QNS investigation of restricted molecular reorientation in the nematic phase. I. The incoherent scattering law for MBBA

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QNS investigation of restricted molecular reorientation in the nematic phase

I. The incoherent scattering law for MBBA

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On the basis of the solution of the random flight problem of a particle between two perfectly reflecting potential barriers the incoherent scattering law for the model of the uniaxial, molecular stochastic reorientation within an arbitrary apex angle Φ_0 has been calculated. In conjunction with the published NMR results evidence is presented, that the along the long axis uniaxial rotation, can be described in terms of the model with an apex angle ϕ_0 of 57°. The model of the restricted uniaxial reorientation, which is expected to be of interest in nematic phases of biaxial molecules, has been applied to the investigation, by quasi elastic incoherent cold neutron scattering, of the rotational dynamics of the rigid benzylidene central part of a magnetically oriented MBBA sample in the nematic phase at 303 K.

1. Introduction

It has been suggested [1] that all cyanobiphenyls in the nematic phase may exhibit local biaxiality in the sense that the ordering matrix, describing the alignment of individual molecules, has the non-vanishing biaxial term $S_{xx} - S_{yy}$. The sufficient condition for this to be true is the requirement that the molecules do not rotate freely about their long molecular z axes. Likewise, in the rectangular modification of the tilted columnar liquid crystalline phase of disc-like molecules [2] the uniaxial, molecular rotational motion like the librational oscillations, might be restricted within an angular interval.

Proton spin–spin relaxation time measurements in the (locally uniaxial) nematic phase of 4-methoxybenzylidene-4'-n-butylaniline (MBBA) [3] as well as broad line NMR and Raman scattering studies [4] of the same compound, have presented evidence of the existence of steric hindrance between adjacent MBBA molecules. In fact, in the nematic phase at 22°C calculation of the spin–spin relaxation time [3] explains the measurements on the basis that the end methyl as well as the end butyl group rotate freely and it is only with increasing temperature that the motion of the

two phenyl rings of the MBBA molecule begins to affect the spectra. The investigations of the molecular motion, the segmental motion as well as the conformation of MBBA molecules in the nematic phase as presented in [3, 4], could not provide the details of the dynamics of the two phenyl rings. Considering the steric hindrance between MBBA molecules and taking into account the observed unusual (undetermined) mobility behaviour of the benzylidene part of the MBBA molecule, this mobility might just correspond to some kind of (temperature dependent) uniaxial librational motion along the long molecular axis in such a way, that most of the time the full 360° revolution (because of the steric hindrance) around the molecular long axis is unlikely to occur.

As is well known [5] the incoherent quasielastic cold neutron scattering (QNS) method is considered to be a unique means for the investigation of various types of random molecular motion. With the technique of the high resolution QNS experiments it has been possible to gain detailed information regarding the different dynamical aspects of liquid-crystalline molecules in various mesomorphic phases. The stochastic motions which have been examined include anisotropic translational diffusion, many possible ways of molecular reorientation about the long molecular axis and also molecular tumbling about the short axes. Generally speaking, the QNS scattering data in liquid crystals are interpreted with the help of different models, describing the relevant molecular dynamical behaviour in question and very often in conjunction with measurements that have been made by other spectroscopic techniques (i.e. NMR, Raman scattering, dielectric relaxation, etc.), it has been possible to elucidate a fair understanding of the molecular motion in different liquid-crystalline phases. The stochastic dynamical models for uniaxial molecular reorientation currently in use [5–10] have in common the fact that the periodic 360° uniaxial reorientation or else 180° flipping motion is allowed for.

In view of the findings [3, 4] that the MBBA molecules in the nematic phase are closely packed, subject to constraint from neighbouring molecules and that their phenyl rings at about 22°C are presumably hindered in their uniaxial rotational dynamics it is the purpose of the paper to present rather a different model of uniaxial rotational molecular diffusion which is characterized by the fact that the proton (rigidly bound in a molecule) is allowed to diffuse continuously on a segment of its circular arc in such a way that the molecule is constrained to reorient itself along its long body axes only within an angular interval denoted by Φ_0. An approximate account (valid for small Φ_0) of the envisaged model has already appeared [11]. However the present formulation, based upon the method of one dimensional random flight of the particle between two perfectly reflecting potential barriers [12] is general, the advantage being the fact that it could be suitably extended to allow for the description of molecular biaxiality. The purpose of this paper is, therefore, to offer detailed information concerning the stochastic, confined uniaxial angular reorientational molecular motion by studying the motion in an oriented nematic MBBA sample since it was established that MBBA molecules should be closely packed, subjected to some constraint from neighbouring molecules [4] and the structural data can be taken to be known [13] for this compound. The MBBA nematic phase has been reported to be locally uniaxial in the sense that the biaxiality of the ordering matrix is small.

2. Theory

Scattering of cold neutrons by hydrogenous compounds is, to a good approximation, described by the incoherent scattering law, $S_{inc}(Q, \omega)$, which yield information

concerning the dynamics of individual protons bound to the molecule because of the exceedingly large incoherent cross-section of protons. Following Sears [14], the incoherent cold neutron scattering law (normalized per molecule) for the classical system is,

$$S_{inc}(Q, \omega) = \frac{1}{2\pi} \int \exp(-i\omega t) I_{inc}(Q, t) \, dt, \tag{1}$$

where the intermediate scattering function is defined by [14],

$$I_{inc}(Q, t) = \sum_{v=1}^{n} (a_{inc}^v)^2 \langle \exp[-i\mathbf{Q}\mathbf{R}(0)] \exp[i\mathbf{Q}\mathbf{R}(t)] \rangle \langle \exp[-i\mathbf{Q}\mathbf{r}_v(0)] \exp[i\mathbf{Q}\mathbf{r}_v(t)] \rangle, \tag{2}$$

assuming that the translational and rotational motion of the molecule are mutually independent. In this expression, $\mathbf{Q}$, is the linear momentum, (in units of $\hbar$), transferred to the system, $\mathbf{R}$ is the position vector of the centre of mass of the molecule, $\mathbf{r}_v$ is the position vector of the vth proton in the molecule as measured from the molecular centre of mass, n is the number of protons in the molecule, $\hbar\omega$ is the energy transfer in the scattering and a_{inc}^v is the incoherent scattering length of the vth nucleus within the molecule. We proceed by expanding the exponential in terms of spherical harmonics, i.e.

