Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy 98 (2012) 479–480

Contents lists available at SciVerse ScienceDirect

Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy

journal homepage: www.elsevier.com/locate/saa

Short Communication

Comment on: “FT-IR, FT-Raman and UV spectral investigation; computed frequency estimation analysis and electronic structure calculations on 1-nitronaphthalene” by M. Govindarajan and M. Karabacak [Spectrochim. Acta A 85 (2012) 251–260]

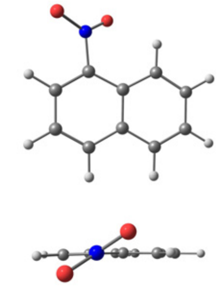
Andrea Alparone [a], Vito Librando [a,b,*]

[a] Research Centre for Analysis, Monitoring and Minimization Methods of Environmental Risk, viale A. Doria 6, Catania 95125, Italy
[b] Department of Chemistry, University of Catania, viale A. Doria 6, Catania 95125, Italy

HIGHLIGHTS

- Geometries, energetics and IR spectra of 1-nitronaphtahlene forms are discussed.
- The planar C_s form of 1-nitronaphtahlene is an unstable structure.
- The C_1 form is the global minimum energy structure for 1-nitronaphtahlene.

GRAPHICAL ABSTRACT



Molecular structure of 1-nitronaphthalene

ARTICLE INFO

Article history:
Received 29 January 2012
Received in revised form 12 August 2012
Accepted 21 August 2012
Available online 28 August 2012

Keywords:
1-Nitronaphthalene
Vibrational spectroscopy
DFT calculations

ABSTRACT

The title paper [1] incorrectly establishes that, in gas phase the global minimum energy structure of 1-nitronaphthalene is planar (C_s symmetry). By contrast, present calculations indicate that the planar C_s form is an unstable structure on the potential energy surface, exhibiting an imaginary vibrational wavenumber value corresponding to the torsional mode of the nitro group around the C–N bond. At the B3LYP/6-311++G(d,p) level of calculation the global minimum energy structure of 1-nitronaphthalene in gas phase has a non-planar geometry, characterized by O–N–C–C dihedral angles of ca. 30° and lying 0.35 kcal/mol below the C_s form.

In their recent paper [1], Govindarajan and Karabacak have state that at the DFT-B3LYP/6-311++G(d,p) level of calculation the equilibrium geometry of 1-nitronaphthalene (**1-NN**) is planar (C_s symmetry). Unfortunately this statement contradicts many earlier reports [2–8], which suggested that the global minimum energy structure of **1-NN** is non-planar. As well-known in literature, the structures of nitro polycyclic aromatic hydrocarbons are rather sensitive to the steric repulsions between the oxygen atoms and the neighbouring hydrogen atoms in *peri* position [9]. These interactions principally influence the O–N–C–C dihedral angles, (Fig. S1 of the Supplementary data) which can deviate also significantly from the planarity. In particular, previous theoretical investigations in gas phase at AM1 [2], PM3 [3], B3LYP/6-31G(d) [4], B3LYP/cc-pVDZ [5,6], and PBE0/6-311G(d,p) [7] levels, all concordantly reported a non-planar ground-state structure (C_1

---

* Corresponding author at: Research Centre for Analysis, Monitoring and Minimization Methods of Environmental Risk, viale A. Doria 6, Catania 95125, Italy. Tel.: +39 957385201.
E-mail address: vlibrando@unict.it (V. Librando).

1386-1425/$ - see front matter © 2012 Elsevier B.V. All rights reserved.
http://dx.doi.org/10.1016/j.saa.2012.08.070

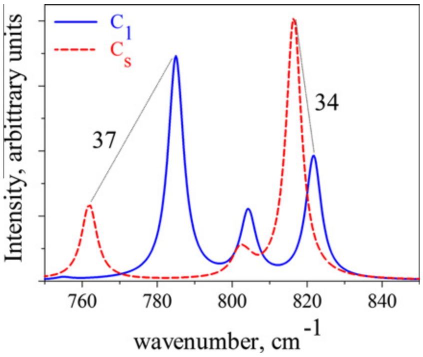


Fig. 1. IR spectral region between 750 and 850 cm^{-1} of 1-nitronaphthalene in the C_1 and C_s forms. B3LYP/6-311++G(d,p) results.

symmetry) for **1-NN**, characterized by O–N–C–C dihedral angles between 23° and 60°. Additionally, the equilibrium geometry of **1-NN** in various solvents is predicted to be non-planar [7,8]. At the B3LYP/cc-pVDZ and IEFPCM-B3LYP/6-311++G(d,p) levels, the relaxed rotation of the nitro group around the C–N bond of **1-NN** produces two saddle-points at the O–N–C–C torsion angle of 0° and 90° [6,8]. The vibrational analysis performed at the B3LYP/cc-pVDZ level confirms that, the non-planar structure with the O_{12}–N_{11}–C_1–C_8 and O_{13}–N_{11}–C_1–C_9 dihedral angles of 23° and 24° (Fig. S1 of the Supplementary data) is the global minimum energy structure of **1-NN** (all the vibrational wavenumbers are real) [5]. Unfortunately, experimental geometrical data for **1-NN** are not available so far. Therefore, it is of great importance to establish rigorously the equilibrium structure of **1-NN**, since the consequences of planarity might be dramatic. As widely recognized in literature, the mutagenic behaviour of nitroaromatic compounds is closely linked to the structure [9,10]. On the whole, compounds with the nitro group co-planar to the aromatic moiety exhibit mutagenic activities higher than those of isomers with the nitro group rotated. In the specific case of nitronaphthalenes, **1-NN** is predicted to be ca. 2–4 times less mutagenic than the planar 2-nitronaphthalene isomer [11,12].

