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Ab initio and DFT study on 1,4-dinitroglycoluril configurational isomers: *cis*-DINGU and *trans*-DINGU

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Abstract

cis-1,4-Dinitroglycoluril (1,4-dinitrotetrahydroimidazo[4,5-d]imidazole-2,5-(1H,3H)-dione, $C_4H_4N_6O_6$, known as DINGU in the literature) is an important explosive regarded as one of the potential ingredients for LOVA (low vulnerability ammunition) applications. However, there is no study concerning *trans*-DINGU, to the best of our knowledge. Thus, in the present study the structural and electronic properties of the configurational isomers of DINGU (*cis*- and *trans*-isomers) have been investigated by performing density functional theory (DFT) calculations at B3LYP/6-31G(d,p), UB3LYP/6-31G(d,p) levels and also ab initio calculations at RHF/6-31G(d,p) and UHF/6-31G(d,p) levels. The optimized geometries, vibrational frequencies, electronic structures, and some thermodynamical values for the presently considered DINGU isomers have been obtained in their ground states. Comparing the calculated energy data (total electronic energy, heat of formation values and homolytic bond dissociation values of N–NO_2) and the calculated bond lengths, *cis*-DINGU was found to be a more stable molecule than the *trans*-isomer.

Keywords: *cis*-DINGU; *trans*-DINGU; Dinitroglycoluril; Explosives; Nitro compounds; Nitramines

1. Introduction

cis-1,4-Dinitroglycoluril (*cis*-DINGU) [1] is an important explosive, that has been of interest to the HEMs (high energy materials) community recently. *cis*-DINGU was prepared as early as 1888 by Franchimont and Klobbie [2,3]. The synthesis of *cis*-DINGU and its derivatives were described in the literature [4–6]. *cis*-DINGU is regarded as one of the potential ingredients for LOVA (low vulnerability ammunition) applications [7]. It has been as an insensitive alternative to RDX (hexahydro-1,3,5-trinitro-*s*-triazine) and TNT (trinitro-toluene) [8]. *cis*-DINGU based PBXs (polymer bonded explosives) possess high explosion energy, good physico-chemical stability and low vulnerability, which is comparable to TATB (triamine-trinitro-bezene)-based PBXs. Since, preparation of *cis*-DINGU is very simple and uses inexpensive starting materials as compared to TATB, *cis*-DINGU based PBXs have a definite edge over TATB based PBXs [9]. Toxicological study of *cis*-DINGU was also investigated [10] and according to the classical guidelines, it would be considered only slightly toxic.

In the literature, there are many studies on *cis*-DINGU including its synthesis [4–6], structure determination (X-ray diffraction for *cis*-DINGU) [11], evaluation of the solid-state formation enthalpy [12], spectro-thermal decomposition [13], mass-spectral fragmentation pathways [14], modelization by molecular mechanics [15], modelization by using AM1 and PM3 methods [16]. However, to the best of our knowledge, there is no study on *trans*-DINGU (neither any X-ray crystallographic investigation nor computational study for it). In the present work, ab initio calculations and the density functional theory (DFT) calculations have been carried out concerning *cis*-DINGU and *trans*-DINGU and the results are compared.

2. Method of calculation

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 [17,18] at the restricted level [19,20]. Then, geometry optimizations were achieved within the framework of density functional theory (DFT, B3LYP) [21,22]

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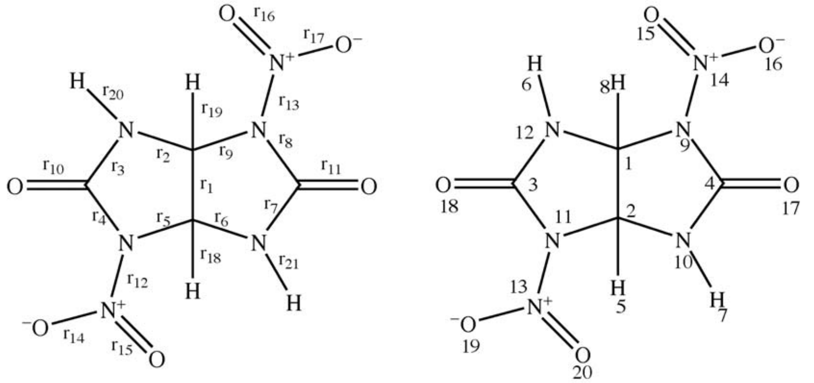

Fig. 1. Numbering of the atoms and bonds of DINGU (for both isomers).

at the level of 6-31G(d,p) (restricted closed-shell, and also unrestricted open-shell)[19]. 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 [22,23]. The correlation term of B3LYP consists of the Vosko, Wilk, Nusair (VWN3) local correlation functional [24] and Lee, Yang, Parr (LYP) correlation correction functional [25].

