**Intramolecular inversions, structure and conformational behavior of gaseous and liquid
N-cyanopiperidine. Comparison with other 1-cyanoheterocyclohexanes**

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ABSTRACT

The molecular structure and intramolecular inversions of N-cyanopiperidine (**CNP**) were studied by various quantum chemical methods and using synchronous gas electron diffraction/mass spectrometry (GED/MS) and IR spectroscopy. The contribution of the equatorial conformer was found **GED** 52(6), **IR** 60(6), **B3LYP** 77, **B3LYP-GD3** 67, **M062X** 59, **MP2** 54%. Interpolation using **CCSD(T)-F12/CBS** predicts $E_{\text{ax}}-E_{\text{eq}}=0.26$ kcal/mol. The NBO analysis shows a strong ~~hyper~~conjugation of the nitrogen atom lone pair with the triple bond making the $r(\text{N}-\text{C}_{\text{CN}})=1.355(3)$ Å distance as short as a typical sesquilateral bond.

A low energy barrier for the Eq→Ax transition of 1.0–2.3 kcal/mol in **CNP** leads to difficulties in NMR conformational ratio studies. This leaves the GED method almost as the only experimental method to study both structural and conformational properties.

Conformational properties of the related compounds are found to depend on the X–C_{CN} bond distance and ~~hyper~~conjugation between the CN group and the lone pair on the heteroatom. The contribution of the axial form of 1-cyano-heterocyclohexanes increases in the series of heteroatoms X in the cyclohexane ring: N→C→Si→P.

Keywords: N-Cyanopiperidine, Conformational analysis, Gas-phase electron diffraction, IR spectra, Quantum chemical calculation.

1. INTRODUCTION

Derivatives of saturated six-membered heterocyclic compounds are widely used in pharmacy, polymer chemistry and other fields. Representative molecules are cyclohexane derivatives in which the ring methylenes are substituted by either one or more heteroatoms (mainly nitrogen, oxygen, silicon, phosphorus or sulfur). Substitution of a hydrogen atom attached to the ring heteroatom by another atom or functional group (halogen, alkyl, phenyl, etc.) creates options for the substituent to occupy an equatorial or axial position relative to the ring. The determination of equatorial-axial equilibria in derivatives of saturated six-membered heterocyclic compounds has provided valuable information regarding the nature of steric interactions in organic molecule. The conformational properties of saturated heterocyclic six-membered rings were reviewed, for example, in Ref. [1].

The investigation of equatorial-axial conformational preferences of carbonitrile group in saturated six-membered ring traces back to the 1960s. Both equatorial and axial conformers of **cyanocyclohexane** were found to exist in the gas phase and in solution [2–5] and for **1-cyano-silacycloxane** in the gas phase [6,7].

1-cyanopiperidine (**CNP**, also known as 1-piperidinecarbonitrile) was mentioned as trapping reagent and solvent [8], but, to our knowledge, no results of theoretical calculations or experimental data on the molecular structure and conformational behavior of **CNP** are available.

For a variety of alkyl-, alkenyl-, alkynyl-, aryl-piperidine and R_nX-piperidine (R=H, CH₃; n=1: X=O, S; n=2: X=N, P) derivatives the conformations and conformational preferences were described recently [9–12]. The present study continues our systematic investigations of N-piperidine derivatives by exploring the conformational behavior and geometric structure of **CNP**, which was studied by gas-phase electron diffraction/mass spectrometric (GED/MS) experiments, IR spectroscopy and extended quantum chemical (QC) calculations.

2. EXPERIMENTAL

2.1. GED-MS experiment

A sample of **CNP** was purchased from the Aldrich-Sigma Company, 99%. The diffraction patterns were recorded during a combined gas-phase electron diffraction and mass-spectrometric experiment carried out using the *EMR-100/APDM-1* unit [13,14]. The sample of **CNP** was evaporated from a molybdenum cell with a cylindrical effusion nozzle of $0.6 \times 1.2 \text{ mm}^2$ size (diameter $\times$ length) at 305(3) K. The conditions of the GED/MS experiment and data refinement details are given in Supporting Information, Table S1 and related chapters.

Mass spectra (EI, 50 eV) of the effusing molecular beam were recorded simultaneously with the collection of the diffracted electrons. The mass spectrum is in good agreement with the NIST data [15], Figure S1. The major peaks corresponds to ions C_3H_6^+ , C_2H_4^+ , NCNCH_3^+ , $\text{NCNC}_2\text{H}_5^+$, $\text{C}_6\text{N}_2\text{H}_9^+$ and M^+ , with intensities 100, 35, 45, 28, 35 and 45%, respectively. No ions with m/e higher than 111 Da (M^+) were detected. The relative intensities of the ions in the mass spectra showed no change during the course of the experiment. In addition, we recorded mass spectra at different ionizing electron energies. The contribution of the fragment ions decreases with lower electron energy. At the energy as low as *ca.* $E_i=10 \text{ eV}$, the electron impact produces the molecular ion, $m/z=111 \text{ Da}$, exclusively (see Figure S2) which is the evidence that the only species present in the gas is **CNP**.

