Liquid Crystals

Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713926090

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To cite this Article Ternieden, Sabine , Muller, Diana and Muller, Klaus(1999) 'Substituted cyclohexanes in liquid crystalline solution: the molecular behaviour of bromocyclohexane', Liquid Crystals, 26: 5, 759 — 769

To link to this Article: DOI: 10.1080/026782999204859

URL: http://dx.doi.org/10.1080/026782999204859

Liquid Crystals, 1999, Vol. 26, No. 5, 759–769

Substituted cyclohexanes in liquid crystalline solution: the molecular behaviour of bromocyclohexane

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(*Received 6 August 1998; in final form 12 October 1998; accepted 20 October 1998*)

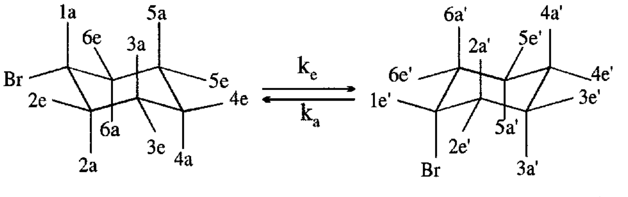
Selectively and perdeuteriated samples of bromocyclohexane, dissolved in a liquid crystalline solution, are studied by dynamic ^{2}H NMR spectroscopy. The analysis of variable temperature ^{2}H NMR spectra between 238 and 333 K, as well as 2D exchange NMR experiments provide the assignment of the various NMR lines in terms of the equatorial and axial bromocyclohexane conformers that exist in a dynamic equilibrium in relative amounts of about $p_e = 0.7$ and $p_a = 0.3$, respectively. By taking into account the molecular geometries of the two conformers (as obtained from molecular mechanics calculations) it is possible to derive the molecular order parameters of both species as a function of temperature. The observed temperature dependent lineshape changes can be attributed to the ring inversion process of the solutes, i.e. a mutual exchange of both conformers. The lineshape analysis yields an activation enthalpy for this internal process of $\Delta H = 44.5 \pm 4.5$ kJ mol^{-1}, in close agreement with earlier findings for isotropic solution.

1. Introduction

In recent years NMR spectroscopy has been extensively used for the characterization of liquid crystalline systems of quite different chemical structures [1–3]. For instance, NMR investigations have been reported for thermotropic low molecular mass and polymeric liquid crystals [4, 5], as well as for various lyotropic systems, such as biomembranes [6], etc. In this connection it has been shown that ^{2}H NMR spectroscopy, applied to selectively or partially deuteriated samples, is of particular use for the evaluation of the molecular features in such systems.

Apart from the studies that were focused on the properties of the molecules that form liquid crystalline phases [7–11], there was also an interest in the molecular behaviour of small guest molecules that were dissolved in liquid crystalline matrices [12–16]. Here, ^{1}H, ^{2}H or ^{13}C NMR techniques have been used to probe a great number of different guest molecules [17–21], extending from the rather rigid (e.g. benzene) [17, 19] to the more flexible compounds (e.g. *n*-alkanes, cycloalkanes) [22–27]. The application of dynamic NMR methods (lineshape studies, relaxation experiments, 2D exchange experiments) gave further access to the dynamics of the solutes in terms of overall (reorientational) and internal (conformational) motions. Recent ^{2}H NMR studies were addressed to the ordering behaviour and the kinetic parameters for the ring interconversion of deuteriated, non-polar cycloalkane derivatives, such as dimethylcyclohexanes and *cis*-decalin [24–26]. It could be shown that the liquid crystalline matrix has only a minor impact on the corresponding kinetic parameters; the activation energies and rate constants were thus found to be very close to those reported from earlier studies of isotropic solutions.

In the following report we describe a ^{2}H NMR investigation on partially and perdeuteriated bromocyclohexane, i.e. a cyclohexane derivative with a polar substituent, that was dissolved in a liquid crystalline solution. In contrast to the cycloalkanes mentioned above [25] (where the ring inversion took place between conformers of identical structure), now—see the scheme—two conformers of different structure and in different amounts are present, coupled with a greater complexity of the expected experimental ^{2}H NMR spectra.



In order to facilitate the assignment of the various ^{2}H NMR signals of the perdeuteriated sample, selectively deuteriated bromocyclohexanes are examined that have been further used during an independent study on bromocyclohexanes in thiourea inclusion compounds

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[28]. From the complete assignment of all NMR signals (exploiting also 2D exchange NMR experiments [27]) and with the knowledge of the molecular geometry from molecular mechanics calculations, it is possible to determine the molecular order parameters of both the axial and equatorial conformers. In addition, from the analysis of variable temperature 1D NMR spectra, the kinetic parameters of the ring interconversion process can be derived. It is also shown that during the synthesis of the specifically deuteriated bromocyclohexanes, additional by-products are formed which again can be characterized by the application of dynamic ^{2}H NMR spectroscopy.

2. Experimental

2.1. *Materials*

All chemicals for the synthesis were obtained from Aldrich Chemicals (Steinheim/Germany). Perdeuteriated bromocyclohexane was purchased from Merck, Sharpe and Dohme (Canada). During the present NMR study, the nematic mixture ZLI 2452 (Merck, Darmstadt) with a nematic range between – 40° and 110°C was used. For the NMR measurements solutions containing 3 to 5 wt % of deuteriated bromocyclohexane were sealed in 5 mm NMR tubes.

2.2. *Synthesis*

In this section we briefly describe the synthesis of the selectively deuteriated bromocyclohexanes used during the present work. Bromocyclohexane-*trans*-2-d$_1$ was obtained by bromination of cyclohexene. In all other cases, the preparation route involved reduction of the cyclohexanone to cyclohexanol, followed by the conversion of the cyclohexanol to bromocyclohexane.

2.2.1. *Bromocyclohexane-trans-2-d$_1$*

Bromocyclohexane-*trans*-2-d$_1$ was obtained by the reaction of cyclohexene with DBr [29]. The reaction mixture contained cyclohexene and the bromination reagent, which was formed by slowly adding a slight excess of D_2O to acetic anhydride and acetyl bromide in a molar ratio of 1:0.93:0.64. The reaction mixture was then kept at 50°C for 2 h. The mixture was worked up by shaking it with *n*-pentane. The organic layer was dried, evaporated and the product purified by distillation. The yield of pure bromocyclohexane-*trans*-2-d$_1$ was 49%.

