

**NMR Spectra of Oriented  $^{13}\text{C}$ -Acetylene.  
Redetermination of the Shrinkage Effects and  
Analysis of the Apparent Temperature Dependence of the Molecular Geometry**

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Abstract

The NMR spectra of the  $^{13}\text{C}$  isomers of acetylene oriented in two nematic liquid crystals (EBBA and Phase IV) have been analyzed in order to determine the distance ratios and the shrinkage effects. In the case of the EBBA samples, the results agree with the IR data except for a small discrepancy in the distance ratios. In the Phase IV samples, we have found an unusually strong temperature dependence of the direct coupling constants and of the corresponding apparent distance ratios. In this case the discrepancies between NMR and IR are as large as 30%. We interpret this phenomenon on the basis of a two-site theory. The following assumptions have to be made in order to explain the apparent anomalies: (i) the enthalpy difference between the two sites is 200-400 cal/mol, (ii) the orientation parameters at the two sites have opposite signs, and (iii) at the site with the lower energy (complex ?) the ratio  $r_{\text{CH}}/r_{\text{CC}}$  is smaller by 0.5-1%. It is interesting that such modest conditions can lead, if neglected, to a 30% error in the distance ratios. With regard to this fact, it is probable that similar effects are not uncommon.

Keywords: NMR, Oriented molecules, Acetylene, Liquid crystal

# NMR Spectra of Oriented $^{13}\text{C}$ -Acetylene: Redetermination of the Shrinkage Effects and Analysis of the Apparent Temperature Dependence of the Molecular Geometry

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The NMR spectra of the  $^{13}\text{C}$  isomers of acetylene oriented in two nematic liquid crystals (EBBA and Phase IV) have been analyzed in order to determine the distance ratios and the shrinkage effects. In the case of the EBBA samples, the results agree with the IR data except for a small discrepancy in the distance ratios. In the Phase IV samples, we have found an unusually strong temperature dependence of the direct coupling constants and of the corresponding apparent distance ratios. In this case the discrepancies between NMR and IR are as large as 30%. We interpret this phenomenon on the basis of a two-site theory. The following assumptions have to be made in order to explain the apparent anomalies: (i) the enthalpy difference between the two sites is 200–400 cal/mole, (ii) the orientation parameters at the two sites have opposite signs, and (iii) at the site with the lower energy (complex?) the ratio  $r_{\text{CH}}/r_{\text{CC}}$  is smaller by 0.5–1%. It is interesting that such modest conditions can lead, if neglected, to a 30% error in the distance ratios. With regard to this fact, it is probable that similar effects are not uncommon.

## INTRODUCTION

The first analysis of the NMR spectra of the  $^{13}\text{C}$  isomers of acetylene oriented in nematic liquid crystals has been published by Spiesecke (1). Unfortunately, this analysis is not quite correct since the evaluation of the vibrational corrections was carried out with no attention being paid to the anharmonic terms and to the effect of the bending motions. In the light of a recent paper (2) on the vibrationally averaged molecular structure, we are convinced that these terms are not negligible. We have taken a number of acetylene spectra and reanalyzed them in order to determine the correct shrinkage effects. In the course of this study we have encountered a new phenomenon which may prove to be more important than the effects we proposed to study originally. This is the discovery that, under suitable conditions, even rather weak specific interactions may lead to large errors in the conventionally determined

distance ratios. We have been alerted to this problem by a dramatic temperature dependence of the apparent distance ratios in one of the liquid crystals.

#### EXPERIMENTAL

The 60% enriched  $^{13}\text{C}$ -acetylene was obtained commercially from Merck, Sharp, and Dohme. The liquid crystals used were EBBA [*N*-(*p*-ethoxybenzylidene)-*p'*-*n*-butylaniline] and the Phase IV obtained from Merck. The samples contained acetylene solutions in equilibrium with acetylene gas at pressures of 7–10 atm.

The spectrometers used in this study were the Varian HA-60 (operating frequency 56.4 MHz) and the Bruker HX-90 Fourier transform machine operating at 90 MHz for protons and at 15 MHz for  $^{13}\text{C}$ . The spectra were recorded at temperatures ranging from 18 to 90°C; the precision of the temperature measurements was about  $\pm 0.5^\circ\text{C}$ .

