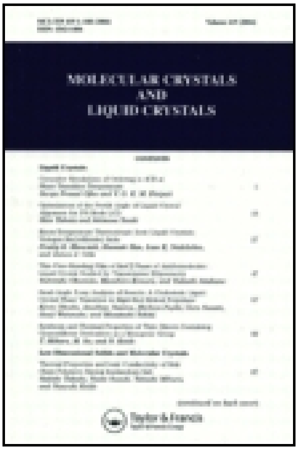

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A Carbon-13 Study of Conformation and Order in 50.7 and 50.7-d $_1$

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A Carbon-13 Study of Conformation and Order in 50.7 and 50.7-d_1

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In principle, liquid crystal spectra should provide information on conformation and orientation as well as on ordering. The quadrupolar spectra of 4-n-pentyloxybenzylidene-4′-n-heptylaniline (50.7) and of three of its homologues have been studied previously. The homologue MBBA-d_1, where a deuteron replaces the proton on the methine carbon of the linkage group has also been studied. The crystal structure of the homologue 40.8 also exists. The aromatic carbon-13 chemical shifts of the 50.7 and the carbon-deuterium dipole-dipole splittings of 50.7-d_1 have been obtained over the entire mesogenic range. The data suggest: (1) that only the order parameter S_{zz} is important in determining the chemical shifts and dipole-dipole splittings of the protonated carbons in the nematic and smectic A and C phases; (2) that the chemical shifts of the unprotonated carbons are, in addition to S_{zz}, influenced either by (S_{xx} − S_{yy}) or by deviations from symmetry in the chemical shift tensor; and (3) that the smectic B and G phases involve distinctly different dependencies than the higher temperature phases.

Keywords: carbon-13, 50.7, NMR relaxation, conformation

INTRODUCTION

The term "liquid crystal" implies a state intermediate between the liquid and crystalline states, partaking somewhat of the properties of both. This description is especially apt for NMR spectra but, in many cases, not for NMR relaxation. Let us limit ourselves to simple NMR interactions, specifically interactions which either do not involve interactions between spins, that is to quadrupolar interactions and/or chemical shift, or else interactions between but two spins, namely dipole-dipole interactions.

In the liquid state the rapid random motion of the molecules leads to simple spectra, with the quadrupolar and dipolar interactions averaged to zero on the NMR time scale and with the chemical shift interaction averaged to a shift proportional to the trace of the chemical shift tensor. In the case of an ideal static single crystal, no such averaging takes place: the dipole-dipole and quadrupole interactions now split the lines, and the shape of the lines is profoundly affected by the entire chemical shift tensor. These spectra will depend on the orientation and conformation of the molecule, and provided the orientation of the crystal is well specified, by say x-ray spectrometry, detailed information on the molecule's orientation and conformation may be obtained. Liquid crystal NMR spectral will depend on the actual phase, but in general the molecular motions will only partially average the interactions and for the dipole-dipole and quadrupolar cases the spectra will resemble crystal spectra where the crystal is oriented so that the long axis lies along the magnetic field and where the splittings are reduced by an amount related to the order tensor. The chemical shift interaction will produce a shift in the frequency of each line from the isotropic value but no splitting and, in this sense at least, the spectra are best described as a modification of the isotropic spectra.

In principle, liquid crystal spectra should allow the determination of the same properties as in the crystalline case specifically, conformation and orientation and, in addition, give information on the order of the liquid crystal.[1-2] In practice, this requires detailed information on the expected conformation and orientation of the molecule involved. For the usual liquid crystal molecule in which a large number of internal rotations are possible and for which any conformation or orientation is in fact an ergodic or ensemble average value, such information may in general be difficult to obtain. A great deal of success has been achieved in the study of the alkyl cyanobiphenyls[2-4] and related substances,[5] for which the straightforward geometry and reasonably rigid core of the biphenyl moeity where only one internal rotation of the core appears possible allows at least some simplifications of the analysis. The study of the various smectic phases appears to have involved some controversy in the past,[6-10] but the disagreements appear to have been resolved.[1,2] However, even an apparently simple nematic like PAA for which the structure in the crystal state exists can raise severe difficulties,[11-13] and even today the lament of over a decade ago remains all too often valid: ". . . we lack the detailed structural parameters necessary for a definitive resolution of the problem."[11] None-the-less, a great deal of information can be obtained from NMR spectra, and we here demonstrate this for the case of 4-n-pentyloxybenzylidene-4′-n-heptylaniline (50.7), presenting the first analysis of ^{13}C–^{2}D splittings in smectic phases.

The molecule 50.7 was chosen because: (1) 50.7 possesses a rich range of phases, a nematic and four smectic phases—A, C, B and G; (2) the quadrupolar spectra of it and three of its homologous have been studied previously[14]; (3) the homologue MBBA has been studied[15] with the same experimental technique used here; (4) there has been much interest in the relaxation properties of 50.7,[16-19] and a complete understanding of these works will require an understanding of the conformation, orientation and order of 50.7; and (5) there is an x-ray determination of the detailed crystal structure of the homologue 40.8,[20] as well as other studies of 50.7 homologues.

EXPERIMENTAL

The 50.7-d_1 sample was purchased from Merck Sharp & Dohme Canada Ltd., and used without further purification. The temperatures for the smectic G-smectic B, smectic B-smectic C, smectic C-smectic A, smectic A-nematic, and nematic-isotropic phase transitions were found to be ~33, 52, 55, 64.3 and 75.5°C. These are somewhat changed from the values obtained in 1980,[16] presumably due to slight decomposition of the sample. The undeuterated 50.7 sample was purchased from Frinton Laboratories Vineland, N.J., U.S.A. and purified by crystallization from ethanol, and had corresponding transition temperatures of ~38, 51.3, 55.6, 63.6 and 77.0 °C. Each sample was degassed by the freeze-pump-thaw method and sealed in a 7.5 mm o.d. NMR tube under vacuum. For better temperature homogeneity, the sample tube was placed in a 10 mm o.d. D_2O bath. The temperature was monitored in the absence of decoupling with a copper-constantan thermocouple placed in the sample bath. The temperature was maintained by a nitrogen gas flow system with an estimated temperature gradient across the sample of less than 0.5 °C. The carbon-13 measurements were made at 22.63 MHz with a Bruker SXP 4-100 spectrometer interfaced to a Nicolet 1180 computer. A proton decoupling field of approximately 10 gauss was applied only during data acquisition to minimize sample heating.[21] The 50.7 measurements were made with a capillary of DMSO inserted in the bath to provide a reference signal. All measurements were performed by cooling from the isotropic phase.

