

Microwave Spectrum, Conformation and *Ab Initio* Calculations for 1-Cyclopropylcyclopropanol

Vladimir Chaplinski,^a K.-M. Marstokk,^b Armin de Meijere^a and Harald Møllendal^{*,b}

^aInstitut für Organische Chemie der Georg-August-Universität Göttingen, Tammannstrasse 2, D-37077 Göttingen, Germany; and ^bDepartment of Chemistry, The University of Oslo, PO Box 1033 Blindern, N-0315 Oslo, Norway

Chaplinski, V., Marstokk, K.-M., de Meijere, A. and Møllendal, H., 1996. Microwave Spectrum, Conformation and *Ab Initio* Calculations for 1-Cyclopropylcyclopropanol – Acta Chem Scand. 50: 486–491. © Acta Chemica Scandinavica 1996.

The microwave spectra of 1-cyclopropylcyclopropanol and one deuterated species (hydroxyl group) have been investigated in the 15.0–17.0 and 24.0–39.0 GHz spectral region at about -10°C . One rotamer, denoted Conformer **II** was assigned. In this conformation the two cyclopropyl rings are *gauche* to one another, and the pseudo π -electrons along the outside of the cyclopropyl ring are in an optimum position for forming a weak intramolecular hydrogen bond with the hydrogen atom of the hydroxyl group of the adjacent cyclopropyl ring. This hydrogen-bonded conformer is at least 2 kJ mol^{-1} more stable than any other hypothetical conformation including the other *gauche* conformer with the same dihedral angle between the planes bisecting the cyclopropyl groups (i.e. Conformer **III**). The microwave work has been assisted by *ab initio* computations at the 6-31G* and MP2/6-31+G** levels of theory.

It is now well established by infrared (IR), microwave (MW), NMR spectroscopy and theoretical *ab initio* methods that the cyclopropyl ring can act as proton acceptor for intramolecular hydrogen (H) bonds.¹ The pseudo π -electrons² presumed to have their maximum electron density along the edges of the ring on the outside, are the acceptor site. Various donor groups attached to the cyclopropyl ring, such as HOCH₂–,^{1e-h,3a-c} H₃CCH(OH)–,^{3d} HOCH₂CH₂–,^{3e} H₂NCH₂–,^{3f} and HSCH₂–,^{3g} have been found to be involved in this kind of interaction. No information about the ability of the cyclopropanol group to act as proton donor and the cyclopropyl ring as proton acceptor within the same molecule has so far been available. 1-Cyclopropylcyclopropanol is the ideal model substance to investigate any such interaction, and this was the motivation to carry out the present research.

1-Cyclopropylcyclopropanol has two internal axes around which rotational isomerism may arise, viz. the C1–O1 and C1–C4 bonds (Fig. 1). A maximum of nine rotamers with staggered atomic arrangements may then exist. However, enantiomers cannot be distinguished by MW spectroscopy, and there are consequently only five different conformations that might be discerned by this method. These five forms are drawn in Fig. 1.

In Conformers **I–III** the H1–O1–C1–C4 chain of atoms is *gauche* (about 60° from *syn* = 0°), whereas these

atoms are *anti* (180° from *syn*) in Conformers **IV** and **V**. The O1–C1–C4–H6 atom linkage is *anti* in Conformers **I** and **V** and *gauche* in the other three forms. Enantiomers exist for all rotamers but Conformer **IV**.

No intramolecular H bonding is of course possible in Conformers **IV** and **V** because of the position of the H1 atom in these two conformations. However, in Conformers **I–III** the H1 atom is rather close to the C4 atom (see Table 1 below), and hence to the pseudo π -electrons of the ring and weak intramolecular interactions may then be possible in each of these conformations. Internal H bonding is definitely most favourable in Conformer **II**, because in this rotamer the pseudo π -electrons on the outside of the ring are oriented such that they are much closer to the H1 atom here than they are in Conformers **I** and **III** (Fig. 1). It is concluded in this work that the more favourable H bond interaction that exists in Conformer **II** is the major reason why this rotamer is preferred.

Experimental

Sample. The sample utilized in this work was synthesized from methyl cyclopropenecarboxylate as recently published.⁴ The sample was purified by repeated preparative gas-phase chromatography. A check of the purified sample by the same method revealed it to be more than 99% pure. The sample was kept at dry-ice temperature (-78°C) or in a refrigerator (-40°C) when not in use.

