

## Open Shell Dianions Likely To Be Stable in the Gas Phase with Respect to Autoionization

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**Abstract:** We address the challenge set by Dreuw and Cederbaum [Dreuw, A.; Cederbaum, L. S. *Chem. Rev.* **2002**, *102*, 181–200] to develop a set of “small” open shell stable dianions. We offer two families of such species, based on a central diradical center with attached anionic sites. Both families achieve dianion stabilization through alternating zones of positive and negative charge. First, quasi-linear systems such as  $\text{NB}(\text{C}_2)_n\text{--Q--}(\text{C}_2)_n\text{BN}$  become diradical dianions stable to autoionization in two cases: (a) for Q a divalent (carbene) carbon when  $n$  is two or greater and (b) for Q a  $\text{C}_4$  ring diradical when  $n$  is one or greater. Second, carbenes with certain anionic aromatic substituents can be stable with respect to autoionization.  $\pi$ -Acid substituted carbenes ( $\text{A}_2\text{Q}$ ) have triplet ground states generally. If A is cyclopentadienyl anion stabilized by cyano substitution, the resulting triplet dianion is stable with respect to autoionization. In bisphenyl carbenes the triplet is relatively stabilized when ortho substituents force the system toward  $D_{2d}$  symmetry. The dianion of bis(orthochlorophenyl) carbene produced by para-substitution with BN retains the triplet preference and is stable with respect to autoionization. These results obtained first by density functional calculations in a small basis, B3LYP/6-31G(d), are confirmed and extended by RMP2 and CCSD calculations in a more flexible basis, 6-31+G(d). DFT has a systematic bias against systems with excess electrons, which is paradoxically a virtue in the screening of candidate dianions since the DFT calculation does not make false predictions of stability.

### Introduction

It seems quite implausible that small dianionic species would persist without stabilizing effects of a medium—one would think that the intense repulsion arising from the excess negative charge would preclude any extended lifetime. Nonetheless the study of small dianions long-lived in the gas phase has advanced strikingly both in experimental and theoretical directions since dianionic alkaline earth tetrahalides such as  $\text{MgF}_4^{2-}$  were first predicted to be stable to electron loss and dissociation in the gas phase.<sup>1</sup> Now the types of dianions known to be stable in these ways have come to include the linear clusters of alternating charges studied by Simons and Boldyrev<sup>2</sup> and also include a

substantial number of variants on the center-ligand sphere in which concentric shells alternate in charge as established by Dreuw and Cederbaum.<sup>3</sup> Other means of stabilization of dianionic systems are known, the simplest of which are the separation of negatively charged sites<sup>4</sup> or the dispersal of the excess charge over large volumes. Substituent-stabilized aromatic dianionic systems have been characterized computationally, most notably derivatives of  $\text{B}_6\text{H}_6$ , e.g. the *closo*  $\text{B}_6(\text{CN})_6^{2-}$  devised by Zink, Dreuw, and Cederbaum.<sup>5</sup> All these dianionic systems are closed shell singlet species. Are there also stable open shell dianionic species? It seems unlikely that the study of the triplet states of those dianions known to be stable in their closed shell ground states would

be rewarding, since the triplet would be an excitation from a ground state itself already marginal in stability. Stable dianionic species with open shell ground states might be expected to be even more elusive than stable closed shell dianionic systems, since few chemically stable neutral systems have open shell ground states. The task of devising a “small” open-shell dianionic molecule stable to autoionization over the transit time in a mass spectrometer has been set.<sup>6</sup> It is among those few systems which have open shell ground states, specifically carbenes and small rings, that we search. They can serve as cores of molecules bearing substituents capable of accommodating excess charges. Here we offer some triplet ground-state systems which according to our computational modeling should be stable with respect to autoionization.

