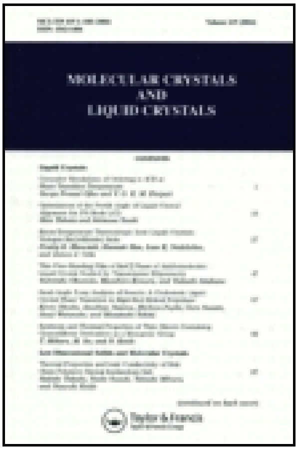

Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl16

Nuclear Magnetic Relaxation and Self Diffusion in a Series of p-Alkanoyl-Benzylidene-P'-Aminoazobenzenes

G. J. Krüger [a] , H. Spiesecke [a] , R. Van Steenwinkel [a] & F. Noack [b]

[a] Magenetic Resonance Laboratory, Physics Division, Euratom CCR, 1-21020, Ispra, Italy

[b] Phys. Inst. der UniversitaUt stuttgar, D-7000, Stuttgart, 80, Germany

Version of record first published: 21 Mar 2007.

To cite this article: G. J. Krüger , H. Spiesecke , R. Van Steenwinkel & F. Noack (1977): Nuclear Magnetic Relaxation and Self Diffusion in a Series of p-Alkanoyl-Benzylidene-P'-Aminoazobenzenes, Molecular Crystals and Liquid Crystals, 40:1, 103-116

To link to this article: http://dx.doi.org/10.1080/15421407708084474

Mol. Cryst. Liq. Cryst., 1977, Vol. 40, pp. 103–116
© Gordon and Breach Science Publishers, Ltd., 1977
Printed in Holland

Nuclear Magnetic Relaxation and Self Diffusion in a Series of *p*-Alkanoyl-Benzylidene-*p'*-Aminoazobenzenes

G. J. KRÜGER, H. SPIESECKE and R. VAN STEENWINKEL
Magnetic Resonance Laboratory, Physics Division, Euratom CCR, I-21020 Ispra, Italy

and

F. NOACK
Phys. Inst. der Universität Stuttgart, D-7000 Stuttgart 80, Germany

(*Received October 28, 1976*)

The self diffusion coefficients and the proton relaxation times have been measured in dependence of temperature in a series of *p*-alkanoyl-benzylidene-*p'*-aminoazobenzenes. Together with the frequency dependence of the relaxation rate of *p*-dodekanoyl-benzylidene-*p'*-aminoazobenzene it could be shown that order fluctuations as well as the translational diffusion process contribute to the relaxation rates.

1 INTRODUCTION

Nuclear magnetic relaxation, together with impurity and self diffusion in *p*-dodecanoyl-benzylidene-*p'*-aminoazobenzene were the subject of earler investigations.[1,2] In the meantime, the measuring technique, especially for the measurement of diffusion coefficients in liquid crystals, has been improved and an investigation of ethyl *p*-(*p*-ethoxybenzylidene)-amino-cinnamate (EBAC) and TBBA has been published.[3] It seemed therefore reasonable to extend these studies to other members of the series of *p*-alkanoyl-benzylidene-*p'*-aminoazobenzenes in order to see the influence of the chain length on the diffusion and relaxation processes. In addition we present here the full frequency dependence of the proton Zeeman relaxation time T_{1Z} of C_{12}–AA which allows a much better interpretation of the relaxation data. For the sake of simplicity we denote the $CH_3(CH_2)_nCOO\phi{=}N\phi N{=}N\phi$ by C_{n+2}-AA.

2 EXPERIMENTAL

As usual, all our experiments were done by first heating the sample to the isotropic regime and then cooling it down to the nematic state. Here, it was allowed to stay for some time in the strong measuring field H_0 in order to orient the molecules. This initial orientation of the molecules in the sample was kept for all subsequent measurements in the different phases.

The temperature dependence of the relaxation rates was investigated at a proton resonance frequency of 15 MHz. The Zeeman relaxation time T_{1Z} of the protons was measured in the usual way, the dipolar relaxation time T_{1D} with a $90°$-τ-$45°_{90°}$-t-$45°$ pulse sequence.[4] In these measurements the temperature of the sample was controlled to better than ±0.05 K and the temperature gradient over the sample was less than ±0.01 K. The errors of T_{1Z} and T_{1D} were $\pm 5\%$ and $\pm 10\%$ respectively.

