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# A Computational Study of the Reactivity of 3,5-(Oxo/Thioxo) Derivatives of 2,7-Dimethyl-1,2,4-Triazepines. Keto−Enol Tautomerization and Potential for Hydrogen Storage

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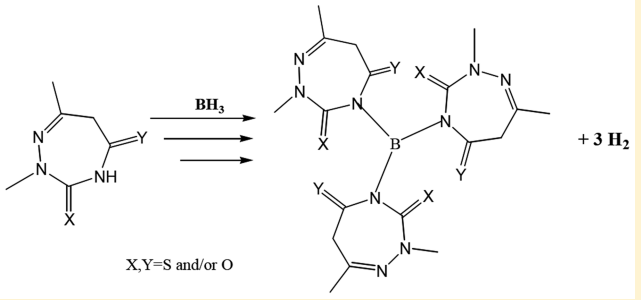
Supporting Information

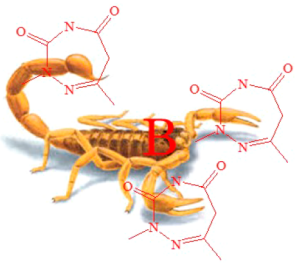
**ABSTRACT:** The G4 level of theory was used to evaluate the acidity of a series of triazepines, that is, 3-thioxo-5-oxo-, 5-thioxo-3-oxo-, 3,5-dioxo-, and 3,5-dithioxo- derivatives of 2,7-dimethyl-[1,2,4]-triazepine. The ability of their available nitrogen lone pair to form a dative bond with $BH_3$ was also studied to highlight the resulting changes in acidity and to understand the behavior of the complexes formed. The effect of the substitution of sulfur by oxygen on the stability of the complex and the activation barrier of dehydrogenation was also evaluated. The formation of these triazepine:$BH_3$ complexes, accompanied by the loss of $H_2$ molecular hydrogen, is a strongly exothermic process. With one triazepine the pathway for $H_2$ elimination from [triazepine]-$BH_3$ is characterized by a small energy barrier ranging from 11 to 23 kJ/mol. The second $H_2$ elimination is relatively more energetic than the first one (~27 kJ/mol). Because of the steric hindrance associated with the addition of two molecules of triazepine $(triazepine)_2$-$BH_2$, the third dehydrogenation step is relatively less favorable than the two preceding steps, particularly in the case of the 3,5-dithio- derivative. The potential energy surface associated with the dehydrogenation reaction of all triazepine derivatives was explored. The thermodynamic favorability reported in this study could allow triazepine-borane to be used as a material for $H_2$ storage applications.




## INTRODUCTION

Almost half a century has elapsed since Trofimenko reported the synthesis of poly(pyrazolyl)borates or Trofimenko ligands.[1] These molecules are represented by the formula $[H_nB(pz)_m]$ ($n$ = 0−3, $m$ = 1−4, pz = pyrazole unit).[2] When a third pyrazole unit is incorporated, the coordination resembles the tail of a scorpion, and these molecules have become known as scorpionate ligands.[3−5] In the early 1970s, Trofimenko introduced other heterocyclic units to replace the pyrazole such as imidazole, triazole, etc. Because of this later work diversifying the structure, these species are now more generally described as boron-centered ligands.[2] Since then, a large number of ligands have been studied, and the central boron atom has been replaced by different atoms.[6−18] In spite of various modifications, the boron-centered tris(pyrazolyl) derivatives remain the most widely used class of these ligands.

To the best of our knowledge, the energetic and conformational behavior of scorpionate ligands such as 1,2,4-triazepines has not been previously studied.



Triazepine derivatives are well-known for their anticonvulsant and antianxiety medicinal properties.[19−24] The oxo and thioxo derivatives have acquired both pharmaceutical and economical relevance.[25] Different triazepine derivatives have exhibited significant biological activities.[19−28] These compounds have been used as drugs to treat various diseases such as cancer,[29] viral

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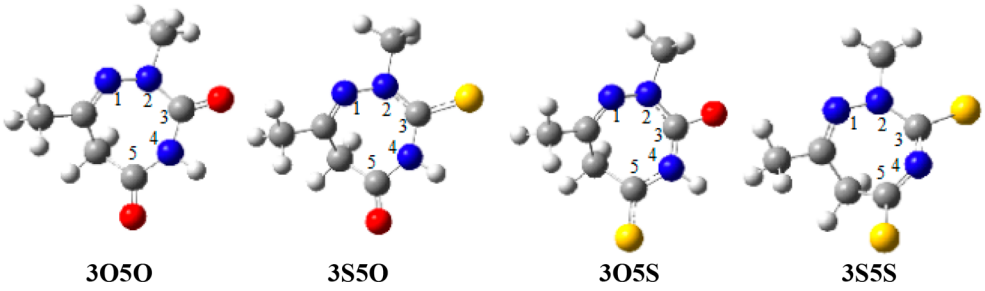
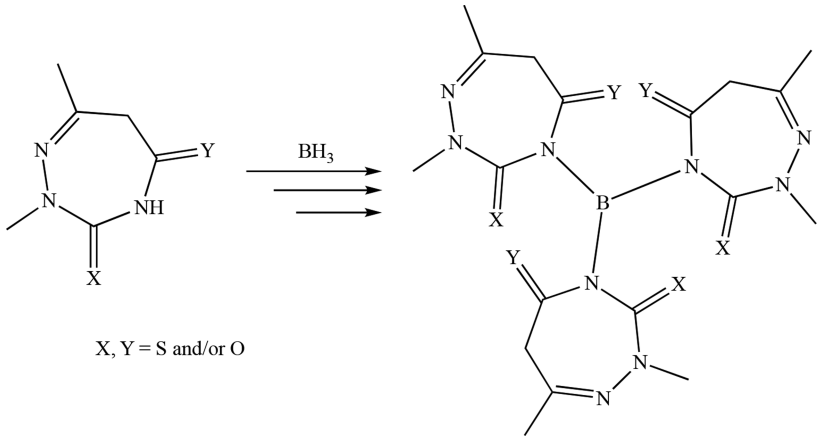
Scheme 1




Scheme 2




infections (HIV),[30] and cardiovascular disorders.[28,31,32] They also associate well with transition metals, which has led to their use in many organometallic chemistry applications.[32−35] Currently there is no evidence of inclusion of these compounds for hydrogen production and storage. Their NH donor groups along with their higher stability could make their behavior similar to hydrazine and ammonia derivatives, which have recently shown their usefulness in the production of $H_2$ fuel.[36−39] Also associated with boron hydride many studies have proposed the feasibility of these latter species in the energetic industry as a good alternative. In this sense we believe that the complex between triazepine derivatives and $BH_3$ could play the same role.

