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Molecular structure of 6-cyclopropyl-1,5-diazabicyclo[3.1.0]hexane: gas phase electron diffraction and theoretical study

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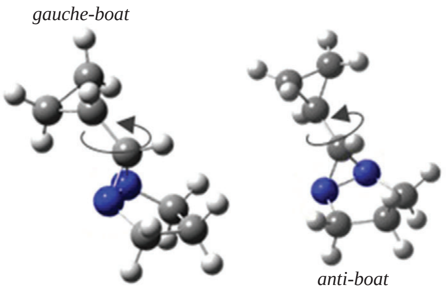
The molecular structure and conformational composition of 6-cyclopropyl-1,5-diazabicyclo[3.1.0]hexane were determined by gas phase electron diffraction and quantum chemical calculations. The gas phase electron diffraction data were well reproduced for the mixture of two conformers with *anti-boat* and *gauche-boat* mutual ring orientation having 15 and 85% relative abundance, respectively. The standard enthalpy of formation of substance under study was calculated using atomization reactions, yielding value of 307.9 ± 3.3 kJ mol^{-1} in gas phase.



Keywords: gas electron diffraction structure, synthesis, *anti-boat* and *gauche-boat* conformers, diazabicyclo[3.1.0]hexanes, diaziridines, enthalpy of formation.

Diaziridine derivatives[1–9] are known to possess neurotropic activity.[10–12] High stability of pyramidal nitrogen atoms of diaziridines makes them simple for study of nitrogen stereochemistry compounds.[7,13,14] The diaziridine ring is vulnerable to ring expansion reactions that leads to formation of various five-eight-membered mono- and bicyclic heterocyclic structures.[16–19] Most alkyl-substituted diaziridines are believed to be promising nontoxic liquid rocket fuel components.[20]

Recently, bonding properties and structural studies of 1,5-diazabicyclo[3.1.0]hexane[2] and 6-methyl-1,5-diazabicyclo-[3.1.0]hexane[8] (Figure 1, structures **1** and **2**) have been carried out by gas electron diffraction and quantum chemical calculations. It has been shown that these compounds exist at 20 °C in the form of *boat* conformation when *n*(N) → σ*(C−C) anomeric effect plays an important role in its stabilization. Adding methyl substituents to C(6) carbon atom of 1,5-diazabicyclo[3.1.0]hexane makes the pyrazolidine moiety of the 6,6-dimethyl-1,5-diazabicyclo[3.1.0.]hexane **3** molecule almost planar.[3] The methyl substituents at C(3) carbon atom in 3,3-dimethyl-1,5-diazabicyclo[3.1.0.]hexane **4** molecule give rise to an equilibrium mixture of 32(8) : 68(8) ratio (*boat*/*chair*) and in 3,3,6-trimethyl-1,5-diazabicyclo[3.1.0]hexane **5** of 26 : 74 ratio in gas phase.[3,9] The obtained results demonstrated great influence of substituents on conformation of 1,5-diazabicyclo[3.1.0]hexane system.

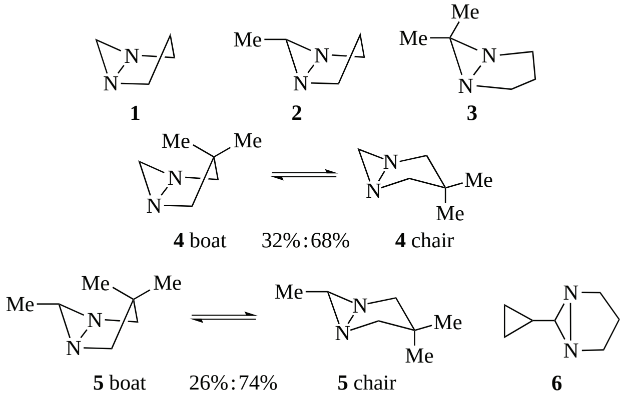


Figure 1 1,5-Diazabicyclo[3.1.0]hexane **1** (ref. 2), 6-methyl-1,5-diazabicyclo[3.1.0]hexane **2** (ref. 8), 6,6-dimethyl-1,5-diazabicyclo[3.1.0]hexane **3** (ref. 3), 3,3-dimethyl-1,5-diazabicyclo[3.1.0]hexane **4** (ref. 3), 3,3,6-trimethyl-1,5-diazabicyclo[3.1.0]hexane **5** (ref. 9), 6-cyclopropyl-1,5-diazabicyclo[3.1.0]hexane **6** (this work).

