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 σ 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 χ_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 χ_2 mixes slightly with the σ_{CC} and σ_{CC}* bond orbitals for the C1C7, C1C8, C5C6, and C5C9 bonds. This is indicated by the small contributions to the χ_2 MO at C6–C9 in Figure 2. As the bridges become unsaturated, the σ_{CC} and σ_{CC}* orbitals are lowered in energy which makes the mixings with χ_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 π_- and χ_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 π or σ 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.

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Elusiveness of Bishomoaromaticity in Anionic Systems: The Bicyclo[3.2.1]octa-3,6-dien-2-yl Anion
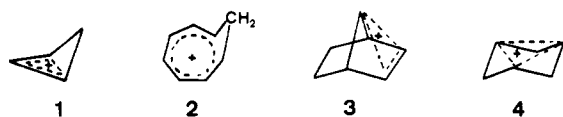
Elmar Kaufmann, Herbert Mayr,* Jayaraman Chandrasekhar, and Paul von Ragué Schleyer

Contribution from the Institut für Organische Chemie der Friedrich-Alexander Universität Erlangen-Nürnberg, Henkestrasse 42, D-8520 Erlangen, Federal Republic of Germany. Received July 11, 1980

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 6π anion **6** and the corresponding 4π 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-π-bonding; an ion (**1**), which resembles the aromatic cyclopropenyl cation electronically, was suggested to result.[1] Winstein generalized this idea: the aromatic stabi-

lization 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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(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*.
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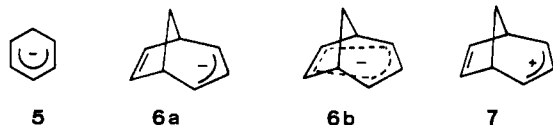
aromatic), and 4[8] (trishomoaromatic) are well-established examples.

Chemists were stimulated to seek further manifestations of this phenomenon; it is common to encounter experimental results interpreted in such terms.[3] The high water mark was reached with the elegant paper of Goldstein and Hoffmann,[9] who analyzed four different topologies for π interactions: pericyclic, spirocyclic, laticyclic, and longicyclic. This treatment included homoaromaticity and homoantiaromaticity as special cases within the pericyclic topology. The authors recognized that stabilizing interactions should be more important with charged species in which the HOMO–LUMO energy differences of the interacting fragments are smaller than in neutral alternatives.

More recently, an ebb is apparent: an increasing number of experimental and theoretical investigations indicate homoconjugative stabilization to be an overrated phenomenon.[10] In particular, the remarkable conclusion of Houk, Paquette, et al.[10b] that *"homoconjugative interactions between neutral closed-shell systems are destabilizing"* is opposite to previous deductions about homoaromaticity. Experimental support for their thesis comes from heats of hydrogenation, photoelectron spectra, and X-ray crystal structures of potentially homoaromatic molecules such as *cis*-1,4,7-cyclononatriene,[11a] triquinacene[11b] and hexaquinacene.[10d] Bicyclo[2.1.0]pent-2-ene,[11c-f] barrelene,[11g,h] and spirenes[11i-k] provide additional examples of destabilizing interactions.

According to Winstein[3b] and to Goldstein and Hoffmann,[9] stabilizing π interactions should be observable in appropriately constituted anions as well as in cations. However, we have already demonstrated that the potentially homoaromatic cyclohexadienyl anion 5 does not show homoconjugative 1,5-interaction.[10c,e] We

5   6a   6b   7

suggested that, in general, monohomoaromaticity should be less significant in anions than in cations.

The bicyclo[3.2.1]octa-3,6-dien-2-yl anion (6), with 6 π electrons, is the most widely cited example of alleged anionic homoaromaticity; the experimental data seem to provide particularly convincing support of the predictions of qualitative π-MO theory. We have examined the degree of π interaction in 6 and related anions by means of quantitative semiempirical and ab initio MO calculations. The corresponding potentially antiaromatic 4π cationic system, 7, and its relatives have also been included in our study.