The presence of three nitrogen atoms within the seven-membered ring makes these species attractive as Lewis donors, and their basicity has been well-described in the literature.[40] However, an enol-to-keto tautomerization produces a relatively acidic NH moiety. This acidity diminishes upon keto-to-enol tautomerization as the proton migrates from the nitrogen to a nearby carbonyl or thiocarbonyl group. Currently, studies of the keto−enol tautomerization and corresponding acidity of these ligands are scarce. We are interested in the energetic and acidity changes associated with the tautomerization of the oxo and thioxo triazepine derivatives 3,5-dioxo (**3O5O**), 3-thioxo-5-oxo (**3S5O**), 5-thioxo-3-oxo(**3O5S**), and 3,5-dithioxo (**3S5S**) 2,7-dimethyl-[1,2,4]-triazepine (Scheme 1).

Our second goal will be the exploration of triazepine coordinate covalent bond formation with a Lewis base such as $BH_3$. We seek to understand the mechanism whereby the ligands interact with $BH_3$, leading to the formation of a B−N bond and the eventual loss of a $H_2$ molecule. This $BH_3$ complexation can occur with up to three triazepine ligands, and we are interested in the energetics of stepwise addition and the formation of products B-$(Triaz)_{1-3}$ (Scheme 2). To this end, we performed a systematic exploration of the potential energy surfaces associated with successive additions and hydrogen release associated with the reaction of triazepine derivatives with borane.

## COMPUTATIONAL DETAILS

We are interested in determining intrinsic acidity with reliable accuracy. Therefore, we used the G4 composite ab initio theory, which provides accurate estimates of reaction enthalpies.[41] Simultaneously, we also utilized the more computationally efficient B3LYP density functional with the 6-311G(d,p) basis set. The G4 composite approach may not be tractable for larger systems, and our systematic comparison between the G4 and B3LYP methods showed very good agreement (Tables S1−S3). Geometry optimization was performed at the B3LYP/6-311G(d,p) level of theory.[42,43] Stationary points were characterized by frequency calculations to verify that transition states have only one imaginary frequency and the minima have real frequencies. The intrinsic reaction coordinate (IRC) path was explored to check the energy profiles connecting each transition state (TS) to the two associated minima of the proposed mechanism.[44] It is to mention that for the acidity calculation the free energy of proton was taken as −6.287 kcal/mol at 298 K.[45] All calculations were performed using the Gaussian 09 suite of programs.[46]

We expect that charge transfer from the triazepine lone pairs into the $BH_3$ orbitals constitutes the main ingredient in the formation of a B−N bond. We analyzed this interaction by examining the orbital interaction energies obtained through a second-order perturbation approach in the framework of the natural bond orbital (NBO) method.[47] We compliment this analysis using the alternative partitioning technique available in the quantum theory of atoms in molecules (QTAIM).[48,49] For each complex formed we constructed the molecular graph as the ensemble of bond critical points (BCPs) and bond paths. The electron



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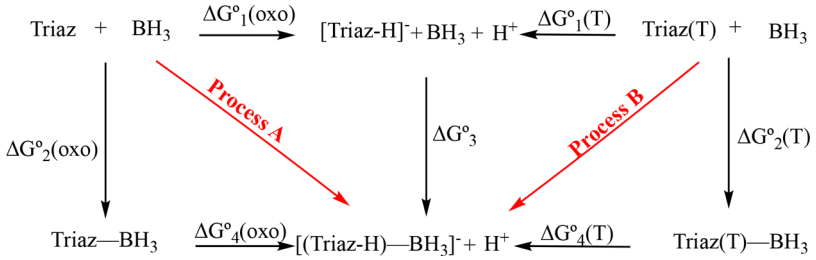
**Scheme 3. Thermodynamic Cycle of the Interaction between Triazepine Keto Oxo/Thioxo Keto Tautomer (Process A) and the Enol Tautomer (Process B), with $BH_3$**[a]




[a]The (oxo) refers to the dioxo/thioxo keto tautomer, while (T) refers to the enol tautomer. $[Triaz\text{-}H]^-$ refers to the deprotonated triazepine.

**Table 1. Free Energies[a] of Processes A and B Calculated at the G4 Level of Theory**

| | $\Delta G^0_1$(oxo) | $\Delta G^0_2$(oxo) | $\Delta G^0_4$(oxo) | $\Delta G^0_1$(T) | $\Delta G^0_2$(T) | $\Delta G^0_4$(T) | $\Delta G^0_3$ |
|---|---|---|---|---|---|---|---|
| **3O5O** | 1410 | 24 | 1261 | 1344 | −84 | 1303 | −125 |
| **3S5O** | 1388 | 62 | 1203 | 1331 | −60 | 1267 | −124 |
| **3O5S** | 1376 | 64 | 1222 | 1311 | −72 | 1294 | −89 |
| **3S5S** | 1359 | 65 | 1200 | 1304 | −73 | 1283 | −94 |

[a]In kilojoules per mole.

density associated with a bond critical point should be a good quantitative measurement of the strength of the linkage, but at the same time, the densities associated with the remainder of the system will provide useful information on the electron density redistribution upon complexation. All the NBO calculations were performed with the NBO6 package,[50] whereas the QTAIM analysis was performed with the AIMALL series of programs.[51]

## RESULTS AND DISCUSSION

**In What Form Does Triazepine React with $BH_3$?** We performed G4 theory and B3LYP/6-311G(d,p) calculations on the oxo and thioxo derivatives of the compounds under study (Tables S1 and S2). In this part of study, our objectives were threefold: (1) estimate triazepine acidity of the keto and enol tautomers, (2) study the effect of triazepine carbonyl and thiocarbonyl substitution, and (3) compare proton donating abilities of triazepine with compounds known to be strongly acidic. Toward this end, we computed the free energy of deprotonation of the oxo and thioxo keto tautomer derivatives $\Delta G^0_1$(oxo) and compared them to the free energies of deprotonation of the enol tautomers $\Delta G^0_1$(T) (Scheme 3 and Table 1).

The values of the acidity ($\Delta G^\circ_1$(oxo)) of the keto tautomer at the G4 level of theory range from 1359 to 1410 kJ/mol. The most acidic compound is **3S5S**, with a $\Delta G^\circ_1$(oxo) that is 51 kJ/mol smaller than **3O5O**, suggesting that when the thiocarbonyl group is present at positions **3** and **5** the departure of the proton becomes easier from the nitrogen at position **4**. The polarizability of the sulfur atom likely encourages resonance between the thiocarbonyl double bond and the nearby C−N bond, which in turn weakens the NH bond. Nevertheless, even with these effects the acidity is small compared to known acids such as $H_2SO_4$, $HNO_3$, or $HBF_4$. For instance, the acidity of these compounds was estimated to be 1269, 1329, and 1207 kJ/mol, respectively, by Koppel et al.[52] using a similar approach to the one taken here and evaluated at the G2 level of theory.

