

Neutral Homoaromaticity in Some Heterocyclic Systems

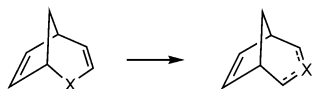
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Neutral Antihomoaromaticity to Homoaromaticity



X = BH, AlH, Be

X = PH, S, NH, O

Neutral homoaromaticity has been evaluated in heterocyclic systems related to the bicyclo[3.2.1]octane skeleton with replacement of CH₂ at C-2 in bicyclo[3.2.1]octa-3,6-diene with X = BH, AlH, Be, Mg, O, S, PH, NH (**12**); replacement of CH at C-3 in bicyclo[3.2.1]octa-3,6-dien-2-yl anion with PH, S, NH, O (**13**); and replacement at C-2 and C-3 with N and O (**14**). Stabilization energies (SE) are evaluated using density functional theory and homodesmotic equations at the B3LYP/6-311+G-(3df,2p)//B3LYP/6-31G(d) level for series **12–14**. Stabilization energies are compared with diamagnetic susceptibility exaltations, Λ , CSGT-B3LYP/6-31G(d)//B3LYP/6-31G(d), and nucleus-independent chemical shifts (NICS), GIAO-B3LYP/6-311+G(2d,p)//B3LYP/6-31G(d). Analysis of frontier orbitals and geometries, B3LYP/6-31G(d)//B3LYP/6-31G(d), and proton affinities of 2-azabicyclo[3.2.1]octa-3,6-diene, pyrrole, and related model systems, B3LYP/6-311+G(2d,2p)//B3LYP/6-31G(d), provide complementary evidence supporting the division of the substrates evaluated into antihomoaromatic (**12**, X = BH, AlH, and Be), nonhomoaromatic (**12**, X = O, S, NH, PH), and homoaromatic (**13**, X = S, PH, NH, O and **14** X = ON), with **12** (X = Mg) appearing as transitional between anti- and nonhomoaromatic.

Studies of homoaromaticity have attracted considerable interest for some time with the foundation provided by early studies by Winstein, Roberts, Woodward, and co-workers.¹ As a consequence, over the intervening years the concept of an aromatic array of orbitals acting across an insulating group is now well established.² Early examples featured cationic systems such as the 7-norbornenyl (**1**) and 8-endo-tricyclo[3.2.1.0^{2,4}]octyl (**2**).^{1,3} Somewhat later, the 2-bicyclo[3.2.1]octadienyl anion (**3**) survived initial skepticism to emerge as an anionic example.⁴

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Examples of neutral homoaromaticity have been rarer and include evidence supporting benzene oxide (**4**),⁵ bis-(ethano) semibullvalene (**5**),⁶ and semibullvalene with BCO replacing CH at carbon positions 2, 4, 6, and 8 (**6**).⁷ Interesting examples of in-plane homoaromaticity (**7**)⁸ and spherical homoaromaticity (**8**)⁹ have been proposed

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TABLE 1. Stabilization Energies (SE), Diamagnetic Susceptibility Exaltations (Λ), Nucleus-Independent Chemical Shifts (NICS), Stabilization of the HOMO, and $\Delta\phi$ for Series 12–14

substrate	SE ^a (kcal/mol)	Λ^b (cgs ppm)	NICS ^c (ppm)	stabilization of HOMO ^d E_h	$\Delta\phi^e$ (deg)
12 , X = BH, C ₁	-5.14	-9.85	2.93		9.0
AlH, C ₁	-3.46	-7.35	0.67		5.2
Be, C ₁	-3.19	-5.05	1.11		6.0
Mg, C ₁	-1.3	-2.53	1.21		1.7
O, C ₁	-0.74	1.38	-1.45	0.002	-3.0
S, C ₁	-0.34	1.27	-2.87	0.007	-2.3
PH, C ₁	0.51	2.93	-1.32	0.002	1.1
NH, C ₁	1.17	2.57	-2.11	0.001	-0.6
13 , X = 3PH, C _s	4.69	11.07	-6.81	0.010	-5.3
3S, C _s	4.34	11.63	-6.47	0.012	-7.9
3NH, C _s	8.16	12.06	-9.35	0.014	-7.6
3O, C _s	8.72	15.56	-13.29	0.016	-11.7
14 , 3ON, C ₁	6.12	9.72	-8.73	0.012	-10.3

