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The Design of “Neutral” Carbanions with Intramolecular Charge Compensation

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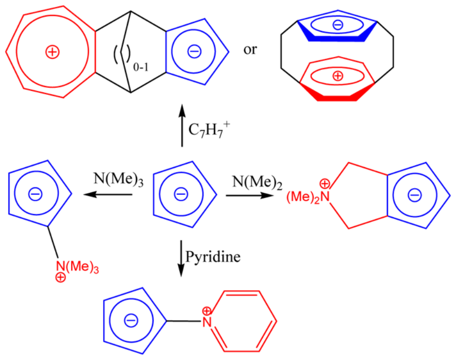
Supporting Information



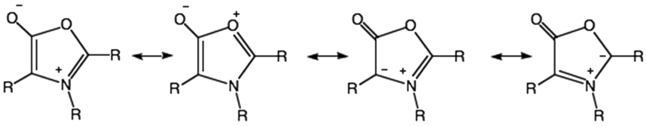
ABSTRACT: Strategies to construct zwitterionic anions from the parent anions are proposed. Two principles are employed; the cationic counterpart is (a) attached as a substituent or (b) inserted as an integral part at a remote location in the assembly. The optimized geometries reveal that a striking similarity exists between the zwitterions and the respective precursor parent anion. The computed vibrational frequencies emphasize that these novel entities are minima on their respective potential energy surfaces. A substantial HOMO−LUMO gap indicates that the proposed structures do not show instability in their respective electronic states and that the higher energy configuration states do not contribute to the ground state viability. The separation of charge between the monopoles in these zwitterions is demonstrated by moderately large nonzero dipole moments. Significant large energy barriers for rearrangement to the closely related positional isomers, demonstrated in a few cases, advocate the thermal stability (associated with spectroscopic viability) of the novel molecules. The donor capacity (basicity) of the anionic subunit in these zwitterions is comparable to that of the respective parent anions. Since the qualitative and quantitative features in the designed charged compensated complexes are conserved as anions, these molecules may perhaps be employed in synthetic organic or organometallic chemistry.

INTRODUCTION

Carbanions are negatively charged reactive species, highly useful in chemistry as synthetic reagents and as organometallic ligands (e.g., cyclopentadienyl).[1] In the gas phase, many carbanions and almost all carbodianions are not bound with respect to electron loss.[2] Stabilization is achieved in condensed phases by the presence of a counterion, typically an alkali metal cation. However, a counterion introduces the complication of strong *external* electrostatic interactions. We now demonstrate that the charges of the typical carbanions can be balanced *internally*, by positively charged substituents that are also present in the molecule. The resulting “charge compensated” (zwitterionic) species are neutral, but have essentially the same electronic structure as the negatively charged carbanions from which they are derived. We had earlier implemented creative strategies in the computational investigation of charge compensated carbocations and further provided evidence that these structural entities were amenable to experimental detection.[3] That research also demonstrated that the geometries of the positively charged counterpart in these zwitterions are similar to those of parent carbocations. In contrast, our present work proposes strategies to design neutral carbanions.

Examples incorporating charge compensation in structures are well-known, amino acids being one of the earliest. In the 1960s sydnones[4] (mesionic compounds) were explored by several research groups. Sydnones are biologically active molecules sharing structural similarity with amino acids. These molecules have a 1,3-oxazole skeleton bearing an oxygen atom attached at the 5-position. The perfect ensemble of various functional groups offers the prospect of resonance stabilization in syndnones, as exemplified in the Scheme 1.

Scheme 1. Possible Resonance Forms of Sydnones (1,3-Oxazole Unit)



Similar to that in syndnones, the stabilization in zwitterionic betaines, dipolar compounds, and ylides may also be ascribed to possible resonance forms. Dipolar compounds can be further categorized into three types: allylic (azo imides, carbonyl imides, carbonyl oxides, carbonyl ylides, nitrones, etc.), propargyl (nitrile imides, nitrile oxides, nitrile ylides, azides, diazo compounds), and the carbene (as in acyl carbenes, imidoyl carbenes, vinyl carbenes). Incorporating electron-donating and -withdrawing groups significantly alters the physical and chemical properties of dipolar compounds. For example, the presence of push−pull groups (electron withdrawing/donating) in charge-compensated species often tends

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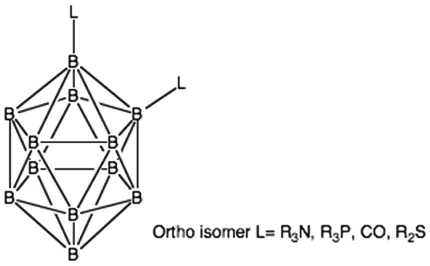
to increase the hyperpolarizabilities leading to an enhanced molecular nonlinear optical (NLO) response.[5] Zwitterionic molecules containing indolino-oxazolidine groups exhibit interesting photo- and acido-tunable NLO properties. Furthermore, these charge-neutralized species have practical applications as novel materials, buffers, enzyme inhibitors, and pharmaceutical drugs.[6] The investigations relating to zwitterionic character in amino acids have recently received theoretical attention.[7] Rios, Amyes, and Richard have experimentally studied the formation and stability of zwitterionic carbanions resulting from enolates of the glycine and its derivatives in aqueous media.[8] Likewise, some studies have focused on theoretically investigating the importance of the existence of the zwitterionic substrate in binding to the active site in proteins.[9]

Similar to zwitterionic carbocations,[3] which contain a parent stabilized carbocation, neutral carbanions may be envisioned as comprising a carbanion and a charge-neutralizing positive moiety. Although the carbanion and a cation could be parts of the same molecule, the positive counterion can either be (1) attached as a substituent or, more elegantly, (2) integrated into the basic structure of the system itself. The computational criteria dictating the prediction and stability of novel entities have been emphasized by Wannere, Chen, and Schleyer[3] and have recently been summarized by Hoffmann, Schleyer, and Schaefer.[10] Based on these ideas, computationally, the predicted structure should be a stable local minimum with a modestly large (in magnitude) lowest positive vibrational frequency. Moreover, the viable species should exhibit appreciable barriers toward rearrangement or dissociation. A large HOMO−LUMO gap is desirable to avoid wave function instability (so that the closest lying high-energy reference states do not contribute to the stability of the ground state). The new species described in the present paper are quite simple. Due to their instability and excessive localized negative charge, carbanions are expected to undergo isomerization (involving tunneling of H), fragmentation, dimerization, or higher chemical aggregation, in the gas phase and in solution, via a variety of chemical pathways. However, consideration of such complex reactions is beyond the scope of this paper; we solely intend to emphasize the principles to designing "*neutral carbanions*". Nevertheless, in a few test cases, we have considered rearrangement reactions to elucidate the stability of zwitterions. We show that all the zwitterionic anions discussed here comply with the above-mentioned computational criteria (discussed in refs 3 and 10) and, hence, are spectroscopically, if not experimentally, viable.

Although not belonging to the carbanion family, $L_2B_{12}H_{10}$ (Scheme 2) is one of the exhaustively studied charge-compensated icosahedron boron complexes.[11,12] Two formally positively charged ligands at the *ortho, meta*, or *para* positions of a 12 vertex boron cage compensate for the charge of the stable icosahedral ($B_{12}H_{10}^{2-}$) counterion; these examples illustrate well the principles we wish to employ. A series of substituents (L = CO, R_3N, R_3P, R_2S) were replaced at the ortho positions in the icosahedral analogues and also in octahedral ($L_2B_6H_4$) *o*-carboranes.[12] Olivia, Schleyer and co-workers demonstrated that there is a direct correlation of the distance between the borons bearing these substituents and the nature of the substituent (electron-donating and -withdrawing groups).[12]

Scheme 2



The concept of designing charge compensated anionic structures is demonstrated by calicene, Scheme 3. Although the parent hydrocarbon calicene is still unknown, several derivatives have been synthesized.[13,14] A possible resonance form of calicene, shown on the left in Scheme 3, indicates a zwitterionic species. Advantage is taken of the aromatic stabilization of the cyclopentadiene anion and the cyclopropenium cation.

