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Microwave and *Ab Initio* Study of the Conformational Properties of 3-Furanmethanol

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The microwave spectra of 3-furanmethanol and one deuterated species (hydroxyl group) have been investigated in the 26.5–39.5 GHz spectral region at 5°C. One conformer was assigned. This rotamer prefers a *skew* arrangement for the C=C–C–O chain of atoms while the H–O–C–C atoms take a *gauche* conformation. This allows the molecule to form a weak intramolecular hydrogen bond between the hydrogen atom of the hydroxyl group and the π-electrons of the nearest double bond. This conformer is estimated to be at least 3 kJ mol^{-1} more stable than any further rotameric form. The microwave work has been assisted by *ab initio* computations at the 6-31*G** and MP2/6-31*G** levels of theory.

The conformational and structural properties of aliphatic allylic alcohols which contain the C=C–C–O–H chain of atoms have attracted considerable attention in the past several years. The simplest of these compounds, allyl alcohol, $H_2C=CHCH_2OH$, has been studied by microwave (MW) spectroscopy,[1a,b] electron diffraction (ED),[1c] *ab initio* computations,[1c,d] and IR[1d–g] and NMR spectroscopies.[1g–i] 3-Buten-2-ol, $H_2C=CHCH(OH)CH_3$, has been investigated by MW spectroscopy[2a] and *ab initio* calculations,[2b,c] as has 2-methyl-2-propen-1-ol (2-methylallyl alcohol), $H_2C=CH(CH_3)CH_2OH$,[3a,b] while *trans*-[4a,b] and *cis*-[4c] buten-1-ol (*trans*- and *cis*-crotyl alcohol), $H_3CCH=CHCH_2OH$, have been subject to MW investigations. MW spectroscopy was used to establish the preferred conformations of 2,3-butadien-1-ol, $H_2C=C=CHCH_2OH$,[5] and 1,4-pentadien-3-ol, $H_2C=CH–CH(OH)–CH=CH_2$.[6]

In all these allyl alcohol derivatives the most stable conformer has been found to take a heavy-atom *skew* conformation with a C=C–C–O dihedral angle about 120° from *syn*. The C–C–O–H dihedral angle was *gauche* (60° from *syn*). This dihedral angle allows for close proximity between the hydrogen (H) atom of the hydroxyl group and the π-electrons of the double bond, which by most workers has been assumed to be a weak intramolecular H bond.

In addition to the 'H-bonded' heavy-atom *skew* conformer, a C=C–C–O *syn* conformer has been found in some of these cases.[1–3,4b] The C–C–O–H conformation is again *gauche*,[1–3,4b] which allows the H atom of the hydroxyl group to come close to the π-electrons of the double bond. Generally, this second rotamer, which may also be said to form an internal hydrogen bond, is slightly less stable than the heavy-atom *skew* conformer.[1–3,4b] $H_2C=CH–CH(OH)–CH=CH_2$ is interesting because it prefers a conformer[6] where the C=C–C–O link of atoms is *syn* with respect to one of the double bonds, and *skew* to the other double bond. The C–C–O–H atoms are *gauche* to one of the double bonds with the formation of an intramolecular H bond.

3-Furanmethanol was chosen for study because it has a C=C–C–O–H atomic arrangement, just as the allylic alcohols do. However, the bonding situation is more complex in this case than with the allylic alcohols because π-electron delocalisation presumably exists to a significant extent in this aromatic molecule. This work was carried out because it was felt that it would be of interest to investigate the influence of delocalisation on the conformational preferences of the C=C–C–O–H chain of atoms.

Fig. 1 shows five conformational possibilities. In the three *skew* forms, the C1=C2–C5–O2 link of atoms is about −120° from *syn*, whereas the C2–C5–O2–H6 dihedral angle is approximately +60° (*Skew 1*), 180° (*Skew 2*) and −60° (*Skew 3*). In the two *syn* rotamers, the C1=C2–C5–O2 dihedral angle is 0°, while C2–C5–O2–H6 dihedral angle is ±60° (*Syn 1*) and 180° (*Syn 2*). The *Skew 1* and *Syn 1* rotamers might be stabilized by intramolecular H bonds formed between the hydroxyl group H atom and the π-electrons of the C1=C2 bond. The corresponding allylic alcohols are generally found to be the two conformers with the lowest energies, as already mentioned. In *Skew 2* and *Syn 2* internal H bonding is