For the investigation of the frequency dependence of T_{1Z} pulse spectrometers with different magnetic fields and frequencies from 7 to 28 MHz were used. At low frequencies a field cycling technique was applied, which consisted in measuring the signals at 7 MHz and switching the magnetic field H_0 between the RF-pulses to the desired relaxation field.[5]

The self diffusion coefficients were measured at 48 MHz using a two pulse proton spin echo. In the smectic phases the sample was practically a "smectic single crystal" since after the initial orientation in the nematic state it was cooled down in the magnetic field. This "smectic single crystal" was then turned by the magic angle and thus a long T_2 for the diffusion coefficient measurement was obtained.[2,6] The pulsed field gradient of up to 1.2 kG/cm was then applied either parallel or perpendicular with respect to the magic angle direction, allowing the measurement of the two self diffusion coefficients parallel ($D_{\parallel}$) and perpendicular ($D_{\perp}$) with respect to the average orientation of the molecular director. The field gradient was generated in a quadrupole coil[7] which was sufficiently symmetric for its gradient to be practically the same for all orientations obtained by rotating the coil about its long axis. As is well known, the direction of the field gradient changes with twice the turning angle of the coil. This effect was already used in our old measurements on C_{12}-AA[2] and in other nematic liquid crystals.[7]

In the nematic regime a $90°$-τ-β pulse sequence was used with $\beta < 90°$, and both RF pulses had the same phase. This sequence creates an echo at time 2τ, which shows modulation by dipolar interaction.[7,8] This particular echo has a rather long T_2, much longer than the $90°$-τ-$90°_{90°}$ solid echo[9,10]

Since it was observed first in nematics,[8] where its amplitude is much larger than in smectics, we call it the "nematic echo" for brevity. The rotation angle β of the second RF pulse was always adjusted to the optimum value β_{opt} for maximum echo amplitude.

The solid echo was also observed in our substances in the nematic regime and decayed completely within about 0.4 ms. The nematic echo, however, could still be measured at pulse spacings of the order of ms e.g. at time intervals of several ms between the 90° pulse and the echo. In contrast to the solid echo the amplitude of the nematic echo for large pulse spacing and at β_{opt} does not depend on the phase difference of the RF pulses. If both pulses have the same phase, the nematic echo has a 180° phase shift with respect to the free induction decay following the first 90° pulse. It behaves, in this respect, as a normal spin echo in a liquid. The value of β_{opt} depends on the substance used. All our observations on different nematics and on impurity molecules dissolved therein, suggest that β_{opt} must be the smaller, the larger is the number of coupled nuclear spins in the molecule e.g. the larger is the total spin of the coupled nuclei in the molecule. This could be similar to the behaviour of β_{opt} of the quadrupolar echo in solids.[11] Boden *et al.*[9] have calculated the nematic echo for the special case of pairs of two spins. They obtained $\beta_{\text{opt}} = 54.7°$ and a rather short (order of 0.1 ms) gaussian decay of the echo amplitude. In all cases observed by us we found $\beta_{\text{opt}} < 54.7°$. For the four *p*-alkanoyl-benzylidene-*p*′-aminoazobenzenes β_{opt} ranged from 39° to 45°. With increasing τ the nematic echo decay was neither exponential nor gaussian.

It seems to be quite complicated to calculate the nematic echo in a multiple spin system. However, since it is observed at a time much longer than the free induction decay (f.i.d.) and since it has a phase behaviour as a liquid echo, we may argue as follows: The nematic echo consists of transverse components of the nuclear magnetization. These are part of the transverse components created by the first 90° pulse. A pair of gradient pulses applied in the same way as in a liquid[12] has an additional effect on each transverse magnetization component, just as in a liquid. Therefore the ratio of the amplitudes of the nematic echo A with, and A_0 without, gradient pulses shows us the additional effect of the gradient pulses and the diffusion of spins in the same way as in a liquid. The cases of multipulse echoes in nematics[13] and smectics[14] are different, because, there, the time intervals between the RF pulses are much shorter than the f.i.d. In our case, the self diffusion coefficient can be measured by A/A_0 provided the adjustment of the RF pulses and their spacing are the same with and without gradient pulses in one particular measurement. Of course, different spacings of the RF pulses and the gradient pulses, must lead to the same value of the diffusion coefficient, and this is indeed observed within the limit of accuracy of our measurements.

The measurement of the diffusion coefficients in a nematic phase using the nematic echo is then as simple as a measurement in an isotropic liquid. $D_{\parallel}$ and $D_{\perp}$ are obtained with field gradients parallel and perpendicular with respect to the direction of the magnetic field H_0 respectively. The measuring accuracy, however, is not very good since the nematic echo is rather small compared with a liquid echo. We assume an error of $\pm 30\%$ for both $D_{\parallel}$ and $D_{\perp}$ in the nematic regime. In the SmA range our measuring accuracy is typically $\pm 10\%$ due to the larger amplitude of the two pulse spin echo at the magic angle orientation of the sample. In the SmB, however, we have again an error of $\pm 30\%$ due to the shorter T_2 and the small values in the order of 10^{-8} cm^{2}s^{-1} of both diffusion coefficients.