THEORY

The theory of NMR spectra of liquid crystals has been given by Doane.[1] We limit ourselves to situations where the interaction of interest is a small perturbation on the Zeeman interaction. If more than one interaction is present it is assumed that they act independently and simply add together. The perturbing interaction may be written as

$$H_p = C_p \sum_j \langle R^H_{j,0} \rangle T^H_{j,0} \tag{1}$$

where C_p is a constant for the p'th interaction ($p = Q$ = quadrupolar, $p = CS$ = chemical shift, $p = D$ = dipole-dipole), $\langle R^H_{j,0} \rangle$ is a time average, and the $R^H_{j,0}$ and $T^h_{j,0}$ are irreducible spherical tensor operators representing the spatial and spin parts of the interaction referred to a laboratory frame with the z-axis along the magnetic field. The $R^H_{j,0}$ are expressed in terms of the $R^L_{j,0}$ which are referenced to a local frame of the interaction by

$$\begin{aligned} \langle R^H_{2,0} \rangle = & \sum_{m_0,m_1=-2}^{2} D^2_{m_0,0}(\theta_0, \phi_0) \langle D^{*2}_{m_0,m_1}(\phi, \theta, \psi) \rangle \langle D^{*2}_{m_1,0}(\beta, \alpha) \rangle R^L_{2,0} \\ & + \sum_{m_0,m_1=-2}^{2} D^2_{m_0,0}(\theta_0, \psi_0) \langle D^{*2}_{m_0,m_1}(\phi, \theta, \psi) \rangle \\ & \times \langle D^{*2}_{m_1,2}(\alpha, \beta, \gamma) + D^{*2}_{m_1,-2}(\alpha, \beta, \gamma) \rangle R^L_{2,\pm 2} \end{aligned} \tag{2}$$

The (θ_0, ϕ_0) give the orientation of the magnetic field with respect to the principal axis of the liquid crystal (z-axis = director) interaction, (ϕ, θ, Ψ) transform from this principal axis to the molecular frame (with z-axis parallel to the long axis of the molecule), and (α, β, γ) refer the principal axis of the local frame (e.g., the frame with z-axis along the vector connecting two spins which interact via the DD interaction) to the molecular frame.

There are some important simplifications. The $T^H_{2,\pm 2}(H)$ are zero for the chemical shift interaction. The $R^L_{2,\pm 2}$ are zero for the dipole-dipole interaction. For the case of deuterium this term is generally very small, indeed zero for perfect axial symmetry and cases exist (cf., the carbon of the CN group in biphenyls) where it is zero for the chemical shift. The isotropic term, $R^L_{0,0}$ is zero for both quadrupolar and dipole-dipole interactions, which is why these interactions have no direct effect on isotropic spectra.

It is convenient to define a frequency term from which the effect of isotropic interactions is removed,

$$\nu_i^p = \nu_i^p\,(\exp) - \nu_i^p\,(j = 0) \tag{3}$$

For Q and D, $\nu_i^p\,(j = 0) = 0$ and ν_i^p is a splitting. For CS $\nu_i^p\,(j = 0)$ is the isotropic frequency and ν_i^p is the frequency difference between the isotropic and mesogenic line positions.

The uniaxial phase is one with axial symmetry about the liquid crystal principal axis. In this case ϕ is undefined, and only $m_0 = 0$ terms in Equation (2) survive. If the second term of Equation 2 is zero, then

$$\nu_i^p = K_i^p\, D^2_{00}\,(\theta_0)[a_i S_{zz} + b_i\,(S_{xx} - S_{yy})] \tag{4}$$

where

$$D^2_{00}(\theta_0) = \frac{3}{2}\cos^2\theta_0 - \frac{1}{2}. \tag{5}$$

The order parameters are

$$S_{zz} = \left\langle \frac{3}{2}\cos^2\theta - \frac{1}{2} \right\rangle \tag{6}$$

$$S_{xx} - S_{yy} = \frac{3}{2}\,\langle \sin^2\theta\cos 2\psi \rangle, \tag{7}$$

the conformational terms[9] are

$$a_i = \left\langle \frac{3}{2}\cos^2\beta_i - \frac{1}{2} \right\rangle \tag{8}$$

$$b_i = \frac{1}{2}\,\langle \sin^2\beta_i \cos 2\alpha_i \rangle, \tag{9}$$

and the interaction strengths are

$$K_i^D = 2\left(\frac{\gamma_i\gamma_k}{4\pi^2}\right)(h/\langle r_i^3\rangle) \tag{10}$$

$$K_i^{CS} = \frac{2}{3}\nu_0(\sigma_\parallel - \sigma_\perp) \tag{11}$$

$$K_i^Q = \frac{3}{2}e^2q^LQ/h \tag{12}$$

The dipolar term[22] is appropriate for a spin i being split by a spin k of a different species of corresponding gyromagnetic ratios γ_i and γ_k, separated by a distance r_i with the vector between oriented in the liquid crystal principal axis frame by β_i and α_i. For the chemical shift $\sigma_\perp = \sigma_{xx} = \sigma_{yy}$ and $\sigma_\parallel = \sigma_{zz}$, and the angles relate the principal axis of the chemical shift tensor to the liquid crystal principal axis with beta between the director and the direction of σ_{zz}. For the quadrupolar case, (e^2q^LQ/h) is the coupling constant measured in the solid state, the quadrupolar asymmetry parameter in the solid state must be zero, and the angles relate to the electric field gradient tensor at the nucleus. For deuterium beta is between the C-D bond and the director. In practice, Equation (4) may be a valid approximation even in situations where it is not rigorously correct.

In the biaxial phase terms in Equation (2) with m_0 not zero must be included, and even if the second term of Equation (2) can be neglected, the results can be very complicated. In practical situations, it is often true that θ_0 is close to zero and that the second term of Equation (2) can be neglected. If in addition the molecular axis can be chosen with the z-axis along the long molecular axis and the x-axis along a two-fold axis of rotational symmetery then[9,13]

$$\nu_i^p = K_i^p\,[a_iS_{zz} + b_i(S_{xx} - S_{yy}) + c_iS_{yz}] \tag{13}$$

where the new terms are

$$S_{yz} = \langle \sin 2\theta \sin \psi\rangle \tag{14}$$

and

$$c_i = \frac{3}{4}\langle \sin 2\beta_i \sin \alpha_i\rangle. \tag{15}$$

It should be kept in mind that Equation (13) is an approximation, that Equation (4) is valid only under limited circumstances generally, in nematic and smectic A phases, and that if θ_0 is not zero it is not appropriate to multiply Equation (13) by Equation (5).

The notation adopted above is convenient, but obscures the fact that for the dipolar case the $\langle r_i^3\rangle$ will depend on the conformational average and will have to be determined simultaneously with the conformational averages of Equations (8), (9) and (15). This determination of $\langle r_i^3 \rangle$ can be a serious drawback in utilizing dipolar shifts, but at the same time may present a very sensitive method of probing possible changes in the conformation of the liquid crystal molecule. The application of the above theory to determine order parameters using any or all of the available interactions requires not only the determination of the conformational terms but also a determination of the coordinate system in which the resulting order parameters are referenced.

RESULTS AND DISCUSSION

Only interactions within the aromatic core and linkage group are considered here. Some typical carbon-13 proton decoupled spectra of this region for 50.7 are given in Figure 1. The chemical shifts as a function of temperature and a numbering diagram of the core are given in Figure 2. The assignments are based on previous studies of carbon-13 spectra of the homologue MBBA[23] and MBBA-d1.[15] It can be seen that the effect on the spectra of decreasing the temperature is to simply increase the shift of the lines from the isotropic values.

Some typical carbon-13 spectra of 50.7-d_1 are given in Figure 3, along with a tentative spectral analysis for one temperature. The spectrum consists of triplets. The central lines of the triplets have frequencies similar to the undeuterated 50.7 spectral lines. The shift due to the deuteron can be ignored so except in the analysis of the 50.7-d_1 spectra, 50.7 shifts will be used in what follows. The analysis was repeated for each spectrum and the region of interest was reproduced quite well.

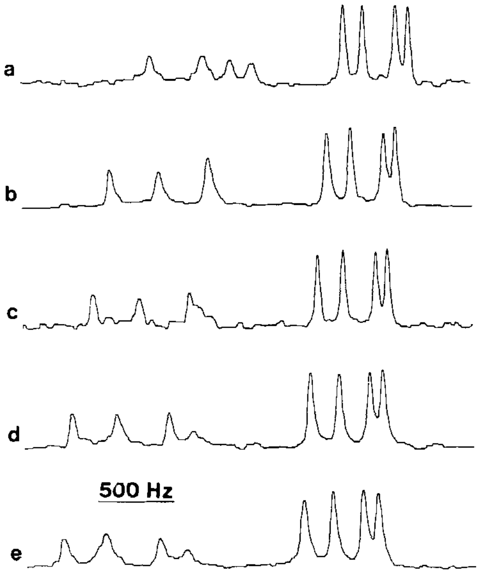

FIGURE 1 Carbon-13 proton decoupled spectra of 50.7: (a) nematic at 71.8°C, (b) smectic A at 62.2°C, (c) smectic C at 53.9°, (d) smectic B at 48.4°C, and (e) smectic G at 29.0°.