We also estimated the acidity of the enol tautomer ($\Delta G^\circ_1$(T)). This tautomer can be obtained by a hydrogen transfer from the NH group to the carbonyl or to the thiocarbonyl at position **3**.[53] The hydroxyl proton in the **3O5O** and **3O5S** enol compounds is found to be less acidic than the sulfhydryl proton in **3S5O** and **3S5S** enols. For instance, the $\Delta G^\circ_1$(T) values for **3O5O** and **3S5S** are 1344 and 1304 kJ/mol, respectively. For all of the enols under study, the free energy associated with the loss of the proton becomes closer to the aforementioned acids. In fact, the 3,5-dithioxo 2,7-dimethyl-1,2,4-triazepine (**3S5S**: 1304 kJ/mol) is more acidic than nitric acid (1329 kJ/mol at the G2 level of theory).

How does this acidity change when the triazepine compounds act as Lewis bases? In other words, what is the acidity of the NH group when the nitrogen lone pair is engaged in a dative bond with $BH_3$? Answers to these questions are fundamental to our study, since it is necessary to know whether the triazepine keto or enol tautomer is the precursor to the loss of molecular hydrogen. After many triazepine ring positions were examined, it was determined that the best site for $BH_3$ interaction is with the nitrogen at position **4**. However, direct complexation between the keto triazepine tautomers and $BH_3$ required an activation barrier (see $\Delta G^0_2$(oxo) of Table 1), whereas the same interaction is favorable when the enol tautomers are involved leading to a reactive complex (Rc) (see $\Delta G^0_2$(T) of Table 1). Regardless of the favorability of reaction, we explored $BH_3$ interaction with both the keto and enol forms of the triazepine derivatives (Scheme 3). This task was achieved considering these interactions as two processes: **Process A** describes the interaction of the keto tautomer with $BH_3$ to produce a deprotonated complex. **Process B** focused on the interaction of $BH_3$ with the enol tautomer. Each process contains multiple thermodynamic steps: $\Delta G^\circ_2$ corresponds to $BH_3$ forming a coordinate covalent bond with NH at position **4**; $\Delta G^\circ_3$ corresponds to dative bonding between $BH_3$ and the deprotonated $\mathbf{N_4}$; and $\Delta G^\circ_4$ corresponds to deprotonation of the triazepine:$BH_3$ complex. The values of the free energy involved in each step were evaluated at the G4 level of theory and are listed in Table 1.

Triazepine acidity increases greatly when it is associated with $BH_3$, particularly for the keto tautomers. For instance, for **3O5O**, $\Delta G^\circ_4$(oxo) = 1261 kJ/mol, whereas $\Delta G^\circ_1$(oxo) = 1410 kJ/mol. The increased acidity in the $BH_3$-complexed keto tautomer can be understood by the nature of the interaction taking place. The change of the deprotonation free energy upon complexation ($\Delta G^0_1$(oxo) − $\Delta G^0_4$(oxo)) ranges from 185 (**3S5O**) to 149 (**3O5O**) kJ/mol for the keto tautomer. The acidity increment is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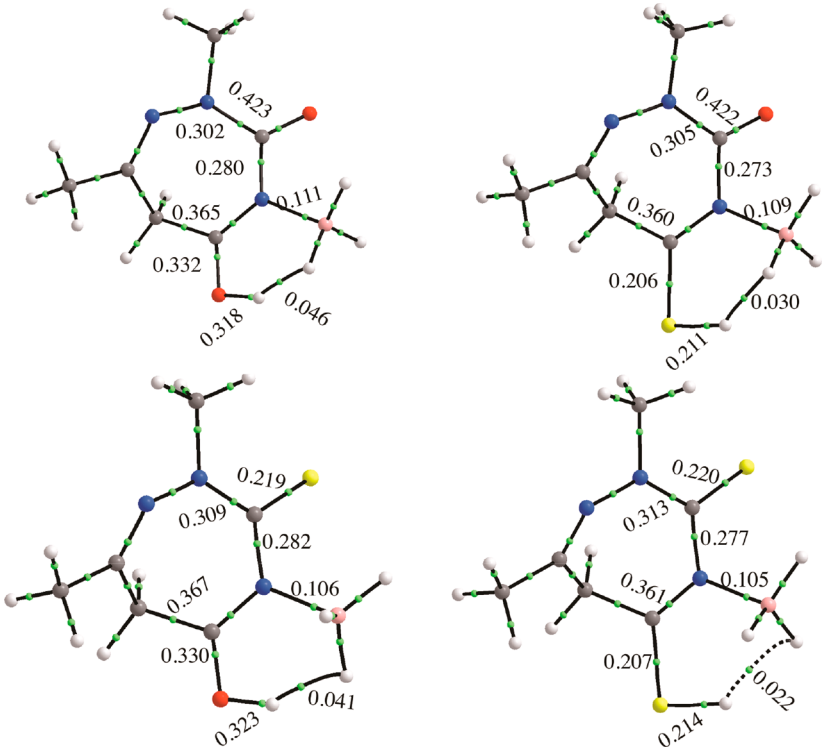


**Figure 1.** Molecular graph for the interaction between triazepine and $BH_3$. Green dots are BCPs.

smaller yet still significant in the enol tautomer, ranging from 17 (**3O5S**) to 64 (**3S5O**) kJ/mol. It is noteworthy that the enol triazepine-$BH_3$ complex contains an H−H bond (Figure 1), which not only contributes to its stability but likely also affects its intrinsic reactivity. All of the enol triazepine-$BH_3$ complexes contain an H−H bond as shown in the AIM analysis (Figure 1). The strength of these bonds can be quantified by the value of the electron density on the corresponding BCP. The interaction between the H atoms was further demonstrated by an NBO analysis showing an attractive interaction between the two oppositely charged hydrogen atoms, that is, the net natural charge on the enol hydrogen is 0.5e, while the hydrogen attached to $BH_3$ carries a −0.08e charge. In the thiol (**3O5S**) the net charge observed is ∼0.22e, while the hydrogen of the Lewis acid is ca. −0.04e. These findings suggest the possibility of an easier departure of $H_2$ when $BH_3$ is associated. Before discussing this possibility let us first mention some characteristics highlighted in the interaction between $BH_3$ and the triazepine to take more insight on their acidities.

