

Deuterium and Carbon-13 NMR of the Solid and Discotic Phases of Three Benzenehexa-*n*-alkanoates

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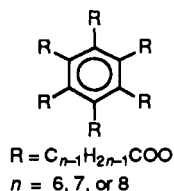
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Deuterium and carbon-13 NMR measurements are reported of the solid and discotic phases of three homologues of the benzenehexa-*n*-alkanoate series, BHA_{*n*}, with *n* (the number of carbons in the alkanoate chains) equal to 6, 7, and 8. All compounds show a high degree of solid polymorphism, and the two higher homologues exhibit a discotic mesophase. The transition between the solid phases is associated with an increase of disorder in the side chains reflecting the increase in the number of populated conformational states. Contrary to a previous interpretation the interconversion rate between the conformers is fast on the NMR time scale and the evolution of the spectrum with temperature mainly reflects changes in the distribution of the populations. Line shape and relaxation measurements are used to estimate relative populations and interconversion rates between different chain conformations. In all solid phases there is no reorientation of the benzene core on the NMR time scale except for the high-temperature phase (I) of benzenehexa-*n*-hexanoate (BHA6). The dynamic NMR features of this phase are very similar to those of the discotic mesophases of benzenehexa-*n*-heptanoate and benzenehexa-*n*-octanoate (BHA7 and BHA8) and are consistent with fast overall molecular reorientation. On this basis, phase I of BHA6 is classified as a discotic mesophase.

Introduction

Thermotropic liquid crystals often exhibit a high degree of polymorphism in the solid state. This polymorphism has been attributed to successive "melting" of the aliphatic chains in the mesogenic molecules and appears to serve as a preamble for the formation of a mesophase.¹ The phenomenon was extensively investigated in several discotic liquid crystals,^{2–5} including ester- and/or ether-substituted benzene and triphenylene, using heat capacity measurements, as well as Raman, infrared, and far-infrared spectroscopy.^{6–11} These techniques provide mainly information about the average disorder in the side chains, however, conclusions regarding the detailed behavior of particular molecular segments remain a matter of interpretation and speculation. In contrast, NMR spectroscopy^{12–15} may under favorable conditions, which often require specific isotopic labeling, provide detailed dynamic information about different parts of the molecules. Such an analysis was attempted a few years ago by some of us using carbon-13 and deuterium NMR of specifically labeled benzenehexa-*n*-hexanoate, BHA6.¹⁵ This compound although claimed to be not mesogenic in the pure state exhibits a solid polymorphism very similar to that of its neighboring homologues, benzenehexa-*n*-heptanoate (BHA7) and benzenehexa-*n*-octanoate (BHA8), which are mesogenic.^{16,17}



The initial purpose of the present work was to extend the previous NMR study¹⁵ of BHA6 to the higher homologues. For

that purpose two series of specifically labeled (with carbon-13 and deuterium) BHA7 and BHA8 were synthesized and their NMR spectra investigated in the solid phases. Despite the similarity of the thermodynamic properties the deuterium NMR spectra of BHA7 and BHA8 appeared in many respects quite different from those obtained earlier for BHA6. On checking for possible reasons for this discrepancy it soon transpired that several of the BHA6 spectra in the earlier work¹⁵ were recorded under saturation conditions (too short delays between successive acquisitions). This led to distorted spectra and consequently to erroneous interpretation of the line shapes. We therefore include in the present work a reinvestigation of the BHA6 homologue. The study contains measurements of the carboxyl and aromatic carbons, as well as of the side chain deuterons in all three homologues. Most detailed measurements were performed on the α and β deuterons of the side chains which limits the discussion to the motional properties of the segments closest to the aromatic core.

Over most of the temperature range of the solid phases of the BHA_{*n*} (*n* = 6, 7, or 8) homologues the deuterium NMR signals exhibit complex line shapes consisting of a superposition of a number of motionally averaged subspectra. These results are interpreted in terms of a jump model in which the aliphatic chains in the solid phases rapidly switch between two (or more) conformations. The situation is complicated by the fact that there appear to be several inequivalent side chains associated either with the same or with different molecules. The rates of the conformational isomerization are fast compared with the quadrupolar splitting, and except at very low temperatures the spectral line shapes are essentially motionally narrowed. Nevertheless, information about the dynamics of the isomerization can still be obtained from the longitudinal relaxation rates of the carbon-13 and deuterium signals. The approach used in the present work is similar to that recently employed by Torchia and co-workers¹⁸ in their study on the side chain dynamics in crystalline methionine. Background theory relevant to the interpretation of the relaxation and line shape measurements may also be found in refs 19–24.

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TABLE I: Phase Transition Temperatures (in °C) and (in Parentheses) the Associated Enthalpies (ΔH , in kJ/mol) and Entropies (ΔS , in J/(mol K)) in the Three BHAn Homologues Studied in the Present Work^a

	IV \rightarrow III	III \rightarrow II	II \rightarrow I	I \rightarrow M	M \rightarrow iso
BHA6	-21.57 (25.66/ 102.67)	-18.31 (12.27/ 46.11)	75.12 (16.26/ 46.68)		95.59 (33.5/ 90.86)
BHA7	-144.15 (1.12/ 8.46)	-50.35 (11.5/ 50.44) ^b	-42.34	80.64 (32.21/ 91.08)	86.13 (21.54/ 59.93)
BHA8			28.74 (48.96/ 164.01)	81.95 (46.07/ 129.81)	83.94 (19.22/ 53.77)

^a The results for BHA6, BHA7, and BHA8 are respectively from refs 6, 7, and 8. The reported transition temperatures were converted to °C by subtracting 273.15. ^b Sums for the III \rightarrow II and II \rightarrow I transitions.

The phase diagrams of the three BHAn homologues studied in the present work are reproduced in Table I, which also gives the corresponding enthalpies and entropies associated with the various transitions. As already indicated pure BHA6 is not mesogenic, but its solid polymorphism is quite similar to that of BHA7 and BHA8. It is shown below that the high-temperature phase I of BHA6 is in fact highly disordered, and on the molecular level as reflected in the NMR spectra it behaves very similar to the mesophases of the two higher homologues.

Experimental Section

Specifically deuterated BHAn ($n = 6, 7$, or 8) homologues were prepared using methods described earlier.^{15,25} The compounds prepared include BHAn deuterated at the α and β methylenes and at most of the other carbons of the aliphatic side chains (BHAn- αd_2 , BHAn- βd_2 , etc.). Also prepared were BHAn homologues enriched, or depleted, in carbon-13 at the carboxyl group by esterification of hexahydroxybenzene with the appropriate alkanoyl chlorides. The latter were prepared²⁵ by carboxylation of the corresponding ($n-1$) alkylmagnesium bromides with carbon dioxide enriched to 95 atom % or depleted to less than 0.1 atom % ^{13}C .