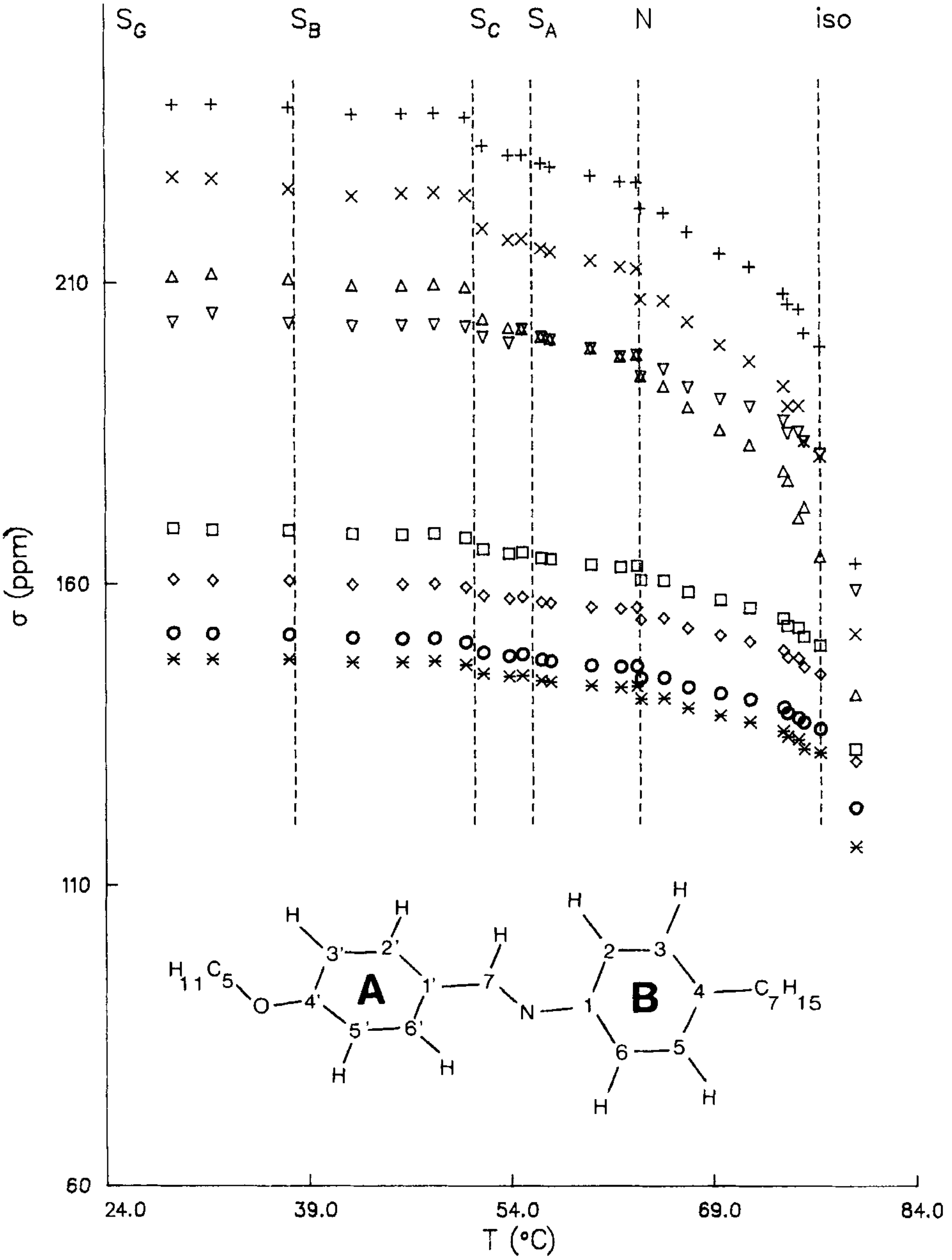

FIGURE 2 Carbon-13 chemical shifts of 50.7 as a function of temperature in ppm from TMS. The symbols are: C4′ = +, C4 = ×, C1′ = Δ, C7 = ∇, C2′ = C6′ = □, C3 = C5 = ◇, C2 = C6 = ○, C3′ = C5′ = *.

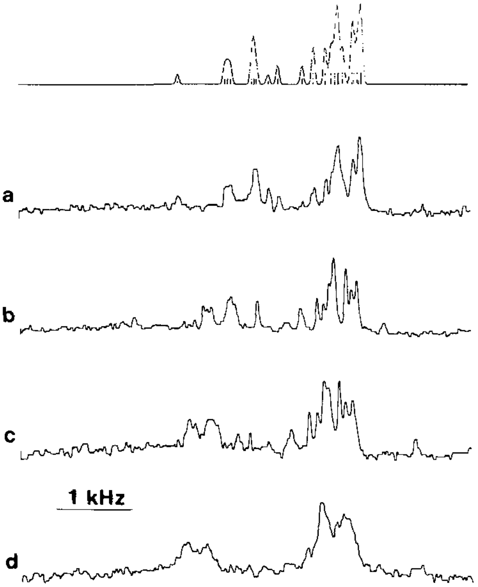

FIGURE 3 Carbon-13 proton decoupled spectra of 50.7-d_1 (a) nematic at 71.4°C, along with spectral analysis and theoretical plot, (b) smectic A at 61.8°C, (c) smectic B at 49.6°C, and (d) smectic G at 32.0°C.

TABLE I

Average C-D distances and angles of C-D with respect to C1′-C4′ axis

CARBON	C-D DISTANCE (angstroms)	ANGLE WITH C1′-C4′ (degrees)
7	1.0733	63.491
1′	2.1421	27.408
2′	2.6230	4.850
6′	3.4008	40.028
2	2.4673	159.526
6	3.8207	127.693

In general, it is possible to find at least two lines for each of the dipole-dipole interactions involving the deuterium and C7, C1′, C2′ and C2. The other couplings can be estimated sufficiently well to verify that the interpretation of the spectra is correct, but are not good enough for quantitative conclusions and will not be considered further at this time. It can also be seen that the 50.7-d_1 spectra are broadened at the lower temperatures by the deuterium-carbon-13 interaction.[15] The deuterium spectra of deuterated 50.7 and their analyses, are found in the literature[14,16,24] and are used in our analysis. Both Hsi et al[14] and Dong[24] have used