In 1982, Yoshida reported the synthesis and structure of cyclic bicalicene (pentacyclo[$11.3.0^{2,4}.0^{5,9}.0^{10,12}$]hexadeca-1,3,5,7,9,11,13,15-octaene), which has a planar geometry despite the 4n electron ring perimeter.[15] Although enclosing a 16π electron system, cyclic bicalicene does not show any characteristics of an antiaromatic compound (based on the proton chemical shifts), as the structure is best described by the zwitterionic form (Scheme 4). For example, the electrochemical or alkali reduction of cyclic bicalicene leads to decomposition. This behavior is in striking contrast to other antiaromatic systems; for example, the parent [16]annulene accepts two electrons to form a stable 18π system.[16]

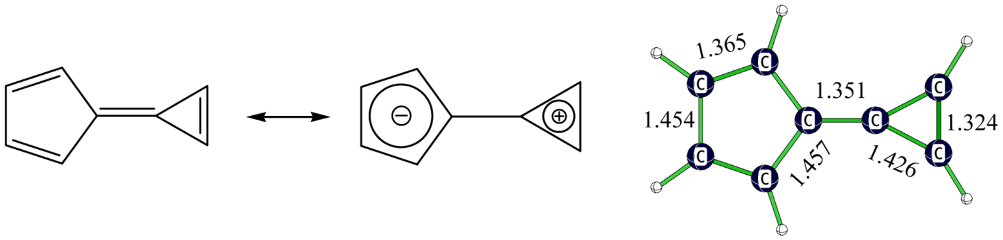
Zwitterions involving quinone related chemical compounds have been well documented. Siri and Braunstein showed that air oxidation of 1,3-dihydroxy-4,6-diaminobenzene leads to a quinonoid charge compensated structure, Scheme 5.[17] In fact, the zwitterionic structure derived from the proton transfer is more stable than the parent aromatic 1,3-dihydroxy-4,6-diaminobenzene. Siri and Braunstein's conclusion for the existence of charge compensated species was based on their NMR and X-ray crystallography analysis. The positive charge is delocalized over the four bonds involving 6π electrons from the amino groups. Likewise, the negative charge is accommodated by delocalization over the C−C−C linkage containing oxygen atoms, Scheme 5 (structure on extreme right).

The bond lengths calculated using the B3LYP/6-311+G** method in benzoquinonemonoimine, Figure 1, indicate that the structure indeed is zwitterionic, with the two charged monopoles separated by 1.546 Å (C1−C5 and C4−C2). Wiberg bond index analysis shows a bond order of 1.6 for C1−O9, 1.3 for C1−C3, and 0.93 for the C1−C5 bonds. Consistent with the bond lengths and bond orders data, **1** (Figure 1) shows a large dipole moment of 8.4 D. These various geometric indices clearly show that **1** is best represented as a zwitterionic quinonoid system. As expected, the NBO population analysis assigns a charge of −0.6 to the O9−C1−C3(H)−C2−O10 unit.

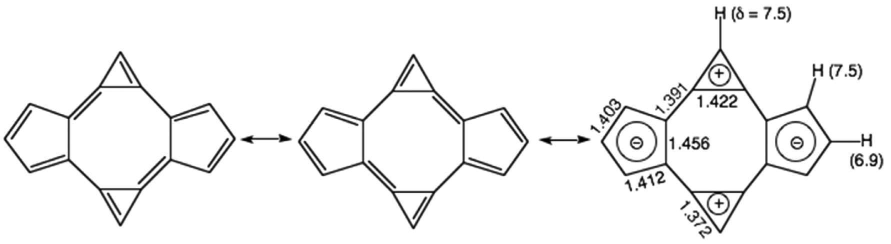
■ COMPUTATIONAL METHODS

All the hydrocarbon structures were optimized at B3LYP/6-31G* and subsequently at the B3LYP/6-311+G** DFT levels using the Gaussian-03 program.[18] Unscaled zero-point energy corrections (ZPE), based on the B3LYP/6-311+G** vibrational frequencies, were applied to the electronic energies. The Nucleus Independent Chemical Shifts (NICS)[19] (at the geometric center of the heavy

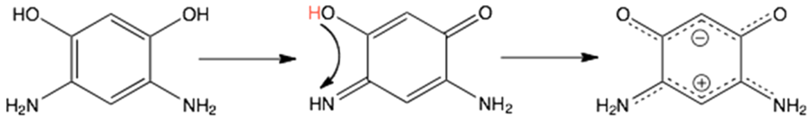
Scheme 3. Geometry (Right) and Zwitterionic Form (Left) of Calicene



Scheme 4. Resonance and Zwitterionic Form (Right) of Bicalicene (Denoted with δ ^{1}H Chemical Shifts)



Scheme 5. Rearrangement and Zwitterionic Form of 1,3-Dihydroxy-4,6-diamino Benzene



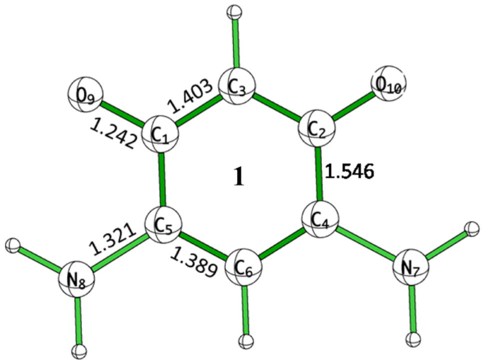


Figure 1. B3LYP/6-311+G** optimized geometry of 1,3-dihydroxy-4,6-diaminobenzene.

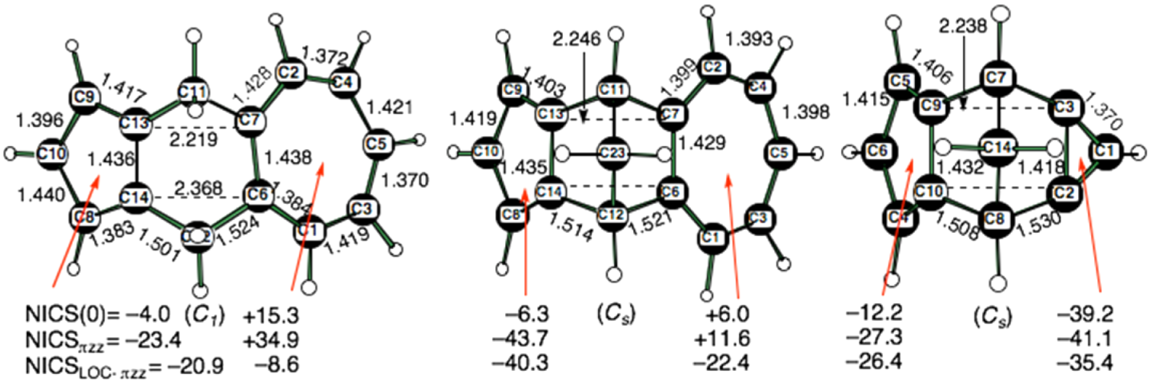
atoms) and the ^{1}H NMR chemical shifts were computed at GIAO[20]-PW91PW91/6-311+G**//B3LYP/6-311+G** refined geometries. The localized MO NICS dissection [denoted as NICS(π)][21,22] employed the deMon-Master program[23] at the SOS-DFPT[24] level with the Perdew−Wang-91 (PW91)[25a,b] exchange correlation functional and the recommended IGLO-III TZ2P[25c] basis set. Note that the NICS(π) refers to the total contributions of the localized π-MO's to the total shielding. The contributions to the isotropic NICS(0), arising from the π-shielding tensors of the component perpendicular to the ring plane ($\text{NICS}_{\pi zz}$), are considerable. Thus, $\text{NICS}_{\pi zz}$, which is regarded as a very reliable aromaticity index, is also evaluated.

■ RESULTS AND DISCUSSIONS

First, we re-examine some of the structures noted in the introduction and extrapolate the construction principles to design new zwitterionic species.

A. Examining Examples from the Literature. *Calicene.* As demonstrated in Scheme 3, calicene can be represented as a potentially zwitterionic structure, which comprises a stabilized cationic 3-membered and an anionic 5-membered ring. Our computed geometry of parent calicene shows significant CC bond alternation in the 5- and 3-membered rings, in agreement with the X-ray analysis reported for the substituted calicene derivatives.[13,14] Note that the CC bond lengths of the 5-membered ring in calicene are closer to those in cyclopentadiene (1.348, 1.468, and 1.505 Å) than to 1.415 Å (computed for the cyclopentadiene anion). Similarly, the C═C bond distance of the 3-membered ring is shorter than that for the cyclopropenium cation, 1.362 Å. The isotropic NICS value in the center of the 5-membered ring is −4.4 ppm while the NICS(π) and $\text{NICS}\pi_{zz}$ indicators also are moderately large in magnitude (−16.3 and −13.6, respectively). These values are closer to those computed for cyclopentadiene (−4.1, −12.2, and −8.6, respectively), but are lower than those for the cyclopentadiene anion (−14.9, 22.7, and −36.0, respectively). Furthermore, it was noted that the Dewar resonance energy of calicene is small, 4.5 kcal/mol,[26] which is consistent with our geometry and NICS finding that calicene prefers a bond localized geometry.