## Computational Methods

We employ B3LYP/6-31G(d) calculations throughout this work, as implemented in the Gaussian 03 suite.<sup>7</sup> This model chemistry makes feasible the investigation of the large systems at issue here but is open to objection on two grounds. The basis seems inadequate to represent loosely bound electrons, lacking diffuse functions. The density functionals now available are not capable *in principle* of representation of anions.<sup>8</sup> Their failure to cancel self-repulsion of electrons would be expected to produce a systematic underbinding of excess electrons. Careful investigations of electron affinities of neutral systems show that the case *in practice* is not bleak; accuracies of ca. 0.2 eV are routine for B3LYP in even modest basis sets.<sup>9</sup> It seems likely that a fortunate error cancellation is at work. The finite basis (lacking continuum or even extensive diffuse components) keeps weakly bound electrons localized at a molecule even when autoionization should be spontaneous. The finite-basis flaw produces a bias in opposition to the DFT underbinding and the errors may tend to cancel in the final estimate of stability of the anion. No such empirical reassurance is available for the electron affinity of monoanions (i.e., the ionization energy of dianions), which are less thoroughly studied. However the choice of B3LYP/6-31G(d) as a model chemistry for closed shell dianions has been tested by comparison to R(O)HF and MP2 calculations in more flexible basis sets and has proved to be a useful semiquantitative guide to the stability of singlet dianions<sup>10</sup> and also to the stability of neutral triplet carbenes.<sup>11</sup> In the following discussion we employ MP2/6-31+G(d) and in some cases CCSD/6-31+G(d) model chemistries, especially to provide an independent view of the dianions predicted in the simplest DFT calculations to be stable with respect to autoionization.

## Design Stratagem

The principles guiding the design of stable dianions, mentioned above and summarized in Table 1, have produced a variety of closed shell singlet dianions stable both with respect to autoionization and unimolecular dissociation and are helpful in the search for an open shell stable dianion. Our design focuses on linear and quasi-linear systems, with the general three-fragment structure anion site—spacer—open-shell center—spacer—anion site. The spacers are always CC

**Table 1.** Ways To Stabilize Molecular Dianions

mode of stabilization	example
separation of charges	long-chain dicarboxylates <sup>4</sup>
alternating charges (spherical shells)	MX <sub>4</sub> , O(BN) <sub>4</sub> <sup>20</sup>
alternating charges (linear)	XXMX <sub>2</sub> <sup>2</sup>
aromaticity or closed-shell stabilization and substituent effects	B <sub>6</sub> H <sub>6</sub> and B <sub>6</sub> (CN) <sub>6</sub> <sup>6</sup>

fragments, the anionic sites are C<sub>2</sub>, BN, or BeO, and the open shell centers are carbene carbons C or cyclobutyl diyl rings CB, which have figured largely in the search for high spin building blocks for magnetic materials. We also investigate the properties of aryl-substituted carbenes, where the anionic site may be a substituent on an aryl ring or the cyclopentadienyl anion. In each type of systems we can find a candidate for the sought open shell dianion stable with respect to autoionization. In this report we define adiabatic ionization energies of the dianions but do not explore details of the dissociation pathways which produce product monoanions. Neither do we explore the repulsive coulomb barrier,<sup>12</sup> which can lend an extended (tunneling) lifetime to metastable dianions.

