

TABLE IV  
VALUES OF  $(1 - 3 \cos^2 \theta) / 3R^3$  FOR VARIOUS BOND CONFIGURATIONS  
(STAGGERED DIAMOND LATTICE WITH A C-C BOND OF 1.542 Å.  
ASSUMED)

Bond	Conformation designation <sup>a</sup>	$(1 - 3 \cos^2 \theta) / 3R^3$ in $10^{22}$ cm. <sup>-3</sup>	Bond	Conformation designation <sup>a</sup>	$(1 - 3 \cos^2 \theta) / 3R^3$ in $10^{22}$ cm. <sup>-3</sup>
$\alpha\beta$		-1.45	$\delta\epsilon$	GTT	-0.02
$\beta\gamma$	T	-1.42		TGG	+ .35
	G	+1.36		TGG'	+ .35 <sup>b</sup>
$\gamma\delta$	TT	-0.27		GTG	+ .35
	TG	+0.35		GTG'	- .02
	GT	-1.05		GGT	- .23
	GG	+0.53		GG'T	-1.42 <sup>b</sup>
	GG'	+1.36 <sup>b</sup>		GGG	-0.23
$\delta\epsilon$	TTT	-0.22		GGG'	+0.53 <sup>b</sup>
	TTG	+ .23		GG'G	-1.45 <sup>b</sup>
	TGT	- .44		GG'G'	+1.36 <sup>b</sup>

<sup>a</sup> Conformations which are mirror images to those given in the table have the same value. <sup>b</sup> These conformations are not allowed between carbon atoms in the paraffin series as two hydrogen atoms would occupy the same lattice position.

C-C bond distance equal to 1.542 Å. The vector  $R$  begins at the carbon for which the chemical shift is determined and terminates at the midpoint of the bond in question.

That the model for magnetic anisotropy of a C-C bond cannot explain the long-range shifts noted here, there can be little doubt; nevertheless, it is interesting

to note that the shifts are correlated in an empirical manner by an expression of the same form. Although no satisfactory explanation of the phenomena is presently available, it seems likely that the effect will only be explained in terms of more direct interactions between remote groups and the electronic structure of the carbon atom under consideration. The possibility of pseudo-six-member ring formation with four carbon atoms in a chain and the two attached hydrogens might well be a better explanation for the  $\gamma$ -carbon effect. This interaction would be very reminiscent of Newman's "rule of six"<sup>22</sup> in which sixth position hydrogen atoms greatly affect reaction rates. The energies associated with such interactions are sufficiently large to change the specific rate constants by several orders of magnitude. An interaction of this nature may well be large enough to modify slightly the electronic structure of the carbon atom. Admixture of higher paramagnetic orbitals or alteration in the degree of bond delocalization at the carbon atom due to this pseudo-six-member ring may be important in changing the chemical shift parameter. Both of these possibilities offer a means of explaining why a carbon atom would be affected by a remote  $\gamma$ -group, whereas no similar shifts of the magnitude discussed here have been observed in proton magnetic resonance spectra.

(22) M. S. Newman, "Steric Effects in Organic Chemistry," John Wiley and Sons, Inc., New York, N. Y., 1956, p. 204.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF COLORADO, BOULDER, COLORADO]

## Nuclear Magnetic Resonance Studies of Hydrogen Bonding.

### II. Calculation of the Shift upon Complex Formation<sup>1a,b</sup>

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The shift upon hydrogen bond formation for the weak hydrogen bonds formed between chloroform and nitrogen bases was assumed to arise from two contributions: (a) the Buckingham electric field effect and (b) the neighbor anisotropy effect. The magnitudes of these two effects were then obtained as functions of the various parameters entering into the calculation. The electric fields were found by integrating over approximate nitrogen lone-pair electron distributions. The Pople-McConnell dipolar approximation was used to estimate effect (b). The results proved to be insensitive to all the parameters except the hydrogen bond length. Therefore, experimental values of the shifts were used to find these lengths, which proved to be in accord with X-ray crystallographic data, and to increase as the hybridization of the lone pair went from  $sp^3$  to  $sp$ . It was concluded for these weak hydrogen bonds that the above two effects are an adequate explanation for the shift upon hydrogen bond formation, and that this shift is a good criterion of "basicity" for weak hydrogen bonds if magnetic anisotropy effects are small, or if they are approximately constant for a series of electron donors.

#### Introduction

It is now well documented that hydrogen bond formation causes a shift to low field of the n.m.r. signal of the proton involved.<sup>2</sup> The principal contributions to this shift were suggested some time ago<sup>2</sup> and are: 1. A contribution to the proton screening (always negative) due to the distortion of the electronic structure of the chemical bond in which the proton is participating. 2. A contribution (negative or positive) to the proton screening due to any magnetic anisotropy

of the molecule to which the proton is hydrogen-bonded.

