Carbon-Carbon Double Bonds with a Covalent σ and an Ionic *p*-Bond in Anti-Bredt Olefins

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Abstract

In the universe of chemical bonds, a spectrum stretches from the almost purely ionic to the perfectly covalent. Yet, amid this intricate zoo of possibilities, one elusive creature remains unseen: a mixed chemical double bond where a covalent σ -bond partners with an ionic p-framework. Using state-of-the-art first-principles computations, we introduce a series of molecules in which adjacent σ -bonded carbon atoms at the branching site and the one-carbon bridge of certain bicyclo-bridged olefins form a stable carbanion-carbocation pair instead of an anti-Bredt π -bond or a diradical. We propose the term *ionic p-bond* to describe this phenomenon, as the bond involves two neighboring, primarily p-based orbitals accommodating a cation and an anion in close proximity. The formation of stable ionic *p*-bonds relies on two key factors: the stabilization of the stabilization of the anion via pyramidalization of the branching carbon. This stability is further reinforced by electron-withdrawing groups substituting the molecule's σ -skeleton.

Ionic bonds are attributed to differences in the intrinsic electronegativity of interacting heteroatoms. In contrast, homoatomic interactions are often associated with varying degrees of electron sharing, resulting in a spectrum of bond types ranging from weak metallic to strong multiple covalent bonds. Among the elements, carbon is particularly notable for its ability to form robust covalent bonds with other carbon atoms, giving rise to a vast array of hydrocarbons and extended networks in its allotropes. However, reports of carbon-based ionic salts remain scarce. A few ionic carbon-carbon bonds have been reported in substituted stable aromatic ions and fullerenes with bulky substituents in polar solvents.^[1–8] In these systems, positive and negative charges are typically delocalized over the conjugated molecular cores and shielded by bulky protecting groups. These groups effectively isolate the carbanion's electron pair from the low-energy orbital of the carbocation, maintaining stability. Here, we present a novel strategy to stabilize a carbanion and a carbocation in close proximity, separated by only the length of a σ -covalent bond.

Our proposal benefits from the intrinsic instability of the anti-Bredt olefins (ABO) characterized by a double bond at the branching position of bridged bicyclic hydrocarbons.^[9–12] Recently, Garg and colleagues reported a series of ABOs in which the R–C=C–R dihedral angles deviate from the ideally planar conformation in unstrained alkenes.^[13] Their theoretical calculations demonstrated that, despite this nonplanarity, the atomic p-orbitals in ABOs retain sufficient overlap to form a π -bond within the distorted σ -backbone of the molecules. Nevertheless, nonplanarity of the σ -framework of ABOs leads to instability and enhanced reactivity. It is worth noting that the reported ABOs consistently feature double bonds on the longer carbon bridges of their bicyclic structures. The dihedral angle between the atomic p-orbitals on the one-carbon bridge (**C7**) and the branching carbon (**C1**) in a bicyclo [2.2.1] heptane is 90° before the distortion of the σ-skeleton of the molecule, **Figure 1a**. Furthermore the branching carbon in bicyclo [2.2.1] heptane, as also discussed by Garg and co-workers, is pyramidal which attenuates the π -bonds. Therefore, a double bond between **C1** and **C7** is likely to break to a diradical. Similarly, a double bond on one-carbon bridges of bicyclo [2.1.1] hexane and bicyclo [1.1.1] pentane are even more difficult to form because pyramidalization in smaller bicyclo olefins is more pronounced. Our CASPT2 computations suggest that in a hypothetical bicyclo[2.2.1]hept-4(7)-ene, or as conventionally known, 7-norbornene, the triplet diradical remains 16 kcal.mol⁻¹ lower in energy than the singlet as a double bond between **C1** and **C7** is too weak to stabilize the associated singlet state, **Figure 1b**.



Figure 1. Structure of hypothetical 7-norbornene. (a) A Schematic representation of atomic porbitals on C1 (branching point) and C7 (the one-carbon bridge) in 7-norbornene. (b) Ground triplet state structure of 7-norbornene and (c) the first singlet state of the molecule. In the singlet state C7 gets notably distorted to permit overlap between p-orbitals.