* To whom correspondence should be addressed.

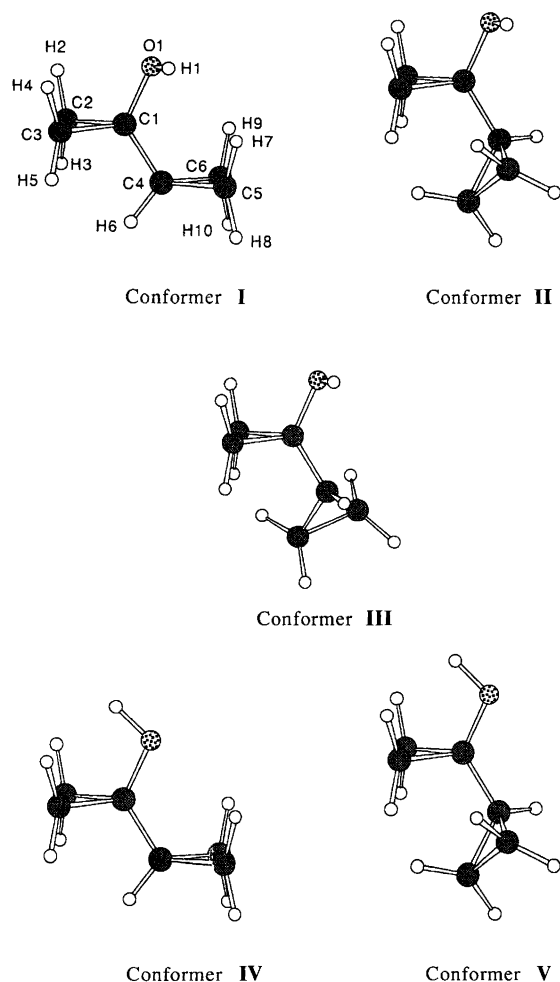


Fig. 1. The five conformations presumed to be possible all-staggered forms of 1-cyclopropylcyclopropanol. Atom numbering is given on the sketch of Conformer I. Conformer II is the only one found in the MW spectrum. This rotamer which is presumed to be stabilized by an intramolecular H bond, is at least 2 kJ mol^{-1} more stable than any other rotameric form of the molecule.

Microwave experiment. The MW spectrum was studied using the Oslo spectrometer which is described in Ref. 5. The 15–17 and 24–39 GHz spectral regions were investigated with the microwave absorption cell cooled to about -10°C . Lower temperatures, which would have increased the MW spectral intensities, could not be employed owing to insufficient vapour pressure of the compound. The pressure was about 4–10 Pa when the spectra were recorded and stored electronically using the computer programs written by Waal.⁶ The accuracy of the spectral measurements is presumed to be better than $\pm 0.10 \text{ MHz}$.

Results

Ab initio calculations. The computations of geometries and energies were first made at the 6–31G* level of theory for all the five conformers shown in Fig. 1 using

the Gaussian 92 program package⁷ running on the Cray Y-MP computer in Trondheim and IBM RS6000 cluster in Oslo. Attempts were made to optimize fully the geometries of these five conformations. However, only Conformers I–III were found as stable minima. (No imaginary vibrational frequencies⁸ were computed for any of these three rotamers). It is noteworthy that no energy minimum was located for either Conformers IV or V using this basis set. Both these conformations are characterized by having the H1–O1 and C1–C4 bonds *anti*. The computations starting with structures close to Conformers IV and V refined to one of the Conformers I–III in all cases. It is presumed that the failure to locate Conformers IV and V as stable minima on the energy surface is not an artefact of the computations, but reflects a genuine property of the title molecule.

Interestingly, only one conformer has been found for cyclopropanol in a MW investigation.⁹ This rotamer has the hydroxyl group in a *gauche* conformation corresponding to that in Conformers I–III. It was questioned whether the *anti* form exists at all for cyclopropanol.⁹

Finally, the computations were repeated for Conformers I–III at the much more elaborate MP2/6–31+G* (frozen core) level of theory with full geometry optimization. These three rotamers were again predicted to be stable minima.⁸ The resulting geometries are given in Table 1, together with other parameters of interest.

