Conformation of the Ethoxy Group in 4-Ethoxy-4'-cyanobiphenyl

J. W. Emsley,* T. J. Horne,

Chemistry Department, University of Southampton, Southampton, S09 5NH U.K.

G. Celebre, M. Longeri,

Dipartimento di Chimica, Universita della Calabria, Calabria, Italy

and H. Zimmermann

Max-Planck-Institut fur Medizinische Forschung, Heidelberg, Germany (Received: January 3, 1992; In Final Form: June 11, 1992)

The deuterium and proton NMR spectra of samples of 4-ethoxy-4'-cyanobiphenyl dissolved in the nematic liquid crystal 4-hexyloxy-4'-cyanobiphenyl have been analyzed to yield quadrupolar splittings and dipolar couplings. The data are compared with values calculated for three models for the conformations adopted by the ethoxy group relative to the attached phenyl ring. These models are (a) a set of four, symmetry-related structures, (b) discrete, minimum-energy structures generated by jumps about the C_4 -O, O- C_7 , and C_7 - C_8 bonds, and (c) the same as (b) except that a continuous potential is adopted for the motion about the O- C_7 bond.

Introduction

The molecules which form liquid-crystal phases are flexible by virtue of internal rotations about bonds, and this flexibility has an important influence on their physical properties. Thus, the melting point is lowered because of the increase in entropy which occurs on going from the solid phase, where the molecule exists in the single, lowest energy conformation, to the liquid-crystalline phase, where there is a distribution among a set of conformational states. There are a number of ways in which this conformational set is viewed. For an isolated molecule the position is clear: there are a set of quantized torsional and vibrational states whose relative energies and eigenfunctions are solutions of a vibration-rotation Hamiltonian.¹ Solving this eigenvalue problem for molecules with the complexity of those which form a liquid-crystalline phase is a formidable and as yet unattempted task. At a less accurate, but for some applications possibly not much less precise level, vibrational motion is neglected, and the torsional motion is described classically by a bond rotation through an angle ϕ under the influence of a rotational potential $V(\phi)$. The finite set of quantized states has been replaced by a continuous potential, and hence such a model is completely inappropriate for calculating torsional energy states, but it has been shown to yield good approximations to quantities whose measured values are averages over all the rotational states. Such averages are calculated much more easily by the classical as opposed to the quantized models, and it is straightforward to use this model when there are several bonds about which rotation occurs. There are, however, still practical difficulties in using the classical, continuous rotor model to calculate averages for molecules which have several bond rotations. To overcome this problem, the continuous motion is often replaced by a jump model in which the molecule resides only in a limited set of minimum-energy structures. When applied to motion about C-C or O-C bonds in alkyl or alkyloxy aliphatic chains, the jump model is often referred to as the rotational isomeric state (RIS) model and was introduced by Flory² in order to calculate statistical averages of the properties of chain molecules. It has been used in most attempts at modeling the conformational distributions of molecules in liquid-crystal phases. The least-biased models² describe the jump motion about the C-X bonds as being between trans and gauche (\pm) states, which are separated in energy by an amount E_{tg} . More restricted models³ consider only those conformations (kinks) which have elongated structures, and the most restricted model considers only conformations of identical shape.⁴ Galland and Volino⁴ adopt their unusual conformational model because of their belief that the shape of a molecule in a liquid phase should be as close as possible to that in the solid. The

case for the adoption of the RIS model, or a restricted variant, is more frequently that the data set under consideration is too sparse for testing less constrained models.

The most frequently employed experimental method for investigating the orientational order of flexible mesogens is deuterium NMR spectroscopy. This yields a quadrupolar splitting, $\Delta \nu_i$, for each set of equivalent deuterons introduced into the molecule, and these splittings are related to order parameters S_{CD}^i for the C-D bonds via

$$\Delta \nu = 3q_{\rm CD}{}^i S_{\rm CD}{}^i/2 \tag{1}$$

where q_{CD}^{i} is the quadrupolar coupling constant for the deuteron in the *i*th C-D bond. The orientational order of several different types of liquid crystals have been studied in this way, with varying degrees of success.⁵ Thus, in the case of the 4-n-alkyl-4'-cyanobiphenyls (NCB), Counsell et al.⁶ adopted the RIS model for the chain conformations and found almost exact agreement between observed values of S_{CD} and those calculated by the mean-field approach first proposed by Marcelja⁷ and developed by Emsley et al.⁸ and which we shall refer to as the additive potential model (AP). The similar series of molecules NOCB, with alkyloxy rather than alkyl chains has been studied by the same method,⁹ but now the agreement between calculated and observed values of S_{CD} is noticeably worse. Clearly, some aspects of the theoretical model or some of the geometrical assumptions made for the NOCB molecules must be incorrect. The present study of 2OCB, whose structure is shown in Figure 1, is an attempt to address these problems.