#### ANALYSIS OF THE SPECTRA

The spectra of acetylene-1- $^{13}\text{C}$  and acetylene-1,2- $^{13}\text{C}$  can be easily interpreted since there are recognizable subspectra (3) of the types  $A_2$  and AB in the A and X parts of the AA'X and AA'XX' spectra of the two molecules. A final refinement of the parameters has been made by means of the LAOCOONOR program (4).

Where possible, the indirect couplings have been also determined from the iterative analysis and their values have been checked in an isotropic solution of acetylene in Phase IV at 90°C. The results of the spectral analysis are summarized in Table 1.

#### THE VIBRATIONAL CORRECTION, THE SHRINKAGE EFFECTS, AND THE EFFECTIVE STRUCTURE

Let us first see the ratios of the effective distances  $r_d$  (the subscript  $d$  indicates "obtained from the direct coupling") as determined from the standard formula

$$D_{ij} = -(h\gamma_i\gamma_j/4\pi^2)S/r_d^3, \quad [1]$$

where  $i$  and  $j$  specify the nuclear pair,  $S$  is the orientation parameter, and  $\gamma_i$  is the gyromagnetic ratio for the  $i$ th nucleus.

In our case, since  $S$  is common for all pairs of the nuclei involved, the distance ratios can be calculated directly from the ratios of the corresponding  $D$  values. The results for the particular case of  $(r_{\text{CH}}/r_{\text{CC}})_d$  are given in Table 2. Surprisingly, the distance ratios determined in this way from the Phase IV spectra depend strongly on the temperature (the total variation is about 24%!). We will defer the discussion of this effect to the next section and concentrate on the results obtained from the EBBA spectra.

Before we try to compare our results with the infrared data, we must correct them for the effect of vibrations. Proceeding along the lines outlined in Ref. (2), we put

$$r_d = r_z + K, \quad [2]$$

where  $r_z = r_e + \langle \Delta z \rangle$ ,  $r_e$  being the equilibrium distance, and, for acetylene,

$$K = (\langle \Delta x^2 \rangle + \langle \Delta y^2 \rangle - 2 \langle \Delta z^2 \rangle) / r_e, \quad [3]$$

where  $\Delta x$ ,  $\Delta y$ , and  $\Delta z$  are the  $x$ ,  $y$ , and  $z$  components of the vibrational amplitudes, respectively. The coordinate axes have been chosen in such a way that the  $z$ -axis

TABLE 1  
RESULTS OF THE SPECTRAL ANALYSIS

Liquid crystal Nucleus studied	EBBA H	EBBA <sup>a</sup> H	EBBA <sup>13</sup> C	Phase IV H	Phase IV H <sub>  </sub>	Phase IV <sup>13</sup> C	Phase IV <sup>13</sup> C
Temperature (°C)	27.5	27.5	26.0	18.0	40.0	44.0	90.0
Pressure (atm)	7	9.5	7	7	7	7	7
$J_{CH}$ (Hz)	249.0 <sup>b</sup>	249.0 <sup>b</sup>	249.0 <sup>b</sup>	249.0 <sup>b</sup>	249.0 <sup>b</sup>	249.0 <sup>b</sup>	248.6 ± 0.4
$J_{CH'}$ (Hz)	49.1 <sup>b</sup>	49.1 <sup>b</sup>	49.1 <sup>b</sup>	49.1 <sup>b</sup>	49.1 <sup>b</sup>	49.1 <sup>b</sup>	49.1 ± 0.4
$J_{HH}$ (Hz)	9.9 ± 1.2	9.5 ± 0.5	9.6 <sup>b</sup>	9.7 ± 0.4	9.3 ± 0.4	9.6 <sup>b</sup>	9.5 ± 0.4
$J_{CC}$ (Hz)	169.7 <sup>b</sup>	169.7 <sup>b</sup>	169.6 <sup>b</sup>	169.7 <sup>b</sup>	169.7 <sup>b</sup>	170.1 ± 1.8	169.8 ± 0.6
$D_{CH}$ (Hz)	1315.0 ± 0.7	783.6 ± 0.2	1340.9 ± 0.9	267.4 ± 0.1	99.0 ± 0.2	77.6 ± 0.6	—
$D_{CH'}$ (Hz)	140.0 ± 0.5	83.3 ± 0.2	143.3 ± 0.3	25.7 ± 0.1	7.7 ± 0.2	6.1 ± 0.6	—
$D_{HH}$ (Hz)	179.8 ± 0.3	106.9 ± 0.2	182.6 ± 0.3	33.9 ± 0.1	11.0 ± 0.1	9.6 ± 1.3	—
$D_{CC}$ (Hz)	224.2 ± 1.2	133.4 ± 0.4	229.4 ± 0.3	37.9 ± 0.7	8.5 ± 1.2	4.9 ± 0.7	—

<sup>a</sup> With addition of CHCl<sub>3</sub> and CH<sub>4</sub> as internal references.

