The Relative Conformation of Ring and Chain in Ethyl- and n-Propyl-benzene studied by Nuclear Magnetic Resonance of Liquid Crystalline Solutions

Anthony G. Avent, James W. Emsley,* Soon Ng, and Sarah M. Venables
Department of Chemistry, The University, Southampton SO9 5NH

Deuteron n.m.r. spectra and proton spin echo spectra of samples of partially deuteriated ethyl- and propyl-benzene dissolved in liquid crystal solvents have been recorded and analysed. The quadrupolar splittings and dipolar couplings obtained have been used to test two possible minimum-energy conformations for the relative orientations of the ring and alkyl chain. These two conformations are those with C_s symmetry and have the phenyl ring either coplanar or orthogonal to the plane containing the first two carbons in the alkyl group and the carbon in the phenyl ring to which the chain is bonded. The data show unambiguously that neither conformation alone correctly describes the conformational state of these alkylbenzenes.

Many of the compounds which form liquid crystalline phases contain alkyl chains directly attached to phenyl groups and the conformational flexibility of the chain has a strong influence on the mesophase properties.[1] There have been many studies of alkyl chain conformational flexibility principally with the aim of understanding polymeric hydrocarbons,[2] and there is a considerable amount of evidence to support the view that in a hydrocarbon chain the C–C–C–C segments adopt two *gauche* and one *trans*-arrangement with high probability and that intermediate forms are of negligible importance. Thus the conformations about each bond are represented as shown in Figure 1. There is no firm evidence, however, for the conformations adopted by the structural unit $C_6H_5CH_2CH_2R$, the structural studies on such fragments giving conflicting results. The simplest molecule containing this unit is ethylbenzene which has been studied by a variety of methods in various phases. The conformation of the ring and the ethyl group is fully described by the form taken by $E(\varphi)$ the internal energy of the molecule expressed as a function of φ, the angle of rotation of the ethyl group about the C–C bond linking chain and ring, as shown in Figure 2. An X-ray diffraction study has yet to be undertaken on ethylbenzene and a search of the literature revealed only one such study on a compound containing an ethyl group bonded to a phenyl group and lacking bulky *ortho*-substituents. In this compound, 1-phthalyl-2-*p*-ethylbenzoylcyclopropane, the ethyl group exists with the single value of φ as $65.2°$, that is structure (c) in Figure 2 with one of the C–H methylene bonds in the plane of the phenyl ring.[3] This result contrasts with an i.r. study of an oriented crystal of ethylbenzene[4] which found evidence for two structural forms. In one the molecule has a single value of φ of $0°$ and in the other φ again was thought to have a single value but it was located only as lying between 0 and 90°. Two separate studies on liquid samples of ethylbenzene by Raman spectroscopy have tried to determine the point group symmetry of the molecule from observed depolarization ratios. Thus, Verdonck and van der Kalen[5] concluded that the molecule has C_1 symmetry and hence cannot be exclusively in the planar or orthogonal forms (a) and (b) in Figure 2, whereas Saunders *et al.*[6] determined the point group to be C_s and hence the structure is one with either a single value of φ of $0°$ or $90°$ or a mixture of these two forms. A study of the dipole moment and Kerr constant of liquid ethylbenzene[7] concluded that the planar form has the highest energy but could not distinguish between models (b) or (c) for $E(\varphi)$. Both models were predicted to have a barrier height to rotation of 9.6 kJ mol^{-1}. Two proton n.m.r. studies of solutions of ethylbenzene have been reported which use empirical correlations of chemical shifts and coupling constants with structure in order to determine the conforma-
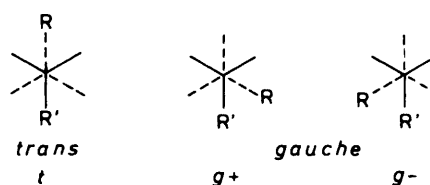

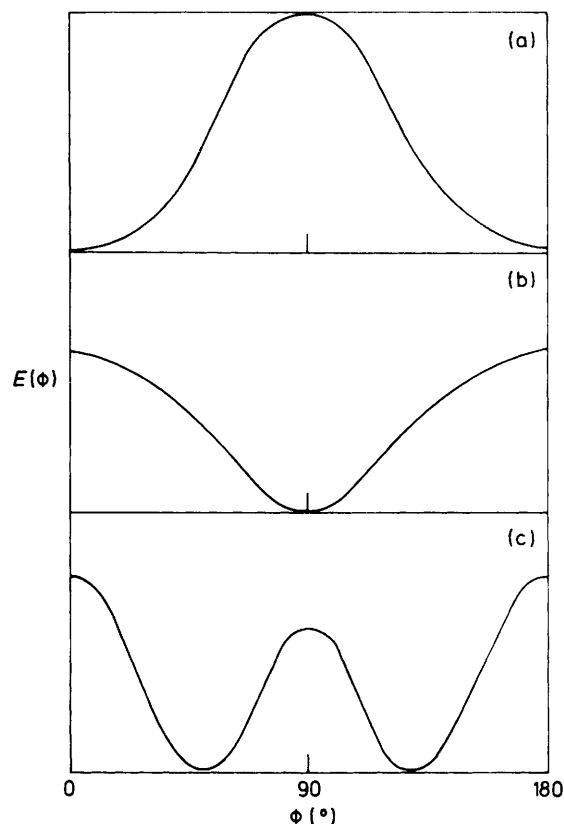**Figure 1.** *Gauche* and *trans* conformations adopted by alkyl chains