Buckingham<sup>3</sup> has suggested how the magnitude of the first effect ( $\Delta_E$ ) might be estimated, if it can be ascribed as solely due to polarization of the H-X bonding electrons by the electric field arising from the proximity of the electron donor molecule. He has derived the relation

$$\Delta_E = k_E \times 10^{-12} E_z - 0.738 \times 10^{-18} E^2 \quad (1)$$

where  $k_E$  is a proportionality constant,  $E_z$  is the magnitude of the field strength along the H-X bond axis, and  $E$  is the total field magnitude. The first term is taken as negative since the lone-pair electrons of the base repel the H-X bonding electrons toward X. Since Buckingham's original paper,<sup>3</sup> values of  $k_E$  from

(1) (a) Supported in part by Directorate of Chemical Sciences, Air Force Office of Scientific Research, under Grant AF-AFOSR-216-63; (b) presented in part at the 146th National Meeting of the American Chemical Society, Denver, Colo., January, 1964; (c) Jersey Production Research Co. Fellow, 1962-1964.

(2) J. A. Pople, J. J. Bernstein, and W. G. Schneider, "High Resolution Nuclear Magnetic Resonance," McGraw-Hill Book Co., Inc., New York, N. Y., 1959, Chapter 15.

(3) A. D. Buckingham, *Can. J. Chem.*, **38**, 300 (1960).

−3.4 to −2.6 have been used in the literature. The successful application of (1) in other areas<sup>4</sup> suggests that it could be used to calculate a good quantitative value for the polarization contribution to the hydrogen-bond shift.

The second effect ( $\Delta_N$ ) can be estimated by the dipolar approximation of Pople<sup>5a</sup> and McConnell<sup>5b</sup>

$$\Delta_N = \frac{\Delta\chi}{3R_N^3} (1 - 3 \cos^2 \gamma) \quad (2)$$

where  $R_N$  is the magnitude of the radius vector drawn from the proton to the center of anisotropy,  $\Delta\chi$  is the difference in the magnetic susceptibilities of the anisotropic group parallel and perpendicular to the bond axis, and  $\gamma$  is the angle between the latter axis and the radius vector.

It is the purpose of this paper to estimate the magnitude of these two effects for the hydrogen bonding of chloroform to nitrogen bases. In these weak complexes, it appears that all of the distortion of the electronic structure of the C–H bond can be ascribed to polarization.<sup>6</sup> Thus the dominant contributions to the hydrogen bond shift are just polarization and magnetic anisotropy. An additional advantage for the study of these particular complexes is that the values of the actual shifts upon complex formation are known, rather than just the observed dilution shifts.<sup>7</sup>

The parameters involved in such a calculation are the hydrogen bond length  $R$ , the magnetic anisotropy of the bond  $\Delta\chi$ , the electric field chemical shift proportionality constant  $k_E$ , and the type of orbitals used to represent the lone-pair electron distribution. It will be shown in this work that the hydrogen bond shift is relatively insensitive to all of these parameters *except* the hydrogen bond length  $R$ .

Calculations of n.m.r. hydrogen bond shifts have been carried out by Granacher for phenol with various bases.<sup>8</sup> These calculations, however, used electric dipoles as the basis for electric field magnitudes, the dangers of which will be discussed below. Also, these systems are more complex than chloroform–nitrogen base systems, owing to possible rehybridization of the electron donor, to the significant lengthening of the OH bond, and to the anisotropy shifts from ring currents.

Hameka has estimated the hydrogen bond shift in ammonia,<sup>9</sup> but later indicated serious doubts concerning the validity of the results.<sup>10</sup>

### Experimental

The values of the shifts upon complex formation,  $\Delta_{AD}$ , for several nitrogen bases, and of the equilibrium constant,  $K$ , are presented in Table I. The methods used, and the data for all except the cyclohexyl cyanide and isocyanide, were given pre-

(4) J. I. Musher, *J. Chem. Phys.*, **37**, 34 (1962).

(5) (a) J. A. Pople, *Proc. Roy. Soc. (London)*, **A239**, 541, 550 (1957);

(b) H. M. McConnell, *J. Chem. Phys.*, **27**, 226 (1957).

