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Density functional theory study of the structural properties of cis-trans isomers of bis-(5-nitro-2*H*-tetrazolato-N^2) tetraammine cobalt (III) perchlorate (BNCP)

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ABSTRACT

In present study, the density functional theory (DFT-B3LYP) method with SVP basis set was used for optimizing and studying the electronic structural properties of cis and trans isomers of bis-(5-nitro-2*H*-tetrazolato-N^2) tetraammine cobalt (III) perchlorate (BNCP) as powerful explosives at 298.15 K temperature and 1 atmosphere pressure. And also, Natural Bond Orbital (NBO) population analysis and the molecular electrostatic potential (MEP) surface of the structures were studied by mentioned level of theory. The effect of ligands sites attached to the transition metal (cobalt) at the BNCP isomers was studied on the HOMO-LUMO energies, the electronic chemical potential, the absolute hardness and electrophilicity index. The geometry optimization of the structures shows the octahedral environment around cobalt. The tetrazole nitrogen atoms have large negative charge. The three-dimensional electrostatic potential maps of the isomers show that the negative charge is located on the nitro and perchlorate groups. The NBO analysis shows that the Co-ligand bonds in the near of perchlorate ion are formed from short, strong and sigma bonds.

Keywords: Theoretical study; Density functional theory; Natural bond orbital population analysis; Electrophilicity index; Molecular electrostatic potential surface

INTRODUCTION

Research in the field of high energy density materials (HEDMs) bolsters the synthesis of organic-inorganic energetic materials containing the nitrogen atoms [1]. Tetrazoles are an increasingly famed functionality with wide ranging application such as explosives [2]. Tetrazoles are five membered heterocyclic rings containing one carbon atom and four nitrogen atoms. Tetrazoles depict a planar structure [3]. The tetrazole ring has strong electron withdrawing property and a number of methods have been reported for the preparation of its [4]. Pletz proposed the classification of "explosophores" and "auxoploses" for functional groups in the energetic materials [5]. An explosophore has been defined as a group of atoms such as azo, azide, nitroso, peroxide, ozonide and perchlorate, which is capable of forming an explosive compound on introduction into a hydrocarbon. Groups such as hydroxyl, carboxyl, chlorine, sulfur, ether, oxygen and amine, which do not themselves produce explosive properties, but may influence them, are called auxoplosives [6]. A main part of energetic materials is related to the

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coordination compounds with transition metals, but a few studies undertaken on the structures of energetic co-ordinate compounds [7]. The bis-(5-nitro-2*H*-tetrazolato-N^2) tetraammine cobalt (III) perchlorate (BNCP) has been reported as an important explosive [8]. This energetic compound has two isomers: cis and trans. In 1997, Bruno Morosin and his coworkers reported the first tactical synthesis of the cis-BNCP [9]. It is formed from the octahedrally coordinated Co atom to four NH_3 groups and two cis-tetrazolato ligands. The trans isomer of this compound was prepared by M. B. Talawar and his coworkwers in 2005 [10]. The structural properties of these isomers weren't studied. In the present work, we report the theoretical study of the cis and trans isomers of BNCP as high energy density materials. A particularly important method is to model a molecular system prior to synthesizing that molecule in the laboratory. This is very useful mean because computational chemistry is in understanding a problem more completely [11-13]. The density functional theory (DFT) methods are theoretical techniques for the prediction of structural of various chemical systems [14]. There are many DFT methods that have been used in the last few decades [15].

COMPUTATIONAL METHOD

The computational studies were performed with the Gaussian 03 package [16] using the B3LYP method with SVP basis set. The term of B3LYP consists of the Vosko, Wilk, Nusair (VWN3) local correlation functional [17] and Lee, Yang, Parr (LYP) correlation correction functional [18, 19]. The computational set was used as implemented in the Gaussian computational study. The geometry of structures was optimized without any structural or symmetry restrictions. Theoretical calculations have been performed in the gas phase [20].

RESULTS AND DISCUSSION

The Geometry of Cis-Trans Isomers of Bis-(5-Nitro-2H-Tetrazolato-N^2) Tetraammine Cobalt (III) Perchlorate (BNCP)

The density functional theory (DFT) has appeared as a useful theoretical method. Hence, we have done all the calculations on the structures with the B3LYP/SVP level of theory. As we mentioned above, we study here structural properties of two high explosive molecules: cis-trans isomers of bis-(5-nitro-2*H*-tetrazolato-N^2) tetraammine cobalt (III) perchlorate (BNCP). The structures with atomic numbers were shown in Figure 1. Our calculated geometries of the structures agree well with the values from XRD analysis [9, 10]. The geometric structures of the molecules are displayed in Figure 2. The Mulliken atomic charges of the molecules at studied level of theory is listed in Table 1. According to the natural bond orbital results, the electron configuration of cobalt atom is [core] 4s(0.29) 3d(7.44) 4p(0.01) and [core] 4s(0.29) 3d(7.45) 4p(0.01) for cis-BNCP and trans-BNCP, respectively. Of the two nitrogen atoms in the tetrazole rings, the N6 and N7 atoms coordinated to cobalt have large negative charge (-0.133e) to the ammonia ligands. It can be explained that the electron withdrawing property of the tetrazole rings is more than NH_3 groups. The Cl atom has larger positive charge. It should be described that the oxygen atoms have large negative charge.