B. Bicalicene. In agreement with the earlier findings,[15] we note that the D_{2h} geometry of Yoshida's cyclic bicalicene is a minimum at B3LYP/6-311+G** with small CC bond alternation along the ring perimeter. The computed ^{1}H NMR chemical shifts of calicene exhibit typical $(4n + 2)\pi$ behavior; all the protons are more downfield (Scheme 4) than those of a typical vinylic H (═C−H). Clearly the [16]annulene perimeter does not contribute to bicalicene's ground state. The isotropic NICS values in the center of the 3- and 5-membered ring, −22.3 and −4.0, respectively, indicate moderate aromatic character. Furthermore, the computed NICS(π) and $\text{NICS}\pi_{zz}$ values show that the 5-membered rings sustain diatropic ring currents (−16.8 and −15.5, respectively). The computed exalted magnetic properties and the delocalized geometry support the conclusion that bicalicene



2 **3** **4**

Figure 2. Optimized geometries of azulene type aromatic analogs.

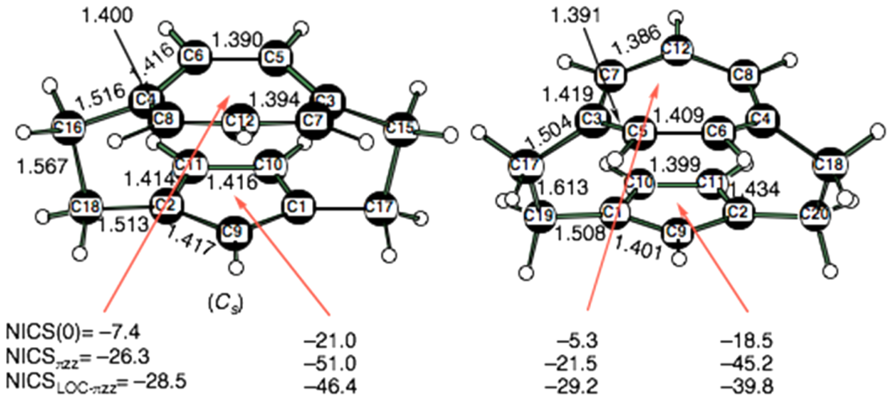
can be more appropriately represented as a zwitterionic species instead of a localized structure.

C. Azulene and Related Systems. Azulene, which is isoelectronic with naphthalene, was discovered and named in 1863 by Septimus Piesse.[27a,b] Lavoslav Ruzicka[27c−e] solved the structure of azulene while Placidus Plattner, in 1937, claimed[27f] its first synthesis. Azulene consists of a fused cyclopentadiene and a cycloheptatriene ring with a 10π electron perimeter. The peripheral bonds have almost similar lengths while the separation of the central CC assembly is representative of almost a single bond. Zwitterionically, azulene may be considered as a fusion of a cyclopentadienide anion and a tropylium cation, each of which contains 6π electrons, much like the naphthalene system. The nonzero computed and measured dipole moment of 1.1 and 1.0 D, respectively, and the associated large diatropic current for azulene is consistent with a zwitterionic picture. However, Aihara and co-workers evaluated the aromaticity in azulene by considering a closed ring circuit perimeter model.[28] We later demonstrate that the zwitterionic picture alone can account for aromaticity in azulene-type charged compensated structures. The NICS(0) values in the centers of the 7-membered ring and the 5-membered ring in azulene (−6.2 and −17.0, respectively) are large. In addition, the NICS(π) and NICS(π_{zz}) values in the center of the 7-membered ring, − 16.0 and −29.7, respectively, and the 5-membered ring, − 28.7 and −54.6, respectively, are close to those for the cyclopentadiene anion (−22.7 and −36.0, respectively) and the cycloheptatriene cation (−17.7 and −35.4, respectively). The various indices suggest the existence of diatropic ring currents due to the 6π electrons in each cyclic ring of azulene. The geometric details, nonzero dipole moment, and the NICS values are consistent with the charge compensated structure of azulene.

Table 1. Smallest Vibrational Frequency (in cm^{-1}), the Dipole Moment (in Debye), and the HOMO−LUMO Gap (in eV) for All the Structures (2 through 24) Computed with the B3LYP/6-311+G Method**

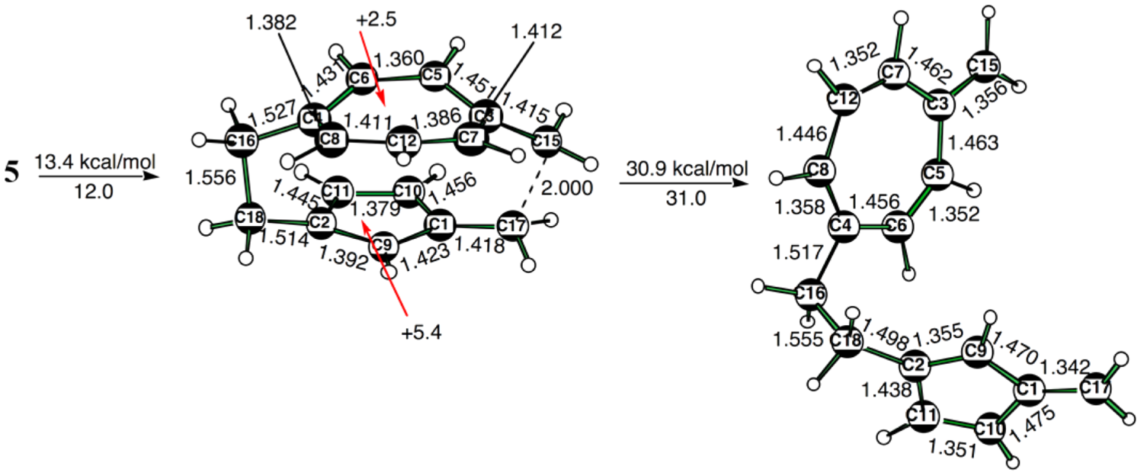
		ν (cm^{-1})	Dipole (D)	HOMO−LUMO (eV)
2	C_1	33.8	5.4	1.8
3	C_s	65.1	4.6	2.0
4	C_s	86.9	4.1	3.5
5	C_s	107.1	3.8	2.1
6	C_s	71.3	3.1	2.3
7	C_{3v}	118.1	10.0	4.9
8a	C_1	132.5	5.6	2.8
8b	C_1	160.1	6.4	2.8
9	C_s	7.7	8.5	3.8
10	C_2	57.2	5.1	2.7
11	C_{2v}	116.3	9.7	3.3
12	C_2	25.2	0.9	1.9
13a	C_{2h}	28.1	0	2.3
13b	C_{2v}	33.2	7.5	2.2
15	C_s	64.3	9.6	3.4
16	C_{3v}	59.3	1.0	5.8
17	C_{3v}	108.6	6.7	2.5
19	C_3	102.9	19.1	2.8
20	C_s	300.6	1.8	2.5
21	C_1	287.8	5.2	1.0
22	C_s	278.3	1.9	4.0
23	C_1	255.0	3.5	3.2
24	C_s	282.3	4.4	3.2

In principle, the two charged moieties of azulene can be separated by a series of intervening saturated rings, as shown in Figure 2, to generate analogous zwitterionic structures. The 7- and 5-membered rings in structure **2** are fused to and are separated by a cyclohexadiene unit, while in **3** these rings are appendages to a norbornadiene unit. Structure **4**, on the other hand, is a charge compensated system with cyclopropenium cation and cyclopentadiene anion rings fused to norbornadiene. As shown in Table 1, these three structures have much larger dipole moments than that of azulene. Strikingly, examples **2** and **3**, which are minima with large real vibrational frequencies, show that a perimeter model theory[28] may not be imperative to explain the delocalization of the π electrons in molecules such as azulene. These examples **2** through **4** conceptually demonstrate how a simple molecule can be transformed into a zwitterion such that the charged rings are distant, but still coexist as in the parent molecule of azulene. The data displayed in Table 1 also show that **2**, **3**, and **4** have large HOMO−LUMO gaps. The CC distances of the 5- and 7-membered rings in **2** and **3**, displayed in Figure 2, exhibit only a small CC bond alternation. Note that the unusually small C7−C13 distance in **2** may be ascribed to through-space interactions of the two zwitterions. To demonstrate that the 5-membered rings in **2**, **3**, and **4** are aromatic, we have computed NICS$_{LOC\text{-}\pi zz}$ values (displayed in Figure 2). NICS$_{LOC\text{-}\pi zz}$, which are more reliable than isotropic NICS,[22,29] denote the *local* π-MO contribution to the zz component of the NICS tensor. For



5 **6**

Figure 3. Optimized geometries of zwitterionic [5,7]paracyclophane analogs.



