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.
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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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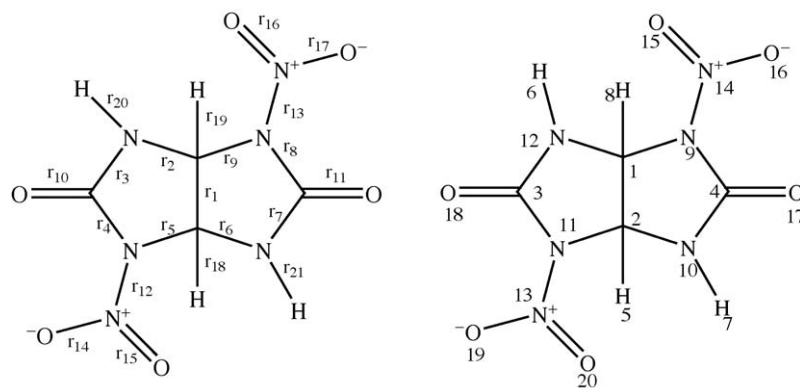*E-mail address:* lturker@metu.edu.tr (L. Türker).

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 cor-

responding 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].
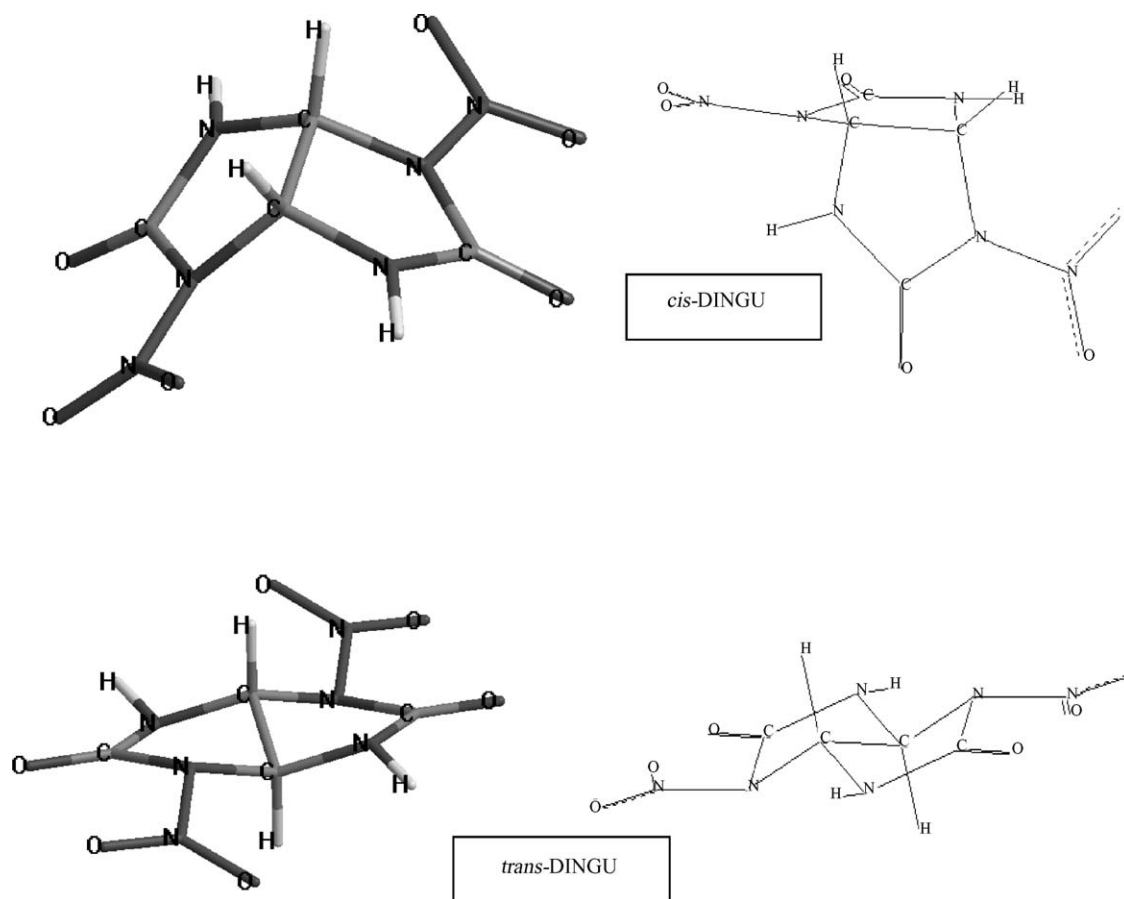
Fig. 2. The geometry optimized structure of *cis*- and *trans*-DINGU (B3LYP/6-31G(d,p)). The molecules at the left-side are oriented as in Fig. 1.

