

Theoretical Investigations on the Reactions of C_6H_5^+ and $\text{C}_{10}\text{H}_7^+$ with D_2

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Abstract. The recent discovery of benzene and polycyclic aromatic hydrocarbons (PAHs) in the interstellar clouds has increased the interest in this entire class of molecules, which result to be the object of several theoretical and experimental investigations. In this work, we have studied the reactions of the phenylium, C_6H_5^+ , and the naphthylum cation, $\text{C}_{10}\text{H}_7^+$, with D_2 . All calculations have been carried out at B3LYP/6-31G* level of theory and they suggest that the addition products, $\text{C}_6\text{H}_5\text{D}_2^+$ and $\text{C}_{10}\text{H}_7\text{D}_2^+$, once formed, can be stabilized by unreactive collisions or lose a neutral molecule (H_2 or HD) or an atom (H or D), respectively.

1 Introduction

Polycyclic aromatic hydrocarbons (PAHs) have been postulated to be an important, ubiquitous component of the interstellar medium based on their high stability against UV radiation. Many members of this class have been already studied [2] [3] [4], even though most of the available information principally concerns the smallest terms of this class, like benzene [5] and naphthalene [6]. By experimental investigations, it has been demonstrated that PAHs are expected to be present as a mixture of free, neutral and ionized gas phase molecules [7] following a large size distribution from small systems (less than 25 carbon atoms) to large graphitic platelets. They can be present both in their neutral and/or ionized forms and are thought to be the origin of a variety of interstellar infrared emission features observed in the 700 to 3100 cm^{-1} range. Recent experimental studies of reactions of the PAHs cations C_6H_6^+ and $\text{C}_{10}\text{H}_8^+$ with H atoms [1] [8] [9] have shown that association channels are dominant and they lead to observable quantities of protonated PAHs. In the same studies, it was also noticed that the cations C_6H_5^+ and $\text{C}_{10}\text{H}_7^+$ did not react with atomic hydrogen whereas they showed particular reactivity towards the hydrogen molecules with a supposed association mechanism [1] [8] [9]. Such kind of reactions, in which PAHs and atomic or molecular hydrogen are involved, are generally postulated to be of fundamental importance in numerous processes which can take place in the interstellar medium [3].

In this paper, we will show the results of our theoretical investigations on the reactions $[\text{C}_6\text{H}_5^+ + \text{D}_2]$ and $[\text{C}_{10}\text{H}_7^+ + \text{D}_2]$. The direct addition of D_2 to

the cations of interest immediately leads to the formation of the intermediates $\text{C}_6\text{H}_5\text{D}_2^+$ and $\text{C}_{10}\text{H}_7\text{D}_2^+$ and both these processes result to be strongly exothermic. These addition complexes may either be stabilized by unreactive collisions or dissociate by losing H_2 (or HD) in the case of $\text{C}_6\text{H}_5\text{D}_2^+$ and H (or D) for the latter cation ^[10].

2 Theoretical Methods

Calculations have been carried out with the B3LYP hybrid exchange correlation functional ^[11] as implemented in GAUSSIAN98 ^[12] in conjunction with the 6-31G* basis set ^[13]. For all the species involved in the investigated reactions, we have optimized their geometries and computed their harmonic frequencies, in order to confirm the presence of either a minimum or a saddle point. All thermochemical calculations have been carried out at 298.15 K and 1 atm by adding, for each species, the zero point correction and the thermal corrections to enthalpy and Gibbs free energy to the calculated B3LYP values. The zero point correction to energy has been considered so that we could evaluate the thermochemistry of our reactions in conditions which are closer to the interstellar ones, since they are characterized by much lower values of temperature.

3 $\text{C}_6\text{H}_5^+ + \text{D}_2$

The relative abundant literature information on the existence and reactivity of the phenylium cation, C_6H_5^+ , indicates that it can be generated by electron impact on benzene ^[14] and two isomeric structures are known to exist for this cation. They are thought to be the cyclic and linear isomers which are readily distinguished by their different reactivities. While linear C_6H_5^+ reacts neither with H_2 nor with H, a reaction between H_2 and cyclic C_6H_5^+ was observed in several studies ^[14] ^[15]. The reaction with D_2 was already experimentally investigated by Sablier et al. ^[16]. The cyclic C_6H_5^+ can exist both in a triplet and a singlet state and we calculated the latter to be more stable by 0.81 eV. In Figure 1, we report a schematic representation of the potential energy surface for the association of D_2 to the phenylium cation and two different mechanisms may be hypothesized.

