

NEW ACCESS TO PLANAR BLATTER RADICALS: π EXTENDED HETEROCYCLES WITH HIGH SPIN DELOCALIZATION

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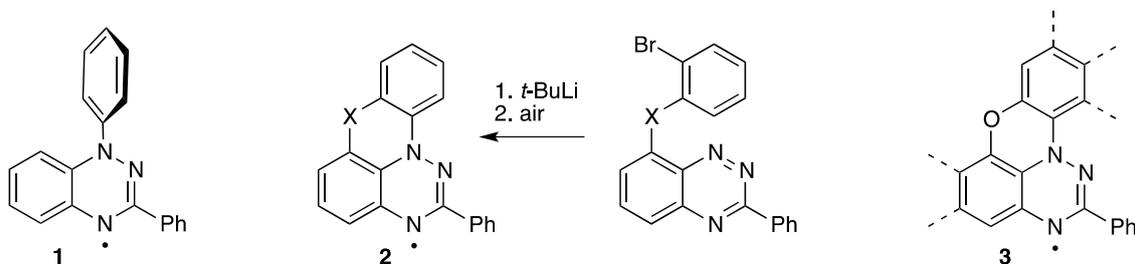
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Open shell organic molecules are becoming important structural elements of advanced functional materials, used in organic electronics and spintronics. In recent years the exceptionally stable, 1,4-dihydrobenzo[*e*][1,2,4]triazin-4-yl radical (e.g. the Blatter radical **1**) is gaining much interest due its high spin delocalization, narrow electrochemical window and low excitation energies. Therefore, development of synthetic methods leading to this radical system is of particular importance.

The general feature of all 1,4-dihydrobenzo[*e*][1,2,4]triazin-4-yl derivatives known to date is the presence of an aryl substituent at the N(1) position, such as Ph in the Blatter radical **1**, which due to steric interactions between the C(8)-H and C(*ortho*)-H forms a large dihedral angle θ (38–82°) with the heterocycle plane [1]. This high torsion angle between the π planes limits spin delocalization from the N(1) position and affects molecular packing in the solid state, which in turn, impacts magnetic properties of the solids [1]. Recently we demonstrated a simple method for the preparation of planarized Blatter radical **2** *via* intramolecular azaphilic addition to the triazine ring [2]. This planarization provides greater spin delocalization, changes packing in the solid state, and offers a new platform for designing of functional materials, such as liquid crystals [3].



Further studies demonstrated some limitations of the azaphilic addition method for the preparation of planar Blatter radicals, which prompted us to develop a new method, which provided access to planarized benzo[*e*][1,2,4]triazinyls **3** with extended π systems. Details of the method and properties (E-Chem, UV, EPR) of these new derivatives **3** supported with XRD and DFT results will be presented.

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[2] P. Kaszyński, C. P. Constantinides, V. G. Young, Jr. *Angew. Chem.* 2016, 128, 11315.

[3] M. Jasiński, J. Szczytko, D. Pocięcha, H. Monobe, P. Kaszyński *J. Am. Chem. Soc.* 2016, 138, 9421. Kapuściński, S.; Gardias, A.; Pocięcha, D.; Jasiński, M.; Szczytko, J.; Kaszyński, P. *J. Mater. Chem. C*, 2018, 6, 3079.