31G(d,p) and in the other set UHF/6-31G(d,p) levels of theories were adopted). The homolytic BDE [27,28] is defined for the present case as $\mathrm{BDE} = E(\mathrm{NO}_2) + E(\mathrm{R}) - E(\mathrm{R}\text{–}\mathrm{NO}_2)$, where E stands for the respective total electronic energy corrected for the zero-point energy for each parent structure and the fragments of the low-energy NO_2 scission reaction. Furthermore, the basis set superposition error (BSSE) analyses were carried out with the counterpoise method, introduced by Boys and Bernardi [29]. The corresponding BSSE analyses were performed at the same theoretical levels (UB3LYP/6-31G(d,p) and UHF/6-31G(d,p)). The normal mode analysis for each fragment resulted in no imaginary frequencies. All these computations were performed by using the Gaussian 98 package program [30].

3. Results and discussion

cis-DINGU is a nitramine type organic explosive and its isomer, yet unknown *trans*-DINGU should exhibit explosive properties too. The chemical structure of DINGU (for both isomers in two-dimensional draw), numbering of atoms and numbering of bond distances (r) are shown in Fig. 1. It has been found that polynitro aliphatics containing at least one N–NO$_2$ (nitramine) linkage are more sensitive than nitro aliphatic explosives containing C–NO$_2$ linkage [31]. On the other hand, the stabilities and impact/shock sensitivities of energetic materials have fre-

quently been related to the strengths of C–NO$_2$ and/or N–NO$_2$ bond strengths [32–34].

In the literature, the structure of *cis*-DINGU was investigated by using X-ray diffraction [11]. However, as mentioned above no work exists in the literature for the *trans*-isomer (to the best of our knowledge). In Table 1, the presently calculated geometric parameters for *cis*- and *trans*-DINGU molecules at the B3LYP/6-31G(d,p),UB3LYP/6-31G(d,p), RHF/6-31G(d,p) and UHF/6-31G(d,p) theoretical levels, as well as the experimental X-ray diffraction data [11] for *cis*-DINGU (bond lengths) are presented. The B3LYP/6-31G(d,p) bond lengths differ from the crystal averages with rms deviations of 0.022 Å. The rms deviations for the UB3LYP/6-31G(d,p) bond lengths are 0.020 Å. Whereas, RHF/6-31G(d,p) and UHF/6-31G(d,p) type calculations cause, the rms deviations to increase to 0.023 Å. Unrestricted calculations give results qualitatively and quantitatively in agreement with those performed by using the restricted formalism. The differences between the experimentally observed (*cis*-DINGU) and theoretical bond lengths can be attributed to crystal packing effects existing in the experimental data. The geometry optimized structures of the *cis*-DINGU and *trans*-DINGU are shown in Fig. 2. Note that the configurational isomerism in DINGU arises from the different spatial orientations of the hydrogen atoms at the bridge head positions.

Table 2
Calculated bond angles (°) of *cis*-DINGU and *trans*-DINGU with basis set 6-31G(d,p)

Bond angles	cis-DINGU B3LYP	cis-DINGU RHF	X-ray diffraction[a]	trans-DINGU B3LYP	trans-DINGU RHF
C(2)–C(1)–N(9)	100.9	100.8	100.2	97.6	97.4
C(2)–C(1)–N(12)	103.8	103.9	104.1	99.6	99.7
C(2)–C(1)–H(8)	114.1	114.1	–	110.3	110.5
N(9)–C(1)–N(12)	115.6	115.3	–	127.3	127.6
H(8)–C(1)–N(9)	110.2	110.2	–	108.7	108.6
H(8)–C(1)–N(12)	111.9	111.9	–	110.9	110.9
C(1)–C(2)–N(10)	103.7	103.9	104.3	99.7	99.7
C(1)–C(2)–N(11)	100.8	100.8	100.1	97.6	97.4
C(1)–C(2)–H(5)	114.1	114.1	–	110.3	110.5
N(10)–C(2)–N(11)	115.5	115.3	–	127.4	127.6
H(5)–C(2)–N(10)	111.9	111.9	–	110.9	110.9
H(5)–C(2)–N(11)	110.2	110.2	–	108.7	108.6
N(11)–C(3)–N(12)	103.8	103.9	105.1	105.4	105.6
N(9)–C(4)–N(10)	103.8	103.9	104.8	105.4	105.6
C(1)–N(9)–C(4)	112.8	113.4	114.2	104.6	104.9
C(2)–N(10)–C(4)	114.6	114.8	116.0	106.4	106.1
C(2)–N(11)–C(3)	112.8	113.4	114.9	104.6	104.9
C(1)–N(12)–C(3)	114.6	114.8	–	106.4	106.1

See Fig. 1 for numbering of the atoms.
[a] X-ray diffraction data for the *cis*-DINGU, the dashed lines mean that no experimental data were reported [11].

The geometry-optimized structures based on the calculations have C_2 and C_1 type molecular point groups for *cis*-DINGU and *trans*-DINGU, respectively. According to the X-ray diffraction study [11], *cis*-DINGU possesses a two-fold symmetry axis passing through the center of the C(1)–C(2) bond and bisecting the dihedral angle of the two rings.