Experimental Data

The π-delocalized intermediate 6b was first suggested by Brown and Occolowitz to account for the rapid base-catalyzed H/D exchange at C-4, $10^{4.5}$ times faster in 8 than in 9.[12] Similarly, rapid H-4 exchange was found for benzo[6,7]bicyclo[3.2.1]octa-2,6-diene[13] and for bicyclo[3.2.2]nona-2,6-diene.[14] The 2.3-ppm high-field shift of H-6 and H-7 in the ^{1}H NMR spectrum of 6 (relative to 8) was considered to be additional evidence for the homoaromatic delocalization of negative charge.[15]

8   9
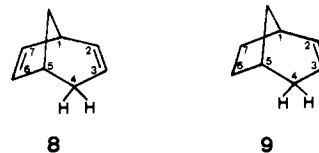
This latter interpretation was questioned by Trimitsis and Tuncay.[16] They demonstrated that the base-catalyzed H-4 exchange is only 3.3 times faster in 10 than in 11, indicating the absence of homoconjugative

10   11   12
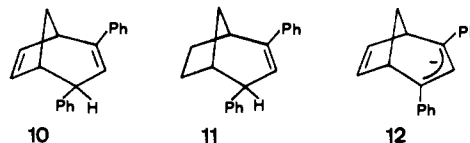
stabilization in anion 12.[16] On the other hand, H-6 and H-7 are 1.4 ppm more shielded in 12 than in 10, approximately half the effect observed for the "homoaromatic" anion 6. This suggested that effects other than homoconjugation might be responsible for the abnormal chemical shifts in 6.

Data for the corresponding cation (7) also do not provide conclusive evidence for interaction between the two π systems. The solvolysis of the *p*-nitrobenzoate 14 was 235 times slower than that of 13.[17] Diaz, Sakai,

13   14
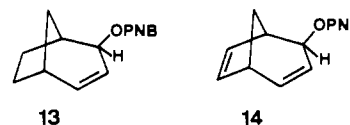
and Winstein considered the magnitude of the rate reduction to be "in line with" the expected antiaromatic character of the dienyl cation 7. They pointed out, however, that the difference between the solvolysis rates might be due partially to the rate-retarding inductive effect of the second olefinic group in 14.

Cyclodelocalization can be analyzed more directly in free radicals than in anions and cations; the coefficients of the singly occupied MO's can be derived from the proton coupling constants in the ESR spectrum.[18]

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Sustmann and Gellert compared the ESR spectra of **15** and **16** and found

15   **16**
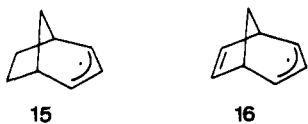
that the allylic hyperfine coupling constants with protons H-2, H-3, and H-4 are not reduced by the extra double bond in **16**.[18a] Furthermore, protons H-6 and H-7 showed only very small couplings in the ESR spectra of both **15** and **16**, thus excluding significant delocalization in **16**. This conclusion was corroborated by INDO calculations.[18a] In addition, Sustmann and Gellert reported that INDO calculations on anion **6** using the optimized geometry of radical **16** did not display homoconjugative interactions. To account for the experimentally observed stabilization of **6**, the authors suggested a distortion of the bicyclic framework in the anion.

Discussion

Systems Examined. Our analysis is based on a comparison of the geometric, electronic, and energetic properties of the 6π anion **6** and the 4π cation **7** with the partially saturated ions **17** and **18**.

Cations   **17**   **19**   **22**
Anions   **18**   **21**   **24**
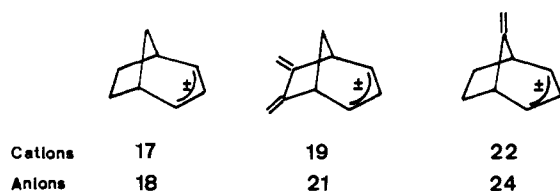
In addition, ions **19** and **21**, derived from the triene **20**, and ions **22** and **24**, formed from **23**, were studied. The exocyclic double bonds are arranged in these systems so that orbital symmetry enforces a different interaction pattern than in **6** and **7** (Figure 1).

