

solutions than were the isomers with no intramolecular bond.

Brooks and Morman observed specific effects on the intramolecular hydrogen bond in nitro derivatives of I and II.<sup>21</sup> The bond appears to be weakened in the 5-nitro derivatives and, in the 3-nitro derivatives, the nitro group competes with the carbonyl group for the intramolecular hydrogen bond. Given these two intramolecularly bonded species, with equilibrium between them possibly altered by other substituents, and the amphiprotic nature of water solvent, the equilibrium situation in water is obviously complex and unpredictable.

There are two general features of interest in the nitro substituent effects. The first is that the effects are practically identical for *p* (to hydroxyl) nitro substitution in phenol, I and III. The second feature is that *p*-substitution in the acetophenone (II) and *o*-substitution in any of the carbonyl molecules causes larger effects than in phenol. A larger substituent effect for molecules with intramolecular hydrogen bonding might be expected from a consideration of the relative stabilization of the parent acid and anion species by the addition of a nitro group to each. If (1) the stabilization of the anions of phenol and one of the *o*-carbonyl acids, say II, is about the same and (2) the stabilization of the acid form of phenol is greater than that of II, the net result would be a larger substituent effect for the dissociation of the nitro derivative of II. One may argue in favor of the plausibility of both conditions. For (1), in addition to the C-N  $\sigma$ -bond formation, which should be about the same for acid and anion, the anion stabilization of phenol and II is formally the same for both, depending largely on the attraction between the polarizable and negatively

charged oxygen and the polarizable nitro dipole. The carbonyl and nitro dipole-dipole interaction (repulsive) may be assumed to be negligible. For (2), stabilization of phenol by the addition of the nitro group will depend on the shift of electron density from the hydroxyl group to the nitro group. The intramolecular hydrogen bond in II implies a larger polarization energy which would oppose shift of electron density toward the nitro group. Condition 2 would appear to be more plausible than 1.

The larger substituent effects in II as compared to I may be accounted for by the argument just given, based on the stronger hydrogen bond in II. The argument clearly does not explain the practically identical results for *p*-nitro substitution in phenol, I and III. It will not be attempted here, but one would examine the validity of condition 1 above with consideration being given to the effects of the orientation of the carbonyl groups. The behavior of the tetralone structure should be useful since the orientation is known in both acid and anion. The substituent effects for the tetralone structure are generally intermediate to those for I and II with the notable exception of the decrease in acidity in the series I, II and III. From the preceding discussion, a parallel increase in the strength of the intramolecular hydrogen bond does not necessarily follow from the decrease in acidity in the series. Information on the strengths of the intramolecular bond in III and its derivatives relative to those of I and II will be of value in estimating the acid and anion contributions to the substituent effects.

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[CONTRIBUTION FROM FRICK CHEMICAL LABORATORY, PRINCETON UNIVERSITY, PRINCETON, N. J.]

## A Survey of C-H Groups as Proton Donors in Hydrogen Bonding<sup>1</sup>

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The ability of C-H groups to act as proton donors in hydrogen bonding was surveyed by infrared spectroscopic techniques, using the strong proton acceptors, pyridine-*d*<sub>5</sub> and dimethyl sulfoxide-*d*<sub>6</sub>, in CCl<sub>4</sub> solution. Pentachlorocyclopropane, pentachloroethane, Br<sub>2</sub>CHCN, bromoform, iodoform and many other compounds gave larger C-H spectral shifts than chloroform, an accepted and well studied proton donor. The order of haloform spectral shifts was CHBr<sub>3</sub> > CHI<sub>3</sub> > CHCl<sub>3</sub>; fluoroform gave inconclusive results. In a C-H compound capable of acting as a proton donor, replacement of Cl by CCl<sub>3</sub> and CN, as well as by Br and I, resulted in an enhancement of the spectral shifts to a common base. X-CH<sub>2</sub>-Y compounds, where X, Y = Cl, Br, I and CN, showed evidence of hydrogen bonding to strong proton acceptors. *cis*- and *trans*-1,2-dichloroethylene also behaved as proton donors; the *trans* isomer gave the larger C-H spectral shifts. Other C(sp<sup>2</sup>)-H compounds giving evidence of proton-donating ability in hydrogen bonding were CHX=CX<sub>2</sub> (X = F, Cl, Br) and poly-substituted benzene derivatives with at least three strongly electron-withdrawing substituents. Aldehydic C-H bands did not give spectral shifts with strong bases; methyl compounds, CH<sub>3</sub>X, also gave no evidence of proton donor ability. Assignment of C-H bands in more complicated spectra was facilitated by observing changes produced by deuterated bases.

That chloroform and acetone form a complex has been known for a long time; as early as 1914, attempts were made to calculate an association constant.<sup>4</sup> In 1937, Glasstone<sup>5</sup> proposed that such complexes of haloforms resulted from X<sub>3</sub>CH...B hydrogen bonding.

(1) Paper X of a series on hydrogen bonding; paper IX, *J. Am. Chem. Soc.*, **85**, 866 (1963). This work was taken from the Ph.D. Thesis of Adam Allerhand, Princeton University, 1962.

(2) Merck Foundation Fellow, 1960-1961; Esso Foundation Fellow, 1961-1962.

(3) Alfred P. Sloan Research Fellow.

(4) E. Beckman and O. Faust, *Z. physik. Chem.*, **89**, 235, 247 (1914).

(5) S. Glasstone, *Trans. Faraday Soc.*, **33**, 200 (1937). Glasstone's proposal found reluctant acceptance. The discussion that followed the presentation of his paper is instructive in the history of the development of the concept of hydrogen bonding.

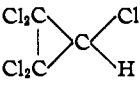
Since then extensive work has been carried out on the subject of C-H groups as proton donors in hydrogen bonding.<sup>6-13</sup> Conclusive infrared and nuclear magnetic

(6) The question of hydrogen bonding involving the C-H group has been reviewed by C. G. Pimentel and A. L. McClellan, "The Hydrogen Bond," W. H. Freeman and Co., San Francisco, Calif., 1960, Ch. 6, pp. 197-201. An extensive list of references is given therein.

(7) E. D. Becker, *Spectrochim. Acta*, **15**, 743 (1959); W. E. Thompson and G. C. Pimentel, *Z. Elektrochem.*, **64**, 748 (1960); D. G. Rea, *J. Chem. Phys.*, **33**, 1875 (1960); A. N. Campbell and E. M. Kartzmark, *Can. J. Chem.*, **38**, 652 (1960); C. F. Jumper, M. T. Emerson and B. B. Howard, *J. Chem. Phys.*, **35**, 1911 (1961); D. K. Anderson and A. L. Babb, *J. Phys. Chem.*, **65**, 1281 (1961); E. R. Kearns, *ibid.*, **65**, 314 (1961); G. S. Denisov, *Optics and Spectry.*, **11**, 232 (1961); K. B. Whetsel and R. E. Kagarise, *Spectrochim. Acta*, **18**, 329 (1962); C. J. Creswell and A. L. Allred, *J. Phys. Chem.*, **66**, 1469 (1962); W. G. Schneider in D. Hadzi, Ed., "Hydrogen Bonding,"

TABLE I

EFFECT OF DIMETHYL SULFOXIDE-*d*<sub>6</sub> AND PYRIDINE-*d*<sub>6</sub> ON  $\nu_{\text{CH}}$  OF COMPOUNDS WITH A SINGLE BAND IN THE C-H STRETCHING FREQUENCY REGION<sup>a</sup>

| Compound  | CCl <sub>4</sub> soln.   | 0.05 M CD <sub>3</sub> SOCD <sub>3</sub> in CCl <sub>4</sub> |                          |             | 2 M pyridine- <i>d</i> <sub>6</sub> in CCl <sub>4</sub> |                          |             |
|---|--------------------------|--|--------------------------|-------------|---|--------------------------|-------------|
|   | $\nu_{\text{CH}}$        | $\nu_{\text{CH}}$ "free"                                     | $\nu_{\text{OH}}$ bonded | $\Delta\nu$ | $\nu_{\text{CH}}$ "free"                                | $\nu_{\text{CH}}$ bonded | $\Delta\nu$ |
| Br <sub>2</sub> CHCN  | 2998                     | sh.  | 2918                     | 80          | 2996  | 2883                     | 113         |
| Cl <sub>2</sub> CHCN  | 2987                     | sh.  | 2921                     | 66          | 2983  | 2891                     | 92          |
|  | 3040                     |  |                          |             | 3039  | 2951                     | 88          |
| CHBr <sub>2</sub> CBr <sub>2</sub>  | 2993                     | 2991   | 2933                     | 58          | 2991  | 2904                     | 87          |
| CCl <sub>3</sub> CHClCCl <sub>3</sub>   | 2961                     |  |                          |             | 2960  | 2878                     | 82          |
| CHBr <sub>3</sub>   | 3031 (3030) <sup>b</sup> | sh.  | 2981                     | 50          | 3029  | 2963                     | 66          |
| CHCl <sub>2</sub> CCl <sub>2</sub> CCl <sub>3</sub>                               | 3005                     | 3004   | 2959                     | 45          | 3005  | 2940                     | 65          |
| CHClBr <sub>2</sub>   | 3027                     | sh.  | 2984                     | 43          |   |                          |             |
| CHCl <sub>2</sub> CCl <sub>3</sub>  | 2988                     | 2986   | 2945                     | 41          | 2987  | 2923                     | 64          |
| CHI <sub>3</sub>  | 3011 (3011) <sup>b</sup> | 3008   | 2968                     | 40          | 3007  | 2952                     | 55          |
| CHCl <sub>3</sub>   | 3020 (3017) <sup>b</sup> | sh.  | 2991                     | 29          | sh.   | 2974                     | 46          |
| <i>trans</i> -CHCl=CHCl   | 3087                     | 3086   | 3053                     | 33          | 3084  | 3050sh.                  | 34          |
| <i>cis</i> -CHCl=CHCl   | 3079                     | 3078   | 3060                     | 18          | 3077  | 3054sh.                  | 23          |
| CHF <sub>3</sub>  | 3036                     | sh.  | 3008                     | 28          | 3037  | None                     | ...         |
| CF <sub>3</sub> SCF <sub>2</sub> CF <sub>2</sub> H                                | 2983                     |  |                          |             | 2981  | None                     | ...         |