However, one can deliberately take advantage of the orthogonality of atomic p-orbitals and pyramidalization of **C1** in norbornane structure to stabilize a carbanion on **C1** while stabilizing a carbocation on **C7** that can easily planarize instead of the usual diradical formation scenario. To achieve this goal, one must break the near-degeneracy of the highest occupied molecular orbitals

(HOMOs) in the triplet diradical state. The orbitals accommodating such ion-pair do not overlap with each other and the neighboring carbons merely benefit from electrostatic stabilization of two adjacent ions, formally accommodated in carbon's atomic p-orbitals. In the following, utilizing this strategy, we introduce a series of novel hydrocarbons with ionic *p*-bonds in which anion and cation are separated by the distortion of the σ -framework.

Starting with bicyclo [2.2.1] heptane (norbornane), we explored two factors: (1) electronic effect of substituents on the stability of the ion pair and (2) the distortion of the σ -framework by extending our quest for stable ionic *p*-bonds in bicyclo [2.1.1] hexane and bicyclo [1.1.1] pentane structures. To verify the ionic *p*-bonding in the selected systems, we examined the relative energies of the singlet and triplet states of the molecules, geometric parameters, atomic charges, and the electronic structure of the molecules. An olefin with ionic *p*-bonding should have a singlet state that is lower than the triplet (biradical) state and a planar **C7** structure in its singlet state to prevent any efficient overlap between **C1** and **C7**. Selected species are listed in **Figure 2**. **Table 1** lists singlet-triplet gaps of the molecules as well as natural atomic charges of anionic and cationic centers computed at ω -B97XD^[14]/def2-TZVP^[15] level in DMF as solvent using SMD^[16] model. More atomic charges and S-T gaps computed at various computational levels are listed on **Tables S1-S4**. Extensive computations using other DFT and post-HF methods are available in the **Supporting Information** section. All data are qualitatively consistent with ω -B97XD/def2-TZVP computations. Therefore, here in the article we refer to these results, unless otherwise is stated.



Figure 2. The structures of three families of bicyclic olefins (1 to 3) with different substituents (a to d, H and F). In the studied structures R stabilizes the carbocation center, therefore, it is selected to be a strong electron-donor. In the case of structures 1, we examined the influence of electron-withdrawing fluorine atoms, two bonds away from the anionic center by substitution of H and F on C3 and C5 of the structure.

Table 1. The singlet-triplet Gibbs free energy gaps, S-T gaps, corrected for zero-point energies at
298.15 K in kcal.mol ⁻¹ , and natural atomic charges, q , of anionic branching carbon (C1) and the
cationic one-carbon bridges (Cb) in structures 1, 2 and 3, listed in Figure 1. All data are computed
for DMF as the solvent model.

Molecule	S-T gap	<i>q</i> (C1)	q(Cb)	Molecule	S-T gap	<i>q</i> (C1)	<i>q</i> (Cb)
1aH	7.8	-0.68	0.35	1bF	10.3	-0.63	0.26
1bH	5.7	-0.67	0.34	1cF	4.5	-0.65	0.36
1cH	2.3	-0.69	0.45	1dF	2.6	-0.64	0.35
1dH	-0.9	-0.67	0.43	2a	23.5	-0.54	0.19
1aF	12.7	-0.64	0.26	3a	26.3	-0.57	0.22

Singlet-triplet energy gaps and natural atomic charges show a correlation with each other. If the substituent on the carbocation is a weakly electron donating one, and more charge is accumulated on the carbocation, the singlet-triplet energy gap decreases notably. This shows that strong localized positive charge prefers an even distribution of electrons on the branching carbon and the one-carbon bridges. Interestingly, the presence of methyl groups on the ortho position of phenyl substituents does not increase the singlet-triplet gap. Looking at the atomic charges shows that although cations are slightly more delocalized via electron donating effect of the ortho-methyl, the proximity of methyl to the anionic carbon puts electrostatic pressure on the anion and lowers the singlet-triplet gaps. This is reflected in the energy levels of HOMOs. For example the HOMO of **1bF** is 0.05 eV higher in energy than that of **1aF** that lacks the ortho-methyl group on the phenyl substituent. In structure 1, the electronic effect of fluorine atoms, two bonds away from the anionic center, still influence the charges and hence the singlet-triplet energy gaps. Therefore, with norbornane's σ-framework, 1, 1aF, with eight fluorine substituents and a para-dimethyl aminophenyl substituent on the cationic carbon has the largest singlet-triplet gap and is most likely to be synthetically achievable in a polar solvent medium.