2.2. IR Spectroscopy

The IR spectrum of **CNP** in liquid phase was registered in the range 400 to 4000 cm^{-1} on an Avatar 360 FT-IR ESP spectrometer at room temperature with KBr windows. Deconvolution of the peaks was performed using the program Fityk, version 0.9.8 [16].

2.3. Computational details

Quantum chemical (QC) calculations of the **CNP** conformers were performed with Gaussian 09 [**Error! Reference source not found.**]; in case of MP2/cc-pVTZ calculations, the Firefly QC package version 8.0.0 [18] was used, which is partially based on the GAMESS (US) [19] source code.

A recent benchmark study of DFT methods confirmed the general success of both M062X and B2PLYP-D functionals in calculating the energies of main-group molecules [20]. Moreover, the B3LYP-D results, where an empirical dispersion correction has been added, of the monosubstituted cyclohexanes and silacyclohexane are in good agreement with the CCSD(T) results [21]. Thus, in this paper, the geometry and vibrational calculations were performed using DFT (with B3LYP-~~GD3~~ and M062X functionals) and MP2 method with the 6-311G** and cc-pVTZ basic sets. The energy difference ΔE of **CNP** also were obtained at the MP4 and CCSD(T) methods on the MP2/6-311G** and/or MP2/cc-pVTZ optimized geometries.

High-level coupled cluster calculations were carried out (using the ORCA package, version 3.0.3) [22] on MP2/def2-TZVP [23,24] optimized geometries in order to get accurate potential energy differences between the axial and equatorial conformers. Electronic energy differences were calculated using explicitly correlated MP2 and coupled cluster theory [25] as implemented in ORCA. The relative electron energy at the CCSD(T)-F12/CBS (CBS=complete basis set) level was estimated with the MP2-F12 method that converges quickly to the complete basis set limit (CBS) and then applying a CCSD(T)-F12 correction to the MP2-F12/large basis value:

$$\Delta E^{\text{CCSD(T)-F12/CBS}} \approx \Delta E^{\text{MP2-F12/large basis}} + (\Delta E^{\text{CCSD(T)-F12/small basis}} - \Delta E^{\text{MP2-F12/small basis}})$$

The MP2-F12 calculations were performed with the correlation consistent basis sets for explicitly correlated methods [21] up to the cc-pVQZ-F12 level. The ΔE value changed by ~ 0.002 kcal/mol when going from the TZ-F12 to QZ-F12 and can be considered converged w.r.t. to basis set size. The $(\Delta E^{\text{CCSD(T)-F12/small basis}} - \Delta E^{\text{MP2-F12/small basis}})$ term was calculated at the CCSD(T)-F12 and MP2-F12 level with cc-pVDZ-F12 basis set and was 0.187 kcal/mol, demonstrating that MP2 calculations can differ considerably from CCSD(T). Auxiliary basis sets (CABS) in the form of cc-pVnZ-F12/OptRI were used in all calculations [24]. Similar CCSD(T)/CBS protocols have been used in studies on silacyclohexanes [7].

The potential energy surface (PES) profile for the nitrogen inversion process was scanned by varying the C5 $\cdots$ N–C6 angle with a step of 10° by B3LYP, M062X and MP2 methods with the 6-311G** basis set. The transition structures were calculated using the Berny algorithm implemented into the Gaussian program package, keyword TS.

The ring inversion for axial-to-equatorial through the *twist* form was studied by scanning the dihedral angle N–C1–C2–C3 with step size of 5° with all other geometric parameters being optimized. The energy pathway for the equatorial-to-axial interconversion of CNP was calculated using the quadratic synchronous transit approach (*Synchronous Transit-Guided Quasi-Newton* – STQN) [26,27] method with keywords QST2 and PATH at M062X/6-311G** level. Transition states were optimized by QST2 calculations.

The Natural Bond Orbital (NBO) analysis was performed at the DFT level with cc-pVTZ basis set using the NBO 6.0 program [28,29].

3. RESULTS AND DISCUSSION

3.1 Energies

The six-membered piperidine ring is *chair*-like in its lowest energy conformations [1,30]. The substituent bonded to a nitrogen atom may exist in axial or equatorial positions about the piperidine ring. The energy difference between the axial and equatorial conformations in N-substituted piperidines arises from the steric repulsion caused by 1,3-syn-diaxial repulsion, which is absent in the equatorial position [21], and also depends on the size of the substituent (see, for example [9,31]).

Calculated relative energies and free Gibbs energies along with the equilibrium population of these conformers in the gas phase at room temperature are summarized in Table 1 (see also Table S2 in Supporting Information for more details). According to the QC calculations, **CNP** can exist in form of equatorial and axial conformations with a C_s symmetry, Figure 1.

The DFT-B3LYP method predicts the equatorial conformer to dominate with the relative total electron energy difference $\Delta E = 0.7\text{--}0.8$ kcal/mol and $\Delta G^\circ = 0.74$ kcal/mol, which corresponds to an **Eq:Ax** ratio of *ca.* 78:22%. The DFT method with B3LYP-~~GD3~~ functional, where an empirical dispersion correction has been added, decreases the ΔE and ΔG° values by 0.4 and 0.3 kcal/mol, respectively. In the case of the M062X functional, the energy differences are even smaller, with ΔE from -0.03 to 0.15 kcal/mol and ΔG° from 0.25–0.31 kcal/mol, implying **Eq:Ax** ratios of 55–62%.