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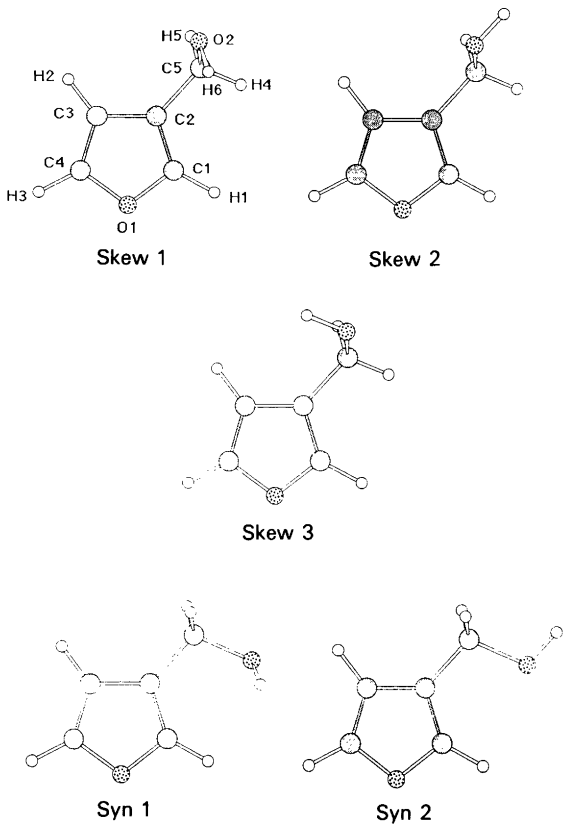

Fig. 1. The five conformations that are presumed to be the stable forms of 3-furanmethanol. Atom numbering is given on the sketch of *Skew 1*, which is the only conformer assigned in this work. The present *ab initio* structures are in nearly complete agreement with this sketch in the cases of *Skew 1*, *Skew 2* and *Syn 2*, whereas the C1–C2–C5–O2 dihedral angle is computed to be smaller by about 34° from the value indicated in this figure (−120°) in *Skew 3*, and deviates by 22° from coplanarity in the case of *Syn 1* (see text).

not possible, while this interaction perhaps cannot be completely excluded for *Skew 3* provided the π-electrons of the furan ring are delocalized to a great extent. Only *Skew 1* was assigned in this work. There is no evidence for large fractions of further rotameric forms.

Experimental

Microwave experiment. The sample utilized in this work was purchased from Aldrich-Chemie, Steinheim, Germany. The compound was purified by preparative gas chromatography. The MW spectrum was studied using the Oslo spectrometer, which is described in Ref. 7. The 25.0–39.5 GHz spectral region was investigated with the microwave absorption cell cooled to about 5°C. Lower temperatures, which would have increased the MW spectral intensities, could not be employed owing to insufficient vapour pressure of the compound. The pressure was about 3–4 Pa when the spectra were recorded. The accuracy of the spectral measurements is presumed to be better than ±0.10 MHz. The deuterated species, $C_4H_3OCH_2OD$, was produced by conditioning the wave guide with heavy water and then introducing the parent species, $C_4H_3OCH_2OH$.

Results

Ab initio *calculations.* 3-Furanmethanol has previously been subject to an *ab initio* calculation with a rather limited basis set and incomplete geometry optimization.[8] It was therefore decided to repeat the computations using a much more sophisticated procedure. The computations were first made employing the 6-31*G** basis set with full geometry optimization for the five rotamers shown in Fig. 1. The Gaussian 92 program package[9] running on the Cray-Y-MP computer in Trondheim was employed. These five rotamers were all found to be stable, as no imaginary vibrational frequencies[10] were computed for any of them.

In order to see whether rotamers other than those depicted in Fig. 1 might be low-energy *stable* conformers, searches for such forms were made using the 6-31*G** basis set starting with the C1=C2–C5–O2 dihedral at 180° (*anti*) and −60° (*gauche*), respectively, allowing for full geometry optimization. However, no stable *anti* or *gauche* rotamers were located. In fact, the Gaussian 92 program always refined to one of the five conformers shown in Fig. 1. It is therefore concluded that the five forms shown in this figure indeed are the *stable* forms of 3-furanmethanol.