For the present comment, we have re-optimized the structure of **1-NN** in gas phase at the same level used by Govindarajan and Karabacak [B3LYP/6-311++G(d,p)], assuming both the C_1 and C_s symmetry. The molecular geometries are given in the Supplementary data (Tables S1 and S2). The vibrational wavenumber and IR intensity values for the two forms, obtained under the harmonic approximation at the same level used for the geometry optimization, are collected in Tables S3 and S4 of the Supplementary data. All calculations have been performed with the Gaussian 09 program [13].

Our results unambiguously indicate that the C_1 form is the global minimum energy structure, the C_s form lying 0.35 kcal/mol above the C_1 structure (the zero-point vibrational energy corrections are considered). The B3LYP/6-311++G(d,p) C_1–C_s relative stability agrees with the results previously obtained at the B3LYP/cc-pVDZ level [6]. Additionally, the O_{12}–N_{11}–C_1–C_8 and O_{13}–N_{11}–C_1–C_9 dihedral angles for the C_1 structure are calculated to be 31.3° and 32.5°, respectively, in agreement with previous theoretical estimates [2–8].

For the C_1 form all the vibrational wavenumbers are real (Table S3 of the Supplementary data), whereas for the C_s structure an imaginary low-lying vibrational mode is computed at 53.8*i* cm^{-1} (Table S4 of the Supplementary data). This vibration corresponds to the torsional mode of the nitro group around the C–N bond. Additionally, wavenumber and IR intensity values of other vibrations are influenced by the planarization of the nitro group. The results are shown in Fig. 1 and in Figs. S2 and S3 of the Supplementary data. In particular, when passing from the C_1 to the C_s form, the peak of the mode No. 37, assigned to an out-of-plane C–H bending, is shifted downward by 23 cm^{-1}, concomitantly decreasing in intensity by ca. a factor of three (Fig. 1). For the vibrational mode No. 34 (ascribed to an out-of-plane C–H bending), when going from the non planar to the planar form, the wavenumber value slightly decreases (5 cm^{-1}), whereas the IR intensity increases by about a factor of two (Fig. 1).

Finally, not surprisingly, on going from the C_1 to the planar structure, some fundamental physicochemical properties (the data are collected in Table S5 of the Supplementary data) such as dipole moment, electronic mean polarizability and polarizability anisotropy increase by 4.6%, 0.7% and 8.2%, respectively. On the other hand, the HOMO–LUMO energy gap and entropy at 298.15 K decrease by 2.8% and 4.6%, respectively.

Acknowledgments

The authors gratefully acknowledge MIUR, Roma, PRIN2009 Program.

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.saa.2012.08.070.

References

[1] M. Govindarajan, M. Karabacak, Spectrochim. Acta A 85 (2012) 251–260.
[2] N. Sera, K. Fukuhara, N. Miyata, H. Tokiwa, Mutat. Res. 349 (1996) 137–144.
[3] S.-T. Lin, Y.-F. Jih, P.P. Fu, J. Org. Chem. 61 (1996) 5271–5273.
[4] K.K. Onchoke, C.M. Hadad, P.K. Dutta, Polycyclic Aromat. Compd. 24 (2004) 37–64.
[5] V. Librando, A. Alparone, J. Hazard. Mater. 154 (2008) 1158–1165.
[6] V. Librando, A. Alparone, Z. Minniti, J. Mol. Struct. (Theochem) 856 (2008) 105–111.
[7] J.S. Zugazagoitia, C.X. Almora-Dìaz, J. Peon, J. Phys. Chem. A 112 (2008) 358–365.
[8] C. Reichardt, R.A. Vogt, C.E. Crespo-Hernández, J. Chem. Phys. 131 (2009). 224518-15.
[9] P.P. Fu, M.W. Chou, D.W. Miller, G.L. White, R.H. Heflich, F.A. Beland, Mutat. Res. 143 (1985) 173–181.
[10] Y.S. Li, P.P. Fu, J.S. Church, J. Mol. Struct. 550–551 (2000) 217–223.
[11] H.S. Rosenkranz, R. Mermelstein, Mutat. Res. 114 (1983) 217–267.
[12] H.S. Rosenkranz, R. Mermelstein, in: C.M. White (Ed.), Nitrated Polycyclic Aromatic Hydrocarbons, Huthig Verlag, Heidelberg, 1985. pp. 267–297.
[13] M.J. Frisch et al., Gaussian 09, Revision A.02, Gaussian, Inc., Wallingford, CT, 2009.