

Internal Rotation Of NO₂ Group In Lower Nitroalkanes From Quantum Chemical Calculations

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Internet Electronic Conference of Molecular Design 2003, November 23 – December 6

Abstract

Motivation. Internal rotation of NO₂ group in nitroethane and 1-nitropropane was investigated. Electron diffraction large-amplitude model approach was used to evaluate geometrical parameters of nitroethane.

Method. Potential energy surfaces of internal rotation around C–C and C–N bonds in nitroethane and 1-nitropropane have been investigated with the GAUSSIAN–03 program package. B3LYP, MP2 and QCISD methods with double and triple basis sets have been applied. Since the MP2/6-31G* method predicts the same form of PES as more accurate calculations, we used it to illustrate our theoretical model, that takes into account intermolecular and dynamic effects in electron diffraction intensity.

Results The barrier height for internal rotation around C-C bond in nitroethane and 1-nitropropane is rather high (800-1200 cm⁻¹ for different ab initio calculations in nitroethane and about 1500cm⁻¹ in 1-nitropropane). Two conformers (gauche – and anti -) should be present. The analysis of internal rotation around C-N bond in these molecules shows that the barrier height is low in nitroethane and in anti-conformer 1-nitropropane. Gauche – conformer of 1-nitropropane is much more rigid.

Conclusions. The low height of the barrier of the internal rotation around C–N bond has to be taken into account in the experimental investigations. Special attention has to be paid on the different shape of the potential energy surfaces in two conformers of 1-nitropropane.

Keywords. ab initio calculations, large amplitude motion, internal rotation, nitroethane, 1-nitropropane.

Abbreviations and notations

PES, potential energy surface

1 INTRODUCTION

Lower nitroalkanes (nitromethane and 1-nitropropane) form catalytic systems with aluminum chloride. As far back as 1941 Wells and Wilson [1] have measured the infra-red spectrum of nitromethane and, using additional data for the liquid, have made assignments of all but one of the fundamental vibrational frequencies. Since that time nitromethane has been widely investigated. However the knowledge of the structure and conformation of the other lower nitroalkanes (nitroethane and 1-nitropropane) is very limited. Smith, Chi-Yang and Nielsen [2] continued the study of the vibrational spectra of the nitroalkanes and have been obtained the infra-red spectra of nitromethane, nitroethane, 1-nitropropane and 2-nitropropane for vapor and liquid phases. But they succeed to get a satisfactory interpretation of the spectra just for nitromethane.

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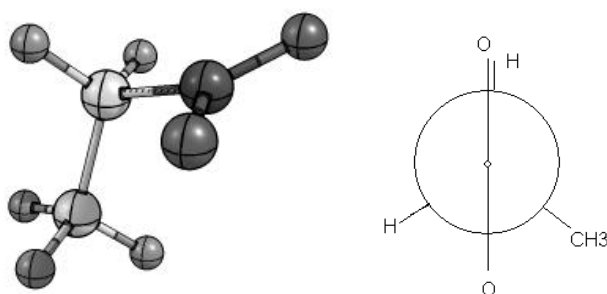
Krishnaji and Pandey [3] made an assignment for microwave spectrum of nitroethane based on a rigid rotor fit, assuming a two-fold barrier around 4-5 kcal/mol for the internal rotation of the nitrogroup. Ekkers, Bauder and Gunthard studied microwave spectrum between 7.5 and 40 GHz and analyzed internal rotation in nitroethane [4]. The spectrum was found typical for an asymmetric rotor with nearly free internal rotation of the nitro group and could not be quantitatively described within the assumption of rigid model [3]. Semirigid model [5], that consists of a rigid frame with C_s symmetry for the ethyl part and a rigid top with C_{2v} symmetry for the nitro group was used in the analysis. Nevertheless, structural parameters have not been determined in [4]. There was no found experimental structural information in the literature on the 1-nitropropane.

We have investigated potential energy surfaces of internal rotation around C–C and C–N bonds in nitroethane and 1-nitropropane with the GAUSSIAN-03 program package [6] and found that the barrier of internal rotation around C–N bond for these molecules is very low, so the rigid rotor models can not be used to describe these molecules. For the correct interpretation of these molecules the model of the large-amplitude motion should be used [7].

