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Conformational analysis of the alkyl spacer of a dimer liquid crystal in the solid and liquid crystalline states by ^{13}C–^{13}C dipolar coupling†

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ABSTRACT: The conformation around the C_ε—$C_{\varepsilon'}$ bond of the alkyl spacer of α,ω-bis[(4,4′-cyanobiphenylyl)oxy] decane (CBA-10) was evaluated in the solid and liquid crystalline states through the detection of the dipolar interaction between C_δ and $C_{\delta'}$. CBA-10 ^{13}C-labelled in the δ position of the alkyl spacer was prepared and for the measurement in the solid state a variation of the Carr–Purcell–Meiboom–Gill sequence was used. The spectra in the nematic state were measured with the pulse saturation method. It was concluded that in the solid state the *trans* conformation is assumed whereas in the liquid crystalline state the fraction of the *trans* conformers is around 0.6. © 1998 John Wiley & Sons, Ltd.

KEYWORDS: NMR; solid-state NMR; ^{13}C–^{13}C dipolar coupling; dimer liquid crystal; nematic state; alkyl spacer; conformation

INTRODUCTION

The interest in dimer liquid crystals arises from the fact that they are often regarded as good model compounds in their polymeric homologues. In our previous studies,[1] a scheme for determining the conformation of the spacer of such compounds was developed. In that method, the rotational isomeric state (RIS) approach and information on molecular orientation derived from either ^2H quadrupolar couplings or ^{13}C chemical shift anisotropy were employed.

In chain molecules, the internuclear distance between a pair of nuclei three bonds apart gives the conformation around the central bond. Since the dipolar coupling between nuclei is inversely proportional to the third power of the distance between them, this gives a means for distance measurements. Many examples in which this principle has been applied have been reported in the literature. Yannoni and Kendrick[2] measured the C—C bond length in a doubly ^{13}C-labelled acetic acid using the nutation spectroscopy method; the same sample was used by Engelsberg and Yannoni[3] and the bond length was determined using a modified type of Carr–Purcell–Meiboom–Gill (CPMG) sequence; Weintraub *et al.*[4] applied simple excitation for the dephasing of rotational-echo amplitudes (SEDRA) to obtain the N—N bond length in 3(5)-methyl-5(3)-phenylpyrazole-$^{15}N_2$; and Tycko and Dabbagh[5] determined the distance between the methyl groups in $(^{13}CH_3)_2C(OH)SO_3Na$ using dipolar recovery at the magic angle (DRAMA). Another method very commonly used is rotational resonance (RR).[6]

Since the intensity of the dipolar interaction decreases considerably with distance, as pointed out previously, relatively short distances were determined in the above examples. However Asakawa[7] succeeded in measuring the intermolecular separation in [1-^{13}C]glycylglycine, which is as large as 5.6 Å.

Our purpose in this work was to determine the conformation around the C_ε—$C_{\varepsilon'}$ bond in α,ω-bis[(4,4′-cyanobiphenylyl)oxy]decane (CBA-10), which forms a nematic phase through the measurement of the internuclear distance *r* between C_δ and $C_{\delta'}$ in the solid and liquid crystalline states (Fig. 1).

EXPERIMENTAL

Material

α,ω-Bis[(4,4′cyanobiphenylyl)oxy]decane is a thermotropic dimer liquid crystal which forms a nematic phase (C · 166.4 °C · N · 186.9 °C · I). The preparation of α,ω-bis[(4,4′-cyanobiphenylyl)oxy]decane-δ-$^{13}C_2$ 99% enriched was accomplished by reacting 4-hydroxy-4′-cyanobiphenyl with ^{13}C-labelled 1,10-dibromodecane-4,7-$^{13}C_2$ 99% as reported elsewhere.[1]

Spectra

Measurements of the dipolar coupling in the solid (polycrystalline) state were carried out with a modified

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† Dedicated to Professor John D. Roberts on the occasion of his 80th birthday.