<sup>b</sup> Assumed.

TABLE 2

ORIENTATION PARAMETERS, DISTANCE RATIOS, AND SHRINKAGE EFFECTS

Liquid crystal	Nucleus studied	Temperature (°C)	$S_{CC}$	$\left(\frac{r_{CH}}{r_{CC}}\right)_d$	$\left(\frac{r_{CH}}{r_{CC}}\right)_z$	$\delta_{CH}$ (Å)	$\delta_{HH}$ (Å)
EBBA	H	27.5	-0.0519	0.878(2) <sup>b</sup>	0.847(2)	0.030(6)	0.065(7)
EBBA <sup>a</sup>	H	27.5	-0.0309	0.878(2)	0.847(2)	0.030(4)	0.065(4)
EBBA	<sup>13</sup> C	26.0	-0.0531	0.879(1)	0.848(1)	0.031(2)	0.060(3)
Phase IV	H	18.0	-0.0088	0.826(7)	0.797(7)	—	—
Phase IV	H	27.5	-0.0056	0.796(9)	0.768(9)	—	—
Phase IV	H	40.0	-0.0020	0.699(30)	0.674(30)	—	—
Phase IV	<sup>13</sup> C	44.0	-0.0011	0.631(30)	0.609(30)	—	—

<sup>a</sup> With internal reference of CHCl<sub>3</sub> and CH<sub>4</sub>.

<sup>b</sup> The values in parentheses represent the expected error in the last decimal digits.

coincides with the  $C_{\infty}$  symmetry axis of the molecule. The values of the  $K$ 's have been calculated from the mean-square amplitudes given by Cyvin (5); at normal temperatures  $K_{CH} = 0.0388 \text{ \AA}$ ,  $K_{CC} = 0.0011 \text{ \AA}$ ,  $K_{CH'} = 0.0114 \text{ \AA}$ , and  $K_{HH} = 0.0155 \text{ \AA}$ . Since the difference between  $r_d$  and  $r_e$  is always very small, the vibrational correction needed to transform  $r_d$  into  $r_z$  is closely approximated by  $v = -K/r_e$  (in %). Using Cyvin's data, we find  $v_{CH} = -3.66\%$ ,  $v_{CC} = -0.09\%$ ,  $v_{CH'} = -0.50\%$ , and  $v_{HH} = -0.47\%$ . The vibrational correction for the distance ratio  $r_{CH}/r_{CC}$ , for example, is then equal to  $v_{CH} - v_{CC}$ , i.e., about  $-3.57\%$ .

The corrected distance ratios can now be compared with the corresponding infrared data. Lafferty and Thibault (6) report  $(r_{CH})_z = 1.064 \text{ \AA}$  and  $(r_{CC})_z = 1.206 \text{ \AA}$ . The IR value of  $(r_{CH}/r_{CC})_z$  is therefore 0.882 (the experimental error of this number is probably less than 0.1%). From the results in Table 2, it is evident that the NMR values are consistently smaller. The discrepancy is only 4% for the EBBA samples but in the Phase IV samples it ranges from 10% to a whopping 31%.

Using the IR value of  $(r_{CC})_z$  and the vibrational corrections derived above, we obtain  $(r_{CC})_d = 1.207 \text{ \AA}$ . This value has been used to calculate the  $S$  parameters from the experimental  $D_{CC}$  values. The most notable feature of the results (see Table 2) is the unusually strong temperature dependence of this quantity. A strong temperature dependence would indicate large orientation energy but that is contrary to the fact that the absolute values of the orientation parameter are very small.

