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An ab initio study on ethylenedinitramine and its monovalent ions

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Abstract

An explosive material, ethylenedinitramine (EDNA), its mono and di *aci* forms, as well as its monovalent cation and anion forms have been considered for 6-31G (UHF) type ab initio quantum chemical treatment in order to investigate the stability of EDNA in the neutral form and when charges develop on it exposed to electrical fields during the storage, handling or explosion process. The calculations indicate stable species. The *aci* forms are less stable than EDNA itself and the anion form is more stable than the neutral and cation forms. Although, the charge development is accompanied by some elongation or contraction of bonds and deviation of bond angles also as compared to the neutral state, no bond rapture occurs.

Keywords: EDNA; Ethylenedinitramine; Explosive; Nitro compound; Ab initio

1. Introduction

EDNA (ethylendinitramine, 1,4-dinitro-1,4-diazabutane) is a nitramine type highly important explosive [1–3]. Nitramines have long been used for technological as well as military purposes [1–5]. In practice, usually new energetic materials are designed by modifying known substances by addition and/or modification of explosophoric group(s) in the molecule(s). However, the research on the subject also accumulates in the direction of synthesis of brand new explosives as well as the development of theoretical methods. These help chemists to develop systematic and scientific approach, thus formulations of appropriate futuristic molecules having ameliorated properties for the desire. These properties might be good thermal stability, impact and friction sensitivity and enhanced explosive performance. The major aim of these methods, apart from being developed as predictive tool in general, is to provide some insight to understanding the molecules which are responsible for higher performance and which are not. Hence, the quantum chemical approaches at various level of sophistication might be helpful to visualize certain aspects of explosion process. For example, electrostatic charges developed during the handling and processing of bulk powder such as explosive, propellant and pyrotechnic powders can be sufficient to cause ignition under certain conditions [6–8]. The propagation of detonation waves could be controlled by means of external magnetic and electrical fields [9]. The influence of these fields on the explosive material might cause polarization or ionization, which may be involved by some means of explosion mechanism. Some explosives, like RDX and TNT, because of their ring shaped geometries are comparatively rigid molecules. While nitrate esters and nitramines are not constrained in such a fashion and are “floppier”. These molecules have more conformational states and might be expected that this would leave the nitrate esters and nitramines more susceptible to fragmentation in external fields [10]. Being a nitramine, the explosion process of EDNA could be triggered by charge development arising from exposure to external fields, static charging by friction or pressure.

Recently, nitramines have been considered for investigation of various properties of them. Especially, the stability and decomposition mechanisms have been the subject of some theoretical treatment [11–15]. Note that storage and handling stability of explosives are as important as their

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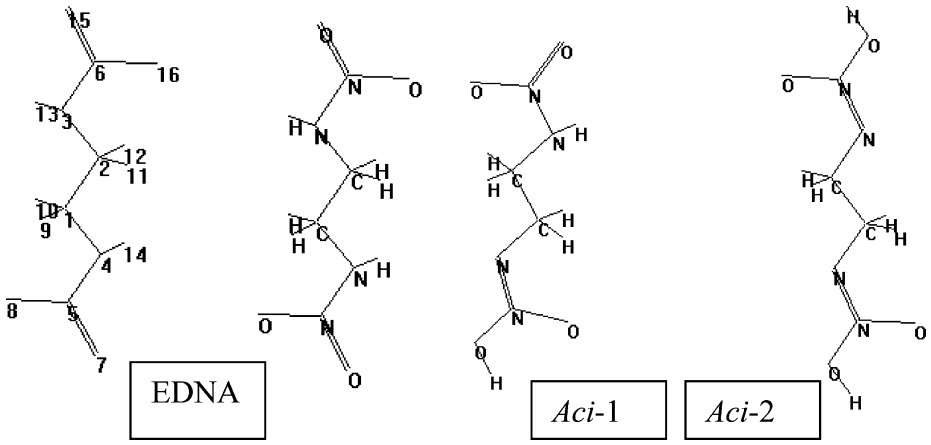

Fig. 1. The chemical structures of EDNA and its *aci* forms.

blasting performances. One of the factors to be considered along this line is whether the development of static charges on the explosive material generates certain hot points. In the present study, to shed some light on the stability of an important nitramine, EDNA, to electrical charging and to investigate whether the charged forms play a role in the explosion process, the neutral as well as its monovalent ions have been subjected to quantum chemical analysis.