Finally, the computations were repeated for these five conformers at the MP2/6-31*G** level, with full geometry optimization using the 6-31*G**-geometries as starting points. The MP2/6-31*G**-geometries and the 6-31*G**-geometries were only slightly different. This was also the case with the energy differences between the conformations and the dipole moment components along the principal inertial axes. Selected results of the MP2/-6-31*G** computations are given in Table 1.

The bond angles and distances shown in this table have rather 'normal' values. The dihedral angles are also close to the expected ones with two exceptions: The C1=C2–C5–O2 dihedral angle is computed to be −86.3° for *Skew 3*, while approximately −120° is expected for this relatively high-energy conformation. No explanation can be offered for this unusual dihedral angle. Repulsion between the H2 and H6 atoms is definitely ruled out because this distance is calculated to be as long as 321 pm.

The same dihedral angle is calculated to be 22.3° from coplanarity in *Syn 1*. Repulsion between the C1 and O2 atoms, which are predicted to be only about 280 pm apart, is perhaps the explanation for this deviation from coplanarity.

Moreover, it is noted (Table 1) that *Skew 1* is computed to be the most stable conformer of 3-furanmethanol. This rotamer is calculated to be only 2.3 kJ mol^{-1} more stable than *Syn 1*. These two conformers are the ones that can form internal H bonds with the π-electrons of the double bond. The small energy difference predicted between

Table 1. Structure, rotational constants, principal-axes coordinates of the hydroxyl-group H atom and dipole moments of five selected rotamers 3-furanmethanol as calculated by *ab initio* methods at the MP2/6-31*G** level.

Conformation:	*Skew 1*	*Skew 2*	*Skew 3*	*Syn 1*	*Syn 2*
Distance/pm					
H1–C1	108.1	108.0	108.0	107.9	107.8
C1–C2	136.8	136.6	136.9	136.8	136.6
C2–C5	149.3	148.7	149.4	149.7	149.1
C5–O2	142.9	143.0	143.1	142.7	142.7
C5–H4	110.0	110.0	109.3	109.4	110.0
C2–C3	143.1	142.9	143.1	142.9	142.9
C3–H2	108.1	108.1	108.3	108.2	108.2
C3–C4	136.3	136.3	136.4	136.5	136.5
C4–H3	108.0	108.0	108.0	108.0	108.0
C4–O1	136.7	136.7	136.5	136.4	136.3
C5–H5	109.3	110.0	109.9	110.0	110.0
O2–H6	97.3	97.3	97.2	97.3	97.1
O1–C1	136.4	136.4	136.3	136.5	136.7
Angles/°					
H1–C1–C2	133.5	133.4	133.3	133.2	133.2
C1–C2–C5	127.6	127.3	127.0	125.6	126.2
C2–C5–O2	112.1	107.8	112.9	112.0	107.6
C2–C5–H4	109.9	109.6	110.6	111.1	110.0
C1–C2–C3	105.8	105.9	105.6	105.8	106.1
C2–C3–H2	126.7	126.8	127.2	127.4	127.5
C2–C3–C4	106.4	106.4	106.6	106.4	106.3
C3–C4–H3	134.0	134.0	134.1	133.9	133.8
C3–C4–O1	110.5	110.5	110.3	110.5	110.5
C2–C5–H5	111.0	110.0	109.6	110.0	110.0
C5–O2–H6	106.5	107.3	106.7	106.4	107.6
C1–O1–C4	106.4	106.4	106.7	106.6	106.7
Dihedral angles[b]/°					
H1–C1–C2–C5	−1.4	0.8	−3.9	−0.4	0.0
C1–C2–C5–O2	−125.3	−124.5	−86.3	22.3	0.0
C1–C2–C5–H4	−0.8	−3.0	31.2	146.7	121.1
H1–C1–C2–C3	179.9	180.3	180.3	180.5	180.0
C1–C2–C4–H2	179.2	178.6	181.0	180.2	180.0
C1–C2–C3–C4	−0.4	−0.1	−0.6	−0.1	0.0
C2–C3–C4–H3	179.9	179.5	180.8	180.4	180.0
C2–C3–C4–O1	0.2	−0.1	0.4	−0.1	0.0
C1–C2–C5–H5	117.8	115.0	149.6	−94.8	−121.1
C2–C5–O2–H6	54.2	186.4	−51.6	59.1	180.0
Rotational constants[c]/MHz					
A	7 129.7	7 213.3	6 954.9	7 229.1	7 328.1
B	1 854.1	1 863.3	1 831.3	1 902.4	1 933.4
C	1 576.7	1 578.8	1 605.1	1 545.0	1 544.6
Principal axis coordinates of hydroxyl-group H atom/pm					
$\|a\|$	216.5	332.4	213.1	226.5	333.3
$\|b\|$	20.3	29.6	71.7	71.3	29.2
$\|c\|$	134.7	31.3	118.3	106.4	0.0
Dipole moment[d]/10^{-30} C m					
μ_a	2.57	5.15	3.30	2.72	4.73
μ_b	2.11	1.54	5.26	4.90	7.62
μ_c	1.04	5.08	1.91	3.47	0.00
Energy difference [e,f]/kJ mol^{-1}					
	0.0	6.7	7.2	2.3	5.5