Ignoring for a moment the 4% discrepancy, let us try to use the EBBA spectra for the determination of the shrinkage effects. The latter are defined (5) by

$$\delta_{CH'} = (r_{CC} + r_{CH} - r_{CH'})_d = K_{CC} + K_{CH} - K_{CH'}, \quad [4]$$

$$\delta_{HH} = (r_{CC} + 2r_{CH} - r_{HH})_d = K_{CC} + 2K_{CH} - K_{HH}. \quad [5]$$

Using the experimental  $D$  values to calculate the effective distance ratios and combining these with the IR value for  $(r_{CC})_d$ , one obtains the  $\delta$  values presented in Table 2. On the other hand, the  $K$  values derived from the normal coordinate analysis (see above) lead to  $\delta_{CH'} = 0.0285 \text{ \AA}$  and  $\delta_{HH} = 0.0632 \text{ \AA}$ . The agreement is excellent but we must point out that similar calculations based on the Phase IV spectra lead to completely wrong results at high temperatures.

#### DISCUSSION OF THE APPARENT ANOMALIES

The anomalous temperature dependence of the  $S$  and  $D$  values and the discrepancies in the apparent distance ratios indicate the presence of an interfering process which modifies the  $D$  values in a nontrivial way. From the discussion in the preceding section it is clear that there is no connection between this interfering process and the vibrational effects. Compared with the observed anomalies, the vibrational corrections are of opposite sign and their magnitudes are too small. We will consider several possible explanations of the anomalies in question. Anticipating somewhat the results, we may say that only one of them is satisfactory and we will start with that one.

Suppose that the solute molecules can be divided into a number of classes according to their surroundings or to their internal state. We will use the rather broad term "site" to describe the particular class of the solute molecules. The existence of such distinct sites may be a general property of the particular liquid crystal or it may be due

to some specific interaction such as complex formation. In both of these cases, the term "site" may be taken quite literally. The same theory would however, also describe the cases in which the molecules are classified according to their different conformations; the term "site" would then coincide with the term "conformer".

We will further assume that the exchange of the molecules between different sites is fast enough so that the observed spectrum can be described in terms of an average Hamiltonian rather than as a superposition of several spectra.

Limiting ourselves to the simplest case of two sites, the effective  $D$  values are

$$D_{ij}(T) = p(T)S_{ij}(T)G_{ij}(T) + p'(T)S'_{ij}(T)G'_{ij}(T), \quad [6]$$

where the prime is used to discriminate between quantities referring to different sites,  $T$  is the absolute temperature,  $p(T)$  is the fraction of the solute molecules which are at the particular site,  $S_{ij}(T)$  is the orientation parameter for the nuclear pair  $ij$ , and  $G_{ij}(T)$  is the corresponding geometric parameter including both the direct coupling term  $-(h\gamma_i\gamma_j/4\pi^2)/r_{ij}^3$  and the anisotropic part of the indirect coupling.

Given the linearity of the molecule,  $S_{ij}(T)$  and  $S'_{ij}(T)$  are the same for all pairs of the nuclei involved so that the subscripts  $i$  and  $j$  can be dropped. We will put

$$S'(T) = \alpha(T)S(T), \quad [7a]$$

$$G'_{ij}(T) = \beta_{ij}(T)G_{ij}(T), \quad [7b]$$

$$p'(T) = \zeta(T)p(T), \quad [7c]$$

introducing thus the quantities  $\alpha(T)$ ,  $\beta_{ij}(T)$ , and  $\zeta(T)$ . The temperature dependence of  $\zeta(T)$  will be assumed to be of the Arrhenius type:

$$\zeta(T) = \kappa e^{\varepsilon/T}, \quad [8]$$

where  $\varepsilon = \Delta H/R$ ,  $\Delta H$  being the enthalpy difference between the two sites, and  $\kappa$  is the weight factor related to the entropy difference.  $\varepsilon$  is a positive quantity provided that the unprimed parameters refer to the site with higher enthalpy (the free form in the case of complex formation). Since  $p + p' = 1$ , Eq. [8] gives

$$p(T) = (1 + \kappa e^{\varepsilon/T})^{-1}. \quad [9]$$

Let us assume that (i) the geometric parameters  $G_{ij}(T)$  and  $G'_{ij}(T)$  are independent of the temperature and (ii) the temperature dependences of  $S(T)$  and  $S'(T)$  are similar since both of them just reflect the temperature dependence of the orientation of the liquid crystal molecules. The first assumption makes it possible to write  $G_{ij}$ ,  $G'_{ij}$ , and  $\beta_{ij}$  instead of  $G_{ij}(T)$ ,  $G'_{ij}(T)$ , and  $\beta_{ij}(T)$ , respectively, while the second amounts to  $\alpha(T) = \alpha$ , where  $\alpha$  is a constant.

