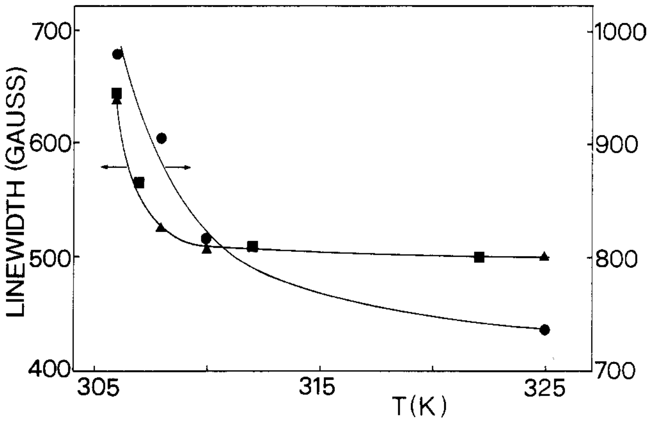

Figure 5. ESR line width as function of temperature: (●) iridium containing sample, (▲) rhodium containing sample, (■) pure chromia.

different atmospheres on the δ-phase signal and to elucidate eventual connections with the diffusion process, Rh^{3+} and Ir^{3+} were supported on α-Cr_2O_3. The ESR spectra below T_N of the Rh containing samples are reported in Figure 4. The sequence of spectra clearly reveals that the δ-phase spectrum is a superpositionof two magnetically nonequivalent sites, one of which is preferentially decreased after treatment at 603 K in an H_2 atmosphere (site a), while the other (site b) persists (Figure 4B). Treatment at 773 K causes also the disappearing of site b (Figure 4C). When N_2 is used in the thermal treatments no alteration of the δ-phase signal is observed until 773 K is reached.

The observed phenomena seem to indicate that progressive diffusion takes place with increasing temperature, the threshold value above which this occurs being lower in a reducing atmosphere. The recorded temperature dependence of the site b spectrum of Figure 4B follows exactly the pattern of the complete δ-phase spectrum of Figure 3, thus suggesting that sites a and b arise from the same defective sites. In principle, this could be represented by two nonequivalent Cr^{3+} ions (e.g., M_2 and M_3) close to the chromium vacancy in the framework depicted above (see Figure 2). There are several reasons for which the occupancy of the vacancy by a Rh ion may cause the disappearance of the ESR spectrum (e.g., Rh in a paramagnetic valence state, electron transfer or change of Cr^{3+} valence state, or simply enhancement of the electron spin relaxation rate). On the other hand, the exchange-narrowed spectrum from regular α-Cr_2O_3 recorded at temperature above T_N is practically unaffected by the presence of rhodium. This suggests that diffusion is limited to the defective sites, which are individually saturated, not influencing the cooperative magnetic phenomena in the α-Cr_2O_3 lattice.

The ESR results concerning the iridium containing samples indicate an analogous trend with respect to the effect of the treatments on the δ-phase signal. However, contrary to rhodium, iridium seems to have a strong effect on the exchange-narrowed spectrum also. Figure 5 shows the ESR line width as function of temperature, as compared with α-Cr_2O_3 and rhodium on α-Cr_2O_3 samples. Furthermore, the antiferromagnetic transition is not sharp and the spectrum grows gradually in intensity between 306 and ~320 K. This behavior suggests that both the chromium vacancies and the regular α-Cr_2O_3 lattice are involved when Ir diffusion occurs. The preferential stabilization of these ions in the regular lattice sites causes spreading of the antiferromagnetic coupling.

In conclusion, experimental evidence exists indicating that rhodium and iridium ions deposited on chromia surface can reasonably diffuse within the support lattice. This phenomenon is influenced by the noble ion concentration,[8] the temperature, and atmosphere of the thermal treatment. We suggest that the relatively low temperature at which diffusion begins is probably related to the high mobility of the defects present in the chromia structure.

Registry No. Rh, 7440-16-6; Ir, 7439-88-5; Cr_2O_3, 1308-38-9.

Deuteron Quadrupole Coupling Constants of the Methyl and Methylene Groups of Ethanol from the Direct ^{13}C–^{2}H and ^{2}H–^{2}H Couplings in ^{2}H NMR Spectra

G. C. Lickfield, A. L. Beyerlein, G. B. Savitsky,*

Department of Chemistry and Geology, Clemson University, Clemson, South Carolina 29631

and L. E. Lewis

Department of Chemistry, Birmingham Southern College, Birmingham, Alabama 35204

(Received: August 29, 1983; In Final Form: February 10, 1984)

The deuteron quadrupole coupling constants, Q_D, of $^{13}C^2H_3CH_2OH$ and $CH_3{}^{13}C^2H_2OH$ were measured in two different nematic solvents by employing the quadrupolar splitting and the ^{13}C–^{2}H and ^{2}H–^{2}H dipolar splittings in ^{2}H NMR spectra. In order to obtain the most accurate values for Q_D, vibrational averaging of the dipolar couplings and ab initio calculations of the C–D bond asymmetry correction were used in the theoretical treatment of the experimental data. The values found in ZLI-1167 are 186.6 and 178.2 kHz and in phase IV are 180.7 and 176.6 kHz for the methyl and methylene groups, respectively. Using the previously obtained ^{2}H NMR relaxation data and the Q_D value determined in ZLI-1167, we calculated the internal rotation coefficient of the methyl group to be 0.68×10^{11} s^{-1}.