$$\exp[i\mathbf{Q}\mathbf{r}_v(t)] = 4\pi \sum_{l=0}^{\infty} \sum_{m=-l}^{l} i^l j_l(Qr_v) Y_{lm}^*(\theta_Q \phi_Q) Y_{lm}(\theta_v \phi_v)_t, \tag{3}$$

where j_l is a spherical Bessel function of order l, and the spherical harmonics are evaluated in the laboratory coordinate system chosen in such a way that its z axis points along the uniaxial macroscopic direction of the nematic sample. The unit vector along this direction defines the usual macroscopic director $\mathbf{n}_0$, which is the preferred orientation of the long axis of all the molecules in the sample. As the molecules are thermally agitated they reorient in a hindered fashion about $\mathbf{n}(\mathbf{r}, t)$, which is the unit vector defining now the instantaneous *local* preferred direction [15] of a small but otherwise undefined number of nematic molecules distributed in a small volume element at $\mathbf{r}$. In general, there are indications that the molecular reorientational motion in liquid crystals can be described in terms of contributions due to uniaxial rotational motion as well as fluctuation of the molecular long axis around the local director [5, 9, 16, 17]. In some cases the correlation time for the axis fluctuation is about the same as that for rotation [9], but there are also examples where the fluctuation of the long molecular axes are slower than 10^{-10} s, for example the smectic E phase of IBPBAC [9] and also the nematic phase of MBBA [15, 18, 19], and hence appear static on the neutron time scale. The derivation presented later applies to those cases when the correlation time for the reorientational molecular motion, occurring along the molecular long axes, is short in comparison with the time for the reorientation of the molecular long axis itself.

In order to see the effect of the angular, uniaxial stochastic molecular reorientational motion confined between two perfectly reflecting potential barriers, on the cold neutron incoherent scattering law the expression

$$\langle \exp[-i\mathbf{Q}\mathbf{r}_v(0)] \exp[i\mathbf{Q}\mathbf{r}_v(t)] \rangle = 16\pi^2 \sum_{l,s} \sum_{m} (-1)^s i^{l+s} j_l(Qr_v) j_s(Qr_v)$$

$$\times Y_{lm}^*(\theta_Q \phi_Q) Y_{sm}(\theta_Q \phi_Q) \langle Y_{lm}(\theta_v \phi_v)_t Y_{sm}^*(\theta_v \phi_v)_0 \rangle, \tag{4}$$

has to be evaluated, where, on account of inversion symmetry of the nematic sample, the summation goes over such integers l and s for which $l + s$ is an even number, and due to the cylindrical symmetry of the sample the value of m takes all integer values between either $-l$ and l, or $-s$ and s, whichever is smaller, i.e. $|m| \leqslant l$ if $l < s$ or the opposite.

Let $\Omega(t)$ denote the set of Euler angles which transform the laboratory system to the instantaneous system defined by the local preferred direction $\mathbf{n}(\mathbf{r}, t)$. Then we have

$$Y_{lm}(\theta_v \phi_v)_t = \sum_{m'} D_{mm'}^{l*}(\Omega(t)) \bar{Y}_{lm'}(\theta_v' \phi_v')_t, \tag{5}$$

where $\bar{Y}$ is written in the local reference frame. Employing this equation twice and noting that the subscript t denotes that proton position at time t, the expression

$$\langle Y_{lm}(\theta_v \phi_v)_t Y_{sm}^*(\theta_v \phi_v)_0 \rangle = \sum_{m'} \sum_{m''} \langle D_{mm'}^{l*}(\Omega(t)) D_{mm''}^{s}(\Omega(0)) \rangle$$

$$\times \langle \bar{Y}_{lm'}(\theta_v'(t)\phi_v'(t)) \bar{Y}_{sm''}^*(\theta_v'(0)\phi_v'(0)) \rangle. \tag{6}$$

is obtained. Here, in view of the large frequency difference of the processes involved, we have separated proton motion from the motion of the local preferred director. For our purposes it is permissible in fact to resort to the approximation that the proton motion is not influenced by slow rearrangement of the local preferred director so that $\Omega(t) = \Omega(0)$. From that it immediately follows that

$$\langle D_{mm'}^{l*}(\Omega(0)) D_{mm''}^{s}(\Omega(0)) \rangle = (-1)^{m-m'} \langle D_{-m,-m'}^{l}(\Omega(0)) D_{m,m''}^{s}(\Omega(0)) \rangle,$$

$$= (-1)^{m-m'} \sum_{\chi} C(l, s, \chi; -m', m'') C(l, s, \chi; -m, m)$$

$$\times \langle D_{0,m''-m'}^{\chi}(\Omega(0)) \rangle$$

$$= (-1)^{m-m'} \sum_{\chi} C(l, s, \chi; -m', m') C(l, s, \chi; -m, m)$$

$$\times \delta_{m'',m'} \langle P_{\chi}(\cos \beta_n) \rangle, \tag{7}$$

where C are Clebsch–Gordan coefficients and the angular bracket denotes the χth order nematic order parameter

$$S_{\chi} = \langle P_{\chi}(\cos \beta_n) \rangle. \tag{8}$$

Here β_n is the angle between the local preferred molecular orientation at the position $\mathbf{r}$ within the sample and the macroscopic uniaxial direction $\mathbf{n}_0$. The second term in equation (6) will now be evaluated under the assumption of stochastic random motion restricted between two potential barriers. The geometry of the assumed proton motion along the molecular long body axis (rigidly bound in the molecule) is shown in figure 1. Transforming the equation (6) to the molecular reference frame, defined by the principal axes of the moment of inertia tensor we obtain

$$\langle \bar{Y}_{lm'}(\hat{r}(t)) \bar{Y}_{sm''}^*(\hat{r}(0)) \rangle = \sum_{m_1} \sum_{m_2} Y_{lm_1}(\hat{r}) Y_{sm_2}^*(\hat{r}) \langle D_{m'm_1}^{l*}(\alpha(t)\beta(t)\gamma(t)) D_{m''m_2}^{s}(\alpha(0)\beta(0)\gamma(0)) \rangle,$$