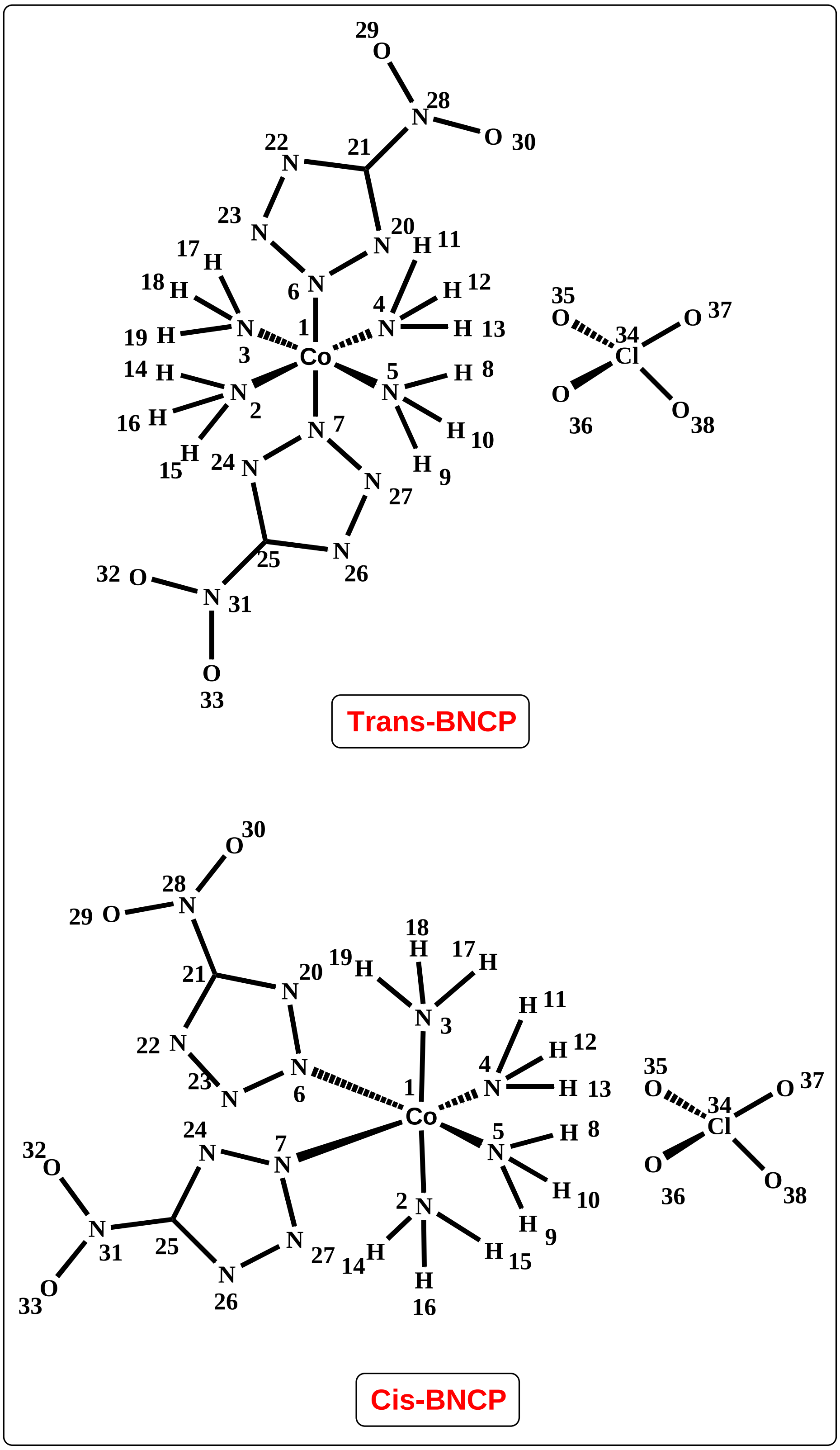

Figure 1. The chemical structures and their atomic numbering.