Introduction

A reinvestigation of the deuteron quadrupole coupling constants (Q_D) in ethanol is prompted by previous investigations:

(1) The Q_D's previously reported by Emsley et al.[1,2] ($Q_D(CD_3)$ = 175.5 ± 15 kHz and $Q_D(CD_2)$ = 164 ± 50 kHz) do not include vibrational averaging of the direct couplings used in determining the orientation parameters, and the experimental error reported approximately spans the entire range of accurately known Q_D values for C–D bonds.

(2) A significant nematic solvent effect was recently discovered on the Q_D value of deuteriochloroform,[3] and there is a need to investigate such solvent effects along with the effects of substitution

---

[1] J. W. Emsley, J. C. Lindon, and J. Tabony, *Mol. Phys.*, **26**, 1485 (1973).

[2] J. W. Emsley and J. C. Lindon, "NMR Spectroscopy Using Liquid Crystal Solvents", Pergamon Press, New York, 1975.

[3] G. C. Lickfield, J. F. McKenna, A. L. Beyerlein, and G. B. Savitsky, *J. Magn. Reson.*, **51**, 301 (1983).

0022-3654/84/2088-3566$01.50/0 © 1984 American Chemical Society

on the carbon to which the deuteron is bound.

(3) Accurate values of Q_D in molecules of different structures and hybridization are needed to establish trends and correlations which will enable one to predict or estimate the Q_D value in deuterated molecules of various types for the quantitative treatment of deuteron relaxation measurements.

(4) There is a need to reevaluate the previous ^2H NMR relaxation study on perdeuterioethanol[4] in terms of the internal rotation rate of the methyl group.

The large errors in the Q_D values are primarily due to problems in relating all of the relevant orientation parameters to the direct couplings between the various nuclei because ethanol is not a rigid molecule.[5] Some simplifying approximations have to be made which in turn result in uncertainties in the value of Q_D. This problem is greatly alleviated by contiguously labeling with ^{13}C and ^2H in the bond of interest. In this way, a very accurate first-order approximation for Q_D (which neglects vibrational and C–D bond asymmetry corrections[2]) can be obtained regardless of molecular symmetry from the quadrupolar and ^{13}C–^2H dipolar splittings along with a value for the C–D bond length without invoking assumptions regarding relations of orientation parameters to direct dipolar couplings.[6] With this technique, these assumptions are only used to apply the relatively small vibrational and C–D bond asymmetry corrections (<10%), thereby introducing negligible error into the overall Q_D measurement. In order to obtain Q_D as accurately as possible, we have obtained the direction of the major axis of the electric field gradient tensor at the deuteron, which may differ slightly from the C–D bond direction, by ab initio calculations. Correcting for the deviation of the electric field gradient major axis direction from the C–D bond direction necessitated the derivation of the most general equations.

Experimental Section

Ethanol-*1*-^{13}C-*1*-$^2H_2$ (60 atom % ^{13}C) was prepared from acetic-*1,1*-^{13}C anhydride (90 atom % ^{13}C, purchased from Merck Sharpe and Dohme) with lithium aluminum deuteride as the reducing and ^2H-labeling agent. Ethanol-*2*-^{13}C-*2*-$^2H_3$ (97–99 atom % ^{13}C) was prepared from sodium acetate-*2*-^{13}C (97–99 atom % ^{13}C, purchased from Cambridge Isotope Laboratories) which was deuterated by acidic exchange in ^2H_2O, and the resulting acetic acid was reduced with lithium aluminum hydride. Samples of 10 mol % of a 2:3 mixture of $^{13}CD_3CH_2OH$:$CH_3{}^{13}CD_2OH$ and 5 mol % of $^{13}CD_3CH_2OH$ were made up in Merck phase IV and Merck ZLI-1167 liquid crystal solvents (E.M. Laboratories Inc., Elmsford, NY). The samples were placed in cylindrical cells and the ^2H NMR spectra taken in the manner previously described.[6] An average of at least eight spectra were recorded on each sample. All observed splittings required to calculate Q_D were obtained from a single ^2H NMR spectrum. The indirect coupling constants, J_{CD}, of the methyl and methylene groups were obtained from the ^{13}C–^2H splittings on samples heated above the nematic range. The nematic phase spectra were recorded over a temperature range of 294–315 K.