In this work, we are reporting experimental and theoretical results on studying structural, conformational and bonding properties of one more 1,5-diazabicyclo[3.1.0]hexane representative, namely, 6-cyclopropyl-1,5-diazabicyclo[3.1.0]-hexane **6** (see Figures 1 and 2), synthesized as described.[1]

One of modern trends of organic and medicinal chemistry is synthesis of medicines by combining two or more pharmacologically active moieties in one molecule.[21] Some drugs based on cyclopropane moiety[22] are already in medical practice, for instance, tranylcypromine as monoamine oxidase

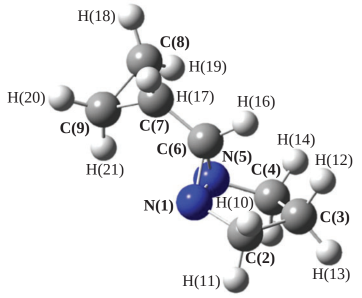


Figure 2 Atom labeling in 6-cyclopropyl-1,5-diazabicyclo[3.1.0]hexane **6**.

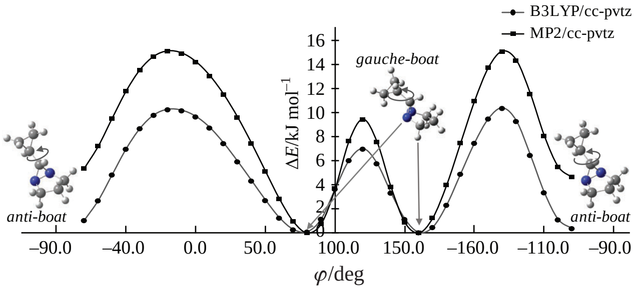


Figure 3 Potential energy curve around C(6)–C(7) bond for 6-cyclopropyl-1,5-diazabicyclo[3.1.0]hexane **6** according to B3LYP/cc-pVTZ and MP/cc-pVTZ calculations with φ = C(9)–C(7)–C(6)–N(1).

inhibitor and ciprofloxacin as antibacterial drug. Existing both diaziridine and cyclopropane rings in one molecule may lead to compounds with new specific action on central nervous system or other useful properties and, therefore, the structure study of such molecules seems relevant.

Using Gaussian 09 program,[23] at the first stage one-dimensional scan was calculated around the C(6)–C(7) bond (see Figure 2) with steps of 10° by applying B3LYP/cc-pVTZ and MP2/cc-pVTZ approaches[24–27] (Figure 3). Geometry optimization and vibrational frequency calculations at minima were performed to prove existence of two low-energy stable configurations of molecule **6**, named *anti* and *gauche* in respect with cyclopropyl ring orientation around the C(6)–C(7) bond. As predicted, *anti* conformer is C_s symmetry one. The six-part cycle, involving diaziriding ring, in both conformers is calculated to be *boat*-shaped. According to B3LYP/cc-pVTZ and MP2/cc-pVTZ calculations, the *gauche-boat* conformer structure is more preferable by energy than the *anti-boat* one. The MP2 calculations predict the *gauche-boat* conformer to be more stable in relative electronic energy by 4.7 kJ mol^{-1}, B3LYP calculations show the preference for *gauche* orientation by about 0.3 kJ mol^{-1}. As to relative abundance of 6-cyclopropyl-1,5-diazabicyclo[3.1.0]hexane **6** conformers in equilibrium mixture, all methods predicted the total abundance of *gauche-boat* conformer: 59% B3LYP/cc-pVTZ *vs*. 86% MP2/cc-pVTZ (Table 1).

The vibration amplitudes and harmonic vibrational corrections to r_{h1} structure were calculated from B3LYP/cc-pVTZ force fields using the SHRINK program.[28] The resulting amplitudes and vibrational corrections (see Online Supplementary Materials, Tables S5, S6) were employed for the GED analysis from the B3LYP/cc-pVTZ computed values. The GED data were analyzed by applying the least squares method to the molecular intensities using UNEX program.[29] The independent parameters used in the structural analysis are given in Table S9 with some geometrical parameter values refined in same groups due to high correlation.