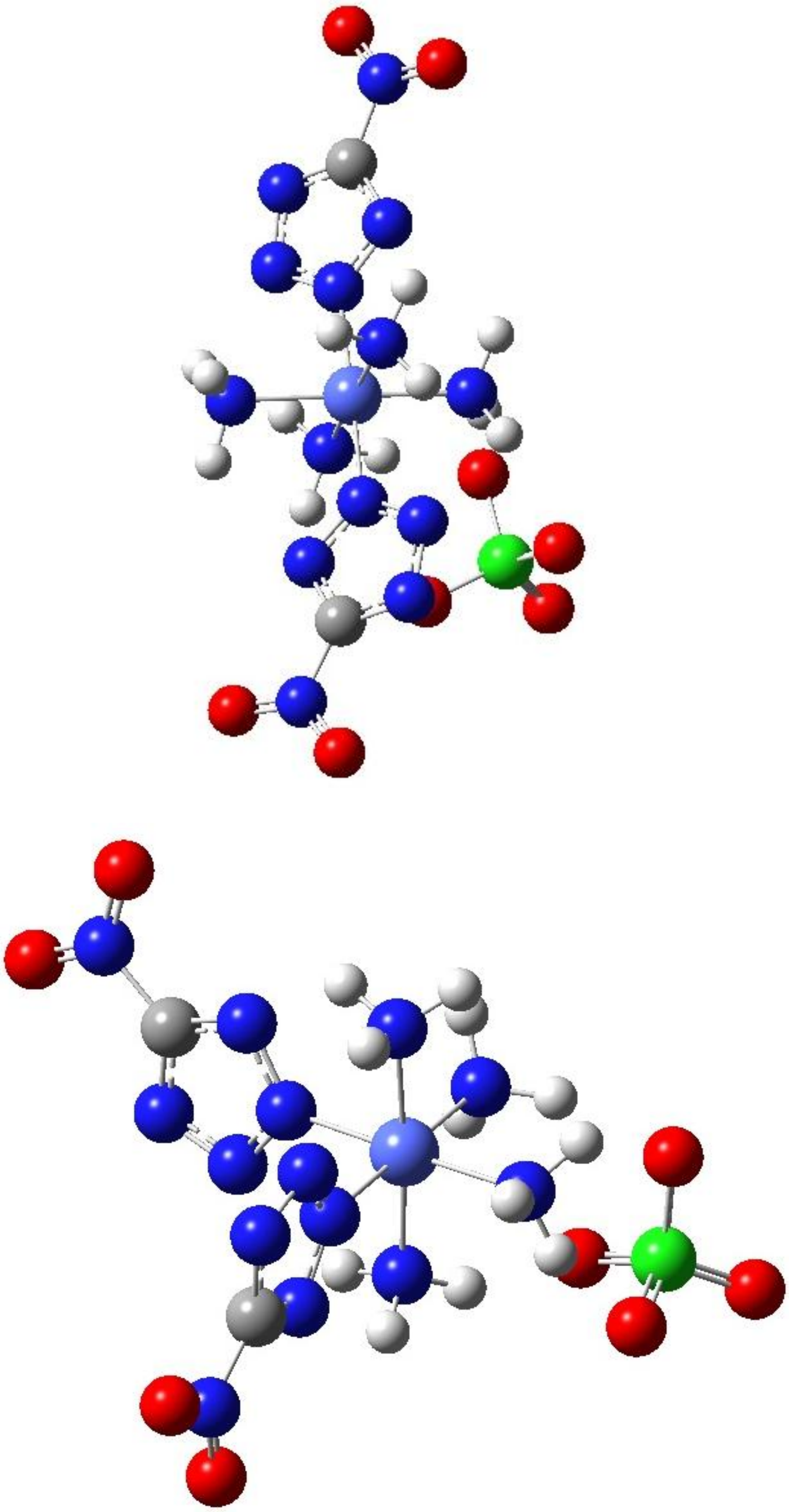

Figure 2. The geometric structures of the BNCP isomers.

Table 1. The Mulliken atomic charges of the BNCP isomers calculated by the B3LYP method with SVP basis set

Atoms	Charge (e)/trans isomer	Charge (e)/cis isomer	Atoms	Charge (e)/trans isomer	Charge (e)/cis isomer
Co1	0.235	0.240	**H15**	0.158	0.156
N6	-0.133	-0.133	**H16**	0.159	0.158
N23	-0.080	-0.082	**N3**	-0.105	-0.093
N22	-0.090	-0.079	**H17**	0.143	0.141
C21	0.110	0.104	**H18**	0.157	0.158
N20	-0.106	-0.076	**H19**	0.159	0.165
N28	0.246	0.247	**N4**	-0.098	-0.111
O29	-0.210	-0.212	**H11**	0.147	0.142
O30	-0.228	-0.228	**H12**	0.151	0.146
N7	-0.135	-0.130	**H13**	0.164	0.145
N27	-0.067	-0.058	**N5**	-0.102	-0.107
N26	-0.088	-0.078	**H8**	0.146	0.139
C25	0.128	0.109	**H9**	0.151	0.139
N24	-0.102	-0.101	**H10**	0.165	0.156
N31	0.247	0.247	**Cl34**	1.141	1.151
O32	-0.203	-0.202	**O35**	-0.477	-0.483
O33	-0.240	-0.242	**O36**	-0.460	-0.472
N2	-0.106	-0.110	**O37**	-0.525	-0.507
H14	0.143	0.136	**O38**	-0.394	-0.374

Bond Lengths of The Structures

The bond lengths data of the molecule have been given in Table 2. It is obtained that Co-N bond lengths related to ammonias 1, 2 are greater than other Co-N bond lengths in both structures. As seen from the table, C-NO_2 bond length on tetrazole ligand is 1.462 A° but C-N bond length in methylamine molecule is 1.469 A°. This behavior can be explained as follows: carbon atom was companied with $sp^{2.3}$ hybrid on C-NO_2 bond in the tetrazole ring structure. And also, the N-H bond length is 1.01 A° in the ammonia legends, but is 1.02 in natural ammonia. The reason for this behavior is participating of nitrogen atom with $sp^{2.85}$ in N-H bonds. Comparing the molecules shows that the structures' bond length is dependent ligands binding site. The molecular electrostatic potential (MEP) is the force acting on a positive test charge (a proton) located at a given point p(x,y,z) in the vicinity of a molecule through the electrical charge cloud generated through the molecules electrons and nuclei. Despite the fact that the molecular charge distribution remains unperturbed through the external test charge (no polarization occurs) the electrostatic potential of a molecule is still a good guide in assessing the molecule reactivity towards positively or negatively charged reactants [21]. The MEP is typically visualized through mapping its values onto the surface reflecting the molecules boundaries [22]. The three-dimensional electrostatic potential maps of the structures are shown in Figure 3. The red loops and the blue loops indicate negative and positive charge development for a particular system respectively. As can be seen from the figures the negative charge is located on the nitrogen and oxygen elements of the nitro and perchlorate groups as expected due to the electron withdrawing character of theirs and positive charge is located on the other sections of the systems.

Table 2. Bond lengths of isomers calculated at B3LYP/SVP level of theory

Bond (A°)	Trans-BNCP	Cis-BNCP	Bond (A°)	Trans-BNCP	Cis-BNCP
Co1-N6	1.926	1.948	**N20-C21**	1.332	1.329
Co1-N7	1.917	1.948	**C21-N22**	1.335	1.336
Co1-N2	2.001	1.993	**N22-N23**	1.313	1.309
Co1-N3	2.000	1.971	**N6-N23**	1.326	1.330
Co1-N4	1.966	1.988	**C21-N28**	1.462	1.463
Co1-N5	1.965	1.990	**N28-O29**	1.214	1.215
N2-H15	1.027	1.034	**N28-O30**	1.218	1.217
N2-H16	1.023	1.032	**N7-N24**	1.316	1.319
N2-H14	1.028	1.022	**N24-C25**	1.330	1.329
N3-H17	1.027	1.031	**C25-N26**	1.336	1.335
N3-H18	1.028	1.026	**N26-N27**	1.311	1.311
N3-H19	1.023	1.033	**N7-N27**	1.325	1.325
N4-H11	1.027	1.023	**C25-N31**	1.461	1.462
N4-H12	1.047	1.039	**N31-O32**	1.219	1.219
N4-H13	1.024	1.025	**N31-O33**	1.214	1.214
N5-H8	1.045	1.024	**Cl34-O35**	1.487	1.505
N5-H9	1.024	1.041	**Cl34-O36**	1.558	1.522
N5-H10	1.029	1.023	**Cl34-O37**	1.491	1.507
N6-N20	1.318	1.315	**Cl34-O38**	1.461	1.456

