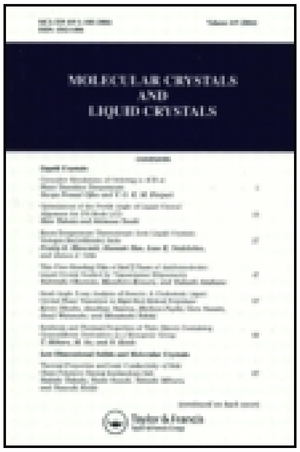

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An NMR Study of the Anisotropic Forces Acting on the Segments of Ammonia and Phosphine in Liquid Crystals

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An NMR Study of the Anisotropic Forces Acting on the Segments of Ammonia and Phosphine in Liquid Crystals

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The dipolar couplings of ammonia and phosphine have been measured in various types of liquid crystals. Striking inconsistencies are encountered if the conventional analysis of these couplings is attempted. It is shown that a recently introduced new method of analysis, allowing for the correlation between the molecular reorientational and vibrational motion, is capable of explaining the couplings by reasonable values of the torques acting on the bonds and lone-pair electron clouds of the molecules in the liquid crystal surroundings. These torques display the same trends as those acting on the bonds of several other small molecules studied earlier, suggesting that there is a common interaction mechanism, possibly the van der Waals interaction, behind these forces.

Keywords: NMR, orienting forces, molecular deformation

1. INTRODUCTION

Recently a new method of analysis has been introduced for the NMR spectral parameters of partially oriented molecules, allowing for the correlation between the reorientational and vibrational motions.[1–3] It is based on a detailed description of the molecular motion in terms of the torques acting on the segments (e.g. bonds) of the molecule. Besides the orientation, these torques give rise also to orientation-

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dependent perturbations on the internal state of the molecule, resulting in the so-called deformational contributions to the spectral parameters (as well as small higher order terms).[3] When the expressions of the deformational contributions are introduced into the equations of the spectral parameters, the torques (and, in favourable cases, molecular geometry etc.) can be determined by the experimental values of the spectral parameters.

In the present work the dipolar couplings of ammonia and phosphine were measured in different liquid crystal solvents. Striking inconsistencies are encountered if the conventional method of analysis is attempted. It is shown that the new method is capable of explaining the couplings by reasonable values of the torques acting on the bonds and lone-pair electron clouds of the molecules. These torques and those acting on the CH bonds of methane in the same liquid crystal environment are shown to be approximately linearly related, in accord with the earlier observations on the torques experienced by the bonds of methyl iodide,[4] methyl fluoride,[4] and hydrogen cyanide.[5]

2. THEORY

According to the general theory of vibration and rotation of partially oriented molecules[1-3] the deformational contribution to the dipolar coupling constant D_{ij} can be written as

$$D_{ij}^{d} = -P_2(\cos\alpha)K_{ij}\sum_{k}\frac{1}{\omega_k^2}$$

$$\cdot\left[\frac{3}{10}\sum_{\alpha,\beta}\phi_{\alpha\beta,k}^{ij}A_{\alpha\beta,k} + \frac{2}{7}\sum_{\alpha,\beta,\mu}(3\phi_{\alpha\mu,k}^{ij}A_{\beta\mu,k} - \phi_{\mu\mu,k}^{ij}A_{\alpha\beta,k})S_{\alpha\beta}^{D}\right]. \quad (1)$$

Here $P_2(x) = 1/2(3x^2 - 1)$ is the Legendre polynomial, α is the angle between the magnetic field direction and the axis of the environment (director), and $K_{ij} = \mu_0\hbar\gamma_i\gamma_j/(8\pi^2)$ where γ_i is the magnetogyric ratio of the nucleus i. Further, $\phi_{\alpha\beta}^{ij} = l_\alpha^{ij}l_\beta^{ij}/r_{ij}^3$ where l_α^{ij} is the direction cosine of the internuclear vector $\mathbf{r}_{ij}$ in the molecular frame, $S_{\alpha\beta}^{D}$ is the ordering tensor (referenced to the director), and $A_{\alpha\beta}$ is the symmetric and traceless *interaction tensor*, defined by the truncated series expansion of the orienting potential energy U_{ext} of the molecule in terms of the direction cosines of the director in the molecular frame, $\cos\theta_\alpha$:

$$U_{ext} = -\frac{3}{2}\sum_{\alpha,\beta}A_{\alpha\beta}\cos\theta_\alpha\cos\theta_\beta. \quad (2)$$

The tensors $\phi^{ij}_{\alpha\beta,k}$ and $A_{\alpha\beta,k}$ are the derivatives of the $\phi^{ij}_{\alpha\beta}$ and $A_{\alpha\beta}$ with respect to the k'th vibrational normal coordinate (with angular frequency ω_k), taken in equilibrium geometry.

