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Adsorption of Tetryl on the Surface of B$_{12}$N$_{12}$: A Comprehensive DFT Study

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**ABSTRACT**

In this study, the adsorption of tetryl on the surface of boron nitride cage was evaluated by density functional theory. For this purpose, the structures of tetryl, B$_{12}$N$_{12}$, and the tetryl-B$_{12}$N$_{12}$ complexes were geometrically optimized. Then, IR and frontier molecular orbital calculations were performed on them. The calculated adsorption energies, Gibbs free energy changes (ΔG$_{ad}$), adsorption enthalpy changes (ΔH$_{ad}$) and thermodynamic equilibrium constants (K$_{th}$) revealed that the adsorption process of both explosives is experimentally feasible, spontaneous, exothermic and non-equilibrium. The specific heat capacity values (C$_V$) showed that the heat sensitivity has been significantly reduced in the tetryl complexes with B$_{12}$N$_{12}$. The N-O and C-N bond lengths and the density values demonstrated that tetryl-derived products with boron nitride cage have higher explosive velocity and blasting pressure in comparison to the pure blasting materials without B$_{12}$N$_{12}$. The frontier molecular orbital parameters such as band gap, chemical hardness, electrophilicity, chemical potential and charge capacity were also studied and the results proved that boron nitride cage is an ideal electroactive sensing material in order to fabricate novel sensors for the determination of tetryl.
**Introduction**

Designing new methods for accurate determination and efficient removal of nitro aromatic explosives is of vital importance. The previous studies showed that the settings that are near to ammunition plants, military munition sites and drowned warships are more susceptible to become polluted by nitro aromatic organic compounds which are commonly utilized in the production of war weapons and bombs [1-3]. Nitro aromatic energetic materials are usually released in the environment via inadequate disposal techniques, open detonations and explosive combustion. Tetryl whose chemical structure is given in Figure 1, is a highly toxic nitro aromatic explosive. Several studies were carried out on the effects of this compound on the health of humans and other living organisms [4-6]. The results showed that exposure to trace amounts of tetryl can lead to liver damage, nausea, allergic dermatitis, anemia, blood damage, cataracts, discoloration of skin and hair, tingling sensation in the nose, skin rashes and irritation, severe headaches, nosebleeds, fatigue and weight loss [7-9]. Moreover, most of the nitro aromatic substances are mutagenic and
carcinogenic. The perniciousness of this type of contaminants is attributed to the oxidation stress which can be created by the synthesis of nitro anion radicals and their redox cycling in the body [10-12]. In this regard, the removal and determination of tetryl is very important. The next matter that accentuates the determination of nitro aromatic chemicals is that many terroristic groups which use explosive bombs and detection of the blasting substances can provide a clue for terroristic activities [13].

Various analytical methods such as high-performance liquid chromatography (HPLC), gas chromatography (GC), fluorescence spectroscopy and mass spectrometry (MS) have been developed for the quantitation of nitro aromatic blasting compounds. On the contrary, the disadvantages make their use challengeable because they are based on costly and intricate instrumentation, all of them are time-consuming and require experienced operators. In addition, the referred techniques consume high amounts of toxic organic solvents and suffer from lack of selectivity [14-16]. Fortunately, sensors are ideally portable and small devices that can be referred to as prominent alternatives for the complicated established methods. In recent years, sensors gathered huge attention all over the world, because of their simplicity, high selectivity, acceptable sensitivity, wide linear working range, being economical, applicability in opaque and coloured samples and short analysis time. But, the most important step in the development of a new sensor is to find a chemical recognition element that interacts strongly with the analyte and this interaction should lead to a change in a measurable property in the local environment near the surface of the transducer [17-27]. On the other hand, boron nitride cage (Figure 1 (b)) is a nanostructure with prominent traits such as high thermal stability, low dielectric constant, great thermal conductance, oxidation resistance, specific surface/area ratio and superb structural stability that make it a suitable adsorbent for the removal of various contaminants and an ideal candidate for the detection of various analytes. Accordingly, the adsorption of HCN, OCN-, amphetamine, proline amino acid and N₂O on the surface of boron nitride cage has been evaluated [28-38].