The presently used calculation methods show a parallelism in reflecting the geometrical differences existing between *cis*- and *trans*-DINGU. Comparing the calculated bond lengths of *cis*-and *trans*-DINGU obtained by using different theoretical methods (shown in Table 1), r_1 bond in *cis*-DINGU is found to be somewhat longer than r_1 bond in the *trans*-DINGU about 0.04 Å. Also, r_4 and r_8 bonds (C–N bonds) in *cis*-DINGU are shorter than those bonds in the other isomer about 0.04 Å. A similar character was also exhibited for r_3 and r_6 bonds (C–N bonds of the amido group linked to the NO_2 moiety). It can be seen from Table 1 that r_1 (C–C bond) stands for the longest bond length of the both isomers. The N–H bond lengths in *cis*- and *trans*-DINGU are about 1.011 Å (B3LYP/6-31G(d,p)). As for the N–N bond lengths, the calculated values are 1.402 and 1.426 Å for the *cis*- and *trans*-isomer, respectively. According to the different theoretical levels performed, the nitramine ($N–NO_2$) bond in the *trans*-isomer is longer than the same bond in the *cis*-isomer about 0.02 Å (see Table 1).

The calculated bond angles of the both isomers presently considered are shown in Table 2. As seen in the table, according to the B3LYP/6-31G(d,p) level of theory, for *cis*-DINGU, N(10)–C(2)–N(11) and N(9)–C(1)–N(12) bond angles are about 115.5°. Whereas, in the case of *trans*-DINGU, these bond angles are about 127.4°. Some of the calculated dihedral angles are shown in Table 3 for the both isomers. For the *cis*-isomer the dihedral angle constituted by atoms H(8)–C(1)–C(2)–H(5) is

Table 3
Some calculated dihedral angles of *cis*-DINGU and *trans*-DINGU with basis set 6-31G(d,p)

Dihedral angles	cis-DINGU B3LYP	cis-DINGU RHF	trans-DINGU B3LYP	trans-DINGU RHF
N(9)–C(1)–C(2)–N(10)	19.5	16.8	49.9	49.8
N(9)–C(1)–C(2)–N(11)	−100.4	−103.0	180.0	180.0
N(12)–C(1)–C(2)–N(10)	139.5	136.5	180.0	180.0
N(12)–C(1)–C(2)–N(11)	19.5	16.7	−49.9	−49.8
H(8)–C(1)–C(2)–H(5)	23.5	20.9	180.0	180.0
C(2)–C(1)–N(9)–N(14)	−170.9	−176.0	−173.8	−178.8
H(8)–C(1)–N(9)–N(14)	−50.0	−55.1	−59.2	−64.5
H(8)–C(1)–N(12)–H(6)	61.8	60.4	59.1	59.6
N(11)–C(2)–N(10)–C(4)	91.3	92.9	−148.6	−148.7
H(5)–C(2)–N(10)–H(7)	61.7	60.4	−59.1	−59.6
C(1)–C(2)–N(11)–C(3)	−16.6	−13.5	41.1	40.9
C(1)–C(2)–N(11)–N(13)	−170.9	−176.1	173.8	178.8
N(12)–C(3)–N(11)–C(2)	6.6	4.5	−17.6	−17.2
N(12)–C(3)–N(11)–N(13)	158.9	165.7	−148.3	−153.1
N(9)–C(4)–N(10)–C(2)	7.9	8.1	15.6	16.1

See Fig. 1 for numbering of the atoms.

Table 4
Some calculated energies for *cis*- and *trans*-DINGU at RHF/6-31G(d,p) and B3LYP/6-31G(d,p) theoretical levels

Energy	RHF[a]	RHF[b]	B3LYP[a]	B3LYP[b]
Total energy	−929.2870980	−929.2351330	−934.3509730	−934.3093840
Total energy (with MP2)	−932.0646039	−932.0252451		

Energies in atomic units (1 hartree = 627.51 kcal/mol, the total energies are corrected for ZPVE).
 [a] *cis*-DINGU.
  [b] *trans*-DINGU.

Table 5
Some calculated energies for *cis*- and *trans*-DINGU, their radicals (after the homolytic cleavage of one of the N–NO$_2$ bonds) and NO$_2$ radical

Energy	*cis*-DINGU	*trans*-DINGU	*cis*-DINGU radical	*trans*-DINGU radical	NO$_2$ radical	BDE[a]	BDE[b]
Total energy[c]	−934.350972	−934.309384	−729.226689	−729.187514	−205.063381	33.51	32.35
Total energy[d]	−929.287098	−929.235125	−725.237222	−725.190556	−204.021641	12.91	10.02

Total energies in atomic units (1 hartree = 627.51 kcal/mol), BDEs in kcal/mol. The total electronic energies are corrected for ZPVE, BDEs are including basis set superposition error (BSSE) and zero-point energy (ZPE) corrections.
  [a] BDE (N–NO$_2$) for *cis*-isomer at 0 K.
  [b] BDE(N–NO$_2$) for *trans*-isomer at 0 K.
  [c] UB3LYP/6-31G(d,p).
  [d] UHF/6-31G(d,p).