2.2.2. *Cyclohexanone-2,2,6,6-d$_4$*

Cyclohexanone-2,2,6,6-d$_4$ was synthesized by basic H/D exchange of cyclohexanone in D_2O with a catalytic amount of Na_2CO_3 [30]. The mixture was stirred for 8 h at 80°C and washed with ether. The organic layer was dried and the solvent evaporated. The crude product was used as starting material for a further exchange cycle. After three cycles, the product was distilled in vacuum. The total yield was 55% with $\geqslant 95\%$ deuteriation at positions C-2 and C-6.

2.2.3. *Cyclohexanol-2,2,6,6-d$_4$*

Cyclohexanone-2,2,6,6-d$_4$ in ether was added slowly to an ethereal solution of $LiAlH_4$ under a nitrogen atmosphere. Afterwards, the mixture was heated under reflux for 8 h and stirred at room temperature for 12 h. After careful hydrolysis, the precipitate was dissolved in 5% H_2SO_4 and the mixture shaken with ether. The organic phase was separated, washed with $NaHCO_3$ solution, dried and evaporated. The product was distilled under vacuum (yield: 76%).

2.2.4. *Cyclohexanol-1-d$_1$*

Here the same procedure was applied as for cyclohexanol-2,2,6,6-d$_4$, except that the reaction was performed with cyclohexanone and $LiAlD_4$ instead of cyclohexanone-2,2,6,6-d$_4$ and $LiAlH_4$ (yield: 70%).

2.2.5. *Bromocyclohexane-1-d$_1$*

Bromine in methylene chloride was added slowly to triphenylphosphine in methylene chloride under a nitrogen atmosphere [31–34]. Cyclohexanol-d$_1$ was added and the mixture was stirred for 30 min under reflux. The solvent was evaporated; the precipitate was dissolved in *n*-hexane and purified by chromatography using a chloroform/*n*-hexane mixture (1:1) and distilled under vacuum. The yield was 66%. As discussed below, only 90% of the product was the desired bromocyclohexane-1-d$_1$. In addition, bromocyclohexane-*cis*-2-d$_1$ (relative amount: 10%) was formed due to the competing elimination/addition reaction.

2.2.6. *Bromocyclohexane-2,2,6,6-d$_4$*

Here, the same procedure was used as for the synthesis of bromocyclohexane-1-d$_1$. In the present case the reaction was performed with cyclohexanol-2,2,6,6-d$_4$ instead of cyclohexanol-1-d$_1$. Again, the product contained the deuteriated by-products, bromocyclohexane-1,3,3-d$_3$ and bromocyclohexane-*cis*-2,6,6-d$_3$. The overall yield was 40%.

2.2.7. *Further attempts at the synthesis of bromocyclohexane-1-d$_1$*

The final reaction step to give selectively deuteriated bromocyclohexane starting from cyclohexanol always gave undesired by-products due to the additional elimination/addition reactions. Further attempts (see table 1) were made to isolate pure bromocyclohexane-1-d$_1$, but it turned out that using the present reaction routes, it was not possible to suppress the additional by-products.

Table 1. Summary of the results from synthetic routes for the preparation of bromocyclohexane-1-d$_1$ from cyclohexanol-1-d$_1$.

Reagents	Reaction conditions	Solvent	Work up	Yield	Rel. amount of by-product[b]
NaBr, H_2SO_4	6 h at 130°C, 12 h at r.t., hydrolysis	H_2O	Vacuum-distillation	72%	approx. 15%[c]
Triphenylphosphine and Br_2 [31–34]	30 min reflux	CH_2Cl_2	Chromatography and vacuum-distillation	66%	10%
	30 min reflux	CCl_4	Chromatography	10%	approx. 20%[c]
	30 min reflux	DMF	Extraction	—	—
	30 min reflux, 12 h at r.t.	DMF	Extraction	—	—
Triphenylphosphine, Br_2 and imidazole	30 min reflux	CH_2Cl_2	Vaccum-distillation	5%	approx. 20%[c]
Triphenylphosphine, Br_2 and DMAP[a]	7 days at r.t.	CH_2Cl_2	Vacuum-distillation	10%	approx. 20%[c]
Triphenylphosphine and CBr_4	1 hr at r.t	THF	Vacuum-distillation	—	—
PBr_3 [45]	2 h in ice bath, 12 h at r.t.	—	Extraction	15%	approx. 20%[c]

[a] DMAP = *N*,*N*-dimethylaminopyridine.

[b] From addition/elimination reaction.

[c] Estimated from ^{13}C NMR spectra.

2.3. *NMR measurements*

All ^{2}H NMR measurements were performed using a Bruker CXP 300 spectrometer at 46.07 MHz, together with a Tecmag control unit (Houston, USA). ^{2}H NMR spectra were recorded with the quadrupole echo sequence $(\pi/2)_x - \tau_1 - (\pi/2)_y - \tau_2$ with a $(\pi/2)$ pulse length of 2 μs and a pulse spacing of $\tau_1 = \tau_2 = 20\,\mu s$. The number of scans varied between 256 and 2048. Recycle delays were chosen to be at least five times T_1, ranging from 1 to 5 s. 2D exchange NMR experiments were performed with a five pulse version of the original experiment [35] and a mixing time of 3 ms. Two separate data sets (cos- and sin-part) were collected, each with 128 t_1 values and a spectral width of 100 kHz in both dimensions, and were processed as described in the literature [36]. The sample temperature during the NMR experiments was controlled with a Bruker BVT 1000 unit with a temperature stability of ±1 K.

2.4. *Molecular mechanics calculations*

The molecular geometries of the bromocyclohexane conformers were determined from molecular mechanics calculations with the MM2 programme [37], implemented in the SYBYL software package (Tripos, St. Louis/USA). The resulting coordinates in the molecule fixed coordinate system x', y', z' are summarized in table 2. The coordinate system is chosen that the molecular x'-axis lies along the C-6/C-5 axis and the x', y'-plane is defined by C-5, C-6 and C-2 (figure 1). The quality of the derived molecular geometries has been checked by a comparison with structures derived by gas phase electron diffraction and FT microwave spectroscopy [38, 39]. It turned out that the theoretical and experimental geometries are in very good agreement. The deviations between the theoretical and experimental values are less than 0.02 Å (bond lengths) and 1° (bond angles).

