[Contribution from the Department of Chemistry, Iowa State College]

Stretching Frequencies as a Function of Distances in Hydrogen Bonds

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Measurements of hydrogenic stretching frequencies of a number of hydrogen bonded compounds have been made in the crystalline state. For "straight" hydrogen bonds, approximately linear relations have been found between X–H. . .Y distances and the X–H stretching frequencies in the systems, O–H. . .O, O–H. . .N, N–H. . .F, N–H. . .O, N–H. . .Cl, N–H. . . N and F–H. . .F, while "bent" hydrogen bonds show large deviation from the regular sequence, always with higher frequencies. The effects of formal charge or coördination number have also been noticed. Based on these results, the crystal structures of several compounds and the nature of hydrogen bonding have been discussed.

Introduction

The lowering of hydrogenic stretching frequencies by hydrogen bonds is well known.[2] Recently it has been shown that for O–H . . . O hydrogen bonds the frequency shift is a monotonic and nearly linear function of the O-H . . . O distance.[3] Since such relationships seem likely to be useful to spectroscopists[4] and molecular crystallographers,[5] we have extended them to a variety of hydrogen bonds X–H . . . Y, where X and Y may be F, O, N and Cl. The main results of this extension are shown in Fig. 1.

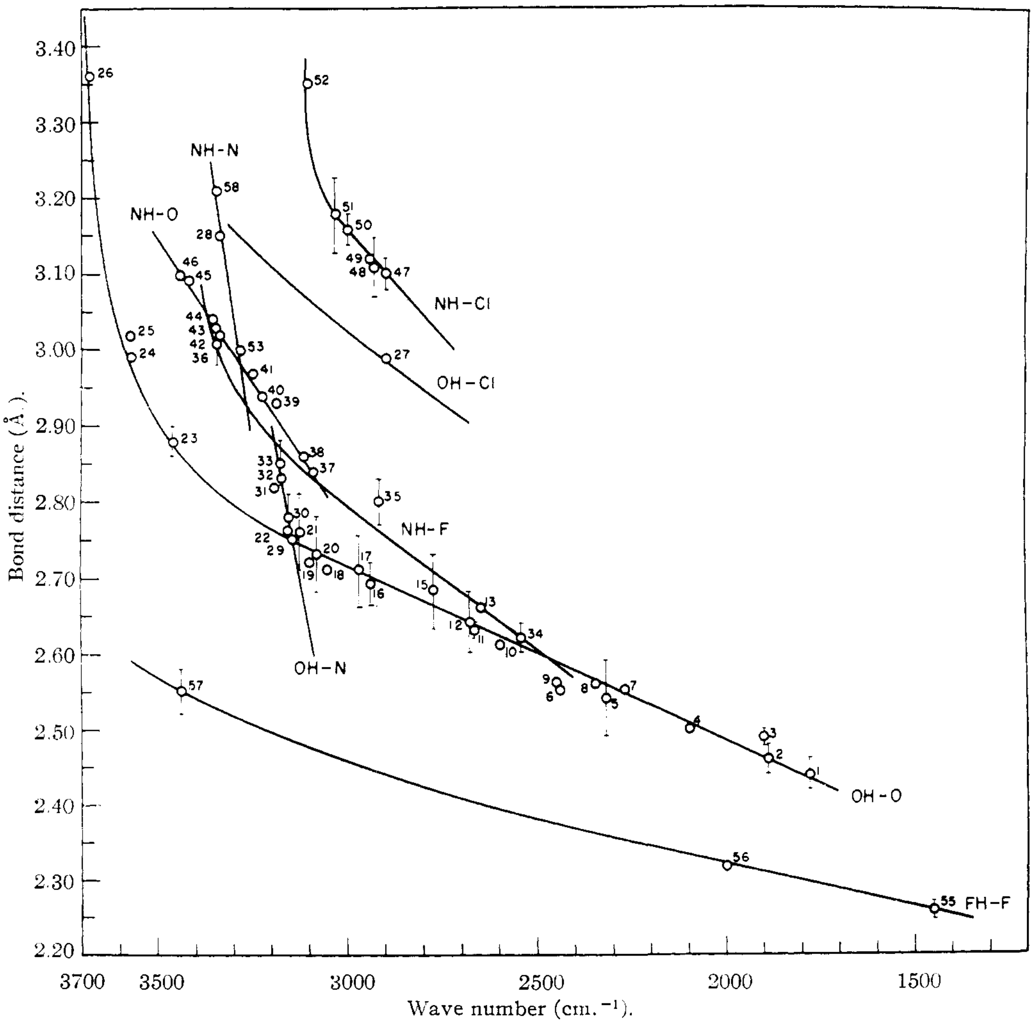

Fig. 1.—Hydrogenic stretching frequency *versus* bond distance for various types of hydrogen bonds.

When such relationships are used there must be definite limitations to their validity, and we have considered some of the more obvious ones, namely, coupling of frequencies, crystalline field effects and geometry of the hydrogen bond. In the latter

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(2) R. M. Badger, *J. Chem. Phys.*, **11**, 288 (1940).

(3) (a) R. E. Rundle and M. Parasol, *ibid.*, **20**, 1487 (1952); (b) R. C. Lord and R. E. Merrifield, *ibid.*, **21**, 166 (1953).

(4) W. Klemperer and G. C. Pimentel, *ibid.*, **22**, 1399 (1954).

(5) M. Kakudo, N. Kasai and T. Watase, *ibid.*, **21**, 1894 (1953).

case, we present evidence indicating that the curves of Fig. 1 are for "straight" hydrogen bonds and that "bent" and "bifurcated" hydrogen bonds give high and low frequency deviations, respectively, from the curves of Fig. 1.

