Computational study of n-butyronitrile in gas and condensed phases: conformational relative stability and thermal properties

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Abstract. Geometrical structures and relative stability of gauche and trans butyronitrile conformers have been investigated by utilizing *ab initio* and DFT calculations. The results showed that the gauche conformer is more stable by 0.27 kcal/mol, outlined as enthalpy change ΔH between the two conformers, at CCSD/6-311G+(d,p), the highest level of theory used. Also, the population analysis displays that the gauche conformer is present at 70% in the gas phase, more predominant than the trans conformer. These results agree well with the previous experimental and theoretical findings. Additionally, thermodynamic properties of the two conformers have been investigated. The data exhibit that the abundance of the gauche conformer increases as the temperature decreases under high-pressure condition. The results help to understand the reasons behind the conformational transitions between the fluid and the solid phases.

Keywords. Butyronitrile conformers; CCSD and DFT methods; relative stability; population analysis; condensed phase.

1. Introduction

Conformational isomerism of a chemical compound, with different functional groups, determines many of its chemical and physical properties. For instance, it determines the activity of some enzymes^{1–3} and determines the phase of the compounds at ambient conditions.^{4,5} Nitriles have a considerable importance in chemistry and astrochemistry. For example, succinonitrile is used as a solvent of inorganic salts and plays an essential role in the research on solid state batteries.^{6–9} Also, it has been used to enhance the conductivity of composite polymers such as poly(methyl methacrylate)-succinonitrile.¹⁰ Some small chain nitriles are likely to be present in interstellar clouds and are believed to produce amino acid when they reacted with water.^{11–13} The largest detected nitriles, in star-forming region Sagittarius B2(N), hereafter denoted as Sgr B2(N), are butyronitrile $\text{CH}_3\text{CH}_2\text{CH}_2\text{CN}$ (also called n-propyl cyanide) and its isomers.¹³ This makes them good candidates in interstellar cloud detection.

Butyronitrile exists in two minima, trans and gauche conformers $\text{CH}_3\text{CH}_2\text{CH}_2\text{CN}$. In the literature, the results of conformational analysis has resulted in a dispute

about the conformational stability of butyronitrile. Very early microwave study by Hirota came to a conclusion that trans conformer is more stable than the gauche.¹⁴ Later, IR study suggested that gauche conformer predominates in the vapor phase. Two conformers are available in liquid and amorphous solid,¹⁵ while in crystalline solid only gauche conformer exists.^{15,16} In a recent microwave study, Włodarczak *et al.*, calculated the energy difference between trans and gauche conformers to be 0.26 kcal/mol, the trans conformer being more stable.¹⁷ The most recent IR and Raman study found that the gauche conformer is 70% more predominate than the trans conformer and more stable by 0.11 kcal/mol.¹⁸ This study is consistent with the gas electron diffraction (GED) study which found that 75.1% gauche conformer is observed in the gas phase of butyronitrile with standard deviation equal to 6.1%.¹⁹

Many theoretical studies have focused on the conformational analysis of butyronitrile.^{18–22} The most recent one by Lamsabhi *et al.*, used the fourth generation method G4 as well as DFT (B3LYP/aug-cc-pVQZ and M06/aug-cc-pVQZ) calculations.²² They have found that, at their highest level of theory M06/aug-cc-pVQZ, that gauche conformer is more stable than the trans conformer by 0.19 kcal/mol.

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The abundance of the conformers depends not only on the relative energy between conformers but also on the ambient conditions such as pressure, temperature and phase changes of the compound.^{18,23} In this work the geometry of butyronitrile conformers and the relative stability of the two conformers was studied in different phases. Moreover, the thermodynamic data of the conformers were computed. The obtained results were compared with the previously reported experimental and theoretical data. Hopefully, the results of this work will help to clarify the conformational transitions under extreme temperature and pressure conditions.

2. Computational details

All the geometry optimization and energy calculations have been done using Gaussian09 package.²⁴ Different levels of theory have been used such as CCSD, B3LYP and M06 using several basis sets 6-31+G(d), 6-311G+(d,p) and aug-cc-pVDZ. The stationary points [minima and the transition states (saddle point of first order)] are characterized using frequency calculations. Mathematically, the minima have no imaginary eigenvalues while the transition states have one imaginary eigenvalue. The relative stability between the most stable conformer and the less stable ones or the transition states are calculated using the equation explained in our previous works.^{25,26}

$$\Delta H_{rel} = (E_o + H_{corr})_{less} - (E_o + H_{corr})_{most} \quad (1)$$

$$\Delta G_{rel} = (E_o + G_{corr})_{less} - (E_o + G_{corr})_{most} \quad (2)$$

where, $(E_o + H_{corr})$ and $(E_o + G_{corr})$ are the corrected electronic energy included the zero-point energy plus the thermal correction to enthalpy (H_{corr}) or the thermal correction of the Gibbs free energy (G_{corr}), respectively.