According to the results on the $[\text{C}_6\text{H}_5 + \text{H}_2]$ reaction ^[17], the process of interest with D_2 should first proceed by the deuterium abstraction mechanism to form $[\text{C}_6\text{H}_5\text{D}^+ + \text{D}]$; successively, the deuterium addition to $\text{C}_6\text{H}_5\text{D}^+$ would give the intermediate of interest. The triplet state C_6H_5^+ can add the deuterium molecule with this proposed mechanism. For the abstraction step, the transition state found on the potential energy surface gives rise to a barrier height of 0.13 eV. The second D atom approaches the $\text{C}_6\text{H}_5\text{D}^+$ intermediate out of the plane of the ring and this addition is exothermic by 3.41 eV and barrierless ^[18] ^[19]. This result is understandable in terms of the electronic structures of the ions involved. The radical cations, with their highly reactive, open-shell structures, readily add a deuterium atom to produce the intermediate $\text{C}_6\text{H}_5\text{D}_2^+$ with a

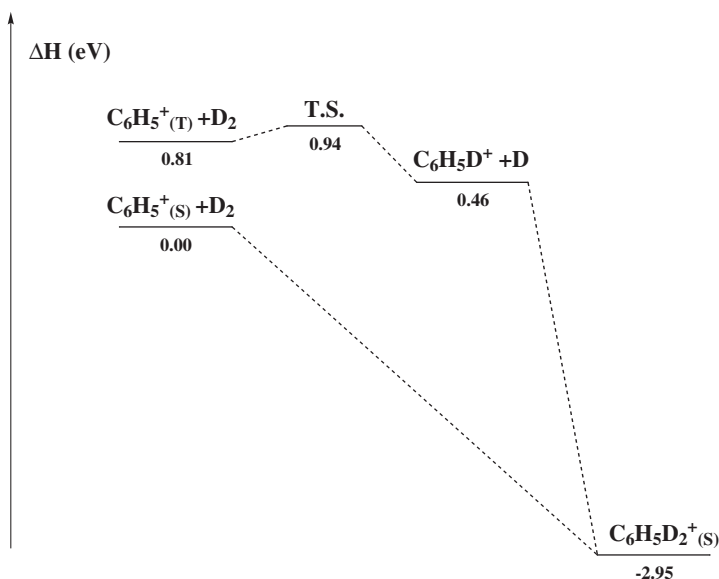


Fig. 1. Schematic representation of the $[\text{C}_6\text{H}_5^+ + \text{D}_2 \rightarrow \text{C}_6\text{H}_5\text{D}_2^+]$ reaction at B3LYP/6-31G* level of theory. (S) and (T) mean singlet and triplet state

more favourable closed-shell electron configuration (singlet state, see Fig. 1). The resultant cation is far less reactive with D (or H) atoms because it already has the preferred closed-shell electron structure and the addition of a second atom would brake this favourable configuration. The singlet isomer does not exhibit the same behaviour and this result is rather foreseeable, since the abstraction step is endothermic of 0.46 eV. It will prefer adding D_2 in a direct 1,1-association mechanism. This addition can be rationalized as an insertion process involving the D-D bond and the vacant sp^2 orbital on the ipso carbon of the phenylium ion. Furthermore, it does not require any energetic barrier and this result is also supported by a similar investigation carried out on the 1,1-elimination process [18]. The exothermicity for this mechanism is computed to be 2.95 eV.

The intermediate $\text{C}_6\text{H}_5\text{D}_2^+$, once formed, can either be stabilized by unreactive collisions with D_2 or form $\text{C}_6\text{H}_3\text{D}_2^+$ and $\text{C}_6\text{H}_4\text{D}^+$ by losing either H_2 or HD, or, finally, it could reform the reactants by releasing D_2 [10]. So as to rationalize the experimental data, we focussed on the fate of the $\text{C}_6\text{H}_5\text{D}_2^+$ intermediate. In Figure 2, we show the potential energy surface of the $\text{C}_6\text{H}_5\text{D}_2^+$ intermediate at B3LYP/6-31G* level of theory.

