Short Communication

Syntheses and Reactions of Some Cyclopropyl-substituted Imines. Part 2. Structural and Conformational Properties of Dicyclopropylketimine as Studied by Microwave Spectroscopy and Quantum Chemical Calculations

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This laboratory is now engaged in research focusing on the syntheses, reactions and properties of cyclopropyl-substituted imines.[1] Another interest has for a long time been the study of intramolecular hydrogen (H) bonding of molecules in the free state.[2] In these imines the H atom of the imine group might perhaps form a weak intramolecular H bond with the pseudo-π electrons of the nearest cyclopropyl ring.

The conformational properties of cyclopropyl-substituted imines in the gaseous state have not previously been investigated. The prototype molecules of this imine series is dicyclopropylketimine (DCK). This compound is small enough to be investigated by microwave (MW) spectroscopy and high-level quantum chemical computations.

The quantum chemical calculations were carried out using the Gaussian 94 program package[3] running on the IBM RS6000 cluster in Oslo. The computations were made in the following manner: A starting geometry was selected. The H1, N1, C1, C2 and C5 atoms (see Fig. 1 for atom numbering) were all assumed to lie in one plane. The conformational properties of DCK are then determined by two dihedral angles conveniently chosen to be the N1–C1–C2–H1 (τ_1 for brevity) and the N1–C1–C5–H7 (τ_2) dihedral angles. These two dihedral angles were each varied systematically in steps of 60°. All structural parameters were fully optimised in HF/4-21G* computations for each combination of these

two dihedral angles. Four low-energy conformers were found in these computations.

Elaborate MP2/6-311++G** computations with full optimisation of the structures were then made for these four rotamers using the 4-21G* geometries as the starting points. Electron correlation is included in this computational scheme using the second-order Møller–Plesset (MP2) perturbation theory[4] with frozen-core electrons.[3] This computational procedure was chosen because it is our experience[5] that the structure (and rotational constants) are rather accurately predicted in computations at this level. Another reason for choosing this computational scheme is that the energy differences between the conformers are normally well reproduced.

The MP2 calculations yielded the same four stable conformers as the HF calculations did. Selected results of the MP2 computations are shown in Table 1. A drawing of the four low-energy conformers is shown in Fig. 1.

B3LYP/6-31G** computations,[6] which are much less expensive than the MP2/6-311++G** calculations, were also carried out. The B3LYP results (not given in Table 1) were rather similar to the MP2 result with regard to the structure and energy differences of the four rotamers. Larger differences were seen for the dipole moments, which are 10–20% less in the B3LYP than in MP2 computations. The vibrational frequencies were not calculated at the MP2 level because of lack of resources. However, no negative frequencies were calculated using the B3LYP procedure. This is another indication that the four rotamers shown in Fig. 1 indeed represent minima on the energy hypersurface.[7]

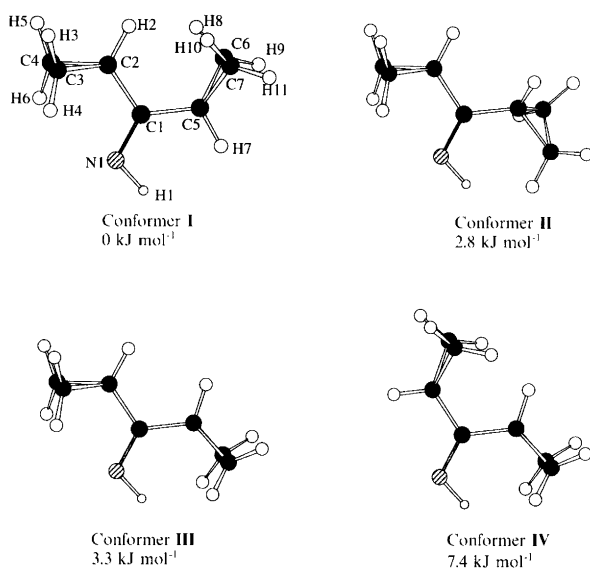* To whom correspondence should be addressed.

Fig. 1. The four low-energy conformers of dicyclopropyl-ketimine found in the quantum chemical calculations. Energy differences were obtained in the MP2/6-311++G** (frozen core) computations. Atom numbering is given on Conformer I.

Comments are warranted for some of the results in Table 1. There is nothing unusual about the bond lengths and bond angles of the four rotamers. The H1, N1, C1, C2 and C5 atoms are co-planar or very nearly so in all of them. Three of the conformers, **I** ($\tau_1 = 180°$, $\tau_2 = 0°$), **III** ($\tau_1 = 180°$, $\tau_2 = 180°$) and **IV** ($\tau_1 = 0°$, $\tau_2 = 180°$), possess a symmetry plane (C_s symmetry), while **II** ($\tau_1 = 182°$, $\tau_2 = -137°$) does not have such a plane. The relative stabilities of the rotamers of **DCK** fall within a narrow range of 7.4 kJ mol^{-1}. It is impossible to say how accurate this number is, but it is expected that each energy difference is accurate to within ± 6 kJ mol^{-1}.

