



Trans-dinitroglycoluril isomers-A DFT treatment



Lemi Türker*

Middle East Technical University, Department of Chemistry, Ankara, Turkey

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ABSTRACT

Isomers of *trans*-1,4-Dinitroglycoluril (*trans*-DINGU) and their 1,3-tautomers are considered within the constraints of B3LYP/6-31++G (d,p) and B3LYP/CC-PVTZ levels of DFT calculations. Additionally, the interactions of these isomers and proton in vacuum are investigated. The data have revealed that two of the three isomers undergo C–H bond cleavage as the result of interaction with proton in vacuum. The total energies, some structural properties, the calculated IR and UV spectra are discussed.

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1. Introduction

The chemical, known as *cis*-1,4-Dinitroglycoluril (*cis*-DINGU) [1,2], is an important explosive and it has been of interest to the high energy materials community recently. *cis*-DINGU was prepared as early as 1888 by Franchimont and Klobbie [3,4]. Then various synthesis of *cis*-DINGU and its derivatives were described in the literature [5–9]. It has been fully characterized [2,10,11]. Nowadays *cis*-DINGU is regarded as one of the potential ingredients for low vulnerability ammunition applications [12]. It has been as an insensitive alternative to RDX (hexahydro-1,3,5-trinitro-s-triazine) and TNT (trinitro-toluene) [13]. Table 1 displays some properties of *cis*-DINGU and some selected explosives.

Furthermore, *cis*-DINGU based PBXs (polymer bonded explosives) [15,16] generally have good physico-chemical stability, high explosion energy and low vulnerability, so that they are comparable to TATB (triamine-trinitro-bezene)-based PBXs. DINGU/Estane PBXs were investigated in detail [11]. Ternary compositions of *cis*-DINGU with TNT and RDX was the subject of a patent work [16].

The preparation of *cis*-DINGU is very simple and make use of inexpensive starting materials as compared to TATB. Therefore, *cis*-DINGU based PBXs have preference over TATB based PBXs [17]. Also

toxicological studies on *cis*-DINGU were done [18] and the data have revealed that it would be considered only slightly toxic according to the classical guidelines. In the literature, there are many studies on *cis*-DINGU including its synthesis [5–7], structure determination (X-ray diffraction for *cis*-DINGU) [19], evaluation of the solid-state formation enthalpy [20], spectro-thermal decomposition [21], mass-spectral fragmentation pathways [22], modelization by molecular mechanics [23], modelization by using AM1 and PM3 methods [24]. In contrast to many reports on *cis*-DINGU, there is no study on *trans*-DINGU (*trans*-1,4-dinitroglycoluril) to the best of our knowledge (neither its synthesis nor X-ray crystallographic investigation) except a computational study exists where the performed DFT and *ab initio* calculations revealed some structural, quantum chemical and thermal properties of DINGU configurational isomers (*cis*- and *trans*-DINGU) in the gas phase [25]. In the present study, isomers of *trans*-1,4-Dinitroglycoluril (*trans*-DINGU) are considered within the constraints of B3LYP/6-31++G (d,p) and partly B3LYP/CC-PVTZ levels of DFT calculations.

2. Method

The initial geometry optimizations of all the structures leading to energy minima were achieved by using MM2 method followed by semi-empirical PM3 self-consistent fields molecular orbital (SCF MO) method [26,27] at the restricted level [28,29].

Subsequent optimizations were achieved at Hartree-Fock level using various basis sets. Then, geometry optimizations were

* Tel.: +90 3122103244.

E-mail address: lturker@metu.edu.tr.

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Table 1
Some properties of selected explosives.

	TNT	RDX	HMX	cis-DINGU
Oxygen balance/%	−73.9	−21.6	−21.6	−27.6
Density/(g·cm ^{−3})	1.654	1.82	1.87 α form 1.96 β 1.82 γ 1.78 δ	1.94 1.98 [11]
Energy of formation/(kJ·kg ^{−1})	−219.0	401.8	353.6	
Heat of formation/(kJ·kg ^{−1})	−295.3	301.4	253.3	−42.3, −46/(kcal·mol ^{−1}) [11]
Volume of explosion/(l·kg ^{−1})	825	903	902	
Heat of explosion (H ₂ O gas)/(kJ·kg ^{−1})	3646	5297	5249	
Velocity of detonation (confined)/(m·s ^{−1})	6900	8750	9100	7580
	ρ :1.60/(g·cm ^{−3})	ρ :1.76/(g·cm ^{−3})	ρ :1.9/(g·cm ^{−3})	ρ : 1.75/(g·cm ^{−3})
Impact sensitivity/Nm	15	7.5	7.4	5–6
Friction sensitivity/N	353	120	120	20–300

Data excerpted from Ref. [14].

managed within the framework of density functional theory (DFT, B3LYP) [30,31] finally at the levels of 6–31++G (d,p) (restricted closed-shell) or CC-PVTZ [28,32]. The exchange term of B3LYP consists of hybrid Hartree–Fock and local spin density (LSD) exchange functions with Becke's gradient correlation to LSD exchange [31,33]. The correlation term of B3LYP consists of the Vosko, Wilk, Nusair (VWN3) local correlation functional [34] and Lee, Yang, Parr (LYP) correlation correction functional [35]. The vibrational analyses were also done. The total electronic energies are corrected for the zero point vibrational energy (ZPE). The normal mode analysis for each structure yielded no imaginary frequencies for the $3N-6$ vibrational degrees of freedom, where N is the number of atoms in the system. This indicates that the structure of each molecule corresponds to at least a local minimum on the potential energy surface. All these calculations were done by using the Spartan 06 package program [36].