Nuclear magnetic resonance measurements were performed on a Bruker CXP300 spectrometer operating at 46.07 MHz and 75.46 MHz for deuterium and carbon-13, respectively. High-power probes were used with 5-mm solenoid coils. The deuterium spectra were recorded using the quadrupole echo method (90° pulse width, 3 μs ; time interval between the 90° pulses, 20 μs ; recycle times ranging between 0.3 and 4 s). Longitudinal relaxation rates of deuterons were measured by the inversion recovery method using quadrupole echo for the signal detection and composite π -pulses²⁶ for the inversion. The carbon-13 spectra were recorded under low-power broad band proton decoupling using a 90°–180° echo sequence (90° pulse width, 3 μs ; time interval between the 90° and 180° pulse, 20 μs ; recycle times, 5–250 s). The carbon T_1 relaxation rates were measured by the

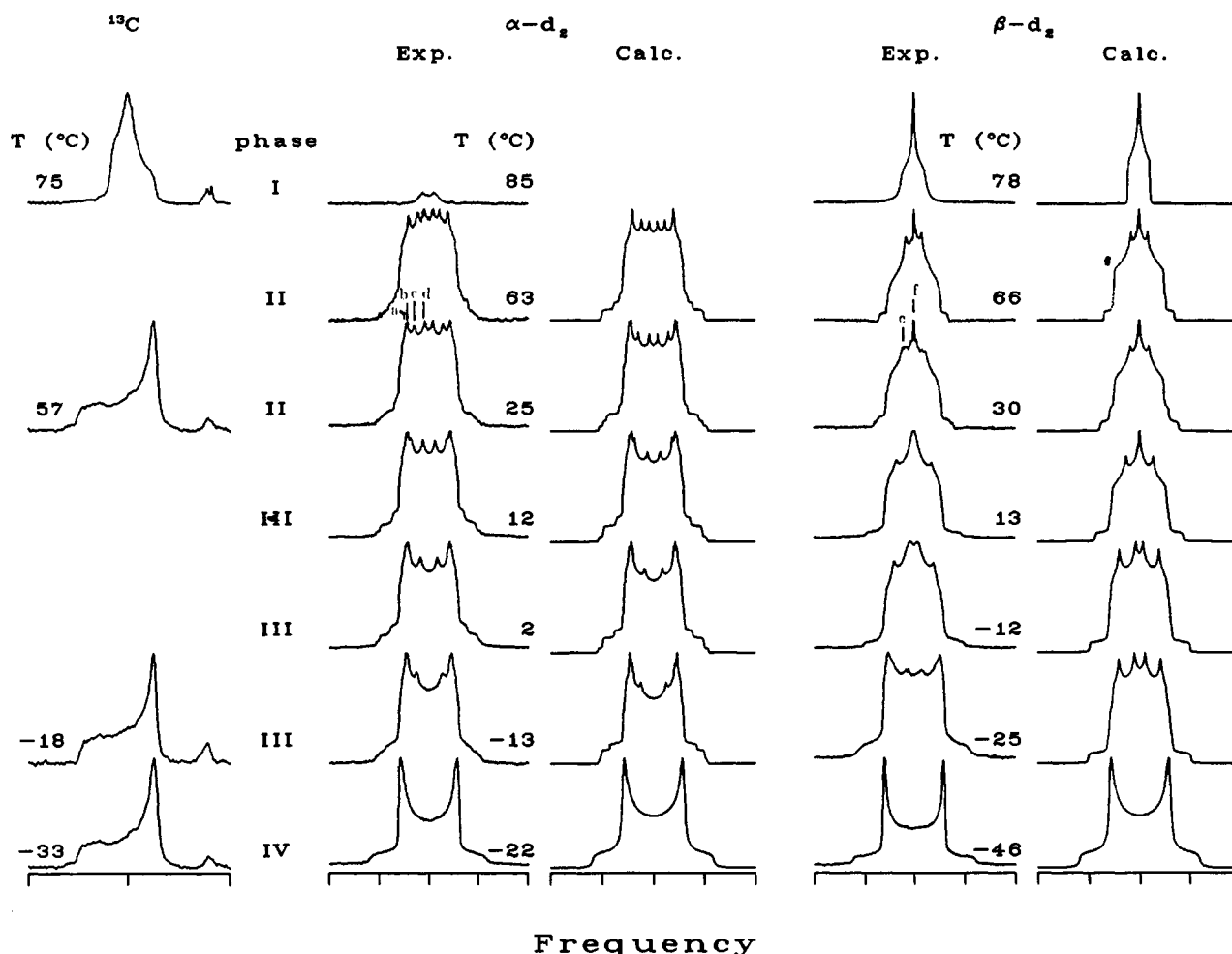


Figure 1. Carbon-13 and deuterium NMR spectra in the various solid phases of BHA6. The first column shows carbon-13 spectra of BHA6 labeled with ^{13}C in the carboxyl groups. The second and fourth columns show respectively experimental deuterium spectra of BHA6- αd_2 and BHA6- βd_2 , while the third and fifth columns show the corresponding simulated spectra. The parameters used in the simulations (in terms of S^2 and η , and using $\nu_Q = 119$ kHz) are shown in Figures 3 and 5 for respectively the α and β deuterons. The experimental spectrum of BHA6- αd_2 in phase I is recorded with the same gain and number of accumulations as in phase II, emphasizing the "disappearance" of the signal in phase I. The overall frequency scales are 30 kHz for the carbon-13 and 400 kHz for the deuterium spectra.

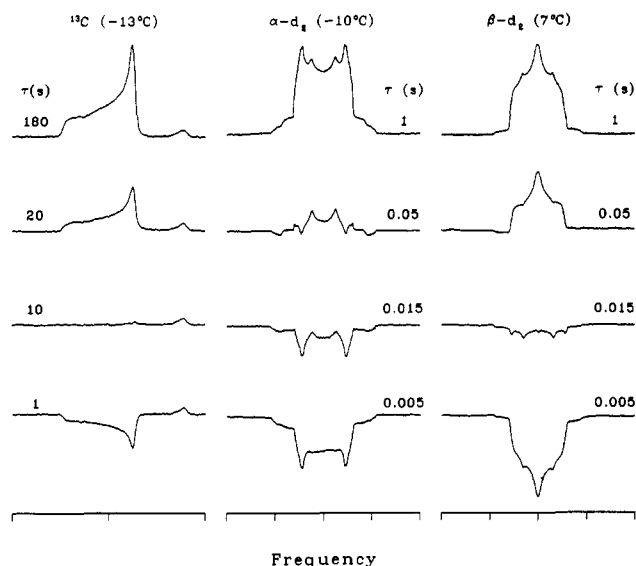


Figure 2. Partially relaxed NMR spectra of the carboxyl carbon (left), α deuterons (middle), and β deuterons (right) of BHA6 obtained by inversion recovery experiments. The spectra were recorded in phase III at the indicated temperatures and recovery delay times. The overall frequency scales are 30 kHz for the carbon-13 and 400 kHz for the deuterium spectra.

inversion recovery method using a 90° – 180° echo sequence for the signal detection.

