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Bicyclo[2.2.1]hepta-2-ene-5-yl-7-ylium Radical Cation: A Theoretical Validation of a Bishomoaromatic Radical Cation Intermediate

Per-Erik Larsson,* Nessima Salhi-Benachenhou, and Sten Lunell

Department of Quantum Chemistry, Uppsala University, S-751 20 Uppsala, Sweden

per-erik.larsson@kvac.uu.se

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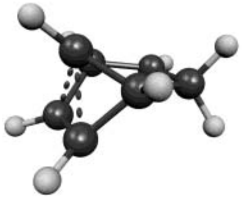
ABSTRACT

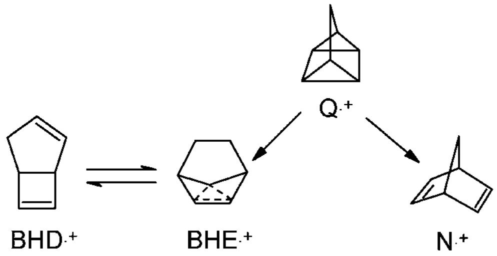


A natural bond orbital analysis of the distonic bicyclo[2.2.1]hepta-2-ene-5-yl-7-ylium radical cation interprets its structure and radical character by a three-center two-electron bond between C2, C3, and C7 (a bishomoaromatic stabilization) and a singly occupied orbital on C5, n_5. Moreover, B3LYP/6-311+G(d,p) ESR parameters, which agree excellently with experiment, are interpreted in terms of spin polarization in the natural hybrids of σ_{C5-H5}, and a dual hyperconjugative effect involving n_5, σ_{C1-H1a}, σ_{C1-H1b}, and antibonding counterparts.

One of the most intriguing aspects of hydrocarbon radical cations is that they often form geometric and electronic structures that differ substantially from their parent molecules. A computational investigation of rearrangements from the quadricyclane radical cation ($\mathbf{Q}^{\bullet+}$) revealed a stationary point with a special structure: the bicyclo[2.2.1]hepta-2-ene-5-yl-7-ylium radical cation ($\mathbf{BHE}^{\bullet+}$).[1] In this letter, we explore the bonding and electronic structure of $\mathbf{BHE}^{\bullet+}$ with natural bond orbitals (NBOs). Furthermore, we show that NBO analysis can be used to reveal how ^{1}H isotropic hyperfine coupling constants (hfcc) arise in hydrocarbon radical cations.

The $\mathbf{Q}^{\bullet+}$ easily rearranges to the norbornadiene radical cation ($\mathbf{N}^{\bullet+}$), but with ESR spectroscopy, an additional radical cation species was discovered.[2] The observed spectrum was assigned to the bicyclo[3,2,0]hepta-2,6-diene radical cation ($\mathbf{BHD}^{\bullet+}$).[2] In a quantum chemical study, we investigated the mechanism for the rearrangement of $\mathbf{Q}^{\bullet+}$ to $\mathbf{BHD}^{\bullet+}$ and localized an intermediate, $\mathbf{BHE}^{\bullet+}$, 2.5 kcal/mol more stable than $\mathbf{BHD}^{\bullet+}$ in CCSD(T)/6-311+G(d,p)//B3LYP/6-311+G(d,p) calculations (Scheme 1). Moreover, a 12.8 kcal/mol conversion barrier back to $\mathbf{Q}^{\bullet+}$ and an 8.1 kcal/mol barrier to $\mathbf{BHD}^{\bullet+}$ were found for $\mathbf{BHE}^{\bullet+}$ on the same level of theory, indicating a certain kinetic stability.[1] A conclusive confirma-

Scheme 1. Quadricyclane Radical Cation Rearrangements



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tion that **BHE**$^{\bullet+}$ was indeed observed in the ESR experiment came from comparing the experimental hfcc[3] (41.5G, 31.6G, 22.5G) with those of the optimized structures **BHD**$^{\bullet+}$ (H2a = 25.6G, H1 = 17.6G, H2b = 16.8G) and **BHE**$^{\bullet+}$ (H6a = 41.0G, H6b = 30.7G, H5 = −22.7G), respectively. We are presently investigating the possible existence of additional rearrangement pathways.