The approach adopted here is to use both deuterium and proton NMR to obtain a larger data set, and one which is more sensitive to the conformational distribution and to the geometry. This involves obtaining resolvable and analyzable proton spectra by proton-{deuterium} decoupling of partially deuteriated molecules. The analysis of these complex spectra yield interproton dipolar couplings, D_{ij} , which are highly sensitive to both structure and the averaging over the bond rotational motions.

Experimental Section

The proton NMR spectrum of 2OCB in the nematic phase is too complex to be analyzable, and we did not attempt to obtain such a spectrum. The proton spectrum can be simplified by partially deuteriating the molecule and removing the H–D spinspin interaction by irradiating at the center of the deuterium spectrum while simultaneously observing the protons. Our principal aim in this study was to investigate the conformations adopted by the ethoxy group, and so we wished to obtain dipolar



Figure 1. Structure of 2OCB showing the atomic labeling and reference axes used in the text.

couplings between protons in both the ring and chain fragments of the molecule. To do this we prepared two partially deuteriated samples:



The proton-{deuterium} spectrum of 20CB- d_9 is much simpler than of 20CB- d_6 and was used simply as an intermediate step in analyzing the spectrum of the d_6 compound. The preparation of these isotopomers was by the reaction



with appropriately deuteriated reagents. The ethylbromide-2,2,2- d_3 was prepared by bromination of CD₃CH₂OH with PBr₃ in pyridine. The preparation of the 4-hydroxy-4'-bromobiphenyl has been described by Zimmermann.¹⁰

Obtaining NMR spectra on the pure 20CB samples in the nematic phase proved to be impossible. The pure compound has a metastable nematic phase below 363.5 K, which is lower than its melting point of 375.2 K. The nematic phase can be observed by microscopy, but the larger samples needed for NMR spectroscopy would not stay supercooled for a sufficiently long time



Figure 2. The 200-MHz proton-{deuterium} spectrum for a sample of $2OCB-d_9$ dissolved (45% w/w) in 6OCB.



Figure 3. The 30.7-MHz deuterium spectrum for a sample of 20CB-d, dissolved (45% w/w) in 60CB.

to enable a good spectrum to be recorded. A stable nematic phase was obtained by the addition of 6OCB and the samples used contained 45% w/w of 2OCB and had $T_{\rm NI}$ values of 349.5 K (d_6) and 348.3 K (d_9). Spectra were obtained at approximately 15 K below $T_{\rm NI}$.

The spectra were obtained on a Bruker MSL 200 spectrometer and are shown in Figures 2-5.

Results and Discussion

Analysis of Spectra. As noted earlier, the spectra from 2OCB- d_9 , were used as an intermediate step in analyzing the proton-[deuterium] spectrum of 2OCB- d_6 , but it is worth noting how much information can be extracted, albeit with low precision on some of the couplings, from the simpler spectra given by the more deuteriated sample. The proton-[deuterium] spectrum of 2OCB- d_9 (Figure 2) yields D_{33}^{HH} , $D_{37}^{HH} = D_{57}^{HH}$ and D_{77}^{HH} as shown in Table I. The deuterium spectrum (Figure 3) shows both broad and sharp lines. The triplets labeled a and a' are probably from deuterons at positions 3' and 5' and the triplet structure arises from a dipolar coupling to deuterons 2' and 6' ($D_{2'3'} = D_{5'6'}$). The peaks labeled b and b' stem from the methyl deuterons and were analyzed as the X₃ part of an AA' BB' X₃ spin system to yield

TABLE I: Dipolar Couplings, D_{ij} , Quadrupolar Splittings, $\Delta \nu_i$, and Chemical Shifts Obtained for a Sample of 20CB-d, Dissolved in 60CB at $T_{\rm Ni} - T = 15$ °C

ij	D _{ij} /Hz	$J_{ij}/{ m Hz}^a$		
	Proton Spectrum			
3,5	396.7 ± 2.8	2		
3,7	-1857.1 ± 1.1	0		
7,7	4227 ± 2.1	0		
$\nu_3 - \nu_7$	289.8 ± 5.2			
	Deuterium Spectrum			
3,8	-88.0 • 1.0	0		
7,8	-170.3 • 1.7	0		
8.8	85.7 ± 0.3	0		
$\Delta \nu_8$	21 000			

^aAssumed, and kept constant in the analysis.

