# Homoarmaticity and Bicycloaromaticity in Carbanions

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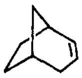
**Abstract:** The proposed homoaromatic and bicycloaromatic stabilization for a series of bicyclic anions is investigated theoretically. Although minimal basis set ab initio calculations reproduce the observed relative acidities of the corresponding hydrocarbons, detailed orbital analyses prove that homoaromaticity and bicycloaromaticity are not involved. It is apparent that the interactions between unoccupied and occupied orbitals necessary to achieve homoaromaticity and bicycloaromaticity cannot be realized in neutral or anionic hydrocarbons without incurring dominating losses of bonding or increases in four-electron repulsions. Thus, these effects are observable only for carbonium ions in which the empty p orbital is energetically and spatially proximate to a high-lying filled $\pi$ or $\sigma$ orbital.

In view of the importance of aromaticity in determining the behavior of organic molecules, the related notion of homoaromaticity has been closely studied since its inception.[2] The concept was generalized to include bicycloaromaticity and the interactions of "ribbons" of $\pi$ orbitals in various topologies.[3] The support for homoaromaticity has been based largely on NMR chemical shift data and on some rates for solvolyses and proton exchange.[3,4] Thus, there is little direct experimental information on the energetic effects of the phenomenon; however, this issue has been addressed in several theoretical studies.[5-8] Molecular orbital (MO) calculations on a series of potential monohomoaromatic neutral hydrocarbons and carbonium ions showed that special stabilization was only unequivocal for the cyclobutenyl and homotropylium cations.[5] Some destabilization is apparent for bicyclo[2.1.0]pent-2-ene and bicyclo[2.1.1]hex-2-enes due to interactions between the small rings and unsaturated bridges,[5,9,10] while bicyclo[3.1.0]hexenyl cation is nonaromatic.[5,11] In a recent paper, Houk et al. have provided additional support that homoantiaromaticity, but not homoaromaticity, is observable in neutral hydrocarbons.[8]

The classic examples of bishomoaromaticity are the 7-norbornenyl and 7-norbornadienyl cations.[4] Solvolytic data and the bridge-flipping barrier for the latter ion indicate stabilization of ca. 20 kcal/mol due to bridging.[12] Similar energetic benefit of bridging is found for the trishomoaromatic Coates' cation and the parent tris(homocyclopropenium) ion.[6,13]

In contrast, little experimental support is available for homoaromaticity in anions. Suitable systems have also received scant theoretical attention. An exception is the combined NMR and MO study of cyclohexadienyl anions by Olah and co-workers.[14] The ions were not found to be homocyclopentadienylic but rather planar, nonaromatic species.[14] So that the analyses could be extended to bridged systems, calculations on **1–5** and the corresponding anions **6–10** are reported here. These systems have been studied experimentally; the enhanced acidities of **2** and **4** relative to **1** and **3** were attributed to homoaromaticity in **7** and **9**.[15-17] Moreover, **10** is claimed to be stabilized further via bicycloaromaticity.[3,17]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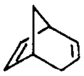
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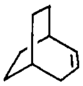
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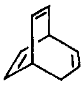
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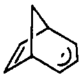
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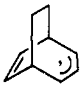
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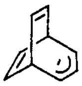
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In the present study, it is first established that ab initio calculations with a minimal basis set can reproduce the observed relative acidities of **1–5**. A thorough analysis of the orbital interactions between the $\pi$-type MO's in the anions then reveals that homoaromaticity and bicycloaromaticity are absent; the critical interactions between the allylic HOMO's and the LUMO's of the ethylenic $\pi$ bonds are simply not present. The LUMO's are too high in energy to mix significantly with the allylic HOMO's, although substantial interaction occurs between occupied $\pi$ and $\sigma$ MO's. The small differences in acidities of **1–5** are attributable to inductive effects; however, it is noted that the increase in energy of the HOMO's as the anions become more saturated results from mixing between the allylic HOMO and $\pi$ bond orbitals of the bridges.

The conclusion is that homoaromaticity is insignificant for hydrocarbon anions as well as neutrals. It is only important for select carbonium ions in which the empty p orbital is proximate to a high-lying occupied $\pi$ or cyclopropyl bond orbital.