It should be noted that X–H frequencies particularly for strong hydrogen bonds are difficult to obtain since as the hydrogen bond distance becomes shorter, the X–H stretching band becomes less prominent in a manner best illustrated in Fig. 2.

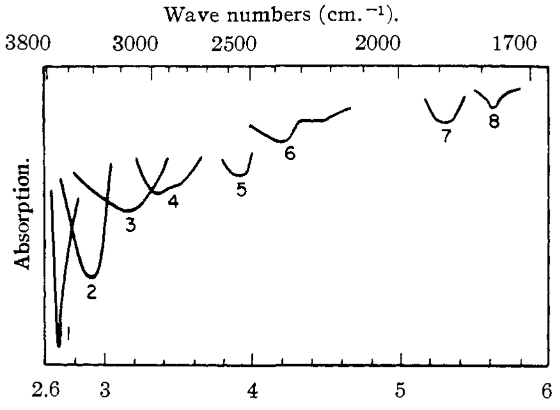


Fig. 2.—Band shape of the O–H stretching vibration for various hydrogen bond distances: 1, $Ca(OH)_2$; 2, $(COOH)_2 \cdot 2H_2O$; 3, H_3BO_3; 4, diaspore; 5, salicylic acid; 6, KH_2PO_4; 7, maleic acid; 8, Ni-dimethylglyoxime.

Collection of Data.—To correlate stretching frequencies with distances it is necessary to use only compounds for which the X–H . . . Y bond distances are known with good accuracy, and for which the X–H band can be identified unambiguously. Most data on hydrogen bond distances come from X-ray crystal structure determinations. Of these data only the more precise are sufficiently accurate for correlation purposes, and, even so, the sensitivity of stretching frequency to distance is so great that the chief error in correlation usually arises from the distance measurement, even when the X–H band is relatively broad.

We have then taken infrared spectra of mulls of crystals of well established structures. Nujol and perfluorokerosene were used in making the mulls, and spectra were obtained using a Perkin-Elmer Model 13 double beam infrared spectrophotometer with a rock salt prism. In some cases data were available in the literature. Data on formic and acetic acid dimers and HF polymer in the vapor phase are included since the distances determined by electron diffraction are available. In all, more than fifty compounds have been examined. Table I summarizes the data and gives references to the structure determinations.

Results

O–H. . .O Hydrogen Bonds.—In Fig. 3 data are plotted for a variety of O–H. . .O bonds. Though there exists a large region of a linear relationship between Δν and O–H . . . O distances, for distances greater than *ca.* 2.80 Å., Δν becomes less sensitive to distance exponentially. Presumably the other lines of Fig. 1 would show curvature for larger distances, but good data are lacking.

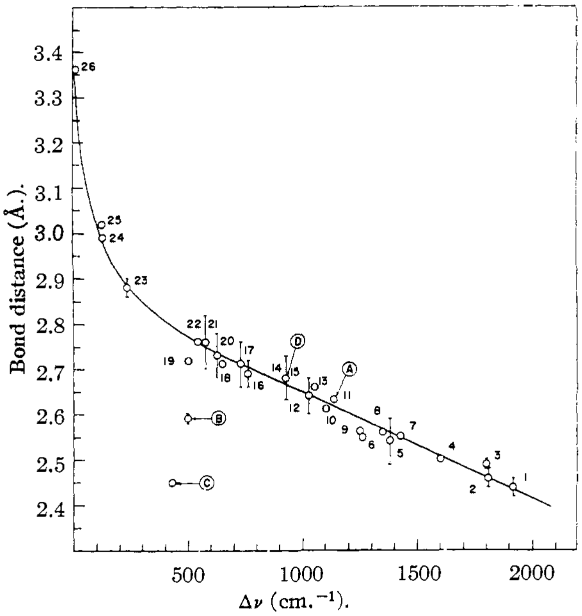
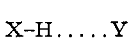


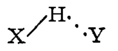
Fig. 3.—Frequency shift *vs.* bond distance for O–H. . .O hydrogen bonds.

It is to be noted that in Fig. 3 data for formic and acetic acid were obtained from the vapor state and agree well with the other data, all from crystals. This tends to confirm that crystalline field effects are small. The X–H frequency, since it is relatively high, apparently couples very little with lattice vibrations.

Bent and Bifurcated Hydrogen Bonds.—Hydrogen bonds may be classified as straight (I), bent (II), and bifurcated (III).



I



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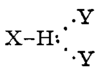

III

Nearly any theory of hydrogen bonding would suggest that if Fig. 1 represents the behavior of straight hydrogen bonds, bent and bifurcated bonds should show high and low frequency deviations, respectively. Most intermolecular hydrogen bonds are straight, but a large number of intramolecular hydrogen bonds must be bent if normal bond angles are preserved. Most of the compounds shown in Fig. 3 have structures suggesting that their hydrogen bonds are of the straight type. Figure 3 contains a few points well off the normal curve, and they are probably due to bent bonds.

For example, Fig. 4a shows the structure of salicylic acid in the crystal.[6] There is an intermolecular hydrogen bond of 2.63 Å., and an intramolecular hydrogen bond of 2.59 Å. The infrared spectrum of the crystal indicates two O–H bands, one at 2564 and the other at 3225 cm.⁻¹. In Table II, O–H stretching frequencies are given for methyl salicylate and the methyl ether of salicylic acid. A comparison with the frequencies in salicylic acid strongly suggests that the 2564 cm.⁻¹ band is due

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(6) W. Cochran, *Acta Cryst.*, **6**, 260 (1953).