TABLE II: Dipolar Couplings and Chemical Shifts Obtained by Analyzing the Proton-{Deuterium} and Deuterium Spectra of a Sample of 2OCB- d_6 (45% w/w) Dissolved in 6OCB at $T_{\rm Ni} - T = 15$ °C

ij	D _{ij} /Hz	ij	D_{ij}/Hz
2,3	-4456 ± 50^{a}	7,7	4228.5 单 1.8
3,5	386.2 ± 1.6	7,8	-1165.5 ± 1.1
3,7	-1851 ± 1.6	8,8	3606.2 ± 0.7
3,8	-440.1 ± 1.1		
	Chemical	Shifts/Hz	
$\nu_3 - \nu_7$	283.8 ± 3.6	$\nu_{3} - \nu_{8}$	833.2 ± 3.1

^aObtained by multiplying the value obtained from the deuterium spectrum by $(\gamma_H/\gamma_D)^2$.

additional dipolar couplings D_{38}^{HD} , D_{78}^{HD} , and D_{88}^{DD} , which are given in Table I. These couplings can be related to their equivalent proton-proton couplings by multiplying by the ratios $(\gamma_H/\gamma_D)^2$ - $(D^{DD} \rightarrow D^{HH})$ and $(\gamma_H/\gamma_D)(D^{HD} \rightarrow D^{HH})$. These couplings were then used as starting parameters in the analysis of the proton-{deuterium} spectrum of 2OCB- d_6 shown in Figure 4; the peaks labeled a and a' in the deuterium spectrum of 2OCB- d_6 in Figure 5 were used to obtain D_{23}^{DD} as shown in Table II together with the parameters obtained from the proton spectrum.

Conformational Analysis. The dipolar couplings in Table II are sensitive to motion about C_4 —O through ϕ_1 , about $O-C_7$ through ϕ_2 , and about C_7 —C₈ through ϕ_3 . The data set is too small to determine the detailed nature of each of these rotational motions, and it is necessary to make some simplifying assumptions based on what is known about such bond rotations.

Rotation about ϕ_1 . The simpler molecule, methoxybenzene (anisole), has been studied very extensively by both experiment and theory,¹¹ and it is concluded that the potential $V(\phi_1)$ is essentially 2-fold, with a small 4-fold term, the absolute minima being at $\phi_1 = 0^\circ$ and 180°, that is with the O-C₇ bond in the ring plane. The interproton dipolar couplings measured for samples of anisole dissolved in liquid-crystal solvents are also consistent with such a potential.¹² The simplest model for this motion is a jump between two planar, mirror-image forms, and for this model the angle C₃C₄O is 124°.

Rotation about ϕ_3 . This is usually assumed to be a 3-fold potential with a barrier high enough that a jump model can be used for averaging dipolar couplings. The minimum energy has one of the C₈-H bonds in the OC₇C₈, plane, and the other two C₈-H bonds are symmetrically disposed above and below this plane. The CH₃ group has close to tetrahedral bond angles and is close to having C₇-C₈ as a 3-fold symmetry axis.

Rotation about O-C7. The potential is usually assumed to have an absolute minimum with $\phi_2 = 0^\circ$, which has the C₄-O-C₇-C₈ atoms in one plane and in a trans configuration. There are two equivalent, secondary minima at ϕ_2 approximately $\pm 120^\circ$, the gauche \pm configurations. The simplest model for the ϕ_2 motion is jumps between these three positions.

The Complete Jump Model. This is the RIS model used by Counsell et al.⁹ to interpret the quadrupolar splittings obtained for deuterons in NOCB molecules. To calculate the averaging



Figure 4. The 200-MHz proton- $\{$ deuterium $\}$ spectrum of a sample of 20CB- d_6 dissolved in 60CB.



Figure 5. The 30.7-MHz deuterium spectrum of a sample of $2OCB-d_6$ dissolved in 6OCB.

produced by such motion it is necessary to use a theoretical model which allows for the dependence of orientational order parameters on molecular shape. We shall adopt the additive potential model, which has been described in detail elsewhere,⁶⁻⁹ and here we shall give only an outline of the method. The model relies on the introduction of a conformationally dependent potential of mean torque $U_{ext}(n,\beta,\gamma)$, where β and γ are the polar angles made by the mesophase director with respect to axes fixed in the molecules. For each conformation n these axes are chosen to be principal axes for the solute-solvent interaction tensor $\epsilon_{2,m}(n)$, so that $U_{ext}(n,\beta,\gamma)$ is given by

$$U(n,\beta,\gamma) = -\epsilon_{2,0}(n)C_{2,0}(\beta,\gamma) - 2\epsilon_{2,2}(n) \text{ Re } C_{2,2}(\beta,\gamma)$$
(2)

where the $C_{2,m}(\beta,\gamma)$ are modified spherical harmonics. The interaction tensor is written as a sum of conformationally independent contributions $\epsilon_{2,p}$ from each rigid subunit of the molecule:

$$\epsilon_{2,m}(n) = \sum_{p} \sum_{j} \epsilon_{2,p} D_{p,m}^2(\Omega_n^{j})$$
(3)

so that the conformational dependence has been transferred to the Wigner rotation matrix $D_{p,m}^{\mathcal{I}}(\Omega_n^j)$ which relates the principal axes of e^{i} to the molecular reference axes.

