

## Thermal stability of N-( $\alpha$ -amino-dodecyl)-benzotriazole

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### Abstract

N-( $\alpha$ -amino-alkyl)-benzotriazole, a derivative of Benzotriazole (BTZ), was synthesized via a Mannich reaction addition. The chemical characterization shows that when C<sub>19</sub>H<sub>32</sub>N<sub>4</sub> supramolecule is subjected to heating process the covalent bonds of aminal carbon are broken, modifying supramolecule structure, this results in a rearrangement to the structure dodecan ammonium-1-benzotriazol-1-ate, [BTZ<sup>-</sup> amine<sup>12+</sup>]. Quantum chemical calculations based on DFT method were performed on the C<sub>19</sub>H<sub>32</sub>N<sub>4</sub> molecule. The results show that in a derivative of BTZ exists a weak bond where its break may occur.

### Keywords

N-( $\alpha$ -amino-alkyl)-benzotriazole; DSC; TGA; Density Functional Theory; Thermal stability.

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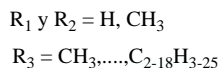
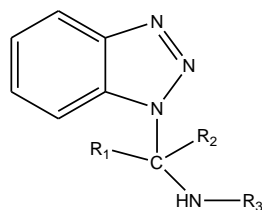
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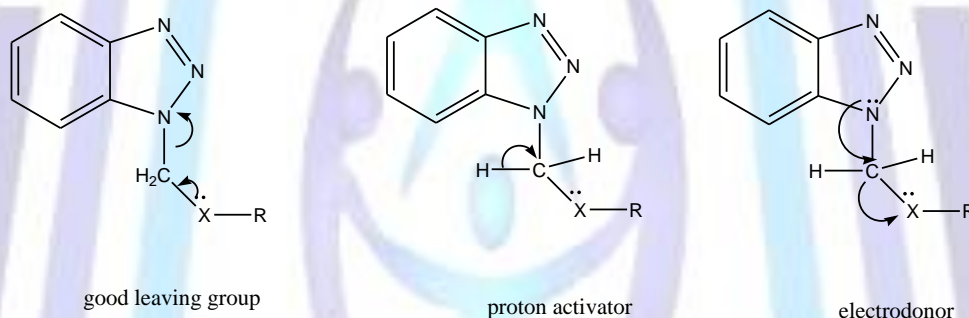
## 1. Introduction

The N-( $\alpha$ -amino-alkyl)-benzotriazoles are important mainly for use in the biological sciences [1-8] and industrial corrosion inhibitors [9-15]. Structurally, the N-( $\alpha$ -amino-alkyl)-benzotriazoles are aminal compounds containing two nitrogen atoms that act as substituents on the same carbon atom [16], wherein one nitrogen corresponds to benzotriazole and another corresponds to a secondary or tertiary amine (**scheme 1**).



**Scheme 1.** General structure of the aminal compound.

These kinds of compounds are characterized by containing within their structure the group known as benzotriazolyl; such is a synthetic auxiliary in the aminal carbon activation. Benzotriazolyl may act as a leaving group; allowing the chain deprotonation; or like electron donor [17]. In each case benzotriazolyl may undergo reductive elimination to form anion, in dependence on X substituent (**Scheme 2**).



**Scheme 2.** Benzotriazolyl group can act in several ways depending on substituent X.

## 2. Experimental procedure

### 2.1 Synthesis and characterization of N-( $\alpha$ -amino-dodecyl)-benzotriazole

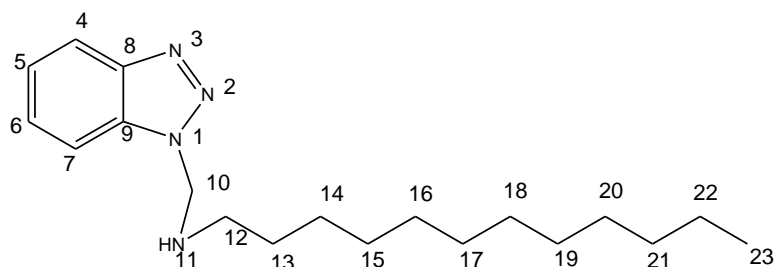
1-n-Dodecylamine (16.78 mmol, 3.12 g) and formaldehyde (16.78 mmol, 0.50 g) were added to a solution of benzotriazole (16.78 mmol, 2.00 g) in methanol (15 ml) and stirred for 3h at room temperature according to the Mannich reaction reported by Katritzky [18]. Yield: 80%. m.p. 68-69°C. Elemental analysis: C 72.10%, H 10.15%, N 17.74% (calcd: C 72.15%, H 10.13%, N 17.72%). IR (KBr  $\text{cm}^{-1}$ ): 3055 (N-H), 2956 (C-H), 2916 (C-H), 1765 (C=C), 1460 (C-N).  $^1\text{HMRN}$  (500 MHz;  $\text{CDCl}_3$ ; ppm): 7.8 (4H,7H), 7.2 (5H, 6H), 5.4 (10HA, 10HB), 2.8 (12HA, 12HB), 2.6 (11H), 1.18 (14H-22H).