## Computational Procedure

So that a consistent set of geometries for **1–10** could be obtained, MINDO/3 calculations were performed. Complete geometry optimization was carried out in each case except one plane of symmetry was assumed for **3** and **5–10**. This assumption was tested for several of the anions and proved to be valid. In particular, complete optimization for **10** predicts the anion to have $C_{2v}$ symmetry. The ion has also been found to be symmetrical on the NMR time scale at −141 °C.[18] The choice of MINDO/3 stems from the ability to optimize systems of this size with reasonable effort and, more importantly, from the facts that for neutral hydrocarbons and carbonium ions the method accounts well for homoaromaticity[5,6] and predicts geometries in good

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[1] Camille and Henry Dreyfus Foundation Teacher-Scholar, 1978–1983, and an Alfred P. Sloan Foundation Fellow, 1979–1981.

[2] Winstein, S. *J. Am. Chem. Soc.* **1959**, *81*, 6524; *Q. Rev. Chem. Soc.* **1969**, *23*, 141.

[3] Goldstein, M. J.; Hoffmann, R. *J. Am. Chem. Soc.* **1971**, *93*, 6193. Goldstein, M. J. *Ibid.* **1967**, *89*, 6357.

[4] For a comprehensive review, see: Warner, P. M. *Top. Nonbenzenoid Arom. Chem.* **1976**, *2*.

[5] Jorgensen, W. L. *J. Am. Chem. Soc.* **1976**, *98*, 6784.

[6] Jorgensen, W. L. *Tetrahedron Lett.* **1976**, 3029, 3033.

[7] Hehre, W. J. *J. Am. Chem. Soc.* **1974**, *96*, 3644.

[8] Houk, K. N.; Gandour, R. W.; Strozier, R. W.; Rondan, N. G.; Paquette, L. A. *J. Am. Chem. Soc.* **1979**, *101*, 6797.

[9] Andrews, G. D.; Baldwin, J. E.; Gilbert, K. E. *J. Org. Chem.* **1980**, *45*, 1523.

[10] Jorgensen, W. L.; Borden, W. T. *J. Am. Chem. Soc.* **1973**, *95*, 6649; Borden, W. T.; Gold, A.; Jorgensen, W. L. *J. Org. Chem.* **1978**, *43*, 491.

[11] Olah, G. A.; Liang, G.; Jindal, S. P. *J. Org. Chem.* **1975**, *40*, 3259.

[12] Brookhart, M.; Lustgarten, R. K.; Winstein, S. *J. Am. Chem. Soc.* **1967**, *89*, 6352.

[13] Coates, R. M.; Fretz, E. R. *J. Am. Chem. Soc.* **1975**, *97*, 2538.

[14] Olah, G. A.; Asensio, G.; Mayr, H.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1978**, *100*, 4347.

[15] Brown, J. M.; Occolowitz, J. L. *Chem. Commun.* **1965**, 376.

[16] Moncur, M. V.; Grutzner, J. B. *J. Am. Chem. Soc.* **1973**, *95*, 6449.

[17] Goldstein, M. J.; Natowsky, S. *J. Am. Chem. Soc.* **1973**, *95*, 6451.

[18] Goldstein, M. J.; Tomoda, S.; Whittaker, G. *J. Am. Chem. Soc.* **1974**, *96*, 3676, footnote 14.

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Table I. Calculated Energetic Results,[a]

| | $\Delta H_f$, MINDO/3 | | $-E$, STO-3G[b] | |
|---|---|---|---|---|
| RH | RH | $R^-$ | RH | $R^-$ |
| 1 | 18.3 | 34.8 | 306.248 22 | 305.433 04 |
| 2 | 54.4 | 71.8 | 305.021 65 | 304.211 72 |
| 3 | 5.1 | 17.3 | 344.824 27 | 344.010 35 |
| 4 | 36.4 | 49.6 | 343.606 64 | 342.797 84 |
| 5 | 69.0 | 83.7 | 342.386 56 | 341.581 98 |
| 11 | 6.1 | 40.3 | 115.651 57 | 114.832 33 |
| 12 | 26.6 | 33.7 | 191.572 41 | 190.813 17 |
| 13 | 41.1 | 43.0 | 190.450 44 | 189.724 68 |

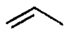
[a] $\Delta H_f$ in kcal/mol; $E$ in au. [b] STO-3G calculations used the MINDO/3 optimized geometries.

