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The conformational composition of 3-buten-1-ol, the importance of intramolecular hydrogen bonding

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Abstract

The conformations of 3-buten-1-ol (1), and its model compounds cis-6-methyl-3-cyclohexen-1-ol (6), 3-cyclopenten-1-ol (7) and epicholesterol (9) have been investigated by FT-IR and ¹H NMR spectroscopy. The energies and geometries of 1, 6 and 7 were also investigated by molecular mechanics, semiempirical molecular orbital and ab initio calculations, while 9 was investigated by molecular mechanics only. The objective of the work was to study the conformational composition and importance of intramolecular OH... π hydrogen bonding for this composition in 1. Only two conformers of 1 have a geometrical possibility for intramolecular hydrogen bonding: Conformers 12 and 13 (Fig. 1). Compounds 6 and 7 were used as models for Conformer 12, while 9 was used as a model for Conformer 13. The investigations showed that Conformer 13 is the only hydrogen-bonded conformer, and that Conformer 12 is not intramolecularly hydrogen bonded. Conformer 13 was the most populated conformer, while Conformer 12 was hardly populated. The combination of experimental and theoretical data, and the use of model compounds was found necessary to obtain this conclusion.[©] 1998 Elsevier Science B.V. All rights reserved.

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1. Introduction

The conformational composition of the homoallylic alcohol 3-buten-1-ol (1) has been the subject of a number of investigations. The question of intramolecular OH... π hydrogen bonding [1–7] has been central to these studies. From the presence of two bands in the OH region in the IR spectrum of 3-buten-1-ol, one at ca. 40 cm⁻¹ lower frequency than the other, Schleyer et al. proposed the existence of an intramo-

lecular hydrogen bond [8]. One year later, Ōki and Iwamura reported the same two bands, but in addition pointed out the possibility of a third one [9]. The presence of this band has later been supported by other workers [10–13]. From the results of the IR spectroscopy investigations, especially from the presence of the low frequency band, 3-buten-1-ol appeared to have at least one conformer stabilised by an intramolecular hydrogen bond. The geometry of the hydrogen-bonded conformers could not be determined by IR spectroscopy.

In 1979, Trætteberg and Østensen reported an electron diffraction (ED) investigation of the conformations of 3-buten-1-ol. They found that in the gas phase, the major conformer (69%) had a geometry

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Fig. 1. Ball and stick models of the 14 3-buten-1-ol (1) conformers (HF/6-31G** geometries).

that made intramolecular hydrogen bonding possible (close to Conformer 13 in Fig. 1). The minor conformer found did not have a geometry with staggered C-C and C-O bonds, or eclipsed H/C-C-C=C bonds [14]. Two years later, Marstokk and Møllendal reported that the results from a microwave spectroscopy (MW) investigation agreed with the main result from the electron diffraction investigation: Conformer 13 was the dominant one in the gas phase

(>80%) with a weak intramolecular hydrogen bond [15].

The conformational composition has been investigated by molecular mechanics calculations [16]. Nine of the conformers have also been examined by ab initio calculations (HF/3-21G*//HF/3-21G*, HF/6-31G*//HF/6-31G* and MP2/6-31G*//MP2/6-31G*) [17]. Conformer **13** was found to be the conformer lowest in energy. However, Conformer **12** was not considered (see Fig. 1 for notation).

We have studied the conformation of several unsaturated alcohols and other compounds with a geometrical possibility for an intramolecular hydrogen bond, and have discussed the importance of intramolecular hydrogen bonding in such compounds [18– 23]. The investigations have been performed by a combination of IR and ¹H NMR spectroscopy to give experimental data, and by calculations at different levels of sophistication to provide theoretical data. We believe that the combination of experimental and theoretical data is necessary to understand the conformational behaviour of these molecules.

2. Synthesis of model compounds

The model compound cis-6-methyl-3-cyclohexen-1-ol (**6**) was obtained from 1,4-cyclohexadiene (**2**) in a four-step synthesis, as shown in Fig. 2. 1,4-Cyclohexadiene was first reacted with m-chloroperbenzoic acid (MCPBA) to give 92% pure 1,4-cyclohexadiene monoepoxide (**3**) in 68% yield. Further reaction with lithium dimethylcuprate gave > 97% pure trans-6methyl-3-cyclohexen-1-ol (**4**) in 37% yield. To obtain the desired product **6** with a cis configuration, its trans



Fig. 2. Syntheses of model compounds.



Fig. 3. Notations and Newman projections of the rotamers of 3buten-1-ol (1) around the C^{1} - O^{5} , C^{1} - C^{2} and C^{2} - C^{3} bonds, and conformational composition from ¹H NMR.

isomer (4) was subjected to a Mitsunobu reaction [24] to give the benzoic acid ester of the inverted alcohol (5). Transesterification of 5 with sodium methoxide in methanol gave the product 6 with a purity of 99%. The yield for the last two steps was 11%. As the aim was to obtain pure model compounds, the yields were not optimized.

3. Experimental

3.1. Materials

1,4-Cyclohexadiene monoepoxide (**3**) was prepared according to Svendsen et al. The spectroscopic data were in accordance with the literature [25–29]. trans-(**4**) and cis-6-Methyl-3-cyclohexen-1-ol (**6**) were prepared as reported [23] with spectroscopic data in accordance with those reported before [30,31].

3-Buten-1-ol (1) and 4-penten-2-ol (10) were commercially available. Both compounds, together with the synthesised trans- (4) and cis-6-methyl-3-cyclohexen-1-ol (6), and 3-cyclopenten-1-ol (7, 89% pure, prepared [32] according to Hess and Brown [33]), were distilled (kugelrohr) before use. All these compounds were kept (neat) over activated 3 Å molecular sieves prior to the preparation of high dilution samples. Cholesterol (8) and epicholesterol (9) were used directly without purification and predrying. Both were commercially available. Epicholesterol was supplied by Steraloids, New Hampshire, USA.

3.2. ¹H NMR

The ¹H NMR spectra were recorded at high dilution at room temperature in CCl₃F on Jeol JNM-FX 100 FT-NMR, Jeol JNM-EX400 and Bruker WM 400 spectrometers, using a sealed capillary tube or coaxial tube with deuterated benzene for locking purposes. The numerical resolution was 0.1 Hz. Chemical shifts are reported as ppm from TMS. The CCl₃F solvent was distilled from freshly activated 3 Å molecular sieves and kept over activated 3 Å molecular sieves in a cold room. The high dilution CCl₃F solutions for NMR (c < 5 mM) were prepared in the NMR tubes in the cold room and were kept over freshly activated 3 A molecular sieves for one-three days before measurement. Spin simulation and spin iteration were performed with the Jeol program COMIC on a Digital PDP-11 computer connected to the Jeol JNM-EX400 spectrometer. Spin simulations were also performed on a PC with the program PMR from Serena Software, Bloomington, Indiana, USA.

3.2.1. 3-Buten-1-ol (1)

¹H NMR (400 MHz): δ 0.88 (1H, t, $J_{\text{H-D,E}} = 5.66 \text{ Hz}, \text{H}^{\text{H}}$), 2.26 (2H, q, $J_{\text{F,G-D,E}} = 5.98 \text{ Hz}, \text{H}^{\text{F,G}}$), 3.56 (2H, q, $\text{H}^{\text{D,E}}$), ca. 5.1 (1H, m, $J_{\text{C-F,G}} = 1.20 \text{ Hz}, \text{H}^{\text{C}}$), ca. 5.1 (1H, m, $J_{\text{B-F,G}} = 1.20 \text{ Hz}, \text{H}^{\text{B}}$), 5.75 (1H, ddt, $J_{\text{A-B}} = 10.20 \text{ Hz}, J_{\text{A-C}} = 17.16 \text{ Hz}, J_{\text{A-F,G}} = 6.98 \text{ Hz}, \text{H}^{\text{A}}$). Not quite stopped exchanging. ¹H NMR (100 MHz): δ 0.91 (1H, t, $J_{\text{H-D,E}} = 5.86 \text{ Hz}, \text{H}^{\text{H}}$). Stopped exchanging. For notation, see Fig. 3.