^a Calculated using eq 1 or 2 at B3LYP/6-311+G(3df,2p)//B3LYP/6-31G(d) + ZPE at B3LYP/6-31G(d)//B3LYP/6-31G(d) uncorrected (Nimag = 0 in all cases, with the exception of **21**, X = PH, and **21**, X = NH, which are C_s with Nimag = 1 and are used for a more accurate comparison with the parent C_s **13** species). ^b Diamagnetic susceptibility exaltations (Λ) determined at CSGT-B3LYP/6-31G(d)//B3LYP/6-31G(d) using eq 1 or 2. ^c Calculated at GIAO-B3LYP/6-311+G(2d,p)//B3LYP/6-31G(d). ^d Stabilization of HOMO = $E_{\text{HOMO } 17} - E_{\text{HOMO } 12}$ or $E_{\text{HOMO } 21} - E_{\text{HOMO } 18}$ at B3LYP/6-31G(d)//B3LYP/6-31G(d). ^e For C_s and **14**, $\Delta\phi = \phi_{6512}$ in **18** - ϕ_{6512} in **20**; for C₁ except **14**, $\Delta\phi = (\text{av of } \phi_{6512} \text{ and } \phi_{7154})$ in **12** - (av of ϕ_{6512} and ϕ_{7154}) in **16**.

and supported by calculations. Recently, we have provided evidence extending neutral homoaromaticity to singlet bivalent carbenes 7-carbenanorbomene (**9**), endo-8-carbenatricyclo[3.2.1.0^{2,4}]octane (**10**),¹⁰ and 6-carbenatricyclo[3.1.1.0^{2,4}]heptane (**11**).¹¹ In light of the relatively few cases of neutral homoaromaticity that have been established, this report presents evidence supporting neutral homoaromaticity in some related heterocyclic systems.¹²

Results and Discussion

The present focus is on heterocyclic systems derived from the bicyclo[3.2.1]octane skeleton with the hetero group placed at position 2 or 3 (**12** and **13**, respectively) and one example of placement at positions 2 and 3 (**14**). Transannular interaction resulting in homoaromaticity should be revealed by analysis of the geometries, stabilization energies, and magnetic properties. Homodesmotic eqs 1 and 2 were employed to determine stabilization energies using density functional calculations. The ener-

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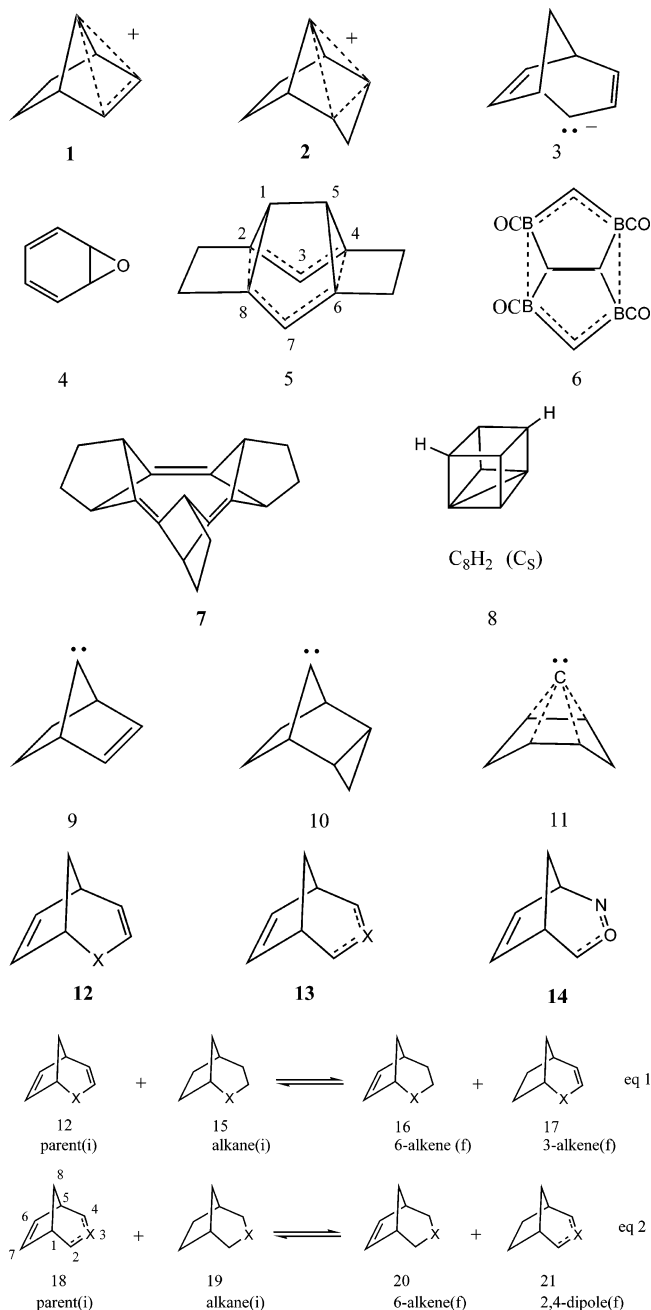
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gies of the individual molecular components of eqs 1 and 2 were evaluated at the B3LYP/6-311+G(3df,2p)//B3LYP/6-31G(d) level plus the ZPE at B3LYP/6-31G(d)//B3LYP/6-31G(d), uncorrected.¹³ The energy changes for eq 1 for X = BH, AlH, Be, Mg, O, S, PH, NH and for eq 2 for X = 3PH, 3S, 3NH, 3O and X = 3ON (based on **14**, eq analogous to eq 2) (Table 1)¹⁴ reveal the stabilization energies and fall into three groups: antihomoaromatic (BH, AlH, Be, Mg), nonhomoaromatic (O, S, PH, NH), and homoaromatic (3PH, 3S, 3NH, 3O, 3ON).