Table II. Relative Acidities of Alkenes[a]

| RH | $\Delta H$, MINDO/3 | $\Delta E$, STO-3G | $\Delta G$, exptl |
|---|---|---|---|
| 1 | −0.9 | 3.3 | 6.9[b] |
| 2 | (0.0) | (0.0) | (0.0) |
| 3 | −2.5 | 5.8 | >9.6[c] |
| 4 | −1.5 | 2.6 | 2.4,[d] 4.0[c] |
| 5 | (0.0) | (0.0) | (0.0) |
| 11 | 32.3 | 58.7 | 34.3[e] |
| 12 | 5.2 | 21.0 | 6.9[f] |
| 13 | (0.0) | (0.0) | (0.0) |

[a] Thermodynamic quantities in kcal/mol. [b] In $Me_2SO$.[15] [c] In $Me_2SO$.[17] [d] In THF.[16] [e] Gas phase.[22] [f] Gas phase.[21]

agreement with experiment and sophisticated ab initio calculations.[5,19,20] Less experimental and theoretical structural data are available for carbanions, though the limited evidence indicates MINDO/3 fares well in this area too.[14,20] To further test the method, it was necessary to carry out calculations on several reference compounds, **11–13**, and their anions, **14–16**, since relative gas-phase acidities have been reported for the molecules.[21,22] As discussed below, the MINDO/3 results are in very good agreement with the experimental values.



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In addition, single point ab initio calculations were executed for the final MINDO/3 optimized geometries of each molecule (**1–16**). The GAUSSIAN/76 program was employed with the minimal STO-3G basis set.[23] The size of the molecules rendered calculations with larger basis sets impractical. Although objections can be raised to performing ab initio calculations on anions with small basis sets and within the Hartree–Fock limit, only relative energetics are considered below so some cancellation of neglected effects is expected.

## Energetic Results

The calculated MINDO/3 $\Delta H_f$'s and STO-3G total energies for **1–16** are recorded in Table I. These numbers are converted to relative acidities for comparison with experiment by computing the $\Delta H$ or $\Delta E$ for the equilibria $RH + R_1^- \rightleftarrows R^- + R_1H$. The results for the three series of compounds **1** and **2**, **3–5**, and **11–13** are summarized in Table II. The experimental relative acidities of **1–5** were obtained from rates of proton exchange in THF or $Me_2SO$ solution.[15-17] Since the anions are allylic and consequently delocalized, differential solvation and ion-pairing effects on the equilibria should be small. The gas-phase experimental results for **11–13** are directly comparable with the theoretical data by assuming an equivalence of $\Delta G$, $\Delta H$, and $\Delta E$.[21,22] This is a reasonable approximation in view of the nature of the equilibria, although small corrections to $\Delta G$ for changes in symmetry numbers and temperature could be considered.

The MINDO/3 results for the reference compounds, **11–13**, are in excellent agreement with experimental results. This supports the choice of the method for the geometry optimizations. The STO-3G values are also in the correct order, although the differences in acidity are exaggerated.

On the other hand, the STO-3G results for **1–5** are in reasonable quantitative agreement with the experimental data, while the MINDO/3 results predict the opposite trends. Several points should be noted here. The experimental data for **1–5** are obtained from kinetic, not equilibrium, measurements. It must also be assumed that there are not significant differential ion-pairing effects on the kinetics. Thus, quantitative accord between the theoretical gas-phase values and the solution-phase results is not expected. In any event, the acidities of **2** and **4** appear to be enhanced by 3–7 kcal/mol relative to those of **1** and **3**. Furthermore, the STO-3G and experimental results agree that **5** is an additional 2–4 kcal/mol more acidic than **4**. Whether it is proper to ascribe these differences to homoaromaticity in **7** and **9** and to bicycloaromaticity in **10** is addressed in the next section. Relative to the stabilization normally associated with aromaticity and to that for the homoaromatic carbonium ions discussed above, the energetic effects for **1–5** are slight.