Inspection of the thermodynamic cycle for the keto tautomer in **process A** shows that, except for **3O5O**, $BH_3$ complexation is favored only if deprotonation occurs before the attachment of $BH_3$. For **3O5O**, the enthalpy of the interaction with $BH_3$ is favorable (−20 kJ/mol); for all other keto triazepine derivatives this enthalpy is positive (Table S3). However, for the enol tautomer (**process B**) the enthalpy of interaction with $BH_3$ is favored for all compounds under study, as can be deduced from Table 1. In the case of the enol tautomer, complexation can be compared to the interaction of $BH_3$ with $NH_3$, which has a free energy cost of ∼118 kJ/mol.[54] For comparison, in the enol triazepine derivatives this interaction is −84 kJ/mol in **3O5O** and −60 kJ/mol in **3S5O**. Evidently, the value of the free energy of $BH_3$ complexation, for both keto and enol tautomers, depends on the carbonyl and the thiocarbonyl groups at the **3** and **5** positions of triazepine. Even with the crowded molecular environment as is present in triazepine derivatives, the approach of the boron to the nitrogen atom is sufficiently favorable to give a strong B···N bond, similar in strength to the $BH_3NH_3$ bonding interaction. According to this analysis, all triazepine derivatives react with $BH_3$ in their tautomeric forms.

**(Triazepines)$_n$-BH$_{3-n}$ Complex Structures.** The formation of the $BH_3NH_3$ complex has been shown to be efficient for the generation of $H_2$ and its storage.[55−59] We were interested in exploring pathways for the generation of molecular hydrogen following the interaction of triazepine with $BH_3$. Our objective is not only to explore the 1:1 stoichiometric complex but also to go further by studying the interaction of three triazepines with $BH_3$ and the successive dehydrogenation that could occur. The analysis of triazepine and triazepine-$BH_3$ complex acidity at the G4 and B3LYP/6-311G(d,p) levels of theory showed similar trends (see Table S3 of Supporting Information). Therefore, for computational tractability, we will use density functional theory (DFT) to study 1:1, 1:2, and 1:3 $BH_3$:triazepene complexation.

The optimized structures of the TSs as well as of the products (Ps) are depicted in Figure 2 and Figure 3. The analysis of these TSs shows that we have two types of forming B···N bonds. At **TS1**, corresponding to 1:1 complexation, the B···N bond is ∼1.56 Å for all molecules. In the case of 1:2 (**TS2**) and 1:3 (**TS3**) complexation, this bond reduces to 1.54 and 1.53 Å, respectively, reflecting that the forming bond strengthens with the substitution of a $BH_3$ hydrogen atom by triazepine. The newly forming H−H bond is, in all cases, ∼0.9 Å, indicating that at the reaction barrier $H_2$ is already formed and substantially detached from the rest of the complex. This is confirmed by the breaking bonds B−H, O−H, or S−H, which are ∼1.34, 1.40, or 1.72 Å, respectively, in the case of **TS1**. These breaking bonds increase in **TS3** particularly in the case of **3S5S**. For **3O5O**, these breaking bonds remain approximately with the same length in all TSs (see Figure 2).

Triazepine derivatives react with borane to form stable compounds having a strong B−N dative bond (Figure 3). Up to three molecules of triazapine can coordinate their N lone-pair electrons



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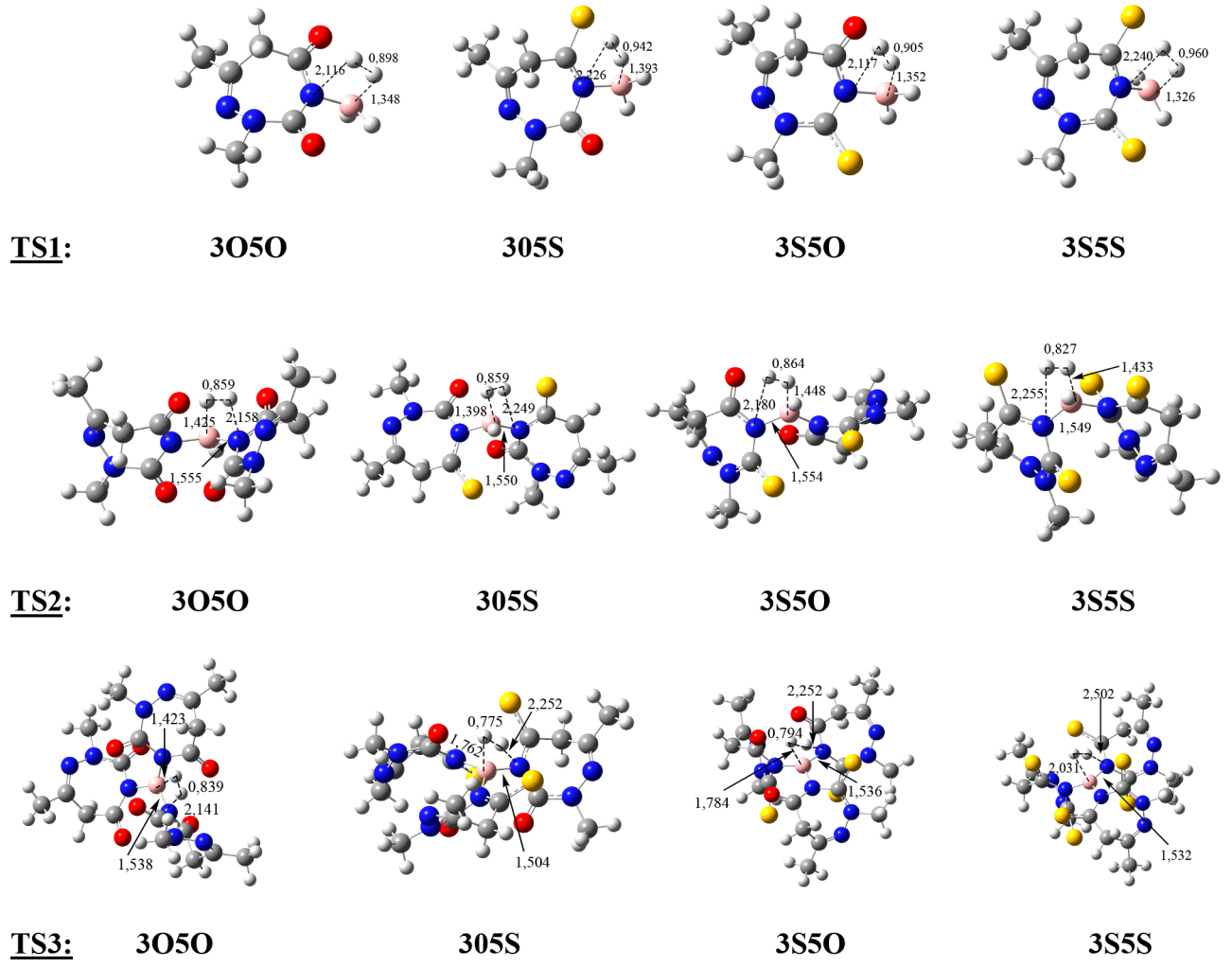


