Acc. Chem. Res. **1987**, *20*, 257–262

Intramolecular Hydrogen Bonding in Some Small Vapor-Phase Molecules Studied with Microwave Spectroscopy

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Received October 9, 1986 (Revised Manuscript Received March 2, 1987)

Introduction

The hydrogen bond has not only generated an immense volume of literature,[1] but it has also been responsible for a proliferation of review articles.[2] This is a demonstration of the great variety of types, descriptions, and applications of this very special mode of bonding.

Our review is limited to hydrogen bonding of the intramolecular type in rather small molecules in the vapor phase. In addition, attention will be focused on the many kinds of information obtainable from microwave spectroscopy, a tool which we believe is particularly well-suited for the study of detailed conformational phenomena in small molecules.

Microwave information for nearly 100 molecules fitting the above specifications has been published,[3] and we will use this body of data in setting up criteria for the presence of hydrogen bonding, observable properties, definitions of bond strength, and other appropriate topics. About one-third of these molecules are also listed in Tables I–VI.

Definition and Properties

A linkage between two molecules (intermolecular bond) or between two parts of a single molecule (intramolecular bond which thereby closes a ring) will be called a *hydrogen bond* if the linkage has the form –X–H···Y–(H), where X is an atom or group of atoms bonded to a hydrogen atom in an approximately normal manner while at the same time this H is weakly bound to the atom or group of atoms Y which is connected to the rest of the molecule.

The atom or group of atoms X is called the *proton donor* because, as the weak linkage H···Y is formed, the bond X–H is slightly lengthened and its stretching force constant reduced so that the H atom is partially donated to the ···Y part. (In special and quite interesting cases, X and Y are identical and the H bond is symmetrical. See Table V.) Common proton donors include O–H, S–H, NH_2, and H–C=C–H which have somewhat acidic H's; in other words, they are good electron acceptors. The *proton acceptors*, such as ···O, ···NH, ···S, O=C, C=C, –C≡N, are rather electronegative; i.e., they are electron donors and also include π orbitals in C=C, C≡N, and benzene and pseudo-π orbitals in cyclopropane.

Table I.
Some Molecules from Our List Which Have Two or More H-Bonded Conformers or Special Structural Information

1. acetic acid [O–H···O=C] (CH_3COOH): (a) Caminati, W.; Scappini, F.; Corbelli, G. *J. Mol. Spectrosc.* **1979**, *75*, 327–332. (b) van Eijck, B. P.; van Opheusden, J.; van Schaik, M. M.; van Zoeren, E. *J. Mol. Spectrosc.* 1981, *86*, 465–479. Recalculation of structure.

3. acrylic acid [O–H···O=C] ($CH_2CHCOOH$): Bolton, K.; Lister, D. G.; Sheridan, J. *J. Chem. Soc., Faraday Trans. 2* **1974**, *70*, 113–125. 2 conformers, double bonds cis and trans, H bonded to carboxylic oxygen.

6. allyl cyanide (CH_2=$CHCH_2CN$): Sastry, K. V. L. N.; Rao, V. M.; Dass, S. C. *Can. J. Phys.* **1968**, *46*, 959–962. Cis and gauche conformers assigned.

14. 2-amino-1-propanol (alaninol) [O–H···N] ($CH_3CH(NH_2)CH_2OH$): Ellingsen, B. H.; Marstokk, K.-M.; Møllendal, H. *J. Mol. Struct.* **1978**, *48*, 9–23.

15. 3-aminopropanol [O–H···N] ($NH_2CH_2CH_2OH$): McMahan, M. A.; Sharma, S. D.; Curl, Jr., R. F. *J. Mol. Spectrosc.* **1979**, *75*, 220–223. 1 conformer only, forms 6-membered ring: gauche/gauche with rather large distortions.

16. 3-aminopropionitrile [N-H···CN] ($NH_2CH_2CH_2CN$): Braathen, O.-A.; Marstokk, M.; Møllendal, H. *Acta Chem. Scand.* **1983**, *A37*, 493–501. Ab initio calculation finds 4 conformers which have total energies within 2 kJ/mol (Skanke, P. N. *Acta Chem. Scand.* **1984**, *A38*, 95–99.

25. chloroacetic acid [O–H···O–C] ($CH_2ClCOOH$): van Eijck, B. P.; Maagdenberg, A. A. J.; Wanrooy, J. *J. Mol. Struct.* **1974**, *22*, 61–67. Derasen, J. L.; Bijen, J. M. *J. Mol. Struct.* **1975**, *24*, 153–164. 3 conformations found.

30. 3-chloro-1-propanol: Fuller, M. J.; Wilson, E. B.; Caminati, W. *J. Mol. Spectrosc.* **1982**, *96*, 131–145. 4 isotopes (parent included) studied, 2 conformers found *no H bond*, no difference in H···Cl if different sets of isotopes used.

