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THE AROMATICITY OF IONS AND RADICALS

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ABSTRACT - Possible reference structures for the computation of ion and radical resonance energies are examined. One is chosen which is analogous to that previously used for molecules, in the sense that both contain localized double and single bonds and the energies of both are obtained additively as the sum of bond energy terms. Although their reference structures are analogous, acyclic ions and radicals are themselves not analogous to molecules; the acyclic molecules are like their reference structures, but acyclic ions and radicals are not. In contrast to graph theoretical predictions, acyclic radicals and ions are found to have considerable aromatic character; and more significantly, it is found that this varies considerably from one system to another. It must be remembered that the fact that a given ion is computed to be more aromatic than some molecule does not necessarily mean that the ion is more stable than the molecule. It means rather that the ion is more stable than its reference by an amount greater than the molecule is more stable than its reference. Resonance energies are also given for a number of cyclic ions and radicals.

INTRODUCTION

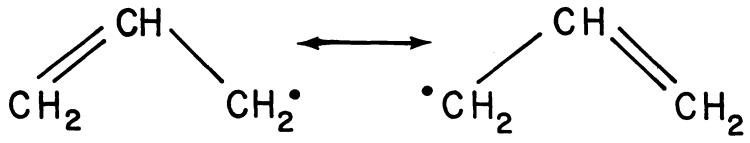
The correlation between Hückel molecular orbital resonance energy and experimental aromaticity of cyclic conjugated molecules has been well established (Refs. 1-7). However, up to now we have not been able to find a similar correlation for radicals and ions, because of our inability to calculate reference energies for those systems. These are required since resonance energy is the difference between the Hückel π energy of the actual structure and the reference energy. In this paper we shall examine several possible reference structures for ions and radicals and choose one that is consistent with our molecule reference and with current experimental usage.

SEARCH FOR REFERENCE STRUCTURE

Graph Theoretical Reference. For conjugated molecules (Ref. 8) it was observed that the π energy of any acyclic hydrocarbon can be expressed to a good approximation as the sum of bond energy terms, while for a cyclic it can not. The sum of bond energy terms defines the energy of the reference structure. Since for acyclics this equals the actual energy, acyclics are computed to have zero, or nearly zero, resonance energies (Refs. 1 & 9).

Trinajstić and his coworkers (Refs. 10 & 11) and Aihara (Ref. 12) have reformulated these ideas in an elegant way using the graph-theoretical theorem of Sachs (Ref. 13), which shows how to find the coefficients in a Hückel secular polynomial by counting certain subgraphs

of the molecular graph. If contributions of cyclic subgraphs are discarded a new polynomial is obtained whose roots are defined as the energy levels of the reference structure. Resonance energies obtained in this way are usually quite similar to ours in the case of conjugated molecules. An advantage of the graph theoretical method is that it can be applied easily to ions and radicals. With this method all conjugated acyclic ions and radicals are computed to have exactly zero resonance energy just as do the corresponding molecules. However allyl radical, like benzene but unlike butadiene and other conjugated acyclics, has two Kekulé structures



and presumably equal C-C bond lengths (Refs. 14 & 15). Consistent with this is the fact that chemists do commonly discuss the resonance stabilization and aromaticity of acyclic ions and radicals (Refs. 16 & 17); hence it is not clear that the graph theoretical reference structure which leads to zero resonance energy is either convenient or correct for ions and radicals.

Infinite Chain Reference. Following Dewar (Ref. 9), the starting point for our theoretical treatment of the aromaticity of conjugated hydrocarbons was the observation that the calculated π energy of linear polyenes is given accurately as a linear function of the number of carbon atoms (Ref. 1). As a consequence, the π energy of these molecules can be written as a sum of bond energy terms. The same turns out to be true for all acyclic conjugated hydrocarbons. Should it also be true for acyclic radicals and ions, then their bond energy terms could be used to define reference structures for radicals and ions, and all acyclic ions and radicals would have zero resonance energy relative to this reference. Such a result would not necessarily imply that acyclic radicals and ions are as stable as acyclic conjugated molecules. It would only mean that all systems have the same energy as their reference structures, but reference structure energies for ions and radicals may be very different from those for molecules. Hence even if energy additivity is found to hold for acyclic ions or radicals, some other reference structure, perhaps one more similar in energy to that used for neutral molecules, might be preferable. On the other hand, if energy additivity is not found for acyclic ions and radicals, then it would not seem reasonable to assign them all zero resonance energy.

We begin by comparing the behavior of the linear conjugated radicals, $CH_2(CH)_nCH_2^{\bullet}$ (n odd), and the linear polyenes, $CH_2(CH)_nCH_2$ (n even). Since these radicals are all odd alternant systems, the highest-filled orbital is nonbonding, and many of the results below apply equally to the singly-charged anions or cations. The secular equations for linear radicals and polyenes can be solved in closed form by the method of finite differences. Summing the results over filled orbitals gives for the polyenes

$$E_\pi = 2\beta[\csc(\pi/2(n+1)) - 1] \ , \quad (n \text{ even}) \tag{1}$$

and for the radicals, anions and cations

$$E_\pi = 2\beta[\cot(\pi/2(n+1)) - 1] \text{ , (n odd)} \quad (2)$$

where n is the number of carbon atoms. Energy and energy differences for the first members of these series are shown in Table I and Fig. 1.