This table reveals some interesting predictions: Conformer II is computed to be approximately 4 kJ mol^{-1} more stable than both Conformer I and Conformer III. In Conformer II the pseudo π -electrons are much more conveniently located for interaction with the H1 atom than in the other two rotamers because the C4–C6 side of the ring is so close to the H1 atom in this case (see non-bonded distances in Table 1). Moreover, it is noted that the H1–O1–C1–C3 dihedral angle is $10\text{--}20^\circ$ larger in Conformer II than in the other two conformations. The widening of this dihedral angle brings the H1 atom into closer contact with the pseudo π -electrons along the C4–C6 edge of the ring, and thus increases the weak H bond interaction in Conformer II.

The bond lengths and bond angles of the three rotamers are predicted to be close to their counterparts in cyclopropane¹⁰ and bicyclopropyl.¹¹

MW spectrum and assignment of Conformer II. The *ab initio* results in Table 1 predict that Conformer II is the most stable form of 1-cyclopropylcyclopropanol. The rotational constants of this table indicate that this compound is a prolate symmetrical top with the asymmetry parameter $\kappa \approx -0.70$. The largest dipole moment component is predicted to lie along the *a*-inertial axis.

A survey spectrum taken in the 15–17 GHz region in order to locate the $J=4\leftarrow 3$ *a*-type transitions met with immediate success and lead to a quick assignment of the *R*-branch transitions shown in Table 2. These lines were rather weak; the maximum intensity of the low- K_{-1} $J=$

Table 1. Structure, rotational constants, principal axes coordinates of the H1 atom, dipole moments and energy differences of the three stable rotamers of 1-cyclopropylcyclopropanol calculated at the MP2/6-31+G** (frozen core) level of theory.

Conformer: ^a	I	II	III
Distances/pm			
H1-O1	96.8	96.9	96.8
C1-O1	141.7	142.1	142.2
C1-C2	149.3	149.1	149.2
C1-C3	150.4	150.5	150.5
C2-H2	108.1	108.1	108.1
C2-H3	108.2	108.1	108.1
C3-H4	108.2	108.1	108.1
C3-H5	108.2	108.1	108.2
C1-C4	149.7	149.2	149.3
C4-C5	150.7	150.4	150.5
C4-C6	150.4	151.1	150.7
C4-H6	108.5	108.5	108.7
C5-H7	108.1	108.1	108.2
C5-H8	108.1	108.1	108.1
C6-H9	108.1	108.3	108.1
C6-H10	108.1	108.1	108.1
Angles/°			
H1-O1-C1	107.5	107.0	107.5
O1-C1-C2	113.9	112.9	112.3
O1-C1-C3	117.0	115.9	116.3
C1-C2-H2	116.5	116.8	115.3
C1-C2-H3	118.0	117.5	119.8
C1-C3-H4	117.3	115.8	117.3
C1-C3-H5	118.1	120.1	117.7
O1-C1-C4	115.0	113.1	113.8
C1-C4-C5	121.3	122.7	119.9
C1-C4-C6	120.2	119.9	122.5
C1-C4-H6	113.4	113.0	113.5
C4-C5-H7	118.3	118.7	116.3
C4-C5-H8	117.9	117.2	118.5
C4-C6-H9	116.6	116.9	118.7
C4-C6-H10	118.2	118.6	117.2
Dihedral angles ^{b/p}			
H1-O1-C1-C2	135.8	155.3	147.5
H1-O1-C1-C3	67.5	87.7	80.1
O1-C1-C2-H2	-1.5	-0.2	-0.9
O1-C1-C2-H3	143.1	144.4	143.9
O1-C1-C3-H4	-2.8	-4.0	-4.8
O1-C1-C3-H5	-148.3	-150.0	-150.5
H1-O1-C1-C4	-81.1	-61.4	-67.5
O1-C1-C4-C5	33.8	158.1	-79.8
O1-C1-C4-C6	-37.6	86.6	208.7
O1-C1-C4-H6	178.5	-55.6	63.4
C1-C4-C5-H7	-2.9	-0.9	-4.6
C1-C4-C5-H8	142.2	143.4	139.2
C1-C4-C6-H9	4.0	6.0	0.9
C1-C4-C6-H10	-140.8	-139.0	-143.2
Non-bonded distances ^c /pm			
H1 ... C4	279.0	260.0	266.8
H1 ... C5	292.9	389.7	368.4
H1 ... C6	336.8	304.7	415.4
Rotational constants ^d /MHz			
A	5 003.6	4 468.1	4 461.0
B	2 003.5	2 227.1	2 230.6
C	1 862.8	1 840.9	1 841.5

(cont.)

