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Donor stabilized borylnitrenes: A theoretical study

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ABSTRACT

Quantum chemical calculations have carried out on some donor stabilized (E = NH, PH and O) borylnitrenes (**5-7**) using density functional theory (DFT) calculations at B3LYP level of theory. Moreover, the effect of non-donor subsituents ($E = CH_2$ and SiH_2) are also studied. All these molecules are found to be ground state triplets. Their zero-field splitting (ZFS) parameters *D* and *E* are also calculated using complete active space self consistent field (CASSCF) theory. The donor atoms are found to have a profound effect on the structure and ZFS parameters of these nitrenes. However, the nature of the C—C back bone has a very little effect on their ground state multiplicity as well as their ZFS parameters.

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1. Introduction

The interelectronic interaction is very crucial so far as molecules containing multiple unpaired electrons are concerned. Electron spin resonance spectroscopy is a valuable tool to characterize such radicals. Determination of zero field splitting (ZFS) parameters *D* and *E* is very important as it provides structure-property information of interelectronic interaction.

One such species are the nitrenes [1–3] which are highly reactive intermediates. Nitrenes generally prefer triplet ground states with large singlet triplet splitting. However, Lewis acidic boron atoms attached to the nitrene centre may stabilize the singlet state ($^1A_1$, π^2) of nitrenes by interacting with their vacant p orbitals. Indeed, previous calculation on parent borylnitrene **1** (Scheme 1), reveals that the singlet state is more stable by 12 kcal mol^{-1} than the triplet state [4,5]. Bettinger et al. reported that the singlet state of parent borylnitrene is 7 kcal mol^{-1} more stable than the triplet state [6]. However, **1** was found to be a first-order stationary point in the C_{2v} symmetry on the potential energy surface, which rearranges to **2** (Scheme 1).

The oxygen donor substituent attached to the boron atoms in **3** and **4** will definitely reduce the Lewis acidity of the boron centre and as a result the π^2 singlet states of **3** and **4** will be destabilized compared to their triplet states [4,5]. Bettinger et. al. have characterized **4** in matrix isolation and the triplet state of **4** was established by EPR analysis [6]. The zero field splitting parameters ($|D/hc| = 1.492\ cm^{-1}$ and $|E/hc| = 0.004\ cm^{-1}$) of **4** was established from the EPR study at 10 K [6].

The potential stabilization of triplet borylnitrene prompted us to investigate the effect of donor atoms (E) on the singlet-triplet splitting and the ZFS parameters of borylnitrenes **5-7** (Chart 1). We have also included non-donor substituents such as CH_2 and SiH_2 (Chart 1) to understand the effect of donor atoms on their spin state properties.

2. Computational details

All the computations were performed using the ORCA suite of program [7]. Geometry of all these molecules were fully optimized at the B3LYP/6-31+G$*$ level of theory [8,9]. Frequency calculations are performed at the same level of theory to characterize the nature of the stationary points. Except a few (see text), all structures are found to be local minimum on the potential energy surface. The same calculations were repeated using improved global-hybrid meta-GGA functional M06-2X using the same basis set [10]. In both the cases, unrestricted formalism has been used for the triplet state optimization. We observed negligible spin contamination of the triplet states as measured by the spin squared expectation value $\langle S^2 \rangle$. The singlet-triplet energy difference designated as $\Delta E_{S\text{-}T}$ is calculated from the energy difference between the singlet and triplet states. Zero point correction has been included in the calculations. The ZFS parameters were calculated using complete active space SCF (CASSCF) level of theory using the 6-31+G$*$ basis set. The complete active space for the molecules consisted of the

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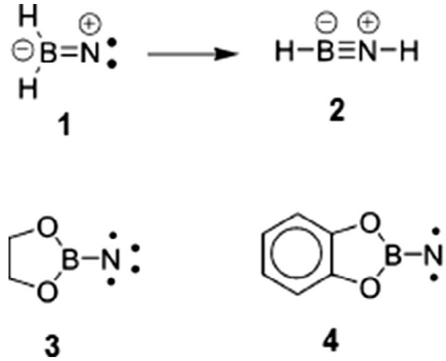

Scheme 1. Rearrangement of the parent borylnitrene **1** to the stable isomer **2** [4]. **3** and **4** are the donor stabilized borylnitrenes [4,5].