ψ_2 of the allyl fragment is antisymmetric (Figure 1) and may interact with π^* in **6** and **7** or with the antisymmetric orbital, π_2, of the butadiene fragment in **19** and **21**. ψ_2 cannot interact with the π or π^* orbitals of the exocyclic double bond in **22** and **24** (Figure 1, right side). Therefore, stabilization of anion **6** and of cation **19** but no stabilization of either cation **22** or anion **24** may be expected from symmetry considerations.

Computational Details. MNDO[19] and ab initio[20a] (with the minimal STO-3G basis set)[21] procedures were used to evaluate the magnitude of these interactions. Complete geometry optimizations were carried out at the MNDO level; C_s symmetry constraints were employed for the ions.[22] These MNDO geometries were then used for the ab initio calculations with one change: all C–H bond lengths were set at 1.09 Å instead of the larger MNDO values. In addition, we performed MINDO/3 calculations,[23] also with complete geometry optimizations, and single-point ab initio calculations (STO-3G) using the MINDO/3 geometries. Since the results were almost identical (deviations of ΔE's in eq 1–6 were less than 1 kcal/mol), they will not be included in this paper. MINDO/3 has previously been demonstrated to reproduce geometries of potentially homoaromatic systems very well.[4d,e,10c] Therefore, we expected the semiempirical methods also to give reliable structures for the systems considered here. This assumption is supported by the agreement between the STO-3G stabilization energies based on semiempirical structures and the

experimental stability order of **6** and **18** as well as of **7** and **17**.

Orbital drawings were carried out with Jorgensen's plotting program[20b] using the STO-3G wave functions.

Geometries. In homoaromatic ions like **1–4**, geometrical distortions take place which increase interaction between the termini of the π systems.[4] Such distortions indicate the presence of homoconjugative interactions.

However, the calculated MNDO geometries of the ions included in Table I do not provide any evidence for homoaromaticity. The allylic bond lengths (C-2–C-3) remain virtually unchanged ($r = 1.395 \pm 0.001$ Å) in anions **6**, **18**, **21**, and **24** in spite of the differing number and positions of additional double bonds. Similarly, almost identical allylic bond lengths are calculated for the various cations **7**, **17**, **19**, and **22** ($r = 1.406 \pm 0.002$ Å).

The presence of cyclic conjugation in **6** might be expected to lead to a reduction of C-2–C-7 distance relative to that in cation **7**. However, the C-2–C-7 distance is only 0.003 Å shorter in the 6π system **6** than in the 4π system **7**. Analogously the C-2–C-7 distances in the other cations are only insignificantly different from those in the corresponding anions. Homoaromatic interaction is thus indicated to be unimportant in these ions.

Wave Functions. If cyclic conjugation occurs in **6**, the antisymmetric allyl HOMO must be stabilized by admixture of the C-6–C-7 π^* fragment. However, the appropriate p-orbital coefficients on C-6 and C-7 are negligible in the HOMO. A plot of the STO-3G wave function (Figure 2) shows this clearly. Slight interaction between the two systems in the ion may, however, be recognized in the LUMO which is primarily localized at C-6 and C-7.

The nonbonding orbitals of ions **6**, **17**, and **18** are also shown in Figure 2. A comparison of the HOMO's of anions **6** and **18** with the LUMO's of cations **7** and **17** is revealing: they are virtually identical. The antisymmetric allyl π orbitals in these systems thus remain essentially unaffected by the presence or absence of additional double bonds.

Charge Distribution and Bond Orders. The results of Mulliken population analyses with STO-3G wave functions are shown in Table II. The charges on the allylic carbons C-2 and C-3 in **6** are not very different from those in the other anions **18**, **21**, and **24**. The charge reduction in **6** relative to **18** is only 0.026 electrons. Similar effects are also found for the cations **7**, **17**, **19**, and **22**, in which the allylic carbons bear nearly identical charges.