Figure 2. Possible forms of the variation of $E(\varphi)$ the internal energy with φ the angle of rotation about the phenyl–C bond in an alkylbenzene. (a) Corresponds to the planar, (b) to the orthogonal, and (c) to an intermediate structure as the most probable conformation
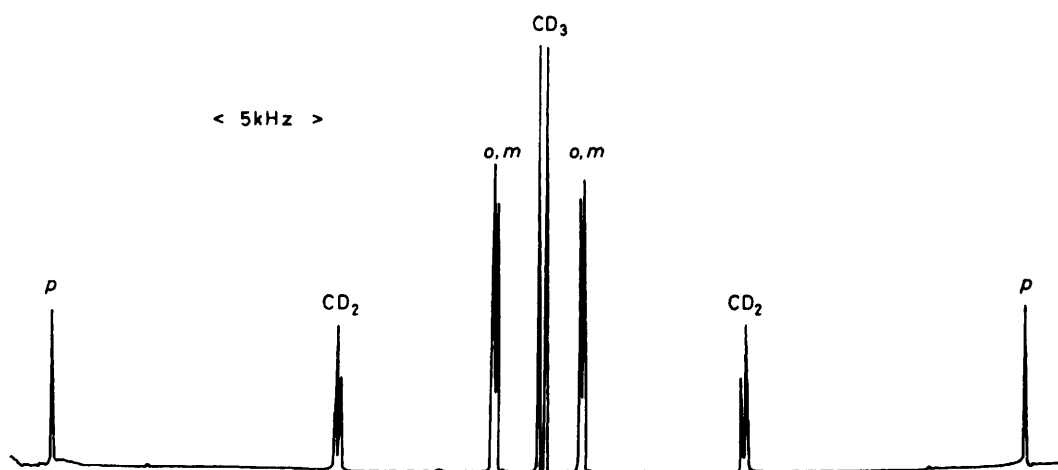
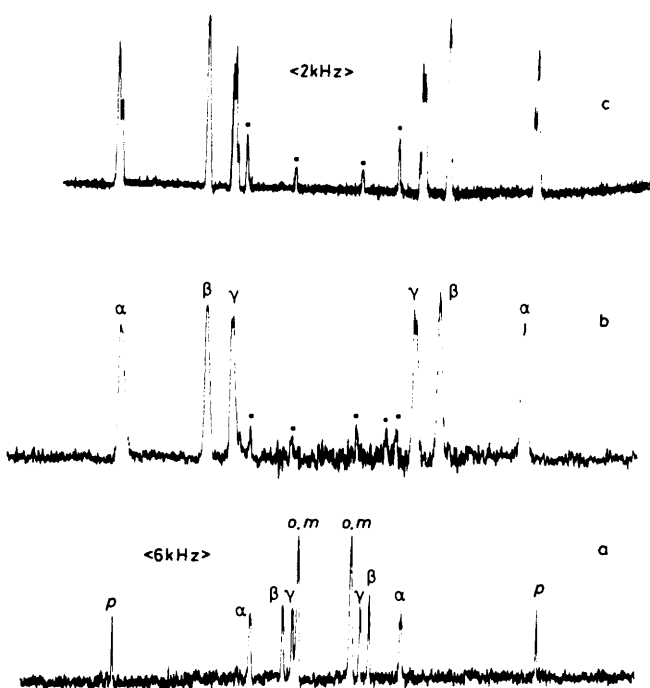**Figure 3.** 30.7 MHz Deuteron spectrum of [^{2}H$_{10}$]ethylbenzene dissolved in ZLI 1167

Figure 4. 30.7 MHz Deuteron spectra of solutions of n-propylbenzene in ZLI 1167. (a) The mixture of $C_6H_5CD_2CD_2CD_3$ and $C_6D_5CH_2$-CH_2CH_3, (b) $C_6H_5CD_2CD_2CD_3$, and (c) $C_6H_5CD_2CD_2CD_3$ with proton decoupling. Peaks marked * are from deuteriated impurities

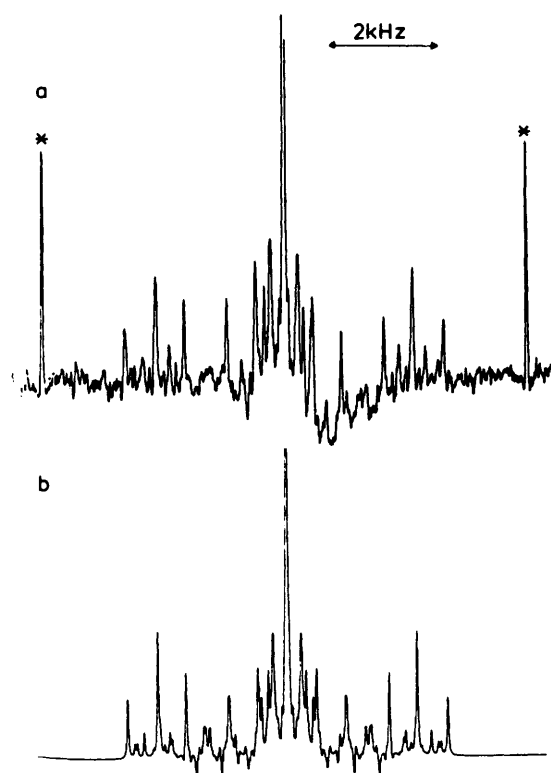**Figure 5.** 200 MHz Proton spin echo spectrum of $C_6D_5CH_2CH_3$ dissolved in ZLI 1167: (a) observed and (b) calculated

