Ground States of Conjugated Molecules. VIII. Bridged Hydrocarbons and Hydrocarbon Ions[1]

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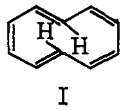
Abstract: The SCF-MO method, described in previous papers of this series,[2] has been applied to bicyclic systems derived from cyclodecapentaene, and the cyclohendecapentaenylium ion, by linking the 1,6-positions with bridging groups.

Previous papers of this series[2] have described a modified SCF-MO procedure which seems to provide a very good description of the ground states of conjugated molecules. In particular, it provided[2b] the first good justification for Hückel's rule, that monocyclic conjugated hydrocarbons can be aromatic only if they contain $(4n + 2)$ π electrons, n being an integer; it also correctly predicted that the higher members of this series should again lack aromatic properties. Here we describe applications of this approach to cyclic systems containing ten or eleven conjugated carbon atoms.

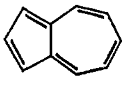
Whether cyclodecapentaene (I), the Hückel polyene with $n = 2$, would be aromatic if it could adopt a planar configuration is largely an academic question, for any planar or near-planar configuration of I would be impossibly strained. The problem of aromaticity in systems of this kind can therefore be studied only by indirect means, by preparing derivatives where the π system of I is retained, but the σ strain in a suitable configuration is reduced by suitable structural alterations.

Some time ago it was suggested,[3] on the basis of a simple perturbational MO approach, that azulene (II) could be regarded as such a derivative of I, the central 9,10 bond being essentially single and contributing little or nothing to the aromaticity of the molecule. However, although this suggestion has been supported by X-ray structure determinations[4] and by our recent calculations,[2b] the relationship to I to II is not immediately obvious; this difficulty does not apply, however, to analogous compounds in which the 9,10 bond is replaced by an inert bridging group (III).

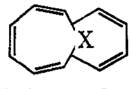
Compounds of this type have recently been reported, with X = CH$_2$[5] or O.[6] We thought it would be of interest to apply our SCF-MO procedure to compounds of this type to see how their structures would be related on the one hand to the hypothetical planar $C_{10}H_{10}$ hydrocarbon (I), and on the other hand to azulene (II).



I



II



IIIa, X = O
b, X = CH$_2$
c, X = S

The geometries of these bridged polyenes are not yet known; two extreme possibilities can be visualized. In the first, the ring carbon atoms are assumed to lie in a plane, this being the nodal plane of their individual 2p orbitals; the C–C bond lengths should then all be close to the "aromatic" value of 1.40 A, and the distance between the bridgehead carbon atoms is a function only of the C–X bond lengths and C–X–C bond angle. This configuration should have the lowest total π energy, but the σ bonds in it will of course be highly strained. The second extreme is one in which the molecule is nonplanar and all the carbon valence angles are 120°; the molecule now has the shape of a half-open oyster, and the 2p orbitals of the individual carbon atoms are no longer parallel.

The calculations were carried out by the modified Pople SCF-MO method, described in detail in part II of this series.[2b] This could be used unchanged in the case of the first (planar) model; however, in the case of the second (oyster) model, allowance had to be made for the deviations from coplanarity.

In the Pople method, the one-electron resonance integrals β are assumed to vanish for pairs of nonbonded atoms; in the oyster model these therefore have normal values, except for bonds linking the bridgehead atoms to their neighbors. These were assumed to vary with the dihedral angle between the 2p orbitals in accordance with a cosine law

$$\beta_\theta = \beta \cos \theta \tag{1}$$

where β_θ is the value of β for dihedral angle θ, and β is the "normal" value corresponding to the same internuclear distance. Nonplanarity has little effect on the values of the repulsion integrals (ii, jj); these were therefore calculated as before by the uniformly charged sphere approximation. The internuclear distances were calculated using the assumed three-dimensional geometry for the molecule.

The nature of the bridging group should have little influence on the total π energy even if X is a heteroatom, for any p orbitals of X will be perpendicular to those of the adjacent bridgehead carbons. A change in the bridging group should therefore affect the π energy only by altering the distance across the bridge. It is true that there might also be inductive effects in the bridgehead carbon atoms, due to polarity of the

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(1) This work was supported by the National Institutes of Health, U. S. Public Health Service, through Grant No. GM-11531-02.