Results and Discussion

A. BHA6. A.1. General Discussion of the NMR Spectra. Experimental carbon-13 spectra of the carboxyl group and deuterium spectra of the α - and β -deuterated isotopomers in the various solid phases of BHA6 are shown in Figure 1. The deuterium spectra of both the α and β deuterons in the low-temperature phase IV exhibit a Pake doublet with full splitting of $2\nu_Q = 210$ – 240 kHz, characteristic of a rigid system. Similar spectra are also obtained in this phase for the γ and δ deuterons (not shown). The deuterium spectrum of the end methyl group also appears as a Pake doublet but with an overall splitting of only 72 kHz indicating rapid reorientation about the C_3 axis (even at the lowest temperature measured of -70°C). Since the chains are rigid we must conclude that the carbon-13 spectrum of the carboxyl group in this phase also corresponds to a rigid state. Its spectrum corresponds to an axially symmetric chemical shift tensor with parameters (taking $\sigma_{\text{iso}} = 170.4$ ppm),¹³ $\sigma_\perp = 124.3$ ppm and $\sigma_\parallel = 262.6$ ppm. The axial symmetry of the tensor is not expected from the structure of the carboxyl group and must be considered accidental. However, the result for σ_\parallel is similar to the values measured for the low-field principal component observed for other carboxylic esters and σ_\perp is very close to the average of the two high-field components.²⁷ In analogy with these results we identify the parallel component of the chemical shift tensor with the perpendicular to the OC(O) plane of the carboxyl group.

On heating to phases III and II the carbon spectrum remains essentially unchanged. This indicates that in these phases no overall molecular reorientation and no conformational changes involving the carboxyl groups take place. (A 180° flip of the carboxyl group about σ_\perp , and with it the whole chain, can be ruled out as highly unlikely.) In contrast, the spectra of all other deuterons in the side chains undergo a discontinuous change in the IV to III transition and to a lesser extent also in the III to II transition. The spectra in these phases cannot be interpreted in terms of a single deuterium species (for each methylene group) but are rather a superposition of a number of distinct subspectra whose parameters change with temperature. For the α deuterons this is clearly seen by the appearance of several shoulders in the

parallel and perpendicular regions of the spectrum and of several cusps in its center. In some of the spectra as many as four such cusps are discerned which we label a, b, c, and d, in order of decreasing splitting (see the trace at 25°C). This is more clearly seen in the inversion recovery spectra shown, e.g., in the middle column of Figure 2. We have therefore interpreted the spectra of the α deuterons in phases III and II in terms of a superposition of four, equally intense, subspectra and, by comparing with simulated line shapes, determined the principal values of their quadrupole tensors over the whole temperature range of these phases. Examples of such simulated spectra are shown in the third column of Figure 1. Several spectra were measured as a function of the time interval between the $\pi/2$ pulses in the quadrupole echo sequence. Only minor effects (other than reduction of the overall intensity) were observed with increasing this time interval, indicating that the spectra correspond essentially to the fast exchange limit.

A similar procedure applied to the β deuterons showed that their spectra can be interpreted in terms of just two species which we label e and f (see Figure 1). A set of inversion recovery spectra for these deuterons is shown in the right column of Figure 2. In this case the relaxation is very nearly isotropic but different for the two subspectra so that their separate line shapes can be obtained by choosing appropriate recovery times. Thus for a recovery time of 15 ms a pure (inverted) spectrum of the slow relaxing species (e) is obtained while the spectrum at 50 ms corresponds predominantly to the fast relaxing species (f).

The multitude of signals from the various methylene groups can be due to inequivalence of the geminal deuterons bonded to the same carbon and/or to different types of chains bonded to either the same or different benzene cores. Carbon-13 MAS spectra of the BHA7 and BHA8 homologues in the solid state exhibit multiplets for both the core and the various side chain carbons indicating a high degree of inequivalence.^{12,13} Since the crystal structure of these compounds is not known, we cannot trace its source, i.e., whether it is due to inequivalent molecules in the unit cell or to inequivalent side chains bonded to the same core. The analysis of the NMR results discussed below suggests that the four subspectra of the α methylene groups correspond to two types of inequivalent chains in a 1:1 ratio, each with two inequivalent geminal deuterons. In the β methylenes the geminal deuterons appear to be equivalent and the two subspectra reflect the two inequivalent types of side chains.

The transition from phase II to phase I exhibits strong discontinuities in both the carboxyl carbon and the deuterium spectra. In many respects the spectra in phase I are very similar to those observed in the mesophases of the BHA7 and BHA8 homologues. In fact we argue below that on the molecular level the dynamic state of phase I is qualitatively the same as in the mesophases of the higher homologues, particularly the presence of fast molecular reorientation about their symmetry axis. The main difference between the two appears to lie in the correlation times associated with the molecular reorientation. In the following sections we first discuss the NMR spectra observed in phases III and II of BHA6 (A.2) and follow with an analysis of the relaxation results in these phases (A.3). The NMR results in phase I are discussed separately in section A.4 and again in section B.2 in connection with the NMR spectra of the mesophases of the higher homologues (BHA7 and BHA8). The solid phases of these homologues are discussed in section B.1.

A.2. Analysis of the NMR Line Shapes in Phases III and II. Analysis of the deuterium NMR spectra of BHA6- αd_2 in phases III and II yields the motionally averaged principal quadrupole frequencies, $\bar{\nu}_i$, of the four species a–d. We define the principal components such that $|\bar{\nu}_z| > |\bar{\nu}_y| \geq |\bar{\nu}_x|$ and express them^{18,19} in terms of the asymmetry parameter η

$$\eta = \frac{|\bar{\nu}_y| - |\bar{\nu}_x|}{|\bar{\nu}_z|} \quad (1)$$

and the order parameter S

$$S^2 = \frac{2}{3} \frac{\bar{\nu}_x^2 + \bar{\nu}_y^2 + \bar{\nu}_z^2}{\nu_q^2} \quad (2)$$

where ν_q is the principal quadrupole interaction (assumed to be axially symmetric) of a deuteron in a rigid aliphatic C-D bond. The order parameter S reflects the averaging of the quadrupolar frequencies by the dynamic processes. From the low-temperature spectra in phase IV where the chains are rigid ($S = 1$) we obtain an average value of $\nu_q = 119$ kHz. Using this result, S^2 and η values, as plotted in Figure 3, were obtained. It may be seen that already in phase IV on increasing the temperature there is a slight reduction in S^2 of the α deuterons which we ascribe to local molecular librations. The transition to phase III is however strongly discontinuous, reflecting the large modulations of the quadrupole interaction due to isomerization between several chain conformations. Each of the four subspectra in this phase corresponds to a particular motionally averaged deuterium species undergoing fast conformational isomerism. For the sake of simplicity we shall assume in the discussion below that the isomerization process involves just two conformations with relative populations depending on temperature. Under these conditions in the fast jump limit the order parameter associated with a particular subspectrum is given by¹⁸

$$S^2 = 1 - 3P_1P_2 \sin^2 \theta_0 \quad (3)$$

where P_1 and P_2 are the fractional populations ($P_1 + P_2 = 1$) and θ_0 is the angle between the C-D bonds in the two conformers. There are thus two unknowns (θ_0 and P_1/P_2) to be determined for each subspectrum from a single measured parameter, S^2 . We therefore assume that the jump angles are constant within a phase and that the temperature dependence of S^2 is solely due to change in populations which are assumed to obey a Boltzmann law,

$$\frac{P_2}{P_1} = \frac{P_2}{1 - P_2} = A \exp\left(-\frac{\Delta E}{RT}\right) \quad (4)$$

so that

$$S^2 = 1 - \frac{3 \exp(-\Delta E/RT)}{[1 + A \exp(-\Delta E/RT)]^2} \sin^2 \theta_0 \quad (5)$$

where $\Delta E = E_2 - E_1$ is the energy difference between the two interconverting isomers and A is related to the entropy difference, $\Delta S = S_2 - S_1 = R \ln A$. The parameters ΔE and A are constant within a phase but may differ from one phase to another. The problem then reduces to determining just three parameters, θ_0 , ΔE , and A , in each of the phases III and II.

