

The proton-decoupled deuterium spectra in the N_U phase are for a pair of magnetically equivalent spin-1 nuclei for which the quadrupolar splitting, $\Delta\nu$, is much smaller than the nuclear Zeeman interaction. The form taken by the spectra depends on $\Delta\nu$ and the residual dipolar coupling, D, between the two ^{2}H nuclei. In principle the spectra also depend on the scalar coupling constant, $J_{^2H^2H}$, between the two ^{2}H nuclei, but in practice this has a magnitude of $(\gamma_{^2H}/\gamma_{^1H})^2 J_{HH}$ which is $\sim$ 0.2 Hz and can be neglected.

IV. SIMULATED DEUTERIUM SPECTRA OF A CD$_2$ GROUP IN AN N_U PHASE

The ^{2}H–{^{1}H} spectrum of a CD$_2$ group in an aligned N_U phase consists of six peaks whose relative intensities depend on the relative signs of the dipolar coupling, D, and q, the partially averaged component of the quadrupolar tensor component along the director. Two simulated spectra are shown in Fig. 5.

The peaks in Fig. 5 are related to q and D by

$$a-b=|2D|;\ \ b-c=|4D|;\ \ b=|3q/4|+|D|;$$
$$d-e=|4D|;\ \ e=-|3q/4|-|D|;\ \ e-f=|2D|.$$

An experimental spectrum gives the relative, but not absolute, signs of q and D, and their magnitudes. Comparison of the simulated spectra with those observed for CB6OCB-d_2 shows that the signs of q and D are opposite.

V. DEUTERIUM SPECTRA IN THE N_{TB} PHASE

The N_{TB} phase is enantiomorphic and as a consequence the two deuterium nuclei in the CD$_2$ group become nonequivalent and there are two quadrupolar splittings in the proton decoupled deuterium spectra, as illustrated in Fig. 6.

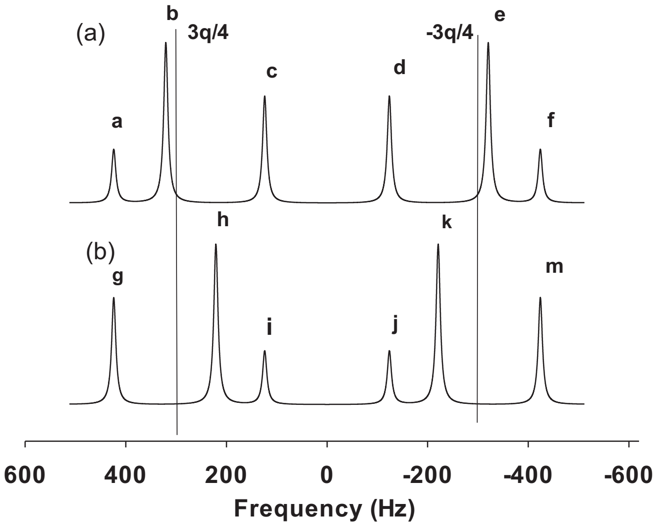

FIG. 5. Simulated ^{2}H spectra of two equivalent deuterium nuclei with q, component of quadrupolar coupling tensor along the liquid crystal director, $\boldsymbol{n}$. (a) opposite in sign to D, the dipolar coupling, and (b) the same sign. Simulations were made with a program written in SpinDynamica [8].

VI. SIMULATED DEUTERIUM SPECTRA OF A CD$_2$ GROUP IN THE N_{TB} PHASE

The lines in each half of the spectrum of the sample in the N_{TB} phase are predicted to have separations and intensities which depend on two different values of q_1 and q_2 and a single value of D, as illustrated in Fig. 7. The values of q_1, q_2, and D in these simulations have magnitudes which are close to the peak separations for the spectra recorded at 381 and 376 K. The computer program used to produce a simulated spectrum first calculates a free-induction decay, (fid), with a single-exponential form characterized by a decay rate, which is chosen to produce peaks each with a linewidth of 100 Hz. Fourier transforming the fid produces the simulated spectrum.

The peak positions in Fig. 7 are related to q_1, q_2, and D by

$$a = |{}^3\!/\!_4 q_1 + 2D|;\; b = |{}^3\!/\!_4 q_1|;\; c = |{}^3\!/\!_4 q_1 - 2D|;$$
$$d = |{}^3\!/\!_4 q_2 + 2D|;\; e = |{}^3\!/\!_4 q_2|;\; f = |{}^3\!/\!_4 q_2 - 2D|.$$

The relative intensities of the peaks in Fig. 7 are seen to depend on the relative signs of D with respect to q_1 and q_2. Comparing the simulated spectra with those obtained from the experiments on CB6OCB-d_2 in the N_{TB} phase shows that D is of opposite sign to both q_1 and q_2. The structure of the CB6OCB-CH$_2$ fragment shown in Fig. 3 suggests that D is positive and q_1 and q_2 are negative.