<sup>a</sup> All frequencies are in cm.<sup>-1</sup>; sh. = shoulder. <sup>b</sup> C. C. Robinson, S. A. Tare and H. W. Thompson, *Proc. Roy. Soc. (London)*, **A269**, 492 (1962).

resonance evidence for C—H...B hydrogen bonding, where B is a strong proton acceptor, exists only for the haloforms,<sup>6</sup> acetylenic C—H groups<sup>6,9</sup> and hydrogen cyanide.<sup>6,10</sup> C—H participation in hydrogen bonding has been proposed for a large variety of compounds,<sup>6</sup> mostly from studies of non-specific properties such as solubility and heat of mixing, but this type of evidence cannot be accepted as conclusive.<sup>6</sup>

Infrared spectroscopy remains the most characteristic and sensitive method for the detection of hydrogen bonding<sup>6</sup>; specific criteria for hydrogen bond formation are the shift, broadening and intensification of the proton donor stretching frequency band. However, two serious experimental problems arise when attempts are made to study C—H...B hydrogen bonding by this method:

1. Interference from the C—H absorption of the proton acceptor, B: strong bases, needed to study the hydrogen bonding capabilities of weak C—H proton donors, all contain C—H groups themselves and absorb in the C—H region.<sup>14</sup> Therefore, measurements of  $\nu_{\text{CH}}$  of the proton donor are obscured by the presence of the necessarily large concentrations of proton acceptor. For example, several infrared studies of the hydrogen bonding capability of haloforms<sup>15</sup> CHCl<sub>2</sub>—CHCl<sub>2</sub><sup>16</sup> and CHCl<sub>2</sub>—CCl<sub>3</sub><sup>16</sup> may not be reliable because C—H containing proton acceptors were used.<sup>17</sup>

Pergamon Press, New York, N. Y., 1959, pp. 55–69; S. Brahm, *Bull. acad. polon. sci., Sér. sci. math., astron. et phys.*, **7**, 449 (1959); **7**, 531 (1959); *Chem. Abstr.*, **54**, 14940 (1960); I. D. Kuntz, Jr., A. B. Thesis, Princeton University, 1961; K. Kurosaki, *Nippon Kagaku Zasshi*, **83**, 655 (1962); R. Kaiser, *Can. J. Chem.*, **41**, 430 (1963).

(8) (a) T. S. Schaefer and W. G. Schneider, *J. Chem. Phys.*, **32**, 1218 (1960); (b) W. G. Schneider, *J. Phys. Chem.*, **66**, 2653 (1962).

(9) A. Allerhand and P. von R. Schleyer, *J. Am. Chem. Soc.*, **85**, 1233 (1963), and lit. cited by them in ref. 13.

(10) G. L. Caldow and H. W. Thompson, *Proc. Roy. Soc. (London)*, **A264**, 1 (1960).

(11) C. G. Cannon, *Spectrochim. Acta*, **10**, 429 (1958).

(12) R. E. Kagari, *ibid.*, **18**, 1385 (1962); **19**, 629 (1963).

(13) (a) D. L. Andersen, R. A. Smith, D. B. Meyers, S. K. Alley, A. G. Williamson and R. L. Scott, *J. Phys. Chem.*, **66**, 621 (1962); J. O. Konecny and C. H. Deal, *ibid.*, **67**, 504 (1963); (b) T. B. Tripp and R. D. Dunlap, *ibid.*, **66**, 635 (1962); (c) C. J. Creswell and A. L. Allred, *J. Am. Chem. Soc.*, **84**, 3966 (1962); **85**, 1723 (1963); cf. ref. 12.

(14) One notable exception is the base NH<sub>3</sub>. Hydrogen bonding, Cl—CH...NH<sub>3</sub>, has been studied in CCl<sub>4</sub> solution.<sup>11</sup> A free band (3017 cm.<sup>-1</sup>) and an associated band (2985 cm.<sup>-1</sup>) were observed ( $\Delta\nu = 32$  cm.<sup>-1</sup>).

(15) R. E. Glick, *Chem. Ind. (London)*, 413 (1956).

(16) E. Halpern, J. B. Bouck, H. Finegold and J. Goldenson, *J. Am. Chem. Soc.*, **77**, 4472 (1955); M. W. Hanson and J. B. Bouck, *ibid.*, **79**, 5631 (1957).

This problem can be avoided in two ways, either by using completely deuterated proton acceptors or by studying C—D proton donor bands instead of C—H bands. Only the second approach has been employed in the literature, for the study of the haloforms.<sup>6,12,18,19</sup>

2. The "solvent effect"<sup>20</sup>; small frequency shifts of  $\nu_{\text{CH}}$  when a proton donor is dissolved in a pure liquid proton acceptor may not necessarily be due to hydrogen bonding, but may be caused by less specific solvent effects.<sup>6,20</sup> It is desirable not to use this procedure, but to carry out measurements in dilute CCl<sub>4</sub> solutions, thus keeping the environment nearly constant.<sup>20,21</sup> Conversely, the absence of a detectable spectral shift ( $\Delta\nu = 0$ ) is not necessarily evidence against hydrogen bonding. The C—D band of CDCl<sub>3</sub> is not shifted in acetone (with respect to its position in CCl<sub>4</sub>) but only broadened and intensified,<sup>12,19</sup> but there is conclusive evidence for chloroform—acetone hydrogen bonding.<sup>12,18,19,22</sup> This example emphasizes the necessity of using the strongest possible proton acceptors, *i.e.*, those capable of producing the largest spectral shifts, for studying C—H hydrogen bonding.

We report here the results of investigations of the effects of dimethyl sulfoxide-*d*<sub>6</sub> and pyridine-*d*<sub>6</sub>, both strong proton acceptors, on the C—H stretching frequencies of a large variety of compounds, some expected to form hydrogen bonds, some not. The behavior of the C—D stretching frequencies of trichloroethylene-*d* and monodeuteriobenzene in the presence of a variety of strong bases was contrasted; the former was expected to form hydrogen bonds, the latter not.

### Experimental<sup>9,20</sup>

Measurements were carried out on a Perkin-Elmer model 21 infrared spectrometer equipped with an LiF prism and a Perkin-Elmer model 421 grating spectrophotometer. Well matched cells, 1 mm. thick, permitted the use of low concentrations of proton donors. Some of the measurements were repeated in

(17) The higher frequencies of acetylenic C—H bands and  $\nu_{\text{CH}}$  of HCN permit the study of these groups as proton donors in the presence of moderate concentrations of C—H containing proton acceptors.

(18) G. M. Barrow and E. A. Yerger, *J. Am. Chem. Soc.*, **76**, 5247 (1954).

(19) R. C. Lord, B. Nolin and H. D. Stidham, *ibid.*, **77**, 1365 (1955); C. M. Huggins and G. C. Pimentel, *J. Chem. Phys.*, **23**, 896 (1955); W. G. Paterson and D. M. Cameron, *Can. J. Chem.*, **41**, 198 (1963).

(20) A. Allerhand and P. von R. Schleyer, *J. Am. Chem. Soc.*, **85**, 371 (1963).

(21) S. S. Mitra, *J. Chem. Phys.*, **36**, 3286 (1962).

(22) C. M. Huggins, G. C. Pimentel and J. N. Shoolery, *ibid.*, **23**, 1244 (1955).

TABLE II

EFFECT OF DIMETHYL SULFOXIDE- $d_6$  AND PYRIDINE- $d_5$  ON  $\nu_{\text{CH}}$  SYM. AND  $\nu_{\text{CH}}$  ANTISYM. IN COMPOUNDS OF THE TYPE X-CH<sub>2</sub>-Y<sup>a</sup>

| Compound             | CCl <sub>4</sub> soln.   | 0.95 M CD <sub>3</sub> SOC <sub>2</sub> D <sub>3</sub> in CCl <sub>4</sub> |                          |                 | 2 M pyridine- $d_5$ in CCl <sub>4</sub> |                          |                 |
|----------------------|--------------------------|--|--------------------------|-----------------|---|--------------------------|-----------------|
|                      | $\nu_{\text{CH}}^b$      | $\nu_{\text{CH}}$ "free"   | $\nu_{\text{CH}}$ bonded | $\Delta\nu$     | $\nu_{\text{CH}}$ "free"                | $\nu_{\text{CH}}$ bonded | $\Delta\nu$     |
| ICH <sub>2</sub> CN  | 3023                     |  | 3016                     | (7)             |   |                          |                 |
|                      | 2968                     | 2967sh.  | 2945                     | 23 <sup>c</sup> |   |                          |                 |
| ClCH <sub>2</sub> CN | 3010                     |  | 3005                     | (5)             |   | 2998                     | (12)            |
|                      | 2966                     | 2963   | 2948                     | 15              | 2960sh.                                 | 2936                     | 30 <sup>d</sup> |
| ICH <sub>2</sub> I   | 3062 (3061) <sup>e</sup> |  | 3058                     | (4)             |   | 3056                     | (6)             |
|                      | 2982 (2983) <sup>e</sup> |  | 2972                     | (10)            |   | 2966                     | (16)            |
| BrCH <sub>2</sub> Br | 3068 (3067) <sup>e</sup> |  | 3065                     | (3)             |   |                          |                 |
|                      | 2991 (2990) <sup>e</sup> |  | 2980                     | (11)            |   |                          |                 |
| ClCH <sub>2</sub> Cl | 3050 (3050) <sup>e</sup> |  | 3049                     | (1)             |   | 3045                     | (5)             |
|                      | 2985 (2984) <sup>e</sup> |  | 2981                     | (4)             |   | 2980                     | (5)             |

<sup>a</sup> All frequencies are in cm<sup>-1</sup>. When ambiguity arises as to whether a band corresponds to a "free" C-H or one bonded to the proton acceptor, the value is placed between the  $\nu_{\text{CH}}$  "free" and  $\nu_{\text{CH}}$  bonded columns and  $\Delta\nu$  is placed in parentheses. See also Fig. 2 and 3. sh. = shoulder. <sup>b</sup> The higher frequency value is the antisymmetric C-H stretching frequency, the lower value being the symmetric stretching band; see ref. 34. <sup>c</sup>  $\nu_{\text{CH}}$  "free" taken 2968 cm<sup>-1</sup>. <sup>d</sup>  $\nu_{\text{CH}}$  "free" taken 2966 cm<sup>-1</sup>. <sup>e</sup> Footnote b in Table I.