(6) This supposition is confirmed by the results obtained in this work. A calculation of the dipole induced in a hydrogen atom by an electric field (the model used by Buckingham for the derivation of eq. 1) provides further evidence. Using an electric field of  $0.5 \times 10^6$  e.s.u. and a polarizability of  $6.7 \times 10^{-25}$  cc., one obtains 0.3 D. in good agreement with the experimental value (0.4 D.) for the chloroform–triethylamine complex found by C. F. Jumper, Thesis, Florida State University, 1961. Undoubtedly, there is some polarization of the lone-pair electrons toward the proton, but this effect is negligible because of the weakness of the C–H bond dipole.

(7) P. J. Berkeley, Jr., and M. W. Hanna, *J. Phys. Chem.*, **67**, 846 (1963).

(8) I. Granacher, *Helv. Phys. Acta*, **34**, 272 (1961).

(9) H. F. Hameka, *Nuovo Cimento*, **11**, 382 (1959).

(10) H. F. Hameka, *Rev. Mod. Phys.*, **34**, 87 (1962).

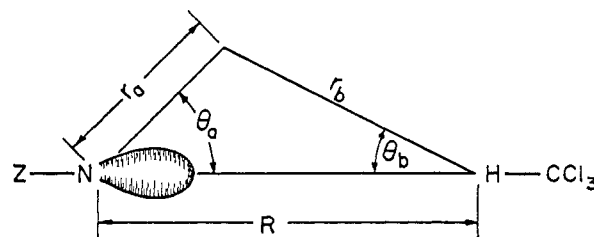


Fig. 1.—Geometric notation used in the calculations.

viously.<sup>7</sup> The isocyanide was prepared as outlined by Ugi and Meyer,<sup>11</sup> and the cyanide as outlined by Tilford, *et al.*<sup>12</sup>

TABLE I  
EXPERIMENTAL PROPERTIES OF  $\text{CHCl}_3$ -NITROGEN BASE  
COMPLEXES

Base	$K$ , mole fraction	$\Delta_{AD}$ , c.p.s., 60 Mc.
N-Methylpyrrolidine	2.2	−123
$\text{CH}_3\text{CH}=\text{NCH}(\text{CH}_3)_2$	5.2	−119
Cyclohexyl cyanide	1.9	−46.6
Cyclohexyl isocyanide	1.8	−45.7

TABLE II  
CONTRIBUTIONS TO THE HYDROGEN BOND SHIFT

Compound	$\Delta_{AD}$ , c.p.s. <sup>a</sup> (exptl.)	$R$ , Å (calcd.)	$\Delta_N$ , c.p.s. <sup>a</sup> (calcd.)	$\Delta_E$ , c.p.s. <sup>a</sup> (calcd.)
N-Methylpyrrolidine	−123	2.42	0	−123
$\text{CH}_3\text{CH}=\text{NCH}(\text{CH}_3)_2$	−119	2.53	−8.2	−111
Cyclohexyl cyanide	−46.6	2.72	+35.9	−82.5

<sup>a</sup> At 60 Mc.

### Evaluation of the Shift Due to Polarization

In order to use the theory of Buckingham,<sup>3</sup> the total electric field,  $E$ , and the field along the C–H bond axis,  $E_z$ , must be calculated. In the case of hydrogen bonding of  $\text{CHCl}_3$  to nitrogen bases, it will be assumed that the C–H bond lies along the axis of symmetry of the nitrogen lone pair, and that this lone pair is responsible for the electric field at the proton.<sup>13</sup> In atomic units, the field due to the lone pair is

$$E' = E_z = 2 \int |\psi_a|^2 \frac{\cos \theta_b}{r_b^2} dV \quad (3)$$

where the geometric notation is given in Fig. 1. The first task in the evaluation of eq. 3 is the choice of a suitable function,  $\psi_a$ . It will be assumed, without further justification, that nitrogen atomic orbitals are a satisfactory description of the lone-pair wave function. There still remain the questions of what atomic orbitals and what hybridization to use; however, it will be shown below that Slater 2s- and 2p-orbitals give essentially the same results for any hybridization from sp to  $sp^3$ . Thus the results are insensitive to the particular form of  $\psi_a$  as long as a reasonable choice is made. It should also be pointed out that the proper  $\psi_a$  for the free molecule is, of course, not the proper

(11) I. Ugi and R. Meyer, *Chem. Ber.*, **93**, 239 (1960).

(12) C. H. Tilford, M. G. Van Campen, and R. S. Shelton, *J. Am. Chem. Soc.*, **69**, 2902 (1947).

