Molecular Crystals and Liquid Crystals Incorporating Nonlinear Optics

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl17

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Version of record first published: 13 Dec 2006.

Mol. Cryst. Liq. Cryst., 1987, Vol. 150b, pp. 201–219
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Printed in the United States of America

Orientational Behaviour of Phosphonic Acid Dialkyl Esters in Nematic and Smectic Phases of Pentoxy-benzylidene-hexylaniline Studied by ^{1}H, ^{2}H, and ^{31}P NMR

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(*Received February 16, 1987*)

The orientational behaviour of a variety of phosphonic acid diesters dissolved in different liquid crystalline phases of pentoxy-benzylidene-hexylaniline was studied. For the complete determination of the orientational ordering of the phosphonate segment, partially deuterated esters were synthesized and a combination of ^{31}P, ^{2}H and ^{1}H NMR was used.

For solutions of hexane phosphonic diethyl ester dissolved in the nematic and S_A phases, the order parameter, S_{33} increases from 0.22 to 0.42 with a biaxiality of 0.1. The $CH_2P(O)O_2$ segment is in the *trans*-conformation and the S_{33} axis makes an angle of 22° with the P=O bond. In the S_B phases the value of S_{33} of the phosphonate segment decreases dramatically to a value of 0.1 in contrast to that of the molecules of the matrix. The reason is that the solute molecules are excluded from the more ordered aromatic region and are forced into the less-ordered hydrocarbon chain region of the matrix. In the S_G phase, a phase separation occurs.

In diethyl esters with *n*-alkyl substituents, S_{33} increases with the chain length of the substituent.

Keywords: spin labels, nematic ordering, smectic ordering, phosphonic acid derivatives, NMR

INTRODUCTION

Phosphonic acid dialkyl esters have been studied in lyotropic liquid crystals in order to throw some light on their behaviour as spin labels

for investigating biological membranes and their influence on the physical properties of membrane systems.[1-5] In thermotropic liquid crystals, interactions due to the hydrophilicity of the phosphonate groups[6] and the ability of the phosphoryl group to form bonds,[7-10] are absent. The comparison of the results obtained in thermotropic and lyotropic matrices should help us to understand the role which the interactions, additionally present in the latter, play in determining the orientational behaviour of these esters in membranes.

The esters studied are relatively large molecules in which large-amplitude conformational changes take place. The determination of the orientation of such large molecules requires many experimental parameters, and special efforts must be made to obtain them from NMR experiments. A further problem is posed by the coupling between the inter- and intramolecular motions of the dissolved molecules.[11-13] The number of protons in the molecules is large and therefore it is not feasible to resolve the dipolar splittings in the proton spectra. In this paper we determine the orientational behaviour of the central part of the molecules only, i.e., of the $—CH_2P(O)O_2$ segment. The corresponding order parameters were deduced from ^{31}P, ^{1}H and ^{2}H NMR experiments. The restriction to this small molecular subunit gives us only local order parameters and no detailed information about the conformation of the whole molecule. The liquid crystalline states of the matrix were studied over a temperature range of about 40°C. We can assume that the intermolecular forces and therefore the molecular conformation do not change appreciably over this relatively small temperature range. Hence the local order parameters also reflect the orientational ordering of the whole molecule.

We used pentoxy-benzylidene-hexylaniline as the liquid crystalline host matrix. This compound has four different smectic phases (A, C, B, G) below the nematic state.[14] This variety of phases allows us to study the phosphonic dialkyl esters in surroundings with different degrees of order.

To our knowledge, this is the first study in which the orientational behaviour of the phosphonate group in a non-rigid molecule and in different liquid crystalline phases has been determined.

MATERIALS AND METHODS

Pentoxy-benzylidene-hexylaniline (PBHA) was purchased from Spezialchemie Leipzig. Its mesophases are well known. The transition temperatures determined by DSC and polarizing microscopy agree

quite well with those published in Ref. 14. The phases transition temperatures in °C (above) and the transition enthalpies in kJ/mol (below) are respectively:

$$\text{cryst.} \underset{25.7}{\overset{34.5}{-}} \text{smG} \underset{.089}{\overset{41.0}{-}} \text{smF} \underset{0.21}{\overset{44.3}{-}} \text{smB} \underset{2.10}{\overset{51.6}{-}} \text{smC} \underset{0}{\overset{53.0}{-}} \text{smA} \underset{0.97}{\overset{61.1}{-}} \text{nem} \underset{1.17}{\overset{72.9}{-}} \text{isotr.}$$

The phosphonic acid diesters of the general type $RP(O)(OR')_2$ are listed in Table I together with their notations.

PAE_{12} and PAE_{16} are gifts from Dr. Haage, Central Institute of Organic Chemistry of the Academy of Sciences of the GDR, Berlin, PAB-T and PAB_6 were supplied by Dr. Günther CKB, Bitterfeld, and PAE-C by Dr. Costisella, Central Institute of Organic Chemistry, Berlin.