TABLE I

BOND DISTANCE AND STRETCHING FREQUENCY FOR VARIOUS HYDROGEN BONDS

Compound	Bond distance (Å.)	Stretching freq. (cm.$^{-1}$)	$\Delta\nu$ (cm.$^{-1}$)	Point and lit.
I O–H...O bond (non-bonded O–H freq., 3700 cm.$^{-1}$)				
Ni-Dimethylglyoxime	2.44 ± 0.02	1780	1920	*1*
Maleic acid	2.46 ± 0.02	1890	1810	*2*
$(COOH)_2 \cdot 2H_2O$	2.49 ± 0.01	1900^a	1800	*3*
Urea oxalate	2.50	2100^a	1600	*4*
KH_2PO_4	2.54 ± 0.05	2320	1380	*5*
$NaHCO_3$	2.55	2440^a	1260	*6*
$CaH_2PO_4 \cdot 2H_2O$	2.55	2270	1430	*7*
N-Acetylglycine	2.56	2350^a	1350	*8*
Phloroglucinol	2.56	2450	1250	*9*
$KHCO_3$	2.61	2600	1100	*10*
Salicylic acid	2.63 ± 0.01	2564	1136	*11*
Succinic acid	2.64 ± 0.04	2680^a	1020	*12*
α-Resorcinal	2.66	2650	1050	*13*
Adipic acid	2.68 ± 0.05	2775^a	925	*14*
α-Iodic acid	2.686 ± 0.009	2778	922	*15*
Pentaerythritol	2.69 ± 0.03	2939	761	*16*
Diaspore	2.71 ± 0.05	2967	733	*17*
Quinhydrone	2.71	3055	645	*18*
Boric acid	2.72	3200	500	*19*
Formic acid dimer	2.73 ± 0.05	3080^b	620	*20*
Acetic acid dimer	2.76 ± 0.06	3125^c	575	*21*
Ice	2.76	3156^d Raman	544	*22*
$(COOH)_2 \cdot 2H_2O$	2.88 ± 0.02	3460	240	*23*
$LiOH \cdot H_2O$	2.99	3570^e	130	*24*
NaOH	3.02	3571	129	*25*
$Ca(OH)_2$	3.36	3690	10	*26*
II. O–H...Cl Bond				
Hydroxylamine HCl	2.99 ± 0.02	2898	802	*27*
Chloral hydrate	3.15	3333	367	*28*
III. O–H...N Bond				
Cyclohexanoxime	2.75	3144	556	*29*
Acetoxime	2.78 ± 0.03	3157	543	*30*
p-Chlorobenzaldoxime	2.82	3190	510	*31*
Dimethylglyoxime	2.83 ± 0.02	3171	529	*32*
p-Aminophenol	2.85 ± 0.03	3175	525	*33*
IV. N–H...F Bond (non-bonded N–H freq., 3400 cm.$^{-1}$)				
$N_2H_4 \cdot 2HF$	2.62 ± 0.02	2548	852	*34*
NH_4HF_2	2.80 ± 0.03	2910	490	*35*
NH_3BF_3	3.01 ± 0.03	3338	62	*36*
V. N–H...O Bond				
Uracil	2.84	3092	308	*37*
Cyanuric acid	2.86	3117	283	*38*
Isatin	2.93 ± 0.02	3193	207	*39*
Oxamide	2.94	$\left.\begin{matrix}3356\\3155\end{matrix}\right\}$ 3255	145	*40*
Acetanilide	2.97	3247	153	*41*
Urea	3.02	$\left.\begin{matrix}3440\\3350\end{matrix}\right\}$ 3350	50	*42*
N-Acetylglycine	3.03	3346	54	*43*
Nicotinamide	3.04 ± 0.01	3356	44	*44*
p-Nitroaniline	3.09	$\left.\begin{matrix}3481\\3359\end{matrix}\right\}$ 3420	−20	*45*
sym-Trinitrobenzene–*p*-iodoaniline	3.10	$\left.\begin{matrix}3479\\3393\end{matrix}\right\}$ 3436	−36	*46*
VI. N–H...Cl Bond				
Hydrazine·2HCl	3.10 ± 0.02	2907	493	*47*
Hexamethylenediamine·2HCl	3.11 ± 0.04	2927	473	*48*
Hydrazine·HCl	3.12	2937	463	*49*
Hydroxylamine·HCl	3.16 ± 0.02	3000	400	*50*
Methylamine·HCl	3.18 ± 0.05	3032	368	*51*
NH_4Cl	3.35	3110	290	*52*
VII. N–H...N Bond				
Melamine	3.00 ± 0.02	3279	121	*53*
Hexamethylenediamine	3.21 ± 0.02	3344	56	*54*
VIII. F–H...N Bond (non-bonded F–H freq., 4140 cm.$^{-1}$)				
KHF_2	2.26 ± 0.01	1450	2690	*55*
NH_4HF_2	2.32 ± 0.03	2000	2140	*56*
$(HF)_n$	2.55 ± 0.03	3440	700	*57*

[a] R. C. Lord and R. E. Merrifield, *J. Chem. Phys.*, **21**, 166 (1953). [b,c] L. G. Bonner and R. Hofstadter, *ibid.*, **6**, 531, 534 (1938). [d] P. C. Cross, J. Burnham and P. A. Leighton, THIS JOURNAL, **59**, 1135 (1937). [e] L. H. Jones, *J. Chem. Phys.*, **22**, 217 (1954).

