Molecular Orbital Theory of Homoaromatic Character
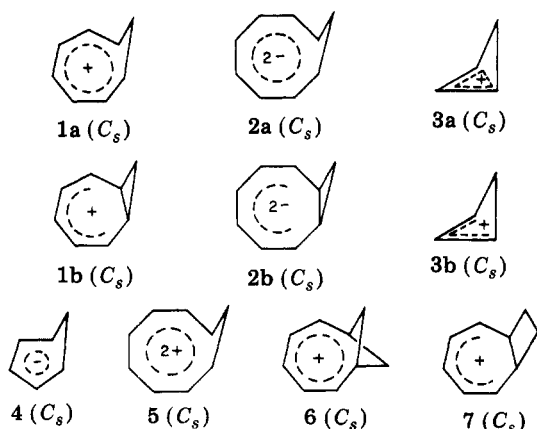
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Ab initio STO-2G geometry optimizations have been carried out for the homotropenylium cation (1) and the cyclooctatrienylium cation [planar (C_{2v}) and nonplanar (C_s)]. The homoconjugate linkage for the homotropenylium cation is found to be 1.578 Å at this theoretical level. This brings the ab initio calculations for 1 into line with previous MINDO/3 studies, frontier molecular orbital theories (FMOs), and the Winstein picture of an open cyclopropane unit in the homotropenylium cation. Both the homotropenylium cation and the cyclooctatrienylium cation are found to be markedly nonplanar when fully optimized. STO-2G, STO-3G, and 4-31G calculations on the STO-2G potential minima indicate that the cyclooctatrienylium cation probably lies no more than 10 kcal/mol higher in energy than the homotropenylium cation. This finding requires a revision of the concept of the homoaromatization energy for 1 and implicates the cyclooctatrienylium cation as an intermediate in the bridge-flipping process which occurs in the homotropenylium cation. MINDO/3 calculations are reported for the homotropenylium and cyclooctatrienylium cations together with results for other ions of interest in the area of homoaromatic chemistry. Evidence for homoaromatic character is found for the homotropenylium cation, the homocyclopropenylium cation, and the homocyclooctatetraene dication. The final frontier—dihomoaromatic character—is illustrated with the aid of calculations on the dihomotropenylium cation which is also found to be nonplanar. The homoaromatic cations show a number of well-defined trends. In particular it is shown that nonplanarity in the basal plane, shortened bond lengths between polyenyl and bridge fragments, bond equalization in the polyenyl segment, and lengthening of the homoconjugate linkage operate in concert to confer homoaromatic character. The bicyclo[5.2.0]nonadienylium cation, in which the cyclopropane group of the homotropenylium cation is replaced by a cyclobutane ring, does not exhibit the above characteristics and is concluded to be nonhomoaromatic. These results are in excellent agreement with previous FMO theories of homoaromatic character. The calculations for the homocyclopentadienyl anion and the homocyclooctatetraene dianion provide some evidence for homoaromatic character, but in contrast to the cations, the results for the anions do not lend themselves to a straightforward interpretation. The full sets of canonical molecular orbitals from the cyclooctatrienylium cation and the homotropenylium cation have been transformed to localized molecular orbitals (LMOs). The three π-type LMOs for the cyclooctatrienylium cation accord well with the notion of a heptatrienylium cation conjugation scheme. The π-type LMOs for 1 are of an entirely different character and most clearly evoke the conjugation of a cyclopropane unit with a pentadienyl cation in which each component has essentially retained its integrity. On this basis it is argued that the homotropenylium cation should be regarded as a resonance hybrid between the fully delocalized ion and the structure with the cyclopropane unit intact, in which the former contributor predominates.

The concept of homoaromaticity[1-3] is now 20 years of age while its forerunner, homoconjugation,[2,3] is a further 10 years older. Both terms are attributed to Winstein,[4] who initiated much of the research in this area.[4,5] Among the simple homoaromatics (those with a single methylene bridge), the best known examples are provided by homotropenylium cation (1) (Pettit and co-workers),[6,7] homocyclooctatetraene dianion (2) (Winstein and co-workers),[8-10] and homocyclopropenylium cation (3) (Olah and co-workers).[2,3,11,12] Notably absent is homocyclopentadienyl anion[13-16] (4) which has never been observed.

1a (C_s) 2a (C_s) 3a (C_s)

1b (C_s) 2b (C_s) 3b (C_s)

4 (C_s) 5 (C_s) 6 (C_s) 7 (C_s)

From the inception of their study, the detailed description of the bonding and structure of these species has

been enveloped in controversy. In his initial formulation, Pettit[6a] was undecided between the classical bicyclo-

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[5.1.0]octadienylium cation formulation **1b** and the homotropenylium cation structure implied by **1a**. Subsequently, on the basis of ^{1}H NMR spectroscopy (particularly the ring current induced chemical shifts) and quenching results in which the cyclopropane ring system was not retained, Pettit[6c] strongly supported the homoaromatic structure **1a**. On the other hand, Deno[17] stated that the properties of **1** are in accord with structure **1b** which only
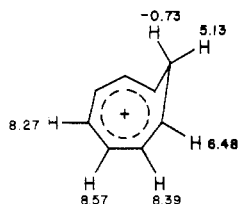

1 (^{1}H NMR δ values[7])

implies the usual stabilization of a carbenium ion by a cyclopropane ring. A careful reexamination of the ^{1}H NMR spectrum of **1** by Warner, Harris, Bradley, and Winstein[7] was interpreted in support of **1a**; this study also suggested for the first time that the basal plane of **1** might not be planar. Subsequent investigations involving NMR spectroscopy,[12a,18] UV spectroscopy,[19] and diamagnetic susceptibility exaltation[20] studies were construed in favor of **1a**.