Table I. Comparison of HMO energies of the linear acyclic radicals (or singly charged anions or cations) with the linear molecules.[a]

Radicals (or ions)				Molecules			
No. of C atoms	HMO Energy (β)	First Difference	Second Difference	No. of C atoms	HMO Energy (β)	First Difference	Second Difference
3	2.828			4	4.472		
		2.636				2.516	
5	5.464		-0.045	6	6.988		0.014
		2.591				2.530	
7	8.055		-0.018	8	9.518		0.006
		2.573				2.536	
9	10.628		-0.009	10	12.053		0.003
		2.564				2.539	
11	13.192		-0.005	12	14.592		0.002
		2.559				2.541	
13	15.750		-0.003	14	17.134		0.001
		2.556				2.542	
15	18.306		-0.002	16	19.676		0.001
		2.554				2.543	
17	20.860		-0.001	18	22.219		0.001
		2.552				2.544	
19	23.412		-0.001	20	24.763		0.000
		2.551				2.544	
21	25.964			22	27.307		

[a] Six decimals were carried in all calculations and final results rounded to three.

For short chains, the radicals deviate somewhat more from additivity than do the polyenes. Further, for short chains inserting a CH unit into a polyene to give the next higher radical lowers the energy only about two-thirds as much as inserting a second CH to go from radical to polyene. But taking the limit of Eqs. (1) and (2) as n becomes infinite shows that for both chains the π energy approaches $4\beta/\pi = 1.273\beta$ per carbon atom (or 2.546β on going from one member to the next in either chain). For long chains the radical energy lies exactly half-way between the next higher and lower polyenes; though Fig. 1 shows that approach to this behavior occurs much more slowly than the approach to additivity in either polyene or radical chains.

Since linear radicals and polyenes go to the same limit, and since linear polyenes are nonaromatic (Ref. 1), it would seem reasonable to use infinite polyenes as reference structures for both molecules and radicals. Consider one of the Kekulé structures of the

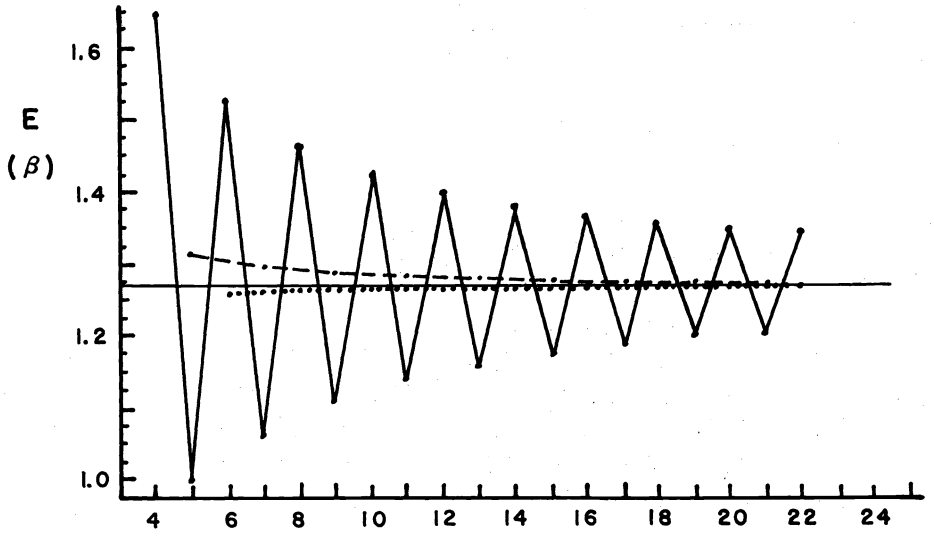
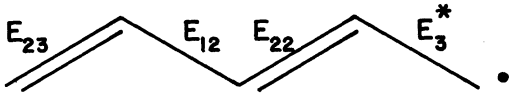


Fig. 1. Linear polyene and radical energy differences. The horizontal line indicates the limiting value of $4/\pi$ for infinite chains. The solid line shows the energy change on adding a CH unit to give a chain with the number of carbon atoms on the abscissa. The dotted line gives half the energy change on adding two CH units starting with a hydrocarbon molecule, and the dashed line shows the corresponding change starting with a hydrocarbon radical.

n-pentadienyl radical

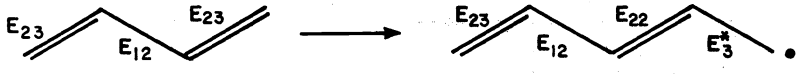


The π energy of this radical might be written in terms of additive bond energies as

$$E_\pi = E_{23} + E_{12} + E_{22} + E_3^* ,$$

where E_{23}, E_{12} and E_{22} are bond energy terms already familiar from the polyenes (Ref. 1), but E_3^* is a new type required for radicals. The first subscript in the polyene bond energy terms indicates whether the bond is double or single, and the second gives the number of hydrogen atoms attached. The new bond types required for radicals will all be formally single, and the first subscript will be deleted. The asterisk will indicate the free electron localized on the one carbon atom of these new bond types. It will turn out that the same new bond energy terms are also valid for monoanions and monocations.

Inserting a CH group into butadiene gives the n-pentadienyl radical, but this same transformation may also be described as the replacement of an E_{23} unit by E_{22} and E_3^* units.



The same is true in forming any linear radical from the next lower polyene. For the infinite chain this energy difference is $4\beta/\pi$. Hence

$$4\beta/\pi = E_{22} + E_3^* - E_{23}, \tag{3}$$

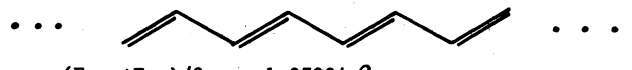
which may then be solved for the new bond energy term E_3^*.