The MP2 calculations predict almost equal abundance conformers: $\Delta E = -0.15$ (6-311G**) and 0.01–0.11 (cc-pVTZ) kcal/mol, and $\Delta G^\circ = 0.01$ (6-311G**) and 0.11–0.20 (cc-pVTZ) kcal/mol. Higher level, MP4 and CCSD(T), single point relative electron energy

calculations with the MP2/6-311G** and MP2/cc-pVTZ optimized geometries did not change the MP2 results.

Table 1: Relative total electron energy ΔE , free Gibbs energy ΔG (kcal/mol) and molar fraction (%) of the equatorial conformer of **CNP**

Quantum chemical calculations ^a				GED, 305K	IR, RT (liquid)
Method/basis set	ΔE^b	$\Delta G^\circ{}^b$	X_{Eq}	X_{Eq}	X_{Eq}
B3LYP	0.71 ÷ 0.80	0.71 ÷ 0.75	77 ÷ 78	52(6) $\Delta G^\circ=0.05(15)^c$	60(6) $\Delta G^\circ=0.24(15)$
B3LYP- GD 3	0.32 ÷ 0.41	0.39 ÷ 0.45	66 ÷ 69		
M062X	−0.03 ÷ 0.15	0.12 ÷ 0.32	55 ÷ 63		
MP2(FC)	−0.15 ÷ 0.11	0.02 ÷ 0.20	51 ÷ 58		
MP2(Full)	−0.15 ÷ 0.01	0.01 ÷ 0.20	51 ÷ 55		
MP4//MP2(FC)	−0.15 ÷ 0.12	—	—		
CCSD(T)//MP2(FC)	−0.04 ÷ 0.24	—	—		
MP2/def2-TZVP	0.05	0.18	57		
MP2-F12/CBS	0.08	—	—		
CCSD(T)-F12/CBS	0.26	—	—		
^a The results obtained with 6-311G**, 6-311G+** and cc-pVTZ are compiled within the indicated intervals, see Table S2 in Supporting Information for more details.					
^b $\Delta E=E_{\text{ax}}-E_{\text{eq}}$, $\Delta G^\circ(298\text{K})=G^\circ_{\text{ax}}-G^\circ_{\text{eq}}$;					
^c Uncertainties were estimated on the base of those for the x value, i.e. ±6%.

Figure 1: Conformers of **CNP** with atom numbering

Similar situations, where the B3LYP functional predicted a noticeably higher contribution of the equatorial conformer, were encountered for several other saturated heterocyclic six-membered compounds, see Refs. [21,32,33]. Those authors concluded that the popular B3LYP functional performs quite badly for those systems, compared to CCSD(T)/CBS, while they found good agreement between the M062X and CCSD(T) results. In our case, the MP2 results are in excellent agreement with and CCSD(T)/CBS results and GED data (see below).

It is to be noted that the contribution of the equatorial conformer increases as the more sophisticated basis set is applied – the lowest values in the intervals (Table 1) correspond to the 6-311G** basis set.

3.2 Intramolecular inversion

The transition path between the equatorial and axial positions of the carbonitrile by *nitrogen inversion* was calculated by optimization of all geometric parameters at fixed C5...N-C6 angle values from 100° to 180° for the axial, and from 150° to 180° for the equatorial conformers, with a 10° step, see Figure 2. The transition state located using the keyword TS in the Gaussian input has a nearly planar shape of the nitrogen atom bond configuration and lies by *ca.* 1.0 (B3LYP), 1.3 (M062X) and 2.3 (MP2) kcal/mol above the equatorial form. The imaginary frequency 63i (B3LYP), 82i (M062X) and 104i (MP2) cm⁻¹ in the transition state corresponds to the nitrogen inversion. These barriers are much lower compared to those estimated for N-methylpiperidine (7.8 – 8.0 [34] and 9.6 [35] kcal/mol) and calculated at the MP2/6-311++G** level for piperidine, 4.9 kcal/mol [36]. This may be due conjugation between the electron lone pair on the nitrogen atom and the carbonitrile group. Moreover, in another derivative with conjugated π -system, phenylpiperidine, the bulkier substituent resulted in a *ca.* 1.0 kcal/mol higher barrier [11], than for the carbonitrile group.

The nitrogen inversion is indeed the lowest energy pathway for the **Eq**⇌**Ax** transition. In our recent papers [9,11], for a dozen of N-piperidine substituted compounds it was shown that the transition via the ring inversion has a much higher energy barrier, up to 14 kcal/mol, as compared with the nitrogen inversion, 1 to 10 kcal/mol.

Such low barriers make the NMR method inapplicable for axial-to-equatorial equilibrium monitoring. Thus the currently most suitable and reliable method, taking into account the controversial QC results, for solving such problems is gas-phase electron diffraction, GED.

Figure 2: The energy pathway for nitrogen inversion of **CNP** calculated at B3LYP, B3LYP-D3, M062X and MP2 levels with 6-311G** basis set.