It was therefore somewhat surprising to find that an ab initio SCF–MO–STO-3G study by Hehre[21] led to a homoaromatic bond length (1–7) of 1.512 Å which represents an almost imperceptible perturbation of the free (STO-3G) cyclopropane bond length of 1.502 Å and is best accommodated by structure **1b**. We[22] therefore restudied the ion with the semiempirical MINDO/3–SCF–MO method and found that the 1–7 distance in **1** was lengthened over the bond length in free cyclopropane (1.504 Å with MINDO/3) to values of 1.579 Å (planar seven-membered ring, as assumed in the ab initio study) and 1.621 Å (full optimization in C_s symmetry)—clearly in favor of structure **1a**. This latter fully optimized, MINDO/3 geometry gave an STO-3G energy which was 1.8 kcal/mol lower[22] than that obtained in the STO-3G structural calculation.[21]

The structure of the homocyclooctatetraene dianion[8–10] has usually been interpreted in terms of **2a**, although some contribution from **2b** has been suggested.[23] Indeed, the
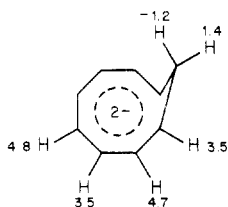
2 (^{1}H NMR δ values[9])

induced diamagnetic ring current in **2** appears to be considerably smaller than that observed in **1**, as evidenced by the differences in ^{1}H NMR chemical shifts for the bridge protons: $\Delta\delta$ 5.85 (**1**),[7] 2.6 (**2**).[9] For fully delocalized ions the larger ring (**2**) should theoretically sustain the greater current;[24] clearly some attenuation of this effect occurs in **2**, and a substantial contribution from **2b** provides a possible explanation.[23] Structural calculations on **2** have not been reported.

The parent homocyclopropenylium cation (**3**) was recently prepared by Olah and co-workers,[12] although methylated derivatives have been known for some time.[11] As regards the structure of **3**, ab initio[25,26] and semiempirical[27–29] calculations are again in disagreement.[30] The ab initio studies favor **3b**, whereas the semiempirical work is best accommodated by **3a**, as are the solution studies. Fortunately an X-ray crystallographic investigation of a derivative of **3** is available[31] —the results of which support **3a**.

The homocyclopentadienyl anion (**4a**) has been searched for both experimentally[13–16] and theoretically[16] without success. It appears that under conditions where the homocyclopentadienyl anion (**4a**) might be generated, the species observed actually corresponds to the cyclohexadienyl anion (**4b**). A recent MINDO/3 study by Olah and co-workers[16] found that **4b** is indeed the ground-state structure for **4**. While we agree that **4b** represents the global minimum for **4**, we have found a local minimum which apparently corresponds to the homoaromatic structure **4a**.

In this paper we report MINDO/3–SCF–MO calculations of all of these species (**1–4**) in the hope of shedding further light on the molecular and electronic structure and energetics of these ions. A full geometry optimization of **1** has also been carried out with ab initio SCF–MO theory and the full set of canonical molecular orbitals (CMOs) for **1** transformed to localized molecular orbitals (LMOs) in accord with the Boys criterion. The results of the studies on **1–4** lead to new insights into homoaromatic chemistry, and some of the results are quite unexpected.

In addition, new ions (**5–7**)[32–34] of potential interest in this field are considered. On the basis of frontier molecular orbital (FMO) theories it has previously been argued that **5** and **6** will be homoaromatic,[32,34] whereas **7** will be nonhomoaromatic.[33] The results of this study support these interpretations.

Computational Methods

Standard SCF–MO theory is applied at the MINDO/3[35] and ab initio STO-2G, STO-3G, and 4-31G levels.[36] In the case of the ab initio method, the STO-2G basis set was employed in the geometry-optimization studies, whereas the other basis sets were used in single-point calculations on the optimized structures. All

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of the geometry optimizations[37] were carried out with gradient search techniques of the quasi-Newton type. The MINDO/3 calculations[35] employed the Davidon, Fletcher, and Powell method,[38] whereas the ab initio calculations utilized the approach developed by Fletcher.[39] This latter program was kindly supplied by Poppinger.[40]

The final geometries were displayed with the ORTEP program[41] by using a version graciously provided by Z. Wasserman.

The LMOs were calculated from the CMOs according to the Foster and Boys criterion,[42] utilizing a modification[44,45] of previous transforms.[43]

Results and Discussion

Homotropenylium Cation (1). Structure. Two structural formulations have been put forward for the cation 1: homotropenylium (1a) and bicyclo[5.1.0]octa-dienylium (1b). We have presented FMO arguments[32,34] and MINDO/3 calculations[22] (Figure 1, supplementary material) in support of 1a, whereas Hehre[21] has published STO-3G calculations in favor of 1b. There is a qualitative disagreement between the results of these two sets of calculations. If we define the difference between the calculated interatomic distance for the homoconjugate linkage in 1 and the calculated bond length in free cyclopropane [1.502 Å (STO-3G), 1.504 Å (MINDO/3),[35] 1.510 Å (experimental)[45]] as Δr, then we obtain Δr values of 0.010 Å (STO-3G)[21] and 0.075 Å (MINDO/3)[22] with the planar seven-membered ring (7-MR) 8; on relaxing the

8 (C_s, 7-MR planar)

constraint on the 7-MR (Figure 1), the MINDO/3 Δr value[22] increases to 0.117 Å. These Δr values represent bond length increases of 0.7, 5.0, and 7.8%, respectively.

The MINDO/3 and STO-3G bond lengths of carbocations are usually in reasonable agreement,[30] so we decided to repeat the ab initio geometry optimization of 1 using a gradient search technique in the hope of rationalizing the preceding differences. Our initial efforts with the STO-3G basis established that such calculations were beyond our computational means, and we eventually settled on the smaller STO-2G basis set. This latter basis set is inferior to STO-3G in structural predictions, but not to any marked extent.[40b] In gradient geometry searches on large molecules, STO-2G is about 3 times faster than STO-3G; nevertheless the calculations represent one of the largest ab initio full optimizations to be published, and the computational requirements were rather heavy (Table I).