Theory

The quadrupolar splitting, Δ, of any given deuteron in the ^2H NMR spectrum of a rigid molecule or rigid portion thereof oriented in a nematic phase of a liquid crystal is given by

$$\Delta = (eQ/h)\sum_{ij} V_{ij} S_{ij} \qquad (1)$$

in which i and j are summed over the xyz molecular axes.[7] Here the V_{ij}'s are the electric field gradients which are defined to be the second partial spatial derivatives of the electric field potential at the deuteron, e is the electron charge, h is Planck's constant, and Q is the electric quadrupole moment of the deuteron. The S_{ij} terms are the orientation parameters, which are defined as

$$S_{ij} = \tfrac{1}{2}\langle 3 \cos \theta_i \cos \theta_j - \delta_{ij} \rangle \qquad (2)$$

where δ is the Kronecker δ, θ_i ($i = x, y$, and z) are the angles the molecular Cartesian axes make with the external magnetic field, and the brackets $\langle\ \rangle$ denote an ensemble average over the thermal molecular motions. The diagonal terms, S_{ii}, are an example of what is referred to as the orientation parameter of a vector which, in this case, is the i axis. If this corresponds to an internuclear vector of two NMR active nuclei, A and B, the corresponding orientation parameters are calculated from the direct dipolar couplings according to the equation

$$D_{AB} = -[(h\gamma_A\gamma_B)/(4\pi^2)]S_{AB}\langle (3 \cos^2 \delta\omega - 1)/2r_{AB}{}^3 \rangle \qquad (3)$$

where γ_A and γ_B are the magnetogyric ratios of nuclei A and B, S_{AB} denotes the orientation parameter of the AB internuclear vector, r_{AB} is the internuclear distance, and $\delta\omega$ is the instantaneous angular deviation of the AB internuclear vector from its equilibrium direction. The brackets $\langle\ \rangle$ indicate vibrational averaging. The term enclosed by the brackets is evaluated as the vibrational averaging correction to the direct couplings. If the nuclei, A and B, are different, one obtains the direct coupling D_{AB} from the observed dipolar splitting ν_{AB} using

$$D_{AB} = \tfrac{1}{2}(\nu_{AB} \pm |J_{AB}|) \qquad (4)$$

where anisotropic contributions to the indirect coupling constant, J_{AB}, are assumed to be small and therefore neglected.[8-10] The appropriate sign preceding $|J_{AB}|$ depends on whether the signs of D_{AB} and J_{AB} are the same or different. For calculations of D_{CD} from ^{13}C–^2H dipolar splittings, this sign is the same as the sign of the intercept obtained from a linear least-squares fit of the quadrupolar splittings, Δ, vs. ν_{CD} where both Δ and ν_{CD} are obtained from the same ^2H NMR spectrum.[6] The variation in Δ and ν_{CD} is achieved by changing sample temperature and concentration. As in the case of previous studies,[3,11] this sign is positive in ZLI-1167 and negative in phase IV for both the methyl and methylene groups. The direct coupling between two deuterons with zero chemical shift (e.g. a CD_2 group) results in an off-centered triplet where the separations between the lines are equal to $2D_{DD}$ and $4D_{DD}$.

For simplification, let $q_{ij} = (eQ/h)V_{ij}$, thus giving eq 1 the following form:

$$\Delta = \sum_{ij} q_{ij} S_{ij} \qquad (5)$$

Using the fact that **q** and **S** are symmetric traceless tensors, we can write eq 5 in a molecular axes system (xyz) as

$$\Delta = \tfrac{1}{2}[3q_{zz}S_{zz} + (q_{xx} - q_{yy}) \times (S_{xx} - S_{yy}) + 4(q_{xy}S_{xy} + q_{yz}S_{yz} + q_{xz}S_{xz})] \qquad (6)$$

Thus, the quadrupolar splitting is a function of the five independent elements of the **q** and **S** tensors. There exists a principal axes system (rst) in which the **q** tensor is diagonalized, i.e. the off-diagonal elements are zero, and therefore contains only three nonzero elements: q_{rr}, q_{ss}, and q_{tt}. The largest of the three is, in general, approximately collinear with the C–D bond. The reason for this is that the greatest effect on the electric field potential at the deuteron is due to the atom (or the charge on the atom) to which the deuteron is bound. Therefore, let the t axis in the

---

(4) T. K. Chen, A. L. Beyerlein, and G. B. Savitsky, *J. Chem. Phys.*, **63**, 3176 (1975).

(5) E. E. Burnell and C. A. de Lange, *Chem. Phys. Lett.*, **76**, 268 (1980).

