

# Conformation of Allylic Alcohols and Intramolecular Hydrogen Bonding

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Bakke, J. M., Schie, A. M. and Skjetne, T., 1986. Conformation of Allylic Alcohols and Intramolecular Hydrogen Bonding. – Acta Chem. Scand. B 40: 703–710.

The conformations of allyl alcohol, *cis*- and *trans*-5-*t*-butyl-2-cyclohexenol, 2-cyclopentenol and 3-methoxycyclopentene were investigated by IR and NMR spectroscopy. Allyl alcohol was found to consist of 51% of the *cis* conformation around the C<sub>1</sub>–C<sub>2</sub> bond with a dominance of the *gauche* rotamer around the C–OH bond. Both *cis*- and *trans*-5-*t*-butyl-2-cyclohexenol exist in a twist-chair conformation, with 50% in the *anti* rotamer around the C–OH bond. In 2-cyclopentenol, the two flip states are equally populated (estimated flip angle 32°), the same being the case for 3-methoxycyclopentene. For 2-cyclopentenol, the *anti* was 56% of the C–OH rotamers, while in the case of its methyl ether, all three rotamers were equally populated. From these data and those from IR spectra, it was concluded that none of these systems show indications of intramolecular hydrogen bonding.

The structure of allyl alcohol has been investigated in the gas phase by electron diffraction<sup>1,2</sup> and microwave spectroscopy<sup>3</sup> and in solution by NMR<sup>4,5</sup> and IR spectroscopy.<sup>6–9</sup> The microwave spectroscopy study led to the conclusion that a conformation with a possibility for intramolecular hydrogen bonding (conformer *IA*, Fig. 1) was important, but that the bond was not strong.<sup>3</sup> The electron diffraction studies offered different conclusions. One indicated *IE* to be dominant (without possibility of a hydrogen bond),<sup>1</sup> and the other a mixture of *IA* and *ID* but without an intramolecular hydrogen bond.<sup>2</sup> The NMR studies resulted in a conclusion close to that of the microwave study.<sup>4,5</sup> The IR results have been interpreted as being caused by an interaction between the hydroxyl group and  $\pi$ -electrons<sup>6</sup> or by an intramolecular hydrogen bond.<sup>7</sup> *Ab initio* calculations did not support the existence of such a bond,<sup>1,10</sup> or found it weak but possible.<sup>11</sup> They agreed that there is a low energy difference between *IA* and *ID*.

We have proposed that the dominance of one conformer in olefinic alcohols may be caused by a repulsion between the oxygen lone pair electrons and the  $\pi$  electrons.<sup>12</sup> In view of this, and of the

conflicting opinions reported above, we have studied the conformations of allyl alcohol at low concentrations in nonhydrogen bonding solvents by IR and NMR spectroscopy. The solvents used were carbon tetrachloride and fluorotrichloromethane. Both of these are of low polarity and show very weak hydrogen bonding interactions.<sup>12</sup>

We have also studied three analogs of allyl alcohol, *cis*- and *trans*-5-*t*-butyl-2-cyclohexenol (2) and 2-cyclopentenol (3). In the case of 2, there is a fixed conformation of the allylic alcohol fragment, close to that of conformations *IA*–*C* of allyl alcohol (the dihedral angle C<sub>6</sub>C<sub>1</sub>C<sub>2</sub>C<sub>3</sub> of 2 is ~15–20°, the corresponding one of conformations *IA*–*C* is 0°). If *IA* were an important conformer of allyl alcohol, stabilised by intramolecular hydrogen bonding, one would expect to find the analogous conformation in the case of 2 with the hydroxyl proton pointing towards the  $\pi$ -electrons (*anti* conformation around the C–OH bond). This would be the case especially for *trans*-2 as both the distance to the  $\pi$  bond and the O–H–acceptor angle are more favourable in this case than for the *cis* isomer.

In conformation 3<sub>ax</sub> (Fig. 3), with the hydroxyl proton in the *anti* rotamer, 2-cyclopentenol also

has a conformation close to *IA* of allyl alcohol. We would therefore expect  $J_{ax}$  to be favoured over  $J_{eq}$  if an intramolecular hydrogen bond was important in allyl alcohol.

These cyclic analogs with fixed geometry should also provide spectroscopic parameters needed for the analysis of the spectra of allyl alcohol itself.

## Results and discussion

The OH stretching frequencies of the alcohols studied are given in Table 1. The NMR parameters are given in Tables 2-6.