No internal H bond is possible for Conformer **I**, which is predicted to be preferred. Conformer **II**, which is calculated to be about 2.8 kJ mol^{-1} less stable than **I**, might, however, be stabilised by this kind of interaction.

The compound used in this work was synthesised as described in Ref. 1 and purified (Experimental) in order to remove minor amounts of cyclopropanecarbonitrile. This was important because this polar nitrile has a strong and comparatively dense spectrum which overlaps with the much weaker imine spectrum.

The MW spectrum was studied in the 27–46 GHz spectral region at a pressure of roughly 5 Pa and a temperature of -10 °C using the Oslo spectrometer.[8] A study at lower temperatures that would have enhanced the spectral intensities was not possible owing to the low vapour pressure of **DCK**.

The observed spectrum was weak as expected because the Boltzmann population of each rotational level is small for a compound as large as **DCK**. The spectrum is rather dense. It is quite likely that small amounts of unidentified impurities contributed to the spectral density.

Searches were first made for Conformer **I**. This rotamer has its largest dipole moment component along the a-inertial axis. The a-type R-branch transitions of this conformer were found close to the frequencies predicted using the MP2 rotational constants. The assignments were confirmed by Stark modulation studies, MW radio frequency double-resonance experiments performed for ^aR-branch K_{-1} doublet transition with $K_{-1} \geqslant 5$ in the manner described in Ref. 9 using the equipment mentioned in Ref. 10, as well as fitting to Watson's Hamiltonian.[11] A total of about 75 transitions were assigned, 61 of which were used to determine the spectroscopic constants (A reduction, I^r-representation[11]) shown in Table 2.* The transitions not used in the fit were in most cases the weaker ^aR-branch high-K_{-1} doublets overlapped by stronger doublets with lower K_{-1} values. Searches for b-type transitions, including the strongest ones (the high-J, Q-branch transitions), proved futile presumably because they were too weak. It was not possible to make definite assignments of vibrationally excited states owing to insufficient intensities.

Attempts were next made to find the other three rotamers **II–IV** using the rotational constants in Table 1 and the B3LYP dipole moments to make predictions. However, no assignments could be made, presumably because these rotamers have higher energies than Conformer **I**, lower Boltzmann populations and hence weaker spectra.

The rotational constants of Table 2 are in very good agreement with those reported for Conformer **I** in Table 1. Cyclopropyl compounds having a symmetry plane and four out-of-plane methylene groups are expected to have the following relation between the principal moments of inertia (I_a, I_b and I_c): $I_a + I_b - I_c \approx 80 \times 10^{-20}$ m^2 u.[12] This is almost the same as the result shown in Table 2 [80.096(14)], and 79.8 (same units) calculated from the entries in Table 1. The good agreement between the experimental (Table 2) and theoretical (Table 1) rotational constants is presumed not to be fortuitous, but in fact reflects that the MP2 structure is indeed very accurate.

The following conclusions can be drawn from the present study: Dicyclopropylketimine prefers Conformer **I** as its most stable form. Three other rotamers (**II–IV**) are expected to be a few kJ mol^{-1} less stable than **I**. Conformer **I** has a symmetry plane (C_s symmetry) and is not stabilised with an intramolecular H bond. The experimental structure that might be determined in the future for this rotamer is presumed to be very close to the MP2 structure shown in Table 1.

Experimental

Purification of dicylopropylketimine. Dicyclopropylket-imine[1] (1.0 g) was dissolved in anhydrous diethyl ether

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* The spectrum is available from the authors upon request, or from the Molecular Spectra Data Center, National Institute of Standards and Technology, Optical Technology Division, Bldg. 221, Rm. B208, Gaithersburg, USA.

Table 1. Structure, rotational constants, dipole moment and energy differences of Conformers I–IV of dicyclopropylketimine as calculated at the MP2/6-311++G** (frozen core) level of theory. Atom numbering is given in Fig. 1.