Secondly, the qualitative error in the MINDO/3 results for **1–5** may at first seem surprising in view of its performance for **11–13**. This is attributable to two factors: (1) the quantitative differences in acidities of **1–5** are small to begin with, and (2) MINDO/3 is well-known to overestimate the strain energies in bridged bicyclic systems, though it still yields good geometrical results for them.[19] The error in the strain energy is aggravated as more $sp^2$ centers replace $sp^3$ carbons in the molecules.[19] Consequently, the overestimate of the strain in the anions should be progressively greater in going from **6** to **7** and **8** to **10**. This is consistent with the trend in the MINDO/3 acidities for **1–5** in Table II. The fact that the STO-3G acidities are quantitatively better for **1–5** than **11–13** is undoubtedly due to the greater structural similarity for the former set of compounds and their anions. Overall, it is clear that the changes in the relative acidities of **1–5** are nicely mirrored in the STO-3G results. Detailed analyses of the composition of the STO-3G molecular orbitals for the anions should then reveal the presence or absence of the proposed homoaromatic and bicycloaromatic interactions.

## Molecular Orbital Analysis

To begin, the analysis will focus on **10** since it is supposed to be a key example of anionic bicycloaromaticity. Consistent with Goldstein and Hoffmann's treatment,[3] an orbital interaction diagram for **10** can be constructed by considering the mixing of the $\pi$ orbitals from the allylic and ethylenic bridges. The familiar allylic orbitals are labeled $\chi_1$, $\chi_2$ and $\chi_3$*.[24] The symmetry combinations of the $\pi$-bond orbitals from the ethylenic bridges yield four orbitals designated $\pi_+$, $\pi_-$, $\pi_+^*$, and $\pi_-^*$ as in norbornadiene.[24] The asterisk superscript indicates an antibonding, unoccupied orbital. The orbitals are classified as symmetric (S) or antisymmetric (A) with respect to the two symmetry planes in **10**; then, mixing orbitals of like symmetry yields the interaction diagram shown in Figure 1.

The diagram has been constructed with the aid of the STO-3G results. In particular, although substantial mixing between the occupied orbitals is found, interaction between occupied and empty orbitals is insignificant. This is illustrated by the drawings of the

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(19) Bingham, R. C.; Dewar, M. J. S.; Lo, D. H. *J. Am. Chem. Soc.* **1975**, *97* 1294.

(20) Haddon, R. C. *J. Org. Chem.* **1979**, *44*, 3608.

(21) Kebarle, P. *Annu. Rev. Phys. Chem.* **1977**, *28*, 445.

(22) Bartmess, J. E.; Scott, J. A.; McIver, R. T. *J. Am. Chem. Soc.* **1979**, *101*, 6046.

(23) Binkley, J. S.; Whitehead, R. A.; Hariharan, P. C.; Seeger, R.; Pople, J. A.; Hehre, W. J.; Newton, M. D. *QCPE* **1978**, *11*, 368.

(24) Jorgensen, W. L.; Salem, L. "The Organic Chemist's Book of Orbitals"; Academic Press: New York, 1973.