The averaged dipolar couplings are given by

$$D_{ij} = \frac{2}{3} \sum_{n} p_n \frac{\text{LC}}{\sum_{\alpha\beta}} D^n_{ij\alpha\beta} S^n_{\alpha\beta}$$
(4)

The $S^n_{\alpha\beta}$ are elements of a conformationally dependent order matrix, which depend on $U_{ext}(n,\beta,\gamma)$ via

$$S_{aa}^{n} = \int C_{2,0}(\beta,\gamma) \exp\{-U_{ext}(n,\beta,\gamma)/kT\} \sin\beta \,d\beta \,d\gamma \quad (5)$$

$$(S_{bb}^n - S_{cc}^n) = \sqrt{6Q_n^{-1}} \int C_{2,2}(\beta,\gamma) \exp\{-U_{ext}(n,\beta,\gamma)/kT\} \sin\beta \,d\beta \,d\gamma \ (6)$$

with

$$Q_n = \int \exp\{-U_{\text{ext}}(n,\beta,\gamma)/kT\} \sin\beta \,d\beta \,d\gamma \qquad (7)$$

and *abc* are principal axes for S^n .

The $D^n_{ij\alpha\beta}$ are elements of the dipolar coupling tensor when the molecule is in the *n*th conformation. The probability, p_n^{LC} , that the molecule is in the *n*th conformation, which has energy E_n independent of the orientational order, is given by

$$p_n^{LC} = Q_n^{-1} Z \exp(-E_n/kT)$$
(8)

where

$$Z = \sum_{n} \int \exp[-[U_{\text{ext}}(n,\beta,\gamma) + E_n]/kT] \sin\beta \, d\beta \, d\gamma \quad (9)$$

Note that $p_n^{\rm LC}$ may differ from $p_n^{\rm ISO}$, the probability of the *n*th conformation in the isotropic phase:

$$p_n^{\rm ISO} = \exp\{-E_n/kT\} / \sum_n \exp\{-E_n/kT\}$$
(10)

but that both p_n^{LC} and p_n^{ISO} are available from the AP method. For 2OCB, the interaction parameters required are $\epsilon_{2,0}^{R}$ and $\epsilon_{2,2}^{R}$ for the biphenyl fragment, $\epsilon_{2,0}^{OC}$ for the O–C₇ bond, and $\epsilon_{2,2}^{CC}$ for the C₇–C₈ bond. In previous studies of the NOCB molecules⁹ and of ethoxybenzenes dissolved in nematic solvents,^{13,14} it was found that setting $\epsilon_{2,0}^{\text{OC}} = \epsilon_{2,0}^{\text{CC}}$ gave equally good fits to the experimental data as keeping them as independent variables, and here we have set them equal to minimize the number of adjustable parameters.

The geometry adopted in these calculations is that assumed for the ethoxybenzenes^{13,14} within the RIS model and has

$$r(H_1,H_2) = 2.48$$
 Å $r(H_1,H_2) = 4.312$ Å

$$r(C_4O) = 1.36 \text{ Å}$$
 $r(OC_7) = 1.42 \text{ Å}$ $r(C_7C_8) = 1.54 \text{ Å}$
 $r_{CH} = 1.1 \text{ Å}$
 $C_3C_4O = 124^\circ$ $C_4OC_7 = 120^\circ$

all other angles are 109.47°. The geometry is fixed in the cal-culations and $\epsilon_{2,0}^{R}$, $\epsilon_{2,2}^{R}$, $\epsilon_{2,0}^{OC} = \epsilon_{2,0}^{CC}$, and E_{tg} are varied, where E_{tg} is the difference in energy between gauche and trans forms. This gives a rms error, R, defined as

$$R = (\sum_{i=1}^{7} = \Delta_{ij}^{2})/7$$
(11)

where

$$\Delta_{ii} = D_{ii} (\text{calculated}) - D_{ii} (\text{observed})$$

for the seven independent couplings of 55 Hz, which is unacceptably large. The value of R can be reduced by changing the geometry and also by moving the positions of the gauche forms, but a more probable cause of the large rms error is the adoption of the jump model for all the bond motions.