The electronic atomic charges were calculated using natural bond orbital (NBO) analysis.²⁷ The obtained data were used in order to calculate the stabilization energy of the most stable conformer. For this purpose, the electrostatic interaction between the point charges C and N atoms of the nitrile group and the staggered CH₃ group are determined using the Coulomb's potential.

$$U_E = k_e \sum_i^N \frac{q_i Q}{r_i} \quad (3)$$

Where, $k_e = \frac{1}{4\pi\epsilon_0} = 8.988 \times 10^9 \text{ Nm}^2\text{C}^{-2}$ is Coulomb's constant, r is the distance between the point charges q of the nitrile group and Q , the point charge of the nearest H atom on CH₃ group.

3. Results and Discussion

3.1 Geometry

The optimized structures of the minima and the transition states are shown in Figure 1. The

corresponding bond length, bond angles and dihedral angles are shown in Table 1. All bond lengths of conformers are comparable with each other at a different level of theory with maximum difference ~ 0.02 Å. The C≡N bond lengths of the gauche and trans conformers are the same at the same level of theory. Whereas, for the same conformer they are a bit different at different levels of theory. The maximum difference is ~ 0.01 Å. In general, all the bond lengths, the bond angles and the dihedral angle of the gauche conformer correlate well with the gas electron diffraction (GED) results.¹⁹ The C≡N bond length of gauche conformer is 1.1576 Å, which is in good agreement with my best results of B3LYP and M06 using aug-cc-pVDZ basis set, and CCSD/6-311G+(d,p). The maximum difference between the current results and GED results is $\sim 2^\circ$ in case of the C4-C1-C2-C3 dihedral angle (Figure 1).

3.2 The relative stability and thermal properties in gas phase

The relative energies of the trans conformer and the transition states (relative to the gauche conformer), outlined by their ΔH_{rel} and ΔG_{rel} , are listed in Table 2. They show that gauche conformer is more stable than trans conformer as indicated by M06 and CCSD methods. While the B3LYP method shows the opposite result. This may be attributed to the fact that the zero point energy and the thermodynamic energies have to be scaled when using the B3LYP functionals.²⁸ The ΔH_{rel} and ΔG_{rel} values obtained by the highest level of theory CCSD/6-311+G(d,p) are comparable with M06/aug-cc-pVDZ results.

To estimate the population of the two conformers at ambient temperature, ΔG_{rel} has to be corrected by $[-RT \ln(1/2) = 0.41 \text{ kcal/mol}]$ because gauche conformer has two forms while the trans has one form. $[\Delta G = \Delta G_{rel} - RT \ln(1/2) = 0.52 \text{ kcal/mol}]$. The population distribution is approximately 30% of trans conformer and 70% of gauche conformer, which agree well with that (30% trans and 70% gauche) by Durig *et al.*,¹⁸ and (75% gauche and 25% trans) of Traetteberg group.¹⁹

The Gibb's free energies $\Delta G^\#$ of the transition states TS1 and TS2 are 3.96 and 4.87 kcal/mol obtained by CCSD/6-311+G(d,p), respectively, relative to the most stable gauche conformer. The results reveal that TS2 Figure 1D has a higher strain than TS1 Figure 1C because of the CH₃ and CN eclipsed configuration. The energies of the transition states are considered to be the energy barriers between the two conformers or the energy of the rotation around the C4-C1-C2-C3 dihedral angle. The rate constants k , of each rotational step,

Figure 1. The optimized stationary points of butyronitrile conformers. (A) Gauche, (B) Trans (C) TS1 (eclipsed H6-C1-C2-C3), (D) TS2 (eclipsed C4-C1-C2-C3). The related optimized parameters are shown in Table 1.

are $\sim 8 \times 10^9 \text{ s}^{-1}$ and $2 \times 10^9 \text{ s}^{-1}$ calculated by using $\Delta G_{TS1}^\ddagger$ and $\Delta G_{TS2}^\ddagger$, respectively, in equation 4.²⁶

$$k(T) = \frac{k_B T}{hc^o} e^{-\Delta G^\ddagger/RT} \quad (4)$$

Where, $c^o = 1$ for the concentration and $T = 298.15 \text{ K}$ for temperature. k_B , h , and R are Boltzmann, Planck and universal gas constants, respectively. The obtained rate constants show a very fast rate of rotation around the dihedral angle at room temperature.