TABLE II

Deuterium-carbon splitting experimental ratios and calculated angles

PHASES		LINES		
		7/1′	7/2′	7/2
N	ratio	3.95±0.12	7.53±0.12	10.0±0.9
	angle	4.5±0.3	4.5±0.2	4.7±0.9
SmA,SmC	ratio	4.53±0.05	7.9±0.4	11.2±0.4
	angle	5.8±0.1	5.2±0.6	5.9±0.4
SmB	ratio	5.1±0.2	9.6±0.4	12.5±0.5
	angle	7.1±0.4	8.2±0.6	7.1±0.4
SmG	ratio	5.1±0.2	9.6±0.4	15.4±0.2
	angle	7.1±0.4	8.2±0.6	9.4±0.2

aromatic deuterium results via the first term of Equation (4). Hsi et al also consider the dipole-dipole interactions of the deuterium as well as the methine deuterium in their analysis. The x-ray crystallographic study of the homologue 40.8[20] reveals two distinct molecules of differing conformation per unit cell. For both molecules the H-C7 = N group is very nearly coplanar with ring A (dihedral angles of 2.9° and 2.7°), but ring B is rotated out of this plane by differing amounts (10.4° and 29.4°). The NMR study[15] of the homologue MBBA (10.4) in the nematic state indicated that ring A and the H-C7 = N group are coplanar within ± 10° and that the dihedral angle between this plane and ring B is 23.7° ± 5.6°. These results are consistent with the x-ray results for 40.8. It appears reasonable, therefore, to take the average of the two 40.8 crystallographic entities as the approximate structure of the 50.7 core. We have converted the given atomic positions[20] to a conventional rectangular coordinate system, calculated appropriate C-D distances, and calculated angles with respect to a coordinate system fixed in ring A with the z-axis along C4′-C1′ and the x-axis in the plane of the ring. The averaged values for the C-D vectors of interest are given in Table I. A coordinate system consisting of the principal axis system of the moment of inertia tensor of the molecules was also investigated but this was not useful. Previous studies of the terms in Equation (4) or (13), or expressions similar to these, indicate that the term a_iS_{zz} is usually dominant. Theoretical studies[25] indicate that the order parameter $(S_{xx} - S_{yy})$ should be smaller than the order parameter S_{zz} by about an order of magnitude, and experimental studies often yield a value of $(S_{xx} - S_{yy})$ which, although sometimes larger than $S_{zz}/10$,[9] are essentially constant within experimental error.[4,9,12,13] The order parameter S_{yz}, however, appears to be about 15% of S_{zz} and to have a distinct temperature dependence. It should be recalled that S_{yz} should not effect the N nor the S_A spectra. Thus in the nematic and perhaps smectic A phases it may be a reasonable approximation to retain only terms in S_{zz} when calculating splittings, but the approximation would be suspect in other phases, and in either case would be expected to hold only for an interaction of appropriate symmetry. The validity

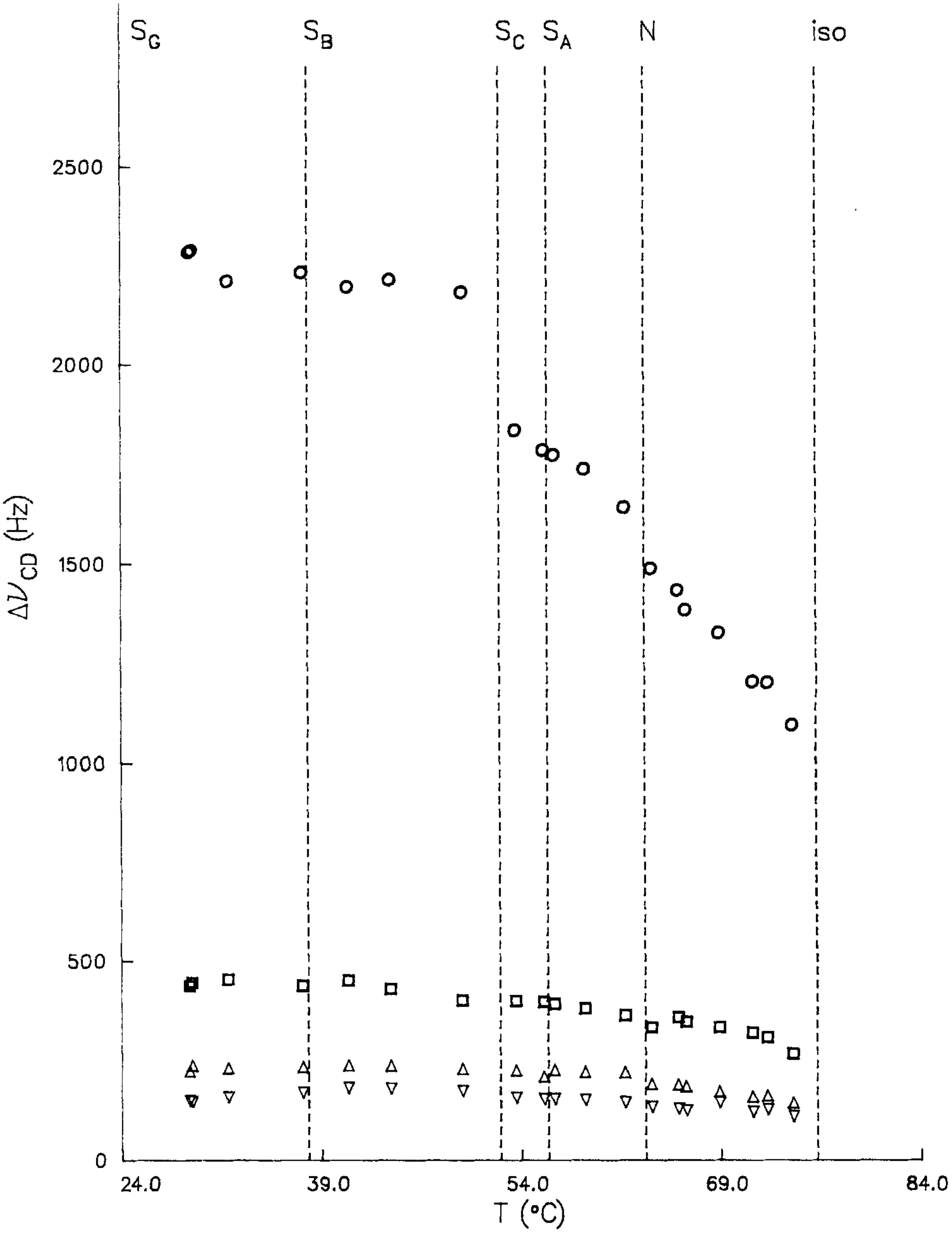

FIGURE 4 Carbon-deuterium splittings of the carbon-13 spectrum of 50.7-d_1 as function of temperature. The splittings of C7, C1′, C2′, and C2 are given by ○, □, Δ, and ∇, respectively.