(6) J. B. Wooten, A. L. Beyerlein, J. Jacobus, and G. B. Savitsky, *J. Chem. Phys.*, **65**, 2476 (1976).

(7) P. Diehl and C. L. Khetrapal in "NMR Basic Principles and Progress", Vol. 1, P. Diehl, E. Fluck, and R. Kosfield, Eds., Springer-Verlag: West Berlin, 1969, p 1.

(8) P. K. Bhattacharyya and B. P. Dailey, *J. Chem. Phys.*, **59**, 3737 (1973).

(9) G. Englert and A. Saupe, *Mol. Cryst.*, **1**, 503 (1966).

(10) A. D. Buckingham and I. Love, *J. Magn. Reson.*, **2**, 338 (1970). These authors cite theoretical calculations which indicate anisotropic contributions to the indirect coupling tensor may be neglected when ^{13}C, ^1H, or ^2H nuclei are involved.

(11) G. C. Lickfield, S. E. Emery, R. V. Gregory, T. C. Chen, A. L. Beyerlein, and G. B. Savitsky, *J. Magn. Reson.*, **54**, 305 (1983).

TABLE I: Independent Elements of the S Matrix for Rigid Molecules of Various Symmetry Types

sym type	no. of independent elements	independent elements
3-fold or greater rotational sym	1	S_{kk}
2 perpendicular mirror planes	2	S_{kk}, $S_{ii} - S_{jj}$
1 mirror plane	3	S_{kk}, $S_{ii} - S_{jj}$, S_{ij}
no sym	5	S_{ii}, S_{jj}, S_{ij}, S_{ik}, S_{jk}

principal axes system be collinear with the direction of the largest component of the electric field gradient. In this principal axes system, eq 5 has the form

$$\Delta = \tfrac{1}{2}[3q_{tt}S_{tt} + (q_{rr} - q_{ss})(S_{rr} - S_{ss})] \qquad (7)$$

The term q_{tt} is referred to as the quadrupole coupling constant, Q_D. The remaining elements, q_{rr} and q_{ss}, are formulated along with q_{tt} to define the asymmetry parameter η

$$\eta = (q_{rr} - q_{ss})/q_{tt} \qquad (8)$$

which essentially describes the deviation from cylindrical symmetry of the electric field gradients about the C–D bond. If one sets $S_{tt} - S_{CD} = \delta S_{tt}$ and uses the above definition of η, eq 7 now has the following form:

$$\Delta = (3/2)Q_D[S_{CD} + \delta S_{tt} + (\eta/3)(S_{rr} - S_{ss})] \qquad (9)$$

where S_{CD} is obtained directly from the measured $^{13}C-^{2}H$ dipolar splitting, using eq 3 and 4, and represents the dominant contribution to the term in square brackets. The term δS_{tt} represents the small difference between S_{tt} and S_{CD} because the C–D bond direction and the major axis of the electric field gradient tensor are not quite in the same direction.

The orientation parameter of any vector α, $S_{\alpha\alpha}$, can be expressed in the molecular axes system by the following transformation:

$$S_{\alpha\alpha} = \tfrac{1}{2}(3\cos^2\beta_{\alpha z} - 1)S_{zz} + \tfrac{1}{2}(\cos^2\beta_{\alpha x} - \cos^2\beta_{\alpha y})(S_{xx} - S_{yy}) + 2(\cos\beta_{\alpha x}\cos\beta_{\alpha y})S_{xy} + 2(\cos\beta_{\alpha x}\cos\beta_{\alpha z})S_{xz} + 2(\cos\beta_{\alpha y}\cos\beta_{\alpha z})S_{yz} \qquad (10)$$

where the angles $\beta_{\alpha x}$, $\beta_{\alpha y}$, and $\beta_{\alpha z}$ are the angles the vector α makes with the xyz molecular coordinate system. Using the above transformation on each of the orientation parameters of the principal axes system (S_{rr}, S_{ss}, and S_{tt}) and S_{CD}, we can express the last two terms in the square brackets of eq 9 as follows:

$$\delta S_{tt} = [\tfrac{1}{2}(3\cos^2\beta_{tz} - 1) - \tfrac{1}{2}(3\cos^2\beta_{CDz} - 1)]S_{zz} + [\tfrac{1}{2}(\cos^2\beta_{tx} - \cos^2\beta_{ty}) - \tfrac{1}{2}(\cos^2\beta_{CDx} - \cos^2\beta_{CDy})](S_{xx} - S_{yy}) + 2[\cos\beta_{tx}\cos\beta_{ty} - \cos\beta_{CDx}\cos\beta_{CDy}]S_{xy} + 2[\cos\beta_{tx}\cos\beta_{tz} - \cos\beta_{CDx}\cos\beta_{CDz}]S_{xz} + 2[\cos\beta_{ty}\cos\beta_{tz} - \cos\beta_{CDy}\cos\beta_{CDz}]S_{yz} \qquad (11)$$