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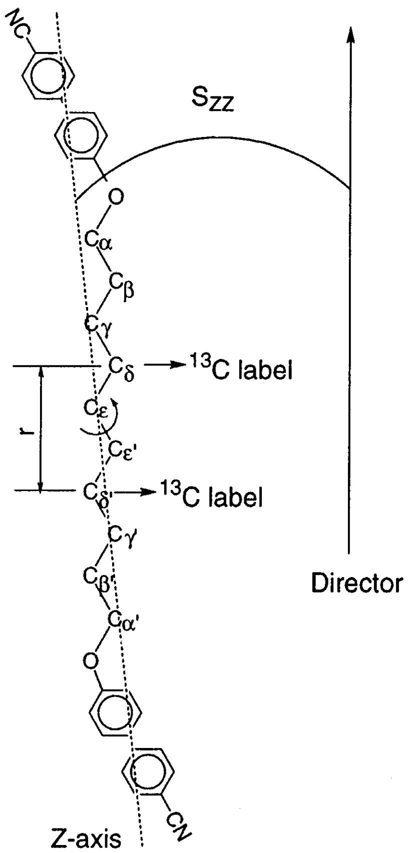

Figure 1. ^{13}C doubly labelled CBA-10 and the conformation around the C_ε—$C_{\varepsilon'}$ bond.

CPMG sequence as indicated in Fig. 2. It is essentially the same as that used by Engelsberg and Yannoni.[3] Here the ^{13}C $\pi/2$ pulse for obtaining the initial transverse magnetization is replaced by a cross-polarization process with the protons. This method was chosen owing to its simplicity and the facility of implementation on our equipment. A JEOL-GSX270 NMR spectrometer (67.8 MHz) was used with the contact time set to 2 ms and a repetition time of 5 s. The protons were irradiated with an r.f. strength of 1.2–1.3 mT for both cross-polarization and decoupling processes and the field strength for ^{13}C adjusted to be on-resonance with C_δ was 5.1–5.3 mT; τ was 600 μs and n varied from 1 to 32. The sample was kept static during the experiment.

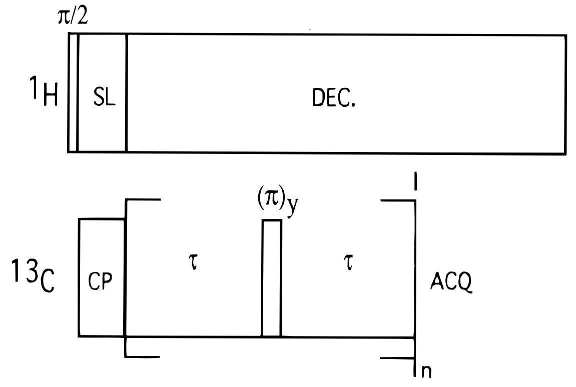

Figure 2. Modified CPMG pulse sequence for determining dipole–dipole couplings in solids.

The spectra of the sample in the nematic state were obtained using the pulse saturation (PST) method in which the carbons are excited with a single pulse with presaturation of the proton spins.[8] The intensity of the signals due to the mobile carbons is thus enhanced. The measurements were carried out on a JEOL-GSX270 NMR spectrometer (67.8 MHz) equipped with a variable-temperature accessory and a variable-temperature CP/MAS probe from Doty Scientific. The r.f. strengths were 1.3 and 5.2 mT for ^{1}H and ^{13}C, respectively, and the repetition time was 10 ms. The sample was kept static and its temperature was determined from the equation

$$T_{\text{real}} = 1.04T_{\text{ind}} - 6.7 \qquad (1)$$

where T_{real} (°C) is the temperature inside the probe and T_{ind} (°C) is the value indicated on the console.[1]

The high-resolution CP/MAS spectrum was measured on a Bruker DSX300 (75.5 MHz) spectrometer with a MAS rate of 5000 Hz. The cross-polarization contact time was set to 2 ms and the repetition times was 5 s. The r.f. strength was 1.5 mT for irradiating the ^{1}H spins for both cross-polarization and decoupling processes.

The ^{13}C chemical shifts in the present study were referred to adamantane as an external reference (29.5 ppm relative to TMS).

RESULTS AND DISCUSSION

Solid state

The CPMG sequence (see Fig. 2) is known to refocus the dephasing in the observed spins which arises from field inhomogeneity, chemical shift anisotropy and dipolar coupling with different nuclear species. However, in the case of dipolar coupling between like nuclei (the observed ones), the π pulse inverts all of them turning the precession rate of a given nucleus into one different from that before the pulse. Consequently, no refocusing occurs,[9] the effect of the dipolar coupling being reflected in the intensities of the echoes, which in the present work were taken directly from the FIDs. Their real and imaginary parts are plotted against the time elapsed from the end of the contact time in Fig. 3 for the undiluted sample (CBA-10-δ-$^{13}C_2$, 99%). It can be seen that the decay with increasing time (or increasing n, see Fig. 2) is not a simple exponential showing the modulation due to the homonuclear dipolar coupling.

