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MAGNETICALLY INDUCED CURRENT DENSITIES IN PHENYLENES IN THE GROUND AND LOWEST LYING TRIPLET EXCITED STATES

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ABSTRACT. Magnetically induced current densities in the lowest lying singlet and triplet states of a series of phenylene molecules were examined at the B3LYP/lanl2DZ level of theory. Previous findings have shown that in the ground singlet state, phenylenes exhibit ring currents with opposed tropicity: diatropic currents within six-membered rings and paratropic currents within four-membered rings. However, for biphenylene in the first excited triplet state, there is a drastic change in aromaticity in comparison to the ground state. Specifically, this molecule in the triplet state sustains a strong diatropic global circulation. In the present work, we showed that higher members of the phenylene family do not exhibit such radical changes in aromaticity when excited to the lowest lying triplet states.

Keywords: biphenylenes, aromaticity, triplet state aromaticity, ring currents.

INTRODUCTION

Aromaticity is a fundamental concept in chemistry that stems from the unique electronic structure and stability found in certain compounds (KRYGOWSKI *et al*., 2014). This concept plays a pivotal role in predicting and understanding the behavior of organic compounds in diverse fields, including medicinal chemistry, where the design of aromatic molecules is integral to drug development (TEWARI *et al*., 2013; WARD and BESWICK, 2014; LANZAROTTI *et al*., 2020) and materials science, where the unique properties of aromatic polymers find applications in a range of materials (KONISHI *et al*., 2019; KALAPOS *et al*., 2022). The intricate interplay between molecular structure and electron delocalization makes the study of aromaticity a cornerstone in the exploration of various fields in chemistry.

The magnetic criteria of aromaticity, particularly magnetically induced current density, provide a distinctive perspective on understanding and characterizing aromatic compounds (FLIEGL *et al*., 2009; GERSHONI-PORANNE and STANGER, 2015; SUNDHOLM *et al*., 2016). Aromatic molecules display a ring current when subjected to an external magnetic field, creating a magnetic response that contributes to their overall stability (SUNDHOLM *et al*., 2016).

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In aromatic systems, the circulation of electrons within the conjugated ring leads to a coherent, circulating current. The presence of significant, diatropic ring currents, as opposed to paratropic ones, signifies the aromatic nature of a compound. This magnetic criterion extends the scope of aromatic analysis beyond traditional methods, providing insights into the electronic delocalization and stability of aromatic molecules from a magnetic perspective. The examination of magnetically induced current density has become an invaluable complement to other aromaticity indices, contributing to a comprehensive understanding of the electronic structure and properties of aromatic compounds in modern theoretical chemistry (Sundholm *et al*., 2016).

Biphenylene is a distinctive hydrocarbon compound that draws attention due to its unique molecular structure: two benzene rings connected through a four-membered ring. Biphenylene is considered as the smallest member of a class of organic compounds characterized by the fusion of multiple benzene units through the four-membered rings. This molecular architecture results in the so-called phenylene family. The representatives of this group exhibit extended conjugation and unique electronic properties, which is the reason for the numerous studies focusing on biphenylene and its derivatives (Vollhardt, 1975; Zimmermann, 1996; Rosokha and Kochi, 2006; Vollhardt and Schore, 2010; Rosenberg *et al*., 2014; Radenković *et al*., 2015; Ayub *et al*., 2017; Gantenbein *et al*., 2019; Liu *et al*., 2021; Plasser, 2021; Leyva-Parra *et al.*, 2024; Radenković *et al*., 2024). Two-dimensional (2D) biphenylene emerges as a promising metal-free catalyst for the electrochemical oxygen reduction reaction (Liu *et al*., 2021). As a newly synthesized allotrope of graphene, the structure of this moiety consists of tetragonal, hexagonal and octagonal rings (Liu *et al*., 2021). Moreover, 2D biphenylene exhibits excellent electrochemical stability, making it as an attractive candidate for use in alkaline fuel cells (Liu *et al*., 2021). The fused biphenylene motif is often found in polycyclic aromatic hydrocarbons (PAHs) and other complex organic molecules. In the paper by Radenković and coauthors the effect of benzo and benzocyclobutadieno annelation in the series of biphenylene derivatives has been investigated (Radenković *et al*., 2015). Calculated ring currents indicate that the angular benzo annelation increases, while the linear decreases the intensity of paratropic ring currents in the four-membered ring in biphenylene molecules (Radenković *et al*., 2015, 2024). In the case of benzocyclobutadieno annelation the effect of annelation is opposite (Radenković *et al*., 2015). Biphenylene can be considered as aromatic chameleon, since it has mixed aromatic and antiaromatic characteristics in the ground S_0 state, while it becomes completely aromatic in the lowest excited T_1 triplet state (Ayub *et al*., 2017; Plasser, 2021; Radenković *et al*., 2024). This intriguing behavior was our motivation to explore whether higher members of the phenylene family undergo similarly drastic changes in aromaticity when excited to their first triplet state. In this work, the electronic structure and magnetic properties of a series of phenylenes were examined in both singlet and triplet spin states (Figure 1).