To take a deeper look about the reason behind the stabilization energy of the gauche conformer, the point charges of each atom have been calculated using NBO analysis by CCSD/6-311+G(d,p) level of theory, Figure 2. Using Coulomb's potential, equation (3), the interaction between CN group and the eclipsed hydrogen (H10) atom is attractive and has a value of 0.12 kcal/mol. This is assumed to be the stabilization energy SE of the gauche conformer. Moreover, the electrostatic potential ESP contours in Figure 2

also shows the attractive interaction between H10 atom and the nitrile group. The SE is absent in trans conformer as there are no attractive interactions between functional groups. SE was estimated using the relative stabilization energy, $\Delta H_{rel} = 0.27 \text{ kcal/mol}$ using CCSD/6-311+G(d,p) method, also taking into account to add the difference of zero-point energy ($\Delta ZPE = -0.11 \text{ kcal/mol}$) and the thermal enthalpy correction ($\Delta H_{corr} = -0.03 \text{ kcal/mol}$): $SE = \Delta H_{rel} + \Delta ZPE + \Delta H_{corr} = 0.13 \text{ kcal/mol}$. This value agrees very well with the value calculated using Coulomb's potential.

3.3 The relative stability and thermal properties in condensed phase

In order to study the thermal properties of the condensed phases, the crystal structure of the solid butyronitrile is needed. Unfortunately, to my knowledge, in literature, there are no experimental or theoretical studies about the condensed phases of butyronitrile. However, based on

Table 1. Selected bond lengths (Å), angles (°) and dihedral angles (torsion angles) (°) of the optimized gauche, trans and transition states (TS) geometries of butyronitrile at the B3LYP, M06, CCSD/ 6-311G+(d,p), (aug-cc-pVDZ) levels of theory.

	Bond (Å)		B3LYP		M06		CCSD	Angles (°)		B3LYP		M06		CCSD	
Structure	expt ^a		/6-311G+(d,p) (/aug-cc-pVDZ) ^b								expt ^a		/6-311G+(d,p) (/aug-cc-pVDZ) ^a		
Gauche	C1-C2	1.5337	1.544	(1.544)	1.530	(1.530)	1.540	C1-C2-C3	113.0	113.2	(113.0)	112.1	(112.1)	112.2	
	C2-C3	1.4621	1.462	(1.468)	1.454	(1.458)	1.476	C2-C1-C4	112.3	113.6	(113.6)	112.5	(112.7)	112.8	
	C1-C4	1.5230	1.529	(1.530)	1.517	(1.517)	1.532	C2-C3≡N5	180.0	179.2	(179.0)	178.8	(178.5)	179.0	
	C3≡N5	1.1576	1.153	(1.161)	1.152	(1.161)	1.161	C4-C1-C2-C3	61.1	63.3	(62.9)	62.2	(61.7)	61.7	
								N5-C3-C4-H10		1.8	(1.4)	1.5	(1.02)	0.1	
Trans	C1-C2		1.543	(1.542)	1.529	(1.529)	1.539	C1-C2-C3		113.0	(112.8)	112.6	(112.6)	112.3	
	C2-C3		1.461	(1.466)	1.452	(1.456)	1.475	C2-C1-C4		111.8	(111.8)	111.2	(111.3)	111.5	
	C1-C4		1.530	(1.530)	1.516	(1.516)	1.531	C2-C3≡N5		179.1	(179.0)	178.8	(178.6)	178.9	
	C3≡N5		1.153	(1.161)	1.152	(1.161)	1.161	C4-C1-C2-C3		180.0	(180.0)	180.0	(180.0)	180.0	
TS1	C1-C2		1.559	(1.559)	1.545	(1.544)	1.556	C1-C2-C3		113.5	(113.4)	113.2	(113.1)	112.7	
	C2-C3		1.460	(1.466)	1.452	(1.456)	1.474	C2-C1-C4		112.8	(112.7)	112.3	(112.2)	112.1	
	C1-C4		1.531	(1.531)	1.517	(1.518)	1.532	C2-C3≡N5		179.2	(179.0)	179.0	(178.8)	179.2	
	C3≡N5		1.154	(1.161)	1.152	(1.161)	1.161	C4-C1-C2-C3		120.2	(120.5)	120.3	(120.8)	119.9	
TS2	C1-C2		1.565	(1.564)	1.550	(1.549)	1.561	C1-C2-C3		115.3	(115.2)	114.9	(114.8)	114.3	
	C2-C3		1.461	(1.467)	1.453	(1.457)	1.475	C2-C1-C4		115.9	(115.8)	115.4	(115.4)	115.4	
	C1-C4		1.531	(1.531)	1.518	(1.518)	1.533	C2-C3≡N5		179.5	(179.7)	180.0	(179.7)	179.8	
	C3≡N5		1.153	(1.161)	1.152	(1.161)	1.161	C4-C1-C2-C3		0.0	(0.0)	0.0	(0.0)	0.0	

^aExperimental value of gauche conformer are taken from reference 19.