Changing the structure from norbornane to smaller bicyclic species dramatically increases the singlet-triplet energy gap through pyramidalization of the branching carbon. Natural Bond Orbital^[17] (NBO) analysis confirms the expected presence of a lone pair on the carbanion localized at the branching carbon. The analysis further demonstrates that increasing the degree of pyramidalization from structure **1** to **3**, **Figure 2**, leads to a progressive increase in the s-orbital contribution to the lone-pair orbital. Specifically, the s-orbital contribution rises from 26.5% in **1aF** to 34.7% in **2a**, and further to 46.7% in **3a**. This trend aligns with a shift in the hybridization of the lone pair from sp³ to sp² and eventually to sp. Such a transition corresponds to the stabilization of the anion, driven by the increased electronegativity of the carbon atom as the sorbital contribution becomes more dominant. NBO analysis confirms the formation of an anion, the stabilization of the cation through π -electron donation from the phenyl rings, and the localization of the cation as a π^* orbital situated between the cationic center and the adjacent phenyl group, **Figure 3**. Natural electron configuration of the carbon's valence orbitals in the cationic centers (**1aF**: 2s (0.93), 2p (2.78), **2a**: 2s (0.94), 2p (2.84), and **2c**: 2s (0.95), 2p (2.80)) reflect lower population than the anionic centers (**1aF**: 2s (1.18), 2p (3.42), **2a**: 2s (1.24), 2p (3.26) and **2c**: 2s (1.40), 2p (3.14)) consistent with the ionic picture of the adjacent atoms.



Figure 3. Natural bonding orbitals of **1aF**, **2a**, and **3a**. All species have a relatively low energy π interaction between the cationic center and its neighboring atom on the phenyl groups denoting π -electron donation. LP in the figure denotes the lone pair of the anionic centers, and π^* corresponds to the carbocationic centers.

The extent of π -donation from the phenyl rings to the cationic center can be quantified by evaluating the electron delocalization between the cationic center and the adjacent atom on the phenyl ring. Electron delocalization serves as a robust metric within the framework of quantum theory of atoms in molecules (QTAIM)^[18], providing a measure of covalency based on the number

of electrons shared between two atoms. The delocalization indices^[19] between the cationic center and the adjacent atom on the phenyl substituent for **1aF**, **2a**, and **3a** are 1.52, 1.45, and 1.48, respectively, indicating a bond order of approximately 1.5. This finding aligns with the expectation of strong electron donation to the carbocation via phenyl groups. To further validate this conclusion, we analyzed 2-propyl cation substituted with a para-dimethylamino phenyl group (substituent **a** in **Figure 2**). The natural atomic charge of this cation was calculated to be 0.32, consistent with the range of charges observed in our model systems. Furthermore, the delocalization index of the corresponding carbon pair in this cationic model was also 1.45, consistent with the other model systems. On the other hand, the delocalization index between the carbanion and carbocation centers in **1aF**, **2a**, and **3a** are 0.98, 1.05, and 0.95, respectively. These values are within the range of ordinary single (σ) carbon-carbon bonds and consistent with the computed bond lengths between carbocation and carbanion centers for **1aF**, **2a**, and **3a** that are 1.514, 1.500, and 1.538 Å, respectively.