The *ring inversion* was furthermore explored by scanning it at fixed N-C1-C2-C3 dihedral angle at the M062X/6-311G** level with a step size of 5°. The procedure turned out to be rather complicated: when starting from the axial conformer, the step next after an almost *half-twist* shape of the ring ($\angle$ N-C1-C2-C3 $\approx$ 5° and $\Delta E\approx$ 10.5 kcal/mol) transforms the molecule to a *boat* structure with equatorial position of the carbonitrile group, see Figure S3 in Supporting information. Further scanning located two minima at -30° and -60°, and relative energies $\Delta E\approx$ 5.5 and 5.8 kcal/mol, both correspond to *twist* conformers indicated as **T2** and **T1**, respectively. However, further steps do not lead to the chair-equatorial structure but instead increase the energy dramatically, resulting in a ‘ring cleavage’ at *ca.* -150°. A similar situation

takes place when starting from the equatorial conformer. The ‘jump’ then occurred after *ca.* 10° and 8.5 kcal/mol, and kept the equatorial position of the substituent attached to a *half-twist* shaped ring.

In a second step, a STQN method with keywords QST2 and PATH aimed to search for a reaction pathway for the *chair-to-twist* and *twist-to-twist* transitions. The combined PES profile is given in Figure 3(a). In this case, the maxima **I** to **III** are of structures different from those located by scanning the N–C1–C2–C3 torsion angle (compare with Figure S3). An attempt to prove these maxima to be transition states by geometry optimization using a keyword TS failed when starting from structures at these maxima.

Finally, a combination of the keywords QST2 and FREQ located three maxima, TS1, TS2 and TS3, to be the transition states for the transitions Ax–T2, T2–T1 and Eq–T2’ as possessing one imaginary frequency each: *i*170 (TS1 and TS3) and *i*80 cm⁻¹ (TS2 and TS2’). Nevertheless, it is to be pointed out that this approach yielded TS1 and TS3 to be identical, see Figure 3(b) with the relative energies lying *ca.* 8.3 kcal/mol above the chair forms.

For comparison, the free Gibbs energy barrier of ring inversion of 1-cyanosilacyclohexane is $\Delta G_{(e \rightarrow a)}^\# = 5.6(1)$ kcal/mol from NMR spectroscopy [7]. Thus, the short N–Ca bond nearly doubles the energy barrier of the ring inversion process as compared with the longer C–Si bond.

Figure 3: The energy pathways for the ring inversion of **CNP** calculated at M062X/6-311G** level.

3.3 GED analysis

The molecular structure of both conformers of **CNP** with atom numbering is shown in Figure 1. The following independent geometric parameters were used to describe the geometry – *equatorial* conformer: bond distances N1–C1, C1–C3, N1–C6, C6–N2 and C1–H1; bond angles C1–N1–C2, N1–C1–C3, C1–N1–C6, N1–C6–N2, H1–C1–N1, H1–C1–C3; dihedral angles C3–C1–N1–C2, C5–C3–C4–C2; *axial* conformer: bond angle C1–N1–C6. For the both conformers,

the Cs symmetry was fixed as found in the QC calculations. All other geometrical parameters for the both conformers were described by the parameters analogous to those in the equatorial conformer and corrected by adding the differences taken from MP2/6-311G** calculations.

Vibrational amplitudes for all three conformers were refined in seven groups according to the specific regions in the radial distribution: 0 – 1.3, 1.3 – 1.8, 1.8 – 2.7, 2.7 – 3.2, 3.2 – 4.4, 4.4 – 5.1, 5.1 – 8.0 Å. The differences between the amplitudes within each group were constrained to the calculated values. The vibrational corrections $\Delta r = r_{hl} - r_a$ and starting amplitudes were calculated with the SHRINK program [37,38] using the so-called second approximation, in which a harmonic approach with a nonlinear relation between Cartesian and internal coordinates were applied on the basis of the force field estimated in the QC calculations at the MP2/6-311G** level.

With these constraints, the independent geometric parameters and seven groups of vibrational amplitudes were refined simultaneously along with molar fractions of the conformers. Experimental and theoretical sM(s) curves along with their difference $\Delta sM(s)$ are given in Figure S4 in Supporting Information. The experimental radial distribution function $f(r)$ derived by Fourier transformation of the molecular intensities is shown in Figure 4, together with difference curves between experimental and calculated (MP2/6-311G**) $f(r)$ functions for the both structures.

Figure 4: Experimental (black dots) and theoretical (black line) radial distribution curves $f(r)$ for refined mixture 52:48% of **Eq:Ax** conformers; colored lines correspond to refinement of all parameters under assumptions of the individual conformers. Differences $\Delta f(r)$ “Experim.–Theor.” are given at the bottom.

The refinement of the molar fraction of equatorial and axial conformers simultaneously with refinement of structural parameters converged to a vapour composition of **Eq:Ax**=52(3):48(3)%, where the uncertainties are $3\sigma_{LS}$.

Results of the refinement of all parameters at fixed conformer contribution are plotted in Figure S5 in Supporting Information. The optimal conformer ratio was found to be **Eq:Ax**=52(6):48(6)% with the uncertainty estimated using Hamilton’s criterion [39] at 0.05 significance level ($R_{f, \min}=2.14\%$). Calculated (MP2/6-311G**) geometric and vibrational

parameters without any refinement demonstrated a somewhat worse fit to the experimental $sM(s)$ function, $R_f = 13.0$ and 10.0 % for **Eq** and **Ax** conformers, respectively.