The partially deuterated compounds are listed in Table II together with their notations. 1,1-d_2-Hexane-1-phosphonic acid diethyl ester was synthesized by the reaction of 1-bromo-1,1-d_2-hexane with sodium diethyl phosphite[15] using a Michaelis–Becker reaction:

$$C_5H_{11}C^2H_2Br + NaP(O)(OC_2H_5)_2 \longrightarrow C_5H_{11}C^2H_2P(O)(OC_2H_5)_2 + NaBr$$

TABLE I

Phosphonic acid diesters $RP(O)(OR')_2$

R	R′	Notation
C_6H_{13}	C_2H_5	PAE_6
C_8H_{17}	C_2H_5	PAE_8
$C_{12}H_{25}$	C_2H_5	PAE_{12}
$C_{16}H_{33}$	C_2H_5	PAE_{16}
C_4H_9	C_4H_9	PAB_4
C_6H_{13}	C_4H_9	PAB_6
	C_4H_9	PAB-P
	C_2H_5	PAE-C
	C_4H_9	PAB-C
	C_2H_5	PAE-B
	C_4H_9	PAB-T

TABLE II

Deuterated hexane phosphonic acid diesters

R	R′	Notation
$H_3C(CH_2)_4C^2H_2$	C_2H_5	PAE_6-d_2
C_6H_{13}	$C_2{}^2H_5$	PAE_6-d_{10}
$^2H_3C(C^2H_2)_4CH_2$	$C_2{}^2H_5$	PAE_6-d_{21}
C_6H_{13}	$CH_2C^2H_2C_2H_5$	PAB_6-d_4
C_6H_{13}	$C^2H_2C^2H_2C_2H_5$	PAB_6-d_8
C_6H_{13}	$C_4{}^2H_9$	PAB_6-d_{18}

For the synthesis of the partially deuterated PAE_6-d_{21} the first step was the production of the perdeuterated diethyl phosphite:

$$3C_2{}^2H_5OH + PCl_3 \xrightarrow{CCl_4} HP(O)(OC_2{}^2H_5)_2 + C_2{}^2H_5Cl + 2HCl$$

After removing the CCl_4, the diethyl phosphite was dissolved in *n*-hexane and the stoichiometric amount of metallic sodium was added:

$$2HP(O)OC_2{}^2H_5)_2 + 2Na \longrightarrow 2NaP(O)(OC_2{}^2H_5)_2 + H_2$$

With partially deuterated 2,2,3,3,4,4,5,5,6,6,6-$^2H_{11}$-1-bromo-hexane one finally obtains PAE_6-d_{21}:

$$NaP(O)(OC_2{}^2H_5)_2 + C^2H_3(C^2H_2)_4CH_2Br \longrightarrow$$

$$C^2H_3(C^2H_2)_4CH_2P(O)(OC_2{}^2H_5)_2 + NaBr$$

The syntheses of the other compounds were performed by the reaction of hexane phosphonic dichloride with the appropriate alcohols in *n*-hexane according to Ref. 16:

$$C_6H_{13}P(O)Cl_2 + HOR' \xrightarrow[-2Py\cdot HCl]{+2Py} C_6H_3P(O)(OR')_2$$

The hexane phosphonic dichloride was obtained from hexane phosphonic acid and phosphorus pentachloride. The pyridine hydrochloride formed has to be extracted with great care in order to obtain products of high purity.

Hexane phosphonic acid-di(ethyl-d_5)-ester and di(butyl-d_9)ester were synthesized using deuterated alcohols (Isocommerz Leipzig). For the

synthesis of partially deuterated hexane phosphonic acid di-(2,2-d_2-butyl)-ester and -(1,1,2,2-d_4-butyl)-esters, the first step was the synthesis of the appropriate alcohols from ethyl malonic acid. $C_2H_5C^2H(COO^2H)_2$ was obtained by threefold isotopic exchange with ^2H_2O. The water-free acid was transformed into butyric acid $C_2H_5C^2H_2COO^2H$ by thermal decarboxylation.[17] 2,2-d_2-butyric acid was reduced with $LiAlCH_4$ or $LiAl^2H_4$,[18] in ether solution giving 2,2-d_2 butanol and 1,1,2,2-d_4-butanol, respectively. The deuterated lithium alanate was obtained from Li^2H (Isocommerz, Leipzig) and $AlBr_3$. Its ether solution was instantly used for the reduction.

All hexane phosphonic dialkyl esters were purified by vacuum distillation.

The structure and the purity of the compounds were proved by ^1H, ^{13}C and ^{31}P NMR. It was found that the impurities were less than 1% and that the deuteration was higher than 90% at the individual positions.

All esters are oily liquids except PAE_{16}, which is a wax at room temperature. The long chain esters possess surface active properties in water.[6,19]

The esters were dissolved in PBHA at 75°C (isotropic phase) in a molar ratio of about 1:100. At large concentrations, the esters are excluded from the thermotropic matrix if it is in the smectic B phase. The temperatures for the NMR measurements were adjusted by decreasing the temperature of the sample slowly (at least 1°K/min) in the magnetic field of the spectrometer to the value wanted. Nevertheless the low temperature smectic G phase can be supercooled by more than 20 K. This procedure yields uniformly oriented samples. The uncertainty of the temperatures is of the order of ± 1 K.

The ^1H FIDs of the PBHA matrix were measured at 32 MHz with a Bruker-Pulse Spectrometer (BKR 322S) and Fourier-transformed by a Nicolet computer BNC 12 (dwell time 2 μs, delay time 6 μs). The measurement of the proton–proton dipole coupling of a small amount of PAE_6-d_{19} dissolved in the PBHA matrix (proton ratio 1:1650) was possible by a delayed FID accumulation (1 ms after the $\pi/2$ pulse) using a Bruker WP-250 spectrometer. After this time, the matrix signal with a T_2 relaxation of about 100 μs has sufficiently decayed with respect to the signal resulting from PAE_6-d_{21}.

The ^2H spectra were recorded on a home-built Fourier transform NMR spectrometer with external stabilization (4096 data points, 512 scans, 25 kHz spectral width, 500 ms repetition time).

The ^{31}P spectra were obtained using Fourier transform techniques (2048 data points, 4098 scans, 20 kHz spectral width, 750 ms repetition

time) and high power proton noise decoupling with a Bruker HX-90 NMR spectrometer operating at 36.43 MHz.

In order to obtain additional information about the phase states present in the mixed systems and the corresponding transitions, a thermal analysis of the system was carried out using a Perkin-Elmer DSC-2 differential scanning calorimeter. Scan speeds used were 5K/*min*.