## Linear Systems I: Carbene Core R—(CC)<sub>n</sub>—C—(CC)<sub>n</sub>—R

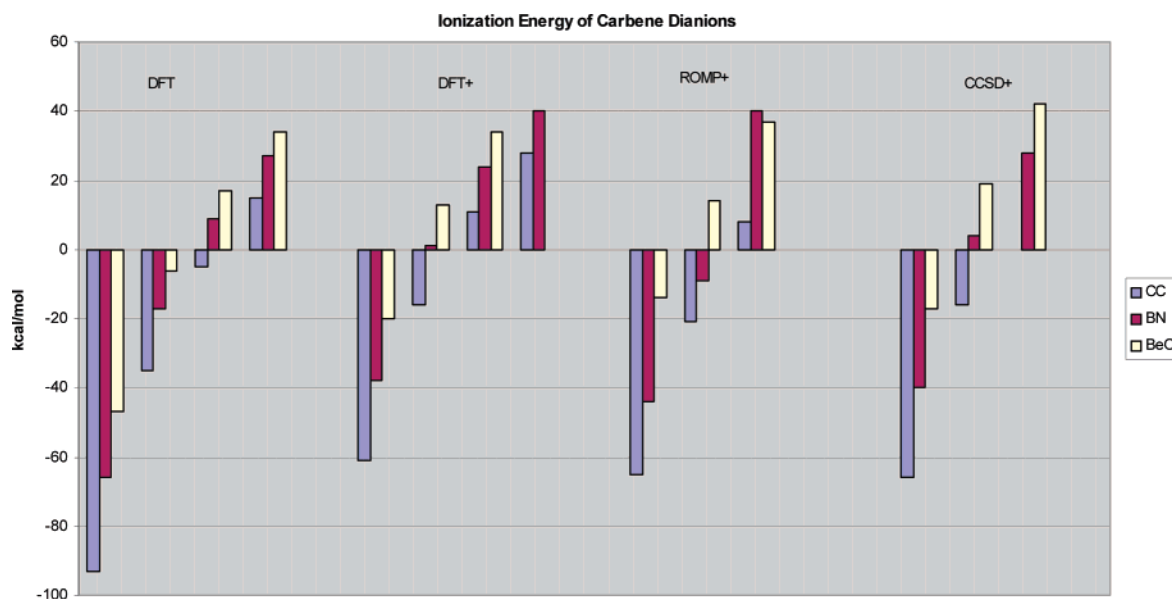
The simplest X-core-X system is derived from the family of carbenes NC(C<sub>k</sub>)C(C<sub>k</sub>)CN studied by Belbruno et al.<sup>13</sup> and Blanksby et al.<sup>14</sup> In analogy to these well-characterized systems we consider the isoelectronic dianions NB—(C<sub>2</sub>)<sub>n</sub>—C—(C<sub>2</sub>)<sub>n</sub>—BN and variants with anionic sites CC and BeO. Watts and Bartlett<sup>15</sup> studied carbon chain dianions by CCSD methods and suggest C<sub>9</sub><sup>2-</sup> may be stable with respect to autoionization. Calabrese et al.<sup>16</sup> reported beam evidence for C<sub>n</sub><sup>2-</sup>, *n* = 7–13, with the species with *n* = 11 most abundant but clear signals from dianions with *n* = 7, 9, and 13. Table 2 shows the computed crossover from autoionizing to stable dianion as *n* increases. For all *n*, BeO is the most effective in stabilizing excess negative charge and C<sub>2</sub> is least effective. As the size of the system increases the dianion takes on diradical character. Only for the smallest system is the closed shell singlet favored over the broken symmetry single-determinant unrestricted open shell “singlet.” That wave function has an expectation value of *S*<sup>2</sup> near 1.0, typical of an equal admixture of singlet and triplet states. For systems with *n* greater than zero the triplet state is favored over a broken symmetry open shell “singlet” state by a small amount. In the limit characteristic of diradicals, i.e., identical geometry and orbitals in singlet and triplet states, we can take this energy difference to be twice the singlet–triplet gap. While no system we studied reached this limit, systems with the BeO anionic site are closest.

We expect enhanced stability of the dianion as *n* increases since the mean separation between anionic sites increases. When *n* = 3 all dianionic species are stable relative to the doublet monoanion produced by autoionization. The DFT calculation predicts triplet ground states for all dianions; the energy differences between symmetry breaking “singlet” and unrestricted triplets approach about 5 kcal/mol. This leads us to estimate the singlet–triplet gap as about 10 kcal/mol.

**Table 2.** Favored State of Dianions and Their Stability Relative to the Anion Produced by Autoionization, for  $R-(C_2)_n-C-(C_2)_n-R^a$ 

$n$ -value	0	0	0	1	1	1	2	2	2	3	3	3
sink	CC	BN	BeO	CC	BN	BeO	CC	BN	BeO	CC	BN	BeO
B3LYP/6-31G(d)	-93	-66	-47	-35	-17	-6	-5	9	17	15	27	34
B3LYP/6-31+G(d)	-61	-38	-20	-16	1	13	11	24	34	28	40	
ROMP/6-31+G(d)	-65	-44	-14	-21	-9	15	8	40	37			
CCSD/6-31+G(d)	-66	-40	-17	-16	4	19	x	28	42			

<sup>a</sup> Adiabatic ionization energies for carbene-based systems, in kcal/mol. Positive values designate endothermic ionization energies and indicate that the triplet dianions are stable with respect to autoionization.