(13) A referee has raised the very important question as to the validity of this approximation. The effects of the electron and nuclear charge distribution from the rest of the molecule can be estimated using the dipole approximation. In all cases the maximum contribution to the electric field at the chloroform proton from the remaining electrical asymmetries is less than 5% of the contribution from the lone pair. Including these other asymmetries automatically compensates for any unscreened charge on the nitrogen atom above the value of +2 which is used in eq. 5. Owing to the great uncertainty in sign, location, and magnitude of the bond dipoles it is not profitable to treat this effect quantitatively. To obtain the 5% figure quoted above we have used a range of reasonable assumptions about the appropriate bond dipoles and calculated the effects on the electric field.

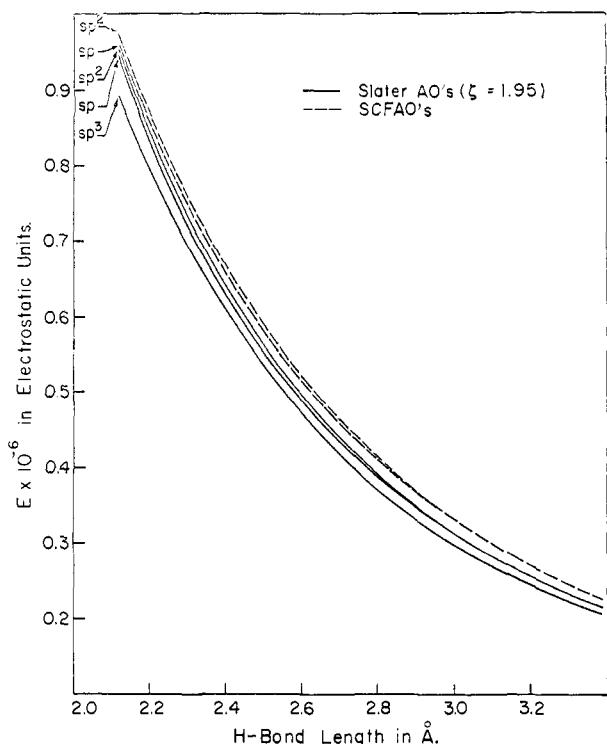


Fig. 2.--Influence of hybridization and choice of atomic orbital upon the electric field at the proton, due to the lone-pair electrons of the base.

$\psi_a$  for the complex. In the first approximation, the latter function is a polarized form of the former.

With these considerations in mind, a lone-pair wave function was used which has the form

$$\psi_a = \frac{2s_a + \lambda 2p_a}{\sqrt{1 + \lambda^2}} \quad (4)$$

where  $\lambda$  is a hybridization parameter. For Slater AO's only three Roothaan<sup>14</sup> charge distributions have to be considered—(2s)(2s), (2s)(2p $\sigma$ ), and (2p $\sigma$ )(2p $\sigma$ )—which give only three different integrals. However, with the SCF function,<sup>15</sup> three additional charge distributions have to be used—(1s)(1s), (1s)(2s), and (1s)(2p $\sigma$ )—which, with the other three, result in fifty-five different integrals when all combinations of orbital exponents are taken into account.

These integrals were evaluated using Geller's expression<sup>16</sup> for integral 3. The calculation was carried out on an IBM 709 computer, the necessary incomplete  $\gamma$ -functions being generated by a subprogram based on recurrence relations. The actual value of the electric field was obtained by subtracting out the field due to a plus two charge at the nitrogen nucleus and converting to electrostatic units

$$E = E_z = \frac{4.80 \times 10^{-10}}{(0.529)^2 \times 10^{-16}} [E' - 2/R^2] \quad (5)$$

Parenthetically, it is of interest to compare the results of Geller's method with those obtained by reducing the triple integrals to single integrals by the Barnett-Coulson technique,<sup>17</sup> and then evaluating these by

(14) C. C. J. Roothaan, *J. Chem. Phys.*, **19**, 1445 (1951).

(15) That for a 5S nitrogen atom as given by C. C. J. Roothaan and E. Clementi, *Phys. Rev.*, **127**, 1618 (1962).

(16) M. Geller, *J. Chem. Phys.*, **39**, 84 (1963).

(17) M. P. Barnett and C. A. Coulson, *Phil. Trans. Roy. Soc. London*, **A243**, 221 (1951).

Simpson's rule on the IBM 709. The values of  $E'$  agree to at least three significant figures. The two methods, therefore, give almost identical results, but there is no reason not to prefer the much faster and more exact method of Geller.

The effect of hybridization (for Slater atomic orbitals with an orbital exponent of 1.95) and of type of atomic orbital is examined in Fig. 2. The differences observed are negligible, especially in light of the uncertainty in converting from electric field to chemical shift, as discussed below. The maximum error in the abscissa is about 0.1 Å. The maximum difference for different types of atomic orbitals with the same hybridization or for different hybridizations with the same atomic orbitals is only about 0.05 Å. Since the hybridization of the compounds of interest is probably quite close to that expected (sp<sup>3</sup> for the amine, sp<sup>2</sup> for the imine, and sp for the nitrile), the error arising from choice of  $\psi_a$  is unlikely to be greater than  $\pm 0.05$  Å.