*Allyl alcohol.* Earlier results, both theoretical and experimental agree that only two rotamers around the  $C_1-C_2$  bond need to be considered, the *gauche* (i.e., *IA-IC*) and the *cis* (i.e., *ID-IE*). Information on the population of these two is available from the coupling constant  $^3J_{b-c,d}$  (Fig. 1). The corresponding  $^3J$  for 3-methoxypropene was estimated to be 2.8 Hz ( $J_g$ ) and 11.5 Hz ( $J_t$ )<sup>13</sup> on the basis of a variable temperature study where the  $^3J$  increased from 5.23 Hz to 5.40 Hz for an increase in temperature from  $-50$  to  $+90$  °C. Data from the study of *cis*- and *trans*-5-*t*-butyl-2-cyclohexenol (*cis* and *trans* 2) give further information on this. The two vinylic coupling

constants  $^3J_{a,b}$  were 1.44 Hz for a dihedral angle  $H_aC_1C_2H_b$  of  $75^\circ$  (*cis*-2) and 4.80 Hz for  $42^\circ$  (*trans*-2). Equations of type (1) have been used for estimations of vinylic coupling constants.<sup>14</sup>

$$J^{est} = A \cos^2\varphi + B \sin^2\varphi \quad (0^\circ < \varphi < 90^\circ) \quad (1)$$

From the values above, eqn. (1a) was obtained for the vinylic coupling constant of allyl alcohol:

$$J^{est} = 7.9 \cos^2\varphi + 0.98 \sin^2\varphi \quad (1a)$$

This gave  $J_g^{est} = 2.7$  Hz, very close to 2.8 Hz from the variable temperature investigation,<sup>13</sup> and we used the values of 2.7 Hz for dihedral angles of  $60^\circ$  and 12 Hz for  $180^\circ$  in this work. These numbers give  $^3J_{b-c,d} = 7.4$  Hz for *IA-C* and 2.7 Hz for *D-E*. The observed  $^3J_{b-c,d} = 5.02$  Hz then gave a mole fraction of *IA-IC* = 0.49 and *ID-IE* = 0.51. This is close to that found in the earlier NMR studies (50% *IA-C*, 50% *ID-E*)<sup>4,5</sup> but different from the result of the electron diffraction study (30% *IA-C*, 70% *ID-E*).<sup>2</sup> The difference is probably best explained by weak solvent-solute interactions in the NMR investigations, interactions absent in the gas phase electron diffraction study. The microwave study indicated *IA* to be the major conformer.<sup>3</sup>

The rotamer composition around the  $C_1-OH$  bond was estimated from  $^3J_{a,b-c}$ . We have earlier

Table 1. Hydroxyl stretching absorption ( $\text{cm}^{-1}$ ) of alcohols in  $\text{CCl}_4$  ( $c < 10^2 \text{ M}$ ).

Compound	$\nu_1$	$\nu_2$	$A_1^\circ$	$A_2^\circ$ <sup>a</sup>	$(\nu_1)_t$	$(\nu_2)_t$
Allyl alcohol <sup>b</sup>	3635	3619	1167	2857	—	20.6
2-Cyclopentenol	3624	3605	900	1205	15.7	15.7
<i>cis</i> -5- <i>t</i> -Butyl-2-cyclohexenol	3623	3605	1456	2092	12.6	16.5
<i>trans</i> -5- <i>t</i> -Butyl-2-cyclohexenol <sup>b</sup>	3624	3616	260	3936	—	18.9

<sup>a</sup>  $A^\circ = \frac{\pi}{2} \cdot \frac{1}{c l} \cdot \ln(I^\circ/I) \cdot \nu_i$  ( $\text{M}^{-1}\text{cm}^{-2}$ ). <sup>b</sup>  $\nu_1$  shoulder.  $\nu_1$  and  $A_1^\circ$  not accurate.

Table 2. Proton chemical shifts ( $\delta$ , ppm from TMS) and proton-proton coupling constants (Hz) for allyl alcohol 5 mM in  $\text{CFCl}_3$ .