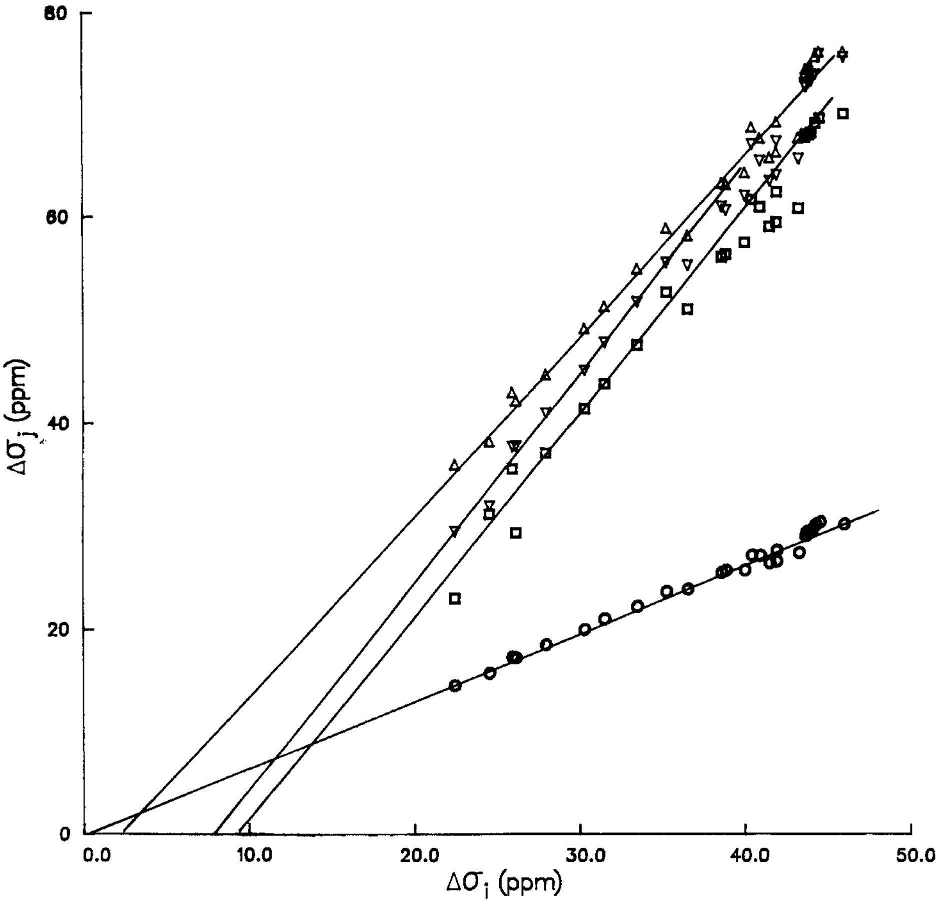

FIGURE 5 Carbon-13 chemical shifts, isotropic shift subtracted from mesogenic shifts, ppm units. Plot of C7 versus C4′ (Δ), C4 (∇), C1′ (□), and C3 (○).

may be investigated by ratio plots,[9] but first we consider the averages involved in the conformational parameters and the orientation of the principal axis of the local frame to the molecular frame.

Hsi, Zimmermann, and Luz described the conformation of 50.7 as resulting from the average of each ring being in one of two symmetrical orientations, such that ring A flips by 180° and thus interchanges 2′ with 6′ and 3′ with 5′, and similarly for ring B. They then calculated the angle delta between the long molecular axis and the C4′-C1′ axis by considering available ratios. The averaging must include both angles and distances, and we define conformational parameters $\hat{a}_i = a_i / \langle r_i^3 \rangle$. Thus, for example, the conformation parameter $\hat{a}_{2'}$, for the splitting of the C2′-D interaction is given by

$$\hat{a}_{2'} = \frac{1}{2}\left\{ \frac{\left(\frac{3}{2}\cos^2(\beta_{2'} - \delta) - \frac{1}{2}\right)}{\langle r_{2'}^3 \rangle} + \frac{\left(\frac{3}{2}\cos^2(\beta_{6'} + \delta) - \frac{1}{2}\right)}{\langle r_{6'}^3 \rangle} \right\} \tag{16}$$

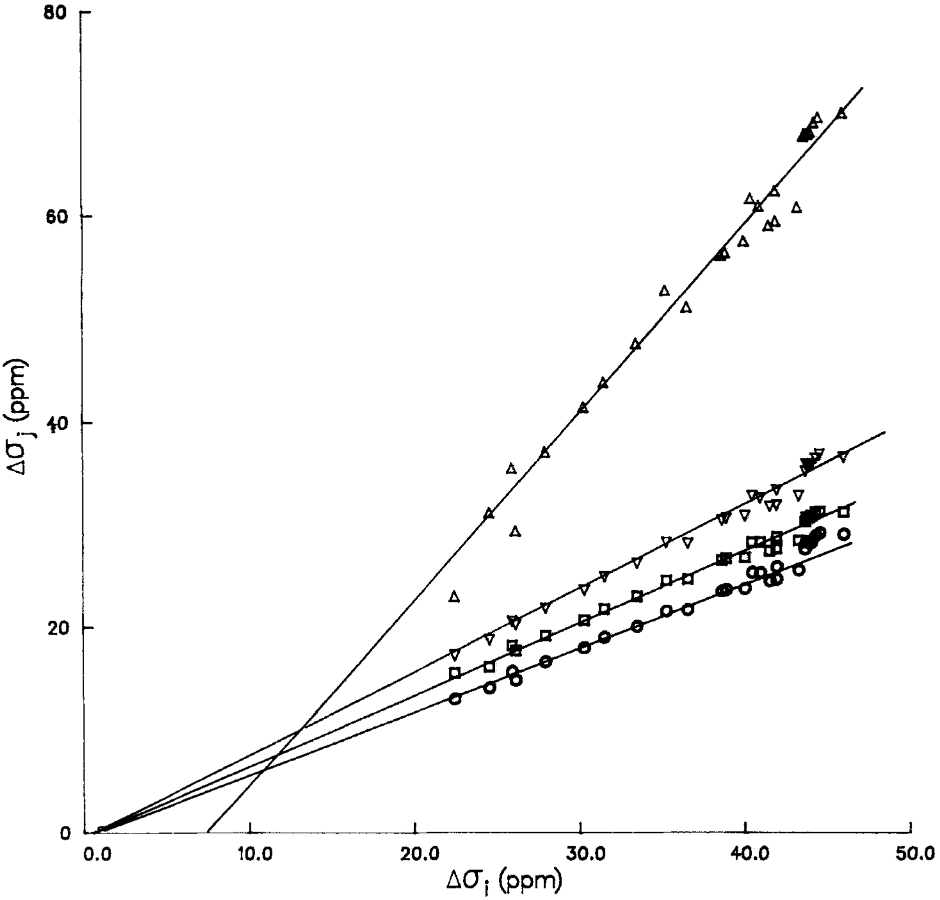

FIGURE 6 As in Figure 5, with C7 versus C1′ (Δ), C2′ (∇), C3′ (□), and C2 (○).

and the C2′-D distance is the average of the C2′-D and C6′-D distances, whereas for $\hat{a}_2$ the angle delta would be subtracted in both terms and for both $\hat{a}_7$ and $\hat{a}_1$, no averaging would occur. Hsi *et al* applied the approach to the ratio of the quadrupolar splittings from the methine and aromatic deutrons, and also to the ratio of the aromatic quadrupolar splittings and deuterium dipole-dipole splittings. The results differed by up to four degrees, possibly because the quadrupole asymmetry parameter of the aromatic carbons invalidated the single order parameter approximation. We have applied the method to three ratios of dipole-dipole interactions, and the results are given in Table II. It should be noted that the ratio 7/1′ does not involve averaging, whereas the ratios 7/2′ and 7/2 do involve averaging.

The agreement between the angles found for the nematic phase is rather spectacular. For the smectic A and smectic C phases the agreement is within experimental error. The conclusions to be drawn are that (1) the method of averaging and the model of ring rotation is correct, a conclusion reinforced by the dependence of dipole-dipole interactions on both angle and distance, and (2) the average con-