In SmB phases we have to use very large field gradient pulses (up to the order of 1 kG/cm). This creates an additional problem due to transient effects in the magnet pole faces. In order to avoid this we used additional gradient pulses of the order of several hundred G/cm and opposite polarity with respect to the large measuring pulses. The whole pulse programme is shown in Figure 1. All the timing of the programme is done by a digital pulse generator constructed in the electronic department of the JRC Ispra.[15] It can easily be shown that the ratio of the amplitudes A_0 and A is given by:

$$\begin{aligned}
\ln\left(\frac{A_0}{A}\right) = \gamma^2 D \Big\{ & \delta^2\left(\Delta - \frac{\delta}{3}\right)g^2 + \delta_1^2\left(\Delta - \frac{\delta_1}{3}\right)g_1^2 \\
& - \delta\delta_1[2(\Delta - \Delta_1) + \delta - \delta_1]gg_1 \\
& + \delta\Big[2\tau^2 - t_1^2 - (t_2 + \Delta_1 - \delta + \delta_1)^2 \\
& - \delta(t_1 + t_2 + \Delta_1 - \delta + \delta_1) - \frac{2\delta^2}{3}\Big]\mathbf{g}_0\mathbf{g} \\
& + \delta_1\Big[2\tau^2 - (t_1 + \Delta_1)^2 - t_2^2 \\
& - \delta_1(t_1 + \Delta_1 + t_2) - \frac{2\delta_1^2}{3}\Big]\mathbf{g}_0\mathbf{g}_1 + \frac{2\tau^3 g_0^2}{3}\Big\}
\end{aligned}$$

(γ is the gyromagnetic ratio, D the self diffusion coefficient, all the times and gradients are given in Figure 1). In our case where $g_0 \approx 1$ G/cm we can neglect the terms containing g_0. In most cases, also the terms with g_1^2 and even with $g \times g_1$ may be neglected depending on the special values of g and g_1.

Due to the gradient coil arrangement, the temperature of the sample head used for the diffusion coefficient measurements could only be controlled to ± 0.4 K and the absolute accuracy was ± 2 K.

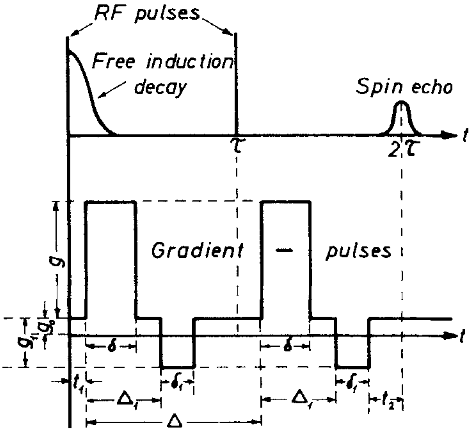

FIGURE 1 Pulse programme used for the measurement of diffusion coefficients.

3 RESULTS

The measured diffusion coefficients of C_6-AA, C_9-AA, C_{10}-AA and C_{12}-AA are shown in Figures 2–5. Figure 5 contains only the remeasured values in the SmB regime, whereas in SmA the least squares fits of the data of Ref. 2 are indicated by solid and broken lines for comparison. The diffusion coefficients in the smectic B range shown in Ref. 2 were only correct for $D_{\parallel} \cdot D_{\perp}$ was erroneously given too big a value due to a defect in the gradient coil.

The diffusion coefficients show a similar behaviour in all cases. In the SmA phases both $D_{\parallel}$ and $D_{\perp}$ obey an Arrhenius type of activation law. The activation energies $E_{\parallel}$ and $E_{\perp}$ and the pre-exponential factors $D_{\parallel 0}$ and $D_{\perp 0}$ are given in Table I. These values were obtained by least squares fits to the measured data and were used for the lines in the corresponding figures. The activation energies $E_{\perp}$ are practically the same for all cases. $E_{\parallel}$ shows some

TABLE I

Activation energies (in kcal/mole) and pre-exponential factors (in cm^2/s) of the self diffusion coefficients in the smectic A regime of C_n-AA. The errors are the probable errors of the least squares fits.

n	$E_{\parallel}$	$E_{\perp}$	$D_{\parallel 0}$	$D_{\perp 0}$
6	33.1 ± 1.4	13.3 ± 0.7	8.9×10^{11}	11.7
9	22.5 ± 0.6	12.9 ± 0.8	4.36×10^{5}	6.82
10	29.0 ± 0.8	13.1 ± 0.5	1.01×10^{9}	6.70
12	25.9 ± 0.7	11.5 ± 0.5	1.60×10^{7}	1.03

