

# Microwave Spectrum, Conformation and Intramolecular Hydrogen Bonding of 1,4-Pentadien-3-ol

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Marstokk, K.-M. and Møllendal, H., 1990. Microwave Spectrum, Conformation and Intramolecular Hydrogen Bonding of 1,4-Pentadien-3-ol. – Acta Chem. Scand. 44: 18–22.

The microwave spectra of  $\text{H}_2\text{C}=\text{CH}-\text{CH}(\text{OH})-\text{CH}=\text{CH}_2$  and one partially deuterated species  $\text{H}_2\text{C}=\text{CH}-\text{CH}(\text{OD})-\text{CH}=\text{CH}_2$  have been investigated in the 28.0–39.5 GHz spectral region at about  $-25^\circ\text{C}$ . One rotamer, called the *skew-syn* conformer, was assigned. In this conformer, the carbon–oxygen bond is *skew* ( $120^\circ$  from *syn*) with respect to one of the double bonds, and *syn* with respect to the other double bond. A five-membered intramolecular hydrogen bond is formed between the hydroxyl-group hydrogen atom and the  $\pi$ -electrons of the double bond which is *skew* to the carbon–oxygen bond. There is no indication of the presence of large fractions of any other rotameric forms.

Allylic alcohols which contain the  $\text{C}=\text{C}-\text{C}-\text{O}-\text{H}$  chain are often found to prefer heavy-atom  $\text{C}=\text{C}-\text{C}-\text{O}$  *syn* or *skew* conformers in the free state.<sup>1–5</sup> In the *syn* conformation the  $\text{C}=\text{C}-\text{C}-\text{O}$  atoms are coplanar, whereas the  $\text{C}-\text{O}$  bond forms an angle of  $120^\circ$  with the  $\text{C}=\text{C}-\text{C}$  plane in the *skew* form. The hydroxyl-group hydrogen atom has invariably been found to be directed towards the double-bond  $\pi$ -electrons.<sup>1–5</sup> Most authors assume that these two conformers are both stabilized by weak intramolecular hydrogen bonds formed between the double-bond  $\pi$ -electrons and the hydroxyl-group hydrogen atom.<sup>1–8</sup> However, Kahn and Hehre have on the basis of theoretical computations, suggested that repulsive effects are much more important for the conformational preferences of allylic compounds than intramolecular hydrogen bonding.<sup>9</sup>

The experimental findings for some selected allylic alcohols studied in the gas phase by microwave (MW) spectroscopy in recent years are as follows: In the simplest compound of this type, *viz.* allyl alcohol,  $\text{H}_2\text{C}=\text{CH}-\text{CH}_2\text{OH}$ , the *skew* conformation has been assigned.<sup>1</sup> There is considerable evidence that another form, presumably *syn*, coexists with the *skew* rotamer, but no assignment has so far been reached, presumably because of extensive tunnelling of the hydroxyl group.<sup>1b</sup> In 3-buten-2-ol,  $\text{H}_2\text{C}=\text{CH}-\text{CH}(\text{OH})\text{CH}_3$ , the *skew* and one of the two possible *syn* conformers were identified, with the *skew* conformer being more stable by  $2.2(6) \text{ kJ mol}^{-1}$ .<sup>2</sup> Both *skew*<sup>4a</sup> and *syn*<sup>4b</sup> were found for  $\text{H}_2\text{C}=\text{C}(\text{CH}_3)\text{CH}_2\text{OH}$ . The energy difference is very small in this case, being  $1.6(18) \text{ kJ mol}^{-1}$ , with *skew* tending to be slightly more stable. Only the *skew* rotamer has been assigned so far for *trans*- $\text{CH}_3\text{CH}=\text{CH}-\text{CH}_2\text{OH}$ ,<sup>3</sup> and this is also the situation for  $\text{H}_2\text{C}=\text{C}=\text{CH}-\text{CH}_2\text{OH}$ .<sup>5</sup> The *syn* form was searched for

extensively for the latter compound, with negative result. The hypothetical *syn* rotamer was estimated to be at least  $4 \text{ kJ mol}^{-1}$  less stable than the *skew*.<sup>5</sup>

