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Assignment of the Deuterium Quadrupolar Splittings for the End-chain of 4-cyano-4′-octylbiphenyl in the Nematic Phase: A Test Between Theoretical Models for End-chain Conformational Motion and Orientational Ordering

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4-Cyano-4′-(1,1,5,5-d_4-octyl)-biphenyl and 4-cyano-4′-(1,1,6,6-d_4-octyl)-biphenyl have been synthesized and the deuterium quadrupole splittings measured for their nematic phases. The results, when combined with previous measurements on other specifically deuteriated derivatives [*Mol. Phys.*, **42**, 565 (1981)], enable a virtually complete assignment to be made of the quadrupolar splittings in the deuterium nmr spectrum of the perdeuteriated end-chain of this mesogen. The assignment is shown to be consistent with that proposed by Emsley, Luckhurst and Stockley [*Proc. Roy. Soc.*, **A381**, 117 (1982)] and with the single frame model proposed by Samulski and Dong [*J. Chem. Phys.*, **77**, 5090 (1982)], but inconsistent with Samulski and Dong's inertial frame model.

INTRODUCTION

The deuterium nmr spectrum of a perdeuteriated mesogen in its liquid crystalline phase consists of a number of doublets. The splitting for each doublet depends on the time-averaged angle between the associated C—D bond and the magnetic field. This, in turn, relates to the reorientational and conformational motion of the molecule. Before information concerning this reorientational and conformational motion can be extracted, however, it is necessary to assign which doublet in the spectrum corresponds to which C—D bond. Often, the only way to do this is to prepare compounds deuteriated at specific sites and this approach has been used to assign the splittings for the end-chains of a number of thermotropic mesogens.[1-5] In previous papers we reported assignments for the end-chains of heptyloxyazoxybenzene[2] and octyloxyazoxybenzene[5] and for the first three segments in the end-chain of octylcyanobiphenyl.[4] One problem with this particular approach to the assignment of a deuterium nmr spectrum is to obtain a large number of specifically deuteriated samples all at the same high level of purity. If this is not achieved then there can be severe problems in correlating the spectroscopic results for the specifically deuteriated mesogens with those for the perdeuteriated mesogen. Whilst purification had not given undue problems in our work on heptyloxyazoxybenzene or on octyloxyazoxybenzene,[2,3,5] it has proved very troublesome in the octylcyanobiphenyl series.[4] For this reason we had not pursued our work on this compound beyond the assignment of the first three segments. However, two recent publications[6,7] which propose different models for the reorientational and conformational motion of molecules in liquid crystals and which use octylcyanobiphenyl as a model mesogen have revived our interest. Samulski and Dong[6] have predicted that for the end-chain of a perdeuteriated mesogen the profile of the plot of deuterium quadrupolar splitting *versus* segment position is very sensitive to the choice of the principal axes system for the molecule. In their 'inertial frame' (IF) model, the molecular fixed frame for each conformer is chosen such that it diagonalises the corresponding moment of inertia tensor. Using this model, the deuterium nmr spectrum of d_{17}-octylcyanobiphenyl (Figure 1a) can be explained provided the signals A, B,...H are assigned, respectively, to segments 1, 3, 2, 4, 5, 6, 7 and 8 of the alkyl chain. This assignment is represented graphically in Figure 2a. Samulski and Dong also discuss a 'single frame' (SF) model in which the molecular fixed frame is chosen such that the Z-axis is fixed parallel to the *para*-axis of the two aromatic rings. This can be used to fit the experimental data provided it is assumed that the signals A to H can be assigned, respectively, to segments 1, 3, 2, 5, 4, 7, 6 and 8 of the end-chain. A more complex model, proposed by Emsley, Luckhurst and Stockley,[7] has elements in common with Marčelja's[8] model for flexible mesogens. It treats the molecule as a system of rigid segments