tional preference of the alkyl group relative to the ring. Oulette et al.[8] compared the chemical shifts of the protons bonded to the carbon directly attached to the phenyl ring in methyl-, ethyl-, and isopropyl-arenes. They concluded that ethylbenzene has a single value of φ such that one C–H of the methylene group lies in the plane of the ring, that is structure (c) in agreement with the X-ray study discussed above. Schaefer et al.[9] used the structural dependence of the six-bond spin–spin coupling between the para-proton and the methylene protons in 3,5-dibromoethylbenzene to conclude that the orthogonal (φ 90°) form is the predominant isomer with a two-fold barrier to rotation of 5.0 kJ mol^{-1}.

There has also been one ab initio molecular orbital calculation reported for ethylbenzene.[10] Unfortunately the complete energy surface for rotation through φ was not explored, only the planar and orthogonal forms were studied and the latter was found to be lower in energy by 9.2 kJ mol^{-1}.

Molecular structures can be determined with high precision from an analysis of the data provided by n.m.r. spectra of samples dissolved in liquid crystalline solvents. However, the proton spectrum of ethylbenzene although resolvable has so far defied analysis, whilst that from propylbenzene is unresolvable. Less precise information can be obtained, yet still valuable in structure investigations, by using partially or fully deuteriated
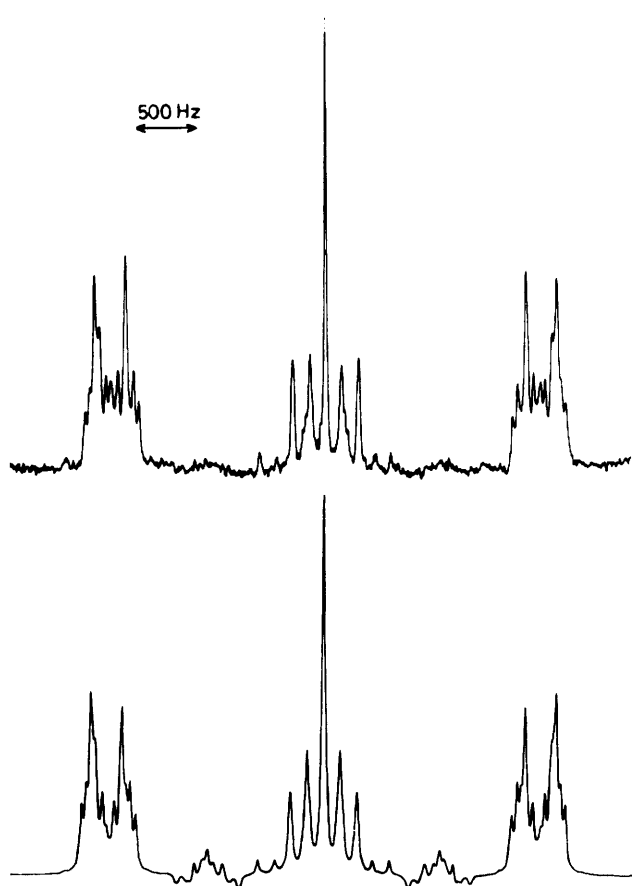
Figure 6. 200 MHz Proton spin echo spectrum of $C_6H_5CD_2CD_2CD_3$ dissolved in ZLI 1167: (a) observed and (b) calculated