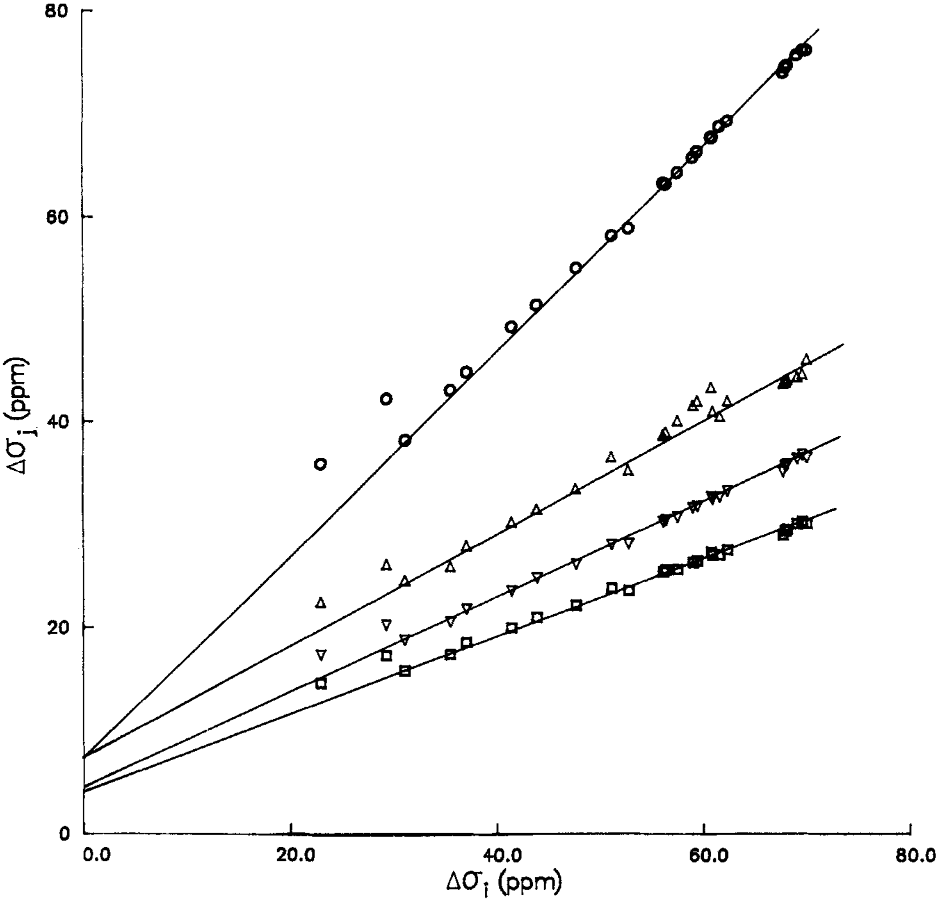

FIGURE 7 As in Figure 5, with C1′ versus C4′ (○), C7 (△), C2 (▽), and C3 (□).

formation determined from x-ray data is valid for the molecular core in the nematic, smectic A and smectic C phases. It is difficult to believe that it must not also be valid for the phases between solid and smectic C. The disagreements in the angles found for the lower phases are presumably due to the expected failure of the single order parameter approximation.

The chemical shifts given in Figure 2 appear under visual inspection to have two distinct types of behaviour as a function of temperature, depending on whether or not the carbon has a proton attached to it. We may investigate this behavior quantitatively by plotting frequencies or ratios of frequencies against each other.[9] Let us absorb the interaction strengths, Equations (10–12) and θ_0 dependence, Equation (5) into the conformational terms, Equations (7–9). Primes are used to indicate this.

If two splittings or shifts ν_p and ν_q are described by Equation [4], then

$$\nu_p = (a'_p/a'_q)\nu_q + (b'_p - (a'_p/a'_q)b'_q)(S_{xx} - S_{yy}). \tag{17}$$

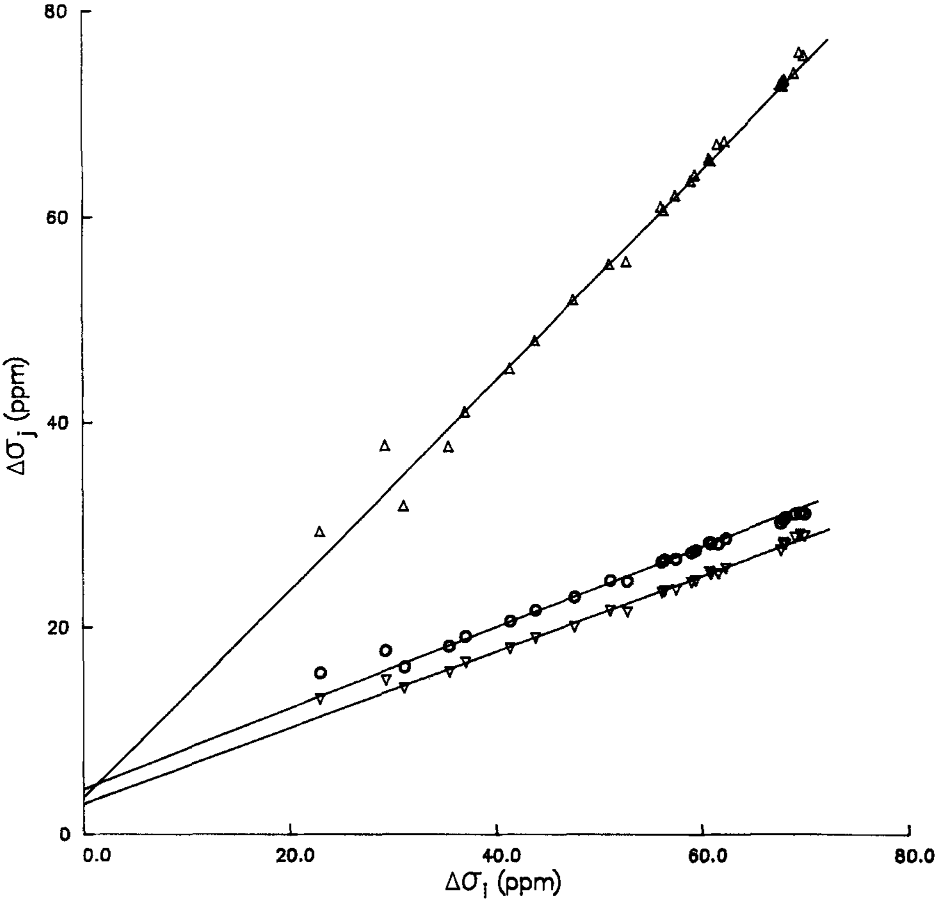

FIGURE 8 As in Figure 5, with C1′ versus C4 (Δ), C3′ (O), and C7 (∇).

If $(S_{xx} - S_{yy})$ is reasonably constant then this is just the equation of a straight line. The intercept will be zero if either the order parameter $(S_{xx} - S_{yy})$ is zero or if the term multiplying it is zero. For conformational terms depending on angles but not distances, this later situation will be fairly common.

Some typical plots of carbon-13 chemical shifts with the appropriate isotropic chemical shifts subtracted out are given in Figures 5 to 8. In general, it is found that: (1) the plots are straight lines in all but the Smectic G phase, (2) plots involving protonated carbons have intercepts at the origin within experimental error, and (3) plots involving non-protonated carbons have intercepts well away from the origin. The general method of plotting ratios has been given in Reference 9.

Consider first the case where $\nu_p = a'_p S_{zz}$ and $\nu_q = a'_q S_{zz}$ but $\nu_r = a'_r S_{zz} + B_r$, B_r is any additional term, for example $B_r = b_r(S_{xx} - S_{yy})$. Then $(\nu_r/\nu_p) = (a'_q/a'_p)(\nu_r/\nu_q)$ and a plot of (ν_r/ν_p) versus (ν_r/ν_q) will be a straight line of zero intercept with slope independent of ν_r. If, on the other hand the dependence of either p or q is more complicated, then the intercept is non-zero. Figure 9 is a plot of $\nu_7/\nu_{1'}$ versus $\nu_{2'}/\nu_{1'}$, and it can be seen that the plot in the nematic, smectic A