cis-DINGU
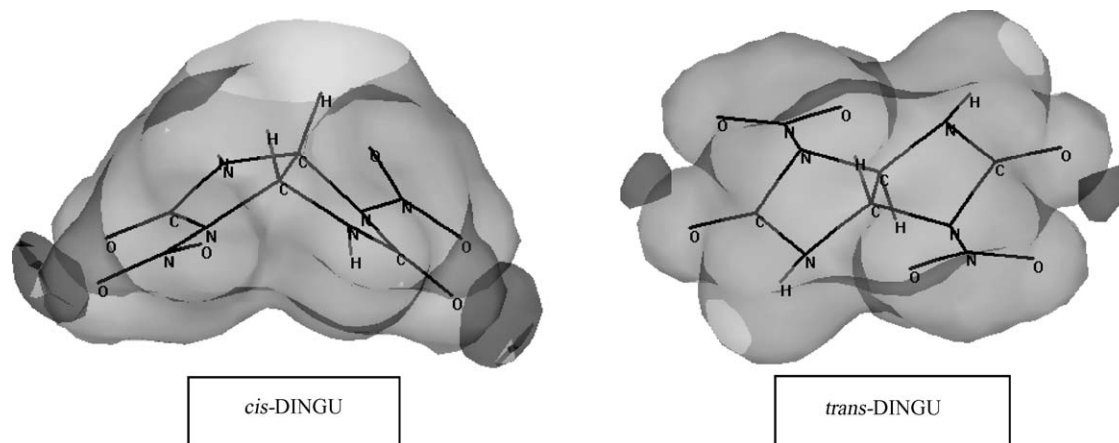
trans-DINGU

Fig. 3. 3D-potential field maps of *cis*- and *trans*-DINGU (B3LYP/6-31G(d,p)).

23.5° (B3LYP/6-31G(d,p) level of theory), however for the *trans*-isomer the respective dihedral angle is 180.0°. In the case of *cis*-isomer, each half of the heterocycle is almost planar (as also found by X-ray diffraction analysis [11]), the nitro substituents directly bonded to the ring onto N atoms, are in the *exo*-position (bent away from the concave side of the bicyclo system). On the other hand, the geometry optimizations indicate that the *trans*-isomer possesses a puckered structure.
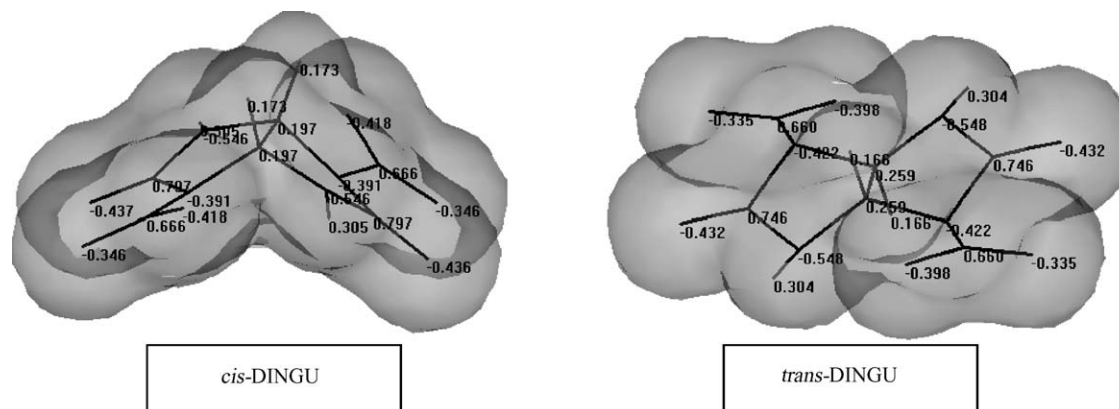

cis-DINGU

trans-DINGU

Fig. 4. 3D-charge density maps and charges of atoms of *cis*- and *trans*-DINGU (B3LYP/6-31G(d,p)).

Table 6
The HOMO and LUMO energies (ε) of *cis*-DINGU and *trans*-DINGU at different theoretical levels

ENERGY	RHF[a]	UHF[a]	RHF[b]	UHF[b]	B3LYP[a]	UB3LYP[a]	B3LYP[b]	UB3LYP[b]
HOMO	−12.662	−12.662	−12.503	−12.503	−8.367	−8.367	−8.488	−8.488
LUMO	2.306	2.306	2.231	2.231	−2.481	−2.481	−2.592	−2.592
$\Delta\varepsilon$	14.968	14.968	14.734	14.734	5.886	5.886	5.896	5.896
Dipole moment	4.8281	4.8279	0.0000	0.0000	4.0894	4.0894	0.0000	0.0000

Energies (in eV) $\Delta\varepsilon = \varepsilon_{LUMO} - \varepsilon_{HOMO}$; dipole moments in Debye. Basis set is 6-31G(d,p) for all the calculations.
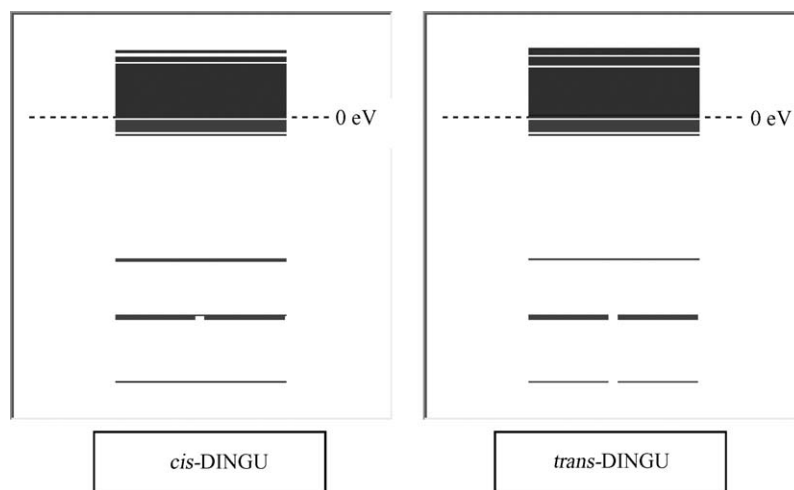 [a] *cis*-DINGU.
  [b] *trans*-DINGU.