The next subject that supports investigating the interaction of B₁₂N₁₂ with tetryl is that some of the former studies showed nanomaterials which can improve the reactivity and energetic features of explosives and reduce their heat sensitivity in some cases [39-44]. Hence, the goal of this study is to evaluate the adsorption of tetryl on the surface of boron nitride cage by density functional theory as it is for the first time.
Experimental

Computational methods
At first, the structures of tetryl, boron nitride cage and the tetryl-B_{12}N_{12} complexes were designed by Gauss View 3.1 and nanotube modeller 1.3.0.3 Softwares. Afterward, geometrical optimizations, IR and frontier molecular orbital computations were performed on them using the density functional theory method in the B3LYP/6-31G (d) level of theory. This basis set was selected because in former studies, it had produced results which were in an admissible agreement with the experimental data [31-40]. All of the calculations were done in the temperature range of 278.15-378.15 at 10° intervals by Spartan software, in the aqueous phase. The investigated processes were as follows:

\[ \text{Tetryl} + \text{B}_{12}\text{N}_{12} \rightarrow \text{Tetryl} - \text{B}_{12}\text{N}_{12} \]  

(1)

Equations 2-6 were used for calculating adsorption energy values (\(E_{\text{ad}}\)) and thermodynamic parameters of the evaluated process including enthalpy changes (\(\Delta H_{\text{ad}}\)), Gibbs free energy variations (\(\Delta G_{\text{ad}}\)), thermodynamic constant (\(K_{\text{th}}\)) and entropy variations (\(\Delta S_{\text{ad}}\)).

\[ E_{\text{ad}} = \left( E_{(\text{Tetryl}\text{--B}_{12}\text{N}_{12})} - (E_{(\text{Tetryl})} + E_{(\text{B}_{12}\text{N}_{12})}) \right) \]  

(2)

\[ \Delta H_{\text{ad}} = \left( H_{(\text{Tetryl}\text{--B}_{12}\text{N}_{12})} - (H_{(\text{Tetryl})} + H_{(\text{B}_{12}\text{N}_{12})}) \right) \]  

(3)

\[ \Delta G_{\text{ad}} = \left( G_{(\text{Tetryl}\text{--B}_{12}\text{N}_{12})} - (G_{(\text{Tetryl})} + G_{(\text{B}_{12}\text{N}_{12})}) \right) \]  

(4)

\[ K_{\text{th}} = \exp(-\Delta G_{\text{ad}}/RT) \]  

(5)

\[ \Delta S_{\text{ad}} = \left( S_{(\text{Tetryl}\text{--B}_{12}\text{N}_{12})} - (S_{(\text{Tetryl})} + S_{(\text{B}_{12}\text{N}_{12})}) \right) \]  

(6)

In the aforementioned equations, \(E\) represents the total electronic energy of each structure, \(H\) denotes the sum of the thermal enthalpy and total energy of the evaluated materials. The \(G\) also stands for the sum of the thermal Gibbs free energy and total energy for each of the studied structures. The \(S\) represents thermal entropy for each material, \(R\) and \(T\) are also ideal gas constants and temperature respectively.

Frontier molecular orbital parameters such as band gap (HLG), chemical hardness (\(\eta\)), chemical potential (\(\mu\)), electrophilicity (\(\omega\)) and the maximum transferred charge (\(\Delta N_{\text{max}}\)) were calculated via equations 5-9.
\[ HLG = E_{LUMO} - E_{HOMO} \quad (7) \]
\[ \eta = (E_{LUMO} - E_{HOMO})/2 \quad (8) \]
\[ \mu = (E_{LUMO} + E_{HOMO})/2 \quad (9) \]
\[ \omega = \mu^2 / 2\mu \quad (10) \]
\[ \Delta N_{\text{max}} = -\mu / \eta \quad (11) \]

\(E_{LUMO}\) and \(E_{HOMO}\) in equations 5 to 7 denote the energy of the lowest unoccupied molecular orbital and the energy of the highest occupied molecular orbital respectively.