Tests

The standard test for the presence of an H bond, at least for molecules containing an O–H, has been a shift of the characteristic O–H stretching frequency to a

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[1] Books: *The Hydrogen Bond*; Schuster, P., Zundel, G., Sandorfy, C. Eds.; North-Holland: New York, 1976. *Hydrogen Bonding*; Joester, M. D., Schaad, L. J., Eds.; Marcel Dekker: New York, 1974. *The Hydrogen Bond*; Pimentel, G., McClellan, A. L., Eds.; W. H. Freeman: San Francisco, 1960.

[2] Reviews: Sandorfy, C. *Top. Curr. Chem.* **1984**, *120*, 41–84. Dyke, T. R. *Top. Curr. Chem.* **1984**, *120*, 85–114. Legon, A. C.; Millen, D. J. *Acc. Chem. Res.* **1987**, *20*, 39–46.

[3] For supplementary material, see paragraph at the end of this article.

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Table II.
H Bonds Connecting O–H or N–H with Lone Pairs on O, N, or F

66. 2-methoxyethanol [O–H···OC2] ($CH_3OCH_2CH_2OH$): (a) Buckley, P.; Brochu, M. *Can. J. Chem.* **1972**, *50*, 1149–1156. (b) Brochu, M.; Buckley, P. *Can. J. Spectrosc.* **1973**, *18*, 165. (c) Caminati, W.; Wilson, E. B.; *J. Mol. Struct.* **1980**, *81*, 356–372. (d) Caminati, W.; Cervellati, R.; Smith, Z. *J. Mol. Struct.* **1983**, *97*, 87–92.

67. 2-(methylamino)ethanol [O–H···N] ($CH_3NHCH_2CH_2OH$): Penn, R. E.; Buxton, L. W. *J. Mol. Spectrosc.* **1975**, *56*, 229–238.

84. pyrrole-2-carboxaldehyde [N–H···O=C] (C_4H_3NHCHO): Marstokk, K.-M.; Møllendal, H. *J. Mol. Struct.* **1974**, *23*, 93–101.

85. pyruvic acid [O–H···O=C] ($CH_3COCOOH$): Marstokk, K.-M.; Møllendal, H. *J. Mol. Struct.* **1974**, *20*, 257–267.

86. salicylaldehyde [O–H···O=C] ($C_6H_4(OH)CHO$): Jones, H.; Curl, Jr., R. F. *J. Mol. Spectrosc.* **1972**, *42*, 65–74.

90. trifluoroethylamine [N–H···F] ($CF_3C_2H_4NH_2$): Warren, I. D.; Wilson, E. B. *J. Chem. Phys.* **1972**, *56*, 2137–2141.

91. triformylmethane[a] [O–H···O=C] ($HC(HCO)_3$): Turner, P. H. *J. Chem. Soc., Faraday Trans. 2* **1980**, *76*, 383–390.

[a] Actually occurs as a compound with a six-membered ring.

Table III.
H Bonds with Sulfur

7. allyl mercaptan [2-propene-1-thiol] (CH_2:$CHCH_2SH$): Sastry, K. V. L. N.; Dass, S. C.; Brooks, W. V. F.; Bhaumik, A. *J. Mol. Spectrosc.* **1969**, *31*, 54–65. No H-bonded form.

9. 2-aminoethanethiol [S–H···N] ($NH_2CH_2CH_2SH$): Nandi, R. N.; Boland, M. F.; Harmony, M. D. *J. Mol. Spectrosc.* **1982**, *92*, 419–430.

27. 2-chloroethanethiol [S–H···Cl] (CH_2ClCH_2SH): Nandi, R. N.; Boland, M. F.; Harmony, M. D. *J. Mol. Spectrosc.* **1982**, *92*, 419–430.

63. 2-mercaptoethanol [O–H···SH] (CH_2OH-CH_2SH): Sung, E. M.; Harmony, M. D. *J. Am. Chem. Soc.* **1977**, *99*, 5603–5608.

64. 3-mercaptopropionitrile [S–H···CN] (CH_2SHCH_2CN): Marstokk, K.-M.; Møllendal, H. *Acta Chem. Scand.* **1983**, *A37*, 477–486.

81. propargyl mercaptan [S–H···CC] ($HCCCH_2SH$): (a) Scappini, F.; Favero, P. G.; Cervellati, R. *Chem. Phys. Lett.* **1975**, *33*, 499. (b) Mirri, A. M.; Scappini, F.; Mader, H. *J. Mol. Spectrosc.* **1975**, *57*, 264. (c) Mirri, A. M.; Scappini, F.; Cervellati, R.; Favero, P. G. *J. Mol. Spectrosc.* **1976**, *63*, 509–520. (d) Scappini, F.; Mader, H.; Sheridan, J. *Z. Naturforsch.* **1973**, *28A*, 77–81. (e) Errata: **1975**, *30A*, 922.

87. thioacetic acid [S–H···O=C] (CH_3C:OSH): Naito, T.; Ohashi, O.; Yamaguchi, I. *J. Mol. Spectrosc.* **1977**, *68*, 32–40.