### 2.2 Modeling of Molecular Structure

In order to understand more about the thermal stability of the [BTZ amine12], (**Scheme 3**), was simulated with the Materials Studio (MS) software [19]. The molecular geometry were fully optimized through Density-Functional-Theory (DFT), energy minimization by using the MS DMol3 code [20,21], taking into account an aqueous environment simulated via water continuum dielectric medium. We have used GGA/PBE functional [22] DNP basis set and TS method for DFT dispersion correlations [23]. We have left predefined run parameters at fine accuracy, it was relaxed until  $1 \times 10^{-5}$  Ha and remaining total force was below 0.002 Ha/Å.

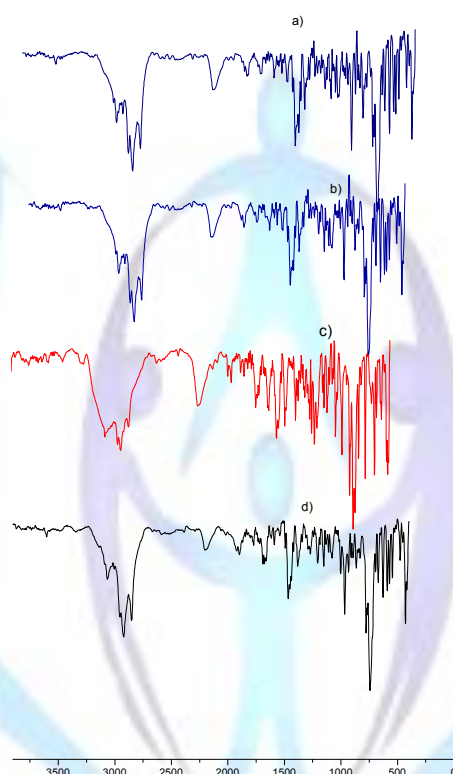
## 3. Results and Discussion

Previously we reported the supramolecular structure of ammonium dodecane-1-benzotriazol-1-ate [24]; obtained from N-( $\alpha$ -amino-dodecyl)-benzotriazole [BTZ amine12] broken during a heating process. In order to determine the temperature which the lattice rearrangement occurs to obtain the dodecane-1-ammonium benzotriazol-1-ate, [BTZ' amine12 $^+$ ]; N-( $\alpha$ -amino-dodecyl)-benzotriazole [BTZ amine12] structure was subjected by 1h to heating process at different temperature (45, 65 and 85°C), (**scheme 3**).



**Scheme 3.** N-( $\alpha$ -amino-dodecyl)-benzotriazole with labels for each atom.

**Figure 1** shows the IR spectra obtained for N-( $\alpha$ -amino-dodecyl)-benzotriazole, [BTZ amine12] characterization obtained after a heating treatment at different temperatures by 1h (r t, 45, 65, 85°C).



**Figure 1.** Infrared spectra [BTZ amine12] molecule corresponding to: a) compound obtained by the reaction at room temperature, b) after heating at 45°C for 1 h c) after heating at 65°C for 1 h, d) keeping at 85°C for 1h.

In all cases appear the bands allocated to the N-H and C-H vibration characteristics ( $3055\text{--}2900\text{ cm}^{-1}$ ). However, when the compound is heated to 45°C is achieved gently flaring seen in this group of signals, is also identified in all cases the vibration corresponding to the C=C band ( $1765\text{--}1780\text{ cm}^{-1}$ ), in the frequency range of  $1460\text{--}1490\text{ cm}^{-1}$  attributable to vibration C-N, the frequency increases with increasing temperature, and there is a small decrease in the intensity of the band as a function of temperature increase. That is at room temperature, frequency is slightly small and the peak is very intense up to 65°C; at 85°C the peak is less intense but its electron density is higher producing an increase in the frequency by  $12\text{ cm}^{-1}$ . This analysis is the first indication that the structure is sensitive to temperature.