In the title compound,  $\text{H}_2\text{C}=\text{CH}-\text{CH}(\text{OH})-\text{CH}=\text{CH}_2$ , there are three single bonds about which rotational isomerism is possible. A large number of conformations is thus possible for this molecule. However, the number of likely conformations is considerably reduced by the requirement that at least one of the  $\text{C}=\text{C}-\text{C}-\text{O}$  chains is likely to take the *skew* conformation with the establishment of an intramolecular hydrogen bond. In fact, only two conformations are probable low-energy forms. Newman projections of these two rotamers are shown in Fig. 1. In

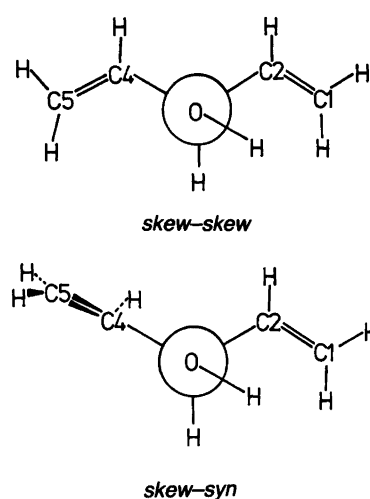


Fig. 1. Newman projections of two possible conformations of  $\text{H}_2\text{C}=\text{CH}-\text{CH}(\text{OH})-\text{CH}=\text{CH}_2$  viewed along the  $\text{O}-\text{C}3$  bond. Only the *skew-syn* conformation was found in this work, and was shown to be  $3 \text{ kJ mol}^{-1}$  more stable than any other rotameric form of 1,4-pentadien-3-ol.

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the *skew-skew* conformation, the C–O bond is *skew* with respect to both double bonds. The hydroxyl-group hydrogen atom is hydrogen-bonded to one of the double bonds. If the hydrogen atom were hydrogen-bonded to the other double bond, an equivalent conformation would arise. A double-minimum potential should thus exist for this conformation, and tunnelling between the two identical forms would be expected. In the *skew-syn* conformation of Fig. 1, the C–O bond is *skew* with respect to one double bond, and the hydroxyl-group hydrogen atom is hydrogen-bonded to its  $\pi$ -electrons. The C–O bond is *syn* with respect to the other double bond. It was found in this work that the *skew-syn* conformer is definitely much more stable than *skew-skew*, or any other rotameric form of 1,4-pentadien-3-ol.

## Experimental

The sample used in this work was purchased from Fluka A.G., Buchs, Switzerland. It was purified by vapour-phase chromatography before use. The spectrum was studied in the 28.0–39.5 GHz spectral region at a temperature of about  $-25^\circ\text{C}$ . Lower temperatures could not be used owing to insufficient vapour pressure of the compound. The pressure was between 1 and 2 Pa during the recording of the spectra. The spectrometer is an improved version of the one described briefly in Ref. 10 employing klystrons as radiation sources. The radiofrequency–microwave double-resonance technique (RFMWDR) was used as described in Ref. 11 employing the equipment mentioned in Ref. 12. The partially deuterated species  $\text{H}_2\text{C}=\text{CH}-\text{CH}(\text{OD})-\text{CH}=\text{CH}_2$  was produced by conditioning the cell with  $\text{D}_2\text{O}$  and then introducing the normal sample. About 50% deuteration was achieved this way.

## Results

**Microwave spectrum and assignment.** Survey spectra revealed a weak, but rather dense MW spectrum for 1,4-pentadien-3-ol. The strongest lines of the spectrum, which are not very numerous, have peak absorption coefficients of roughly  $1.0 \times 10^{-7} \text{ cm}^{-1}$  at about  $-25^\circ\text{C}$ . It turned out later that these transitions are intermediate- $J$   $a$ -type R-branch lines of the *skew-syn* conformer. The numerous remaining very weak lines all have peak absorption coefficients much less than these  $a$ -type R-branch transitions.