Table 1. (continued)

Conformer: ^a	I	II	III
Principal axis coordinates ^d of the H atom of the hydroxyl group/pm			
lal	32.2	77.8	130.9
lbi	192.6	201.5	187.4
lcl	58.4	52.0	79.3
Dipole moment ^e /10 ⁻³⁰ C m			
μ _a	0.60	5.27	2.23
μ _b	2.57	1.77	2.23
μ _c	4.97	2.86	5.17
Energy difference ^f /kJ mol ⁻¹			
	4.1	0.0	4.0

^a See Fig. 1 for definition. ^b Measured from $\text{syn}=0^\circ$. ^c Sum of van der Waals radii: ¹⁵ H ... C (half thickness of aromatic molecule) 290 pm. ^d Calculated from the structures given above in this table. ^e 1 D = $3.335\ 64 \times 10^{-30}$ C m. ^f The total energy of conformer Conformer II was calculated to be $-801\ 955.33$ kJ mol⁻¹ ($-308.876\ 559$ hartree) ^g Energy difference between Conformer II and each of the two other conformations.

9←8 were roughly 2×10^{-7} cm⁻¹. Attempts were next made to find the strongest *b*- and *c*-type transitions of the spectrum, but none was found, presumably because the corresponding components of the dipole moment along the principal inertial axes are too small to produce a spectrum strong enough to be assigned with certainty. This is in keeping with the *ab initio* results of Table 1, which indicate that μ_b and μ_c are considerably smaller than μ_a. The spectroscopic constants (*A*-reduction *I*-representation)¹² obtained by the least-squares method are listed in Table 3. Only Δ_J and Δ_{JK} were fitted with the rest of the centrifugal distortion constants pre-set at zero, because the molecule is not widely different from a prolate symmetrical top ($\kappa = -0.701\ 556$).

Attempts to determine the dipole moment by Stark-effect measurements failed because the transitions were so weak that quantitative measurements could not be made.

The ground-state spectrum was accompanied by the spectra of several vibrationally excited states. The first two excited states of what is presumed to be the torsional vibration around the C1-C4 bond were assigned; their spectroscopic constants are found in Table 4.* Relative intensity measurements using selected transitions performed largely as described in Ref. 13 yielded 72(20) cm⁻¹ for this vibration, compared to 83 cm⁻¹ as calculated by *ab initio* above (MP2/6-31+G** level not given in Table 1).

* 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. B265, Gaithersburg, MD 20899, where they have been deposited.

Table 2. MW spectrum of the ground vibrational state of Conformer II of 1-cyclopropylcyclopropanol.