88. thioformic acid [S–H···O–C] ($H(C{=}OO)SH$): Hocking, W. H.; Winnewisser, G. *Z. Naturforsch.* **1977**, *32A*, 1108–1118.

Table IV.
Examples of Molecular Species in Which a Hydrogen Is Weakly H Bonded to the π Orbitals of a Double Bond Such as C=C

4. allyl alcohol [O–H···C=C] (CH_2:CH_3H): Murty, A. N.; Curl, R. F. *J. Chem. Phys.* **1967**, *46*, 4176–4180.

20. 2,3-butadien-1-ol [O–H···C=C]: Horn, A.; Marstokk, K.-M.; Møllendal, H.; Priebe, H. *Acta Chem. Scand.* **1983**, *A37*, 679–684.

23. 3-buten-2-ol [OH···C=C]: Smith, Z.; Carballo, N.; Wilson, E. B.; Marstokk, K.-M.; Møllendal, H. *J. Am. Chem. Soc.* **1985**, *107*, 1951–1957.

24. 3-butyn-1-ol [O–H···CC] (HCC-CH_2CH_2OH): Szalanski, L. B.; Ford, R. G. *J. Mol. Spectrosc.* **1975**, *54*, 148–155.

31. crotyl alcohol [O–H···C=C] ($CH_3CH{=}CH_2OH$): Lum, D. K.; Bauman, L. E.; Mallory, T. B.; Cook, R. L. *J. Mol. Struct.* **1978**, *50*, 1–6. 1 conformation: skew, H bonded; low-resolution MW.

Table V.
Some Molecules with Double-Minima Potential Functions and Intramolecular Hydrogen Bonds

60. 6-hydroxy-2-formylfulvene [O–H···O=C]: Pickett, H. M. *J. Am. Chem. Soc.* **1973**, *95*, 1770–1774.

62. malonaldehyde [O–H···O=C]: (a) Rowe, W.; Duerst, R.; Wilson, E. B. *J. Am. Chem. Soc.* **1976**, *98*, 4021–4032. (b) Baughcum, S.; Duerst, R.; Rowe, W.; Smith, Z.; Wilson, E. B. *J. Am. Chem. Soc.* **1983**, *103*, 6296–6303. (c) Baughcum, S.; Smith, Z.; Wilson, E. B.; Duerst, R. *J. Am. Chem. Soc.* **1984**, *106*, 2260–2265. (d) Turner, P. H.; Baughcum, S.; Coy, S.; Smith, Z. *J. Am. Chem. Soc.* **1984**, *106*, 2265–2267.

71. 2-methylmalonaldehyde: Sanders, N. D. *J. Mol. Spectrosc.* **1981**, *86*, 27–42.

93. trinitromethane: Caminati, W.; Wilson, E. B. *J. Mol. Spectrosc.* **1980**, *81*, 507–510.

lower frequency when an H bond involving the O–H is formed. This is a direct consequence of the lengthening of the O–H bond when associated with the formation of the H bond, O–H···Y–.

In solution there can be additional complications due to the formation of H-bonded dimers, etc., so that extrapolation to zero concentration may be needed. These data are not always available for molecules in the vapor phase. There can also be confusion as to which spectral line is due to free OH. Although similar frequency shifts should occur for the N–H frequency, etc., these are often harder to identify.

Another test is the shift (usually in the high-field direction) for the nuclear magnetic resonance signal due to the proton in the H bond.[4] Again, in principle, vapor-phase data are best but are not always easy to obtain, especially for low vapor pressure materials.

In our collection[3] of data on about 100 molecules believed likely to have one or more conformations with an intramolecular H bond, most authors have usually inferred the presence of an H bond from the geometry. This structure in turn is obtained by transferring some bond distances and angles from studies on related molecules plus the fitting of dihedral and other angles to the moments of inertia obtained from the microwave spectrum of the molecule being examined and some of its isotopically substituted forms.

It is customary to assume that a given conformer is H-bonded if the structure brings the atoms X and Y somewhat closer to each other than the sum of the van der Waals radii[5] of X and Y. It is also required that there be no other steric crowding that brings atoms which are not bonded to each other appreciably closer than the sum of their van der Waals radii.

In most of our list the lowest energy conformation is one displaying a hydrogen bond, but there are a few exceptions, such as 3-chloro-1-propanol[6] and 2-aminoethanethiol.[7] These few exceptions can mostly be explained as due to special steric repulsions between atoms not directly bonded to each other, repulsions not

(4) Davis, Jr., J. C.; Deb, K. K. In *Advances in Magnetic Resonance*; Waugh, J. S., Ed.; Academic: New York, 1970; Vol. 4, p 201.

(5) Pauling, L. *Nature of the Chemical Bond*; Cornell University Press: Ithaca, NY, 1939; p 174 ff.