**Figure 1.** Adiabatic ionization energies of carbene-based dianions in kcal/mol. Labels: DFT = B3LYP/6-31G(d), DFT+ = B3LYP/6-31+G(d), ROMP+ = ROMP/6-31+G(d)/UMP2/6-31+G(d), CCSD+ = CCSD/6-31+G(d)/UMP2/6-31+G(d).

While it is the case that the terminal anionic sites each bear a local negative charge near the unit value, the interior is not uniformly neutral. Rather there is a marked charge alternation in the CC chain which might be considered a polarization in response to the marked negative charges at the termini. This would complicate, but not preclude, estimates of the coulomb barrier which rely on modeling the charges as well separated.<sup>17</sup>

The patterns discernible in the B3LYP/6-31G(d) model chemistry are also present in the alternative (and, in principle, superior) ROMP2/6-31+G(d)/UMP2/6-31+G(d) and CCSD/6-31+G(d)/UMP2/6-31+G(d) calculations. There is considerable spin contamination in the UMP2 results; ROMP2 (for which one has a pure spin state) gives predictions closely comparable with UCCSD. There are however significant (though not surprising) differences in the pictures provided by the density functional and wave function methods. In keeping with the expected underbinding of excess electrons expected for density functional methods, the stability of the dianions relative to monoanions is always underestimated by B3LYP compared to ROMP and CCSD, by roughly 20 kcal/mol. This is far from the accuracy claimed for electron affinities of medium-sized neutral molecules, 0.2 eV. One might kindly say that the small-basis DFT results are “conservative”; B3LYP/6-31G(d), systematically biased against excess charge, produces no “false positive” predictions of dianion stability. Every DFT prediction of dianion stability

made by B3LYP/6-31G(d) is confirmed by ROMP/- and CCSD/6-31+G(d) estimates. However a small-basis DFT-based survey will overlook some dianions that may be stable with respect to autoionization. We note ROMP/6-31+G(d) and CCSD/6-31+G(d) calculations suggest that OBe(CC)C-(CC)BeO dianion might be stable relative to the monoanion, while B3LYP/6-31G(d) makes the opposite prediction. The obvious step of enhancing the basis set used in the DFT calculations has a strikingly good effect. The results of B3LYP/6-31+G(d) description of the carbene-based systems are in surprising agreement with the wave function based and correlation-corrected ROMP and CCSD calculations in the same basis. It does not appear that the systematic flaw of the functionals in use, which should produce systematic underbinding of excess electrons, has any practical impact here. Figure 1 shows the systematic error in B3LYP/6-31G(d) relative to calculations in the basis augmented with diffuse functions, i.e., 6-31+G(d). A general consistency obtains among B3LYP, ROMP, and CCSD calculations in this basis.

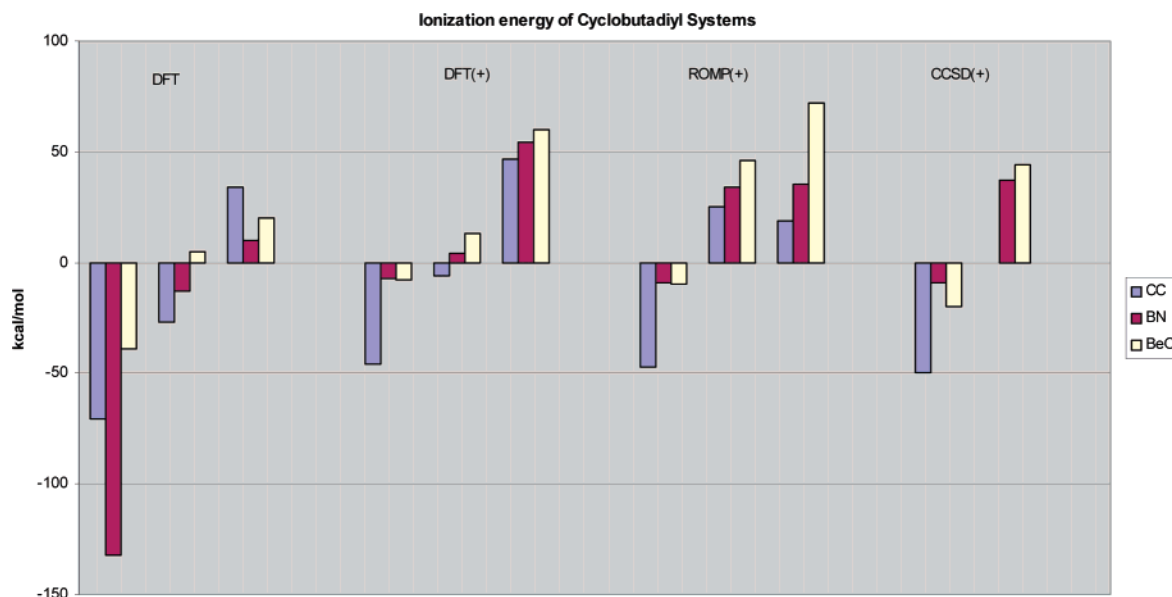
## Linear Systems II: Cyclobutadiyl Core, $R-(CC)_n-CB-(CC)_n-R$