In addition to the DFT calculations, ab initio RHF/6-31G(d,p) and UHF/6-31G(d,p) calculations [26] were performed. Furthermore, single point MP2 calculations were carried out (for the ab initio RHF and UHF calculations) in order to obtain more accurate energy data. For each case (DFT and ab initio calculations, using the same basis set employed in the corresponding geometry optimizations) the vibrational analyses (presented here unscaled) were done. The total electronic energies are corrected for ZPVE. 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.

In this study, in order to compare the N–NO_2 bond strengths in the isomers, homolytic bond dissociation energy (BDE) calculations, for the removal of nitrogen dioxide moiety from the structures, were performed (the geometry optimized structures were considered, and in one set of calculations UB3LYP/6-

Table 1
Calculated bond lengths (in Å) of *cis*-DINGU and *trans*-DINGU at the different theoretical levels and their radicals after cleavage of one of the nitro group from the molecules

	B3LYP[a]	RHF[a]	X-ray diffraction[b]	UB3LYP[c]	UHF[c]	B3LYP[d]	RHF[d]	UB3LYP[e]	UHF[e]
r_1	1.553	1.539	1.574	1.560	1.544	1.518	1.500	1.528	1.504
r_2	1.431	1.420	1.437	1.445	1.429	1.441	1.427	1.444	1.432
r_3	1.381	1.363	1.354	1.383	1.365	1.403	1.388	1.400	1.385
r_4	1.443	1.419	1.406	1.436	1.416	1.483	1.454	1.482	1.451
r_5	1.470	1.459	1.463	1.468	1.460	1.453	1.441	1.456	1.444
r_6	1.430	1.419	1.435	1.425	1.416	1.441	1.427	1.437	1.426
r_7	1.381	1.364	1.337	1.389	1.368	1.403	1.388	1.415	1.399
r_8	1.443	1.419	1.434	1.429	1.422	1.483	1.454	1.457	1.448
r_9	1.469	1.460	1.469	1.453	1.448	1.453	1.441	1.426	1.428
r_{10}	1.201	1.176	1.205	1.201	1.177	1.196	1.173	1.198	1.173
r_{11}	1.200	1.176	1.199	1.211	1.185	1.196	1.173	1.208	1.181
r_{12}	1.402	1.359	1.387	1.398	1.357	1.426	1.375	1.425	1.375
r_{13}	1.402	1.359	1.361			1.426	1.375		
r_{14}	1.211	1.177	1.220	1.213	1.178	1.229	1.175	1.210	1.176
r_{15}	1.234	1.200	1.219	1.233	1.200	1.210	1.197	1.229	1.197
r_{16}	1.211	1.200	1.229			1.210	1.197		
r_{17}	1.235	1.176	1.205			1.229	1.175		
r_{18}	1.092	1.078	–	1.092	1.078	1.098	1.086	1.099	1.086
r_{19}	1.092	1.078	–	1.098	1.083	1.098	1.086	1.109	1.092
r_{20}	1.011	0.994	–	1.010	0.995	1.014	0.997	1.012	0.998
r_{21}	1.011	0.996	–	1.010	0.994	1.014	0.997	1.013	0.997

See Fig. 1 for numbering of the bonds. Basis set is 6-31G(d,p) for all calculations.

[a] *cis*-DINGU.

[b] X-ray diffraction data for *cis*-DINGU.

[c] NO_2 removed *cis*-DINGU radical.

[d] *trans*-DINGU.

[e] NO_2 removed *trans*-DINGU radical, the dashed lines mean that there was no data about corresponding bond lengths in Ref. [11].