VII. TEMPERATURE DEPENDENCE OF q AND D

A sample of CB6OCB-d_2 was introduced into the probe of the NMR spectrometer cooled from the isotropic into the N_U phase and ^{2}H–{^{1}H} spectra recorded manually at intervals of 2 K until 389 K. In a separate experiment the same sample of CB6OCB-d_2 was cooled from the isotropic into the N_U phase and the temperature lowered slowly until 386 K, when the sample is in the N_U phase and ^{2}H–{^{1}H} spectra recorded at intervals of 1 K until 376 K. This second set of spectra allowed changes in the vicinity of $T_{N_{TB}N_U}$ to be monitored with greater precision.

The values obtained for the quadrupolar interactions and the dipolar coupling are given in Tables I and II and shown in Figs. 8 and 9.

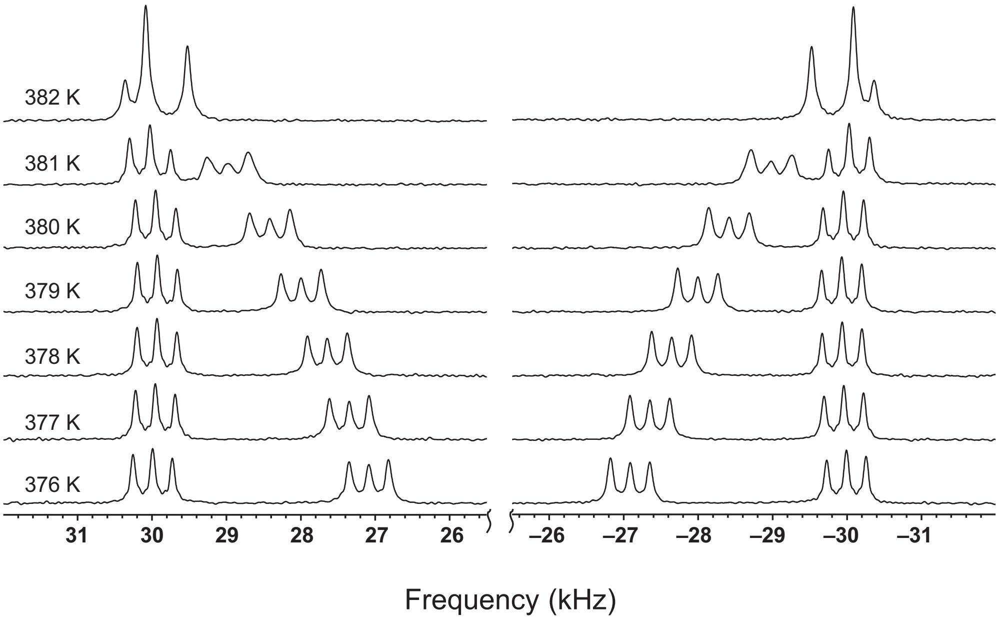

FIG. 6. The 76.77-MHz ^{2}H–{^{1}H} spectra of CB6OCB-d_2 recorded at intervals of 1 K starting at 382 K when the sample is in the N_U phase followed by spectra in N_{TB} phase. The ^{2}H $\pi/2$ pulse was 4.625 µs. ^{1}H decoupling at 25 kHz of rf power, during the whole acquisition time of 13.95 ms. Spectra were acquired with 1585 complex points and are processed with 16 384 complex points and an exponential window function with 5 Hz of line broadening.