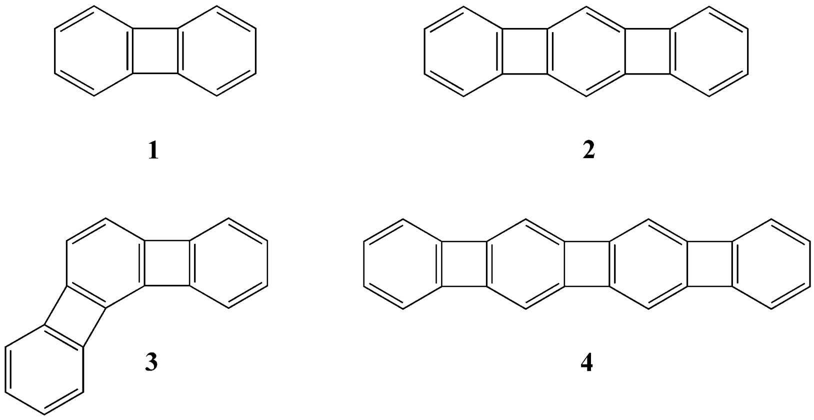

Figure 1. Studied systems

.COMPUTATIONAL METHODS

The structures of examined molecules were optimized in both spin states, singlet and triplet at the B3LYP level of theory in combination with the lanl2DZ basis set using the Gaussian 09 program (FRISCH *et al*., 2009). The calculation of vibrational frequencies validated that these structures correspond to a minimum on the potential energy surface.

Magnetically induced current densities were computed using the diamagnetic zero variant of the continuous transformation of origin of current density (CTOCD-DZ) method (KEITH and BADER, 1993a, 1993b; LAZZERETTI *et al*., 1994; LAZZERETTI, 2012) at the B3LYP/lanl2DZ level of theory. An external magnetic field was applied perpendicular to the molecular plane of the studied systems. The current densities were calculated and mapped 1 bohr above the molecular plane and visualized with the Paraview program (UTKARSH, 2015). In the current density maps, diatropic currents were depicted by counterclockwise circulations, while paratropic currents were shown by clockwise circulations.

RESULTS AND DISCUSSION

The structures of the examined molecules were optimized in the lowest singlet and triplet states. Figure 2 presents the obtained optimized structures. It was found that phenylenes with angular topologies **2** and **4**, adopt a D_{2h} geometry, similar to **1**, while **3** having an angular topology exhibits a C_{2v} symmetry. These molecules share identical symmetry groups in both spin states. Bond lengths for the studied systems are also included in Figure 2. In the triplet state, the carbon-carbon bonds on the perimeter of the four-membered rings are much shorter than in the singlet state. This observation implies that the four membered ring contribute more to cyclic conjugation in the triplet than in the singlet state. Figure 2 displays the adiabatic singlet-triplet energy gaps (ΔE_{ST}) for the studied systems obtained at the B3LYP/lanl2DZ level of theory. The ΔE_{ST} is calculated as the energy difference between the triplet (T_1) and singlet (S_0) state optimized structures. In all cases, ΔE_{ST} is positive indicating that all molecules are more stable in their singlet state, which is the ground state. It can be seen that larger phenylenes have a lower singlet-triplet energy gap than **1**. The ΔE_{ST} of linear **2** and **4** are by 40% and 60 %, respectively, reduced relative to biphenylene. In the case of **3**, the ΔE_{ST} is only 5 kJ mol^{-1} lower than for biphenylene. The molecular topology also influences stability. Since molecules **2** and **3** are isomers, their energy in both spin states can be directly compared. **3S** is 11.71 kJ mol^{-1} more stable than molecule **2S**, while in the triplet state **2T** is 65.61 kJ mol^{-1} more stable than molecule **3T**. The observed order of stability of **2S** and **3S** can be attributed to the reduction of antiaromatic character of the central ring, as reported in the work of Radenković and coauthors (RADENKOVIĆ *et al*., 2015).