	$H_{a\infty}$	$H_{b,c}$	$H_d$	$H_e$	$H_f$	$J_{a,b-c}$	$J_{b-c,d}$	$J_{b-c,e}$	$J_{b-c,f}$	$J_{d,e}$	$J_{d,f}$	$J_{e,f}$
$\delta(\text{ppm})$	0.753	4.037	5.925	5.049	5.198							
J (Hz)						6.18	5.02	1.56	1.66	10.39	17.23	1.71

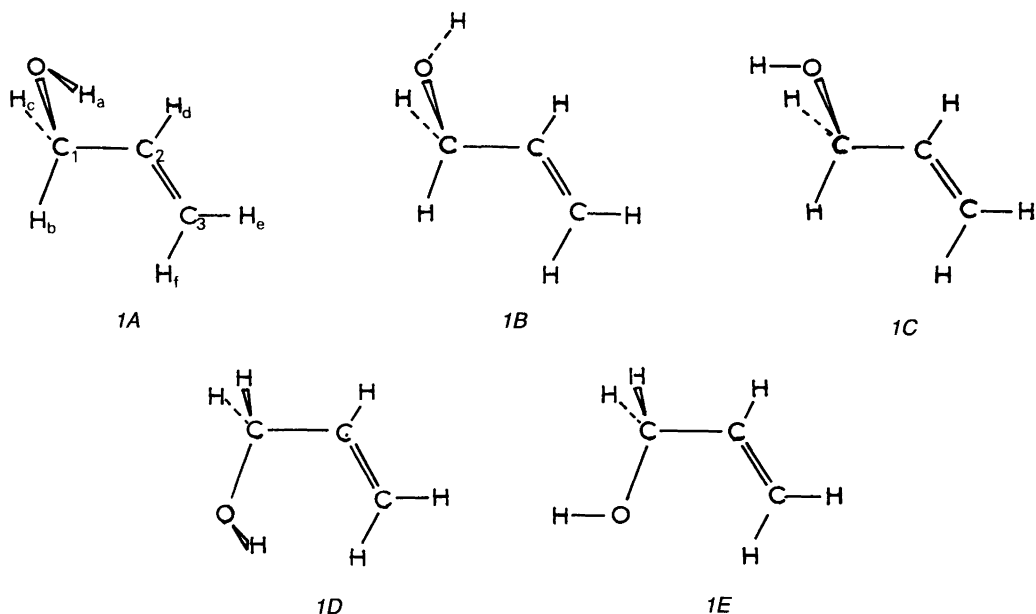


Fig. 1. Conformations of allyl alcohol.

used the value  ${}^3J_{\text{CHOH}} = 2.2$  Hz for a dihedral angle  $\text{H}_a\text{OC}_1\text{H}_b$  of  $60^\circ$ .<sup>15</sup> For the *anti* conformation ( $\text{H}_a\text{OC}_1\text{H}_b$ ,  $180^\circ$ ), we used the value 12.5 Hz, found for *cis*-3,4-epoxycyclopentanol.<sup>16</sup> From these numbers, we obtained a composition around C-OH of 77% *endo* (1A, 1B, 1D) and 12% *exo* (1C, 1E) in allyl alcohol. From this, the major band in the OH region of the IR spectrum was assigned to the *endo* rotamers.

We found above that conformations 1A-C and 1D-E were equally populated and we found that of these, 1A-B and 1D are the major ones. Conformations 1A and 1D appear to have the best possibilities for an intramolecular hydrogen bond. In 1B, the hydroxyl proton points away from the double bond. If we have an intramolecular hydrogen-bonded conformer, this would be assigned to the low frequency band in the OH stretch region ( $3619\text{ cm}^{-1}$ ). A variable temperature investigation ( $-20$ – $+50^\circ\text{C}$ ) gave an inaccurate result due to the overlapping bands,  $\Delta H^\circ = -0.4 \pm 0.1\text{ kcal mol}^{-1}$  for  $\nu_1 \leftrightarrow \nu_2$ , presumably  $(\text{COH})_{\text{exo}} \leftrightarrow (\text{COH})_{\text{endo}}$ . The temperature coefficients of the two integrated extinction coefficients were assumed to be identical. A variable temperature ( $0$ – $60^\circ\text{C}$ ) NMR study of the OH sig-

nal gave, perhaps fortuitously, the same result,  $\Delta H^\circ = -0.4 \pm 0.1\text{ kcal mol}^{-1}$ .

The interactions determining the conformational composition of allyl alcohol are thus weak. We will discuss the question of an intramolecular hydrogen bond after examination of the data obtained for the other allylic alcohols.

*Cis- and trans-5-t-butyl-2-cyclohexenol* (2, Fig. 2). In analogy with cyclohexene, we expect these compounds to adopt a twist-chair conformation, particularly the *cis* isomer where both substituents would be in semiequatorial positions. The conformation of cyclohexene was studied by NMR a few years ago, and the twist-chair conformation was found to be the dominant one,<sup>17</sup> in accordance with the result from an electron diffraction study.<sup>18</sup> The NMR parameters of 2 are given in Tables 3 and 4.