**Figure 2.** Geometries optimized at B3LYP/6-311G(d,p) level of the TSs involved in the dehydrogenation reaction between triazepine derivatives and $BH_3$. Lengths are given in angstroms.

to B, and it is this electron-donor ability of triazepine that contributes to complex stabilization. The strength of the triazepene:$BH_3$ dative bond is reflected in the B−N bond length of 1.55 Å, which is shorter than the bond length in the classic dative complex $H_3B{:}NH_3$ (1.664 Å). The B−N is the shortest for 1:1 complexation (**P1**), and it increases slightly in **P2** and **P3**, except in the case of **3S5S**, where there is a small decrease (See Figure 3).

For all TSs, the NBO perturbation analysis shows that there is clearly an electrostatic interaction between the boron atom (positive center) and the $sp^3$ nitrogen atom (negative center) of the incoming triazepine ($B^{\delta+}\cdots N^{\delta-}$). Furthermore, the approach of the second and the third triazepine to the 1:1 complex increases notably the zwitterionic character of the corresponding TS structure. There is especially an accumulation of positive charges at the boron atom (0.05e at **TS1**, 0.55e at **TS2**, and 1.19e at **TS3**), while the negative charges at the nitrogen ($sp^3$) atoms are −0.63e in the case of **TS1**, −0.70e at **TS2**, and −0.80e at **TS3**.

A closer look at the topological analysis of the charge density of the TSs involved in the reaction pathways by means of the QTAIM theory may offer some clues to understand this type of interaction between triazepine and $BH_3$. The BCPs of the different transition states of **3O5O** and **3O5S** derivatives are depicted in Figure 4.

The values of the charge density ($\rho$) at the BCPs correlate well with the bond distances: the shorter the bond, the larger the $\rho$ value. In addition, three important points must be emphasized. (i) The $\rho$ values at the B···N forming bond are 0.14 a.u. at **TS1** and range from 0.15 to 0.16 a.u. at **TS2** and **TS3**. (ii) The $\rho$ values at the forming (H−H) and breaking (B−H) bonds are ∼0.2 and 0.1 a.u., indicating some synchronicity between these two contrasting processes. (iii) The existence of several BCPs involving the hydrogen atom of the forming $H_2$ molecule and a sulfur or oxygen atom reflects a stabilization of the TS structure (Tables S4−S7).

**Dehydrogenation Reaction Energies.** The total energies as well as the scaled zero-point energy (ZPE), thermal correction of enthalpy (TCE), and entropy values for all minima and transition states of the investigated structures are reported in Table S1 of the Supporting Information. The thermodynamic state functions pertaining to the formation of various complexes and the release of $H_2$ as computed in this work are given in Table 2. The values of this Table correspond to processes of complexation between the enol tautomer of enol/thiol triazepine and $BH_3$ leading to the loss of molecular hydrogen $H_2$, which can also be called dehydrogenation reactions. The reaction involves the initial formation of a 1:1 reactive complex (Rc) more stable than the separated reactants. This complex then overcomes the TS leading to the 1:1 product complex (**P**) and the evolution of molecular hydrogen. This $(\text{triazepine})_n\cdots BH_{3-n}$ interaction can generate up to three $H_2$ molecules via several direct pathways with energy barriers ranging from 11 to 23 kJ/mol in terms of enthalpy ($\Delta H_m$) and from 14 to 26 kJ/mol in terms of Gibbs



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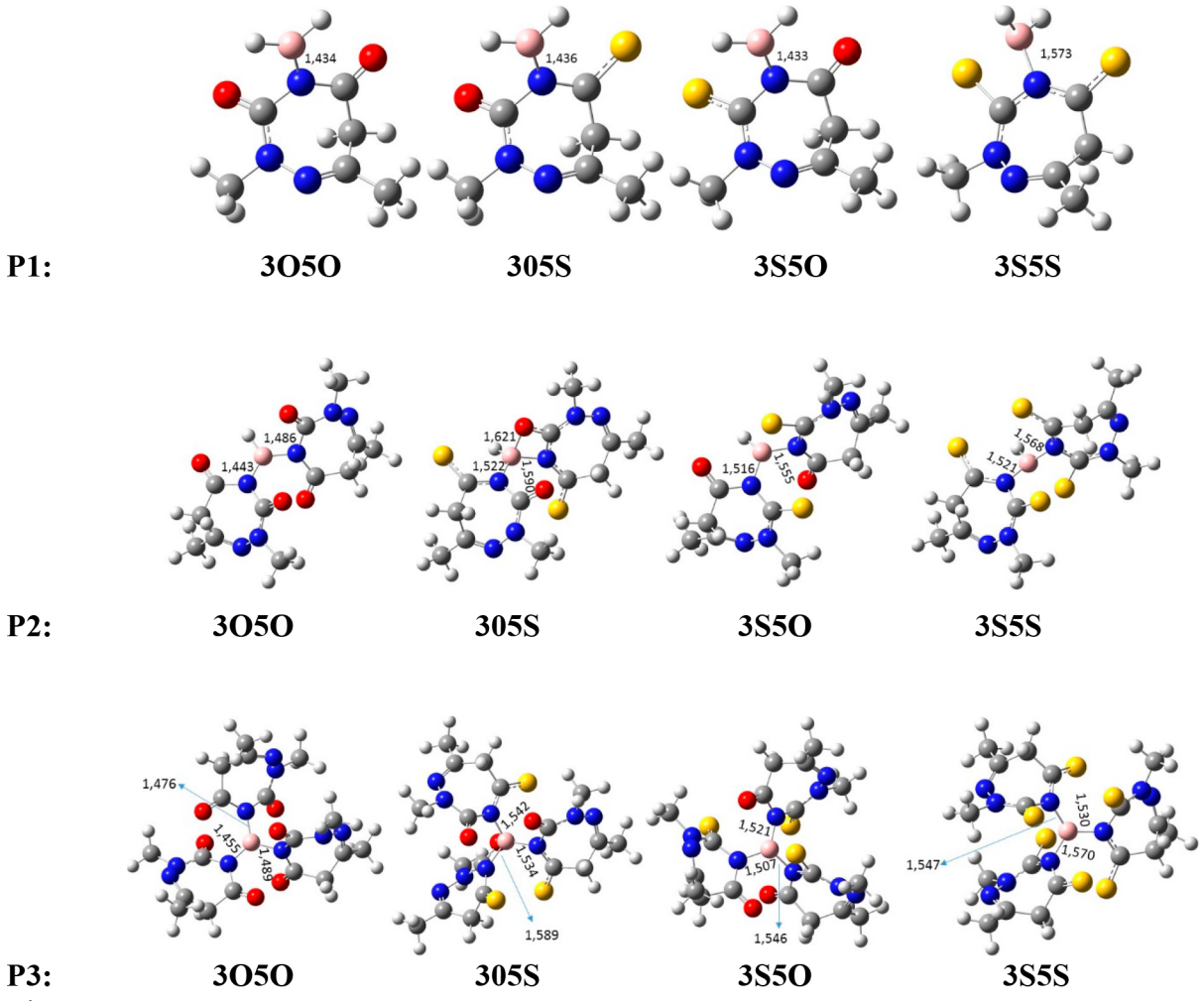