The free Gibbs energy was estimated on the base of the conformer ratio determined from the least squares analyses of GED data, **Eq**:**Ax**=52(6):48(6)%, as $\Delta G(305K)=0.05(15)$ kcal/mol. Within the uncertainty limit, the conformer ratio and free Gibbs energy coincide with that predicted the MP2 and M062X calculations.

In addition, we estimated the temperature-dependence of the conformer ratio. Based on the relative electronic energies and vibrational characteristics obtained from the QC calculations, we calculated the equilibrium constants of the process **Eq** $\rightleftharpoons$ **Ax** at different temperatures from 100 to 1000K with a 50 K step using the programs TDF and KP-IZ (by Dr. V.V. Sliznev). With increasing temperature, the concentration of the **Eq** conformer approaches a value of *ca.* 55%, see Figure 5.

Figure 5: Temperature dependence of conformer contribution estimated on a basis of quantum chemical calculations, and the GED value at 305 K

3.4 Geometry

Select experimental (GED) and calculated (QC) geometric parameters of the **Eq** and **Ax** conformers of **CNP** are compiled in Table 2, see also Tables S3, S4 and S5 in Supporting Information for more details.

Comparing the molecular parameters of the conformers, one can see that the C–N bonds are not affected by the axial or equatorial position of the substituent. The vicinity with the C–N bond leads to a shorter C1–C3 distance as compared with the more distant C3–C5 pair of atoms, by 0.004–0.006 Å in both conformers. The endocyclic C–N bonds are by 0.120(5) (GED) and *ca.* 0.14 Å (QC) longer than the exocyclic one due to the influence of conjugation between the LP electrons on the nitrogen atom N1 and the C6 $\equiv$ N2 triple bond. Caused by the interaction between the LP and the C–H_{ax} bond, the elongation of the latter in relation to the C–H_{Eq} bond is more pronounced in the case of the C _{α} atoms environment, 0.006 to 0.010 Å, rather than for the β - and γ -carbons, 0.003–0.004 Å. The in-ring CNC angle is smaller than the outer ones by 1–2° in equatorial and by 1–3° in the axial conformer. The exocyclic CNC bond angle in the equatorial conformer is slightly larger than that in the axial one, by 0.7°.

Table 2: Theoretical (with 6-311G** basis set) and experimental geometric parameters ^a of **CNP**

Conformer	Equatorial				Axial			
Method	B3LYP- GD 3	M062X	MP2	GED	B3LYP- GD 3	M062X	MP2	GED
Bond distance, Å								
N1–C1	1.477	1.472	1.474	1.474(4)	1.480	1.475	1.477	1.477(4)
N1–C6	1.333	1.337	1.347	1.354(3)	1.335	1.340	1.349	1.356(3)
C6≡N2	1.160	1.155	1.179	1.179(2)	1.161	1.155	1.180	1.180(2)
C1–C3	1.529	1.523	1.525	1.529(3)	1.533	1.527	1.528	1.533(3)
C3–C5	1.535	1.530	1.531	1.535(3)	1.537	1.532	1.533	1.538(3)
C1–H _{ax}	1.101	1.100	1.103	1.106(2)	1.095	1.094	1.097	1.100(2)
C1–H _{eq}	1.091	1.090	1.093	1.096(2)	1.090	1.090	1.093	1.096(2)
Bond angle, °								
N1C1C3	109.7	109.4	109.1	109.5(5)	111.5	111.3	111.7	112.1(5)
C1C3C5	111.0	110.7	110.5	110.1(5)	110.7	110.4	110.4	110.0(5)
C3C5C4	110.6	110.5	110.5	112.9(5)	111.2	111.0	110.9	113.1(5)
C1N1C2	115.3	114.8	113.6	112.8(13)	113.8	113.1	112.3	111.4(13)
C1N1C6	117.1	115.9	114.5	114.4(5)	116.8	114.9	113.6	115.9(8)
N1C6N2	178.2	178.4	177.8	185.3(16)	178.1	178.4	177.7	185.2(16)
Torsion angle, °								
N1C1C3C5	54.4	55.3	56.3	55.1(14)	54.0	54.9	55.2	54.2(14)
C1C3C5C4	–55.0	–55.6	–55.4	–51.9(14)	–54.0	–54.5	–54.3	–50.9(14)
α ^b	20	17	14	15(3)	85	89	85	88(3)

^a See Figure 1 for atom numbering. ^b α is an angle between the C≡N group and the piperidine ring planar frame C1C3C4C2; dependent parameter; the uncertainty was estimated from those for the N1C1C3, C1N1C2 and C1N1C6 variables.

The theoretical bond distances and dihedral angles are in good agreement with the GED values, though with two of exceptions: (i) the experimental exocyclic N1–C6 bond distance was found to be 0.01–0.02 Å longer than all the theoretical predictions; (ii) the N1–C6–N2 fragment is practically linear, *ca.* 178° (QC) and 185(2)° (GED); the latter tends to a slight deviation of the C≡N bond to a ‘*cis*’ orientation relative to the C_αC_α–N plane.