3.2.2. cis-6-Methyl-3-cyclohexen-1-ol (6)

¹H NMR (400 MHz): δ 0.89 (1H, d, $J_{C-I} = 6.83$ Hz, H^I), 0.97 (3H, d, $J_{H-J} = 6.84$ Hz, CH₃ (J)), 1.73–1.93 (2H, m, H^{G or F, H}), 2.00–2.12 (2H, m, H^{E or D, F or G}), 2.20–2.32 (1H, dm, $J^{d} \approx 18$ Hz, H^{D or E}), 3.76 (1H, ddt, $J_{C-I} = 7.0 \pm 0.2$ Hz, $J_{C-H} = 2.2 \pm 0.2$ Hz, $J_{C-E} =$ 4.5 \pm 0.2 Hz, $J_{C-D} = 4.5 \pm 0.2$ Hz, H^C), 5.45–5.55



Fig. 4. Notations, and ball and stick models of the two Anti ring conformers of cis-6-methyl-3-cyclohexen-1-ol (6) as examples of the 6_{ax} and 6_{eq} conformers (HF/6-31G** geometries).

 $(1H, m, H^{B})$, 5.55–5.65 (1H, m, H^A). For notation, see Fig. 4.

3.2.3. 3-Cyclopenten-1-ol (7)

¹H NMR (400 MHz): δ 0.94 (1H, d, $J_{C-H} = 6.59$ Hz, H^H), 2.24 (2H, br. d, H^{F,G}), 2.57 (2H, br. dd, $J_{D-F} = 16-$ 17 Hz, $J_{C-D} = 6.34$ Hz, H^{D,E}), 4.40 (1H, dtt, $J_{C-F,G} =$



Fig. 5. Notations, and ball and stick models of the two Anti ring conformers of 3-cyclopenten-1-ol (7) as examples of the 7_{ax} and 7_{eq} conformers (HF/3-21G geometries).

2.3 Hz, H^{C}), 5.64 (2H, br. s, $H^{A,B}$). For notation, see Fig. 5.

3.2.4. Epicholesterol (9)

¹H NMR (400 MHz): δ 0.97 (1H, d, ³J_{CH-OH} = 7.57 Hz, OH), 3.84 (1H, m, *H*COH). The OH signal and its coupling were identified by a *J*-resolved NMR experiment and from its disappearance on shaking with D₂O.

3.3. IR

The IR spectra were recorded at high dilution at room temperature in CCl₄ on a single beam Nicolet 20SXC FT-IR spectrometer equipped with a Nicolet 620 Data Station and TGS detector using IR quartz cells with 10 mm path length (transparent in the hydroxyl stretch frequency region in IR), 256 scans and 2 cm^{-1} resolution. The instrument was purged with dry air. The CCl₄ solvent was refluxed over and subsequently distilled from P2O5 under N2 atmosphere, and kept over activated 3 Å molecular sieves in a dry box under N2 atmosphere. The high dilution CCl_4 solutions for IR (c < 5 mM) were prepared and added to the IR cells in the dry box, and were kept over freshly activated 3 Å molecular sieves for 24 h before measurement. Overlapping bands were resolved by the FOCAS 2.1 program from Nicolet using a linear baseline approach. The number of bands and their positions were assessed by use of Fourier Self Deconvolution.

Note: keeping a dilute solution over activated molecular sieves will reduce the concentration and make it impossible to measure absolute values of integrated absorptions. However, relative values are valid.

3.4. Theoretical calculations

Molecular mechanics calculations were performed with the program MMPMI 1.0 [34] on a PC using the default dipole–dipole electrostatic mode, or, where noted, charge–charge interaction mode. MMPMI consists of MM2 (N.L. Allinger, QCPE Program no. 395) and MMP1 (N.L. Allinger, QCPE Program no. 318), as implemented by Serena Software, Bloomington, Indiana, USA. Input files for MMPMI were made on a PC using PCMODEL version 1.0 or 4.0 from Serena Software. The individual point charges for MMPMI in charge–charge mode were calculated with CHARGE2, version 1.0 [35–39] on a PC.

The semiempirical MNDO, AM1 and PM3 MO calculations were performed with MOPAC 3.13 [40] on a Digital MicroVax II, or with MOPAC 6.00 [41] on a Digital Vaxstation 3100 M38. Input files were made by PCMODEL.

Ab initio calculations were performed with GAUSSIAN 90, Revision I [42], GAUSSIAN 92, Revision C or G.2 [43], or with GAUSSIAN 94, revision B.1 [44], on the Cray X-MP/216 and Cray Y-MP4D/464 supercomputers in Trondheim. The calculations were done using Restricted Hartree-Fock (RHF) and Restricted Møller-Plesset of second order (RMP2) theory (closed-shell species, HF and MP2). Input files were made by PCMODEL as MOPAC input files. MOPAC without geometry optimization was used to transform MOPAC style Zmatrixes to GAUSSIAN style Z-matrixes. Standard GAUSSIAN basis sets were used (with 6 d polarization functions on heavy atoms for basis sets derived from 6-31G). Geometries were gradient-optimised without symmetry restrictions using the Berny optimiser and default convergence criteria. For the MP2 calculations, both the valence and core orbitals were included in the calculations. Analytical second derivatives were used in the geometry optimisations for all compounds using 3-21G and 6-31G** basis sets (except for 7), and for the calculations of hydroxyl stretch IR frequencies. All vibrational frequencies for all calculated conformers were positive, confirming that stationary points were all local minima. For the geometry optimisation of 7 and MP2 calculations of 1, numeric force constants were calculated at each point, using gradient information from previous points. No numeric vibrational frequencies were calculated.

For calculations of thermodynamical properties based on scaled vibration frequencies with GAUSSIAN 92, revision C, a modified version of link 716, which includes a scale factor, was used in the recalculations.

The conformational compositions were calculated from the relative energies, using the Boltzmann's law of distribution at 298 K. For the ab initio calculations, the compositions were calculated based on: (i) total energy; and also for one molecule on (ii) total energy together with zero point energy; (iii) total energy together with zero point energy and ΔH_{vib} connected with the increase in temperature from 0 K to 298.15 K; and (iv) Gibbs free energy based on (iii) and the calculated total entropy S_{tot} at 298.15 K. The calculations using the options (ii)–(iv) were performed both with and without scaling of the frequencies. The GAUSSIAN program package uses the Rigid Rotor-Harmonic Oscillator approximation to calculate the thermodynamical properties (no special treatment for low-frequency modes).

4. Results and discussion

If one assumes that staggered conformations are the stable ones for sp³-sp³ C-C and C-O bonds, and for sp³-sp² C-C=C bonds the eclipsed ones [45], there are 27 possible conformers of 3-buten-1-ol (1). Of these, 26 make up 13 enantiomeric pairs. The 14 conformers are shown in Fig. 1, while notation for the numbering of atoms and naming of the rotamers is shown in Fig. 3.

