NMR Studies of the Molecular Dynamics of Biphenylcyclohexans BCH52 and BCH5CN Liquid Crystals

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Abstract

The motional behaviour of proton has been investigated in the liquid crystalline BCH52 and BCH5CN compounds using 90 MHz NMR continuous and pulse techniques. The continuous spectra showed magnetic transitions at various regions. The reorientation of the terminal CH_3 group of the pentyl chain have been observed from the temperature dependence of proton spin-lattice relaxation time in the low temperature region. In the high temperature region, molecular motions are observed at lower activation energy value in BCH5CN than in BCH52. Values of relaxation parameters indicate that the nematic phase in BCH5CN has a smectic-like ordering.

INTRODUCTION

The biphenylcyclohexans (BCH's) were first reported by Eidenschink[1] and Eidenschink et.al.[2]. The diamagnetic properties[3], the densities and the optical properties[4], and the thermal data[5] of a number of these compounds have been reported. Haase et.al.[6] have determined the X-ray structures of some of BCH's in the solid and liquid crystalline states. Recently, Ibrahim[7] has studied the nematogen structures of the halogen and peseudo halogen-derivatives of BCH, as well as the binary mixture of BCH5CN and BCH52 by X-ray diffraction method.

Proton spin-lattice relaxation mechanisms in nematic liquid crystals seem to be reasonably well understood[8], while little is known about the nature of the spin-lattice processes in the various smectic phases[9]. Three types of relaxation mechanisms are dominated in the smectic phase, namely, order fluctuations, self-diffusion and molecular rotation[10]. The molecular reorientation has the usual BPP type[11], and the relaxation rate can be written as[12],

$$\frac{1}{T_1} = C \left[\frac{\tau_c}{1+(\omega\tau_c)^2} + \frac{\tau_c}{1+4(\omega\tau_c)^2} \right] \quad , \qquad (1)$$

where T_1 is the spin-lattice relaxation time, ω is the larmor frequency and τ_c is the correlation time which is given by,

$$\tau_c = \tau_o \, e^{Ea/RT}.$$

τ_o is the preexponential factor, E_a is the activation energy, R is the gas constant and T is the absolute temperature. The dipole coupling constant C can be written as $C = \varepsilon C'$, where ε is the parameter measuring the anisotropy[8] of the local reorientations. The constant C' equals,

$$C' = \frac{9}{8} \, \gamma^4 \, \hbar^2 \, \frac{1}{15} \sum_k U_k \, (3 \, l_k^2 - 1)^2 / r_k^6 \qquad (2)$$

where γ is the proton magnetogyric ratio, $\hbar$ is defined as $h/2\pi$, h being Planck's constant, U_k is the relative weight of protons belonging to the kth group and l_k is the cosine of the angle between the internuclear vector r_k of kth group and the long molecular axis. For the rotation of three-proton group (CH_3) about C_3-axis in powdered samples, O'Reilly and Tsung[12] have calculated the constant C in equation (1) to be

$$C = \frac{9 \, \gamma^4 \, \hbar^2}{20 \, r^6}$$

Moreover, the minimum relaxation time can be obtained at which $\omega\tau_c = 0.616$ as,

$$T_{1min} = \frac{20 \; r^6 \omega}{9 \; \gamma^4 \; \hbar^2 \; (1.42)} \qquad (3)$$

In the present work, the molecular relaxation in BCH5CN and BCH52 are investigated by measuring the temperature dependence of spin-lattice relaxation time T_1. Whereas, the relaxation parameters are deduced by fitting the experimental data to equation (1).

Experimental

The following are the compounds which have been studied, BCH52 ($X = C_2H_5$) and BCH5CN ($X = CN$) samples as obtained from E.Merck, Darmstadt, Germany were used without further purification. A powder sample was mounted in a sealed glass tube (8 mm in diameter) in a Bruker SXP 4-100 NMR pulse spectrometer at 90 MHz. The relaxation time T_1 has been measured using π-τ-$\pi/2$ pulse sequence over a temperature range from 400 K to 130 K, The temperature were set and stabilized with an accuracy of ± 1 K using nitrogen gas flow unit. Single exponential decay of magnetization was observed in the considered temperature range allowed the determination of T_1. Proton-NMR spectra were recorded using a Varian EM-390 90 MHz spectrometer (at Alex. Univ.) for the dissolved samples in CCl_4 solution at 293 K.