The complex Fourier transform of the decay consists of a superposition of a sharp peak on a doublet. The doublet is a typical pattern (the 'Pake doublet') obtained for isolated pairs of coupled nuclei randomly oriented as in a polycrystalline sample. The central peak may originate from spin locking,[3] which is reported to occur when the CPMG sequence is used unless a particular phase alternation of the pulses in the sequence is

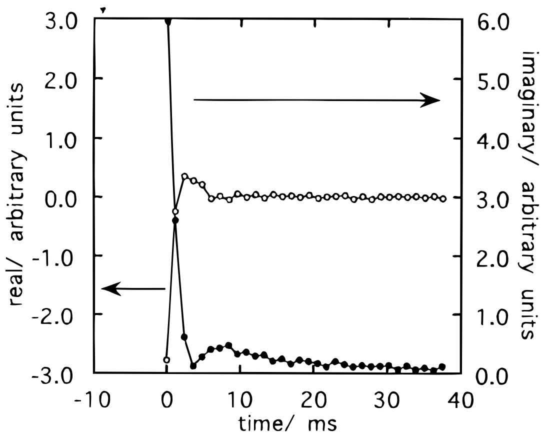

Figure 3. Intensity of the measured echoes as a function of time for the undiluted CBA-10-δ-$^{13}C_2$. Open and filled circles indicate the real and imaginary parts, respectively (see text).

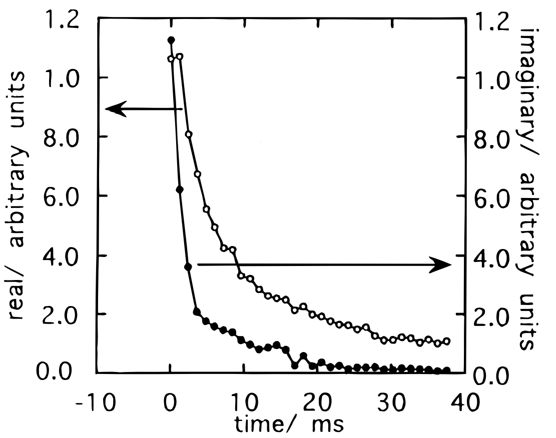

Figure 5. Intensity of the measured echoes as a function of time for the 10% diluted CBA-10-δ-$^{13}C_2$. Open and filled circles indicate the real and imaginary parts, respectively (see text).

applied.[10] Other explanations such as a peak due to a 'high' mobility component or due to molecules with a single ^{13}C nucleus are believed to be less probable in this crystalline and highly ^{13}C-enriched sample.

The spectrum was analysed as a Gaussian superimposed on a Pake doublet using the equations reported elsewhere.[11] Since the J coupling between vicinal carbons is reported to be small[12] (< 5 Hz), it was not considered in the analysis. Also, the value of the duty factor L defined[3] as

$$L = \frac{2\tau}{2\tau + t_w} \tag{2}$$

where t_w is the width of the ^{13}C π pulse (see Fig. 2), is 0.99 in the present work and therefore was approximated to unity.

The best fit was obtained with the calculations using $r = 3.55$ Å as shown in Fig. 4. The internuclear distance between C_δ and $C_{\delta'}$ obtained by the above procedure is between those for the *trans* (3.90 Å) and *gauche* (3.11 Å) conformers calculated using the geometrical parameters reported previously.[1]

On the other hand, the chemical shift of C_δ is 32.6 ppm, as shown in the CP/MAS spectrum of CBA-10-δ-$^{13}C_2$. From this result it is concluded[13] that the C_ε—$C_{\varepsilon'}$ bond assumes the *trans* conformation, suggesting that the experimental spectrum obtained is broadened. One possible cause may be the imperfection of the ^{13}C π pulse which would result in incomplete refocusing of the spins and consequently in spectral line broadening. Ishii *et al.*[14] also reported that ^{13}C–^{1}H dipolar recoupling can occur under ^{1}H decoupling conditions when a π-pulse train is applied in ^{13}C, unless the intensity of the r.f. field for the ^{1}H decoupling is set to a value at least three times that for the ^{13}C π pulses, i.e. $\omega_{1^1H}/\omega_{1^{13}C} = 3, 5, 7, \ldots, \omega_{1i} = \gamma B_{1i}$ (rad s^{-1}). In the present work this was not done. Finally, the intermolecular interaction may also contribute to the spectral broadening of this undiluted sample.