5_{TS} **5_{PDT}**

Figure 4. Reaction barrier for the opening of zwitterionic *cis*-[5,7]paracyclophane.

example, the NICS$_{LOC-\pi zz}$ value for the 7-membered ring does not contain contributions from the isolated three π-bonds of the cyclopentadienyl anion.[29] Large negative NICS$_{LOC-\pi zz}$ values computed in the ring centers clearly show that the 5- and 7-membered ring appendages in **2** and **3** sustain diatropic ring currents due to six π electrons. Likewise, the 3- and 5-membered rings in **4** show exalted NICS values. Notably, the aromaticity of neither **2** nor **3** can be explained by invoking Aihara's perimeter model.[28] Clearly the π-ring current circuit of the 5- and 7-membered rings is discontinued due to the intervening saturation. However, the existence of diatropic currents in these structures can be adequately explained only by emphasizing the ionic forms in each subunit.

The separation between the cyclopentadienyl anion and the tropylium cation can also be achieved by integrating these rings as a constituents of paracyclophanes, as demonstrated in Figure 3. Two different orientations of the 5- and 7-membered rings are possible, as shown in Figure 3. The computed positive vibrational frequencies (Table 1) and HOMO−LUMO gap indicate that both **5** and **6**, with significantly large dipole moments, are minima. The evaluated NICS$_{LOC-\pi zz}$, depicted in Figure 3, show that 5- and 7-membered rings in both structures are aromatic with 6π electrons. The computed isotropic NICS(0) values for the individual rings also are large and negative and advocate diatropic character. Notably, the CC bond lengths in the 5- and 7-membered rings in the optimized geometries exhibit insignificant bond alternation.

The thermal stability of **5** is also revealed from the computed ring opening barrier, which is reasonably high (12 kcal/mol at the B3LYP/6-311+G**). Notably, the structural isomer **5_{pdt}** is thermodynamically preferred by 19 kcal/mol. The large ~12 kcal/mol barrier toward rearrangement reveals that **5** should be isolable at low temperatures. The optimized geometry of TS (**5_{TS}**) reveals that the CC bonds in the cyclic rings are not delocalized. The formation of exocyclic double bonds at C3−C15 and C1−C17, leading to loss of aromaticity of the 5- and 7-membered rings in **5_{TS}**, also is corroborated by the positive isotropic NICS values (Figure 4).

D. Acetylenic and Allylic Anions. Although previous examples (**2** through **6**) demonstrated that the stabilization offered by the aromaticity of the (4n + 2)π electron systems can be utilized in constructing charge compensated structures, zwitterionic carbanions can be designed from something as primitive as the acetylene monoanion, H−C≡C:(−). Substitution of the hydrogen by *a positively charged group without any multivalent capability* results in a stable, neutral acetylene carbanion surrogate. We have chosen the trimethylammonium group, $(CH_3)_3N(+)-$, for illustrative purposes (from among numerous alternatives). Substitution of H in H−C≡C:(−) (rCC 1.25 Å) results in $(CH_3)_3N(+)-C\equiv C:(-)$ (**7**), which

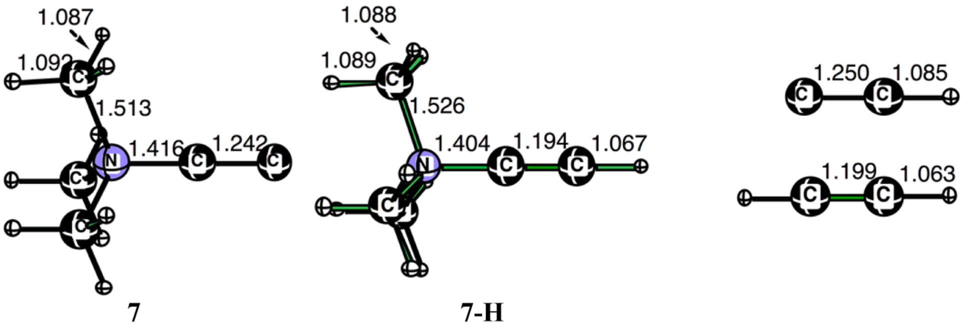


Figure 5. Optimized geometries of *N,N,N*-trimethylamine acetyl anion (**7**) and its protonated form (**7-H**). The geometries of acetylene and its corresponding anionic are displayed for comparison.

retains the CC triple bond (with four π electrons) and has nearly the same CC distance (rCC 1.24 Å), Figure 5. The computed proton affinity (PA) of $(CH_3)_3N(+)-C\equiv C:(-)$ is large, 278 kcal/mol with B3LYP/6-311+G**, compared to that of the amines (e.g., 226.8 kcal/mol for gaseous trimethylamine).[30] Note that this value is slightly smaller than that for the anionic species like the propynyl anion (380 kcal/mol). Such a large PA indicates that the $-C\equiv C:(-)$ in the zwitterion has a strong anionic character and can exhibit comparable nucleophilicity (electron pair donating ability). The charge density plot (Figure 6) clearly indicates that the negative charge (blue region) in the zwitterionic **7** is localized on the terminal carbon of the acetylenic bond.

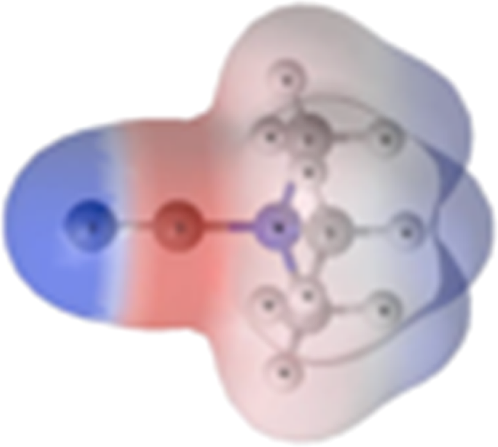


Figure 6. Charge density plot for the zwitterionic *N,N,N*-trimethyl acetyl anion.

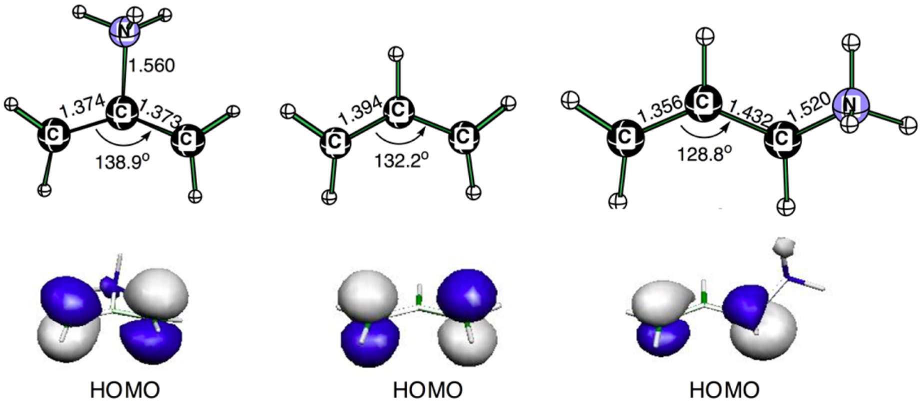
Another commonly encountered anion is the allyl carbanion, which not only has been widely utilized in synthetic organic chemistry but also is an exhaustively employed ligand in organometallic chemistry (η^1 or η^3 as a one or three electron donor, respectively). The substitution of a hydrogen on the allyl anion by the trimethylammonium or ammonium cation leads to zwitterionic structures (Figure 7). The ammonium cation can replace the proton attached to either the terminal or the central carbon atom leading to two different isomers (Figure 7). Both zwitterionic species **8a** and **8b** (C_1 symmetry) are minima with large lowest vibrational frequencies (133 and 160 cm^{-1}, respectively). The B3LYP/6-311+G** energies indicate that the terminal isomer (**8b**) is only 1.9 kcal/mol higher in energy than **8a**. The CC bond lengths and the C−C−C angle in the structures **8a** and **8b** are remarkably similar to those in the allyl anion. Furthermore, the highest occupied molecular orbitals of the allyl anion structures, **8a** and **8b**, are qualitatively similar. The NBO population analysis indicates that the allyl moiety in both zwitterions, as expected, is negatively charged, −0.5.