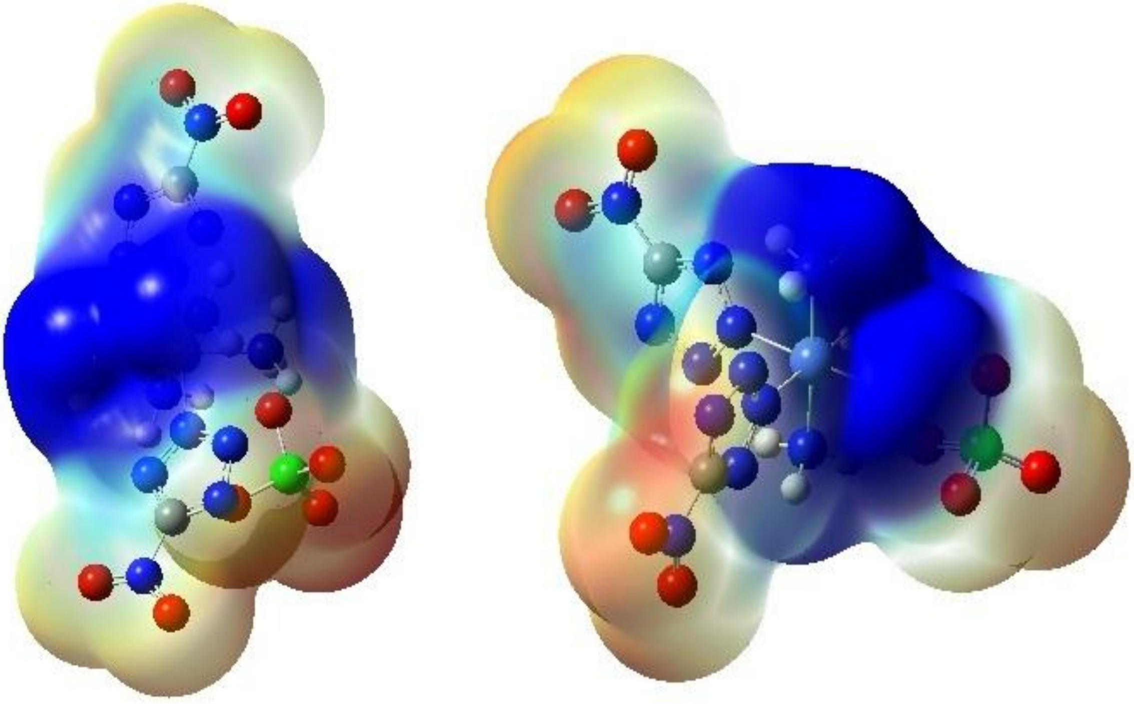

Figure 3. The 3-D electrostatic potential maps of the structures**.**

The Frontier Molecular Orbital Energies

Table 3 shows the HOMO and LUMO energies (ε) of the molecule computed at the B3LYP/SVP level of theory. Density functional theory (DFT) methods have many important applications to chemistry. In DFT methods, two important parameters, the electronic chemical potential μ and the absolute hardness η help us to characterize chemical systems. The electronic chemical potential (the negative of the electronegativity, $-\chi = \mu$) is a thermodynamic measure of the electron tendency to scarper from the electron cloud, and is pertained to both electronic affinity and ionization potential characters. The absolute hardness η is defined as a feature that branched from the μ. If $\eta > 0$, the charge transfer process is energetically adjutant [23]. The ionization energy and electron affinity can be tabernacle by the frontier molecular orbitals HOMO and LUMO energies, respectively ($I = -\varepsilon_{HOMO}$ and $A = -\varepsilon_{LUMO}$) [24]. The electronic chemical potential is half-way between the HOMO and the LUMO on the energy scale. The gap of the HOMO and the LUMO energies is equal to 2η (both the electronic chemical potential and the hardness are measured in electron-volts). Electron transfer between reactants occurs between the molecular orbitals of HOMO and LUMO. The index ω is defined as electrophilicity character that measures the energy stabilization when the system obtains an additional electronic charge from the environment. So, we can acquire the reactivity indexes such as μ, η and ω from frontier orbitals energies by following equations:

$$\mu\ (\mathrm{eV}) = (\varepsilon_{LUMO} + \varepsilon_{HOMO})/2$$
$$\eta\ (\mathrm{eV}) = \varepsilon_{LUMO} - \varepsilon_{HOMO}$$
$$\omega\ (\mathrm{eV}) = \mu^2/2\,\eta$$

The index ω denotes electrophilicity power 1.62, 2.06, 1.52, 1.72, 1.64, 1.59, 1.22, 1.17 and 1.31 for C_2H_2, C_2HF, BH_3, HNO_3, CS_2, C_4H_4, Azulene, Anthracene and Perylene respectively [25]. In this study, index ω value of the structures has been calculated by the application of density functional theory using B3LYP/SVP basis set (Table 3). From the data, it is obtained that the molecules have high electrophilicity.

Natural Bond Orbital (NBO) Population Analysis of Bncp Isomers

A natural bond orbital (NBO) is a calculated bonding orbital with maximum electron density [26]. The NBOs are intermediate between various localized basis atomic orbitals (AO) and molecular orbitals (MO) [27]. The NBO population analysis provides a method for studying intra and intermolecular bonding and interaction among bonds [28]. The results from NBO computations can prepare the electronic structure details of the compound [29]. The natural bond orbital calculation was carried out at the B3LYP/SVP level of theory. He calculated occupancies of the natural orbitals are listed in Tables 4 and 5. According to calculations, the transition metal has used d orbitals to form bonds with the ligands that the d values are more for Co-NH_3 bonds to Co-tetrazole bonds. In the cis-BNCP, σ(Co-tetrazole) bond is formed from an $sd^{1.98}$ hybrid on Co atom, whilst in the trans-BNCP, it is formed from an $sd^{1.93}$ hybrid on Co atom. On the other hand, σ (Co-NH_3) bond is formed from the $sp^{0.01}d^{2.14}$ hybrid and the $sp^{0.01}d^{2.04}$ hybrid on the Co atom in the cis and trans isomers, respectively. As seen from the data, the cobalt atom forms three sigma (single) bonds and three dative bonds with ligands. While the dative bonds between cobalt with two NH_3 and one tetrazole ligands can be described as a donation of electron density from a lone pair (LP) on each nitrogen atom on ligand molecular orbitals. And also, the Co-ligand bonds in the near of perchlorate ion are formed from shorter and sigma bonds.