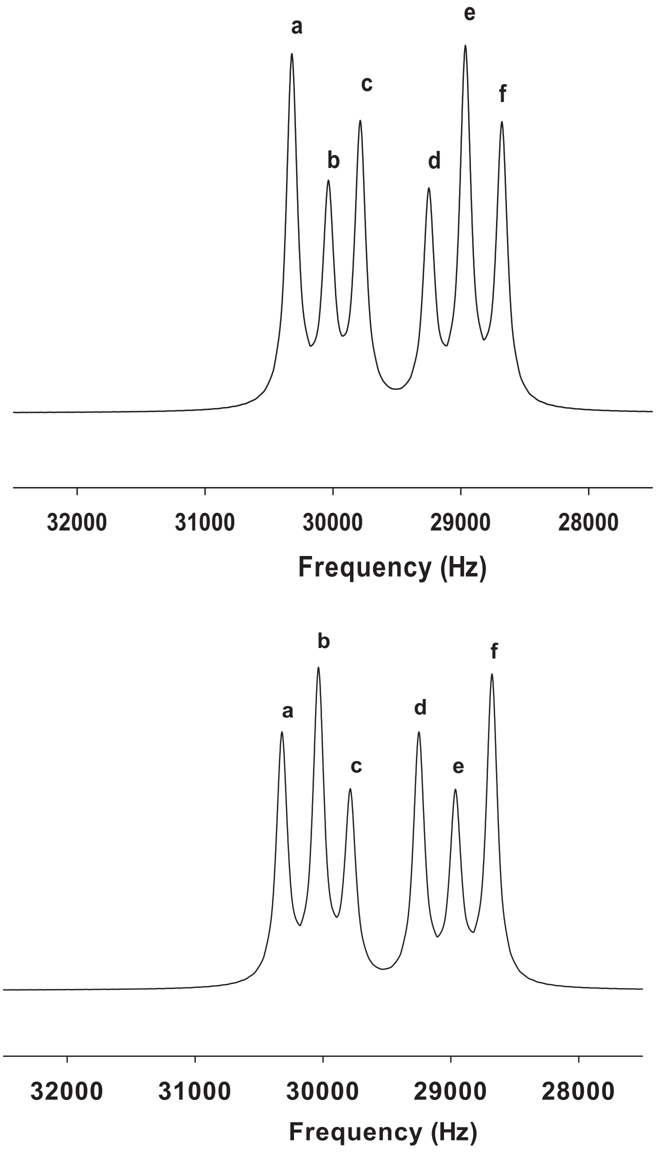

FIG. 7. Simulation of ^{2}H spectra recorded at 381 K in N_{TB} phase. Spectra are symmetric about their center and only the high-frequency side of the spectrum is shown. Nonequivalent deuterium nuclei have $q_1 = -40\,040$ Hz, $q_2 = -38\,641$ Hz, and $D = -137$ Hz (top) and $+137$ Hz (bottom).

Note that the data for the two experiments do not match exactly at 389 K. The small difference is a result of removing the sample from the spectrometer after recording the first set of spectra and reinserting it to record the second set and reflects the precision with which temperature profiles of q and D can be obtained with the NMR spectrometer used in these experiments.

VIII. MOLECULAR ORIENTATIONAL ORDER PARAMETERS S_{CD} AND S_{DD}

The component, q, along the director is related to the C-D bond-order parameters $S_{\mathrm{CD1}} = S_{\mathrm{CD2}} = S_{\mathrm{CD}}$ by

$$q = S_{\mathrm{CD}}\,[q_{\mathrm{CD}} + \eta(S_{\mathrm{BB}} - S_{\mathrm{CC}})/3], \tag{3}$$

TABLE I. Quadrupolar, q, and dipolar, D, couplings obtained for CB6OCB-d_2 in N_U phase.

T/K[a]	q/Hz[b]	D/Hz[c]
426.0	−29 914	97
423.7	−31 655	112
421.4	−32 990	116
419.1	−34 056	121
416.7	−34 952	123
414.4	−35 754	126
412.1	−36 456	128
409.8	−37 068	131
407.5	−37 621	133
405.2	−38 126	134
402.8	−38 587	136
400.5	−38 980	137
398.2	−39 334	139
395.9	−39 636	139
393.6	−39 887	140
391.3	−40 082	141
388.9	−40 201	141
386.6	−40 237	140
385.5	−40 218	140
384.3	−40 174	141
383.2	−40 104	140
382.0	−40 020	140

[a] Calibrated by locating values of T_{NI} and $T_{N_{TB}N_U}$ from spectra and linearly interpolating between them.
[b] q has a precision of 1.0 Hz.
[c] D has a precision of 0.4 Hz.

where axes (A, B, C) have A along a C–D bond and B and C perpendicular to A and to each other.

The asymmetry parameter η is

$$\eta = (q_{\mathrm{BB}} - q_{\mathrm{CC}})/q_{\mathrm{AA}}. \tag{4}$$

The value of q_{CD} has been calculated for 5CB-d_2 to be 168.8 kHz with an asymmetry parameter of 0.027 [9], so that, to a good approximation,

$$q = S_{\mathrm{CD}} q_{\mathrm{CD}}. \tag{5}$$

For the pair of ^{2}H nuclei in CB6OCB-d_2 the value of the partially averaged dipolar coupling D is given by

$$D = -2K_{\mathrm{DD}} S_{\mathrm{DD}}/r^3, \tag{6}$$

TABLE II. Quadrupolar, q_1 and q_2, and dipolar, D, couplings obtained for CB6OCB-d_2 in N_{TB} phase.

T/K[a]	q_1/Hz[b]	q_2/Hz[b]	D/Hz[c]
381	−40 040	−38 641	138
380	−39 938	−37 893	136
379	−39 905	−37 333	135
378	−39 913	−36 931	134
377	−39 942	−36 468	132
376	−39 987	−36 114	132

[a] Calibrated by locating value of $T_{N_{TB}N_U}$ from spectra.
[b] q_1 and q_2 have a precision of 1.0 Hz.
[c] D has a precision of 0.8 Hz.