^bThe values in parentheses are for aug-cc-pVDZ basis set.

Table 2. The relative energies of the trans conformer and the transitions state compared with the most stable gauche conformer.

Geometry	Method	Basis set	ΔH_{rel}^a	ΔG_{rel}^a
Trans	CCSD	6-311G+(d,p)	0.27	0.11
		M06	0.41	0.45
	B3LYP	aug-cc-pVDZ	0.27	0.09
		6-311G+(d,p)	-0.10	-0.17
		aug-cc-pVDZ	-0.12	-0.20
TS1 ^b	CCSD	6-311G+(d,p)	2.88	3.96
		M06	2.95	4.07
	B3LYP	aug-cc-pVDZ	2.88	3.97
		6-311G+(d,p)	2.42	3.42
		aug-cc-pVDZ	2.39	3.41
TS2 ^b	CCSD	6-311G+(d,p)	3.87	4.87
		M06	3.69	4.90
	B3LYP	aug-cc-pVDZ	3.23	4.33
		6-311G+(d,p)	3.58	4.50
		aug-cc-pVDZ	3.44	4.42

^aAll energies are in kcal/mol.

^b $\Delta H_{rel} \equiv \Delta H^\#$ and $\Delta G_{rel} \equiv \Delta G^\#$ for transition state.

and inspired with the crystal structure of succinonitrile $P2_1/a$ space group,²⁹ a dimer, tetramer and hexamer structures of butyronitrile have been optimized using M06/6-31+G(d) level of theory (Figure 3). To imitate the succinonitrile $P2_1/a$ structure the tetramer or hexamer were treated as the unit cells of the solid-state crystal and then extended using 2-D periodic boundary conditions

(PBC) in XY plane as shown in Figure 3.³⁰⁻³⁴ The interactions between the cells were represented at the boundary between each cell and the neighboring cell. On the other hand, the third dimension (Z) of the boundary condition was extended by increasing the unit cell itself (dimer $\rightarrow$ tetramer $\rightarrow$ hexamer). Beyond the hexamer structure, the calculation becomes very expensive and time-consuming. The dimer structure with only head-to-head interaction cannot represent all crystal structure interactions, so it has not been extended using PBC. The tetramer and hexamer with two head-to-head and two side-by-side interactions are shown in Figure 3.

To calculate the thermodynamic data ΔH_{cryst} , ΔG_{cryst} and ΔS_{cryst} , (Table 3), the following change between the gas phase and the predicted dimer (n=2) or tetramer (n=4) are considered.

Here, equations are similar to equations 1 and 2.

$$\Delta H_{cryst} = (E_o + H_{corr})_{dimer, tetramer \text{ or } hexamer} - n(E_o + H_{corr})_g \quad (5)$$

$$\Delta G_{cryst} = (E_o + G_{corr})_{dimer, tetramer \text{ or } hexamer} - n(E_o + G_{corr})_g \quad (6)$$

$$\Delta S_{cryst} = S_{total(dimer, tetramer \text{ or } hexamer)} - nS_{total(g)} \quad (7)$$

Where, S_{total} includes translational, rotational, and vibrational entropy.

Figure 2. The NBO analysis of atomic charge distributions and the electrostatic potential (ESP) of the gauche and the trans butyronitrile conformers using CCSD/6-311+G(d,p) method.

The following notes about the data in Table 3 are very interesting. First, the ΔH_{cryst} values are negative, which means that the interaction is attractive between molecules. Second, the ΔG_{cryst} values are positive, which reveals that the crystallization process is nonspontaneous at room temperature. And finally, the ΔS_{cryst} values are negative, because, as expected the crystal (solid) is less entropic than the molecules in the gas phase. As depicted in Table 3, the attraction energy between the gauche molecules is higher than the trans ones. The difference is 0.2 kcal/mol for both dimer and tetramer.