TABLE III

EFFECT OF DIMETHYL SULFOXIDE- $d_6$  AND PYRIDINE- $d_5$  ON THE SPECTRA OF SOME ETHYLENE AND BENZENE DERIVATIVES IN THE C-H STRETCHING REGION<sup>a</sup>

| Compound  | CCl <sub>4</sub> soln.   | 0.95 M CD <sub>3</sub> SOC <sub>2</sub> D <sub>3</sub> in CCl <sub>4</sub> |       |             | 2 M pyridine- $d_5$ in CCl <sub>4</sub> |   |             |
|---|--------------------------|--|-------|-------------|---|---|-------------|
|   | $\nu$                    | $\nu$  | $\nu$ | $\Delta\nu$ | $\nu$                                   | $\nu$                                       | $\Delta\nu$ |
| CHF=CF <sub>2</sub> <sup>b</sup>                    | 3153s <sup>c</sup> 3102s |  |       |             | 3150s                                   | 3101s 3079m                                 | 22          |
| CHCl=CCl <sub>2</sub> <sup>b</sup>                  | 3160w <sup>d</sup> 3084s | 3155w  | 3083s | 3042s       | 41                                      | 3157w 3083s 3038s                           | 45          |
| CCl <sub>2</sub> =CHCCl <sub>3</sub> <sup>b</sup>   | 3191w <sup>d</sup> 3072s |  |       |             |   | 3189w 3070s 3006s                           | 64          |
| CHBr=CBr <sub>2</sub> <sup>b</sup>                  | 3103s <sup>e</sup> 3067s | 3102s  | 3067s | 3027s       | 40                                      | 3101s 3066s <sup>f</sup> 3014s <sup>g</sup> | 52          |
| 1,3,5-Trichlorobenzene <sup>h,i</sup>               | 3086                     |  |       |             |   | 3086 3051                                   | 34          |
| 1,2,4,5-Tetrabromobenzene <sup>h,i</sup>            | 3084                     |  |       |             |   | 3083 3032                                   | 51          |
| 1,2,4,5-Tetrachlorobenzene <sup>h,h,k</sup>         | 3092s 3034w              | 3092s  | 3052m | 3035m       | 40                                      | 3091s 3049m 3032m                           | 42          |
| 1-Nitro-2,3,5,6-tetrachlorobenzene <sup>h,h,l</sup> | 3083s 2967w              |  |       |             |   | 3081s 3036s 2969s                           | 45          |
| 3,5-Dinitro-2,4,6-trichlorobenzene <sup>h,h,m</sup> | 3085s 2978w              | 3086s  | 3039s | 2974s       | 47                                      | 3085s 3032s 2966s                           | 53          |

<sup>a</sup> All frequencies are in cm<sup>-1</sup>; abbreviations: s = strong, m = medium, w = weak. <sup>b</sup> C-H stretching bands, free and hydrogen bonded, are italicized. <sup>c</sup> This band is probably the first overtone of the C=C stretching frequency. Its high intensity is probably due to Fermi resonance with  $\nu_{\text{CH}}$ ; see footnote e. <sup>d</sup> First overtone of  $\nu_{\text{C}=\text{C}}$ ; see ref. 24. <sup>e</sup> First overtone of the C=C stretching frequency (at 1557 cm<sup>-1</sup>), intensified by Fermi resonance with  $\nu_{\text{CH}}$ ; see ref. 29, 37. <sup>f</sup> 3061 cm<sup>-1</sup> in pure liquid pyridine- $d_5$ . <sup>g</sup> 3013 cm<sup>-1</sup> in pure liquid pyridine- $d_5$ . <sup>h</sup> Several weak bands are also present. <sup>i</sup> See Fig. 4C. <sup>j</sup> See Fig. 4D. <sup>k</sup> See Fig. 5A. <sup>l</sup> See Fig. 5B. <sup>m</sup> See Fig. 5C.

TABLE IV

EFFECT OF DIMETHYL SULFOXIDE- $d_6$  AND PYRIDINE- $d_5$  ON THE SPECTRA OF MISCELLANEOUS COMPOUNDS IN THE C-H STRETCHING REGION<sup>a</sup>

| Compound  | $\nu_{\text{CH}}$ in CCl <sub>4</sub> soln. | 0.95 M CD <sub>3</sub> SOC <sub>2</sub> D <sub>3</sub> in CCl <sub>4</sub> |                          |             | 2 M pyridine- $d_5$ in CCl <sub>4</sub> |                          |                  |
|---|---|--|--------------------------|-------------|---|--------------------------|------------------|
|   | $\nu_{\text{CH}}$                           | $\nu_{\text{CH}}$ "free"   | $\nu_{\text{CH}}$ bonded | $\Delta\nu$ | $\nu_{\text{CH}}$ "free"                | $\nu_{\text{CH}}$ bonded | $\Delta\nu$      |
| BrCH <sub>2</sub> C≡CH <sup>b</sup>                               | 3311  | 3311   | 3209 <sup>c</sup>        | 102         | 3311                                    | 3201                     | 110 <sup>d</sup> |
| CH <sub>3</sub> (CH <sub>2</sub> ) <sub>3</sub> C≡CH <sup>b</sup> | 3315  | 3315   | 3233                     | 82          |   |                          |                  |
| CHCl <sub>2</sub> CHClCHCl <sub>2</sub> <sup>e</sup>              | 3004  | 3004   | 2973                     | 31          | 3003                                    | 2965sh.                  | (38)             |
|   | 2956  | 2956sh.  | 2935sh.                  | (21)        | 2955                                    | 2919                     | 36               |
| CHCl <sub>2</sub> CHCl <sub>2</sub>                               | 2983 <sup>f</sup>                           | 2984sh.  | 2959                     | (25)        |   |                          |                  |
| CHBr <sub>2</sub> CHBr <sub>2</sub>                               | 2991 <sup>g</sup>                           | 2990   | 2949                     | 41          |   |                          |                  |
| CHCl <sub>2</sub> COOCH <sub>3</sub>                              | 3009 <sup>h</sup>                           | 3006   | 2980sh.                  | 26          |   |                          |                  |

<sup>a</sup> Frequencies are in cm<sup>-1</sup>; sh. = shoulder. <sup>b</sup> Only the acetylenic C-H band is shown. Stretching vibrations of the methylene and methyl groups were not affected by the proton acceptors. <sup>c</sup> CH<sub>3</sub>SOCH<sub>3</sub> was used for this measurement. <sup>d</sup> The spectral shift is 113 cm<sup>-1</sup> if ordinary pyridine is used instead of pyridine- $d_5$ , showing that the deuterium substitution in the proton acceptor has negligible effect on the hydrogen bonding spectral shifts. <sup>e</sup> The 3004 cm<sup>-1</sup> band corresponds to  $\nu_{\text{CH}}$  of the terminal -CHCl<sub>2</sub> group, while the band at 2956 cm<sup>-1</sup> is  $\nu_{\text{CH}}$  of the internal -CHCl- group; see H. Gerding and G. W. A. Rijnders, *Rec. trav. chim.*, **65**, 143 (1946). <sup>f</sup> There is also a shoulder at about 2998 cm<sup>-1</sup>. <sup>g</sup> There is also a shoulder at about 3012 cm<sup>-1</sup>. <sup>h</sup> A shoulder at about 3033 cm<sup>-1</sup> and a strong band at 2957 cm<sup>-1</sup> are unaffected by 0.95 M CD<sub>3</sub>SOC<sub>2</sub>D<sub>3</sub> (Fig. 6B); see text.

0.1-mm. cells, using proportionately larger concentrations of proton donors but without changing the proton acceptor concentrations. Identical results were obtained in both types of measurements. Spectral grade solvents were used without further purification. Other compounds used were purified by fractional distillation or recrystallization. Dimethyl sulfoxide- $d_6$ ,<sup>23</sup> trichloroethylene- $d_4$ ,<sup>24</sup> monodeuteriobenzene<sup>25</sup> and dibromoacetonitrile<sup>26</sup> were prepared by known methods. Commercially available pyridine- $d_5$  (Merck, Sharpe and Dohme of Canada, Ltd.) was used without further purification.

(23) F. A. Cotton, J. H. Fassnacht, W. D. Horrocks, Jr., and N. A. Nelson, *J. Chem. Soc.*, 4138 (1959).

(24) T. J. Houser, R. B. Bernstein, R. G. Miekka and J. C. Angus, *J. Am. Chem. Soc.*, **77**, 6201 (1955).

(25) W. M. Lauer and W. E. Noland, *ibid.*, **75**, 3689 (1953).

(26) J. W. Wilt and J. L. Diebold, *Org. Syntheses*, **38**, 16 (1958).