Preliminary sets of rotational constants were predicted for both conformers shown in Fig. 1 using the plausible structural parameters listed below in Table 4. The *skew-skew* conformation was predicted to have the following rotational constants:  $A = 5.05$ ,  $B = 2.59$  and  $C = 1.93$  GHz, respectively. The dipole-moment components along the principal inertial axes were predicted to be approximately  $\mu_a = 1.7$ ,  $\mu_b = 1.9$  and  $\mu_c = 4.7$  (in units of  $10^{-30} \text{ C m}$ ) using the bond-moment method.<sup>13</sup> The corresponding values for *skew-syn* are  $A = 6.95$ ,  $B = 2.34$  and

$C = 1.91$  GHz for the rotational constants, and  $\mu_a = 5.1$ ,  $\mu_b = 0.3$  and  $\mu_c = 0.5$  (same units as above).

Strong and numerous  $c$ -type Q-branch transitions scattered all over the spectrum were predicted to occur for the hypothetical *skew-skew* conformation. This feature was not seen for the strongest lines of the spectrum. Attention was therefore focused on the *skew-syn* conformer. The rotational constants of the *skew-syn* rotamer predicted that the high- $K_{-1}$  transitions of the  $J = 7 \leftarrow 6$ ,  $8 \leftarrow 7$ , and  $9 \leftarrow 8$   $a$ -type R-branch transitions falling in the investigated spectral range should coalesce two by two. This was exploited in an RFMWDR search<sup>11</sup> for these transitions, which were readily found very close to their predicted frequencies using this mode of operation. Extension of the assignments to include the lower- $K_{-1}$   $a$ -type R-branch transitions was then made using normal Stark effect modulated MW spectroscopy. Transitions of types  $b$  and  $c$  were searched for

Table 1. Selected transitions of the ground-state MW spectrum of the *skew-syn* conformer of 1,4-pentadien-3-ol.