(*1*) L. E. Godycki and R. E. Rundle, *Acta Cryst.*, **6**, 487 (1953).
(*2*) M. Shahat, *ibid.*, **5**, 763 (1952).
(*3*) F. R. Ahmed and D. W. J. Cruickshank, *ibid.*, **6**, 385 (1953).
(*4*) A. F. Schuck, L. Merritt and J. H. Sturdivant, to be published.
(*5*) J. West, *Z. Krist.*, **74**, 306 (1930).
(*6*) W. H. Zachariasen, *J. Chem. Phys.*, **1**, 634 (1933).
(*7*) W. L. Hill and S. B. Hendricks, *Ind. Eng. Chem.*, **28**, 441 (1936).
(*8*) G. B. Carpenter and J. Donohue, THIS JOURNAL, **72**, 2315 (1950).
(*9*) T. Ohashi and I. Nitta, to be published.
(*10*) I. Nitta, Y. Tomiie and C. H. Koo, *Acta Cryst.*, **5**, 292 (1952).
(*11*) W. Cochran, *ibid.*, **6**, 260 (1953).
(*12*) J. D. Morrison and J. M. Robertson, *J. Chem. Soc.*, 980 (1949).
(*13*) J. M. Robertson, *Proc. Roy. Soc.* (*London*), **A157**, 79 (1936).
(*14*) J. D. Morrison and J. M. Robertson, *J. Chem. Soc.*, 987 (1949).
(*15*) M. T. Rogers and L. Helmholtz, THIS JOURNAL, **63**, 278 (1941).
(*16*) F. J. Llewellyn, E. G. Cox and T. H. Goodwin, *J. Chem. Soc.*, 883 (1937).
(*17*) F. J. Ewing, *J. Chem. Phys.*, **3**, 203 (1935).
(*18*) K. Osaki and H. Matsuda, to be published.
(*19*) J. M. Cowley, *Acta Cryst.*, **6**, 522 (1953); H. Zachariasen, *ibid.*, **7**, 305 (1954).
(*20*) and (*21*) J. Karle and L. O. Brockway, THIS JOURNAL, **66**, 574 (1944).
(*22*) W. H. Barnes, *Proc. Roy. Soc.* (*London*), **A125**, 670 (1929).
(*23*) Same to (*3*).
(*24*) R. Pepinsky, *Z. Krist.*, **A102**, 119 (1940).
(*25*) T. Ernst, *Nachr. Ges. Wiss. Göttingen*, 76 (1946).
(*26*) T. Ernst, *Z. physik. Chem.*, **B20**, 65 (1933).
(*27*) B. Jerslev, *Acta Cryst.*, **1**, 21 (1948).
(*28*) S. Kondo and I. Nitta, *X-Ray*, **6**, 53 (1950).
(*29*) Y. Okaya, I. Nitta and A. Shimada, to be published.
(*30*) T. K. Bierlein and E. C. Lingafelter, *Acta Cryst.*, **4**, 450 (1951).
(*31*) B. Jerslev, *Nature*, **166**, 741 (1950).
(*32*) L. L. Merritt and E. Lanterman, *Acta Cryst.*, **5**, 811 (1952).
(*33*) C. J. Brown, *ibid.*, **4**, 100 (1951).
(*34*) M. Kronberg and D. Harker, *J. Chem. Phys.*, **10**, 309 (1942).
(*35*) L. Pauling, *Z. Krist.*, **85**, 380 (1933).
(*36*) J. L. Hoard and S. Geller, *Acta Cryst.*, **4**, 396 (1951).
(*37*) G. S. Parry, *ibid.*, **7**, 313 (1954).
(*38*) E. H. Wiebenga, THIS JOURNAL, **74**, 6156 (1952).
(*39*) G. H. Goldschmidt and F. J. Llewellyn, *Acta Cryst.*, **3**, 294 (1950).
(*40*) E. M. Ayerst and J. R. C. Duke, *ibid.*, **7**, 588 (1954).
(*41*) C. J. Brown and D. E. C. Corbridge, *ibid.*, **7**, 711 (1954).
(*42*) P. Vaughan and J. Donohue, *ibid.*, **5**, 530 (1952).
(*43*) Same to (*8*).
(*44*) W. B. Wright and G. S. D. King, *ibid.*, **7**, 288 (1954).
(*45*) S. C. Abrahams and J. M. Robertson, *ibid.*, **1**, 252 (1948).
(*46*) H. M. Powell, G. Huse and P. W. Cooke, *J. Chem. Soc.*, 153 (1943).
(*47*) J. Donohue and W. N. Lipscomb, *J. Chem. Phys.*, **15**, 115 (1947).
(*48*) W. P. Binnie and J. M. Robertson, *Acta Cryst.*, **2**, 180 (1949).
(*49*) K. Sakurai and Y. Tomiie, *ibid.*, **5**, 293 (1952).
(*50*) Same to (*27*).
(*51*) E. W. Hughes and W. N. Lipscomb, THIS JOURNAL, **68**, 1970 (1946).
(*52*) L. Vegard, *Z. Physik*, **5**, 17 (1921).
(*53*) E. W. Hughes, THIS JOURNAL, **63**, 1737 (1941).

(*54*) W. P. Binnie and J. M. Robertson, *Acta Cryst.*, **3**, 424 (1950).

(*55*) L. Helmholtz and M. T. Rogers, THIS JOURNAL, **61**, 2590 (1939).

(*56*) Same to (*35*).

(*57*) E. Westrum and K. Pitzer, THIS JOURNAL, **71**, 1940 (1949).

to the intermolecular bond, while the 3225 cm.$^{-1}$ band is due to the intramolecular bond. In this case the frequency of the intermolecular bond falls on the curve of Fig. 3 (point A), while that of the intramolecular bond falls far off the curve on the high frequency side (point B), in agreement with the interpretation that the intermolecular hydrogen bond is straight, the intramolecular bond bent.