Because the orienting potential energy U_{ext} (2) determines the ordering tensor $S^D_{\alpha\beta}$, there is one-to-one correspondence between the tensors $S^D_{\alpha\beta}$ and $A_{\alpha\beta}$.[1,2] If the ordering tensor is known, the interaction tensor $A_{\alpha\beta}$ can be calculated, which gives information on the anisotropic forces acting on the molecule. Actually the dipolar couplings D_{ij} include more detailed information on these forces than the ordering tensor does, because their deformational contributions D^d_{ij} (1) depend also on the derivatives $A_{\alpha\beta,k}$. These derivatives describe the dependence of the anisotropic forces on the deformations of the molecule. Thus, they provide information on the distribution of these forces within the molecule.[1,2] To this end, the molecular interaction tensor $A_{\alpha\beta}$ is regarded as the sum of the contributions associated with the relatively rigid segments (e.g. bonds) of the molecule, considered as isolated entities. Then, assuming that the orienting forces acting on these segments do not change their internal states significantly (e.g. do not stretch the bonds appreciably), the elements of the segmental interaction tensors in the *segment fixed* axis systems can be treated as deformation-independent constants. In the *molecule fixed* Eckart axis system the segmental interaction tensors do depend on deformations, because the orienting forces tend to bend the segments (as a whole), rotating the axis systems fixed in these segments. Therefore the molecular interaction tensor $A_{\alpha\beta}$ can be expressed as a function of the molecular geometry and the set of deformation-independent segmental interaction tensors (in the segment fixed axis systems) which describe the anisotropic forces acting on the segments. The derivatives $A_{\alpha\beta,k}$ are obtained by differentiating this function with respect to the normal coordinates and can also be expressed as functions of the segmental interaction tensors.[1-3]

The basic segments of the molecules NH_3 and PH_3 are their bonds and lone-pair electron clouds directing away from the positive ends of the molecules. If the interaction tensors associated with these segments are taken to be axially symmetric, they are specified by their anisotropies $\Delta A = A_\parallel - A_\perp = 3/2\ A_\parallel$, where $A_\parallel$ and $A_\perp = -1/2\ A_\parallel$ are the principal values of the tensor along the symmetry axis and perpendicular to it, respectively. Physically, ΔA determines the torque acting on the segment, because the orienting potential energy of the segment is, by equation (2)

$$U_{ext} = -\Delta A\ P_2(\cos\theta) \tag{3}$$

where θ is the angle between the symmetry axis and the director.

In the molecule fixed axis system the elements of the segmental interaction tensor are

$$A_{\alpha\beta} = \Delta A \left(\cos\phi_\alpha \cos\phi_\beta - \frac{1}{3}\delta_{\alpha\beta} \right) \tag{4}$$

where $\cos\phi_\alpha$ are the direction cosines of the symmetry axis of the segment in the molecular frame.[4] The elements of the molecular interaction tensor are obtained by summing the contributions (4) over the four segments of the molecule (the lone-pair electron cloud and the three XH bonds). At the equilibrium geometry the resulting molecular interaction tensor is axially symmetric and has the anisotropy

$$\Delta A = \Delta A_e + 3\Delta A_{\mathrm{XH}} \cos\beta \tag{5}$$

where ΔA_e and ΔA_{XH} are the anisotropies of the interaction tensors associated with the lone-pair electron cloud and XH bonds, and β is the HXH bond angle.[4] With this ΔA, equation (3) gives the orienting potential energy of the molecule. Hence, ΔA (5) determines the ordering tensor, which is specified by the order parameter of the molecular symmetry axis, S.

The derivatives of the segmental interaction tensors (4) with respect to the normal coordinates can be calculated, if the dependence of the direction cosines $\cos\phi_\alpha$ on the molecular geometry is known (taking the ΔA's to be deformation-independent constants). For bonds the calculation presents no problems: the symmetry axis of the (isolated) bond coincides with the bond direction, which is simply determined by the positions of the nuclei. Hence the derivatives of the bond interaction tensors can be calculated by the general equations given in Reference 3. For the lone-pair electron cloud the direction of the symmetry axis is not a simple function of the nuclear positions. The six independent force constants in the general harmonic force field of XH_3 do not completely specify the interactions between the lone-pair electrons and the other parts of the molecule. Thus, these force constants cannot be used to calculate the bending of the symmetry axis of the lone-pair electron cloud due to displacements of the nuclear positions. The relevant interactions could be specified by some model force field, for example by a modification of the Urey-Bradley model in which the lone-pair electrons are treated as a fourth substituent.[6] However, these interactions can be expected to be of minor importance in calculating the deformational contributions to the dipolar couplings. The D_{ij}^{d} (1) is determined by the displacements of the positions of the nuclei *i* and *j*, specified by the derivatives $A_{\alpha\beta,k}$. The displacements of the nuclear positions are primarily determined by the torques acting on the *bonds*: the forces acting on the lone-pair electron cloud bend it but induce only indirectly deformations in the other parts of the molecule. Thus, the neglect of the derivatives of the interaction tensor associated with the lone-pair electrons should be a reasonable approximation in calculating the molecular $A_{\alpha\beta,k}$'s, with the present special object of determining the displacements of the *nuclear* positions. Hence, in the present work the forces acting on the lone-pair electrons are simply neglected in calculating the molecular deformations. Nevertheless, these forces are allowed for in calculating the *order parameter* of the molecule, using equation (5). There they cannot be neglected, particularly because the forces acting on the bonds tend to cancel out (the "attenuation factor" 3cosβ of ΔA_{XH} in (5) is -0.862 for ammonia and -0.183 for phosphine).

