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Intramolecular forces: the molecular structure and conformation of 2-cyclopropylpyridine and 4-cyclopropylpyridine

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Abstract

The molecular structure and conformation of 2-cyclopropylpyridine and 4-cyclopropylpyridine have been studied experimentally by gas-phase electron diffraction as well as by ab initio quantum chemical calculations.

2-Cyclopropylpyridine appears exclusively in the bisected form, with the cyclopropyl group pointing towards the nitrogen atom. The 4-cyclopropylpyridine molecules are, however, present as a mixture of conformers, dominated by the bisected one (71.0(6.5)%) along with the perpendicular conformer. The energies of the two cyclopropylpyridines are being compared to the energy of cyclopropylbenzene. The presence of the nitrogen atom is generally found to lower the energy of these molecules. When the orbitals of the cyclopropyl group may interact with the nitrogen lone-pair electrons, as in one of the bisected 2-cyclopropylpyridine conformers, this has a profound effect on the stability of the molecule, resulting in a lowering of the energy by ca. 3 kcal mol^{-1}.

The expected shortening of the distal cyclopropyl C–C bond length is observed in 2-cyclopropylpyridine, while the calculated difference between vicinal and distal C–C bonds had to be assumed in the experimental study of 4-cyclopropylpyridine.

Keywords: Gas-phase electron diffraction; Quantum-chemical calculations; Conformation; Cyclopropyl groups; Intramolecular interactions

1. Introduction

The conjugation between a cyclopropyl group and an unsaturated system is optimal when the plane of the unsaturated group bisects the distal C–C bond of the cyclopropyl group [1–3]. The bisected form of cyclopropylbenzene was, for example, found to be the preferred form in the gas phase, while the energy of the perpendicular form was estimated to be about 1 kcal mol^{-1} above that of the bisected form [4]. Both NMR [5] and solvolysis experiments [6] performed on substituted cyclopropylbenzenes showed that the bisected conformation could be retained when the electronic interaction between the cyclopropyl and phenyl rings had been altered from that of the parent system. When steric effects are important, such as in α-naphthyl- and 9-anthrylcyclopropanes [7] as well as in hexacyclopropylbenzene [8], the perpendicular form was observed in the solid state. A recent gas electron diffraction (GED) study of another sterically crowded molecule, 2,2-dichlorocyclopropylbenzene [9], showed that the stable conformer was rotated 20–30° (away from the chlorine atoms) from the perpendicular form. Essentially, the electronic interaction in cyclopropylbenzene comes about as a donor-acceptor relationship [1]. Due to the higher electronegativity of nitrogen, the pyridyl group is a stronger electron acceptor than the phenyl group. Thus, in 2- and 4-cyclopropylpyridine, the bisected conformers should be more strongly favored than in cyclopropylbenzene. In addition, 2-cyclopropylpyridine may assume two different bisected conformations, one with the cyclopropyl group pointing towards the α-C–H bond (PYR2-C), the other one with it pointing towards the nitrogen atom (PYR2-N). In the latter case the lone-pair electrons on the nitrogen might also interact with the electrons of the cyclopropyl group. In order to gain insight into these problems, we studied the molecular structures and conformations of 2-cyclopropylpyridine (PYR2) and 4-cyclopropylpyridine (PYR4).

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2. Experimental section

Samples of 2- and 4-cyclopropylpyridine were prepared by cyclopropanation of 2- and 4-vinylpyridine, respectively, with dimethylsulfoniummethylide as reported by Levine et al. [10]. The IR- and ^{1}H-NMR-spectroscopic data agreed with the previously reported ones [11]. ^{13}C-NMR data have been published only for 4-cyclopropylpyridine [12]. The ^{13}C-NMR data for 2-cyclopropylpyridine in $CDCl_3$ are as follows: 162.6 (C_{quat}), 149.1 (C-6), 135.7 (C-3), 121.1 (C-5), 120.2 (C-4), 17.0 (C-7), 9.7 [C-8(9)].

The electron diffraction patterns were collected on Kodak Image plates using the Balzers Eldigraph KDG-2 instrument [13,14] at nozzle temperatures of 24/23 °C for PYR2 (LC/SC) and 57 °C for PYR4. The voltage/distance calibration was done with benzene as a reference. The nozzle-to-plate distances were 498.80 (LC: long camera distance) and 248.80 (SC: short camera distance) mm for both molecules, and the electron wavelength was 0.058615 Å. For PYR2 six LC plates and five SC plates were selected for use in the least squares analysis, while three (LC) and five (SC) plates were used for PYR4. The optical densities were measured with a Joyce Loebl microdensitometer.