**Figure 2** shows the signals corresponding to the Nuclear Magnetic Resonance Proton ( $^1\text{H NMR}$ ) of [BTZ amine12], small peaks suggesting the presence of small amounts of a byproduct can be appreciated, the singlet at 5.4 ppm appears for integrating protons H10A and H10B, double doublet of 7.8 corresponds to proton H4 and H7, which appears in the doublet 7.2 ppm correspond H5 and H6.

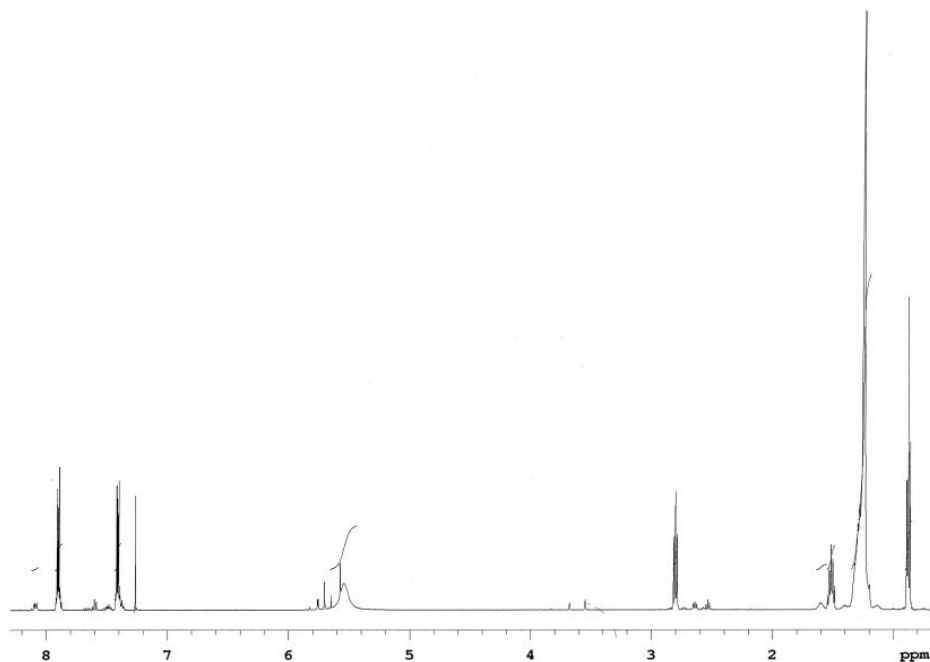


Figure 2.  $^1\text{H}$  NMR of [BTZ amine12].

The triplet located at 2.8 ppm correspond to H12A and H12B, the triplet at 2.6 ppm shift corresponds to  $-\text{NH}-$ , indicating that the compound [BTZ amine12] is effectively a secondary amine, while quintet that appears at 1.5 ppm shift corresponds to hydrocarbonated chain (C14 to C21), upon heating [BTZ amine12] at  $45^\circ\text{C}$  for one hour the spectrum of  $^1\text{H}$  NMR is observed unchanged.

After heating at  $65^\circ\text{C}$  for 1h., the observed aromatic signals (8.05-7.2 ppm) are duplicated and maintained a 1:1 proportion, (Figure 3). At 5.5 ppm shift the C-H signal disappears while the triplet at 2.8 ppm increase in intensity and the signal of neighbor triplet reduces.

When [BTZ amine12] is heated to  $85^\circ\text{C}$ , the proportions of the aromatic signals are modified again, the triplet at 2.8 ppm of chemical shift are lower than those observed at lower temperatures, the triplet signal at 2.6 ppm of chemical shift corresponding to H11 is bigger. The obtained information from spectra described before indicates that the N-( $\alpha$ -amino-dodecyl)-benzotriazole structure is unstable with increasing temperature; furthermore, since  $65^\circ\text{C}$ , the presence of ammonium dodecane-1-benzotriazol-1-ate, [BTZ $^+$  amine12 $^-$ ] compound predominates at the end of heating process.