**Figure 3.** Structures optimized at B3LYP/6-311G(d,p) level for all products involved in the dehydrogenation reaction between triazepine derivatives and $BH_3$. Lengths are given in angstroms.

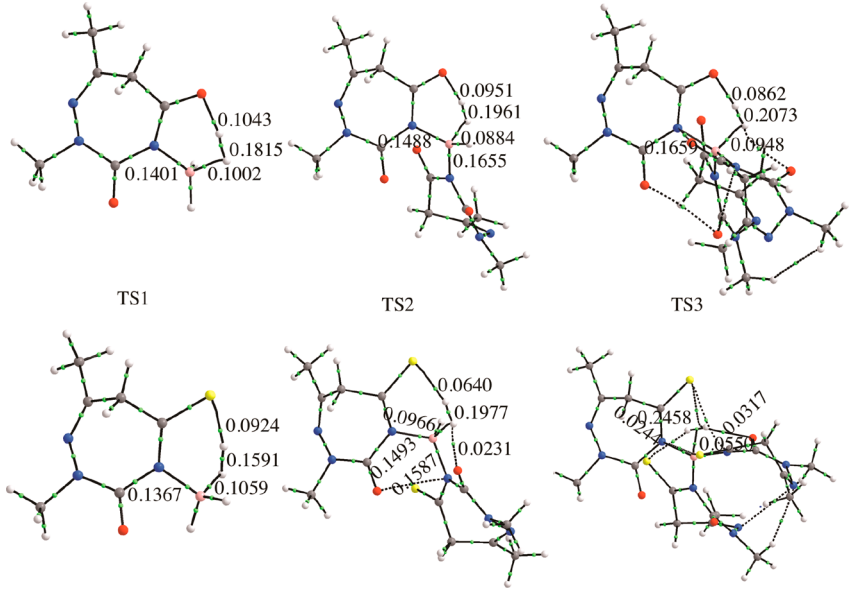


**Figure 4.** Molecular graph for TSs of **3O5O** and **3O5S**. Green dots are BCPs.

energy ($\Delta G_m$) at the first dehydrogenation. The dehydrogenation enthalpy changes ($\Delta H_m$) are strongly exothermic relatively to those found by Das et al.[60] in the case of the dehydrogenation reactions of the borane adducts of azeridine (−6 kJ/mol), pyrrolidine (−13 kJ/mol), piperidine (−13.0 kJ/mol), and azepane (−15 kJ/mol). These values are significantly less exothermic than



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Table 2. B3LYP/6-311G(d,p) Energies ($\Delta E_m$), Enthalpies ($\Delta H_m$), Entropies ($\Delta S_m$), and Gibbs Energies ($\Delta G_m$)[a] for All the Stationary Points Relative to the Separated Reactants

| 3S5S | (A.C)1 | TS1 | P1 | (A.C)2 | TS2 | P2 | (A.C)3 | TS3 | P3 |
|---|---|---|---|---|---|---|---|---|---|
| $\Delta E$ | −75.65 | −59.80 | −153.55 | 14.64 | 40.58 | −56.90 | 69.87 | 143.26 | 16.32 |
| $\Delta H$ | −80.71 | −67.36 | −152.72 | 13.72 | 36.62 | −50.79 | 67.61 | 142.67 | 22.47 |
| $T\Delta S$ | −50.71 | −55.73 | −17.49 | −59.54 | −60.96 | −22.17 | −59.04 | −65.61 | −30.96 |
| $\Delta G$ | −30.00 | −11.63 | −153.27 | 73.30 | 99.58 | −28.66 | 136.98 | 208.32 | 53.43 |
| **3S5O** | | | | | | | | | |
| $\Delta E$ | −92.05 | −76.57 | −135.98 | −92.88 | −2.09 | −125.10 | 20.08 | 67.36 | −42.13 |
| $\Delta H$ | −97.36 | −83.09 | −133.93 | −95.14 | −3.72 | −118.28 | 18.91 | 66.53 | −34.56 |
| $T\Delta S$ | −50.71 | −53.55 | −14.22 | −60.16 | −56.82 | −21.59 | −63.55 | −62.70 | −22.51 |
| $\Delta G$ | −46.69 | −29.54 | −119.75 | −34.98 | 53.05 | −96.69 | 82.47 | 129.29 | −12.01 |
| **3O5S** | | | | | | | | | |
| $\Delta E$ | −51.46 | −76.15 | −115.06 | −53.55 | −18.83 | −110.88 | −2.09 | 56.48 | −26.48 |
| $\Delta H$ | −94.68 | −83.34 | −113.80 | −56.90 | −21.76 | −106.15 | −3.05 | 55.90 | −19.92 |
| $T\Delta S$ | −51.67 | −54.64 | −15.19 | −64.77 | −61.67 | −25.90 | −64.73 | −64.22 | −25.40 |
| $\Delta G$ | −43.01 | −28.66 | −98.62 | 7.86 | 37.91 | −80.25 | 61.67 | 120.12 | 5.48 |
| **3O5O** | | | | | | | | | |
| $\Delta E$ | −107.95 | −83.68 | −143.09 | −59.41 | −31.80 | −109.20 | −72.80 | −1.26 | −90.83 |
| $\Delta H$ | −113.55 | −90.16 | −140.92 | −60.88 | −33.85 | −102.42 | −76.06 | −3.51 | −84.06 |
| $T\Delta S$ | −51.34 | −53.97 | −13.93 | −58.37 | −60.42 | −18.91 | −72.34 | −65.14 | −26.15 |
| $\Delta G$ | −62.22 | −36.23 | −126.98 | −2.51 | 26.61 | −83.51 | −3.72 | 61.63 | −57.90 |

[a]In kilojoules per mole, at 25°C.

our results, which are −153, −136, −114, and −141 kJ/mol in the case of the first dehydrogenation of **3S5S**-, **3S5O**-, **3O5S**-, and **3O5O**-borane, respectively. The second dehydrogenation reaction is relatively less exothermic than the first one, but it is still more exothermic than that found by Das et al. It is −51 (**3S5S**), −118 (**3S5O**), −106 (**3O5S**), and −102 kJ/mol (**3O5O**). It is remarkable that even the third step of dehydrogenation is exothermic, in spite of the steric effects present, which may disadvantage the release of $H_2$, (−35 kJ/mol for **3S5O**, −20 kJ/mol for **3O5S**, −84 kJ/mol for **3O5O**). The **3S5S** compound is the only exception to the favorability of the third step.