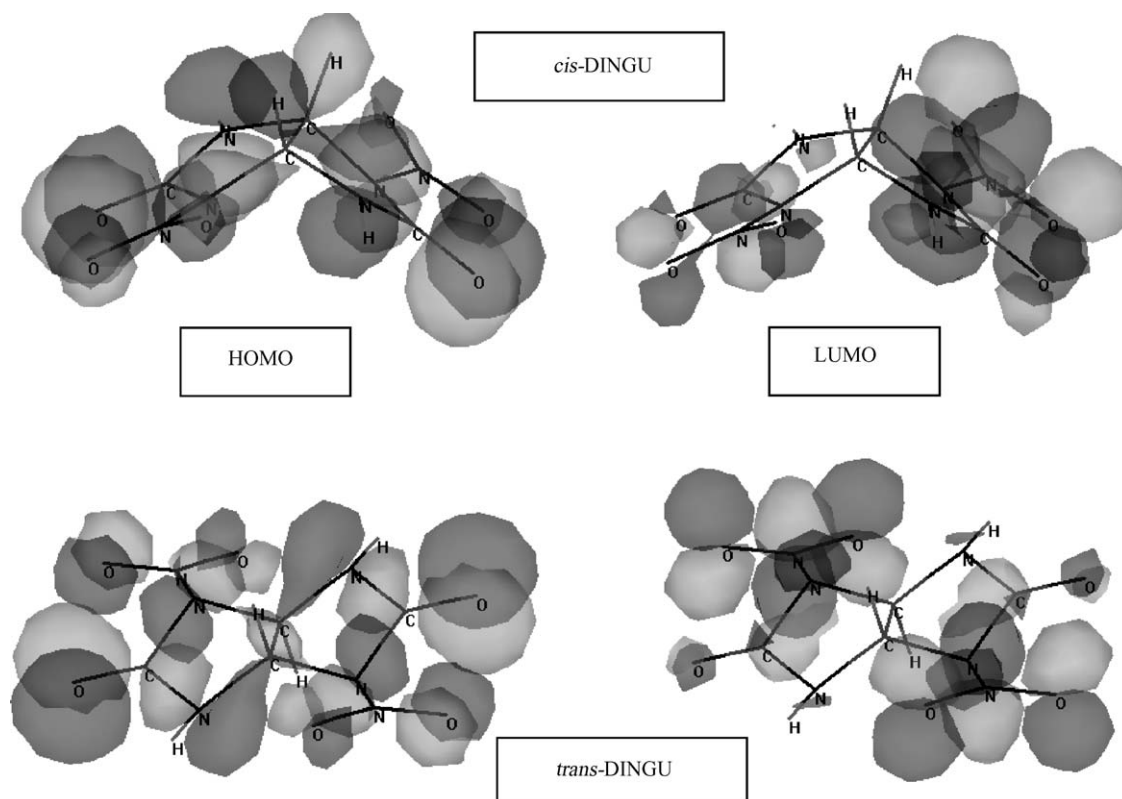Fig. 5. The molecular orbital energy spectra of *cis*- and *trans*-DINGU (B3LYP/6-31G(d,p)).

Fig. 6. The frontier molecular orbitals, the LUMO and HOMO of *cis*- and of *trans*-DINGU (B3LYP/6-31G(d,p)).