Only two conformers have the geometrical possibility for intramolecular hydrogen bonding: Conformers **12** and **13**. We have studied the conformational composition of 3-buten-1-ol and model homoallylic alcohols by IR and ¹H NMR spectroscopy, and by theoretical calculations. For Conformer **12** we chose cis-6-methyl-3-cyclohexen-1-ol **(6)** and 3-cyclopenten-1-ol **(7)** as models, and for Conformer **13** the OH epimer of cholesterol **(8)**: epicholesterol **(9)**. From inspection of models and the theoretical calculations, these molecules have geometries of the homoallylic alcohol fragments close to those of Conformers **12** and **13** of 3-buten-1-ol.

cis-6-Methyl-3-cyclohexen-1-ol (6) has six possible conformers. Two Anti conformers are shown in Fig. 4. In these, H^I and H^C have an anti conformation around C¹-O⁸, and the OH group has either an axial ($\mathbf{6}_{ax}$) or equatorial position ($\mathbf{6}_{eq}$). The shown example of $\mathbf{6}_{ax}$ (Anti-Ax) is the conformer that models Conformer 12 of 3-buten-1-ol. 3-Cyclopenten-1-ol (7) has four possible conformers, and these are shown with two Anti conformers as examples of the axial ($\mathbf{7}_{ax}$) and equatorial ($\mathbf{7}_{eq}$) conformers of the ring in Fig. 5. The conformer that models Conformer 12 of 3-buten-1-ol is the shown example of $\mathbf{7}_{ax}$ (Anti-Ax). Fig. 6 shows the Anti conformer of epicholesterol that acts as a model for Conformer 13 of 3-buten-1-ol. Anti denotes that the hydroxyl proton is antiperiplanar



Fig. 6. Ball and stick model of the Anti conformer of epicholesterol (9, MMPMI geometry).

to the vicinal proton. The other conformers of the model compounds have a Gauche C–O rotamer.

The IR and ¹H NMR spectra were obtained at concentrations lower than 5 mM in CCl_4 or CCl_3F . Under these conditions, intermolecular hydrogen bonding is not important, and interactions with the solvent are at a minimum since both CCl_4 and CCl_3F are non-polar non-hydrogen bonding solvents [2,3,18–22,46]. CCl_4 and CCl_3F have equivalent solvent properties [47].

4.1. IR spectroscopy

The pertinent IR data for 3-buten-1-ol (1) and the model compounds are given in Table 1. The data for 3-buten-1-ol were close to those reported earlier [8–13]. However, this appears to be the first time the relative areas of the three OH stretch bands have been reported as the result of a numerical analysis.

The band at 3624.9 cm⁻¹ (ν_2) only showed as a shoulder on the large v_1 band in the experimental spectrum (Fig. 7). The most striking part of the spectrum is the band at 3596.2 cm⁻¹, 42 cm⁻¹ lower than the major band and with 37% of the total OH band area. 3-Buten-1-ol is the only open chain olefinic alcohol that, in addition to two OH stretch bands at standard frequencies [48-51] in IR, has an extra band at such a low frequency and with a significantly greater band half width than all the other OH bands of open chain olefinic alcohols [18]. This band has accordingly been assigned to an intramolecularly hydrogen-bonded conformer [8-13]. The identity and population of the hydrogen-bonded conformer(s) are, however, somewhat uncertain. It has been reported [7] that hydrogen bonding increases the hydroxyl stretch molecular absorption coefficient (Band 3). But it has also been reported that the other two bands (Bands 1 and 2) may not have the same hydroxyl stretch molecular absorption coefficients due to differences in delocalisation possibilities [49].

cis-6-Methyl-3-cyclohexen-1-ol (**6**) and 3-cyclopenten-1-ol (**7**) have geometries of the homoallyl alcohol fragment close to that of Conformer **12**, while trans-6-methyl-3-cyclohexen-1-ol (**4**) has a geometry in its dominant conformation that makes an intramolecular hydrogen bond impossible. The low frequency hydroxyl stretch IR band of **6** at 3599.1 cm⁻¹ (Fig. 8) was only 7 cm⁻¹ lower than that of the trans isomer (**4**), and 3-cyclopenten-1-ol (**7**) had its lowest band at 3601.3 cm⁻¹ (Fig. 8). Neither the low frequency band of **6** nor that of **7** had such a large band half width as that of 3-buten-1-ol

Table 1

IR spectroscopic data for 3-buten-1-ol (1) and some other homoallylic alcohols in the OH stretch region

	Frequencies	Band areas/%					
Compound	ν_1	ν_2	<i>v</i> ₃	ν_1	ν_2	ν_3	
-Buten-1-ol (1) ^a	3638.0 (19.8)	3624.9 (21.0)	3596.2 (32.8)	48	15	37	
rans-6-Methyl-3-cyclohexen-1-ol (4)	3633.0 (15.3)	3621.9 (17.9)	3605.7 (17.5)	55	23	23	
is-6-Methyl-3-cyclohexen-1-ol (6) ^b	3626.1 (23.8)	3599.1 (17.6)		67	33		
-Cyclopenten-1-ol (7) ^b	3624.6 (18.1)	3601.3 (17.0)		71	29		
Cholesterol (8) ^b	3623.1 (15.0)	3611.6 (18.5)		73	27		
Epicholesterol (9) ^b	3621.6 (20.1)	3589.0 (32.1)		36	64		
-Penten-2-ol (10)	3626.7 (18.0)	3610.4 (22.4)	3590.0 (26.3)	45	13	42	

All spectra recorded at c < 5 mM in CCl₄. All frequencies in cm⁻¹. Numbers in parentheses are band half widths.

^aSee Fig. 7 for experimental spectrum with resolved bands and the reconstructed curve (sum of the resolved bands).

^bSee Fig. 8 for experimental spectra and reconstructed curves.



Fig. 7. IR spectrum of the hydroxyl stretch region of 3-buten-1-ol (1) at high dilution (c < 5 mM) in CCl₄. The uppermost curve is the experimental followed by the reconstructed curve which is the sum of the three shown resolved bands at 3638.0, 3624.9 and 3596.2 cm⁻¹. See Table 1.

(1). These data did not indicate the presence of intramolecular hydrogen bonds in these compounds.

On the other hand, epicholesterol (9) with a geometry of the homoallyl alcohol fragment close to that of Conformer 13, had its lowest hydroxyl stretch IR frequency band (3589.0 cm^{-1} , Fig. 8) 23 cm⁻¹ lower than that of cholesterol (8, Fig. 8), 7 cm^{-1} lower than the low frequency band of 3-buten-1-ol and at approximately the same frequency as the low frequency band of the homoallylic alcohol 4-penten-2-ol (10) with a secondary OH group. This low frequency epicholesterol band also had a band half width comparable to that of the low frequency band of 3-buten-1-ol. Cholesterol has no possibility for an internal hydrogen bond. This suggests that epicholesterol (9) has an intramolecularly hydrogen-bonded conformer. Infrared hydroxyl stretch frequencies for 7 [52], 8, 9 [8,53] and **10** [11,13,54] have been reported earlier.

It is to be expected according to the rules of Oki et al. [50,51] that if the model compounds are intramolecularly hydrogen bonded, their IR spectra should have a hydroxyl stretch IR band at a lower frequency than the low frequency band of 3-buten-1-ol (1). The reason for this is that both Conformers 12 and 13 of 3buten-1-ol have a gauche C–O rotamer (Type II, Fig. 3), while the conformers of the model compounds with geometrical possibility for intramolecular hydrogen bonding have an Anti C–O rotamer (Type III) $(\nu_{II} > \nu_{III})$.