E. Anionic Aromatic Systems. Similar to the previous two examples (demonstrated in Figures 5 and 7), the $(CH_3)_3N(+)-$ group can stabilize the cyclopentadiene anion. Johannes Thiele discovered the unusual acidity of cyclopentadiene in 1900.[31] The cyclopentadienyl anion, $C_5H_5(-)$, the first aromatic carbanion, is a versatile molecule that is important both in organic and in organometallic chemistry, where it serves as the basis of a host of sandwich and half-sandwich compounds. Substitution of H by a $(CH_3)_3N(+)-$ group gives the neutral $C_5H_4N(CH_3)_3$ (**9**) derivative (Figure 8), which, astonishingly, is computed to have five nearly equal CC bond lengths (1.410 ± 0.003 Å); these are closer to that of neutral benzene (1.40 Å) and the anionic $C_5H_5(-)$ (1.415 Å).

The aromatic character due to six π electrons in **9** is demonstrated by its isotropic NICS of −14.2 in the five-membered ring center [vs −14.9 for $C_5H_5^-$]. The large and negative magnitude of the NICS(π) and the NICS$_{\pi zz}$ values (−22.4, −25.1) clearly shows the existence of diatropic ring currents in **9** (−22.7 and −36.0, respectively, cyclopentadiene anion). The computed δ ^{1}H NMR values of the protons attached to the five-membered ring (δ = 6.0 and 6.1) in **9** are comparable to those calculated for the cyclopentadienyl anion (5.6 ppm, while the measured value is δ = 5.37).[32] Furthermore, the extent and stability of delocalization in **9** is indicated by the very large HOMO−LUMO separation of 3.8 eV. Not only is **9** a minimum, but also the barrier for the [1,2]methyl shift to form 5-[*N,N*-dimethyl]amino-5-methylcyclopentadiene is 48 kcal/mol at B3LYP/6-311+G** (Figure 9). Due to its stability and a large barrier for rearrangement, isolation of **9** at room temperature is viable. Note that the rearranged product 5-[*N,N*-dimethyl]amino-5-methyl cyclopentadiene is predicted to be about 19 kcal/mol lower in energy than **9**.

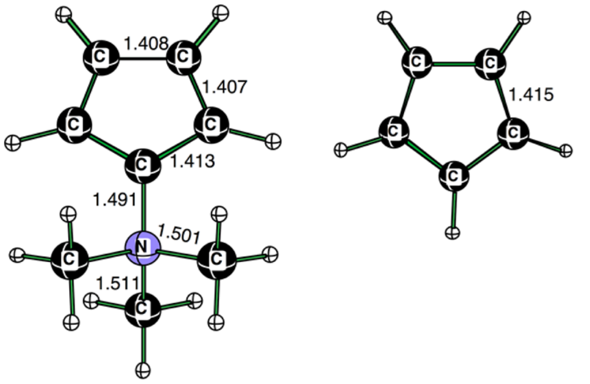
As opposed to the trimethylammonium cation group utilized in examples **7** through **9**, the pyridinium cation can be used for charge compensation. Thus, a hydrogen atom of cyclopentadiene or an acetylene anion can be replaced by a pyridinium cation (Figure 10), which acts as a pendant that helps localize the positive charge. Unlike the $(CH_3)_3N(+)-$ moiety, where the methyl attached to the nitrogen shows a tendency for migration (Figure 9), rearrangement of the pyridinium cation is less likely.

The cyclopentadienyl anion of the zwitterion **10** displays a small degree of CC bond alternation (0.051 Å). The various



8a (C_1) **Allyl anion (C_{2v})** **8b (C_1)**

Figure 7. Optimized geometries of allyl anion (center) and its corresponding zwitterionic analogs (left and right). Molecular orbitals displayed in the figure below demonstrate a striking similarity between the three structures.



9 **Cyclopentadiene anion (D_{5h})**

Figure 8. Cyclopentadienyl anion (left) and its zwitterionic *N*,*N*,*N*-trimethyl derivative.

structural features of **11** and its protonated state (**11-H**) are the same; e.g., the CC and the CN distances in both these structures are close. Remarkably, the similar CC bond length of the ethynyl unit in **11** (1.251 Å) and that computed for the parent acetylene anion (1.250 Å) demonstrate that the anionic moiety in the zwitterion is conserved. The optimized geometries of **10** and **11** have real vibrational frequencies (the smallest are 57 and 116 cm^{-1}, respectively). Furthermore, the viability of **10** and **11** can be inferred from the large HOMO−LUMO gaps (2.7 and 3.3 eV, respectively). Notably, the HOMO of the 5-membered ring of structure **11** shares its qualitative similarity with that of the cyclopentadiene anion. As expected, the HOMO of **11** (second structure from the right in Figure 11) shows a marked qualitative resemblance to that of the H−C≡C in the ethynyl anion; the negative charge resides in the σ-bond orbital due to the elimination of the proton. The charge density plot of the dipolar species **11** confirms the HOMO representation; Figure 11 show that the negative charge is indeed localized on the acetylenic carbons. The zwitterions **10** and **11** exhibit large dipole moments of 5.0 and 9.7 D, respectively, implying a charge separation between the polar groups. A further characteristic of **10** is its remarkable structural resemblance with biphenyls. Like the biphenyls, structure **10** prefers a C_2 symmetry. However, the computed barrier to rotation around the central bond (13 kcal/mol) in **10** (via a C_{2v} structure) is much larger as compared to 1.5 kcal/mol,[33] measured for biphenyl, possibly due to a slight double bond character at the C−N bridge. The HOMO, and the subsequently occupied lower orbitals, demonstrates that the C−N bridge possesses a bond order much greater than 1, perhaps due to the excess negative charge in the cyclopentadienyl subunit, which is shared with the vacant nitrogen π^* of the pyridinium moiety (also indicated by the natural

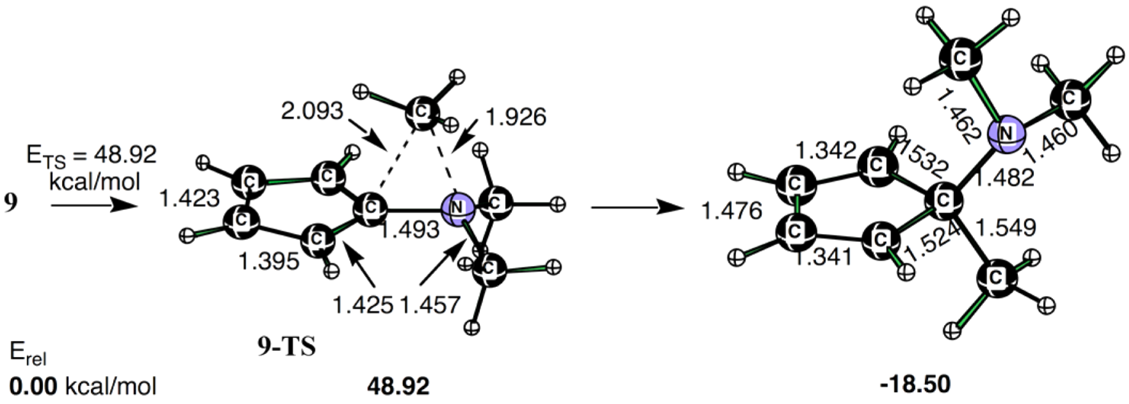
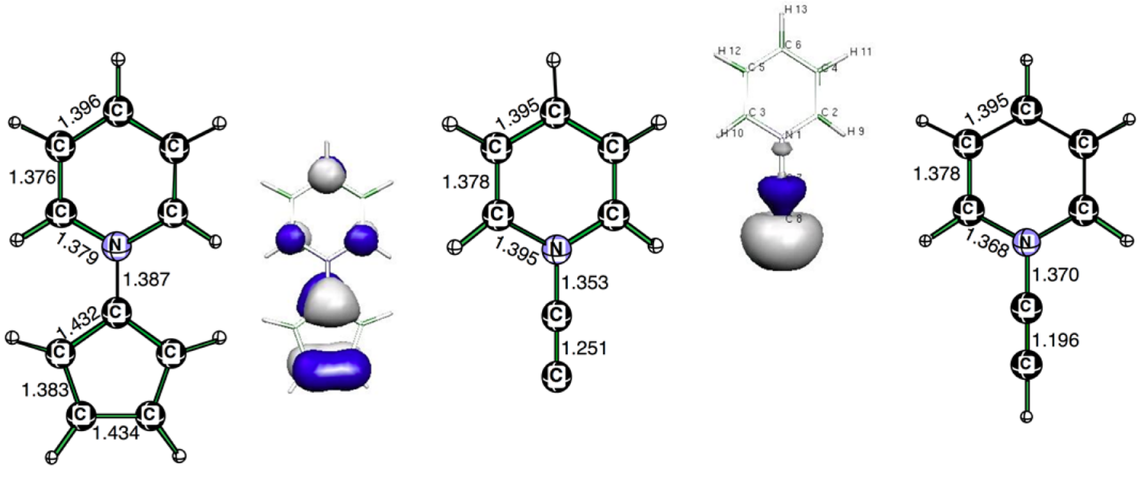


Figure 9. Barrier for rearrangement of the *N*,*N*,*N*-trimethyl cyclopentadienyl anion to the more stable 1-methyl-1-[*N*,*N*-dimethyl]amine cyclcopentadiene.