	I	II	III	IV
Distance/pm				
C2–C3	152.0	152.1	152.1	151.9
C3–C4	149.9	149.8	149.7	150.4
C5–C6	152.0	150.6	152.0	151.9
C6–C7	150.3	151.1	150.0	150.1
C2–H2	108.4	108.5	108.5	108.5
C5–H7	108.7	108.7	108.5	108.4
N1–H1	102.3	102.3	102.4	102.5
C1–N1	129.1	128.8	129.0	129.1
C1–C2	149.0	148.8	148.9	148.4
C1–C5	148.8	149.6	149.5	149.6
C3–H3	108.3	108.4	108.4	108.4
C3–H4	108.4	108.4	108.4	108.4
C4–H5	108.4	108.4	108.4	108.4
C4–H6	108.4	108.4	108.4	108.4
C6–H8	108.4	108.5	108.5	108.5
C6–H9	108.4	108.4	108.4	108.4
C7–H10	108.4	108.5	108.5	108.5
C7–H11	108.4	108.4	108.4	108.4
Angle/°				
H1–N1–C1	109.6	109.5	110.6	110.1
N1–C1–C2	118.1	119.1	118.4	116.9
C1–C2–C3	117.9	118.2	118.2	121.2
C2–C3–C4	60.5	60.4	60.5	60.3
N1–C1–C5	123.7	126.3	125.8	125.3
C1–C5–C6	121.0	122.0	119.5	119.3
C1–C5–H7	114.0	114.4	115.4	116.5
C2–C1–C5	118.1	114.6	115.8	117.8
C5–C6–C7	60.4	60.5	60.4	60.4
C1–C2–H2	117.2	115.7	116.1	112.7
C2–C3–H3	117.2	117.3	117.1	116.6
C2–C3–H4	115.0	115.0	114.9	117.7
C2–H4–H5	117.2	117.0	117.1	116.6
C2–C4–H6	115.0	115.1	114.9	117.7
C5–C6–H8	117.2	118.2	116.2	116.3
C5–C6–H9	116.7	117.4	117.3	117.3
C5–C7–H10	117.2	116.5	116.2	116.3
C5–C7–H11	116.7	118.0	117.3	117.3
Dihedral angle/°[a]				
H1–N1–C1–C2	180.0	171.2	180.0	180.0
N1–C1–C2–C3	33.9	37.7	34.0	−144.7
C1–C2–C3–C4	−107.5	−108.0	−107.7	−110.1
H1–N1–C1–C5	0.0	3.2	0.0	−0.0
N1–C1–C5–C6	144.8	17.4	−34.5	−34.5
C1–C5–C6–C7	109.9	106.1	108.7	108.6
N1–C1–C2–H2(τ_1)	180.0	−176.4	−179.9	−0.0
C1–C2–C3–H3	143.7	143.1	143.4	141.0
C1–C2–C3–H4	0.5	−0.0	0.5	−2.0
C1–C2–C4–H5	−143.7	−143.6	−143.4	−141.0
C1–C2–C4–H6	−0.5	−0.5	−0.5	2.0
N1–C1–C5–H7(τ_2)	0.0	−137.2	180.0	180.0
C1–C5–C6–H8	1.4	−0.6	−0.1	−0.0
C1–C5–C6–H9	−141.3	−145.4	−142.5	−142.7
C1–C5–C7–H10	−1.4	−5.4	0.1	0.0
C1–C5–C7–H11	141.3	138.9	142.5	142.7
Rotational constants/MHz				
A	3783.4	4891.8	5356.0	3720.4
B	1430.2	1234.3	1162.4	1432.2
C	1240.5	1134.0	1123.6	1236.1

Table 1. (Continued.)

	I	II	III	IV
Dipole moment components[b] and total dipole moment/10^{-30} C m				
μ_a	7.70	5.40	5.37	1.63
μ_b	5.67	6.64	7.47	10.24
μ_c	0.0	2.87	0.0	0.0
μ_{tot}	9.57	9.00	9.21	10.37
Energy difference[c]/kJ mol^{-1}				
	0.0	2.8	3.3	7.4

[a]Measured from *syn*=0°. Clockwise rotation corresponds to positive dihedral angle. [b]Along the principal inertial axes. 1 debye=3.3356×10^{-30} C m. [c]Relative to Conformer I. Total energy of I obtained in the MP2 computations: -858873.10 kJ mol^{-1}.

Table 2. Spectroscopic constants[a,b] of the ground vibrational state of Conformer I of dicyclopropylketimine.

No. of transitions:	61
R.m.s. dev.[c]/MHz:	0.112
A_0/MHz	3771.64(29)
B_0/MHz	1428.6807(65)
C_0/MHz	1239.7779(69)
Δ_J/kHz	0.212(61)
Δ_{JK}[d]/kHz	$-0.182(16)$
$I_a+I_b-I_c/10^{-20}$ m^2 u	80.096(14)

[a]A-reduction I^r-representation.[11] [b]Uncertainties represent one standard deviation. [c]Root-mean-square deviation. [d]Further centrifugal distortion constants pre-set at zero. [e]Conversion factor $505379.05 \times 10^{-20}$ m^2 u MHz.

(50 ml). Dry HCl gas was passed in to the solution for 20 min. The white precipitate (ketimine HCl) was filtered and carefully washed with diethyl ether and dried in a desiccator. The hydrochloride was then suspended in dry diethly ether, and gaseous NH_3 was passed into the solution for 30 min. The precipitate (NH_4Cl) was filtered off, the filtrate was evaporated and the residue was distilled. 0.62 g, b.p. 74 °C (25 mmHg). This procedure was then repeated to give a satisfactory sample for MW examination.

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