



Research paper

Remote modulation of singlet–triplet gaps in carbenes

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ABSTRACT

The modulation of the singlet–triplet (*S/T*) gap of phenyl-carbene derivatives by hydrogen bond formation has been studied using the G4(MP2) computational method. The complexation of the aromatic ring substituents ($-\text{NH}_2$, $-\text{OH}$, $-\text{PH}_2$, $-\text{SH}$) in *meta*- and *para*-positions with water and the protonation or deprotonation of such groups have a remarkable influence on the *S/T* gaps, reaching *S/T* gap variations from 25.7 to 93.7 kJ mol⁻¹. This variation is linearly related to the binding energy difference of the *S/T* configurations. Importantly, the triplet and singlet electronic configurations are systematically favored in the protonated and deprotonated forms, respectively, in all cases.

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1. Introduction

Carbenes are intriguing molecules containing a divalent carbon atom, leaving two of its valence electrons not used for bonding. From a formal point of view, there are two possible arrangements for these two electrons. Depending on whether they are located in a same or a different orbital, they give place to a singlet (*S*) or a triplet (*T*) configuration, respectively. The preference for one or the other electronic configuration has profound implications on the geometry and reactivity of carbenes [1,2]. Aromatic substitution on carbenes has been shown to play an important role on the *S/T* gap [3]. It has been also reported that the *S/T* gap is relevant for the reactivity of π -systems [4–7].

The carbene group, especially in the singlet configuration, is known to act as electron donor in different non-covalent interactions [8–19]. A number of reports have indicated the influence of the polarity of the solvent on the *S/T* gap [20–23]. In the same way, the formation of hydrogen [24–26], halogen [27] and triel bonds [28] with the carbene group have been shown to favor the singlet configuration. With these precedents in mind, we study in this article the influence of hydrogen bonds distant from the carbene moiety on the *S/T* gap. A series of 3/4-substituted phenylcarbenes have been chosen for this purpose (see the H_nX groups in Scheme 1). To modulate the *S/T* gap, we consider a series of complexes between suitable small molecules and the H_nX substituents, acting as HB donors or HB acceptors depending on the case. Additionally, the effect on the gap of the protonation and deprotonation of the H_nX substituents is also included in the study. The results obtained have been rationalized based on the molecular

electrostatic potential of the isolated molecules in their singlet and triplet configurations. Along with that, we analyze the relationship between the *S/T* gap and the energies involved in the complexation processes.

2. Computational details

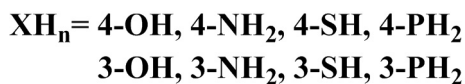
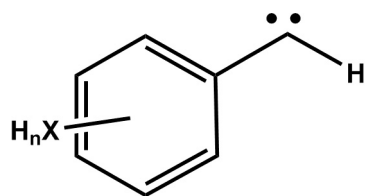
All geometries were fully optimized using the G4(MP2) formalism [29], which typically provides thermodynamic magnitudes with an accuracy of ± 4 kJ mol⁻¹, as shown by a recent study of our group on the *S/T* gap in carbenes [30]. All these calculations were carried out with the Gaussian09 program [31]. The molecular electrostatic potential (MEP) of the isolated molecules was calculated at the B3LYP/6-31G(2df,p) computational level, the level of theory used by the G4(MP2) formalism in the optimization procedure. The Multiwfn program [32,33] was used to analyze the critical points of the MEP on the 0.001 au electron density isosurfaces, and represented with the Jmol program [34]. Finally, binding energies are defined as the enthalpy difference between the complex and the isolated interacting units, all in their fully relaxed conformations, whereas the *S/T* gaps are defined as the enthalpy difference $H(\text{triplet}) - H(\text{singlet})$.

3. Results and discussion

We start by analyzing the *S/T* gaps for our set of isolated carbenes, collected in Table 1 following the definition given in the previous section. The results indicate that the ground state is a triplet in almost all cases, finding small gaps between -5.7 and -13.3 kJ mol⁻¹. The only exceptions are the 4-OH and 4-NH₂ derivatives, where the singlet is more stable than the triplet by 1.9 and 8.4 kJ mol⁻¹, respectively. As a general trend, for all the

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Scheme 1. Carbenes considered in the article.

Table 1

S/T gap (kJ mol^{-1}) for the isolated systems calculated at G4(MP2) computational level^a.

Position/ H_nX	OH	NH_2	SH	PH_2
4- H_nX	1.9	8.4	-5.7	-12.1
3- H_nX	-12.8	-12.3	-13.0	-13.3

^a Negative values indicate that the triplet is more stable than the singlet (see the gap definition in the Computational Details section).

substituents, the S/T gaps of the 3- H_nX derivatives are larger than the corresponding 4- H_nX ones, being the triplet the most stable configuration. Previous calculations of the S/T gap at the G3 (MP2) level [35] showed similar results for the 3- NH_2 and 4- NH_2 derivatives (7.1 and $-14.6 \text{ kJ mol}^{-1}$) although for the 3-OH and 4-OH derivatives, the G3(MP2) results (gaps of 7.8 and -5.4 kJ mol^{-1}) favor the singlet about 6 kJ mol^{-1} when compared to the G4(MP2) ones.