An idea about the possible range of θ_0 and $\Delta P = P_1 - P_2 = (1 - 4P_1P_2)^{1/2}$ can be obtained from plots of ΔP versus θ_0 (eq 3) for S^2 values consistent with those observed experimentally. Such plots are shown in Figure 4. Considering first the curve for $S^2 = 0.8$ which approximately corresponds to species a and b of the α deuterons, we note that this curve allows for a wide range of θ_0 and ΔP , including $\theta_0 \sim 30^\circ$ with $P_1 = P_2$ ($\Delta P = 0$) or $\theta_0 \sim 45^\circ$ with $P_1 \approx 5P_2$. For the c and d species, S^2 varies between 0.35 and 0.70 allowing a much narrower range for θ_0 and ΔP . The experimental S^2 results for these subspectra are more strongly temperature dependent and therefore more reliable values for ΔE , A , and θ_0 can be expected.

In preliminary attempts to analyze the data of Figure 3 we noticed that the results for the population ratios P_1/P_2 of species a and b are quite similar and likewise for species c and d. This suggests that each of these pairs of species corresponds to a pair of geminal α deuterons. In the final analysis we therefore assumed that P_2/P_1 and therefore ΔE and A for the species a and b are equal and likewise for the pair of species c and d. The values of θ_0 were however allowed to be different for each species. The

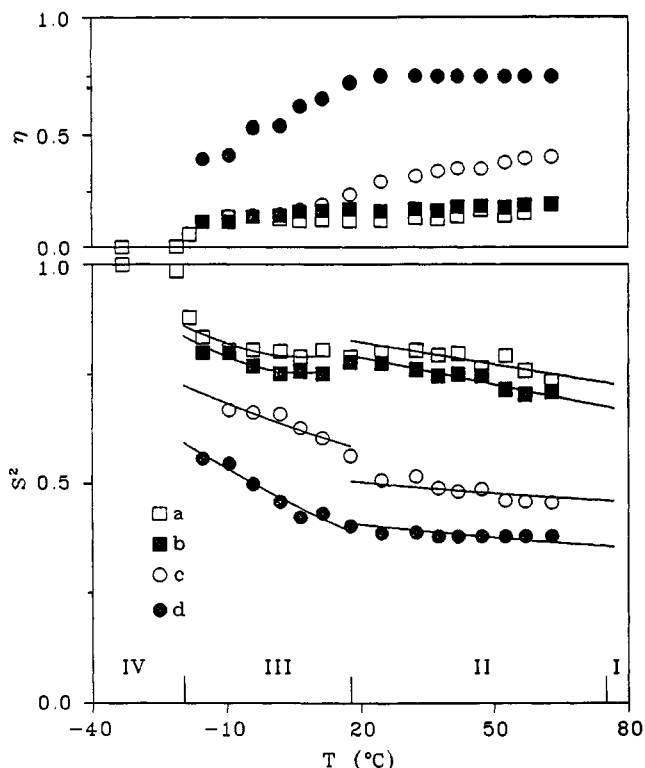


Figure 3. Derived values of η and S^2 (eqs 1 and 2) for the α deuterons in BHA6- αd_2 in phases IV, III, and II at different temperatures. The different symbols a, b, c, and d in phases III and II correspond to the four subspectra as indicated in Figure 1. The continuous curves are calculated from eq 5 using parameters given in Table II.

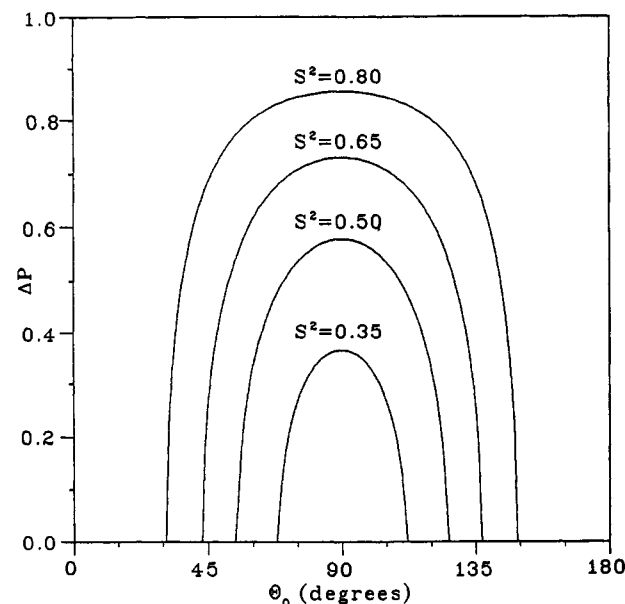


Figure 4. Plots of $\Delta P = P_1 - P_2$ versus θ_0 for a number of S^2 values realized in the experimental results of the subspectra a-d in Figure 3.

results derived from eq 5 using the nonlinear least squares fitting program, STEPIT,²⁸ for the various species in phase III and II are summarized in Table II. These parameters were used to calculate the continuous curves in Figure 3. The analysis thus suggests that in the solid phases III and II of BHA6 there are two inequivalent types of side chains which undergo fast but distinctly different modes of isomerization. Whether the two types of chains belong to the same molecule or to different molecules the NMR results do not tell. It is likely that the chains belong to the same molecule and are alternately oriented above and below the plane of the benzene core. Such a structure was proposed for the esters of triphenylene on the basis of X-ray

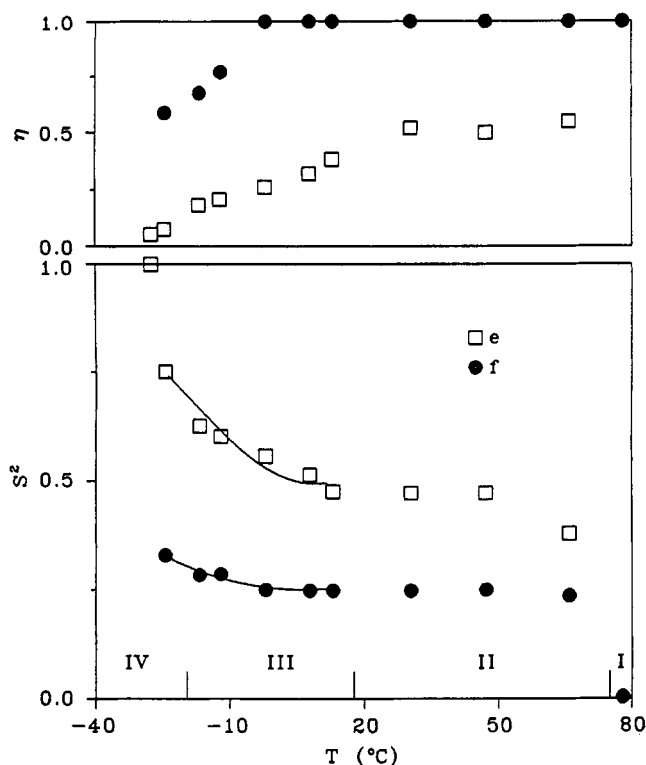


Figure 5. Same as in Figure 3 for the β deuterons of BHA6.