and

$$(\eta/3)(S_{rr} - S_{ss}) = (\eta/3)\{[\tfrac{1}{2}(3\cos^2\beta_{rz} - 1) - \tfrac{1}{2}(3\cos^2\beta_{sz} - 1)]S_{zz} + [\tfrac{1}{2}(\cos^2\beta_{rx} - \cos^2\beta_{ry}) - \tfrac{1}{2}(\cos^2\beta_{sx} - \cos^2\beta_{sy})](S_{xx} - S_{yy}) + 2[\cos\beta_{rx}\cos\beta_{ry} - \cos\beta_{sx}\cos\beta_{sy}]S_{xy} + 2[\cos\beta_{rx}\cos\beta_{rz} - \cos\beta_{sx}\cos\beta_{sz}]S_{xz} + 2[\cos\beta_{ry}\cos\beta_{rz} - \cos\beta_{sy}\cos\beta_{sz}]S_{yz}\} \qquad (12)$$

Thus, in order to calculate the C–D bond asymmetry correction and δS_{tt} of eq 9, the values of the asymmetry parameter, the angles β_{ij}, and, in general, the orientation parameters for the molecule must be determined.

For a rigid molecule and, to a good approximation, for rigid portions of a molecule with internal motions,[5] elements of symmetry will reduce the number of independent orientation parameters to a number less than five. Consequently, the number of dipolar couplings needed to calculate Q_D may be correspondingly reduced. Table I gives the nonzero orientation parameters needed for various molecular symmetries provided the ijk molecular coordinate system is appropriately selected.[2] For 3-fold or greater symmetry, the k axis must be collinear with the symmetry axis. For molecules with two perpendicular mirror planes, the ik and jk planes must define these mirror planes. For molecules with one mirror plane, the k axis is set up to be perpendicular to this mirror plane.

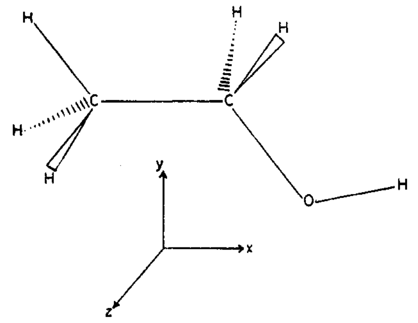

Figure 1. Molecular axes system for the trans conformation of ethanol.

Table I is strictly applicable to the symmetry of the entire rigid molecule but, with some assumptions, can also be applied to a given rigid group in the molecule.[5] Figure 1 shows the molecular axes system used in this work for the ethanol molecule in the trans conformation. Since in this conformation the molecule has mirror plane symmetry, the axes system is set up such that the xy plane defines the mirror plane with the x axis lying along the carbon–carbon bond. It is not known what the preferred conformation of the methyl group is in the nematic solvent, but it is usually assumed to have a 3-fold axis of symmetry,[1,2,12] which in this case would be collinear with the C–C bond and therefore with the x axis in Figure 1. This approximation can be justified on experimental grounds and will be discussed in the following section. Thus, in these approximations, the orientation of the methylene group is completely described by three orientation parameters (S_{zz}, $S_{xx} - S_{yy}$, and S_{xy}) and the methyl group by only one (S_{xx}).

The three orientation parameters needed to calculate Q_D(methylene) are obtained from three of the observed dipolar splittings in the ^2H NMR spectrum of the mixture of $^{13}CD_3CH_2OH$ and $CH_3{}^{13}CD_2OH$. Two are from the methylene-labeled ethanol ($\nu_{CD(2)}$ and ν_{DD}), and one is from the methyl-labeled ethanol ($\nu_{CD(3)}$). Substitution of the values for $D_{CD(2)}$, $D_{CD(3)}$, obtained from eq 4, and D_{DD} into eq 3 yields the values of $S_{CD(2)}$, S_{DD}, and $S_{CD(3)}$. Insertion of the appropriate values for the angles that the three internuclear vectors make with the molecular coordinate system into eq 10 allows us to solve for S_{zz}, $S_{xx} - S_{yy}$, and S_{xy}. The results of this are

$$S_{zz} = S_{DD}$$

$$S_{xx} - S_{yy} = 2S_{CC} + S_{DD}$$

$$S_{xy} = \{S_{CD} - \tfrac{1}{2}(3\cos^2\beta_z - 1)S_{DD} - \tfrac{1}{2}(\cos^2\beta_x - \cos^2\beta_y) \times (2S_{CC} + S_{DD})\}/(2\cos\beta_x\cos\beta_y) \qquad (13)$$

where the S_{CC} term is the orientation parameter of the C–C internuclear vector and the angles (β_x, β_y, and β_z) are the angles a C–D bond in the methylene group makes with the xyz molecular coordinate system. The S_{CC} term is estimated from $S_{CD(3)}$ by

$$S_{CC} = \tfrac{1}{2}(3\cos^2\beta_\alpha - 1)S_{CD(3)} \qquad (14)$$

which assumes 3-fold rotational symmetry for the methyl group. The angle β_α is the angle a C–D bond of the methyl group makes with the C–C bond. For the calculation of the Q_D of the methyl group, S_{CC} is the same as the orientation parameter of the 3-fold axis of symmetry, i.e. S_{xx} according to Figure 1.