(6) Fuller, M. J.; Wilson, E. B.; Caminati, W. *J. Mol. Spectrosc.* **1982**, *96*, 131–145.

(7) Nandi, R. N.; Boland, M. F.; Harmony, M. D. *J. Mol. Spectrosc.* **1982**, *92*, 419–430.

Table VI.
Some Molecules Showing Several Conformations with Different Dipole Moments (Interatomic Distances in angstroms, Diple Moments in debye)[a]

5. allylamine [N–H···C═C]: (a) Roussy, G.; Demaison, J.; Botskor, J.; Rudolph, H. D. *J. Mol. Spectrosc.* **1971**, *38*, 535–544. (b) Botskor, J.; Rudolph, H. D.; Roussy, G. *J. Mol. Spectrosc.* **1974**, *52*, 457–484. (c) Botskor, J.; Rudolph, H. D.; Roussy, G. *J. Mol. Spectrosc.* **1974**, *53*, 15–36. (d) Botskor, J.; Rudolph, H. D. *J. Mol. Spectrosc.* **1978**, *71*, 430–445. Conformer I: N-cis, lone pair trans to C–C. Conformer II: N-skew, lone pair gauche; exptl μ_a = 0.169 (2), μ_b = 0.807 (3), μ_c = 0.829 (2). Conformer III: N-skew, lone pair trans to C–C; exptl μ_a = 0.766 (10), μ_b = 0.700 (5), μ_c = 0.290 (20). Conformer IV: N-cis, lone pair gauche; exptl μ_a^{eff} = 0.804 (3)8 μ_b = 0.78 (1), μ_c = 0.78 (1) tunneling.

11. (aminomethyl)cyclopropane [N–H···Δ] ($CH_2CH_2CH{-}CH_2X$): Marstokk, K.-M.; Møllendal, H. *Acta Chem. Scand.* **1984**, *A38*, 387–398 (X = NH_2). 2 conformers, both H-bonded. Conformer I: exptl μ_a = 0.144 (2), μ_b = 0, μ_c = 1.068 (16), μ_{tot} = 1.077 (16); calcd BM μ_a = 0.3, μ_b = 0.4, μ_c = 1.2. Conformer II: exptl μ_a = 1.018 (26), μ_b = 0.39 (16), μ_c = 0.833 (55), μ_{tot} = 1.372 (16); BM μ_a = 0.6, μ_b = 0.8, μ_c = 1.0.

39. 2,2-difluoroethylamine [N–H···F] ($CHF_2CH_2NH_2$): Marstokk, K.-M.; Møllendal, H. *Acta Chem. Scand.* **1982**, *A36*, 517–533. 3 H-bonded conformers were found, one with 2 bonds has the lowest energy, *E*; Δ*E* measured. H-bonded probably electrostatic; see discussion. Conformer I: exptl μ_a = 2.042 (15), μ_b = 1.101 (29), μ_c = 0, μ_{tot} = 2.230 (27); calcd BM μ_a = 2.1, μ_b = 0.4, μ_c = 0, μ_{tot} 2.1. Conformer II: exptl μ_a = 1.073 (14), β_b = 0.22 (23)8 μ_c = 1.483 (26), μ_{tot} = 1.844 (57); calcd BM μ_a = 1.1, μ_b = 0.2, μ_c = 1.6. Conformer III: exptl μ_a = 0.09 (3), μ_b = 0, μ_c = 1.427 (28), μ_{tot} = 1.430 (30); calcd BM μ_a = 0.1, μ_b = 0, μ_c = 0.82, μ_{tot} = 0.83.

41. 1,3-dioxan-5-ol [O–H···O2]: Alonso, J. L.; Wilson, E. B. *J. Am. Chem. Soc.* **1980**, *102*, 1248–1251. 1 conformer, chair, bifurcated hydrogen bond. O···H, 2.59 Å; O–H···O, 100.4; O(H)···O, 2.94 Å. Shrinkage of O···O upon deuteriation: 0.002 Å. exptl μ_a = 1.61, μ_b = 2.09; calcd BM μ_a = 1.35, μ_b = 1.99. IR: 3594 cm^{-1}, H-bonded, stronger absorption; 3635 cm^{-1} interpreted as nonbonded. *Tetrahedron* **1959**, *7*, 10–18. 2 conformers in IR.

46. 2-fluoroethanol [O–H···F]: Buckton, K. S.; Azrak, R. G. *J. Chem. Phys.* **1970**, *52*, 5652–5655. OH, OD; H···F, 2.42 (2); FCCO, 62.2°; CCOH, 55.5°. μ_a = 0.38 (2), μ_b = 1.47 (1), μ_c = 0, μ_{tot} = 1.5112, consistent with bond moment calculation.