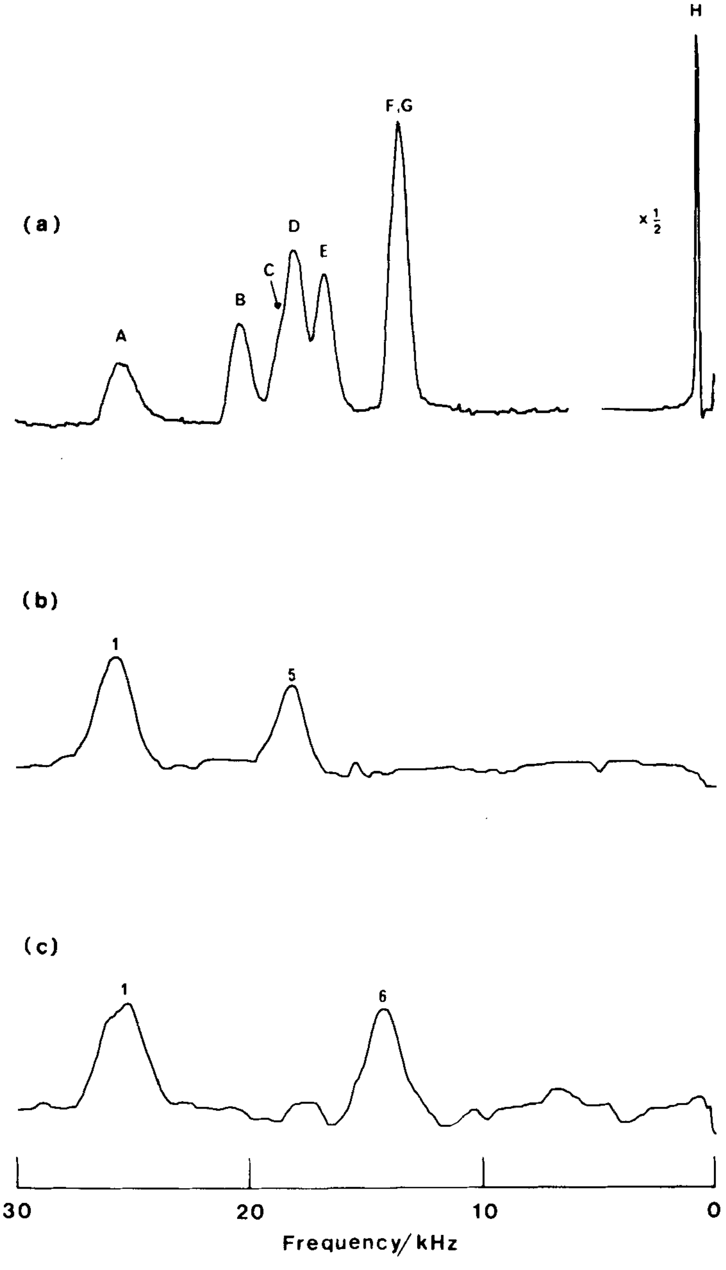

FIGURE 1 Deuterium nmr spectra measured at 9.8 MHz for the nematic phase at a reduced temperature of 0.985—(a) 4-cyano-4'-(d_{17}-octyl)-biphenyl; (b) A mixture of 4-cyano-4'-(1,1,5,5-d_4-octyl)-biphenyl and 4-cyano-4'-(1,1-d_2-octyl)-biphenyl; (c) A mixture of 4-cyano-4'-(1,1,6,6-d_4-octyl)-biphenyl and 4-cyano-4'-(1,1-d_2-octyl)-biphenyl.