At this point, it might be well to point out the danger of calculating  $E$  using the dipole approximation. Even if it is assumed that the proper value of the dipole moment is known, its location is ambiguous. The importance of this location can be shown by a simple calculation on acetonitrile. Using the molecular geometry found by Thomas, *et al.*,<sup>18</sup> the electric field along the C-H bond is

$$E_z = (\mu/33.6) \times 10^{24} \quad (6)$$

(where  $\mu$  is the dipole moment) if the dipole is taken to be at the nitrogen nucleus. However, if  $\mu$  is taken to be at the midpoint of the triple bond, one obtains

$$E_z = (\mu/16.4) \times 10^{24} \quad (7)$$

which differs by a factor of two, for a movement of the dipole by 0.6 Å. (a reasonable allowance for the uncertainty in the location of  $\mu$ ). Of course, the difficulty arises because of the  $r^3$  dependence of  $E$  upon  $\mu$  and can be expected to reoccur whenever the uncertainty of the location of  $\mu$  is not very small compared with the distance of the proton from the dipole.

Having found a relation between  $R$  and  $E$ , eq. 1 can be used to calculate  $\Delta_E$  as a function of  $R$ . Figure 3 shows the resulting curves for  $k_E = -2.6$ ,  $-3.0$ , and  $-3.4$  and Slater atomic orbitals with sp<sup>3</sup> hybridization. The difference in calculated length for a specific value of  $E_z$  between the two extreme values of  $k_E$  is about 0.16 Å. If  $k_E = -3.0$  is used, it probably is safe to assume an error, due to this choice, of  $\pm 0.08$  Å. in length for a given  $\Delta_E$ .

Since it is unlikely that  $\Delta_{AD}$  for the amine contains any significant contribution from anisotropy (*i.e.*,  $\Delta\chi = 0$ ),<sup>19</sup>  $\Delta_{AD}$  can be set equal to  $\Delta_E$ . Thus, reading the distance from Fig. 3 for  $\Delta_{AD} = 123$  c.p.s., one finds an N...H length of 2.42 Å. This value seems to be quite reasonable. The N-N distance in solid NH<sub>3</sub>, where the hydrogen bonds are similar, is 3.38 Å,<sup>20</sup> and, for a N-H distance of 1.00 Å., this would correspond to a N...H distance of 2.38 Å.

(18) L. F. Thomas, E. I. Sherrard, and J. Sheridan, *Trans. Faraday Soc.*, **51**, 619 (1955).

(19) J. A. Pople, *J. Chem. Phys.*, **37**, 34 (1962).

(20) G. C. Pimentel and A. L. McClellan, "The Hydrogen Bond," W. H. Freeman and Co., San Francisco, Calif., 1960.

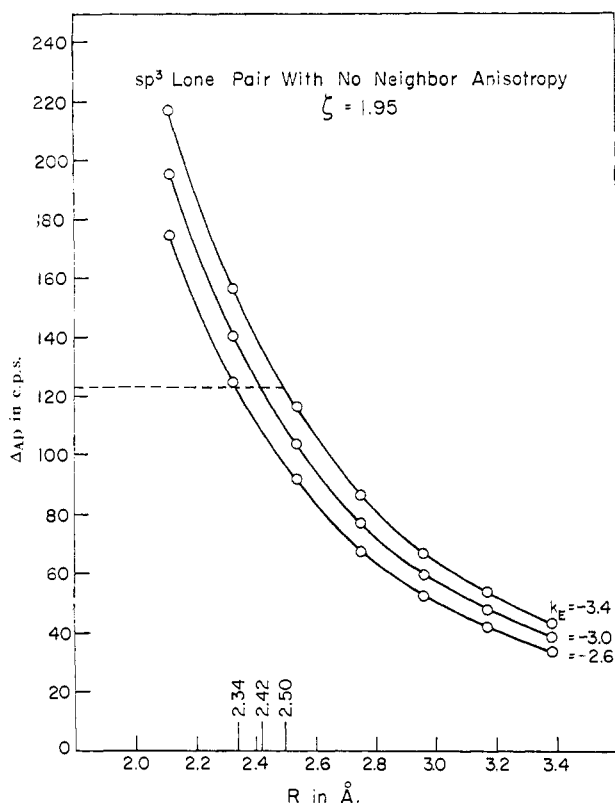


Fig. 3.—Importance of choice of proportionality constant,  $k_E$ , in the calculation of shifts from fields with eq. 1. Note that the ordinate is labeled  $\Delta_{AD}$  since the calculations are for the amine where  $\Delta_N$  is assumed negligible (thus,  $\Delta_E = \Delta_{AD}$ ).