A comparison of stabilization energies with magnetic properties¹⁵ appears to offer additional insight. Homoaromaticity should result in an increased diatropic ring current. As a consequence, as first pointed out by Dauben,^{14i-k} the species in question will exhibit a diamagnetic susceptibility exaltation relative to a standard that lacks aromatic conjugative geometry. Diamagnetic

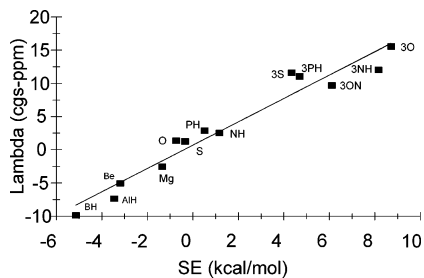


FIGURE 1. Plot of stabilization energy (SE), kcal/mol, versus diamagnetic susceptibility exaltation (Lambda), cgs ppm.

susceptibility exaltations in the present case were determined at CSGT-B3LYP/6-31G(d)//B3LYP/6-3G(d).^{12a} A positive value for the change in diamagnetic susceptibility for eq 1 or 2 indicates diamagnetic susceptibility exaltation (Λ) and aromaticity.¹⁴ The same division into three groups as noted for stabilization energies is revealed for diamagnetic susceptibility exaltation (Table 1). A plot of stabilization energy versus Λ (Figure 1) provides a correlation ($R = 0.97$) and helps to visualize the three groupings, suggesting, however, that $X = \text{Mg}$ represents a transition between anti- and nonhomoaromaticity.

Nucleus-independent chemical shifts (NICS), representing a second magnetic property, were calculated at the centers of the potentially interactive five-atom systems and should provide complementary evidence of aromaticity.^{11,14a,b,e} The results listed in Table 1 allow a plot of stabilization energy (SE) versus NICS (Figure 2, $R = 0.97$), which reveals the same groupings as in Figure 1. For comparison purposes, NICS for benzene is -7.6 , pyrrole is -13.3 , and cyclopentadiene is -2.8 (B3LYP/6-311+G(2d,p)//B3LYP/6-31G*), which supports 3PH, 3S, 3ON, 3NH, and 3O as homoaromatic species. Frontier orbital analysis of the systems where the three-atom bridge is analogous to allyl anion (i.e., **12**, where $X = \text{O}$, S, PH, NH; **13**, where $X = 3\text{PH}$, 3S, 3NH, 3O; and **14**,

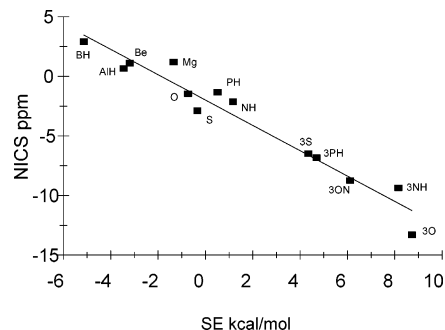


FIGURE 2. Plot of stabilization energy (SE), kcal/mol, versus NICS, ppm.