$$\tag{9}$$

where α, β, γ are the set of Euler angles transforming the local reference frame, defined by $\mathbf{n}$, into the body system and $Y_{lm}(\hat{r})$ is an lth order spherical harmonic evaluated in the molecular frame. Since the assumed motion occurs along the body ξ axis, and the
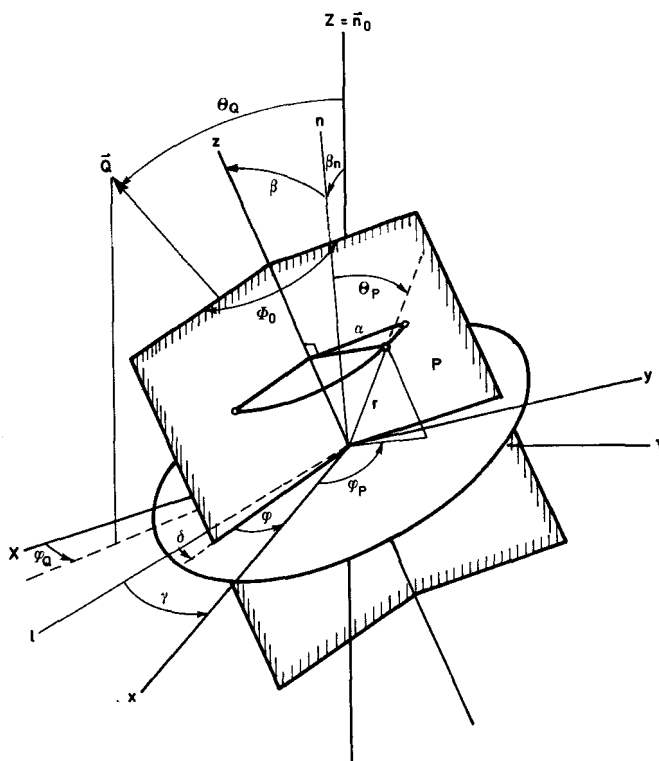
Figure 1. The model of the angular, between two perfectly reflecting barriers confined uniaxial simple rotational diffusion of a proton P within the molecule. The radius of the circle is denoted by a and the angular interval of the segment of the circular arc allowed to the proton is Φ_0. The laboratory coordinate system is X, Y, Z defined by the macroscopic uniaxial direction of the nematic sample n_0, the local director is defined by the unit vector n and the molecular principal axes system (in which P is fixed) is denoted by xyz, where z points along the direction corresponding to the smallest eigenvalue of the moment of inertia tensor. l denotes the line of nodes between the local and the molecular frame of reference. The origins of the coordinate systems are chosen in the molecular centre of mass. The spherical coordinates of the proton P in the body fixed system are given by the time independent values r, θ_P, and ϕ_P.

processional molecular motion around n is unlikely to occur, $\alpha(t) = \alpha(0)$, and so equation (9) reduces to

$$\langle D^{l*}_{m'm_1}(\alpha(t)\beta(t)\gamma(t)) D^s_{m'm_2}(\alpha(t)\beta(0)\gamma(0)) \rangle$$

$$= \langle d^l_{m'm_1}(\beta(t)) d^s_{m'm_2}(\beta(0)) \rangle \langle \exp[-im_1\gamma(t)] \exp[im_2\gamma(0)] \rangle. \tag{10}$$

Here the first term is associated with the long molecular axes orientational fluctuations with respect to the preferred molecular direction $n(r, t)$. It was precisely this term which was studied in [17], utilizing the model of confined stochastic angular molecular orientational motion, which is obtained by extending Feller's [12] result on the random walk of a particle between two perfectly reflecting potential barriers. However, in this publication it is the second term with which we are concerned.

The intermediate scattering function for the general case of molecular motion including the simple translational diffusion of the molecular centre of mass (for

one proton) is,

$$I_{\text{int}}(Q, t) = I_{\text{trans}}(Q, t)I_{\text{rot}}(Q, t), \quad (11)$$

where in the gaussian approximation

$$I_{\text{trans}}(Q, t) = \exp(-Q^2Dt). \quad (12)$$

Here D being an average molecular centre of mass translational self diffusion constant and

$$\begin{aligned}
I_{\text{rot}}(Q, t) = \ & 16\pi^2 \sum_{l,s} \sum_m (-1)^s i^{(l+s)} j_l(Qr) j_s(Qr) Y_{lm}^*(\theta_Q, \phi_Q) Y_{sm}(\theta_Q, \phi_Q) \\
& \times \sum_{m'} (-1)^{m-m'} \sum_\chi C(l, s, \chi; -m', m') C(l, s, \chi; -m, m) S_\chi \\
& \times \sum_{m_1,m_2} \langle d_{m'm_1}^l(\beta(t)) d_{m'm_2}^s(\beta(0)) \rangle \langle \exp[-im_1\gamma(t)] \exp(im_2\gamma(0)) \rangle \\
& \times Y_{lm_1}(\theta, \phi) Y_{sm_2}^*(\theta, \phi).
\end{aligned} \quad (13)$$

The intermediate scattering function for the molecular rotational motion, equation (13), is derived for the case when the long molecular axis is itself subject to an as yet unspecified orientational motion (in the fixed plane passing through the local director) as well as some sort of rotational motion along its long body (i.e. principal) axis. This clear exhibition of the way the various complicated molecular motions enter into the incoherent scattering law is an advantage of the present formulation in which the exponentials are expanded in terms of spherical waves (see equation (3)). In addition to this, the relevant expressions, after averaging over all directions of the scattering vector $\mathbf{Q}$, are immediatley applicable to the unoriented or even isotropic samples.

The conditional probability density, $P(\varphi_0/\varphi; t)$, that after a large number of (angular) steps the proton will be found at the angle φ at time t providing it was at φ_0 at the beginning, can be immediately given [12, 17];

$$P(\varphi_0/\varphi; t) = \frac{1}{\Phi_0} + \frac{2}{\Phi_0} \sum_{r=1}^{\infty} \exp\left(-\frac{\pi^2 r^2 Rt}{\Phi_0^2}\right) \cos\left(\frac{\pi r \varphi_0}{\Phi_0}\right) \cos\left(\frac{\pi r \varphi}{\Phi_0}\right), \quad (14)$$

here R is the angular diffusion constant for this type of motion, and Φ_0 is the angular span between the two barriers (see figure 1). In equation (14) the angles φ and φ_0 are measured from one barrier onwards. It is convenient to introduce an angle δ such that

$$\gamma = \delta + \varphi, \quad (15)$$

where δ is the angle between the potential barrier (from which φ is measured) and the axis from which γ is measured. The initial distribution over γ_0 is thus written as

$$P(\gamma_0) = P(\delta)P(\varphi_0), \quad (16)$$

where the intervals available to δ and φ_0 are $0 \leqslant \delta \leqslant 2\pi$ and $0 \leqslant \varphi_0 \leqslant \Phi_0$; respectively. The conditional probability needed in equation (10) is, therefore, equal to

$$P(\gamma_0/\gamma; t) = P(\varphi_0/\varphi; t)\frac{d\varphi}{d\gamma} = P(\varphi_0/\varphi; t). \quad (17)$$