(2) (a) A. L. H. Chung and M. J. S. Dewar, *J. Chem. Phys.*, 42, 756 (1965); (b) M. J. S. Dewar and G. J. Gleicher, *J. Am. Chem. Soc.*, 87, 685 (1965); (c) *ibid.*, 87, 692 (1965); (d) M. J. S. Dewar and C. C. Thompson, Jr., *ibid.*, 87, 4414 (1965).

(3) M. J. S. Dewar, *ibid.*, 74, 3345 (1952), Theorem 24.

(4) J. M. Robertson, H. M. M. Shearer, G. A. Sim, and D. G. Watson, *Acta Cryst.*, 15, 1 (1962).

(5) E. Vogel and H. D. Roth, *Angew. Chem. Intern. Ed. Engl.*, 3, 228 (1964); E. Vogel and W. A. Ball, *ibid.*, 3, 642 (1964).

(6) F. Sondheimer and A. Shani, *J. Am. Chem. Soc.*, 86, 3168 (1964).

Table I. $E_{\pi b}$ (ev) for Bridged Conjugated Systems

Parent molecule	Bridging group	$E_{\pi b}$ Planar PPP	Planar SPO	Nonplanar PPP	Nonplanar SPO
Cyclodecapentaene	O	11.763	10.622	10.243	9.348
	CH_2	11.740	10.595	10.189	9.295
	S	11.700	10.550	9.959	9.090
Cyclohendecapentaenylium ion	O	15.536	14.215	13.931	12.836
	CH_2	15.523	14.198	13.890	13.796
	S	15.502	14.171	13.679	12.613

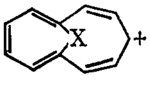
Table II. Electrophilic Localization Energies[a] (ev)

Molecule	Bridging group	Position	Localization energy Planar PPP	Planar SPO	Nonplanar PPP	Nonplanar SPO
Naphthalene	...	1	−0.907	−0.905	...	...
		2	−0.498	−0.539	...	...
Cyclodecapentaene	O	1	−1.343	−1.506	−1.422	−1.498
		2	−1.266	−1.415	−1.202	−1.344
	CH_2	1	−1.361	−1.530	−1.444	−1.524
		2	−1.289	−1.444	−1.228	−1.377
	S	1	−1.392	−1.570	−1.493	−1.571
		2	−1.332	−1.497	−1.273	−1.432
Benztropylium	...	3	4.801	4.858	...	...
		4	4.464	4.483	...	...
		5	5.534	5.656	...	...
		10	4.537	4.603	...	...
		11	3.966	4.119	...	...
Cyclohendecapentaenylium	O	3	3.967	3.935	3.927	3.958
		4	3.780	3.670	4.229	4.188
		5	4.209	4.278	4.189	4.217
		10	3.984	3.936	4.211	4.172
		11	3.919	3.865	3.939	3.979
	CH_2	3	3.926	3.888	3.875	3.901
		4	3.741	3.625	4.197	4.150
		5	4.152	4.206	4.113	4.126
		10	3.937	3.882	4.168	4.126
		11	3.878	3.817	3.904	3.928
	S	3	3.850	3.800	3.754	3.771
		4	3.676	3.550	4.180	4.137
		5	4.040	4.064	3.965	3.914
		10	3.851	3.784	4.089	4.039
		11	3.802	3.729	3.818	3.845
Perinaphthindenylium	...	1	4.480	4.638	...	...
		2	3.987	3.968	...	...

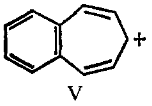
[a] For definition see ref 2d.

C–X bonds; however, since it is difficult to assess the importance of such effects, we preferred to neglect them.

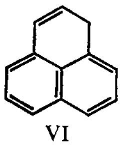
Calculations were also carried out for the analogous bridged C_{11} carbonium ions (IV), since Vogel and his collaborators have recently reported a synthesis of IVb.[7] In this case the simple system, with atoms 1 and 6 directly linked, is not analogous; the resulting ion V (benzotropylium) differs from azulene (II) in being a true bicyclic aromatic system in which the central bond must have a large π component.