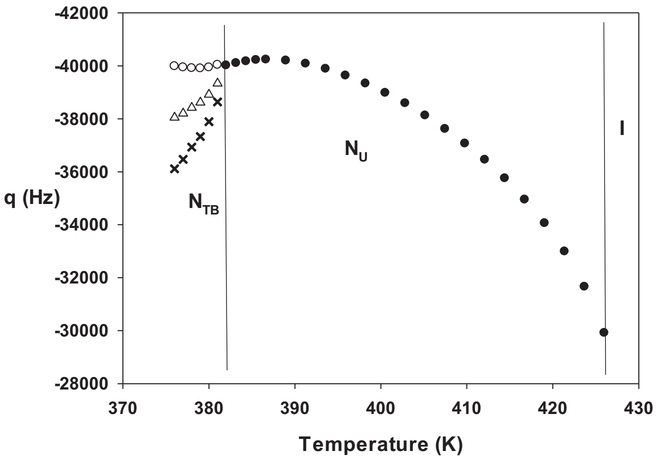

FIG. 8. Temperature variation of q in N_U (●) phase, q_1 (○) and q_2 (×), and their mean (Δ) in N_{TB} phase.

where r is the magnitude of the vector $\boldsymbol{r}$ connecting the two ^{2}H nuclei and K_{DD} is 1414.6 Hz. A density-functional theory (DFT) calculation on CB6OCB in the minimum energy conformation [5] gives $r = 1.755$ Å, for which

$$S_{\mathrm{DD}} = -0.001\,91\,D, \tag{7}$$

with the units of D being in hertz.

Figure 10 shows the temperature dependences of S_{CD} and of S_{DD}.

Both S_{CD}(mean) and S_{DD} change discontinuously at $T_{N_{TB}N_U}$ by ~1.7% compared with the discontinuous change at this transition of 1.4% in S_{zz} obtained previously for CB6OCB from ^{13}C shift anisotropies [5]. The similar changes in the three order parameters are consistent with the structure of the biphenyl–C fragment being unchanged at the transition from the N_U to N_{TB} phase.

Beguin *et al.* [10] proposed that the changes at $T_{N_{TB}N_U}$ in the two order parameters for the C–D bonds and S_{DD} can be understood by transforming to axes fixed on the CD$_2$ groups shown in Fig. 11.

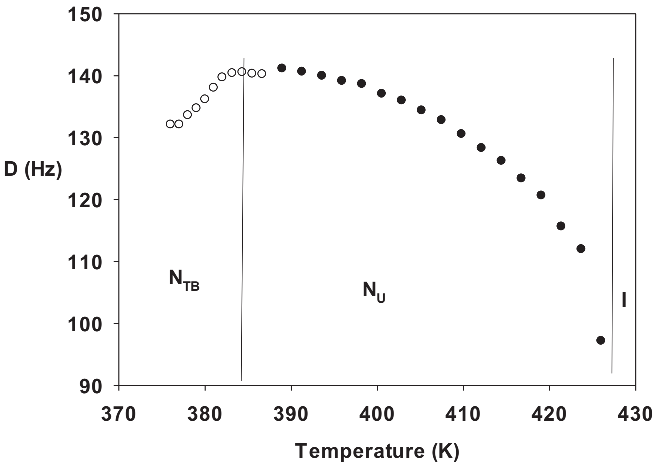

FIG. 9. Temperature variation of D in N_U and N_{TB} phases for CB6OCB-d_2. Spectra were recorded manually in two different experiments, the first from the isotropic phase to 389 K in 2 K steps and the second from 386 K in 1 K steps.

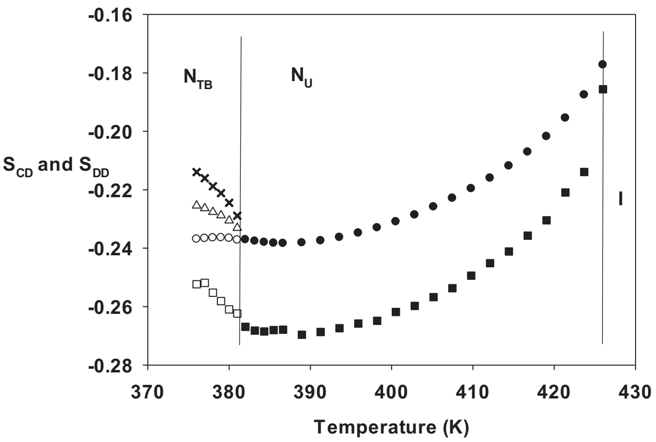

FIG. 10. Dependence, on temperature for CB6OCB-d_2, of order parameters S_{CD} (●) in N_U phase. For N_{TB} phase the two values of q_1 and q_2 yield two values, S_{CD1} (○) and S_{CD2}(×), and their mean, S_{CD}(mean) (Δ). In N_U phase, ^{2}H nuclei in CD$_2$ group are symmetrically equivalent and there is just one measured value of D at each temperature and hence just one value (■) for S_{DD} order parameter. In N_{TB} phase, two values for D at each temperature could be measured, but these are equal within experimental error and just their average value is shown for S_{DD} (□).