Our values in Table 2 are calculated with respect to the first entrance channel, also referred to above as the Rc. Dixon et al. have found that in the case of $NH_3$:$BH_3$ and $CH_3NH_2$:$BH_3$ the reaction enthalpies are −21 and −15 kJ/mol, respectively.[61] Another study performed by Németh et al.[62] found that the molecular hydrogen elimination reaction for cyclopropylamine- and cyclopropylmethylamine-borane is −31 and −25 kJ/mol, respectively. These values are consistent with our results suggesting that the triazepines may hold promise as chemical hydrogen storage materials. The free energy values of the dehydrogenation reaction of all triazepine-borane derivatives are negative (except **3S5S**). This indicates that all dehydrogenation reactions are spontaneous with the exception of the **3S5S** derivative, where $\Delta G_m$ for the third dehydrogenation is 54 kJ/mol. The Gibbs activation energies for these dehydrogenations are much higher than those of the enthalpy reactions. The standard entropies are strongly negative (in range from −11.2 to −58 $J \cdot mol^{-1} \cdot K^{-1}$) with respect to the separate reactants, and they are responsible for the increase in the Gibbs energy of all the stationary points.

Special attention must be paid to the intermediates and the transitions states of these processes to predict the reliability of $H_2$ lost during reaction with the different triazepine derivatives. While the reaction of **3O5O** is kinetically and thermodynamically feasible in all process steps, the **3S5S** compound presents some peculiarities that must be mentioned.

In Figures 5−7, we present the different steps of the four triazepines interacting with $BH_3$. Figure 5 shows the first interaction between triazepine and $BH_3$ leading to the first dissociation of $H_2$ and the formation of the first product. Figure 6 shows the reaction of the first dehydrogenation product interacting with a second triazepine molecule. This produces a second elimination of $H_2$ and a product compound, where the boron atom is bonded to two triazepine molecules. Figure 7 represents the final step, where a third triazepine molecule enters into interaction to lead to the final product by eliminating a third molecule of hydrogen.

In the first dehydrogenation reaction (Figure 5), all the triazepine derivatives lead to a stable complex with respect to the entrance channel. The activation energies to release $H_2$ are favorable in all cases. However, in the second dehydrogenation step (Figure 6), note that, for the **3S5S** reaction channel, the formation of the complex and the activation barrier of the dehydrogenation process are higher in energy than the entrance channel. Hence, one can assume that the dehydrogenation process for this compound cannot take place. However, the overall process for **3S5S** is exothermic relative to the initial complex. The same reasoning can be proposed for the third dehydrogenation step (Figure 7). In this case, we see that **3S5S** and **3O5S** lead to initial complexes and barriers that are higher in energy than their corresponding entrance channel energies. Two factors could explain these findings. First, even while the formation of the new H−H bond stabilizes the complex, the incoming third triazepine molecule creates a destabilizing, sterically hindered interaction. (Note that the activation barrier to release $H_2$ depends on the triazepine derivative under study and differs slightly from the one obtained in the first step.) The second factor might be that the increased resonance in the complex alters the basicity of the B atom and reduces its ability to coordinate with a third triazepine. This suggests that the third hydrogen molecule could be chemisorbed into the system, and its departure may become more difficult.

## CONCLUSION

The capability of triazepines to donate a proton, under oxo/thioxo or enol/thiol forms, has been highlighted in the present study.



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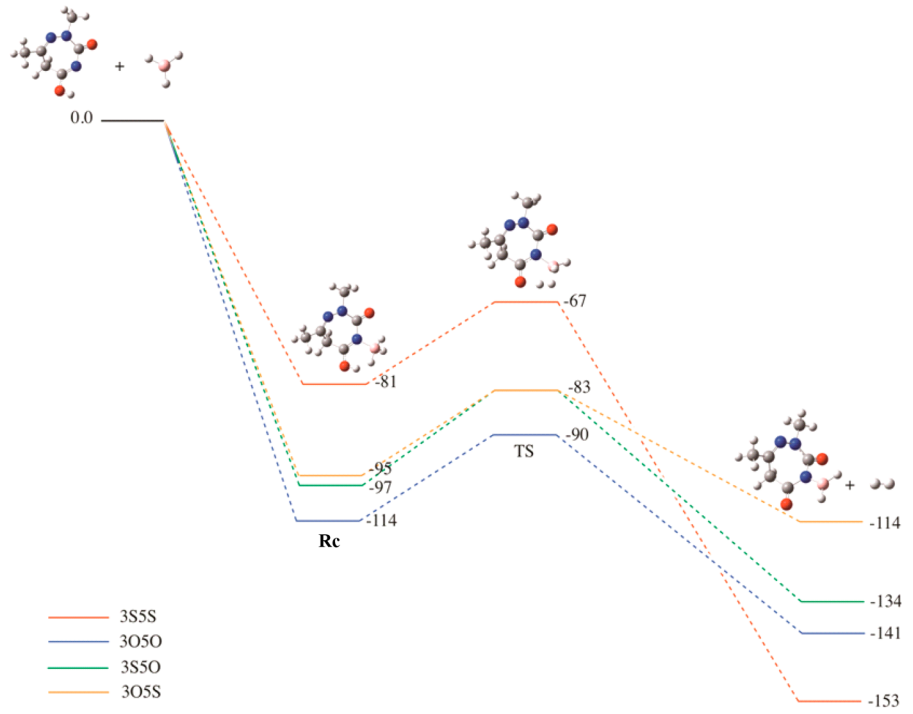


**Figure 5.** Enthalpy (kJ/mol) profiles for the reaction of $BH_3$ and triazepines as computed at the B3LYP/6-311G(d,p) level corresponding to the first dehydrogenation reaction.