The greater shielding of the protons on C-6 and C-7 in **6** compared to those in **8** observed in the ^{1}H NMR spectra[15] is partially reflected by the calculated charge distribution. There is a net increase of 0.05 electrons on C-6 and C-7 in **6** relative to neutral **8**. However, a similar charge redistribution is seen in ions **21** and **24** as well: carbons 6, 7, and 9 in **21** and carbons 8 and 9 in **24** bear 0.05 and 0.03 more electrons, respectively, relative to their neutral counterparts. The charge polarization in these systems appears to be relatively insensitive to the orientation of the additional double bonds. Thus, the increased shielding of H-6 and H-7 in **6** does not necessarily imply the presence of cyclic delocalization.

Comparisons of the calculated C-2–C-7 and C-2–C-8 overlap populations in the different ions do not indicate any special stabilizing interaction in **6**. On the contrary, the values are all small and negative and indicate weak antibonding interaction in all cases. In particular, the C-2–C-7 overlap population in **6** is nearly the same as that in the corresponding cation **7** (–0.043 vs. –0.041).

Energies. The energetic impact of the C-6–C-7 double bond in the ions **6** and **7** can be assessed by eq 1 and 2; the reaction

					STO-3G	(MNDO)	
Anion	**18**			**6**	–4.2	(+0.6)	(1)
Cation	**17**	**8**	**9**	**7**	+2.9	(+1.0)	(2)
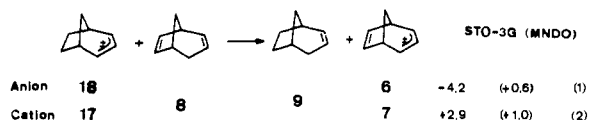
enthalpies are obtained from the data in Table III. Whereas MNDO predicts eq 1 and 2 to be almost thermoneutral, the ab initio calculations indicate a stabilization (4 kcal/mol) of anion **6** relative to its saturated counterpart in agreement with the experimental data. Furthermore, the experimentally observed

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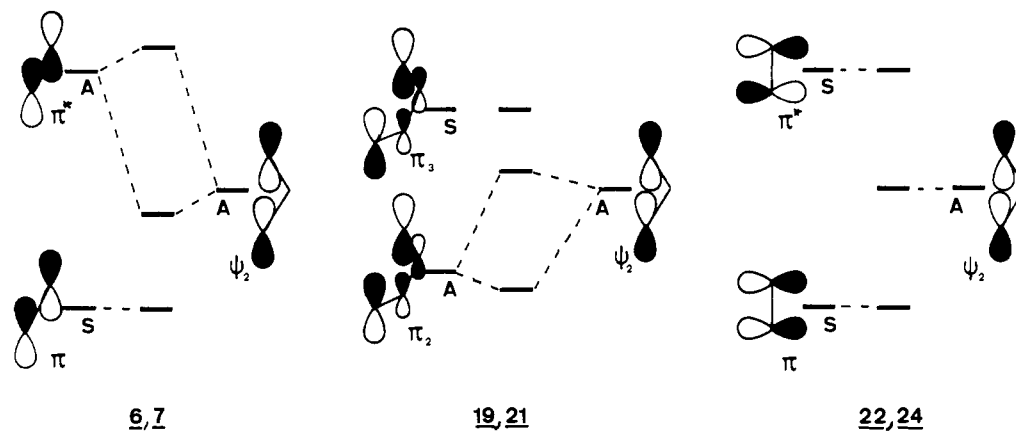
6,7   **19,21**   **22,24**

Figure 1. Symmetry-allowed interactions of the allylic π_2 orbital with ethylene fragments in different orientations.