In order to investigate the contribution of the intermolecular interaction, a measurement using the modified CPMG sequence was carried out with a sample diluted to 10% with the unenriched sample. The decay curve and its complex Fourier transform are shown in Figs 5 and 6, respectively. As can be observed, only a singlet was obtained, suggesting that the peak due to

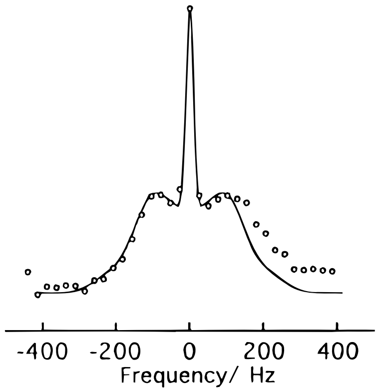

Figure 4. Experimental spectrum (open circles) and the best fitted theoretical spectrum (solid line) which was calculated with $r = 3.55$ Å.

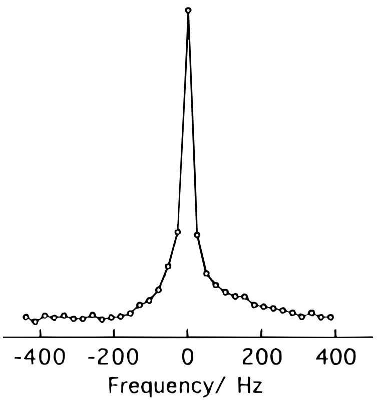

Figure 6. Spectrum resulting from the complex Fourier transform of the decay shown in Fig. 5.

spin locking was enhanced by the signal due to molecules with only one ^{13}C nucleus, surpassing the doublet in intensity. This can only be confirmed if dilution is carried out with ^{13}C-depleted sample.

Liquid crystalline state

Typical spectra for CBA-10-δ-$^{13}C_2$ in the isotropic and nematic states are shown in Fig. 7. The spectrum taken in the isotropic state is a singlet whereas that in the nematic state is split into a doublet by the dipolar coupling. The splitting is not very convincing, but it is validated by the temperature variation experiments, the results of which are shown in Fig. 8. The splitting $\Delta\nu$ is expressed by

$$\Delta\nu = \frac{3\gamma^2 h}{4\pi^2 r^3}\frac{(3\langle\cos^2\theta\rangle - 1)}{2} = \frac{3\gamma^2 h}{4\pi^2 r^3} S_{zz}^{C_\delta C_{\delta'}} \qquad (3)$$

where γ is the ^{13}C gyromagnetic ratio, h is Planck's constant and r is the internuclear distance between C_δ and $C_{\delta'}$. $S_{zz}^{C_\delta C_{\delta'}}$ is the order parameter of the internuclear vector which forms an angle θ with the magnetic field.

The dipolar splitting increases with decrease in temperature, as shown in Fig. 8. This implies that either $S_{zz}^{C_\delta C_{\delta'}}$ increases or r decreases. The latter is improbable since C_ε—$C_{\varepsilon'}$ assumes the *trans* conformation in the crystalline state, suggesting that the variation of r with temperature in the nematic phase should be in the opposite direction and small, implying an almost constant conformation around C_ε—$C_{\varepsilon'}$, in agreement with previous results.[1]