Some small systems in the substituted cyclobutadiyl dianion family show imaginary frequencies in  $D_{2h}$ , but larger systems have a  $D_{2h}$  minimum energy structure. For the sink BeO the triplet and “singlet” dianion for  $n = 1$  is predicted in B3LYP/

**Table 3.** Favored B3LYP/6-31G(d) State of Dianions and Their Stability Relative to the Anion Produced by Autoionization, for  $R-(C_2)_n$ -Cyclobutadiyl- $-(C_2)_n-R^a$ 

$n$ -value	0	0	0	1	1	1	2	2	2
sink	CC	BN	BeO	CC	BN	BeO	CC	BN	BeO
B3LYP/6-31G(d)	-71	-132	-39	-27	-13	5	34	10	20
B3LYP/6-31+G(d)	-46	-7	-8	26	4	13		54	60
ROMP/6-31+G(d)	-47	-9	-10	25	34	46	19 <sup>b</sup>	35 <sup>b</sup>	72 <sup>b</sup>
CCSD/6-31+G(d)	-50	-9	-20	x	37	44			

<sup>a</sup> Adiabatic ionization energies for cyclobutadiyl-based systems, in kcal/mol. Positive values designate endothermic ionization energies and indicate that the triplet dianions are stable with respect to autoionization. <sup>b</sup> The ROMP entries for  $n = 2$  refer to ROMP/6-31+G(d)/UHF/6-31+G(d).

**Figure 2.** Adiabatic ionization energies of cyclobutadiyl-based dianions in kcal/mol. Labels: DFT = B3LYP/6-31G(d), DFT+ = B3LYP/6-31+G(d), ROMP+ = ROMP/6-31+G(d)/UMP2/6-31+G(d), CCSD+ = CCSD/6-31+G(d)/UMP2/6-31+G(d).

6-31G(d) to be stable with respect to autoionization, as is the case for all dianionic species with  $n = 2$ . (See Table 3.)

The cyclobutadiyl system is antiaromatic and thus should either prefer an open shell ground state or spontaneously distort from 4-fold symmetry to achieve a stable closed shell state. The cyclobutadiyl system could perhaps favor the open shell singlet, which is an intrinsically multiconfigurational state and hence not strictly representable by a UHF symmetry breaking single determinant wave function. Neither is this state strictly represented by the analogous broken symmetry DFT calculation reported here. The observed preference for this broken-symmetry singlet over the triplet in the larger systems is an interesting outcome, worth testing by independent methods. In these systems we are close to the diradical limit for which the energy gap between UHF "singlet" and triplet is about twice the value predicted by the simplest two-configuration representation of the open-shell singlet.

Ab initio MP2/6-31+G(d) (and where available, CCSD/6-31+G(d)) representations of the cyclobutadiyl-based dianions confirm that dianions with  $n = 2$  are stable with respect to autoionization and also suggest that triplets with  $n = 1$  are stable with respect to autoionization. These methods place the triplet state lower than any open or closed shell singlet. Unrestricted MP2 states are again strongly spin-contaminated—projection makes a large difference in energy