Table 3. The frontier orbitals energy of the structures calculated at B3LYP/SVP level of theory

Structures	**ε_{HOMO} (a.u.)**	**ε_{LUMO} (a.u.)**	**μ (eV)**	**η (eV)**	**w (eV)**
Trans-BNCP	-0.27699	-0.13686	5.630	3.812	4.163
Cis-BNCP	-0.30941	-0.13327	6.022	4.792	3.782

Table 4. Natural bond orbital population analysis in Trans-BNCP

Donor Lewis type NBOs	**Occupancy**	**Population/Bond orbital/Hybrids**
σ (Co1-N4)	1.96714	18.52% Co1 ($sp^{0.01}d^{2.04}$), 81.48% N4 ($sp^{4.56}$)
σ (Co1-N5)	1.96761	18.49% Co1 ($sp^{0.01}d^{2.04}$), 81.51% N5 ($sp^{4.49}$)
σ (Co1-N7)	1.94710	16.72% Co1 ($sd^{1.93}$), 83.28% N7 ($sp^{2.61}$)
σ (N3-H17)	1.99481	70.20% N3 ($sp^{3.34}$), 29.80% H17 (s)
σ (N3-H18)	1.99520	71.78% N3 ($sp^{2.92}$), 28.22% H18 (s)
σ (N3-H19)	1.99519	72.19% N3 ($sp^{2.85}$), 27.81% H19 (s)
σ (N4-H11)	1.99535	70.76% N4 ($sp^{2.87}$), 29.24% H11 (s)
σ (N4-H12)	1.99398	74.95% N4 ($sp^{2.32}$), 20.05% H12 (s)
σ (N4-H13)	1.99519	72.06% N4 ($sp^{2.83}$), 27.94% H13 (s)
σ (N5-H8)	1.99538	70.69% N5 ($sp^{2.88}$), 29.31% H8 (s)
σ (N5-H9)	1.99521	72.40% N5 ($sp^{2.79}$), 27.60% H9 (s)
σ (N5-H10)	1.99417	74.74% N5 ($sp^{2.37}$), 25.26% H10 (s)
σ (N2-H14)	1.99537	72.16% N2 ($sp^{2.84}$), 27.84% H14 (s)
σ (N2-H15)	1.99513	71.75% N2 ($sp^{2.94}$), 28.25% H15 (s)
σ (N2-H16)	1.99481	70.21% N2 ($sp^{3.33}$), 29.79% H16 (s)
σ (C25-N31)	1.98934	37.92% C25 ($sp^{2.31}$), 62.08% N31 ($sp^{1.91}$)
σ (C25-N24)	1.98637	39.53% C25 ($sp^{1.91}$), 60.47% N24 ($sp^{1.62}$)
σ (C25-N26)	1.99140	41.12% C25 ($sp^{1.83}$), 58.88% N26 ($sp^{1.81}$)
π (C25-N26)	1.74148	45.54% C25 ($sp^{99.99}d^{6.56}$), 54.46% N26 (p)
σ (C21-N28)	1.98938	37.96% C21 ($sp^{2.31}$), 62.04% N28 ($sp^{1.92}$)
σ (C21-N20)	1.98708	39.68% C21 ($sp^{1.91}$), 60.32% N20 ($sp^{1.68}$)
σ (C21-N22)	1.99160	41.10% C21 ($sp^{1.83}$), 58.90% N22 ($sp^{1.8}$)
π (C21-N22)	1.74733	45.63% C21 (p), 54.37% N22 (p)
σ (N7-N24)	1.98196	51.77% N7 ($sp^{1.76}$), 48.23% N24 ($sp^{2.85}d^{0.01}$)
π (N7-N24)	1.87382	56.31% N7 (p), 43.69% N24 (p)
σ (N7-N27)	1.99124	52.95% N7 ($sp^{1.75}$), 47.05% N27 ($sp^{2.73}d^{0.01}$)
σ (N6-N20)	1.97956	51.57% N6 ($sp^{2.27}$), 48.43% N20($sp^{2.75}d^{0.01}$)
π (N6-N20)	1.87198	55.86% N6 (p), 44.14% N20 (p)
σ (N6-N23)	1.98884	52.63% N6 ($sp^{2.29}$), 47.37% N23 ($sp^{2.66}d^{0.01}$)
σ (N31-O32)	1.99495	48.45% N31 ($sp^{2.07}$), 51.55% O32 ($sp^{2.72}d^{0.01}$)
σ (N31-O33)	1.99496	48.52% N31 ($sp^{2.04}$), 51.48% O33 ($sp^{2.69}d^{0.01}$)
π (N31-O33)	1.98275	42.53% N31 (p), 57.47% O33 (p)
σ (N28-O30)	1.99500	48.52% N28 ($sp^{2.06}$), 51.48% O30 ($sp^{2.72}d^{0.01}$)
σ (N28-O29)	1.99501	48.48% N28 ($sp^{2.04}$), 51.52% O29 ($sp^{2.68}d^{0.01}$)

Continued Table 4.