The angles α between the C≡N group and the piperidine ring planar frame C1C3C4C2 from GED is 15(4)° (**Eq**) and 88(4)° (**Ax**), which are, within the estimated uncertainty, in good agreement with calculated values, except for **Eq** by B3LYP-~~GD~~3, see Table 2.

3.5 NBO analysis

The natural charges of the atoms do not change essentially when going from one conformer to another, see Table 3. Among the three carbons directly linked to the piperidinic nitrogen atom, only one of them, the C_{CN} atom, is positively charged, while the two others are slightly negative.

Table 3: The natural charges of nitrogen and carbon atoms, total electronic energy $E^{(tot)}$, the second-order perturbation energy $E(2)$ $Lp(N1) \rightarrow BD^*(C \equiv N)$, total steric $E^{(ST)}$ and electrostatic $E^{(NCE)}$ energies at the DFT level of theory with cc-pVTZ basis set. Relative energies are in kcal/mol.

Method	B3LYP		B3LYP- GD3		M062X	
Conformer	Eq	Ax	Eq	Ax	Eq	Ax
N1	-0.487	-0.478	-0.487	-0.477	-0.509	-0.497
N2	-0.387	-0.394	-0.387	-0.392	-0.383	-0.388
C _{α}	-0.170	-0.170	-0.170	-0.170	-0.172	-0.172
C _{CN}	0.409	0.397	0.409	0.396	0.419	0.405
$\Delta E^{(tot)}$	-0.78	0.00	-0.41	0.00	-0.15	0.00
$\Delta E(2)$	1.34	0.00	0.93	0.00	-1.19	0.00
$\Delta E^{(ST)}$	3.04	0.00	-5.68	0.00	-0.63	0.00
$\Delta E^{(NCE-tot)}$	3.24	0.00	3.18	0.00	3.91	0.00
$\Delta E^{(NCE-L)}$	4.13	0.00	3.79	0.00	4.41	0.00

The second-order perturbation energy $E(2)$ $Lp(N1) \rightarrow BD^*(C \equiv N)$ is 0.93–1.34 kcal/mol higher in the **Eq** than in the **Ax** conformer as calculated by the B3LYP and B3LYP-~~GD3~~ methods. On the other hand, the M062X calculation resulted in an opposite trend – this interaction is 1.19 kcal/mol lower in the **Ax** form. The orbital interaction between the Lp on the nitrogen atom with the $C \equiv N$ triple bond is illustrated in Figure 6.

The total steric energy E^{ST} from the NBO analysis was calculated as described in Refs [40–42]. The Natural Coulomb Electrostatic energies E^{NCE} , total and its Lewis components, were calculated as described in Ref. [42]. Table 3 shows that from B3LYP-~~GD3~~ and M062X calculations, the steric interactions in the **Ax** conformer are more pronounced than in the **Eq** conformer. At the same time, from the all calculations, the electrostatic effect stabilizes the equatorial conformer. Thus, as follows from M062X calculations, the second-order perturbation energy $E(2)$ $Lp(N1) \rightarrow BD^*(C \equiv N)$ and the steric effect stabilize the axial form, while the electrostatic effect plays a destabilizing role.

Figure 6: Orbital interaction between the Lp on nitrogen atom and the $C \equiv N$ triple bond

A tendency of increase of the $N_{ring}-C_{subst}$ bond orders, estimated as ‘Wiberg bond indices’ in the NBO analyses performed for the series: N-alkyl, N-aryl, N-alkenyl, N-alkynyl, N-carbonitrile (0.99, 1.06, 1.10, 1.11, 1.14) does clearly correlate with the bond distance shortening (1.455-1.475 [9], 1.410-1.420 [11], 1.383-1.402, 1.349-1.350 [9] and 1.333-1.349 Å), respectively, getting very close to the sesquilateral bond in pyridine 1.3376 (4) [43], but still larger than for the double $C=N$ bond in imines, *ca.* 1.27 Å [44].

3.6 IR spectra

Experimental IR vibrational spectra of **CNP** were recorded in the range from 400 to 4000 cm^{-1} for the neat liquid at room temperature. The experimental IR spectra are compared with those obtained from QC calculations; the graphical representation of the theoretical spectra was performed using the software package ChemCraft [45] with a band width half height of 10 cm^{-1} , see Figure 7.

The experimental IR spectrum in the liquid phase obtained in this work is in good agreement with the data of Sigma Aldrich Library [46] and the Spectral Database for Organic Compounds SDBS [47]. The vibrations in the region 3100–2850 cm^{-1} are all CH stretches, those in the region 1520–1480 cm^{-1} are HCH scissoring. The HCH, CCC, CCN and CCN deformation and rocking modes occur in the region 1450–400 cm^{-1} , while the region 400–230 cm^{-1} contains mainly ring deformations and torsions. One peak, the vibration of the cyano mode in the range of 2100–2250 cm^{-1} , is observed in both experimental spectra.