IVa, X = O
b, X = CH_2
c, X = S



V



VI

Results

Table I shows π-binding energies calculated for III and IV by the PPP[2b] and SPO[2b] methods, for both planar and nonplanar structures. The geometries of these were calculated using standard values for C–X bond lengths and C–X–C bond angles.

The difference in π-binding energy between the planar and nonplanar systems is in each case close to 1.5 ev. This seems very reasonable. The results also indicate that there is a linear relation between the π-binding energy and the separation of the bridgehead atoms.

Localization energies[2d] were also calculated for these compounds, for electrophilic, nucleophilic, and radical substitution; the results are shown in Tables II, III, and IV. The localization energies are given relative to benzene, so that a negative value corresponds to a site that is more reactive than a single position in benzene. For comparison, values are also listed for naphthalene (from part IV[2d]), and for benzotropylium (V) and perinaphthindenylium (VI), the latter being new results.

Discussion

These calculations suggest that the bridged polyenes (III) and bridged cyclic ions (IV) must be nonplanar, as ordinary chemical intuition would in any case lead one to expect, for the differences in π-binding energy be-

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[7] W. Grimme, H. Hoffmann, and E. Vogel, *Angew. Chem.*, 77, 348 (1965).

Table III. Nucleophilic Localization Energies[a] (ev)

Molecule	Bridging group	Position	Localization energy			
			Planar		Nonplanar	
			PPP	SPO	PPP	SPO
Naphthalene	...	1	−0.915	−0.912	...	...
		2	−0.500	−0.544	...	...
Cyclodecapentaene	O	1	−1.340	−1.498	−1.421	−1.496
		2	−1.266	−1.415	−1.202	−1.345
	CH_2	1	−1.358	−1.525	−1.443	−1.522
		2	−1.289	−1.444	−1.228	−1.377
	S	1	−1.389	−1.563	−1.492	−1.570
		2	−1.332	−1.497	−1.273	−1.434
Benztropylium	...	3	−7.546	−7.701	...	...
		4	−6.548	−6.790	...	...
		5	−7.469	−7.653	...	...
		10	−6.372	−6.669	...	...
		11	−6.501	−6.765	...	...
Cyclohendecapentaenylium	O	3	−7.148	−7.485	−7.439	−7.735
		4	−7.089	−7.441	−7.149	−7.528
		5	−7.122	−7.463	−7.273	−7.612
		10	−7.083	−7.431	−7.167	−7.536
		11	−7.119	−7.463	−7.387	−7.698
	CH_2	3	−7.146	−7.489	−7.432	−7.730
		4	−7.092	−7.447	−7.153	−7.543
		5	−7.121	−7.468	−7.265	−7.606
		10	−7.086	−7.439	−7.164	−7.534
		11	−7.121	−7.469	−7.391	−7.707
	S	3	−7.151	−7.496	−7.455	−7.760
		4	−7.097	−7.460	−7.158	−7.551
		5	−7.117	−7.475	−7.273	−7.624
		10	−7.092	−7.455	−7.181	−7.561
		11	−7.123	−7.481	−7.418	−7.735
Perinaphthindenylium	...	1	−7.408	−7.427	...	...
		2	−4.764	−4.705	...	...

[a] For definition see ref 2d.

Table IV. Radical Localization Energies[a] (ev)