Table 1 Equilibrium distribution of *anti-boat* and *gauche-boat* conformers of 6-cyclopropyl-1,5-diazabicyclo[3.1.0]hexane **6**.[a]

Conformer	ΔE_e	ΔH	S_{298}	ΔG_{298}	p_{298}
		B3LYP/cc-pVTZ			
gauche-boat	0.0	0.0	373.6	0.00	58.8
anti-boat	0.3	–0.2	369.8	0.88	41.2
		MP2/cc-pVTZ			
gauche-boat	0.0	0.0	370.5	0.00	86.0
anti-boat	4.7	4.1	369.0	4.49	14.0

[a] ΔE_e (kJ mol^{-1}) is the relative electronic energy; $H = E_e$ + ZPE (kJ mol^{-1}), where ZPE is the zero point energy correction calculated from vibrational frequencies; S_{298} (J K^{-1} mol^{-1}) is the entropy value at 298 K calculated using frequencies and including the entropy of mixing (Rln2) for *gauche-boat* conformer with C_1 symmetry, which are present as an equimolar mixture of the two optical isomers; ΔG_{298} is the Gibbs free energy difference (kJ mol^{-1}); p_{298} is the mole fraction of conformers (%) according to Boltzmann distribution law.

Natural bond analysis was carried out to locate orbital interactions giving structural stabilization of conformers. In most abundant boat conformers, the strong n(N) → σ*(C−C) interactions with stabilization energy, E(2) = 4.2 kcal mol^{-1}, for both *anti-boat* and *gauche-boat* forms have been pointed out. The lone pair of N(5) atom interacts with antibonding orbital of the C(3)–C(4) bond {n[N(5)] → [C(3)–C(4)]} as well as the lone pair of N(1) atom interacts with the antibonding orbital of C(2)–C(3) bonds {n[N(1)] → σ*[C(2)–C(3)]}. Meanwhile, the stabilization energies of the same interactions for *anti-chair* and *gauche-chair* conformers were significantly less and equal to 1.1 kcal mol^{-1} according to B3LYP/cc-pVTZ calcualtion. Anomeric effect reported for 1,5-diazabicyclo[3.1.0]hexane **1** and 6-methyl-1,5-diazabicyclo[3.1.0]hexane **2** structures also occurs in 6-cyclopropyl-1,5-diazabicyclo[3.1.0]hexane **6**, causing stabilization of all possible boat conformations.

Comparison between results of orbital interaction stabilization for *anti-boat* and *gauche-boat* forms reveals the similar trending. The strongest interactions with E(2) varying from 4.3 up to 5.0 kcal mol^{-1} interactions are related to the three-membered ring orbital overlapping, σ(C–C) → σ*(C–C), where C is C(7), C(8) or C(9), and σ[N(5)–N(1)] → σ*[C(6)–N(5)(1)]. Atom in Molecules (AIM) theory calculation resulted in no critical points between any nitrogen and hydrogen atoms. NBO orbital interaction analysis was neither showed the presence of possible hydrogen bond.

Structural analysis performed for 6-cyclopropyl-1,5-diazabicyclo[3.1.0]hexane **6** conformer mixture according to mole fraction conformer estimation found from MP2/cc-pVTZ values led to better quality-of-fit disagreement factor being equal to 0.053. Radial distribution curve (Figure 4) gives similar arrangement of atom–atom distances of two stable conformation. Most different terms such as C(9)···N(1); C(8)···N(5) are seen to be effected by *anti* or *gauche* position of cyclopropyl fragment. Because of fixing amplitudes for internuclear distances involving hydrogen atoms, some dissimilarity in radial distribution curve is taking place. Reasonable disagreement factor and refining error values along with molecular intensities similarities let the data obtained to be concerned as reliable.