Table 7
Calculated vibrational frequencies and intensities for both isomers

RHF/6-31G(d,p) *cis*-DINGU		B3LYP/6-31G(d,p) *cis*-DINGU		RHF/6-31G(d,p) *trans*-DINGU		B3LYP/6-31G(d,p) *trans*-DINGU	
Intensity	Frequency	Intensity	Frequency	Intensity	Frequency	Intensity	Frequency
1.7011	45	1.7873	45	1.5141	69	1.4011	64
0.9511	73	1.7135	71	0.5474	85	0.3666	80
1.5352	83	1.2592	78	0.0000	85	0.0000	83
0.3433	93	0.0418	85	11.096	113	7.8633	108
5.1428	109	3.5639	93	8.2581	150	5.2653	134
1.7340	154	0.4726	158	0.0000	167	0.0000	154
1.6329	173	2.1579	169	0.0000	214	0.0000	189
1.5602	235	0.9377	205	0.0000	246	0.0000	232
11.6417	250	9.5316	223	3.3436	310	1.8764	278
0.0558	351	0.0810	311	4.0186	326	3.8768	293
5.3477	372	3.2118	330	0.0000	364	0.0000	323
0.9687	472	0.1192	428	0.0000	447	0.0000	406
14.9301	508	10.4399	457	6.7467	505	5.7271	450
17.6654	514	14.0416	460	0.0000	523	13.8534	459
5.6914	551	7.6798	489	3.7870	530	0.0000	463
90.5406	577	89.5972	536	40.0524	588	26.8073	544
196.6232	578	147.6016	540	0.0000	658	0.0000	593
10.6720	670	30.4398	605	0.0000	685	0.0000	628
74.5347	720	60.1630	651	269.8574	716	234.5247	657
5.3649	765	0.3595	691	75.1232	748	59.8261	675
2.4379	789	7.6077	718	0.0000	831	0.0000	738
152.1338	812	28.8188	724	0.0000	841	30.7089	745
3.3363	823	97.3322	739	52.3289	849	0.0000	753
58.5595	845	11.6210	748	0.0000	871	0.0000	764
10.1673	892	1.1032	766	198.9463	877	175.0512	784
111.6652	902	69.5465	772	65.9270	920	29.8918	806
73.1922	942	78.6836	843	0.0000	925	0.0000	816
2.8028	944	2.4519	844	0.0000	988	0.0000	871
25.4802	975	20.0600	877	94.0126	995	90.1487	879
7.2740	1078	4.7754	978	0.0000	1164	388.4266	992
24.0865	1192	0.2988	1088	148.5353	1170	0.0000	1004
4.6752	1203	18.6574	1093	0.0000	1180	0.0000	1056
3.2974	1263	1.5374	1106	55.6011	1242	41.5590	1117
34.3111	1285	175.2279	1139	0.0000	1260	0.0000	1118
0.2888	1315	1.5705	1153	158.4111	1271	0.0000	1148
171.7896	1349	363.7441	1170	0.0000	1309	92.3096	1152
341.6120	1380	28.6166	1218	280.8182	1409	543.9906	1225
25.9690	1386	422.1650	1233	0.0000	1411	0.0000	1251
11.1733	1491	663.5658	1312	295.4897	1456	225.6959	1298
537.7428	1502	1.5116	1319	0.0000	1522	0.0000	1351
273.7526	1514	1.6731	1335	338.3429	1537	321.1889	1356
0.0466	1531	176.4132	1359	523.7773	1570	0.0007	1356
728.8546	1582	45.4914	1402	0.0000	1572	130.1419	1377
0.0680	1584	0.6703	1421	0.0000	1593	0.0000	1423
100.8448	1589	137.7488	1432	186.1296	1630	77.4454	1474
4.4301	1608	5.7265	1445	0.0000	1652	0.0000	1496
169.0571	1871	87.3234	1688	0.0000	1889	0.0000	1707
470.7357	1880	278.5983	1692	765.9166	1894	401.9574	1709
1368.2950	2079	840.0076	1903	1567.705	2094	952.6918	1913
410.2577	2098	229.0634	1914	0.0001	2108	0.0002	1921
2.3309	3317	2.5339	3122	0.0000	3218	0.0000	3025
10.8752	3326	9.6530	3128	30.1824	3229	26.7768	3035
265.9185	3893	0.5665	3656	36.5517	3854	0.0133	3613
1.2144	3894	188.7430	3656	174.9656	3854	144.6149	3613

Harmonic frequencies in cm^{-1} and IR intensities in km/mol.

Table 4 shows some of the calculated energies of the compounds (the total electronic energies are corrected for ZPVE). According to the DFT geometry optimization at the level of B3LYP/6-31G(d,p), *cis*-DINGU is more stable than the *trans*-isomer about 26.1 kcal/mol in terms of the total electronic energy. Furthermore, according to the ab initio results the *cis*-isomer is again more stable than the *trans*-one about 32.6 kcal/mol and after MP2 single point calculation, energy dif-

ference between *cis-* and *trans*-isomers was 24.7 kcal/mol and *cis*-isomer has lower energy. All these results show that the stability order is *cis*-DINGU > *trans*-DINGU. Also the additional calculated energy data (UHF/6-31G(d,p), UB3LYP/6-31G(d,p)) are consistent with this result (see Table 5).

Also the heats of formation in the gas phase for the both isomers were calculated by a semiempirical method, PM3, based on the DFT optimized geometry. *cis*-DINGU has the heat of formation of −26.23 kcal/mol (exothermic), but the respective value for *trans*-DINGU is 6.41 kcal/mol (endothermic). Also, these data confirm that *cis*-DINGU is a more stable molecule than the *trans*-isomer in terms of the heat of formation values.

Thermal stability of nitramines is mainly related to the energy required for the initial reaction of decomposition [35]. The common initial step of thermal decomposition of nitramines is the NO_2 fission reaction through breaking of N–NO_2 bond as known in the decomposition of hexahydro-1,3,5-trinitro-*s*-triazine (RDX) and 1,3,5,7-tetranitro-1,3,5,7-tetraazacyclooctane (HMX) [36].