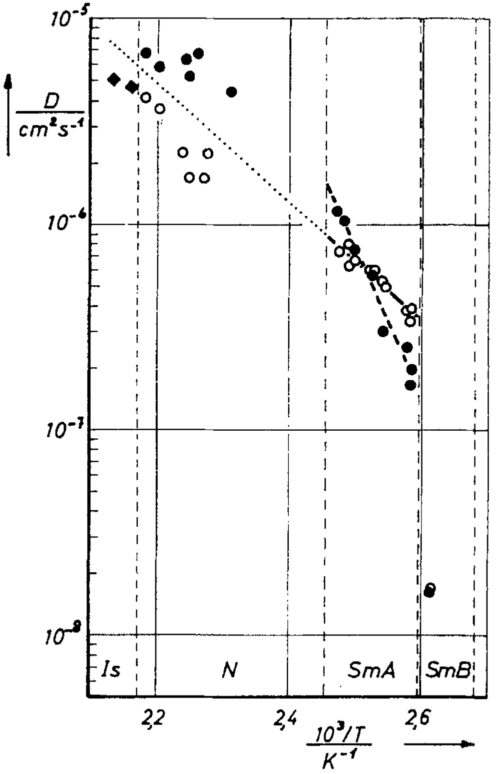

FIGURE 2 Self diffusion coefficients $D_\perp$ (○——○), $D_\parallel$ (●----●) and D_{is} (◆) of C_6–AA vs. reciprocal temperature. Transition temperatures are indicated by broken lines. .... extrapolation of $D_\perp$ into the nematic and isotropic phases.

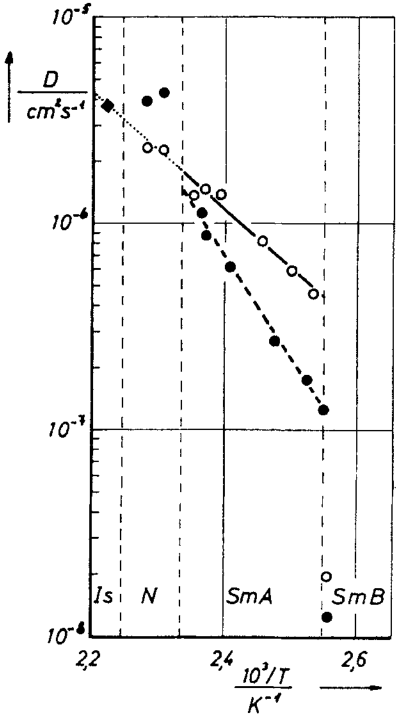

FIGURE 3 Same as Figure 2 for C_9–AA.

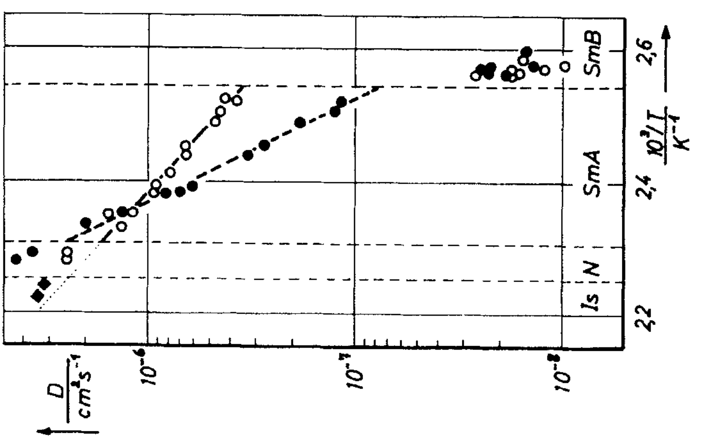

FIGURE 4 Same as Figure 2 for C_{10}–AA.

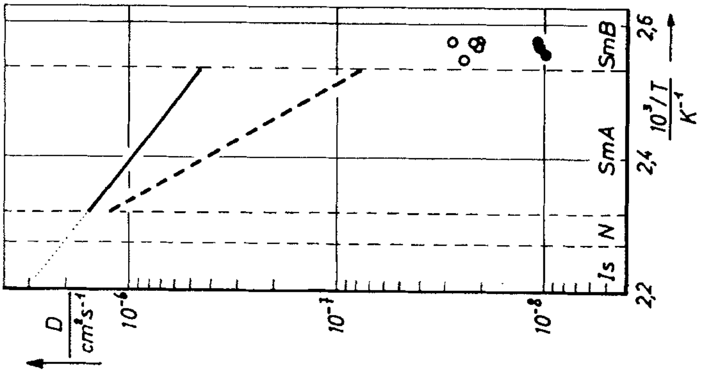

FIGURE 5 Same as Figure 2 for C_{12}–AA.