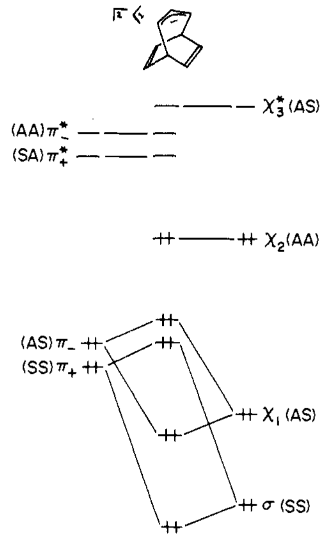

**Figure 1.** Molecular orbital interaction diagram for bicyclo[3.2.2]nonatrienyl anion (**10**).

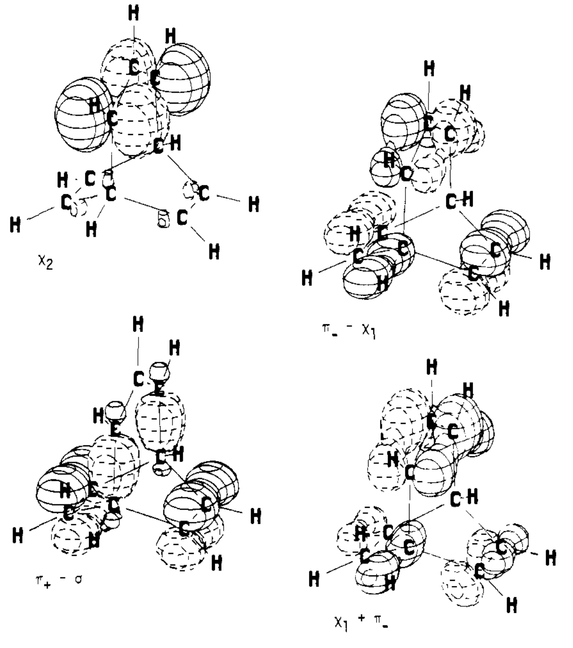

**Figure 2.** Orbital drawings for the four highest occupied MO's of **10** from the STO-3G wave function.

four highest occupied and three lowest unoccupied MO's presented in Figures 2 and 3. The drawings were generated by the PSI/77 program using the STO-3G wave functions and a contour level of 0.08 au.[24,25]

The four HOMO's may be described in order of increasing energy as $\chi_1 + \pi_-$, $\pi_+ - \sigma$, $\pi_- - \chi_1$, and $\chi_2$. It is noted that the $\pi_+$ orbital has mixed with $\sigma$ components of the same symmetry centered on the allylic bridge. Analogous "through-bond" mixing occurs for the $\pi_+$ orbital of norbornadiene,[24] though the interactions of the $\pi$ orbitals in this molecule are usually taken as a classic case of "through-space" interactions.[26] Goldstein and Hoffmann identified the key stabilizing interactions for bicycloaromaticity in **10** to be between $\chi_2$ and $\pi_-^*$ and $\pi_-$ and $\chi_3^*$. The illustrations of $\chi_2$ and $\chi_3^*$ in Figures 2 and 3 and perusal of the actual MO coefficients unequivocally assert that these interactions are insignificant in **10**. Therefore, bicycloaromaticity is not the source of the enhanced acidity of **5**. For comparison as an example of homoaromatic delocalization, the HOMO of the parent bis(homocyclopropenium) ion (**17**) which can be derived from 4-cyclopentenyl cation (**18**) is shown in Figure 4. This orbital reveals strong stabilization of the filled $\pi_{CC}$ bond orbital by mixing with the formally empty 2p orbital on C4 to yield a highly delocalized homoaromatic cation. The geometry in this case was also optimized with MINDO/3. It should be noted that MINDO/3 predicts the 2-cyclopentenyl cation to be more stable than **17** and **18** by 11 and 17 kcal/mol, respectively, which is consistent with the experimental difficulties in attempting to prepare **17** and **18**.[27]