The last terms in eq 11 and 12 that need to be determined are the angles between the molecular axes system and the principal axes system and the value of the asymmetry parameter η. Instead of assuming both the directionality of the principal axes system and the value of η, we have performed ab initio calculations on

---

[12] J. W. Emsley and J. Tabony, *J. Magn. Reson.*, **17**, 223 (1975).

TABLE II: Experimental Data (Hz)

methylene[a]			methyl[b]	
Δ	ν_{CD}	D_{DD}	Δ	ν_{CD}
		Phase IV		
8566.6	252.2	25.3	4207.7	129.4
8555.8	250.7	25.4	4201.7	128.6
8289.7	244.6	24.4	4121.3	127.4
7537.2	223.3	22.7	3599.8	113.5
7533.2	223.7	22.7	3594.6	112.3
7525.2	221.1	22.2	3592.2	114.4
7520.3	221.9	22.1	3588.2	112.3
7495.6	220.5	22.2	3553.7	112.6
			4645.2	140.8
			4635.2	141.1
			4503.4	137.6
			4502.4	138.1
			4498.2	137.9
		ZLI-1167		
5264.1	118.1	11.6	3724.6	75.1
5236.8	117.4	11.8	3687.0	74.8
5231.7	116.2	11.8	3684.0	75.1
5230.9	115.8	11.5	3685.7	74.8
5228.4	116.6	11.4	3684.1	73.5
5223.1	115.2	11.9	3678.7	74.5
4636.8	100.8	10.4	3237.0	62.7
4624.8	100.9	10.5	3241.3	62.0
4622.4	101.4	10.8	3226.2	62.5
4593.5	99.2	10.5	3199.7	63.0
4576.0	98.3	10.4	3170.8	60.7
4571.0	97.3	10.5	3168.2	60.3
			4273.6	90.3
			4268.1	88.3
			4262.5	88.7
			4245.4	89.9
			3587.1	72.1

[a] J_{CD} = 21.5. [b] J_{CD} = 19.2.

TABLE III: Rotation Angles (deg) and Asymmetry Parameters

	rotation angles			
	r	s	t	asym parameter
		Methylene		
x	46.949	129.895	69.503	−0.0634
y	62.279	41.326	62.051	
z	124.303	99.037	35.806	
		Methyl (in plane)		
x	90.000	19.940	109.940	−0.0305
y	90.000	70.060	19.940	
z	0.000	90.000	90.000	
		Methyl (out of plane)		
x	77.633	23.705	109.891	−0.0318
y	151.997	88.139	117.930	
z	114.698	66.378	35.375	

TABLE IV: Vibrational Averaging Corrections (%) to the Direct Couplings

	ZLI-1167	phase IV
Methylene		
D_{CD} (CD_2)	3.067	3.039
D_{DD} (CD_2)	1.445	1.397
D_{CD} (CD_3 in plane)	2.351	6.225
D_{CD} (CD_3 out of plane)	4.481	4.863
Methyl		
D_{CD} (in plane)	4.205	4.205
D_{CD} (out of plane)	3.963	3.963

TABLE V: Quadrupole Coupling Constants (Q_D) (kHz)

	Q_D	
	ZLI-1167	phase IV
	Methylene	
in plane	178.3 ± 1.1	176.5 ± 1.0
out of plane	178.1 ± 1.1	176.6 ± 1.0
	Methyl	
in plane	186.8 ± 1.5	181.0 ± 1.2
out of plane	186.3 ± 1.5	180.4 ± 1.2

the ethanol molecule. This was done with the double zeta basis sets of Snyder and Basch[13] using the GAUSSIAN 70 program[14] and POLYATOM (version II) system of programs.[15]

Results and Discussion

The observed splittings and indirect coupling constants used in the Q_D determinations are given in Table II. The internuclear distances used in the calculations are r_{CD}(methyl) = 1.100 Å, r_{CD}(methylene) = 1.093 Å, and r_{DD}(methylene) = 1.775 Å.[16] Table III contains the results of the ab initio calculations for the trans conformation of ethanol. The calculated asymmetry parameters of the in-plane and out-of-plane hydrogens of the methyl group are slightly different, which is most likely a result of the proximity of the oxygen. The vibrational averaging corrections to the direct couplings were calculated as a percent correction from the equations of Snyder[17] and Lucas[18] and are listed in Table IV. These calculations use the orientation parameters obtained from the uncorrected direct couplings and are therefore dependent on the nematic solvent. We have estimated these corrections using the force field for 2-chloroethanol.[19] This force field was modified by changing all the force constants pertaining to the chlorine atom to those of the methyl hydrogens. The resulting frequencies approximated those for ethanol. These force constants were assumed not to change significantly upon deuteration, and the vibrational corrections listed are for the deuterated molecules. The effect of each correction, being positive in sign, is to increase the value of the corresponding direct coupling.