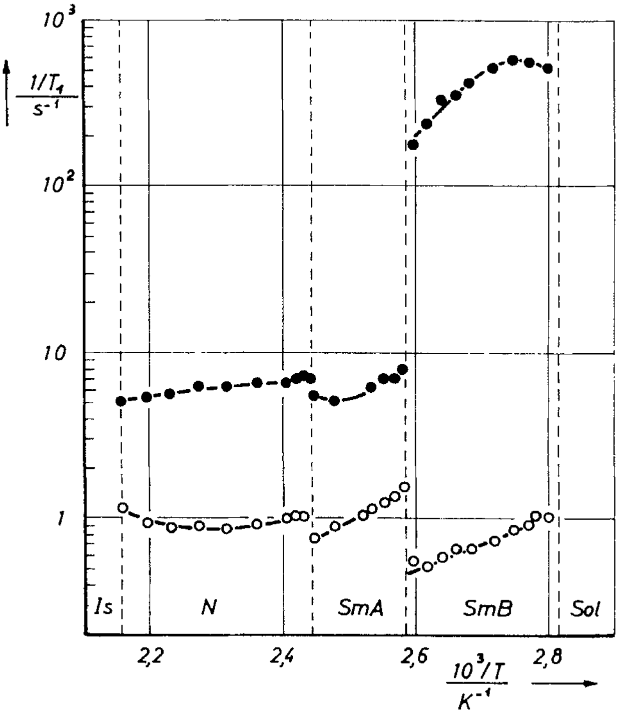

FIGURE 6 Proton Zeeman (○) and dipolar (●) relaxation rates of C_6–AA vs. reciprocal temperature.[†]

changes in dependence of the chain length. C_6–AA, particularly, has a larger $E_{\|}$ than the others.

At the smectic A to B phase transition, both $D_{\|}$ and $D_{\perp}$ show a discontinuity of about one order of magnitude. In the smectic B regime the anisotropy of the diffusion is small and it seems that always $D_{\perp} > D_{\|}$. The same behaviour was observed in EBAC[3].

The temperature dependence of the relaxation rates is shown in Figures 6 to 8. The corresponding Figure for C_{12}–AA was already shown in Ref. 1. The relaxation rates of all four components behave similarly. All relaxation rates show discontinuities at the phase transitions indicating that they must be of first order. In contrast to all the others, C_9–AA shows opposite slopes for $1/T_{1D}$ and $1/T_{1Z}$ in the nematic regime. This was the only odd chain length

---

[†] We call the phase between SmA and solid in the case of C_6–AA a smectic B phase, although it has been quoted in the literature as a SmC phase,[24] because the relaxation rates and diffusion coefficients behave in that phase and at the phase transition from the SmA range into that phase exactly as in the SmB phase of the other C_n–AAs.

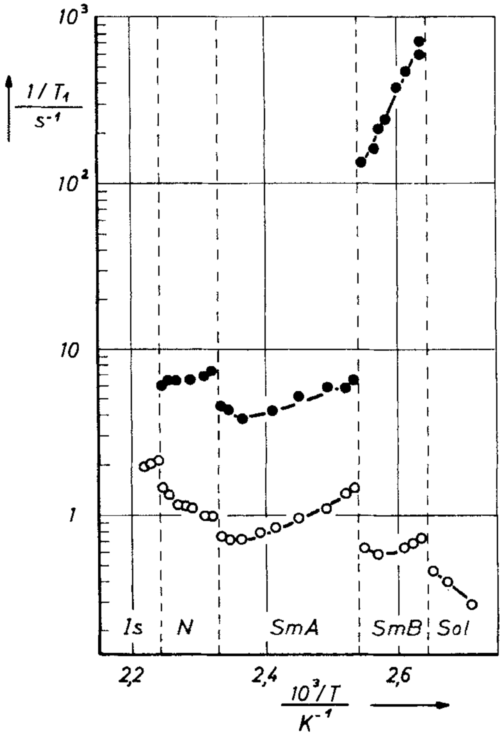

FIGURE 7 Same as Figure 6 for C_9-AA.

investigated so we do not know whether this particular relaxation behaviour is due to an even–odd effect. The relaxation rates $1/T_{1Z}$ and $1/T_{1D}$ at the nematic to smectic A and SmA to B phase transitions do practically not depend on the chain length.

Finally, the frequency dependence of $1/T_{1Z}$ in different mesophases of C_{12}-AA is given in Figure 9. It is obvious that we have very different frequency dependences in different phases.