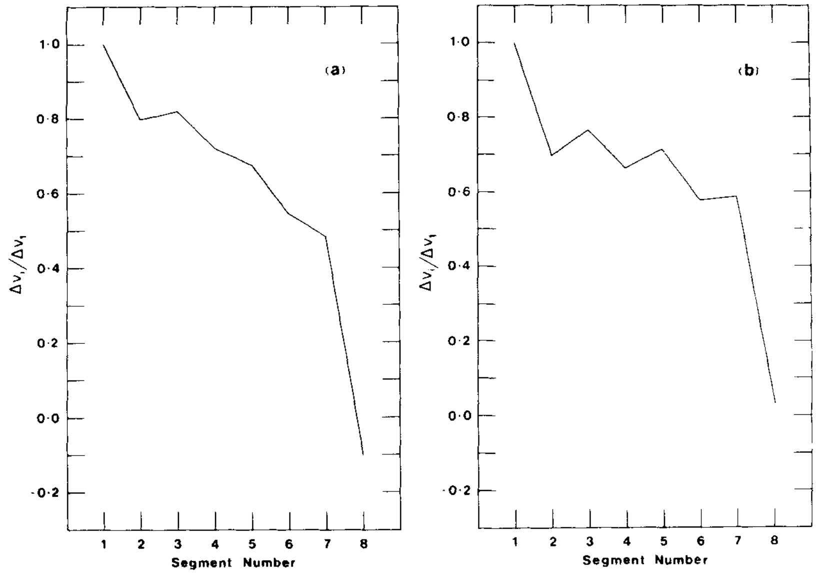

FIGURE 2 Variation of the relative deuterium quadrupolar splittings ($\Delta\nu_i/\Delta\nu_1$) with chain position for (*a*) the end chain of octylcyanobiphenyl at a reduced temperature (T/T_{NI}) of 0.98 as predicted by the inertial frame model of Samulski and Dong,[6] and (*b*) the end chain of octylcyanobiphenyl at a temperature 6.3 K below T_{NI} as predicted by the model of Emsley, Luckhurst and Stockley.[7]

and takes the molecular fixed frame for a particular conformer as the principal axis system of the tensor for the potential of mean torque. They assume an assignment of the deuterium nmr spectrum of d_{17}-octylcyanobiphenyl (Figure 1a) which is the same as that proposed in the SF model of Samulski and Dong, i.e., A, B...H are assigned to segments 1, 3, 2, 5, 4, 7, 6 and 8 respectively, as illustrated in Figure 2b. Clearly, before further progress can be made with the theoretical modelling of these systems it is essential to establish which, if any, of the proposed assignments is correct.

RESULTS

All of the models discussed above agree with our earlier assignment[4] of signals A, B and C to, respectively, segments 1, 3 and 2 and with the assignment of signal H to the methyl group (segment 8). To distinguish between these models we have now assigned the signals from segments 5 and 6. Since previous experience had led us to anticipate (correctly) problems in purifying these specifically deuteriated cyanobiphenyls, we have employed a 'double-label' technique and prepared mesogens labelled at positions 1 and 5 and at positions 1 and 6. The label on each molecule at the previously assigned 1-position acts as an internal marker and helps to match the nmr spectra of the perdeuteriated and selectively deuteriated materials. The precursors with selectively deuteriated chains were prepared as before by a mixed Kolbé reaction,[5] elaborated into the cyanobiphenyl molecule by the method of Gray and Mosley[9] and purified as far as possible by repeated column chromatography and bulb distillation. Details of the preparation are given in the experimental section. The deuterium nmr spectra of these mesogens are shown in Figures 1b and 1c. It is clear that segment 5 is associated with signal D and segment 6 with either signal F or signal G. This enables the assignment of the spectra assumed in the 'inertial frame' model of Samulski and Dong (Figure 2a) to be discounted, although it is compatible with either their second (SF) model or with the model proposed by Emsley *et al.*

EXPERIMENTAL

The nmr spectroscopic methods used for the neat liquid crystalline samples have been described elsewhere.[2-4] In comparing the spectra of the selectively and perdeuteriated samples, approximately the same reduced temperature was used in each case and this was also the temperature which produced a satisfactory matching of the quadrupolar splittings of segment 1.