The theoretical expressions of the dipolar couplings D_{XH} and D_{HH} were derived by using the harmonic force field of Benedict and Plyler[7] for ammonia and of Duncan and Mills[8] for phosphine. The geometrical parameters r_{XH} and β were taken from these papers: for ammonia $r_{\mathrm{NH}} = 1.0116$ Å, $\beta = 106.7°$ and for phosphine $r_{\mathrm{PH}} = 1.419$ Å, $\beta = 93.5°$. The resulting equations for the dipolar couplings contain two unknowns, ΔA_e and ΔA_{XH}, which can be determined from the experimental values of D_{XH} and D_{HH}.

3. EXPERIMENTAL

Commercially available enriched ammonia-^{15}N was used without further purification. Phosphine was prepared by the reaction of PCl_3 with $LiAlH_4$ in diethylether.[9] Ammonia and phosphine were distilled from a vacuum system into the NMR double-walled tubes which contained the degassed liquid crystal solvents. The ammonia samples contained also methane-^{13}C at approximately 1 atm, as well as some NaOH to make the solvents more basic for obtaining good spectra. All the spectra (a total of 28 and 22 spectra of NH_3 and PH_3, respectively, in 8 and 9 different liquid crystal solvents at different temperatures) were recorded on a Bruker WH-90 DS spectrometer locked on D_2O in the interwall space of the sample.

The indirect spin–spin coupling constants were measured in different isotropic and smectic solvents, with the results shown in Tables

TABLE I

Measured values of the indirect coupling constant J_{NH} of ammonia.

Solvent[a]		Temperature [K]	J_{NH} [Hz]	Resonance
Gas		302	60.30(21)[b]	^1H
HAB	smectic	312	60.87(20)	^1H
ZLI 1167	isotropic	350	60.45(90)	^2D
EBBA	isotropic	340	60.08(90)	^2D

[a] HAB = p,p'-di-n-heptylazoxybenzene
ZLI 1167 = a mixture of three cyclohexyl-cyclohexanes by Merck
EBBA = N-(p-ethoxybenzylidene)-p-n-butylaniline.
[b] Uncertainties in parentheses are one standard deviation in the last figure quoted.

1 and 2. For the relevant part the values are in agreement with the earlier measurements.[10,11] Because J_{PH} displays considerable solvent dependence, the values used in the spectral analyses (by the computer program LEQUOR[12]) were taken from the measurements in the corresponding or related liquid crystals.

The resulting dipolar couplings together with the liquid crystal solvents and temperatures are shown in Tables 3 and 4. For the types of liquid crystals used earlier by Spiesecke[13] and Zumbulyadis and Dailey[14] the couplings are similar to the ones reported by these authors.

4. RESULTS AND DISCUSSION

The experimental values of the dipolar couplings reveal immediately that the conventional method of analysis is not applicable to them.

TABLE II

Measured values of the indirect coupling constant J_{PH} of phosphine.

Solvent[a]		Temperature [K]	J_{PH} [Hz]	Resonance
ZLI 1167	isotropic	355	185.55(37)	^{31}P
EBBA	isotropic	355	186.25(59)	^{31}P
K 24	smectic	302	186.69(30)	^1H
HAB	smectic	302	185.22(30)	^1H
C_6D_6		302	186.52(21)	^1H
C_6D_{12}		302	182.62(30)	^1H
$CDCl_3$		302	188.96(23)	^1H

[a] K 24 = 4-cyano-4'-n-octylbiphenyl by BDH Chemicals Ltd.

TABLE III

Dipolar coupling constants $D^D_{ij} = D_{ij}/P_2$ (cos α) (referenced to the director) of ammonia and methane in various liquid crystal solvents.