TABLE II

THE O–H STRETCHING FREQUENCY IN SALICYLIC ACID DERIVATIVES

Compound	ν_{OH}	ν_{OH}
Salicylic acid	3225	2564
Methyl salicylate	3220	..
Methyl ether of salicylic acid	..	2630

In the nickel complex of salicylaldoxime (Fig. 4b) the case for a bent hydrogen bond is even better. Here the intramolecular hydrogen bond has an O . . . . O distance of 2.45 Å.,[7] and an O–H frequency of 3270 cm.$^{-1}$. As can be seen in the figure, a normal NOH angle would lead to a badly bent hydrogen bond and the frequency is particularly high (point C).

Few other compounds with intramolecular hydrogen bonds have been given accurate X-ray study, but O–H . . . O distances can be estimated rather reliably from known bond distances and angles. In Table III, expected distances are compared with observed O–H stretching frequencies. In nearly all cases the observed frequency is far higher than the frequency expected from Fig 3. The most probable interpretation is that R–O–H angles are nearly normal in intramolecular hydrogen bonds so that the bonds are of the bent type. There is too little exact information to permit correlation of frequencies with distances and angles in bent bonds.

TABLE III

INTRAMOLECULAR HYDROGEN BOND

Compound	Calcd. distance (Å.)[a]	ν Obsd.	ν Calcd.	$\Delta\nu$
Catechol	2.75	3333	3050	283
Salicylaldehyde	2.60	3100	2500	600
Salicylic acid	2.60	3225	2500	725
Methyl salicylate	2.60	3220	2500	720
o-Nitrophenol	2.50	3270	2100	1170
2-Nitroresorcinol	2.50	3280	2100	1180

[a] The following bond distances and angles were assumed: C–C (benzene), 1.40 Å., C–O (phenolic), 1.36 Å., C=O (carbonyl), 1.24 Å., C–N (nitro), 1.48 Å. and N–O (nitro), 1.26 Å. All the angles were assumed to be 120°. These assumptions lead to a calculated O. . .O distance of 2.50 Å., for salicylic acid *vs.* 2.60 Å. observed. Thus the idealized angles and bond distances may lead to errors of the order of 0.1 Å. in O. . .O distances, but even errors of this size will by no means explain the difference between $\nu_{obsd.}$ and $\nu_{calcd.}$

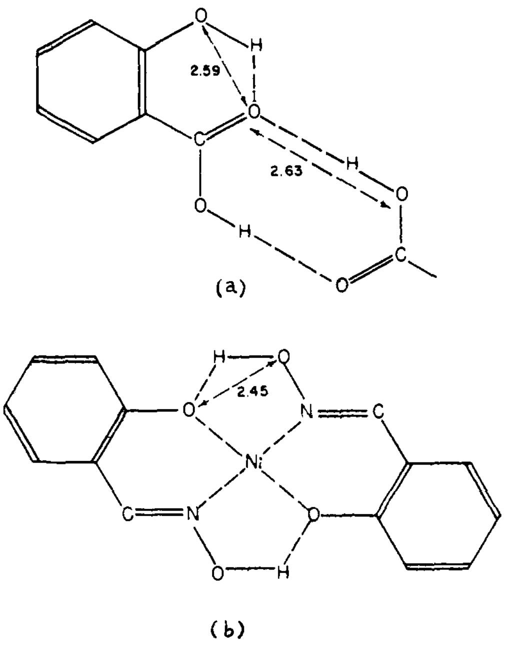

Fig. 4.—Molecular structures of salicylic acid (a) and Ni-salicylaldoxime (b).

Bifurcated hydrogen bonds apparently are rare. They have been reported for α-iodic acid[8a] and glycine.[8b] A recent neutron diffraction study[9] of α-iodic acid shows, however, that there is a normal straight hydrogen bond of 2.68 Å. rather than bifurcated bond of 2.76 Å. as previously reported.[7] (Neutron diffraction is more sensitive to oxygen positions than X-ray diffraction which is dominated by iodine scattering. The two results are similar but differ enough to alter the interpretation of the hydrogen bonding.) The O–H stretching frequency is in good agreement with the neutron diffraction result (point D).

In glycine there are several hydrogen bonds of the N–H . . . O type, and only one prominent N–H frequency at 3160 cm.$^{-1}$. This frequency is rather low for the N–H . . . O distances reported, in agreement with the expected deviation for a bifurcated bond, but interpretation is complicated by the zwitterion structure, with the consequent positive formal charge and four bonds to nitrogen. It has been found that this lowers N–H frequencies (see below), so that it is difficult to be sure of any agreement relative to bifurcated bonds using glycine as an example.

N–H . . . . O Hydrogen Bonds.—In the case of O–H. . .O hydrogen bonds, interpretation is relatively simple. There is usually but one hydrogen covalently attached to an oxygen, and a unique frequency to be assigned to the O–H stretching mode. In N–H . . . O hydrogen bonds considerably more difficulty arises in making assignments, since often two hydrogens are bonded to one nitrogen and several N–H bands result. Sometimes these are due to symmetrical and unsymmetrical stretching modes which often show quite different

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(7) L. L. Merritt and C. Quare, *Acta Cryst.*, **7**, 650 (1954).

(8) (a) M. T. Rogers and L. Helmholz, THIS JOURNAL, **63**, 278 (1941); A. F. Wells, *Acta Cryst.*, **2**, 128 (1948); (b) G. Albrecht and R. B. Corey, THIS JOURNAL, **61**, 1087 (1939).

(9) B. S. Garrett, Oak Ridge National Laboratory Report, No. 1745.

frequencies. In this case an average is necessary, or alternatively, symmetrical and unsymmetrical stretching frequencies could be plotted separately. In comparing a variety of compounds of differing symmetries, the averaging method seemed most practical and was adopted.