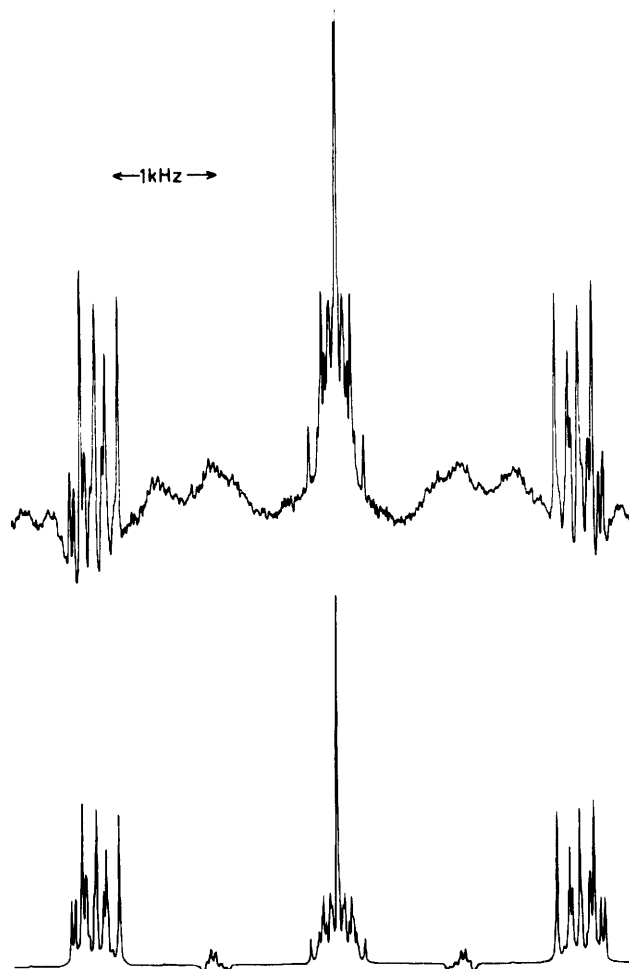**Figure 7.** 200 MHz Proton spin echo spectrum of $C_6H_5CD_2CD_2CD_3$ dissolved in Phase V: (a) observed and (b) calculated
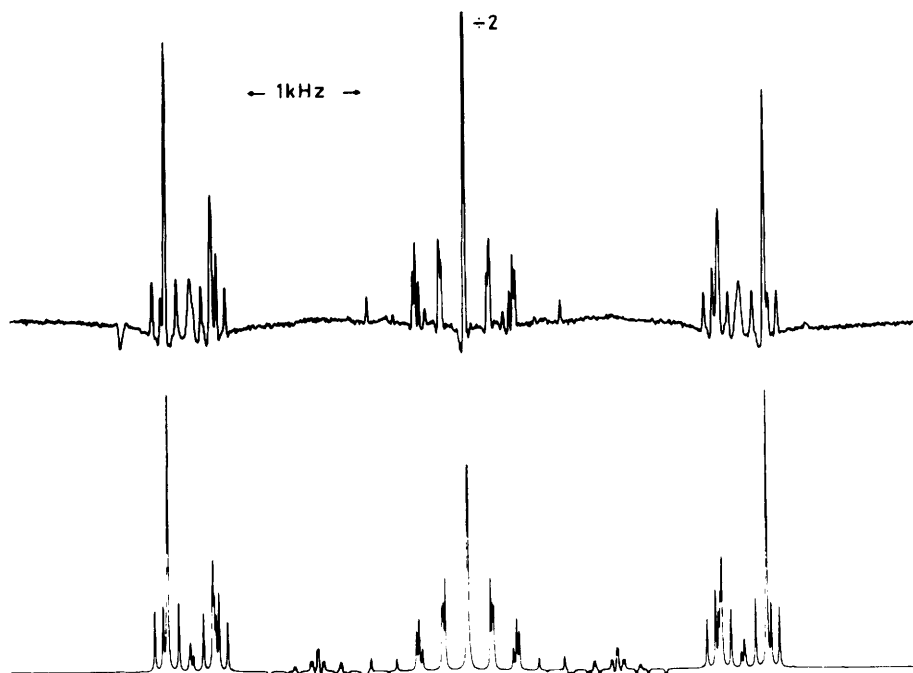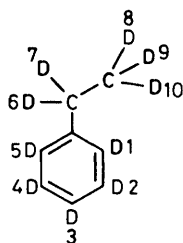
Figure 8. 200 MHz Proton spin echo spectrum of $C_6H_5CD_2CD_2CD_3$ dissolved in E7: (a) observed and (b) calculated

Table 1. Quadrupolar splittings, $\Delta\tilde{v}$, and dipolar coupling, $\tilde{D}$, for the mixture of $C_6D_5C_2H_5$ and $C_6D_5CD_2CD_3$ in the liquid crystal ZLI 1167.

Position	$|\Delta\tilde{v}_i|/Hz$	$|\tilde{D}_{ij}|/Hz$
1,5	9 533 ± 8	
2,4	9 533 ± 8	
3	40 173 ± 8	
6,7	14 123 ± 8	29 ± 2
8,9,10	1 350 ± 8	

samples dissolved in liquid crystalline solvents and we have used this approach on ethyl- and propyl-benzenes.

Figure 9. Molecule of ethylbenzene showing the bond lengths and angles used in the calculation and the location of xyz and pqr axes

Experimental

Samples of perdeuteriated ethyl- and n-propyl-benzene were obtained from Merck, Sharp and Dohme. Samples of the two alkylbenzenes deuteriated only in the ring were prepared by exchange of deuterium between the alkylbenzene and [$^2H_6$]-benzene catalysed by trace amounts of ethylaluminium di-chloride,[10] 90% deuterium being achieved in both cases.

Two samples were used for the study of ethylbenzene, both using the liquid crystal solvent ZLI 1167 (E. Merck, Darmstadt). The best resolved deuteron spectra were obtained using a 5% solution by weight of fully deuteriated ethylbenzene, whilst a solution containing $C_6D_5C_2H_5$ and $C_6D_5CD_2CD_3$ in the ratio of 2:1 and of ca. 5% total concentration in ZLI 1167 was used for proton and deuterium experiments. The samples used for the studies on propylbenzene were the chain-deuteriated form dissolved in three liquid crystal solvents: ZLI 1167, Phase V (E. Merck), and E7 (B.D.H. Chemicals Limited). Samples of equal amounts of ring- and chain-deuteriated propylbenzenes in these same solvents were also used to obtain deuteron spectra.

