

Short Communication

Structure, Conformation and Intramolecular Hydrogen Bonding of Dicyclopropyl Carbinol as Studied by Microwave Spectroscopy and *Ab Initio* Computations

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It is now well established by means of microwave (MW) spectroscopy that the most stable conformations of α -hydroxy,^{1–3} α -cyclopropanol,⁴ α -amino⁵ and α -mercapto⁶ cyclopropanes are stabilised by intramolecular hydrogen (H) bonds formed between one H atom of the said groups and the pseudo- π electrons of the cyclopropane ring.⁷

Rotational isomerism is possible around the C1–O1, C1–C2 and C1–C5 bonds in the present case of dicyclopropyl carbinol (Fig. 1), and many rotamers may thus exist for this compound. This study was undertaken as a continuation of our H bond investigations⁸ to see what conformer(s) dicyclopropyl carbinol prefers and the role internal H bond might play for its conformational choice(s). A combined approach using reasonably high-level *ab initio* quantum mechanical computations and microwave (MW) spectroscopy has proved rather effective and was therefore chosen.

Ab initio computations employing the Gaussian 92 program package⁹ were made in order to locate minima, i.e. 'stable' rotamers, on the conformational energy surface. Calculations were carried out at the rather high MP2/6-31G** (frozen core) level of theory and were restricted for economic reasons to five (Fig. 1) of the rather large number of rotamers that is actually possible for this compound. These five rotamers were selected because steric conditions seem to be better in them than in other forms of the molecule. The fully optimised structures as well as some other parameters of interest of these five rotamers are listed in Table 1.

The *ab initio* calculations predict that *Conformer I* is considerably more stable than the other rotamers

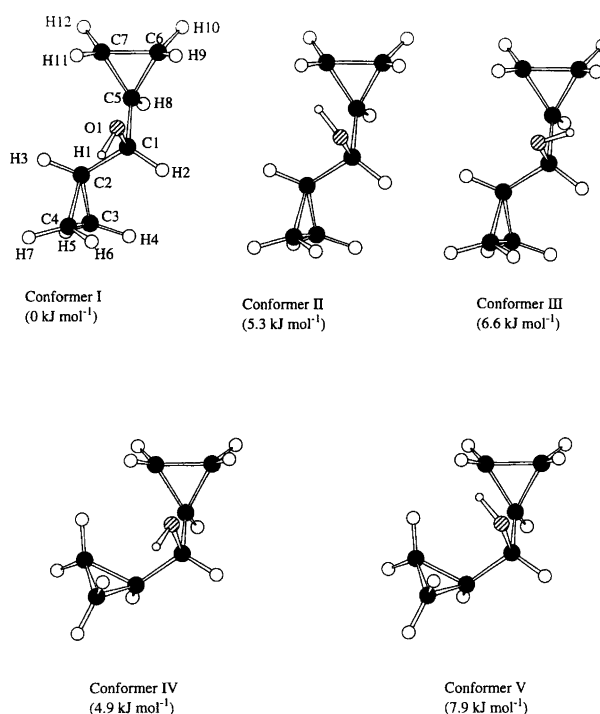


Fig. 1. The five conformers of dicyclopropyl carbinol for which *ab initio* computations were carried out. Atom numbering is given on *Conformer I*.

(Table 1). This conformation is stabilised by an intramolecular H bond formed between the H1 atom and the pseudo- π electrons along the C2–C3 edge of the cyclopropyl ring, as the non-bonded H1...C2 and the H1...C3 distances are calculated to be 245.5 and 284.5 pm, respectively, from the structure in Table 1. The sum of the van der Waals radii of hydrogen and aromatic carbon

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Table 1. Structure,^a rotational constants, dipole moments and energy differences of five rotamers of dicyclopropyl carbinol obtained by *ab initio* computations at the MP2/6-31G** (frozen core) level.