With these assumptions, Eq. [6] can be written in a much simpler form:

$$D_{ij}(T) = p(T)S(T)G_{ij}(1 - \mu_{ij}e^{\varepsilon/T}), \quad [10]$$

where

$$\mu_{ij} = -\alpha\kappa\beta_{ij}.$$

We have already noticed that the experimental  $D$  values decrease with temperature much faster than could be expected from the decrease of orientation of the liquid crystal itself. According to Eq. [9],  $p(T)$  increases with temperature. The fast decrease of  $D_{ij}(T)$  must therefore be due to the bracketed term in Eq. [10]. This necessarily

means that  $\mu_{ij} > 0$  and, in consequence,  $\alpha < 0$ . In other words, the orientation parameters at the two sites must be of opposite sign in order to give the observed effect. This is in agreement with the small magnitudes of the apparent (average)  $S$  values (see Table 2).

It is convenient to introduce new parameters  $T_{ij}$  such that

$$\mu_{ij} = \exp(-\varepsilon/T_{ij}). \quad [11]$$

Then

$$D_{ij}(T) = p(T)S(T)G_{ij}\{1 - \exp[\varepsilon(T^{-1} - T_{ij}^{-1})]\}. \quad [12]$$

$T_{ij}$  is obviously the temperature at which the extrapolated  $D_{ij}(T)$  curve would pass through zero.

Consider now two pairs of nuclei ( $ij$ ) and ( $kl$ ) and write

$$A_{kl}^{ij}(T, T_1) = \frac{D_{ij}(T)}{D_{kl}(T)} \bigg/ \frac{D_{ij}(T_1)}{D_{kl}(T_1)} = \frac{\exp[\varepsilon(T^{-1} - T_{ij}^{-1})] - 1}{\exp[\varepsilon(T^{-1} - T_{kl}^{-1})] - 1} \bigg/ \frac{\exp[\varepsilon(T_1^{-1} - T_{ij}^{-1})] - 1}{\exp[\varepsilon(T_1^{-1} - T_{kl}^{-1})] - 1}, \quad [13]$$

where  $T_1$  is a chosen reference temperature. If the dominant contribution to the  $D$ 's comes from the direct interactions,  $A_{kl}^{ij}(T, T_1)$  is just the cube of the factor by which the apparent distance ratio  $r_{kl}/r_{ij}$  is multiplied when the temperature is changed from  $T_1$  to  $T$ . That large effects are feasible is evident from the fact that if  $T_{ij} \neq T_{kl}$ , then  $A_{kl}^{ij}(T_{ij}, T_1) = 0$  and  $A_{kl}^{ij}(T_{kl}, T_1) = \pm \infty$ . It is also interesting to notice that if  $T_{ij} = T_{kl}$ , then  $A_{kl}^{ij}(T, T_1) = 1$ . The anomalous temperature dependence of the  $D$ 's therefore does not necessarily imply the temperature dependence of the apparent distance ratios. For the latter to occur, it is necessary that  $T_{ij} \neq T_{kl}$ , i.e.,  $\beta_{ij} \neq \beta_{kl}$ . In other words, the bond lengths  $r_{ij}$  and  $r_{kl}$  must change by different relative amounts when going from one site to another.

Since the values of  $A_{kl}^{ij}(T, T_1)$  can be determined from the experimental data, one can use them for a least-squares adjustment of the parameters  $\Delta H$ ,  $T_{ij}$ , and  $T_{kl}$ . In our case, it turned out that the  $A_{kl}^{ij}(T, T_1)$  curves were strikingly insensitive to  $\Delta H$ . Adjusting the parameters  $T_{ij}$  and  $T_{kl}$ , an excellent fit can be obtained for any value of  $\Delta H$  ranging from 0 to about 12 kcal/mole. The optimal parameters  $T_{ij}$  and  $T_{kl}$  thus become functions of  $\Delta H$ . In our case, however, they were practically constant throughout the whole range of  $\Delta H$ , their values being  $T_{CC} = 323.9^\circ\text{K}$ ,  $T_{CH} = 331.4^\circ\text{K}$ ,  $T_{HH} = 333.4^\circ\text{K}$ , and  $T_{CH} = 338.6^\circ\text{K}$ .