Molecule	Bridging group	Position	Localization energy			
			Planar		Nonplanar	
			PPP	SPO	PPP	SPO
Naphthalene	...	1	−0.424	−0.452	...	...
		2	−0.161	−0.248	...	...
Cyclodecapentaene	O	1	−0.867	−1.164	−1.306	−1.553
		2	−0.851	−1.146	−0.992	−1.281
	CH_2	1	−0.885	−1.186	−1.337	−1.586
		2	−0.869	−1.166	−1.017	−1.310
	S	1	−0.917	−1.224	−1.436	−1.682
		2	−0.902	−1.211	−1.079	−1.375
Benztropylium	...	3	−0.155	−0.320	...	...
		4	+0.080	−0.150	...	...
		5	+0.105	−0.271	...	...
		10	+0.067	−0.313	...	...
		11	−0.130	−0.420	...	...
Cyclohendecapentaenylium	O	3	−0.426	−0.919	−0.795	−1.258
		4	−0.444	−0.953	−0.457	−0.982
		5	−0.407	−0.895	−0.573	−1.086
		10	−0.423	−0.931	−0.510	−1.048
		11	−0.423	−0.927	−0.793	−1.259
	CH_2	3	−0.442	−0.938	−0.818	−1.283
		4	−0.457	−0.969	−0.472	−1.001
		5	−0.423	−0.915	−0.593	−1.111
		10	−0.438	−0.948	−0.526	−1.061
		11	−0.439	−0.949	−0.818	−1.285
	S	3	−0.468	−0.971	−0.897	−1.359
		4	−0.481	−0.999	−0.502	−1.031
		5	−0.452	−0.951	−0.649	−1.171
		10	−0.465	−0.979	−0.574	−1.101
		11	−0.467	−0.979	−0.902	−1.361
Perinaphthindenylium	...	1	−0.066	−0.403	...	...
		2	+0.519	−0.328	...	...

[a] For definition see ref 2d.

Table V. Calculated Resonance Energies and Heats of Formation (ev) at 25° for Nonplanar Forms of III and IV

Molecule	Bridge	E_R PPP	E_R SPO	ΔH_f,[b] kcal/mole
I[a]	. . .	1.061	1.079	. . .
III	O	0.892	0.857	92.536 ± 0.050
III	CH_2	0.869	0.830	101.451 ± 0.053
III	S	0.829	0.785	91.370 ± 0.055
Naphthalene	. . .	2.282	2.280	. . .
Azulene	. . .	1.225	1.226	. . .
IV	O	3.578	3.473	104.520 ± 0.089
IV	CH_2	3.565	3.456	113.435 ± 0.090
IV	S	3.544	3.429	103.383 ± 0.094

[a] Values for planar I. [b] Listed limits of error are estimated average deviations.

tween the planar and nonplanar forces are too small to outweigh the much greater σ-bond strains in the former case.

Table V lists resonance energies and heats of formation for III and IV, calculated[2] from the data in Table II; previous[2] values for cyclodecapentaene (I), naphthalene, and azulene are included for comparison. The resonance energies of III are close to that of I, and much less than that of naphthalene; naphthalene is, of course, best regarded as a bicyclic aromatic system, with a resonance energy twice that of analogous monocyclic systems. On this basis, azulene is also best regarded as a monocyclic aromatic system, the transannular bond making only a small additional contribution to the total π-binding energy. Note that the resonance energies of III are somewhat less than that of the parent I; this again would be expected in view of the noncoplanar model assumed for III.

The localization energies listed in Tables II–IV also seem generally reasonable. The monocyclic systems III are all predicted to be significantly more reactive than naphthalene to reagents of all three types; as would be expected for substitution in a neutral hydrocarbon, no type of reagent is specially favored. The positive ions IV on the other hand are predicted to show extremely low reactivity to electrophilic reagents, extremely high reactivity to nucleophilic reagents, and a reactivity to radicals quite similar to naphthalene or III; this pattern would, of course, be expected for reactions of positive ions, and the values are in line with those predicted for benzotropylium. The values for the bridged systems III and IV differ from those for naphthalene or benzotropylium in that the variations in reactivity between the various positions are predicted to be much smaller; this again seems very reasonable since III and IV approximate quite closely in structure to simple monocyclic systems where all the positions would be essentially equivalent. One might also expect the reactivities to show a systematic dependence on the length of the transannular bridge, this increasing in the order $O < CH_2 < S$; the localization energies in Tables II–IV confirm this intuition. Thus the reactivities of the bridged cyclic polyenes III to reagents of all three types are predicted to increase in the order IIIa < IIIb < IIIc.

The localization energies lead to the prediction that all three bridged polyenes III should undergo substitution preferentially in the α positions (*i.e.*, those adjacent to the bridge). Vogel and his collaborators[8] have studied various electrophilic substitution reactions of IIIa and IIIb, in particular, nitration, bromination, and acetylation; in each case products were isolated with the substituent in the α positions.

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(8) E. Vogel, W. Mackel, and W. Grimm, *Angew. Chem.*, **76**, 786 (1964).