2. Method

The initial geometry optimizations of all the structures leading to energy minima were achieved by using MM+ method followed by semiempirical PM3 self-consistent fields molecular orbital (SCF MO) method [16,17] at the unrestricted Hartree-Fock (UHF) level [18] (by the application of the steepest-descent method followed by conjugate gradient methods, Fletcher-Reeves and Polak-Ribiere, consecutively; convergence limit of 4.18×10^{-4} kJ/mol and RMS gradient of 4.1810^{7} kJ/m mol) and then by, ab initio treatment at the level of 6-31G [18,19] (UHF type, convergence limit 10^{-5} kcal/mol and RMS gradient of 10^{-3} kcal/A mol) by using Polak-Ribiere technique. The Raffenetti integral format (cut-off 1×10^{-10} Hartree) was used for two-electron integral control. For the molecular orbital initial guess, the core-Hamiltonian option [19,20] was applied with involvement of six d-orbitals. The geometry optimized structures were subjected to vibrational analysis (UHF, 6-31G) for the judgment of their stabilities. Furthermore, all the bond lengths were thoroughly searched. All these computations were performed by using the Hyperchem (release 5.1) package program.

3. Results and discussion

EDNA (Haleit) forms orthorhombic white crystals. EDNA is a nitramine type organic explosive and it was found that polynitro aliphatics containing at least one N–NO_2 (nitramine) linkage are more sensitive than nitroaliphatic explosives containing C–NO_2 linkage [5].

Krygowsky et al. have claimed that, in the crystalline state pyridylnitramines exist in the nitrimino forms [21,22] whereas a detailed ab initio study of N-(2-pyridyl)-nitramine, contrary to the structural data, favors the nitramino form [21,22]. Keeping these literature data in mind, presently, various forms of EDNA have been screened for their relative stabilities. In the case of EDNA, 1,3-proton tautomerism involving the shift of hydrogen from amino nitrogen to oxygen site (by analogy called mono and di *aci* forms) may be possible. Because of that the calculations extended to these forms. The chemical structures of EDNA and its tautomeric *aci* forms are shown in Fig. 1. Whereas, Table 1 shows some of the calculated energies of EDNA and its tautomeric *aci* forms. The geometry optimized structures of the *aci* forms are shown in Fig. 2. The data in Table 1 reveal that EDNA in its nitramine form is far more stable than its *aci* forms.

The stability order is EDNA > *Aci*-1 > *Aci*-2. Since the nitrimine forms are attainable via *aci* forms and they are less stable than EDNA, the nitrimine forms are not considered. Hence, in the present study, EDNA in nitramine form has been adopted to investigate the effect of charge development on the stability and some quantum chemical properties of it.

The geometry optimized structures based on 6-31G (UHF) type ab initio calculations (see Fig. 3) have C_2, C_1 and C_1 type molecular point groups for the neutral, cation and anion forms, respectively. Table 2 shows the calculated bond

Table 1
Some calculated energies for EDNA and its *aci* forms

Energy	EDNA	*Aci*-1	*Aci*-2
Total	−1564429	−1564407	−1564364
Electronic kinetic	1565811	1565773	1565664
EK, ee, and eN	−3029517	−2992808	−3008516
Nuclear repulsion	1465088	1428401	1444152
Viral	1.9991	1.9992	1.9991
Total (MP2)	−1567518	−1567382	−1567231

Energies in kJ/mol.