Transition	Observed frequency <sup>a</sup> /MHz	Obs. – calc. frequency/MHz	Centrifugal dist./MHz
$7_{0,7} \leftarrow 6_{0,6}$	28429.41	0.09	–0.54
$7_{1,6} \leftarrow 6_{1,5}$	30763.15	0.06	–0.50
$7_{2,5} \leftarrow 6_{2,4}$	30787.53	0.03	–0.46
$7_{2,6} \leftarrow 6_{2,5}$	29501.75	0.11	–0.44
$7_{5,2} \leftarrow 6_{5,1}$	30030.46	0.06	–0.51
$7_{3,4} \leftarrow 6_{3,3}$	27709.42	0.11	–0.34
$7_{3,5} \leftarrow 6_{3,4}$	29887.47	–0.03	–0.34
$7_{5,2} \leftarrow 6_{5,1}$	29821.24	–0.06	0.03
$7_{5,3} \leftarrow 6_{5,2}$	29821.24	0.01	0.03
$7_{6,1} \leftarrow 6_{6,0}$	29800.14	–0.11	0.27
$7_{6,2} \leftarrow 6_{6,1}$	29800.14	–0.10	0.27
$8_{0,8} \leftarrow 7_{0,7}$	32221.17	–0.08	–0.76
$8_{1,7} \leftarrow 7_{1,6}$	34955.47	–0.11	–0.75
$8_{1,8} \leftarrow 7_{1,7}$	31827.83	–0.11	–0.76
$8_{2,6} \leftarrow 7_{2,5}$	35355.86	0.06	–0.72
$8_{2,7} \leftarrow 7_{2,6}$	33624.70	0.01	–0.69
$8_{3,5} \leftarrow 7_{3,4}$	34451.21	–0.03	–0.59
$8_{3,6} \leftarrow 7_{3,5}$	34173.82	–0.11	–0.57
$8_{4,5} \leftarrow 7_{4,4}$	34159.53	0.10	–0.39
$8_{6,2} \leftarrow 7_{6,1}$	34073.47	0.01	0.12
$8_{6,3} \leftarrow 7_{6,2}$	34073.47	0.01	0.12
$8_{7,1} \leftarrow 7_{7,0}$	34055.12	0.07	0.46
$8_{7,2} \leftarrow 7_{7,1}$	34055.12	0.07	0.46
$9_{0,9} \leftarrow 8_{0,8}$	35998.43	0.04	–1.09
$9_{1,8} \leftarrow 8_{1,7}$	39053.29	0.01	–1.06
$9_{1,9} \leftarrow 8_{1,8}$	35709.13	0.07	–1.09
$9_{2,8} \leftarrow 8_{2,7}$	37713.94	0.04	–1.00
$9_{3,6} \leftarrow 8_{3,5}$	38937.97	–0.02	–0.91
$9_{3,7} \leftarrow 8_{3,6}$	38452.23	–0.01	–0.88
$9_{4,5} \leftarrow 8_{4,4}$	38501.61	–0.05	–0.69
$9_{4,6} \leftarrow 8_{4,5}$	38470.41	0.01	–0.68
$9_{6,3} \leftarrow 8_{6,2}$	38353.09	–0.03	–0.10
$9_{6,4} \leftarrow 8_{6,3}$	38353.09	–0.02	–0.10
$9_{7,2} \leftarrow 8_{7,1}$	38326.74	–0.03	0.28
$9_{7,3} \leftarrow 8_{7,2}$	38326.74	–0.03	0.28
$9_{8,1} \leftarrow 8_{8,0}$	38310.12	0.03	0.71
$9_{8,2} \leftarrow 8_{8,1}$	38310.12	0.03	0.71

<sup>a</sup>  $\pm 0.10$  MHz.

Table 2. Spectroscopic constants<sup>a,b</sup> for the ground vibrational state of the *skew-syn* conformer of the parent and the partially deuterated species of 1,4-pentadien-3-ol.

Species	No. of transitions	R.m.s. <sup>c</sup> /MHz	A <sub>0</sub> /MHz	B <sub>0</sub> /MHz	C <sub>0</sub> /MHz	Δ <sub>J</sub> <sup>d</sup> /kHz	Δ <sub>JK</sub> /kHz
Parent	36	0.066	6916.59(18)	2335.7231(46)	1910.0706(52)	0.390(28)	-1.608(37)
Deuterated	35	0.079	6535.65(22)	2334.3249(45)	1879.0883(72)	0.521(33)	-1.008(44)

<sup>a</sup>A-reduction *I'*-representation.<sup>14</sup> <sup>b</sup>Uncertainties represent one standard deviation. <sup>c</sup>Root-mean-square deviation. <sup>d</sup>Further quartic centrifugal distortion constants preset at zero.

Table 3. Spectroscopic constants<sup>a,b</sup> for vibrationally excited states of the parent species of the *skew-syn* conformer of 1,4-pentadien-3-ol.

Vibrational state <sup>c</sup>	No. of transitions	R.m.s. <sup>d</sup> /MHz	A <sub>0</sub> /MHz	B <sub>0</sub> /MHz	C <sub>0</sub> /MHz	Δ <sub>J</sub> <sup>e</sup> /kHz	Δ <sub>JK</sub> /kHz
First excited state of lowest torsional vibration	33	0.085	7017.52(11)	2337.7947(63)	1912.9318(78)	0.407(39)	-2.359(58)
Second excited state of lowest torsional vibration	13	0.124	7131.72(59)	2339.922(23)	1915.910(26)	0.60(17)	-2.75(18)
First excited state of second torsional vibration	31	0.056	6800.73(18)	2343.4154(42)	1911.6192(52)	0.561(27)	-0.634(39)