Magnetically induced current densities were calculated for the studied systems in both spin states, and the obtained current density maps are shown in Figures 3, 5-7. In all studied systems there are weak paratropic circulations inside the hexagonal rings, opposing the more pronounced diatropic currents outside these rings. This behavior is a typical characteristic of aromatic rings. For instance, in benzene, the weak paratropic circulation inside the ring contributes to the deshielding effects at its center. However, the presence of such paratropic currents in hexagonal rings does not affect the overall conclusion about the aromatic characteristics of the hexagonal rings. In the singlet state of **1S**, paratropic currents in the four-membered ring are more pronounced than the diatropic currents observed in the six-membered rings. This goes in line with the results on previous studies of aromaticity of biphenylene (RADENKOVIĆ *et al*., 2015; GANTENBEIN *et al*., 2019).

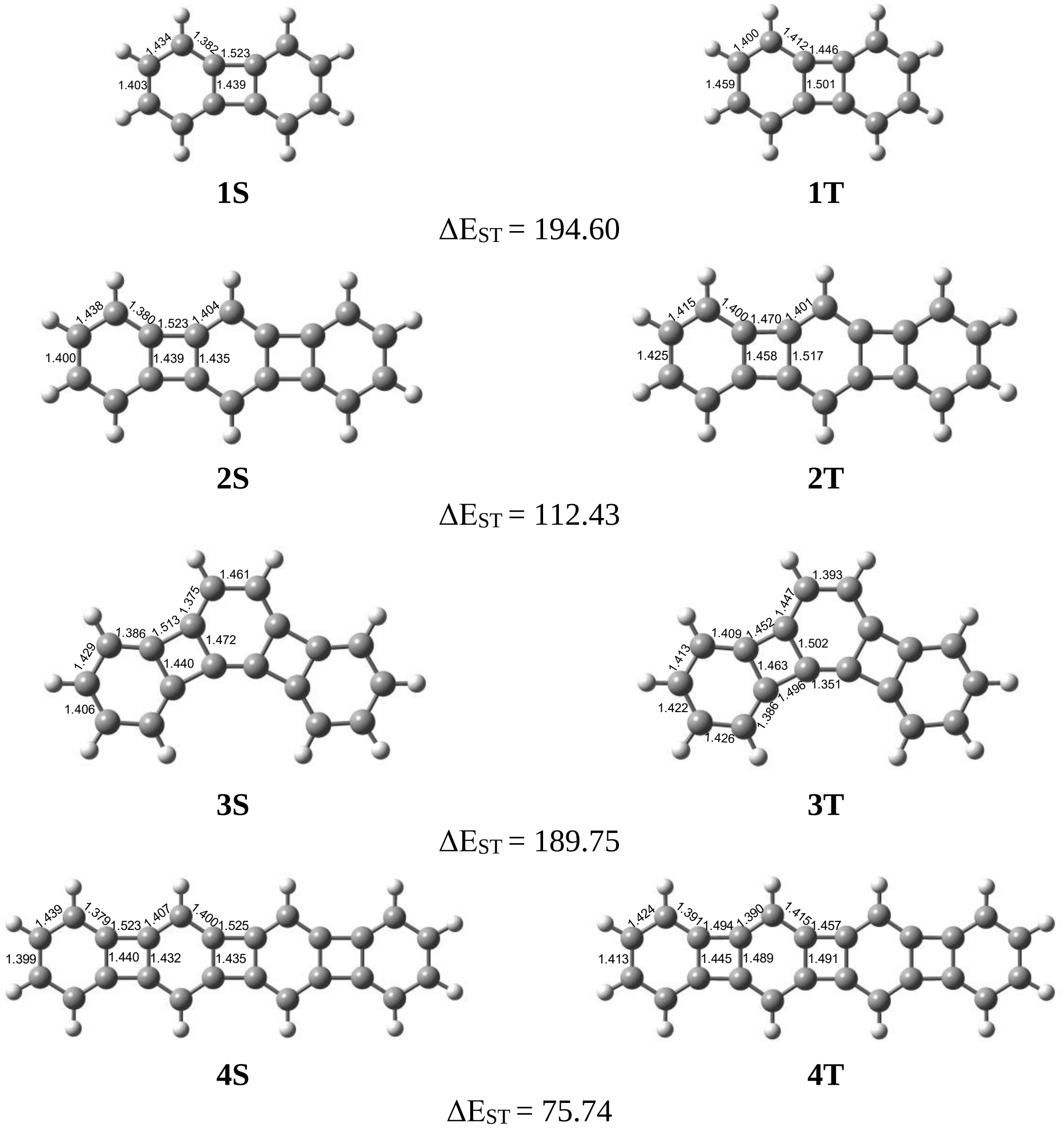

Figure 2. Optimized structures of studied molecules in the low-lying singlet (S) and triplet (T) states at the B3LYP/lanl2DZ level of theory. ΔE_{ST} represents the singlet-triplet energy gap obtained at the B3LYP/lanl2DZ level of theory in kJ mol^{-1}.