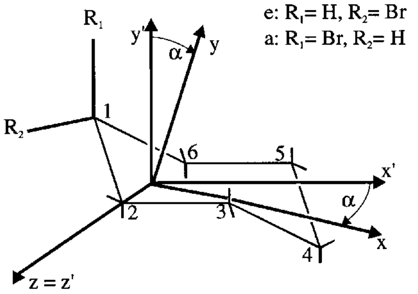

Figure 1. Definitions of coordinate systems used during the present study. The molecular-fixed system is given by x' and y' in the symmetry plane of the molecule; z' is perpendicular to the symmetry plane. The origin is halfway between carbons C-2 and C-6. The principal axis system x, y, z is related to the molecular-fixed system by a rotation about an angle α about $z' = z$.

2.5. *Simulations*

Lineshape simulations were made with a FORTRAN programme that accounts for an $I = 1$ spin-system undergoing two-site exchange. The ‘best fit’ spectra were obtained by visual inspection of the theoretical spectra and the experimental counterparts. The data processing of the experimental and simulated NMR

Table 2. Coordinates of the carbon and deuterium atoms in bromocyclohexane as derived from molecular mechanics calculations (MM2 force field [37]).

Equatorial conformer				Axial conformer			
Atom	x'/Å	y'/Å	z'/Å	Atom	x'/Å	y'/Å	z'/Å
C-1	– 0.542	0.697	0.000	C-1′	– 0.542	0.698	0.000
C-2	0.000	0.000	1.274	C-2′	0.000	0.000	1.274
C-3	1.551	0.000	1.274	C-3′	1.551	0.000	1.274
C-4	2.091	– 0.701	0.000	C-4′	2.092	– 0.700	0.000
C-5	1.551	0.000	– 1.274	C-5′	1.551	0.000	– 1.274
C-6	0.000	0.000	– 1.274	C-6′	0.000	0.000	– 1.274
D-1a	– 0.237	1.757	0.000	D-1e′	– 1.644	0.668	0.000
D-2a	– 0.369	– 1.038	1.308	D-2a′	– 0.368	– 1.039	1.308
D-2e	– 0.371	0.525	2.169	D-2e′	– 0.371	0.524	2.171
D-3a	1.919	1.039	1.308	D-3a′	1.919	1.039	1.308
D-3e	1.922	– 0.524	2.169	D-3e′	1.922	– 0.524	2.171
D-4a	1.778	– 1.758	0.000	D-4a′	1.779	– 1.757	0.000
D-4e	3.194	– 0.671	0.000	D-4e′	3.195	– 0.668	0.000
D-5a	1.919	1.039	– 1.308	D-5a′	1.919	1.039	– 1.308
D-5e	1.921	– 0.524	– 2.171	D-5e′	1.922	– 0.524	– 2.171
D-6a	– 0.369	– 1.038	– 1.308	D-6a′	– 0.368	– 1.039	– 1.309
D-6e	– 0.372	0.526	– 2.169	D-6e′	– 0.371	0.524	– 2.171

signals was performed on a SUN Sparc 10 work station using the NMRi and Sybyl software packages (Tripos, St. Louis/USA).

3. Results and discussion

Partially and perdeuriated bromocyclohexanes, dissolved in ZLI 2452, were studied by ^{2}H NMR spectroscopy. The major advantage of the deuteron nucleus stems from the fact that the magnetic interactions are governed by the dominant quadrupolar interaction, having its main interaction axis along the C–D bond. Experimental ^{2}H NMR spectra of deuteriated solutes in a nematic liquid crystalline phase can be understood by recalling the following: in a strong external magnetic field, the liquid crystalline domains along with the embedded solutes usually become aligned. In addition, fast (anisotropic) reorientational motions give rise to a reduction of the static quadrupolar splitting. As a result, ‘single crystal’-like spectra are observed where each inequivalent C–D bond is accompanied by a distinct signal doublet. The actual size of this doublet, the experimental quadrupolar splitting $2\langle \nu_Q \rangle$, depends on the molecular geometry and on the molecular order parameters, as discussed below.

3.1. ^{2}*H NMR experiments and spectral assignment*

To begin with, we report on the interpretation of the experimental ^{2}H NMR spectra, i.e. the assignment of the observed NMR signals, achieved by the consideration of various partially and perdeuteriated samples. In figure 2 representative ^{2}H NMR spectra are given for perdeuteriated bromocyclohexane-d$_{11}$ in ZLI 2452 as a function of temperature. It can be seen that the spectra consist of various lines due to different inequivalent deuterons. At 238 K, eight different quadrupolar splittings can be distinguished. At elevated temperatures the spectra exhibit distinct lineshape changes which have been attributed to the ring inversion process, analogously to previous observations for other substituted cyclohexanes [24–26].

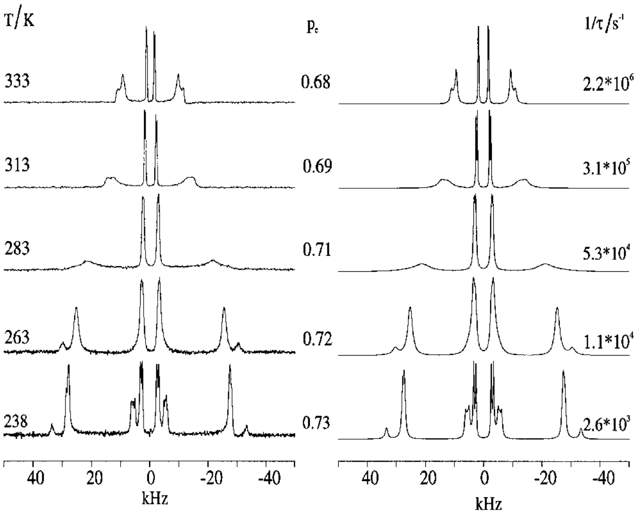

Figure 2. Experimental (left column) and simulated (right column) ^{2}H NMR spectra of bromocyclohexane-d$_{11}$ at various temperatures. The rate constants for the ring inversion process and the relative amounts of equatorial conformers are given in the figure.