The **BHE**$^{\bullet+}$ B3LYP/6-311+G(d,p)-optimized structure is shown in Figure 1. Both the optimization and the NBO[4] analysis were carried out with Gaussian 98.[5] This structure has similarities to **N**$^{\bullet+}$ but presents two striking differences. The most obvious one is the strong tilting of the C7 bridge toward the C2−C3 bond, which is shown by the difference between the two dihedral angles, Φ_1 and Φ_2. This tilting also affects the C2−C3 bond, which has a length of 1.40 Å, indicating an elongated double bond. The other major difference between **BHE**$^{\bullet+}$ and **N**$^{\bullet+}$ is the C5 and C6 coordination: C5 is a three-coordinated carbon with bonds that are only partly shortened C−C single-bonds, and it does not show any pyramidalization; C6 is similar to the methyl carbons found in norbornenyl.

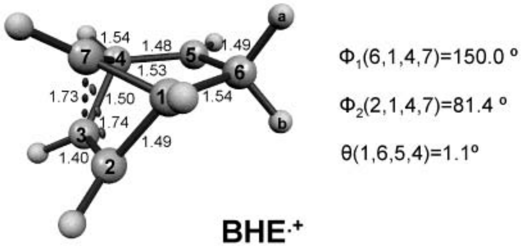
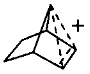


Figure 1. Selected distances and dihedral angles for the **BHE**$^{\bullet+}$ stationary point, optimized with B3LYP/6-311+G(d,p).

In carbocation chemistry, this type of structure is well-known from both experiment and computations.[6] Two examples that show behavior similar to **BHE**$^{\bullet+}$ are the 7-norbornenyl cation, **1**, and the bicyclo[2.1.1]hex-2-en-5-ylium cation, **2**. To highlight this close correspondence, we compare the C2−C7 (1.73 Å) and C3−C7 (1.74 Å) distances of **BHE**$^{\bullet+}$ with the equivalent distances in **1** and **2**. An MP2/6-31G* calculation[6c] for **1** gives 1.72 Å for both distances, and X-ray crystal structure data of a derivative of **1** give 1.88 and 1.87 Å, respectively.[6a] For structure **2**, a B3LYP/6-31G* calculation[6b] gives two equal distances of 1.74 Å, and the X-ray structure[6b] for a methylated derivative gives 1.76 Å. Another feature that indicates a close resemblance in bond character between **BHE**$^{\bullet+}$ and **1** and **2** is the similar size and direction of the pyramidalization on C2 and C3. The derivative of **1** has, for example, bonds C2−C21 and C3−C31 bent out of the plane in the *exo* direction by 15.4 and 14.2°,[6a] respectively, which is close to the **BHE**$^{\bullet+}$ values of 22.9 and 21.6° for the equivalent bending. These close similarities in geometric parameters suggest a strong resemblance between the bonds formed in **BHE**$^{\bullet+}$ and the two cations **1** and **2**. Therefore, **BHE**$^{\bullet+}$ should have a bishomoaromatic, three-center two-electron bond between C2−C3−C7 with strong cationic behavior.



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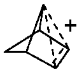

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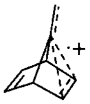

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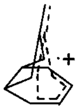

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Actually, this type of conjugative stabilization has also been suggested for radical cations.[7] Of particular interest for this work is the exocyclic stabilization, between C2−C3 and the C7−C8 double bonds, in 7-methylidenenorbornene[7a,b] and 7-methylenenorbornadiene,[7c] **3**. Another example of a bishomoaromatic stabilization is the bishomoheptafulvene, **4**.[7d] However, none of these examples are as well documented as the bishomoaromatic carbocation structures.