On the other hand, in triplet state **1T**, diatropic circulations are found around the four-membered ring and along the molecular perimeter. Aromaticity of the triplet state of biphenylene is not so much studied, but this result agrees with the chemical shielding tensors as reported in Plasser's paper (PLASSER, 2021). The CTOCD-DZ method can directly link induced current densities to electronic structure (Figure 4). As shown previously, the pronounced paratropic currents in the four-membered ring of **1S** come from the rotational transition from HOMO ($2b_{2g}$) to LUMO ($2b_{1g}$) level (Figure 4) (RADENKOVIĆ *et al.* 2015). In the triplet state of **1**, the highest singly occupied MOs α-$2b_{2g}$ and α-$2b_{1g}$ correspond to the HOMO and LUMO of the singlet state of this molecule. In **1T** there are only translational transitions: α-HOMO ($2b_{1g}$) to α-LUMO ($2a_u$), α-HOMO ($2b_{1g}$) to α-LUMO+1 ($3b_{3u}$), α-HOMO-1 ($2b_{2g}$) to α-LUMO ($2a_u$) and α-HOMO-1 ($2b_{2g}$) to α-LUMO+1 ($3b_{3u}$), and β-HOMO ($2b_{3u}$) to β-LUMO ($2b_{2g}$), β-HOMO ($2b_{3u}$) to β-LUMO+1 ($2b_{1g}$), β-HOMO-1 ($1a_u$) to β-LUMO ($2b_{2g}$) and β-HOMO-1 ($1a_u$) to β-LUMO+1 ($2b_{1g}$). These translational transitions have the main contribution to the diatropic current densities in molecule **1T** (Figure 4). In addition, the proposed transition diagram can explain the obtained current density maps calculated separately for α and β electrons (Figure 5). In **1T**, both α and β electrons induce diatropic currents of similar intensities.

1S **1T**

Figure 3. Current density maps calculated 1 bohr above molecular plane for **1S** (left) and **1T** (right).