Since bromocyclohexane has a C_s symmetry with a single symmetry element, namely a mirror plane, the expected number of quadrupolar splittings from inequivalent deuterons is reduced from eleven to seven with an intensity ratio of 1 : 2 : 2 : 2 : 2 : 1 : 1 (1 : 2a : 2e : 3a : 3e : 4a : 4e, a = axial, e = equatorial). This number of signals, however, is doubled due to the existence of axial and equatorial conformers. It should be noted that the latter holds only if a signal averaging due to the ring inversion process can be neglected, i.e. if this process occurs in the 'slow exchange' limit. In fact, the lineshape analysis revealed that this is the case for the NMR experiments performed at 238 K, as shown below. The experimental observation of only eight resolved splittings further implies that some of the inequivalent deuterons accidentally exhibit the same quadrupolar splittings or that several lines are unresolved due to the finite experimental linewidths. In summary, the ^{2}H NMR spectra of perdeuteriated bromocyclohexane, given in figure 2, appeared to be too complex for an unequivocal assignment of the different lines with respect to the two bromocyclohexane conformers. For this reason selectively deuteriated bromocyclohexanes—also used in an independent study on inclusion compounds [28]—have been examined, again using the nematic solvent ZLI 2452.

In figure 3 variable temperature ^{2}H NMR spectra of bromocyclohexane-*trans*-2-d_1 are given. At 238 K, two splittings of 5.4 and 11.9 kHz are observable that can be attributed to the signals from the equatorial and axial conformers. Moreover, the relative amounts of these species with $p_e = 0.73$ and $p_a = 0.27$ are identical with those from earlier studies for isotropic solutions [40, 41]. The observed lineshape changes at elevated temperatures again stem from the earlier mentioned ring inversion process. Eventually, at 333 K this motion reaches the 'fast exchange limit', as can be taken from the remaining single splitting of 3.2 kHz.

A second selectively deuteriated compound, bromocyclohexane-1-d_1, should exhibit similar spectral features to bromocyclohexane-*trans*-2-d_1, i.e. two splittings at low temperatures and a single exchange-averaged splitting at high temperatures. However, as shown in figure 4, at 333 K two splittings occur. It emerged that the signal of lower intensity (relative amount: 10%) belongs to bromocyclohexane-*cis*-2-d_1, a by-product from the bromination of cyclohexanol-1-d_1 that cannot be separated from the main product. This additional compound originates from an elimination/addition reaction that competes with the desired substitution reaction, where during the elimination step cyclohexene-1-d_1 is formed. HBr is then added by an anti-addition to the double bond which results in the formation of either bromocyclohexane-*cis*-2-d_1 or bromocyclohexane-1-d_1. In order to obtain pure bromocyclohexane-1-d_1 various other preparation methods and changes in the reaction conditions were examined (see table 1). However, so far it has not been possible to suppress the undesired elimination/addition reaction that yields bromocyclohexane-*cis*-2-d_1. On the other hand it should be mentioned that in the present case this by-product is of advantage, since it allows the assignment of additional NMR signals.

It can be further seen that in the low temperature spectrum at 238 K the signals from the main and the by-product are superimposed. They can be separated in

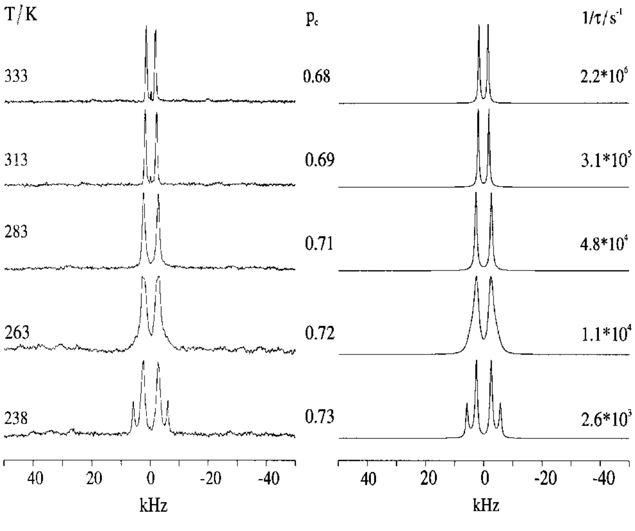

Figure 3. Experimental (left column) and simulated (right column) ^{2}H NMR spectra of bromocyclohexane-*trans*-2-d_1 at various temperatures. The rate constants for the ring inversion process and the relative amounts of equatorial conformers are given in the figure.

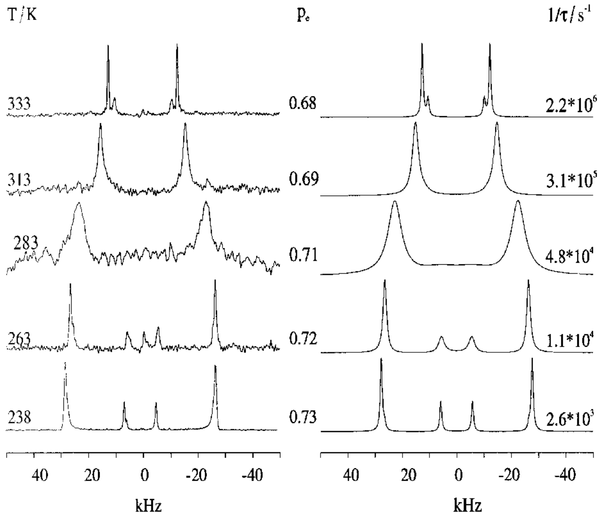

Figure 4. Experimental (left column) and simulated (right column) ^{2}H NMR spectra of bromocyclohexane-1-d_1 and 10% bromocyclohexane-*cis*-2-d_1 at various temperatures. The rate constants for the ring inversion process and the relative amounts of equatorial conformers are given in the figure.

a 2D exchange NMR spectrum, as depicted in figure 5. Here, for each nuclear spin transition, two cross-peaks of different intensities are visible that connect the ^{2}H NMR signals due to the exchanging sites, i.e. the corresponding C–D bonds of the axial and equatorial conformers that undergo chemical exchange due to the ring inversion process. The 2D exchange experiment thus allows the assignment of the signals to the various C–D bonds in bromocyclohexane-1-d_1 and bromocyclohexane-*cis*-2-d_1. In addition, the 2D exchange spectrum contains information about the relative signs of the quadrupolar couplings of the exchanging sites [25, 26]. Hence, a change of the relative sign is reflected by a cross-peak that connects signals at opposite sides relative to the centre of the spectrum. Likewise, the same relative sign is given by a cross-peak connecting signals within the same half of the spectrum. In the present case, the exchanging signals for one pair (bromocyclohexane-1-d_1; 1e′, 1a) possess the same sign, while for the other pair (bromocyclohexane-*cis*-2-d_1; 2e′, 2a) the relative sign of the quadrupolar couplings changes.