Table I. MNDO Geometries of Hydrocarbons and Ions (Distances in Å)

	X	species	C-1-C-2 (C-4-C-5)	C-2-C-3 (C-3-C-4)	C-5-C-6 (C-1-C-7)	C-6-C-7	C-1-C-8 (C-5-C-8)	C=CH$_2$	C-2-C-7 (C-4-C-6)	C-2-C-8 (C-4-C-8)
	+	17	1.511	1.406	1.573	1.549	1.563		2.543	2.488
	H	9	1.519	1.351	1.560	1.551	1.557		2.529	2.481
			1.556	1.514	1.561		1.557		2.593	2.538
	−	18	1.502	1.394	1.567	1.551	1.562		2.547	2.484
	+	7	1.513	1.407	1.542	1.352	1.573		2.483	2.489
	H	8	1.520	1.351	1.531	1.354	1.567		2.484	2.486
	−	6	1.558	1.517	1.533		1.565		2.543	2.540
	+	19	1.513	1.404	1.543	1.487	1.565	1.347	2.470	2.497
	H	20	1.524	1.353	1.535	1.495	1.560	1.344	2.492	2.498
			1.561	1.507	1.533		1.558	1.342	2.551	2.547
	−	21	1.500	1.394	1.545	1.497	1.563	1.344	2.503	2.489
	+	22	1.512	1.405	1.573	1.548	1.533	1.340	2.549	2.439
	H	23	1.518	1.351	1.560	1.550	1.531	1.337	2.542	2.438
			1.559	1.512	1.562		1.529		2.609	2.498
	−	24	1.502	1.394	1.567	1.552	1.537	1.337	2.552	2.449

Table II. Charges on Carbon and Overlap Populations (STO-3G) in Hydrocarbons and Ions

	X	species	C-1 (C-5)	C-2 (C-4)	C-3	C-6 (C-7)	C-8	C-9	$\rho(2\text{-}7)$ $\rho(4\text{-}6)$	$\rho(2\text{-}8)$ $\rho(4\text{-}8)$
	+	17	−0.052	+0.134	−0.099	−0.100	−0.091		−0.033	−0.049
	H	9	−0.037	−0.068	−0.065	−0.107	−0.103		−0.047	−0.050
			−0.026	−0.112		−0.103			−0.041	−0.044
	−	18	−0.024	−0.255	−0.065	−0.104	−0.105		−0.057	−0.050
	+	7	−0.055	+0.137	−0.098	−0.044	−0.078		−0.041	−0.049
	H	8	−0.044	−0.065	−0.064	−0.070	−0.094		−0.048	−0.050
			−0.032	−0.111		−0.063			−0.044	−0.045
	−	6	−0.032	−0.242	−0.068	−0.093	−0.099		−0.043	−0.053
	+	19	−0.056	+0.133	−0.100	−0.004	−0.087	−0.094	−0.035	−0.049
	H	20	−0.045	−0.065	−0.063	+0.004	−0.102	−0.136	−0.047	−0.048
			−0.034	−0.111		+0.008		−0.137	−0.044	−0.043
	−	21	−0.034	−0.247	−0.061	+0.019	−0.105	−0.174	−0.051	−0.050
	+	22	−0.059	+0.134	−0.098	−0.098	+0.012	−0.104	−0.034	−0.055
	H	23	−0.048	−0.064	−0.064	−0.106	+0.020	−0.153	−0.045	−0.052
			−0.037	−0.110		−0.102			−0.039	−0.048
	−	24	−0.036	−0.251	−0.060	−0.104	+0.037	−0.199	−0.056	−0.050