and even increases the expectation value of  $S^2$ . Owing to the erratic behavior of the dianion—monoanion energy gaps predicted by unrestricted and projected-unrestricted MP2, we rely on ROMP results. These are assured to have pure spin states and produce energies consistent with available CCSD values. For the largest cyclobutadiyl-based systems ( $n=2$ ) we used UHF-optimized geometries rather than the UMP2-optimized structures, the basis for all other estimates. Comparison for the  $n = 2$  BN system was possible and showed that although there are appreciable differences in details of the geometry, the dianion—monoanion energy gaps are similar. The mean difference between wave function results in the augmented basis and B3LYP/6-31G(d) results for the dianion—monoanion energy gap is systematic (DFT underbinds dianions) and large (roughly 40 kcal/mol). Enhancing the basis set employed in DFT to 6-31+G(d) does bring some improvement, but this is not so impressive as what we found for the carbene-based systems. We may observe that DFT estimates of stability of dianions in this structural class are conservative regardless of the basis, in the sense that all predictions of dianion stability made in DFT are confirmed by ab initio methods. As we found for the carbene systems, DFT does not produce "false positives". Figure 2 displays estimates of the adiabatic ionization energies and shows the systematic error in B3LYP/6-31G(d) estimates relative to those obtained in an augmented



**Table 4.** Bisaryl Dianions in B3LYP/6-31G(d)<sup>a</sup>

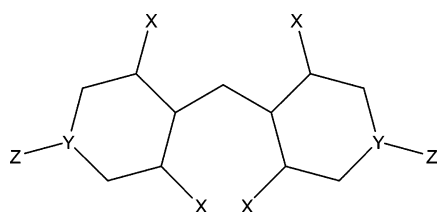
X	Y	Z	singlet angle	triplet angle	doublet angle	AEA kcal/mol
H	B	H	121	144	144	-68
H	B	F	121	143	143	-71
H	B	CN	121	146	143	-39
H	C	BN	120	142	139	-7
o-Cl	B	H	121	158	157	-42
o-Cl	B	F	129	154	155	-46
o-Cl	B	CN	132	178	159	-17
<b>o-Cl</b>	<b>C</b>	<b>BN</b>	<b>133</b>	<b>170</b>	<b>180</b>	<b>8</b>
perfluoro	B	F	124	144	145	-47
Candidate in ROMP2/6-31+G(d)//UHF/6-31+G(d)						
<b>o-Cl</b>	<b>C</b>	<b>BN</b>		<b>156</b>	<b>155</b>	<b>22</b>

<sup>a</sup> The entry in bold identifies an open shell dianion which is stable with respect to autoionization.

6-31+G(d) basis. For this system, in contrast to the perfectly linear carbene-based dianions, B3LYP underbinds dianions relative to ROMP and CCSD even in the augmented basis.

## Bisaryl Carbenes

Bisphenyl carbenes are known to favor a triplet ground state,<sup>18</sup> so we constructed a series of dianions following the structural theme (aryl ring)—methylene—(aryl ring). We transformed the known neutral bisphenyl species to dianions by substituting B for C in the ring or by attaching a BN fragment at the para position. (See Table 4.)



The longest-lived bisaryl triplets are ortho-substituted with bulky CF<sub>3</sub>, Br, or Cl groups.<sup>19</sup> This substitution has the effect of opening the central angle and orienting the ring systems orthogonal to one another. Attending this structural change is a shortening of the central CC bonds and considerable delocalization of the spin into the aryl rings. Fluoro-substitution (even perfluorination) is ineffective in inducing this major structural change, but ortho-chloro substitution accomplishes it. In the most extreme cases with near-linear

central CCC angles, these systems approach the diradical limit, and an open shell singlet is close in energy and structure to the ground state triplet. The only system in this structural class we have found thus far to be autoionization stable according to B3LYP/6-31G(d) is such a linearized diradical, bis(2,6-dichloro-4-BN-phenyl) carbene. The DFT prediction is confirmed by ab initio estimates in ROMP2/6-31+G(d)//UHF/6-31G(d). The geometry differences between DFT and ab initio representations of these bisaryl systems have been discussed elsewhere.<sup>11</sup>

## Biscyclopentadienyl Carbenes

The family of bisaromatic carbenes A—C—A could contain a dianion if the six- $\pi$ -electron cyclopentadienyl anion is used as A. The unsubstituted species is liable to autoionization and has a closed shell singlet ground state. (See Table 5.) The perfluorinated dianion likewise has a closed shell ground state, but the monoanion is still more stable. Replacement of fluorine by the  $\pi$ -acid CN produces a triplet dianion stable with respect to autoionization. This is confirmed by an approximate ab initio calculation using the model chemistry MP2/6-31+G(d)//UHF/6-31+G(d). Spin contamination is minor in these systems. Related species bis(2,5-dicyanocyclopentadienyl)carbene dianion and bis(3,4-dicyanocyclopentadienyl)carbene dianion are not predicted to be autoionization-stable in this model chemistry.