2 MATERIALS AND METHODS

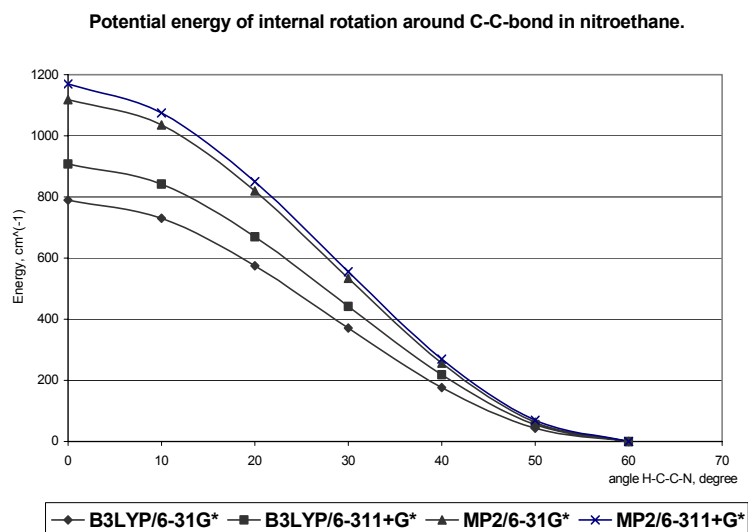
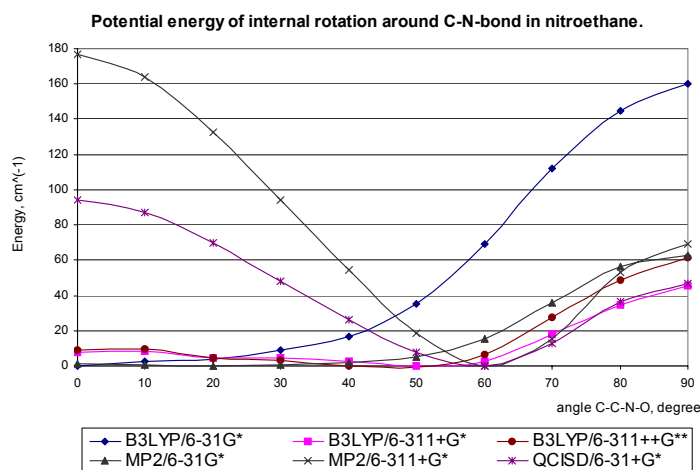
NITROETHANE

Potential energy surface (PES) of internal rotation around C–C and C–N bonds in nitroethane has been investigated with the GAUSSIAN-03 program package. B3LYP, MP2 and QCISD methods with double and triple basis sets have been applied.



The internal rotation around C – C bond is essentially frozen the barrier height varying in the limits of 800 – 1200 cm^{-1} . Quantum chemical results for PES of internal rotation around C–N bond is essentially different. All B3LYP calculations predict broad and shallow minimum with the center at 0 degree corresponding to the *syn* position of the C–C–N–O unit (*i.e.* C–C bond is eclipsed with

respect to the N–O bond) whereas MP2/6-311+G* and QCISD/6-31+G* calculations predict the minimum in the region near 60 degrees. In all cases the barrier height is very low, resulting in approximately free internal rotation around this axis.



Electron diffraction large-amplitude model approach [2] was used to evaluate geometrical parameters of this molecule. Rotation around C–N bond was chosen as a large-amplitude coordinate and separated from the rest of vibrations. All other vibrations were treated as anharmonic vibrations of relatively small amplitude. Since we did not have any spectroscopic data, *ab initio* calculated force field was not refined during fitting process. Since rotation around C–N bond is nearly free, the molecule does not possess equilibrium geometry in a strict sense of this term; we have evaluated

reference geometry corresponding to the minimum of potential function shown at the previous pictures.