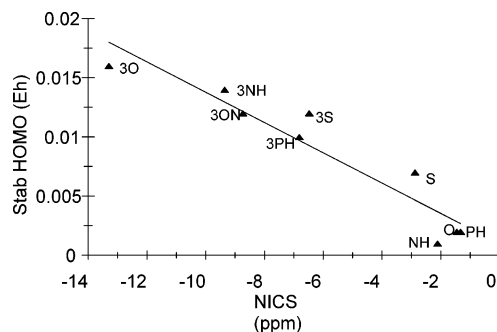


FIGURE 3. Plot of NICS (ppm) versus stabilization of the HOMO (E_h).

where $X = 3\text{ON}$) may be analyzed in terms of the C_s systems where symmetry allows interaction between the allyl nonbonding MO (χ_2) and the transannular π^* and between the transannular π MO and the allyl LUMO (χ_3^*). For the non- C_s systems that are isoelectronic with the C_s systems, these interactive features should be operative as well. The energy gap between χ_2 and the transannular π^* is less than that for transannular π with χ_3^* in all cases, and, therefore, it seems reasonable to focus attention on the nonbonding allyl- π^* MO interaction and suggest that the resulting stabilization of the allyl HOMO is related to homoaromaticity. The stabilization of the HOMO is estimated by the difference in the energy of HOMO of the system without the transannular double bond (e.g., **17**) and the HOMO of the corresponding system of interest (e.g., **12**) (Table 1). A plot of NICS versus stabilization of the HOMO does indeed reveal a correlation (Figure 3, $R = 0.95$), and we see a separation of the nonhomoaromatic from the homoaromatic. Thus, the interaction for $X = \text{S}$, NH, PH, and O is insufficient to provide homoaromaticity. In the case of the systems where the three-atom bridge is isoelectronic with the allyl cation, the symmetry-allowed transannular interaction of filled allylic MO with the transannular π orbital should be destabilizing.

The changes in geometry as one travels along the series are more subtle but, nevertheless, still consistent with the features revealed by stabilization energies and magnetic properties. The expectation is that the two wings for the species of series **12**, **13**, or **14** would move closer together in the homoaromatic cases and farther apart for the antiaromatic. For the C_s species, the wings in question are represented by the planes containing C1, C7, C6, C5 and C1, C2, C4, C5 in **18** and **20**, respectively, and the change in the angle between these two wings is

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(14) The number 3 preceding the substituent symbols serves to indicate the geometric placement on the ring skeleton.

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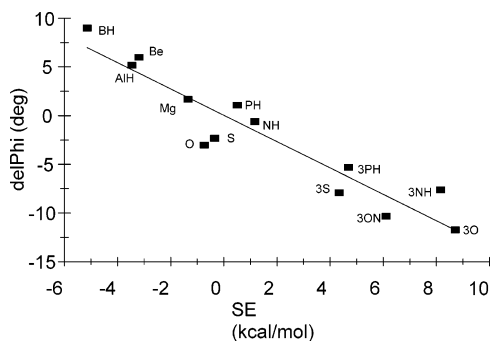


FIGURE 4. Plot of stabilization energy (SE), kcal/mol, versus $\Delta\phi$ (delPhi), deg.

TABLE 2. Proton Affinities at 25 °C (kcal/mol)

	PA ^a	PA ^b	PA _{exp} ^c	PA _{exp} ^d
NH ₃	203.9		205.0	203.5
pyrrole, H ⁺ at C-3	205.0	201.9		
pyrrole, H ⁺ at C-2	210.4	206.9	208.9	209.2
pyrrole, H ⁺ at NH	189.6	187.8		
aza-2-cyclopentene, H ⁺ at C-3	230.3			
aza-2-cyclopentene, H ⁺ at NH	218.2			
pyrrolidine	227.0		224.3	
2-azabicyclo[3.2.1]octa-3,6-diene (12 X = NH) H ⁺ at C-4	232.2			
2-azabicyclo[3.2.1]octa-3,6-diene (12 X = NH) H ⁺ at NH	218.8			

^a Calculated at B3LYP/6-311+G(2d, 2p)//B3LYP/6-31G(d) (thermal energy correction to H²⁹⁸ calculated at B3LYP/6-31G(d)).