The molecular electrostatic potential (MEP) helps us to trace the most suitable positions for the interaction with electron acceptors and electron donors. The MEP of the singlet and triplet carbenes on the 0.001 au electron density isosurface was calculated to identify these binding sites, as exemplified in Fig. 1 for the 4-OH derivatives, and the minimum and maximum values associated with each type of substituent on the aromatic ring are summarized in Table 2. These values provide a tool for a direct comparison of the donor/acceptor abilities of a given structure. Although the minimum and maximum MEP values are located at approximately the same

Table 2

MEP stationary points (au) on the 0.001 au electron density surface associated to the XH_n groups.

XH_n	Singlet		Triplet	
	X	H	X	H
4-OH	-0.018	0.100	-0.035	0.082
4- NH_2	-0.006	0.079	-0.037	0.058
4-SH	-0.010	0.056	-0.026	0.043
4- PH_2	-0.018	0.033	-0.032	0.015
3-OH	-0.026	0.086	-0.037	0.078
3- NH_2	-0.031	0.065	-0.042	0.054
3-SH	-0.019	0.045	-0.028	0.039
3- PH_2	-0.024	0.019	-0.032	0.011

places for both the singlet and triplet configurations, a simple look at Fig. 1 allows visualizing the effect of the carbene configuration on the phenyl ring.

In all cases, as summarized in Table 2, the minimum values of the triplet are larger than those of the singlet in absolute value, while the opposite is found for the maximum values. Thus, the interaction of electron acceptors with these molecules should favor the triplet configuration, whereas electron donors should favor the singlet configuration. Another interesting feature of these systems is the smaller differences found between the maximum and minimum MEP values in the *meta* derivatives compared to the *para* ones. This fact should lead to smaller energetic differences for the complexes with the singlet vs. the triplet configurations for a same substituent in the former case.

Once analyzed the characteristics of the isolated carbenes, we proceed to study the complexes between a series of HB donors and acceptors (H_2O , OH^- and H_3O^+) and the substituted aromatic rings, interacting through the H_nX group (see Fig. 2). This kind of complexes were conceived and proposed by Radom and colleagues as partial protonation and deprotonation states [36]. In addition, the protonated and deprotonated isolated species can be considered as an extension of the partial protonation/deprotonation complexes, as visualized in Fig. 2. In Table 3, the S/T gaps of the complexes are gathered along with the values of the isolated protonated, deprotonated and neutral systems for comparative purposes. In all cases, the deprotonation of the side group favors the singlet configuration between 60.6 and $102.1 \text{ kJ mol}^{-1}$ in the *para* derivatives and between 17.5 and 21.7 kJ mol^{-1} in the *meta*

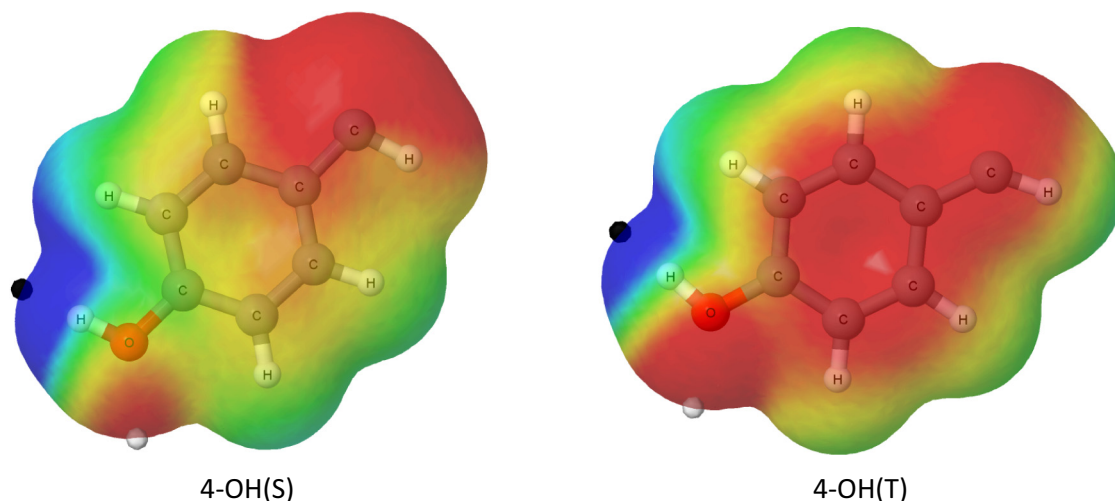


Fig. 1. MEP on the 0.001 au electron density isosurface of the 4-OH derivative in the singlet (S) and triplet (T) electronic configurations. The color code range between -0.015 (red) and 0.05 (blue) au. The location of the minimum and maximum MEP values associated to the OH group are indicated by white and black dots, respectively. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

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