10 (C_2) **HOMO of 10** **11 (C_{2v})** **HOMO of 11** **11-H (C_{2v})**

Figure 10. Optimized geometries of cyclopentadiene and acetyl anions stabilized by the pyrdinium cation.

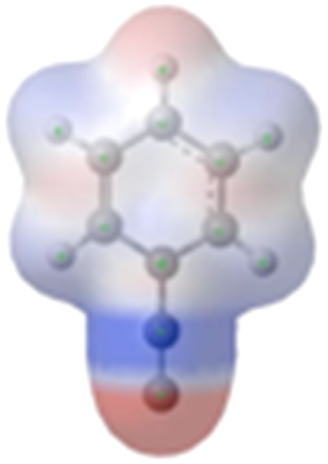


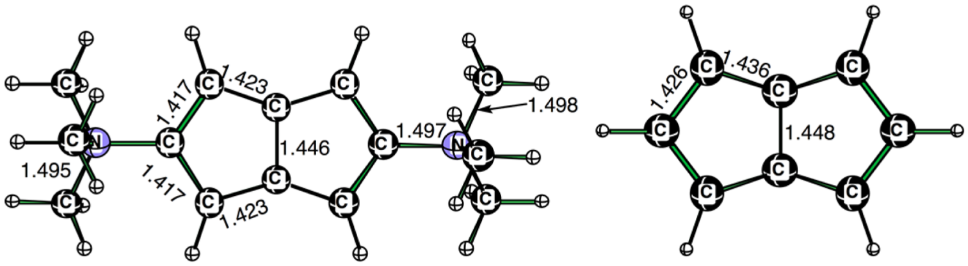
Figure 11.

bond orbital analysis). In sharp contrast, each benzene ring in biphenyl retains its aromaticity and, therefore, exhibits a bond order close to one at the C−C bridge. Based on these bond order differences, the barriers for rotation for these two isoelectronic species are distinctly different.

F. Antiaromatic (Aromatic Dianions) Systems. Pentalene has been the subject of numerous Hückel-type and *ab initio* studies.[34] Due to the presence of 8π electrons in the circuit this antiaromatic molecule sustains a paratropic ring current. Because of its high reactivity, pentalene has only been observed spectroscopically in matrix isolation.[35] However, the addition of 2π electrons to this antiaromatic molecule generates the aromatic pentalene dianion, which is isoelectronic with naphthalene. The pentalene dianion was synthesized in 1962 by Katz et al.[36] as a lithium salt and later by Schleyer et al.[37] Substitution of two hydrogen atoms by $(CH_3)_3N(+)-$ groups gives the neutral $C_8H_4(N(CH_3)_3)_2$ (**12**) derivative. Zwitterion **12** shows nearly equal CC bond lengths along the ring perimeter (1.420 ± 0.003); these match closely to those for the pentalene dianion (Figure 12). A moderately large HOMO−LUMO separation of 1.90 eV shows that the zwitterion **12** does not have instabilities with respect to the mixing of closely related configurations.

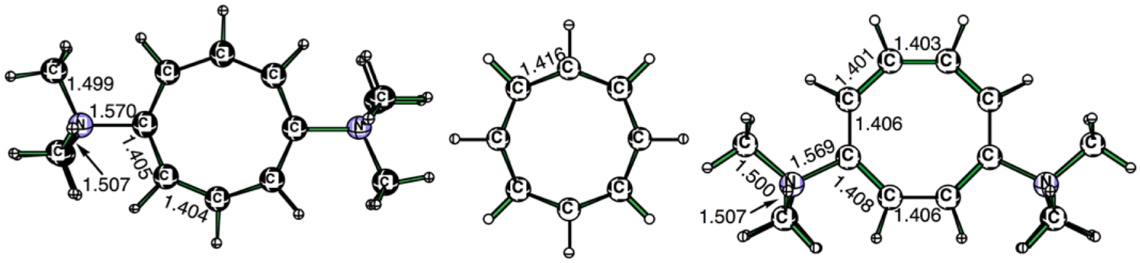
The aromaticity in **12**, due to the presence of 10π electrons, is indicated by the large and negative isotropic NICS, −13.2, in the five-membered ring center; the corresponding value for parent pentalene dianion is −12.9. Not only is the NICS(π) in **12** (−21.6 ppm) close to that for the cyclopentadiene anion (−21.4), but also similar are the NICS$_{\pi zz}$ values (−32.6 vs −34.8, respectively). The NICS(π) and NICS$_{\pi zz}$ values for the pentalene dianion are much smaller, −14.2 and −24.2, respectively. The computed δ ^{1}H NMR of the protons attached to the five-membered ring (5.4 ppm) in **12** is comparable to those measured for the pentalene dianion (5.1 ppm).

Cyclooctatetraene (COT), also known as [8]annulene, incorporates 8π electrons. Since the D_{8h} symmetry geometry



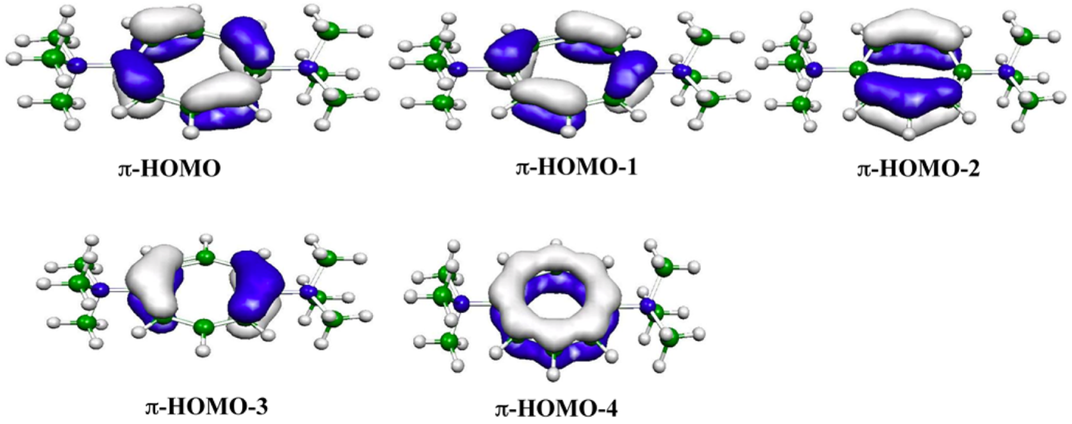
12 (C_2) **Pentalene Dianion (D_{2h})**

Figure 12. Optimized geometries of pentalene dianion (right) and its zwitterionic di-[*N*,*N*,*N*-trimethyl] analog.



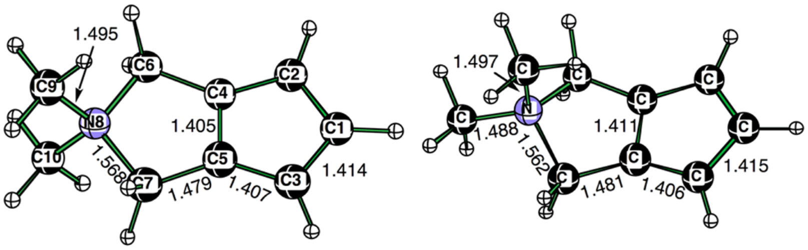
13a (C_{2h}) **Cyclooctatetraene Dianion** (D_{8h}) **13b** (C_{2v})

Figure 13. Optimized geometries of the cyclooctatetraene dianion (center) and its corresponding zwitterionic *cis*- and *trans*-di-[*N*,*N*,*N*-trimethyl] analogs.


π-HOMO π-HOMO-1 π-HOMO-2

π-HOMO-3 π-HOMO-4

Figure 14. Occupied π-orbitals of the cyclooctatetraene zwitterion (**13a**).