Experiment number	Liquid[a] crystal	Temperature [K]	$D^D_{HH}(NH_3)$ [Hz]	$D^D_{NH}(NH_3)$ [Hz]	$D^D_{CH}(CH_4)$ [Hz]
1	HAB nematic	332	−4.91(5)	−6.00(15)	1.35(15)
2	HAB nematic	322	−7.08(14)	−4.93(28)	0.86(11)
3	HAB nematic	318	−12.32(5)	−3.25(13)	0.00(8)
4	HAB smectic	312	−14.97(8)	−1.27(21)	−1.47(20)
5	PHASE IV	322	160.24(5)	−47.32(13)	7.38(19)
6	PHASE IV	312	198.56(5)	−58.04(14)	8.29(27)
7	PHASE IV	302	232.95(4)	−67.20(11)	8.91(35)
8	PHASE IV	292	264.55(4)	−75.47(11)	10.12(25)
9	EBBA	332	159.74(11)	−47.05(30)	5.90(50)
10	EBBA	322	250.38(5)	−72.50(14)	8.82(32)
11	EBBA	312	308.22(5)	−88.26(13)	10.28(35)
12	EBBA	302	364.75(5)	−102.89(13)	11.02(30)
13	ZLI 1167/EBBA	312	28.30(9)	−4.37(3)	0.30(12)
14	ZLI 1167/EBBA	302	20.67(2)	−1.71(6)	0.18(9)
15	ZLI 1167/EBBA	295	16.94(4)	−0.22(9)	0.17(15)
16	ZLI 1167/EBBA	292	12.67(2)	1.05(6)	−0.07(10)
17	ZLI 1167/EBBA	286	10.54(3)	2.15(7)	−0.20(10)
18	ZLI 1167/EBBA	282	5.98(2)	3.50(6)	−0.32(9)
19	ZLI 1167	322	−115.76(4)	36.54(10)	−4.26(14)
20	ZLI 1167	312	−150.22(2)	46.62(8)	−5.00(14)
21	ZLI 1167	302	−176.16(2)	54.34(6)	−5.48(10)

TABLE III (*continued*)

Experiment number	Liquid[a] crystal	Temperature [K]	$D^{P}_{HH}(NH_3)$ [Hz]	$D^{P}_{NH}(NH_3)$ [Hz]	$D^{P}_{CH}(CH_4)$ [Hz]
22	ZLI 1167	292	−177.70(2)	55.76(8)	−5.96(12)
23	ZLI 1695	312	−161.02(8)	48.04(22)	−4.74(18)
24	ZLI 1695	302	−200.04(6)	59.08(18)	−5.72(24)
25	ZLI 1132	312	−74.16(4)	27.07(8)	−3.98(13)
26	ZLI 1132	302	−108.08(4)	36.99(10)	−4.96(11)
27	ZLI 1083	312	−40.89(5)	15.79(13)	−2.47(19)
28	ZLI 1083	302	−100.47(4)	33.69(11)	−4.42(13)

Note. The $D_{\parallel}$ values are converted to the $D^{P}_{\parallel}$ values by multiplying $D_{\parallel}$ by −2, if the director is perpendicular to the applied magnetic field (in experiments 19–24).

[a] Phase IV = eutectic mixture of p-methoxy-p′-n-butyl-azoxybenzenes by Merck
ZLI 1695 = a mixture of cyclohexyl-cyclohexanes by Merck
ZLI 1132 = a mixture of three phenylcyclohexanes and one biphenylcyclohexane by Merck
ZLI 1083 = eutectic mixture of three phenylcyclohexanes by Merck
Samples 13–18 are mixtures composed of 65 wt% ZLI 1167 and 35 wt% EBBA.

TABLE IV

Dipolar coupling constants $D_{ij}^{D} = D_{ij}/P_2(\cos \alpha)$ (referenced to the director) of phosphine and methane in various liquid crystal solvents.

Experiment number	Liquid crystal	Temperature [K]	$D_{HH}^{D}(PH_3)$ [Hz]	$D_{PH}^{D}(PH_3)$ [Hz]	$D_{CH}^{D}(CH_4)$[a] [Hz]
1	K 24 nematic	312	38.74(11)	6.51(18)	0.89(13)
2	K 24 smectic	302	38.90(14)	6.02(21)	−2.03(13)
3	HAB nematic	325	31.58(25)	5.05(28)	1.01(15)
4	HAB nematic	312	35.42(9)	6.42(16)	−1.47(20)
5	HAB nematic	302	26.92(11)	4.65(18)	−2.88(50)
6	HAB smectic	294	8.17(13)	1.14(13)	−4.01(50)
7	PHASE IV	312	145.22(25)	27.54(39)	8.29(27)
8	PHASE IV	302	145.18(14)	27.48(32)	8.91(35)
9	EBBA	312	177.74(25)	34.56(39)	10.28(35)
10	EBBA	302	191.18(26)	37.15(39)	11.02(30)
11	ZLI 1167/EBBA	312	51.17(15)	9.00(24)	0.30(12)
12	ZLI 1167/EBBA	302	52.25(12)	9.28(22)	0.18(9)
13	ZLI 1167	347	2.13(30)	−0.74(48)	−2.84(50)
14	ZLI 1167	336	0.98(24)	−1.47(44)	−3.50(50)
15	ZLI 1167	312	−17.18(30)	−5.72(48)	−5.00(14)
16	ZLI 1167	302	−22.12(30)	−6.84(48)	−5.48(10)
17	ZLI 1695	312	−13.92(44)	−4.76(58)	−4.74(18)
18	ZLI 1695	302	−21.64(40)	−6.58(54)	−5.72(24)
19	ZLI 1132	312	2.55(12)	−0.77(22)	−3.98(13)
20	ZLI 1132	302	−4.98(13)	−2.35(23)	−4.96(11)
21	ZLI 1083	312	3.58(15)	−0.25(24)	−2.47(19)
22	ZLI 1083	302	−4.56(15)	−2.20(24)	−4.42(13)

[a] Couplings obtained in the samples without PH_3.