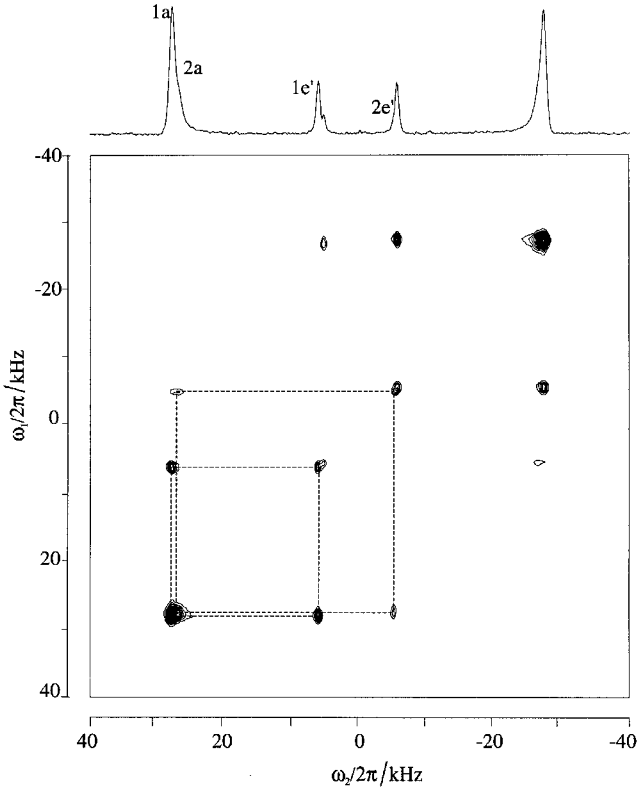

Figure 5. 2D exchange NMR spectrum of bromocyclohexane-1-d_1 and 10% bromocyclohexane-*cis*-2-d_1, recorded at 238 K with a mixing time of 3 ms.

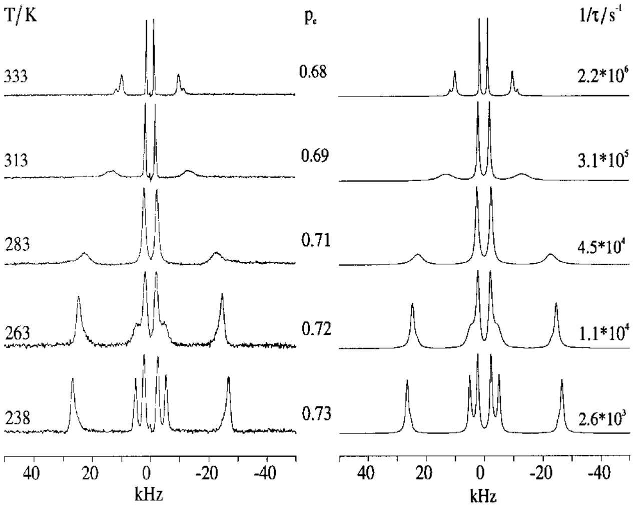

Figure 6. Experimental (left column) and simulated (right column) ^{2}H NMR spectra of bromocyclohexane-2,2,6,6-d_4, 10% bromocyclohexane-*cis*-2,6,6-d_3 and 10% bromocyclohexane-1,3,3-d_3 at various temperatures. The rate constants for the ring inversion process and the relative amounts of equatorial conformers are given in the figure.

We proceed with bromocyclohexane-2,2,6,6-d_4 that was prepared from cyclohexanol-2,2,6,6-d_4 by substitution. As for bromocyclohexane-1-d_1, the elimination/addition reaction (see reaction scheme in figure 7) gives rise to partially deuteriated by-products, bromocyclohexane-1,3,3-d_3 and bromocyclohexane-*cis*-2,6,6-d_3 in amounts of 10% of each, that are visible in the 1D and 2D NMR spectra of figures 6 and 8. The 2D exchange NMR spectrum in figure 8 again can be used for the separation of the exchanging signal pairs and the relative signs of their quadrupolar couplings. With the assignment from the previous selectively deuteriated compounds, it was possible to attribute each observed ^{2}H NMR signal to a particular C–D bond in one of the two conformers. It should be noted that the assignment, given in the 2D exchange NMR spectrum, was based upon the additional assumption that the signals at C-3 behave similarly to those at C-2. This assumption was confirmed later (see next paragraph) during the analysis of the molecular order parameters.

At this stage the signals that are related to the deuterons at C-1, C-2 and C-3 have been assigned. The remaining signals due to the deuterons at C-4 (4a, 4e′, 4a′, 4e) could be derived from the experiments with perdeuteriated bromocyclohexane-d_{11}, as given in figures 2 and 9, where the 2D exchange spectrum could be used for the identification of the missing (exchanging) signal pairs at C-4. The final assignment of these signals to a specific C–D bond, however, could not be made unequivocally. To do so, the molecular geometry from the MM2 calculations had to be taken into account, as will be outlined below.