In conclusion on this point, the model compounds with geometries close to that of Conformer **12** of 3-buten-1-ol showed IR spectra without low frequency IR hydroxyl stretch bands, indicative of intramolecular hydrogen bonding. This suggests that this conformer was not the source of the low frequency band in 3-buten-1-ol (**1**). On the other hand, the model for Conformer **13**, epicholesterol (**9**), showed such a band. The IR study therefore indicated that this conformer gave rise to the hydroxyl stretch band at 3596.2 cm⁻¹ in the IR spectrum of 3-buten-1-ol.

4.2. ¹H NMR spectroscopy

The vicinal coupling constants contain information on the conformational composition. In 3-buten-1-ol (1), there are three single bonds. Different relationships exist between the dihedral angles and vicinal coupling constant for each of these bonds. The observed coupling constants are the weighed average of the coupling constants for each of the three



Fig. 8. IR spectra of the hydroxyl stretch region of (a) cis-6-methyl-3-cyclohexen-1-ol (6), (b) 3-cyclopenten-1-ol (7), (c) cholesterol (8) and (d) epicholesterol (9) at high dilution (c < 5 mM) in CCl₄. The uppermost curves are the experimental ones, while the curves slightly below are the reconstructed ones made up of the sum of the resolved bands given in Table 1.

rotamers around each of these bonds (Fig. 3). To determine the composition around the C¹-O⁵ bond we have used ${}^{3}J_{60^{\circ}} = 2.2 \text{ Hz}$ and ${}^{3}J_{180^{\circ}} = 12.5 \text{ Hz}$ [19,20,46]. This gives $J_{anti} = 2.2$ Hz and $J_{gauche} = 7.35$ Hz. For the H₂C¹-C²H₂ fragment, we have used the values $J_{\text{gauche}} = 5.1 \text{ Hz}$ and $J_{\text{anti}} = 8.6 \text{ Hz}$ which we used for the analysis of the CH2CH2 fragment of 2-phenylethanol [20]. For the H_2C^2 -C³H fragment we used the Garbisch equations developed for this system [55], and obtained $J_{\text{gauche}} = 7.6 \text{ Hz}$ and $J_{cis} = 3.6$ Hz. From these relationships and the observed vicinal coupling constants, the rotamer distributions were obtained (Fig. 3). It should be noted that only the average A_2X_2 spectrum was observed for the CH2CH2 fragment (not the AA'XX' one) and an A_2X for the CH_2CH = fragment.

Conformers 12 and 13 in 3-buten-1-ol (1) are the

only conformers that can be intramolecularly hydrogen bonded. Both have a gauche relationship around $C^{1}-O^{5}$ and a gauche one around $C^{1}-C^{2}$ (Fig. 3). The vicinal coupling constants indicate the gauche rotamers to be the major ones around both \tilde{C}^1 -O⁵ (71%) and C^{1} - C^{2} (75%). However, the two conformers have different rotamers around C²-C³. Conformer 12 has a cis relationship, i.e. with C^1 in the plane of the double bond. Conformer 13, on the other hand, has a gauche rotamer around this bond with one of the hydrogens on C^2 in the plane of the double bond. The vicinal coupling constant ${}^{3}J_{A-F,G}$ indicates the major rotamer to be the gauche one (84%, 16% anti). From the IR spectrum it was evident that the intramolecularly hydrogen-bonded conformer(s) had a relative large population. This excludes Conformer 12 (maximum population 16%) as a major component. Therefore, Conformer **13** appears to be the major intramolecularly hydrogen-bonded conformer. This result is consistent with the result from IR spectroscopy on the model compounds. Whether the less populated Conformer **12** is also intramolecularly hydrogen bonded can not be decided from ¹H NMR on 3-buten-1-ol (**1**) alone.

The ¹H NMR results from the model compounds 6, 7 and 9 gave further information on this. In these compounds, the major conformers have geometries of the homoallyl alcohol fragments close to those of Conformers 12 or 13 of 3-buten-1-ol. We will first discuss the geometry and intramolecular hydrogen bonding of the models for Conformer 12. cis-6-Methyl-3-cyclohexen-1-ol (6) has two stable ring conformations, one with the hydroxyl group in an axial position and the methyl group equatorial, the other with an equatorial hydroxyl group ($\mathbf{6}_{ax}$ and $\mathbf{6}_{eq}$, Fig. 4). From data for conformations of the cyclohexane system [45], we expected $\mathbf{6}_{ax}$ to be the more stable one of these two. In this ring conformer, the hydroxyl group can occupy a position with a geometrical possibility for an intramolecular hydrogen bond to the π electron system of the double bond. The ¹H NMR spectrum at 400 MHz did not permit an estimate of the dihedral angles of the ring due to overlapping bands. However, the signal from H^C was well separated, and we used the ${}^{3}J_{C-E}$ (see Fig. 4 for notation) for an estimate of the $6_{ax}/6_{eq}$ ratio. For 6_{ax} , both H^C and H^{E} are equatorial, and a small ${}^{3}J_{C-E}$ would be expected. For $\mathbf{6}_{ea}$, they would both be axial with a corresponding large coupling constant. The observed coupling constant 4.5(2) Hz showed ring conformer $\mathbf{6}_{ax}$ to be the dominant one. To obtain a more accurate estimate, the HF/6-31G** geometries for $\mathbf{6}_{ax}$ and $\mathbf{6}_{eq}$ were used as inputs for PCMODEL 4.0, and ${}^{3}J_{C-E}$ was evaluated by Haasnoot's equations implemented in that program [56]. This gave ${}^{3}J_{C-E} = 2.3$ Hz for $\mathbf{6}_{ax}$ and 10.4 Hz for $\mathbf{6}_{eq}$. From these values and the observed ${}^{3}J_{C-E}$, the conformational composition of the ring of **6** was found to be 72(3)% $\mathbf{6}_{ax}$ and 28% $\mathbf{6}_{eq}$.

For the ring conformer $\mathbf{6}_{ax}$, one of the rotamers around the C-O bond (Anti) points towards the double bond with a geometry favourable for an intramolecular hydrogen bond. This is the conformer Anti-Ax given in Fig. 4 as an example of $\mathbf{6}_{ax}$. From the observed ${}^{3}J_{C-I} = 6.83$ Hz and the ${}^{3}J_{S}$ for the rotamers of the CH-OH fragment ($J_{Anti} = 12.5$ Hz and $J_{Gauche} =$ 2.2 Hz for secondary alcohols, see above), the composition around the CH–OH bond is close to 50% anti and 50% Gauche (45/55). From these results, there is a maximum of ca. 45% and a minimum of ca. 20% of the conformer of **6** with a possibility for an internal hydrogen bond from the hydroxyl group to the π -bond (Anti-Ax). Even the lowest estimate would give a high enough concentration to have its OH stretch band observed by IR spectroscopy. No low frequency IR OH stretch band was observed for **6** (Table 1).