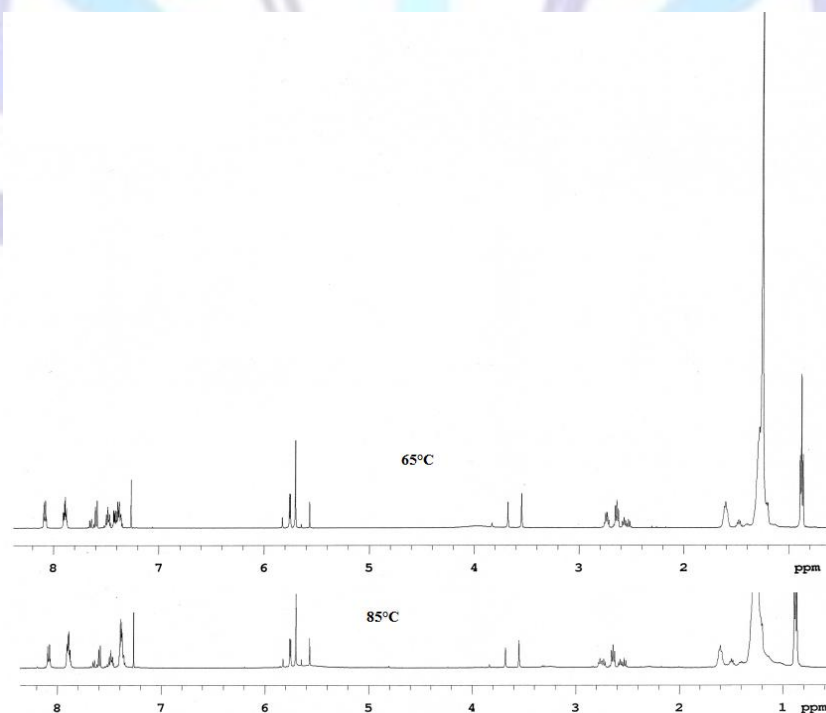
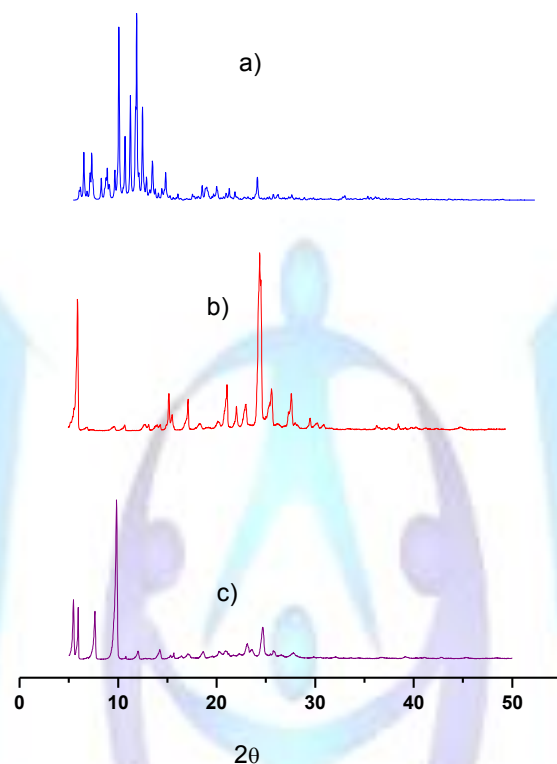


Figure 3.  $^1\text{H}$  NMR after heating [BTZ amine12] 65 and  $85^\circ\text{C}$ .

Due the observed change in the structure at 65°C modifications on molecular packing are expected. The X-ray characterization by diffraction of powders of [BTZ amine12] synthesized at room temperature and after heating at 65°C is shown in (Figure 4). After heating at 85°C the compound structure is totally amorphous so that diffraction patterns can be not obtained.