We assume a uniform initial probability distribution for φ_0

$$P(\varphi_0) = \frac{1}{\Phi_0} \quad (18)$$

and a uniform distribution of potential barriers along the molecular long axes, i.e.

$$P(\delta) = \frac{1}{2\pi}. \quad (19)$$

Thus, under the conditions described we obtain,

$$
\langle \exp[-im_1\gamma(t)]\exp[im_2\gamma(0)]\rangle = \delta_{m_1,m_2}\frac{2}{\Phi_0^2}\Bigg\{\frac{1-\cos(m_1\Phi_0)}{m_1^2}
$$
$$
+ 2\sum_{r=1}^{\infty}\exp\left(-\frac{\pi^2 r^2 Rt}{\Phi_0^2}\right)\frac{m_1^2(1-(-1)^r\cos(m_1\Phi_0))}{((\pi r/\Phi_0)^2 - m_1^2)^2}
$$
$$
+ \frac{\Phi_0^2}{4}\exp(-m_1 Rt)\sum_{r=1}^{\infty}\delta_{m_1^2,(\pi r/\Phi_0)^2}\Bigg\}, \tag{20}
$$

where the prime denotes that only those terms are to be taken into account for which the denominator in the second term is (exactly) non-zero. In all of the following expressions the explicit distinction of the summation of terms over r will be, suppressed for compactness. It is to be stressed that the equation (20) is derived for the case where the apex angle Φ_0 is limited within an interval $0 \leqslant \Phi_0 \leqslant 2\pi$. However, if $\Phi_0 = 2\pi$ the model does not simply correspond to the simple uniaxial rotation diffusion model. Namely, the random flight of a particle between two potential barriers is set up [12] in such a way that the particle can come arbitrarily close to the barrier (in the continuous limit) but the probability of finding it at the potential barrier itself is exactly zero. Consequently, even for $\Phi_0 = 2\pi$, the particle cannot describe a full circle. Detailed numerical evaluation of equation (20) in the limit $\Phi_0 = 2\pi$ presents the following characteristics: for $t = 0$ and arbitrary $m \neq 0$ the second term is to a very good approximation equal to $\frac{1}{2}$ and thus equal to the third one. For $t \neq 0$ the second term is slightly larger than the third term, the difference increases with increasing t. Hence, the main distinction between the two models is expected to be observed at small energy transfer, ω, while at large ω the two models yield almost identical, i.e. the rotational diffusion model, results. The reason that the two models differ for $\Phi_0 = 2\pi$ is mathematically quite clear; the probability densities are the solution of the same diffusion equation but for different boundary conditions.

Providing that it is permissible to neglect the molecular orientational fluctuations (for which now a model would be needed) we assume that $\beta(t) = \beta(0) = 0$. This simplifies the expressions obtained considerably to

$$
\langle d_{m'm_1}^l(0)d_{m'm_2}^s(0)\rangle = \delta_{m'm_1}\delta_{m'm_2}. \tag{21}
$$

In this approximation, assuming uncoupled simple translational diffusion of the molecular centre of mass and angular confined stochastic libration along the long molecular axis, the incoherent scattering law is

$$
S(Q, \omega) = 32\pi\sum_{v}(a_{inc}^v)^2\sum_{l,s}(-1)^{s_i(l+s)}j_l(Qr_v)j_s(Qr_v)
$$
$$
\times \sum_{m}Y_{lm}^*(\theta_Q, \phi_Q)Y_{sm}(\theta_Q, \phi_Q)\sum_{m'}(-1)^{m-m'}
$$
$$
\times \sum_{\chi}C(l, s, \chi; -m', m')C(l, s, \chi; -m, m)S_\chi Y_{lm'}(\theta_v, \phi_v)Y_{sm'}^*(\theta_v, \phi_v)
$$
$$
\times \Bigg\{\frac{1-\cos(m'\Phi_0)}{m'^2\Phi_0^2}\frac{Q^2 D}{(Q^2 D)^2 + \omega^2} + 2\sum_{p=1}^{\infty}\frac{m'^2(1-(-1)^p\cos(m'\Phi_0))}{\Phi_0^2((\pi p/\Phi_0)^2 - m'^2)^2}
$$
$$
\times \frac{Q^2 D + \dfrac{\pi^2 p^2 R}{\Phi_0^2}}{\left(Q^2 D + \dfrac{\pi^2 p^2 R}{\Phi_0^2}\right)^2 + \omega^2}\Bigg\}. \tag{22}
$$

Here D is an isotropic, average translational diffusion constant of the molecular centre of mass, l, s are integers such that their sum is an even number and m, m' run, at fixed l and s, over all values of either l or s, whichever is the smaller. In the derivation of equation (22) no orientational fluctuations of the molecular axes was assumed and furthermore it was taken that during the stochastic confined angular uniaxial rotational motion, the barriers themselves do not rotate.

The zeroth moment of the scattering law $S(Q, \omega)$, in equation (22) determines the convergence criterion of the series evaluation, since

$$
\begin{aligned}
1 = \int_{-\infty}^{\infty} S(Q, \omega) \, d\omega &= 32\pi^2 \sum_{l,s} (-1)^s i^{(l+s)} j_l(Qr) j_s(Qr) \\
&\times \sum_{m} Y_{lm}^*(\theta_Q, \phi_Q) Y_{sm}(\theta_Q, \phi_Q) \sum_{m'} (-1)^{m-m'} \\
&\times \sum_{\chi} C(l, s, \chi; -m', m') C(l, s, \chi; -m, m) S_\chi Y_{lm'}(\theta, \phi) Y_{sm'}^*(\theta, \phi) \\
&\times \left\{ \frac{1 - \cos(m'\Phi_0)}{m'^2 \Phi_0^2} + 2 \sum_{p=1}^{\infty} \frac{m'^2(1 - (-1)^p \cos(m'\Phi_0))}{\Phi_0^2((\pi p/\Phi_0)^2 - m'^2)^2} \right\},
\end{aligned} \tag{23}
$$

is valid, (written for one proton only); this has been numerically verified for various arbitrary values of the parameters r, $\mathbf{Q}$ and Φ_0. From equation (22) it is possible to obtain certain limiting cases such as:

(a) no uniaxial angular confined stochastic reorientation, i.e. $\Phi_0 = 0$. This limit corresponds to the case where the molecules do not rotate, but their molecular planes (now specified by the angle δ, in figure 1), are randomly oriented around the local directors. Taking the limit $\Phi_0 \to 0$ the expression in the curly bracket, (see equation (22)), reduces to

$$
\left\{ \ldots \right\} = \frac{1}{2} \frac{Q^2 D}{(Q^2 D)^2 + \omega^2}.
$$

In this limit the first term inside the curly bracket of the normalization of equation (23) is equal to $\frac{1}{2}$, while the second is zero, consequently the scattering function, equation (22) in conjunction with, equation (23), gives

$$
\lim_{\Phi_0 \to 0} S(Q, \omega) = \frac{1}{\pi} \frac{Q^2 D}{(Q^2 D)^2 + \omega^2} \sum_{\nu} (a_{inc}^\nu)^2 \tag{24}
$$

and only the translational motion of the molecular centre of mass contributes to the incoherent scattering law, as expected.

(b) Let us now assume that all of the molecular long axes are parallel to the macroscopic uniaxial direction $\mathbf{n}_0$ while each molecule is subject to the uniaxial along the long body axis angular confined stochastic reorientation between two angular potential barriers separated by Φ_0. In the limit $S_\chi \equiv 1$, and as

$$
\sum_{\chi} C(l, s, \chi; -m', m') C(l, s, \chi; -m, m) = \delta_{m',m} \tag{25}
$$

the normalization condition (equation (23)) is greatly simplified. If we assume that the neutron scattering vector $\mathbf{Q}$ is parallel to the uniaxial direction $\mathbf{n}_0$, it follows that

$$
Y_{lm}(\theta = 0°, \phi) = \sqrt{\left[\frac{2l + 1}{4\pi} \right]} \delta_{m,0} \tag{26}
$$

and taking into account the normalization condition (equation (23)), the (single) proton incoherent scattering law is given simply by

$$S(Q, \omega)_{\parallel} = \frac{1}{\pi} \frac{Q^2 D}{(Q^2 D)^2 + \omega^2} \tag{27}$$

and is consequently once again independent of the rotational effects (and now also of the molecular structure factor) as expected.

For later use, we write down the expression for the incoherent scattering function for the case that the molecule is subject to simple uniaxial rotational diffusion along the long body axis, (the principal axis of the moment of inertia tensor), characterized by the uniaxial simple rotational diffusion constant D_1. As well known [7],

$$\langle \exp[-im_1 \gamma(t)] \exp[im_2 \gamma(0)] \rangle = \exp(-D_1 m_1^2 |t|)_{\delta_{m_1, m_2}} \tag{28}$$

is valid and consequently the incoherent scattering law for the molecules in the nematic subject to simple translational and simple uniaxial rotational diffusion, is given by equation (22) providing the curly bracket there is substituted by

$$\left\{ \cdots \right\} = \frac{1}{2} \frac{Q^2 D + D_1 m'^2}{(Q^2 D + D_1 m'^2)^2 + \omega^2}, \tag{29}$$

while all other terms in equation (22) remain the same.

Within the approximation of a uniaxial, perfectly homogeneous nematic sample it is easy to derive the equivalent expression, to the equation (22) but written in terms of cylindrical Bessel functions, which reads

$$S(Q, \omega) = \frac{1}{\pi} J_0^2(Qa \sin(\theta_Q)) \frac{Q^2 D}{(Q^2 D)^2 + \omega^2}$$

$$+ \frac{4}{\pi \Phi_0^2} \sum_{k=1}^{\infty} J_k^2(Qa \sin(\theta_Q)) \left\{ \frac{1 - \cos(k\Phi_0)}{k^2} \frac{Q^2 D}{(Q^2 D)^2 + \omega^2} \right.$$

$$\left. + 2 \sum_{r=1}^{\infty} \frac{k^2(1 - (-1)^r \cos(k\Phi_0))}{\left(\left(\frac{\pi r}{\Phi_0} \right)^2 - k^2 \right)^2} \frac{Q^2 D + \dfrac{\pi^2 r^2 R}{\Phi_0^2}}{\left(Q^2 D + \dfrac{\pi^2 r^2 R}{\Phi_0^2} \right)^2 + \omega^2} \right\}, \tag{30}$$

where a is the perpendicular distance of the proton to the molecular principal axis corresponding to the smallest eigenvalue of the moment of the inertia tensor. Incidentally, substitution of equation (29) into equation (30) yields the incoherent scattering law for the well-known case of an ensemble of perfectly oriented molecules subject to simple uniaxial rotational diffusion and simple translational diffusion of their centres of mass [7]. The incoherent scattering law for the simple molecular uniaxial rotational motion and its centre of mass translational diffusion only, is usually expressed [7] in the reference frame where the Q dependent coefficients are the cylindrical Bessel functions. The equivalent expression as given by equations (22) and (29), which is formulated

in terms of spherical Bessel waves, equation (3), is however particularly suitable for powder samples as the isotropic averaging can be performed immediately. The importance of the spherical harmonics formulation is evident in the case when one has to take into account the molecular *biaxiality* (and which seems to be present in all cyanobiphenyls [1]) in which case the quantities $S_{xx} - S_{yy}$ as well as $S_{zz} (= S_z)$ are both non-zero. For this to be true the molecule should not rotate freely (i.e. 360° revolution) about its long axis.

3. Experiment and data treatment

The experiment was performed at the time-of-flight spectrometer for cold neutrons at the R2 reactor in Studsvik. The spectrometer is described in detail elsewhere [20, 21] and hence only some relevant facts are given. The energy of the neutrons was 3·34 meV corresponding to the neutron wavelength of 4·95 Å. The detectors were placed at 14 different scattering angles ranging from 8° to 83° which is equivalent to a covered wavevector transfer region of $Q = 0·2 \text{Å}^{-1}$ to $Q = 1·6 \text{Å}^{-1}$. The energy and wavevector resolution at zero energy transfer were nearly constant and equal to $\Delta E = 0·25 \text{meV}$ (FWHM) and $\Delta Q = 0·1 \text{Å}^{-1}$, respectively.