Table V contains the Q_D's for the methyl and methylene groups in each nematic solvent. The terms "in-plane" and "out-of-plane" correspond to the methyl hydrogens which were used in the calculations. Even though the asymmetry parameters, rotation angles, and vibrational corrections corresponding to the in-plane and out-of-plane hydrogens of the methyl group are different, the differences (~0.1 kHz) in the Q_D's obtained by using these different values are well within experimental error and the average values: 186.6 and 178.2 kHz in ZLI-1167 and 180.7 and 176.6 kHz in phase IV, for the methyl and methylene groups, respectively, represent the Q_D measurements within ±1.5 kHz.

The calculation of Q_D from eq 9 required detailed information on the molecular geometry in order to estimate from eq 11 and 12 the δS_{tt} and asymmetry corrections. The estimation of these corrections also requires the assumptions (i) that the methyl- and methylene-labeled ethanol molecules have the same overall orientation in the nematic phases and (ii) that the methyl group has a 3-fold axis of symmetry. However, these assumptions and possible uncertainties in the molecular geometry resulting from bond angle distortions in the nematic phase do not introduce significant error into the measured Q_D because they do not affect S_{CD} which dominates the correction terms (which are about 5% of S_{CD}) in eq 9. Rather, S_{CD} is calculated directly from eq 3 and 4 by using measured $^{13}C-^{2}H$ dipolar splittings and only one molecular parameter, the C–D bond length, which is usually known accurately and does not change significantly upon solution in the nematic phase.

Even though for our purposes high accuracy is not required for assumptions (i) and (ii), it is worthwhile noting that they are

---

(13) L. C. Snyder and H. Basch, "Molecular Wavefunctions and Properties", Wiley, New York, 1972.

(14) W. J. Hehre, W. A. Lathan, R. Ditchfield, M. D. Newton, and J. A. Pople, *QCPE*, **No. 236**.

(15) D. B. Neumann, H. Basch, R. L. Kornegay, L. C. Snyder, J. W. Moskowitz, C. Hornback, and S. P. Liebmann, *QCPE*, **No. 238**.

(16) Ch. O. Kadzhar, I. Dzh. Isaev and L. M. Imanov, *Zh. Strukt. Khim.*, **9**, 445 (1968).

(17) L. C. Snyder, *J. Chem. Phys.*, **43**, 4041 (1965).

(18) N. J. D. Lucas, *Mol. Phys.*, **22**, 147 (1971).

(19) P. A. Giguere and M. Schneider, *Can. J. Chem.*, **50**, 152 (1972).

reasonably accurate. The validity of the first assumption was verified by adding a small amount of perdeuterioethanol to a sample containing the mixture of labeled ethanols. The resulting ^2H NMR spectra showed essentially the same spectral splittings except for some line broadening due to ^2H–^2H direct coupling in the perdeuterioethanol. If this assumption were not valid, additional spectral lines would have appeared since the quadrupolar splittings are dependent upon the orientation of the solute molecules. The second assumption is justified by the spectra themselves which showed the characteristic septet for a CD_3 group,[2] indicating that all three deuterons of the methyl group are experimentally indistinghishable, probably because of the rapid reorientation of the methyl group.

As in previous studies,[3,11,20] the Q_D's determined in phase IV are lower than the corresponding values obtained in ZLI-1167. Previous investigations of Diehl et al.[21] indicated ZLI-1167 to be the most inert nematic solvent because it gave the "best" r_α structure of benzene. Hydrogen-bonding interactions or electronic interactions of the solute with the nematic solvent are less likely for ZLI-1167 because its single polar group (a nitrile group) is much less active than the alkoxy groups and/or aromatic rings in phase IV and other nematic solvents.

The effect of substitution on Q_D of a highly polar group is readily apparent from Table V. The electron-withdrawing effects of a hydroxyl group tend to lower the Q_D of the group to which it is bound. This is in agreement with the results of Rinne and Depireux[22] on a variety of substituted molecules. Whether or not substitution on the methylene carbon has any effect on the Q_D of the methyl group cannot be discerned. Further studies employing different electron-donating and -withdrawing substituents are needed to provide such information.