Further, the textures of the phases and their changes with temperatures were observed in some selected systems by a polarizing microscope equipped with a heating stage.

THEORY

The orientational order of a rigid molecule or a rigid molecular segment in a liquid crystalline phase can be described by the Saupe ordering matrix[20]:

$$S_{\alpha\beta} = \left\langle \frac{3}{2}(\mathbf{e}_\alpha \mathbf{e}_z)(\mathbf{e}_\beta \mathbf{e}_z) - \frac{1}{2}\delta_{\alpha\beta} \right\rangle \tag{1}$$

$\mathbf{e}_\alpha, \mathbf{e}_\beta (\alpha, \beta = \xi, \eta, \zeta)$ are unit vectors of an arbitrary molecular system M and $\mathbf{e}_z$ defines the director orientation of the uniaxial liquid crystalline phases (nematic, smectic A and B). The brackets indicate an ensemble average.

In NMR the structural information as well as the orientational order are deduced from dipolar and quadrupolar interactions and from the chemical shift. These parameters are second rank tensors with the values $W_{ii} (i = 1, 2 \text{ and } 3)$ in the principal axis system. The splittings and the chemical shifts of the lines observed in NMR are determined by the components of the corresponding interaction tensors parallel to the external magnetic field W_{zz}

$$W_{zz} = \sum_{i=1}^{3} (\mathbf{e}_i \mathbf{e}_z)(\mathbf{e}_i \mathbf{e}_z) W_{ii} \tag{2}$$

In most cases, it is useful to introduce the molecular system M which can be more or less arbitrarily defined. The connection between the principal system and the NMR parameters observed is then given by a two-step transformation from the principal frame via the molecular system, to the laboratory system

$$\overline{W}_{zz} = \frac{2}{3}\sum_{\alpha\beta} S_{\alpha\beta} W_{\alpha\beta} = \frac{2}{3}\sum_{\alpha\beta} \sum_{i} S_{\alpha,\beta}(\mathbf{e}_\alpha \mathbf{e}_i)(\mathbf{e}_\beta \mathbf{e}_i) W_{ii} \tag{3}$$

The symmetry of the molecular subunit under consideration simplifies this expression. The phosphonate group possesses a local mirror plane, defined by the O = P—C atoms. In the case of identical ester groups and an alkyl substituent, *R* in all-*trans* conformation, the whole molecule has this symmetry. We choose a molecular frame where ξ and ζ lie in this symmetry plane where ζ is parallel to the phosphoryl bond (cf. Figure 1). According to this symmetry, only the 3 elements $S_{\xi\xi}$, $S_{\zeta\zeta}$ and $S_{\xi\zeta}$ of the order matrix differ from zero.[20] In this frame Eq. (3) simplifies to

$$\overline{W}_{zz} = \frac{2}{3}(W_{\zeta\zeta} - W_{\eta\eta})S_{\zeta\zeta} + \frac{2}{3}(W_{\xi\xi} - W_{\eta\eta})S_{\xi\xi} + \frac{4}{3}W_{\xi\zeta}S_{\xi\zeta} \quad (4)$$

For the determination of the 3 unknown elements of the ordering matrix we need at least 3 experimental parameters. The ^{31}P chemical shift is one suitable quantity. The principal values of the solid state ^{31}P chemical shift tensors in some compounds containing the phosphonate group are known. For the phosphonate group in PAE_6 we

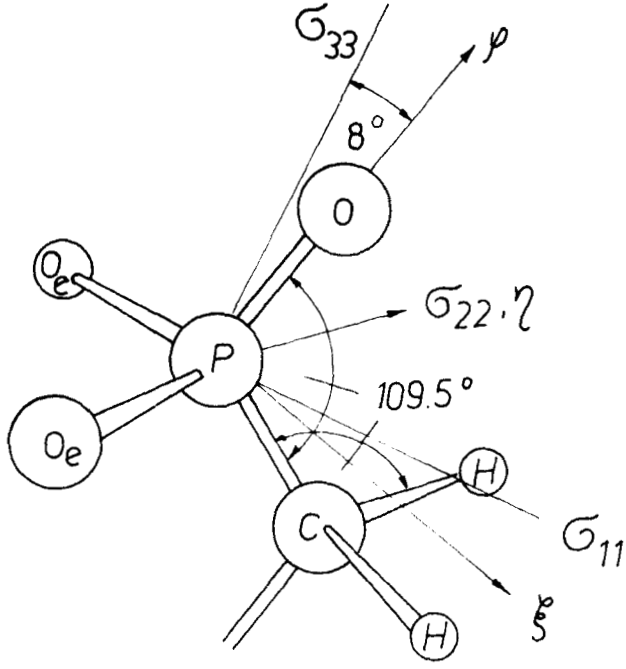

FIGURE 1 Geometry of the $CH_2P(O)O_2$ segment, the positions of the ^{31}P chemical shift tensor and of the molecular axis system.

used the values $\sigma_{11} = -96.3$, $\sigma_{22} = -77.0$ and $\sigma_{33} = 78.9$ ppm obtained for hexadecyl phosphonic diethyl ester.[21] According to quantum chemical calculations[22] the phosphoryl group and the direction of σ_{33} make an angle of about 8°. The principal value σ_{11} lies in the symmetry plane of the phosphonate group and σ_{22} is perpendicular to this plane (cf. Figure 1).

In principle, the chemical shifts of the carbon atom and the phosphoryl oxygen could be used as the two other experimental parameters. But unfortunately these tensors are unknown and there would be further difficulties related to the isotropic enrichments and the experimental determination of the chemical shifts at the low concentration of PAE_6 in PBHA.