By considering the cation $\text{C}_6\text{H}_5\text{D}_2^{+a}$, which is the species directly formed from the phenylium ion according to the mechanism previously described, a 1-2 deuterium shift can be observed, with the consequent formation of the intermediate $\text{C}_6\text{H}_5\text{D}_2^{+b}$. The barrier is 0.55 eV at B3LYP/6-31G* level of theory. $\text{C}_6\text{H}_5\text{D}_2^{+b}$ evolves in different manners; firstly, it can lose a HD molecule in a barrierless process and form $\text{C}_6\text{H}_4\text{D}^+$ ($\Delta H = 2.92$ eV). Alternatively, by a fur-

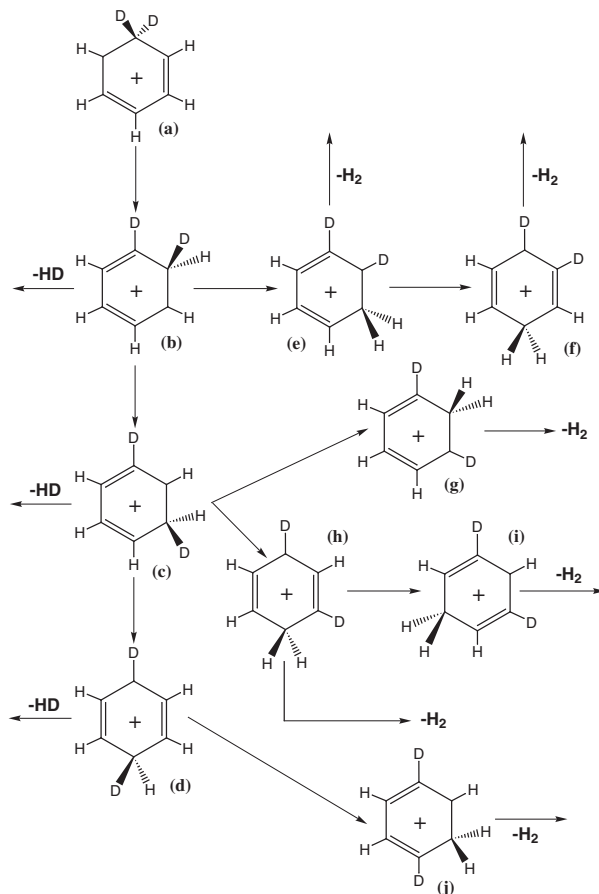


Fig. 2. Schematic representation of the $\text{C}_6\text{H}_5\text{D}_2^+$ potential energy surface at B3LYP/6-31G* level of theory

ther shift of a D atom, it can evolve into $\text{C}_6\text{H}_5\text{D}_2^+_c$ with an activation barrier of 0.55 eV. Finally, a hydrogen shift can be considered with the formation of $\text{C}_6\text{H}_5\text{D}_2^+_e$ and the energetic barrier of this third process is 0.52 eV. At this point, $\text{C}_6\text{H}_5\text{D}_2^+_e$ will be able either to lose a H_2 molecule forming $\text{C}_6\text{H}_3\text{D}_2^+$ ($\Delta H = 2.88$ eV) or to shift a further H atom to give $\text{C}_6\text{H}_5\text{D}_2^+_f$. In Table 1, we present the energetics for all the reactions drawn in Figure 2, reporting their ΔE_0 , ΔH , ΔG and E_a values at B3LYP/6-31G* level of theory.

By comparing the thermochemical values for the loss of HD and H_2 from the intermediate $\text{C}_6\text{H}_5\text{D}_2^+$ with the exothermicity of the association reaction [$\text{C}_6\text{H}_5^+ + \text{D}_2$] (2.95 eV), the production of $\text{C}_6\text{H}_4\text{D}^+$ and $\text{C}_6\text{H}_3\text{D}_2^+$ results to be exothermic by 0.03 eV and 0.07 eV with respect to the reactants, explaining, thus, their presence in the experimental apparatus^[10]. However, it is also worth noticing that all the activation barriers for the isomerization processes

lie much lower in energy than the release of a neutral molecule. Therefore our calculations can rationalize why in the experimental analysis large concentrations of $\text{C}_6\text{H}_5\text{D}_2^+$ were detected together with lower quantities of $\text{C}_6\text{H}_4\text{D}^+$ and $\text{C}_6\text{H}_3\text{D}_2^+$ [10].