47. 2-fluoroethylamine [N–H···F]: Marstokk, K.-M.; Møllendal, H. *Acta Chem. Scand.* **1980**, *A34*, 15–19. Conformer I: FCCN gauche, NH gauche and trans: H-bond; N···F, 2.87; vd W, 2.85; H··F, 2.55; N–H···F, 99°. Conformer II: FCCN gauche, NH gauche and gauche: H-bond; N···F, 2.94; H···F, 2.63; N–H···F, 97°. Conformer I: exptl μ_a = 1.148 (3), μ_b = 1.380 (8), μ_c = 0.332 (21), μ_{tot} = 1.826 (12); calcd BM μ_a = 1.1, μ_b = 0.9, μ_c = 1.002 (5), μ_{tot} = 1.671 (10). Conformer II: exptl μ_a <0.03, μ_b = 1.337 (8), μ_c = 1.002 (5), μ_{tot} = 1.671 (10); calcd BM μ_a = 0.1, μ_b = 0.9, μ_c = 1.9.

50. 2-fluoropropanol [O–H···F] (CH_3CHFCH_2OH): Braathen, O.-A.; Marstokk, K.-M.; Møllendal, H. *Acta Chem. Scand.* **1982**, *A36*, 173–181. Calcd BM μ_a = 1.1, μ_b = 0.9, μ_c = 0.2. 1 conformation: CH_3 anti to OH. OH 0.966 assumed; H···F, 2.48; F···O, 2.87; O–H··F, 104°. exptl μ_a = 1.41 (1), μ_b = 1.19 (2), μ_c = 0.1 (3), μ_{tot} = 1.15 (4); calcd BM μ_a = 1.1, μ_b = 0.9, μ_c = 0.2.

51. 3-fluoro-1-propanol [O–H···F]: Caminati, W. *J. Mol. Spectrosc.* **1982**, *92*, 101–116. OH + OD; 3 conformers, 1 H bonded; O··F, 2.85; H···F, 2.07. Dipole moments measured and calculated for all conformers from bond moments.

[a] Obtained by examining the changes in splittings of microwave absorption transitions when an external electric field is applied to the gas. Dipole moments and their components μ_a, μ_b, μ_c can be obtained for different rotamers, for different topamers, for different vibrational states, and, in favorable cases, for molecules distorted by being spun rapidly in high rotational states; some experimental values are compared with values calculated from bond moments (BM).

easily avoided without a high energy cost arising from a reduction of the bonding energy when the molecule is deformed so as to reduce the repulsion.

Various other criteria can be used to strengthen the conclusion from the structure. For example, the components of the observed electric dipole moment can be compared with those calculated from tables[8] of bond dipole moments, helping to define the structure.

In many studies it has been found that H-bonded molecules tend to have larger dipole moments than would be predicted from additivity rules,[8] but this effect is not present in all cases here.

When a molecule contains one or more nuclei with nuclear spin greater than $I = {}^1/_2$, these nuclei may have nonvanishing electrical nuclear quadrupole moments. These may then show a nonvanishing field gradient component, $\partial^2V/\partial x^2$, etc., arising from the electron distribution and from the other nuclear charges. Thus, the presence of any of the nuclei ^2D, ^{14}N, ^{17}O, ^{35}Cl, ^{37}Cl, etc., may produce a hyperfine structure in the rotational transitions from which the field gradient components can often be determined. (*V* is the electrical potential due to the electrons and other nuclei, etc.) These field gradients $\partial^2V/\partial x^2$ can sometimes be predicted, at least approximately, thus providing information about the structure which many support structural conclusions originally obtained by different approaches. In particular, formation of an H bond will often change the field gradients at critical nuclei. These changes may strengthen the case for the presence of an H bond. On the other hand, the effect may be too small to be detectable, even in cases where other criteria indicate the presence of an H bond.

For intermolecular bonding, the H bond tends to be approximately linear;[9,10] i.e., the angle X–H–Y is near 180°. However, this is seldom the case for intramolecular bonds which are likely to be governed by the constraints of the other bonds.

In a number of examples from our list the X–H and H–Y bonds are found to be essentially parallel, as one might expect from a crude electrostatic model. Examples of such parallelism include chloroethanol,[10] bromoethanol,[10] and hydroxypropionitrile[11] (see Figure 1).

In some cases, the microwave spectrum may provide specific evidence for molecular distortions such as might be anticipated as a result of expected forces from an H bond. Examples include dihedral angles deviating measurably from an expected gauche or skew conformation.

A special example of a distortion due to H-bond forces is provided by hydroxyacetone ($CH_3{-}CO{-}CH_2O{-}H$)[12] in which microwave A–E splittings due to rotational tunnelling by the CH_3 group lead to an unusually small CH_3 internal rotational barrier of 193 ± 10 cal/mol. Similar molecules without H bonds show distinctly higher values. This effect has been explained in terms of forces arising from the hydrogen bond. If further examples substantiate this phenomenon, it could turn

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[8] Smyth, C. P. *Dielectric Behavior and Structure*; McGraw-Hill: New York, 1955.

[9] Dyke, T. R. *Top. Curr. Chem.* **1984**, *120*, 85–114.