The C–D bond directions are at angles $\pm\phi$ with axis a so that

$$S_{\mathrm{CD1}} = S_{aa}\cos^2\phi + S_{cc}\sin^2\phi - S_{ac}\sin 2\phi, \tag{8}$$

and

$$S_{\mathrm{CD2}} = S_{aa}\cos^2\phi + S_{cc}\sin^2\phi + S_{ac}\sin 2\phi, \tag{9}$$

so that,

$$S_{\mathrm{CD}}(\text{mean}) = \tfrac{1}{2}(S_{\mathrm{CD1}} + S_{\mathrm{CD2}}) = S_{aa}\cos^2\phi + S_{cc}\sin^2\phi, \tag{10}$$

$$\Delta S_{\mathrm{CD}} = |S_{\mathrm{CD1}} - S_{\mathrm{CD2}}| = |2S_{ac}\sin 2\phi|. \tag{11}$$

ΔS_{CD}, and hence S_{ac}, is nonzero only in the chiral N_{TB} phase. For the geometry obtained by the DFT calculation for the minimum energy, rigid conformation of CB6OCB [5], the value of ϕ is 54.7 ° so that

$$\Delta S_{\mathrm{CD}} = |S_{\mathrm{CD1}} - S_{\mathrm{CD2}}| = |1.886 S_{ac}|. \tag{12}$$

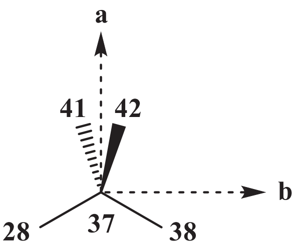

FIG. 11. Local axes (abc) with a in the plane defined by C37, H41, and H42, and bisecting the angle $\angle 41,\ 37,\ 42 = 2\phi$. Axis c is normal to the plane defined by C28, C37, and C38.

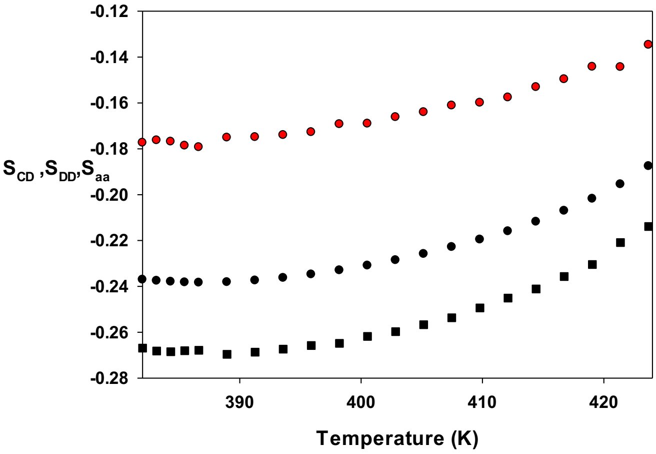

FIG. 12. Values of S_{aa} (●) together with S_{CD} (●) and S_{DD} (■) in N_U phase.

The order parameter S_{DD} is obtained from the direction of the vector $\boldsymbol{r}$ connecting the two ^{2}H nuclei which coincides with axis c so that

$$S_{\mathrm{DD}} \equiv S_{cc}. \tag{13}$$

S_{CD}(mean) from Eq. (10) is also dependent on the value of the angle ϕ, and when this is 54.7 ° as predicted by the DFT calculation for the minimum energy, rigid conformation of CB6OCB [5], this gives

$$S_{\mathrm{CD}}(\text{mean}) = 0.333 S_{aa} + 0.667 S_{cc}. \tag{14}$$

Accordingly,

$$S_{\mathrm{CD}}(\text{mean}) = 0.333 S_{aa} + 0.667 S_{\mathrm{DD}}. \tag{15}$$

Values of S_{aa} in the N_U phase were calculated from Eq. (15) and are shown together with S_{CD} and S_{DD} in Fig. 12.