![Tetryl and Boron Nitride Nanocage](image)

**Figure 1.** The chemical structure of tetryl and optimized structures of B\(_{12}\)N\(_{12}\) and its complexes with tetryl at four different configurations

Results and discussion

Structural properties
As can be seen from Figure 1, tetryl was inserted near the boron nitride cage at four different positions, for more convenient understanding, each configuration was remarked by an abbreviated name. The naming method is explained in the following:

The I-Isomer abbreviation was considered for the derivative in which the benzene ring is inserted in parallel form near the $\text{B}_{12}\text{N}_{12}$ surface. The II-Isomer symbol was also assigned to the derived product that was originated from placing the boron nitride cage near to the first carbon atom of tetryl. The next derivative which was formed by situating the 7th carbon of the methyl group of tetryl near the surface of $\text{B}_{12}\text{N}_{12}$ was remarked by III-Isomer. IV-Isomer also represents the last configuration in which the third nitrogen atom of tetryl’s nitro group is placed near the surface of the boron nitride cage. The reported adsorption energy values in Table 1, were calculated via equation 2. As can be seen from the Table, this parameter is considerably negative for all of the configurations, therefore, it can be deduced that the adsorption process of tetryl is experimentally feasible [26-36]. Therefore, this nanostructure can be applied for the removal of this nitroaromatic contaminant from the environmental specimens.

Owing to the fact that N-O, N-NO$_2$ and C-NO$_2$ bond lengths are appropriate standards for estimating the blasting power in the nitroaromatic explosives, after implementing geometrical optimization on the studied structures, the mentioned bond lengths were measured and tabulated in Table 1. As the provided data in Table 1 clearly reveal, the N-O, N-NO$_2$ and C-NO$_2$ bond lengths have increased in tetryl after being adsorbed on the surface of boron nitride cage at all of the evaluated derivatives. The incrementing of the referred bond lengths exhibits that the existed bonds between nitrogen and oxygen as well as nitrogen and carbon have become much weaker and they can be ruptured more easily by interacting with boron nitride cage. In other words, tetryl derivatives with $\text{B}_{12}\text{N}_{12}$ can take part in the combustion reaction more conveniently in comparison to the pure explosive and their blasting power have ameliorated substantially [33-35]. Density was the next investigated structural parameter which was obtained by dividing the weight of the structures to the calculated volumes after the optimization step. According to equations 12 and 13, density has a direct and obvious relationship with explosion velocity and detonation pressure [39].

$$D^{1/4} = 1.01 \left(\frac{NM^{1/2}Q^{1/2}}{Q^{1/2}}\right)^{1/2} (1 + 1.30\rho)$$ (12)

$$P^{1/4} = 1.558NM^{1/2}Q^{1/2}\rho^2$$ (13)

In these formulas, D is the explosion velocity, P is the detonation pressure, M represents the average molecular weight of gaseous products, N stands for the number of moles of gaseous explosion products per gram of explosives, Q is the blasting Heat and $\rho$ is the density of blasting.
material. As can be seen from the table, the density of tetryl has enhanced after adsorbing on the surface of B\textsubscript{12}N\textsubscript{12}. Among the studied derivatives, I-Isomer has the highest density. Hence, coating tetryl on the surface of boron nitride cage leads to a significant rise in the explosion velocity and detonation pressure of the inspected blasting material in all of the configurations [40].

**Table 1.** The values of the total energy, adsorption energy, lowest frequency, bond lengths, weight, volume and density for tetryl and its complexes with B\textsubscript{12}N\textsubscript{12}