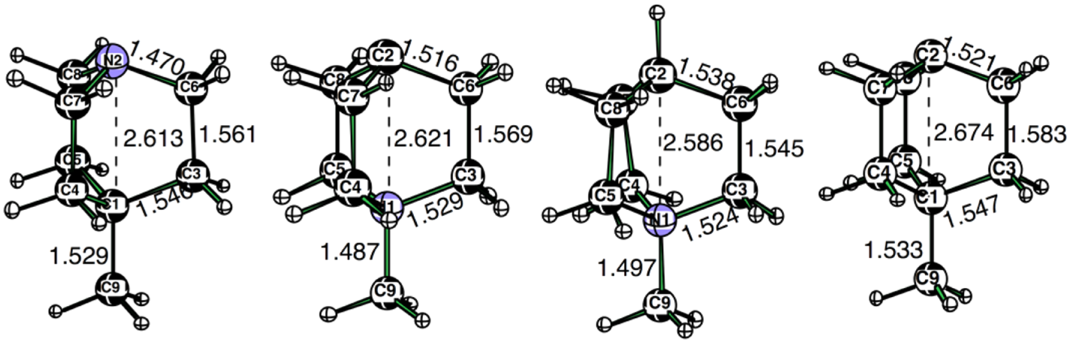


14 (C_{2v}) **15** (C_2)

Figure 15. Alternative strategy for stabilizing cyclopentadiene anion. The structure on the left with C_{2v} symmetry represents a transition state for interconversion of the axial and equatorial C_2 forms demonstrated on the left.

displays a Jahn−Teller distortion, COT adopts a nonplanar tub-shaped geometry. In sharp contrast, the dianion of COT, which prefers a planar conformation, is aromatic due to the presence of 10π electrons.[38] The strategy of replacing two hydrogens of an antiaromatic compound by $(CH_3)_3N(+)-$ to form a zwitterionic aromatic compound can be applied to cyclooctatetraene (COT) as well (Figure 13). The B3LYP/6-311+G** geometry of zwitterion **13a** shows nearly equal CC bonds (1.405 Å) along the COT perimeter. Although the lowest vibrational frequency is small (27 cm^{-1} at the B3LYP/6-31G*), it corresponds to the noncritical rotation of the methyl group of the ammonium ion. The large negative values of NICS (−14.9), NICS(π) (−19.8), and $NICS_{\pi zz}$ (−46.4) in the center of the 8-membered (dianonic) ring of **13a** justifies the presence of diamagnetic ring currents; the corresponding values for the parent COT dianion are −14.8, − 19.1, and −49.0, respectively. The computed δ ^1H NMR values of the protons attached to the 8-membered ring ($\delta_{average}$ ≈ 5.9 ppm) in **13a** are similar to those for the COT dianion (5.5 ppm).

Thus, the geometric and magnetic evidence indicate that the 8-membered ring in zwitterionic **13a** is aromatic with 10π electrons. Charge compensated structures differing in placements of trimethylammonium groups in **13a** lead to a positional isomer (for example, **13b**), which also is aromatic. The CC bonds in **13b** show small bond alternation along the ring perimeter, similar to that in **13a**. The computed magnetic properties (NICS = −14.9, NICS(π)= −19.9, $NICS_{\pi zz}$= −45.9, and δ ^1H NMR chemical shifts of the protons attached to the ring = 5.9 ± 0.3 ppm) indicate that the COT ring in **13b** also is aromatic. Notably the qualitative features of delocalization of the π-orbitals of **13a** (and also **13b**) resemble those for the COT dianion (Figure 14). The examples **12**, **13a**, and **13b** clearly demonstrate that substitution of hydrogens of an antiaromatic compound by a positively charged counterion



16 (C_{3v}) **17** (C_{3v}) **17-H** (C_3) **18** (C_{3v})

Figure 16. Geometry of zwitterionic 4-methyl-[2,2,2]-azabicyclooctane (**17**) and its isomeric analog (**16**). The protonated form of **17** (17-H) and the corresponding 4-methyl-[2,2,2]-bicyclooctane are displayed to illustrate structural similarities.

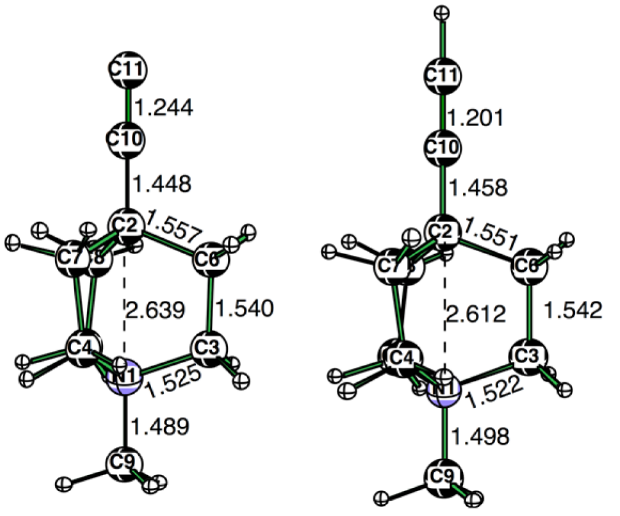
generates aromatic counterparts of the respective parent structure. This strategy can be creatively employed to other antiaromatic compounds so that isolation of these, rather, unstable structures is effortlessly achieved even at room temperature.

The principle of integrating the cationic moiety at a remote location in the parent anionic structure to design a charge compensated molecule is illustrated by an example in Figure 15. Alternatively, the zwitterion **14** (Figure 15) containing a pendant cation, such as $(CH_3)_2N-$, can possibly be introduced at an isolated position in the adjoining ring that is an appendage to the cyclopentadiene anion. The resulting structure **14** (C_{2v}) is a transition state, with a barrier of 3.4 kcal/mol, corresponding to the out of plane motion of the $(CH_3)_2N-$ group. Following the negative eigenvector leads to structure **15** (C_s), which is a minimum with a large smallest vibrational frequency of 64 cm^{-1}. Note that both **14** and **15** show nearly equal CC bond lengths for the cyclopentadiene anion subunit.

The aromatic character due to the 6π electrons in the 5-membered anionic ring in **14** is demonstrated by its large negative isotropic NICS(0) value of −12.0 ppm. Likewise, the NICS(π) and the NICS$_{\pi zz}$ values (−22.0 and −34.1 ppm) also indicate aromaticity of the cyclopentadiene ring in **14**. The ^{1}H NMR chemical shifts of the protons attached to C1 and C2 (δ = 5.6 and 6.9 ppm, respectively) are comparable to those for the cyclopentadiene anion (5.6 ppm). Consistent with a large charge separation between the monopoles, **14** shows a substantial computed dipole moment (9.6 D) compared to that for **9** (8.5 D). A very large HOMO−LUMO separation of 3.39 eV testifies to the stability of **14**.

G. [2,2,2]-Azabicyclooctanes. 4-Methyl-[2,2,2]-azabicyclooctane (**16** in Figure 16), also known as quinuclidine, not only is well-known as a (σ-donor) ligand in organometallic chemistry but also serves as a classical Hammett molecular probe.[39] *N*-Methyl-[2,2,2]-azabicyclooctane (**17**), which is an isomer of **16**, is a charge compensated molecule with a carbanionic center at the C2 position. However, **16** is 80 kcal/mol lower in energy than the charge compensated species **17** at the B3LYP/6-311+G** level. The computation at this level reveals that structure **17** is also a minimum with a large smallest positive vibrational frequency, 109 cm^{-1}. A very large HOMO−LUMO gap (2.5 eV) reveals the absence of wave function instability in the singlet ground state of **17**. The optimized geometry reveals that there is a remarkable geometric resemblance between the protonated *N*-methyl-[2,2,2]-azabicyclooctane (**17-H**), [2,2,2]-bicyclooctane anion (**18**), and the zwitterion **17**. Likewise, the NBO population analysis indicates that both **17** and **18** have similar charges at the C2 carbon (−0.34 and −0.30). The large dipole moment, 6.7 D, computed for **17** is justified by a large separation of the formal positive and negative centers. The computed proton affinity (PA) of **17** is large, 241 kcal/mol, and is not much different from the value measured[30,40] for **16**, 236 kcal/mol. The comparable PA reveals that, similar to **16**, the zwitterionic isomer, **17**, displays marked nucleophilic character.