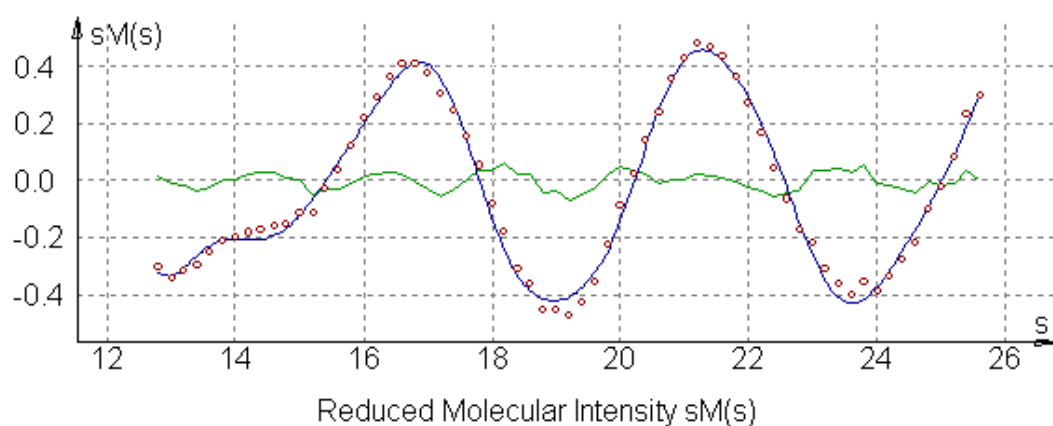
Six geometrical parameters were adjusted; five of them are listed in the table below, the sixth one being average C–H bond length (all C–H bond lengths and N–O bond lengths were refined in groups). In accordance with the overall approach, amplitudes were not independently adjusted. The following figures show only preliminary results and are subject to further verification since experimental data used in the fitting procedure was obtained only in a limited range of the scattering coordinate.

Internuclear distances in nitroetane.

	Ab initio(r_e)	Electron diffraction (r_e)	Electron diffraction (r_g)	Microwave spectroscopy (r_o) ^[3]
r (C-N)	1.497	1.452	1.471	1.505 (3)
r (N-O)	1.232	1.264	1.270	1.213 (3)
r (C-C)	1.521	1.526	1.538	1.540 (fixed)
\angle O-N-O	125.4	122.1		134.0 (fixed)
χ (CN-NO ₂) ^{a)}	2.8	2.4		

a) angle between C-N bond and NO₂ plane

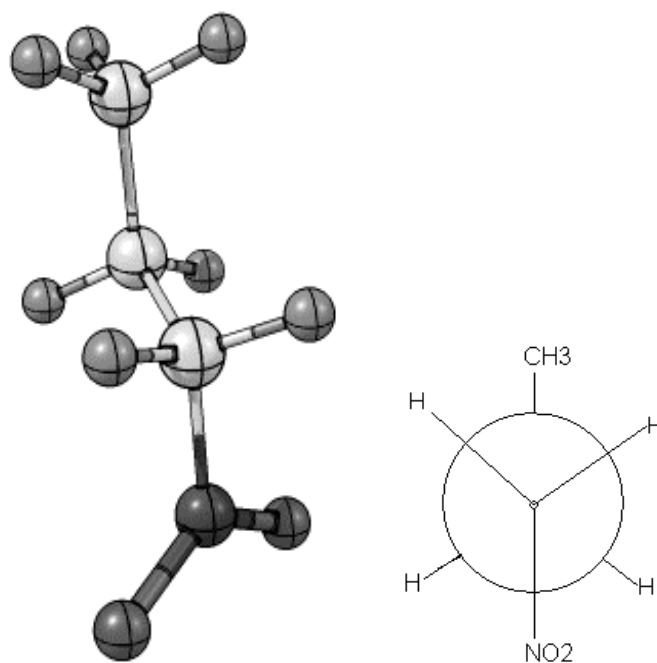
The following picture shows the agreement of calculated and experimental diffraction intensity curves.



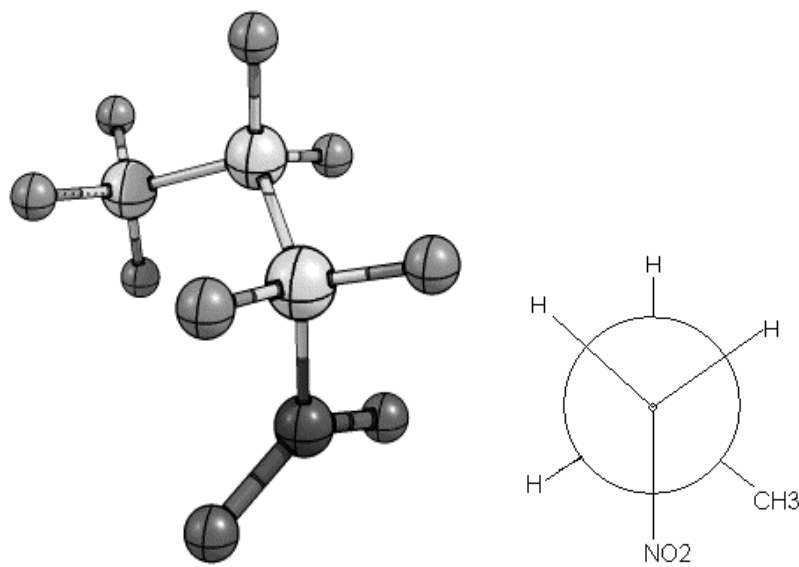
Electron diffraction reduced reliability factor in this particular calculation is equal 10.6 %. Further experimental and theoretical investigations are in progress.