4 DISCUSSION

The discussion of the temperature dependence of the relaxation rates together with the diffusion in the smectic phases of EBAC was given in our earlier paper.[3] It could be shown that diffusion inside the SmA planes ($D_\perp$) is liquid like, whereas from plane to plane ($D_\parallel$) we have a pseudolattice jump process.[14] In the SmB regime we have jump processes in all directions and therefore $D_\parallel$

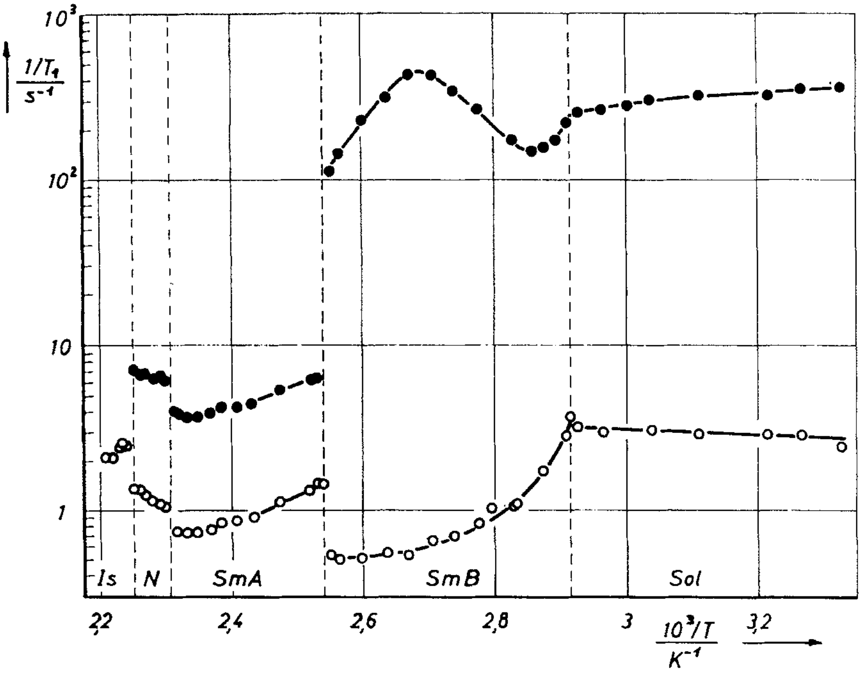

FIGURE 8 Same as Figure 6 for C_{10}-AA.

and $D_\perp$ have rather similar behaviours. The *p*-alkanoyl-benzylidene-*p*′-aminoazobenzenes behave in the same way. In the nematic range, the diffusion is liquid like in the sense that, unlike in a lattice, no defined jump distance exists in any direction. It shows, however, an anisotropy and we find always $D_\parallel > D_\perp$ as in all nematic systems investigated so far.[7,13,16] The average ratios $D_\parallel/D_\perp$ are given in Table II. For averaging we assume that $D_\parallel/D_\perp$ is not temperature dependent in a nematic.[7,13] In our present set of substances only C_6–AA has a sufficiently large nematic range to show the temperature dependence of the diffusion coefficients. The measurement accuracy, however, is not sufficient to determine $E_\parallel$ and $E_\perp$. The measured values in combination with the error of ±30% are compatible with the assumption of equal

TABLE II

Ratio of $D_\parallel/D_\perp$ in the nematic phase of C_n-AA

n	6	9	10
$D_\parallel/D_\perp$	2.6	1.8	1.6

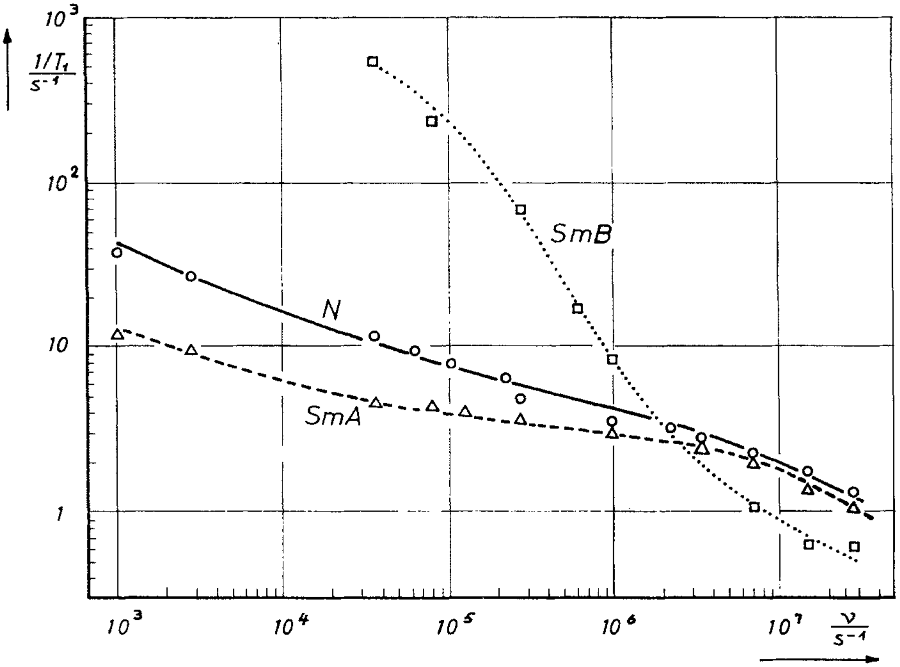

FIGURE 9 Frequency dependence of the proton Zeeman relaxation rate of C_{12}-AA. The solid, dashed and dotted curves correspond to the theoretical fits (see text).

activation energies of both $D_{\parallel}$ and $D_{\perp}$ in the nematic regime[7,13] and these activation energies are about equal to that of $D_{\perp}$ in the SmA region.