[10] Azrak, R. G.; Wilson, E. B. *J. Chem. Phys.* **1970**, *52*, 5299–5316.

[11] Marstokk, K. M.; Møllendal, H. *Acta Chem. Scand., Ser. A* **1985**, *39*, 15–31.

[12] Kattya-Ari, M.; Harmony, M. D. *Int. J. Quantum Chem., Quantum Chem. Symp.* **1980**, *No. 14*, 443.

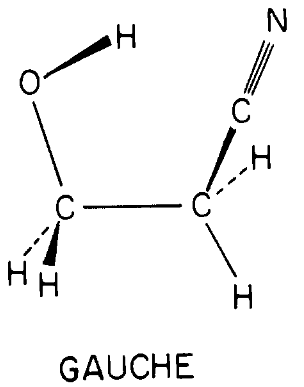


Figure 1. Gauche H-bonded form of ring for $OHCH_2CH_2CN$. Reprinted with permission from ref 11. Copyright 1985 Acta Chemica Scandinavia.

out to be an important test for H bonding in fairly special situations.

A rather more subtle indication is sometimes found. From a large number of X-ray determinations of H-bond structures in crystals, it has been found that substitution of D for H in $X{-}H\cdots Y$ can change the effective X to Y distance (the Ubbelhode effect).[13-15] This can show up, for example, as a difference in the r_s coordinates[16] calculated by using different atoms as the standard basis. This effect may be too small to see for sufficiently weak H bonds but can show up for stronger ones and sometimes can support the presence of an H bond.

Strength of H Bonds

A reasonable measure of the strength of a hydrogen bond would be the energy or enthalpy difference from the H-bonded conformation to an open conformation with a geometry in which the $X\cdots Y$ separation is too large to allow H bonding. There are indeed possible ambiguities; for example, there may be some steric crowding which varies for different conformations. We might or might not want to include this steric energy separately or as a negative term in the binding energy.

The intensity ratio (at thermal equilibrium) of two completely resolved spectral transitions, one associated with one conformer and the other with a different conformer, after corrections for the different dipole moments, line breadths, statistical weights, frequencies, etc.,[17] leads to a value for the energy difference between the lower levels involved in the two resolved transitions.

For example, the energy difference from the H-bonded conformer of 3-hydroxypropionitrile[11] to the open form was found to be 1.77 ± 5.7 kcal/mol.[18]

To obtain thermodynamic quantities (ΔG, ΔS, ΔH, etc.) for the reaction

$$\text{conformation I} \rightarrow \text{conformation II}$$

we would have to calculate partition functions for I and II, which would require sums over the Boltzmann factors of all the rotation–vibration–nuclear spin states of I and of II.

A simpler, but only semiquantitative, estimate of strength is the X- - -Y distance compared with the sum of the van der Waals radii of X and Y. Another is the magnitude of the shift of the O–H stretch in the infrared region.

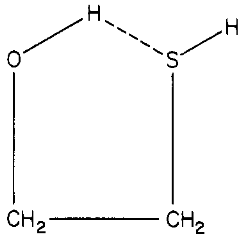
One could also imagine using the deviation of the displacement of one or more dihedral twist angles away from the normal staggered configuration. One expects and normally finds larger deviations for the dihedral angles controlling the positions of X and Y. The main chains tend to keep their twist angles close to those of a staggered configuration.

When we examine cases in which both X and Y can act as donors, we would expect sometimes to see two conformers present

$$X{-}H\cdots Y{-}H \quad \text{and} \quad Y{-}H\cdots X{-}H$$

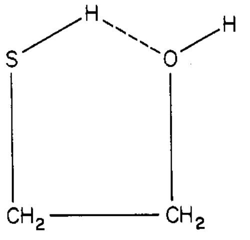
In the first form X is the donor and Y is a proton acceptor (forward conformer), whereas in the second rotamer X is the acceptor and Y–H is the donor (reversed form). Actually this is found, plus complications, in glycine,[19] CH_2NH_2–COOH, which has $N{-}H\cdots O$ and also $O{-}H\cdots N$ forms (see Figure 2).

One direction for the H bond is almost always so much stronger than the other direction that the population and intensity for the high-energy form are unobservably too small. Even so, we can usually tell whether the X type or the Y type bond is the stronger from the geometrical information given by the microwave results. For example, consider the donor–acceptor pairs -O-H and -S-H. The molecule



A

is found to have O–H as the donor and S–H as the acceptor, but the conformer



B

is not observed and is thus presumed to be of higher energy. From similar data, we can then list our dual

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[13] Hamilton, W. C.; Ibers, J. A. *Hydrogen Bonding in Solids*; W. A. Benjamin: New York, 1968.

[14] Penn, R. E.; Birkenmeier, J. A. *J. Mol. Spectrosc.* **1976**, *62*, 416–422.