In 2, the average of the vinylic coupling constants  ${}^3J_{c,d}$  and  ${}^3J_{c,e}$  was close to that found for cyclohexene (averaged by flipping): 3.69 Hz for *cis*-2, 3.86 Hz for *trans* 2 and 3.73 Hz for cyclohexene.<sup>17</sup> From this, we assumed that both *cis*- and *trans*-2 are in the twist-chair conformation, and we used the molecular geometry reported

Table 3. Proton chemical shifts ( $\delta$ , ppm from TMS) for 5-*t*-butyl-2-cyclohexenols (2) and their acetates. (Fig. 3 for proton assignments.)

Substance	H <sub>a</sub>	H <sub>b</sub>	H <sub>c</sub>	H <sub>d</sub>	H <sub>e</sub>	H <sub>f</sub>	H <sub>g</sub>	H <sub>h</sub>	H <sub>i</sub>	COCH <sub>3</sub>	<i>t</i> -Bu
<i>Cis</i> -2-acetate <sup>a</sup> (X=H <sub>a</sub> , Y=OAc)	5.380	5.572	5.860	2.038	1.831	1.456	2.128	1.212	—	2.048	0.862
<i>Cis</i> -2-ol <sup>b</sup> (X=H <sub>a</sub> , Y=OH <sub>i</sub> )	4.080	5.526	5.609	1.939	1.734	1.339	2.036	0.962	0.753	—	0.894
<i>Trans</i> -2-acetate <sup>a</sup> (X=OAc, Y=H <sub>a</sub> )	4.842	5.342	5.614	1.705	1.326	1.100	1.506	0.923	—	2.045	0.874
<i>Trans</i> -2-ol <sup>b</sup> (X=OH <sub>i</sub> , Y=H <sub>a</sub> )	4.010	5.685	5.753	2.008	1.658	1.423	1.840	1.195	0.813	—	0.887

<sup>a</sup>In CDCl<sub>3</sub>. <sup>b</sup>5mM in CFCI<sub>3</sub>.Table 4. Proton-proton coupling constants (Hz) for 5-*t*-butyl-2-cyclohexenols and their acetates.

Couplings	Compound			
	<i>Cis</i> -2-acetate X=H <sub>a</sub> , Y=OAc	<i>Cis</i> -2-ol X=H <sub>a</sub> , Y=OH <sub>i</sub>	<i>Trans</i> -2-acetate X=OAc, Y=H <sub>a</sub>	<i>Trans</i> -2-ol X=OH <sub>i</sub> , Y=H <sub>a</sub>
J <sub>a,b</sub>	1.57	1.44	5.04	4.80
J <sub>a,c</sub>	-2.24	-2.24	0.00	0.00
J <sub>a,d</sub>	2.24	1.71	0.00	0.00
J <sub>a,e</sub>	2.57	-3.44	-2.47	-2.47
J <sub>a,f</sub>	0.00	0.00	0.00	0.00
J <sub>a,g</sub>	5.92	6.63	1.75	1.75
J <sub>a,h</sub>	10.51	-10.51	4.09	4.09
J <sub>a,i</sub>	—	7.31	—	7.15
J <sub>b,c</sub>	10.01	10.17	9.95	9.75
J <sub>b,d</sub>	-1.56	-1.68	-1.69	-1.70
J <sub>b,e</sub>	-3.00	-3.17	-1.96	-1.86
J <sub>b,f</sub>	0.00	0.00	0.00	0.00
J <sub>b,g</sub>	-1.64	-1.59	-1.90	-1.69
J <sub>b,h</sub>	0.00	0.00	0.00	0.00
J <sub>c,d</sub>	5.21	5.28	5.48	5.56
J <sub>c,e</sub>	2.17	2.33	2.21	2.08
J <sub>c,f</sub>	0.00	0.00	0.00	0.00
J <sub>c,g</sub>	0.00	0.00	0.00	0.02
J <sub>c,h</sub>	0.00	0.00	0.00	0.00
J <sub>d,e</sub>	-19.03	-17.72	-17.98	17.75
J <sub>d,f</sub>	4.89	4.94	4.83	4.83
J <sub>d,g</sub>	-2.50	-2.21	-1.73	1.50
J <sub>d,h</sub>	0.00	0.00	0.00	0.00
J <sub>e,f</sub>	11.06	11.15	11.61	11.69
J <sub>e,g</sub>	0.92	0.77	0.00	-0.02
J <sub>e,h</sub>	0.00	0.00	-0.46	-0.46
J <sub>f,g</sub>	2.06	2.07	2.36	2.23
J <sub>f,h</sub>	13.09	13.08	13.28	13.06
J <sub>g,h</sub>	-11.73	-12.50	-13.96	-13.31

from the NMR study of cyclohexene in the analyses of the spectral data of 2.<sup>17</sup> Furthermore, the olefinic coupling constants <sup>3</sup>J<sub>b,c</sub> of 2 were close to that of allyl alcohol: 10.01 Hz for *cis*-2, 9.72 Hz for *trans*-2 and 10.39 for allyl alcohol. This indicated that the ring system of 2 was an acceptable model for allyl alcohol, and that the spectral parameters obtained from 2 could be used in the analyses of allyl alcohol.

