[8]RADIALENE: A DENSITY FUNCTIONAL THEORY COMPUTATIONAL INVESTIGATION OF THE THEORETICAL CONFORMATIONAL STRUCTURE OF THE MOLECULE

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Abstract

Density functional theory calculations at the ωB97X-D/6-311++G level of theory were performed on [8]radialene conformers, based initially on the reported conformational variability of a cyclo-octane ring and also employing additional initial trial geometries to further investigate the potential energy surface of [8]radialene. The most stable conformer was related to the "boat-boat" structure of cyclo-octane. No planar structures for the neutral molecule or for the singlet dication or singlet dianion (or for higher multiplicities) could be established as stable minima, and [8]radialene was computationally predicted to be a flexible, cyclic, non-conjugated poly-alkene. All structures were fully optimized and vibrational frequencies were performed on all molecules to ascertain that the molecules were stable minima on the potential energy surface.**

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Introduction

Radialenes[1] (Figure 1) are well-known, reactive alicyclic compounds, $C_{2n}H_{2n}$, $n \geq 3$, containing sp^2-hybridized carbon atoms in a ring of three or more carbon atoms, surrounded by exocyclic methylene groups attached to the central ring by C=C double bonds. Simple [*n*]radialenes are characterized by the ring size (*n*), and four simple radialenes from [3]radialene through [6]radialene have been synthesized: [3]radialene[2] in 1965 and 1966,[3] [4]radialene[4] in 1962 and 1963,[5] [5]radialene[6] in 2015, and [6]radialene[7] in 1977 and 1978.[8] The next member of the series, [7]radialene, has yet to be synthesized, but was the subject[9] of a brief density functional computational investigation, which demonstrated that the molecule was predicted to be flexible and was unlikely to be planar. However, no calculations on a hypothetical planar [7]radialene structure were reported.

Like [7]radialene, [8]radialene has not been synthesized. What little is known of [8]radialene is based upon the molecule being assumed to be a planar system, as was experimentally deduced for [3]radialene through [6]radialene. Theoretical investigations[10] have included an SCF-LCAO-MO study, using Hückel theory,[11,12] and calculation of resonance energies[13] based on π-bond energies. In addition, total π-electron energy indexes[14] have been used in developing an understanding of the stability of radialenes and the diamagnetic susceptibility exaltations in the molecules. A graph theoretical method[15] indicated that radialenes exhibit little conjugative stabilization, and a localized molecular orbital investigation demonstrated[16] the presence of little, if any, resonance energy in these molecules.

Unsubstituted [8]radialene, even if planar, is expected to be a simple cyclic molecule with isolated, non-conjugated, exocyclic double bonds, but the actual structure of the molecule has not been calculated or discussed. To fill that void and to address the question of whether [8]radialene could exist as a planar singlet dication or dianion (or of higher multiplicities), herein is reported a density functional computational investigation of the structures and properties of [8]radialene and the hypothetical planar structures of neutral [8]radialene and the dication and the dianion of the planar molecule, at the ωB97X-D/6-311++G** level of theory.

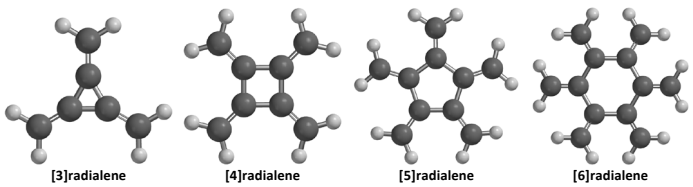


Figure 1. The four synthesized simple radialenes. Dark gray, carbon; light gray, hydrogen.

Computational Methods

The *Spartan* computational packages[17] were used to perform all calculations, and the range-separated hybrid generalized gradient approximation (RSH-GGA) density functional method[18] ωB97X-D/6-311++G** was applied to all species. This method is reported[18,19] to perform well for covalent species, such as were investigated herein. All molecules were fully optimized and vibrational frequencies were calculated to determine that no imaginary frequencies were present and that a stable minimum was located on the potential energy surface.

The initial trial geometries (ITGs) for the calculations were originally structured to be similar to the reported conformers[20] of cyclo-octane. In addition, ITGs with alternative structures were investigated to further address and investigate the potential energy surface of the molecule. Other ITGs with all atoms co-planar or with some or all of the methylene groups non-planar were also used in the calculations. For the examinations of the singlet dication and dianion, and higher multiplicities, partially and fully planar structures were used for the ITGs. No conformational analysis was performed on [8]radialene; the similarity of the calculated conformers to those of cyclooctane, and the small energy differences between them, indicated that a reasonable examination of the conformations of the molecule had been performed.

Results and Discussion

The calculated results for [8]radialene are reported, first for the neutral molecule, and then the hypothetical dianion and dica-

tion are briefly discussed.

Neutral [8]radialene

Calculations at the ωB97X-D/6-311++G** level of theory indicated that [8]radialene may exist as four distinct conformational isomers, and the properties of these conformations are listed in the Table. The identifiers for the conformers have been adopted from the similarity of the [8]radialene structures to the reported conformers[20] of cyclo-octane, and these conformers are illustrated in the Figure 2. Based on the differences in electronic energies of the four conformers, [8]radialene is expected to exist primarily as the boat-boat conformer. No planar conformations for [8]radialene could be identified, either as a singlet species or with two, four, six, or eight unpaired electrons.

Despite the obvious structural differences in the four conformers of [8]radialene, little variation was calculated to exist in the C–C single bond ranges or in the C=C double bond ranges, save for a slight lengthening of the C–C single bond length ranges in the higher energy conformers.