#### Evaluation of the Shift Due to Neighbor Anisotropy

With the other three compounds, anisotropy effects must be considered. For the nitrile and the imine, the relation 2 developed by Pople<sup>19</sup> and McConnell<sup>5b</sup> was used for estimating the contribution,  $\Delta_N$ , to  $\Delta_{AD}$  due to neighbor anisotropy. The values of  $\Delta\chi$  used for the nitrile and the imine were those calculated by Pople<sup>19</sup> for acetylene and ethylene,  $-19.4 \times 10^{-6}$  and  $8.6 \times 10^{-6}$  e.m.u. per mole, respectively. The validity of Pople's calculations has been shown recently by the crystal susceptibility measurements of de Villepin.<sup>21</sup> She has found for the C=C bond,  $\chi_x - \chi_z$  to be  $8.92 \times 10^{-6}$  and  $\chi_y - \chi_z$  to be  $6.10 \times 10^{-6}$  ( $x$  is along the bond axis and  $z$  normal to the nodal plane). Although Pople estimated cylindrical symmetry for the susceptibility of olefinic bonds, these values very closely approximate his.

The justification for using, for our compounds, values derived for hydrocarbons is: With the imine, the anisotropy contribution to the total  $\Delta_{AD}$  is small (less than 10%), and thus any reasonable estimate of  $\Delta\chi$  will do. Experimental evidence is available in the case of the nitrile. The anisotropies of C≡N and C≡C have been examined by Goldstein and Reddy<sup>22</sup> and by Zeil and Buchert.<sup>23</sup> Goldstein and Reddy find that  $-\Delta\chi$  is the same for both types of compounds and equals  $10.5 \times 10^{-6}$  e.m.u./mole. Zeil and Buchert find that  $-\Delta\chi$  for C≡N is  $31.6 \times 10^{-6}$ , and for C≡C is  $34.2 \times 10^{-6}$  e.m.u./mole. These latter values show that the  $-\Delta\chi$  values are about the same, but the values

(21) J. de Villepin, *Compt. rend.*, **267**, 2278 (1963).

(22) G. S. Reddy and J. H. Goldstein, *J. Chem. Phys.*, **39**, 3509 (1963).

(23) W. Zeil and H. Buchert, *Z. physik. Chem. (Frankfurt)*, **38**, 47 (1963).

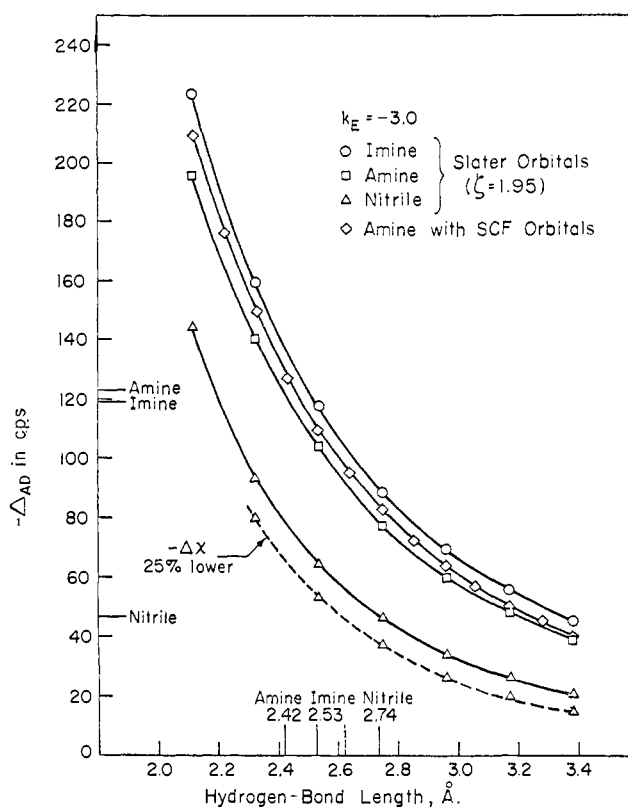


Fig. 4.—Final results of combining electric field shifts and anisotropy shifts so that hydrogen bond lengths can be found from the experimental  $\Delta_{AD}$ 's (indicated along the ordinate). The solid lines along the abscissa correspond to the lengths using the Slater orbitals.

themselves are too large, possibly due to neglect of carbon-carbon bond anisotropy.