The frequency dependence of the spin lattice relaxation rate caused by order fluctuations in a nematic is given by[17,18]

$$\frac{1}{T_{1Z(OF)}} = A + B\nu^{-1/2} \tag{4.1}$$

Blinc showed that Eq. (4.1) holds even in a SmA phase and even if the order fluctuation is diffusion induced.[19] We have tried, therefore, to adopt such a process in both smectic A and B phases. On the other hand, the measured frequency dependence of Figure 9 shows clearly that other relaxation processes must contribute. From the similarity with the EBAC data[3] we conclude, with the same reasoning used there, that translational diffusion must play an important role in the relaxation of both the smectic phases. Its contribution in the nematic regime is less certain. There may be also contributions from intramolecular interactions other than order fluctuations.[18] Since the additional process turns out to be less important in the nematic than in the smectic regimes, we use for a first approach the translational diffusion process in all three phases and call its contribution to the relaxation rate $1/T_{1Z(t)}$. We must bear in mind, however, that in the nematic it may well be an intramolecular process or a mixture of processes with a similar intensity function. The details of the translational diffusion relaxation have not been evaluated, so far, for liquid crystals. We take therefore the intensity function calculated by Torrey[20] for isotropic liquids and for cubic lattice jump processes. We also have to remember that the correlation time for such a process may be different from the jump time.[21] We think that this approach is reasonable to account for the frequency dependence since the intensity functions of translational diffusion are not very sensitive to changes in the microscopic model of the process. Of course we can then achieve only the relative frequency dependence and the correlation time τ_c of $1/T_{1Z(t)}$, whereas the absolute value does not allow us to draw further conclusions. In the nematic regime, where the contribution of $1/T_{1Z(t)}$ is only important over a small frequency range from 100 kHz to 10 MHz, we arbitrarily assumed Torrey's parameter $\alpha \approx 0$, which corresponds to very small jump lengths as compared with the molecular dimensions. In the SmA range we took $\alpha = \frac{1}{12}$ corresponding to jump lengths of the order of the molecular dimension in order to account for the $D_{\parallel}$ jumps with a jump length of about the smectic layer distance.[3] In this case $1/T_{1Z(t)}$ is the most important contribution to $1/T_{1Z}$ for frequencies between 100 kHz and 20 MHz. Only at frequencies lower than 100 kHz and larger than 20 MHz do we find an important contribution of $1/T_{1Z(OF)}$. This can be seen also from the temperature dependence of $1/T_{1Z}$ at 15 MHz.[1] The similar but somewhat smaller slope of $1/T_{1Z}$ as compared to the slopes of the diffusion coefficients (their average value should give the slope of the correlation time τ_c) is due to the fact that we are already close to the maximum relaxation rate where $1/T_{1Z(t)}$ has a smaller slope than τ_c.[20,21] In the SmB phase we took Torrey's intensity function for cubic lattices,[22] the relative frequency dependence of which is practically indistinguishable from the case of isotropic diffusion in a liquid with $\alpha = \frac{1}{12}$. Thus we have the same frequency dependence of the intensity function as in the SmA regime. In SmB we find that $1/T_{1Z(t)}$ is much more important than $1/T_{1Z(OF)}$ at low frequencies up to 1 MHz. At high frequencies, however, $1/T_{1Z(OF)}$ becomes more important. The parameters, A and B of Eq. (4.1), used in the fit are given in Table III together with the correlation time τ_c (not the jump time) of the translational diffusion process. Equal values of τ_c in the nematic and SmA phases do not mean that the jump times τ are also equal. For $\alpha \approx 0$ we have $\tau_c \gg \tau$.[21] Further we give the values of $1/T_{1Z(t)0}$ at zero frequency. Since the contribution of the order fluctuations in the smectic phases is only important over very small frequency ranges either at low or at high frequencies, the fit of $1/T_{1Z(OF)}$ is not so accurate and the values of A and B are less meaningful than in the nematic regime.

TABLE III

Fitting parameters of the frequency dependence of $1/T_{1Z}$ of C_{12}-AA (see text).