Rotamer:	Conformer I	Conformer II	Conformer III	Conformer IV	Conformer V
Distances/pm					
O1-H1	96.6	96.5	96.4	96.4	96.6
C1-O1	143.0	143.3	143.1	143.2	142.7
C1-H2	110.2	109.5	110.1	109.9	109.4
C1-C2	150.6	150.7	150.2	151.6	151.7
C2-H3	108.4	108.6	108.3	108.5	108.4
C2-C3	150.1	150.5	150.4	150.3	149.9
C2-C4	150.8	150.2	150.0	149.9	150.4
C3-H4	108.2	108.2	108.2	108.1	108.0
C3-H5	108.0	108.0	108.0	108.1	108.0
C4-H6	108.2	108.1	108.1	108.0	108.1
C4-H7	108.0	108.1	108.0	108.0	108.0
C1-C5	150.9	151.5	151.6	151.1	151.7
C5-H8	108.4	108.4	108.4	108.4	108.4
C5-C6	150.1	149.9	150.3	150.1	149.9
C5-C7	150.3	150.4	150.0	150.2	150.4
C6-H9	107.9	108.0	108.1	108.0	108.0
C6-H10	108.1	108.1	108.0	108.1	108.0
C7-H11	108.0	108.1	108.2	107.9	108.1
C7-H12	108.1	108.0	108.0	108.1	108.0
Angles/°					
H1-O1-C1	106.1	106.7	107.1	107.1	106.8
O1-C1-H2	109.8	104.7	109.9	109.4	103.9
O1-C1-C2	110.8	111.7	106.9	111.4	112.1
C1-C2-H3	113.9	114.1	113.8	113.5	113.3
C1-C2-C3	119.7	119.7	119.1	121.2	120.4
C1-C2-C4	119.3	119.5	119.8	119.9	121.6
C2-C3-H4	117.5	117.4	117.6	118.1	116.2
C2-C3-H5	118.2	118.2	118.2	118.2	118.6
C2-C4-H6	117.7	116.8	117.2	116.5	119.1
C2-C4-H7	117.5	118.4	118.2	118.5	117.9
O1-C1-C5	107.6	111.4	111.9	107.5	112.1
C1-C5-H8	113.1	113.5	113.3	113.2	113.3
C1-C5-C6	120.8	120.3	121.8	120.5	120.4
C1-C5-C7	119.9	120.2	119.5	120.5	121.6
C5-C6-H9	116.9	116.4	118.6	116.8	116.2
C5-C6-H10	118.0	118.4	118.0	118.2	118.6
C5-C7-H11	116.9	118.0	116.3	117.2	119.1
C5-C7-H12	118.1	118.2	118.7	117.9	117.9
Dihedral angles ^b /°					
H1-O1-C1-H2	-73.2	-156.1	50.9	-38.8	180.0
H1-O1-C1-C2	46.3	-38.7	168.2	81.4	-63.1
O1-C1-C2-H3	62.7	72.1	63.3	-177.4	179.6
O1-C1-C2-C3	-151.9	-143.7	-152.4	-32.6	-36.2
O1-C1-C2-C4	-81.7	-73.5	-82.2	38.6	35.3
C1-C2-C3-H4	1.1	1.1	2.0	2.8	4.2
C1-C2-C3-H5	-143.0	-142.7	-142.1	-142.3	-140.5
C1-C2-C4-H6	-2.4	-0.9	-0.4	-4.1	-2.9
C1-C2-C4-H7	142.5	142.7	143.2	140.6	141.8
H1-O1-C1-C5	168.6	86.4	-70.3	-156.5	63.1
O1-C1-C5-H8	177.3	179.1	177.1	-175.0	-179.7
O1-C1-C5-C6	32.1	33.9	31.5	40.3	36.1
O1-C1-C5-C7	-38.9	-37.0	-39.7	-30.9	-35.4
C1-C5-C6-H9	-2.1	-2.8	-2.1	-3.1	-4.1
C1-C5-C6-H10	142.5	142.0	143.1	141.6	140.5
C1-C5-C7-H11	3.7	3.5	5.1	3.2	2.9
C1-C5-C7-H12	-141.2	-141.7	-139.8	-141.5	-141.8

Table 1. (Continued.)

Rotamer:	Conformer I	Conformer II	Conformer III	Conformer IV	Conformer V
Rotational constants ^c /MHz					
A	4363.6	4331.7	4236.5	4397.8	4437.3
B	1282.1	1267.2	1301.0	1356.6	1311.2
C	1130.0	1121.9	1136.5	1260.9	1227.5
Dipole moment ^d /10 ⁻³⁰ C m					
μ_a	6.11	2.56	1.66	2.95	0.0
μ_b	1.66	4.37	2.31	1.81	4.54
μ_c	0.44	3.63	5.23	4.24	0.99
Energy difference ^{e,f} /kJ mol ⁻¹					
	0.0	5.3	6.6	4.9	7.9

^aSee Fig. 1 for definition. ^bMeasured from $\text{syn}=0^\circ$. ^cCalculated from the structures given above in this table. ^d $D=3.33564 \times 10^{-30}$ C m. ^eThe total energy of *Conformer I* was calculated to be -913777.24 kJ mol⁻¹ (-348.0393548 hartree). ^fEnergy difference between each of the other four rotamers and *Conformer I*.