3-Cyclopenten-1-ol (7) also has two ring system conformations, one with the hydroxyl group in an axial position (7_{ax}) and one with the hydroxyl group in an equatorial position (7_{eq} , Fig. 5). Only 7_{ax} has a geometry which makes an internal hydrogen bond possible if the hydroxyl proton points towards the π bond. The ¹H NMR spectrum contains information on both the conformational composition and the flip angle of the cyclopentene ring. The observed two vicinal coupling constants ${}^{3}J_{C-D}$ and ${}^{3}J_{C-F}$ (for notation, see Fig. 5) are the weighted average of those of the two ring conformations $\mathbf{7}_{ax}$ and $\mathbf{7}_{eq}$. If we assume the flip angle of the ring to be the same in the two ring conformations, the cis vicinal coupling constant, ${}^{3}J_{C}$ D, will be the same in both ring conformations. We have earlier used Eq. (1), a modified Karplus equation, for these systems [19,47].

$${}^{3}J = 12.9\cos^{2}\theta - 0.32\cos\theta$$
 (1)

From Eq. (1) and the observed ${}^{3}J_{C-D}$ (6.34 Hz), we obtain a dihedral angle $H^{C}-C^{1}-C^{5}-H^{D} = 44^{\circ}$ (ϕ). For angles of this magnitude, the dihedral angle is close to the angle of pucker [47] and the ¹H NMR results thus indicate this to be ca. 40°. This is somewhat larger than that reported for 2-cyclopenten-1-ol (32°, [19]) and a few other cyclopentene systems $(27-37^{\circ})$, [47,57,58]). From the estimated dihedral angle H^C- $C^{1}-C^{5}-H^{D}(\phi)$, the observed trans vicinal coupling constant ${}^{3}J_{C-F}$ (2.3 Hz) and Eq. (1), a 7_{ax} population of 86% is obtained when assuming that the dihedral angle H^F-C-C-H^C = $120^{\circ} - \phi$ for 7_{ax} and $120^{\circ} + \phi$ for 7_{eq} . This is the same population (85%) as obtained using the measured ${}^{3}J_{C-F}$ and the Haasnoot's equation [56] to obtain values for ${}^{3}J_{C-F}$ from HF/3-21G geometries for 7_{ax} and 7_{eq} . The major ring conformation of the cyclopentene ring therefore places the hydroxyl group in the axial position. From the vicinal coupling constant ${}^{3}J_{CH-OH}$, the rotamer composition around

Table 2

	1	1 ,	·			0		2			
						3-21G// 3-21G based on	6-31G**//6-31G** based on				
Conformer	MMPMI	MMPMI ^a	MNDO	AM1	PM3	Total energy	Total energy	Total energy + ZPE ^b	Total energy + ZPE + ΔH_{vib}^{b}	$\Delta G^{\circ b}$	
1	4	3	0	0	0	0	1	1	1	1	
2	21	22	12	1	1	5	8	10	9	12	
3	2	3	1	6	3	1	1	1	1	1	
4	6	11	10	20	17	5	7	8	7	9	
5	6	12	10	22	17	6	8	9	8	10	
6	4	1	1	0	0	1	0	0	1	0	
7	17	3	13	0	0	0	2	2	2	3	
8	14	8	11	1	0	21	11	13	12	13	
9	1	1	1	2	1	5	1	1	1	1	
10	5	4	10	4	7	2	3	4	3	5	
11	4	4	8	10	8	18	8	8	8	8	
12	1	2	2	5	4	1	2	2	2	1	
13	9	18	13	16	27	31 ^c	43 ^d	36	40	30	
14	6	8	8	13	15	4	5	5	5	6	

Calculated conformer populations (%) for the 14 3-buten-1-ol (1) conformers using Hartree-Fock theory

^aCharge-charge interaction modus.

^bZPE denotes the zero point energy. ΔH_{vib} denotes the extra vibrational energy connected with increasing the temperature from 0 K to 298.15 K. ΔG° is calculated from the calculated entropy S_{tot} and total energy + ZPE + ΔH_{vib} . Scaled frequencies were used for the calculations of ZPE, ΔH_{vib} , S_{tot} and ΔG° . HF/6-31G** scale factor: 0.87800 [48]. The adjustments are based on the rigid rotor-harmonic oscillator approximation as implemented in the GAUSSIAN program package after scaling of the frequencies.

[°]The zero of energy was: – 229.6746618 hartrees.

^dThe zero of energy was: - 230.9725784 hartrees.

the CH-OH bond can be estimated. The observed ${}^{3}J_{\text{CH-OH}} = 6.59$ Hz together with the vicinal coupling constants for each rotamer (see above) indicate that the rotamer with the hydroxyl proton pointing towards the π -bond constitutes 43% of this rotamer composition. From this and the ring conformational composition with 86% 7_{ax} , at least 28% and maximum 43% of the conformational population will have a geometrical possibility for an internal hydrogen bond. This is the conformer Anti-Ax shown in Fig. 5 as an example of 7_{ax} . The IR OH stretch band of this conformer would certainly be observable in the spectrum. No low frequency OH stretch IR band was observed for 7 (Table 1).

The theoretical calculations indicated the two models for Conformer **12** of 3-buten-1-ol, cis-6-methyl-3cyclohexen-1-ol (**6**) and 3-cyclopenten-1-ol (**7**), to have geometries of the homoallyl fragment close to that of Conformer **12** (see Section 4.3.2 for details). As the two models did not show an IR band at a frequency indicative of internal hydrogen bonding (Table 1), the ¹H NMR results indicate that the hydrogen-bonded hydroxyl stretch IR band in **1** was not caused by Conformer **12**.

For Conformer 13, epicholesterol (9) was chosen as a model (Fig. 6). In this compound, the geometry of the homoallyl fragment is close to that of the C-C-C-O skeleton of Conformer 13 (see Section 4.3.2 for details) and the ${}^{3}J_{CH-OH}$ would give information on the rotamer composition around the C-O bond. The observed ${}^{3}J_{\text{CH-OH}} = 7.57 \text{ Hz}$ shows 52% of the Anti rotamer with the hydroxyl proton pointing towards the 5,6-double bond and 48% of the Gauche one with the hydroxyl group pointing away $(J_{Anti} =$ 12.5 Hz and $J_{\text{Gauche}} = 2.2$ Hz). This is consistent with the results from the IR spectroscopy. The IR spectrum of epicholesterol (9) had a low frequency hydroxyl stretch band at 3589 cm⁻¹ with 64% of the band area (Table 1). From its position and also its bandwidth, this was assigned to an intramolecularly hydrogen-bonded conformer. The ¹H NMR results confirm this, ca. 50% of the C-O rotamers have hydroxyl groups pointing towards the π -bond. The integrated molecular absorption coefficient for Band 2 was 64% larger than for Band 1. It is well known that the IR band intensity may increase on hydrogen bonding [7]. However, other factors also influence the relative molecular absorption coefficients [48–51].

The conclusion from the IR and ¹H NMR spectroscopic investigations of 3-buten-1-ol (**1**) and the model compounds is that Conformer **13** of 3-buten-1-ol is the intramolecularly hydrogen-bonded conformer. This conformer gives rise to the IR band at 3596 cm^{-1} for 3-buten-1-ol. Conformer **12** of 3-buten-1-ol (**1**) is not intramolecularly hydrogen bonded.

4.3. Theoretical calculations

We have performed calculations on the geometries and energies of 3-buten-1-ol (1) and its model compounds cis-6-methyl-3-cyclohexen-1-ol (6), 3-cyclopenten-1-ol (7) and epicholesterol (9). The calculations were effected at various levels, depending on the number of atoms in the molecules. 3-Buten-1-ol (1) itself was the smallest of the studied compounds and was accordingly calculated at the highest level.