On the other hand, the relative positions of exchanging signal pairs (i.e. the relative signs of the splittings) were sufficient to perform lineshape simulations of the variable

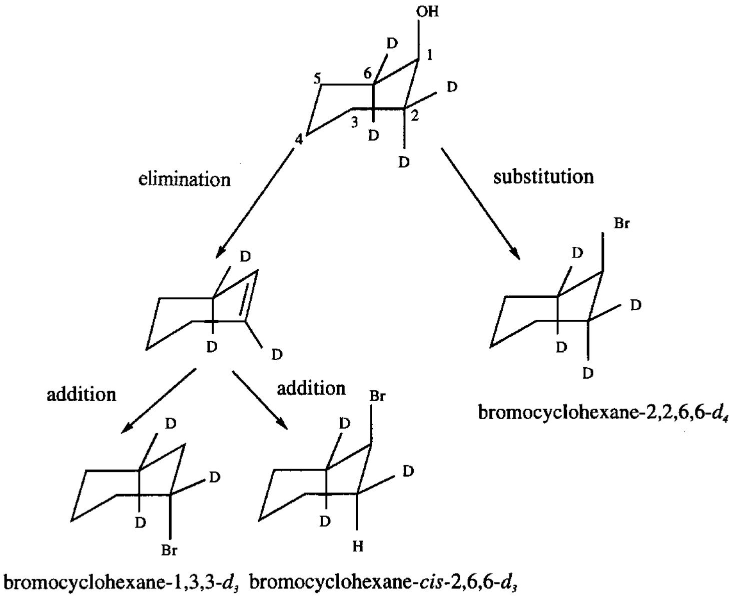

Figure 7. Reaction scheme for the synthesis of deuteriated bromocyclohexane-2,2,6,6-d_4.

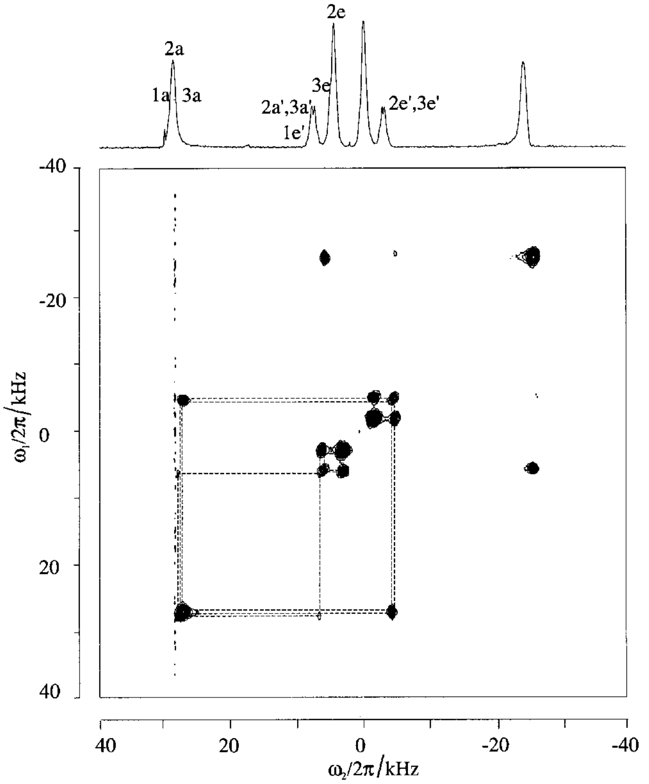

Figure 8. 2D exchange NMR spectrum of bromocyclohexane-2,2,6,6-d_4, 10% bromocyclohexane-*cis*-2,6,6-d_3 and 10% bromocyclohexane-1,3,3-d_3, recorded at 238 K with a mixing time of 3 ms.

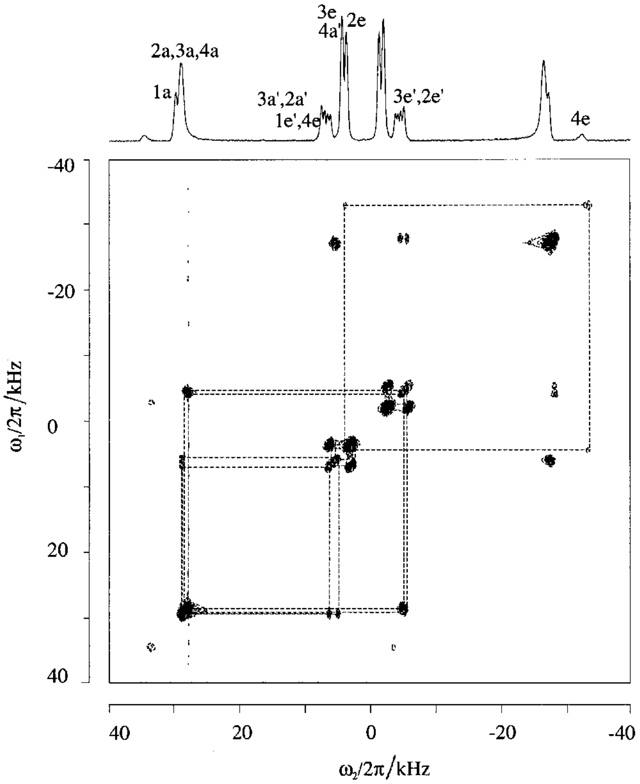

Figure 9. 2D exchange NMR spectrum of bromocyclohexane-d_{11}, recorded at 238 K with a mixing time of 3 ms.

temperature ^{2}H NMR spectra. Here, the simulation parameters were (i) the rate constant of the inversion process, (ii) the quadrupolar couplings of the exchanging sites that vary with temperature due to changes of the molecular order parameters, and (iii) the relative populations of the two conformers. At low temperatures ('slow exchange limit') these populations were found to be consistent with previous data from studies using isotropic solutions [40, 41]. Therefore, the thermodynamic data from that study were used for the calculations of the populations at higher temperatures [41]. The best fit spectra from these lineshape simulations are depicted in figures 2, 3, 4 and 6.