Three kinds of spectra were recorded. (a) Deuteron spectra which were the Fourier transform of the average of free induction decays obtained by single pulse excitation as shown in Figures 3 and 4. These are 'normal' spectra. (b) Similar spectra but obtained with proton decoupling, an example being shown in Figure 4 for propylbenzene chain deuteriated in ZLI 1167. (c) Spin echo spectra of the protons, as shown in Figure 5 for ring-deuteriated ethylbenzene and in Figures 6—8 for chain-deuteriated propylbenzene. These spin echo spectra are virtually free from the effects of proton–deuteron coupling, as discussed by Avent et al.[11] The spectra were recorded at 300 K on a Bruker CXP 200 spectrometer.

Results and Discussion

Ethylbenzene.—The deuteron spectra are dominated by the quadrupolar splittings $\Delta\tilde{v}_i$, which may be assigned to deuterons on the basis of intensity and the expectation that $|\Delta\tilde{v}_1| = |\Delta v_2| \simeq |\Delta\tilde{v}_4| \equiv |\Delta\tilde{v}_5|$ as shown in Figure 3. The CD_2 peak shows fine structure which results from dipolar coupling and a value for the coupling $\tilde{D}_{67}^{DD}$ was obtained by fitting the shape of this
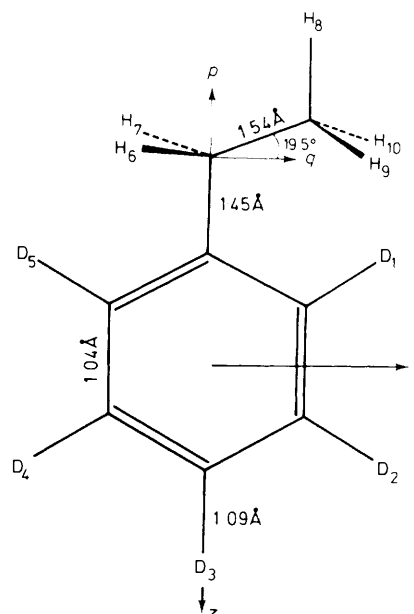
group of peaks. The data obtained from the deuteron spectrum of ethylbenzene are given in Table 1. Note that the signs of the $\Delta\tilde{v}_i$ and $\tilde{D}_{ij}$ are not available from the spectra. However, the structure on the peaks from the *ortho*- and *meta*-deuterons, and the peak from the methylene deuterons, are consistent with the dipolar and quadrupolar couplings being of opposite sign.

For a rigid fragment of a molecule the quadrupolar splitting at the ith site is related to elements of S^L a local order matrix[12] by $\Delta\tilde{v}_i = (3/2) q_{ibb}[S_{zz}{}^L(l_{zi} + \eta_i l_{xi}{}^2/3) + S_{xx}{}^L(l_{xi}{}^2 + \eta_i l_{zi}{}^2/3) - \eta_i S_{yy}{}^L/3 + 2(S_{xz}{}^L l_{xz} l_{zi} + S_{xy}{}^L l_{xi} l_{yi} + S_{yz}{}^L l_{yi} l_{zi})(1 + \eta_i)]$ where a, b, and c are principal axes for the electric field gradient tensor V_i and hence of q_i; the quadrupolar tensor, $q_i = eQV_i/h$. For deuterons in hydrocarbons the b axis, defined so that q_{bb} is the largest component, lies along the C–D bond, and the asymmetry parameter, $\eta = (q_{aa} - q_{cc})/q_{bb}$, is defined to be positive. We use the quadrupolar splittings for the aromatic deuterons to evaluate the principal elements of S^R, the local order matrix for the phenyl ring. To do this we use $q_{ibb} = 185 \pm 5$ kHz and $\eta_i = 0.03 \pm 0.03$ at each position.[13] The direction cosines, l_{xi} etc., are of the ith C–D bond with respect to x, y, and z and were evaluated from the assumed regular hexagon shape of the benzene ring with all CCD bonds equal to 120°. Rotations about the phenyl–C bond are subject to a potential of at least C_{2v} symmetry which means[12] that S^R is diagonal in the xyz axes shown in Figure 9. Thus, the two resolved quadrupolar splittings, $\Delta\tilde{v}_3$ and $\Delta\tilde{v}_1 \simeq \Delta\tilde{v}_2$, can be used to determine $S_{zz}{}^R$ and $S_{xx}{}^R - S_{yy}{}^R$. The ethylbenzene molecule most probably aligns with z tending to lie parallel to the mesophase director. The director and magnetic field for this liquid crystal are orthogonal hence the sign of $S_{zz}{}^R$ is most probably negative. This leads to $\Delta\tilde{v}_3$ being negative and $\tilde{D}_{12}$ positive. The quadrupolar splittings $\Delta\tilde{v}_1$ and $\Delta\tilde{v}_2$ are opposite in sign to $\tilde{D}_{12}$ and hence are negative. With these signs of the quadrupolar splittings we obtained the local order parameters shown in Table 2.