Continuous Rotation about the O-C₇ Bond. The data set is too small to consider continuous rotation about all three bonds, and so the jump model is retained for motion about the C_4 -O and

TABLE III: Residuals, $\Delta_{ij} = D_{ij}$ (calculated) - D_{ij} (observed), Potential Coefficients V_1 and V_3 (kJ mol⁻¹) and Interaction Parameters $\epsilon_{2,0}^{R}$, $\epsilon_{2,2}^{R}$, $\epsilon_{2,0}^{OC} = \epsilon_{2,0}^{OC}$ (kJ mol⁻¹) Obtained from the Analysis of the Dipolar Couplings by the AP Method

itj	Δ_{ij}/Hz	inj	Δ_{ij}/Hz	
2,3	-1.5	7,7	0.3	
3,5	-1.7	7,8	-0.6	
3,7	2.9	8,8	-0.2	
3,8	-2.0			
		Rms Error = 1.6 Hz		
V_1	3.3 ± 0.1	62 2 ^R	1.05 ± 0.02	

 12.4 ± 0.1



Figure 6. Potential curve $V(\phi_2)$ obtained by the AP method.

 C_7 - C_8 bonds. The potential governing rotation about the O- C_7 bond, $V(\phi_2)$, is written as

$$V(\phi_2) = V_1(1 - \cos \phi_2) + V_3(1 - \cos 3\phi_2)$$
(12)

This potential has minima at $\phi_2 = 0^\circ$ and at

$$\phi_2^{\min} = 180^\circ - \sin^{-1} \left[(V_1/12V_3) + \frac{3}{4} \right]^{1/2}$$
 (13)

and maxima at 180° - ϕ_2^{\min} and 180°. Note, however, that $V(\phi_2^{\min})$ and $V(\phi_2^{\max})$ also depend on the adjustable coefficients V_1 and V_3 , so that this potential does not allow the positions of the minima to be varied independently of their relative heights. To achieve such a flexible form for the potential involves including five Fourier coefficients, and our data set is too small to test such a potential. The rotation through ϕ_2 is sampled at 73 equal intervals between $\pm 180^{\circ}$, and the three interaction parameters plus V_1 and V_3 varied to obtain a minimum value for R. Reducing the C-H bond lengths to 1.085 Å in the CH and CH₃ groups reduced R still further to 1.6 Hz and the individual residuals and optimized parameters are given in Table III. The shape of the potential $V(\phi_2)$ is shown in Figure 6. The values of ϕ_2^{\min} and ϕ_2^{\max} are 118.5° and 61.5°, and the difference $V(\phi_2^{\min}) - V(0) = E_{\text{tg}}$ is 4.91 kJ mol⁻¹, which are close the values adopted in the RIS model. The barriers to rotation $V(\phi_2^{\text{max}}) - V(0)$ and $V(180^\circ)$ $V(\phi_2^{\min})$ are both 26.5 kJ mol⁻¹. $V_2(\phi_2)$ can be used to calculate $p^{1SO}(\phi) \equiv p_n^{1SO}$ from eq 11, and this is compared with $p^{LC}(\phi)$ in Figure 7. Conformations close to $\phi_2 = 0^\circ$, the trans form, are enhanced in the nematic phase, and there is a diminution in the probabilities of the conformations close to the gauche \pm positions. This effect has been noted before for the NOCB series⁹ of liquid crystals, and the magnitude of the changes depends on N, and the relatively small changes found for 2OCB are as expected.

Orientational Order Parameters. When a molecule adopts conformations with different shapes, it is no longer possible to describe the orientational order with a single-order matrix.^{15,16} Each conformation has a characteristic order matrix, S^n , and it is interesting to note how these change, for example, between the trans and gauche isomers. The values of $S^{t}_{\alpha\beta}$ and $S^{g}_{\alpha\beta}$ are given in Table IV in both reference, xyz, and principal, abc, axes. The changes in the principal order parameters in going from the trans

 0.38 ± 0.02



Figure 7. Comparison of $p^{ISO}(\phi)$ (dashed line) with $p^{LC}(\phi)$ (full line) obtained for a sample of 2OCB dissolved (45% w/w) in 6OCB.

TABLE IV: Order Parameters for the Trans Conformer, $S^{i}_{\alpha\beta}$, and Gauche + $S^{s}_{\alpha\beta}$, with Respect to the Reference Axes xyz Shown in Figure 1 and Also in Principal Axes, abc^{a}

S ¹ 22	0.573	St ag	0.573	α	0.0°
$S_{xx}^{t} - S_{yy}^{t}$	0.058	$S^{t}_{bb} - S^{t}_{cc}$	0.058	β	-0.5°
S ^t xz	0.007			γ	0.0°
S ⁸ 22	0.546	S ⁸ aa	0.546	α	29.1°
$S_{xx}^{s} - S_{yy}^{s}$	0.060	$S^{B}_{bb} - S^{B}_{cc}$	0.060	β	-1.1°
S ⁸ xv	-0.005			γ	-23.9°
S ⁸ xz	0.013				
S ⁸ yz	0.0064				

^a The relative orientations of these axes is given by the Euler angles α , β , and γ .

to the gauche form are relatively small, which is because the potential of mean torque for 2OCB is dominated by the contribution from the biphenyl fragment, as can be seen from the relative magnitudes of ϵ_{20}^{R} and $\epsilon_{20}^{OC} = \epsilon_{20}^{CC}$ in Table III. That the trans form has the larger value of S_{aa} and a small biaxiality is in accord with the idea that orientational order is strongly correlated with the molecular shape, particularly with the length to breadth ratio, which is largest for the trans conformer.

