



X-ray, conformation and electronic structures of 1-nitropyrrolidine



Katarzyna Gajda ^a, Krzysztof Ejsmont ^a, Zdzisław Daszkiewicz ^a,
Christopher G. Gianopoulos ^b, Bartosz Zarychta ^{a, b, *}

^a Faculty of Chemistry, University of Opole, Oleska 48, 45-052 Opole, Poland

^b Department of Chemistry, University of Toledo, Toledo, OH 43606, United States

ARTICLE INFO

Article history:

Received 13 July 2015

Received in revised form

16 December 2015

Accepted 17 December 2015

Available online 20 December 2015

Keywords:

1-nitropyrrolidine

X-ray

DFT

Conformation

Disorder

ABSTRACT

The chemistry of pyrrolidine compounds has drawn much attention because of their biological activities. The crystal and molecular structure of 1-nitropyrrolidine ($C_4H_8NNO_2$) at 150K, along with calculated structures (DFT and MP2), are reported herein. In the solid-state, the asymmetric part of the unit cell is composed of one quartermolecule at the position of two perpendicular mirror planes and the five-membered ring is disordered over a mirror plane, revealing the twisted conformation. Both geometries suggest slight sp^3 hybridization of the amine nitrogen atom. The non-planar geometry suggests the lack of conjugation of the amine nitrogen lone pair with the nitro group, however the N–N bond distance indicates oppositely.

© 2015 Elsevier B.V. All rights reserved.

1. Introduction

Substituted pyrrolidine compounds are well documented in the literature because of their wide spread application to the synthesis of biologically active compounds and natural products [1–5]. Accordingly, pyrrolidines are used as building blocks in pharmaceutical and fine chemical manufacturing [6,7]. Pharmaceutically active pyrrolidines possess anticonvulsant, antimicrobial and antifungal activities against various pathogens [8]. As a building block of many biological systems such as proline and furanose, the structure and conformation of five-membered rings may play a key role in the understanding of some processes in which these compounds participate [9]. Stereochemically, 1-nitropyrrolidines are among the most interesting nitroamines. A study of these compounds permits one to investigate such problems as the local geometry of the nitroamine group (degree of nonplanarity of the nitrogen atoms and/or torsion about the N–N bond) and the conformation of the five-membered ring (envelope or asymmetric envelope). The structure determination of saturated five-membered ring compounds poses a challenging problem as the small energy differences between differing conformations results

in facile interconversion between the various conformations [9]. The structure and conformation of the five-membered ring of 1-nitropyrrolidine and several derivatives were investigated previously by means of gas-phase electron diffraction [10] and theoretically at many levels of theory, i.e. RHF, DFT (B3LYP) and MP2 using 6-31G(d) [11] and HF and MP2 using 6-311++G(d,p) basis sets [9]. In the present work, the crystal structure of 1-nitropyrrolidine at 150 K and the molecular structure calculated using B3LYP and MP2 methods at the 6-311++G(d,p), 6-311++G(3df,3dp) and aug-cc-pvdz basis sets level are presented and compared.

2. Experimental

1-nitropyrrolidine was prepared by oxidation 1-nitrosopyrrolidine, according to literature procedures [12]. The product was crystallized from acetone (mp. 56–57 °C). FTIR (KBr) (cm^{-1}): 1493 ($\nu_a(NO_2)$), 1313 ($\nu_s(NO_2)$). 1H NMR (400 MHz, DMSO); δ (ppm): 3.769–3.734 (4H, m, H1), 1.973–1.909 (6H, m, H2A, H2B). ^{13}C NMR (400 MHz, DMSO); δ (ppm): 23.40 (C2, C2C), 49.70 (C1, C1A).

The IR spectrum was recorded with a Philips PU 9800 FT instrument in the range 400–4000 cm^{-1} employing KBr pellet technique. NMR spectra were recorded with a Bruker Ultrashield spectrometer operating at 400 MHz.