Table 1. Thermochemical parameters (eV) calculated at B3LYP/6-31G* level of theory for the processes described in Figure 2. ΔH , ΔG and E_a values have been calculated at the temperature of 298.15 K. ΔE_0 , ΔH and ΔG for the isomerization processes are in meV.

Reaction	ΔE_0	ΔH	ΔG	E_a
$\text{C}_6\text{H}_5\text{D}_2^+{}_a \rightarrow \text{C}_6\text{H}_5\text{D}_2^+{}_b$	-5.09	-4.90	-5.42	0.55
$\text{C}_6\text{H}_5\text{D}_2^+{}_b \rightarrow \text{C}_6\text{H}_5\text{D}_2^+{}_c$	-1.42	-1.61	-1.18	0.55
$\text{C}_6\text{H}_5\text{D}_2^+{}_c \rightarrow \text{C}_6\text{H}_5\text{D}_2^+{}_d$	0.82	0.84	0.49	0.55
$\text{C}_6\text{H}_5\text{D}_2^+{}_b \rightarrow \text{C}_6\text{H}_5\text{D}_2^+{}_e$	-7.54	-8.54	-6.20	0.52
$\text{C}_6\text{H}_5\text{D}_2^+{}_e \rightarrow \text{C}_6\text{H}_5\text{D}_2^+{}_f$	-0.60	-0.76	-0.68	0.53
$\text{C}_6\text{H}_5\text{D}_2^+{}_c \rightarrow \text{C}_6\text{H}_5\text{D}_2^+{}_g$	-4.71	-4.49	-3.84	0.52
$\text{C}_6\text{H}_5\text{D}_2^+{}_c \rightarrow \text{C}_6\text{H}_5\text{D}_2^+{}_h$	-5.31	-5.25	-4.54	0.52
$\text{C}_6\text{H}_5\text{D}_2^+{}_h \rightarrow \text{C}_6\text{H}_5\text{D}_2^+{}_i$	-2.20	-2.45	-1.66	0.53
$\text{C}_6\text{H}_5\text{D}_2^+{}_d \rightarrow \text{C}_6\text{H}_5\text{D}_2^+{}_j$	-6.91	-6.94	-5.50	0.52
$\text{C}_6\text{H}_5\text{D}_2^+{}_b \rightarrow \text{C}_6\text{H}_4\text{D}^+ + \text{HD}$	2.83	2.92	2.51	-
$\text{C}_6\text{H}_5\text{D}_2^+{}_c \rightarrow \text{C}_6\text{H}_4\text{D}^+ + \text{HD}$	2.83	2.92	2.51	-
$\text{C}_6\text{H}_5\text{D}_2^+{}_d \rightarrow \text{C}_6\text{H}_4\text{D}^+ + \text{HD}$	2.83	2.91	2.51	-
$\text{C}_6\text{H}_5\text{D}_2^+{}_e \rightarrow \text{C}_6\text{H}_3\text{D}_2^+ + \text{H}_2$	2.79	2.88	2.48	-
$\text{C}_6\text{H}_5\text{D}_2^+{}_f \rightarrow \text{C}_6\text{H}_3\text{D}_2^+ + \text{H}_2$	2.79	2.87	2.48	-
$\text{C}_6\text{H}_5\text{D}_2^+{}_g \rightarrow \text{C}_6\text{H}_3\text{D}_2^+ + \text{H}_2$	2.79	2.88	2.48	-
$\text{C}_6\text{H}_5\text{D}_2^+{}_h \rightarrow \text{C}_6\text{H}_3\text{D}_2^+ + \text{H}_2$	2.79	2.88	2.48	-
$\text{C}_6\text{H}_5\text{D}_2^+{}_i \rightarrow \text{C}_6\text{H}_3\text{D}_2^+ + \text{H}_2$	2.79	2.88	2.48	-
$\text{C}_6\text{H}_5\text{D}_2^+{}_j \rightarrow \text{C}_6\text{H}_3\text{D}_2^+ + \text{H}_2$	2.79	2.88	2.48	-

4 $\text{C}_{10}\text{H}_7^+ + \text{D}_2$

In analogy with C_6H_5^+ , even the naphtylium cation, $\text{C}_{10}\text{H}_7^+$, is known to react with the H_2 molecule, whereas no reactions occur with atoms [8] [9]. Previous theoretical calculations on the naphtylium cation indicated this species is planar with the positive charge largely delocalized on the deprotonated ring [20] and our B3LYP/6-31G* calculations are in good agreement with these results. Then, we have been able to locate two different isomers of $\text{C}_{10}\text{H}_7^+$ and they can be indicated as $\text{C}_{10}\text{H}_7^+-\alpha$ and $\text{C}_{10}\text{H}_7^+-\beta$, where α and β denote the sites where the hydrogen atom has been abstracted (see Figure 3).