|                  | Tetryl | I-Isomer | II-Isomer | III-Isomer | IV-Isomer |
|------------------|--------|----------|-----------|------------|-----------|
| Total energy (a.u) | -1123.575 | -2007.645 | -2007.687 | -2007.548 | -2007.915 |
| Adsorption energy (KJ/mol) | --- | -407.215 | -517.701 | -152.317 | -1117.478 |
| Lowest frequency (cm\textsuperscript{-1}) | 31.169 | 15.392 | 27.387 | 14.83 | 14.80 |
| C=N (Å) | 1.512 | 1.521 | 1.533 | 1.522 | 1.585 |
| C-N (Å) | 1.507 | 1.517 | 1.514 | 1.517 | 1.526 |
| C=N (Å) | 1.515 | 1.522 | 1.531 | 1.523 | 1.540 |
| N-O (Å) | 1.477 | 1.490 | 1.483 | 1.484 | 1.480 |
| N-O (Å) | 1.268 | 1.282 | 1.281 | 1.282 | 1.278 |
| N-O (Å) | 1.512 | 1.584 | 1.539 | 1.551 | 1.545 |
| N-O (Å) | 1.236 | 1.283 | 1.392 | 1.243 | 1.270 |
| N-O (Å) | 1.275 | 1.282 | 1.291 | 1.286 | 1.287 |
| N-O (Å) | 1.279 | 1.291 | 1.286 | 1.294 | 1.293 |
| N-O (Å) | 1.278 | 1.290 | 1.397 | 1.291 | 1.356 |
| N-O (Å) | 1.277 | 1.294 | 1.289 | 1.285 | 1.345 |
| C-B (Å) | --- | 1.615 | --- | --- | --- |
| C-N (Å) | --- | --- | 1.411 | --- | --- |
| C-B (Å) | --- | --- | --- | 1.613 | --- |
| C-N (Å) | --- | --- | --- | 1.297 | --- |
| Weight (amu) | 287.144 | 569.945 | 569.945 | 569.945 | 569.945 |
| Volume (Å\textsuperscript{3}) | 220.210 | 426.180 | 433.300 | 429.910 | 431.030 |
| Density=m/v (amu/Å\textsuperscript{3}) | 1.304 | 1.337 | 1.315 | 1.326 | 1.322 |

**Thermodynamic parameters of the adsorption process**

The reported $\Delta H_{\text{ad}}$ values in Table 2, which was calculated from equation 3, clearly indicate that the interaction of boron nitride cage with tetryl is extremely exothermic at all of the configurations. Indeed, the heat or energy is transferred from the system to the environment in the adsorption process of tetryl. In this regard, B\textsubscript{12}N\textsubscript{12} can be utilized for the detection of tetryl by thermal sensors. These types of sensors determinate the amount of analyte by measuring the alterations in the environmental temperature by a sensitive thermistor [41, 42]. Among the evaluated derivatives, IV-Isomer has the most negative $\Delta H_{\text{ad}}$ value which shows that the formation of this configuration is more exothermic and experimentally feasible in comparison to other derived products. The influence of temperature on this parameter was also investigated. As it is obvious from the Table, by increasing of temperature, $\Delta H_{\text{ad}}$ does not experience any meaningful variations. Therefore, on
the basis of this parameter, the optimum temperature for the adsorption process cannot be
determined [31].

The reported $\Delta G_{\text{ad}}$ values in Table 2 which were calculated from equation 4, exhibit that the
interaction of boron nitride cage with tetryl is spontaneously at all of the configurations because of
the achieved negative Gibbs free energy alterations. The impact of changing the temperature on this
parameter was also checked out and the findings demonstrate that by rising of temperature, $\Delta G_{\text{ad}}$
has gradually incremented. In other words, the adsorption process has become less spontaneous
with temperature increasing. In this regard, 278.15 K was selected as the optimum temperature for
the adsorption of tetryl on the surface of boron nitride ca
gue. This phenomenon was not out of
expecting because tetryl and is more reactive at higher temperatures and it has more tendency to
participate in explosive reactions. However, in lower temperatures, they are more stable and
consequently can take part in other interactions more conveniently [32-36].

### Table 2. The values of enthalpy changes and Gibbs free energy changes for the adsorption process of tetryl on
the surface of $B_{12}N_{12}$ in the temperature range of 278.15-378.15 K