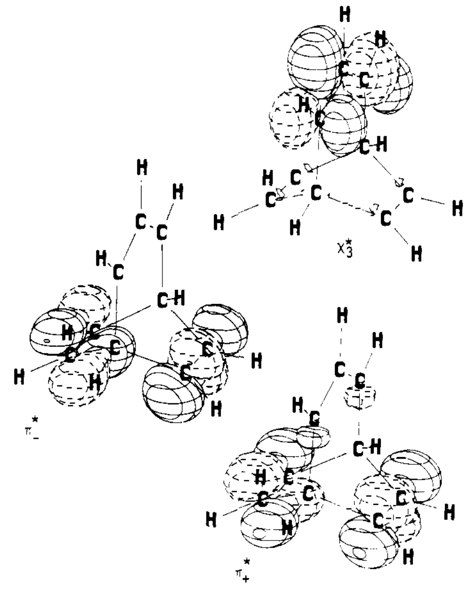

**Figure 3.** Orbital drawings for the three lowest unoccupied MO's of **10** from the STO-3G wave function.

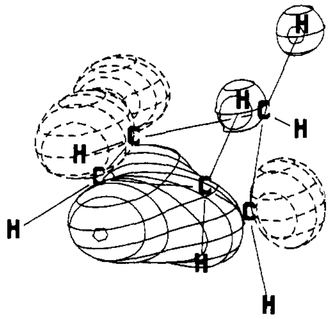

**Figure 4.** The HOMO of the parent bis(homocyclopropenium) ion.

For **7** and **9**, the key interactions that would lead to homoaromaticity are between $\chi_2$ and $\pi^*$, and $\pi$ and $\chi_3^*$.[3] Again, the MO coefficients from STO-3G, MINDO/3, and extended Hückel calculations indicate that such mixings are negligible. Furthermore, the geometric results are consistent with the lack of homoaromaticity predicted by MINDO/3. For example, if homoaromaticity were operative, the C6C7 bonds should lengthen appreciably in going from the neutral to the anions for **2**, **4**, and **5**. In fact, these bond lengths increase by only 0.002 Å according to the MINDO/3 results. Such changes are at the limits of the Fletcher–Powell optimization procedure. In contrast, for homoaromatic carbonium ions, MINDO/3 calculations yield increases of 0.1–0.2 Å for corresponding bonds.[5,6,20]

The reason for the lack of mixing between the filled and empty $\pi$ orbitals in **7**, **9**, and **10** appears to be that the energy gap is too great between the two manifolds. Overlap is not the problem as witnessed by the interaction of $\chi_1$ and $\pi_-$ illustrated in Figure 2. A similar conclusion primarily accounts for the lack of homoaromaticity in neutrals.[8] In this context it is noted that the

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[25] Jorgensen, W. L. *QCPE* **1978**, *11*, 340.

[26] Hoffmann, R. *Acc. Chem. Res.* **1971**, *4*, 1.

[27] Olah, G. A.; Surya Prakash, G. K.; Rawdah, T. N.; Whittaker, D.; Rees, J. C. *J. Am. Chem. Soc.* **1979**, *101*, 3935. Olah, G. A.; Liang, G.; Mo, Y. K. *Ibid.* **1972**, *94*, 3544.

STO-3G orbital energies for the four highest occupied MO's of **10** (Figure 2) are within 6.4 eV, whereas the energy gap between the HOMO and the three LUMO's (Figure 3) is 10.3–13.0 eV. For carbonium ions, the energy of the empty p orbital is close to that of occupied orbitals so homoaromaticity is permitted. It might be questioned whether minimal basis set calculations underestimate mixings between occupied and virtual orbitals. Actually, they tend to overestimate such charge-transfer interactions.[28]

At this point, it may be asked what is controlling the relative acidities of **1**–**5**? One must be cautious in attempting to explain differences of only a few kilocalories/mole in MO terms. With this in mind some proposals may be considered. The most obvious possibility is inductive effects. With increasing unsaturation the $\sigma$ frameworks of the ions become more electronegative and better able to accommodate the negative charge. The effect is manifested in a general lowering of MO energies for the more unsaturated species. For example, the energy of the $\chi_2$ HOMO decreases by 0.15 eV in going from **8** to **10** according to the STO-3G results. It may also be noted that the MO coefficients show that $\chi_2$ mixes slightly with the $\sigma_{CC}$ and $\sigma_{CC}^*$ bond orbitals for the C1C7, C1C8, C5C6, and C5C9 bonds. This is indicated by the small contributions to the $\chi_2$ MO at C6–C9 in Figure 2. As the bridges become unsaturated, the $\sigma_{CC}$ and $\sigma_{CC}^*$ orbitals are lowered in energy which makes the mixings with $\chi_2$ less energetically unfavorable.

Finally, the preference for $C_{2v}$ symmetry in **10** is easily understood from the orbital analyses. Tilting the allylic fragment toward an ethylenic bridge increases the four-electron repulsion between $\pi_-$ and $\chi_1$ much faster than it increases stabilizing interactions between occupied and unoccupied orbitals. This effect has been corroborated by both MINDO/3 and STO-3G calculations.

