

Oxidized Forms of Antiaromatic Oligomers of Biphenylene

Abel Cárdenas,^[a] Francisco J. Ramírez,^[a] Yan Xia^[b], and Juan Casado*^[a]

^a Department of Physical Chemistry, University of Málaga, Andalucía-Tech (Campus de Teatinos s/n, 29071 Málaga, Spain)

^b Department of Chemistry, Stanford University, Stanford, California 94305, United States
casado@uma.es

Keywords: conjugated oligomers • biphenylene • oxidation • electronic and Raman spectroscopies

The importance of antiaromatic molecules in Chemistry and more recently in material science is rising. In the particular case of applications in electronics, the antiaromatic skeleton offers the favorable situation of high energy (i.e., destabilized) occupied molecular orbitals allowing to ease oxidation, doping or electron transfer to form conductive and photo-active substrates.

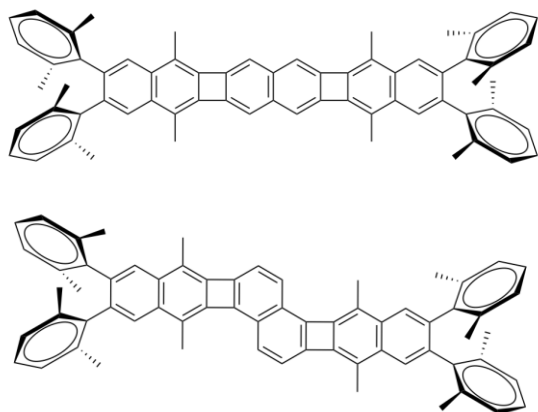


Figura 1. Oligomers of biphenylene with linear (top) and angular disposition of the fused rings.

In this contribution, we will show new recently synthesized polycyclic compounds based on fused antiaromatic bis-phenylene which have resulted to be stable enough to be spectroscopically characterisable^{1,2}. We study two different isomer such as shown in Figure 1, either with linear arrangement of the rings or with angular disposition. The research is based on the study of neutral and oxidized species of the two molecules. Oxidation was carried out by electrochemistry and the generated species were analyzed by UV-Vis-NIR absorption spectroscopy. On the other hand, the redox forms were formed by chemical oxidation on which the Raman spectra were also obtained. All results are interpreted and guided theoretically through the use of DFT quantum chemical calculations. We conclude that oxidation generates the radical cation and the dication species which have completely different electronic and molecular structures which are in consonance with the varying degree of antiaromatic character. Stable cations and dications of antiaromatic molecules are scarce and therefore unexplored. We contribute to this knowledge by studying these in oligomers of biphenylene.

References

- [1] Zexin Jin, Yew Chin Teo, Simon J. Teat, and Yan Xia. *J. Am. Chem. Soc.* **2017**, *139*, 15933-15939 .
- [2] Zexin Jin, Ze-Fan Yao, Kayla P Barker, Jian Pei, and Yan Xia. *Angew. Chem. Int. Ed.* **2018**, *57*, 10.1002/anie.201812581