Based on main conformer geometry information from GED and quantum chemical calculations, the standard enthalpy of formation of 6-cyclopropyl-1,5 diazabicyclo[3.1.0]hexane **6** in the gas phase was estimated using calculations of Gaussian-4 composite method. To obtain it, atomization reaction approach was employed; the resulting value of enthalpy formation of *gauche-boat* conformer is found 307.9 ± 3.3 kJ mol^{-1}. As can be calculated from B3LYP/cc-pVTZ approximation, the *anti-boat* conformation of 6-cyclopropyl-1,5-diazabicyclo[3.1.0]hexane **6** is less by energy (ΔE_0) by 11.8 kJ mol^{-1} than the *anti-chair* conformer (Figure S10), and the *anti-chair* conformer presence was excluded from structural GED analysis consideration due to insignificant amount in equilibrium total conformer mixture. For unsubstituted 1,5-diazabicyclo[3.1.0]hexane **1** and for 6-cyclopropyl-1,5-diazabicyclo[3.1.0]hexane **6**, the *boat* conformation is in abundance; meanwhile, for 3,3-dimethyl-1,5-diazabicyclo[3.1.0]hexane **4** and 3,3,6-trimethyl-1,5-diazabicyclo[3.1.0]hexane **5** structures, the *chair* conformation rather than *boat* one is preferable.

Main geometrical parameters of 6-cyclopropyl-1,5-diazabicyclo[3.1.0]hexane **6** and related molecular structures **1**–**5** are collected in Table 2. It might be emphasized that N–N bond distance of *boat* conformer is shorter by approximately 0.03 Å than that for *chair* conformer. Worthwhile is a good

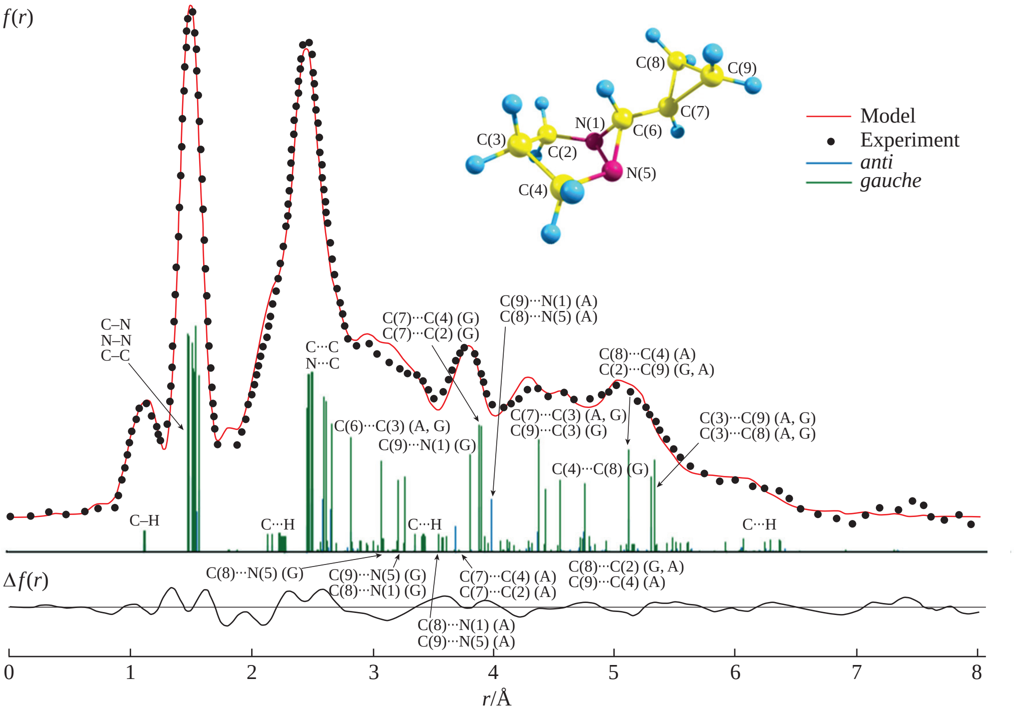


Figure 4 Radial distribution curve of 6-cyclopropyl-1,5-diazabicyclo[3.1.0]hexane **6**.

Table 2 Structural parameters of 6-cyclopropyl-1,5-diazabicyclo[3.1.0]hexane **6** in comparison to related substances from GED data analysis.