The STO-2G optimized geometries for 8 and 1 are given in Figure 2 (supplementary material) and Figure 3, respectively. The geometry in Figure 2 was calculated with

(37) The C–H bond lengths were set equal to 1.1 Å. Apart from this simplification, all geometries were fully optimized, subject only to the constraints specified in the text.

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Table I. UNIVAC 1108 Computing Times (min) for the Homotropenylium Cation (1, C_s)[a]

operation	MINDO/3	STO-2G	STO-3G
integral evaluation	~0	8	25
iteration to self-consistence	1	10	10
total for SCF calculation	1	18	35
number of geometrical variables to be optimized	19	19	
gradient evaluation	~0	165	
number of SCF calculations	17	22	
number of cycles required	7	9	
total for optimization	17	32[b]	
number of localization cycles			10
total for calculation of LMOs			100

[a] The STO-2G geometry search began with the optimized MINDO/3 structure, and vice versa. The C–H bond lengths in all molecules were set equal to 1.1 Å. [b] Hours.
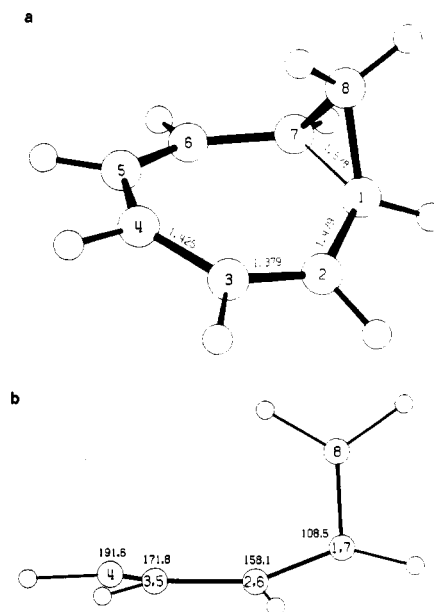
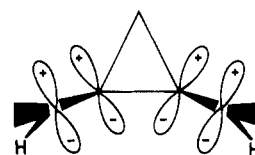**Figure 3.** STO-2G structure for the homotropenylium cation (1).

Figure 4. Homoaromatic orbital overlap between the FMOs of cyclopropane and the termini of the polyenyl fragment.

the 7-MR of 1 constrained to be planar (8), as in the previous ab initio study.[21] The structure in Figure 3 was obtained without any geometrical assumptions, although C_s symmetry[22] was imposed. In the first case (8) we find a Δr value of 0.031 Å (2.1% increase in cyclopropane bond length), with a corresponding figure of 0.070 Å (4.6%) for the full optimization (1).

The 7-MR in the STO-2G structure is markedly nonplanar, as was found in the previous MINDO/3 study.[22] The nonplanarity follows directly from our arguments[22,32,34] regarding the interaction between the FMOs of the pentadienyl cation and the cyclopropane unit in conferring

homoaromatic character on 1. Due to the orientation of the Walsh orbitals of cyclopropane, efficient overlap with the pentadienyl fragment requires a continuous deformation in the π-orbital array of the ring, and the flexing of the ring and the out-of-plane bending of the C–H bonds are manifestations of this effect (Figure 4).

These results (Figures 2 and 3) are quite compatible with the MINDO/3 structures (Figure 1), and although there are differences, these are now of a qualitative nature, characteristic of previous discrepancies between the two methods.[30] *It is apparent, however, that both the semiempirical and ab initio techniques do favor the Winstein formulation for 1 with an open cyclopropane unit, as embodied in 1a.* We conclude that the structural questions regarding 1 are now resolved in favor of 1a.

It seems that the previous differences between the MINDO/3 and ab initio studies of 1 may have arisen because the latter work utilized the axial iteration technique in the geometry search. Such methods are known to be unreliable for treating structures with strongly coupled variables (as occur in cyclic molecules), due to the inadequacy of the convergence properties (which are linear, rather than quadratic as in the case of the gradient search methods) near the minimum. As we show later, the previous STO-3G structure[21] does not correspond to a true minimum on the potential surface and was apparently prey to the above difficulty.

We also studied the cyclooctatrienylium cation with the planar 8-MR (C_{2v} symmetry), **9**, as this seemed to be a possible candidate for the transition state in the bridge-flipping process which has been shown to occur in solution studies[4,19] of 1. The heptatrienylium cation (**10**) (cf. ref

9 (C_{2v}, 8-MR planar)

10 (C_{2v}, A, STO-2G)
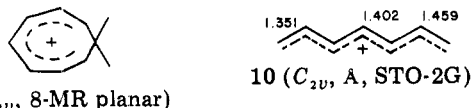
46) clearly provides a good model for **9**, as the STO-2G calculated bond lengths for these two ions correspond to within 0.002 Å (Figure 5). A further comparison is provided by the tropenylium cation (**11**).

11 (D_{7h}, A, STO-2G)
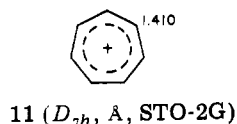
Finally we report a new and unexpected minimum on the potential surface of 1. It is most appropriately termed the cyclooctatrienylium cation (**12**) and differs from 1

12 (C_s)
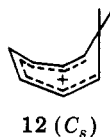
principally in the 1–7 interatomic distance, which can no longer be considered a bond (homoconjugate or otherwise). Nevertheless, it is apparent from the calculated ring bond lengths of **12** (Figure 6), which show a consistent trend toward equilization (in comparison to those of **9** and **10**), that there is a homoaromatic *interaction*[34] present in **12**. We have previously shown that this type of interaction can be an important influence on bond lengths in such situations.[48] The 1–7 interatomic distance of 2.303 Å cal-
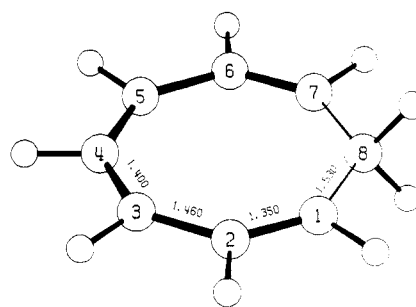
(46) O. Bastiansen, F. N. Fritsch, and K. H. Medberg, *Acta Crystallogr.*, **17**, 538 (1964).