The geometry of *trans*-2 is more favourable for the formation of an internal hydrogen bond than that of conformer 1A of allyl alcohol. For *cis*-2 as compared to 1A, the opposite is the case. If intramolecular hydrogen bonding is important for the conformational population of allylic alcohols, we would expect this difference to be manifested by the *anti* rotamer around the C—OH bond being more populated in *trans*-2 than in *cis*-2 and the hydroxyl group absorption occurring at a lower frequency in the spectrum of *trans*-2 than that of *cis* 2. Inspection of Tables 1 and 4 shows that this is not the case. The coupling constants <sup>3</sup>J<sub>a,i</sub> are almost the same: 7.31 Hz for *cis*-2 and 7.15 Hz for *trans*-2 corresponding to 50% and 48%, respectively, for the *anti* rotamer around the C—OH bond; that is, the same composition for both isomers, and certainly no great dominance of the *anti* rotamer.

The chemical shifts of the hydroxyl protons are close to that of allyl alcohol:  $\delta_i = 0.753$  ppm for *cis*-2, 0.813 ppm for *trans*-2 and 0.753 ppm for allyl alcohol, indicating all to be in almost identical chemical environments.

The IR spectra (Table 1) of both compounds have two OH stretch bands, one at 3624 cm<sup>-1</sup> common for both, one at 3605 cm<sup>-1</sup> for *cis*-2 and

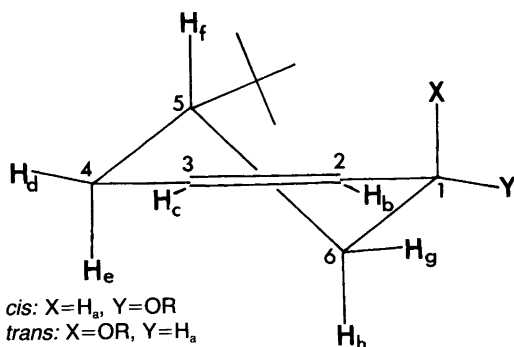


Fig. 2. Conformations of *cis*- and *trans*-5-*t*-Butyl-2-cyclohexenol (2).

one at  $3616\text{ cm}^{-1}$  for *trans*-2; that is, at a higher frequency for *trans*-2 than for *cis*-2. Furthermore, the band at  $3616\text{ cm}^{-1}$  corresponds to  $\sim 94\%$  of the total area. This indicates the band to be an overlap of the band of the *anti* and that of one of the *gauche* rotamers (from the composition obtained from NMR). The *anti* rotamer (with geometry making an intramolecular hydrogen bond possible) has thus the same  $\nu_{\text{OH}}$  as that of one of the *gauche* rotamers (without that possibility). We therefore concluded that the interactions determining the conformation of the hydroxyl group in 2 are weak, and that they cannot be hydrogen bonds since they do not result in a shift in the hydroxyl group frequency.

**2-Cyclopentenol (3, Fig. 3).** In this compound also, the geometry of the C=C-C-O fragment is close to that of 1A-C of allyl alcohol. We used it as a probe for intramolecular hydrogen bonding, as the molecule has the ability to flip between the two states  $3_{\text{ax}}$  and  $3_{\text{eq}}$  (Fig. 3), the former more favourable for such a bond than the latter.

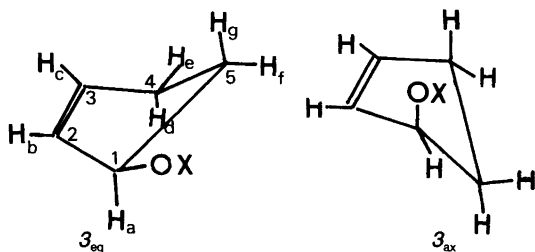


Fig. 3. The skeletal conformers of 2-cyclopentenol.