## Conclusion

An important finding in the present study is that reasonable relative acidities for alkenes can be obtained from minimal basis set ab initio calculations, particularly for structurally similar molecules. Furthermore, in view of the present results and other studies,[8,14,29,30] it is apparent that stabilization from homoaromaticity and bicycloaromaticity is not possible in neutral or anionic hydrocarbons. The molecules' occupied and unoccupied orbitals are well separated energetically. Consequently, their interaction cannot be realized without forcing geometrical distortions that yield too much loss of bonding or increases in four-electron repulsive interactions. Thus, homoaromaticity is found only for a small class of carbonium ions in which stabilization occurs by mixing the empty p orbital with properly oriented, high-lying, occupied $\pi$ or $\sigma$ orbitals. Bicycloaromaticity, which is an enhanced form of homoaromaticity resulting from the presence of additional unsaturated bridges, is likely only relevant for the 7-norbornadienyl cation. Invocation of these effects outside of the restricted contexts described here should be viewed with great skepticism.

**Acknowledgment** is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for support of this work.

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(28) Umeyama, H.; Morokuma, K. *J. Am. Chem. Soc.* **1977**, *99*, 1316.

(29) Grutzner, J. B. *J. Am. Chem. Soc.* **1976**, *98*, 6385.

(30) Kaufmann, E.; Mayr, H.; Chandrasekhar, J.; Schleyer, P. v. R. *J. Am. Chem. Soc.*, following paper in this issue.

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# Elusiveness of Bishomoaromaticity in Anionic Systems: The Bicyclo[3.2.1]octa-3,6-dien-2-yl Anion

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**Abstract:** The electronic structure of the bicyclo[3.2.1]octa-3,6-dien-2-yl anion (**6**), considered to be the prototype bishomoaromatic anion, was analyzed by semiempirical (MNDO) and ab initio (STO-3G) MO calculations. No evidence for homoaromatic stabilization (i.e., cyclic delocalization) was found. C-2–C-7 distances and Mulliken overlap populations between these carbons are almost identical in the $6\pi$ anion **6** and the corresponding $4\pi$ cation **7**. The calculated stabilization energy of anions **21** and **24** is similar to that of the alleged homoaromatic species **6** even though the orientation of the additional double bonds in **21** and **24** does not permit homoconjugative interaction with the allyl HOMO (eq 1, 3, 5). The experimentally observed stabilizing effect of the C-6–C-7 double bond in **6** is due to an inductive effect. In general, homoaromatic stabilization is not expected to be an important phenomenon in anions.

Applequist and Roberts recognized the unusual stability of the cyclobutenylium ion (**1**).[1] The geometry of the small ring facilitates substantial 1,3-$\pi$-bonding; an ion (**1**), which resembles the aromatic cyclopropenyl cation electronically, was suggested to result.[1] Winstein generalized this idea: the aromatic stabilization of conjugated systems with $(4n + 2)\pi$-electrons may not be destroyed completely by the insertion of one or more intervening groups.[2] This concept, "homoaromaticity", won rapid acceptance.[3,4] Cations **1**[5] and **2**[6] (monohomoaromatic), **3**[7] (bishomo-


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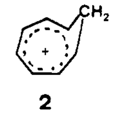
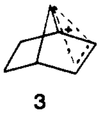


**2**


**3**


**4**

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(1) Applequist, D. E.; Roberts, J. D. *J. Am. Chem. Soc.* **1956**, *78*, 4012.

(2) Winstein, S. *J. Am. Chem. Soc.* **1959**, *81*, 6524.

(3) For reviews see: (a) Winstein, S. *Q. Rev. Chem. Soc.* **1969**, *23*, 141; *Spec. Publ.—Chem. Soc.* **1967**, *No. 21*, 5; (b) *Carbonium Ions* **1972**, *3*, Chapter 22. (c) Paquette, L. A. *Angew. Chem., Int. Ed. Engl.* **1978**, *17*, 106. (d) Warner, P. M. *Top. Nonbenzoid Aromatic Chem.* **1976**, *2*.

(4) For theoretical treatments, see: (a) Goldstein, M. J. *J. Am. Chem. Soc.* **1967**, *89*, 6357. (b) Hehre, W. J. *Ibid.* **1972**, *94*, 8908; **1973**, *95*, 5807; **1974**, *96*, 5207. (c) Haddon, R. C. *Ibid.* **1975**, *97*, 3608. (d) Jorgensen, W. L. *Ibid.* **1976**, *98*, 6784. (e) Haddon, R. C. *J. Org. Chem.* **1979**, *44*, 3608.

0002-7863/81/1503-1375$01.25/0