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Figure 5. STO-2G structure for the planar cyclooctatrienylium cation (**9**).
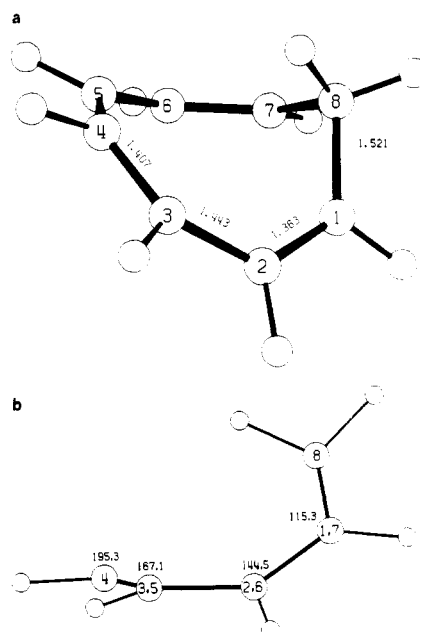

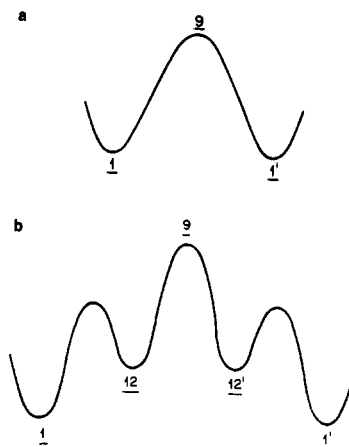**Figure 6.** STO-2G structure for the cyclooctatrienylium cation (**12**).

Figure 7. Energy profile for bridge flipping in the homotropenylium cation (1): (a) previous scheme,[4,19] (b) proposed scheme.

culated for **12** is well within the range expected for a homoaromatic interaction,[48] and the ring geometry at these carbon atoms allows efficient overlap underneath the ring[5b] (cf. Figure 4), which is a characteristic of homoaromatic bonds and interactions.

Energies. The results of our energy calculations are summarized in Table II, together with the sole piece of experimental data. This experimental information derives from a study of Winstein and co-workers[4,19] on the bridge-flipping process in the homotropenylium cation (1)

Table II. Energies on the Homotropenylium Cation Potential Surface (1, 8, 9, and 12)

		energy[a]								
		MINDO/3		STO-2G		STO-3G		4-31G		
structure	geometry	ΔH_f	rel	total	rel	total	rel	total	rel	exptl[b]
9	MINDO/3	211.0	0.5	-295.265 93	25.6					22.3
12	MINDO/3	208.9	-1.6	-295.281 88	15.6					
8	MINDO/3	213.4	2.9	-295.301 33	3.4	-304.188 38	3.5			
1	MINDO/3	210.5	0	-295.306 71	0	-304.193 92	0	-307.423 19		0
9	STO-2G			-295.270 39	29.4	-304.162 63	25.2	-307.410 15	10.0	22.3
12	STO-2G			-295.301 85	9.7	-304.192 69	6.3	-307.441 84	-9.9	
8	STO-2G			-295.309 87	4.7	-304.195 56	4.5	-307.417 81	5.2	
1	STO-2G			-295.317 32	0	-304.202 73	0	-307.426 10	0	0
8	STO-3G[c]					-304.191 04	7.3			

[a] Heats of formation (ΔH_f) and relative (rel) and experimental (exptl) energies are in kcal/mol, whereas total energies (total) are in hartrees. [b] See text. [c] Reference 21.

which was assumed to proceed via the planar cyclo-octatrienylium cation (9) transition state (Figure 7a). If
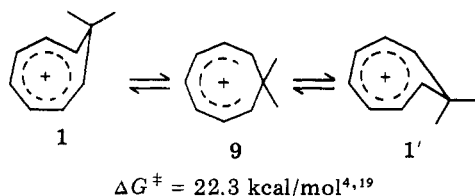
$$\Delta G^\ddagger = 22.3 \text{ kcal/mol}^{4,19}$$

changes in zero-point energy are neglected, then the ring-inversion study places 9 22.3 kcal/mol higher in energy than 1 (Table II). If we now use the energy difference between 1 and 9 as a calibration, then it is clear that the ab initio minimal basis set results are in closest agreement with experiment.

The energies of the STO-2G-optimized structures 1 and 9 give an energy difference of 29.4 kcal/mol, in reasonable agreement with the experimental value of 22.3 kcal/mol.[4,19] STO-3G and 4-31G calculations on the STO-2G optimized structures lead to energy differences of 25.2 and 10.0 kcal/mol, respectively. The STO-3G energy calculation apparently provides the best description of this portion of the $C_8H_9{}^+$ potential energy surface. The 4-31G-level calculations lead to a large change in the relative energies of 1 and 9, and the energy difference is appreciably underestimated. The energies of the MINDO/3-optimized structures accentuate this trend to the point where 1 and 8 are found to be of comparable energy—a result which is at variance with current thought.

All methods predict an energy gain on allowing the 7-MR to relax from planarity; this calculated energy difference between 1 and 8 ranges from 3 to 5 kcal/mol. Attention is drawn to the large structural changes which accompany this distortion. It is clear that the total energy is a poor criterion for the convergence of geometry optimizations on flexible molecules (those with low force constants). It is also apparent from Table II that the previous STO-3G geometry optimization[21] on 8 does not represent a true minimum on the potential surface, as our STO-2G structure gives an STO-3G energy which is 2.8 kcal/mol lower in energy; this value provides a lower energy bound on the error in the STO-3G structure.

