

Towards Organic Conductors - the Structure and Stability of Cyano-[n]-Radialenes and Their Dianions

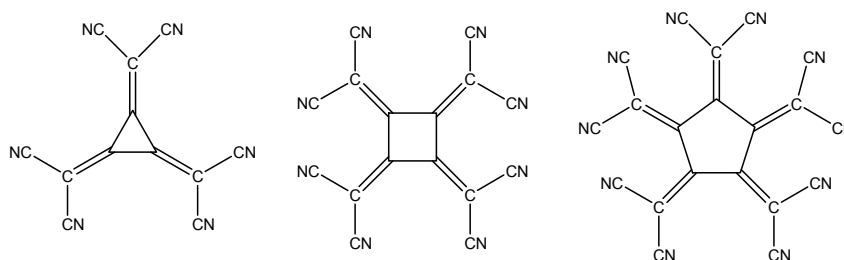
I. Despotović¹, Z.B. Maksić²

¹Quantum Organic Chemistry Group, Division of Organic Chemistry and Biochemistry, Ruđer Bošković Institute, Bijenička 54, 10000 Zagreb, Croatia; e-mail: idespoto@irb.hr

²Faculty of Science, Department of Physical Chemistry, The University of Zagreb, Horvatovac 102A, 10000 Zagreb, Croatia

It is well known that molecular anions play important role in organic chemistry and biochemistry. Special attention has been focused on dianions and higher anions lately, because they might prove very useful in storage and transport of electrons in the fields of photo-and/or electrically conducting polymers [1]. It follows that anions are likely to provide a bridge between organic chemistry and material science. It is therefore very important to get insight into the structure, stability and reactivity of mono- and higher anions.

In the present work we consider the structure and energetic properties of some neutral [n]-radialenes (n = 3, 4, 5) substituted by various groups and their mono- and dianions utilizing B3LYP/6-311+G* computational scheme [2]. It is found that cyano substitution enables efficient stabilization of dianions, which is higher the greater number of the CN groups is present. Hexacyano-[3]-radialene dianion is by 126 kcal mol⁻¹ more stable than the initial



neutral compound, and by 13.3 kcal mol⁻¹ than its monoanion. Other examined [3]-radialene dianions dissociate to monoanions, which are significantly more stable. The underlying principle governing strong stabilization of hexacyano-[3]-radialene dianion is highly effective anionic resonance, which distributes the excessive negative charge predominantly on the peripheral parts of the dianions. The latter is corroborated by examination of the bond lengths and redistribution of the electron density upon reduction and by calculation of the perpendicular NICS(1)_{zz} component of the magnetic shielding tensor calculated 1 Å above the center of the three-membered ring. Higher [n]-radialenes (n = 4, 5) involving larger number of CN substituents provide even more stable dianions [3], giving excellent candidates for polyanions which could make strong complexes with the electron accepting system and eventually yielding strong organic conductors or perhaps the organic “metals”. It is shown that hexacyano-[3]-radialene is strong oxidant in MeCN.

[1] M. Baumgarten, U. Müller, *Synth. Met.* 57 (1993) 4755-4761.

[2] I. Despotović, Z.B. Maksić, *J. Mol. Struct. THEOCHEM* 811 (2007) 313-322.

[3] To be published.