The MBBA sample of area 3–5 cm² and thickness 0·7 mm was kept in a flat container of aluminium and the aligning magnetic field **H**, being produced by a permanent magnet, had a strength of about 1200 G. The sample made a 30° angle relative to the direction of the incoming neutron beam. This implies that when the orienting magnetic field is in the scattering plane the true parallel orientation of **Q** and **H** occurs at a scattering angle of 60°. This circumstance is noted when the comparison between measured and calculated spectra is made later. Four different measurements on the MBBA sample were performed. The nematic and the amorphous phases were measured with the magnetic field direction parallel and perpendicular to the scattering plane.

The measured spectra of scattered neutrons were corrected for trivial experimental effects by standard methods and normalized to absolute cross section units via vanadium calibration measurements. The contribution from multiple scattering was calculated by use of the computer code developed by Copley [22]. In order to derive the scattering kernel the scattering cross section obtained according to a Langevin diffusion model [23] was used. This is not strictly applicable for MBBA but does describe the measured spectra well enough to be used for this purpose. From these measurements the absolute incoherent scattering function per molecule, $S(Q, \omega)$, (expressed in units $(\text{meV})^{-1}$) were deduced and are reported in this work. The error in the absolute normalization is of the order of 5 per cent except for the spectrum at the largest scattering angle where, due to experimental difficulties, the normalization error may be as large as 20 per cent. However, the statistical errors are smaller than the points when not visible as vertical lines in the figure.

Models describing molecular motion in liquid crystals usually yield a scattering function for the quasielastic scattering only. Thus, all scattering of an inelastic nature should be accounted for in the measured spectra when making a comparison between model predictions and experimental results meaningful. This is an important fact in cases such as ours when the spectrometer has a rather broad resolution. Assuming that the inelastic contribution to the spectra does not change appreciably in the temperature interval of 10–20 K the variation in the measurements is attributed to the quasielastic scattering processes. For this purpose the measured $S(Q, \omega)$ in the

amorphous phase, in a wide range of energy transfer around the energy of the incident neutron, were used to determine the resolution function. This was convoluted, at all scattering angles, with the approximate model scattering law multiplied by the appropriate Debye–Waller factor and compared to the measurements.

4. Results and discussion

Equation (22) which is to be compared to the experimental results is a rather complicated function of S_χ (the even order parameters) the molecular structure and of the assumed molecular dynamical behaviour in the nematic phase. Long axis orientational fluctuations were omitted in the derivation. It is to be noted that the stochastic angular confined motion as envisaged, enters the expression in second order only, i.e. for l, s non-zero and $m' \neq 0$, thus the translational diffusion term is the dominant term.

Liquid crystal molecules are long molecules at least of the order of $20\,\text{Å}$ and usually quite longer. For this reason to ensure convergence of the series, equation (22), a large number of terms (say $l + s = 18$) ought to be included, the criterion for convergence is of course,

$$\int S(Q, \omega)\, d\omega = 1$$

(for one proton). Thus the exact knowledge of all (even) order parameters, S_χ, is required ($l + s < \chi < |l - s|$) but experimentally only S_2 and S_4 have been determined [24].

The mean field evaluation of the very high rank order parameters required in the calculations furnishes unreliable results and for this reason perfect molecular order is assumed, i.e. $S_\chi = 1$, which necessitates the experiment to be performed on an oriented sample. This choice precludes, of course, any temperature variation motional study. Such an expression has been utilized for comparison with the experimental data obtained on a magnetically oriented nematic sample of MBBA. The value of $1200\,\text{G}$ for the orienting magnetic field might cast some doubt that the limit for S_χ is indeed attained. Consequently, depending on the degree of misaligned the magnitude of ϕ_0 quoted further in the paper should be taken as an approximation being, by a crude estimate, up to 40 per cent in error.

Yasuniwa *et al.* [4] have investigated the dynamics of MBBA and EBBA molecules in solid, nematic, and isotropic phase by broad line NMR and Raman scattering methods and have in conjunction with the published volumetric and X-ray data, analysed the segmental motions of these compounds as well as the conformation of the end butyl chains. From the temperature dependency of the splitting widths of the broad line NMR spectra, corresponding to the protons of aromatic ring and azomethyn (–CHN–) group of MBBA an important conclusion has been made namely that this segment in the nematic phase experiences the motion of the single entity. The observed $310\,\text{cm}^{-1}$ Raman peak, which appears in the nematic and isotropic phases offers evidence of the existence of the constraint which adjacent molecules exert on a given MBBA molecule and in conjunction with the specific volume, clearing point and X-ray analysis it was concluded, that MBBA molecules are closely packed in the nematic phase. In order to interpret the measured NMR splitting the authors have found that the stem part of the end butyl chain of the MBBA molecule is rather loosely attached to the benzene ring. Namely in their calculations it was observed that

of all nine protons of the butyl chain the contribution to the splitting width of only those two closest to the benzene ring had to be taken into account and even then only to a small extent.

Ito *et al.* [3] have measured the (modified) spin–spin relaxation time, T_2^*, (it is qualitatively different from the T_2 as obtained by the usual free induction decay or the spin echo method) of the MBBA sample over the large temperature range from the solid to the isotropic phase and studied the relation between the structural changes and molecular dynamics. In the solid and nematic phases two discrete relaxation times were measured, characterized as long, T_{2L}^* and short T_{2S}^*, respectively which, however coalesce in the isotropic phase. These two relaxations were attributed to two groups within the MBBA molecule possessing different mobility. The T_{2L}^* component has been associated with the free rotation of the end methyl and butyl groups. Limiting ourselves to the nematic phase only, the study has advanced the following conclusions regarding the segmental motion of MBBA molecule in the temperature interval between 20°–46°C:

(1) at $T = 22$°C the methyl and *n*-butyl groups of MBBA molecule are uniformity rotating, while the motion of both phenyl rings linked together by the azomethyn group is, at this temperature, almost unobservable

(2) the motion of this rigid benzylidene unit of the MBBA molecule is, with increasing temperature, rapidly activated; its mobility being largest at the nematic–isotropic transition; and

(3) the measurements of the temperature dependence of both relaxation times during the cooling process in the nematic phase exhibit similar functional dependence indicating the gradual restriction of the mobilities of the molecular groups. On the warming process, however an anomaly of the long relaxation time behaviour within the temperature interval between 20°–25°C was observed.