TABLE II: Best Fit Parameters of Eq 5 for the Various Subspectra of the α and β Deuterons of BHA6

deuterium	subspectra	phase	θ_0^a (deg)	ΔE (kJ/mol)	A
α	a, b	III	32, 35	30.0	2.5×10^{-6}
α	a, b	II	66, 90	8.1	0.44
α	c, d	III	55, 90	11.9	1.8×10^{-2}
α	c, d	II	66, 90	-3.1	1.31
β	e	III	55	30.4	2.4×10^{-6}
β	f	III	90	12.4	4.8×10^{-3}

^a The subspectra a and b and likewise c and d were fitted with common ΔE and A but different (right and left, respectively) θ_0 .

studies and SCF/CNDO calculations²⁹ and is also predicted by molecular mechanics calculations.^{30,31} A recent molecular dynamics simulation of BHA7 in the liquid phase also indicates alternation of the chain relative to the benzene ring.³² The appearance of four subspectra for the α deuterons in phases III and II is, however, still puzzling. Since we know that the carboxyl groups are rigid in these phases the only isomerization process that could modulate the quadrupole interaction of the α deuterons involves a reorientation about the $C^1 - C^\alpha$ bond (where C^1 is the carboxyl carbon). This should result in identical spectra for the geminal deuterons as both must be associated with the same angle θ_0 . The fact that this is not so indicates that an additional averaging process, e.g., fast local libration of the side chain takes place. Such a motion will in general reduce the quadrupole interaction of the two geminal deuterons to a different extent, depending on the detailed geometry of the libration.

As indicated in the previous section we interpret the spectra of the β deuterons of BHA6 (Figures 1 and 2) in terms of a 1:1 superposition due to two deuteron species e and f. For the β methylene the number of possible states that each deuteron may acquire is larger than that for the α deuterons since in addition to reorientation about the $C^1 - C^\alpha$ bond, reorientation about $C^\alpha - C^\beta$ also contributes to the averaging. Attempts to fit the results using eq 5 with common ΔE and A for both the e and f species (but different θ_0) were unsuccessful suggesting that the two species correspond to two different side chains. We therefore interpreted the two subspectra separately with different ΔE , A , and θ_0 , and the results for phase III are summarized in Figure 5 and Table

II. In principle we would expect to obtain four subspectra, as for the α deuterons, but apparently the increase in the conformational disorder for methylenes further out along the chains makes the geminal pairs more nearly equivalent and therefore indistinguishable by NMR. In fact, throughout the phases III and II all the methylenes (except the α 's) and methyl deuterons exhibit just two subspectra which we identify with the two types of inequivalent chains discussed in connection with the α deuterons. On the basis of the experimental NMR spectra alone we are unable to extract further information concerning the conformational equilibria of the alkyl chains, although additional information related to the isomerization dynamics can be derived from the longitudinal relaxation data as discussed in the next section.

A.3. Longitudinal Relaxation Rates and the Dynamics of the Conformational Isomerization. Longitudinal relaxation rates from about -40°C to the isotropic liquid point are shown in Figure 6a for the α and β deuterons of BHA6 as well as for the carboxyl carbons in the three BHA homologues (Figure 6b). Although relaxation rates in solids may be anisotropic, those for the carbon-13 and for the two species of the β deuterons were found to be fairly isotropic (Figure 2). For the four species of the α deuterons the relaxation appears to be anisotropic, but in practice we could only follow the evolution of the cusps of the various subspectra in the inversion recovery experiments. The deuteron T_1 for the species a and b were essentially identical and likewise for the subspectra c and d, and they are therefore plotted together in Figure 6a. An additional result of $T_1 = 0.73$ s not indicated in the figure was measured for the deuteron static spectrum in phase IV (-40°C). For both the carbon-13 and the deuteron signals there is a discontinuous drop in T_1 on going from phase IV to phase III which we associate with the onset of the chain isomerization processes. From the temperature dependence of the relaxation times within phases III and II we may conclude that both the carbon-13 and the deuteron relaxations correspond to the extreme fast motion limit, i.e., $\omega_0\tau \ll 1$ where ω_0 is the appropriate Larmor frequency and τ the correlation time. This conclusion is also consistent with the derived values for τ (see below). Convenient equations for nuclear relaxation rates due to modulation of various anisotropic interactions by jump processes in solids were given by Torchia and Szabo.²⁰

We consider first the relaxation of the deuterons which we assume to be dominated by modulation of the quadrupole interaction. For a two-site jump model in the extreme narrowing limit the expression for T_1 becomes

$$\frac{1}{T_1} (^2\text{H}) = \frac{4\pi^2\nu_q^2\tau}{3} (1 - S^2) f(\theta, \phi) \quad (6)$$

where θ and ϕ are the polar and azimuthal angles of the magnetic field with respect to the principal directions of the average quadrupole tensor, and $f(\theta, \phi) = 1 + 3 \sin^2 \theta \sin^2 \phi$. Thus for the cusps, $f(\theta, \phi) = 1$, and using the experimental T_1 and S^2 values (Figures 3 and 6) the correlation times for the isomerization process in phases III and II as plotted in Figure 7 are obtained. Note that despite the different relaxation rates of the two pairs of subspectra, the calculated correlation times are nearly the same due to the compensating effect of the $1 - S^2$ term. Since for the β deuterons the dynamic process involves more than just two sites we refrain from performing a similar analysis on their relaxation data. We note, however, that the relaxation rates of the e and f species differ by almost an order of magnitude (Figure 6a) supporting the inference that they belong to different alkyl chains.

The relaxation of the carboxyl carbon-13 in phases III and II must, according to our model, predominantly be due to modulation of the dipolar interaction with protons in the alkyl chains. Considering only the two α protons the relevant equation in the