It may seem surprising that our theory does admit a pronounced temperature dependence of the apparent distance ratios even for an arbitrarily small  $\Delta H$ . Actually, whenever the critical temperatures  $T_{ij}$  and  $T_{kl}$  are outside the nematic range of the liquid crystal (our case), the effect becomes less pronounced for larger values of  $\Delta H$ . This is due to the easily verifiable fact that if  $\Delta H \rightarrow \infty$ , then  $A_{kl}^{ij}(T, T_1) \rightarrow 1$ . A strict lower limit for  $\Delta H$  can, however, be derived from Eq. [12] or its equivalent,

$$D_{ij}(T) = p'(T)S'(T)G'_{ij}\{1 - \exp[-\varepsilon(T^{-1} - T_{ij}^{-1})]\}, \quad [14]$$

since  $D_{ij}(T) \rightarrow 0$  whenever  $\Delta H \rightarrow 0$ . In our case, the  $D$ 's are positive, the  $G$ 's are negative, and  $T < T_{ij}$  so that  $S > 0$  and  $S' < 0$ . Then  $|p'S'| < \frac{1}{2}$  and Eq. [14] gives

$$\Delta H > -R(T^{-1} - T_{ij}^{-1})^{-1} \ln(1 - 2S_{ij}^*) = \Delta H_{\min}, \quad [15]$$

where  $S_{ij}^* = D_{ij}(T)G'_{ij}$  is the apparent orientation parameter. The value  $\Delta H = \Delta H_{\min}$  is actually unattainable since it would imply  $p' = 1$ . A realistic lower limit for  $\Delta H$  is about  $2\Delta H_{\min}$ . Using the value of  $S_{CC}^*$  at  $18^\circ\text{C}$  (see Table 2), this gives  $\Delta H \gtrsim 200$  cal/mole.

The  $D_{ij}(T)$  curves cannot be directly fitted since only a guess can be made for the temperature dependence of  $S(T)$ . In order to check whether our theory is consistent with the shape of the empirical  $D_{ij}(T)$  curves, we have inverted the argument and examined the ratio

$$\frac{S(T)}{S(T_1)} = \frac{D_{ij}(T) p(T_1)}{D_{ij}(T_1) p(T)} \frac{\exp[\varepsilon(T_1^{-1} - T_{ij}^{-1})] - 1}{\exp[\varepsilon(T^{-1} - T_{ij}^{-1})] - 1}, \quad [16]$$

where  $p(T)$  is given by Eq. [9]. Using the experimental values of  $D_{ij}(T)$  and the values of  $T_{ij}$  derived above, Eq. [16] yields a two-parametric family of curves, the parameters being  $\Delta H$  and  $\kappa$ . It turns out that for small  $\Delta H$ , the curves are almost insensitive to  $\kappa$  within its whole range  $0 \leq \kappa < \infty$ . For higher values of  $\Delta H$ , the sensitivity to  $\kappa$  becomes more pronounced. For any  $\Delta H$  from 0 to 12 kcal/mole, however, there exists a rather wide region of  $\kappa$  values leading to quite reasonable shapes of the  $S(T)/S(T_1)$  curve. This proves that although the shapes of the  $D_{ij}(T)$  curves cannot be used to delimit better the parameters involved, they are at least consistent with our theory.

We will now try to determine the magnitudes of the changes in the molecular geometry when going from one site to the other. Let

$$r'_{ij} = r_{ij}(1 + d_{ij}). \quad [17]$$

Then, assuming that  $D_{ij}$  is strictly proportional to  $r_{ij}^{-3}$ ,

$$(1 + d_{kl})^3 / (1 + d_{ij})^3 = \beta_{ij} / \beta_{kl} = \mu_{ij} / \mu_{kl} = \exp[\varepsilon(T_{kl}^{-1} - T_{ij}^{-1})]. \quad [18]$$

When  $d_{ij} \ll 1$ , this equation reduces to

$$d_{kl} - d_{ij} = 1/3\{\exp[\varepsilon(T_{kl}^{-1} - T_{ij}^{-1})] - 1\} = \Delta_{kl}^{ij}. \quad [19]$$