The previously introduced acetylenic anion and quinuclidinyl subunit, in combination, can be utilized as building blocks to fabricate other charge compensated species, such as **19** (Figure 17). Indeed, a substitution of the proton on the C2 carbon of the carbocation **17-H** by $-C{\equiv}C^-$ gives the zwitterionic structure **19**, which is a minimum (smallest vibrational frequency is 103 cm^{-1}) with a large HOMO−LUMO gap (2.76 eV). The various CC and CN distances in the bicyclooctane ring of **19** are similar to those in **17** and to those of its protonated form, **19-H**. Despite the many structural similarities with **17**, the protonated form **19** displays a substantially larger dipole moment of 19.1 D solely due to



19 (C_3) **19-H** (C_3)

Figure 17. Optimized geometry of the zwitterionic acetyl anion and its protonated form stabilized by the 4-methyl-[2,2,2]-azabicyclooctane cation.

the larger separation between the formal positive and negative centers. Consistent with expectation, the charge density plot for **19**, shown in Figure 18, indicates that the anion is localized at the terminal acetylenic C11 atom. A relatively larger proton affinity (314 kcal/mol) as compared to that of **17** (241 kcal/mol) and of **7** (278 kcal/mol) indicates that the anionic moiety in **19** behaves as the strongest nucleophile in this series.

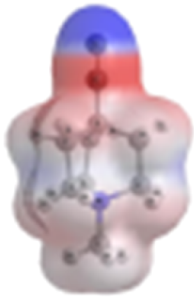


Figure 18. Charge density plot for the zwitterionic 4-methyl-[2,2,2]azabicyclooctane acetylene anion.

H. Homoaromaticity of the Neutral Zwitterionic Carbanion Analogs. The concept of homoaromaticity[41] was coined to explain the unusual stability of charged molecules. Such stabilization arises due to delocalization of the charge, despite one or more interrupting saturated linkages, due mostly to through space interaction. Winstein,[41a−c] who introduced homoaromaticity, first observed this phenomenon in cationic species. Later Goldstein and Hoffmann proposed that stabilizing π-interactions should be observable in appropriately constituted anions.[42] Homoaromaticity is firmly established in cationic[43] and more recently in anionic[44] systems. However, homoaromaticity in neutral[45] and radical[46] hydrocarbons is much debated and remains controversial. Various carbenes have been computationally explored to extend the concept of homoaromaticity to neutral structures.[47] After considering several examples, Cremer et al. concluded that the bicyclo[3.2.1]octadienyl anion, **20** (Figure 19), is most likely a potential contender for homoaromaticity.[48] Brown and Occolowitz proposed that the stability of the bicyclo[3.2.1]-octadienyl anion, **20a** and **20b**, can be explained by invoking the possibility of a π-delocalized resonance structure, **20c** (Figure 19).[49]

Using the zwitterionic principles discussed above, we demonstrate here that a stable anion can be constructed by elegantly integrating a cationic center in the parent anion. Thus, in principle, any of the carbons, either involved or not involved in the charge delocalization of the bicyclooctadienyl anion **20**, can be substituted with a nitrogen atom. Similar to the parent (**20**), from which they are derived, **21** through **24** are also anticipated to show homoaromaticity. As expected, these charge compensated structures (**21**, **22**, **23**, and **24** in Figure 20) are all minima with substantially large positive smallest vibrational frequencies, Table 1. In the neutral carbanions **21** and **22**, nitrogen is involved in the homoaromatic delocalization, while, in **23** and **24**, nitrogen is embedded in the basic structure at a remote location. Freeman investigated the energies and magnetic properties (NICS and magnetic susceptibility exaltations) of only **21** and **22** and concluded that the latter structure is homoaromatic.[50]

The geometries of the newly proposed homoaromatic zwitterionic carbanions **23** and **24** are close to that of **22** and also to that of the parent system **20**; for example, the crucial C7−C8, C7−C5, C5−C8, C4−C5, and C4−C6 distances in these four structures are very similar. Furthermore, the isotropic NICS and NICS(π) values at the geometric center of atoms 4−5−6−7−8 in **23** (−10.8, −8.4) and **24** (−7.5, −8.8) are similar to those for **22** (−10.8, −9.3) and **20** (−9.8, −7.5); the corresponding NICS values for **21** are −3.7 and −5.3, respectively. A very large HOMO−LUMO gap (Table 1) reveals additionally that the ground state singlet configuration contributes primarily to the electronic structures of **22**, **23**, and **24**.

■ CONCLUSIONS

Other than the universally present amino acids, only a few examples that contain anionic zwitterionic moieties are experimentally known. The fundamental concept of charge compensation may be utilized in enhancing our chemical bonding knowledge of carbanions. The preservation of carbanionic features in such zwitterions illustrates that the resulting structures may well be employed as excellent ligand targets in organometallic chemistry. The existence of large dipole moments shows that the monomeric units, in addition, can be utilized in the design of novel material with enhanced NLO properties.

In general, commonly known carbanions are not amenable to isolation in the solid state, except as salts. The presence of a counterion introduces some perturbation to the parent carbanoinic subunit. Our research demonstrates that carbanions can be explicitly isolated by segregating a positively charged subunit at a remote position in the zwitterionic assembly. We have successfully employed this strategy to a variety of commonly encountered carbanions such as the allyl anion, acetylenic anion, and, also, to nonclassical carbanions such as the norbornyl anion. Computations of the HOMO−LUMO gaps, lowest vibrational frequencies, and barriers to rearrangement (in some cases) suggest that all the computed structures

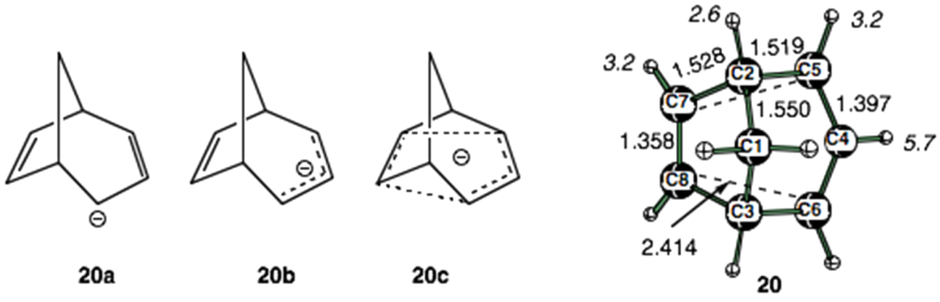
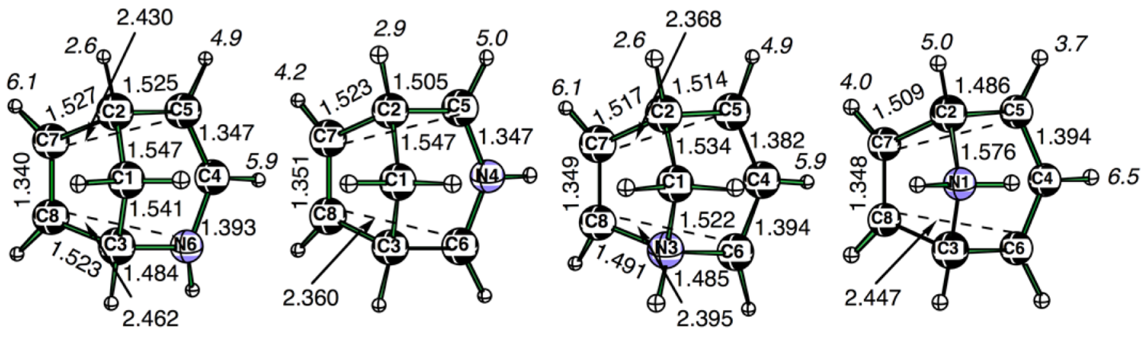


Figure 19. Homoaromaticity of the bicyclo[3.2.1]octadienyl anion.



21 (C_1) **22** (C_s) **23** (C_1) **24** (C_s)

Figure 20. Optimized geometries of isolobal N-substituted bicyclo[3.2.1]octadienyl carbanionic analogs stabilized by homoaromaticity.

are genuine and, hence, are viable spectroscopically. Simple aromatics such as pentalene and cyclooctatetraene dianions and the cyclopentadienyl anion have been conceived as simple models of interest to illuminate the electron delocalization. However, these aromatic anions have been isolated in the gas matrix (at low temperatures) or in the liquid phase. Using the internal compensation strategy, we have demonstrated that pentalene and COT dianions, if synthesized, can be stabilized and isolable in the solid state. The computational design of several new zwitterionic carbanions in this work extends a challenge to experimental chemists to devise creative ways to synthesize these molecules. In addition, our investigations of the construction of novel molecules open routes to a potentially rich carbanion chemistry.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.joc.5b02695.

B3LYP/6-311+G** optimized geometries (in the form of spatial coordinates) for all the structures described in the text (PDF)

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