The dependences on temperature of the bond-order parameters $S_{\mathrm{CD}}(T)$ and $S_{\mathrm{DD}}(T)$ are almost parallel throughout the whole N_U phase, including the region ~10 °C before the transition to the N_{TB} phase is reached and are in the ratio 0.882 ± 0.004. From Eqs. (5) and (6) the ratio $S_{\mathrm{CD}}(T)/S_{\mathrm{DD}}(T)$ will be constant when the product $q_{\mathrm{CD}} r^3$ is constant, which will hold when the asymmetry parameter, η, remains negligible and r is constant throughout the N_U phase. Note too that the ratios $S_{\mathrm{CD}}/S_{aa} (= 1.37 \pm 0.02)$ and $S_{\mathrm{DD}}/S_{aa} (= 1.55 \pm 0.03)$ are also constant, which from Eq. (10) holds only when ϕ is independent of temperature.

The local directors, $\boldsymbol{n}$, in the N_{TB} in the model proposed by Dozov (see Fig. 2) are tilted through an angle θ with respect to the helix axis $\boldsymbol{h}$. This tilt is predicted to increase with decreasing temperature in the *NTB* phase and should reduce both S_{CD}(mean) and S_{DD} by the same factor $R[\Delta(T)]$ [see Eq. (2)], predicting that the ratio $S_{\mathrm{CD}}(\text{mean})\,(T)/S_{\mathrm{DD}}(T)$ should be constant. This ratio is found for the sample of CB6OCB–d_2 to have a constant value of 0.859 ± 0.008 in the N_{TB} phase and is equal to the value of the ratio of $S_{\mathrm{CD}}(T)/S_{\mathrm{DD}}(T)$ in the N_U phase of 0.882 ± 0.004 and shows that the angle ϕ remains constant throughout both nematic phases.

The temperature independence of all these ratios is consistent with the structure of the biphenyl-CD$_2$ group being constant throughout both nematic phases.

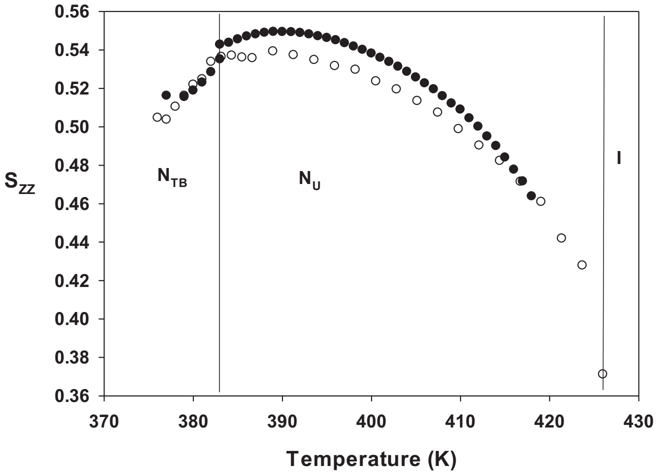

FIG. 13. Dependence on temperature, T, of S_{zz} obtained from ^{13}C chemical-shift anisotropies in CB6OCB [5] (●) and from dipolar coupling between deuterons in CB6OCB-d_2 (○).

IX. TILT OF THE DIRECTORS IN BOTH NEMATIC PHASES AWAY FROM THE MAGNETIC FIELD

The occurrence of a maximum value of S_{zz}, a local order parameter for the fragment shown in Fig. 3 in the N_U phase ~10 K above the transition to the N_{TB} phase was attributed [5] to a tilting of the directors of these phases away from the direction of the applied magnetic field through an angle θ_{tilt}. Values of θ_{tilt} were obtained by comparing the temperature profile of S_{zz} obtained from the ^{13}C–{^{1}H} experiments, $S_{zz}\,(\Delta T)$ with that predicted, $S(\Delta T)$ from a Haller function [11]:

$$S(\Delta T) = S(0)(\Delta T/T^*_{\mathrm{NI}})^{\gamma}, \tag{16}$$

where $\Delta T = T_{\mathrm{NI}} – T$, and $S(0)$ is the value of S when the sample is at 0 K. For a rigid, axially symmetric nematogen the value of $S(0) = 1$, but for real nematogens it is treated as a fitting parameter, as is the exponent γ. The value of T^*_{NI} is set to 1–2 K above T_{NI} so that $S(\Delta T)$ at T_{NI} has a predicted finite value similar to that found experimentally.

The values of θ_{tilt} are then obtained from the difference, ΔS_{zz}, between predicted and observed values of S_{zz} as

$$S_{zz}(T, \text{obs}) = S_{zz}(T, \text{pred})(3\cos^2\theta_{\mathrm{tilt}} - 1)/2. \tag{17}$$

Values of S_{zz} can be obtained from S_{DD} by noting that the direction of $\mathbf{r}_{\mathrm{DD}}$ in the fragment biphenyl-CD$_2$ (see Fig. 3) in the minimum energy conformation is parallel to axis x. Furthermore, it was assumed when deriving S_{zz} from ^{13}C chemical-shift anisotropies [5] that $S_{xx} = S_{yy} = -1/2 S_{zz}$ so that the same level of approximation gives $S_{zz} = -2 S_{\mathrm{DD}}$. Figure 13 compares the values of S_{zz} obtained by these two methods.