[a]See Fig. 1 for definition. [b]Measured from *syn* = 0°. [c]Calculated from the structures given above in this table. [d]1 D = 3.335 64 × 10^{-30} C m. [e]The total energy of conformer *Skew 1* was calculated to be −899 201.6 kJ mol^{-1}. [f]Energy difference between *Skew 1* and each of the other four conformations.

Table 2. Selected MW transitions of the ground vibrational state of *Skew 1* of 3-furanmethanol.

Transition $J''_{K''-1,K''+1} \leftarrow J'_{K'-1,K'+1}$		Observed frequency[a]/MHz	Obs. − calc. freq./MHz
$8_{5,3}$	← $7_{5,2}$	27 397.59	0.02
$8_{5,4}$	← $7_{5,3}$	27 397.59	0.03
$8_{7,1}$	← $7_{7,0}$	27 379.68	−0.04
$8_{7,2}$	← $7_{7,1}$	27 379.68	−0.04
$9_{0,9}$	← $8_{0,8}$	29 806.02	−0.02
$9_{1,8}$	← $8_{1,7}$	31 622.93	0.04
$9_{2,7}$	← $8_{2,6}$	31 560.12	0.03
$9_{2,8}$	← $8_{2,7}$	30 599.10	0.02
$9_{3,6}$	← $8_{3,5}$	30 980.87	0.03
$9_{4,6}$	← $8_{4,5}$	30 860.38	0.06
$9_{6,3}$	← $8_{6,2}$	30 816.66	0.03
$9_{6,4}$	← $8_{6,3}$	30 816.66	0.04
$9_{7,2}$	← $8_{7,1}$	30 807.09	−0.03
$9_{7,3}$	← $8_{7,2}$	30 807.09	−0.03
$10_{0,10}$	← $9_{0,9}$	32 953.58	−0.06
$10_{1,9}$	← $9_{1,8}$	35 030.88	0.10
$10_{2,9}$	← $9_{2,8}$	33 949.66	0.01
$10_{3,7}$	← $9_{3,6}$	34 490.55	0.04
$10_{4,7}$	← $9_{4,6}$	34 307.84	−0.01
$10_{5,5}$	← $9_{5,4}$	34 270.64	−0.06
$10_{5,6}$	← $9_{5,5}$	34 270.64	0.08
$10_{6,4}$	← $9_{6,3}$	34 249.19	0.00
$10_{6,5}$	← $9_{6,4}$	34 249.19	0.00
$10_{7,3}$	← $9_{7,2}$	34 236.26	−0.01
$10_{7,4}$	← $9_{7,3}$	34 236.26	−0.01
$10_{9,1}$	← $9_{9,0}$	34 221.57	−0.06
$10_{9,2}$	← $9_{9,1}$	34 221.57	−0.06
$11_{0,11}$	← $10_{0,10}$	36 088.41	0.04
$11_{1,11}$	← $10_{1,10}$	35 775.25	−0.01
$11_{2,10}$	← $10_{2,9}$	37 285.49	0.00
$11_{3,8}$	← $10_{3,7}$	38 027.52	−0.02
$11_{4,7}$	← $10_{4,6}$	37 774.29	−0.01
$11_{6,5}$	← $10_{6,4}$	37 684.44	0.00
$11_{6,6}$	← $10_{6,5}$	37 684.44	0.00
$11_{8,3}$	← $10_{8,2}$	37 656.12	0.00
$11_{8,4}$	← $10_{8,3}$	37 656.12	0.00
$11_{10,1}$	← $10_{10,0}$	37 642.24	0.04
$11_{10,2}$	← $10_{10,1}$	37 642.24	0.04
$9_{1,9}$	← $8_{0,8}$	31 478.46	−0.02
$10_{0,10}$	← $9_{1,9}$	31 281.16	−0.02
$10_{1,10}$	← $9_{0,9}$	34 245.16	0.01
$11_{1,11}$	← $10_{0,10}$	37 066.75	−0.04
$12_{0,12}$	← $11_{1,11}$	38 239.60	0.00
$13_{4,9}$	← $13_{3,10}$	36 150.04	−0.05
$15_{3,13}$	← $15_{2,14}$	31 759.62	0.02
$16_{4,12}$	← $16_{3,13}$	33 910.89	0.01
$18_{3,16}$	← $18_{2,17}$	35 588.17	0.03
$19_{4,15}$	← $19_{3,16}$	30 723.24	−0.03
$21_{2,19}$	← $21_{1,20}$	33 660.35	0.01
$22_{3,19}$	← $22_{2,20}$	25 086.41	−0.01
$23_{4,19}$	← $23_{3,20}$	27 331.78	−0.02
$25_{3,22}$	← $25_{2,23}$	32 051.41	0.00
$26_{4,22}$	← $26_{3,23}$	27 576.97	0.02
$27_{4,23}$	← $27_{3,24}$	28 417.55	0.02
$28_{5,23}$	← $28_{4,24}$	35 733.58	0.00
$30_{4,26}$	← $30_{3,27}$	33 401.37	−0.09
$32_{5,27}$	← $32_{4,28}$	33 366.76	0.01
$35_{5,30}$	← $35_{4,31}$	35 685.98	0.04
$36_{5,31}$	← $36_{4,32}$	37 363.23	0.01