TABLE V

Anisotropies of the interaction tensors of the lone-pair electron cloud and NH bonds of ammonia and of the CH bonds of methane (calculated from the dipolar couplings D_{CH} by the equation given in Reference 4) as well as the values of the order parameter of ammonia (referenced to the director) calculated from ΔA_e and ΔA_{NH}

Experiment number	ΔA_{NH} [10^{-22} J]	ΔA_e [10^{-22} J]	ΔA_{CH} [10^{-22} J]	S
1	−3.93(12)	−3.27(10)	−0.65(7)	0.00050(1)
2	−5.35(23)	−4.67(20)	−0.41(5)	−0.00028(1)
3	−4.98(11)	−4.44(9)	0.00(4)	−0.00066(1)
4	−3.88(17)	−3.54(15)	0.70(10)	−0.00089(1)
5	−7.83(11)	−4.21(9)	−3.53(9)	0.01149(1)
6	−9.21(11)	−4.91(10)	−3.97(13)	0.01421(1)
7	−10.08(9)	−5.25(8)	−4.26(17)	0.01665(1)
8	−10.75(9)	−5.51(8)	−4.84(12)	0.01888(1)
9	−7.71(24)	−4.04(21)	−2.82(24)	0.01145(1)
10	−11.05(11)	−5.60(10)	−4.22(15)	0.01790(1)
11	−12.80(11)	−6.36(9)	−4.92(17)	0.02201(1)
12	−13.87(11)	−6.63(9)	−5.27(14)	0.02599(1)
13	1.85(3)	2.00(3)	−0.14(6)	0.00190(1)
14	2.55(5)	2.48(4)	−0.09(4)	0.00134(1)
15	3.05(7)	2.84(6)	−0.08(7)	0.00106(1)
16	3.26(5)	2.97(4)	0.03(5)	0.00076(1)
17	3.75(6)	3.35(5)	0.10(5)	0.00059(1)
18	3.98(5)	3.48(4)	0.15(4)	0.00026(1)
19	7.59(8)	4.67(7)	2.04(6)	−0.00837(1)
20	9.20(7)	5.58(6)	2.39(6)	−0.01084(1)
21	10.52(5)	6.40(4)	2.62(4)	−0.01270(1)
22	11.38(7)	7.20(6)	2.86(6)	−0.01284(1)
23	8.30(18)	4.64(15)	2.27(8)	−0.01156(1)
24	9.75(15)	5.38(13)	2.74(12)	−0.01436(1)
25	7.83(3)	5.56(3)	1.90(6)	−0.00548(1)
26	9.41(8)	6.46(7)	2.37(5)	−0.00791(1)
27	5.02(11)	3.67(9)	1.18(9)	−0.00305(1)
28	8.19(9)	5.52(8)	2.12(6)	−0.00733(1)

TABLE VI

Anisotropies of the interaction tensors of the lone-pair electron cloud and PH bonds of phosphine and of the CH bonds of methane (calculated from the dipolar couplings D_{CH} by the equation given in Reference 4) as well as the values of the order parameter of phosphine (referenced to the director) calculated from ΔA_e and ΔA_{PH}.

Experiment number	ΔA_{PH} [10^{-22} J]	ΔA_e [10^{-22} J]	ΔA_{CH} [10^{-22} J]	S
1	−0.58(13)	1.10(2)	−0.43(6)	0.00563(1)
2	−0.22(15)	1.13(3)	0.97(6)	0.00563(1)
3	−0.29(20)	0.97(4)	−0.48(5)	0.00458(1)
4	−0.85(12)	0.95(2)	0.70(10)	0.00516(1)
5	−0.49(13)	0.72(2)	1.38(10)	0.00392(1)
6	0.04(9)	0.24(2)	1.92(5)	0.00117(1)
7	−4.32(27)	3.71(5)	−3.97(13)	0.02120(1)
8	−4.28(22)	3.57(4)	−4.26(17)	0.02120(1)
9	−5.87(27)	4.42(5)	−4.92(17)	0.02598(1)
10	−6.30(27)	4.56(5)	−5.27(14)	0.02795(1)
11	−1.04(17)	1.40(3)	−0.14(6)	0.00745(1)
12	−1.12(15)	1.37(3)	−0.09(4)	0.00761(1)
13	0.73(34)	0.20(6)	1.36(7)	0.00027(2)
14	1.11(30)	0.22(5)	1.67(7)	0.00009(1)
15	2.21(33)	−0.15(6)	2.39(6)	−0.00259(2)
16	2.48(33)	−0.24(6)	2.62(4)	−0.00332(2)
17	1.88(40)	−0.11(7)	2.27(8)	−0.00210(2)
18	2.35(37)	−0.24(7)	2.74(12)	−0.00324(2)
19	0.79(15)	0.22(3)	1.90(6)	0.00033(1)
20	1.12(16)	0.04(3)	2.37(5)	−0.00077(1)
21	0.53(17)	0.20(3)	1.18(9)	0.00049(1)
22	1.05(17)	0.05(3)	2.12(6)	−0.00071(1)

Namely, if there are no orientation-dependent perturbations on the internal state of the molecule, all the dipolar couplings are directly proportional to the order parameter S. This is not the case: for example, the couplings D_{XH} and D_{HH} do not vanish simultaneously (in the liquid crystal mixture where $D_{NH} = 0$ the corresponding $D_{HH} =$ 16 Hz!).