Let us assume for a moment that the changes in geometry are additive (this might not be true, for example, if the effect were due to a difference in the mean-square vibrational amplitudes at the two sites). Then

$$\begin{aligned} d_{\text{CH}'} &= (r_{\text{CC}}/r_{\text{CH}'})d_{\text{CC}} + (r_{\text{CH}}/r_{\text{CH}'})d_{\text{CH}}, \\ d_{\text{HH}} &= (r_{\text{CC}}/r_{\text{HH}})d_{\text{CC}} + 2(r_{\text{CH}}/r_{\text{HH}})d_{\text{CH}}, \end{aligned} \quad [20]$$

which, when combined with Eqs. [19], gives

$$\Delta_{\text{CC}}^{\text{HH}} = 2(r_{\text{CH}}/r_{\text{HH}})\Delta_{\text{CC}}^{\text{CH}} \quad [21]$$

and

$$\Delta_{\text{CC}}^{\text{CH}'} = (r_{\text{CH}}/r_{\text{CH}'})\Delta_{\text{CC}}^{\text{CH}}. \quad [22]$$

Equations [21, 22] can be used as a check of the additivity. Using  $r_{\text{CH}}/r_{\text{CH}'} = 0.469$  and  $r_{\text{CH}}/r_{\text{HH}} = 0.319$  (values based on the IR data), the values of  $\Delta_{\text{CC}}^{\text{HH}}$  and  $\Delta_{\text{CC}}^{\text{CH}'}$  determined via Eqs. [21, 22] differ from those calculated directly from Eq. [19] by less than 10% for any  $\Delta H$  from 0 to 12 kcal/mole. Given the smallness of the quantities involved and



the uncertainties due to the experimental errors in the temperature measurements, this is not a bad agreement.

In Table 3 we have listed the values of  $\Delta_{CC}^{CH} = d_{CC} - d_{CH}$  calculated from Eq. [19] as a function of  $\Delta H$ . These show that the ratio  $r_{CH}/r_{CC}$  is smaller at the primed site (the complex) than at the unprimed site (the free form). The dominant contribution to  $\Delta_{CC}^{HC}$  is most likely due to a shortening of the CH-bond in the complex.

TABLE 3

SITE-DEPENDENT VARIATIONS IN BOND LENGTHS AND THE CORRECTED DISTANCE RATIOS AS FUNCTIONS OF  $\Delta H$ .

$\Delta H(\text{cal/mole})$	$\Delta_{CC}^{CH}$	$(r_{CH}/r_{CC})^a$	$(r_{CH}/r_{CC})_z$
200	0.45	0.923(7)	0.890(7)
400	0.91	0.925(7)	0.892(7)
600	1.36	0.927(7)	0.894(7)
800	1.83	0.929(7)	0.896(7)
1000	2.31	0.931(7)	0.898(7)
1200	2.79	0.934(7)	0.900(7)
1600	3.77	0.938(7)	0.905(7)

<sup>a</sup> Calculated via Eq. [23] from the Phase IV spectra at 18°C. The critical temperatures are (in °K):  $T_{CC} = 323.9$ ,  $T_{CH} = 331.4$ ,  $T_{HH} = 333.4$ , and  $T_{CH} = 338.6$ .

The absolute value of  $\Delta_{CC}^{CH}$  is a sensitive function of  $\Delta H$ . Since changes in the bond-lengths ratios greater than ~3% are very unlikely,  $\Delta H$  should not exceed about 1.5 kcal/mole. The most remarkable thing however, is, that even changes in geometry as small as 0.5% can, under suitable conditions, result in the apparent distance ratios differing from the true values by as much as 30% or more.

Neglecting the contributions to the  $G$ 's due to the anisotropy of the indirect couplings, Eq. [12] gives

$$\frac{G_{ij}}{G_{kl}} = \frac{D_{ij}(T) \exp[\varepsilon(T^{-1} - T_{kl}^{-1})] - 1}{D_{kl}(T) \exp[\varepsilon(T^{-1} - T_{ij}^{-1})] - 1} = \frac{\gamma_k \gamma_l r_{ij}^3}{\gamma_i \gamma_j r_{kl}^3} \quad [23]$$

This relation can be used for determination of the true distance ratios. Unfortunately, the uncertainty in  $\Delta H$  makes it again necessary to calculate the distance ratios as functions of this parameter. The value of  $r_{CH}/r_{CC}$  obtained in this way from the data for  $T = 18^\circ\text{C}$  (see Table 3) increases slightly with increasing  $\Delta H$ . When corrected for the vibrational effects, it is in a very good agreement with the IR value of 0.882 provided that  $\Delta H \approx 200\text{--}400$  cal/mole. The ratios derived from Eq. [23] refer to the unprimed site (the free form); at the primed site the ratio  $r'_{CH}/r'_{CC}$  is slightly smaller.