Thus MBBA molecule is a likely candidate with which to test our predictions. Molecules in the nematic phase are constrained as far as their mobility is concerned. It is only at temperatures above 22°C that the phenyl rings are flexible enough that their dynamical reorientation, presumably of a uniaxial nature, become noticeable in the measured NMR spectra. In addition its structural data are known [13] since the MBBA molecule is obtained from EBBA just subtracting a CH_2 unit from the C_2H_5O group. It has been shown [18, 19], that the frequency dependence of the longitudinal spin–lattice relaxation time T_1 in the nematic phase of MBBA is, at large frequencies, dominantly influenced by the molecular translational self-diffusion and not the long axis orientational fluctuations. This dynamic process is expected therefore to be, on the cold neutrons scattering frequency scale, a relatively less important motional contribution to the scattering spectra and this is the reason that the contribution of the long axes molecular orientational fluctuation has not been included in the derivation of the equation (22).

Yasuniwa *et al.* [4] findings that the benzylidene part of an MBBA molecule in the nematic phase acts as a single unit and that the molecules are hindered, and Ito *et al.* [3] findings that close to the solid–nematic transition the dominant molecular motion consists of the uniform rotation of the end methyl and butyl groups, naturally lead to the description of the central molecular part rotational motion in the nematic phase as being approximated by the model of the angular confined uniaxial stochastic reorientation of the MBBA body and uniaxial simple rotational diffusion of the

molecular tails. The incoherent scattering law, is then of the form

$$S_{inc}(Q, \omega) = [S_{inc}(Q, \omega)]_{ACR} + [S_{inc}(Q, \omega)]_{RD}, \tag{31}$$

where the first term on the right hand side is given by equation (22) and the second is obtained by the appropriate substitution of equation (29). In equation (30) there are three unknown parameters, ϕ_0, R and D_1 and in principle they could be determined in fitting the theoretical predictions to the measured spectra. Such a division of the incoherent scattering law is necessary since the rotating methyl and butyl chains contain 12 protons and the remaining nine protons are attached to the benzylidine part of the MBBA molecule. In what follows the perfect molecular order, $S_\chi \equiv 1$, has been invoked. In view of the expression given by equation (25) the incoherent scattering law, equation (22), simplifies further and now becomes completely equivalent to the corresponding expression derived for the perfect homogeneous case written with the cylindrical symmetry, (see equation (30)).

In the computation the molecular centre of mass translational diffusion constant was taken to be $D = 2 \times 10^{-11}$ m^2/s the value reported in [18]. However, for a start it is more appropriate to fit the data for the $\mathbf{Q} \perp \mathbf{H}$ geometry with each model separately since then it is possible to investigate directly the sensitivity of the (rather broad spectrometer resolution) data to the two alternative descriptions of the molecular rotational motion in the nematic phase, at 30°C. To this purpose assuming the whole molecule to be rigid, we can determine separately the values of the parameters Φ_0 and R on the one hand, and D_1 on the other hand. Later, the measurements are easily refined according to equation (31). It ought to be emphasized that the required convolution of the model scattering law with the resolution function, for the case of our resolution, cannot be performed by the usual discrete fast Fourier transform method because of its lack of sensitivity. In the present case we used the analytical expression for the measured resolution function (obtained at $T = 10$°C) of the form

$$R(E) = x_1(1 - x_2 E)\exp[-(E/x_3)^2],$$

where the parameters x_1, x_2 and x_3 were determined for each particular Q separately.

The best fitting using the angular confined uniaxial reorientation model is obtained with the apex angle Φ_0 of 57° and the rate constant R of 2.3×10^{10} s^{-1}. For future reference we note that the experimental, absolute, incoherent scattering law, $S_{inc}(Q, E)$, is normalized to a single proton within the molecule.

The uniaxial rotational motion of all liquid-crystalline molecules studied by quasielastic incoherent cold neutron scattering has been successfully interpreted in terms of simple or jump rotational molecular diffusion. As jump rotational diffusion for $N \geqslant 6$, where N is the number of equilibrium sites, yields almost identical results to the simple rotational diffusion predictions, the later has been, as an alternative model of motion, also utilized in comparison to the measured spectra. The results of the fitting, in the $\mathbf{Q} \perp \mathbf{H}$ geometry, is such that for the value of the parameter D_1 of 1×10^{10} s^{-1} obtained in the fitting the measured spectra are described equally well in terms of uniaxial rotational diffusion of the assumed rigid MBBA. It is to be emphasized that the uniaxial rotation diffusion model can describe the measurements only for values of D_1 which do not differ from the quoted value by more than, say 10 per cent. Furthermore, also equation (30) where the (rigid) benzylidene group is subject to the angular confined uniaxial reorientation type of motion but the motion of both the alkoxy and butyl chains is represented by the uniaxial simple rotational diffusion,
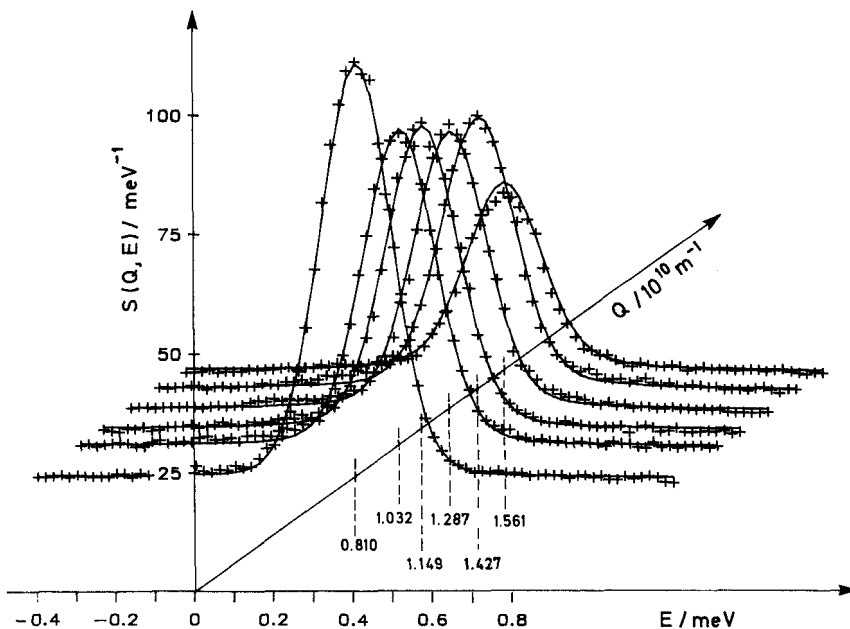
Figure 2. The measured incoherent scattering function normalized to one proton for the
MBBA molecule in the nematic phase at 303 K in the $\mathbf{Q} \perp \mathbf{H}$ geometry is compared to
the resolution broadened calculated scattering law describing the simple translational
diffusion of the molecular centre of mass $D = 2 \times 10^{-11}$ m^2/s, uniaxial rotational
motion of the rigid benzylidene molecular part represented by the stochastic, between
two perfectly reflecting potential barriers, angular confined librational motion charac-
terized by the apex angle Φ_0 of 57° and the rate constant R of 2.5×10^{10} s^{-1} and the
uniaxial simple rotational diffusion of the alkoxy and butyl chains of the diffusion
constant D_1 of 1×10^{10} s^{-1}, as obtained in the fitting procedure described in the text. The
measurements refer to the absolute values of the incoherent scattering law expressed per
one proton of the MBBA molecule. The error is of the order of 5 per cent and increases
with increasing scattering vector. At the largest Q shown the error is estimated to be 20
per cent.