These values for the quadrupole coupling constants of the methyl and methylene groups can be combined with the measured ^2H relaxation times[4] to estimate the internal rotation rate of the methyl group. This is calculated to be 0.68×10^{11} s^{-1} by using the Q_D value measured in the more inert nematic solvent, ZLI-1167. This is in excellent agreement with Levine et al.,[23] who estimated an average internal rotation rate of 0.5×10^{11} s^{-1} for terminal methyl groups on short hydrocarbon chains (less than 10 carbon atoms) from ^{13}C relaxation times. Since the estimate of the methyl group internal rotation rate for ethanol from ^2H relaxation studies[4] was not possible until the more accurate quadrupole coupling constants reported herein became available, it serves to illustrate how important accurate quadrupole coupling constants are to the development of ^2H NMR for molecular motion studies.

Acknowledgment. Support for this work was provided by the donors of the Petroleum Research Fund, administered by the Americal Chemical Society (Grant PRF-13066-AC6). We greatly appreciate the assistance of Dr. H. K. McDowell with the ab initio calculations.

Registry No. $^{13}CD_3CH_2OH$, 1759-87-1; $CH_3{}^{13}CD_2OH$, 1859-09-2; ZLI-1167, 67009-49-8; Phase IV, 11106-54-0.

---

(20) J. Jokisaari, P. Diehl, J. Amrein, and E. Ijas, *J. Magn. Reson.*, **52**, 193 (1983).

(21) P. Diehl, H. Bösiger, and H. Zimmermann, *J. Magn. Reson.*, **33**, 113 (1979).

(22) M. Rinne and J. Depireux, *Adv. Nucl. Quadrupole Reson.*, **1**, 357 (1974).

(23) Y. K. Levine, N. J. M. Birdsall, A. G. Lee, J. C. Metcalfe, P. Partington, and G. C. K. Roberts, *J. Chem. Phys.*, **60**, 2890 (1974).

Two Crystal Modifications of 4-Hydroxybiphenyl: The Biphenyl Structure without an Inversion Center and a Fully Ordered Structure Containing Nearly Planar Molecules[1]

Carolyn Pratt Brock* and Kurt L. Haller

Department of Chemistry, University of Kentucky, Lexington, Kentucky 40506-0055

(Received: November 7, 1983; In Final Form: April 2, 1984)

The structures of two polymorphs of 4-hydroxybiphenyl have been determined. Crystals grown by sublimation under reduced pressure are essentially isostructural with biphenyl but belong to the space group C_{2h}^5-$P2_1/a$ [$a = 8.067$ (2), $b = 5.449$ (1), $c = 20.022$ (5) Å, $\beta = 95.14$ (2)° at 295 K] and have a full molecule, rather than a half-molecule, in the asymmetric unit. Even in the absence of any symmetry restriction, the atomic distribution corresponds to a nearly planar molecule [ψ, the conformation angle about the phenyl–phenyl bond, = 1.6 (2)°]. As in the case of biphenyl, the structure seems to be complicated by subtle static and/or dynamic disorder. Satellite reflections have been observed at room temperature that may correspond to a structure modulation involving rotation about the long molecular axis. The structure has been refined both in the usual way (570 observations, 118 variables, final R index on F_o of 0.042) and by using a rigid-group least-squares procedure that incorporates the TLS description of rigid-body motion (38 variables, final R index on F_o of 0.071). The latter refinement indicates that the motion about the long molecular axis is significantly different for the two phenyl groups; the libration components in this direction are 62 (6) and 95 (7) deg^2 respectively for the substituted and unsubstituted rings. Crystals grown from solution belong to the space group D_2^4-$P2_12_12_1$ [$a = 15.472$ (8), $b = 5.469$ (7), $c = 20.600$ (14) Å at 295 K] and contain two independent, nearly planar molecules [$\psi = 2.3$ (2), 2.0 (3)°]. For this latter polymorph (1171 observations, 235 variables, final R index on F_o of 0.042) an analysis of the refined atomic U tensors in terms of the Schomaker–Trueblood rigid-body model reveals no abnormally large thermal motion that might hide disorder. The libration components associated with the long molecular axes are 78 (5) and 65 (6) deg^2 for the two independent molecules and do not differ significantly for the two rings within a single molecule.

The biphenyl molecule has been extensively studied for 20 years, and its structure often cited, because of the important conformational change it undergoes during crystallization. In discussions of "crystal packing effects", biphenyl is the paradigm. The inter-ring torsion angle ψ averages 42 (2)° in the gas phase[2] but is apparently compressed to 0° in the solid state at both room

---

(1) This paper is dedicated to Prof. Jack D. Dunitz on the occasion of his 60th birthday.

(2) Almenningen, A.; Bastiansen, O. *Kgl. Nor. Vidensk. Selsk. Skr.* **1958**, *4*, 1–16.

0022-3654/84/2088-3570$01.50/0