Both $S_{zz}(T)$ obtained from the chemical shift anisotropy and that derived from D are affected by experimental errors, which are ~1–2%, but also from systematic errors from assumptions made about molecular geometries, and the effect of vibrational motion. The magnitudes of the systematic errors are probably about 2–3%, making the total uncertainties in the curves ~5%. Despite these large uncertainties affecting the two curves it is concluded that their shapes are so similar

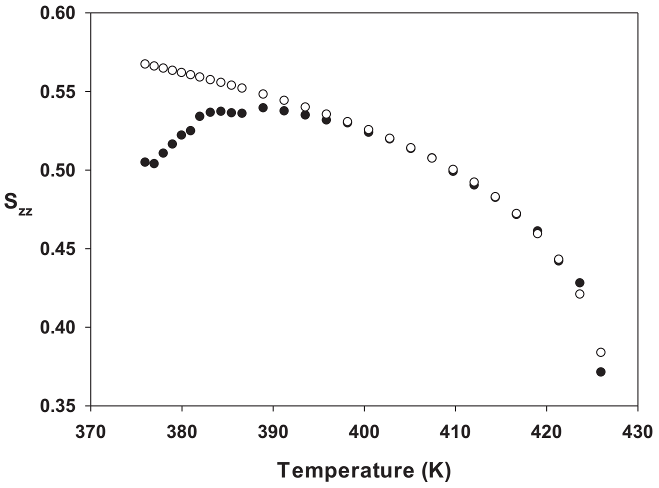

FIG. 14. $S_{zz} = -2S_{\rm DD}$ (●) compared with a Haller plot (○) with $\gamma = 0.12$ and $S_{zz}(0) = 0.735$, $T^*_{\rm NI} = 428$ K.

as to be attributed to a common source: a tilt of the directors through an angle $\theta_{\rm tilt}$ away from the direction of the applied magnetic field.

The two temperature profiles shown in Fig. 13 have similar but not exact forms, with the main difference being the values of S_{zz} obtained from the dipolar couplings extend until $T_{\rm NI}$. Fitting the values of $S_{zz} = -2S_{\rm DD}$ to a Haller function gives the result shown in Fig. 14.

The values of $\theta_{\rm tilt}$ derived from $S_{zz} = -2S_{\rm DD}$ shown in Fig. 14 were used with Eq. (16) to give the temperature variation shown in Fig. 15.

The tilt angle determined from values of $S_{zz} = -2S_{\rm DD}$ range from ~ 16° at the freezing point of the sample decreasing in the N_{TB} phase to ~ 12°, and after a small discontinuity on entering the N_U phase decrease until becoming indistinguishable from zero within the precision of their measurement at ~405 K. This variation with temperature of $\theta_{\rm tilt}$ is similar to that determined previously [5] from ^{13}C shift anisotropies as shown in Fig. 16.

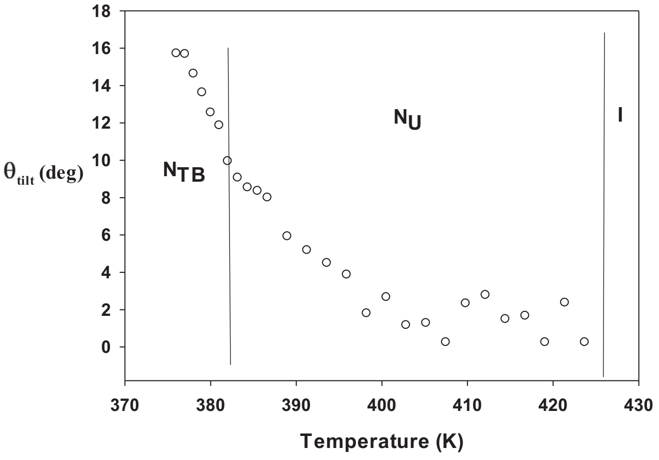

FIG. 15. Tilt, $\theta_{\rm tilt}$, of the director away from direction of applied magnetic field obtained for CB6OCB-d_2 using $S_{zz} = -2S_{\rm DD}$ and a Haller plot with $\gamma = 0.12$ and $S_{zz}(0) = 0.735$ with $T^*_{\rm NI} = 428$ K.