The most unexpected result is provided by the cyclo-octatrienylium cation (12), which all methods agree is a true minimum on the potential surface. The STO-2G and STO-3G energy calculations, which are apparently the most reliable in the present context, place 12 only 9.7 and 6.3 kcal/mol, respectively, above the homotropenylium cation (1) itself.

This will require some revision of the concept of the homoaromatization energy,[23,29] which in the present context was equated with the energy difference between 1 and 9, that is, the 22.3 kcal/mol implicated in the bridge-flipping process.[4,19] Our results suggest that the homoaromatization energy in 1 should be associated with the energy difference between 1 and 12. The calculations suggest that this energy is considerably less than 22.3 kcal/mol and probably below 10 kcal/mol. It is apparent that the very existence of homoaromaticity is a matter of a few kcal/mol. A revised reaction-profile diagram for bridge flipping in 1 is given in Figure 7b. Although we have placed the transition state between 1 and 12 lower than 9 we have no computational evidence for their relative energies. The fact that 12 has not been experimentally observed, however, does suggest that the energy barrier for collapse of 12 to 1 is insufficient to inhibit this transformation at the temperatures which have been employed.

The MINDO/3 and 4-31G energy calculations erroneously suggest that 12 is the global ground state on the homotropenylium potential surface. Nevertheless, it appears possible that appropriate substitution could lead to a situation where 12 is favored over 1 (that is, electron-donating groups in the 1, 3, 5, and 7 positions).

While the calculations have not provided a uniformly good picture of the energies of the different structures on the $C_8H_9{}^+$ potential energy surface, it is apparent from the total energies that the calculated structures are reasonably consistent with one another.

Homocyclooctatetraene Dianion (2). The MINDO/3 structure calculated for the homocyclooctatetraene dianion (2) is shown in Figure 8 (supplementary material). The geometry found for the molecule is remarkable for two reasons. First, the basal 8-MR is virtually coplanar, and second, the homoconjugate linkage seems barely perturbed from that of cyclopropane ($\Delta r = 0.030$ Å). These results are at variance with previous predictions,[32] and for comparison purposes we therefore decided to investigate the structure of neutral "homocyclooctatetraene" [cis-bicyclo[6.1.0]nonatriene (13)]. The MINDO/3 geometry

13 (C_s)
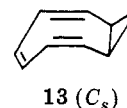
is shown in Figure 9 (supplementary material). The 1–8 bond distances in 2 and 13 turn out to have precisely the same value (1.534 Å). As expected, the conformation[18b] and ring bond lengths (apart from 1–8) in 13 are quite distinct from those found in 2.

It is difficult to assess the reliability of the MINDO/3 structure calculated for 2. There are a number of natural objections to the use of SCF–MO methods in geometry

Table III. Structures Obtained for the
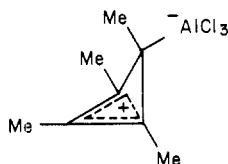Homocyclopropenylium Cation

3

14
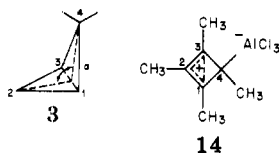
spe-cies	method	bond lengths, Å			α, deg	ref
		1-2	1-3	1-4		
3	MINDO/2	1.384	1.661	1.473	149.6	27
3	MINDO/3	1.402	1.739	1.502	149.3	28, 29
3	STO-2G	1.406	1.926	1.546	155.4	26
3	STO-3G	1.392	1.99	1.545	170.0	25
3	STO-3G	1.392	1.916	1.539	156.2	26
3	4-31G	1.385	1.915	1.532	157.5	26
14	X-ray	1.387	1.775	1.510	148.5	31

calculations on anions, but in general the results have been favorable.[49-51] Nevertheless, particular doubt must be attached to the significance of the MINDO/3 results in this connection, as a result of the neglect of overlap. In arguing for a lengthening of the homoconjugate linkage in 2, we relied on electron donation into an orbital which is antibonding with respect to the 1–8 bond. It is conceivable that the neglect of overlap approximations implicit in MINDO/3 may underestimate this effect. We therefore believe that these results must serve as a stimulus to further work rather than a final resolution of the problem.

It is appropriate to draw attention to our introductory remarks regarding 2, where we pointed out the experimental evidence for inhibition of resonance in this anion. This observation might lend some support to the above results. It would be of great interest if 2 could be utilized as a ligand, particularly in bishomouranocene (cf. ref 52).

Homocyclopropenylium Cation (3). The MINDO/3 geometry for the homocyclopropenylium cation[28,29] (3) is shown in Figure 9. The previous semiempirical[27-29] and ab initio[25,26] structural calculations are collected in Table III together with the results of an X-ray crystallographic study[31] of a derivative of 3—the aluminum trichloride complex of tetramethylcyclobutadiene (14). With the

14 (C_s)

exception of the STO-3G results, there is reasonable agreement as to the structure of the homocyclopropenylium cation (Table III), which accords well with FMO arguments.

In a low-temperature solution study of 3, Olah and co-workers[12] found a free energy of activation for bridge flipping in 3 of 8.4 kcal/mol. Assuming that 15 corre-

15 (C_{2v})

sponds to the transition state for this process, theoretical

calculations give energy barriers of 9.8[29] (MINDO/3), 1.0[26] (STO-2G), 0.4[25] and 0.7[26] (STO-3G), and 0.4[25] and 0.7[26] kcal/mol (4-31G).

With regard to structure and energy on the homocyclopropenylium cation potential surface, the semiempirical methods seem to acquit themselves considerably better than the present level of ab initio calculations.

Homocyclopentadienyl Anion (4). The MINDO/3 structure for the homocyclopentadienyl anion (4) is shown in Figure 11 (supplementary material). FMO arguments[32] for the lengthening of the homoconjugate bond in 4 have been based on the idea of electron donation into an orbital which is antibonding with respect to the 1–5 bond. This effect is apparent in the MINDO/3 results which show a homoconjugate bond length of 1.586 Å ($\Delta r = 0.082$ Å).