In the analysis we used, in addition to the ^{31}P chemical shift, the deuterium quadrupolar splitting, $\Delta\nu_Q$ and the proton dipole–dipole interaction, $\Delta\nu_D$ of the α-methylene group which could be experimentally determined by studying PAE_6-d_2 and PAE_6-d_{21} dissolved in PBHA at the same concentration as PAE_6. The use of experimental quantities obtained from these different solutes is justified since the deuterium does not influence the inter- and intramolecular interactions and motions.

A serious question is whether there is an intramolecular motion of the α-methylene group. If it rotates freely or if there is an equal population of the three rotamers possible then the quadrupolar and the dipolar splittings are averaged to the same axial-symmetric tensor orientation and therefore they are linearly dependent. An analysis is, in principle, not possible using these parameters. But a free rotation seems unlikely because the phosphonate ester group and the substituent R are relatively bulky groups and because the potential field for the rotation about the P—C bond is asymmetric. Since these spectra exhibit no indication of a gauche rotamer of the PO_3CH_2 segment, we assume that only the *trans*-rotamer is present (represented in Figure 1). This is supported by the ratio of the splittings observed experimentally, which do not agree with the ratio of the tensor interactions calculated. Finally, Monte Carlo simulations also yield only the *trans*-rotamer.[23]

Further, we will not consider the influence of small amplitude motions. On these assumptions Eq. 4 holds also for the quadrupolar splitting and the dipolar interaction.

The nematic, as well as the smectic A and B phase are axial-symmetric. In the smectic phases the director orientation is frozen (cf. e.g., Ref. 24) and the angular dependence of the NMR spectra can be measured. The three interactions observed vary with the ori-

entation according to the function $3/2\cos^2\theta' - 1/2$. The phosphorus chemical shift obeys the relation

$$\nu_{cs} - \nu_{iso} = \frac{1}{3}\Delta\nu_{eff}(3\cos^2\theta' - 1) \tag{5}$$

θ' is the angle between the director $\mathbf{e}_z$ and the magnetic field B_0, ν_{iso} the chemical shift in the isotropic phase and $\Delta\nu_{eff} = \nu_{cs}(\theta' = 0°) - \nu_{cs}(\theta' = 90°)$ the chemical shift anisotropy.

For the quadrupole coupling constant of the C^2H_2 group we use $e^2qQ/h = 170$ kHz and $\eta = 0$.[25] The solid state quadrupole splitting for $\theta' = 0°$ amounts then to $\Delta\nu_Q = 3/2\ e^2qQ/h = 255$ kHz. Under the same conditions and with $r_{HH} = 178$ pm, the dipolar splitting in the CH_2 group has the value

$$\Delta\nu_D = \frac{3}{2}\left(\frac{\mu_0}{4\pi}\right)\frac{\gamma^2\hbar}{\pi r_{HH}^3} = 62.3 \text{ kHz}$$

With these solid state NMR interactions and the geometry of Figure 1 we obtain the following 3 equations for the determination of the ordering matrix of the phosphonate group ($\theta' = 0°$):

$$\begin{aligned}
\Delta\nu_{cs} &= \nu_{cz} - \nu_{iso} = \nu_0[101.7S_{\zeta\zeta} - 10.4S_{\xi\xi} - 32.1S_{\xi\xi}]10^{-6} \\
\Delta\nu_Q &= 255 \text{ kHz}\left[-5/9\ S_{\zeta\zeta} - 4/9\ S_{\xi\xi} + \frac{2\sqrt{2}}{9}S_{\xi\zeta}\right] \\
\Delta\nu_D &= 62.3 \text{ kHz}[-S_{\zeta\zeta} - S_{\xi\xi}]
\end{aligned} \tag{6}$$

We obtain the principal values of the ordering matrix S_{11}, S_{22} and S_{33} and their orientation in the molecular system (angle between ζ and S_{33}) wanted from the three order parameters $S_{\zeta\zeta}$, $S_{\xi\xi}$ and $S_{\xi\zeta}$ by diagonalisation.

RESULTS

Figure 2a shows the ^1H dipole–dipole splitting arising from the benzene protons of PBHA doped with and without PAB-T as a function of temperature. The discontinuities of the splitting at the phase transitions nem $\rightarrow S_A$ and $S_A \rightarrow (S_C)S_B$ slightly visible in the pure PBHA

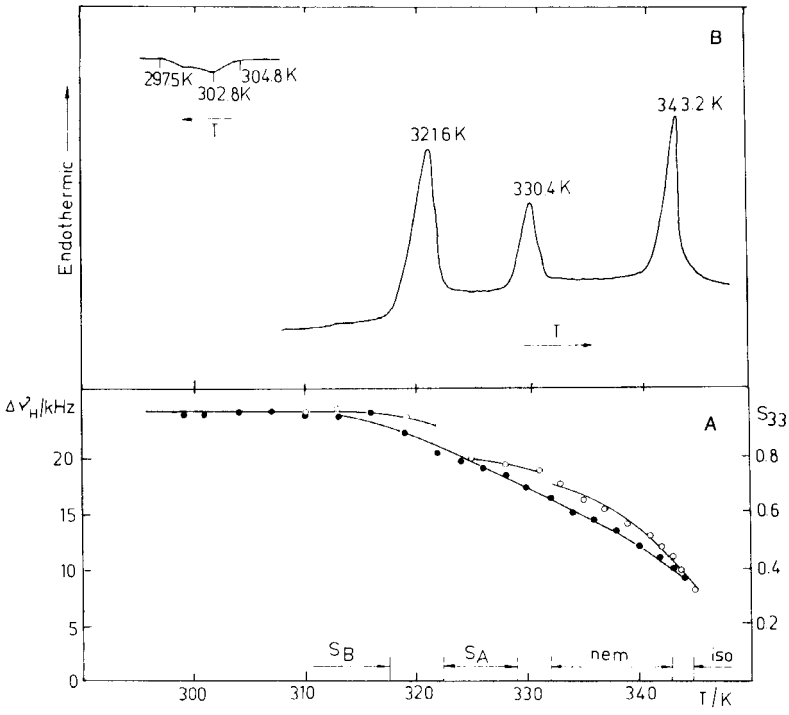

FIGURE 2 The ^1H dipolar splitting of the benzene protons in PBHA doped with (solid circles) and without (open circles) PAB-T at $\theta' = 0$ as a function of temperature (a) and the DSC scans of the doped sample (b).