The head-to-head attraction can be estimated by -4.0 and -3.8 kcal/mol for di-gauche and di-trans, respectively outlined as ΔH . By subtracting the two head-to-head interactions in case of the tetramer, the side-by-side interactions are -6.0 and -6.1 kcal/mol, for gauche and trans conformers, respectively. As noticed, the side-by-side attraction of the trans conformer is a bit higher than that of the gauche conformer. This may be referred to the steric hindrance of the staggered methyl group in the case of the gauche conformer.

The experimental freezing point of butyronitrile is 161.25 K.³⁵ The transition temperature between the fluid (gas) phase and the crystalline phase (sublimation) is in good agreement with the experimental freezing point of butyronitrile (Table 3). This may reveal that the freezing and the sublimation points are very close in the phase diagram.

At high pressure, the change of the equilibrium between trans and gauche conformers is affected by their molar volume.

The molar volume in gas phase of gauche butyronitrile = $63.406 \text{ cm}^3/\text{mol}$, while the trans conformer = $69.937 \text{ cm}^3/\text{mol}$ with $\Delta V = -6.531 \text{ cm}^3/\text{mol}$ using CCSD/6-311G+(d,p). Using the following thermodynamic equation,

$$\left(\frac{\partial \ln(K_e)}{\partial P} \right)_T = -\frac{\Delta V}{RT} \quad (8)$$

obtain $-\frac{\Delta V}{RT} = 2.67 \times 10^{-4} \text{ atm}^{-1}$ A pressure of $\sim 3700 \text{ atm}$ will change $\ln(K_e)$ by 1 unit (i.e., K_e will

Figure 3. The optimized structure of (A) Dimer; Unit cells (B) Tetramer, (C) Hexamer and the corresponding (D) Tetramer and (E) Hexamer 2-D XY plane 3×3 supercell packing to represent the PBC structure of the condensed phase butyronitrile.

change by 2.718) and $K_e^{new} .718(70/30) = 6.34$). This will increase the predominance of gauche conformer to $\sim 84\%$. When the tetramer structure (Figure 3) is

considered, $\Delta V = -6.04 \text{ cm}^3/\text{mol}$, $\sim 4000 \text{ atm}$ is needed for the same effect. On the other hand, using van't Hoff equation:

Table 3. The thermodynamic data of the transition point between the crystalline phase and the fluid (gas) phase, using M06/6-31+G(d).

Geometry	ΔH_{cryst}^a (kcal/mol)	ΔG_{cryst}^a (kcal/mol)	ΔS_{cryst}^a (cal.mol ⁻¹ .K ⁻¹)	$T_{trs} = \frac{\Delta H_{trs}}{\Delta S_{trs}}$ (K)
Di-gauche	-4.0	5.5	-182.8	—
Di-trans	-3.8	6.0	-184.3	—
Tetra-gauche	-20.0	15.8	-120.2	166.4
Tetra-trans	-19.8	14.6	-115.2	171.8
Hexa-gauche	-36.6	25.7	-209.0	175.1
Hexa-trans	-34.7	25.6	-202.0	171.8
ΔH_{trs}^b	-1.2	0.4	-5.4	225

^aThe temperature at which the data obtained = 298.15 K.^bThe transition between (trans)_{cryst}(gauche)_{cryst}.

$$\frac{d \ln(K_e)}{d(1/T)} = -\frac{\Delta H}{R} \quad (9)$$

H/R= 93 K from equation (9), this means to change K_e by 2.718, the temperature has to drop down to less than 100 K in the gas phase. However, if the phase change of the tetramer structure is considered, the values of $\Delta H = -1.2$ kcal/mol and $\Delta S = -5.4$ cal. K⁻¹.mol⁻¹, and the phase change temperature occurs at ~225 K. That is higher than the freezing point which means the conformational change occurs during the crystallization process.

4. Conclusions

The geometry and thermal properties of butyronitrile have been investigated using *ab initio* CCSD and two DFT (B3LYP and M06) methods. The results show that butyronitrile has two conformers, gauche and trans. The geometrical outcomes of the gauche conformer agree very well with the experimental GED results. Also, the thermal properties of the two conformers have been studied in the gas and crystalline phases. The gauche conformer has been found to be more stable in the gas phase, which correlates with many experimental and theoretical results. In addition, the data show that the crystalline phase contains only the gauche conformer. Moreover, at high pressure, the gauche conformer is preferred over the trans conformer not only because the gauche is more stable but also because the gauche has lower molar volume than the trans conformer. Finally, the present results show that as the temperature decreases and the pressure increases, the predominance of gauche butyronitrile structure increases, which explains the experimental findings.

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