Before proceeding to get all the new radical bond energy terms in this way, our eight polyene bond energies should be revised slightly. They were obtained originally by a least squares fit to the π energy of 40 small acyclic hydrocarbons (Ref. 1). With them, the REPE of infinite linear polyenes and infinite annulenes turns out to be (Ref. 18)

$$4\beta/\pi - (E_{22} + E_{12})/2 = 0.005\beta\ , \tag{4}$$

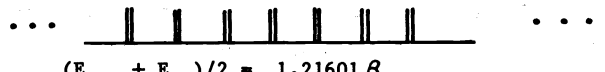
making these compounds essentially nonaromatic. To be exactly consistent with our planned radical reference structure, we should require the right-hand side of Eq. (4) to be exactly zero instead of 0.005β. There are eight polyene bond energy terms, but because of linear relations connecting them (Refs. 1 & 19), two must be fixed arbitrarily. Let $E_{23} = E_{22'} = 2.0000$ as before (Ref. 1). The remaining six are to be determined by equating additive π energy per electron to that actually computed by the Hückel method (see Appendix) for the six infinite hydrocarbon chains

a)



$$(E_{22} + E_{12})/2 = 1.27324\beta \tag{5}$$

b)

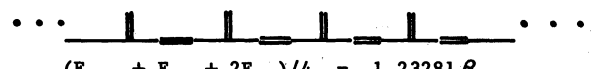


$$(E_{22'} + E_{10})/2 = 1.21601\beta \tag{6}$$

c)

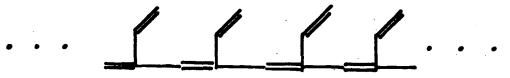
$$(2E_{23} + 2E_{11} + E_{10} + E_{20})/6 = 1.24741\beta \tag{7}$$

d)



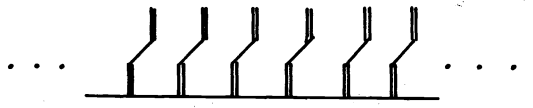
$$(E_{22'} + E_{22} + 2E_{11})/4 = 1.23281\beta \tag{8}$$

e)



$$(E_{23} + E_{21} + 2E_{11})/4 = 1.24941\beta \tag{9}$$

f)



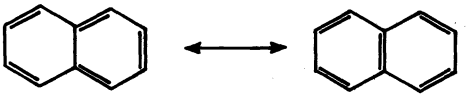
$$(E_{23} + E_{12} + E_{21} + E_{10})/4 = 1.24485\beta\,. \tag{10}$$

Unfortunately the left sides of Eqs. (5)-(10) are linearly dependent. It turns out that in addition to the two linear dependences holding for all conjugated hydrocarbons, for all infinite acyclic chains a third

$$n_{23} = 2n_{20} + n_{21} \tag{11}$$

also holds, where n_{ij} equals the number of bonds of type ij.

To provide a sixth independent equation, we considered imposing the condition that the additive energies of all Kekulé structures be equal for any conjugated hydrocarbon. This condition simplifies the computation of REPE and was found very nearly to hold with our original bond energies (Ref. 1). Comparing two Kekulé structures of naphthalene



it is see that the (10) bond in one becomes a (20) bond in the other, two (21) bonds become (11) bonds, and a (12) becomes a (22). Additive energies will be equal for the two structures if

$$E_{10} + 2E_{21} + E_{12} = E_{20} + 2E_{11} + E_{22}\,. \tag{12}$$

In fact Eq. (12) is general enough to ensure the equality of additive energies for all Kekulé forms of any conjugated hydrocarbon. But Eq. (12) also turns out to be a linear combination of the left-hand sides of Eqs. (5)-(10). Therefore a further condition must be sought to fix all six independent E_{ij}'s. Equating additive and Hückel energies of butadiene or some other small acyclic could be used to give the remaining condition, but the following is more like what was planned to obtain the radical bond energy, E_3^*. The additive energy of $CH_2{=}CH{-}(-CH{=}CH-)_m{-}CH{=}CH_2$ is

$$2E_{23} + E_{12} + m(E_{12} + E_{22}) = 4 + E_{12} + m(8/\pi) \tag{13}$$

in units of β. Equating this to the Hückel energy from Eq. (1) with $n = 2m + 4$ and taking the limit as m becomes infinite gives

$$E_{12} = \lim_{m\to\infty} [2\csc(\pi/(4m+10)) - 6 - 8m/\pi]\beta$$
$$= (20/\pi - 6)\beta = 0.366198\,\beta . \tag{14}$$

Then solving Eqs. (5)-(8) and (12) gives a set of hydrocarbon bond energy terms which however do not give satisfactory predictions of aromaticity. For example butadiene is predicted to be over twice as aromatic as azulene. Roughly stated the difficulty seems to be that all the lack of additivity of the long chains is thrown into the E_{12} term by using Eq. (14). This can be corrected by retaining Eqs. (5)-(8) and (12), but varying E_{12} to minimize the REPE of our orginal 40 acyclics (Ref. 1). Resulting bond energy terms do predict reasonable aromaticities, but our intended method of computing E_3^* no longer seems reliable, and a new route must be sought.

Mulliken-Parr Reference. The π energy of our conjugated hydrocarbon reference is gotten by adding contributions of double bonds (all approximately 2β) and of single bonds (all about $\beta/2$). This is reminiscent of the Mulliken-Parr reference structure (Ref. 20) which consisted of alternating long and short bonds. We are treating only the π electrons while Mulliken and Parr included σ electrons also; but we have shown (Ref. 4) how, since the two affect the resonance energy in a parallel way, the latter might be ignored. We shall first make a simple application of the Mulliken-Parr reference structure to several small hydrocarbons to see whether results are similar to ours. Considering only the π electrons, resonance energy (RE) is given by

$$RE = E_\pi - E_\pi(\text{ref}) \tag{15}$$

where E_π is the π energy of the actual molecule and E_π(ref) is that of the reference structure with alternating long and short bonds. The long and short bond lengths were taken to be 1.54 Å and 1.34 Å. The Wolfsberg-Helmholtz approximation (Ref. 21) was used to obtain resonance integrals as a function of interatomic distance