<sup>a,b</sup>Comments as for Table 2. <sup>c</sup>See text for discussion of the assignments of these excited states. <sup>d</sup>As for Table 2. <sup>e</sup>Further quartic centrifugal distortion constants preset at zero.

next in the dense but very weak spectrum, but no assignments could be made. This finding was expected, since rather low values were predicted above for the dipole-moment components along the *b*- and *c*-inertial axes. Table 1 shows the identified <sup>a</sup>R-spectrum.\* The spectroscopic constants (*A*-reduction, *I'*-representation)<sup>14</sup> derived from the transitions listed in Table 1 are shown in Table 2.

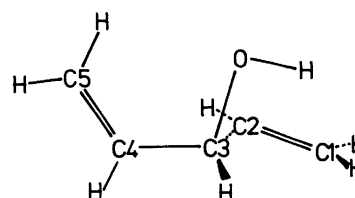
Unfortunately, the spectrum was too weak to allow a determination of the dipole moment of 1,4-pentadien-3-ol.

**Vibrationally excited states.** The ground-state transitions were accompanied by a relatively strong spectrum presumably belonging to vibrationally excited states of the molecule. As shown in Table 3, these excited states have been attributed to the two lowest heavy-atom torsional modes presumed to occur around the C2–C3 and C3–C4 bonds, because this has been found in other similar molecules.<sup>1–5</sup> Relative intensity measurements performed largely as described in Ref. 15 yielded 76(30) cm<sup>-1</sup> for the lowest torsional mode, and 95(30) cm<sup>-1</sup> for the second lowest torsional mode. These values are very similar to those in Refs. 1–5. It is quite likely that the lowest bending mode is rather low in wavenumber, just as in the cases of other allylic compounds,<sup>2,5</sup> but the first excited state of this mode was not identified, presumably because of the low absolute intensity of this spectrum.

\* The complete spectra are available from the authors upon request, or from the Molecular Spectra Data Center, Bldg. 221, Room B 268, National Bureau of Standards, Gaithersburg, MD 20899, U.S.A., where they have been deposited.

**The existence of further conformations.** The assignments reported above include all the strong lines of the spectrum. Moreover, the absolute intensities of the assigned transitions are roughly what one would predict for 1,4-pentadien-3-ol if the identified *skew-syn* conformer were the only conformation which was present. Bond-moment computations<sup>13</sup> indicate that any hypothetical rotamer of 1,4-pentadien-3-ol should possess a sizable dipole moment. The fact that the remaining unassigned lines are less than one third as intense as the identified ones leads us to conclude that the *skew-syn* conformer shown in Figs. 1 and 2 is at least 3 kJ mol<sup>-1</sup> more stable than any further hypothetical conformation. This conclusion is also supported by RFWDR<sup>11</sup> searches which were made over a wide spectral range.

**Structure.** The six rotational constants of Table 2 furnish insufficient information for a full structure determination of the identified *skew-syn* conformer of 1,4-pentadien-3-ol.



*skew-syn*

Fig. 2. Model of the identified *skew-syn* conformation of H<sub>2</sub>C=CH–CH(OH)–CH=CH<sub>2</sub>.

Table 4. Plausible molecular structure<sup>a</sup> (bond lengths/pm; angles/°) of the *skew-syn* conformer of 1,4-pentadien-3-ol.