Although this result is in accord with predictions[32] on the structure of 4, it is surprising in the light of the geometry found for 2, where the lengthening of the homoconjugate linkage was very slight even though similar FMO arguments apply to both anions.[32] Both anions, however, retain an essentially coplanar basal ring, in contrast to the homoaromatic cations.

There have been a number of experimental[13-16] and theoretical[16] studies on the cyclohexadienyl anion (16), but

16 (C_s)

no evidence has been produced for 4. Olah and co-workers[16] studied 16 with MINDO/3 (found to possess C_{2v} symmetry), and our own work shows that 16 is the global minimum for the $C_6H_7^-$ potential surface, lying some 36 kcal/mol lower in energy than 4 according to MINDO/3.

Homocyclooctatetraene Dication (5). It has previously been pointed out that the homocyclooctatetraene framework (13) could be homoaromatic both as a dianion and as a dication.[32] The MINDO/3 geometry for the homocyclooctatetraene dication (5) is given in Figure 12 (supplementary material) and may be seen to be quite unlike its reduced counterparts 13 and 2. In particular, the ion bears a strong resemblance to the other homoaromatic cations such as 1. The homoconjugate linkage of 1.679 Å ($\Delta r = 0.175$ Å) is the longest found in the present study, and in contrast to 13 and 2, the dication 5 adopts the boat conformation.

We are unaware of experimental approaches to 5, but our results would seem to encourage such an endeavor.
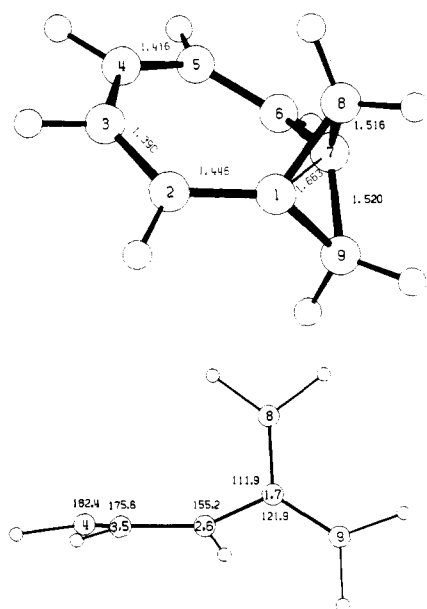
Dihomotropenylium Cation (6). On the basis of FMO arguments we have promulgated a new concept in the area of homoaromatic chemistry—dihomoaromatic character.[32] The MINDO/3 structure for the dihomotropenylium cation (6; see Figure 14) optimized in C_{2v} symmetry (17) is shown in Figure 13 (supplementary material). The

17 (C_{2v})

homoconjugate bond length of 1.620 Å is similar to that found in the homotropenylium cation (1). The MINDO/3[35] bridge bond length of bicyclobutane is 1.555 Å (experimental[53] 1.497 Å), which gives a Δr value of 0.065 Å.

On relaxing the symmetry to C_s (6) and allowing the 7-MR to distort from planarity, one observes that the

(49) L. Radom, *Aust. J. Chem.*, **29**, 1635 (1976).

(50) A. L. Hinde, D. Poppinger, and L. Radom, *J. Am. Chem. Soc.*, **100**, 4681 (1978).

(51) D. W. Boerth and A. Streitwieser, Jr., *J. Am. Chem. Soc.*, **100**, 750 (1978).

(52) A. Streitwieser, Jr., U. Muller-Westerhoff, G. Sonnichsen, F. Mares, D. G. Morrell, K. O. Hodgson, and C. A. Harmon, *J. Am. Chem. Soc.*, **95**, 8644 (1973).

(53) K. W. Cox, M. D. Harmony, G. Nelson, and K. B. Wiberg, *J. Chem. Phys.*, **50**, 1976 (1969).

Figure 14. MINDO/3 structure for the dihomotropenylium cation (6).

interaction of the bicyclobutane and conjugated segments is enhanced, and the homoconjugate linkage is further lengthened to 1.663 Å (Δr = 0.108 Å). The conformations and bond lengths of the 7-MRs of 1 and 6 (fully optimized) are strikingly similar. We hope that the final frontier in homoaromatic chemistry, dihomoaromatic character,[32] will soon receive experimental attention.

Bicyclo[5.2.0]nonadienylium Cation (7). The MINDO/3 geometry calculated for the bicyclo[5.2.0]nonatrienylium cation (7) is shown in Figure 15 (supplementary material). The 1–7 bond length of 1.575 Å found for 7 (see also ref 29) represents a slight increase over the MINDO/3[35] value of 1.548 Å (experimental[54] 1.525 Å) for cyclobutane which gives a Δr of 0.027 Å for 7. Even more striking is the conformation found for the 7-MR of 7. The planarity found for 7 stands in marked contrast to the 7-MR conformations found for the homoaromatic cations, in which the basal rings are buckled. Clearly, the vicinal interactions of polyenyl systems with cyclopropane and cyclobutane are entirely distinct. Whereas the former may confer homoaromatic character, the latter is apparently incapable of transmitting this type of conjugation. These results are in complete accord with previous arguments regarding the noninvolvement of the cyclobutane ring in homoaromatic conjugation.[33] The ring bond lengths found for 7 show a strong resemblance to those calculated[16] for the cyclohexadienyl cation (18). The bonds from the
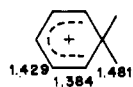

18 (C_{2v}, A, MINDO/3)

termini of the incipient pentadienyl cation fragment to the attached carbon(s) are shorter (and apparently stronger) in 18 (cf. ref 34) than in 7.