$$\beta_{ij}(R) = 0.5\ K\ (\alpha_{ii} + \alpha_{jj})\ S_{ij}(R) \tag{16}$$

where $S_{ij}(R)$ is the overlap integral between AO's ϕ_i and ϕ_j separated by a distance R. All AO's to be considered are $2p\pi$ orbitals on carbon so that β will depend upon R only and the

subscripts i and j can be dropped. Applying Eq. (16) to β_o, the standard resonance integral at the benzene distance of R = 1.397 Å; and dividing the result into Eq. (16) gives simply

$$\beta(R) = \beta_o S(R)/S(1.397\ \text{Å}) \tag{17}$$

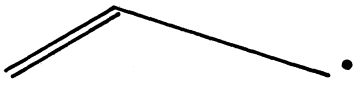
where the troublesome parameter K has canceled out. The standard Slater exponent (Ref. 22) of 1.625 was used (with R in a. u.) in the evaluation of overlap integrals. E_π was computed by starting with a Hückel calculation using all resonance integrals equal to β_o, taking the resulting bond orders to get bond lengths, then using these in Eq. (17) to get new resonance integrals and the final E_π. The bond order-bond length relation used was that of Coulson and Goŀebiewski (Ref. 23) as recommended by Salem (Ref. 24).

$$R = (1.517 - 0.18\rho)\text{Å} \tag{18}$$

Eq. (18) is consistent with the use of R_o = 1.397 Å.

REPE's (Ref. 25) computed in this way for the first several linear polyenes varied from 0.002 for butadiene (original value (Ref. 1) = 0.002) to 0.009 for the C_{14} chain (original value (Ref. 1) = 0.001); for benzene this method gave REPE = 0.053 instead of 0.065; and +0.055 and +0.047 for the two distinct Kekulé forms of naphthalene instead of our original value of 0.055 for both. Several variations of the Mulliken-Parr method were tried including using experimental rather than calculated bond lengths for the actual structure, setting all resonance integrals equal to β_o for the actual structure, changing lengths of the long, short and standard bonds (these bond length changes produced large effects), and changing the $2p\pi$ orbital exponent (this had surprisingly little effect), but nothing worked significantly better than the first version. We conclude that REPE's from this version of the Mulliken-Parr model are in sufficiently close agreement with our original values (Ref. 1) to justify computing the allyl resonance energy in this way and then using it to get our E_3^* bond energy term.

The Mulliken-Parr reference structure for allyl radical is



with a double bond of 1.34 Å and a single bond of 1.54 Å. Using Eq. (17), the corresponding resonance integrals are β_2 = 1.099402 and β_1 = 0.781716 in units of β_o, and E_π of the reference is $2\sqrt{\beta_1^2 + \beta_2^2}$ = 2.697973. The actual allyl radical is computed to have two equal bonds with bond order = 0.70711 and hence of length = 1.38972 Å, leading to a π energy of 2.863192. The resonance energy is then the difference between these two π energies, i.e., 0.16522. In our method, resonance energy is also computed according to Eq. (15), but E_π(ref) for allyl is simply the sum of the bond energy terms E_{23} = 2.0000 and

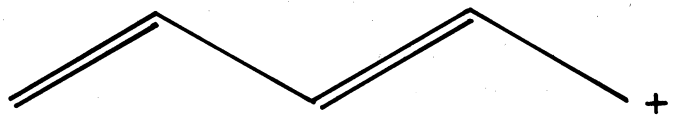
E_3^* (which is as yet unknown), and E_π is computed by the Hückel method with all resonance integrals = 1 (in units of β_o) as 2.828427. Equating this resonance energy to that from the Mulliken-Parr model gives

$$0.16522 = 2.828427 - (E_{23} + E_3^*) \tag{19}$$

or $E_3^* = 0.6632$.

The Coulson-Rushbrooke pairing theorem (Ref. 26) has been shown by Longuet-Higgins (Ref. 27) to hold even in the case of unequal resonance integrals. Hence the odd electron in all acyclic radical reference structures is in a non-bonding orbital, and hence E_3^* and the other radical bond energy terms to be obtained below hold for singly charged anions and cations as well. In the sections above it was convenient to carry out the discussion in terms of the radicals, but we shall actually be more interested in applying our results to ions. At this point we shall therefore change our focus to cations and derive the remaining bond energy terms needed.

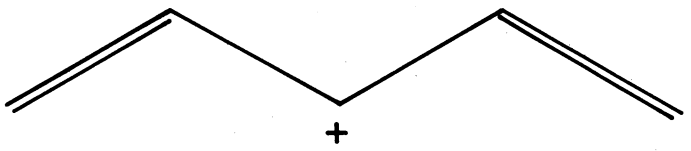
With E_3^* and the condition that all resonance structures of an ion have the same reference energy it is now quite simple to compute all necessary ion bond energy terms. To obtain the $HC-\overset{+}{C}H$ bond energy (E_2^*) the pentadienyl or any linear acyclic cation may be used. Using the resonance structure which has the positive charge on a terminal carbon,



the energy of the reference structure for the pentadienyl cation is

$$E_{ref} = E_{23} + E_{22} + E_{12} + E_3^* = 5.1991 \ . \tag{20}$$

Equating this to the reference energy of the resonance structure with a positive charge on the central carbon



gives

$$2E_{23} + 2E_2^* = 5.1991 \ . \tag{21}$$

E_2^* is found to be equal to 0.5996 regardless of the linear acyclic cation used. There are four additional single bond types which bear a positive charge, and these can be obtained in a similar fashion using branched acyclic cations. All six bond types and their energies are given in Table II. In all cases the simplest acyclic system in which the bond type

Table II. Bond energies of single bonds bearing a positive charge.