Although they result to be both planar, the abstraction of a H atom destroys the aromaticity of the naphthalene π system and they own only a C_S symmetry.

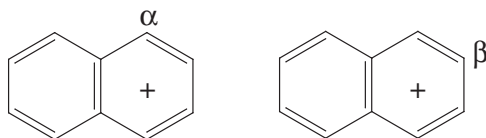


Fig. 3. Schematic representation of $\text{C}_{10}\text{H}_7^+-\alpha$ and $\text{C}_{10}\text{H}_7^+-\beta$

By a comparison of their energies, the $\text{C}_{10}\text{H}_7^+-\alpha$ isomer is more stable than β by nearly 0.058 eV and, by calculating the energies of the $\text{C}_{10}\text{H}_7\text{D}_2^+-\alpha$ and $\text{C}_{10}\text{H}_7\text{D}_2^+-\beta$ intermediates, which can be directly originated from the previous reactants by D_2 addition, the α isomer results to be lower in energy by 0.13 eV. We can therefore assume that our process of interest will principally involve the α isomers. The association reaction $[\text{C}_{10}\text{H}_7^+ + \text{H}_2]$ is known to occur under low density conditions [1] [8] [9]. Additional information is available on the reaction $[\text{C}_{10}\text{H}_8^+ + \text{H}]$ [21]. Ho et al. [22] supposed the reaction $[\text{C}_{10}\text{H}_7^+ + \text{H}_2 \rightarrow \text{C}_{10}\text{H}_8^+ + \text{H}]$ to be slightly endothermic, while our calculations suggest the same process to be exothermic by 0.34 eV. When D_2 reacts with the naphthyl cation, the intermediate $\text{C}_{10}\text{H}_7\text{D}_2^+$ is mainly produced with lower quantities of the cationic species $\text{C}_{10}\text{H}_7\text{D}^+$ and $\text{C}_{10}\text{H}_6\text{D}_2^+$ which could be formed by the further loss of a D or a H atom respectively [10].

On the D_2 addition to $\text{C}_{10}\text{H}_7^+$, we have optimized a transition state for the abstraction-addition mechanism ($E_a = 0.17$ eV), whereas the 1,1-addition is a barrierless process exothermic by 3.17 eV. In Figure 4, we report a schematic representation of the $\text{C}_{10}\text{H}_7\text{D}_2^+$ potential energy surface, where we concentrate only on the possible shifts of a deuterium atom around the molecular rings. Ten different structural isomers have been optimized and they all reveal comparable stabilities, except those cations in which the coordination of the deuterium atom involves the carbons in common with the two six-membered rings. These latest species have been indicated by the letters *e* and *f* and they can only lose the D atom to form the $\text{C}_{10}\text{H}_7\text{D}^+$ cations. At this point of the study, we focussed our attention only to the shifts involving the D atoms, without considering the same phenomenon in the case of the H atoms (see Figure 4).

As shown in Figure 4, by starting from $\text{C}_{10}\text{H}_7\text{D}_2^{+a}$, which is our initial isomer, three different pathways can be followed. Firstly, we can consider the breaking of a C-D bond with the formation of $\text{C}_{10}\text{H}_7\text{D}^+$ and this reaction is endothermic by 2.82 eV. Alternatively, $\text{C}_{10}\text{H}_7\text{D}_2^{+b}$ is formed: this reaction is slightly endothermic and it requires an activation barrier of 0.72 eV. The cation *b* can evolve by losing either a D ($\Delta H = 2.69$ eV) or a H atom ($\Delta H = 2.61$ eV) or give $\text{C}_{10}\text{H}_7\text{D}_2^{+c}$. A third possible channel involves the isomerization $\text{C}_{10}\text{H}_7\text{D}_2^{+a} \rightarrow \text{C}_{10}\text{H}_7\text{D}_2^{+f}$ with an activation energy of 1.10 eV. In Table 2, we report the thermochemical parameters for all the processes drawn in Figure 4, considering both the activation barriers and the loss of the D and H atoms.