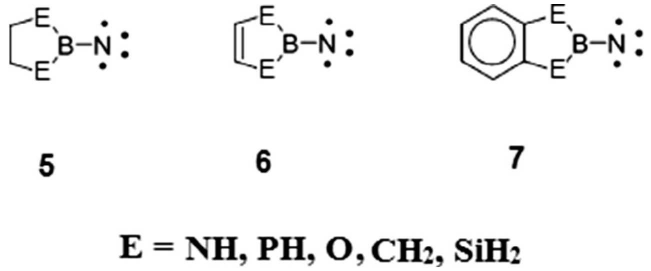
5
6
7
E = NH, PH, O, CH₂, SiH₂

Chart 1. Schematic representation of the nitrenes selected for the study.

complete π systems and the in-plane p orbital at the nitrene centre. This resulted in (6,5)-CASSCF for **5**, (8,7)-CASSCF for **6** and (12,11)-CASSCF for **7**.

3. Results and discussions

3.1. Molecular geometries

The optimized geometries of the lowest energy triplet T_0 states with $\sigma^1\pi^1$ configurations of **5-7** are shown in Fig. 1.

The ground state triplets (T_0) of the molecule are planar with E = NH and O. However, P substituted derivatives are pyramidal at the P centre. The P—H bonds are *trans* to each other. The pyramidalization at the P centre arises due to the high inversion barrier at the P centre.

The E-B distance in **6** and **7** are found to be longer while the B-$N_{nitrene}$ distance are shorter in **6** and **7** than that in **5**. This might be due to the fact that in **6** and **7**, the lone pairs at the E atoms are also delocalized to the adjacent $>$C=C$<$ moiety which results in slightly weaker delocalization of the lone pairs at E atom to the adjacent B centre. As a result, the E-B distances in **6** and **7** increases. This weaker E-B delocalization in **6** and **7** resulted in stronger B-$N_{nitrene}$ interaction. However, there is very little change in E-B distance going from **6** to **7**. This indicates that the strength of the E-B bond remains constant with olefenic $>$C=C$<$ as in **6** or the aromatic $>$C=C$<$ as in **7**.

The shortest B-$N_{nitrene}$ distance is found for phosphorous substituted borylnitrenes, **5-PH**, **6-PH** and **7-PH**. This might be due to the bigger size of P atom which can accept more spin density from the nitrene centre resulting in more delocalization of the spin density of the nitrene centre (see text below). Thus, donor atoms (E) have a profound effect on the B-$N_{nitrene}$ distance of these borylnitrenes.

The singlet-triplet energy separation $\Delta E_{S\text{-}T}$ of these molecules is an important parameter. Table 1 contains the $\Delta E_{S\text{-}T}$ values of the nitrenes computed at B3LYP/6-311++G**//B3LYP/6-31+G* level of theory. For the triplet states, we observed very less spin contamination (Table 1) which justifies the reliability of the level of theory used. Moreover, the calculation at M06-2X level of theory produces