| Temperature (K) | $\Delta H_{\text{ad}}$ (KJ/mol) | $\Delta G_{\text{ad}}$ (KJ/mol) |
|-----------------|-------------------------------|-------------------------------|
|                 | I-Isomer | II-Isomer | III-Isomer | IV-Isomer | I-Isomer | II-Isomer | III-Isomer | IV-Isomer |
| 278.15          | -444.128 | -559.458  | -188.003   | -1299.619 |
| 288.15          | -444.427 | -559.682  | -188.358   | -1299.996 |
| 298.15          | -444.722 | -559.908  | -188.686   | -1300.342 |
| 308.15          | -445.009 | -560.137  | -188.981   | -1300.657 |
| 318.15          | -445.291 | -560.363  | -189.258   | -1300.980 |
| 328.15          | -445.533 | -560.550  | -189.521   | -1301.278 |
| 338.15          | -445.755 | -560.729  | -189.764   | -1301.574 |
| 348.15          | -445.974 | -560.898  | -189.972   | -1301.864 |
| 358.15          | -446.177 | -561.059  | -190.172   | -1302.131 |
| 368.15          | -446.376 | -561.189  | -190.363   | -1302.362 |
| 378.15          | -446.572 | -561.306  | -190.536   | -1302.603 |

As can be observed from the presented thermodynamic constants in Table 3, tetryl adsorption
process is irreversible, one-sided and non-equilibrium. The main advantage of this $K_{\text{th}}$ is that it can
show the impact of temperature more evidently than other thermodynamic parameters. As it is
obvious, the thermodynamic constant values have reduced significantly by increasing of
temperature. The values of adsorption entropy changes ($\Delta S_{ad}$) were also calculated by equation 6
and the results are tabulated in Table 3. As can be seen, this parameter is negative for all of the
evaluated configurations which indicate that tetryl interaction with $\text{B}_{12}\text{N}_{12}$ is inappropriate due to
the aggregation in tetryl complexes with boron nitride cage [37-40].

Table 3. The values of thermodynamic constant and entropy changes for the adsorption process of
tetryl on the surface of $\text{B}_{12}\text{N}_{12}$ in the temperature range of 278.15-378.15 K

| Temperature (K) | $K_{th}$ (J/mol K) | $\Delta S_{ad}$ (J/mol K) |
|----------------|-------------------|---------------------------|
|                |                   | I-Isomer                  | II-Isomer                 | III-Isomer                | IV-Isomer                |
| 278.15         |                   | 2.818×10$^{-117}$         | 2.818×10$^{-117}$         | 2.818×10$^{-117}$         | 2.818×10$^{-117}$         |
| 288.15         |                   | 6.896×10$^{-112}$         | 6.896×10$^{-112}$         | 6.896×10$^{-112}$         | 6.896×10$^{-112}$         |
| 298.15         |                   | 3.423×10$^{-108}$         | 3.423×10$^{-108}$         | 3.423×10$^{-108}$         | 3.423×10$^{-108}$         |
| 308.15         |                   | 3.310×10$^{-104}$         | 3.310×10$^{-104}$         | 3.310×10$^{-104}$         | 3.310×10$^{-104}$         |
| 318.15         |                   | 5.664×10$^{-100}$         | 5.664×10$^{-100}$         | 5.664×10$^{-100}$         | 5.664×10$^{-100}$         |
| 328.15         |                   | 1.596×10$^{-97}$          | 1.596×10$^{-97}$          | 1.596×10$^{-97}$          | 1.596×10$^{-97}$          |
| 338.15         |                   | 7.448×10$^{-93}$          | 7.448×10$^{-93}$          | 7.448×10$^{-93}$          | 7.448×10$^{-93}$          |
| 348.15         |                   | 5.354×10$^{-90}$          | 5.354×10$^{-90}$          | 5.354×10$^{-90}$          | 5.354×10$^{-90}$          |
| 358.15         |                   | 5.756×10$^{-87}$          | 5.756×10$^{-87}$          | 5.756×10$^{-87}$          | 5.756×10$^{-87}$          |
| 368.15         |                   | 8.939×10$^{-84}$          | 8.939×10$^{-84}$          | 8.939×10$^{-84}$          | 8.939×10$^{-84}$          |
| 378.15         |                   | 1.943×10$^{-82}$          | 1.943×10$^{-82}$          | 1.943×10$^{-82}$          | 1.943×10$^{-82}$          |

