Journal of Molecular Structure 1080 (2015) 145–152

Contents lists available at ScienceDirect

Journal of Molecular Structure

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

Quantum mechanical and experimental analyses of TNT metabolite 2-hydroxylamino-4,6-dinitrotoluene

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HIGHLIGHTS

- Quantum mechanical MP2/aug-cc-pVDZ simulations of 2-HADNT for geometry optimizations and conformational energy profile.
- Single point MP2/aug-cc-pVDZ calculations of chemical properties.
- Energy minimum structures are found to be very close to the crystal structure.
- The 4-nitro group exhibits co-planarity with the phenyl ring in both crystal and energy minimization structures.
- This work demonstrates considerable discrepancies of some results between MP2 and B3LYP methods.

ARTICLE INFO

Article history:
Received 22 July 2014
Received in revised form 21 September 2014
Accepted 21 September 2014
Available online 5 October 2014

Keywords:
2-HADNT
MP2
HUMO–LUMO separation
Conjugation
Dipole

ABSTRACT

In this study, a combined quantum mechanical and experimental analyses were performed to investigate crystal structure of the immediate degradation product of TNT, 2-hydroxylamino-4,6-dinitrotoluene (2-HADNT) and to reveal its important chemical properties. Leakage of 2-HADNT has caused serious environmental pollution and therefore raises widespread concerns. In the quantum mechanical analysis, the B3LYP/6-311+G**, B3LYP/aug-c-pVDZ, M06HF/aug-cc-pVDZ, and MP2/aug-cc-pVDZ methods were employed for geometrical optimization and single point calculations of chemical properties of the compound. Such properties include highest unoccupied molecular orbitals (HOMO) – lowest occupied molecular orbitals (LUMO) separation, dipole moment, atomization energy, and vibrational frequencies. Experimental analysis and validation showed that the energy minimized structures acquired from the quantum mechanical analysis were very similar to those obtained by X-ray crystallography. The 6-NO_2 groups twist out of plane with respect to the benzene ring in both the crystallographic and energy minimized structures. The 4-NO_2 group exhibits co-planarity with the phenyl ring in both the crystallographic and energy minimized structures as well. Unlike TNT, however, the energy barrier to orthogonal conformation is only 3.8 kcal/mol. In addition, considerable discrepancies between results obtained from the MP2 and B3LYP methods were observed, which suggest that it has to be very careful when applying B3LYP method to study such class of compounds. Through this study, a more accurate description of the chemical properties of dispersion-dominated aromatic systems was acquired. The chemical properties found from this study can help researchers to better understand the compound of 2-HADNT and to develop effective management plans for such compound so as to minimize its impact on the environment.

Introduction

The explosive 2,4,6-trinitrotoluene (TNT) has been widely used for military and commercial purposes for centuries [1–3]. However, the extensive application of TNT resulted in significant environmental contaminations through carcinogenic TNT and its metabolites, and environmental remediation is therefore highly wanted [4,5]. It is well known that TNT mineralizes slowly, mostly follows reductive pathways and gives rise to toxic intermediates including 2-hydroxylamino-4,6-dinitrotoluene [6–11]. In order to effectively implement environmental remediation, analytical and toxicological evaluations of contaminated sites are required and therefore a thorough knowledge of the properties of the reduction

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http://dx.doi.org/10.1016/j.molstruc.2014.09.058
0022-2860/

products such as hydroxylamino-, amino-, azo-, and azoxytoluenes is highly wanted. It was found that initial products of TNT reductive degradation are 2-hydroxylamino-4,6-dinitrotoluene (2-HADNT) and its isomer 4-hydroxylamino-2, 6-dinitrotoluene (4-HADNT), as shown in Fig. 1 [11–13]. Homma-Takeda et al. found that 4-HADNT damages DNA, prompts the generation of 8-oxodG, and causes cleavage of DNA at sites with consecutive guanines [14]. It was also agreed that an understanding of the chemical properties of these initial TNT reduction products may provide insight into their reductive pathways and environmental fates [15]. Unfortunately, as pointed out by Junk, Catallo, and Maeda, limited access to various TNT degradation products remains a significant barrier in collecting experimental data from those materials and performing experimental analysis [11,13]. Quantum mechanical simulation can be an advanced and alternative method to evaluate their thermo-chemical properties. However, such method has to be validated by comparing the quantum mechanical simulation results with the experimental data.