HOMO **6**

LUMO **6**

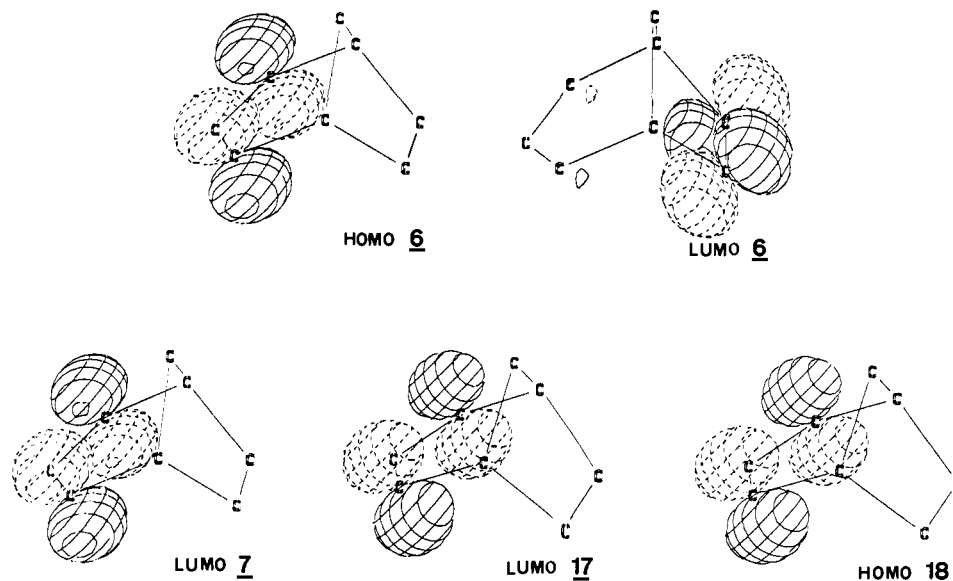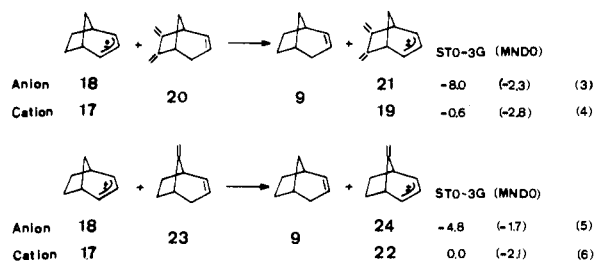LUMO **7**   LUMO **17**   HOMO **18**

Figure 2. Frontier orbitals (STO-3G) of some bicyclic anions and cations.

Table III. Calculated Heats of Formation (kcal/mol) and Total Energies (au) of Hydrocarbons and Ions Derived from Bicyclo[3.2.1]octane

species	ΔH_f° (MNDO)	E_{tot} (STO-3G)
17	202.4	−305.461 72
9	0.2	−306.260 70
18	7.7	−305.445 42
7	236.8	−304.225 57
8	33.6	−305.029 16
6	41.7	−304.220 64
19	243.6	−380.183 77
20	44.2	−380.981 86
21	49.4	−380.179 30
22	222.0	−342.817 40
23	21.9	−343.616 29
24	27.7	−342.808 67

destabilization of cation **7** by the C-6–C-7 double bond is also reproduced by the STO-3G calculations. We thus regard the STO-3G energies to be more reliable.

How can the stabilization of **6** and the destabilization of **7** be explained, even though we do not find any evidence for π interactions? Homoconjugative interactions may be present in **6** and **7** but are too small to be seen in the wave functions. Alternatively, the stabilization of **6** and the destabilization of **7** may be due to the inductive effect of the additional double bonds. The reaction enthalpies of eq 3–6 may be used to differentiate these two


						STO-3G	(MNDO)	
Anion	**18**		**20**	→	**9**	**21**	−8.0 (−2,3)	(3)
Cation	**17**					**19**	−0.6 (−2,8)	(4)

						STO-3G	(MNDO)	
Anion	**18**		**23**	→	**9**	**24**	−4.8 (−1.7)	(5)
Cation	**17**					**22**	0.0 (−2.1)	(6)

possibilities. In anions **21** and **24**, the additional double bonds are orientated so that HOMO–LUMO interactions with the allylic fragment are symmetry inhibited. Nevertheless, the stabilization of **24** is similar in magnitude to that of **6** (eq 5); **21**, with two exo double bonds, is stabilized to an even greater extent than **6** (eq 3). This demonstrates the operation of an inductive effect. Unlike **7**, cations **19** and **22** are not affected significantly by the extra double bonds (eq 2, 4, and 6). Homoconjugative interactions of small magnitude, destabilizing **7** and stabilizing **19** (see Figure 1), may be involved. C–C hyperconjugation, different for sp³- and sp²-hybridized carbons, may also contribute to the differences

found. We prefer to defer detailed analysis of possible effects in alleged homoaromatic cations to the next paper in this series where systems better constituted for favorable interactions of π fragments will be considered.