The lowest calculated frequency correspond to the nitrogen inversion and lies in a range 56(B3LYP)–96(MP2) cm^{-1} for both conformers, suggesting that this molecule is relatively rigid. Thus, the harmonic approximation applied in QC calculations for evaluating the vibrational frequencies is applicable. Moreover, the shape of the PESs, see Figure 3, supports this suggestion as not being too shallow, except for the B3LYP case.

Figure 7: IR spectra of **CNP**: calculated (B3LYP and MP2(FC) with 6-311G** basis set) of equatorial and axial conformers along with the experimental data in liquid.

According to the DFT method, the carbonitrile group in both conformers should be in a range of 2317–2329 cm^{-1} (B3LYP and B3LYP- ω B3) and 2374–2393 cm^{-1} (M062X). These values are by *ca.* 110 cm^{-1} (B3LYP and B3LYP- ω B3) and *ca.* 180 cm^{-1} (M062X) shifted to violet region compared to the experimental bands. At the same time, the MP2 calculations predict this band only *ca.* 10 cm^{-1} (FC) and 20–30 cm^{-1} (FULL) away from the experimental data. Except for the MP2 method with full core, increasing sophistication of the basis set decreases the wavenumber of the CN mode.

A most informative part of the experimental IR-spectra of liquid **CNP** is in the region from 2100 to 2250 cm^{-1} . According to the QC calculations, the vibrational frequency $\nu(\text{CN})$ is by 5–11 cm^{-1} lower in the **Ax** conformer than in the **Eq** one. The wavenumbers, intensities and their ratio of the CN mode in both conformers of **CNP** are given in Table 4. For comparison, the wavenumber of the CN mode in cyanocyclohexane is 2205 (**Ax**) and 2210 (**Eq**) from MP2(Full)/6-31G* calculation, 2246 from IR spectrum in Xe solution and 2243 cm^{-1} from Raman spectrum in liquid [4]. Our calculations for 1-cyanosilacyclohexane show these values as

Ax–Eq, 2301–2304 (B3LYP) and 2107–2109 (MP2/6-311G**) and 2113–2114 (MP2/cc-pVTZ) cm^{-1} .

Table 4: Vibrational frequencies and intensities of carbonitrile group in both conformers of **CNP**

Conformer	ν , cm^{-1}		$\Delta\nu$ cm^{-1}	I, km/mole		$I_{\text{Eq}}/I_{\text{Ax}}$
	Eq.	Ax.		Eq.	Ax.	
B3LYP/6-311G**	2326.8	2321.7	5.1	205.781	198.012	1.040
B3LYP/cc-pVTZ	2322.0	2316.5	5.5	219.188	216.785	1.011
B3LYP- G D3/6-311G**	2328.7	2322.5	6.3	204.229	182.562	1.119
B3LYP- G D3/cc-pVTZ	2323.8	2317.5	6.3	218.081	199.296	1.094
M062X/6-311G**	2392.7	2382.0	10.7	207.476	170.358	1.218
M062X/cc-pVTZ	2384.4	2374.0	10.4	224.762	188.821	1.190
MP2(FC)/6-311G**	2222.7	2215.1	7.6	106.894	83.471	1.281
MP2(FC)/cc-pVTZ	2219.7	2213.0	6.7	126.980	103.658	1.225
MP2(Full)/6-311G**	2229.8	2222.1	7.7	109.232	85.021	1.285
MP2(Full)/cc-pVTZ	2245.1	2237.7	7.4	134.412	107.876	1.246
Experiment in liquid	2213(10)	2204(8)	9(10)	–	–	1.489

We performed an experimental band deconvolution of the $\text{C}\equiv\text{N}$ mode of **CNP** in liquid. The peak positions were obtained by calculating the second derivative, which clearly indicates the presence of two overlapping peaks. Deconvolution was achieved by free peak fitting using Lorentzian band shapes with the use of the program Fityk, version 0.9.8 [16], see Figure 8. The deconvolved peaks at 2204 and 2213 cm^{-1} were assigned to the $\text{C}\equiv\text{N}$ mode of axial and equatorial conformers, respectively. This difference of about 10 cm^{-1} coincides with the theoretical predictions, Table 4.

Figure 8: Appearance and deconvolution of the $\text{C}\equiv\text{N}$ mode of **CNP** in the IR spectrum in liquid at room temperature.

The experimental ratio of ~~intensities~~ peak heights was found as $I_{\text{Eq}}/I_{\text{Ax}}=1.489$; the theoretical IR intensities ratio for **Eq:Ax**=1:1 varies from 1.01 (B3LYP) to 1.29 (MP2), see Table 4. Applying these values, the derived experimental conformers ratio in liquid **CNP** at room temperature varies from **Eq:Ax**=60:40% to 54:46% with an average value of 57(3):43(3)% and corresponding $\Delta G=0.17(7)$ kcal/mol for the equilibrium **Eq** $\rightleftharpoons$ **Ax**. The experimental ratio of the peak areas is $A_{\text{eq}}/A_{\text{ax}}=2.015$ which gives **Eq:Ax**=67:33 to 61:39% with an average

64(3):36(3). The two approaches of the IR data treatment are very close to the GED result, 52(6):48(6)%, for the gas phase.