Due to the fact that the specific heat capacity has an obvious and direct relationship with heat
sensitivity, this parameter was also calculated and presented in Table 4. Specific heat capacity is
defined as the heat or energy, which is required for raising the temperature of a certain amount of
material to one Celsius degree. Therefore, a compound with higher $C_v$ will have a lower sensitivity
to the heat because it needs more energy to increase its temperature. On the other hand, a molecule
with a low specific heat capacity value will be more sensitive to heat because its temperature can be
enhanced by a lower amount of heat. As the provided results in the table obviously reveal, the
specific heat capacity has dramatically increased after the adsorption of tetryl on the surface of
boron nitride cage, in all of the derivatives [41-45]. Therefore, the heat sensitivity has declined
tangibly after tetryl adsorption on the $\text{B}_{12}\text{N}_{12}$. The next point which can be perceived from the
Tables is that by increasing of temperature specific heat capacity values have also augmented linearly.

**Table 4.** The specific heat capacity values for tetryl and its complexes with B\(_{12}\)N\(_{12}\) in the temperature range of 278.15-378.15 K

| Temperature (K) | Tetryl  | I-Isomer | II-Isomer | III-Isomer | IV-Isomer |
|-----------------|---------|----------|-----------|------------|-----------|
| 278.15          | 240.376 | 420.705  | 428.910   | 413.074    | 399.273   |
| 288.15          | 246.136 | 434.702  | 442.947   | 427.337    | 413.674   |
| 298.15          | 251.824 | 448.565  | 456.825   | 441.471    | 427.956   |
| 308.15          | 257.440 | 462.282  | 470.534   | 455.459    | 442.103   |
| 318.15          | 262.986 | 475.840  | 484.065   | 469.289    | 456.100   |
| 328.15          | 268.461 | 489.229  | 497.409   | 482.948    | 469.936   |
| 338.15          | 273.866 | 502.439  | 510.559   | 496.425    | 483.597   |
| 348.15          | 279.200 | 515.460  | 523.507   | 509.710    | 497.074   |
| 358.15          | 284.463 | 528.285  | 536.247   | 522.795    | 510.355   |
| 368.15          | 289.654 | 540.907  | 548.773   | 535.670    | 523.433   |
| 378.15          | 294.772 | 553.319  | 561.082   | 548.330    | 536.299   |

**Frontier molecular orbital analysis**

As stated before, in chemistry, HOMO is described as the highest occupied molecular orbital and LUMO is defined as the lowest unoccupied molecular orbital, and the energy discrepancy between these orbitals is known as band gap (HLG) which can be calculated via equation 7. Determination of this variable is important because of its relevance to the conductivity. Indeed, the compounds with lower values of HLG demand less energy for transmitting their electrons from the ground state to the excited one in comparison to the materials with higher values of the band gap. Hence, a molecule with a little value of HLG will be more conductive than a compound with a high amount of energy gap. As it can be observed from the density of states (DOS) diagrams in Figure 2 and the provided data in Table 5, this parameter has abated significantly after the adsorption of tetryl on the surface of boron nitride cage. In other words, the conductivity has increased remarkably by the interaction of B\(_{12}\)N\(_{12}\) with tetryl. Therefore, it can be concluded that this nanostructure can be used for the detection of this toxic explosive by conductometric electrochemical sensors [46]. The second investigated parameter was chemical hardness (\(\eta\)) which was calculated by equation 8. This variable has a clear relationship with the reactivity. In fact, the soft molecules that have lower values of \(\eta\) will be more reactive because they can alter their electron density so conveniently, and electronic transmissions that are essential for the implementation of reaction can be done more easily in them. The presented results in the table indicate that the reactivity of tetryl has improved considerably after the adsorbing of tetryl on the B\(_{12}\)N\(_{12}\). The chemical potential (\(\mu\)) which is necessary for acquiring other indices was also calculated by equation 9.
Table 5. The calculated $E_H$ and $E_L$, HLG, chemical hardness ($\eta$), electrophilicity index ($\omega$), and the maximum amount of electronic charge index ($\Delta N_{\text{max}}$), dipole moment and zero-point energy for tetryl and its complexes boron nitride cage