Bond Type	Designation	Bond Energy (β)
$HC—\overset{+}{C}H_2$	E_3^*	0.6632
$HC—\overset{+}{C}H$	E_2^*	0.5996
$C—\overset{+}{C}H_2$	$E_{2'}^*$	0.5950
$HC—\overset{+}{C}$	E_1^*	0.5480
$C—\overset{+}{C}H$	$E_{1'}^*$	0.5697
$C—\overset{+}{C}$	E_0^*	0.5430
$H\overset{+}{C}—\overset{+}{C}H_2$	E_3^{**}	0.7967
$H\overset{+}{C}—\overset{+}{C}H$	E_2^{**}	0.7330
$\overset{+}{C}—\overset{+}{C}H_2$	$E_{2'}^{**}$	0.7067
$\overset{+}{C}—\overset{+}{C}H$	E_1^{**}	0.6815
$\overset{+}{C}—\overset{+}{C}$	E_0^{**}	0.6570

occurred was used to obtain the bond energy. With these bond energies one can calculate the additive energy or reference energy and therefore the resonance energy of any conjugated monocation, acyclic or cyclic.

RESULTS

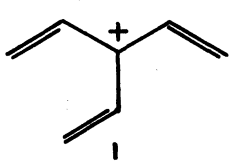
Acyclic Cations. We shall first examine the resonance energies of the linear acyclic cations (Table III). It is misleading to compare total resonance energies for molecules of different size since the general trend of increasing total resonance energy with increasing size will obscure differences in aromaticity. We and others have compared resonance energies per π electron. Zahradník, Michl and Pancíř (Ref. 28) and also Aihara (Ref. 29) have used π energies per bond. In the case of three-dimensional polyhedral molecules Aihara (Ref. 30) has also proposed resonance energy per face. Trinajstić and coworkers

Table III. Resonance energies of the acyclic linear cations.

no. of atoms	HMO energy	reference energy	RE	REPA
3	2.828	2.663	0.165	0.055
5	5.464	5.199	0.265	0.053
7	8.055	7.735	0.320	0.046
9	10.628	10.271	0.357	0.040
11	13.192	12.807	0.385	0.035
13	15.750	15.343	0.408	0.031
15	18.306	17.879	0.428	0.029
17	20.860	20.415	0.446	0.026
19	23.412	22.950	0.462	0.024
21	25.964	25.486	0.477	0.023
23	28.514	28.022	0.492	0.021
25	31.064	30.558	0.506	0.020
27	33.613	33.094	0.519	0.019
29	36.162	35.630	0.532	0.018
31	38.711	38.166	0.545	0.018
33	41.259	40.702	0.558	0.017
35	43.808	43.238	0.570	0.016

(Ref. 31) compared resonance energies per electron with those per bond, for charged and uncharged species, and found that the two led to similar predictions. We are inclined to agree with Lewis and Peters' conclusion (Ref. 32) that there is no clear answer to how this normalization should be made. Nevertheless, we prefer to use resonance energy per atom in the conjugated system (REPA) rather than resonance energy per π electron (REPE) in the case of ions. That is, we prefer a description of how strongly each atom is bonded in the molecule, rather than one of how much bonding is being done by each electron. REPE and REPA are identical in the case of hydrocarbons and their radicals. They will differ somewhat for ions and for heterosystems where the heteroatom contributes more than one π electron to the conjugated system.

REPA is shown in Table III for the first seventeen linear cations. In all cases where more than one kind of resonance structure can be written for an ion the reported RE was obtained using the average of the additive energies of all the resonance structures. As was found for the conjugated hydrocarbons (Ref. 1) there was never any significant difference in reference structure energies from the various resonance structures of an ion. It is seen that the first members of the series have a substantial positive REPA. Examination of small branched acyclic ions (e.g., 1 and 2) also indicates they have significant resonance



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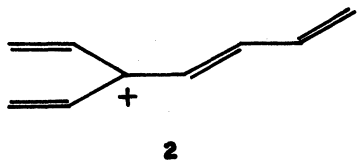

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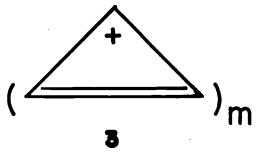
stabilization (0.051) and 0.043). The only previously calculated resonance energies of conjugated ions (Refs. 11,12) were based on graph theory in which all acyclic ions, by definition, have zero resonance energy.

Cyclic Monocations. Of the cyclic monocations perhaps the most interesting ones are the monocyclic annulenium ions (3) which have received considerable attention in recent years.



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REPA's of the first members are in Fig. 2 and Table IV.

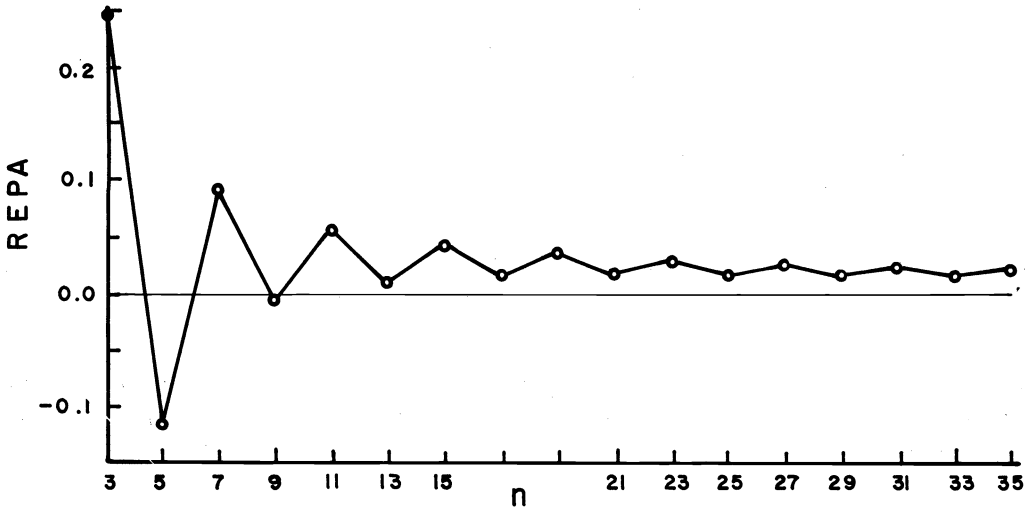


Fig. 2. A plot of REPA (β) vs. number of carbon atoms (n) of the monocyclic cations.