Thus in Table I, frequencies of individual N–H bands are given together with the average frequencies which were used in obtaining the plots in Figs. 1 and 6. For some compounds, *e.g.*, N-acetylglycine, there is but one hydrogen atom bonded to nitrogen and only one N–H . . . O distance and frequency. In comparing this frequency with an average of symmetrical and unsymmetrical frequencies from more complex cases, the best type of averaging is unknown. We have used an arithmetic mean which seems to be satisfactory at least where frequencies do not differ widely.

In some cases there were several X–H . . . Y distances in crystals of a given compound, and then average distances were used if the X–H . . . Y distances differed no more than 0.1 Å., since the X–H . . . Y band was broadened, but usually not resolved. When the X–H bands were resolved, we have, perhaps optimistically, assigned lower frequencies to shorter hydrogen bonds, higher ones to longer bonds.

For cyanuric acid we have plotted an average distance and frequency even though combined X-ray study and polarized infrared study of the crystal makes possible the resolution of the two distances and frequencies. However, present interpretation of the X-ray and infrared results are, we believe, incompatible. Cyanuric acid in the crystal has the structure shown in Fig. 5. The N–H . . . O bonds along b and roughly normal to b have reported lengths[10] of 2.83 and 2.88 Å., respectively, as determined by a recent X-ray examination. From a polarized infrared study of the crystals[11] the N–H frequencies along and normal to b are, respectively, 3210 and 3060 cm.$^{-1}$. As Newman and Badger noted, the infrared data indicate that the longer N–H . . . O bond is along b. This is in disagreement with the crystal structure determination, which should be one of high accuracy. We believe that our correlation is accurate enough to suggest that the bonds along b and roughly normal to b are 2.92 and 2.82 Å., respectively, accepting Newman and Badger's infrared study. It seems likely to us that the crystal structure refinement went astray or, alternatively, perhaps (110) and (010) directions were somehow mixed in the infrared study. (X-Ray and infrared distances would be in satisfactory agreement if this change were made.)

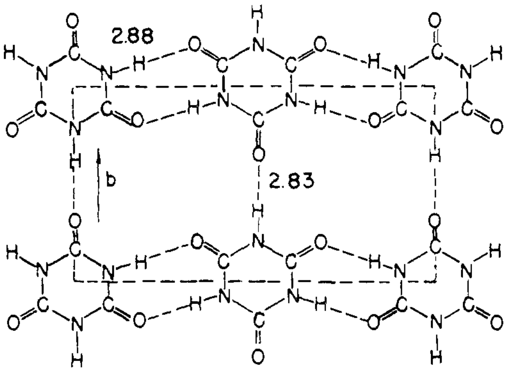


Fig. 5.—Crystal structure of cyanuric acid projected onto the (101) plane.

It is to be noted that all of the N–H . . . O bonds reported here are for a nitrogen with a covalence of three (no formal charge). As will be discussed later, we have reason to believe that the N–H frequency is lowered considerably for quadricovalent nitrogen (formal charge + 1), and that the N–H . . . O curve of Fig. 1 would not be applicable.

O–H. . .N Hydrogen Bonds.—The relation between bond distances and ν for O–H . . . N and N–H . . . O bonds, shown in Fig. 6, indicates that the linear portion of the slopes of these two types of hydrogen bonds are distinctly different. Such a difference could conceivably be useful in deciding between tautomers, such as the isatin case (which unfortunately lies at the intersection of the two lines).

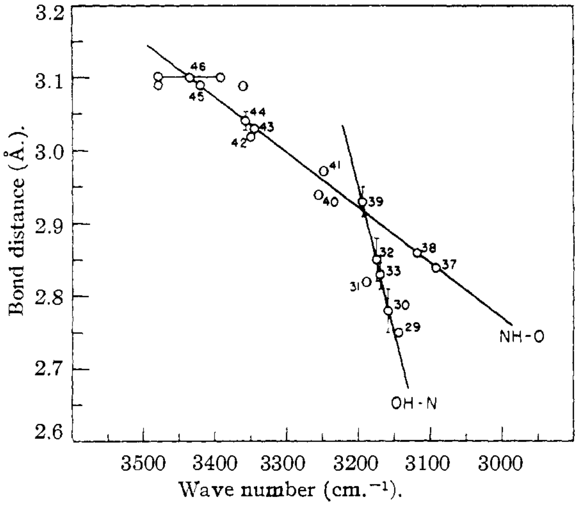
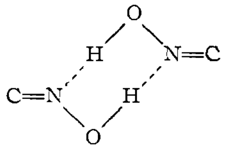


Fig. 6.—N–H and O–H stretching frequencies *versus* hydrogen bond distance.

Upon examining the crystal structures of compounds possessing O–H . . . N hydrogen bonds it was noted that most of these were oximes, and that of four oxime structures[12] all but acetoxime formed bonds of type I shown below, where the reported N–O . . . N′ angles lie in the neighborhood of 75 ~ 82°. This is a disturbingly low angle and suggests either that the O–H . . . N bond is bent, or



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that within the crystal there has been a transfer of H from O to N. Since the O–H frequency is low, the assumption that the O–H. . .N bond is badly

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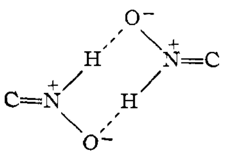
(10) E. H. Wiebenga, This Journal, **74**, 6156 (1952).

(11) R. Newman and R. M. Badger, *ibid.*, **74**, 3545 (1952).