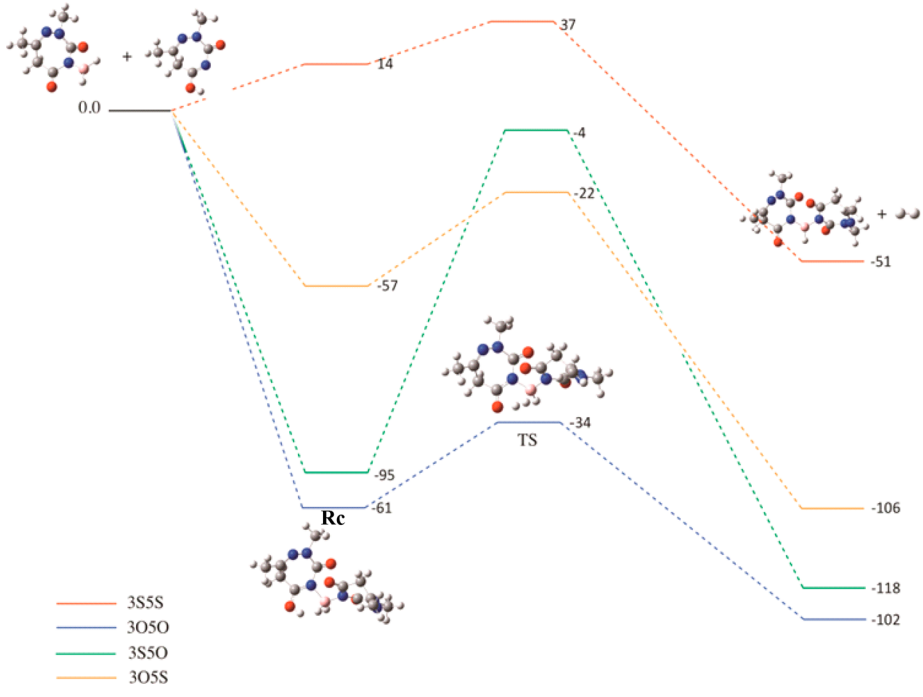


**Figure 6.** Enthalpy (kJ/mol) profiles for the reaction of $BH_3$ and triazepines as computed at the B3LYP/6-311G(d,p) level corresponding to the second dehydrogenation reaction.

The enol tautomer has been shown, by high-level calculations, to be more acidic than the keto tautomer. In this context, the **3S5S** triazepine derivative was found to be as acidic as nitric acid. Dative bonding between triazepine and $BH_3$ increases the acidity of these compounds. Moreover, the interaction of $BH_3$ with triazepines facilitated the release of molecular hydrogen. For this reason, we have investigated the reaction pathways and the molecular mechanisms for $H_2$ release from 1,2,4-triazepine and their thioxo and oxo derivatives. A computational mechanism based on the energetic profile of the considered reaction, supported by NBO and Bader's analysis of the transition states, fully rationalizes the nature of the donor−acceptor interaction between triazepines and $BH_3$. Successive additions of triazepine molecules to $BH_3$ led to B-(triazepine)$_3$ complex with a loss of three $H_2$ molecules via 3TSs and three intermediate products. A smaller energy barrier characterizes the first dehydrogenation, which is substantially lower than the barrier for the second and third dehydrogenation. The thermodynamic stabilities, as well as



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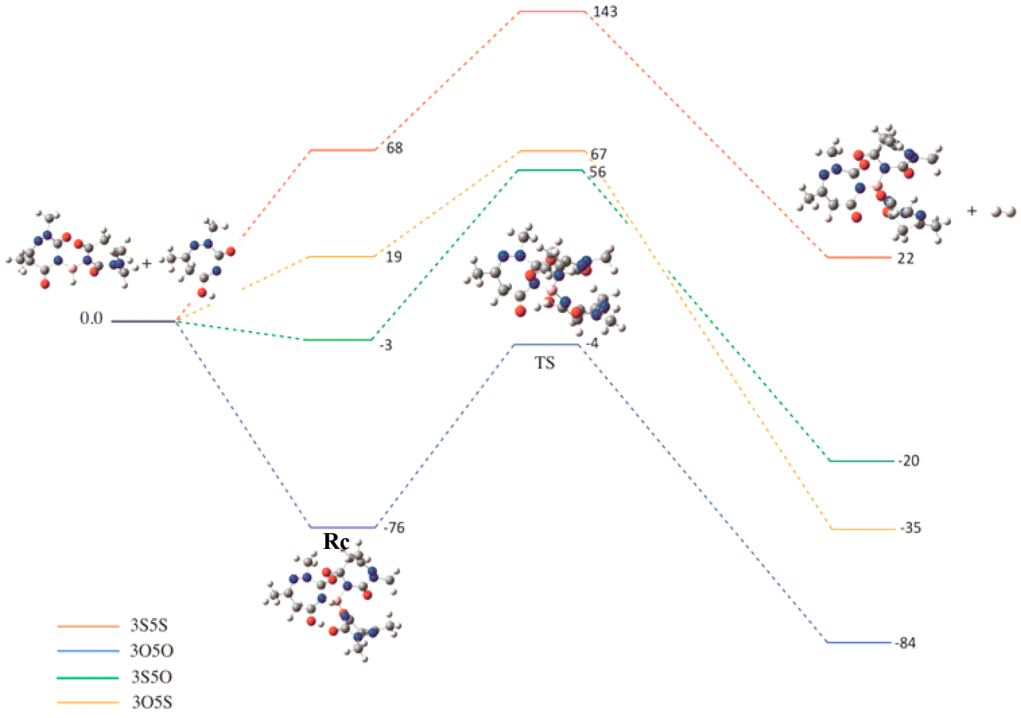


**Figure 7.** Enthalpy (kJ/mol) profiles for the reaction of $BH_3$ and triazepines as computed at the B3LYP/6-311G(d,p) level corresponding to the third dehydrogenation reaction.

exothermic and exergonic character of the dehydrogenation reactions of the compounds considered in this study, indicate their potential as hydrogen storage material. The dioxo-derivative may prove to be a good material for chemical $H_2$ storage. Because of the satisfactory results of this study, our compounds are expected to trigger new experimental investigations as potential candidates for hydrogen storage.

## ■ ASSOCIATED CONTENT

### Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.jpca.8b00251.

Total energy (in a.u.) achieved at B3LYP/6-311G(d,p) and G4 levels of theory of the structures involved in Scheme 3. Enthalpies and free energies (kJ/mol) of keto and enol forms of the studied compounds calculated at B3LYP/6-311G(d,p) level of theory. Electron density (e/bohr3), Laplacian of the electron density, and total energy density (hartree/bohr3) of **TSs** of **3O5O**, **3O5S**, **3S5O**, and **3S5S** derivatives (PDF)

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### Notes

The authors declare no competing financial interest.

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