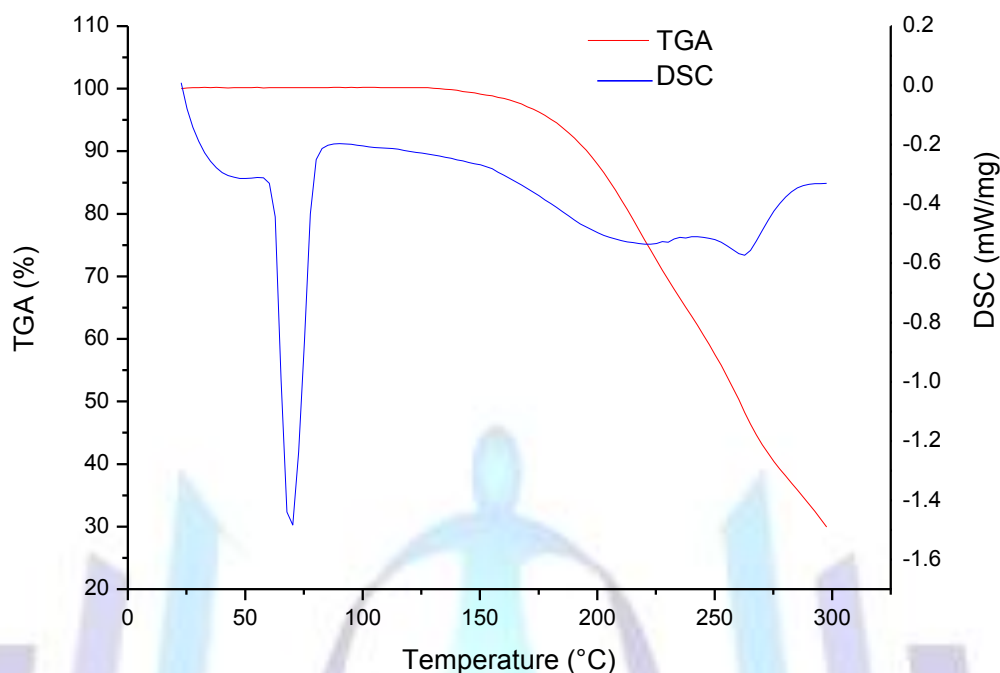
**Figure 4.** XRD: a) [BTZ amine12] monocrystal, b) [BTZ amine12] after heating at 65°C in xylene, c) at room temperature [BTZ amine12].

Considering as reference the diffractogram of monocrystal (Figure 4a) [24], can be noted marked differences in the diffraction patterns obtained at room temperature and after heating at 65°C, indicating that a structural intramolecular rearrangement occurs as a result of a function of temperature variations.

### 3.1 Thermogravimetric Analysis (TGA) and Differential Scanning Calorimetry (DSC).

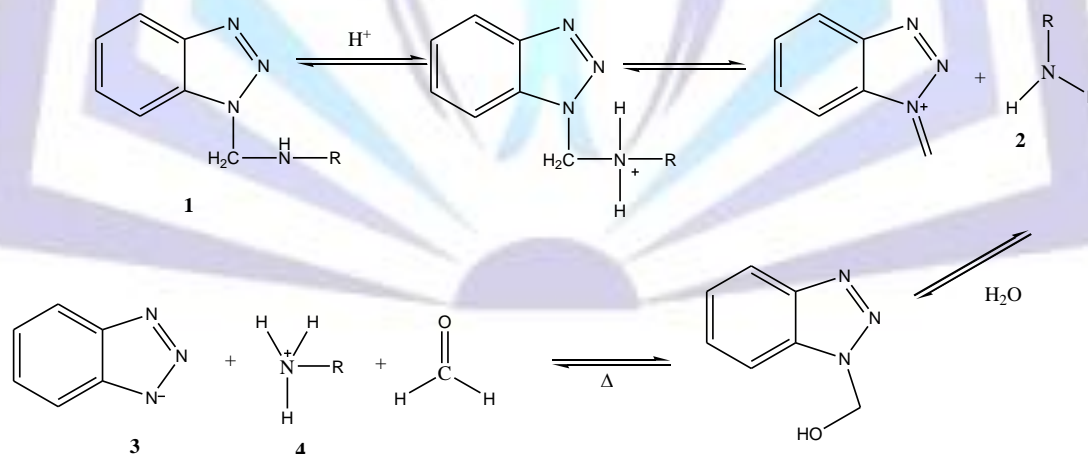
As was depicted before, temperature has an important effect on N-( $\alpha$ -amino-dodecyl)-benzotriazole supramolecule, in this sense thermal analysis, by means of both thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) of [BTZ amine12] can be useful to determine the compound's stability. These analyses are presented in (Figure 5).





**Figure 5.** TGA and DSC of N-( $\alpha$ -amino-dodecyl)-benzotriazole, obtained from 25°C to 300°C under nitrogen with a heating rate of 5°C / min.

Thermal analysis of N-( $\alpha$ -amino-dodecyl)-benzotriazole indicates a strong endothermic process occurring between 63°C and 79°C, with a peak maximum at 70°C, however in the TGA no weight loss is appreciated, that is, the thermal transition indicates that [BTZ amine12] structure experiments a chemical change, which suggests a structural rearrangement indicating that the aminal group is unstable at high temperatures. Aminal bond rupture is favored by heating generating a stable ionized supramolecular structure by the counterion presence as can be seen in (Scheme 4).



**Scheme 4.** Mechanism of ionic species forming reductive elimination.

The DSC shows that an increment in temperature generates the apparition of small peaks associated with endo and exothermic reactions, which is in agreement with TGA weight loss of 33.79% due to the release of H<sub>2</sub>O and CO<sub>2</sub>.