sample, are smeared out in the doped sample. Thus, this parameter is not appropriate for determining the phase transition temperatures. For this purpose we used DSC scans (cf. Figure 2b). All transition temperatures shifted to lower temperatures by about 3°C. The smectic C phase between 51.6° and 53° observed in pure PBHA, is suppressed in the doped samples.

The ^{31}P NMR spectra of the esters dissolved in PBHA consist of one line, the position of which changes with temperature. Figure 3 shows the $\Delta\sigma_{eff} = -\Delta\nu_{eff}/\nu_0$ of some selected phosphonic acid esters as a function of temperature. $\Delta\sigma_{eff}$ of PAE_{12} has qualitatively the same temperature dependence as PAE_{16}. The $\Delta\sigma_{eff}$ of all the other esters behave like PAE_6. In the case of PAE_6, for example, a second signal with a smaller $|\Delta\sigma_{eff}|$ (see below) value appears at 47°C the position of which has the same dependence on the angle θ' as the first signal. The ratio of the signal intensities changes in favour of that with the smaller $|\Delta\sigma_{eff}|$ with decreasing temperature. These facts prove that at these temperatures two phases coexist.

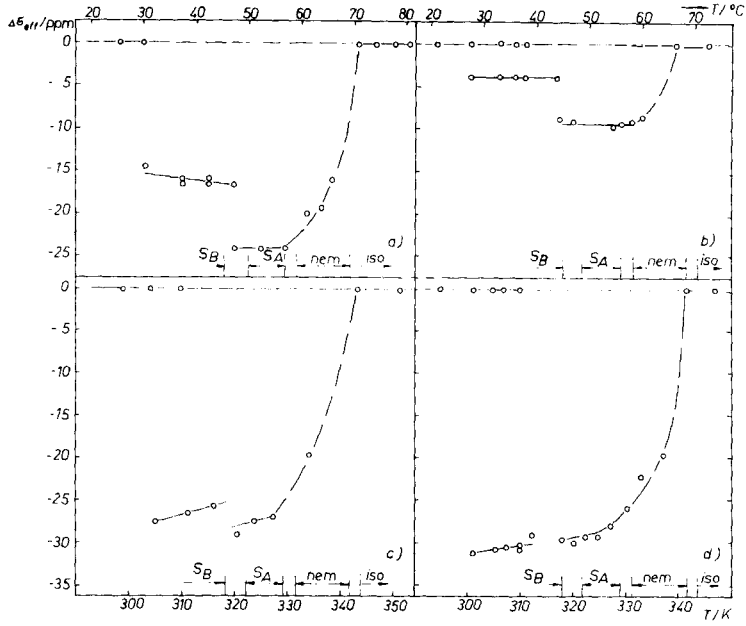

FIGURE 3 The effective ^{31}P chemical shift anisotropies in PAE_6: a; in PAB-T b; in PAE_{12} c; and in PAE_{16} d as a function of temperature.

At low temperatures, a signal appears at ν_{iso} (cf. Figure 3) whose position does not depend on θ' and whose intensity increases at the expense of the other signal with decreasing temperature. Obviously it is due to a phase separation which leads to an exclusion of the esters from the PBHA matrix at appropriately low temperatures. The temperature at which it starts lies between 38 and 27°C, depending on the structure of the ester and its concentration. The ^{31}P chemical shift anisotropies $\Delta\sigma_{eff}$ in the smectic phases, determined by fitting the experimental values at different θ' according to Eq. 5, are listed in Table III. In the nematic phase $\Delta\sigma_{eff}$ was obtained using

$$\Delta\sigma_{eff} = -\frac{1}{\nu_0}\frac{3}{2}(\nu_{cs} - \nu_{iso}) \qquad (7)$$

The line width of the ^{31}P lines of the esters in the liquid crystalline phases of PBHA is large. PAE_6-d_{21} also gives a line width not less than 500 Hz. The broadening is mainly due to very small amounts of paramagnetic impurities present in the samples, which could not be removed. In the deuterated compounds the different ^2H–^{31}P dipole interactions present, also contribute to the broadening. Because

TABLE III

Phosphorus chemical shift anisotropies $\Delta\sigma_{eff}$ in ppm

Ester	S_B (43°C)	S_A (50°C)	Ester	S_B (43°C)	S_A (50°C)
PAE_{16}	−30.0	−29.0	PAE-C	−18.8	−25.7
PAE_{12}	−26.0	−27.5	PAB-C	−9.6	
PAE_8	−25.1		PAB-P	−9.1	
PAE_6	−16.2	−24.0	PAB-B	−12.6	
PAB_6	−7.3	−21.9	PAB-T	−4.0	−9.5
PAB_4	−6.7				

of the relatively large line width we could not determine the $^1H-^{31}P$ dipole interaction in PAE_6-d_{21} by ^{31}P NMR.

The ^2H spectrum of PAE_6-d_2 shows a sharp line pair in the liquid crystalline phases of PBHA. The temperature dependence of the quadrupolar splitting as well as those of the dipolar splitting in PAE_6-d_{21} and of the ^{31}P chemical shift anisotropy are represented in Figure 4. These are the three experimental quantities at each temperature which we employ for the determination of the ordering matrix by solving Eq. 6.