* Corresponding author. Faculty of Chemistry, University of Opole, Oleska 48, 45-052 Opole, Poland.

E-mail address: bzarychta@uni.opole.pl (B. Zarychta).

Single crystals of the 1-nitropyrrolidine were selected directly from the crystalliser. The experimental data were obtained on a KM4 CCD Xcalibur diffractometer (graphite monochromatic, MoK α radiation, $\lambda = 0.71073$ Å) at 150.0 (1) K. Corrections to the Lorentz and polarization factors were applied to reflection intensities. Data collection: CrysAlis CCD [13]; cell refinement: CrysAlis RED [13]; data reduction: CrysAlis RED [13]. A correction for absorption was not applied. The structure was solved by Superflip and EDMA [14,15] software. Hydrogen atoms were determined from the geometric concepts and refined with isotropic temperature factors of 1.2 times the U_{eq} value of the parent atom. All non-hydrogen atoms were located from difference Fourier synthesis and refined by least squares method in the full-matrix anisotropic approximation by SHELXL14 software [16].

The crystallographic data for the compound and details of X-ray experiment are collected in Table 1. Structure drawings were prepared by using the SHELXTL program [16]. Crystallographic data have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC 1409554; 12 Union Road, Cambridge CB2 1EZ, UK(Fax, 44-(1223)336-033, E-mail deposit@ccdc.cam.ac.uk.

The starting geometry of the molecule was modeled with a planar five-membered ring and the nitro group twisted by ca. 90°. The geometry was optimized by using the B3LYP hybrid functional [17–19] with the 6-311++G(d,p), 6-311++G(3df,3dp) and aug-cc-pvdz basis sets. All species correspond to the minima calculated at the DFT/B3LYP level with 6-311++G(d,p), 6-311++G(3df,3dp) and aug-cc-pvdz basis sets as determined by frequency analysis. Additionally, geometry optimization was performed at the MP2 level [20,21] with the same basis sets. The bonding was further analyzed by the NBO for all species. All calculations were performed using the GAUSSIAN09 program package [22].

3. Results and discussion

The experimental and calculated geometric parameters of 1-nitropyrrolidine are reported in Table 2. The solid-state and theoretical molecular structure of the title compound, along with the atom-numbering schemes is presented in Figs. 1 and 2. In the asymmetric part of the unit cell, there is one chemically equivalent but crystallographically independent quartermolecule. The crystal packing is shown in Fig. 3.

Table 1
Crystal data and refinement parameters.

Compound	C ₄ H ₈ N ₂ O ₂
M_w (g mol ⁻¹)	116.12
Temperature (K)	150.0 (1)
Crystal system	Orthorhombic
Space group	Cmcm
a (Å)	10.3292 (3)
b (Å)	7.8385 (3)
c (Å)	6.9076 (3)
Volume (Å ³)	559.28 (4)
Z	4
μ (mm ⁻¹)	0.11
F(000)	248
Index ranges	$h = \pm 13$; $k = \pm 10$; $l = -6, 9$
No. of reflections collected	2209
No. of unique reflections	418
Data/restraints/parameters	418/0/38
Goodness-of-fit	1.106
q_{calc} (Mg m ⁻³)	1.379
R[F ² > 2 σ (F ²)] Final R indices	$R_1 = 0.033$, $wR_2 = 0.0981$
R indices (all data)	$R_1 = 0.0447$, $wR_2 = 0.102$
Largest difference peak and hole (eÅ ⁻³)	0.14/–0.18