|          | $E_H$ (eV) | $E_L$ (eV) | HLG (eV) | $\eta$ (eV) | $\mu$ (eV) | $\omega$ (eV) | $\Delta N_{\text{max}}$ (eV) | Dipole moment (deby) | Zero-point energy (KJ/mol) |
|----------|------------|------------|----------|-------------|------------|-------------|-----------------------------|-----------------------|--------------------------|
| Tetryl   | -8.154     | 2.660      | 10.814   | 5.407       | -2.747     | 0.698       | 0.508                      | 3.170                 | 444.080                  |
| Boron nitride cage | -8.290     | 6.690      | 14.980   | 7.490       | -0.800     | 0.043       | 0.107                      | 0.000                 | 349.518                  |
| I-Isomer | -7.194     | 1.411      | 8.605    | 4.303       | -2.892     | 0.972       | 0.672                      | 3.729                 | 877.067                  |
| II-Isomer| -3.515     | 2.916      | 6.431    | 3.215       | -0.299     | 0.014       | 0.093                      | 14.481                | 763.855                  |
| III-Isomer| -7.594    | 1.388      | 8.982    | 4.491       | -3.103     | 1.072       | 0.691                      | 3.397                 | 773.550                  |
| IV-Isomer| -4.115     | 2.505      | 6.621    | 3.310       | -0.805     | 0.098       | 0.243                      | 8.595                 | 823.630                  |

Electrophilicity ($\omega$) and maximum transferred charge ($\Delta N_{\text{max}}$) that were calculated by equations 10 and 11 consecutively, show the tendency of a molecule towards electron. If a material has a great and positive value of $\omega$ and $\Delta N_{\text{max}}$, it will have more tendency to absorb an electron. However, if a molecule has a low amount of these indices, it will act as an electron donor [47]. The obtained results in the tables reveal that tetryl can act as a Lewis acid or an electron acceptor because of their high electrophilicity and maximum transferred charge values. While, boron nitride cage can play the role of an electron donor due to its low electrophilicity, hence, it can be elicited that the nanostructure and the explosive can take part in electron transfer reactions. Thus, boron nitride cage is an ideal electroactive sensing material for the fabrication of novel tetryl sensitive electrochemical sensors.

Dipole moment is the last investigated parameter. The dipole moment is a key clue which demonstrates the solubility of the investigated structures. A substance with higher dipole moment will have stronger solubility in the polar solvents like water. On the other hand, a low amount of dipole moment indicates the poor solubility in polar solvents. As can be seen, the dipole moment of $B_{12}N_{12}$ is zero, so, this nanostructure is insoluble in water. This fact is of great importance because many sensors lose their sensitivity, stability and selectivity after a short period of time because of the leakage of the recognition element from the membrane to the sample solution. In this regard, sensing materials with lower solubility in polar solvents are more suitable for the construction of new sensors. Fortunately, boron nitride cage meets this requirement. Besides, the dipole moment of
tetryl has enhanced significantly after its interaction with B_{12}N_{12}. So, it can be deduced that tetryl has become more soluble in water after the adsorbing on the surface of boron nitride cage [48].

**Figure 2.** The density of states (DOS) diagrams for tetryl and its complexes with boron nitride cage

**Conclusions**

Tetryl is a toxic nitroaromatic explosive that has adverse effects on the health of human and other living organisms. Therefore, its detection and removal is of vital importance. In this regard, the adsorption of the tetryl on the surface of boron nitride cage was evaluated by DFT method in the
B3LYP/6-31G (d) level of theory. The results of the calculations revealed that the adsorption of tetryl on the surface of B$_{12}$N$_{12}$ is experimentally possible. In addition, the interaction of tetryl with boron nitride cage is exothermic as this nanostructure can be used for the thermal detection of tetryl. The effect of temperature on the studied process was also checked out and it was found out that 278.15 K is the optimum temperature. The obtained specific heat capacity values proved that tetryl adsorbing on the B$_{12}$N$_{12}$ leads to a significant decrease in the heat sensitivity. The structural properties including bond lengths and density values proved that the boron nitride cage complexes with tetryl have higher detonation velocity, blasting pressure and explosive power in comparison to pure tetryl. The frontier molecular orbital parameters also showed that boron nitride cage can be used as an electroactive sensing material for the determination of tetryl.

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**Conflict of Interest**

We have no conflicts of interest to disclose.

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