Conclusions

Since the bicyclo[3.2.1]octa-3,6-dien-2-yl anion (**6**) is clearly not a bishomoaromatic system, the same may well be true for other bicyclic anions which have similar structures as **6**. Anions **25**,[14a]

25   **26**   **27**   **28**
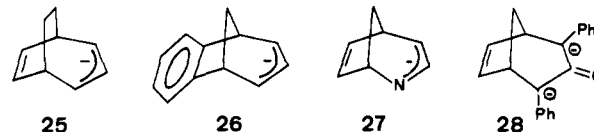
26,[13] **27**,[24] and **28**,[25] for example, probably do not have the suggested delocalized structures. The 10π electron system **29**, which has been demonstrated experimentally not to be a bishomoaromatic species,[26] is another example in this series.

In parallel work, Grutzner and Jorgensen concluded that the experimentally observed stability of anion **30** is not due to long-

29   **30**   **31**
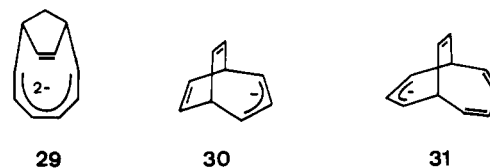
icyclic stabilization.[22] The failure to observe longicyclic stabilization of **31**[27] experimentally is thus not an exception but is representative of the general rule that bicyclohomoaromaticity is not observable in anionic systems.

Qualitative MO theory that does not consider the magnitude of the overlap is obviously not sufficient for predicting stabilizations through interactions of π fragments. It is likely that most of the systems that were thought to display aromatic stabilization on the basis of the symmetry properties of the fragment orbitals and the topology of their interactions[9] do not do so because both the geometrical separation and the energy difference between the interacting ribbon orbitals are too large. In combination with

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previous conclusions that homoaromaticity does not exist in neutral molecules[10b] and that monohomoaromaticity is not an important effect in anions,[10c] this work suggests that homoaromaticity may be restricted to cationic systems which can distort to increase the overlap of the interacting orbitals.

Na+ Complexes with Acyclic Polyethers. Stabilities, Enthalpies, and Entropies of Reaction in Acetonitrile and Pyridine. A Sodium-23 NMR Study

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Abstract: Multinuclear NMR (^{1}H, ^{13}C, and ^{23}Na) is applied to complex formation between Na+ and a series of linear polyethers. The most interesting finding is the considerable difference in complexation enthalpies and entropies: while $\Delta H = -18 \pm 3$ kJ·mol^{-1} and $\Delta S = -11 \pm 3$ J·K^{-1}·mol^{-1} for the sodium complex of 1,20-bis(o-(methylamido)phenoxy)-3,6,9,12,15,18-hexaoxaeicosane (2·Na), the homologous ligand 1,11-bis(o-(methylamido)phenoxy)-3,6,9-trioxaundecane (1·Na) has $\Delta H = -66 \pm 10$ kJ·mol^{-1} and $\Delta S = -185 \pm 45$ J·K^{-1}·mol^{-1}. This difference reflects pyridine solvent participation in 1·Na (but not in 2·Na) complex formation. When the weaker electron-donor solvent acetonitrile is used, solvent coordination to the cation is no longer significant for the 1·Na complex.
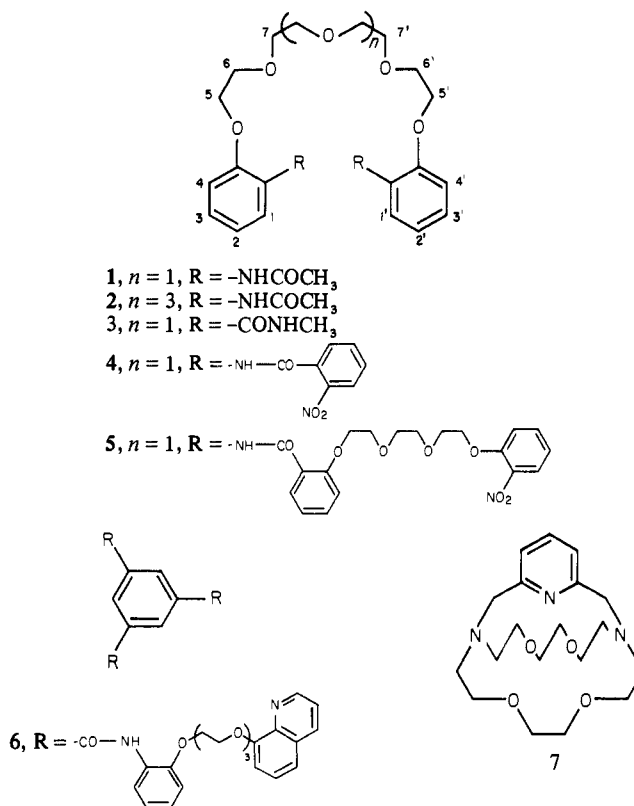
Introduction