Parameter^{a,b}	1,5-Diazabicyclo[3.1.0]hexane derivatives								
	6 (this work)		**2** (ref. 8)	**1** (ref. 2)	**3** (ref. 3)	**4** *boat*⇔*chair* (ref. 3)		**5** *boat*⇔*chair* (ref. 9)	
	anti- *boat* 15%	*gauche-* *boat* 85%	GED *boat* (Cs)	GED *boat*	GED *boat*	GED *boat*	GED *chair*	*boat* 26%	*chair* 74%
C(6)–N(1), C(6)–N(5)	1.451(21)	1.455(21) /1.448(21)	1.440(2)	1.442(2)	1.455(6)	1.444(7)	1.443(7)	1.443(2)	1.442(2)
N(1)–N(5)	1.518(17)	1.516(17)	1.512(2)	1.506(13)	1.522(7)	1.512(7)	1.545(7)	1.520(2)	1.554(2)
C(2)–N(1), C(4)–N(5)	1.483(18)	1.483(18) /1.483(18)	1.466(2)	1.469(4)	1.472(7)	1.468(7)	1.475(7)	1.465(2)	1.471(2)
C(2)–C(3), C(3)–C(4)	1.538	1.538/1.538	1.523(2)	1.524(7)	1.538(7)	1.541(7)	1.527(2)	1.539(2)	1.525(2)
C(6)–C(7)	1.502(21)	1.508(21)	1.487(2)	–	1.505(7)	–	–	1.490(2)	1.490(2)
C–H	1.097(4)	1.096(4)	1.073–1.077(7)	1.100(5)$_{av}$	1.095(6)$_{av}$	1.091(6)$_{av}$	1.091(6)$_{av}$	1.102(9)	1.103(9)
∠N(1)–C(2)–C(3), ∠N(5)–C(4)–C(3)	108.0(21)	108.1(21) /108.0(21)	110.2(4)	106.5(9)	109.3(18)	109.8(24)	106.0(22)	108.8(14)	105.7(14)
∠C(2)–C(3)–C(4)	102.7(27)	102.7(27)	99.9(4)	104.0(10)	105.1(20)	102.3(28)	100.4(24)	101.5(15)	103.6(15)
∠N(1)–N(5)–C(4), ∠N(5)–N(1)–C(2)	107.3(9)	107.6(9) /107.2(9)	106.1(2)	107.7(4)	108.2(7)	107.6(9)	105.8(9)	105.9(5)	107.9(5)
∠N(1)–N(5)–C(6), ∠N(5)–N(1)–C(6)	58.5(3)	58.7(3) /58.3(3)	58.3(1)	58.5^c	58.5^c	58.4^c	57.6^c	57.4(1)	58.2(1)
∠N(1)–C(6)–N(5)	63.1(6)	63.0(6)	63.3(1)	63.0(11)	63.1^c	63.2^c	64.7^c	65.2(1)	63.6(1)

[a] Bond lengths are in Å, bond angles and torsional angles are in degrees. [b] Values in parentheses are estimated total errors (2.5σ). [c] Assumed at the value from B3LYP/cc-pVTZ quantum chemical calculations.

agreement between structural parameter of related compounds and 6-cyclopropyl-1,5-diazabicyclo[3.1.0]hexane **6**. The C(2)–N(1) and C(4)–N(5) bond distances are being in error limits by 0.01 Å longer than those for other 1,5-diazabicyclo-[3.1.0]hexane derivatives.

In conclusion, the fist molecular structural and conformational behavior investigation of 6-cyclopropyl-1,5-diazabicyclo[3.1.0]-hexane **6** has been performed by gas phase electron diffraction experiment complemented by quantum chemical calculations. The two most stable conformers of 6-cyclopropyl-1,5-diazabicyclo[3.1.0]hexane **6** at 298 K possess *anti-boat* and *gauche-boat* mutual ring orientation. The anomeric effect arisen from $n(\mathrm{N}) \rightarrow \sigma^*(\mathrm{C{-}C})$ interaction impacts on stabilization of *boat* conformation of 6-cyclopropyl-1,5-diazabicyclo[3.1.0]-hexane molecular structure.

We respectfully dedicate this paper to the memory of our esteemed late colleague, Professor Nina N. Makhova, N. D. Zelinsky Institute of Organic Chemistry, one of the leader scientists in nitrogen-containing heterocycles chemistry.

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Online Supplementary Materials

Supplementary data associated with this article can be found in the online version at doi: 10.1016/j.mencom.2022.07.015.

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