Let us first consider the conformation around the C-OH bond, then the conformation of the cyclopentene ring. From  $^3J_{\text{CHOH}}$  (7.93 Hz, Table 6) a composition of 56% *anti* and 44% *gauche* was obtained using the values referred to above. This is close to that found for 5-*t*-butyl-2-cyclohexenol and indicates no strong interaction to be present. Again, the chemical shift of the hydroxyl proton is almost the same as that of allyl alcohol.

The IR spectrum at high dilution showed two hydroxyl bands, one at  $3624\text{ cm}^{-1}$  (43% of the area) and one at  $3605\text{ cm}^{-1}$  (57% of the area). In this case, the ratio of the band areas corresponded very closely to the *gauche/anti* ratio derived from  $^3J_{\text{CHOH}}$  (above), and we assigned the high frequency band to the *gauche* rotamers, the low frequency one to the *anti*. It is interesting to note that cyclopentanol showed one band at  $3624\text{ cm}^{-1}$ , the same frequency as that assigned to the *gauche* rotamer of 2-cyclopentenol. Cyclopentanol consists of 88% of the *gauche* C-OH rotamer ( $^3J_{\text{CHOH}} = 3.42\text{ Hz}$ ).

In addition to the rotation of the hydroxyl group, the conformation of 2-cyclopentenol is determined by the flip of the five-membered ring. We assumed the ring to have an envelope conformation as found for cyclopentene with planarity of C<sub>1</sub>C<sub>2</sub>C<sub>3</sub>C<sub>4</sub> (Fig. 3).<sup>19,20</sup> By flipping out of plane, C<sub>5</sub> gives two conformers with a pseudoaxial and pseudoequatorial hydroxyl group ( $3_{\text{ax}}$  and  $3_{\text{eq}}$ ). These two forms are not energetically equivalent, but we assume the angle of pucker ( $\alpha$  between C<sub>1</sub>C<sub>2</sub>C<sub>3</sub>C<sub>4</sub> and C<sub>1</sub>C<sub>4</sub>C<sub>5</sub>) for the two conformers to be identical; the hydroxy group does not constitute a major perturbation of the ring. The NMR spectrum contains enough information both for determination of the angle of pucker ( $\alpha$ ) and the conformational population. However, the spectrum was complex due to strong couplings between the protons on C<sub>4</sub> and C<sub>5</sub>. To analyse it, it was necessary first to analyse that of 3-methoxycyclopentene (3, X=CH<sub>3</sub>), and also to prepare 1,5,5-D<sub>3</sub>-cyclopentenol to obtain some of the spectral parameters.

The dihedral angles and the vicinal coupling constants of the *cis* oriented protons H<sub>4</sub>-H<sub>f</sub> and H<sub>e</sub>-H<sub>g</sub> are a function only of the angle of pucker.<sup>21</sup> The *trans* couplings (H<sub>e</sub>-H<sub>f</sub> and H<sub>4</sub>-H<sub>g</sub>) are, on the other hand, dependent on the conformational composition, being nearly equatorial-equatorial in one and axial-axial in the other. We used a modified Karplus eqn. to obtain

Table 5. Proton chemical shifts ( $\delta$ , ppm from TMS) for 2-cyclopentanol (3, X=H) and 3-methoxycyclopentene (3, X=Me).

Substance	$\delta_a$	$\delta_b$	$\delta_c$	$\delta_d$	$\delta_e$	$\delta_f$	$\delta_g$	$\delta_x$
X = Me <sup>a</sup>	4.472	5.887	6.032	2.268	2.484	2.124	1.776	3.318
X = H <sup>b</sup>	4.673	5.709	5.823	2.184	2.413	2.132	1.572	0.733

<sup>a</sup>In CDCl<sub>3</sub>. <sup>b</sup>5mM in CFCl<sub>3</sub>.

Table 6. Proton-proton coupling constants (Hz) for 2-cyclopentanol (3, X=H) and 3-methoxycyclopentene (3, X=Me).

Substance	$J_{a,b}$	$J_{a,c}$	$J_{a,d}$	$J_{a,e}$	$J_{a,f}$	$J_{a,g}$	$J_{b,c}$	$J_{b,d}$
X = CH <sub>3</sub>	2.40	-1.16	1.12	2.32	7.41	3.60	5.63	-2.42
X = H	2.20	-1.20	1.20	2.32	7.58	3.60	5.60	-2.20