The deformational contributions to the dipolar couplings are not directly proportional to S, and can account for the observed behavior. The interaction parameters ΔA_e and ΔA_{XH} which explain the experimental dipolar couplings are given in Tables 5 and 6. Their values—ranging from -13.9×10^{-22} J to 11.4×10^{-22} J—are reasonable, in the sense that this is the order of magnitude which can be inferred from the normal order parameters of small molecules in liquid crystals. A typical value $S = 0.1$ corresponds to the value of molecular ΔA of 19.5×10^{-22} J (at 300 K), which means that the ΔA's of the bonds are expected to fall just on the range resulting from the present analyses. It should be noted that the equation of the order parameter of NH_3 and PH_3 does not prevent the interaction parameters from having large values: it constrains only the linear combination (5). Thus, the smallness of the resulting values of the ΔA's shows that the forces responsible for the orientation are also capable of accounting for the deformations.

At first sight the negative sign of some of the interaction parameters may seem to be counter to intuition: in these cases the preferred orientation of the segment is perpendicular to the director. That this phenomenon is not an artifact of the present method of analysis is revealed by the fact that negative molecular ΔA is in some cases obtained directly from the order parameter. For example, the order parameter of the hydrogen molecule is in some liquid crystals negative,[15] showing unambiguously that the corresponding ΔA is also negative. It has been shown recently that the van der Waals forces between the atoms of the solute molecule and the liquid crystal surroundings may explain the behavior of hydrogen, methane and their deuterated analogues in different solvents.[3] Hence, if the interactions of the ammonia and phosphine molecules with their surroundings are dominated by the van der Waals forces, the appearance of negative ΔA's may be considered natural. This is valid also for the interaction parameter of the lone-pair electron cloud, because all of the attraction of the van der Waals forces, and much of the repulsion, results from the interaction of the electrons of one center of force with those of the other center of force. Hence, the presence of a nucleus inside the electron cloud is not essential for the van der Waals forces.

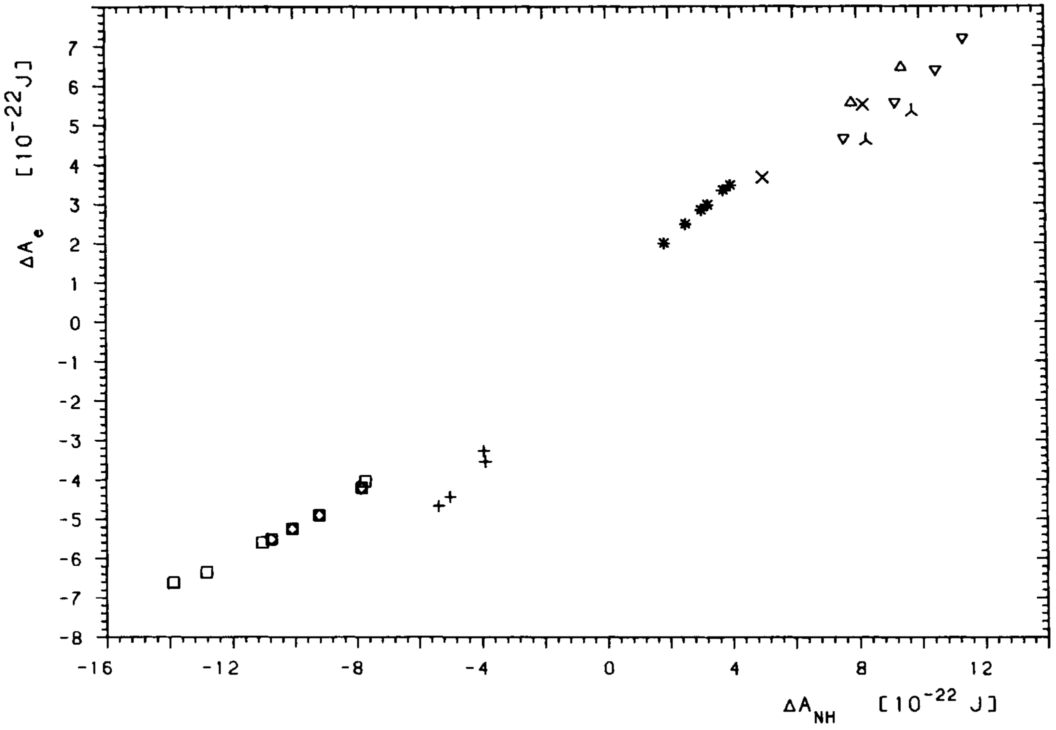

FIGURE 1 The relations between the anisotropies of the interaction tensors of the lone-pair electron cloud and NH bonds of ammonia. The symbols refer to different liquid crystal solvents as follows: HAB (+), Phase IV (⊠), EBBA (□), ZLI 1167/EBBA (*), ZLI 1167 (▽), ZLI 1695 (⅄), ZLI 1132 (△), ZLI 1083 (×).