4.3.1. Theoretical calculations on 3-buten-1-ol (1)

In Table 2, we present the calculated populations of the conformers of **1** from the obtained relative energies and Boltzmann's law of distribution. Conformers **12** and **13** (see Fig. 1) are the only ones with a possibility for an internal hydrogen bond. From the spectroscopic investigations (see above), Conformer **13** appeared to be the one giving rise to the low frequency hydroxyl stretch band in the IR spectrum.

The calculations on **1** were performed by molecular mechanics, semiempirical molecular orbital and ab initio methods. The results were very dependent on the method of calculation. The molecular mechanics calculation in the dipole–dipole interaction mode gave Conformers **2**, **7** and **8** as the most stable ones with only a minor population of Conformer **13**. In the charge–charge interaction mode this changed, and this calculation indicated Conformer **13** to be a major one together with Conformers **2**, **4** and **5**. The semiempirical molecular orbital calculations by the PM3 method gave Conformer **13** as the most populated one, 27%,

but overestimated the gauche rotamer around the C^{1} - O^{5} bond (see below), as did the AM1 calculations.

We also used ab initio calculations at various levels. The conformer populations from some of the Hartree-Fock calculations using the same basis sets for both geometry optimisation and energy calculations are given in Table 2. By using the small basis set 3-21G, a population of 31% of Conformer 13 was obtained. The largest basis set used was 6-31G**. For this, we have tabulated the populations based on total energy and total energy corrected for thermodynamical parameters. The tabulated values are based on scaled frequencies. However, the difference between calculations using scaled and non-scaled frequencies were hardly visible. The HF/6-31G** calculations indicate Conformer 13 with a possibility for an internal bond to be the dominant one (30-43%). It is important to note that Conformer 12, the other conformer with a geometry which makes an internal hydrogen bond possible, is only populated at 1-2%by the HF/6-31G** calculations. AM1 was the method that gave the highest population for this conformer, only 5%. Of these calculations, the HF/6-31G** results are believed to be the most reliable and the HF/6-31G** geometries of the conformers of 1 are given in Fig. 1. Thus, the calculations support that Conformer 13 is the major conformer of 1 that gives rise to the low frequency IR hydroxyl stretch band. Whether the less populated Conformer 12 is also intramolecularly hydrogen bonded can not be decided by energy calculations alone.

The optimized HF/6-31G^{**} geometries for these two conformers are given in Table 3. For reference, we also give the MP2/6-31++G^{**} geometry of Conformer **13** in this table. From the optimised geometries and energies of all 14 conformers, the rotamer compositions around the three bonds C^1-O^5 , C^1-C^2 and C^2-C^3 (see Fig. 3 for notation) were calculated. These are given in Table 4 together with those calculated from the observed vicinal ¹H NMR coupling constants. Except for the C^2-C^3 composition for which the gauche rotamer was slightly overestimated, the compositions calculated by HF/6-31G^{**}//HF/6-31G^{**} were close to those found from ¹H NMR spectroscopy. For the calculations performed on a lower level, there were larger discrepancies.

From the HF/6-31G** calculations of **1**, the hydroxyl group geometry was available (Table 5). The O-H

Table 3

	HF/6-31G**		MP2/6-31++G**		
	12	13	13 ^b		
Bond distances/Å					
$C^{3}=C^{4}$	1.3204	1.3198	1.3418		
C^2-C^3	1.5110	1.5056	1.4974		
C^1-C^2	1.5238	1.5298	1.5275		
$O^{5}-C^{1}$	1.4005	1.3983	1.4254		
H ^C -C ⁴	1.0768	1.0772	1.0820		
H ^B -C ⁴	1.0755	1.0760	1.0805		
H ^A -C ³	1.0793	1.0806	1.0863		
$H^{G}-C^{2}$	1.0896	1.0884	1.0929		
H ^F -C ²	1.0872	1.0855	1.0910		
H ^E -C ¹	1.0830	1.0832	1.0878		
$H^{D}-C^{1}$	1.0889	1.0906	1.0952		
H ^H -O ⁵	0.9432	0.9441	0.9677		
Angles/°					
$C^{2}-C^{3}=C^{4}$	127.35	125.17	124.16		
$C^{1}-C^{2}-C^{3}$	115.80	111.96	111.02		
$O^{5}-C^{1}-C^{2}$	112.76	112.43	111.90		
$H^{C}-C^{4}=C^{3}$	122.96	121.67	121.08		
$H^{B}-C^{4}=C^{3}$	120.92	121.60	121.53		
$H^{A}-C^{3}-C^{2}$	114.72	115.96	116.79		
$H^{G}-C^{2}-C^{3}$	108.46	109.58	110.25		
$H^{F}-C^{2}-C^{3}$	108.62	110.14	110.00		
$H^{E}-C^{1}-C^{2}$	109.15	109.76	110.48		
$H^{D}-C^{1}-C^{2}$	110.45	109.83	109.95		
$H^{H}-O^{5}-C^{1}$	109.48	109.24	107.48		
Dihedral angles/°					
$C^{1}-C^{2}-C^{3}=C^{4}$	- 16.3	108.9	106.9		
$O^{5}-C^{1}-C^{2}-C^{3}$	- 66.5	- 65.2	- 63.8		
$H^{C}-C^{4}=C^{3}-C^{2}$	0.1	2.0	3.3		
$H^{B}-C^{4}=C^{3}-C^{2}$	- 179.1	- 178.8	- 177.9		
$H^{A}-C^{3}-C^{2}-C^{1}$	164.6	- 69.3	- 70.2		
$H^{G}-C^{2}-C^{3}=C^{4}$	106.7	- 130.4	- 132.5		
$H^{F}-C^{2}-C^{3}=C^{4}$	- 138.3	- 12.2	- 13.4		
$H^{E}-C^{1}-C^{2}-C^{3}$	175.8	176.7	179.0		
$H^{D}-C^{1}-C^{2}-C^{3}$	58.4	58.8	59.6		
$H^{H}-O^{5}-C^{1}-C^{2}$	54.4	54.2	51.2		

Ab initio HF/ $6-31G^{**}$ and MP2/ $6-31++G^{**}$ optimised geometries for the two conformers of 3-buten-1-ol (1) with geometrical possibility for internal hydrogen bonding (Conformers 12 and 13)^a

^aAtom numbering given in Fig. 3.

^bThe zero of energy was: - 231.7570757 hartrees.

bond lengths for the anti C^{1} -O⁵ conformers were all within the interval 0.9423–0.9425 Å, while the ethanol anti conformer had a O-H bond length of 0.9424 Å [48]. For conformers of **1** with a gauche conformation around the C¹-O⁵ bond, the O-H bond length was calculated to be 0.9430–0.9432 Å. The corresponding value for the ethanol gauche conformer was 0.9431 Å [48]. Both Conformers **12** and **13** with geometrical possibilities for an internal hydrogen bond have gauche C^{1} -O⁵ rotamers. For Conformer **12** the O-H bond length was calculated to be 0.9432 Å, very close to those of the other conformers with a gauche conformation. However, the O-H bond length of Conformer **13** deviated from this pattern with a bond length of 0.9441 Å, but only by 0.0010 Å. Although the effect is significant, it is small, and alone it would not strongly indicate the presence of an internal hydrogen bond. However, the same calculation gave

Table 4

Calculated rotamer compositions (%) around the C¹-O⁵, C¹-C² and C²-C³ bonds in 3-buten-1-ol (1) as compared with the compositions from ¹H NMR (c < 5 mM in CCl₃F)

	C^1-O^5		$C^{1}-C^{2}$	$C^{1}-C^{2}$		C^2-C^3	
Method	gauche	anti	gauche	anti	gauche	cis	
MMPMI	40	60	60	40	88	12	
MMPMI ^a	63	37	49	51	90	10	
MNDO	62	38	66	34	95	5	
AM1	97	3	50	50	87	13	
PM3	99	1	63	37	92	8	
HF/3-21G//HF/3-21G HF/6-31G**//HF/6-31G**	72	28	83	17	92	8	
based on:							
Total energy	77	23	75	25	95	5	
Total energy $+ ZPE^{b}$	73	27	71	29	95	5	
Total energy + ZPE + ΔH_{vib}^{b}	75	25	74	26	95	5	
ΔG^{ob}	70	30	67	33	96	4	
¹ H NMR ^c	71	29	75	25	84	16	

^aCharge-charge interaction modus.