Structural Trends. Among the cations a number of clear trends are evident. The homoaromatics are markedly nonplanar, in contrast to the nonhomoaromatics such as 7 (see figures). The bond lengths of the cations are equally instructive (Table IV). As the homoconjugate linkages
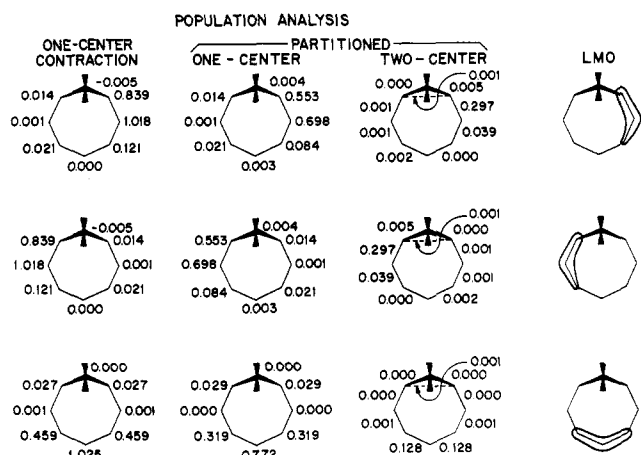
Figure 16. STO-3G π-type localized molecular orbitals for the STO-2G structure of the cyclooctatrienylium cation (12).
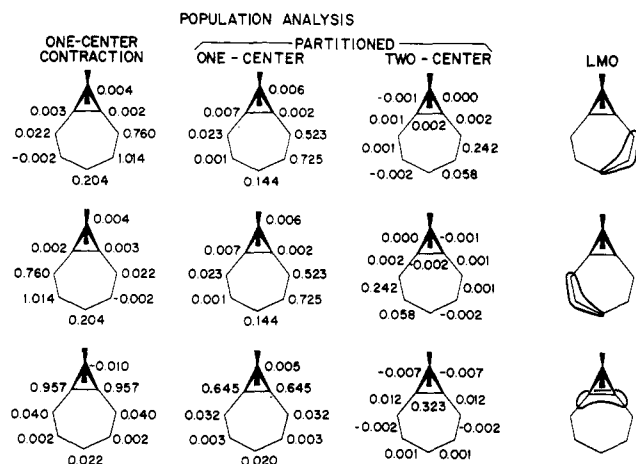
Figure 17. STO-3G π-type localized molecular orbitals for the STO-2G structure of the homotropenylium cation (1).

increase in length, the 1–2 bonds to the cyclopropane fragment decrease, indicative of an enhanced conjugation between the polyenyl cation and the bridge group. Paralleling this strengthened interaction is the trend toward bond length equalization in the basal plane. It is clear that these four effects, nonplanarity in the basal plane, shortened bond lengths between polyenyl and bridge fragments, bond equalization in the polyenyl segment, and lengthening of the homoconjugate linkage, operate in concert to confer homoaromatic character, providing, of course, that the $(4n + 2)\pi$-electron rule[55] is satisfied.

The structures obtained for the anions represent something of an enigma. There is no obvious relationship between homoconjugate and vicinal bond lengths. Thus while 2 has a short homoconjugate bond length (indicative of weak electron donation into the bridge group), the vicinal bond lengths are clearly shortened (indicative of appreciable conjugation between the polyene and cyclopropane segments of the molecule. The opposite behavior obtains in the case of 4, and it is clear that these molecules warrant further study.

Localized Molecular Orbitals (LMOs) for the Homotropenylium Cation (1). Localized molecular orbitals have become an increasingly powerful aid in the interpretation of molecular and electronic structure.[56,57]
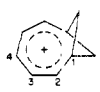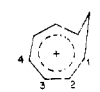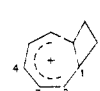
(54) (a) A. de Meijere, *Acta Chem. Scand.*, **20**, 1093 (1965); (b) S. Meiboom and L. C. Snyder, *J. Chem. Phys.*, **52**, 3857 (1970).
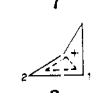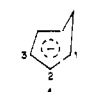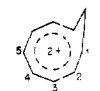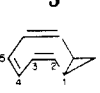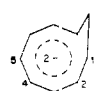
(55) R. C. Haddon, *J. Am. Chem. Soc.*, **101**, 1722 (1979), and references therein.
(56) W. England, L. S. Salmon, and K. Ruedenberg, *Top. Curr. Chem.*, **23**, 31 (1971).

Table IV. MINDO/3 Calculated Bond Lengths (Å)

molecule	bridge to C-1	homoconjugate	1-2	2-3	3-4	4-5
11			1.405	1.405	1.405	
6	1.518	1.663	1.446	1.390	1.416	
1	1.498	1.621	1.449	1.387	1.412	
7	1.550	1.575	1.489	1.375	1.418	
3	1.502	1.738	1.402			
4	1.511	1.586	1.477	1.404		
5	1.497	1.679	1.427	1.411	1.390	1.432
13	1.521	1.534	1.482	1.345	1.460	1.348
2	1.521	1.534	1.459	1.407	1.374	1.454

STO-3G LMOs for the STO-2G structures of the cyclo-octatrienylium cation (**12**) and the homotropenylium cation (**1**) are shown in Figures 16 and 17, respectively. The three LMOs shown for each cation correspond to π-type MOs.

From the three LMOs of **12** it is easy to recognize the underlying heptatrienylium cation conjugation scheme. In the case of the LMOs of **1** we had expected a similar scheme, but with a substantial development of the 1-7 electron density. Inspection of Figures 16 and 17, however, shows that this is not the case.

The LMOs for **1** are of an entirely different character than those found for **12**. The LMOs for **1** most clearly evoke the vicinal conjugation of a cyclopropane unit with a pentadienyl cation, in which each component has essentially retained its integrity. *Our calculated LMOs for* **1** *clearly favor the electronic structure connoted by* **1b**.