results in the very good fit to the measurements providing the parameters are
$\Phi_0 = 57°$, $R = 2.5 \times 10^{10}$ s^{-1} and $D_1 = 1 \times 10^{10}$ s^{-1}. All three approaches
described here yield almost identical fits, within the experimental error being almost
indistinguishable among themselves. In the computation the attenuation effect in the
quasielastic region on account of the short time positional fluctuations of the proton
mass was taken into account by the Debye–Waller factor, $\exp(-Q^2 u^2)$. The mean
square displacement of the protons (an average over all protons in the molecule), u^2,
is in the nematic phase equal to 0.21 Å^2 ($T = 30°$C) and in the amorphous phase
0.16 Å^2 ($T = 10°$C). It is to be noted that within the given resolution we have
obtained, in the sense of the least square method (the χ^2 test), the best fits for the
parameters Φ_0, R and separately for D_1. A slight variation of these values from the
values quoted here for each of the three cases described, does worsen the agreement.
The elimination of one or perhaps even two among the three motional possibilities
mentioned, might be possible, providing the parameter D_1 could be known indepen-
dently or the sample could be selectively deuteriated. Evidently this is not the case in
the present study so we are left with three possibilities for the MBBA molecular

motion in the oriented nematic phase at 303 K which, judging on the basis of QNS method alone, would be:

(1) the (rigid) benzylidene part of MBBA molecule is subject to the angular confined stochastic diffusion within the apex angle Φ_0 of 57° and associated rate constant R of $2 \cdot 5 \times 10^{10} \, \text{s}^{-1}$ while both the alkoxy and butyl chains perform uniaxial simple rotational diffusion, the diffusion constant being $D_1 = 1 \times 10^{10} \, \text{s}^{-1}$, or

(2) the whole rigid molecule subject to angular confined stochastic diffusion within the apex angle Φ_0 of 57° and the associated rate constant R of $2 \cdot 3 \times 10^{10} \, \text{s}^{-1}$, or

(3) the whole rigid MBBA molecule is subject to uniaxial simple rotational diffusion where the rotational constant D_1 is $1 \times 10^{10} \, \text{s}^{-1}$.

The NMR studies clearly show the existence of two groups with different mobilities within the MBBA molecule. The mobility of one of them, identified as its benzylidene part, is at 29·5°C almost negligible and increases with increasing temperature. However, as shown in figure 3 of [4], the mobility of this central molecular part is a monotonic function of temperature. This finding is in direct contradiction with cases 2 and 3 proposed here, as they do not account for the existence of the two groups with different dynamical behaviour. Furthermore case 3 has to be ruled out completely as in order, that the model of the uniaxial rotational diffusion of the rigid molecular body would indeed correspond to our QNS measurements at 303 K, a discontinuity in the temperature dependence of the NMR splitting widths at $T = 295 \, \text{K}$ (or above) would be required. Existence of such a discontinuity would present evidence that a strong and fast motion, absent at 295 K had been activated. But no such behaviour has been observed.

The incoherent scattering law of case 1 is the one which can therefore straightforwardly accommodate the findings as obtained by the T_2^* measurements of Ito *et al.* [3], as well as, to a large degree, of Yasuniwa *et al.* [4]. For this reason the findings of the present QNS investigation seem to be that the gradient of flexibility occurring along the two phenyl rings of MBBA in the temperature interval between 22°C and 30°C is now qualitatively modelled and if the Ito *et al.* description of MBBA molecular motion is correct it is then required that at 22°C the apex angle Φ_0 within which the aromatic rings rotationally diffuse is small indeed and it is likely to increase with the increasing temperature.

In part II of the series, we deal with the geometry of the MBBA motion as well as the deuteron quadrupole spin–lattice relaxation rate evaluation of the nematic liquid crystal 4-*n*-pentyl-4'-cyanobiphenyl. There, an additional support to the claim that, even in this phase the uniaxial reorientation of the central molecular segments might be restricted, is presented.

5. Conclusions

The model of the uniaxial, angular restricted, molecular rotational diffusion on the segment of an arc with the apex angle Φ_0, which in a further elaborated form, could accommodate the requirement for the molecular motion in nematics, with biaxial molecules has been described. The incoherent cold neutron scattering data from the magnetically oriented sample of MBBA in the locally uniaxial nematic phase at 303 K for six spectra in $\mathbf{Q} \perp \mathbf{H}$ and 1 spectrum in $\mathbf{Q} \parallel \mathbf{H}$ orientations have been interpreted

on the basis of simple translational diffusion of the molecular centre of mass and two different models for the benzylidene groups uniaxial rotation. These were either the model of simple uniaxial rotational diffusion or, alternatively, the model of stochastic, between two perfectly reflecting potential barriers, angular confined uniaxial librational motion. The motion of the alkoxy and butyl chains has been, on the basis of the published NMR investigations, represented by simple uniaxial rotational diffusion. Within the limit of the available energy resolution of the spectrometer the measurements are equally well described in terms of either of the two uniaxial rotational models. In conjunction with the published NMR spin–spin relaxation time measurements, NMR broad line study and Raman scattering results the QNS investigation provides a description according to which the rotational motion of the MBBA molecule in the nematic phase at 303 K is composed of (assuming uniaxial simple rotational diffusion of both the end methyl and butyl chains the corresponding diffusion constant being $D_1 = 1 \times 10^{10}\,\mathrm{s}^{-1}$) uniaxial small step stochastic angular displacements restricted within an angular interval of $\phi_0 = 57°$, with the associated rate constant $R = 2.5 \times 10^{10}\,\mathrm{s}^{-1}$, of the rigid benzylidene central molecular part. The uniaxial axis in question is identified as the one corresponding to the smallest principal value of the moment of inertia tensor.

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