1-NITROPROPANE

Two dimensional potential energy surface (PES) of internal rotation around C-C(N) and C-N bonds has been investigated with the GAUSSIAN-98 program package. B3LYP, MP2 and QCISD methods with different basis sets have been applied. Since the MP2/6-31G* method predicts the same form of PES as more accurate calculations, we used it to illustrate our theoretical model, that takes into account intermolecular and dynamic effects in electron diffraction intensity. The PES analysis of internal rotation around C-C(N) bond shows that there are two stable pseudo-conformers: anti and gauche. The barrier between them is rather high – about 1500cm^{-1} . Gauche-conformer is more stable and two minima in PES correspond to it. We also make the PES analysis of internal rotation around C-N bond for both conformers and some intermediate conformations. The PES for anti-conformer looks like PES for nitroethane with low barrier (about 100cm^{-1}). For gauche-conformer the PES is not symmetric and the barrier is much higher in comparison with anti-conformer (about 600cm^{-1}). The low height of the barrier is resulting in approximately free internal rotation around C-N bond. The structure of 1-nitropropane yet has not been investigated experimentally.

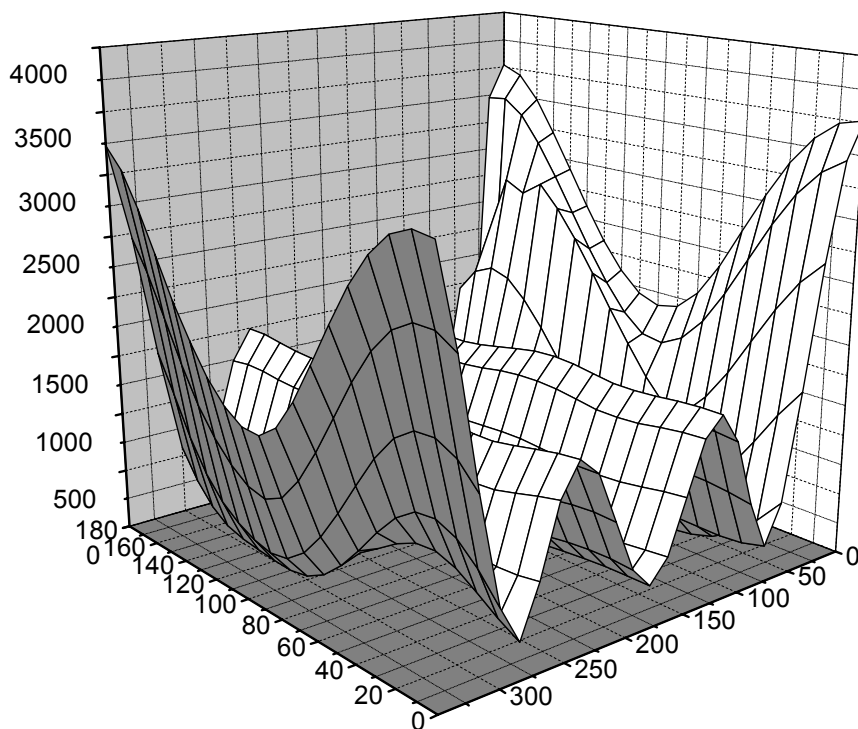


1-nitropropane (anti - conformer)