	$J_{b,e}$	$J_{c,d}$	$J_{c,e}$	$J_{d,e}$	$J_{d,f}$	$J_{d,g}$	$J_{e,f}$	$J_{e,g}$	$J_{f,g}$	$J_{a,x}$
	-2.25	2.31	2.33	-16.99	9.02	4.66	4.69	8.84	-13.72	
	-2.20	2.32	2.20	-17.00	8.98	4.70	4.82	8.84	-13.71	7.93

the conformational parameters from the coupling constants, (eqn. 2).<sup>21</sup>

$${}^3J = 12.9 \cos^2\varphi - 0.32 \cos\varphi. \quad (2)$$

From  ${}^3J_{d,e}$  and eqn. (2), a dihedral angle of 32.7° was obtained; from  ${}^3J_{e,g}$  one of 31.8°; average 32.3 ± .5°. For angles of this magnitude, the dihedral angles are close to the angle of pucker of the ring ( $\alpha$ ),<sup>22</sup> and we concluded that this angle is 32 ± .5° for 2-cyclopentanol, close to that found for 1-indanol (35.3°) and for other substituted cyclopentenes (27–37°).<sup>19-21</sup>

From this result, eqn. (2) was used, together with the two *trans* coupling constants to calculate the relative populations of the two conformers  $3_{ax}$  and  $3_{eq}$ . With a flip angle of 32°,  ${}^3J_{ax,eq} = 0.0$  Hz and  ${}^3J_{ax,ax} = 10.4$  Hz was obtained, and from  ${}^3J_{e,f}$  and  ${}^3J_{d,g}$  percentages of  $3_{ax}$  of 54% and 45% were calculated, averaging 50 ± 5% of the axial conformer. There is thus no energetic preference for any one of the two flip states. A flip angle of 32° corresponds to a dihedral angle C<sub>5</sub>C<sub>1</sub>C<sub>2</sub>C<sub>3</sub> of ±15°, indicating the allylic alcohol fragment to have a conformation close to that of conformations IA-C of allyl alcohol.

Conformer  $3_{ax}$  has a better possibility for an intramolecular hydrogen bond than  $3_{eq}$  as both the O-H-acceptor distance and angle are more favourable in this conformation. If there were such a bond, we would therefore expect a predominance of  $3_{ax}$ , together with the *anti* rotamer around the C-OH bond. We have then the following data to probe the existence of an internal hydrogen bond: a slight preference for the *anti* C-OH rotamer (56%); a small frequency shift for the OH band (19 cm<sup>-1</sup> lower than the unbonded band); and no preference for the most favourable ring conformation ( $3_{ax}$ ). The only conclusion thus far is that any interaction is weak and probably does not involve a hydrogen bond.

To obtain quantitative information on this question, we performed variable temperature IR and NMR investigations. As the two bands in the OH stretch region were further separated than those of allyl alcohol, better determinations of the band areas were possible. Assuming the temperature coefficients of the integrated molar extinction coefficients to be identical,  $\Delta H^\circ = -0.25 \pm 0.04$  kcal mol<sup>-1</sup> was obtained for the reaction C-OH<sub>gauche</sub> ↔ C-OH<sub>anti</sub> (-22°C-+55°C). A variable temperature NMR study (8-60°C) of the

OH signal gave  $\Delta H^\circ = -0.35 \pm .01$  kcal mol<sup>-1</sup>. From these experiments, we conclude that there is no intramolecular hydrogen bond in 2-cyclopentenol. The interactions are so weak that they can not be termed "bonds". It is worth mentioning that, for example in 1,2-difluoroethane, the conformer with the two fluoro atoms *gauche* has been shown to be favoured by 1 kcal mol<sup>-1</sup> over the *anti*, an interaction three times as large as that found here, without the term "bond" being invoked.<sup>23</sup>

**3-Methoxycyclopentene.** The NMR parameters for this compound were close to those of 2-cyclopentenol (Tables 5 and 6). By applying the same methods as for that compound, we found a flip angle ( $\alpha$ ) of  $32.3 \pm .5^\circ$  and again an equal population of the two flip states ( $50 \pm 5\%$ ). The only variable left to be determined for this molecule was the rotamer population around the C–OCH<sub>3</sub> bond. Information on this was available from the three-bond hydrogen-carbon CH–O–CH<sub>3</sub> coupling constant. We used this in the investigation of the rotamer composition of 9-methoxyfluorene and found  $^3J_{\text{CH}(anti)} = 8.5$  Hz and  $^3J_{\text{CH}(gauche)} = 1.3$  Hz applicable for those systems.<sup>24</sup> For 3-methoxycyclopentene  $^3J_{\text{CH}} = 3.66$  Hz was observed, corresponding to 33% *trans*, 67% *gauche*. This is the statistical distribution, indicating that none of the rotamers is energetically favoured. These results show that the lack of intramolecular hydrogen bonding in 2-cyclopentenol is not caused by steric repulsion in the conformer with a possibility for such a bond ( $J_{ax}$  with the hydroxyl proton in the *anti* position).