Are the Data Consistent with There Being Only a Single Set of Symmetry-Related Conformations? The dipolar couplings for ethoxybenzene and 4-chloro- and 4-fluoroethoxybenzenes obtained for samples dissolved in the nematic solvent I52 were analyzed by Celebre et al.^{13,14} with the AP model to give very similar results to that obtained here for 2OCB. However, Galland and Volino⁴ have shown that the same data are consistent with a single set of four conformations each with the same shape. For such a situation it is not necessary to use a conformationally dependent potential of mean torque to analyze the data, since the only changes in the order matrix elements in the frame xyz are predictable changes in the signs of the off-diagonal elements $S_{\alpha\beta}$. The calculated dipolar couplings must be brought into agreement with those observed by adjusting the molecular geometry and five order parameters. Galland and Volino varied ϕ_1 , ϕ_2 , and θ , the angle between z and the C₄-O bond and obtained good agreement for ethoxybenzene with $\theta = 6^{\circ}$, $\phi_1 = 23^{\circ}$, and $\phi_2 = 39^{\circ}$, and very similar structures were obtained for 4-chloro- and 4-fluoroethoxybenzene. We have carried out the same kind of analysis for 20CB, and in this case an acceptable solution was found which has $\theta = 18^{\circ}$, $\phi_1 = -48^{\circ}$, and $\phi_2 = 55^{\circ}$.

Clearly, what Galland and Volino showed for the case of the ethoxybenzenes and which we also find to be the case for 2OCB is that there are at least two possible solutions for the conformational distribution which are consistent with the experimental D_{ij} values. The choice between them must rest on other evidence, and here we disagree with Galland and Volino, in that the geometry they obtain for the ethoxybenzenes and that found here for 2OCB are not in accord with what is known about molecules with the same structural features. To justify the twist about the C_4 -O bond of 23°, they argue that methoxybenzene in the solid

phase is planar, while in the gas phase it has $\phi_1 = 90^\circ$ according to a quantum mechanical calculation on this compound.¹⁷ In the liquid-crystal phase, therefore, the structure could have $0^\circ < \phi_1$ $< 90^\circ$. However, more recent, more accurate ab initio calculations quite clearly reach the conclusion that the minimum energy structure has the COC and ring coplanar,^{11,18} which is the conclusion too of an electron diffraction study.¹⁹ The value of 39° found for ϕ_2 by Galland and Volino for ethoxybenzene and that of 55° for 2OCB are clear evidence in our view that the molecule does not exist in a single set of symmetry-related structures.

Galland and Volino make a general argument that in liquid phases a molecule should have only a single shape, and internal motion is restricted to conformations which form a symmetryrelated isomorphous set. However, there are numerous examples of molecules studied in the liquid phase which contradict this view.²⁰

Galland and Volino⁴ also make a general criticism of the AP method, which is also known as the ELS method. The point at issue is the use of a mean potential $U(n,\beta,\gamma)$ of the form:^{7,8,15}

$$U(n,\beta,\gamma) = U_{\text{ext}}(n,\beta,\gamma) + U_{\text{int}}(n)$$
(14)

Galland Volino argue that $U(n,\beta,\gamma)$ cannot be a mean-field potential since this should vanish in the isotropic phase. However, only the anisotropic part of the mean-field potential, $U_{ext}(n,\beta,\gamma)$, must vanish in the isotropic phase. There is always a nonzero scalar contribution to a mean potential and $U_{int}(n)$ is simply that part which is conformationally dependent; the part which does not vary with conformation does not need to be considered in the AP method. The value of $U_{int}(n)$ may, therefore, contain a density-dependent contribution, or be solvent dependent. Such gas-liquid changes in $U_{int}(n)$, or $V(\phi)$ when $U_{int}(n)$ can be identified with rotational potentials, should be revealed by comparing the results of analysis by the AP method, or by similar approaches to analyzing dipolar and quadrupolar couplings, with experiments on gaseous samples. There is indeed a growing body of evidence that rotational potentials can be phase and solvent dependent.^{11,21}

Conclusion

Previous studies of the conformational distributions of NOCB molecules in liquid-crystalline phases approximated the conformational distribution by the rotational isomeric state model. Our analysis of the dipolar couplings obtained for 2OCB was done by adopting a continuous potential for rotation about the O-C₇ bond. The particular model chosen for this potential is the simplest truncated cosine expansion which is consistent with the symmetry of the potential, and which has minima at trans and gauche positions. The results obtained support the basic view of the conformational distributions in molecules of this type, that is, that the C₄OC₇ and the attached ring are coplanar, and that rotation about the O-C₇ bond is described by a potential function with minima at trans ($\phi_2 = 0^\circ$) and gauche \pm foms ($\phi_2 = \pm 118.5^\circ$).