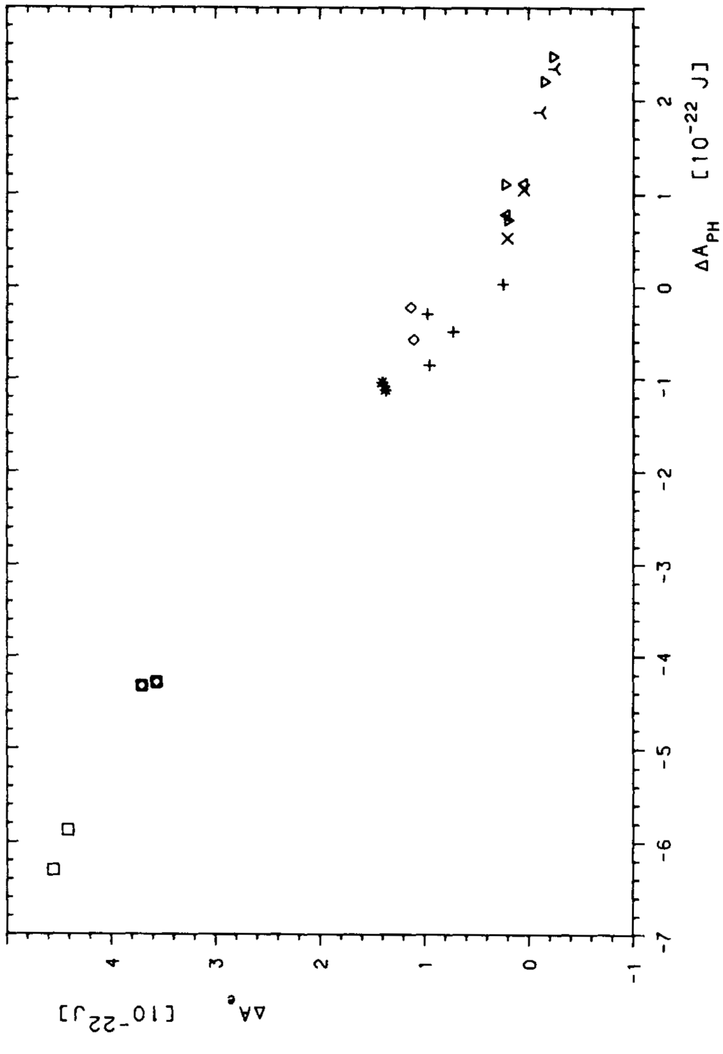

FIGURE 2 The relations between the anisotropies of the interaction tensors of the lone-pair electron cloud and PH bonds of phosphine. The symbol (◇) is used for the liquid crystal K 24. The other symbols are defined in Figure 1.