[a] ±0.10 MHz.

Table 3. Ground-state spectroscopic constants[a,b] of the *Skew 1* conformer of 3-furanmethanol.

Species:	Parent	Deuterated
No. of transitions:	103	39
R.m.s. dev.[c]/MHz:	0.037	0.067
A_0/MHz	7 095.145 1(45)	6 925.946(32)
B_0/MHz	1 840.652 6(13)	1 797.722 4(45)
C_0/MHz	1 578.353 6(13)	1 554.607 9(47)
Δ_J/kHz	0.251 4(63)	0.301(21)
Δ_{JK}/kHz	2.070 5(78)	1.916(28)
Δ_K/kHz	2.94(22)	2.94[d]
δ_J/kHz	0.014 27(20)	0.0141 5(44)
δ_K/kHz	0.185(13)	0.185[d]

[a] *A*-reduction, *I*^{r}-representation.[11] [b] Uncertainties represent one standard deviation. [c] Root-mean-square deviation. [d] Fixed at this value in the least-squares fit.

Skew 1 and *Syn 1*, with the former rotamer as the more stable, is reminiscent of the findings made for the aliphatic allylic alcohols,[1-6] as discussed above.

Skew 2, *Skew 3* and *Syn 2* are all calculated to be high-energy forms of 3-furanmethanol, with energy differences in the 5.5–7.2 kJ mol^{-1} range (Table 1). Since no stabilization of the H6 atom with the π-electrons of the double bond is possible for any of these three rotamers, it is indeed expected that they are less stable than *Skew 1*.