π (N28-O29)	1.98299	42.29% N28 (p), 57.71% O29 (p)
σ (N27-N26)	1.98015	50.64% N27 (sp$^{2.22}$), 49.36% N26 (sp$^{2.62}$d$^{0.01}$)
σ (N23-N22)	1.98043	50.53% N23 (sp$^{2.29}$d$^{0.01}$), 49.47% N22 (sp$^{2.62}$d$^{0.01}$)
σ (Cl34-O36)	1.98182	46.49% Cl34 (sp$^{2.87}$d$^{0.05}$), 53.51% O36 (sp$^{5.64}$d$^{0.01}$)
σ (Cl34-O37)	1.97871	46.22% Cl34 (sp$^{3.42}$d$^{0.06}$), 53.78% O36 (sp$^{7.36}$d$^{0.01}$)
σ (Cl34-O35)	1.98174	46.39% Cl34 (sp$^{2.91}$d$^{0.05}$), 53.61% O35 (sp$^{5.65}$d$^{0.01}$)
σ (Cl34-O38)	1.98355	46.62% Cl34 (sp$^{2.67}$d$^{0.04}$), 53.38% O38 (sp$^{5.23}$d$^{0.01}$)
LP (N3)	1.74358	N3 (sp$^{2.92}$)
LP (N2)	1.74433	N2 (sp$^{2.92}$)
LP (N6)	1.70834	N6 (sp$^{1.54}$)
LP1 (Co1)	1.98880	Co1 (sp$^{0.13}$d$^{99.99}$)
LP2 (Co1)	1.98514	Co1 (d)
LP3 (Co1)	1.96445	Co1 (d)

Table 5. Natural bond orbital population analysis in Cis-BNCP

Donor Lewis type NBOs	**Occupancy**	**Population/Bond orbital/Hybrids**
σ (Co1-N2)	1.97169	18.34% Co1 (sp$^{0.01}$d$^{2.14}$), 81.66% N2 (sp$^{4.87}$)
σ (Co1-N4)	1.97488	15.86% Co1 (sd$^{1.91}$), 84.14% N4 (sp$^{4.12}$)
σ (Co1-N6)	1.94799	15.91% Co1 (sd$^{1.98}$), 84.09% N6 (sp$^{2.59}$)
σ (N2-H14)	1.99520	72.93% N2 (sp$^{2.37}$), 27.07% H14 (s)
σ (N2-H15)	1.99504	72.10% N2 (sp$^{2.75}$), 27.90% H15 (s)
σ (N2-H16)	1.99434	72.66% N2 (sp$^{2.75}$), 27.34% H16 (s)
σ (N4-H11)	1.99619	70.23% N4 (sp$^{2.94}$), 29.77% H11 (s)
σ (N4-H12)	1.99460	73.99% N4 (sp$^{2.31}$), 26.01% H12 (s)
σ (N4-H13)	1.99592	71.43% N4 (sp$^{3.02}$), 28.57% H13 (s)
σ (N5-H8)	1.99559	71.35% N5 (sp$^{2.70}$), 28.65% H8 (s)
σ (N5-H9)	1.99631	70.60% N5 (sp$^{2.75}$), 29.40% H9 (s)
σ (N5-H10)	1.99502	73.98% N5 (sp$^{2.35}$), 26.02% H10 (s)
σ (N3-H17)	1.99460	73.02% N3 (sp$^{2.49}$), 26.98% H17 (s)
σ (N3-H18)	1.99412	73.26% N3 (sp$^{2.52}$), 26.74% H18 (s)
σ (N3-H19)	1.99642	70.02% N3 (sp$^{2.60}$), 29.98% H19 (s)
σ (C21-N20)	1.98681	39.37% C21 (sp$^{1.91}$), 60.63% N20 (sp$^{1.60}$)
σ (C21-N22)	1.99112	41.20% C21 (sp$^{1.82}$), 58.80% N22 (sp$^{1.81}$)
σ (C21-N28)	1.98936	37.92% C21 (sp$^{2.31}$), 62.08% N28 (sp$^{1.91}$)
σ (C25-N26)	1.99110	41.02% C25 (sp$^{1.84}$), 58.98% N26 (sp$^{1.81}$)
σ (C25-N24)	1.98631	39.68% C25 (sp$^{1.90}$), 60.32% N24 (sp$^{1.63}$)
σ (C25-N31)	1.98928	37.98% C25 (sp$^{2.31}$), 62.02% N31 (sp$^{1.92}$)
σ (N7-N27)	1.99270	52.94% N7 (sp$^{1.48}$), 47.06% N27 (sp$^{2.74}$d$^{0.01}$)
σ (N7-N24)	1.98323	52.16% N7 (sp$^{1.44}$), 47.84% N24 (sp$^{2.81}$d$^{0.01}$)
π (N7-N24)	1.87132	56.59% N7 (sp$^{99.99}$d$^{8.77}$), 43.41% N24 (p)
σ (N6-N23)	1.99199	52.83% N6 (sp$^{1.75}$), 47.17% N23 (sp$^{2.71}$d$^{0.01}$)
σ (N6-N20)	1.98254	51.50% N6 (sp$^{1.77}$), 48.50% N20 (sp$^{2.84}$d$^{0.01}$)
π (N6-N20)	1.87294	55.51% N6 (p), 44.49% N20 (p)
σ (N23-N22)	1.98012	50.67% N23 (sp$^{2.22}$), 49.33% N22 (sp$^{2.61}$d$^{0.01}$)

Continued Table 5.

π (N23-N22)	1.82193	51.02% N23 (p), 48.98% N22 (p)
σ (N27-N26)	1.98073	50.84% N27 ($sp^{2.19}$), 49.16% N26 ($sp^{2.61}d^{0.01}$)
π (N27-N26)	1.83307	51.89% N27 (p), 48.11% N26 (p)
σ (N31-O33)	1.99498	48.49% N31 ($sp^{2.05}$), 51.51% O33 ($sp^{2.69}d^{0.01}$)
π (N31-O33)	1.98302	42.22% N31 (p), 57.78% O33 (p)
σ (N31-O32)	1.99502	48.48% N31 ($sp^{2.05}$), 51.52% O32 ($sp^{2.71}d^{0.01}$)
σ (N28-O29)	1.99499	48.51% N28 ($sp^{2.04}$), 51.49% O29 ($sp^{2.69}d^{0.01}$)
π (N28-O29)	1.98288	42.52% N28 (p), 57.48% O29 (p)
σ (N28-O30)	1.99500	48.44% N28 ($sp^{2.07}$), 51.56% O30 ($sp^{2.72}d^{0.01}$)
σ (Cl34-O36)	1.79397	37.41% Cl34 ($sp^{2}d^{1.14}$), 62.59% O36 ($sp^{6.07}d^{0.01}$)
σ (Cl34-O38)	1.97431	45.97% Cl34 ($sp^{2.66}d^{0.09}$), 54.03% O38 ($sp^{5.29}d^{0.01}$)
π_1 (Cl34-O38)	1.93385	9.88% Cl34 ($sp^{88.85}d^{75.22}$), 90.12% O38 ($sp^{99.99}d^{0.47}$)
π_2 (Cl34-O38)	1.93673	9.59% Cl34 ($pd^{0.85}$), 90.41% O38 (p)
σ (Cl34-O35)	1.79918	37.58% Cl34 ($sp^{1.88}d^{1.08}$), 62.42% O35 ($sp^{6.04}d^{0.01}$)
σ (Cl34-O37)	1.78756	36.74% Cl34 ($sp^{2.06}d^{1.22}$), 63.26% O37 ($sp^{6.33}d^{0.01}$)
LP1 (Co1)	1.98842	Co1 (d)
LP2 (Co1)	1.98689	Co1 (d)
LP3 (Co1)	1.97282	Co1 (d)
LP (N5)	1.70874	N5 ($sp^{5.07}$)
LP (N3)	1.71638	N3 ($sp^{5.58}$)
LP (N7)	1.66257	N7 ($sp^{4.27}$)