Khire and co-workers [13] studied spectro-thermal decomposition of *cis*-DINGU and they proposed that the thermal decom-

position mechanism of *cis*-DINGU should involve N–NO_2 bond cleavage as the primary step. They also proposed that the bond dissociation energy for N–H bond was involved in the rate determining step. The average N–N bond distance in *cis*-DINGU was reported to be 1.375Å [37]. Compounds with long N–N bonds in general favor NO_2 liberation on fast thermolysis [38]. Whereas, the tendency to form HONO(g) early in the thermolysis depends on the H/NO_2 ratio in the parent secondary nitramine [39]. Keeping these in mind, and the results of presently performed different theoretical methods, which yield longer N–N bonds in *trans*-DINGU as compared to the *cis*-form, one expects the *trans*-isomer should decompose by NO_2 liberation and even should be a more sensitive explosive than the *cis*-isomer (in terms of the bond length data). Furthermore homolytic bond dissociation energy (BDE) of the nitramine group (N–NO_2) for the both isomers was performed at UB3LYP/6-31G(d,p) and UHF/6-31G(d,p) theoretical levels (see Table 5, the total electronic energies are corrected for ZPVE). The BDEs were calculated at the same levels with correction for the basis set superposition error (BSSE), using the Boys–Bernardi counterpoise technique [29].
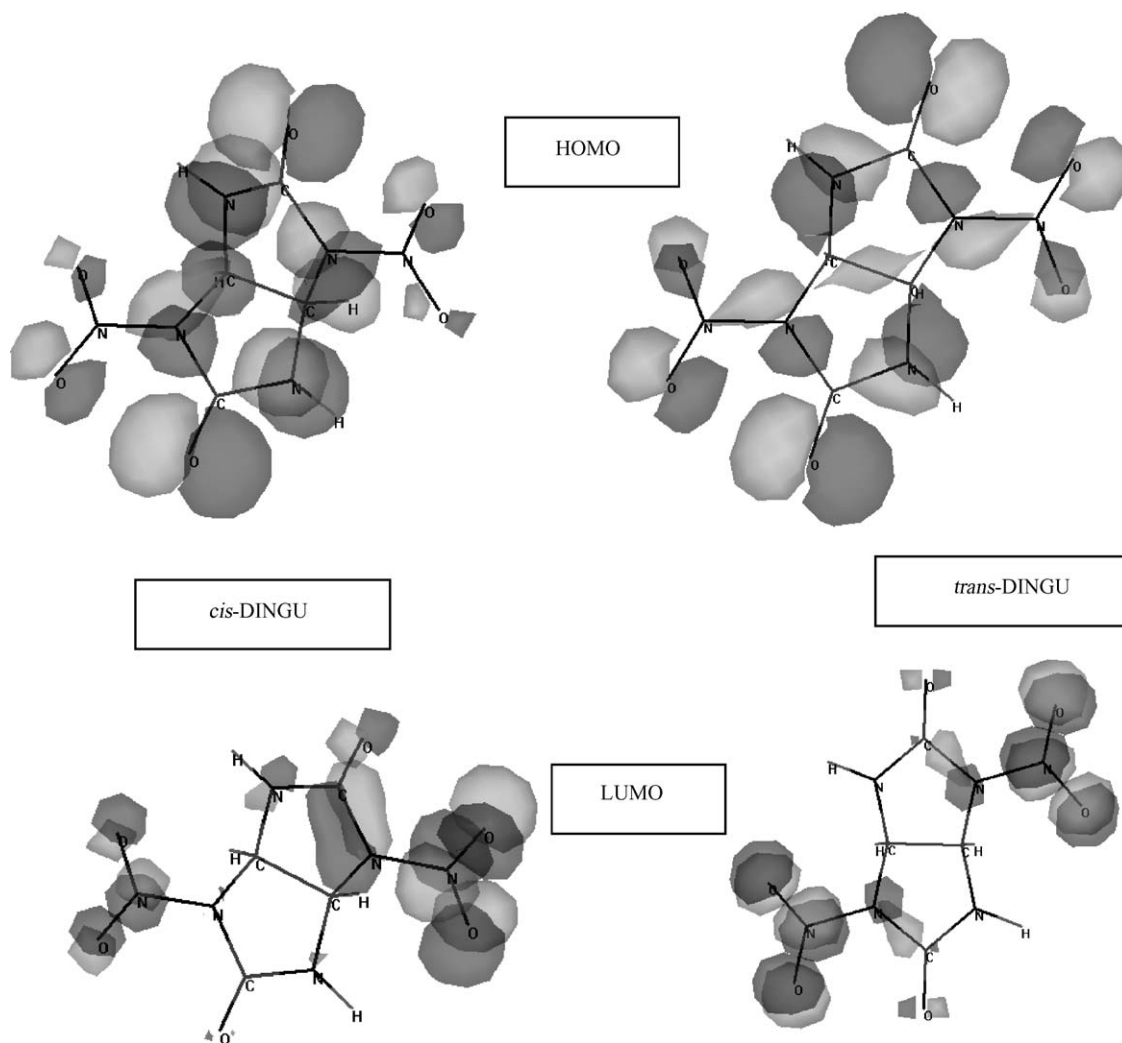

Fig. 7. Top view of the HOMO and LUMO of both DINGU isomers (B3LYP/6-31G(d,p)).