## Results and Discussion

Results of C-H...B hydrogen bonding studies are given in Tables I-IV and Fig. 1-6. C-D...B hydrogen bonds are illustrated in Table VI, and Table V shows the effect of both "inert" and proton accepting solvents on  $\nu_{\text{CD}}$  of monodeuteriobenzene. Additional infrared spectroscopic results on haloform- $d$  hydrogen bonding have been given in a previous report.<sup>9</sup>

For the hydrogen bonding equilibrium  $\text{R}_3\text{CH} + \text{B} \rightleftharpoons \text{R}_3\text{CH} \cdots \text{B}$  in dilute CCl<sub>4</sub> solution,  $\nu_{\text{CH}}$  will designate the CH stretching frequency of the "free" R<sub>3</sub>CH molecule and  $\nu_{\text{CHB}}$  will refer to the R<sub>3</sub>CH...B hydrogen bonded complex;  $\Delta\nu = \nu_{\text{CH}} - \nu_{\text{CHB}}$ . If  $\Delta\nu$  is suf-

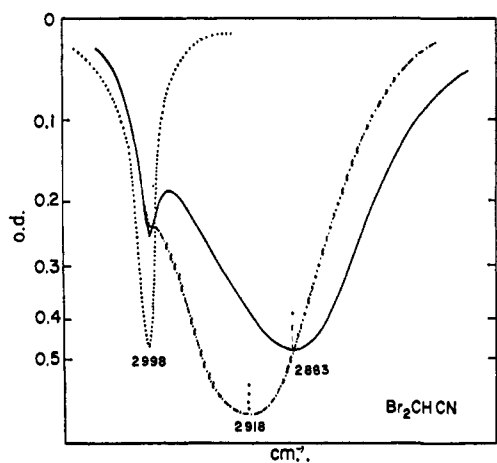


Fig. 1.—Effect of proton acceptors on  $\nu_{\text{CH}}$  of dibromoacetonitrile. Conditions:  $\cdots\cdots$ ,  $\text{CCl}_4$  solution;  $\text{—}$ , 2 M pyridine- $d_5$  in  $\text{CCl}_4$ ;  $\text{- - -}$ , 0.95 M  $\text{CD}_3\text{SOCD}_3$  in  $\text{CCl}_4$ . Concentration of proton donor: 10  $\mu\text{l./ml.}$ ; 1-mm. cells.

ficiently large, at least 10 or 15  $\text{cm.}^{-1}$ ,  $\nu_{\text{CH}}$  and  $\nu_{\text{CHB}}$  can be resolved<sup>27</sup> and two bands may be observed. In order to extend the spectral shift criterion to very weak proton donors, very strong proton acceptors must be used. The deuterated analogs of dimethyl sulfoxide and pyridine were chosen for the present studies.  $\Delta\nu_{\text{OH}}$  for methanol in  $\text{CCl}_4$  solution is 237  $\text{cm.}^{-1}$  with dimethyl sulfoxide,<sup>20</sup> 286  $\text{cm.}^{-1}$  with pyridine<sup>28</sup> and, in contrast, only 140  $\text{cm.}^{-1}$  with diethyl ether,<sup>20</sup> a widely used proton acceptor. In spite of the larger spectral shift with pyridine, hydrogen bonding equilibria are more favorable for dimethyl sulfoxide, perhaps because of the availability of two equivalent p-orbital bonding sites on oxygen in the latter compound (see Fig. 1). The largest shifts and the most favorable equilibria are obtained with tetraalkylammonium halides as proton acceptors<sup>9</sup> ( $\Delta\nu_{\text{OH}}$  methanol-tetraethylammonium chloride is 371  $\text{cm.}^{-1}$  in  $\text{CCl}_4$ ), but the deuterated analogs would be difficult to obtain. A complication which arises in the study of many  $\text{R}_3\text{CH}$  proton donors is the presence of several bands in the C-H stretching region. X- $\text{CH}_2$ -Y compounds have both a symmetrical and an antisymmetrical vibrational band. The first overtone of the C=C stretching frequency falls in this spectral region. This overtone may be a weak band (as in trichloroethylene, Table III) or an intense one due to Fermi resonance with the CH band (as in tribromoethylene).<sup>29</sup> The study of aromatic CH bands is rendered difficult by the complex patterns observed in the spectra of these compounds.<sup>30</sup> In the case of nitro compounds an additional complication may be the presence of an overtone of the strong band at 1570–1500  $\text{cm.}^{-1}$ .<sup>30</sup> Compounds such as  $\text{CHCl}_2\text{-CHCl-CHCl}_2$  contain two non-equivalent types of hydrogen, both of which may form hydrogen bonds with strong proton acceptors. The study of oxygenated analogs of chloroform, such as  $\text{HC(OCH}_3)_3$ , and of other interesting cases such as  $\text{CHCl}_2\text{-COOCH}_3$  is complicated by the presence of  $\text{CH}_3$  absorption bands.

**Compounds with a Single Band in the C-H Stretching Frequency Region.**—Results are summarized in Table I. Typical spectra are shown in Fig. 1 and 2.  $\Delta\nu_{\text{CH}}$  for dibromoacetonitrile with pyridine- $d_5$  is quite large, 113  $\text{cm.}^{-1}$ , a value not much less in absolute magnitude than  $\Delta\nu_{\text{OH}}$  for methanol-diethyl ether (140  $\text{cm.}^{-1}$ )<sup>20</sup>

(27) The limiting factor here is the band width of  $\nu_{\text{CH}}$  and  $\nu_{\text{CHB}}$ .

(28) E. D. Becker, *Spectrochim. Acta*, **17**, 436 (1961); T. Gramstad, *Acta Chem. Scand.*, **16**, 807 (1962), reported  $\Delta\nu = 300 \text{ cm.}^{-1}$ .

(29) J. C. Evans and H. J. Bernstein, *Can. J. Chem.*, **33**, 1171 (1955).

(30) L. J. Bellamy, "The Infrared Spectra of Complex Molecules," John Wiley and Sons, Inc., New York, N. Y., 1958.

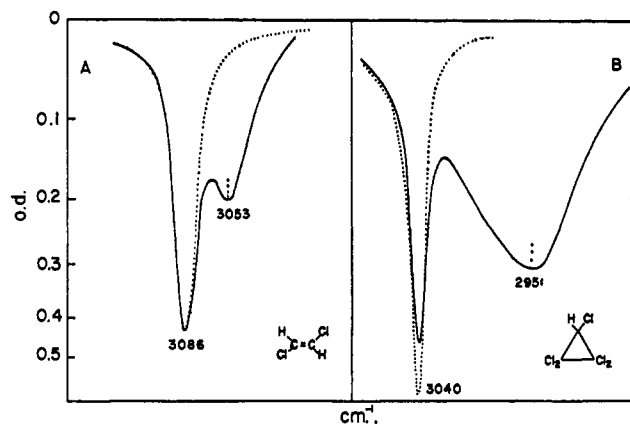


Fig. 2.—Effect of proton acceptors on CH stretching frequencies. Conditions: A, 10  $\mu\text{l./ml.}$  of *cis*-1,2-dichloroethylene in:  $\cdots\cdots$ ,  $\text{CCl}_4$  solution;  $\text{—}$ , 0.95 M  $\text{CD}_3\text{SOCD}_3$  in  $\text{CCl}_4$ ; B, 18  $\mu\text{l./ml.}$  of pentachlorocyclopropane in:  $\cdots\cdots$ ,  $\text{CCl}_4$  solution;  $\text{—}$ , 2 M pyridine- $d_5$  in  $\text{CCl}_4$ . 1-mm. cells were used for all measurements.

and greater than the values for methanol-acetonitrile (78  $\text{cm.}^{-1}$ )<sup>31</sup> and propargyl bromide-dimethyl sulfoxide (102  $\text{cm.}^{-1}$ ) (Table IV) considered to be well established examples of hydrogen bonding. For the compounds with large  $\Delta\nu$ 's,  $\nu_{\text{CHB}}$  was very broad (Fig. 1 and 2). Table I is arranged in order of decreasing spectral shifts. Chloroform, the most widely investigated and accepted example of C-H participation in hydrogen bonding, is nearly at the bottom of the list ( $\Delta\nu$  for  $\text{CHCl}_3$ -pyridine- $d_5$  is 46  $\text{cm.}^{-1}$ ).

From Table I it follows that: (a) Haloform  $\Delta\nu$ 's are in the order  $\text{CHBr}_3 > \text{CHI}_3 > \text{CHCl}_3$ . The same order has been observed for haloform-triethylamine spectral shifts.<sup>15</sup> Fluoroform behaves in an ambiguous way and will be discussed together with other fluorinated compounds. (b) When one of the halogens of a haloform is replaced by a cyano group there is a very large increase in  $\Delta\nu$ . Thus, the  $\Delta\nu$ 's on bonding to pyridine- $d_5$  are 46 and 92  $\text{cm.}^{-1}$  for chloroform and dichloroacetonitrile, respectively. (c)  $\Delta\nu_{\text{CH}}$  increases when X (Cl, Br) in  $\text{X}_3\text{CH}$  is replaced by the respective  $\text{CX}_3$  group. Thus,  $\Delta\nu$ 's increase appreciably in the series  $\text{CHCl}_3 < \text{CHCl}_2\text{CCl}_3 < \text{CCl}_3\text{CHClCCl}_3$  and  $\text{CHBr}_3 < \text{CHBr}_2\text{CBr}_3$ . (d)  $\Delta\nu$ 's are much larger for *trans*-1,2-dichloroethylene than for the *cis* isomer. Both compounds show clear evidence of hydrogen bonding to  $\text{CD}_3\text{SOCD}_3$  and pyridine- $d_5$  (Table I and Fig. 2). (e) Fluoroform showed evidence of hydrogen bonding to  $\text{CD}_3\text{SOCD}_3$  but not to pyridine- $d_5$ .  $\text{CF}_3\text{SCF}_2\text{CF}_2\text{H}$  showed no evidence of hydrogen bonding to pyridine- $d_5$ . Both available samples of  $\text{CF}_3(\text{CF}_2)_6\text{H}$  in  $\text{CCl}_4$  solution had two bands, at 3004 and 2978  $\text{cm.}^{-1}$ ; in the presence of pyridine- $d_5$ , slight intensity increases and possibly larger band widths were observed, but no detectable spectral shifts. More work is necessary before any conclusions can be drawn about partially fluorinated hydrocarbons as proton donors in hydrogen bonding by this method. Other evidence for this type of hydrogen bonding has been reported, e.g., for the systems  $\text{CF}_3(\text{CF}_2)_6\text{H}\cdots\text{acetone}$ <sup>13a</sup>,  $\text{CF}_3\text{CF}_2\text{CF}_2\text{H}\cdots\text{O}(\text{CH}_3)_2$ <sup>13b</sup> and  $\text{CHF}_3\cdots\text{tetrahydrofuran}$ .<sup>13c</sup>

In summary, all the compounds in Table I, except perhaps the fluorinated ones, are demonstrated by infrared spectroscopy to be proton donors in hydrogen bonding.

**Compounds of the Type X- $\text{CH}_2$ -Y.**—Results are summarized in Table II and Fig. 3.  $\Delta\nu$ 's are small in all

(31) P. von R. Schleyer and A. Allerhand, *J. Am. Chem. Soc.*, **84**, 1322 (1962).