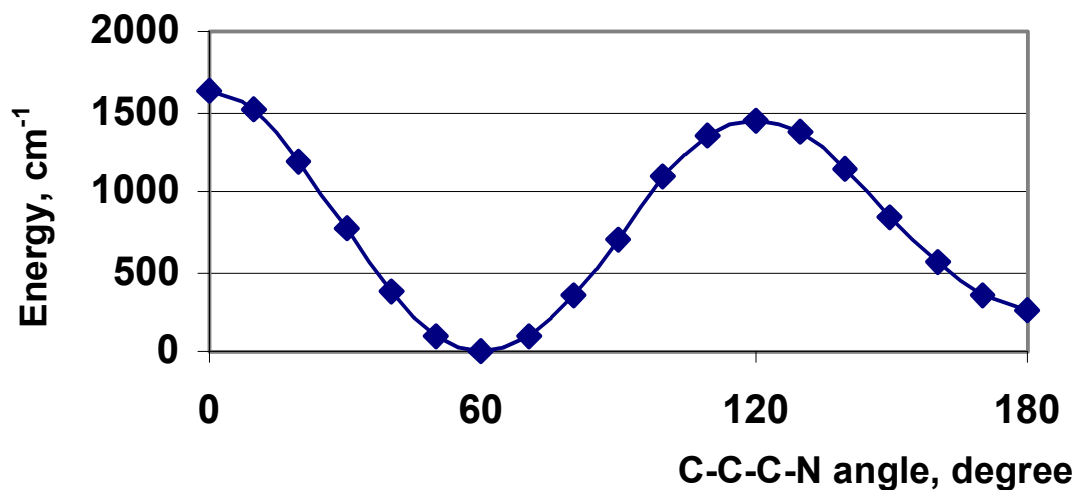


1-nitropropane (gauche-conformer)

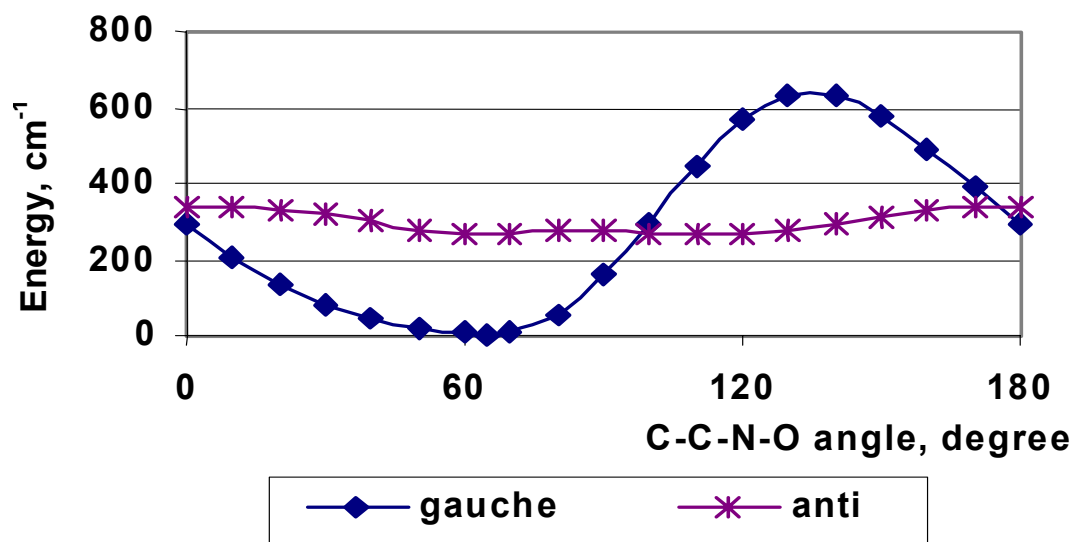
**Two dimensional potential energy surface of internal rotation around C-C(N)
and C-N bonds in 1-nitropropane**



Potential energy of internal rotation
around C - C(N) bond in 1-nitropropane



Potential energy of internal rotation
around C-N bond in 1-nitropropane.