The preparation by Pedersen[2] of cyclic polyethers which form strong complexes with metallic ions has ushered in a new era in chemistry. Crown ethers[3] and cryptands[4] are now routinely used in many industrial and chemical processes, for enhancing the solubility of salts in organic solvents and also for their cation-binding selectivity.[5] Crown ethers are synthetic analogues of natural macrocycles such as those present in many antibiotic ionophores, which are known for their efficiency and selectivity in binding ions. Examples of *acyclic* ionophore antibiotics include monensin, nigericin, grisorixin, X-537 A (lasalocid), alborixin, and emericid.[6] These biomolecules wrap themselves around the cation, in a manner very similar to the cyclic species.[6] Acyclic synthetic analogues should behave likewise and thus should be useful additions to the available crown ethers and cryptands. Furthermore, acyclic oligoethers, called podands,[5,6] are obtained simply and cheaply; there is no need for high-dilution techniques or for template effects in their preparation.[8] Vögtle's group has synthesized numerous such open-chain ligands.[6]

We have already shown the potential utility of ^{23}Na nuclear magnetic resonance for studying cation binding by organic and biological ionophores.[9] In a preliminary communication the complexing properties of ligand 1 toward the Na+ cation were described.[10] We report here results obtained also with the podands listed in Chart I.

We have selected these ligands, from a row of polyethers synthesized in the laboratory of Professor Vögtle in Bonn, because

Chart I

1, n = 1, R = –NHCOCH₃
2, n = 3, R = –NHCOCH₃
3, n = 1, R = –CONHCH₃

4, n = 1, R = -NH—CO—(o-nitrophenyl)

5, n = 1, R = -NH—CO—(...)—NO₂

6, R = -CO—NH—(...)

7

1, 1,11-bis(o-(methylamido)phenoxy)-3,6,9-trioxaundecane; **2,** 1,20-bis(o-(methylamido)phenoxy)-3,6,9,12,15,18-hexaoxaeicosane; **3,** 1,11-bis(o-(methylamido)phenoxy)-3,6,9-trioxaundecane; **4,** 1,11-bis[o-((o-nitrophenyl)amido)phenoxy]-3,6,9-trioxaundecane; **5,** 1,11-bis[o-[[o-(10-(o-nitrophenyl)-1,4,7,10-tetraoxadecyl)phenyl]amido]phenoxy]-3,6,9-trioxaundecane; **6,** 1,3,5-tris[[o-(9-(8-quinolyloxy)-1,4,7-trioxanonyl)phenyl]amido]benzene; **7,** pyridinophane cryptand ((2.2.1)py)[13]

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they include pentaethers (compounds **1, 3,** and **4**), having also two nitrogen heteroatoms available for coordination to the cation.