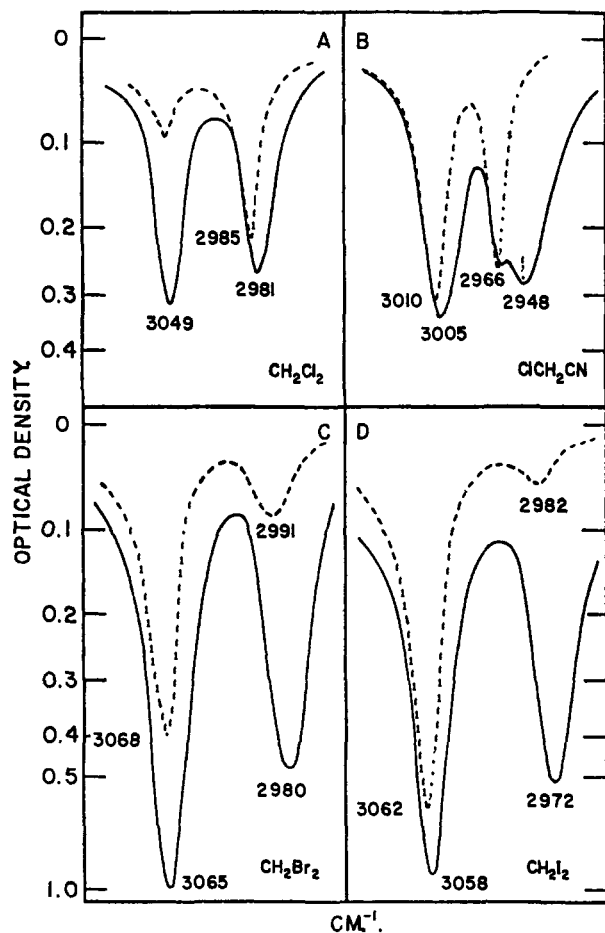


Fig. 3.—Effect of proton acceptors on  $\nu_{\text{CH}}$  of  $\text{XCH}_2\text{Y}$  compounds. Conditions: .....  $\text{CCl}_4$  solution; —, 0.95  $M$   $\text{CD}_3\text{SOCD}_3$  in  $\text{CCl}_4$ . Concentration of proton donors: A, 15  $\mu\text{l./ml.}$ , 1-mm. cells; B, 100  $\mu\text{l./ml.}$ , 0.1-mm. cells; C and D, 30  $\mu\text{l./ml.}$ , 1-mm. cells.

cases, but are much larger for the symmetrical than for the asymmetrical vibrations. A comparison can be made with other  $-\text{XH}_2$  proton donors, primary amines and water.  $\nu_{\text{NH}}$  sym. and  $\nu_{\text{NH}}$  asym. hydrogen bonding shifts are about equal in primary amines.<sup>32</sup> For water, the hydrogen bonding spectral shifts are somewhat larger for the asymmetrical than for the symmetrical band.<sup>33</sup>

In the case of  $\text{X}-\text{CH}_2-\text{CN}$  ( $\text{X} = \text{Cl}, \text{I}$ ) there is good spectral shift evidence for hydrogen bonding to strong proton acceptors (Table II and Fig. 3). For  $\text{CH}_2\text{X}_2$  ( $\text{X} = \text{Cl}, \text{Br}, \text{I}$ ) the spectral shifts were small (Table II), but the large intensity enhancements are strong indications of hydrogen bonding (Fig. 3).

**Vinylic Compounds.**—*cis*- and *trans*-1,2-dichloroethylene (Table I and Fig. 2), already discussed, and  $\text{CHX}_2=\text{CX}_2$  compounds (Table III and Fig. 4) form hydrogen bonds with strong proton acceptors. The spectral shift order for the latter was  $\text{X} = \text{Br} > \text{X} = \text{Cl} > \text{X} = \text{F}$ . The spectra of  $\text{CHF}=\text{CF}_2$  and  $\text{CHBr}=\text{CBr}_2$  also display a strong  $\nu_{\text{C}=\text{C}}$  first overtone, intensified by Fermi resonance with  $\nu_{\text{CH}}$ .<sup>29</sup> There was some evidence for a very weak hydrogen bond between acrylonitrile and pyridine- $d_5$ . The spectrum of  $\text{CH}_2=\text{CHCN}$  in  $\text{CCl}_4$  is not simple. In the presence of pyridine- $d_5$  there are intensity increases and very small shifts (*ca.* 5  $\text{cm.}^{-1}$ ). The spectrum of  $\text{CBr}_2\text{C}=\text{CHCH}_3$  was not appreciably altered by  $\text{CD}_3\text{SOCD}_3$  in  $\text{CCl}_4$ .

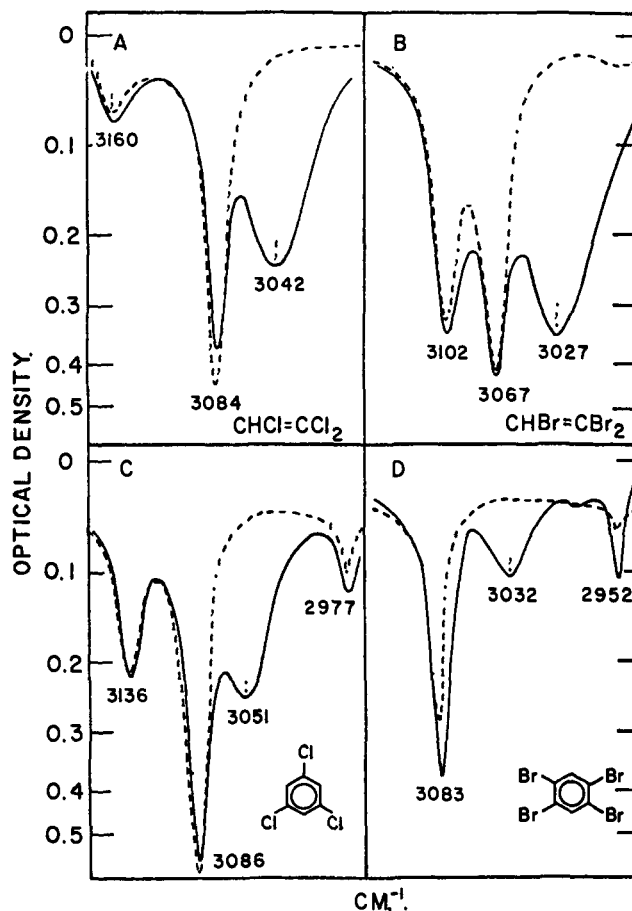
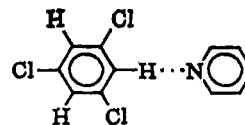


Fig. 4.—Effect of proton acceptors on the CH stretching region of unsaturated compounds. A, 10  $\mu\text{l./ml.}$  of trichloroethylene in: .....  $\text{CCl}_4$  solution; —, 0.95  $M$   $\text{CD}_3\text{SOCD}_3$  in  $\text{CCl}_4$ ; B, 20  $\mu\text{l./ml.}$  of tribromoethylene in: .....  $\text{CCl}_4$  solution; —, 0.95  $M$   $\text{CD}_3\text{SOCD}_3$  in  $\text{CCl}_4$ ; C, 42  $\text{mg./ml.}$  of 1,3,5-trichlorobenzene in: .....  $\text{CCl}_4$  solution; —, 2  $M$  pyridine- $d_5$  in  $\text{CCl}_4$ ; D, saturated solution of 1,2,4,5-tetrabromobenzene in: .....  $\text{CCl}_4$ ; —, 2  $M$  pyridine- $d_5$  in  $\text{CCl}_4$ ; 1-mm. cells were used for all measurements.

$\text{CHCH}_3$  was not appreciably altered by  $\text{CD}_3\text{SOCD}_3$  in  $\text{CCl}_4$ .

**Aromatic Compounds.**—Results are summarized in Table III and typical spectra are given in Fig. 4 and 5. The C-H spectra of the aromatic compounds (Table III) are complicated by the presence of overtone and combination bands. The changes caused by pyridine- $d_5$  in the 1,3,5-trichlorobenzene and 1,2,4,5-tetrabromobenzene spectra (Fig. 4) are simple to interpret. In  $\text{CCl}_4$  solution, 1,3,5-trichlorobenzene showed a C-H band at 3086  $\text{cm.}^{-1}$  and several weaker bands.<sup>30</sup> In the presence of 2  $M$  pyridine- $d_5$  an additional broader band at 3051  $\text{cm.}^{-1}$  appeared, assigned to  $\nu_{\text{CHB}}$  of the H-bonded complex with a  $\Delta\nu$  of 35  $\text{cm.}^{-1}$ . Similar



results were obtained with 1,2,4,5-tetrabromobenzene (Fig. 4D); the spectral shift was 51  $\text{cm.}^{-1}$  with pyridine- $d_5$ , larger than  $\Delta\nu_{\text{CH}}$  of chloroform-pyridine- $d_5$  (46  $\text{cm.}^{-1}$ , Table I)! We believe this to be the first reported specific evidence for hydrogen bonds involving aromatic hydrogens. (An earlier claim of detecting benzene-benzene hydrogen bonding by n.m.r.<sup>8a</sup> has now been retracted.<sup>8b</sup>) It appears that at least three

(32) E. A. Cutmore and H. E. Hallam, *Trans. Faraday Soc.*, **58**, 40 (1962).

(33) E. Greinacher, W. Lüttke and R. Mecke, *Z. Elektrochem.*, **59**, 23 (1955).