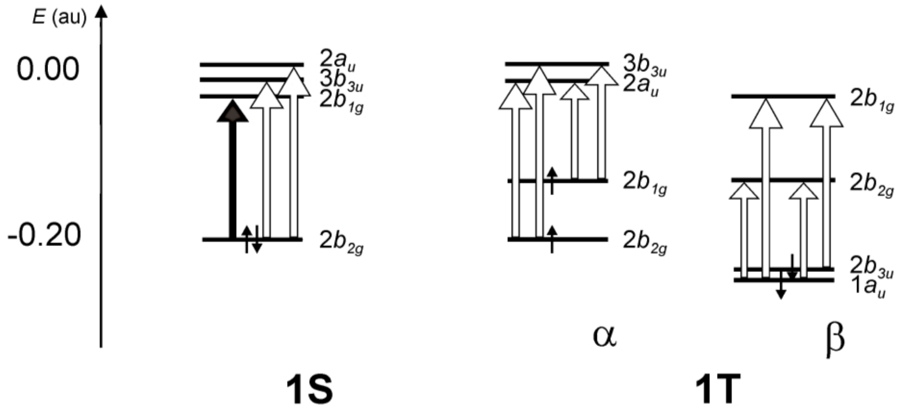

Figure 4. Frontier molecular orbitals and their energies (in au). Full (empty) arrows denote rotationally (translationally) allowed transitions.

α **β**

Figure 5. α- (left) and β- (right) electron current density maps calculated 1 bohr above molecular plane for **1T**.

In molecule **2S**, pronounced paratropic circulations are observed in the four-membered rings, while diatropic circulations within the six-membered rings are weakened in comparison to **1S** (Figure 6). In the triplet state, paratropic currents along four-membered rings are still present, but they are weakened compared to the S_0 state. Diatropic currents along the six-membered rings in **2T** are more pronounced than in **2S** (Figure 6). Also, the current density map of **2T** reveals that the diatropic currents are more conspicuous in the two terminal rings than in the central six-membered ring of the molecule. These findings suggest that the antiaromatic character of **2S** is reduced in **2T**.

In the case of molecule **3**, its magnetic response is very similar in both spin states (Figure 7), with pronounced paratropic currents along the four-membered rings and diatropic currents in the six-membered rings. These results correlate well with the singlet-triplet energy gaps and stability of molecules **2** and **3**. In particular, diatropic currents in six-membered rings in **3S** are more pronounced than in **2S**, which goes along with the finding that **3S** is 11.71 kJ mol^{-1} more stable than **2S**. On the other side, in the triplet state, diatropic currents are more pronounced in **2T**, but also paratropic currents are more pronounced in **3T** than in **2T,** which corresponds with the stability order of these molecules. Based on the limited number of molecules, it can be expected that in the singlet state phenylenes with angular constellation are more stable than linear, while in the triplet the order of stability is reversed.

2S **2T**

Figure 6. Current density maps calculated 1 bohr above molecular plane for **2S** (left) and **2T** (right).

3S **3T**

Figure 7. Current density maps calculated 1 bohr above molecular plane for **3S** (left) and **3T** (right).

In **4S**, the dominant circulations consist of paratropic currents within the four-membered rings (Figure 8). These paratropic circulations persist in the triplet state, although weakened (Figure 8). The diatropic circulations within the six-membered rings show the opposite behavior: they are weaker in **4S** and become more intensive in the triplet state **4T** (Figure 8). If one compares the circulations within the four membered rings in **1T**, **2T** and **4T**, it can be concluded these rings become more antiaromatic as the size of molecules increases.

4S **4T**

Figure 8. Current density maps calculated 1 bohr above molecular plane for **4S** (left) and **4T** (right).

CONCLUSIONS

In this research, magnetic properties of a series of phenylenes were studied in their singlet and triplet spin states. It was found that the molecular topology has a significant influence on the singlet-triplet energy gap of phenylenes. Higher members of the phenylene family having linear topology exhibit significantly lower singlet-triplet energy gap than biphenylene, while in those with angular topology the singlet-triplet energy gap is only slightly reduced relative to biphenylene. Our study confirmed that biphenylene can be described as an aromatic chameleon, displaying a drastic change of the aromatic character when going from the singlet state, where it exhibits both aromatic and antiaromatic properties, and its lowest excited T_1 state, where it becomes aromatic. On the other hand, other phenylenes studied in this work do not exhibit such radical change in aromaticity. In general, in the triplet excited state phenylenes tend to reduce the antiaromatic character and enhance aromaticity compared to the singlet state.

Acknowledgments

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