3.2. *Molecular ordering*

The final signal assignment and the determination of the ordering matrix of bromocyclohexane in the nematic solvent ZLI 2452 have been made using the procedure outlined previously [24, 25]. The complete spectrum simulation requires the knowledge of three Euler angles between the molecular-fixed coordinate system (x', y', z') and the principal axes system of the ordering matrix (x, y, z), as well as the order parameters S_{xx}, S_{yy}, S_{zz} in the x, y, z coordinate system [42]. For molecules having a C_s symmetry (such as the bromocyclohexane conformers) one axis, assigned here as the z'-axis, must be taken to be perpendicular to the symmetry plane. The principal coordinate system of the ordering matrix then is defined by a z-axis that is colinear with the z'-axis. The remaining principal axes x and y then must lie in the $x'y'$ plane, rotated about $z = z'$ by the angle α (see figure 1). In the x, y, z coordinate system the averaged quadrupolar interaction, i.e. half of the experimental splitting, of a particular deuteron i is given by

$$\begin{aligned}\langle \nu_Q^i \rangle &= \nu_Q^i (S_{xx}\cos^2\theta_x^i + S_{yy}\cos^2\theta_y^i + S_{zz}\cos^2\theta_z^i)\\ &= \nu_Q^i S_{xx}\left[\frac{1}{2}(3\cos^2\theta_x^i - 1) + \frac{1}{2}\eta(\cos^2\theta_z^i - \cos^2\theta_y^i)\right].\end{aligned} \tag{1}$$

In the above equation ν_Q^i is 3/4 of the static quadrupolar coupling constant e^2qQ/h, with a typical value of 168 kHz for an aliphatic C–D bond, that also has been used during the following analysis. For the derivation of this equation, the static quadrupolar tensor has been assumed to be axially symmetric. $\theta_\gamma^i = \theta_\gamma^i(\alpha)$ is the angle between the C–D^i bond direction and the principal axis γ, while $\eta = (S_{zz} - S_{yy})/S_{xx}$ is the asymmetry parameter. Furthermore, the x-axis was chosen to be the major ordering axis that is connected with the longest molecular axis. The ^{2}H NMR splittings thus depend on three parameters, namely S_{xx}, η and α.

These quantities were determined for each conformer separately by a best fit analysis in such a way that the difference between the theoretical splittings from equation (1) and the experimental splittings was minimized. To do so, the angles θ_γ^i were calculated from the molecular coordinates—as given by the MM2 calculations—for a series of angles α. In this connection, it was also necessary to check for each molecule the different relative signs for the experimental $\langle \nu_Q^i \rangle$. They, however, could not be changed independently, since the relative signs of each exchanging signal pair were fixed by the cross-peaks in the 2D exchange experiments (see above). Likewise, S_{xx} was restricted to be positive. This ensured that the molecular long axis is connected with a positive order parameter [25].

At the beginning of the analysis, only the known signals for the deuterons at carbons C-1, C-2 and C-3 were taken into account. After the minima had been found, the procedure was repeated by considering the various possibilities for the signals due to the deuterons at C-4. Eventually, we were able to give a complete assignment of the whole experimental ^{2}H NMR spectrum.

At first, the above analysis was made for the low temperature spectrum at 238 K by taking the experimental splittings directly from the 1D ^{2}H NMR spectrum. At higher temperatures, i.e. at temperatures where the ring inversion affects the NMR lineshapes, the splittings were taken from the input parameters for the lineshape simulations of the ring inversion process. The derived order parameters $S_{\gamma\gamma}$, asymmetry parameters η and angles α are reported in table 3. Plots of the quadrupolar interactions $\langle \nu_Q^i \rangle$ for both conformers as a function of temperature are given in figure 10. In figure 11 S_{zz}-S_{yy} is plotted versus S_{xx}. In addition, the final assignments are depicted in the 2D NMR spectra of figures 5, 8 and 9.

As demonstrated by the data given in table 3 and figures 10 and 11, there is a significant influence of the particular orientation of the substituent (i.e. at the axial or equatorial position) on the ordering characteristics of bromocyclohexane. The axial conformer thus exhibits lower order parameters $S_{\gamma\gamma}$ along with a larger asymmetry parameter η and angle α. These findings certainly reflect a more globular shape of the axial conformer, while the equatorial conformer is characterized by an elongated (anisotropic) shape with a major ordering axis, being close to the line connecting C-1 and C-4, by analogy with other substituted cyclohexanes.

Table 3. Derived order parameters $S_{\gamma\gamma}$, asymmetry parameters η and angles α for both conformers of bromocyclohexane in ZLI 2452.

Temperature/K	S_{xx} [a]	S_{yy} [a]	S_{zz} [a]	η	α/°
Equatorial conformer					
238	0.294	− 0.216	− 0.078	0.47	14.0
263	0.271	− 0.198	− 0.073	0.46	14.5
283	0.234	− 0.17	− 0.064	0.45	14.5
313	0.216	− 0.158	− 0.058	0.46	17.2
333	0.240	− 0.178	− 0.058	0.52	19.2
Axial conformer					
238	0.140	− 0.125	− 0.015	0.79	53.2
263	0.128	− 0.115	− 0.013	0.79	53.2
283	0.116	− 0.103	− 0.012	0.79	53.2
313	0.087	− 0.078	− 0.009	0.79	53.0
333	0.070	− 0.063	− 0.007	0.79	53.2

[a] Estimated errors: ± 4%.

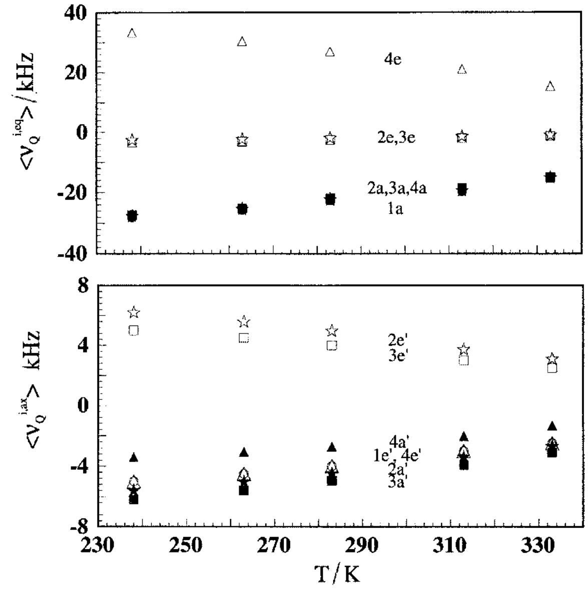

Figure 10. Experimental quadrupolar interactions $\langle \nu_Q^i \rangle$ (half of the experimental splitting) for the various deuterons in the equatorial (upper figure) and axial conformer (lower figure) of bromocyclohexane. The signs of the $\langle \nu_Q^i \rangle$ are fixed by the choice that S_{xx} is positive.