The BDE (N–NO$_2$) for *cis*-isomer is slightly higher than the *trans*-one as a result of ab initio and DFT(B3LYP) calculations. The BDE (N–NO$_2$) difference between the *cis*- and *trans*-isomers at ab initio and DFT levels were found to be 2.9 kcal/mol and 1.16 kcal/mol, respectively (see Table 5). Hence, N–NO$_2$ bond strength for *cis*-isomer is slightly greater than the corresponding bond strength for the *trans*-isomer at these theoretical levels.

Figs. 3 and 4 show the 3D-electrostatic potential field and charge density maps (as well as the atomic charges) for the species, respectively. The *cis*- and *trans*-isomers generate an electrostatic potential field around them due to the overall effect of positive and negative charge distribution. In Fig. 3, the darker and lighter regions are negative and positive electrostatic potential fields, respectively. As evident from the figure, the lighter regions (positive field) predominate in both of the isomers. Some explosive materials are sensitive to electromagnetic and electrostatic fields they are exposed [40,41]. The effect is due to interaction of the external field with electron distribution within the molecule thus with the electrostatic potential field, such that in some sensitive explosives this interaction causes the rupture of chemical bonds.

It is clear from Fig. 4 that why the *cis*-isomer has higher dipole moment than the *trans*-isomer. In the case of the *trans*-isomer, bond dipoles oriented in the molecule so that the net dipole moment is almost zero. Whereas, *cis*-DINGU is a polar compound and has the calculated dipole moment value of 4.0894 and 4.8281 Debye at DFT and ab initio results, respectively (see Table 6). Fig. 5 shows the molecular orbital energy spectra of the species presently considered (B3LYP/6-31G(d,p)). As seen in the figure, the occupied molecular orbitals of the isomers constitute three distinct groups of nearly spaced levels and some of them are degenerate. The span of molecular orbital energies for *cis*-DINGU is in between −522.92 and 130.67 eV, whereas for the *trans*-isomer molecular orbital energies range between −523.07 and 130.17 eV (Fig. 5). Figs. 6 and 7 show the HOMO and LUMO, whereas their energies are shown in Table 6. The LUMO–HOMO energy difference in the *cis*- and *trans*-isomers were calculated at DFT (B3LYP/6-31G(d,p)) method as 5.886 and 5.896 eV, respectively. As seen in Figs. 6 and 7, although in both of the isomers many of the atoms of DINGU contribute to the HOMO, only a part of the structure including the nitro groups contribute to the LUMO.

The DFT geometry optimized structure of *cis*-DINGU reveals that due to the ring geometry, the nitramine nitrogen is under a better influence of the amido carbonyl as compared to the *trans*-isomer. Consequently, the electron pair is localized on the nitrogen atom rather than being shifted to the NO$_2$ group. Whereas, in the optimized geometry of *trans*-DINGU, the lone pair of the nitramine nitrogen can conjugate better with the nitro group. Thus, the NO$_2$ groups exert their electron withdrawing effects on the adjacent amino (nitramine) groups more effectively. Thus, the HOMO and LUMO energies of the *trans*-DINGU turns out to be lower than the corresponding energies for the *cis*-isomer for the restricted and unrestricted DFT calculations (see Table 6), whereas the ab initio calculations predict the HOMO energy of *cis*-DINGU to be lower but the LUMO energy

to be higher than the respective values of the *trans*-isomer. Moreover, the LUMO energy for both of the isomers was found to be quite high (positive values, see Table 6).

Fundamental normal modes of the both isomers calculated at the Hartree–Fock and DFT(B3LYP) levels of theories using the standard 6-31G(d,p) basis set were presented in Table 7 (raw calculated frequencies are shown in the table). These data (especially concerning the vibrational frequencies of *trans*-DINGU) do not exist in the literature.

4. Conclusion

The presently performed DFT and ab initio calculations have revealed some quantum chemical and thermal properties of DINGU configurational isomers in the gas phase. The stabilities and impact/shock sensitivities of energetic materials have frequently been related to the strengths of C–NO$_2$ and/or N–NO$_2$ and some experimental studies revealed that the thermal decomposition mechanism of *cis*-DINGU should involve N–NO$_2$ bond cleavage as the primary step. Thus, it is logical to assume that the same mechanism should be operative for *trans*-DINGU. Presently, comparing the bond lengths of nitramine functional groups for the both isomers, it has been found that the values of the N–NO$_2$ bonds in *cis*-DINGU are shorter than the same bonds in the *trans*-isomer which suggests that the N–NO$_2$ bond is weaker in the case of *trans*-DINGU. Also the greater homolytic BDE value of this bond, for the *cis*-isomer than the *trans*-isomer, additionally indicates the possibility of rupture of those bonds in *trans*-DINGU more favorably than *cis*-DINGU. Moreover, considering the energy data (total electronic energy and heat of formation) *trans*-DINGU should be less stable. Hence, in the light of all these results, *trans*-DINGU so far not mentioned in the literature, may be a more powerful explosive than *cis*-DINGU.

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