[15] Penn, R. E.; Curl, R. F. *J. Chem. Phys.* **1971**, *55*, 651–658. Penn, R. E.; Olsen, R. J. *J. Mol. Spectrosc.* **1976**, *62*, 423–428.

[16] The so-called r_s coordinates are atomic coordinates obtained by fitting coordinate values to the changes in the molecular moments of inertia brought about by isotopic substitution instead of fitting the coordinates to the absolute values of the moments of inertia for a set of isotopic species.

[17] See: Gordy, W.; Cook, R. L. *Microwave Molecular Spectra*; Interscience: New York, 1970; Section 3.1.

[18] McMahan, M. A.; Sharma, S. D.; Curl, Jr., R. F. *J. Mol. Spectrosc.* **1979**, *75*, 220–233.

[19] Suenram, R. D.; Lovas, F. J. *J. Am. Chem. Soc.* **1978**, *72*, 372–382. (b) Hollis, J. M.; Snyder, L. E.; Suenram, R. D.; Lovas, F. J. *Astrophys. J.* **1981**, *241*, 1001–1006. (c) Snyder, L. E.; Hollis, J. M.; Suenram, R. D.; Lovas, F. J.; Brown, L. W.; Bukl, D. *Astrophys. J.* **1983**, *268*, 123–128. (d) Suenram, R. D.; Lovas, F. J. *J. Am. Chem. Soc.* **1980**, *102*, 7180–7184.

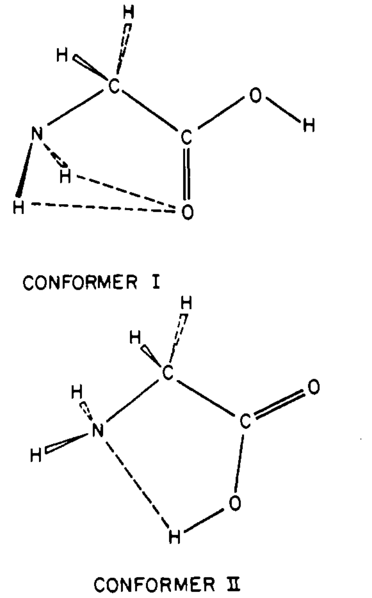

Figure 2. Structures of two H-bonded conformers of glycine (vapor). Reproduced from ref 19.

purpose donor–acceptor groups in the order –OH, –SH, $-NH_2$, $-C{=}C-H$ if in fact this order always predicts the more stable bond, as seems to be the case for our limited sample. The –O–H already appears in our list to give the most stable form with OH as donor, regardless of the acceptor used.

Some Structural Generalizations

For the discussion of the regularities found in the H-bonded structures, it is convenient to set up a few categories. Thus, our list contains a number of molecules which can be considered as derivatives of ethane, as for example CH_2OHCH_2Y with Y = OH, SH, NH_2, CN, etc. Similarly, in this series OH could be replaced by NH_2.

In these substituted ethanes, generally the gauche configuration with the OCCY (or NCCY) dihedral angles near 60° occurs in order to minimize the barrier energy about the C–C bonds. Generally the deviations from a staggered configuration are small, only a few degrees, and it is possible that the size of this deviation from 60° is correlated with the strength of the H bond.

Still another series (substituted propanes) is generated by replacing the first (or second) CH_2 group by CH_3CH. Again, the preferred conformation is gauche for the basic chain, and it is reasonable to assume that there is a relationship between the deviation from an exactly staggered configuration and the strength of the H bond. In addition, the barrier to internal rotation of the methyl group is probably related to the H-bond strength also, but we now have too few cases to draw a firm conclusion.

Many of our listed molecules have a five-membered ring, counting the hydrogen (see structure A). There are some which show a six-membered ring, 3-aminopropanol[18] being an example (see Figure 3). The main ring in this example is somewhat puckered but roughly near-planar. One would expect a six-membered ring to introduce less crowding and therefore cause less constraint on the H bond. The H bond would therefore have more freedom to seek a lower energy bond configuration. This would suggest a hydrogen bond tending more toward linearity.

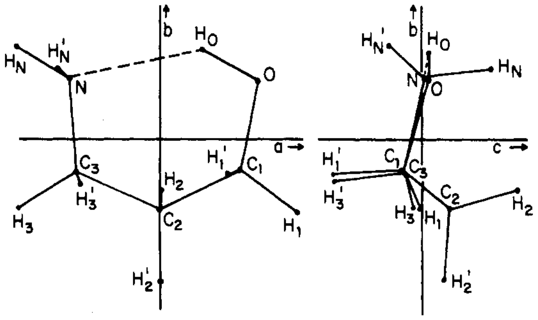

Figure 3. Example of six-membered ring, 3-aminopropanol. Reprinted with permission from ref 18. Copyright 1979 Academic Press.