Analysis of the proton spin echo spectrum of ethyl[$^2H_5$]-benzene, shown in Figure 5, yields the values of the three dipolar coupling constants shown in Table 3, which together with the assumed geometry of Figure 9 gives three elements of S^c the local order matrix of the ethyl group; the assumption is also

Table 2. Local order parameters for the phenyl ring of ethylbenzene derived from the quadrupolar splittings and for the ethyl group determined from proton dipolar couplings. The axes are those in Figure 9

Phenyl ring	S_{zz}^R	-0.143 ± 0.004*	
	$S_{xx}^R - S_{yy}^R$	-0.133 ± 0.012	
		$\tilde{D}_{67} - \text{ve}$	$\tilde{D}_{67} + \text{ve}$
Ethyl group	S_{pp}^c	-0.1321 ± 0.0008	0.1244 ± 0.0008
	$S_{qq}^c - S_{rr}^c$	0.0125 ± 0.0002	-0.0048 ± 0.0002
	S_{qp}^c	-0.0543 ± 0.0003	0.0454 ± 0.0003

* Errors represent the effect of the uncertainty in q_{bb} and η.

Table 3. Chemical shifts and dipolar coupling constants obtained from the 200 MHz proton spin echo spectrum of a mixture of $C_6D_5CH_2CH_3$ and $C_6D_5CD_2CD_3$ in ZLI 1167

	$\tilde{D}_{67} + \text{ve}$	$\tilde{D}_{67} - \text{ve}$
δ_{68}(p.p.m.)	2.41 ± 0.03	2.20 ± 0.07
J_{68}/Hz*	7	7
$\tilde{D}_{67}$/Hz	$1\,273.5 \pm 1.9$	$-1\,272.5 \pm 2.4$
$\tilde{D}_{89}$/Hz	-160.7 ± 1.0	165.0 ± 1.1
$\tilde{D}_{68}$/Hz	243.3 ± 1.2	-250.7 ± 1.3

* Fixed at the value found in the isotropic phase.

Table 4. Quadrupolar splittings obtained for the deuterons in a sample of $C_6H_5C_3D_7$ plus $C_6D_5C_3H_7$ in ZLI 1167 and E7

Position	$\Delta\tilde{v}_i$/Hz	
	ZLI 1167	E7
1,5	$\pm 5\,165 \pm 100$	$\pm 7\,324 \pm 30$
2,4	$\pm 5\,165 \pm 100$	$\pm 7\,324 \pm 30$
3	$-40\,603 \pm 30$*	$43\,750 \pm 30$*
6,7	$\pm 14\,451 \pm 30$	$\pm 15\,308 \pm 30$
8,9	$\pm 8\,332 \pm 30$	$\pm 8\,569 \pm 30$
10,11,12	$\pm 6\,500 \pm 30$	$\pm 6\,836 \pm 100$

* Signs based on the expected signs of S_{zz}^R.

made of rotation of the methyl group about the C–C bond between three equivalent sites. The p and z axes coincide and therefore S_{zz}^R and S_{pp}^c should be equal independently of the relative conformation of the ring and chain, assuming only that the geometry of the molecules does not change appreciably in the different rotational forms. The set of dipolar couplings based on a negative value for $\tilde{D}_{67}$ does yield S_{pp}^c almost identical with S_{zz}^R and can be selected, therefore, as the correct set. The small difference between S_{pp}^c and S_{zz}^R is attributable in part at least to a difference in the sample temperature when recording the proton and deuteron spectra. Both spectra were recorded with the sample temperature set at 300 K, but the reproducibility of the sample temperature is of the order of 0.5 K and hence it is possible that the experiments were not run at exactly the same temperature. It is, however, more probable that S_{pp}^c and S_{zz}^R differ because of errors in the geometrical parameters assumed. In calculating S_{pp}^c it is necessary to assume a value for the angles and bond lengths of the ethyl fragment, and the CCC bond angle is almost certainly greater than the assumed tetrahedral value; X-ray studies of compounds with alkyl chains attached to aromatic rings find this angle to be between 3 and 11° larger than the tetrahedral value.[3,14-19] The values of S_{pp}^c and S_{zz}^R can be brought into exact agreement by increasing the $\widehat{CCC}$ bond angle to $118.0 \pm 0.5°$, which lies within the range found for other compounds.

The values of $S_{xx}^R - S_{yy}^R$ and $S_{qq}^c - S_{rr}^c$ would also be equal if the planes of the ring and ethyl fragments are coplanar, and equal in magnitude and opposite in sign if the two planes are orthogonal. Clearly, neither of these two structures alone is an adequate description of the structure of ethylbenzene. The same conclusion is reached in perhaps a more direct way by comparing the observed value for $\tilde{D}_{67}^{HH}$ of $-1\,272.5 \pm 2.4$ Hz with values calculated assuming ethylbenzene to be either the planar or orthogonal structure. For the planar form $\tilde{D}_{67}^{HH}$ is given by $\tilde{D}_{67}^{HH} = -\gamma_H^2 h\, S_{yy}^R/4\pi^2 r_{67}^3$ and with $r_{67} = 1.78$ Å, the value for the structure in Figure 9, $\tilde{D}_{67}^{HH} = -2\,942 \pm 219$ Hz. For the orthogonal form, $\tilde{D}_{67}^{HH} = -\gamma_H^2 h\, S_{xx}^R/4\pi^2 r_{67}^3$, and calculation yields -112 ± 110 Hz. These two structures clearly predict totally unacceptable values for $\tilde{D}_{67}^{HH}$ which could not be brought into reasonable agreement with experiment by acceptable changes in the geometrical assumptions.