Good agreement between the observed and calculated dipolar couplings was achieved by allowing for a continuous distribution in ϕ_2 , rather than restricting this rotation to being a jump motion between trans and gauche forms. The poor agreement found between observed and calculated quadrupolar splittings for the NOCB molecules studied by Counsell et al.⁹ may also be a consequence of using the jump model. One should note, however, that rotations about more than one bond are probably not independent but strongly correlated. Evidence for such correlated motion is suggested by theoretical calculations^{11,22} and experimental²³ studies on anisole and by a recent study of ethoxybenzenes by Di Bari et al.²⁴ The latter used the maximum entropy approach to analyze the LC NMR data on ethoxybenzenes, as well as obtaining the dependence on ϕ_1 and ϕ_2 of the energy as calculated by an ab initio molecular orbital method. They find a strong correlation between the two bond rotations. Perhaps their most important result is that $P(0^{\circ},\phi_2)$ has only a barely discernible second maximum close to where gauche \pm forms are thought to be located, and this disappears at larger values of ϕ_1 . This suggests that the secondary maximum shown in Figure 7 is an artifact introduced by the adoption of a two-term Fourier expansion for $V(\phi_2)$, and our use of a jump motion about O-C₇. The data set obtained for 2OCB is too small to test models for correlated motion.

Acknowledgment. We thank the S.E.R.C for a postgraduate studentship for T.J.H., the CNR-Royal Society exchange programme, the CNR for additional financial support, and Professor Veracini for a preprint of ref 24.

References and Notes

- (1) Veracini, C. A.; Longeri, M. In NMR of Liquid Crystals; Emsley, J. W., Ed.; Reidel: Dordrecht, 1985.
- (2) Flory, P. J. Statistical Mechanics of Chain Molecules; Interscience: New York, 1969.
 - (3) Hsi, S.; Zimmermann, H.; Luz, Z. J. Chem. Phys. 1978, 69, 4126.
 (4) Galland, D.; Volino, F. J. Phys. II 1991, 1, 209.
 (5) NMR of Liquid Crystals; Emsley, J. W., Ed.; Reidel: Dordrecht, 1985.

 - (6) Counsell, C. J. R.; Emsley, J. W.; Heaton, N. J.; Luckhurst, G. R. Mol.
- Phys. 1985, 54, 847.
- (7) Marcelja, S. J. Chem. Phys. 1974, 60, 3599.
- (8) Emsley, J. W.; Luckhurst, G. R.; Stockley, C. P. Proc. R. Soc. London 1962, A381, 117.

- (9) Counsell, C. R. J.; Emsley, J. W.; Luckhurst, G. R.; Sachdev, H. S. Mol. Phys. 1988, 63, 33.
- (10) Zimmermann, H. Lig. Cryst. 1989, 4, 591
- (11) Spellmeyer, D. C.; Grootenhuis, P. D. J.; Miller, M. D.; Kuyper, L. F.; Kollman, P. A. J. Phys. Chem. 1990, 94, 4483.
- (12) Diehl, P.; Huber, H.; Kunwar, A. C.; Reinhold, M. Org. Magn. Reson. 1977, 6, 374.
- (13) Celebre, G.; Longeri, M.; Emsley, J. W. J. Chem. Soc., Faraday Trans. 2 1988, 84, 1041.
 - (14) Celebre, G.; Longeri, M.; Emsley, J. W. Liq. Cryst. 1989, 6, 689. (15) Emsley, J. W.; Luckhurst, G. R. Mol. Phys. 1980, 41, 19.
 - (16) Zannoni, C., in ref 5.

 - (17) Perrin, H.; Berges, J. J. Phys. (France) 1984, 85, 1947.
 (18) Schaefer, T.; Sebastian, R. Can. J. Chem. 1989, 67, 1148.
 - (19) Seip, H. M.; Seip, R. Acta Chem. Scand. 1973, 27, 4024.
- (20) Internal rotations in molecules; Orville-Thomas, W. J., Ed.; Wiley:
- London, 1974. (21) Wilson, M. R.; Allen, M. P. Mol. Cryst. Liq. Cryst. 1991, 198, 465. (22) Konschin, H.; Tylli, H.; Grundfeldt-Forsius, C. J. Mol. Struct. 1981,
- 77, 51
- (23) Celebre, G.; De Luca, G.; Longeri, M.; Emsley, J. W. J. Phys. Chem. 1992, 96, 2466.
- (24) Di Bari, L.; Persico, M.; Veracini, C. A. J. Chem. Phys. 1992, 96, 4782.