In this paper, two Density Functional Theory (DFT) methods and high level second order Møller–Plesset perturbation theory (MP2) method were applied to calculate the chemical properties of 2-HADNT and the simulation results were compared with the experimental data obtained from X-ray crystallography. Important chemical properties include the LUMO–HOMO separation [10,16], dipole moment, and atomization energy. Especially, in this study, the structural parameters of 2-HADNT were compared with the published structural parameters for TNT [17–20] and their differences were highlighted.

Regarding the employed research tools, the DFT methods have been widely used in theoretical simulations of TNT and its derivatives [10,16,21–31], whereas the application of MP2 methods are relatively limited due to its high computational cost [24,29,31]. However, the most popular DFT method B3LYP [32–35] was found being inaccurate in simulating dispersion-dominated non-covalent interactions [36]. In fact, mPWB1K/TZVP was found to be the most accurate DFT for computing the reduction potential of nitrobenzenes [37]. On the other hand, the vibrational frequencies calculated using B3LYP/6-311+G** were found to best agree with those determined by infrared spectrum (IR) [30]. Based on these reasons, this study targeted the quantum mechanical simulation of 2-HADNT using the B3LYP and MP2/aug-cc-pVDZ methods. The simulation results were then compared with the data obtained from X-ray crystallography as well as the published results for TNT. A more accurate description of the chemical properties of dispersion-dominated aromatic systems was acquired through this study.

Research approach

Computational method

In the mechanical simulation, computer models were generated for molecular structure, which was the optimized structure at MP2 level based on the compound's crystal structure (the molecular structure can be seen from Fig. 1). Initial coordinates derived from the crystal structure of 2-HADNT were optimized with MP2/aug-cc-pVDZ using Gaussian-09 [38]. Based on the computer models, important chemical properties such as LUMO–HOMO gap, dipole moment and atomic energy were then calculated using the B3LYP, M06HF, and MP2 methods. The calculated conformational energy profile of 2-HADNT was then compared with a published conformational energy profile of TNT (entry ZZZMUC01), obtained from the Cambridge Crystallographic Data Centre [17]. The aug-cc-pVDZ basis sets were used throughout all single point calculations, and the results were compared with those obtained using the basis set 6-311+G**. In order to compare with the experimental data, solvation effects need to be considered [39,40]. In this work, solvation effects were considered for single point calculations only and solvation corrections were implemented using the polarizable continuum model (SMD) [41] with a dielectric constant of 4.7 for an aqueous solution [42]. Minimized structures were confirmed by an absence of negative frequencies in vibrational frequency calculations. All the computational simulations and calculations were performed on a quad-core cluster canpe01 and dual-core canfire04 at the Center for Advanced Computer Studies (CACS) at the University of Louisiana at Lafayette with support of high performance computational resources provided by the Louisiana Optical Network Initiative (LONI).

Experimental method

In experimental analysis 2-HADNT was synthesized following a procedure presented by Junk and Catallo [11]. In that procedure, a Fourier transformation infrared (FTIR) sample of 2-HADNT was first mixed with KBr and was compressed to a thin layer for IR analysis. In our study, FTIR spectra were determined using a JASCO FI/IR-480 spectrometer with an attached continuum micro-

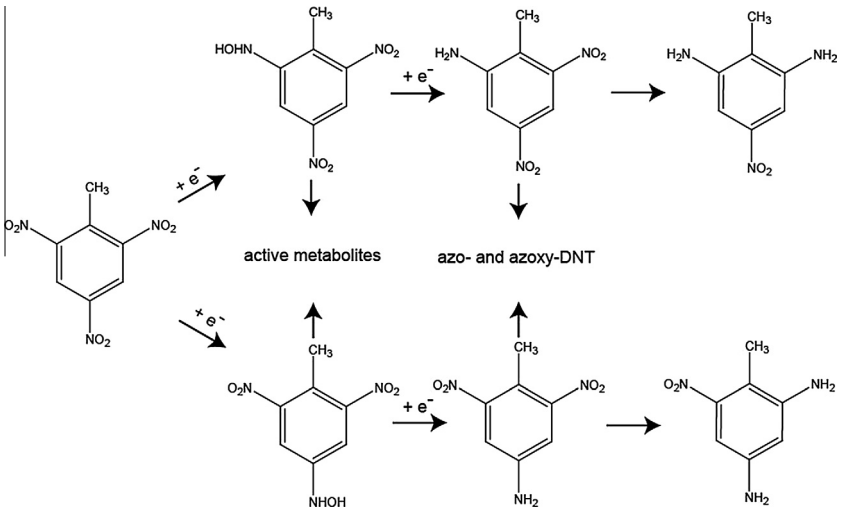

Fig. 1. Reductive degradation pathway of TNT.