Transition	Observed frequency ^a /MHz	Obs. – calc. freq./MHz
$J''_{K''-1, K''+1} \leftarrow J''_{K-1, K+1}$		
4 _{0,4} ← 3 _{0,3}	15 891.72	0.08
4 _{1,3} ← 3 _{1,2}	16 997.15	0.03
4 _{1,4} ← 3 _{1,3}	15 464.95	–0.06
4 _{2,2} ← 3 _{2,1}	16 719.60	–0.05
4 _{2,3} ← 3 _{2,2}	16 287.52	0.07
6 _{1,5} ← 5 _{1,5}	25 179.44	0.19
6 _{2,4} ← 5 _{2,3}	25 463.37	0.02
6 _{2,5} ← 5 _{2,4}	24 277.25	–0.01
6 _{3,3} ← 5 _{3,2}	24 841.60	–0.08
6 _{3,4} ← 5 _{3,3}	24 654.13	0.05
6 _{4,2} ← 5 _{4,1}	24 650.24	–0.01
6 _{4,3} ← 5 _{4,2}	24 642.45	0.10
7 _{0,7} ← 6 _{0,6}	26 944.56	–0.15
7 _{1,6} ← 6 _{1,6}	26 775.07	0.00
7 _{2,5} ← 6 _{2,4}	29 807.57	–0.03
7 _{2,6} ← 6 _{2,5}	28 211.26	–0.06
7 _{3,4} ← 6 _{3,3}	29 160.11	–0.06
7 _{3,5} ← 6 _{3,4}	28 769.91	–0.05
7 _{4,3} ← 6 _{4,2}	28 815.57	–0.13
7 _{4,4} ← 6 _{4,3}	28 789.93	0.08
8 _{0,8} ← 7 _{0,7}	30 602.18	–0.03
8 _{1,7} ← 7 _{1,6}	32 908.91	–0.14
8 _{1,8} ← 7 _{1,7}	30 500.36	0.02
8 _{2,6} ← 7 _{2,5}	34 077.12	–0.07
8 _{2,7} ← 7 _{2,6}	32 100.65	–0.11
8 _{3,5} ← 7 _{3,4}	33 563.06	0.00
8 _{3,6} ← 7 _{3,5}	32 862.07	0.03
8 _{4,4} ← 7 _{4,3}	33 017.77	–0.05
8 _{4,5} ← 7 _{4,4}	32 948.91	0.10
8 _{5,4} ← 7 _{5,3}	32 876.91	0.17
8 _{6,2} ← 7 _{6,1}	32 824.54	0.05
8 _{6,3} ← 7 _{6,2}	32 824.54	0.10
8 _{7,1} ← 7 _{7,0}	32 792.70	–0.12
8 _{7,2} ← 7 _{7,1}	32 792.70	–0.12
9 _{0,9} ← 8 _{0,8}	34 270.19	0.04
9 _{1,8} ← 8 _{1,7}	36 603.01	–0.01
9 _{1,9} ← 8 _{1,8}	34 212.28	0.10
9 _{2,8} ← 8 _{2,7}	35 946.22	0.03
9 _{3,7} ← 8 _{3,6}	36 921.40	–0.01
9 _{4,5} ← 8 _{4,4}	37 272.13	0.02
9 _{4,6} ← 8 _{4,5}	37 113.79	–0.06
9 _{7,2} ← 8 _{7,1}	36 916.90	0.03
9 _{7,3} ← 8 _{7,2}	36 916.90	0.04

^a ± 0.10 MHz.Table 3. Ground-state spectroscopic constants^{a,b} of Conformer II of 1-cyclopropylcyclopropanol.

Species:	Parent	Deuterated
No. of transitions:	44	27
R.m.s. dev. ^c /MHz:	0.087	0.077
A_0 /MHz	4 453.230(91)	4 299.201(81)
B_0 /MHz	2 235.045 7(43)	2 225.440 1(59)
C_0 /MHz	1 845.988 1(50)	1 816.421 0(63)
Δ_J /kHz	0.280(29)	0.191(81)
Δ_{JK} ^d /kHz	1.947(68)	2.079(76)

^a A-reduction, I'' -representation.¹² ^b Uncertainties represent one standard deviation. ^c Root-mean-square deviation. ^d Further quartic constants pre-set at zero.Table 4. Spectroscopic constants^{a,b} of Conformer II of 1-cyclopropylcyclopropanol in vibrationally excited states of the C1–C4 torsional vibration.

Vibrational state:	1st ex.	2nd ex.
No. of transitions:	29	23
R.m.s. dev. ^c /MHz:	0.090	0.103
A_v /MHz	4 456.42(10)	4 459.68(13)
B_v /MHz	2 233.626 7(54)	2 232.017 2(75)
C_v /MHz	1 844.622 2(64)	1 843.310 9(96)
Δ_J /kHz	0.281(40)	0.288(55)
Δ_{JK} ^d /kHz	1.71(10)	1.54(16)

^{a-d} Comments as for Table 3.

The deuterated species (deuterioyl group) was studied to locate the position of the H atom of the hydroxyl group. The assignment of this spectrum was straightforward. The spectroscopic constants are found in Table 2. The substitution coordinates¹⁴ for the H atom of the hydroxyl group were calculated as $|a| = 81.35(11)$, $|b| = 194.619(42)$ and $|c| = 56.44(17)$ pm using these spectroscopic constants. These values are in quite good agreement with those predicted for Conformer II (Table 1) and represent conclusive evidence that Conformer II has indeed been assigned and not confused with Conformer III, which would have rotational constants close to those of Conformer II, but widely different coordinates for the H1 atom, as seen in Table 1. Another evidence that the spectrum of Table 2 undoubtedly belongs to Conformer II is the fact that this rotamer has its largest dipole moment along the *a*-axis, whereas Conformer III is predicted to have its largest dipole moment component along the *c*-axis (Table 1).