The bond properties in **BHE**$^{\bullet+}$ were evaluated through an NBO analysis.[4] The purpose is to obtain the NBO Lewis structure (LS), i.e., to construct localized chemical bonds and lone pairs from the delocalized molecular orbitals.[8] For open-shell systems, this is done with the different hybrids for different spins NBO, which yields separate LSs for α and β spins.[9]

As a first step we tried the default NBO search routine and located an α-LS with 96.47% population and a β-LS with 97.33% population. However, when investigating these LSs, several flaws were detected that would complicate an NBO analysis.[10] Therefore we found it judicious to add the three-center search, which results in a slight improvement of the NBO occupancy: the α-LS has 98.55% occupation and the β-LS has 98.53% occupation.[11] Yet, more important

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(3) Three major hfcc components are taken from ref 2a, and the theoretical values are from ref 1.

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(8) Weinhold, F. In *Encyclopedia of Computational Chemistry*; Schleyer, P. v. R., Allinger, N. L., Clark, T., Gasteiger, J., Kollman, P. A., Schaefer, H. F., III, Schreiner, P. R., Eds.; Wiley & Sons: Chichester, UK, 1998; Vol. 3.

(9) Carpenter, J. E.; Weinhold, F. *J. Mol. Struct. (THEOCHEM)* **1988**, *169*, 41−62.

C2-C3-C7
3-center bond

n_5
Unpaired Orbital

Figure 2. Contour plots of the α-PNBO for the three-center bond and the singly occupied orbital. The PNBO are taken from a B3LYP/6-311+G(d,p) NBO-calculation.

is that both LSs have very similar NBOs, with only relatively small polarizations, and no bonds with low occupancy appear.

Most of the located bonds are of the σ_{C-C} or the σ_{C-H} type, with two important exceptions (see below). The two σ-bonds with the lowest electron occupation are the σ_{C1-C7} ($\alpha = 0.952$e, $\beta = 0.953$e) and σ_{C4-C7} ($\alpha = 0.951$e, $\beta = 0.942$e), which in both cases is close to a two-electron Lewis bond. This fact can also be noticed from the atomic distances in Figure 1 of C1−C7 (1.53 Å) and C4−C7 (1.54 Å); a C−C single bond is 1.54 Å. Therefore, the NBO located σ-bonds indicate a σ-bonded backbone that has little radical character.

The special characteristics of **BHE**$^{\bullet+}$ can be explained by the two remaining occupied NBO. First, a three-center NBO between C2−C3−C7, plotted to the left in Figure 2 (with electron occupations $\alpha = 0.974$e and $\beta = 0.976$e), is responsible for the C7 tilt toward C2−C3. Further, a 0.64 positive charge is located around the C2−C3−C7 bond[12] using natural population analysis,[13] implying a large cationic character in this part of the molecule. Second, a nonbonding orbital, n_5, is located on C5, plotted on the right in Figure 2 (with electron occupation $\alpha = 0.918$e and $\beta = 0.074$e). Hence, most of the radical character is localized on n_5. Less positive charge is localized (0.18) on this part. Hence, the spin and charge are to a large extent separated in **BHE**$^{\bullet+}$.

A hfcc measures a net unpaired electron density at the proton. The difference in occupancy for α and β NBOs can capture the spin-unpairing mechanisms behind the hfcc values. Traditionally, this type of analysis is done with simple wave functions, e.g., Hückel.[14] When the NBO method is used instead, any type of wave function is applicable, and the result of the analysis has a more general validity. Since the large calculated hfcc values (H5, H6a, and H6b) are localized around n_5, it is from the interactions between n_5, σ_{C5-H5}, σ_{C6-H6a}, σ_{C6-H6b}, and their antibonding counterparts that spin-unpairing appears.