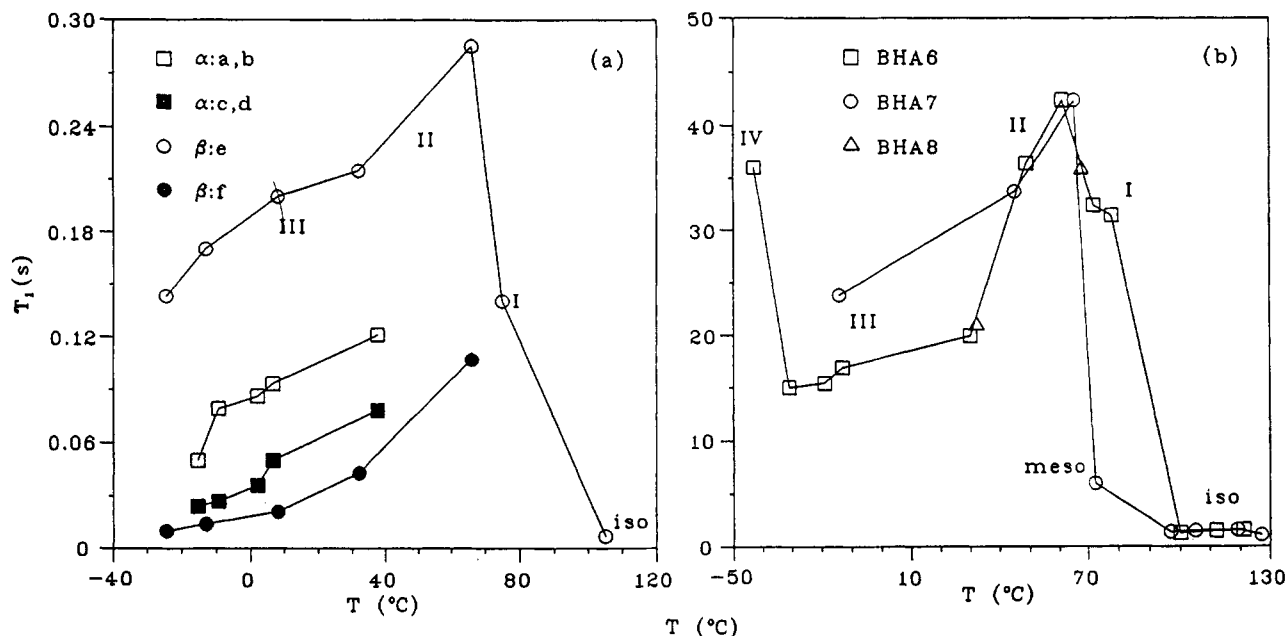


Figure 6. Longitudinal relaxation times of the α and β deuterons in BHA6 (a) and of the carboxyl carbon-13 in the various phases of BHA6, BHA7, and BHA8. The indications of the phases I–IV refer to the compound BHA6 (b). The continuous lines are drawn to guide the eye.

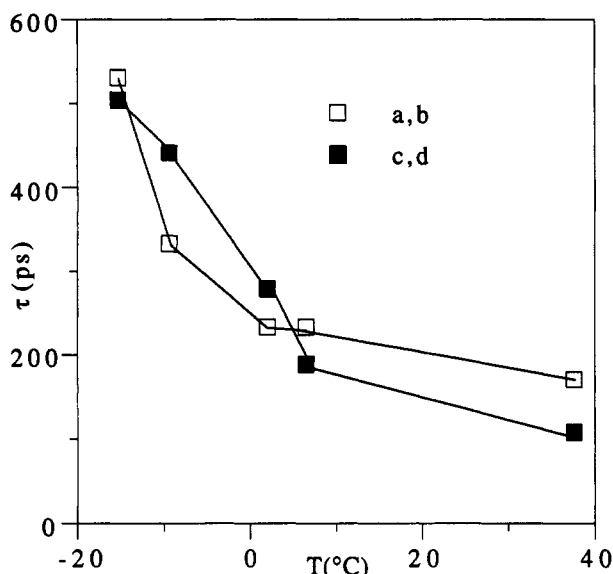


Figure 7. Correlation times for the chain isomerization calculated from the longitudinal relaxation rates of the α deuterons in phases III and II of BHA6.

extreme narrowing limit becomes

$$\frac{1}{T_1}({}^{13}\text{C}) = 2 \left[\frac{\hbar \gamma_{\text{H}} \gamma_{\text{C}}}{r_{\text{CH}}^3} \right]^2 \tau (1 - S^2) \quad (7)$$

where r_{CH} is the distance between the carboxyl carbon and the α hydrogens. Taking $r_{\text{CH}} = 2.15 \text{ \AA}$ yields correlation times within a factor of 2 from those derived from the deuterons (Figure 7), which considering the approximation used is quite satisfactory.

A.4. Phase I of BHA6. The transition from phase II to phase I is accompanied by sharp discontinuities in the deuterium and carbon-13 spectra: (i) The rigid carbon-13 signal of the carboxyl groups transforms into a much narrower biaxial spectrum with chemical shift components (assuming again $\sigma_{\text{iso}} = 170.4 \text{ ppm}$)¹³ $\sigma_{11} = 208.1 \text{ ppm}$, $\sigma_{22} = 178.8 \text{ ppm}$, $\sigma_{33} = 124.3 \text{ ppm}$, ($\eta = 0.64$). (ii) The spectrum of the α deuterons broadens to the extent that it becomes unobservable. (The narrow peak in the upper trace of Figure 1 corresponds to about $\sim 8\%$ of the signal intensity observed in the other phases and may be ascribed to natural abundance and/or accidentally labeled deuterons in other

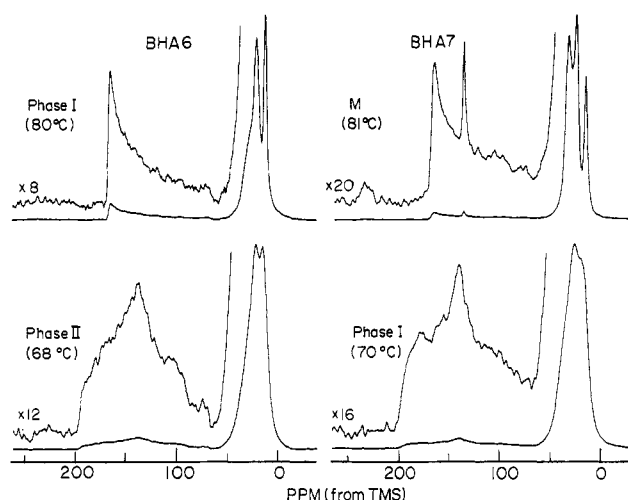


Figure 8. Carbon-13 NMR spectra in BHA6 (left) and BHA7 (right) with the carboxyl carbons depleted to less than 0.1 atom % ${}^{13}\text{C}$ at the indicated temperatures and phases. Delay times of 90 s were used, and the signals correspond to 2200–3300 accumulations. The enlarged part of the spectra represents the aromatic carbons.

methylene or methyl groups.) (iii) The resonances of the β , γ , and δ deuterons undergo strong narrowing compared to their overall width in phase II and appear as single asymmetric spectra. Finally, (iv) the relaxation rates of both the carboxyl carbon and the chain deuterons shorten relative to their values in the high-temperature region of phase II. Many of these features are similar to those found on transition from the solid to the mesophases in the higher homologues BHA7 and BHA8, suggesting similar motional properties in particular the setting in of fast reorientation about the molecular symmetry axes. A direct indication for this mode of motion can be obtained from the carbon-13 signal of the benzene core. However this signal strongly overlaps that of the carboxyl carbon hindering its study in normal (unenriched) compounds. Labeling of the benzene moiety with carbon-13 is extremely difficult and expensive. Fortunately, however, we had in stock carbon dioxide depleted in carbon-13 from which we were able to synthesize BHA6 and BHA7 with carboxyl groups containing more than 99.9% carbon-12. This allowed us to record the naturally abundant carbon-13 of the benzene ring without interference from the carboxyl signals. The spectra obtained for