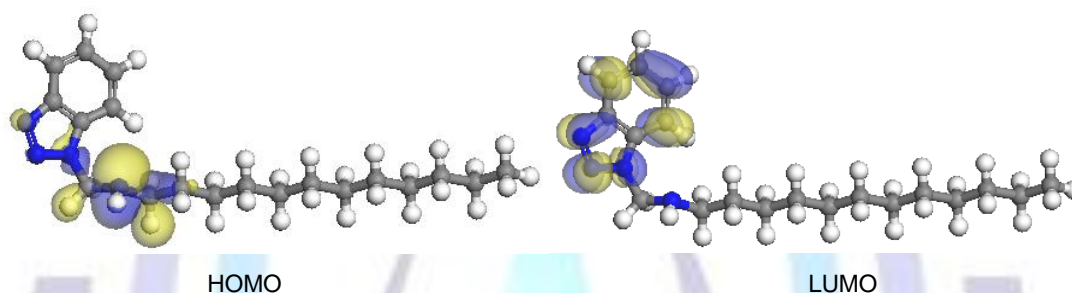
To support the experimental data, a theoretical study was conducted to provide a molecular level understanding of the observed experimental behavior for the N-( $\alpha$ -amino-dodecyl)-benzotriazole structure. The reactive ability of the inhibitor is closely bonded to their frontier molecular orbital, including the highest occupied molecular orbital (HOMO), the lowest unoccupied molecular orbital (LUMO) and the energy band gap  $\Delta E_{\text{gap}} = E_{\text{LUMO}} - E_{\text{HOMO}}$ , where  $E_{\text{LUMO}}$  and  $E_{\text{HOMO}}$ , where LUMO and HOMO are the LUMO and HOMO energies, respectively [25]. The reactivity may be related to stability, because if the molecule is very reactive, it will be less stable. The determined quantum parameters  $E_{\text{LUMO}}$ ,  $E_{\text{HOMO}}$  and  $\Delta E_{\text{gap}}$  (are listed in Table 1). The energy of the HOMO characterizes the susceptibility of the molecule toward attack by

electrophiles.  $E_{HOMO}$  is often associated with the electron donating ability of a molecule, high values of  $E_{HOMO}$  are likely indicate the tendency of the molecule to donate electrons to appropriate acceptor moieties, as hematite surface, with lower energy  $E_{LUMO}$  (Table 1).

**Table 1.** Energy differences in kcal/mol among LUMO and HOMO for the [BTZ amine12] and the hematite surface.

Molecule	Total Energy	$E_{HOMO}$	$E_{LUMO}$	$\Delta E_{gap}$
[BTZ amine12]	-603296.694	-125.863	-49.880	75.984
Hematite	-21316646.930	-131.859	-131.306	0.553

Frontier molecular orbitals (Figure 7) allow to gain a major comprehension about the electron transfer process, the location of the molecule that can give electrons is mainly located over the aminal fragment and neighboring carbon atoms, meanwhile the location of the part that can accept electrons is around the both rings. The N1-C10 bond is considered as antibonding with a node on the bond indicating a weak union.



**Figure 7.** Frontier orbitals of the [BTZ amine12]. Blue and yellow isosurfaces of the HOMO and LUMO denote positive and negative values respectively.

The bond order, frequently used to discuss the stability of molecules, is the distribution of the electron density between a pair of atoms [26]. We have obtained the bond order and the [BTZ amine12] species presents two weak bonds, the first is 0.757 for N1–N2 connection and the second is 0.526 for N1–C10 bond. In accordance with the energy of the frontier molecular orbitals, their location over the molecule, and the bond orders, it indicates that could exist a bond breaking process between N1-C10 atoms.

#### 4. Conclusion

The supramolecular structure of N-( $\alpha$ -amino-dodecyl)-benzotriazole, considered an aminal structure having a stability at room temperature up to 45°C as indicated by the chemical characterization. At 65°C starts a gradual process of structural breaking up through aminal carbon generating a supramolecular ammonium salt, ammonium dodecan-1-benzotriazol-1-ate, [BTZ<sup>+</sup> amine12<sup>+</sup>]. The transformation to the ionized structure was shown by the thermal analysis. Quantum chemical results done using DFT have revealed that the  $E_{HOMO}$  showed in [BZ amine12] has a high tendency to donate electrons, therefore, exists a high probability that the molecule breaks up in the bond between the N1-C10 bond where the HOMO is located.

#### Acknowledgement

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