NBO analysis shows the intermolecular orbital interactions in the complex. This is performed by studying all possible interactions between donor and acceptor natural bond orbitals and guesstimating their energetic value by second-order perturbation theory [30]. The stabilization energy (E^2) for natural bond orbitals (donor NBO = i and acceptor NBO = j) is guessed as follows:

$$E^2 = -q_i \times (F_{i,j})^2/(\varepsilon_j - \varepsilon_i)$$

where:

q_i = orbital occupancy

ε_j, ε_i = diagonal elements

$F_{i,j}$ = off-diagonal natural bond orbital Fock matrix element

As seen from Tables 6 and 7, the tetrazole rings are strongly conjugated by the electron density donations of the bonds and lone pairs in the rings. So, there is an aromaticity property in the rings. This mechanism can be describe a relatively high occupancy of the sigma and pi antibonding orbitals of the elements of the rings, as shown in Tables 4 and 5. From the data, it is deduced that the Co-ligand bonds in the near of perchlorate ion are stronger than other Co-ligand bonds. The reason can be expound by the occupancy of the metal-ligand antibonding orbitals. And also, The nitro groups on the tetrazole rings have high occupancy and high electron density in their antibonding orbitals. Then, at the time of the blast, nitro molecules are released as stable state of nitrogen oxide compounds.

Table 6. Second-order interaction energy between donor-acceptor orbitals in Trans-BNCP

Donor → acceptor	**E^2 (kcal/mol)**	**E(j)-E(i)**	**F (i,j)**
σ (Co1-N4) → σ* (Co1-N5)	2.85	0.47	0.035
σ (Co1-N4) → σ* (Co1-N7)	2.92	0.48	0.036
σ (Co1-N5) → σ* (Co1-N4)	2.80	0.47	0.035
σ (Co1-N5) → σ* (Co1-N7)	2.81	0.48	0.035
σ (Co1-N7) → σ* (Co1-N4)	2.34	0.53	0.033
σ (Co1-N7) → σ* (Co1-N5)	2.31	0.53	0.033
σ (Co1-N7) → σ* (C25-N24)	4.25	1.05	0.060
σ (Co1-N7) → σ* (N7-N24)	1.88	0.97	0.038
σ (Co1-N7) → σ* (N7-N27)	1.85	0.95	0.038
σ (Co1-N7) → σ* (N26-N27)	3.96	1.01	0.057
σ (C25-N24) → σ* (Co1-N7)	2.66	0.86	0.047
σ (C25-N26) → LP2 (N27)	75.31	0.10	0.108
σ (C25-N26) → σ* (N7-N24)	22.46	0.23	0.072
σ (C25-N26) → σ* (N31-O33)	12.31	0.22	0.051
σ (N7-N24) → σ* (C25-N31)	7.39	1.23	0.087
π (N7-N24) → LP2 (N27)	32.08	0.17	0.096
π (N7-N24) → π* (C25-N26)	19.09	0.37	0.082
π (N31-O33) → LP3 (O32)	13.26	0.19	0.082
π (N31-O33) → π* (C25-N26)	5.30	0.43	0.048
π (N31-O33) → π* (N31-O33)	7.35	0.33	0.053
σ (N26-N27) → σ* (C25-N31)	7.13	1.20	0.085
LP2 (O32) → σ* (C25-N31)	14.19	0.57	0.080
LP2 (O32) → σ* (N31-O33)	18.47	0.75	0.106
LP3 (O32) → π* (N31-O33)	167.24	0.15	0.141
LP2 (O33) → σ* (C25-N31)	14.79	0.57	0.082
LP2 (O33) → σ* (C25-N24)	1.21	0.77	0.028
LP2 (O33) → σ* (N31-O32)	19.18	0.73	0.107
LP1 (N24) → σ* (C25-N31)	1.41	0.72	0.029
LP1 (N24) → σ* (C25-N26)	5.95	0.92	0.067
LP1 (N24) → σ* (N7-N27)	7.27	0.83	0.070
LP1 (N27) → σ* (C25-N26)	5.93	0.94	0.067
LP1 (N27) → σ* (N7-N24)	6.67	0.86	0.068
LP2 (N27) → π* (C25-N26)	48.61	0.20	0.098
LP2 (N27) → π* (N7-N24)	102.23	0.12	0.102
LP1 (N26) → σ* (C25-N31)	1.55	0.68	0.029
LP1 (N26) → σ* (C25-N24)	7.39	0.89	0.073
LP1 (N26) → σ* (C25-N27)	7.99	0.79	0.071
LP1 (N3) → σ* (Co1-N4)	2.55	0.45	0.031
LP1 (N3) → σ* (Co1-N5)	71.56	0.45	0.162
LP1 (N3) → σ* (Co1-N7)	2.47	0.46	0.031
LP1 (N2) → σ* (Co1-N4)	71.43	0.45	0.162
LP1 (N2) → σ* (Co1-N5)	2.53	0.45	0.030
LP1 (N2) → σ* (Co1-N7)	2.46	0.46	0.031
LP1 (N6) → σ* (Co1-N4)	2.44	0.50	0.031
LP1 (N6) → σ* (Co1-N5)	2.38	0.50	0.031
LP1 (N6) → σ* (Co1-N7)	82.88	0.51	0.186