The C–C bond lengths[21] in gas-phase cyclo-octane, however, average 154.0 pm, which is significantly longer than the C–C bond length ranges calculated herein for [8]radialene. Of course, that average bond distance in cyclo-octane represents sp^3–sp^3 carbon-carbon bonds, while the bonds in [8]radialene are sp^2–sp^2 carbon-carbon single bonds. While none of the synthesized parent [*n*] radialenes (*n*=3–6) have lifetimes long enough for structural studies, structural studies[22] on the symmetrically-substituted planar hexaethyl[6]radialene and on the symmetrically-substituted chair-shaped[23] hexamethyl[6]radialene have been successful. The exocyclic C=C double bond length ranges in the former were found to be 133.6–134.7 pm, and in the latter 133.2–133.7 pm, while the C–C single bond length ranges for the former were 148.0–150.0 pm and in the latter 149.3–149.5 pm. These experimentally-derived distances compare well with the computational distances calculated for the [8]radialene conformers.

Table. Electronic energies and selected structural properties of the four conformers of [8]radialene

conformer[a]	electronic energy (a.u.)	Δ[b]		bond ranges (pm)[c]	
		a.u.	kJ/mol	C–C	C=CH_2
"boat-boat"	-619.108459	0.000000	0.00	149.1–149.2	133.4–133.6
"tub"	-619.105410	0.003049	8.01	149.1–149.8	133.3–133.8
"boat-chair"	-619.104527	0.003932	10.3	148.2–150.2	133.1–133.5
"twist-chair-chair"	-619.103608	0.004851	12.7	149.2–150.1	133.1–133.5

[a]See Figure 2. [b]Relative energy differences between the most stable conformer and the higher energy conformers. [c]C–C, single bond distance ranges for the eight-membered ring; C=CH_2, double bond distance ranges to the exocyclic methylene groups.

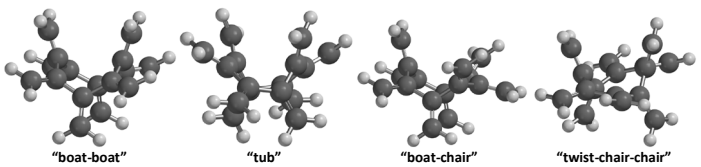


Figure 2. The four conformers of [8]radialene calculated to be stable minima on the [8]radialene potential energy surface. Dark gray, carbon; light gray, hydro-

[8]radialene dication and dianion

Despite prior assumptions of planarity made for [8]radialene (*vide supra*), the molecule, if synthesized, would likely have a boat-boat conformation similar to the boat-boat structure observed for cyclo-octane. However, what of either a dianion or a dication? In the former case, the hypothetical planar molecule could be thought to contain an eight-membered ring containing ten π-electrons, while in the latter, the eight-membered ring could be assumed to contain six π-electrons; in either case, an argument for "4*n*+2" Hűckel aromatic character might be advanced (with the strong caveat that with the central ring containing either ten or six paired π-electrons, the ring would be surrounded by up to eight exocyclic [$\cdot CH_2$] radicals, and the molecule could have up to eight unpaired electrons). For comparison, the uranocene sandwich molecule[24] contains two planar di-anionic cyclo-octatetraene rings (when, during "electron-counting", the uranium center is given a charge of 4+ to maintain the aromatic character of the cyclooctatetraene with ten electrons) bound to a uranium(IV) moiety, yet cyclooctatetraene exists in a tub conformation in the solid state[25] and in the gas-phase.[26]

Unfortunately, calculations beginning with singlet, neutral ITGs for [8]radialene that were completely planar or contained a planar eight-membered ring and non-planar methylene groups could not be optimized without multiple imaginary vibrational frequencies. Similar calculations for neutral molecules with higher multiplicities also could not be optimized. Attempts to locate systems containing planar rings for either the singlet dianion or singlet dication, again with ITGs which were either completely planar or which contained a planar eight-membered ring and non-planar methylene groups were unsuccessful. Similar calculations for the dianion or the dication with higher multiplicities also could not be optimized.

The electronic energies for those completely planar [8]radialene molecules that converged, disregarding the multiple imaginary frequencies (in parentheses), and the (significantly greater) positive energy differences with respect to the lowest energy non-planar [8]radialene conformer, were as follows:

planar [8] radialene, neutral (8) -618.827569 a.u. +737.5 kJ/mol
planar [8]radialene, dication (8) -618.141631 a.u. +604.8 kJ/mol
planar [8]radialene, dianion (8) -618.740887 a.u. +965.1 kJ/mol

Note that a comparison of the dication or the dianion to the neutral "boat-boat" conformer is not correct, as the molecule does not have the same number of electrons as does the dication or dianion. The energy differences are provided here as an approximate benchmark. Based on these large positive energy differences, it is unlikely that either the dication or the dianion would exist independently, but the potential for complexation of the dication or dianion to a metal center remains.

Conclusions

Based upon calculations at the ωB97X-D/6-311++G** level of theory, neutral [8]radialene is predicted to adopt a non-planar twisted boat-boat conformation with bond length ranges in line with the previous calculations for [7]radialene and for structural

studies of symmetrically-substituted [6]radialenes. Planar structures for the neutral molecule, or for the dianion or dication could not be optimized, although the possibility remains that the molecule could adopt a planar structure if complexed to an appropriate metal atom moiety, as is the case for uranocene. This possibility remains open for further investigations.

Supplementary Material

Supplementary material includes final atomic coordinates for all optimizable systems, and is available upon request from the corresponding author.

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