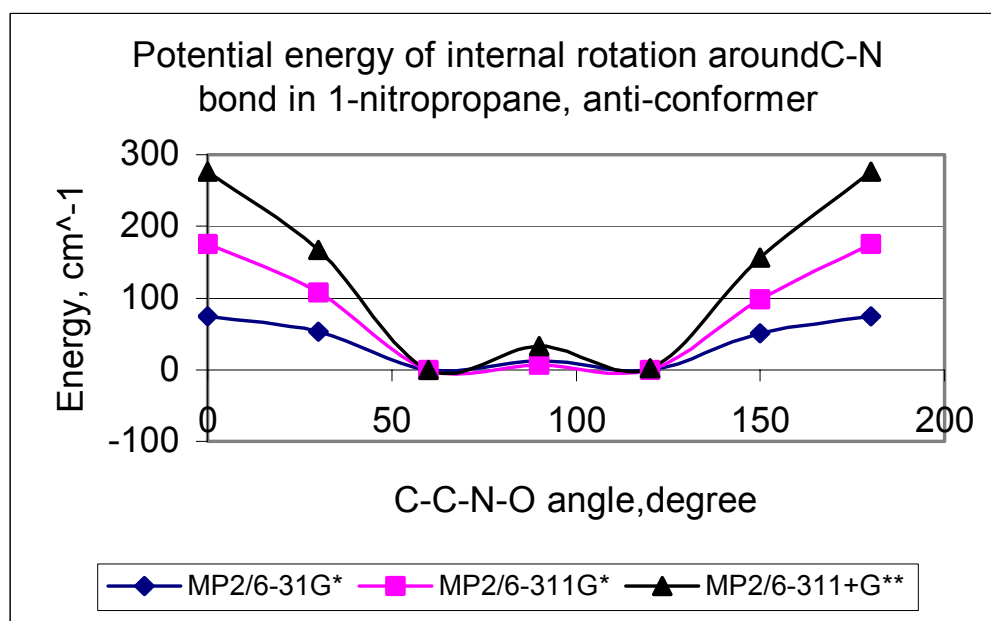
—◆— gauche —*— anti

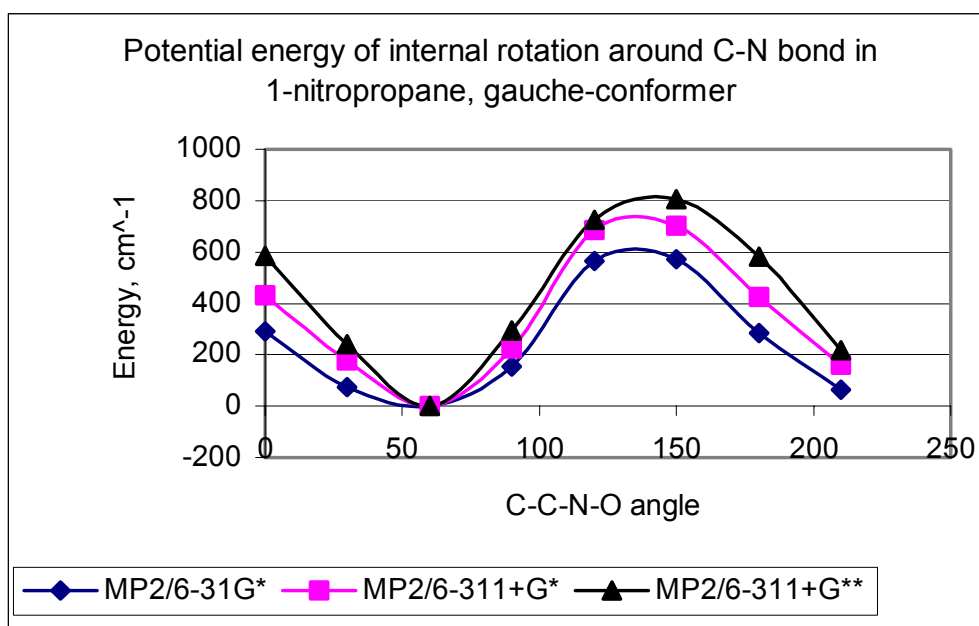
Molecular geometry of 1-nitropropane calculated with MP2 method with different basis sets :

Basis set	anti-conformer		gauche-conformer	
	6-311G*	6-311+G**	6-311G*	6-311+G**
C–N	1.494	1.496	1.495	1.498
N–O	1.230	1.231	1.230	1.231
C(N)–C(H2)	1.522	1.524	1.523	1.524
C(H2)–C(H3)	1.527	1.529	1.527	1.528
<O–N–C	116.5	116.6	116.5	116.6
<C–C–N	109.8	109.8	109.2	109.3
<C–C–C	111.0	110.9	111.3	111.0
<H–C–N	106.2	106.2	106.2	106.1
τ (C–C–N–O)	67.2	66.0	65.0	61.8
τ (C–C–C–N)	179.0	178.8	58.3	58.8

Energy barrier in cm^{-1} , torsion around C–N bond

Method	gauche-conformer	anti-conformer
MP2/6-31G*	628	75
MP2/6-311G*	702	176
MP2/6-311+G**	808	277





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