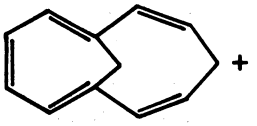
The initial strong alternation between aromatic and antiaromatic is similar to that found in annulenes. However it is seen that with n>9 both 4N and 4N + 2 systems have a positive REPA. Although similar behaviour is found with the annulenes, REPA of the 4N annulenes does not become positive until they are considerably larger and even then the value is insignificantly small. (The number of carbon atoms in the ring, n, the m of structure 3 and the Hückel index, N, are related by n = 2m + 1 = 4N or 4N + 2.)

Experimental results compare very favorably with our calculated REPA's for these monocylic cations. Breslow has prepared a number of derivatives (Ref. 33) of cyclopropenyl cation (REPA = 0.244) and was even able to isolate stable salts of the unsubstituted cyclopropenyl cation (Ref. 34). Using pK_{R+} data he has estimated that this ion is stabilized by 18 kcal/mole relative to the allyl cation. In contrast the cyclopentadienyl cation (REPA = -0.114) has been characterized from experimental results by both Breslow (Ref. 35) and Lossing (Ref. 36) as antiaromatic. The unusual stability of the tropyllium ion has been well documented (Ref. 37) and is in agreement with our large calculated positive REPA of +0.092. The cyclononatetraenyl cation has been proposed as an unstable intermediate in solvolytic reactions (Refs. 38 & 39). As the ring size increases in these monocyclic ions

Table IV. Resonance energies of monocyclic cations

ring size	HMO energy	reference energy	RE	REPA
3	4.000	3.269	0.731	0.244
5	5.236	5.805	-0.569	-0.114
7	8.988	8.341	0.647	0.092
9	10.823	10.877	-0.054	-0.006
11	14.053	13.413	0.641	0.058
13	16.110	15.949	0.162	0.012
15	19.134	18.485	0.649	0.043
17	21.307	21.020	0.286	0.017
19	24.219	23.556	0.663	0.035
21	26.464	26.092	0.372	0.018
23	29.307	28.628	0.679	0.030
25	31.601	31.164	0.437	0.017
27	34.397	33.700	0.697	0.026
29	36.725	36.236	0.490	0.017
31	39.487	38.772	0.716	0.023
33	41.842	41.308	0.535	0.016
35	44.578	43.844	0.735	0.021

their stabilities will surely be affected by the bond angle strain required for them to obtain planarity. Vogel has overcome this difficulty by preparing a methylene bridged [11]annulenium cation (4)



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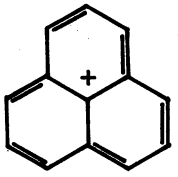
which is isolable and extremely stable (mp = 190° C) (Ref. 40). An X-ray structure determination of the hexafluorophosphate salt of 4 indicates very little bond alternation in the peripheral bonds, again supporting its aromaticity (Ref. 41).

In contrast to the polycyclic mono-anions, relatively few polycyclic monocations have been observed. The best known example is the phenalenium ion (5) which Pettit isolated as the



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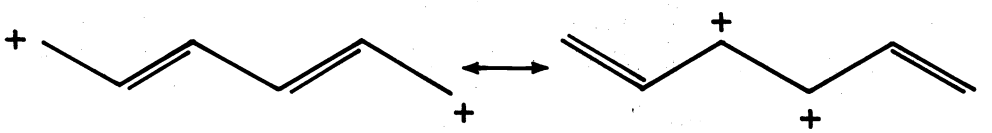
perchlorate salt (Ref. 42). 5 has a large positive REPA. A related system is cation 6 which was isolated as an extremely stable tetrafluoroborate salt (Ref. 43). Resonance energies of 6 and other polycyclic systems are given in Table V.

Table V. Resonance energies of polycyclic ions

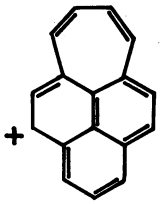
compound	HMO energy	reference energy	RE	REPA
5	17.827	16.877	0.950	0.073
6	23.573	22.429	1.144	0.067
7	8.906	8.792	0.114	0.014
8	11.581	11.328	0.253	0.028
9	9.857	9.525	0.332	0.042
10	9.514	9.527	-0.013	-0.002
11	21.099	20.628	0.471	0.029
12	15.618	14.597	1.021	0.085
13	20.962	19.894	1.068	0.071
14	23.262	22.430	0.832	0.049
15	17.213	16.906	0.307	0.024
16	10.456	9.525	0.931	0.116
17	16.231	15.049	1.182	0.099
18	23.446	22.207	1.239	0.062
19	19.410	18.090	1.320	0.094
20	14.996	14.597	0.399	0.033
21	16.050	15.074	0.976	0.081
22	21.956	20.628	1.328	0.083
23	9.104	8.945	0.160	0.020

Dications. Consideration of resonance energies of dications requires additional bond energy terms. For example the dication of cyclobutadiene

has four equivalent resonance structures which possess a single bond with a positive charge on each of the two carbons. The bond energy of this type of bond (E_2^{**}) was determined as above using the dication of hexatriene.