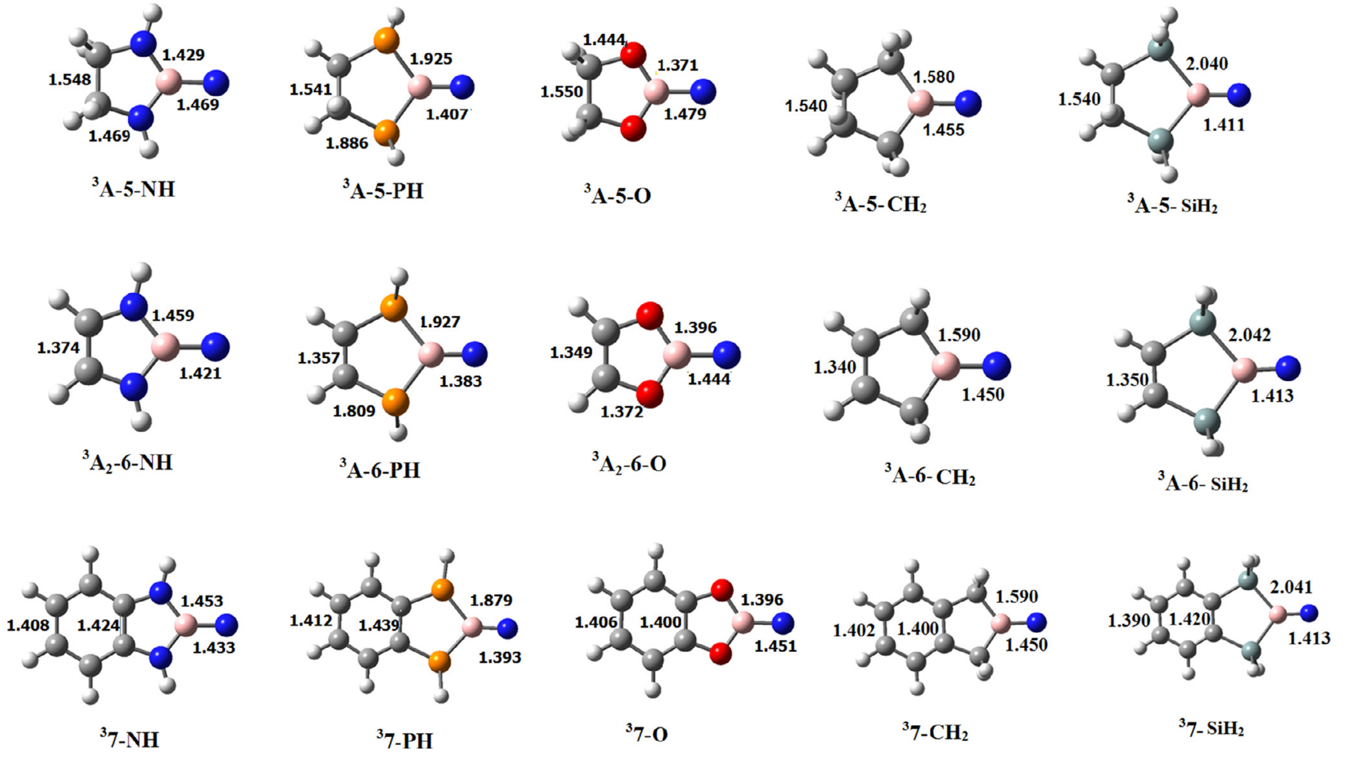
1.548
1.429
1.469
1.469
^{3}A-5-NH
1.541
1.925
1.407
1.886
^{3}A-5-PH
1.444
1.371
1.550
1.479
^{3}A-5-O
1.580
1.540
1.455
^{3}A-5-CH₂
2.040
1.540
1.411
^{3}A-5- SiH₂
1.459
1.374
1.421
^{3}A₂-6-NH
1.927
1.357
1.383
1.809
^{3}A-6-PH
1.396
1.349
1.444
1.372
^{3}A₂-6-O
1.590
1.340
1.450
^{3}A-6- CH₂
2.042
1.350
1.413
^{3}A-6- SiH₂
1.453
1.408
1.424
1.433
^{3}7-NH
1.879
1.412
1.439
1.393
^{3}7-PH
1.396
1.406
1.400
1.451
^{3}7-O
1.590
1.402
1.400
1.450
^{3}7-CH₂
2.041
1.390
1.420
1.413
^{3}7- SiH₂

Fig. 1. B3LYP/6-31+G* optimized triplet T_0 states geometries of **5-7**.

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