As we can observe in Table 2, the activation energies for the investigated isomerization processes result to be lower than the calculated values for the

loss of the D and H atoms from the same intermediates. This result implies that $C_{10}H_7D_2^+$, once formed, can easily allow the atomic shifts all along its structure with the consequent formation of a remarkable number of isomers which differ one another for the position of the isotopically labelled atoms.

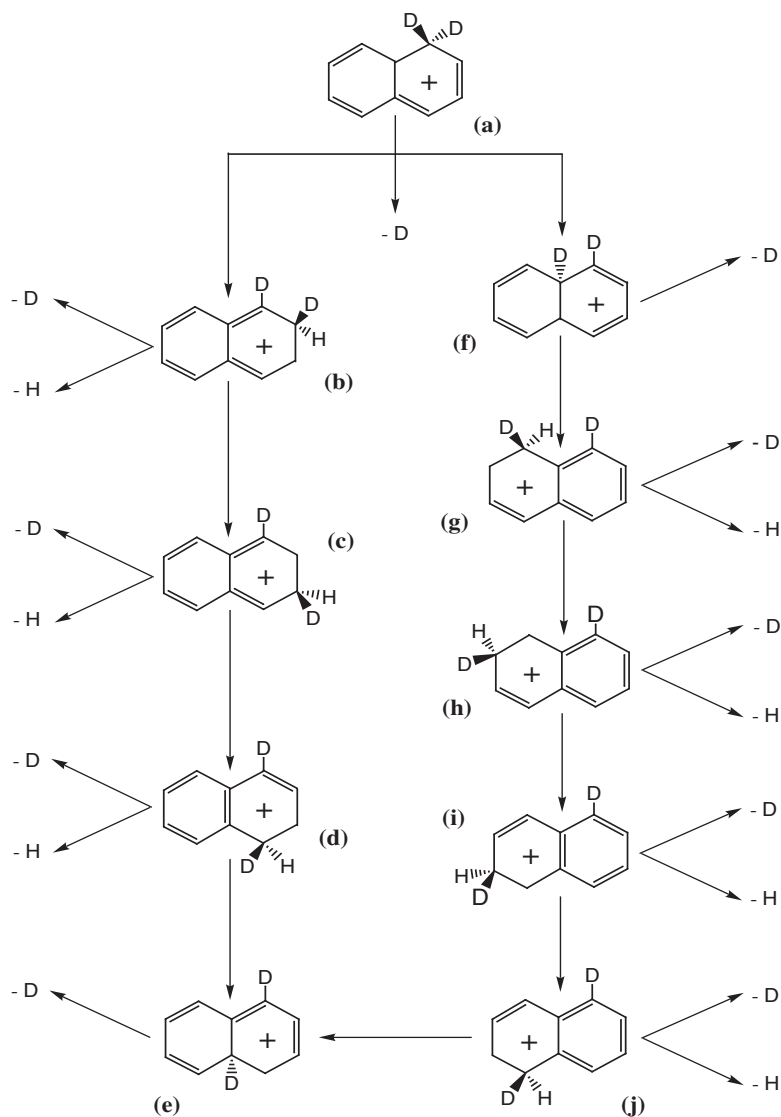


Fig. 4. Schematic representation of the $C_{10}H_7D_2^+$ potential energy surface at B3LYP/6-31G* level of theory

Table 2. Thermochemical parameters (eV) calculated at B3LYP/6-31G* level of theory for the processes described in Figure 4. ΔH , ΔG and E_a values have been calculated at the temperature of 298.15 K.