Conformation of 1,2-Dimethoxyethane in the Gas Phase: A Rotational Isomeric State Simulation of NMR Vicinal Coupling Constants

Katsuhiro Inomata and Akihiro Abe*

Department of Polymer Chemistry, Tokyo Institute of Technology, 2-12-1 Ookayama, Meguro-ku, Tokyo 152, Japan (Received: February 11, 1992; In Final Form: June 25, 1992)

Conformational characteristics of 1,2-dimethoxyethane (DME) in the gas phase have been studied by the NMR method. Observed ${}^{1}H-{}^{1}H$ and ${}^{1}C-{}^{1}H$ NMR vicinal coupling constants are compared with those previously determined in nonpolar solvents. The values observed in the gas phase and in solution do not exhibit any appreciable discontinuity at the transition. Rotational isomeric state simulations of these vicinal coupling constants yielded conformational energies of the gauche state relative to the trans in the gas phase: $E_{\rho} = 1.0$ kcal mol⁻¹ for the C–O bond and $E_{\sigma} = -0.4$ kcal mol⁻¹ for the C–C bond. In these treatments, the neighbor-dependent character of the bond rotation has been rigorously taken into account. The conformational energies thus determined were found to be nearly identical with those previously derived from the measurement in nonpolar solvents such as c- C_6D_{12} . Accordingly, it has been confirmed that the gauche oxygen effect, i.e., the gauche preference for the OC-CO bond, is not a feature caused by the surrounding solvent molecules in solution. This is contrary to the expectation emerging from the classical consideration of Coulombic interactions between partial charges residing on the oxygen atoms. The value of E_{α} estimated above is inconsistent with the results of recent MO calculations (0.5 kcal mol⁻¹) reported by Barzaghi et al. The discrepancy between the calculated and observed values amounts to about 1 kcal mol⁻¹. Finally, the fractions of the conformer estimated in this work are compared with those derived from the electron diffraction measurement by Astrup. The agreement was found to be only qualitative.

Introduction

In a series of papers,¹⁻⁴ we have been studying the conformation of 1,2-dimethoxyethane (DME) in relation to the gauche oxygen effect⁵ associated with the internal rotation around the OC-CO bond. Tasaki and one of the present authors^{2,3} previously reported the results of NMR measurements on vicinal coupling constants ${}^{3}J_{\rm HH}$, ${}^{3}J'_{\rm HH}$, and ${}^{3}J_{\rm CH}$ in various solvents and in the neat liquid. The rotational isomeric state (RIS) analysis of these experimental data yielded conformational energies E_{σ} and E_{ρ} for the constituent bonds OC-CO and CC-OC, respectively. The values of E_{σ} , representing the energy of the gauche state expressed relative to the trans, were found to vary in a range -0.5 to -1.2 kcal mol⁻¹ depending on the solvent system. As has been demonstrated for a variety of compounds, polar conformers tend to be better stabilized in the high dielectric media.⁶ The results are compared with those reported previously by Viti et al.⁷ and Matsuzaki et al.⁸ Although the trans and gauche coupling constants adopted in the analysis are quite different among research groups, all yielded negative values of E_{σ} on the basis of the NMR ¹³CH satellite side band spectra.

The gauche oxygen effect, i.e., the gauche preference about the OC-CO bond of DME, has been difficult to interpret in the classical concept of chemistry. Since the DME molecule is relatively small, theoretical calculations can be easily carried out. Various methods including semiempirical molecular force field^{9,10} as well as MO calculations¹¹ have been applied to predict conformational energies of the rotational isomers. Most of these calculations suggest that the all-trans ttt form should be the lowest energy conformation when a single molecule remains in the isolated state. For a strict test of these theoretical predictions, the experimental data derived from the gas phase should be better suited. Astrup¹² estimated fractions for several representative rotational isomers from the electron diffraction studies in the vapor phase. The value of the trans fraction f_t^{CC} (= $1-f_g^{CC}$) for the central C-C bond is in good agreement with our estimation in solution at room temperature.² However, his analysis gave a larger fraction for tgg ($tg^{\pm}g^{\pm} + tg^{\pm}g^{\mp}$) than tgt, being inconsistent with those derived from the NMR analysis.

In the present work, we have attempted to examine the conformation of DME in the vapor phase by employing the same NMR technique as adopted in solution.² Some preliminary results derived from the analysis of ¹³CH satellite side band spectra have

[•] To whom correspondence should be sent.