The proton echo spectrum yields the magnitude of $\tilde{D}_{67}^{HH}$ with high precision and, as we have shown, the sign of this coupling can be inferred by combining the data from proton and deuteron spectra. The deuteron spectrum yields a value for the magnitude of $\tilde{D}_{67}^{DD}$ of 29 ± 2 Hz, which may also be used to test the hypotheses of planar or orthogonal structures with the advantage that all the data used in making such a test comes from the same spectrum whereas in combining data from two spectra we had to rely on the temperature of the sample being identical for the two experiments. The deuteron–deuteron dipolar coupling, which is in good agreement with the proton–proton dipolar coupling when scaled by the ratio of γ_H^2/γ_D^2, is, however, determined with considerably lower precision than $\tilde{D}_{67}^{HH}$.
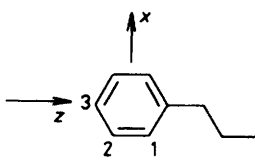
Propylbenzene.—Our approach to investigating the conformational possibilities in n-propylbenzene is similar to that used in the case of ethylbenzene but differs in some details because of the increased complexity of the spectra and more mundanely because of the compounds available to us. Our first approach was to record deuteron spectra of a sample of a mixture of $C_6D_5C_3H_7$ and $C_6H_5C_3D_7$ in ZLI 1167 and E7 to yield the quadrupolar splittings shown in Table 4. Unfortunately the peaks from the methylene group were unresolved and values for the dipolar coupling could not be obtained. These spectra, therefore, served only to calculate possible sets of values of S^R, corresponding to different relative signs of the quadrupolar splittings $\Delta\tilde{v}_3$ and $\Delta\tilde{v}_1$. A second approach was to record deuteron spectra from samples of $C_6D_5C_3H_7$ dissolved in several liquid crystalline solvents and on the same samples to record proton echo spectra. However, the echo spectra are very complex and so far have defied analysis. A third, and more successful approach was to record proton spin echo spectra of $C_6H_5C_3D_7$ dissolved in liquid crystal solvents, as shown in Figures 6—8, and analysis of these spectra gave the results in

Table 5. Dipolar coupling constants obtained from the analysis of the 200 MHz proton spin echo spectra of $C_6H_5C_3D_7$ dissolved in ZLI 1 167, Phase V, and E7‡

	$\tilde{D}_{ij}$/Hz		
i,j	ZLI 1167	Phase V	E7
12	1 182.1 ± 0.4	−1 481.5 ± 0.9	−1 616.3 ± 0.2
13	163.6 ± 4.9	−186.3 ± 4.6	
14	15.7 ± 0.4	4.9 ± 0.6	−27.7 ± 0.2
15*	−43.9 ± 0.5	105.0 ± 0.8	44.1 ± 0.2
23	113.7 ± 4.5	39.8 ± 3.3	
24*	−43.9 ± 0.5	105.0 ± 0.8	44.1 ± 0.2
13 + 23†			−447.9 ± 2.0

* Assumed equal since the analysis yields only their sum with good precision. † Only the sum of $D_{13} + D_{23}$ obtained with good precision for E7. ‡ The chemical shifts and coupling constants were kept constant in the interations at values appropriate to the isotropic phase of $\delta_{12} = 0.09$ p.p.m., $\delta_{13} = 0.03$ p.p.m., $J_{12} = 8$ Hz, $J_{13} = 1.5$ Hz, $J_{14} = 0.6$ Hz, $J_{15} = 1.5$ Hz, $J_{23} = 8$ Hz, $J_{24} = 1.5$ Hz.

Table 6. Local order parameters $S_{\alpha\beta}^R$ and proton co-ordinates (Å) for the phenyl ring of $[^2H_7]$-n-propylbenzene in the liquid crystal solvents ZLI 1167, Phase V. and E7

	ZLI 1167	Phase V	E7
x_1	2.119 ± 0.011	2.171 ± 0.017	2.156 ± 0.010
z_1	2.647 ± 0.001	2.637 ± 0.002	2.645 ± 0.001
x_2	2.192 ± 0.011	2.143 ± 0.017	2.156 ± 0.010
z_2	0.158 ± 0.001	0.147 ± 0.002	0.155 ± 0.001
x_3	0.0	0.0	0.0
z_3	0.0	0.0	0.0
S_{xx}^R	0.029 ± 0.001	−0.070 ± 0.001	−0.030 ± 0.001
S_{yy}^R	0.123 ± 0.001	−0.120 ± 0.001	−0.177 ± 0.001
S_{zz}^R	−0.152 ± 0.001	0.191 ± 0.001	0.207 ± 0.001