3. Theoretical calculations

Quatum-chemical calculations have been performed on PYR2 and PYR4 using the GAUSSIAN 98 package [15] at the second-order Möller–Plesset (MP2) level of perturbation theory, using 6-31G* and 6-311G** basis sets. The optimized geometric parameters for the two bisected PYR2 conformers and for the bisected and the perpendicular PYR4 conformers are presented in Table 1, together with the calculated energies. The numberings of the atoms are shown in Fig. 1.

The torsional potential function about the C–C bond connecting the cyclopropyl and pyridinyl groups has been calculated for both molecules at 30° interval. Due to the symmetry of PYR4 it was sufficient to perform the calculations between 0° (bisected) and 90° (perpendicular form) for this molecule, while the calculations for PYR2 covered the interval from 0 to 180°. For PYR2 the bisected

Table 1
Structural parameters obtained by MP2 ab initio calculations for 2-cyclopropylpyridine and 4-cyclopropylpyridine (and pyridine), using the 6-311G** basis set

2-cyclopropylpyridine, Bisected			Pyridine	4-cyclopropylpyridine		
	PYR2-N (0°)	PYR2-C (180°)			Bisected (0°)	Perp. (90°)
N^1–C^2	1.347	1.348	1.344	N^1–C^2	1.344	1.344
N^1–C^6	1.342	1.344	1.344	N^1–C^6	1.343	1.344
C^5–C^6	1.397	1.396	1.398	C^5–C^6	1.397	1.398
C^4–C^5	1.397	1.397	1.396	C^4–C^5	1.401	1.401
C^3–C^4	1.395	1.394	1.396	C^3–C^4	1.403	1.401
C^2–C^3	1.404	1.405	1.398	C^2–C^3	1.396	1.398
C^7–$C^{8/9}$	1.517	1.517			1.517	1.511
C^8–C^9	1.501	1.504			1.503	1.512
C^2–C^7	1.483	1.484		C^4–C^7	1.482	1.493
∠C^2–N^1–C^6	117.8	117.7	116.6	∠C^2–N^1–C^6	116.0	116.4
∠N^1–C^2–C^3	122.4	122.3	123.9	∠N^1–C^2–C^3	124.2	124.0
∠N^1–C^6–C^5	123.8	124.0	123.9	∠N^1–C^6–C^5	124.1	124.0
∠C^4–C^5–C^6	118.3	118.2	118.7	∠C^4–C^5–C^6	119.7	119.4
∠C^3–C^4–C^5	118.5	118.6	118.2	∠C^3–C^4–C^5	116.5	117.0
∠C^2–C^3–C^4	119.3	119.3	118.7	∠C^2–C^3–C^4	119.5	119.4
∠C^2–C^7–H	115.3	112.5		∠C^4–C^7–H	114.4	114.9
∠N^1–C^2–C^7	116.6	115.3		∠C^3–C^4–C^7	122.9	121.5
∠C^3–C^2–C^7	121.0	122.4		∠C^5–C^4–C^7	120.7	121.5
∠C^2–C^7–$C^{8/9}$	118.7	120.8		∠C^4–C^7–$C^{8/9}$	120.3	119.8
∠H–$C^{8/9}$–H	116.6	115.2		∠H–$C^{8/9}$–H	115.3	115.4
∠N^1–C^6–H	115.7	115.6	115.8	∠N^1–C^2–H	115.8	115.8
∠C^5–C^6–H	120.5	120.4	120.3	∠C^3–C^2–H	120.0	120.2
∠C^4–C^5–H	121.4	121.4		∠C^2–C^3–H	119.2	120.4
∠C^6–C^5–H	120.3	120.4		∠C^4–C^3–H	121.3	120.3
∠C^3–C^4–H	120.6	120.5	120.9	∠N^1–C^6–H	115.9	115.8
∠C^5–C^4–H	120.9	120.9	120.9	∠C^5–C^6–H	120.1	120.2
∠C^2–C^3–H	119.8	120.5	120.1	∠C^4–C^5–H	120.3	120.3
∠C^4–C^3–H	121.0	120.2	121.2	∠C^6–C^5–H	119.9	120.4
E (molecule^{-1}) (−363.x) x:	0.9735014	0.969527	(−247.6004983)		0.9680231	0.966248
ΔE (kcal mol^{-1})	0.0	+2.494			0.0 (+3.438)*	+1.114 (+4.552)*

*Relative to PYR2-N. Distances in Å, angles in degrees.