The conformational studies of 1-nitropyrrolidine play a crucial role in the previously reported structural analyses. Interestingly, the structure of 1-nitropyrrolidine [10] was interpreted in terms of an envelope conformation with a twisted nitro group on the basis of gas-phase electron diffraction. However, high level calculations [MP2/6-311++G(d,p)] suggest that the asymmetric envelope conformation is most favorable [11]. In both cases, the geometry about the amine nitrogen atom is markedly pyramidal. This has been confirmed in the solid-state structure presented herein, the sum of angles around the amine nitrogen atom N3 (357.5 (2)°) demonstrates slight pyramidalization. The atom is disordered over two sides by a (001) mirror plane. Accordingly, the nitro group is not coplanar with the plane formed by the C1/N3/C1^I atoms [symmetry code (I) 1–x, y, z]. Nevertheless the atom lies only 0.13 (5) Å above the C1/N2/C1^I plane indicating partial conjugation with the nitro group. In the molecular structure the N2–N3 bond length is shorter (1.328 (6) Å) than the distance characteristic of an N–N single bond (1.42 Å) [23] but longer than the distance characteristic of an N–N double bond (1.24 Å) [23] indicating partial double bond character. The conformation of the five-membered ring is not so obvious here as C2 and C2^{II} [symmetry code (II) x, y, 0.5–z] are disordered over a mirror plane (in the plane of the molecule) with occupancy factors of 0.5. Additionally, a perpendicular (100) mirror plane generates two symmetry equivalents of these atoms, forming an apparent envelope-like conformation. Due to this confluence both conformations (envelope and asymmetric envelope) could be considered plausible (Fig. 1a). However, upon closer inspection, there ought to be considerable steric strain between hydrogen atoms in the presumed envelope conformation, where the distance between H2b and H2b^I is 1.219 (6) Å [Symmetry code: (III) 1–x, y, z]. On the other hand, there are no apparent steric interactions in the asymmetric conformation. Moreover, the bond distances between C2–C2^{II} (envelope conformation) and C2–C2^{III} [asymmetric envelope conformation; symmetry code (III) 1–x, y, 0.5–z] are 1.373 (5) Å and 1.513 (5) Å respectively, while the average C–C bond distance in cyclopentane is 1.543 (18) Å [23]. Moreover, the asymmetric envelope conformation was predicted to be the most stable by Shustov and co-workers [11], on the basis of MP2 calculations. In this context it is evident that 1-nitropyrrolidine adopts the asymmetric envelope conformation with a 2-fold axis passing through the N2–N3 bond and the midpoint of the C2–C2^{III} bond (Fig. 1).

The bond distances and angles are in good accordance with values for the calculated structures. Some differences are observed for the nitroamine torsion angles. In the calculated structures, the values of the torsion angles O1–N2–N3–C1(C11) are in the range of 14.32° – 24.18° and –10.50° – –18.26°. Similar to the crystal structure, the amine nitrogen atom lies, on average, 0.17 Å above the plane defined by the C1–N2–C1^I atoms in structures calculated at the DFT/B3LYP level of theory. The nitro group is not coplanar with the plane formed by the neighboring pyrrolidine atoms. In structures calculated at the MP2 level of theory, the geometry of the amine group is even more pyramidal than the structure in the solid-state or the DFT structures. In the MP2 structure, the displacement of the nitrogen atom from the plane defined by the three neighboring atoms amounts to 0.29 Å. In light of the differences in the distance of the amine nitrogen from the plane defined by its neighbors (solid-state: 0.13 (5) Å, DFT: 0.17 Å, MP2: 0.29 Å), it is interesting to consider the presence of N_{pyrrolidine} → N_{nitro} π -interactions in the gas-phase structures. The N–N bond order is indeed suggestive of partial multiple bond character, regardless of the level of theory, as determined by NBO calculations (Table 3; Wiberg bond index DFT: 1.11, MP2: 1.12). Accordingly, the conformation of 1-nitropyrrolidine does appear to be sensitive to N_{pyrrolidine} → N_{nitro} π -interactions. The observed structures of the nitroamine group can be further rationalized as a mesomeric

Download English Version:

<https://daneshyari.com/en/article/1405174>

Download Persian Version:

<https://daneshyari.com/article/1405174>

[Daneshyari.com](https://daneshyari.com)