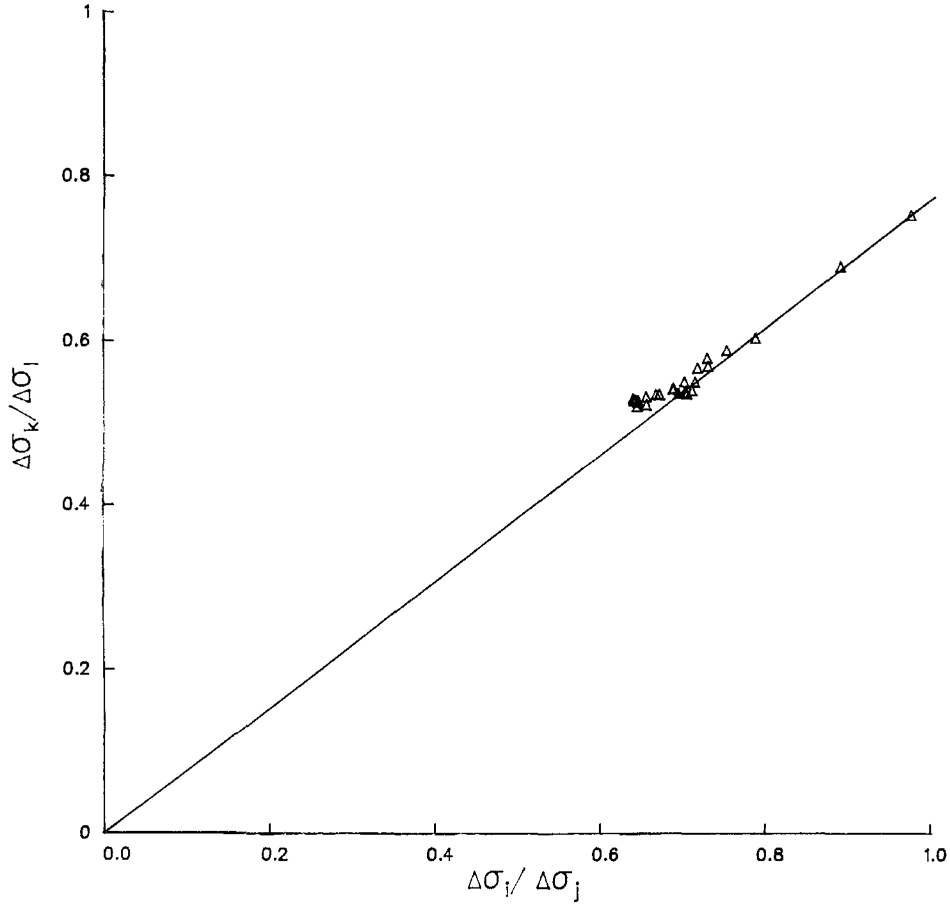

FIGURE 9 Ratios of carbon-13 chemical shifts, isotropic shifts subtracted from mesogenic shifts. Plot of C7/C1′ versus C2′/C′.

and B regions is a straight line of zero intercept. Thus the protonated carbons in these regions must have shifts that are just proportional to S_{zz}. The shift $\nu_{1'}$, and in general the shifts of the other non-protonated carbons, must have additional terms. These could arise from terms in Equation (4) or (13), or they could arise from the fact that most chemical shift tensors are not axially asymmetric[26] and so additional terms from the second half of Equation (2) may have to be considered.

In general ratio plots will not have zero intercepts. Consider the case where $\nu_p = a'_p S_{zz}$, $\nu_r = a'_r S_{zz} + b'_r(S_{xx} - S_{yy})$, and $\nu_s = a'_s S_{zz} + b'_s(S_{xx} - S_{yy})$. Then the slope of ν_p/ν_r versus ν_p/ν_s will be b'_s/b'_r. The two ratio plots of Figure 10 test the possibility that the unprotonated lines arising from C4′ and C1′ can be described in terms of the order parameters S_{zz} and $(S_{xx} - S_{yy})$, and it appears that they fail the test.

Consider now the dipole-dipole splittings. Figure 11 gives plots of C1′-D, C2′-D, and C2-D versus C7-D. The plots for the nematic, the smectic A and C, and

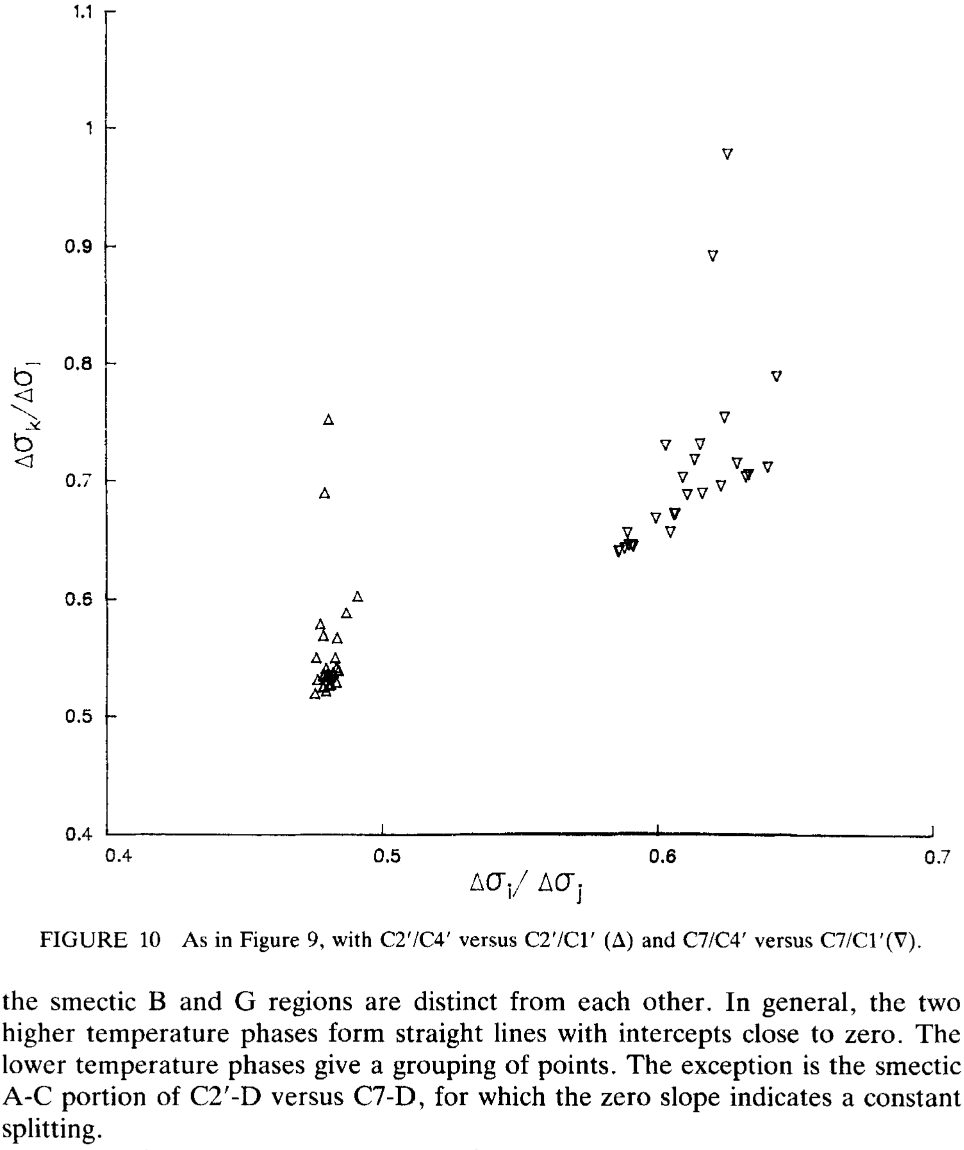

FIGURE 10 As in Figure 9, with C2′/C4′ versus C2′/C1′ (Δ) and C7/C4′ versus C7/C1′(∇).

the smectic B and G regions are distinct from each other. In general, the two higher temperature phases form straight lines with intercepts close to zero. The lower temperature phases give a grouping of points. The exception is the smectic A-C portion of C2′-D versus C7-D, for which the zero slope indicates a constant splitting.