Unfortunately the signs of the quadrupolar and dipolar splittings are not known. However, according to the orientation of the proton–proton vector perpendicular to the axis ζ (cf. Figure 1) it is reasonable to assume a negative sign for the dipolar splitting $\Delta\nu_D$. If we assume that the sign of the quadrupolar splitting $\Delta\nu_Q$ is positive, then after solving Eq. 6 and diagonalisation of the ordering matrix we obtain an order parameter S_{33} which lies between 0.4 and 0.7. These values are larger than, or similar to, the order parameter of the matrix itself (cf. Figure 2). Therefore we exclude this solution and assume a negative sign for the quadrupolar splitting $\Delta\nu_Q$ observed. The principal values of the ordering matrix S_{11}, S_{22} and S_{33}, and its orientation in the molecular system obtained with negative signs for the quadrupolar and dipolar splittings by solving Eq. 6 and diagonalisation are given in Figure 5.

In order to obtain some information about the behaviour of the ester segments, some esters partially deuterated in the ester groups were synthesized (cf. Table II) and the ^2H NMR spectra measured.

In the liquid crystalline states of PBHA the spectra are superpositions of doublets. The doublet with the highest intensity and the smallest peak separation, observed at temperatures between 64 and 50°C, apparently results from the C^2H_3 groups. The $O—C^2H_2$ seg-

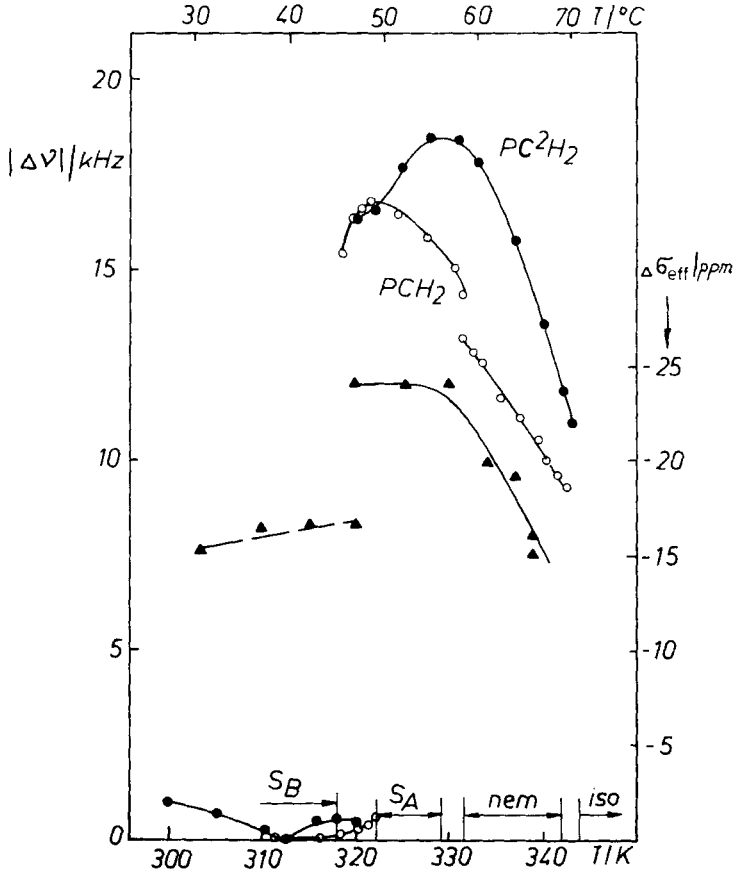

FIGURE 4 The quadrupolar splitting of PAE_6-d_2 (solid circles), the dipolar splitting of PAE_6-d_{21} (open circles), and the ^{31}P chemical shift anisotropy (solid triangles) as a function of temperature. All esters were dissolved in PBHA at a molar ratio of 1:100.

ments give rise to two splittings, because of different orientational behaviours of the two C—^{2}H bonds in the methylene groups. The same non-equivalence was also found in the $OC(O)C^2H_2$ segment in the sn 2 chain of lipids[26–28] and is in agreement with the results of Monte Carlo simulation.[23] At a temperature of 45°C, we observe a superposition of the spectra of two phases (cf. insert in Figure 6) as in the other NMR spectra where the doublets with the smaller peak distance are due to the smectic B phase. At the end of the smectic B phase a small central line, characteristic of a completely disordered state appears, whose intensity increases progressively on account of the intensity of the doublets as the temperature is lowered.