It is appropriate to point out that as the 1-7 interatomic distance passes between 1.578 Å (**1**) and 2.303 Å (**12**), there must occur a fundamental change in the character of the LMOs as expressed in the extremes of Figure 18. The *exact* value of the 1-7 interatomic distance in **1**, of course, remains a matter of some uncertainty (cf. Figures 1a and 3a). By the same token the correct set of LMOs for **1** is also therefore somewhat in doubt (and may be basis-set dependent).
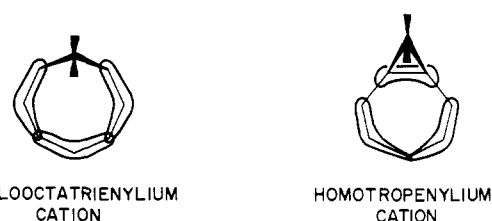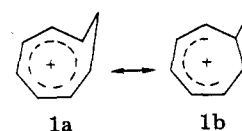
(57) (a) D. A. Kleier, D. A. Dixon, and W. N. Lipscomb, *Theor. Chim. Acta*, **40**, 33 (1975); (b) D. A. Dixon, D. A. Kleier, and W. N. Lipscomb, *J. Am. Chem. Soc.*, **100**, 5681 (1978).

CYCLOOCTATRIENYLIUM
CATION

HOMOTROPENYLIUM
CATION

Figure 18. STO-3G π-type localized molecular orbitals for the STO-2G structures of the cyclooctatrienylium cation (**12**) and the homotropenylium cation (**1**).

The precise answers to these questions are of much less importance than the realization that our results indicate that structures **1a** and **1b** are not incompatible in the overall description of the homotropenylium cation (**1**). It seems that on the basis of our molecular and electronic structure calculations, *the homotropenylium cation should be considered as a resonance hybrid of* **1a** *and* **1b**.

1a   **1b**

As the calculated structures favor **1a**, it is natural to assume that **1a** is the principal resonance contributor; nevertheless, the LMOs indicate that **1b** cannot be totally neglected. Indeed, **1b** emphasizes the important role of

the cyclopropane group, the presence of which we have argued to be an essential ingredient for the occurrence of homoaromaticity.[22,32-34]
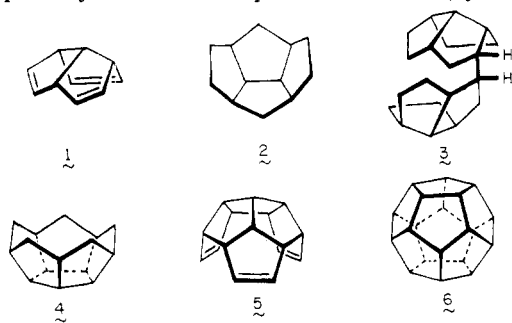

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Details of the efficient conversion of dimethyl 3,3a,3b,4,6a,7a-hexahydro-3,4,7-metheno-7H-cyclopenta[a]-pentalene-7,8-dicarboxylate (9a), a product of the domino Diels–Alder addition of dimethyl acetylenedicarboxylate and 9,10-dihydrofulvalene, to a pair of C2-symmetric hexaquinane dilactones are presented. The initial phase of the strategy, which was to retain minimal C2 symmetry in all intermediates, required exclusive "cross-corner" oxygenation of the double bonds in 9a. This objective was realized by sequential iodolactonization of the derived dicarboxylic acid, methoxide-promoted opening of the dilactone at room temperature, oxidation, and reductive deiodination. Cyclopentenone annulation of the resulting dimethyl decahydro-1,5-dioxo-3,4,7-metheno-7H-cyclopenta[a]pentalene-7,8-dicarboxylate 13 involved condensation with diphenylsulfonium cyclopropylide and Baeyer–Villiger oxidation or alkylation with (trimethylsilyl)allyl anion and oxidative cyclization, followed by acid-promoted rearrangement. Catalytic hydrogenation of 18 provided 22 whose borohydride reduction delivered the "closed" dilactone tetradecahydro-5H,6H-1,5b,12:5a,10,11-dimethenodicyclopenta[e,e']benzo[2,1-c:3,4-c']-dipyran-5,6-dione (7). Results of alkali metal reduction of both 7 and 18 are given. In the first instance, the "open" dilactone 8 was formed stereoselectively as a consequence of exclusive protonation from the convex surface. The behavior of 18 comprises the first example of a π-mediated 1,6-dicarbonyl reduction. The chemical behavior of dilactones 7 and 8 is described; indications of the effects of their highly spherical topology, conformational character, and essentially solvent-free cavity on the differing product-forming steps are pointed out and discussed.

The unusual topological features of triquinacene (1), noted first by Woodward[2] and Jacobson,[3] have more recently been incorporated into structures of greater complexity. Tetracyclo[7.2.1.0^{4,11}.0^{6,10}]dodecane (2),[4,5] dl-bivalvane (3),[6] peristylane (4),[7] and C16-hexaquinacene (5)[8] are especially notable examples. The all-cis,syn stereo-

chemistry of these frameworks has assumed central importance because of their obvious model relationship to the still unknown pentagonal dodecahedrane structure 6. The carbon skeletons of 2–5, like that of 1, are rigid, bowl-shaped, relatively strain free,[9] and in certain cases rather highly symmetric.[10]

There is associated with 6 a particular fascination because this (CH)20 hydrocarbon possesses the highest known point-group symmetry (I_h, icosahedral), encloses a cavity incapable of solvation, and appeals to one's scientific curiosity and imagination. As a result, the molecule has recently become the focal point of intense synthetic[2,3,6-8,11-15] and theoretical research.[9,16-18]

In principle, a variety of methods are available for the tactical elaboration of 6. Although all are necessarily complex, we have had particular interest in schemes which would capitalize on the inherent symmetry of the target molecule. In this way, the number of individual laboratory steps should be appreciably reduced. An additional ad-

(1) (a) National Science Foundation Graduate Fellow, 1972–1975. (b) Postdoctoral Fellow of the Deutsche Akademische Austauschdienst (NATO), 1974–1975. (c) Dissertation Fellow, 1977–1978. (d) Postdoctoral Fellow of the Science Research Council, 1975–1977.

(2) Woodward, R. B.; Fukunaga, T.; Kelly, R. C. *J. Am. Chem. Soc.* **1964**, *86*, 3162.

(3) Jacobson, I. T. *Acta Chem. Scand.* **1967**, *21*, 2235.

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