Structural parameters

C3-O	142.8	∠H-O-C	106.0
C=C	133.7	∠H-C3-O	109.47
C-C	150.2	∠H-C3-C	109.47
C3-H	109.3	∠C3-C2-C1	124.3
O-H	96.0	∠C3-C4-C5	124.3
=C-H	108.5	∠C3-C2-H	116.7
		∠C3-C4-H	116.7
		∠H-C1-C2	121.5
		∠H-C5-C4	121.5
		∠H-O-C3-H	60.0 from <i>syn</i> <sup>b</sup>
		∠O-C-C-C	120.0 from <i>syn</i> <sup>b</sup>

Kraitchman's coordinates for the hydroxyl-group hydrogen atom

Calculated from rotational constants:

$$a = 33.73(25) \quad b = 206.694(39) \quad c = 11.92(81)$$

Calculated from plausible structure:

$$a = 31.9 \quad b = 208.4 \quad c = 7.3$$

Rotational constants / MHz

Parent species:

Observed:	$A_0 = 6916.59$	$B_0 = 2335.72$	$C_0 = 1910.07$
Calculated:	$A_0 = 6949.66$	$B_0 = 2342.14$	$C_0 = 1914.54$

Deuterated species:

Observed:	$A_0 = 6535.65$	$B_0 = 2334.32$	$C_0 = 1879.09$
Calculated:	$A_0 = 6559.88$	$B_0 = 2340.95$	$C_0 = 1883.01$

Hydrogen-bond parameters

H...C2	252	∠O-H...C2	72
H...C1	332	∠O-H,C2-C1 <sup>c</sup>	51

Sum of van der Waals radii<sup>d</sup>

H...C	290
O...C	310

<sup>a</sup>See text. <sup>b</sup>Dihedral angle. <sup>c</sup>Angle between O-H and C1-C2 bonds. <sup>d</sup>Taken from Ref. 17; van der Waals radius of carbon assumed to be 170 pm, as for aromatic carbon atoms.

However, the structural parameters shown in Table 4, which were selected from recent, accurate studies, reproduce the rotational constants of the parent as well as for the partially deuterated species well, as shown in this table. The substitution (or Kraitchman's) coordinates<sup>16</sup> for the hydroxyl-group hydrogen atom are also close to the values calculated for the plausible structure shown in Table 4. There can thus be no doubt that the *skew-syn* conformer shown in Figs. 1 and 2 has indeed been identified, and this conformer is likely to have structural parameters close to the ones listed in Table 4. The substitution coordinates of the hydroxyl-group hydrogen atom show conclusively that this hydrogen atom is hydrogen-bonded to the  $\pi$ -electrons

of the C1-C2 double bond. The geometry of the intramolecular hydrogen bond of the identified *skew-syn* conformer (Table 4) is similar to the geometries of the related molecules referred to in Refs. 1-5, and is characterized by the fact that the OH...C2 non-bonded distance is approximately 40 pm shorter than the sum of the van der Waals radii of hydrogen and aromatic carbon.<sup>17</sup> This indicates that a rather weak hydrogen bond is present in the title molecule.

Another notable feature of the preferred *skew-syn* conformer is the rather short O...C5 distance, which is calculated to be 274 pm from the plausible structure of Table 4. This is about 35 pm shorter than the sum of the van der Waals distances of an aromatic-type carbon and oxygen, as shown in Table 4.<sup>17</sup>

## Discussion

The fact that 1,4-pentadien-3-ol prefers the *skew-syn* conformation (Figs. 1 and 2) is probably a compromise between several effects. The finding that the C1=C2-C3-O-H chain of atoms has a *skew* arrangement including an intramolecular hydrogen bond to the double-bond  $\pi$ -electrons comes as no surprise, because this conformational arrangement has been found as the preferred form in the other cases so far investigated.<sup>1-5</sup> Hydrogen bonding is of course not the only force stabilizing this *skew* arrangement. Repulsion is likely to be quite important, as advocated by Kahn and Hehre.<sup>9</sup>

The reason why the C5=C4-C3-O chain of atoms takes a *syn* arrangement instead of *skew* is perhaps a result of repulsion between the oxygen atom lone electron pairs and the  $\pi$ -electrons of the C4=C5 double bond. This repulsion would probably be larger if this chain of atoms were in a *skew* conformation than if it were in the preferred *syn* conformation.

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Received March 20, 1989.