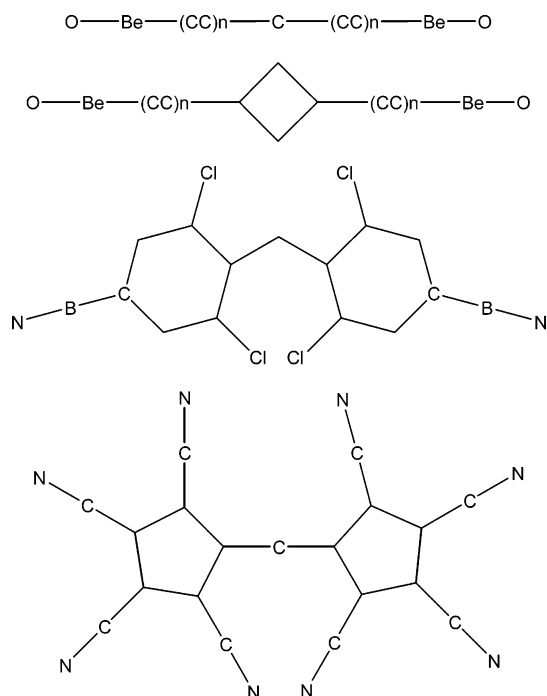
The fully CN-substituted system has a broken symmetry UB3LYP/6-31G(d) “singlet” (expectation value of  $S^2 = 1.0297$ ) at -1161.938014 Hartrees, about 4.1 kcal/mol below the triplet. Its geometry is similar to that of the triplet (1.3508 Å, 179.9 deg), so we may consider the stable open shell species to have a degree of diradical character, comparable with other long-lived triplet carbenes.

## Conclusions

We present three kinds of open shell autoionization stable dianions, based on a simple structural theme. Chart 1 illustrates the structural types of the stable dianions: (1) systems built from diatomic anion centers connected by the methylene triplet linker; (2) systems built from diatomic anion centers connected by the cyclobutadienyl open shell singlet linker; and (3) systems built from diatomic anion centers connected by the bisphenyl carbene triplet linker.

**Table 5.** Variations on the Structure Cyclopentadienyl Anion—Carbene Carbon—Cyclopentadienyl Anion

substituent	(unsubstituted)	perfluoro	percyano	percyano
model chemistry	B3LYP/6-31G(d)	B3LYP/6-31G(d)	B3LYP/6-31G(d)	ROMP/6-31+G(d)//UHF/6-31+G(d)
Dianions				
central bond length	1.4387	1.4255	1.4059	
central angle	120	124	124	
Triplet				
central bond length	1.4118	1.4004	1.3592	1.4068
central angle	144	144	177	144
Monoanion Doublet				
central bond length	1.3727	1.3690	1.3592	1.3694
central angle	143	145	177	147
gap (kcal/mol)	-102	-47	14	14

**Chart 1.** Structural Types of Triplet Dianions Stable with Respect to Autoionization

The triplet dianion biscyclopentadienyl methylene also appears to be stable with respect to autoionization, if the cyclopentadienyl ring is fully substituted by the stabilizing CN  $\pi$ -acid.

The challenge to devise open-shell dianionic systems potentially stable with respect to autoionization has been met insofar as calculations in a modest basis and in the B3LYP variant of DFT can be trusted. Comparison with MP2 and CCSD results obtained with a more flexible 6-31+G(d) basis show that the bias against dianions in these B3LYP/6-31G-(d) calculations is severe. This may be an advantage in the search for stable dianions however, since such a method will not yield false positives.

The systems described here include a number of dianionic species which may be stable with respect to autoionization. They are however not “small” as was specified in the challenge to identify small stable open-shell dianions. They should be considered only a step toward the study of much smaller systems. Smaller molecules can be more reliably characterized, and identification of stable smaller systems would be more responsive to the intention of the challenge.

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**Supporting Information Available:** Detailed energies and structures of all species. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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