Table 7. Second-order interaction energy between donor-acceptor orbitals in Cis-BNCP

Donor → acceptor	**E^2 (kcal/mol)**	**E(j)-E(i)**	**F (i,j)**
σ (Co1-N2) → σ* (Co1-N4)	2.24	0.46	0.031
σ (Co1-N2) → σ* (Co1-N6)	2.43	0.46	0.032
σ (Co1-N4) → σ* (Co1-N2)	1.97	0.48	0.030
σ (Co1-N4) → σ* (Co1-N6)	1.96	0.48	0.030
σ (Co1-N6) → σ* (Co1-N2)	2.03	0.52	0.031
σ (Co1-N6) → σ* (Co1-N4)	1.86	0.53	0.030
σ (Co1-N6) → σ* (C21-N20)	4.30	1.04	0.060
σ (Co1-N6) → σ* (N6-N23)	1.96	0.94	0.038
σ (Co1-N6) → σ* (N6-N20)	2.23	0.95	0.041
σ (Co1-N6) → σ* (N23-N22)	4.07	1.00	0.057
σ (C21-N20) → σ* (Co1-N6)	2.41	0.86	0.044
σ (C21-N20) → σ* (N28-O29)	1.18	1.34	0.036
σ (C21-N22) → σ* (C21-N20)	1.14	1.35	0.035
σ (C21-N22) → σ* (N28-O30)	1.12	1.31	0.035
σ (C21-N28) → σ* (N6-N20)	1.34	1.23	0.036
σ (C21-N28) → σ* (N23-N22)	1.18	1.28	0.035
σ (N26-N23) → σ* (Co1-N2)	0.65	0.92	0.024
σ (N26-N23) → σ* (Co1-N4)	0.90	0.92	0.028
σ (N26-N20) → σ* (Co1-N2)	0.94	0.91	0.028
σ (N26-N20) → σ* (Co1-N4)	0.87	0.92	0.027
σ (N26-N23) → σ* (C21-N28)	2.20	1.22	0.048
σ (N26-N20) → σ* (C21-N28)	7.29	1.22	0.087
σ (N26-N20) → LP1 (C21)	29.85	0.23	0.102
σ (N26-N20) → π* (N23-N22)	17.58	0.34	0.076
σ (N23-N22) → σ* (Co1-N6)	1.68	0.89	0.038
σ (N23-N22) → σ* (C21-N28)	7.27	1.19	0.085
π (N23-N22) → LP1 (C21)	40.39	0.20	0.106
π (N23-N22) → π* (N6-N20)	20.87	0.25	0.076
σ (N28-N29) → σ* (C21-N20)	1.22	1.60	0.040
σ (N28-N29) → σ* (C21-N28)	1.22	1.39	0.038
π (N28-O29) → LP3 (O30)	13.23	0.19	0.082
π (N28-O29) → π* (N28-O29)	7.38	0.33	0.053
σ (N28-O30) → σ* (N28-O29)	0.55	1.56	0.026
LP1 (C21) → π* (N6-N20)	246.53	0.06	0.112
LP1 (C21) → π* (N23-N22)	110.75	0.10	0.107
LP1 (C21) → π* (N28-O29)	170.18	0.04	0.084
LP1 (N23) → σ* (C21-N22)	6.07	0.94	0.068
LP1 (N23) → σ* (N6-N20)	6.46	0.85	0.067
LP1 (N20) → σ* (C21-N22)	5.95	0.92	0.067
LP1 (N20) → σ* (N6-N23)	6.85	0.83	0.068
LP1 (N22) → σ* (C21-N20)	7.34	0.89	0.073
LP1 (N22) → σ* (N6-N23)	8.10	0.79	0.072
LP1 (N5) → σ* (Co1-N2)	2.57	0.40	0.029
LP1 (N5) → σ* (Co1-N4)	3.22	0.40	0.032
LP1 (N5) → σ* (Co1-N6)	81.84	0.40	0.163
LP1 (N3) → σ* (Co1-N2)	76.98	0.39	0.156
LP1 (N3) → σ* (Co1-N4)	3.11	0.40	0.032
LP1 (N3) → σ* (Co1-N6)	2.54	0.40	0.029

Continued Table 7

LP1 (N7) → σ* (Co1-N2)	1.38	0.42	0.022
LP1 (N7) → σ* (Co1-N4)	84.02	0.42	0.169
LP1 (N7) → σ* (Co1-N6)	2.07	0.42	0.026

CONCLUSION

In the present work, structural properties of cis-trans isomers of bis-(5-nitro-2*H*-tetrazolato-N^2) tetraammine cobalt (III) perchlorate (BNCP) as powerful explosives have been investigated theoretically by using quantum chemical treatment. Full geometrical optimization of the structures was performed using density functional theory (DFT, B3LYP) at the level of SVP. According to the results, we can be concluded as follows:

a. The geometry optimization of BNCP isomers computed by the B3LYP/SVP theory shows the octahedral environment around cobalt.

b. The two nitrogen atoms in the tetrazole rings that joined to cobalt have larger negative charge than the ammonia ligands.

c. The three-dimensional electrostatic potential maps of the structures show that the negative charge is located on the nitrogen and oxygen elements of the nitro and perchlorate groups as expected due to the electron withdrawing character of theirs and positive charge is located on the other sections of the systems.

d. Index ω value of the structures shows that the molecules have low electrophilicity.

e. The Natural Bond Orbital (NBO) analysis has provided the detailed insight into the nature of bonding in the isomers of BNCP.

f. We understand from the NBO analysis that the Co-ligand bonds in the near of perchlorate ion are formed from short, strong and sigma bonds.

g. The Natural Bond Orbital (NBO) analysis shows the nitro molecules are released as stable state of nitrogen oxide compounds at the time of the blast.

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