4-Cyano-4′-(1,1,6,6-d_4-octyl)-biphenyl

Ethyl iodide (31.2 g) was interreacted with the sodium salt of diethyl malonate (from 33.0 g of ester) to give diethyl ethylmalonate (30.1 g, 80%, b.p. 78–82 °C/0.1 mm).[10] This ester (11.2 g) was α-deuteriated and hydrolysed by the procedure of Katoh *et al.*[11] to give 2,2-d_2-butanoic acid (2.2 g, 42%, b.p. 60–80 °C/0.1 mm). Dimethyl adipate (50.5 g) and adipic acid (73 g) were also interreacted[12] to give methyl hydrogen adipate (46.8 g, 59%, b.p. 130–135 °C/0.1 mm). A mixed Kolbé reaction[5] between methyl hydrogen adipate (19.3 g) and 2,2-d_2-butanoic acid (2.2 g), followed by isolation of the neutral products, distillation, column chromatography on kieselgel (eluting with 30% chloroform-light petroleum) and bulb distillation gave methyl 6,6-d_2-octanoate (2.2 g, 56%) which was pure by g.l.c. After an initial attempt using milder conditions had failed, the ester (2.2 g) was hydrolysed by heating with 25% aqueous potassium hydroxide at 115° for 1 h. The mixture was cooled to room temperature, poured into 2M-hydrochloric acid (200 cc), and extracted into ether. The ether extracts were dried with anhydrous magnesium sulphate, filtered and the solvent removed under reduced pressure to give the crude 6,6-d_2-octanoic acid as an oil (1.12 g 56%). The crude acid (1.12 g) was added dropwise to boiling thionyl chloride (4 cc). After 1.5 h the excess of thionyl chloride was removed under reduced pressure and the resultant oil was bulb distilled to give 6,6-d_2-octanoyl chloride (0.55 g, 46%, b.p. 90–100 C, oven temperature/0.5 mm). The 6,6-d_2-octanoyl chloride (0.55 g) was diluted with undeuteriated octanoyl chloride (0.54 g) and used to acylate 4-bromobiphenyl under the conditions described by Gray and Mosley[9] to give a mixture of 4-bromo-4′-octanoylbiphenyl and 4-bromo-4′-(6,6-d_2-octanoyl)-biphenyl (1.1 g, 46%, m.p. 99–101 °C, lit. 104–105 °C[13]). Reduction of this material with lithium aluminium deuteride/aluminium trichloride[9] gave a mixture of 4-bromo-4′-(1,1-d_2-octyl)-biphenyl and 4-bromo-4′-(1,1,6,6-d_4-octyl)-biphenyl which was recrystallised from ethanol (0.90 g, 85%, m.p. 87–100 °C, lit. 87–9 °C[13]). Treatment with cuprous cyanide in *N*-methyl pyrrolidone gave a mixture of 4-cyano-4′-(1,1-d_2-octyl)-biphenyl and 4-cyano-4′-(1,1,6,6-d_4-octyl)-biphenyl (1.06 g crude). Chromatography on silica (eluting with chloroform), followed by bulb distillation and repeated chromatography on kieselgel (eluting with chloroform/petrol mixtures) and further bulb distillation gave a sample of the biphenyl (0.43 g, 57%) with transition temperatures T_{S_AN} 26 °C, T_{NI} 33 °C (literature values[14] for undeuteriated 4-cyano-4′-octylbiphenyl T_{S_AN} 33.6 °C, T_{NI} 40.6 °C).

4-Cyano-4′-(1,1,5,5-d_4-octyl)-biphenyl

Was prepared in a similar manner starting from propyl iodide and glutaric acid. The final product which was a mixture of 4-cyano-4′-(1,1-d_2-octyl)-biphenyl and 4-cyano-4′-(1,1,5,5-d_4-octyl)-biphenyl had T_{S_AN} 24 °C, T_{NI} 35 °C.

4-Cyano-4′-(d_{17}-octyl)-biphenyl

Was synthesised by Professor G. W. Gray and Dr. A. Mosley of the University of Hull[14] and had transition temperatures T_{S_AN} 33.0 °C, T_{NI} 39.1 °C.

The transition temperatures for the two mixtures of selectively chain-deuteriated materials are lower than would be anticipated bearing in mind that the transition temperatures for chain-predeuteriated and fully hydrogenous 4-cyano-4′-octylbiphenyl are only slightly different. However, all the materials prepared appeared pure by ^{1}H nmr spectroscopy and in most cases they were also shown to give satisfactory mass spectra.

Acknowledgments

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