## Conclusions

The cyclic alcohols 2 and 3 with fixed conformations close to *IA* and *IB* of allyl alcohol (Fig. 1) showed no indications of intramolecular hydrogen bonds. It is therefore reasonable to assume that *IA* is not stabilised by such a bond either. From NMR spectroscopy, the ratio of *ID* to *IA* + *IB* was close to unity. The implication is therefore that *ID* is not stabilised relative to these two by a hydrogen bond or by any other interaction. As *IA* and *ID* are the only conformers with possibilities for such bonds, we conclude that intramolecular hydrogen bonds are not of any importance for the conformational composition of allyl alcohol. This is supported by its IR

spectrum (Table 1). The low frequency OH stretch band was only 18 cm<sup>-1</sup> below the corresponding one of ethanol.<sup>28</sup> This is the same as the shift found for the alcohols 2 and 3 which had no indications of intramolecular hydrogen bonds. The conformational population of allyl alcohol therefore appears to be determined by weak interactions. These may include repulsion between the lone pair electrons of the oxygen and the  $\pi$  electrons of the double bond<sup>12</sup> and an overlap between the lone pair orbital of the oxygen (HOMO) and the LUMO of the  $\pi$  bond.<sup>2</sup> None of these interactions is strong, as seen, for example, from the conformation of 3-methoxycyclopentene where the rotamers were equally populated in contrast to what was found for 9-methoxyfluorene.<sup>24</sup> Neither is the HOMO-LUMO interaction important; there is no predominance of *ID–E* (where that interaction is possible). Finally, the conformation of allyl alcohol is not influenced by an intramolecular hydrogen bond.

## Experimental

The preparations of 2-cyclopentenol and 3-methoxycyclopentene were by published methods.<sup>26</sup>

**5,5-D<sub>2</sub>-2-Cyclopentenone.** Two grams of 2-cyclopentenone<sup>26</sup> in D<sub>2</sub>O (15 ml) were kept at 90°C for 9 days. The solution was saturated with NaCl and extracted continuously with ether for 3×8 h, then filtered, dried (Na<sub>2</sub>SO<sub>4</sub>), the ether removed and the product distilled in a Kuegelrohr apparatus. Yield 1.8 g (90%) (CDCl<sub>3</sub>):  $\delta$  6.3–6.2 (1H, m),  $\delta$  6.2–6.1 (1H, m),  $\delta$  2.7 (2H, s, bd),  $\delta$  2.4 (0.06H, m). (97% deuterated at C<sub>5</sub>).

**1,5,5-D<sub>3</sub>-2-Cyclopentenol.** Half a gram of 5,5-D<sub>2</sub>-2-Cyclopentenone in dry ether (10 ml) was kept at –60°C, and LiAlD<sub>4</sub> (0.12 g) added during 5 min. After 4 h at –60°C, water (0.15 ml) was added and the cooling removed. After 15 min, aqueous sodium hydroxide (12%, 0.15 ml) was added. After 10 min, more water (0.3 ml) was added. The mixture was stirred for 1 h, filtered, dried (Na<sub>2</sub>SO<sub>4</sub>) and the ether evaporated (Vigreux column). The product was distilled (Kuegelrohr) and was 85% pure (GC), the major impurity being deuterated cyclopentanol. IR (liq.): 3350, 3060, 2940, 2860, 2210, 2180, 2130 cm<sup>-1</sup>. The NMR spectrum at 400 MHz showed the product to be 1,5,5-D<sub>3</sub>-2-cyclopentenol and pro-

vided the spectral parameters for the analyses of 2-cyclopentanol. ( $J_{b,c}$ ,  $J_{b,d}$ ,  $J_{b,e}$ ,  $J_{c,d}$ ,  $J_{c,e}$  reported in Table 3) The procedures for obtaining the NMR and IR spectra have been reported.<sup>12,27</sup> The NMR spectra were analysed by the PANIC program on the Bruker instrument. The probable errors on the reported coupling constants were  $\pm 0.02$  Hz.

*Acknowledgements.* The gift of *cis*- and *trans*-5-*t*-butyl-2-cyclohexanol and their acetates from Professor Y. Senda, Tohoku University, Japan, is gratefully acknowledged.

The 400 MHz NMR spectra were obtained at the Norwegian National NMR Laboratory at the University of Trondheim.

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Received February 4, 1986.