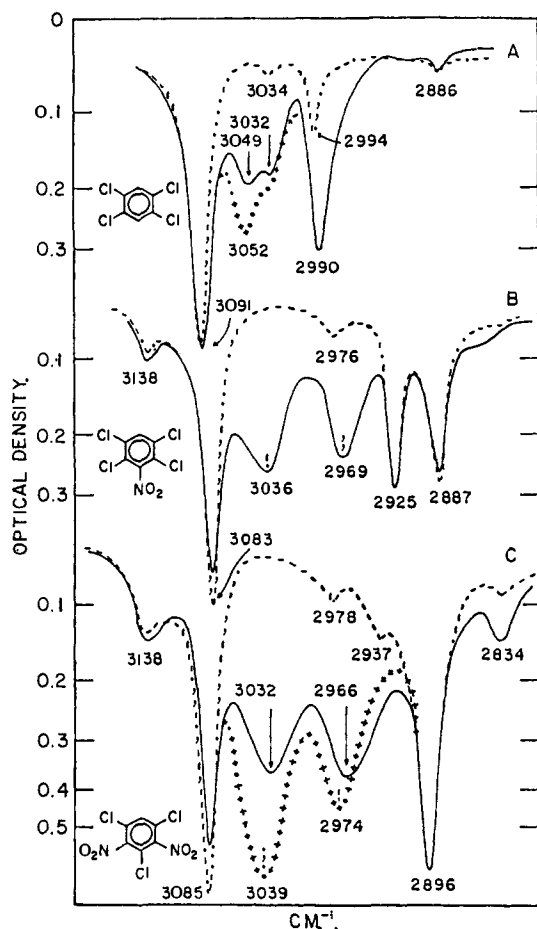


Fig. 5.—Effect of proton acceptors on the CH stretching region of substituted benzene derivatives. Conditions: ..... ,  $\text{CCl}_4$  solution; ———, 2 M pyridine- $d_6$  in  $\text{CCl}_4$ ; + + +, 0.95 M  $\text{CD}_3\text{SOCD}_3$  in  $\text{CCl}_4$ . Concentration of proton donors: A, 50 mg./ml.; B and C, 60 mg./ml.; 1-mm. cells were used for all measurements.

chlorines are necessary to increase the aromatic proton acidity sufficiently for hydrogen bonding. *m*-Dichlorobenzene and chlorobenzene showed several strong bands in the C-H region in  $\text{CCl}_4$  solution. The chlorobenzene spectrum was not altered by 2 M pyridine- $d_6$ , while the *m*-dichlorobenzene spectrum was very slightly modified. Benzene itself showed three bands in  $\text{CCl}_4$  solution: at 3092, 3073 and 3038  $\text{cm}^{-1}$ . The spectrum was not modified by introducing  $\text{CD}_3\text{SOCD}_3$  (0.95 M) or pyridine- $d_6$  (2 M). These results were confirmed by studying several deuterated compounds. The behavior of  $\nu_{\text{CD}}$  of monodeuteriobenzene showed no evidence of hydrogen bonding even to the strongest proton acceptors, such as pyridine,<sup>6</sup> triethylamine<sup>6</sup> and tetrabutylammonium bromide<sup>9</sup> (Table V).

TABLE V  
EFFECT OF SOLVENTS OF THE C-D STRETCHING FREQUENCY OF MONODEUTERIOBENZENE

| Solvent              | $\nu_{\text{CD}}$ , $\text{cm}^{-1}$ | Solvent  | $\nu_{\text{CD}}$ , $\text{cm}^{-1}$ |
|----------------------|--------------------------------------|--|--------------------------------------|
| Perfluoroöctane      | 2273                                 | Benzene  | 2267                                 |
| Hexane               | 2270                                 | Diethyl ether                                      | 2267                                 |
| Carbon tetrachloride | 2270                                 | Bromoform  | 2267                                 |
| Dichloromethane      | 2270                                 | 1 M pyridine in $\text{CCl}_4$                     | 2270                                 |
| Triethylamine        | 2268                                 | 0.5 M tetrabutylammonium bromide in $\text{CCl}_4$ | 2270                                 |

Preliminary results indicated that the C-D bands of *p*-dichlorobenzene-2-*d* and *m*-dichlorobenzene-2-*d* in  $\text{CCl}_4$  were only very slightly affected by 2 M pyridine.

Therefore, benzene and chlorobenzene do not behave as proton donors; 1,3,5-trichlorobenzene and more highly substituted analogs (Table III) form hydrogen bonds with strong proton acceptors, while *m*-dichlorobenzene is a borderline case.

The behavior of 1,2,4,5-tetrachlorobenzene, 1-nitro-2,3,5,6-tetrachlorobenzene and 3,5-dinitro-2,4,6-trichlorobenzene was more complicated. These compounds are good proton donors (Fig. 5), but the presence of the deuterated base not only causes the appearance of  $\nu_{\text{CHB}}$  (Table III) but also large increases in intensity and small shifts to lower frequency in bands close to  $\nu_{\text{CHB}}$  (Fig. 5). Thus, the very weak band at 3034  $\text{cm}^{-1}$  in the 1,2,4,5-tetrachlorobenzene spectrum (Table III) appears as a much stronger band at about the same frequency in the presence of  $\text{CD}_3\text{SOCD}_3$  or pyridine- $d_6$  (Fig. 5A). One possible explanation for this behavior is that  $\nu_{\text{CHB}}$  is close enough to the 3034  $\text{cm}^{-1}$  band for Fermi resonance to occur.<sup>34,35</sup> In all three cases (Fig. 5) only bands on the lower frequency side of  $\nu_{\text{CH}}$  are affected.  $\nu_{\text{CH}}$  and a weak overtone or combination band at a lower frequency may be too widely separated for Fermi resonance to occur,<sup>34</sup> but hydrogen bonding makes the separation smaller since  $\nu_{\text{CHB}}$  is less than  $\nu_{\text{CH}}$  and Fermi resonance may be possible (providing the two vibrational energy levels are of the same symmetry species<sup>34</sup>). Relative to the unperturbed vibrational energy levels, the perturbed energy levels will be shifted; their separation will be larger than in the absence of Fermi resonance.<sup>34</sup> This results in a displacement to lower frequency of the overtone or combination band and a displacement to higher frequency of  $\nu_{\text{CHB}}$  with respect to the positions of the unperturbed bands. As a consequence, the observed  $\Delta\nu$  of hydrogen bonding may be smaller than expected. This behavior apparently was exhibited by 1-nitro-2,3,5,6-tetrachlorobenzene (Fig. 5B) and 3,5-dinitro-2,4,6-trichlorobenzene (Fig. 5C). Both compounds in  $\text{CCl}_4$  showed strong C-H bands at about 3084  $\text{cm}^{-1}$  and very weak bands at about 2977  $\text{cm}^{-1}$ . In the presence of a strong proton acceptor, pyridine- $d_6$ , new broad bands ( $\nu_{\text{CHB}}$ ) appeared and the 2977  $\text{cm}^{-1}$  bands were greatly intensified and shifted slightly (7–12  $\text{cm}^{-1}$ ) to lower frequencies (Fig. 5B and C). In the absence of Fermi resonance,  $\nu_{\text{CHB}}$  should be at a lower frequency and  $\Delta\nu$  should be larger than was actually observed. If the intensity of the unperturbed overtone is negligible with respect to that of the participating fundamental vibration, then the zero-order separation of the two vibrational energy levels participating in a Fermi resonance interaction and the "true"  $\Delta\nu$  can be calculated.<sup>34,36,37</sup>

**Aldehydes.**—Arguments both in favor<sup>6,38</sup> and against<sup>6,39</sup> hydrogen bonds involving the aldehydic C-H as proton donor have been presented. The  $\text{CCl}_4$  solution spectra of acetaldehyde, *p*-chlorobenzaldehyde, dimethylformamide and chloral in the absence and presence of pyridine- $d_6$  or dimethyl sulfoxide- $d_6$  were examined. Chloral reacted with the proton acceptors.

(34) G. Herzberg, "Molecular Spectra and Molecular Structure. II. Infrared and Raman Spectra of Polyatomic Molecules," D. Van Nostrand Co., Inc., Princeton, N. J., 1945, pp. 215–217 and 265–266.

(35) The possibility that the original weak bands discussed above are caused by impurities was also considered. The compounds were carefully recrystallized. Melting points were sharp. Spectroscopic results after one or two recrystallizations were identical with those after five or more recrystallizations.

(36) E. L. Saier, L. R. Cousins and M. R. Basila, *J. Phys. Chem.*, **66**, 232 (1962).

(37) R. N. Dixon, *J. Chem. Phys.*, **31**, 258 (1959).

(38) C. M. Lee and W. D. Kumler, *J. Am. Chem. Soc.*, **84**, 571 (1962).

(39) (a) W. F. Forbes, *Can. J. Chem.*, **40**, 1891 (1962); and references cited therein; (b) I. D. Kuntz, Jr., A.B. Thesis, Princeton University, 1961; (c) R. E. Klinck and J. B. Stothers, *Can. J. Chem.*, **40**, 1071 (1962).

The spectra of the other compounds were unaffected both in the region of the aldehydic C-H band and of the other C-N stretching vibrations. Methyl formate was also examined. Dimethyl sulfoxide- $d_6$  had no effect on the "aldehydic" C-H band<sup>36</sup> at 2837  $\text{cm}^{-1}$  but caused slight intensity changes in bands at 2954 and 2931  $\text{cm}^{-1}$ . Thus we find no evidence of "aldehydic" C-H participation in *intermolecular* hydrogen bonding,