Phase	A/s^{-1}	$B/s^{-3/2}$	τ_c/s	$T^{-1}_{1Z(\omega 0)}/s^{-1}$
Nematic	0.6	1200	9.4×10^{-9}	3.5
SmA	0.6	320	9.4×10^{-9}	2.6
SmB	0	2700	1.8×10^{-6}	1000

In smectic B phases we have a high dipolar relaxation rate which normally has its maximum in this regime. The modulation frequency of the free induction decay, which corresponds to the frequency of the local dipolar field, is about 10 kHz. With the correlation time of the translational diffusion we obtain, therefore, $\Delta\omega\tau_r \approx 0.1$, which is not an unreasonable value at the maximum of $1/T_{1D}$. This confirms our assumption of $1/T_{1D}$ being caused mainly by the translational diffusion process.[3]

5 CONCLUSION

It appears from this study that diffusion inside smectic A layers is liquid like and that from plane to plane there is a pseudolattice jump process as was the case in other smectics.[3] The main argument for this are the different activation energies of $D_\parallel$ and $D_\perp$ in smectic A phases.[3] In smectic B we assume jump diffusion of a pseudolattice type in all directions. The diffusion process contributes to the spin lattice relaxation rates $1/T_{1Z}$ at low frequencies and to $1/T_{1D}$ in the smectic B range. Its contribution in the smectic A regime is weaker but still significant. The order fluctuations contribute to $1/T_{1Z}$ over a large frequency range in both nematic and smectic A phases, whereas in smectic B they only contribute at high Larmor frequencies. In the nematic phase we cannot state that the second process contributing to $1/T_{1Z}$ is diffusion. It can as well be an intramolecular process or a sum of processes with a similar intensity function.

Acknowledgements

The authors wish to thank Mr. J. Cametti and Mr. R. Weiss for their valuable help with the measurements and Dr. G. A. Helcké for revision of the manuscript.

References

1. G. J. Krüger, H. Spiesecke, and R. Van Steenwinkel, *J. Physique Colloq.*, **36**, C1-91 (1975).
2. G. J. Krüger, H. Spiesecke, and R. Weiss, *Phys. Lett.*, **51A**, 295 (1975).
3. G. J. Krüger, H. Spiesecke, and R. Van Steenwinkel, *J. Physique Colloq.*, **37**, C3-123 (1976).

4. J. Jeener, *Adv. in Magnetic Resonance*, **3**, 205 (1968).
5. M. Stohrer and F. Noack, Proc. 18th Ampere Congress, p. 245, Nottingham (1974).
6. J. W. Doane and R. S. Parker, Proc. 17th Congress Ampere, p. 410, North Holland Publishing Co., Amsterdam (1973).
7. G. J. Krüger and H. Spiesecke, *Z. Naturforsch.*, **28a**, 964 (1973).
8. G. J. Krüger and H. Spiesecke, *Ber. Bunsenges.*, **75**, 272 (1971).
9. N. Boden, Y. K. Levine, D. Lightowlers, and R. T. Squires, *Chem. Phys. Letters*, **31**, 511 (1975).
10. N. Boden, Y. K. Levine, D. Lightowlers, and R. T. Squires, *Chem. Phys. Letters*, **34**, 63 (1975).
11. M. Mehring and O. Kanert, *Z. Naturforsch.*, **24a**, 768 (1969).
12. E. O. Stejskal and J. E. Tanner, *J. Chem. Phys.*, **42**, 288 (1965).
13. I. Zupančič, J. Pirš, M. Luzar, R. Blinc, and J. W. Doane, *Solid State Commun.*, **15**, 227 (1974).
14. R. Blinc, M. Burgar, M. Luzar, J. Pirš, I. Zupančič, and S. Žumer, *Phys. Rev. Letters*, **33**, 1192 (1974).
15. A. Sajeva and L. Stanchi, *Nucl. Instr. and Methods.*, **106**, 549 (1973).
16. A. J. Leadbetter, F. P. Temme, A. Heidemann, and W. S. Howells, *Chem. Phys. Letters*, **34**, 363 (1975).
17. W. Wölfel, F. Noack, and M. Stohrer, *Z. Naturforsch.*, **30a**, 437 (1975) and further references cited there.
18. P. Ukleja, J. Pirš, and J. W. Doane, *Phys. Rev.*, **A14**, 414 (1976).
19. R. Blinc, M. Luzar, M. Vilfan, and M. Burgar, *J. Chem. Phys.*, **63**, 3445 (1975).
20. H. C. Torrey, *Phys. Rev.*, **92**, 962 (1953).
21. G. J. Krüger, *Z. Naturforsch.*, **24a**, 560 (1969).
22. H. A. Resing and H. C. Torrey, *Phys. Rev.*, **131**, 1102 (1963).
23. R. Blinc, M. Luzar, M. Mali, R. Osredkar, J. Seliger, and M. Vilfan, *J. Physique Colloq.*, **37**, C3-73 (1976).
24. D. L. Fishel and P. R. Patel, *Mol. Cryst. Liq. Cryst.*, **17**, 139 (1972).