Polycyano Derivatives of Some Cyclic and Polycyclic Hydrocarbons Provide Stable Anions and Dianions – A Density Functional Study

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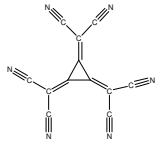
Introduction

Negatively charged molecular systems are ubiquitous in living species and play important role in chemistry, biochemistry and solid state materials. In contrast to these cases where anions are stabilized by the interactions with the environment, they are highly elusive in the gas phase due to electron repulsion. In our previous study we have shown that some cyanated radialenes (e.q. hexacyano-[3]-radialene) are capable of forming dianions in the gas phase.



EA_1 = 112,8 kcal mol^{-1}
EA_2 = 13,3 kcal mol^{-1}

Hexacyano-[3]-radialene

The aim of this study is to find stable anions and dianions of monocyclic and polycyclic organic compounds dessed by the CN and CF_3 goups using the concepts of anionic resonance and aromaticity.

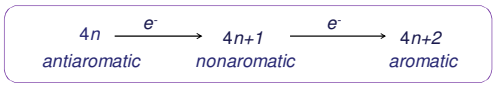
Methods

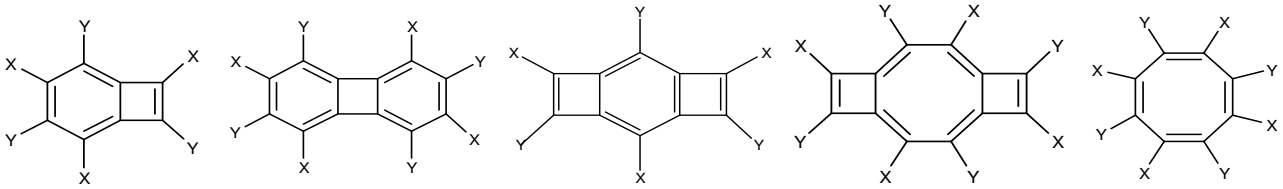
Electron affinity of tetracyanoethene was calculated using several teoretical models as denoted in Table below. Good agreement with experiment was obtained using BLYP/cc-pVTZ//B3LYP/6-311+G(d) method. Geometries were fully optimized with B3LYP/6-311+G(d) model and frequency analysis confirmed that the structures are minima on potential energy surface. Calculation of energy was done at equilibrium structures using BLYP/cc-pVTZ model. The radical anion species were treated by the unrestricted UBLYP/cc-pVTZ//UB3LYP/6-311+G(d) formalism. All calculations were performed using the Gaussian03 program.

model	EA / kcal mol^{-1}
B3LYP/6-311+G(d)	81.4
BLYP/aug-cc-pVTZ	75.1
B3LYP/cc-pVDZ	72.0
BLYP/cc-pVTZ//B3LYP/6-311+G(d)	72.3
G3	75.5
G3MP2	74.7
CCSD(T)/6-311+G(d)//experiment	63.9
experiment	73.1 ± 4.6

Results

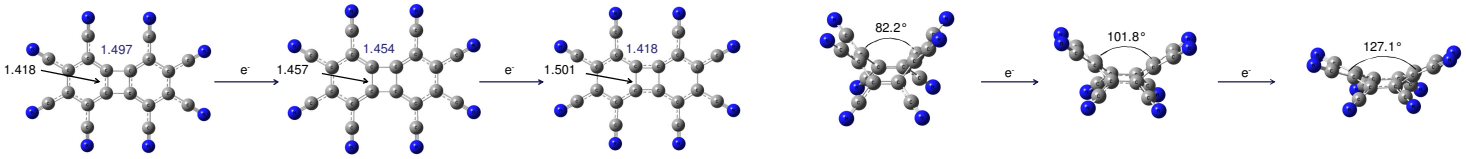
First (EA_1) and second (EA_2) electron affinities in kcal mol^{-1}.





X	Y	EA_1	EA_2	EA_1	EA_2	EA_1	EA_2	EA_1	EA_2	EA_1	EA_2
H	H	3.3	-116.5	4.1	-106.9	14.5	-94.6	11.3	-103.3	16.6	-89.3
CF_3	CF_3	68.6	-26.6	60.3	-65.7	72.0	-18.2	24.8	-22.2	60.2	-28.4
CF_3	CN	80.8	-15.8	79.2	-6.3	85.6	-10.4	84.2	-7.1	82.4	0.5
CN	CN	92.7	-4.2	91.5	**6.1**	94.1	**2.9**	97.8	**3.9**	100.9	**19.2**

Change of geometry upon electron attachment:



*octacyano*biphenylene (anion) (dianion) *octacyano*cyclooctatetraene (anion) (dianion)

Conclusion

All investigated antiaromatic compounds have shown to be stable upon electron attachment, having positive value of the first electron affinity. Substitution with electron withdrawing CF_3 and CN groups resulted in enhanced electron affinity, and this effect was more pronounced in case of CN group. Percyanated structures, except in case hexacyanobenzocyclobutadiene, have positive second electron affinities and can provide stable dianions. The highest value of second electron affinity was obtained for octacyanocyclooctatetraene which is 19.2 kcal mol^{-1}. Attachment of first and then second electron results in structural changes that indicate aromatic delocalization of electrons on the perimeter of the molecule. In case of systems which contain cyclooctatetraene part, there occurs a significant planarization of the central ring.