This bond energy and those of the other four possible bonds with two positive charges (obtained from branched acyclic dications) are given in Table II. To obtain the reference structure energy for a dication the bond energies given in Table II are used along with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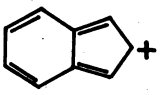
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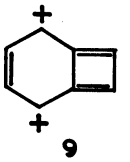
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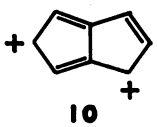
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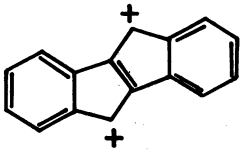
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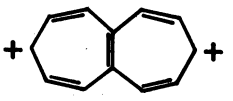
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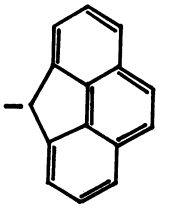
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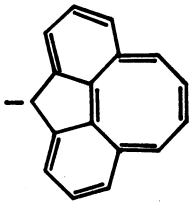
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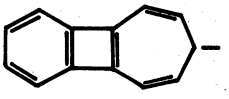
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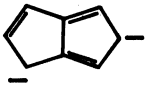
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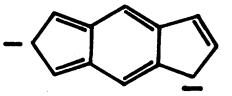
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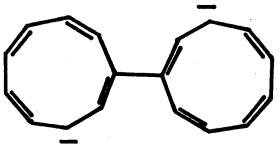
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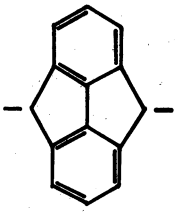
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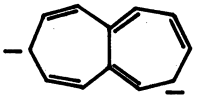
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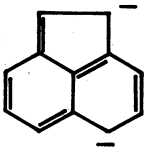
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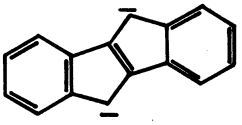
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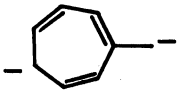
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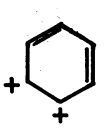
those in Table I in Ref. 1. For example for the dication of benzene there are six resonance structure of type A and three of type B.


A


B

Hence to compute the reference energy of this dication:

$$E^{A}_{ref} = 2E_{22} + E_{12} + E^{*}_{2} + E^{**}_{2} = 6.5380 \quad (22)$$

$$E^{B}_{ref} = 2E_{22} + 4E^{*}_{2} = 6.5382 \quad (23)$$

$$E_{ref} = (6E^{A}_{ref} + 3E^{B}_{ref})/9 \quad (24)$$

and its resonance energy:

$$RE = E_{HMO} - E_{ref} = 6.0000 - 6.5381 = -0.5381 \quad (25)$$

In Fig. 3 and Table VI we have plotted the REPA's of the annulene dications containing 4 to

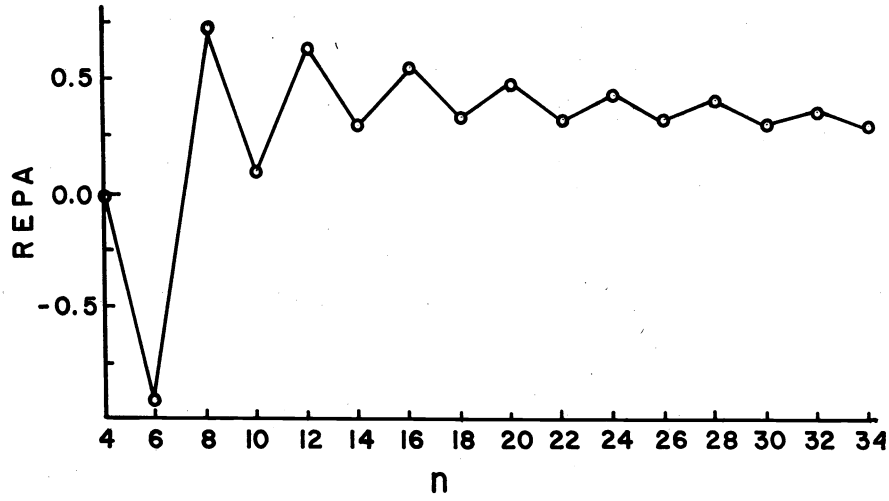


Fig. 3. A plot of REPA (β) vs. number of carbon atoms (n) of the annulenyl dications.

to 34 carbons. Perhaps the most remarkable result is the predicted nonaromatic character of the dication of cyclobutadiene (REPA = -0.001) even though it is a 4N + 2 system (N=0). This prediction appears to have some experimental support. Attempts to synthesize it have been unsuccessful (Ref. 44), including an attempt to observe it at very low temperature (Ref. 45). Olah has reported the synthesis of the tetramethyl derivative, but even it is unstable above -65°C. Recent ab initio calculations have predicted that cyclobutadiene dication should have a puckered geometry, perhaps also an indication of its antiaromaticity (Ref. 46). Although the dication of cycloocatatetraene has not been observed, a tetramethyl derivative was prepared at low temperature; but undergoes a rearrangement at -20°C (Ref. 47). The only other monocyclic dication that has been reported is that of [16]annulene (Ref. 48).