^bSee footnote b in Table 2.

°Calculated from measured coupling constants and model coupling constants.

that the C¹-O⁵-H^H bond angle for Conformer **13** (109.24°, Table 5) is smaller than the corresponding bond angles for all the other conformers of **1**, in accordance with the change in geometry necessary for an hydroxyl group to form an internal hydrogen bond to the π -bond. Together, we take these two changes as an indication of a weak intramolecular hydrogen bond for Conformer **13**. The C¹-O⁵-H^H bond angle for Conformer **12** was only slightly larger than the corresponding angle for Conformer **13** and smaller than

the corresponding bond angles for all the other conformers of **1**. However, the O-H bond length of Conformer **12** did not deviate from the O-H bond lengths of the other gauche C^{1} -O⁵ conformers. This indicates that the interaction between the OH group and the π -electron system in Conformer **12** is very weak, much weaker than for Conformer **13**. Conformer **14** also deviated from the bond length pattern, but this was believed to be caused by a repulsion between the hydroxyl proton and another proton in the molecule.

Table 5

Ab initio HF/6-31G** calculated hydroxyl group geometries for the conformers of 3-buten-1-ol (1)

	C ¹ -O ⁵ bond length/Å		
Conformer	gauche	anti	$C^{1}-O^{5}-H^{H}$ bond angle/°
1		0.9424	109.84
2		0.9424	109.92
3	0.9430		109.69
4	0.9430		109.73
5	0.9430		109.68
6		0.9425	109.76
7		0.9424	109.90
8		0.9423	110.00
9	0.9431		109.79
10	0.9432		109.86
11	0.9432		109.62
12	0.9432		109.48
13	0.9441		109.24
14	0.9424		109.79

Table 6 Ab initio hydroxyl stretch frequencies^a calculated with the 6-31G** basis set at the Hartree–Fock level for the conformers of 3-buten-1ol (1)

Conformer	C ¹ -O ⁵ gauche	C^1 - O^5 anti
1		3680.8
2		3680.0
3	3671.5	
4	3670.7	
5	3671.4	
6		3678.0
7		3680.4
8		3681.8
9	3669.9	
10	3669.1	
11	3668.6	
12	3672.2	
13	3658.3	
14	3681.9	

All frequencies in cm⁻¹.

^aThe frequencies are scaled. HF/6-31G** scale factor: 0.87800 [48].

We have also calculated the ab initio HF/6-31G** O-H stretch IR frequency for each of the 14 conformers of 3-buten-1-ol (1, Table 6). These frequencies follow the same pattern as the O–H bond lengths. For all gauche conformers (Type II) around the C-O bond, except for Conformer 13 (and Conformer 14), a frequency of $3670 \pm 2 \text{ cm}^{-1}$ (Band 2) was calculated after scaling to the gas phase O-H stretch frequency of methanol, $\nu_{gas} = 3681 \text{ cm}^{-1}$ [59]. However, for Conformer 13, a frequency of 3658 cm^{-1} (Band 3) was found, significantly lower than those of the other conformers, which together with the small C^{1} -O⁵-H^H bond angle indicates intramolecular hydrogen bonding. For all anti conformers (Type I) around the C-O bond, a frequency of $3680 \pm 2 \text{ cm}^{-1}$ (Band 1) was found. The frequency difference between the calculated highest frequency bands is ca. 10 cm^{-1} , while the difference between band 2 and the low frequency band of Conformer **13** (Band 3) is 12 cm⁻¹. The corresponding values from high dilution IR spectroscopy (Table 1) were 13.1 and 28.7 cm^{-1} , respectively. The calculated difference between Bands 1 and 2 was in good agreement with the experimental result, while the calculated frequency difference between Bands 2 and 3 was much smaller than the experimental value. This was not surprising. We have previously shown that HF/6-31G** frequency calculations semiquantitatively

can reproduce the experimental IR hydroxyl stretch frequency pattern for an acyclic saturated alcohol [48]. However, even a medium–large basis set, (6-31G**) at the Hartree–Fock level, can not fully reproduce the effect of intramolecular hydrogen bonding.

A clear sign for the presence of an intramolecular hydrogen bond is that the distance between the donor and acceptor functions of the presumed hydrogen bond is less than the sum of the van der Waals radii of the contributing atoms, in this case C and O. For very weak hydrogen bonds, this test criteria may not be satisfied. Instead, the test criteria is modified to use the distance between C and H(O) as compared to the sum of the van der Waals radii of C and H [4,60]. The sum of the van der Waals radii of C and O is 3.1-3.2 Å, while the sum of the van der Waals radii for C and H is 2.7–2.9 Å [4,61,62]. However, the use of this criteria for a hydrogen bond to C=C is not as straightforward as for a hydrogen bond to O, because it is difficult to define the acceptor point. From the ab initio HF/6-31G** geometries for 3-buten-1-ol Conformer **13**, the C⁴-O (3.54 Å) and C⁴-H(O) (2.94 Å) distances were larger then the sum of the van der Waals radii of C and O/C and H, while both the C^3 -O (3.00 Å) and C³-H(O) (2.62 Å) distances were 0.1 Å shorter (see Fig. 3 for notation). We take this as an indication of a weak intramolecular hydrogen bond in Conformer 13. For Conformer 12, the calculated distances were C^4 -O (3.30 Å), C^4 -H(O) (2.70 Å), C³-O (3.09 Å) and C³-H(O) (2.72 Å). Some of these distances fell in the intervals of the van der Waals radii, but none of them was shorter than the sum of the van der Waals radii. If Conformer 12 is intramolecularly hydrogen bonded, this bond must be weaker than the hydrogen bond in Conformer 13.

The results from the ab initio HF/6-31G** calculations on the energy and geometries for 3-buten-1-ol (1) are in accordance with and support the experimental IR and ¹H NMR results. Only for Conformer **13** did we find a shorter O-H bond length and a smaller C-O-H angle than for the other conformers, and only for this conformer did we calculate a significantly lower O-H stretch frequency than for the other conformers and found a short enough hydrogen bond length for hydrogen bonding to take place.

4.3.2. Theoretical calculations on model compounds The theoretical calculations on structures and

energies were done at various levels of sophistication for the models of the homoallylic alcohol 3-buten-1-ol (1) Conformers 12 and 13. Only the results from the highest levels of calculations will be given here.