a conclusion confirmed by a companion n.m.r. study.<sup>39b</sup>

**Miscellaneous Compounds.**—For the acetylenic C-H band of propargyl bromide  $\Delta\nu_{\text{CH}}$  was 110  $\text{cm}^{-1}$  with pyridine- $d_5$  and 113  $\text{cm}^{-1}$  with ordinary pyridine (Table IV); the difference was within experimental error, as expected.  $\text{CHCl}_2\text{CHClCHCl}_2$  has two non-equivalent protons; both have hydrogen bonding ability (Table IV and Fig. 6A). The  $\text{CCl}_4$  solution spectrum of methyl dichloroacetate is not simple (Fig. 6B). The band at 3009  $\text{cm}^{-1}$  probably corresponds to  $\nu_{\text{CH}}$  of the  $\text{CHCl}_2$ -group ( $\nu_{\text{CH}}$  of  $\text{CHCl}_3 = 3020 \text{ cm}^{-1}$ ) while the strong band at 2957  $\text{cm}^{-1}$  can be assigned to the symmetrical stretching mode of the  $\text{CH}_3$  group.<sup>34</sup> In the presence of  $\text{CD}_3\text{SOCD}_3$  an additional strong band appears at about 2980  $\text{cm}^{-1}$  (Fig. 6B), indicating hydrogen bonding of the proton in the  $\text{CHCl}_2$  group to dimethyl sulfoxide- $d_6$ . This hydrogen bonding method may be used similarly to help assign C-H bands. Triphenylmethane, 1,1,1-trichloroethane and methyl iodide gave no indication of hydrogen bonding to strong proton acceptors. The spectrum of  $\text{CH}_3\text{SOCH}_3$  in  $\text{CCl}_4$  solution was not concentration dependent, up to 100% dimethyl sulfoxide. This is evidence against self-association. Changes are observed in the C-H region of the nitromethane spectrum in  $\text{CCl}_4$  solution as the concentration of  $\text{CH}_3\text{NO}_2$  varies.<sup>40</sup> This is not attributed to hydrogen bonding but to "charge transfer" interactions between  $\text{CH}_3\text{NO}_2$  molecules.<sup>40,41</sup> The effects of dimethyl sulfoxide- $d_6$  and pyridine- $d_5$  on the nitromethane spectrum in  $\text{CCl}_4$  solution (Fig. 6C) are very similar to those resulting when the concentration of nitromethane is increased.<sup>40,42</sup> This would indicate some type of association between nitromethane and the proton acceptors, but the spectral changes would be difficult to explain on the basis of hydrogen bonding. Similarly, the effect of our proton acceptors on the acetonitrile spectrum, which was not as pronounced as for nitromethane, is not indicative of hydrogen bonding. The complete alteration of the spectra of trimethyl and triethyl orthoformates in the C-H region by dimethyl sulfoxide- $d_6$  was indicative of a chemical reaction. Pyridine- $d_5$  had no effect on the CH stretching region of the  $\text{CH}(\text{OCH}_3)_3$  spectrum. Since the observed spectrum is complicated,  $\text{CD}(\text{OCH}_3)_3$  should be investigated before asserting that the trimethoxy analog of chloroform is not a proton donor.

**Compounds with C-D Bonds.**—It would be desirable to study the hydrogen bonding ability of the deuterated analogs of many of the compounds in Fig. 1-6. Only a few of these were investigated. Results with monodeuteriobenzene (Table V) and two of its dichloro derivatives have been mentioned in a previous section. As expected, deuteriohaloforms form hydrogen bonds with strong proton acceptors.<sup>9,12,18,19</sup>

(40) P. A. D. de Maine, *J. Mol. Spectry.*, **4**, 407 (1960).

(41) P. A. D. de Maine, M. M. de Maine and A. G. Goble, *Trans. Faraday Soc.*, **53**, 427 (1957), and references cited therein.

(42) The C-H region spectrum of nitromethane in  $\text{CCl}_4$  solution (Fig. 6C) is similar in pattern and relative intensities of the bands to that of ref. 40, but there are large discrepancies in the positions of the bands. Our measurements were carried out on both available high resolution spectrometers (see Experimental section), with similar results on both.

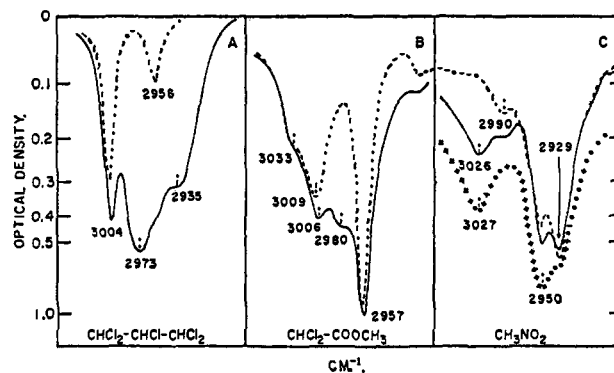


Fig. 6.—Effect of strong proton acceptors on the CH stretching region. A,  $\text{CHCl}_2\text{CHClCHCl}_2$ ; conditions:  $\cdots\cdots$ , 15  $\mu\text{l./ml.}$  in  $\text{CCl}_4$ ;  $\text{—}$ , 20  $\mu\text{l./ml.}$  in 0.95  $M$   $\text{CD}_3\text{SOCD}_3$  in  $\text{CCl}_4$ ; B,  $\text{CHCl}_2\text{COOCH}_3$ ; conditions: 20  $\mu\text{l./ml.}$  in:  $\cdots\cdots$ ,  $\text{CCl}_4$  solution;  $\text{—}$ , 0.95  $M$   $\text{CD}_3\text{SOCD}_3$  in  $\text{CCl}_4$ ; C,  $\text{CH}_3\text{NO}_2$ ; conditions: 30  $\mu\text{l./ml.}$  in:  $\cdots\cdots$ ,  $\text{CCl}_4$  solution;  $\text{—}$ , 2  $M$  pyridine- $d_5$  in  $\text{CCl}_4$ ; + + +, 0.95  $M$   $\text{CD}_3\text{SOCD}_3$  in  $\text{CCl}_4$ . All measurements were carried out in 1-mm. cells.

Hydrogen bonds with trichloroethylene- $d$  as proton acceptor are demonstrated in Table VI.

**Hydrogen Bonds Involving the Si-H Link.**—The Si-H band of  $\text{SiHCl}_3$ , at 2257  $\text{cm}^{-1}$  in  $\text{CCl}_4$  solution,<sup>43</sup> is unshifted by the addition of dibutyl ether. Under the same conditions the shift of the C-H band of  $\text{CHCl}_3$  would be small, but easily detectable.<sup>19</sup> Instantaneous reactions in  $\text{CCl}_4$  solution occurred with the stronger proton acceptors pyridine and dimethyl sulfoxide; tetrabutylammonium bromide<sup>9</sup> produced an ambiguous spectral change. Smith and Angelotti<sup>43b</sup> stated, "Hydrogen bonding in SiH compounds has never been found, and, if it exists, the effect on the frequency must be small." An n.m.r. study<sup>44</sup> reporting hydrogen bonding involving  $\text{SiHCl}_3$  cannot now be regarded as conclusive, since two component systems were employed (compare ref. 8a and 8b). In our opinion, more work is necessary to establish whether silicochloroform can function as a proton donor.

**Interpretation and Conclusions.**—A spectral shift of appreciable magnitude constitutes definite evidence for hydrogen bonding,<sup>6</sup> but the lack of such a shift does not necessarily indicate the absence of hydrogen bonding (see above).<sup>19</sup> Nevertheless, if there is no detectable alteration of an infrared spectrum either in position or in intensity in the presence of the strongest available proton acceptors, it seems reasonable to assume that hydrogen bonding is unimportant and that physical properties are not influenced significantly by such interactions. We believe that the evidence indicates that a single electron-withdrawing group attached to a  $\text{sp}^3$ -hybridized carbon is not sufficient to make the hydrogens attached to such a carbon proton donors. Methyl groups in any molecule do not hydrogen bond,<sup>45</sup> nor apparently do C-H groups in alkyl chains, nor in aldehydes,<sup>45</sup> formates and formamides.

All kinds of deviations from "expected" or "ideal" behavior have at one time or another been attributed, often over-enthusiastically, to C-H hydrogen bonding.<sup>46</sup> A referee has commented, "One point which should be

(43) Reported at 2258  $\text{cm}^{-1}$ : (a) H. W. Thompson, *Spectrochim. Acta*, **16**, 238 (1960); (b) A. L. Smith and N. C. Angelotti, *ibid.*, **15**, 412 (1959).

(44) C. M. Huggins and D. R. Carpenter, *J. Phys. Chem.*, **63**, 238 (1959).

(45) A conclusion confirmed by n.m.r. studies, ref. 8b and 39b.

(46) See, for example: E. A. Braude and J. A. Coles, *J. Chem. Soc.*, 2085 (1951); J. L. H. Allan and M. C. Whiting, *ibid.*, 3314 (1953); Mmc. and M. J. Martinet, *Bull. soc. chim. France*, 71 (1948); D. Jerchel and W. Melloh, *Ann.*, **613**, 144 (1958); P. J. Elving, J. M. Markowitz and I. Rosenthal, *Chem. Ind. (London)*, 1192 (1959); I. Brown and F. Smith, *Australian J. Chem.*, **13**, 30 (1960); J. Radell and L. A. Harrah, *J. Chem. Phys.*, **36**, 1571 (1962); additional examples are given in Chapter 6 of ref. 6.

TABLE VI

EFFECT OF SOLVENTS ON THE C-D STRETCHING FREQUENCY OF  $\text{CDCl}=\text{CCl}_2^a$ 

| Solvent <sup>b</sup>                          | $\nu_{\text{CD}}$<br>"free" | $\nu_{\text{CD}}$<br>bonded | $\Delta\nu$       |
|---|-----------------------------|-----------------------------|-------------------|
| "Inert" solvents                              |                             |                             |                   |
| Perfluorooctane                               | 2306                        | None                        | ...               |
| Carbon tetrachloride                          | 2302                        | None                        | ...               |
| Tetrachloroethylene                           | 2300                        | None                        | ...               |
| Carbon disulfide                              | 2296                        | None                        | ...               |
| Weak proton acceptors                         |                             |                             |                   |
| Benzene                                       | 2296                        | None                        | ...               |
| Nitromethane                                  | 2302                        | None                        | ...               |
| Ethers  |                             |                             |                   |
| Dioxane                                       | 2290 <sup>c</sup>           |                             | (10) <sup>d</sup> |
| Tetrahydrofuran                               | sh.                         | 2285                        | 15 <sup>d</sup>   |
| Diethyl ether                                 | 2298sh.                     | 2287                        | (11)              |
| Dibutyl ether                                 | 2300                        | 2286                        | 14                |
| Sulfoxides                                    |                             |                             |                   |
| Dimethyl sulfoxide                            | None                        | 2266                        | 34 <sup>d</sup>   |
| Diisopropyl sulfoxide                         | 2297sh.                     | 2261                        | 36                |
| Tetramethylene sulfoxide                      | None                        | 2260                        | 40 <sup>d</sup>   |
| Tertiary amines                               |                             |                             |                   |
| N,N-Dimethylaniline                           | 2292 <sup>e</sup>           |                             | (8) <sup>d</sup>  |
| Triethylamine                                 | 2300                        | 2241                        | 59                |
| Tripropylamine                                | 2300                        | 2246                        | 54                |
| Tributylamine                                 | 2300                        | sh.                         | ?                 |
| N-Methylmorpholine                            | sh.                         | 2287 <sup>e</sup>           | (13) <sup>d</sup> |
|   |                             | 2251sh. <sup>f</sup>        | (49) <sup>d</sup> |
| Pyridine derivatives                          |                             |                             |                   |
| Pyridine                                      | 2297                        | 2268                        | 29                |
| 2-Chloropyridine                              | 2297                        | 2282sh.                     | 17                |
| 3-Picoline                                    | 2296                        | 2265                        | 31                |
| 5-Ethyl-2-picoline                            | 2297                        | 2257                        | 40                |
| 2,6-Lutidine                                  | 2297                        | 2260                        | 37                |
| Quinoline                                     | 2296                        | 2263                        | 33                |
| Proton acceptors in $\text{CCl}_4$ soln.      |                             |                             |                   |
| 1 M dimethyl sulfoxide                        | 2301                        | 2273                        | 28                |
| 0.5 M tetrabutylammonium bromide <sup>g</sup> | 2301                        | 2235                        | 66                |