Results and Discussion

The spectra Figure (1) showed magnetic transitions at various regions. The peak at $\delta = 0.87$ ppm is attributed to the methyl protons of both the pentyl and the ethyl groups in compound BCH52 and of the pentyl group of compound BCH5CN. The carful study of the peak shows signs of multiplicity and a triplet is observed. A stronger peak at $\delta = 1.26$ ppm is attributed to the methylene groups. The integral ratio is corresponding to the number of methylene protons in each compound. The cyclohexyl protons resonated at $\delta = 1.85$ ppm. The characteristic pattern of the restricted rotation was evident and the perturbation of the adjacent phenyl group showed a week multiplet around $\delta = 2.4$ ppm. The spectra of BCH52 Figure (1-a) showed a quartet at $\delta = 2.63$ ppm attributed to the methylene protons of the ethyl group, thus obscuring the weak multiplet at $\delta = 2.4$ ppm. The aromatic protons appeared in the low field region as two doublets for compound BCH52 Figure (1-a) at $\delta = 7.25$ ppm,

whereas those of BCH5CN appeared as a multiplet Figure (1-b) at $\delta = 7.33$ ppm. The less multiplicity of the peak arising from BCH52 around $\delta = 7.25$ ppm could be attributed to chemical equivalence of the biphenyl protons.
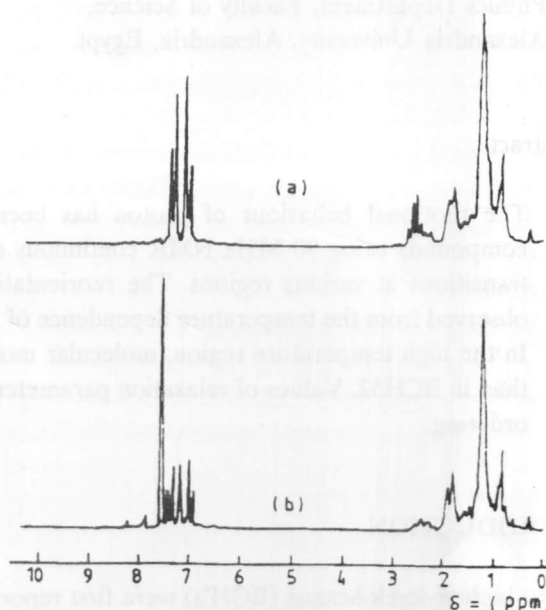

Figure 1. Proton spectrum at 293 K for BCH52 (a) and BCH5CN (b), dissolved in CCl_4.

The T_1 data for BCH52 and BCH5CN as a function of temperature are plotted in Figures (2) and (3), respectively. These figures show a single T_1 minimum in the low temperature regions. The fitting of these data yields the relaxation parameters, see Table (1), and the number of protons are found to be equal to 3. This suggests that we have only seen the reorientation relaxation of the terminal CH_3 group in the pentyl chain, assuming that the magnetization of aliphatic protons spreads along the alkyl chain according to the fast spin-diffusion case. Moreover, the free induction decay remains typical for solids when the temperature increases to the liquid crystalline state.

Table (1). Proton Spin-lattice relation parameters in solid and liquid crystalline states for BCH52 and BCH5CN.

sample	Liquid crystalline state						CH_3 motion		
	τ_0 (s)	T_{1min} (ms)	T^* (K)	E_a (kcal/mol)	C' (s⁻²)	ϵ	E_a (kcal/mol)	T_{1min} (ms)	T^* (K)
BCH52	0.2×10^{-13}	660	317	6.85	3.9×10^7	15	2.1	354	148
BCH5CN	5.8×10^{-13}	660	360	5.8	4.7×10^7	12.7	1.27	580	172

$$T_{1min} = \frac{20 \; r^6 \omega}{9 \; \gamma^4 \; \hbar^2 \; (1.42)} \qquad (3)$$

In the present work, the molecular relaxation in BCH5CN and BCH52 are investigated by measuring the temperature dependence of spin-lattice relaxation time T_1. Whereas, the relaxation parameters are deduced by fitting the experimental data to equation (1).

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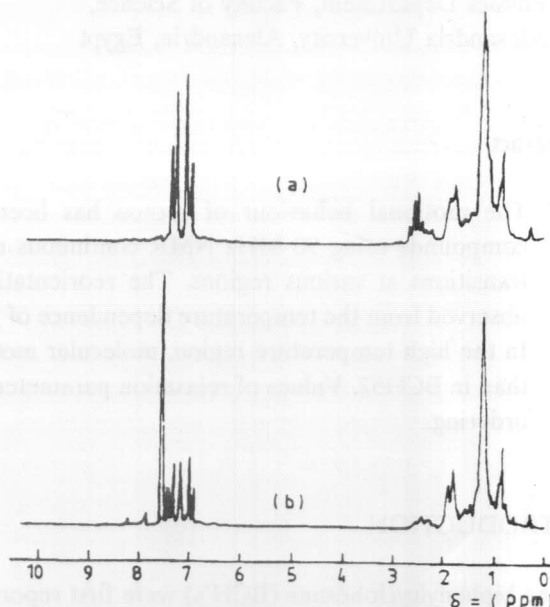Figure 1. Proton spectrum at 293 K for BCH52 (a) and BCH5CN (b), dissolved in CCl_4.

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