TABLE III: Principal Components of the Aromatic Carbon-13 Chemical Shift Tensors in the Rigid and Rotor Phases of BHA6 and BHA7^a

compd (phase, temp (°C))	σ_{11} (ppm)	σ_{22} (ppm)	σ_{33} (ppm)	σ_{iso} (ppm)
BHA6 (phase I, 80)	168.9	168.9	67.4	135.0
BHA6 (phase II, 68)	197.0	139.2	68.9	135.0
BHA7 (M, 81)	168.0	168.0	69.1	135.0
BHA7 (phase I, 70)	196.7	139.3	69.1	135.0

^a For the calculations, the isotropic chemical shift, σ_{iso} , was taken as 135.0 ppm (relative to TMS).¹³

the aromatic carbons in phases I and II of BHA6 and in the mesophase and the high-temperature solid phase I of BHA7 are shown in Figure 8. It is evident that the signals in the mesophase of BHA7 and phase I of BHA6 are essentially identical and correspond to an axially symmetric chemical shift tensor. Likewise the signals in the solid phases I of BHA7 and II of BHA6 are similar and correspond to an asymmetric chemical shift tensor. The principal components of the various tensors are summarized in Table III. The values for the asymmetric tensors are in the range found for other substituted benzene derivatives²⁷ with σ_{11} and σ_{22} in the benzene ring and σ_{33} perpendicular to it. This indicates that in these phases the benzene core is rigid. The values for the symmetric tensors in phase I of BHA6 and in the mesophase of BHA7 are related to the corresponding asymmetric tensors in the rigid phases by $\sigma_{\perp} = 1/2(\sigma_{11} + \sigma_{22})$ and $\sigma_{\parallel} = \sigma_{33}$, reflecting the effect of fast reorientation of the benzene core about its symmetry axis.

The main difference between phase I of BHA6 and the mesophases of the higher homologues appears to lie in the correlation time τ_R for the molecular reorientation. Evidently τ_R

is considerably longer in phase I of BHA6 as reflected in the relaxation times and particularly in the "disappearance" of the signal due to the α deuterons. This effect corresponds to a situation where $2\pi\nu_Q\tau_R \sim 1$, i.e., $\tau_R \sim 1 \mu s$. The contribution of this motion to the carboxyl carbon T_1 is approximately given by

$$\frac{1}{T_1} = \frac{2}{15}[\omega_0(\sigma_{\parallel} - \sigma_{\perp})]^2(1 - S_{\sigma}^2) \frac{\tau_R}{1 + \omega_0^2\tau_R^2} \quad (8)$$

where

$$S_{\sigma}^2 = \frac{3}{2} \frac{\bar{\sigma}_x^2 + \bar{\sigma}_y^2 + \bar{\sigma}_z^2}{(\sigma_{\parallel} - \sigma_{\perp})^2} = 0.28 \quad (9)$$

Inserting $\tau_R = 1 \mu s$ gives $T_1 = 540 s$, which is much longer than that observed experimentally (Figure 6b). Clearly, other mechanisms, particularly dipolar interactions with the aliphatic protons, dominate the carboxyl carbon-13 relaxation in this phase. Using an analysis similar to that of Cole and Torchia²⁴ involving both chemical shift anisotropy and dipolar interaction as relaxation mechanisms (their eqs 2 and 3) yields a correlation time for the latter of $\tau \approx 80 ps$ (with an associated order parameter of 0.7). This value of τ is in agreement with the value of 90 ps obtained by extrapolation of the relaxation data of the α deuterons in Figure 7.

B. BHA7 and BHA8. B.1. NMR Spectra in the Solid Phases. The two mesogenic homologues BHA7 and BHA8 exhibit a similar solid polymorphism to that found in BHA6. In both compounds throughout the solid phases the carboxyl carbon-13 spectrum is identical to that found in phases IV, III, and II of BHA6 with essentially the same chemical shift parameters. The NMR spectra of the α and β deuterons in the solid phases of these

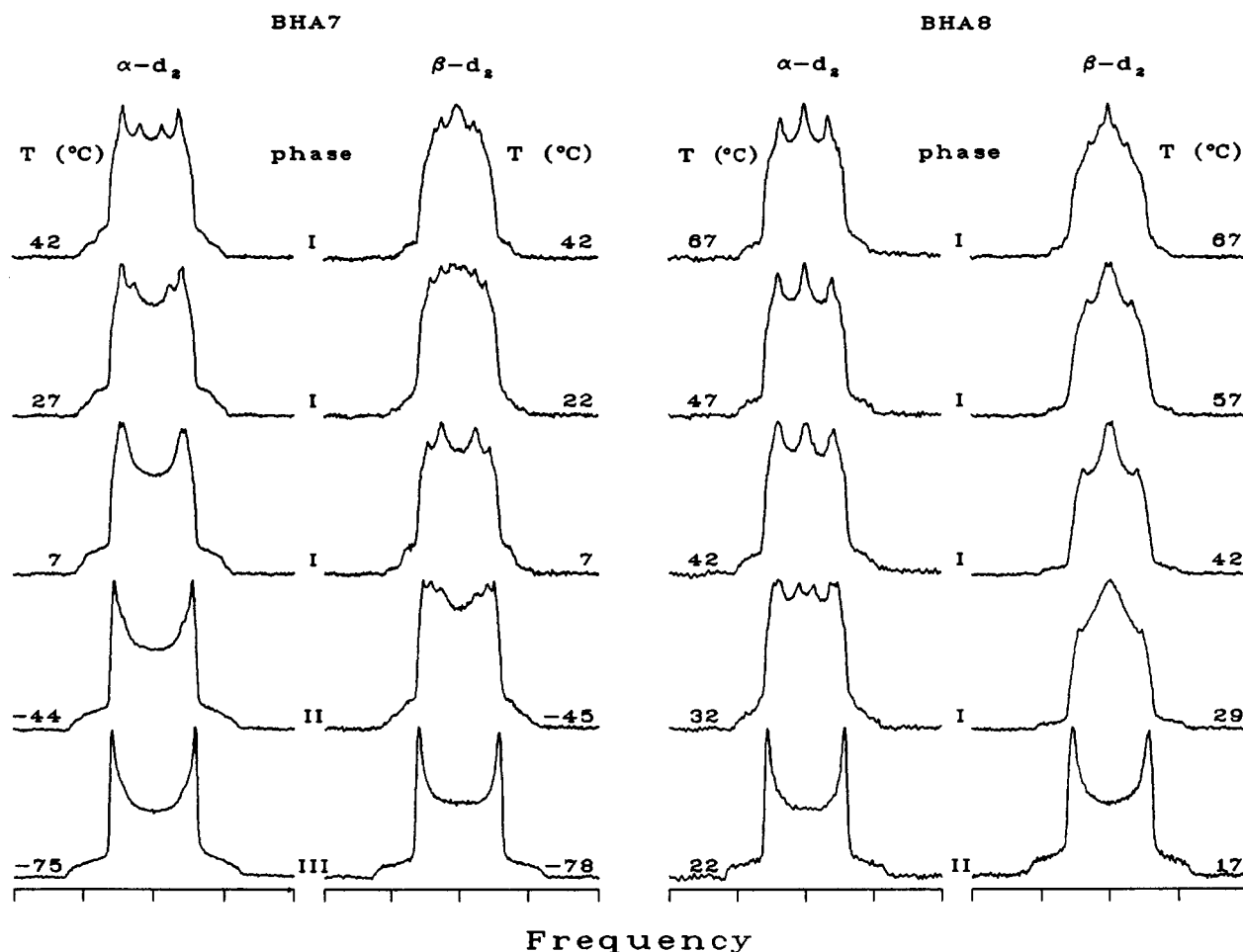


Figure 9. NMR spectra of the α and β deuterons in the solid phases of BHA7 and BHA8 at the indicated temperatures and phases.