<sup>a</sup> All frequencies are in  $\text{cm}^{-1}$ . <sup>b</sup> Pure liquid proton acceptor, unless otherwise stated. <sup>c</sup> Assignment of this band to the "free" or bonded category would be arbitrary; see ref. 19. <sup>d</sup> "Free" band assumed at  $2300 \text{ cm}^{-1}$ . <sup>e</sup> Hydrogen bonding to the oxygen. <sup>f</sup> Hydrogen bonding to the nitrogen. <sup>g</sup> See ref. 9.

clearly and explicitly made...is that most of the H-bonds under study are very weak ones. The reason for doing so is that many chemists do not differentiate quantitatively between such bonds and more powerful ones of the OH...O type, for example. In the reviewer's experience, it is not unusual to find organic or even physical chemists rationalizing conformations, postulated reaction intermediates, and other structural features with the help of hydrogen bonds of the type studied here when the energy contribution of the bonds is an order of magnitude too small to produce the supposed effects." We agree that discretion should be used before attributing a physical datum to C-H hydrogen bonding, but the referee has overstated the case. It is apparent from the present survey that C-H groups can have a very wide range of proton donor abilities. C-H spectral shifts range from 0 to well over  $100 \text{ cm}^{-1}$  and in some cases are comparable even in absolute magnitude to OH spectral shifts involving methanol as proton donor. Hydrogen bonding enthalpies of C-H proton donors have not been studied

widely, but the available data for chloroform indicate  $-\Delta H$ 's from 2.5 to 6 kcal./mole to common oxygen-containing proton acceptors<sup>6,12,13c</sup>; these values are not inferior to those reported for methanol hydrogen bonding to similar bases.<sup>6</sup>

What is the significance of the magnitude of the observed spectral shifts? The Badger-Bauer rule,<sup>47</sup> ascribing a proportionality between the enthalpy of a hydrogen bond and the spectral shift, has been seriously questioned recently.<sup>6,9,13,28,48-50</sup> Although a  $\Delta H-\Delta\nu$  relationship can be demonstrated for a series of similar compounds,<sup>49,51</sup> the rule may not have general validity; for example, enthalpies for the association of phenol with cyclohexyl halides are just opposite to those predicted from the observed spectral shifts.<sup>48</sup> For C-H proton donors, the same lack of correlation seems to hold. Very recently, Creswell and Allred have determined the thermodynamics of haloform-tetrahydrofuran association in cyclohexane solution by an n.m.r. method.<sup>13c</sup> Their results— $\Delta H$ 's for  $\text{CHF}_3$ ,  $\text{CHCl}_3$ ,  $\text{CHBr}_3$  and  $\text{CHI}_3$  were  $-2.4$ ,  $-3.6$ ,  $-2.6$  and  $-1.6$  kcal./mole, respectively—do not correspond in any simple way to the order of spectral shifts reported for these haloforms in Table I and by Glick.<sup>15</sup> Proton donor spectral shifts evidently are due to a subtle interplay of hybridization, inductive, resonance, polarizability and medium effects as yet quite imperfectly understood. Complementary thermodynamic studies are desirable, but determination of spectral shifts—experimentally easy—reveal which systems are interesting enough for enthalpy measurements, which are experimentally tedious to do.

Spectral shifts also do not appear to correlate with conventional acidities. Phenol, an excellent proton donor in hydrogen bonding, and nitromethane, which we believe is not a proton donor, both have roughly the same  $pK_a$  values.<sup>52</sup> The rates of carbanion formation of the haloforms,  $\text{CHI}_3 \approx \text{CHBr}_3 \gg \text{CHCl}_3 \gg \text{CHF}_3$ ,<sup>52</sup> mirror neither the spectral shift order (Table I) nor the hydrogen bonding enthalpy order.<sup>13</sup> In a hydrogen bonded complex the proton donor X-H bond is weakened, but only slightly (*ca.* 1-5%) and there is little change in charge distribution. Conventional acidities reflect energy differences between an un-ionized acid and its anion, in which resonance effects stabilizing the negative charge play a prominent role. In hydrogen bonding such resonance effects at best must be minor. Nevertheless, C-H compounds which give appreciable spectral shifts appear to be sufficiently acidic to undergo facile base-catalyzed H-D exchange, *e.g.*, haloforms<sup>52</sup> and  $\text{ClCH}=\text{CCl}_2$ .<sup>24</sup> Benzene derivatives, substituted with two *ortho* electron-withdrawing groups, have recently been found to change readily.<sup>53</sup>

We conclude that the ability of a C-H group to act as a proton donor in hydrogen bonding depends on the carbon hybridization,  $\text{C}(\text{sp})-\text{H} > \text{C}(\text{sp}^2)-\text{H} > \text{C}(\text{sp}^3)-\text{H}$ , and increases with the number of adjacent electron-withdrawing groups. Terminal acetylenes are pro-

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(53) J. Hine and P. B. Langford, *J. Org. Chem.*, **27**, 4149 (1962); also see references therein cited.



ton donors even in the absence of electronegative substituents.<sup>6,9</sup> In compounds  $R_2C=CHX$ , X and at least one of the R groups have to be strongly electron withdrawing for the molecule to give a well detectable hydrogen bond. Benzene needs three such substituents to be a proton donor, since the grouping  $=CHX$  is impossible. In  $C(sp^3)-H$  compounds at least two substituents X in  $CHX_3$  have to be strongly activating in order for the compound to exhibit proton donor characteristics. The effectiveness of activation by electron-withdrawing substituents, as measured by the infrared spectral shift criterion, is:  $CN \gg CCl_2Cl_3 > CBr_3 > CCl_3 > Br > I > CHClCHCl_2 \sim Cl > F > COOCH_3 > CHBr_2 > CHCl_2$ . Each of these substituents can be assigned a "spectral shift increment" for a given proton acceptor; in compounds  $CHXYZ$  the sum of individual contributions for each group X, Y and Z can be used to predict  $\Delta\nu$ 's accurately. This additivity relationship is reminiscent of that observed for  $^{13}C-H$  n.m.r. coupling constants in the same compounds; the magnitudes of such coupling constants are used to estimate the hybridization of carbon.<sup>54</sup> However, the infrared and n.m.r. additivity

increments agree only in a very general way suggesting that hybridization of carbon cannot be the only significant factor in determining infrared spectral shifts. The spectral shifts of C-H proton donors do not appear to correlate with the enthalpy of hydrogen bonding.

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## The Hydrogen Bonding Propensities of the Haloforms

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Thermodynamic constants for the association of tetrahydrofuran with fluoroform, chloroform, bromoform and iodoform were measured by nuclear magnetic resonance techniques. The magnitudes of the enthalpy of association decrease in the order chloroform > bromoform  $\approx$  fluoroform > iodoform.

### Introduction

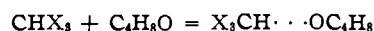
Conflicting results were obtained in previous studies of the relative strengths of hydrogen bonds formed by the haloforms. From dielectric polarizations of solutions of haloforms in various donors, the following orders of complex formation are indicated<sup>1</sup>

Acetone: chloroform > bromoform > iodoform  
Diethyl ether: chloroform = bromoform > iodoform  
Diisopropyl ether: chloroform > bromoform  
Quinoline: chloroform > bromoform > iodoform

The heat of mixing is slightly greater for the addition of a given donor solvent to chloroform than to bromoform.<sup>2,3</sup> It may also be noted<sup>2</sup> that, for a given donor, heats of mixing decrease in the order methylene chloride > methylene bromide  $\gg$  methylene iodide where hydrogen bonding is probably much less important. The heats of mixing for the systems chloroform-ethylene glycol dimethyl ether, dichlorofluoromethane-ethylene glycol dimethyl ether, chloroform-tetraethylene glycol dimethyl ether and dichlorofluoromethane-tetraethylene glycol dimethyl ether have been presented<sup>4</sup> for a wide range of concentrations. The maxima of the corresponding heat of mixing-composition curves for chloroform and dichlorofluoromethane were reported to be the same within experimental error. The solubilities of chloroform, dichlorofluoromethane and chlorodifluoromethane in several ethers were found to increase in the order given, and it was concluded<sup>5</sup>

that the hydrogen bonding ability of the  $\begin{array}{c} \diagup \\ C-H \\ \diagdown \end{array}$  group is increased as fluorine atoms are substituted for the chlorine atoms of chloroform. With the recent appearance<sup>6-9</sup> of considerable evidence for only limited validity of the Badger-Bauer rule<sup>10</sup> which relates spectral shifts in the infrared to the energies of hydrogen bonds, the earlier conflicting interpretations of spectral shifts<sup>11,12</sup> can be understood.

The present paper reports the determination of the thermodynamic constants for the association of tetrahydrofuran with fluoroform, chloroform, bromoform



and iodoform in the solvent cyclohexane.

### Experimental

**Preparation of Compounds and Solutions.**—Fluoroform was prepared from the reaction of trifluoromethyl iodide with potassium hydroxide in the solvent acetone.<sup>13</sup> The fluoroform was separated from impurities by bulb-to-bulb distillation and shown to be pure by hydrogen and fluorine nuclear magnetic resonance (n.m.r.).

Chloroform was washed with concentrated sulfuric acid, dilute sodium hydroxide and ice-water.<sup>14</sup> The chloroform was then

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