3.7 Comparison with analog compounds

We compared relative total electron energies and free Gibbs energies between axial and equatorial conformers of 1-cyano-heterocyclohexanes: cyanocyclohexane **CNC**, 1-cyanopiperidine **CNP**, 1-cyanosilacyclohexane **CNSiC** and 1-cyanophosphorinane **CNPhr** (see Table 5, Figure 9 and Table S6 in Supporting Information).

Table 5: Relative total electron energies $\Delta E = E_{ax} - E_{eq}$, free Gibbs energies $\Delta G^\circ(298K) = G_{ax} - G_{eq}$ (kcal/mol) and X–C_{CN} bond distance ^a (Å) of 1-cyano-heterocyclohexanes from QC calculations ^b and experimental data

QC calculations				Experiment	Ref.
	ΔE	ΔG°	r(X-C _{CN})		
	Cyanocyclohexane				
B3LYP	+0.41 to +0.57	+0.57 to +0.72	1.462-1.468	$\Delta G(303K)=0.11(8)$ NMR (CCl ₄)	3
M062X	−0.56 to −0.15	−0.21 to +0.02	1.463-1.469	$\Delta H=−0.18(3)$ IR (Xe)	4
MP2	−0.73 to −0.34	−0.40 to −0.28	1.460-1.468	$\Delta H=−0.13(5)$ Raman (liquid)	4
	1-Cyanopiperidine				
B3LYP	+0.71 to +0.80	0.71 to 0.75	1.330-1.333	$\Delta G(298K)=0.24(15)$ IR (liquid)	
M062X	−0.03 to +0.15	0.12 to 0.32	1.335-1.340	$\Delta G(305K)=0.05(15)$ GED	
MP2	−0.15 to +0.11	0.01 to 0.20	1.341-1.349		
	1-cyanosilacyclohexane				
B3LYP	−0.36 to −0.35	−0.19 to −0.17	1.866-1.872	$\Delta G(279K)=−1.0(4)$ GED	7
M062X	−1.02 to −0.94	−0.94 to −0.85	1.867-1.874	$\Delta G(120K)=0.14$ ¹³ C NMR	
MP2	−1.02 to −0.98	−0.90 to −0.88	1.860-1.867		
	1-cyanophosphorinane				
B3LYP	−1.59 to −1.34	−1.42 to −1.18	1.796-1.803		
M062X	−2.52 to −2.10	−2.28 to −1.94	1.798-1.805		
MP2	−2.45 to −2.15	−2.21 to −2.01	1.788-1.794		

^a values of both, axial and equatorial, forms;

^b see also Table S6 in Supporting Information for more details.

As follows from Table 5, the DFT method with B3LYP functional overestimates ΔE and ΔG° values for the conformer ratio of these compounds. At the same time, the M062X and MP2 methods predict similar results, which are in good agreement with the experimental data. The ΔE and ΔG° values increase from the C to N atoms, then decrease to the Si and P atoms, see Figure 9. From the bond length values given in Table 5, a tendency of the ΔE and ΔG values decrease in the series of the heteroatom X N>C>Si with increase the r(X–C_{cyano}) distance between the ring and carbonitrile group. This trend is easily argued as arising from a lowering of the steric repulsion, more pronounced for the axial configuration, when the substituent is more distanced from the hydrogens of the ring. On the other hand, a situation with the phosphorus compound is somewhat different: the ΔE and ΔG values in **CNPhr** are smaller than those in **CNSiC** (despite the shorter X–C_{cyano} bond length), which may be caused by hyperconjugation between the Lp on the phosphorus atom and the triple bond of the carbonitrile group that stabilizes the axial form in **CNPhr**.

Figure 9: The change of ΔE and $\Delta G(298\text{ K})$ values on heteroatoms

4. CONCLUSIONS

According to the QC calculations, **CNP** may exist as two conformers, equatorial and axial. The DFT method with the B3LYP and B3LYP-GD3 functionals overestimate the ΔE and ΔG values, while the M062X functional calculates these values very well. The results from the MP2 level are in good agreement with the CCSD(T)/CBS level with $\Delta E=0.26$ kcal/mol and with experimental GED data $\Delta G(305\text{K})=0.05(15)$ kcal/mol, corresponding to a ratio **Eq:Ax**=52(6):48(6)%. Based on the intensity of CN modes of the equatorial and axial forms in the IR spectrum in liquid, the ratio of conformers is **Eq:Ax**=60(6):40(6)%.

Thus, as follows from the QC calculations and experimental GED data for N-substituted piperidines, the equatorial conformer is more stable than axial one. However, the proportion of the axial conformer increases with increasing multiplicity of the bond of the substituents that directly links with the nitrogen atom of the piperidine ring: alkyl < alkenyl $\approx$ aryl < alkynyl < carbonitrile [9–11].

The contribution of the axial form of 1-cyano-heterocyclohexanes increases in the series **CNP**<**CNC**<**CNSiC**<**CNPhr**. The position of the carbonitrile group relative to the ring influences the competition between two types of interactions: 1,3-diaxial repulsion and hyperconjugation between the Lp on heteroatoms with the π -system of carbonitrile group.

The NBO analysis shows that in the case of **CNP** the hyperconjugation stabilizes the axial form, while the electrostatic effect destabilizes it.

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GRAPHICAL ABSTRACT