Table 7. The interdeuteron geminal dipolar coupling in Hz for the methylene group of $[^2H_7]$n-propylbenzene obtained from the deuteron spectrum and calculated from the planar and orthogonal structures

	ZLI 1167	Phase V	E7
Observed	±29.0 ± 0.5	48.8 ± 0.2	50.5 ± 0.2
Calculated planar	−62 ± 1	60 ± 1	55 ± 1
orthogonal	−15 ± 0	35 ± 0.5	14 ± 0.5

Table 5. These coupling constants were used to calculate S_{zz}^R and $S_{xx}^R − S_{yy}^R$; r_{12} was set equal to 2.49 Å, the value for the geometry of Figure 9, and with this constraint the x and z co-ordinates of protons 1,2,4, and 5 together with S_{zz}^R and $S_{xx}^R − S_{yy}^R$ were found which gave an exact fit to the five independent dipolar couplings and the results are shown in Table 6. The small variations found for the co-ordinates reflect the neglect of vibrational averaging as well as the small solvent effects usually found in these analyses.

The deuteron spectra of the samples of $C_6H_5C_3D_7$ dissolved in the three samples do not show resolvable structure on the methylene peaks. However, the line shapes obtained with proton decoupling, as shown in Figure 4, clearly reveal the effect of geminal dipolar coupling and values of $\tilde{D}_{67}^{DD}$ were obtained by line-shape fitting and are given in Table 7 together with values calculated for the planar and orthogonal models for n-propylbenzene. In this molecule we use planar and orthogonal to denote the orientation of the phenyl plane and the plane of the phenyl C–C–C atoms; it does not of course imply that the methyl carbon also lies in these planes. The lack of agreement between the observed and calculated values of $\tilde{D}_{67}^{DD}$ shown in Table 6 is clearly too large to be attributed to reasonable changes in the geometrical assumptions and we conclude that neither structure correctly describes the conformation of n-propylbenzene.

Conclusions.—We have shown that ethyl- and n-propyl-benzene do not exist exclusively with the phenyl ring and the phenyl C–C–C planes either coplanar or orthogonal to one another. The data from the present experiments yield no further information on this conformational question. There are insufficient data to test either the structure with a single, deep minimum in $E(\varphi)$ at some angle between 0 and 90° (see Figure 2), or a mixture of planar and orthogonal forms. The results found here, by ruling out the two structures with C_s symmetry, provide a stimulus to pursue the problem by obtaining more data on these and similar compounds.

References

1 G. W. Gray in 'Molecular Physics of Liquid Crystals,' eds. G. R. Luckhurst and G. W. Gray, Academic Press, London, 1979.
2 P. J. Flory, 'Statistical Mechanics of Chain Molecules,' Interscience, New York, 1969.
3 V. G. Andrianov, H. A. Karapetyan, and Yu. T. Struckhov, Cryst. Struct. Commun., 1978, 7, 552.
4 J. Strokr, H. Pivcova, B. Schneider, and S. Divilikov, J. Mol. Struct., 1974, 12, 45.
5 L. Verdonck and G. P. Van der Kelen, Spectrochim. Acta, 1972, 28, 51.
6 J. E. Saunders, J. J. Lucier, and J. N. Willis Jr., Spectrochim. Acta, 1968, 24, 2023.
7 M. Camail, A. Proutiere, and P. Verlaque, J. Phys. Chem., 1975, 79, 1962.
8 R. J. Oulette, B. K. Sinha, J. Stolfo, C. Lewis, and S. Williams, J. Am. Chem. Soc., 1970, 92, 7145.
9 T. Schaefer, L. Kruczyniski, and W. Niemezura, Chem. Phys. Lett., 1976, 38, 498.
10 J. L. Garnett, M. A. Long, R. F. W. Vining, and T. Mole, J. Am. Chem. Soc., 1972, 94, 5913.
11 A. G. Avent, J. W. Emsley, and D. L. Turner, J. Magn. Reson., 1983, 52, 57.
12 J. W. Emsley, G. R. Luckhurst, and C. P. Stockley, Mol. Phys., 1981, 44, 565.
13 J. W. Emsley and M. Longeri, Mol. Phys., 1981, 42, 315.
14 J. Doucet, J.-P. Mornon, R. Chevalier, and A. Lifchitz, Acta Crystallogr., 1977, B33, 101.
15 U. Baumeister, H. Hartung, and M. Jaskolski, Mol. Cryst. Liq. Cryst., 1982, 88, 167.
16 T. Ottersen, E. Rosenquist, C. E. Turner, and F. S. El-Feraly, Acta Chem. Scand., Ser. B, 1977, 31, 781, 807.
17 M. A. Kravers, M. Yu. Antipin, and Yu. T. Struchkov, Cryst. Struct. Commun., 1978, 7, 405.
18 T. Ottersen and E. Rosenquist, Acta Chem. Scand., Ser. B, 1977, 31, 749.
19 V. G. Andrianov, H. A. Karapetyan, and Yu. T. Struchkov, Cryst. Struct. Commun., 1979, 8, 423.