In Fig. 4,  $\Delta_{AD}$  calculated with the anisotropy contribution included is plotted vs. hydrogen bond length for the amine, imine, and cyanide (using Slater orbitals with  $\zeta = 1.95$  and  $k_E = -3.0$ ). Then, from the measured values of  $\Delta_{AD}$  for N-methylpyrrolidine, ethylideneisopropylimine, and cyclohexyl cyanide, the hydrogen bond lengths are read off. These are listed in Table II along with  $\Delta_{AD}$ ,  $\Delta_N$ , and  $\Delta_E$ . The lengths increase nicely as the basicity of the compounds decreases.<sup>7</sup>

Two other lines are plotted on this figure. The solid line with the diamonds is for  $sp^3$  SCF atomic orbitals with no anisotropy correction (that is, for the amine). Again, it is clear that the choice of atomic orbitals makes little difference in the calculated hydrogen bond length—only about 0.04 Å. at 123 c.p.s. The other line, the dashed line with the triangles, shows the effect of increasing  $-\Delta\chi$  by 25% for the cyanide, a more than adequate allowance for the uncertainty in the anisotropy. Now, if the hydrogen bond length read off for this line, 2.62 Å., is reduced by another 0.1 Å. to allow for any unknown errors, the length for the amine is still 0.1 Å. greater than for the cyanide. The point is that, even with a very bad choice of parameters, the trend of length with basicity is still observed. It should be noted that the error due to choice of  $k_E$  is not involved here, since this constant, if variable at all, should be a function of the acid (not the base).

Not so quantitative a picture can be obtained for the isocyanide. The resonance of the methyl protons of acetonitrile is known to occur considerably upfield

( $\sim 0.9$  p.p.m.) of methyl isocyanide,<sup>24</sup> yet the dipole moments of these two compounds are almost indistinguishable.<sup>25</sup> If the dipole moments of the two compounds can be located anywhere near the same position, this must mean that the anisotropy effect for methyl isocyanide is less than that for acetonitrile. If this is so, then the hydrogen bond length must be greater for the isocyanide, since the  $\Delta_{AD}$  values are essentially the same, and  $\zeta$  for the carbon is less than that for nitrogen. This is not surprising in light of the lower boiling points of isocyanides, though infrared

(24) I. D. Kuntz, P. von R. Schleyer, and A. Allerhand, *J. Chem. Phys.*, **35**, 1533 (1961).

(25) C. P. Smith, "Dielectric Behavior and Structure," McGraw-Hill Book Co., Inc., New York, N. Y., 1955.

spectral shifts upon hydrogen bond formations are smaller for the cyanide.<sup>26</sup>

In conclusion, we feel that the electric field effect and the neighbor-anisotropy effect are sufficient to explain the n.m.r. shift upon complex formation for weak hydrogen bonds. Thus, where anisotropy is constant, this shift could be used to compare hydrogen bond lengths and, as far as the two are proportional, strengths. Furthermore, a fair estimate of the actual length can be obtained. The connection between the weaker basicity of nitriles compared with amines and the prediction of longer hydrogen bond lengths is being investigated.

(26) A. Allerhand and P. von R. Schleyer, *J. Am. Chem. Soc.*, **85**, 866 (1963).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF WASHINGTON, SEATTLE, WASHINGTON, AND THE RESEARCH COUNCIL OF ALBERTA, EDMONTON, ALBERTA, CANADA]

## Inverse Secondary Intermolecular Isotope Effects in the Low Pressure Thermal Isomerization of Cyclopropane<sup>1a</sup>

BY B. S. RABINOVITCH,<sup>1b</sup> P. W. GILDERSON,<sup>1b</sup> AND A. T. BLADES<sup>1c</sup>

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The experimental study of quantum statistical intermolecular secondary isotope effects in the rate of thermal decomposition of cyclopropane and of cyclopropane-*d*<sub>6</sub> has been extended down to pressures of  $10^{-4}$  mm. at  $510^\circ$  by an internal comparison method. The expected inversion of the ratio  $k(h_6)/k(d_6)$  occurs at  $\sim 10^{-2}$  mm. Below this pressure complications attributed to wall effects obscure the behavior, and a limiting value of  $k(h_6)/k(d_6) \simeq 0.8$  was obtained. The results are discussed briefly, along with mixed isotope effects, and are compared with theoretical computations.