is 290 pm.¹⁰ The angle between the H1–O1 bond and the C2–C3 bond is 21.7°. These values are quite similar to the corresponding parameters in related H-bonded cyclopropyl derivatives.^{1–5}

Conformers II–V may also be stabilised by weak internal H bonds in a similar manner as *Conformer I*. However, the H1 atom is further away from the pseudo- π electrons in these cases, resulting in a weaker interaction. This may explain why they are less stable than the last-mentioned rotamer. The energy differences, suggested by the *ab initio* computations (Table 1) to be ca. 5–8 kJ mol⁻¹ in these cases, are reasonable.

The rotational constants computed for *Conformer I* (Table 1) indicate that this rotamer is quite prolate with the asymmetry parameter $\kappa \approx -0.9$. The largest component of the dipole moment is calculated to be about 6.1×10^{-30} C m and to lie along the *a*-inertial axis (Table 1). Characteristic *a*-*R*-branch pile-ups of transitions should thus occur for this rotamer at frequencies given approximately by $(B+C) \times (J+1)$.

The microwave spectra of a commercial sample were taken in the 23–39 GHz spectral range at about 0 °C using the Oslo spectrometer.¹¹ The *a*-*R*-pile-ups, which were immediately noted, were remarkably weak, as the strongest transitions had peak absorption coefficients of only roughly 4×10^{-8} cm⁻¹. The reason for this weakness is presumed to be the large partition function resulting in relatively few molecules in each quantum state.

The assignments started with the *a*-*R* pile-ups; the ground and one vibrationally excited states were ultimately assigned.* The spectroscopic constants (*A*-reduction, *I'*-representation)¹² of the ground vibrational state and the lowest excited vibrational state are listed in Table 2. Only *a*-*R*-lines were assigned. Two of the quartic centrifugal distortion constants (Δ_J and Δ_{JK}) were fitted,

*The complete spectra are available from the authors upon request, or from the Molecular Spectra Data Center, National Institute of Standards and Technology, Molecular Physics Division, Bldg. 221, Rm. B208, Gaithersburg, MD 20899, USA, where they have been deposited.

Table 2. Spectroscopic constants^{a,b} the ground and one vibrationally excited state of dicyclopropyl carbinol.

Vibrational state:	Ground	1st ex. tors. state
No. of transitions:	70	55
R.m.s. dev. ^c /MHz:	0.119	0.130
A_v /MHz	4376.98(55)	4424.69(37)
B_v /MHz	1277.6988(50)	1278.8312(46)
C_v /MHz	1123.9566(51)	1122.4960(51)
Δ_J /kHz	0.0590(72)	0.0180(82)
Δ_{JK} ^d /kHz	-0.164(15)	-0.098(17)
J_{max} ^e	16	16

^a*A*-reduction, *I'*-representation.¹² ^bUncertainties represent one standard deviation. ^cRoot-mean-square deviation. ^dFurther quartic centrifugal distortion constants preset at zero. ^eMaximum value of *J*.

while the other three constants were pre-set at zero. Attempts to find *b*- and *c*-type transitions failed, presumably because the two corresponding principal-axes dipole moment components are small (Table 1), resulting in intensities that are too low. The frequency of the lowest excited state was determined by rather crude relative intensity measurements to be ca. 90 cm⁻¹.

It is seen in Table 2 that the rotational constants of the ground vibrational state agree with those calculated for *Conformer I* (Table 1) to within better than 0.6%. However, the experimental rotational constants differ little from those of *Conformers II* and *III*, and cannot be used alone to discriminate unambiguously between these three forms. Nevertheless, the principal-axes dipole moment components are quite different in these three cases and can be used for this purpose. The observation that only *a*-type lines were observed is in agreement with the predictions for *Conformer I* (Table 1). The *C* rotational constants of *Conformers IV* and *V* are quite different (several per cent) from those of *Conformer I*. Moreover, neither *Conformer IV* nor *Conformer V* are predicted (Table 1) to have a large μ_a . There is thus no

doubt that *Conformer I* has indeed been assigned and not confused with any other rotamer.

The following conclusions can be drawn from the present study: dicyclopropyl carbinol prefers *Conformer I* as its most stable form. Steric conditions are favourable in this rotamer. The intramolecular H bond is providing additional stabilisation of this rotamer making it several kJ mol^{-1} more stable than other forms. The H bond found in dicyclopropyl carbinol is similar to those in related cyclopropyl derivatives.¹⁻⁵

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