3. Results and discussion

A nitramine type explosive, known as simply DINGU, is constitutionally *cis*-1,4-dinitroglucuril [25]. However, it should have also *trans* form which has not been synthesized yet. In addition to that either *cis* or *trans* forms of dinitroglucuril should have other isomers which possess the nitramine group at different positions of the bicyclic system. In the present study, *trans*-dinitroglucuril skeleton is considered in which three isomers exist arising from positional variations of the nitramine groups and they are indicated by capital letters as A, B and C.

3.1. *Trans*-dinitroglucuril isomers

In the present study, three possible structural isomers of *trans*-dinitroglucuril have been considered (Fig. 1). As seen in the figure, the *trans* forms of DINGU isomers possess bridge-head hydrogens oriented on opposite sites of the molecular plane, namely in the case of DINGU, *cis* and *trans* are defined with respect to the orientation of those hydrogens but not the nitro groups. The figure also shows the direction of the dipole moments they have. The isomers possess two nitramine groups which are flanked by at least one pure amide carbonyl group arising from the particular structure of glucuril backbone. Fig. 2 shows the bond lengths and Table 2 contains their area, volume and dipole moment values. In structure-A the nitramine bond lengths are almost the same, C=O bonds comparable and the amide C–N bonds are symmetrically equal. Structure-B possesses unequal nitramine bond lengths, whereas in structure-C, they are comparable (see Fig. 2 for details). The dipole moments of these isomeric structures follow the order of $B > A > C$.

Inspection of the bond length data reveals that in structure-B, one of the nitramine bonds is longer (1.49 Å) than the others. It is the longest of all the nitramine bonds in structure-A through C. Also the carbonyl bond flanked by that particular nitramine bond is longer (1.20 Å) than all the carbonyl bonds of these isomers. Based on classical resonance treatment, this fact could be explained if the nitramine, amine nitrogen lone-pair shifts towards the carbonyl group rather than to the nitro group. It might arise because of the geometrical factors operative in that particular ring, thus preventing the conjugation with the nitro group (see Figs. 1 and 2).

Table 3 shows the total energies (E), the zero point vibrational energies (ZPE) and the corrected total energies (E_c) which contain the ZPE values at the level of B3LYP/6-31++G (d,p). E_c value of DINGU (*cis*-1,4-dinitroglucuril) is -2453243.40 kJ/mol. Thus, the stability order based on E_c values is DINGU > C > A > B. Note that isomer-B has the greatest dipole moment among the set and the dipole moment of isomer-C is zero. Aqueous energies are obtained based on SAM5.4 model of Cramer and Truhlar [37]. In water the stability order is C > B > A. It means solvation effects on A and B in aqueous medium reverses the stability order of them while C remains the most stable one as it is in vacuum. Table 4 shows the similar energies obtained at the level of B3LYP/CC-PVTZ. Note that CC-PVTZ is a correlation consistent basis set. The stability order based on E_c values in this case is again DINGU > C > A > B.

The stability orders in vacuum and water indicate that isomer-C where the nitramine groups are crossly located is more stable than the others. Isomer-A having two nitramine groups on the same ring is the least stable in water. Isomer-B, the least stable in vacuum is somewhat stabilized by solvation and becomes more stable than isomer-A.

Fig. 3 displays the IR-spectra of the isomers considered. The N–H stretchings occur around 3600 cm^{−1}. In the spectra of isomer-

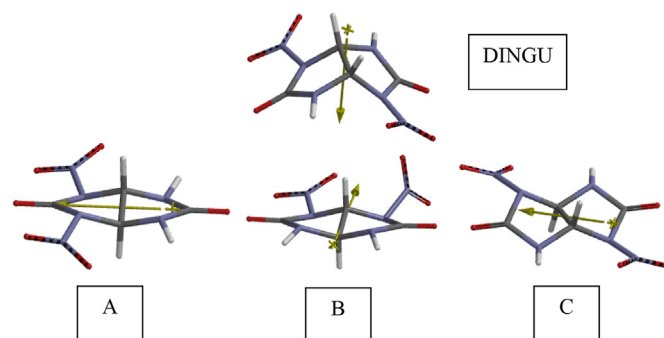


Fig. 1. *cis*-1,4-Dinitroglucuril (DINGU) and isomers of *trans*-dinitroglucuril (B3LYP/6-31++G (d,p) level of calculations).

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