Kinetic isotope effects for the thermal unimolecular isomerization of cyclo-C<sub>3</sub>H<sub>6</sub> and cyclo-C<sub>3</sub>D<sub>6</sub> were first measured by Blades.<sup>2</sup> His experiments at  $482^\circ$ , made at pressures down to 0.18 mm., gave ratios which declined with pressure from the limiting high pressure value  $[k(h_6)/k(d_6)]_\infty = 1.96$  to  $[k(h_6)/k(d_6)]_{0.18} = 1.35$ . Rabinovitch, Setser, and Schneider<sup>3</sup> (RSS) pointed out that this inequality, which at high pressures reflects a primary isotope effect mainly, should invert at sufficiently low pressures, where opposing secondary quantum statistical isotope effects would eventually overtake the primary effect. They calculated a low pressure limiting value on a harmonic oscillator model of  $[k(h_6)/k(d_6)]_0 = 0.25$ . This inverse isotope effect is a quite general phenomenon, and explicit confirmation of its existence has since been given for the isomerization of the pair CH<sub>3</sub>NC and CD<sub>3</sub>NC.<sup>4</sup>

The present paper describes the extension of the cyclopropane system to lower pressures. Although the expected inversion has been realized, wall effects at still lower pressures<sup>5</sup> obscure the quantitative aspects.

(1) (a) This work was supported by the National Science Foundation; (b) University of Washington; (c) Research Council of Alberta, Contribution No. 253.

(2) A. T. Blades, *Can. J. Chem.*, **39**, 1401 (1961).

(3) B. S. Rabinovitch, D. W. Setser, and F. W. Schneider, *ibid.*, **39**, 2609 (1961).

(4) F. W. Schneider and B. S. Rabinovitch, *J. Am. Chem. Soc.*, **85**, 2365 (1963); this effect has now also been demonstrated for CH<sub>2</sub>DNC, unpublished results of P. W. Gilderson.

(5) A. D. Kennedy and H. O. Pritchard, *J. Phys. Chem.*, **67**, 161 (1963); B. S. R. thanks Dr. Pritchard for a private communication which clarified the fact that a  $k_\infty$  value derived from data of W. E. Falconer, T. E. Hunter, and A. F. Trotman-Dickenson [*J. Chem. Soc.*, 609 (1961)] has been used in the  $\log k/k_\infty$  plot of this reference.

## Experimental

**Materials.**—The mixture of cyclo-C<sub>3</sub>H<sub>6</sub> and -C<sub>3</sub>D<sub>6</sub>, in the proportions of 4.00:1, was the same as that used previously.<sup>2</sup> The C<sub>3</sub>D<sub>6</sub> component was of 93% isotopic purity, with the remainder chiefly C<sub>3</sub>HD<sub>5</sub>.

**Apparatus and Procedure.**—The reactor was a 12-l. spherical Pyrex flask, fitted with a thermometer well, and heated in a stirred air furnace to an average temperature of  $510.7^\circ$ . The maximum temperature variation from the mean over the vessel was  $\pm 2^\circ$ . A conventional vacuum system was employed.

After production of a sticking vacuum, the reactor was seasoned as follows: Following a flush with 1 mm. of C<sub>3</sub>H<sub>6</sub>, the reactor was allowed to stand at  $510^\circ$  and 1 mm. pressure for 2 hr. The procedure was repeated. After evacuation of the reactor, any exchange of a surface film was allowed to occur by flushing for 10 min. with the isotopic mixture. After the first exchange treatment, no isotopic alteration of the mixture or products could be detected.

Measured samples were expanded into the reactor from a trap at Dry Ice temperature in order to prevent transport of mercury vapor. At the end of the run, the contents of the reactor were analyzed.

**Analytical.**—Analysis of products was made by g.l.p.c. on an 80-ft. silver nitrate-glycol column.<sup>6</sup> Standard mixtures of propene-*h*<sub>6</sub> and -*d*<sub>6</sub> were prepared for the calibration of peak heights and their ratios. Three mixtures, of *h*<sub>6</sub>/*d*<sub>6</sub> composition 0.971:1, 2.305:1, and 4.96:1, were used. The calibration factor (actual ratio/measured ratio) was found to be the same for each mixture. There was no recognizable trend of the factor with sample size. A calibration run was performed with each set of analyses. Variations were within  $\pm 2\%$ .

Parent peak analysis with a Consolidated 21-103 mass spectrograph of the propene-*d*<sub>6</sub> used in the calibrations showed that there was 6% propene-*d*<sub>5</sub> present; this did not introduce appreciable inaccuracy because its retention time is virtually identical with that of propene-*d*<sub>6</sub>.

(6) R. J. Cvetanovic, F. J. Duncan, and W. E. Falconer, *Can. J. Chem.*, **41**, 2095 (1963).