(12) See the references of Table I on the crystal structures of *p*-chlorobenzaldoxime, dimethylglyoxime and cyclohexanoxime.

bent seems to be in conflict with our observations of O-H frequencies in intramolecular hydrogen bonding. On the other hand, interpreting the bonding as II, leads to better angles, but makes these N-H...O bonds fall on a different curve than the other N-H...O bonds of Fig. 6. Since the nitrogen for the latter structure is quadricovalent and is involved in double bond formation to C, a different curve may well be satisfactory. The local dielectric constant is no doubt high in the region of the hydrogen bond, so that the proposed ionization does not seem to be unreasonable, but neutron diffraction or possibly nuclear magnetic resonance measurements will have to be called upon to settle the hydrogen positions.



II

Charge and Coördination Effects on N-H Stretching Frequencies.—The N-H...Cl bonds reported here are for quadricovalent nitrogen and a chloride ion, N^+-H...Cl^-. It is noted that though the slope of the N-H...Cl curve is typical of weak hydrogen bonding the actual N-H frequencies are rather low. Recently Mr. Russell Bonham, in our laboratories, has examined N-H frequencies for the various salts of the $[(C_2H_5)_xNH_y]^+(C_6H_5)_4B^-$ type where $x + y = 4$, and finds that, for quadricovalent nitrogen, non-hydrogen-bonded N-H frequencies are near 3100 cm.$^{-1}$. This lower frequency for quadricovalent nitrogen is in accord with observations of N-H frequencies in other ammonium salts where hydrogen bonding is probably not an important factor. Thus, the low frequencies found in the N^+-H...Cl^- bonds reported arises only partly from hydrogen bonding.[13] In plotting $\Delta\nu$ *versus* distance, as Lord and Merrifield[8] have done, such charge and coördination effects must be taken into account. For these and other reasons their curve should be used only for straight O-H...O bonds.

It is to be noted that C-H stretching frequencies are highest for triple-bonded C-H, intermediate for double-bonded C-H, and lowest for single-bonded C-H (Table IV), presumably because increasing the *s*-character in the C-H bond shortens and strengthens the C-H bond.

TABLE IV

BOND DISTANCE AND STRETCHING FREQUENCY IN VARIOUS C-H BONDS

Bond	Hybridization	Bond distance[a] (Å.)	C-H stretching frequency[b] (cm.$^{-1}$)
—C—H	sp^3	1.094	2850 ∼2960
=C—H	sp^2	1.079	3010 ∼3095
≡C—H	sp	1.057	3300

[a] C. A. Coulson, "Valence," Oxford Press, London, 1953, p. 200. [b] L. F. Bellamy, "The Infrared Spectra of Complex Molecules," John Wiley and Sons, Inc., New York, N. Y., 1954.

A similar effect may occur for N-H bonds, though it has not been so well established. At any rate, it would seem likely that in comparing N-H...Y bonds, only like types could be correlated with one curve. Thus, R_2N-H...Y, R_3N^+-H...Y^-, $R_2C{=}N$-H...Y, and $R_2C{=}N^+R$-H...Y^- probably constitute four different types and require different curves, even where Y is held constant. Unfortunately the number of compounds whose structures have been accurately determined is not yet sufficient to carry out correlations for many of these types.

On the Nature of the Hydrogen Bond.—The slopes and intercepts of Fig. 1 have interesting implications to the nature of hydrogen bonding. The slopes of the curves for N-H...Y and O-H...Y are plotted in Fig. 7 *versus* the electronegativity of Y. We have used Pauling's electronegativities of 3.0, 3.5 and 4.0 for N, O and F, and on this basis Cl falls on the curve if given an electronegativity of 3.35, rather than 3.0. Since F and Cl occurred as negative ions in these hydrogen bonds, and since size, charge and polarizability must be factors of importance, Fig. 7 is somewhat hard to interpret, but in general it indicates that X-H frequencies become increasingly sensitive to the position of Y as the charge on Y increases. This result agrees with expectations based on electrostatic models, and the apparent high electronegativity of the chloride ion is, then, understandable.

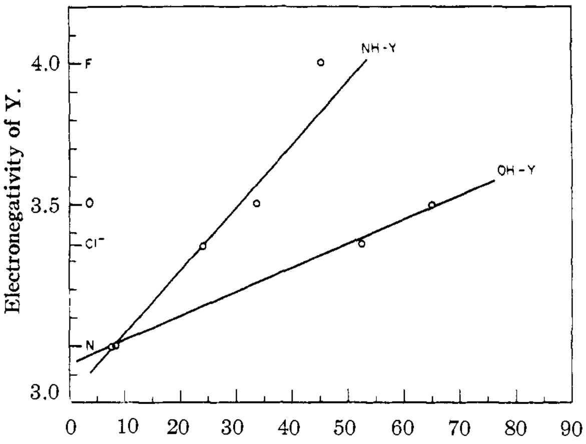


Fig. 7.—Relation between electronegativity and slope of straight line of Fig. 1.

On the other hand, if one looks at effectiveness in lowering X-H frequencies at large distances, then

TABLE V

RELATION BETWEEN THE VAN DER WAALS OR IONIC RADIUS, POLARIZABILITY AND N-H OR O-H STRETCHING FREQUENCY IN LONG HYDROGEN BONDS

Atom or ion	Van der Waals or ionic radius (Å.)	Polarizability (10^{-24} cm.^{3})	N-H freq. (at 3.0 Å.)	O-H freq. (at 2.9 Å.)
Cl^-	1.81	3.66	2720	2670
Cl	1.80			
N	1.5	..	3280	3200
O	1.40	..	3310	3500
F^-	1.36	1.04	3340	..
F	1.35			

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(13) Similar charge effects would be expected for R_2O^+-H...Cl^- hydrogen bonds but data are lacking.

the order of the shift of the O–H and N–H frequencies is Cl > N > O > F. As is shown in Table V, this is in good accord with the order of the van der Waals radii of these atoms.