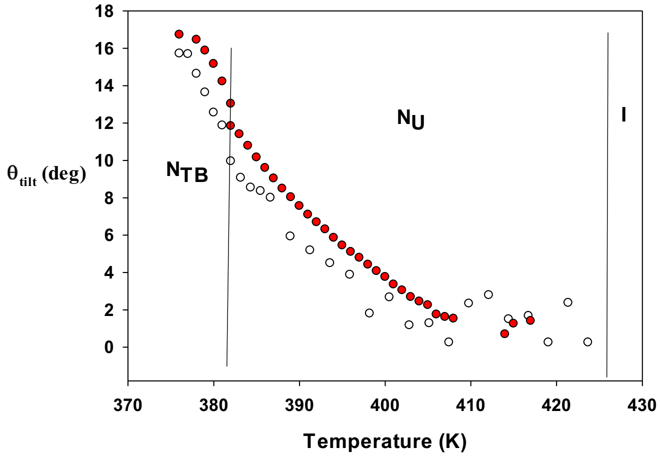

FIG. 16. Tilt, $\theta_{\rm tilt}$, of the director from direction of applied magnetic field obtained from difference between values of $S_{zz} = -2S_{\rm DD}$(○) compared with values (●) derived previously [5] from ^{13}C chemical-shift anisotropies.

The finite values for $\theta_{\rm tilt}$ obtained from ^{13}C shift anisotropies for the sample in the N_U phase were ascribed previously [5] to either the presence above $T_{N_{TB}N_U}$ of a splay-bend phase extending until about ($T_{\rm NI}$–10) K, or as being a pretransitional effect similar to those detected in N_U phases near a transition to a phase with positional order. This uncertainty is essentially not resolved by the present results.

X. CONCLUSIONS

Proton decoupling increases the useful information which can be obtained from the deuterium spectra of liquid crystals containing a single CD$_2$ group by dramatically reducing the linewidths to reveal the fine structure which is the result of the dipolar coupling between the two deuterium nuclei within each CD$_2$ group, and allows a value of the residual dipolar coupling, D, to be obtained. Analysis of the fine structure yields values of the quadrupolar interaction q and D and their relative sign. For the deuterons in CB6OCB-d_2 the relative sign is found to be opposite throughout the whole range of the N_U and N_{TB} phases.

The temperature-dependent bond-order parameters $S_{\rm CD}(T)$ and $S_{\rm DD}(T)$ derived from $q(T)$ and $D(T)$ were found to be in a constant ratio with a value of 0.882 ± 0.004 in the N_U phase from $T_{\rm NI} - 2$ °C to $T_{N_{TB}N_U}$ +1 °C, which is consistent with the product $q_{\rm CD}r^3$ being unchanged in this phase. This ratio of bond-order parameters is also constant in the N_{TB} phase at almost the same value (0.859 ± 0.008), which shows not only that the structure of the CD$_2$ group is unchanged from that in the N_U phase, but that the decreasing values of $S_{\rm CD}$ and $S_{\rm DD}$ in the N_{TB} phase have a common origin, the tilting of the local directors, as proposed by Dozov [3].

The high precision with which the order parameters, $S_{\rm CD}$ and $S_{\rm DD}$, are measured from the ^{2}H–{^{1}H} spectra allows their discontinuous changes at $T_{N_{TB}N_U}$ to be quantified and to show that they both decrease by the same amount of 1.7%.

The previous study [5] of the ^{13}C chemical-shift anisotropies in CB6OCB enabled the order parameter, S_{zz}, to be measured for the local z axis fixed in the biphenyl-CH_2 fragment (see Fig. 3) and to reveal the presence of a maximum in the temperature dependence of S_{zz} in the N_U phase about 10 K before the transition to the N_{TB} phase is reached. This was attributed to a tilting of the local directors in the N_{TB} phase through an angle θ_{tilt} being continued into the N_U phase. Values of θ_{tilt} were obtained by comparing the values of S_{zz} predicted for a bent mesogen like CB6OCB by a modified Haller function with those observed. A similar temperature profile for S_{zz} in CB6OCB-d_2 was found but now obtained from values of S_{DD} and, using the same approach of comparison with predictions of a modified Haller function, leads to values of θ_{tilt} being obtained, which are in good agreement with those derived from the ^{13}C chemical-shift anisotropies in CB6OCB.

It is perhaps surprising that proton decoupling has not been used previously when recording the ^{2}H NMR spectra of liquid crystal samples. This can be attributed to two impediments. The first is the availability of a spectrometer with the ability to apply ^{1}H rf fields with sufficient power to fully decouple the proton-deuterium interactions. The second is the requirement to synthesize liquid crystals containing a single -CD_2- group: deuteriation of multiple sites will produce proton-decoupled spectra with fine structure from multiple ^{2}H–^{2}H residual dipolar interactions which *may* be unresolved or may be difficult to interpret.

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