MW search for further conformations. The above assignments include all the strongest transitions seen in the MW spectrum. However, many unassigned weaker lines remained. It is of course possible that some, or all, of these weak transitions belong to unidentified impurities. Many unsuccessful attempts were made to assign these unassigned transitions to either Conformer I or to Conformer III, both of which were predicted to have one rather large dipole moment component, and to be roughly 4 kJ mol^{–1} less stable than Conformer II (Table 1). The low intensities of the unassigned lines is one indication that both Conformers I and III are considerably less stable than Conformer II. The failure not to obtain an assignment for these transitions points in the same direction.

Zero-point energy corrections are presumed to be small in this case because the lowest fundamental vibrational frequencies (not given in Table 1) calculated at the MP2/6–31+G** level for the three stable rotamers, are rather similar in each case.

Intensity considerations of assigned as well as unassigned transitions lead us to conclude that Conformer II is at least 2 kJ mol^{–1} more stable than any other rotameric form of 1-cyclopropylcyclopropanol. This

experimental estimate is considered to be conservative and is in agreement with the theoretical prediction that Conformer II is about 4 kJ mol^{-1} more stable than I or III.

Structure. It is seen from Table 3 that the experimental rotational constants of Conformer II are very close to those calculated from the MP2/6-31+G** structure (Table 1). In fact, the agreement is better than about 1% for all three rotational constants. This is as good as one can expect because the *ab initio* structure is an approximation of the equilibrium structure, and the rotational constants in Table 3 reflect the r_0 -structure. Moreover, the structural parameters of the cyclopropyl ring are very similar to their experimental counterparts in cyclopropane¹⁰ and bicyclopropyl.¹¹ The substitution coordinates¹⁴ of the H1 atom are also close to the theoretical prediction (Table 1), as remarked above. No experimental data are at hand that could really improve the MP2/6-31+G* structure of Conformer II. The structure shown in Table 1 is therefore adopted as a plausible structure for Conformer II of 1-cyclopropylcyclopropanol. It is expected that any full experimental structure that might be determined in the future will be very close to this one.

Discussion

The choice of Conformer II as the most stable form of 1-cyclopropylcyclopropanol demonstrates the important role even such weak intramolecular H bonding as the present one plays for the conformational properties. The finding made for the title compound thus parallels those made for the other molecules^{1,2} possessing a cyclopropyl ring as proton acceptor.

The H bond in Conformer II is calculated from the structural parameters of Table 1 to have non-bonded H1...C4 and H1...C6 distances of approximately 260 and 305 pm, respectively. The sum of the van der Waals radii of hydrogen and aromatic carbon is 290 pm.¹⁵ The pseudo π -electrons which are the acceptor, are of course not located to a particular atom in this case, but it is quite clear that the distance between the H1 atom and the pseudo π -electrons is so small that the interaction in this case undoubtedly can be called a weak internal H bond. It is also evident that the conditions for H bonding are much better in Conformer II than in the other two rotamers of Fig. 1, because the cyclopropyl group is now rotated to its most favourable position.

The H bond in Conformer II is also characterized by having a O1-H1...C4 angle of approximately 69° , and a O1-H1...C6 angle of about 98° . The O1-H1 and C4-C6 bonds are approximately 26° from being parallel. It is interesting to note that the structure of the H bond in 1-cyclopropylcyclopropanol is actually quite similar to that those seen in cyclopropylmethanol^{3a-c} and 1-cyclopropylethanol^{3d} (where the corresponding values for the structural parameters have been given.^{3d}) The

great similarity between the title compound on the one hand and cyclopropylmethanol^{3a-c} and 1-cyclopropylethanol^{3d} on the other, indicates that the H bond interaction is of similar magnitude in these three compounds.

Acknowledgement. Mrs. Anne Horn is thanked for drawing the figure. Mr. Gunnar Isaksen is thanked for purifying the compound by gas-phase chromatography. V. C. is indebted to the Gottlieb Daimler- and Karl Benz-Stiftung for a graduate fellowship. This work has received support from the Norwegian Supercomputer Committee (TRU) of the Norwegian Research Council through a grant of computer time.