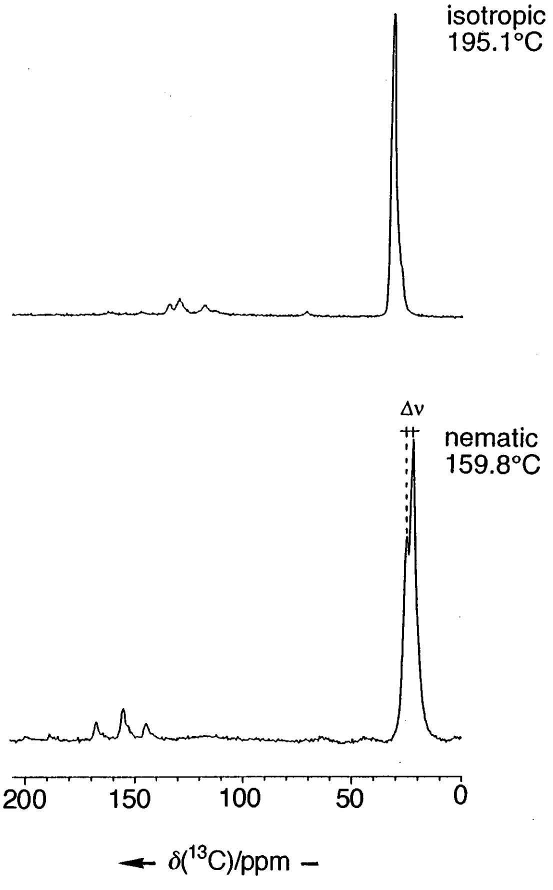

Figure 7. Typical high-resolution solid-state ^{13}C NMR PST spectrum of α,ω-bis[(4,4′-cyanobiphenylyl)oxy]decane-δ-$^{13}C_2$ in the isotropic state, 195.1 °C (top) and in the nematic state, 159.8 °C (bottom). The sample was not spun. The splitting $\Delta\nu$ due to the dipolar interaction is indicated.

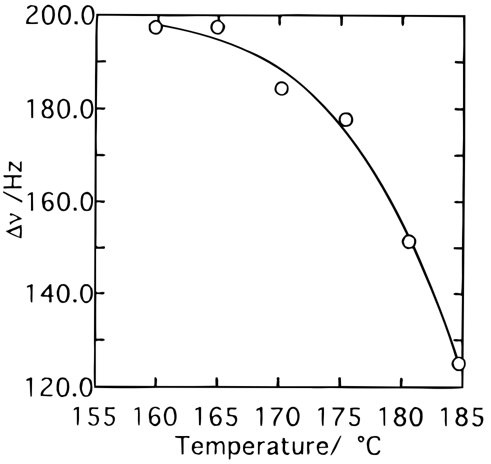

Figure 8. Dipolar splitting $\Delta\nu$ measured in the liquid crystalline state as a function of temperature.

$S_{zz}^{C_\delta C_{\delta'}}$ was calculated from Eqn (3) and is plotted in Fig. 9 against the temperature for the *trans* fraction of the C_ε—$C_{\varepsilon'}$ bond indicated. Assuming that the value of $S_{zz}^{C_\delta C_{\delta'}}$ in the flat part of the curve is near to that obtained for the C_γ—C_ε axis[1] (*ca.* 0.4 and almost constant with temperature), it can be concluded that the proportion of the *trans* conformation around C_ε—$C_{\varepsilon'}$ is around 0.6, supporting our previous studies.[1] More accurate evaluation of $S_{zz}^{C_\delta C_{\delta'}}$ can only be done using the method proposed previously[1] and the chemical shift anisotropy information on C_ε, a ^{13}C-labelled sample in the ε position of the spacer being necessary in this case.

CONCLUSION

The dipolar coupling between a pair of ^{13}C nuclei three bonds apart was successfully detected under a strong magnetic field. It is concluded that the C_ε—$C_{\varepsilon'}$ bond

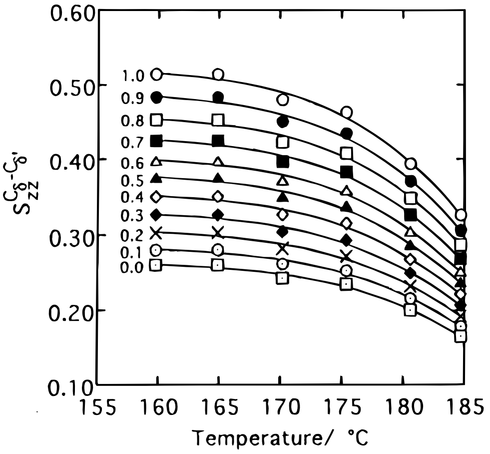

Figure 9. Order parameter of the C_δ–$C_{\delta'}$ internuclear vector calculated for the indicated *trans* fraction of the C_ε—$C_{\varepsilon'}$ bond as a function of temperature.

assumes the *trans* conformation in the crystalline state. In the nematic phase, on the other hand, the *trans* fraction of the C_ε—$C_{\varepsilon'}$ bond is approximately 0.6. It is also suggested that the variation of the temperature is due to an increase in the value of $S_{zz}^{C_\delta C_{\delta'}}$, the conformation being almost unaltered. This is in agreement with our previous results.[1]

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