In Conformer 12, the dihedral angle C^1 - C^2 - C^3 = C^4 is -16° (HF/6-31G**), while in the Anti-Ax conformers of 6 (Fig. 4) and 7 (Fig. 5), the corresponding dihedral angles are -18° (HF/6-31G**) and -17° (HF/3-21G), respectively (see Figs. 3–5 for notation). For the $O-C^1-C^2-C^3$ dihedral angle, the corresponding values were -67° , -76° and -93° , while for the H-O-C¹-C² dihedral angle, the values were 54° , 48° and 57°. In Conformer 13, the dihedral angle C^1 - C^2 - $C^3 = C^4$ is 109° (HF/6-31G**), while the corresponding dihedral angle for the Anti conformer of 9 (Fig. 6) is 129° (MMPMI). For the O-C¹-C²-C³ dihedral angle, the corresponding values were -65° and -68°, while for the H-O-C¹-C² dihedral angle, 54° and 55°. As can be seen, the homoallylic geometries of the models are close to those of Conformers 12 and 13 of 3-buten-1-ol (1).

We will first discuss the geometries and energetics of the models of Conformer 12. Ab initio Hartree-Fock 6-31G**//6-31G** calculations on cis-6methyl-3-cyclohexen-1-ol (6) gave 83% of the ring conformer with an axial hydroxyl group, 6_{ax} (Fig. 4), and 56% of the conformer Anti-Ax, while ¹H NMR predicted 72(3)% 6_{ax} and a maximum of 45% Anti-Ax (minimum ca. 20%) by using the observed coupling constants together with Haasnoot's equations on the HF/6-31G** geometries (Section 4.2). For 3-cyclopenten-1-ol (7), the Hartree-Fock calculations predicted 79% (3-21G//3-21G) and 61% (6-31G**//3-21G) of the ring conformer 7_{ax} with an axial hydroxyl group (Fig. 5), and 73% (3-21G//3-21G) and 42% (6-31G**//3-21G) of the conformer Anti-Ax. For comparison, ¹H NMR gave 86% 7_{ax} from a modified Karplus equation, and 85% 7_{ax} and a maximum of 43% Anti-Ax (minimum 28%) based on HF/3-21G geometries and the Haasnoot's equations, see Section 4.2. The reason for the discrepancies between the ab initio and ¹H NMR results for 7 might be the use of HF/3-21G instead of HF/6-31G** for geometry optimisation. This confirms the result from ¹H NMR: the Anti-Ax conformers of **6** and 7 have high enough populations to have their OH stretch bands observed by IR spectroscopy. Since an IR hydroxyl stretch band at a frequency indicative of intramolecular hydrogen bonding was not present in the IR spectrums of 6 and 7, this indicates that the hydrogen-bonded band in 1 was not caused by its Conformer 12.

From the HF/6-31G** calculated O-H bond lengths and hydroxyl stretch frequencies for **6**, no conclusions about the presence of intramolecular hydrogen bonding could be drawn due to lack of a pattern. Nor for the Hartree–Fock calculations on **7** could a conclusion be drawn, since these calculations were done with the small basis set 3-21G which is not accurate enough for this kind of calculation: the pattern for O-H bond length and hydroxyl stretch frequencies found for 3buten-1-ol (**1**) with HF/6-31G** (Section 4.3.1) was not that obvious from the corresponding HF/3-21G geometry and frequency calculations.

The distances C⁴-O, C³-O, C⁴-H(O) and C³-H(O) for the Anti-Ax conformer of cis-6-methyl-3-cyclohexen-1-ol (**6**) calculated with HF/6-31G** were 3.28, 3.09, 2.79 and 2.71 Å, respectively (for notation, see Fig. 4). None of these distances is shorter than the sum of the van der Waals radii of the donor and acceptor functions for a hydrogen bond, although some of the distances fell in the intervals of the van der Waals radii (Section 4.3.1). Thus, if Conformer **12** of 3-buten-1-ol (**1**) is intramolecularly hydrogen bonded, this bond must be very weak. The calculated distances are very close to the corresponding distances calculated for Conformer **12** (Section 4.3.1).

For the other model of Conformer **12**, 3-cyclopenten-1-ol (**7**), the HF/3-21G calculated distances in the symmetrical Anti-Ax conformer were $3.15 \text{ Å} (\text{C}^3\text{-O})$ and 2.87 Å (C³-H(O)) [see Fig. 5 for notation]. Both these values fell in the upper part of the intervals of the van der Waals radii (Section 4.3.1). An intramolecular hydrogen bond in this model molecule is thus not very probable.

We will now focus on the model for 3-buten-1-ol (1) Conformer 13. Epicholesterol (9, Fig. 6) is too large to allow calculations with HF/3-21G or larger basis sets, and was accordingly only calculated by molecular mechanics (MMPMI). For the geometry of the homoallyl fragment, the only dihedral angle of interest is C-C-O-H. All the other dihedral angles of the homoallylic C-C-C-O skeleton are fixed in a chair form. The MMPMI calculations on 9 gave 24% of the Anti conformer, which is the conformer responsible for the hydrogen-bonded hydroxyl band at low

frequency in IR (Table 1). ¹H NMR, however, gave 52% Anti. The explanation for this discrepancy is that MMPMI underestimates weak hydrogen bonds. Since this calculation was only done with molecular mechanics and not with ab initio using a mediumlarge basis set, no O-H bond lengths or hydroxyl stretch IR frequencies can be safely compared. However, since the molecule is locked into a ring, the calculated C^4 -O, C^3 -O, C^4 -H(O) and C^3 -H(O) distances are assumed to be reasonably accurate. Note that the superscripts denote the position in the homoallylic system (see Fig. 3 for notation) and not the numbering normally used for the cholesterol skeleton. The calculated values for these distances were 3.70, 2.97, 3.15 and 2.58 Å, respectively, while the corresponding values for 3-buten-1-ol (1) Conformer 13 for comparison were 3.54, 3.00, 2.94 and 2.62 Å, respectively (HF/6-31G** geometries). As for Conformer 13, the C^4 -O and C^4 -H(O) distances of epicholesterol's Anti conformation were larger than the sum of the van der Waals radii (see Section 4.3.1), while both the C³-O and C³-H(O) distances were 0.1 Å shorter. This is an indication of weak intramolecular hydrogen bonding in the model 9 and in 3-buten-1-ol Conformer 13.

The results from the theoretical calculations on the model compounds are also in accordance with and support the results from experimental IR and ¹H NMR. We have shown that the geometries of the models are close to those of 3-buten-1-ol Conformers 12 and 13. Furthermore, as also shown by ¹H NMR, the populations of the conformers with a geometric possibility for intramolecular hydrogen bonding in the models for Conformers 12 and 13 were large enough to be visible in the IR spectrum, indicating that the hydrogen-bonded band in 1 was not caused by Conformer 12 but by Conformer 13, since only the model of Conformer 13 had an intramolecularly hydrogenbonded hydroxyl band in IR. From calculations of bond distances between the acceptor and donor functions for a hydrogen bond, it was shown that only the model for Conformer 13 had a short enough hydrogenbond length for hydrogen bonding to take place.

5. Conclusions

A combination of experimental (FT-IR and ¹H

NMR spectroscopy) and theoretical methods at different levels of sophistication (molecular mechanics, semiempirical molecular orbital and ab initio methods) have been used in the study of conformational composition, and the importance of intramolecular OH... π hydrogen bonding for this composition in 3-buten-1-ol (1) and model compounds. The combination of experimental and theoretical data, and the use of model compounds was necessary to understand the conformational behaviour of these molecules. All investigations on both 1 and its model compounds showed that the Conformer 13 of 1 (see Fig. 1) is the only intramolecularly hydrogen-bonded conformer, and that the only other conformer that by visual inspection of models might have a geometrical possibility for an intramolecular hydrogen bond, Conformer 12, is not intramolecularly hydrogen bonded. Conformer 13 was the most populated conformer, while Conformer 12 was hardly populated.

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