The above result is not to be expected from a point charge type of model, and suggests that if Y is large and polarizable the important effect at large distances is an overlap of the outer electrons of Y with the proton.

Both the very low frequencies found in strong hydrogen bonds and the recent neutron diffraction data (Fig. 8 and Table VI) indicate that in strong hydrogen bonds the X–H distance increases exponentially as the X–H...Y distance decreases. This seems to be in serious disagreement with semi-theoretical treatments of hydrogen bonding, such as that of Coulson and Danielsson.[14] In several recent treatments[15] it is either assumed or found that the amount of covalent character in the long H...Y bond is negligible, and it seems possible that these treatments fail to account for the rapid increase of the X–H distance in strong hydrogen bonds because they grossly underestimate the covalent character in the H...Y bond as Y approaches the hydrogen. In any case, the bad disagreement with hydrogen positions in strong hydrogen bonds does not justify faith in recent theoretical treatments.

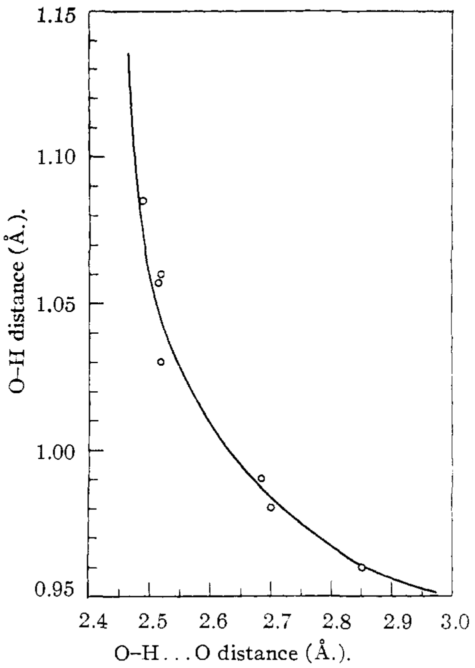

Fig. 8.—O–H...O distance *versus* O–H distance.

TABLE VI

THE RELATION BETWEEN O–H...O DISTANCE AND O–H DISTANCE

Compound	O–H...O distance (Å.)	O–H Distance (Å.)	Method[f]
$(COOH)_2 \cdot 2H_2O$	2.85[a]	0.96[a]	N.D.
$CaSO_4 \cdot 2H_2O$	2.70[b]	0.98[c]	P.M.R.
α-HIO_3	2.686 ± 0.009[a]	0.990 ± 0.017[a]	N.D.
KD_2AsO_4	2.52[a]	1.03[a]	N.D.
KH_2AsO_4	2.52[a]	1.06[a]	N.D.
$(COOH)_2 \cdot 2H_2O$	2.518 ± 0.008[a]	1.057 ± 0.016[a]	N.D.
KH_2PO_4	2.487 ± 0.005[d]	1.085 ± 0.013[e]	N.D.

[a] B. S. Garrett, Oak Ridge National Laboratory Report, No. 1745. [b] W. A. Wooster, *Z. Krist.*, **94**, 375 (1936). [c] G. E. Pake, *J. Chem. Phys.*, 16, 327 (1948). [d] G. E. Bacon and R. S. Pease, *Proc. Roy. Soc.* (*London*), **A220**, 397 (1953). [e] S. W. Peterson, H. A. Levy and S. H. Simmonsen, *J. Chem. Phys.*, 21, 2084 (1953). [f] N. D., neutron diffraction; P.M.R., proton magnetic resonance.

Figure 8 suggests that for hydrogen bonds of ~2.45 Å. the hydrogen will be centered, tending to confirm that the hydrogen bond in nickel dimethylglyoxime, where O–H–O = 2.44 Å., is symmetric.

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(14) C. A. Coulson and U. Danielsson, *Arkiv Fysik*, **8**, 239, 245 (1955).

(15) For example, N. D. Coggeshall, *J. Chem. Phys.*, **18**, 978 (1950).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, PURDUE UNIVERSITY]

The Raman and Infrared Spectra of Tin Tetramethyl[1]

BY WALTER F. EDGELL AND CURTIS H. WARD[2]

RECEIVED FEBRUARY 8, 1955

The Raman and infrared spectra of $Sn(CH_3)_4$ have been studied and compared with the results of earlier investigations. The fundamental frequencies of vibration are determined and the large number of combination and overtone bands in both spectra are explained in terms of them. The coupling between the skeletal vibrations and those modes characteristic of the methyl groups is discussed and the results compared to those for the other tetramethyl compounds of Group IVA elements.

Introduction

The Raman and infrared spectra of several organotin compounds have been studied recently in this Laboratory. Such a study is of theoretical interest in connection with the nature of "group frequencies" and in particular with regard to the extent of coupling between the skeletal modes and those of the methyl groups. This paper deals with the study of tin tetramethyl. Although several previous workers have studied this compound,[3–8] considerable disagreement still appears to exist as

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(1) Based upon a portion of the Ph.D. thesis of C. H. Ward, Purdue University, September, 1953.

(2) Purdue Research Foundation Fellow, 1950–1952; Allied Chemical and Dye Fellow, 1952–1953.

(3) C. F. Kettering and W. W. Sleator, *Physics*, **4**, 39 (1933).

(4) G. Pai, *Proc. Roy. Soc.* (*London*), **149A**, 29 (1935).

(5) C. W. Young, J. S. Koehler and D. S. McKinney, THIS JOURNAL, **69**, 1410 (1947).

(6) H. Siebert, *Z. anorg. Chem.*, **263**, 82 (1950).

(7) H. Siebert, *ibid.*, **268**, 177 (1952).

(8) E. R. Lippincott and M. C. Tobin, THIS JOURNAL, **75**, 4141 (1953).