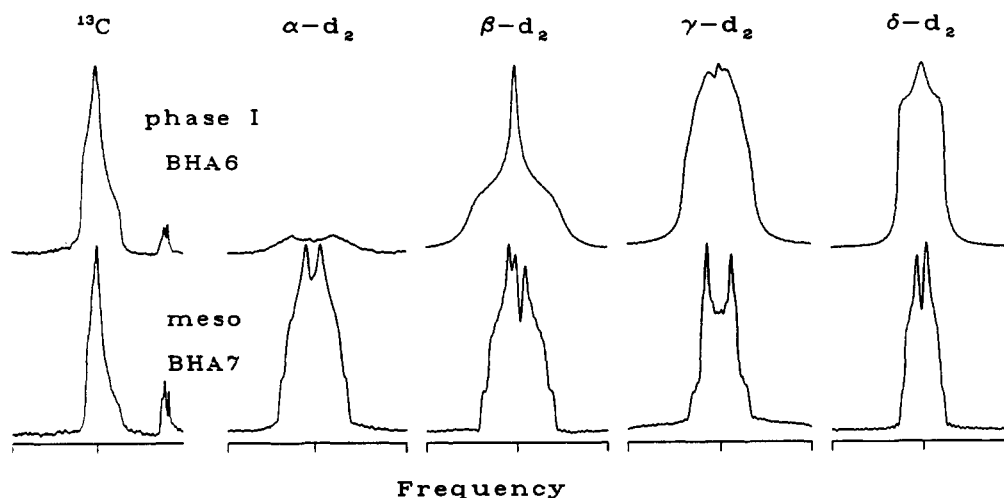


Figure 10. NMR spectra of the carboxyl carbon-13 and of the aliphatic deuterons in phase I of BHA6 and in the mesophase of BHA7.

TABLE IV: Principal Frequencies^a of the Deuterium Quadrupole and Carbon-13 Anisotropic Chemical Shift Tensors in the Mesophase of BHA7 and Phase I of BHA6

nucleus	BHA7 (mesophase)				BHA6 (phase I)			
	$\bar{\nu}_x$	$\bar{\nu}_y$	$\bar{\nu}_z$	η^b	$\bar{\nu}_x$	$\bar{\nu}_y$	$\bar{\nu}_z$	η^b
αd_2	-4.0	-12.8	16.8	0.52	not obsd			
βd_2	-5.0	-15.0	20.0	0.50	0	-22.1	22.1	1.0
γd_2	-6.6	-8.8	15.4	0.14	0	-34.0	34.0	~1.0
δd_2	-2.5	-8.5	11.0	0.55	0	-24.0	24.0	~1.0
carboxyl $^{13}\text{C}^c$	0.90	2.15	-3.05	0.41	0.63	2.85	-3.48	0.63
aromatic $^{13}\text{C}^c$	2.49	2.49	-4.97	0	2.55	2.55	-5.10	0

^a Frequencies are relative to the corresponding ν_{iso} in kHz. ^b Asymmetry parameter as defined in eq 1. ^c Calculated for a Larmor frequency of 75.46 MHz.

homologues are shown in Figure 9. For BHA7 no spectra for phase IV were recorded since the transition to this phase (-144°C) is not readily accessible with our spectrometer. The spectra in phase III at -75°C already exhibit motional effects which become gradually more pronounced throughout phase II and phase I resulting for both the α and β deuterons in two-component spectra. Close examination of the α deuteron spectra reveal that they can indeed better be fitted in terms of four species as was the case in the phases III and II of BHA6. For BHA8 there are two solid phases. In the low-temperature phase II the deuterium spectra are nearly static while the transition to phase I is discontinuous with motionally averaged spectra similar to those of phase I of BHA7.

B.2. Mesophases of BHA7 and BHA8 and the "Solid" Phase I of BHA6. The carbon-13 and deuterium spectra observed in the mesophases of BHA7 and BHA8 are essentially identical, and they are closely related to those observed for the "solid" phase I of BHA6. Examples of spectra for BHA6 and BHA7 are shown in Figures 8 and 10. Except for the aromatic carbon-13 (Figure 8) all other signals exhibit average asymmetric tensors typical of biaxial liquid crystals. Their average principal frequencies and asymmetry parameters are summarized in Table IV. The biaxiality of the BHA n mesophases was noted earlier both by X-ray³³ and by NMR³⁴ and reflects deviation from hexagonal order of the columns and/or tilting of the average molecular symmetry axes relative to the columnar axes. For rigid, axially symmetric molecules in a biaxial mesophase the asymmetry parameters of all tensors should be identical.³⁴ The fact that this is not the case for the results in Table IV most likely reflects the high disorder of the alkyl chains. The results for the aromatic carbons (Figure 8) are outstanding in that in the mesophase (and in phase I of BHA6) they correspond to an axially symmetric tensor with parameters almost exactly those expected for planar averaging of a benzene moiety. This indicates that except for the fast reorientation the symmetry axes of the benzene cores are highly ordered and undergo very little out of plane fluctuations.

Summary

There are two main conclusions concerning the polymorphism of the BHA n series that emerge from the present work. The first concerns the disorder of the side chains in the various solid phases, as reflected in the deuterium NMR spectra. In the earlier work¹⁵ on BHA6 these were interpreted as dynamic line shapes which evolve with temperature due to an increase in the interconversion rate between a fixed distribution of conformers. Here we have shown that the line shapes actually evolve due to changes with temperature of the conformational distribution, under conditions where the interconversion rates are fast on the NMR time scale. The increase of the interconversion rate with temperature does not affect the line shape but is reflected in the longitudinal relaxation times from which in fact estimates of correlation times are derived.

The second point concerns the classification of the phase I of BHA6. The carbon-13 and deuterium NMR spectra of this phase are very similar to those observed in the mesophase of BHA7 (and BHA8). The main difference between the two appears to be the lower mobility of the molecules in the former phase compared to that in the mesophases of the higher homologues. The classification of the high-temperature "solid" phase of BHA6 has already concerned Sorai et al.⁶ in their thermodynamic study of this compound. On one hand the X-ray and optical microscopy studies by Chandrasekhar and co-workers^{16,17,33} indicate a highly ordered crystalline structure. On the other hand the melting entropy of BHA6 is similar to the clearing entropies of the BHA7 and BHA8 mesophases and its magnitude is very small compared to the overall entropy changes in this compound (although not small enough to fulfill Timmerman's³⁵ criterion of crystalline plasticity). Clearly the transition between rigid molecular crystals, plastic crystals, and liquid crystals is not discrete and phase I of BHA6 occupies the gray area between a highly "fluid" solid and a highly viscous discotic liquid crystal.

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