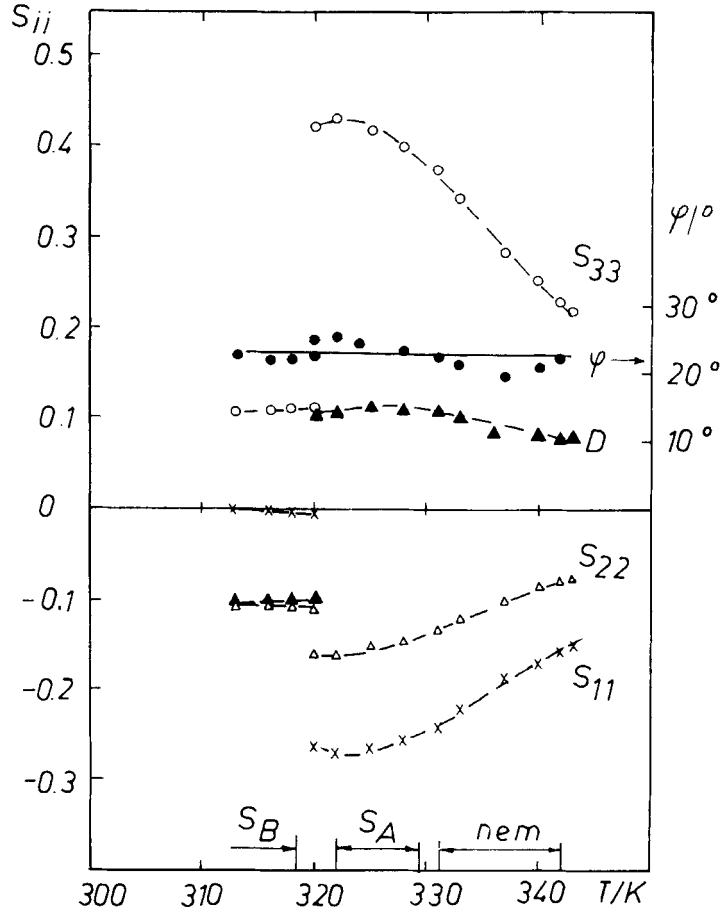

FIGURE 5 The ordering matrix of PAE_6 dissolved in PBHA and its orientation as a function of temperature.

The ^2H spectra also indicates a transition temperature region between the isotropic and the nematic state of PBHA.

The unambiguous assignments of the various splittings obtained for PAB_6-d_{18} (Figure 6) to the different segments were possible using the spectra of the partially deuterated compounds PAB_6-d_4 and PAB_6-d_8.

DISCUSSION

The phosphonic acid dialkyl esters dissolved in PBHA in a molar ratio of 1:100 broaden the temperature regions of the phase transi-

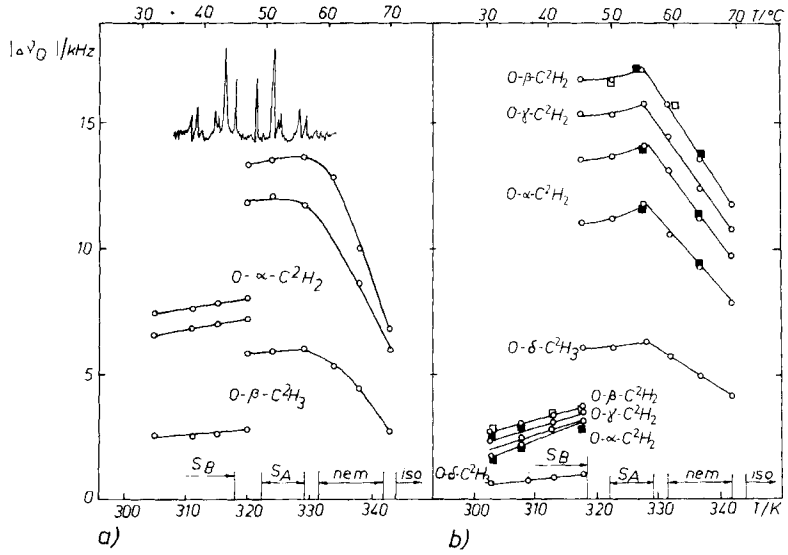

FIGURE 6 The quadrupolar splittings measured in hexane phosphonic diethyl (a) and dibutyl esters as a function of temperature (b).

tions up to about 3 K (Figure 2). Coincidental depressions of nearly 3°C of the phase transition temperatures, as detected by the maximum DSC peak, occur. (These facts which are well known for mixed systems, are not the subject of our paper.)

The existence of a smectic C state in the mixed systems could not be proved either by microscopy or by NMR or DSC. In pure PBHA the temperature region of its existence of 1.4 K is already very small. The smectic C phase is probably suppressed by the dopant molecules. Below 311 K, the exclusion of the esters from the thermotropic matrix starts (cf. Figure 3). But DSC does not indicate any transitions. The appearance of the DSC peak between about 297 and 305 K (cf. Figure 2a) is not clear.

From the ^{1}H dipolar splitting $\Delta\nu_D$ of the benzene protons of PBHA (Figure 2a) the order parameter of the benzene moiety can be obtained as $\Delta\nu_D/25$ (25 kHz is the splitting observed for the benzene protons with $S = 1$). It is about 0.36 at the transition to the nematic state and increases almost continously to about 1. These extreme values are the same in pure PBHA obtained in the same way but ^{13}C measurements give a slightly smaller order parameter of 0.9[29] in the smectic B state.

The different phase regions and phase transitions are much better reflected in the ^{31}P and ^{2}H parameters of the dissolved solutes

(Figures 4 and 6) than in the ^1H dipolar splittings of the matrix (Figure 2a). They agree with those obtained with DSC.

The orientational order of the phosphonate group, determined in PAE_6 is relatively high, with S_{33} values from about 0.2 to 0.4 (cf. Figure 6). It increases continuously in the nematic and S_A phases with decreasing temperature. With further decrease of temperature at the end of the S_A phase region it remains constant and decreases in the transition region to the S_B phase. The same behaviour was observed also for other molecules.[30]

At the transition to the S_B phase, the orientational ordering decreases drastically and remains practically constant in the S_B phase. The deuterium splittings of the ester groups exhibit the same behaviour (cf. Figure 6). At the same transition, the ordering of the matrix molecules reaches its maximum (Figure 2a). The drastic reduction in the ordering of the phosphonate group and in the deuterium splittings of the ester groups in the S_B phase is evidence that the solute molecules essentially retain their conformation, but are excluded from the well-ordered aromatic core region and are forced into the less-ordered hydrocarbon chains of PBHA. The intermolecular forces responsible for the increase in the order in the layers push the dissolved impurities to the outer region. This is still more strongly marked in the more ordered smectic G phase at lower temperatures. Therefore, the solute molecules form a separate phase.