First, the electron density around H5 (−22.7G) has an excess of β spin: the 1s natural atomic orbital has 0.020e higher occupation in the β spin (α-1s = 0.371e, β-1s = 0.391e). This appears from an inequivalent polarization of the natural hybrids in the σ_{C5-H5}: α-σ_{C5-H5} is $0.792(sp^{1.90})_C + 0.610(s)_H$ and β-σ_{C5-H5} is $0.775(sp^{1.88})_C + 0.632(s)_H$ (both with 0.992e occupation). Thus, it is the difference in polarization coefficients that unpair the bond, i.e., the α-σ_{C5-H5} polarization coefficient of the C5 hybrid is higher (0.792) than α-σ_{C5-H5} (0.775) and lower in the α-σ_{C5-H5} H5 hybrid (0.610) than β-σ_{C5-H5} (0.632).

Second, both H6a (41.0G) and H6b (30.7G) involve a dual hyperconjugative mechanism. In H6a, the population has 0.048e (α-1s = 0.397e, β-1s = 0.349e) more α than β spin, while that in H6b has 0.037e (α-1s = 0.392e, β-1s = 0.355e) more α than β spin. Since hyperconjugation is a stabilization due to delocalization into unoccupied NBO, an estimate of their importance can be obtained from second-order perturbation interaction energies, $\Delta E^{(2)}$.[8] Substantial $\Delta E^{(2)}$ for the α-LS appears from n_5 into $\sigma_{C6-H6a*}$ ($\Delta E^{(2)} = 4.35$ kcal/mol), 0.017e, and into $\sigma_{C6-H6b*}$ ($\Delta E^{(2)} = 4.02$ kcal/mol), 0.015e, which is a delocalization that increases the α-electron density around H6a and H6b. Moreover, to compensate for this increase of electron density in $\sigma_{C6-H6a*}$ and $\sigma_{C6-H6b*}$, β-σ_{C1-H1a} and β-σ_{C6-H6b} delocalize electron density into β-n_5. The $\Delta E^{(2)}$ for the electron transfer from σ_{C6-H6a} into n_5 is 4.67 kcal/mol, and that from σ_{C6-H6b} into n_5 is 3.67 kcal/mol. Thus, the hyperconjugative effect that gives rise to the spin-unpairing is actually two mechanisms that both increase the spin density around H6a and H6b.

In conclusion, the radical character of **BHE**$^{\bullet+}$ is mainly located in the singly occupied orbital, and its charge is located mainly in the three-center bond. From the NBO analysis, the strong resemblance of atom distances between **BHE**$^{\bullet+}$ and **1** and **2**, and the excellent correspondence with the experimental hfcc, it can unequivocally be concluded that **BHE**$^{\bullet+}$ is a bishomoaromatic distonic radical cation. Finally, the NBO analysis indicates the validity of interpreting the hfcc as a spin polarization and a hyperconjugative effect, with a dual mechanism, for **BHE**$^{\bullet+}$. This analysis supports the standard type of reasoning based on simpler wave functions often used in ESR spectroscopy.

Acknowledgment. We are indebted to Prof. O. Matsson for valuable discussions.

Supporting Information Available: Details of computational procedures, Cartesian coordinates, and software citations. This material is available free of charge via the Internet at http://pubs.acs.org.

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(10) The most problematic aspect was that peculiar bonds and nonbonding orbitals were formed and that the α and β spin LS had several large differences. For example, the α-LS had a nonbonding orbital on C4 with an occupation of 0.45e, and the β-LS had a nonbonding orbital on C3 with an occupation of 0.36e.

(11) The three-center search gives two well balanced LSs that have no large population in Rydberg (<0.003e) or antibonding orbitals (<0.089e).

(12) This value was obtained by summing up the natural population charges for α and β spin for C2(−0.01, −0.02), C3(−0.05, 0.02), C7(−0.03, 0.00), H2(0.13, 0.13), H3(0.13, 0.14), and H7(0.14, 0.14). Another area where a substantial part of the positive charge is located is around C5−H5 (0.18): C5(−0.50, 0.42), H5(0.11, 0.14). The remaining charge (0.18) is delocalized.

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