Reaction	ΔE_0	ΔH	ΔG	E_a
$C_{10}H_7D_2^+{}_a \rightarrow C_{10}H_7D_2^+{}_b$	0.13	0.13	0.13	0.72
$C_{10}H_7D_2^+{}_b \rightarrow C_{10}H_7D_2^+{}_c$	0.01	0.01	0.01	0.81
$C_{10}H_7D_2^+{}_c \rightarrow C_{10}H_7D_2^+{}_d$	-0.13	-0.13	-0.14	0.59
$C_{10}H_7D_2^+{}_d \rightarrow C_{10}H_7D_2^+{}_e$	0.88	0.88	0.89	1.11
$C_{10}H_7D_2^+{}_a \rightarrow C_{10}H_7D_2^+{}_f$	0.88	0.88	0.89	1.10
$C_{10}H_7D_2^+{}_f \rightarrow C_{10}H_7D_2^+{}_g$	-0.88	-0.88	-0.89	0.23
$C_{10}H_7D_2^+{}_g \rightarrow C_{10}H_7D_2^+{}_h$	0.13	0.13	0.14	0.72
$C_{10}H_7D_2^+{}_h \rightarrow C_{10}H_7D_2^+{}_i$	0.00	0.00	0.00	0.81
$C_{10}H_7D_2^+{}_i \rightarrow C_{10}H_7D_2^+{}_j$	-0.13	-0.13	-0.14	0.59
$C_{10}H_7D_2^+{}_j \rightarrow C_{10}H_7D_2^+{}_e$	0.88	0.88	0.89	1.11
$C_{10}H_7D_2^+{}_a \rightarrow C_{10}H_7D^+ + D$	2.77	2.82	2.45	-
$C_{10}H_7D_2^+{}_b \rightarrow C_{10}H_7D^+ + D$	2.64	2.69	2.32	-
$C_{10}H_7D_2^+{}_b \rightarrow C_{10}H_6D_2^+ + H$	2.55	2.61	2.25	-
$C_{10}H_7D_2^+{}_c \rightarrow C_{10}H_7D^+ + D$	2.64	2.69	2.32	-
$C_{10}H_7D_2^+{}_c \rightarrow C_{10}H_6D_2^+ + H$	2.55	2.61	2.25	-
$C_{10}H_7D_2^+{}_d \rightarrow C_{10}H_7D^+ + D$	2.78	2.83	2.46	-
$C_{10}H_7D_2^+{}_d \rightarrow C_{10}H_6D_2^+ + H$	2.69	2.74	2.39	-
$C_{10}H_7D_2^+{}_e \rightarrow C_{10}H_7D^+ + D$	1.89	1.95	1.57	-
$C_{10}H_7D_2^+{}_f \rightarrow C_{10}H_7D^+ + D$	1.89	1.94	1.57	-
$C_{10}H_7D_2^+{}_g \rightarrow C_{10}H_7D^+ + D$	2.77	2.83	2.46	-
$C_{10}H_7D_2^+{}_g \rightarrow C_{10}H_6D_2^+ + H$	2.69	2.74	2.39	-
$C_{10}H_7D_2^+{}_h \rightarrow C_{10}H_7D^+ + D$	2.64	2.69	2.32	-
$C_{10}H_7D_2^+{}_h \rightarrow C_{10}H_6D_2^+ + H$	2.55	2.61	2.25	-
$C_{10}H_7D_2^+{}_i \rightarrow C_{10}H_7D^+ + D$	2.64	2.69	2.32	-
$C_{10}H_7D_2^+{}_i \rightarrow C_{10}H_6D_2^+ + H$	2.55	2.61	2.25	-
$C_{10}H_7D_2^+{}_j \rightarrow C_{10}H_7D^+ + D$	2.77	2.83	2.46	-
$C_{10}H_7D_2^+{}_j \rightarrow C_{10}H_6D_2^+ + H$	2.69	2.74	2.39	-

5 Conclusions

In this paper, we present a theoretical study at B3LYP/6-31G* level of theory of the reactions $[C_6H_5^+ + D_2]$ and $[C_{10}H_7^+ + D_2]$. They both involve PAHs and the deuterium molecule, which are well-known constituents of the interstellar clouds. The 1,1-addition of the D_2 molecule to the phenylium and naphthylum cations does not require any activation energy and the products of this reactions are the experimentally revealed cations $C_6H_5D_2^+$ and $C_{10}H_7D_2^+$. The fate of these two species is different. From the experimental results on both systems^[10], it was noticed that the intermediate $C_6H_5D_2^+$ could dissociate by losing either

a HD or a H₂ molecule giving the cations C₆H₄D⁺ and C₆H₃D₂⁺, whereas the intermediate C₁₀H₇D₂⁺ could lose a H atom forming C₁₀H₆D₂⁺ or a D atom with the consequent synthesis of C₁₀H₇D⁺. All our calculations rationalize these surveys and, in addition, offer a more complete view of the possible reactive pathways which may be followed by both the systems of interest.

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