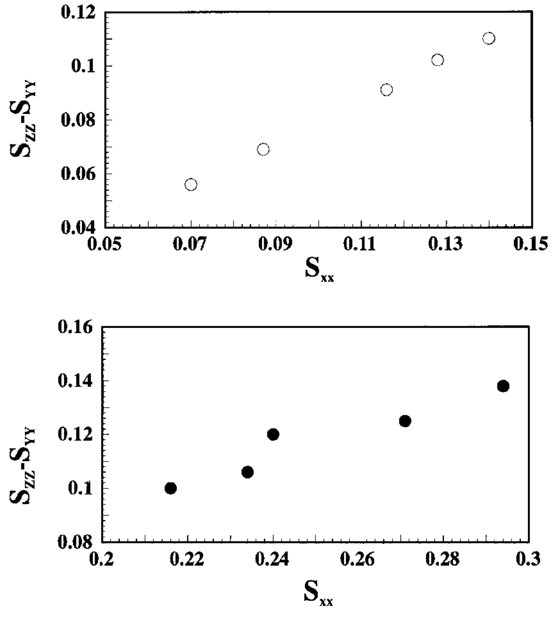

Figure 11. Plots of S_{zz}-S_{yy} versus S_{xx}. Open and filled symbols refer to the equatorial and axial conformers of bromocyclohexane, respectively.

In fact, the comparison of the present data for the ordering behaviour of the bromocyclohexane conformers with those reported earlier for substituted cyclohexanes (bearing non-polar substituents) reveals a close resemblance between bromocyclohexane in the equatorial conformation, methylcyclohexane and 1,4-*cis*-dimethylcyclohexane [25, 26]. This implies that the polarity of the substituent is of minor importance for the ordering behaviour of substituted cyclohexanes in liquid crystalline solvents. It therefore would be interesting if the above experimental results could be confirmed by appropriate theoretical calculations [43].

3.3. *Conformational properties*

This section deals with the conformational properties of bromocyclohexane in the nematic solvent ZLI 2452 which can be derived by analysing the variable temperature ^{2}H NMR spectra. As mentioned earlier, the observed lineshape changes can be traced back to the influence of the ring inversion process. The low temperature ^{2}H NMR spectra thus refer to the slow exchange region with separate signals from the equatorial and axial conformers. As reported for the isotropic solution [40, 41], both bromocyclohexane conformers exist at $T = 238$ K in relative amounts of $p_e = 0.73$ and $p_a = 0.27$, respectively. In the intermediate and fast exchange limit the conformational ratios could not be determined independently from the present NMR data. In this case they were derived from the thermodynamic data given by a previous ^{1}H NMR study involving the isotropic solution [41].

The remaining parameters for the lineshape simulations were the rate constant and the quadrupolar splittings (along with the relative signs) of each exchanging signal pair. In addition, for the simulations an exchange and temperature independent linewidth has been used which varied between 175 and 860 Hz for the various deuterons. The derived exchange rates $1/\tau$ $(= k_a + k_e = k_e/p_a = k_a/p_e)$ for the ring inversion process are plotted in figure 12 as a function of the reciprocal temperature. From this, an activation enthalpy $\Delta H = 44.5 \pm 4.5$ kJ mol^{-1} has been derived which is rather close to the value of $\Delta H = 48.9$ kJ mol^{-1} obtained from the former ^{1}H NMR

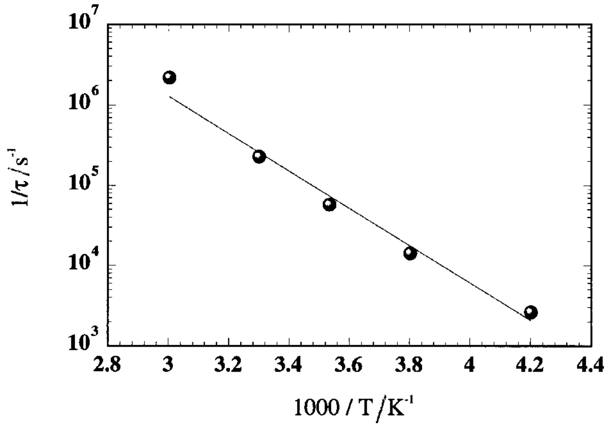

Figure 12. Arrhenius representation for the rate constants of the ring inversion process of bromocyclohexane in ZLI 2452.

solution study. As found for the conformational equilibria, the conformational dynamics again seem to be almost independent of the nature of the particular solvent. On the other hand, it should be noted that from a solid state ^{13}C NMR study on the thiourea inclusion compound with bromocyclohexane, a somewhat smaller value of $\Delta H = 39.3\,\mathrm{kJ\,mol^{-1}}$ has been reported [44]. Obviously, upon changing the surrounding matrix from a liquid medium to a solid thiourea channel, the conformational dynamics appear to be strongly affected. The same is true for the conformational ordering. Thus, the conformational ratio in thiourea is given by $p_e : p_a = 0.05 : 0.95$, which reflects a considerable stabilization of the axial conformer by the thiourea channels.

4. Summary

Selectively and perdeuteriated bromocyclohexanes have been studied using a liquid crystalline solution and employing dynamic ^{2}H NMR methods. From a complete analysis of the 2D exchange experiments and variable temperature ^{2}H NMR lineshapes, it was possible to derive quantitative information about the ordering and conformational features of the bromocyclohexane molecules in the anisotropic matrix. The ordering characteristics of both conformers (which exist in a dynamic equilibrium) are expressed by various order parameters and an angle α between a molecular fixed and the molecular ordering coordinate system. It was found that these quantities strongly depend on the actual conformational state of bromocyclohexane, also reflecting the different overall shapes of both conformers.

The conformational properties are expressed by the conformational equilibria and the ring interconversion dynamics. They were found to be almost unaffected by the surrounding matrix, as can be seen from the comparison with the data from a former study involving the isotropic solution. Further work along these lines using other substituted cyclohexanes is in progress.

We thank Mrs H. Seidel for help during the synthesis of the deuteriated compounds used in the present study. Financial support by the Deutsche Forschungsgemeinschaft and the Fonds der Chemischen Industrie is gratefully acknowledged.

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