In the nematic and S_A phases the solute molecules prefer to reside near the more ordered aromatic core. The exclusion of solute molecules at the transition from the nematic to smectic phases was observed also in other systems.[24,31,32]

The biaxiality $D = S_{22}-S_{11}$ is larger than the values usually observed for solute molecules.[33] Maybe it is the result of the very different chemical not use of the substituents attached to the phosphorus atom. As predicted for mesogenic molecules D exhibits a flat maximum, dependent on temperature.[33]

The ratio between the biaxiality $D = S_{22}-S_{11}$ and the order parameter, S_{33} depends on the deviation of the potential of the mean torque of the solute molecule from cylindrical symmetry.[33] Figure 7 shows the dependence of D on S_{33} obtained from the nematic and S_A phases of PBHA.

The orientation of the main axis of the ordering tensor (S_{33}) makes an angle of about 22° with the P=O bond, nearly independent of temperature (cf. Figure 5). The S_{33} orientation might agree with the long axis of the whole molecule.

Now we will qualitatively discuss the behaviour of the other phos-

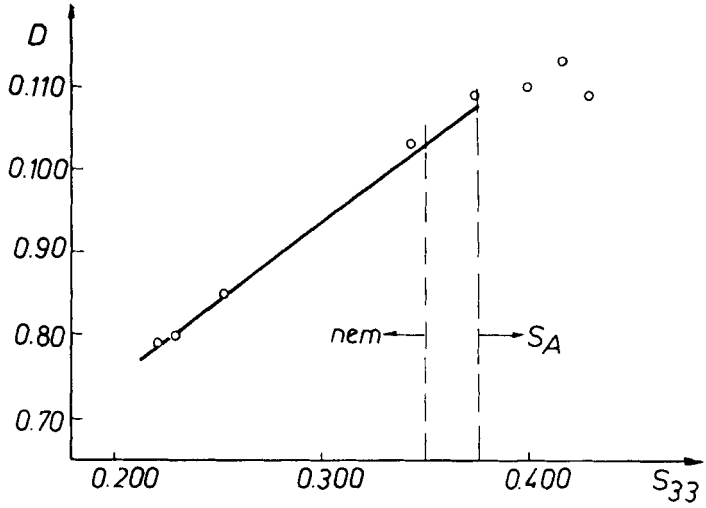

FIGURE 7 The biaxiality $D = S_{22} - S_{11}$ as a function of S_{33}.

phonic acid diesters than PAE_6 on the basis of the ^{31}P chemical shift anisotropies measured (Table III). Only the ester groups of PAB_6 were partially deuterated and additionally the deuterium splitting determined (Figure 6b).

Eqs. (6) were solved as a function of $\Delta\sigma_{eff}$ on the assumption of a constant $\Delta\nu_Q = -17.7$ kHz and $\Delta\nu_D = -16.5$ kHz (PAE_6, S_A phase, 325 K) (Figure 8). The order parameter S_{33} increases and the biaxiality decreases linearly with growing absolute values of $|\Delta\sigma_{eff}|$. Using these results, we can conclude that S_{33} increases and D decreases with growing chain length of the hydrocarbon substituent of the solute molecule in the S_A phase (cf. Table III, $\Delta\sigma_{eff}$ of PAE_n with $n = 6$, 12, 16). This is what we could expect, since different motions as rotation, fluctuation and diffusion of the solute molecules are more restricted for the longer hydrocarbon substituents. Further, with growing chain length the effective molecular asymmetry decreases.[23] According to Reference 33 this leads to a smaller biaxiality, in agreement with our qualitative result.

PAB-T exhibit the smallest S_{33} and the largest D compared to the other esters (cf. Table III and Figure 8). This can be explained in terms of the bulky hydrocarbon substituent in PAB-T, which reduces the ordering.

At the transition to the S_B phase, the ordering of all esters, with the exception of the long chain esters PAE_{12} and PAE_{16}, is drastically

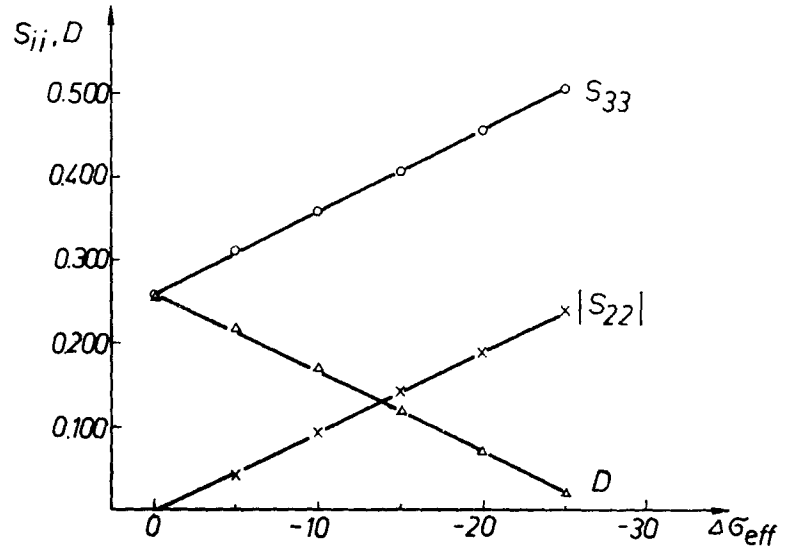

FIGURE 8 The ordering matrix of the phosphonate group calculated as a function of the ^{31}P chemical shift anisotropy and constant quadrupolar and dipolar splittings ($\Delta\nu_Q = -17.7$ kHz and $\Delta\nu_D = -16.5$ kHz).

reduced (cf. Table III and Figure 8), because of the exclusion of the solute molecules from the aromatic region of the PBHA matrix. This fact indicates that PAE_{12} and PAE_{16} are not excluded from the aromatic region, in contrast to the other esters studied. The reasons might be that these esters fit the packing of the matrix molecules and/or that there are strong intermolecular interactions between the solute and PBHA molecules.

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