Ordering Acceptors and Donors

Suppose that one molecular species can form an intramolecular H bond X–H···Y while another species forms the bond X–H···Y′; then it seems reasonable to assume that the difference in the strengths of these two bonds will be, at least to a considerable extent, determined by the difference Y–Y′ in the acceptor powers. Microwave intensity measurements given by the ratio of bonded to nonbonded conformers of the first species can therefore be combined with similar intensity measurements on the conformers of the second species. Such data then lead to the establishment of an order for the acceptor power of the groups Y, Y′, etc.

Unfortunately, relatively little microwave intensity data of adequate accuracy on such conformers have been obtained, so that this potentially valuable method of ordering the proton acceptor power of atoms and groups has been little used. This is just one more example of the high payoff one can expect from improved techniques for intensity measurements.

Very similar results can be expected from application of intensity measurements on pairs of donor groups, the acceptors being the same in the two species. Let [S–H···Y] and [NH_2–H···Y] be two H-bonded species whose bond strengths have been obtained by making microwave intensity measurements on the bonded vs. open forms. Further, the two species share a common acceptor, here Y. Then if [S–H···Y] is stronger than [NH–H···Y], it is reasonable to infer that the donor SH is a stronger donor than NH_2. Microwave studies have seldom been carried out with these goals in mind so examples are not at hand, but it is hoped that this gap will be filled in the future.

Comparisons with Quantum Chemical Calculations

Our data list contains a few molecules for which ab initio quantum chemical calculations of one or more of the conformations, the structure, etc., of the various conformations have been published. It is therefore possible to compare these calculated values with the microwave results. This is a difficult test because the energy differences are quite small, the number of electrons is fairly large, and not too much experience has been gained on efficient basis sets and configurations suitable for such calculations. As one could expect, the results are mixed but somewhat encouraging.

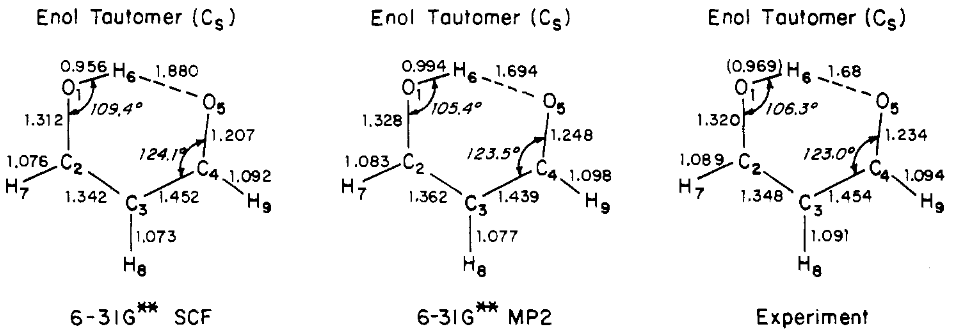

Figure 4. Structure of malonaldehyde. Two levels of theory compared with experiment. Reprinted with permission from ref 22. Copyright 1985 American Institute of Physics.

A striking positive result was the successful prediction of a second conformer of the amino acid glycine.[19] This calculation was apparently practically useful in finding and analyzing the second microwave spectrum.

With malonaldehyde[20–22] (see Figure 4) even moderately high level (near Hartree–Fock) calculations were only partly successful on the structure and rather poor on the vibration frequencies. (But these are not well-known experimentally either.) Finally, by going to a still higher order calculation,[22,23] an excellent structure and better vibration frequencies were obtained despite the fact that malonaldehyde contains 9 atoms and 56 electrons and has complications such as a double-minimum potential energy function.

A donor has to have a hydrogen capable of being donated and thereby forming a bond with an acceptor. We have examples of only a few donor–acceptor dual purpose groups. It would be of interest to find new ones.

By addition of groups with large inductive effects, it may be possible to extend the list of donor–acceptor groups just as the three fluorines in CF_3H give the group H bond[24] forming properties.

Conclusions

The discussion of some of these H-bonded molecules shows the level of detail obtainable from resolved microwave spectra. As the available data are further analyzed, it should be possible to choose molecules for future study which will lead to a deeper understanding and more sets of rules about the structure of these H-bonded species, the strength of these bonds, their electron distributions, and further correlations with other properties such as the donor and acceptor strengths. It should be possible to gain more predictive power with respect to the local properties of intramolecular hydrogen bonds in large biologically important macromolecules.

This work was supported by NSF Grant CHE-83-10534. We are grateful to Dr. Stephen Coy for his help on a number of occasions.

Supplementary Material Available: Listing of hydrogen-bonded molecules and some of their properties (12 pages). Photocopies of the supplementary material from this paper or microfiche (105 × 148 mm, 24× reduction, negatives) may be obtained from Microforms & Back Issues Office, American Chemical Society, 1155 16th Street, NW, Washington, DC 20036. Orders must state whether for photocopy or microfiche and give complete title of article, names of authors, journal issue date, and page numbers. Prepayment, check or money order for $23.50 for photocopy ($25.50 foreign) or $10.00 for microfiche ($11.00 foreign), is required and prices are subject to change.

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