Finally, Figure 12 gives some selected ratio plots for the dipole-dipole interactions. They are consistent with the proposal that order parameters other than S_{zz} are involved in the spectra of 50.7, but to a very small degree.

CONCLUSION

It has been shown that the structure found by crystallographic means for the core of the homologue 40.8 provides a description of the conformation of the core of 50.7 in the mesogenic phases. Because of the dependence of C-D dipole-dipole

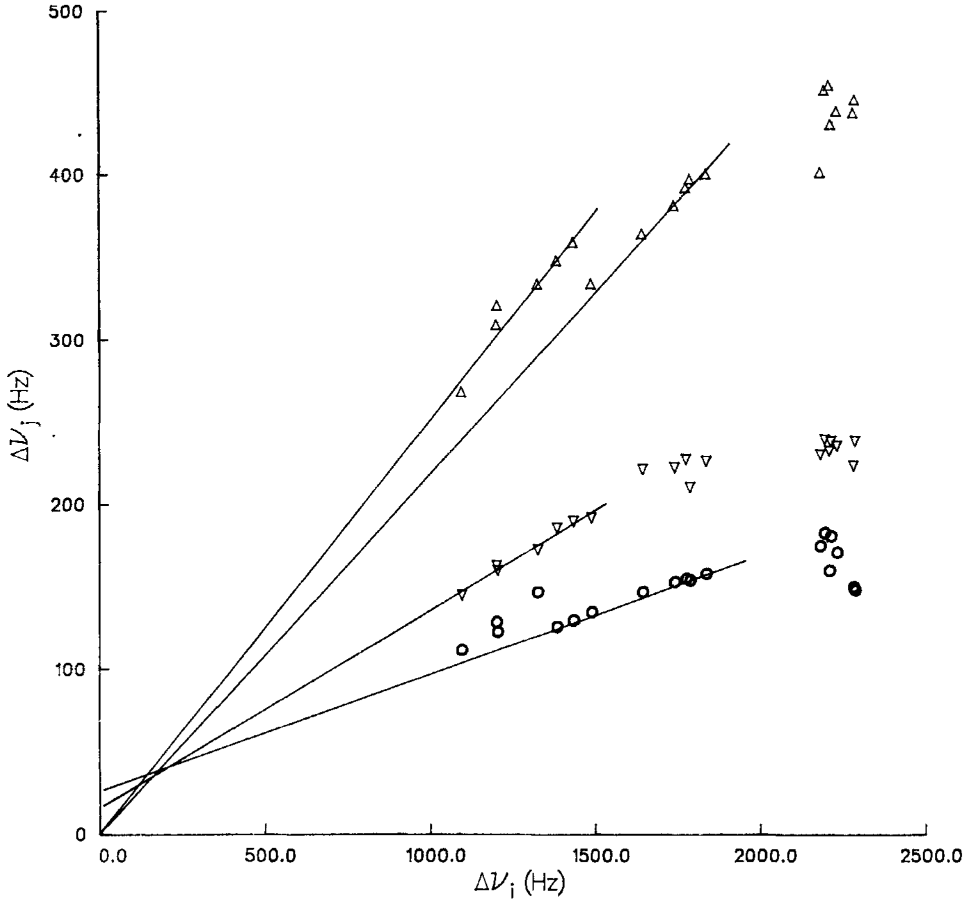

FIGURE 11 Carbon-deuterium dipole-dipole splittings. Plot of C7-D versus C1′-D (Δ), C2′-D (∇), and C2-D(○).

interactions on distance as well as angle, Table II provides convincing evidence for this, and substantiates the previous conclusions about conformation reached[1,9] indirectly through ratio plots.

Studies of the relative values of both the carbon-13 chemical shifts and of the carbon-deuterium dipole-dipole splittings have indicated (1) that only S_{zz} is important in determining these values in the nematic and smectic A and C phases, at least for dipole-dipole interactions and chemical shifts of protonated carbons, (2) that the unprotonated carbon chemical shifts are influenced by another term due either to $(S_{xx} - S_{yy})$ or to the lack of axially symmetry of the chemical shift tensor, and (3) that the Smectic B and G phases involve distinctly different dependencies.

We have, to date, been less successful at utilizing the carbon-deuterium splittings to study order parameters. It is hoped that a complete analysis of all the splittings (see Figure 3) will remedy this situation.

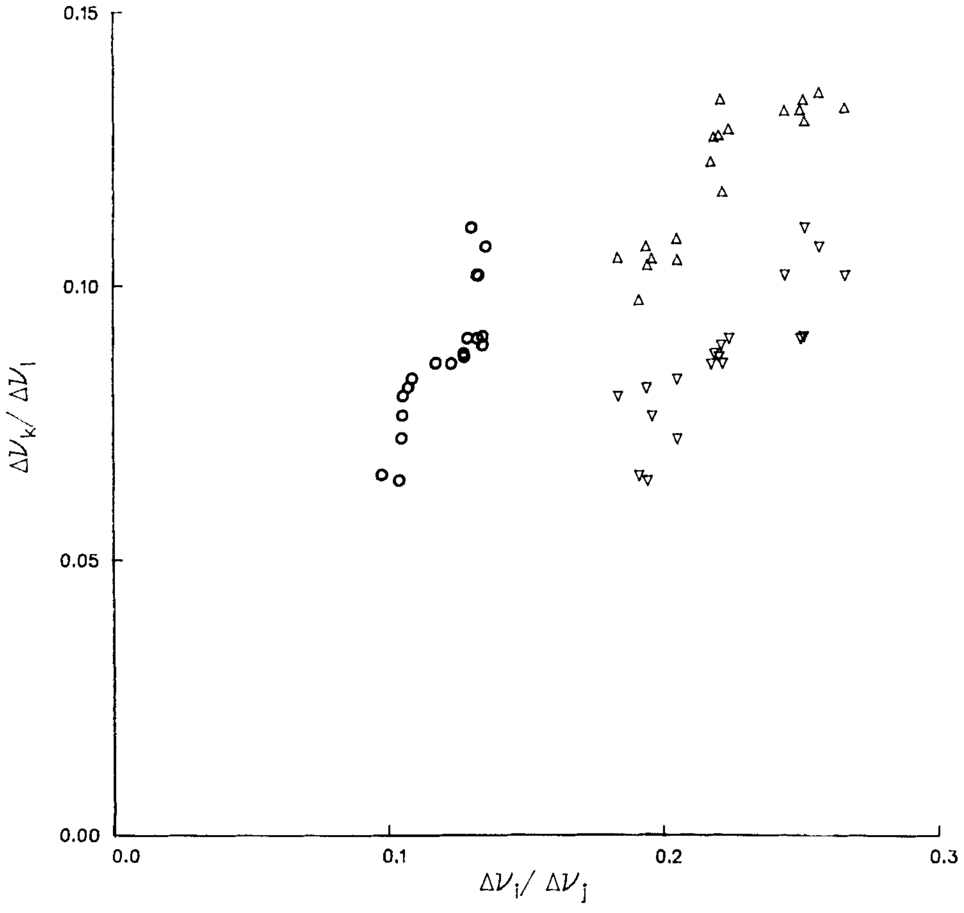

FIGURE 12 Ratios of carbon-deuterium dipole-dipole splittings. Plot of C1′-D/C7-D versus C2′-D/C7-D (Δ), C1′-D/C7-D versus C2-D/C7-D (∇), and C2′-D/C7-D versus C2-D/C7-D (○).

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