The effect of Eq. [23] on the temperature dependence of the apparent distance ratio can be seen from Fig. 1.

Considering the smallness of the required enthalpy difference in the two-site theory, it would surely be more realistic to consider a continuous distribution of sites rather than just two of them. In such a theory, the sum over the two sites in Eq. [6] would be

substituted by an integral over the site distribution. From the preceding analysis of the two-site case, it is clear, however, that such an approach would involve so many free parameters as to make it virtually intractable. Moreover, it is extremely unlikely that the qualitative conclusions of the preceding case would be altered.

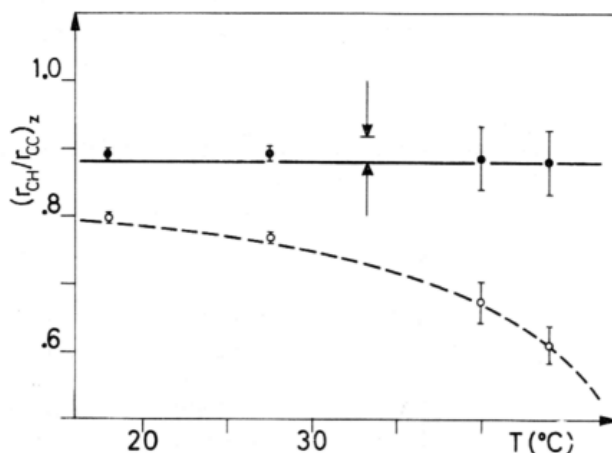


FIG. 1. The apparent (○) and corrected (●) distance ratios for acetylene in Phase IV. The solid line is the IR value while the broken curve has been calculated from Eq. [23] using the IR value as a basis and assuming  $\Delta H = 300$  cal/mole. The arrows indicate the magnitude of the vibrational correction.

We have also considered the possibility that none of the many-site theories might be correct and that the anomalies arise from a correlation between the orientation and the geometry of the molecule. Although such an effect could explain the behaviour of the apparent distance ratios, it can not explain the strong temperature dependence of the  $D$ 's. The details of the relevant theory will be presented elsewhere on their own merits. Here, we can just say that numerical calculations show that in order to explain the observed temperature dependences, one would have to assume orientation-dependent variations in the molecular geometry comparable to the apparent distance ratio anomalies.

### CONCLUSIONS

We have shown that our data can be interpreted within the two-site theory under quite reasonable assumptions. The molecular geometry determined in this way is in excellent agreement with the IR data, and the anomalous temperature dependences of the  $D$  values and of the apparent distance ratios are all properly explained. The most important feature of the theory, however, is the realization that even very small deformations connected with complex formation can lead to large errors in the determination of distance ratios. This "amplification effect" will become pronounced whenever (i) the orientations at the two sites are of opposite sign and (ii) some of the critical temperatures at which the extrapolated  $D(T)$  curves change sign fall near to or within the nematic range of the liquid crystal. An accompanying symptom of this situation is the unusually strong temperature dependence of the  $D$  (and  $S$ ) values.

As to the nature of the acetylenic complex, the most obvious (though speculative) possibility is a bond between the acetylenic hydrogen and the  $\pi$ -orbitals of the aromatic rings of the liquid crystal. Such a complex formation would also explain why

the preferred orientation of acetylene in most liquid crystals is such that the  $C_{\infty}$  molecular axis and the optical axis of the nematic phase are mutually perpendicular (1, 7, 8). The observed discrepancy between the distance ratios derived from the EBBA spectra and those determined from the IR data might be due to the same phenomenon provided that the critical temperatures in this case are far above the nematic-isotropic transition.

The existence of two sites with substantially different orientation distributions had been observed earlier in at least two cases (9, 10). Since even quite weak specific interactions can in some cases lead to considerable errors in the apparent distance ratios, the phenomena discussed in this paper are possibly not uncommon.

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