Polar solvents play an important role in stabilization of ionic species. In the absence of a polar medium in the gas phase, the singlet-triplet energy gap for all species decreases, **Table S5**. Among the studied species only in **2a** and **3a** the singlet state remains notably lower than the triplet states in the gas phase. Interestingly, the singlet-triplet gap in **2a** and **3a** switch and **2a** in the gas phase sustains a larger singlet-triplet gap. NBO analysis and inspecting the geometry of **2a** reveal that while, the branching carbon is negatively charged (q(**Cb**) = -0.35) the σ -framework of the molecule is distorted in a way that now a polarized double bond is formed between the formal carbonand carbocation, **Figure 4**. This picture is consistent with bond shortening from 1.500 Å in solvent to 1.442 Å in the gas phase.



Figure 4. Natural molecular orbitals of 2a in gas phase. The molecule in the absence of a polar medium forms a distorted π bond.

In summary, we report an unexpected mechanism of chemical bonding between carbon atoms: ionic *p*-bonding. In these bonds, steric hindrance imposed by the rigid σ -skeleton of bicyclo-bridged olefins prevents the formation of a conventional π -bond. The substitution of threecoordinated carbon atoms with electron-withdrawing and electron-donating groups promotes charge separation, resulting in the formation of adjacent ion pairs instead of a triplet diradical species. Efficient ionic p-bonding requires asymmetric substitution of carbons with strong electron-withdrawing and electron-donating groups, and it is further facilitated by the pyramidalization of the branching carbon in bicyclo-bridged olefins. Our computational results indicate that as pyramidalization of the branching carbon increases from bicyclo[2.2.1]heptane to bicyclo[1.1.1]pentane, the s-character of the lone pair on this carbon also increases, providing additional stabilization to the carbanion.

Computational Methods

All molecular structures in both singlet and triplet states were initially optimized at the ω -B97XD/def2-TZVP computational level. The eigenvalues of the Hessian matrix were used to

characterize local minima. To evaluate the impact of different functionals on the results, all local minima were reoptimized using the M06-2X^[20], B3LYP^[21-23], and BLYP functionals with the same basis set. The results obtained with M06-2X and B3LYP were quantitatively similar to those of ω -B97XD, while GGA-BLYP predicted significantly larger singlet-triplet gaps. All density functional theory (DFT) computations were carried out in both the gas phase and in N,N-dimethylformamide (DMF) as a solvent, using the SMD solvation model. The quality of open-shell DFT computations for triplet states was assessed by examining spin contamination, and all unrestricted DFT (UDFT) results were confirmed to be free of significant spin contamination as spin-squared operator values for triplet states remain close to 2, **Table S6**.

To further validate the DFT results, single-point CCSD/def2-SVP computations were performed on the ω -B97XD/def2-TZVP-optimized geometries, as ω -B97XD has been demonstrated to be reliable for modeling strained molecules. Vertical singlet-triplet gaps were calculated at both singlet and triplet geometries. At the singlet geometries, all olefins exhibited high-energy triplet states. However, at the triplet geometries, several olefins with low singlettriplet gaps were found to have more stable triplet states. Nonetheless, for compounds **1aF**, **2a**, and **3a**, the singlet state was consistently more stable at the CCSD level, regardless of the geometry used, **Table S7**.

The potential multireference character of the molecules was assessed using the T1 diagnostic test, which indicated single-reference wavefunctions for all cases, **Table S8**. For 7-norbornene, a discrepancy was observed between CCSD and DFT results. To resolve this, the singlet and triplet structures of 7-norbornene were optimized at the CASSCF(4,4)/def2-TZVP level, and single-point CASPT2(4,4)/def2-TZVP computations were performed to determine the relative energies of the states. The triplet state was found to be 16 kcal·mol⁻¹ more stable than the

singlet, indicating a dominant diradical character for 7-norbornene. All first-principles computations were performed using Gaussian 16 C01.^[24]

The electronic structures of the molecules were analyzed using Natural Bond Orbital (NBO) and Quantum Theory of Atoms in Molecules (QTAIM) methods . NBO analyses were conducted using NBO 3, implemented in Gaussian, while QTAIM analyses were performed using AIMAll (Version 19.10.12).^[25]

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Conflict of interests

The authors declare no conflict of interest.

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TOC

Orthogonal natural frontier orbitals of an anti-Bredt olefin, shown below, accommodating an

anion (green) and a cation (blue-yellow) nearby.