^b Calculated at MP2(fc)/6-31G(2d,p)//HF/6-31G(d,p), ref 16. ^c Experimental values from ref 18. ^d Experimental values from ref 19.

evaluated by determining the difference between the dihedral angle ϕ_{6512} in **18** and ϕ_{6512} in **20**, $\Delta\phi$. For the C1 species we approximate the plane of C1, X2, C4, C5 and its angle with C1, C7, C6, C5 (essentially coplanar) using the following: (av of ϕ_{6512} and ϕ_{7154} in **12**) - (av ϕ_{6512} and ϕ_{7154} in **16**) = $\Delta\phi$ (Table 1). The plot of SE versus $\Delta\phi$ provides a correlation ($R = 0.94$) (Figure 4) and shows the homoaromatics with a narrowing of the angle between the two rings and the antiaromatics with an increased angle. The nonaromatic species are clustered near zero.

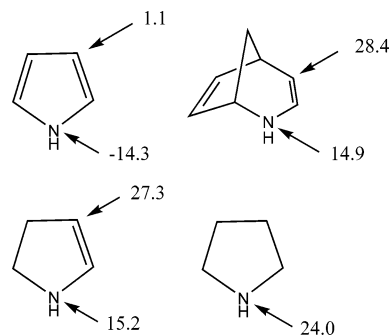
Since 2-azabicyclo[3.2.1]octa-3,6-diene (**12**, X = NH) was initially viewed as a key prospect for homoaromaticity, a bishomopyrrole, it seemed reasonable to view a direct comparison with pyrrole. Pyrrole exhibits a very low basicity for an amine due to the participation of its nitrogen electron pair in 6π electron delocalization, with protonation occurring on carbon rather than nitrogen.¹⁶ The proton affinities of azabicyclooctadiene **12** (X = NH), pyrrole, and related model systems were evaluated by calculations at the B3LYP/6-311+G(2d,2p)//B3LYP/6-31G(d) level¹⁷ (Table 2). The proton affinity of ammonia

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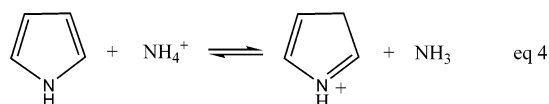
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SCHEME 1. Proton Affinities for Proton Attack at N and C Relative to NH₃ (kcal/mol), Calculated at the B3LYP/6-311+G(2d,2p)//B3LYP/6-31G(d) Level



is the negative of the enthalpy for eq 3; consequently, the proton affinity for C-3 attack on pyrrole relative to ammonia is the negative of the enthalpy for eq 4. Since the agreement with experiment for ammonia, pyrrolidine, and attack at C-2 of pyrrole is good (Table 2), one can picture the comparison as in Scheme 1. The proton affinities for attack at N and at C-4 in azabicyclooctadiene **12** (X = NH) are much greater than for the analogous positions in pyrrole. Thus, the reduction of basicity and reactivity realized in pyrrole due to the consequent loss of aromaticity upon reaction is not reflected in the proton affinities for N and C-4 attack on azabicyclooctadiene **12** (X = NH). In fact, we see that the proton affinities evaluated for **12** (X = NH) are quite close to those calculated for the nonaromatic aza-2-cyclopentene. This provides strong reinforcement for categorizing azabicyclooctadiene **12** (X = NH) as nonhomoaromatic.



Thus, analyses of stabilization energies, magnetic properties, geometric changes, frontier orbitals, and proton affinities all point to a division of the components of series **12**, **13**, and structure **14** into antihomoaromatic (**12**, X = BH, AIH, Be), nonhomoaromatic (**12**, X = O, S, NH, PH), and homoaromatic (**13**, X = 3S, 3PH, 3NH, 3O; and **14**, X = 3ON) groups, with **12** (X = Mg) appearing as transitional between antihomoaromatic and nonhomoaromatic.

Acknowledgment. Support from the Oregon State University Research Council and the MRF fund is gratefully acknowledged.

Supporting Information Available: Tables providing the energies and diamagnetic susceptibilities used to calculate stabilization energies (SE), diamagnetic susceptibility exaltations (Λ), and proton affinities, as well as the Cartesian coordinates for all optimizations described. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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