MW spectrum and assignments. The first survey spectra revealed a very weak spectrum. The peak intensities of strongest lines observed were as low as roughly 4×10^{-8} cm^{-1} at 5°C. Such a weak spectrum was expected, since the dipole moment of the *Skew 1* conformer, which is predicted to be the most stable one (Table 1), is computed to be rather small, as seen in the same table. The largest principal-axis component of the dipole moment is μ_a for this prolate rotor, which is predicted to have Ray's asymmetry parameter[11] $\kappa \approx -0.9$. High-K_{-1} pile-up regions were therefore expected for the ^aR-transitions. Fortunately, such pile-ups were soon noted and easily assigned. μ_b is calculated to be almost as large as μ_a, and the high-J ^bQ-transitions were thus expected to be the strongest *b*-type transitions. These lines were searched for and readily assigned. No *c*-type transitions were seen, although their hypothetical frequencies could be predicted very accurately. This is not surprising, since μ_c is predicted to be so small (Table 1). Ultimately 103 transitions were used to determine the spectroscopic constants. Selected lines* are listed in Table 2, and the spectroscopic constants (*A*-reduction *I*^{r}-representation)[12] of the ground vibrational state are found in Table 3.

* The complete spectra of the parent and deuterated species are available from the authors upon request, or from the National Institute of Science and Technology, Molecular Spectra Data Center, Bldg. 221, Rm. B 268, Gaithersburg, MD 20899, U.S.A., where they have been deposited.

Very weak signals from vibrationally excited states were noted, but no assignments have been made owing to their weakness. The dipole moment could not be determined because the spectrum is too weak.

It is seen in Table 1 that the MP2/6-31*G** rotational constants of all the three *skew* conformations are rather similar to the experimental ones (Table 3), although the best agreement is found for *Skew 1*, as expected. The deuterated species (hydroxyl group) was studied to corroborate that the identified spectrum indeed belongs to *Skew 1*, and not to *Skew 2* or *Skew 3*. The MW spectrum of this isotopomer was assigned in a straightforward manner; its rotational constants are found in Table 3. The principal-axes coordinates of H6 are calculated as $|a| = 210.844(14)$, $|b| = 18.36(16)$ and $|c| = 126.6600(23)$ pm using Kraitchman's equations.[13] These are close to the values predicted for *Skew 1* (Table 1) and show beyond doubt that this conformer has been identified.

The existence of further conformations. The *ab initio* computations (Table 1) predict that only small energy differences exist between the five conformations of Fig. 1. *Skew 1* is predicted to have the *smallest* dipole moment of the five conformers. The intensities of the MW transitions are proportional to the square of the components of the dipole moment components along the principal inertial axes. The fact that *all* the strongest lines observed in this weak spectrum belong to *Skew 1* is therefore strong evidence that *Skew 1* is the most stable conformer, in agreement with the theoretical computations. *Skew 1* must be considerably more stable than any of the other four forms shown in Fig. 1, since much larger dipole moments are predicted for them, as seen in Table 1. Intensity considerations thus lead us to the rather conservative estimate that *Skew 1* is at least 3 kJ mol^{-1} more stable than any other hypothetical conformation.

Structure. It is seen from Tables 1 and 3 that the experimental rotational constants are very close (better than 1%) to those calculated from the structure in Table 1. Moreover, the MP2/6-31*G** structural parameters of *Skew 1* are very similar to their counterparts in closely related molecules, such as furan[14] in the case of the ring and methanol[15] in the case of the substituent. No experimental data are at hand that could really improve the structure in Table 1. The MP2/6-31*G** structure is therefore adopted as a *plausible* structure of the *Skew 1* conformer of 3-furanmethanol.

Discussion

This work has shown that 3-furanmethanol prefers the same conformation that aliphatic allylic alcohols[1-6] do as their most stable form. The delocalisation of the π-electrons, or aromaticity, thus seems to play a minor role for the conformational preference in this molecule.

Is *Skew 1* stabilized by a weak H bond? The evidence for this is the fact that the preferred conformation is the one that brings the H6 atom close to the π-electrons of the C1=C2 double bond. The H6···C2 non-bonded distance is 253 pm, slightly less than 290 pm, which is the sum of the van der Waals radii of *H* and the half-thickness of aromatic carbon.[16] The internal H bond is further characterized by a non-bonded H6···C1 distance of 344 pm, an O2–H6···C1 angle of 72.5° and an O2–H6···C1 angle of 89.6°. The angle between the O2–H6 and C1=C2 bonds is 57.5° from being parallel. These geometrical characteristics of the intramolecular *H* bond are close to their counterparts in the aliphatic allylic compounds.[1-6] There is thus no great difference between 3-furanmethanol and its aliphatic congeners. However, it should be stressed that the H bonds in allylic compounds are undoubtedly very weak and clearly borderline cases.

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