References

- (a) Wilson, E. B. and Smith, Z. *Acc. Chem. Res.* 20 (1987) 257; (b) Møllendal, H. *J. Mol. Struct.* 97 (1983) 303; (c) Møllendal, H. *Structures and Conformations of Non-Rigid Molecules*, Ed. Laane, J., Dakkouri, M., van der Veken, B. and Oberhammer, H., Kluwer Academic Publishers, Dordrecht, Netherlands (1993) 277; (d) Landolt-Börnstein, *Numerical Data and Functional Relationships in Science and Technology, New Series, Vol. II/7 (1976), Vol II/15 (1987) and Vol. II/21 (1992)*, Ed. K.-H. Hellwege, Springer-Verlag, Berlin, Heidelberg, New York; (e) Harmony, M. D., Laurie, V. W., Kuczkowski, R. L., Schwendeman, R. H., Ramsay, D. A., Lovas, F. J., Lafferty, W. J. and Maki, A. G. *J. Phys. Chem. Ref. Data* 8 (1979) 619, (f) Joris, L., Schleyer, P. v. R. and Gleiter, R. *J. Am. Chem. Soc.* 90 (1968) 327; (g) Oki, M., Iwamura, H., Murayama, T. and Oka, I. *Bull. Chem. Soc. Jpn.* 42 (1969) 1986; (h) Oki, M. and Iwamura, H. *Tetrahedron Lett.* 41 (1973) 4003.
- Walsh, A. D. *Trans. Faraday Soc.* 45 (1949) 179.
- (a) Bhaumik, A., Brooks, W. V. F., Dass, S. C. and Sastry, K. V. L. N. *Can. J. Chem.* 48 (1970) 2949; (b) Brooks, W. V. F. and Sastri, C. K. *Can. J. Chem.* 56 (1978) 530; (c) Badawi, H. M. *J. Mol. Struct. (Theochem)* 228 (1993) 93; (d) Marstokk, K.-M. and Møllendal, H. *Acta Chem. Scand., Ser. A* 39 (1985) 429; (e) Hopf, H., Marstokk, K.-M., de Meijere, A., Mlynek, C., Møllendal, H., Svecizer, A., Stenström, Y. and Trætteberg, M. *Acta Chem. Scand.* 47 (1993) 739; (f) Marstokk, K.-M. and Møllendal, H. *Acta Chem. Scand. Ser. A* 38 (1984) 387; (g) Marstokk, K.-M. and Møllendal, H. *Acta Chem. Scand.* 45 (1991) 354.
- de Meijere, A., Kozhushkov, S. I., Späth, T. and Zefirov, N. S. *J. Org. Chem.* 58 (1993) 502.
- Guirgis, G. A., Marstokk, K.-M. and Møllendal, H. *Acta Chem. Scand.* 45 (1991) 482.
- Ø. Waal, Personal communication 1995.
- Frisch, I. M., Trucks, G. W., Head-Gordon, M., Gill, P. M. W., Wong, M. W., Foresman, J. B., Johnson, B. G., Schlegel, H. B., Robb, M. A., Replogle, E. S., Gomperts, R., Andres, J. L., Raghavachari, K., Binkley, J. S., Gonzalez, C., Martin, R. L., Fox, D. J., Defrees, D. J., Baker, J., Stewart, J. J. P. and Pople, J. A., *Gaussian 92*, Revision C, Gaussian, Inc., Pittsburgh, PA 1992.
- Hehre, W. J., Radom, L., Schleyer, P. v. R. and Pople, J. A. *Ab Initio Molecular Orbital Theory*, Wiley, New York 1985, p. 227.
- Macdonald, J. N., Norbury, D. and Sheridan, J. J. *Chem. Soc. Faraday Trans. 2* 74 (1978) 1365.

10. Endo, Y., Chang, M. C. and Hirota, E. *J. Mol. Spectrosc.* 126 (1987) 63.
11. (a) Bastiansen, O. and de Meijere, A. *Acta Chem. Scand.* 20 (1966) 516; (b) Hagen, K., Hagen, G. and Trøttestad, M. *Acta Chem. Scand.* (1972) 3649.
12. Watson, J. K. G. In: Durig, J. R., Ed., *Vibrational Spectra and Structure*, Elsevier, Amsterdam 1977, 6.
13. Esbitt, A. S. and Wilson, E. B. *Rev. Sci. Instrum.* 34 (1963) 901.
14. Kraitchman J., *Am. J. Phys.* 21 (1953) 17.
15. Pauling, L. *The Nature of the Chemical Bond*, 3rd Edn., Cornell University Press, New York 1960, p. 260.

Received June 2, 1995.