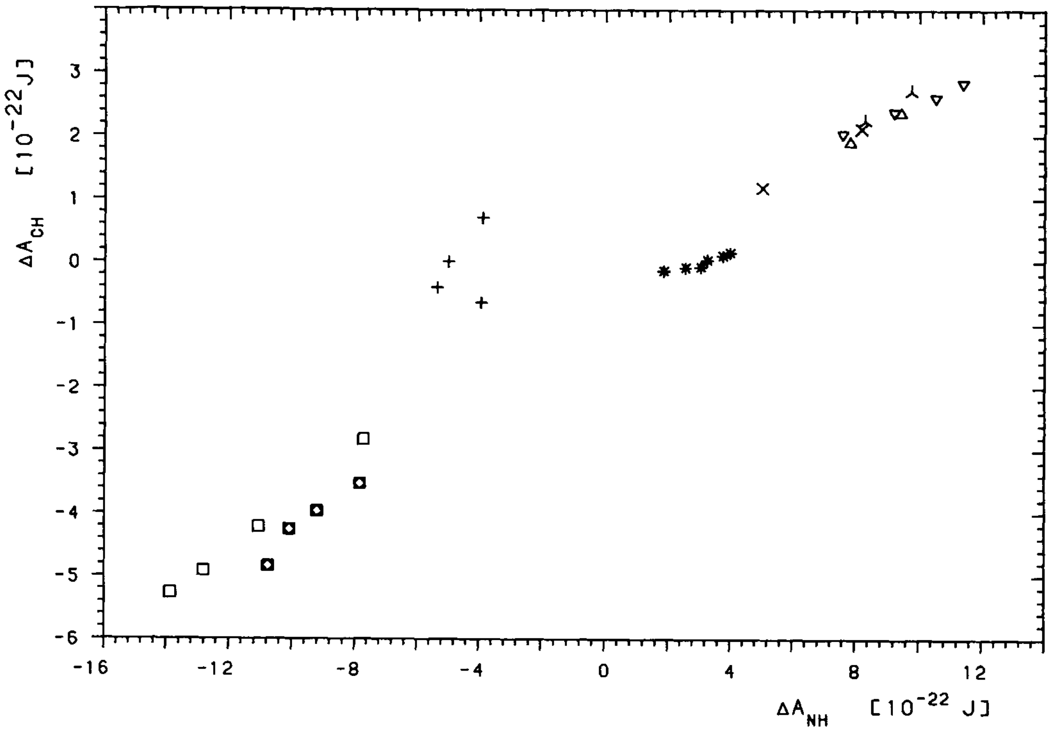

FIGURE 3 The relations between the anisotropies of the interaction tensors of the NH bonds of ammonia and the CH bonds of methane.

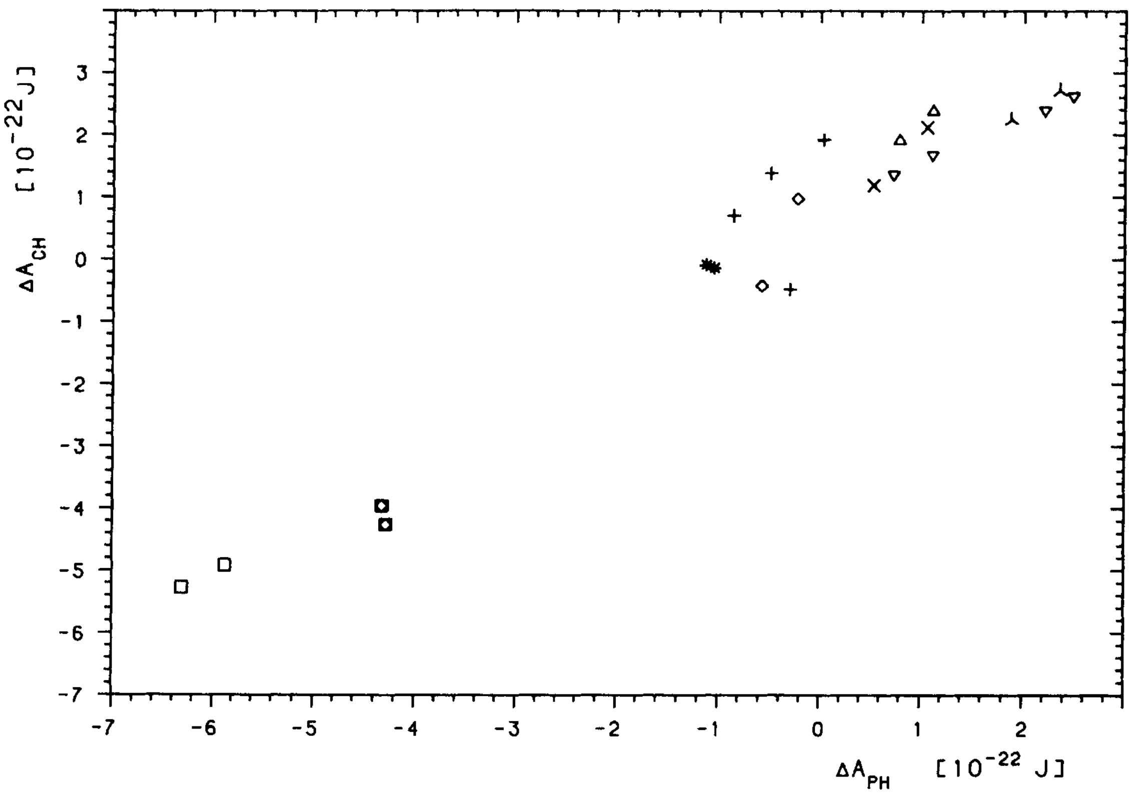

FIGURE 4 The relations between the anisotropies of the interaction tensors of the PH bonds of phosphine and the CH bonds of methane.

The interaction parameters resulting from the present analyses display the same trends as those of the bonds of methyl iodide,[4] methyl fluoride,[4] and hydrogen cyanide.[5] As is shown in Figures 1 and 2, there is an approximately linear relation between the parameters ΔA_e and ΔA_{XH}. Furthermore, the interaction parameters of the CH bond of methane in the same liquid crystals are also approximately linearly related to the ΔA_e and ΔA_{XH}, as is shown in Figures 3 and 4. This behavior implies that the torques acting on the segments of CH_4, CH_3I, CH_3F, HCN, NH_3, and PH_3 stem, at least partly, from a common interaction mechanism. The obvious candidate for this mechanism is the van der Waals interaction, which appears to account for the forces experienced by the methane molecule.[3]

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