Table VI. Resonance energies of monocyclic dications

ring size	HMO energy	reference energy	RE	REPA
4	4.000	4.002	-0.002	-0.001
6	6.000	6.538	-0.538	-0.090
8	9.657	9.074	0.583	0.073
10	11.708	11.610	0.098	0.010
12	14.928	14.146	0.782	0.065
14	17.086	16.682	0.404	0.029
16	20.109	19.218	0.892	0.056
18	22.340	21.754	0.587	0.033
20	25.255	24.290	0.966	0.048
22	27.537	26.825	0.712	0.032
24	30.383	29.361	1.022	0.043
26	32.703	31.897	0.806	0.031
28	35.501	34.433	1.068	0.038
30	37.849	36.969	0.880	0.029
32	40.613	39.505	1.108	0.035
34	42.983	42.041	0.942	0.028

Of the dications of polycyclic systems, the pentalenyl dication (10) is of particular interest. It is predicted to be very slightly antiaromatic (REPA = -0.002). A recent report by Johnson supports this finding (Ref. 49). He found that electrochemical oxidation of tri-t-butylpentalene yielded exclusively the radical-cation and concluded that the inability to form the dication was perhaps due to its antiaromaticity. However, Rabinovitz has more recently reported (Ref. 50) the preparation of the dication of dibenz[b,f]pentalene (11). Unlike pentalene itself it has a positive REPA (0.029). In contrast to the dication of pentalene the dication of heptalene (12) is predicted to be strongly aromatic.

Anions and Dianions. Since all acyclic monocations are alternant and contain an odd number of carbon atoms the LUMO is nonbonding ($\epsilon = 0$), and therefore all acyclic monoanions will have the same HMO energy as the monocations. The result of this is that the calculation of acyclic bond energy terms of single bonds which contain a negative charge (i.e. 2 electrons) on one of the carbons leads to bond energy terms for the monoanions which are identical to those of the monocations. Hence values in Table II for the monocation bonds (E^*_{ij}) can also be used in computing reference structure energies of all acyclic and cyclic monoanions. Because of the pairing theorem the same relation holds between the dianions and dications. Note also that the acyclic dianions will have the same total resonance energy as the corresponding dications, as not only are the reference energies always identical but so also are the HMO binding energies.

The behavior of the monocyclic annulenyl anions is similar to that of the annulenyl cations as shown in Fig. 4 and Table VII and the REPA's are in good agreement with experimental results. pK_a studies by Breslow have led him to characterize the cyclopropenyl anion

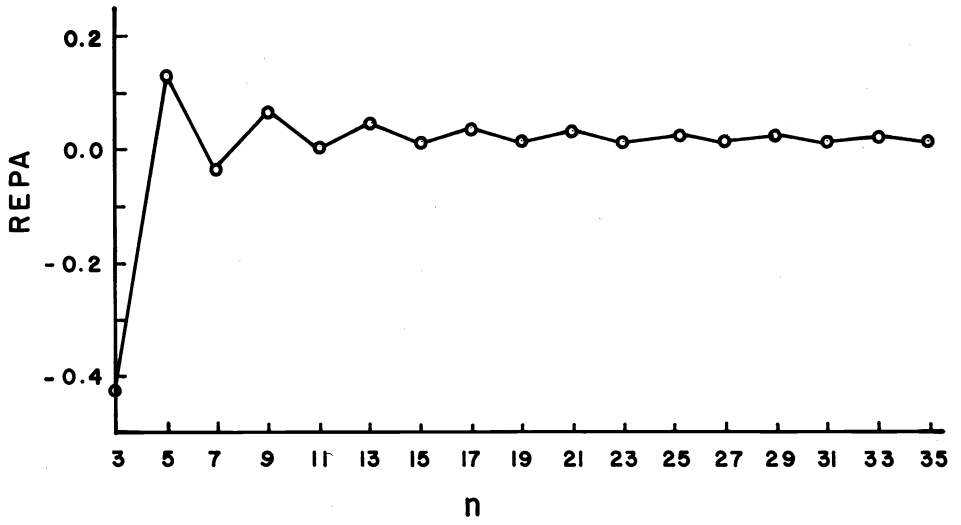


Fig. 4. A plot of REPA (β) vs. number of carbon atoms (n) of the monocyclic anions.

Table VII. Resonance energies of monocyclic anions

ring size	HMO energy	reference energy	RE	REPA
3	2.000	3.269	-1.269	-0.423
5	6.472	5.805	0.667	0.133
7	8.098	8.341	-0.243	-0.035
9	11.518	10.877	0.641	0.071
11	13.484	13.413	0.071	0.006
13	16.592	15.949	0.644	0.050
15	18.715	18.485	0.231	0.015
17	21.676	21.020	0.656	0.039
19	23.889	23.556	0.333	0.018
21	26.763	26.092	0.671	0.032
23	29.034	28.628	0.406	0.018
25	31.852	31.164	0.688	0.028
27	34.164	33.700	0.464	0.017
29	36.942	36.236	0.706	0.024
31	39.285	38.772	0.513	0.017
33	42.033	41.308	0.725	0.022
35	44.399	43.844	0.555	0.016

(REPA = -0.423) as antiaromatic (Ref. 51). On the other hand the high stability of the cyclopentadienyl anion (REPA = +0.133) has been known for many years. The cyclononatetraenide ion (REPA = +0.071) has been well characterized and appears to be aromatic (Refs. 52-55). Staley has noted the high degree of puckering in a methylene bridged [11]annulenyl anion and ascribed it to the antiaromaticity of this system (Ref. 56). We find it be be essentially nonaromatic. The [17]annulenyl anion was

synthesized in solution and found to be stable at 100°C for one hour (Refs. 57 & 58). A number of benzo-substituted annulenyl anions have also been reported (Refs. 59-61). Several polycyclic conjugated anions have been observed (Refs. 62 & 63) (13-15) and their resonance energies are given in Table V.

Total resonance energies and REPA's of the monocyclic annulenyl dianions are the same as the corresponding dications. The cyclobutadienyl dianion is calculated to be nonaromatic (REPA = -0.001) even though it is a 4N + 2 Hückel system. Pettit has postulated its existence as an intermediate but characterized it as very reactive since it abstracts protons from tetrahydrofuran (Ref. 64). On the other hand the next few 4N + 2 members of the monocyclic dianions are calculated to have strong resonance stabilization. In agreement with this the dianions of [8]- (Refs. 65 & 66), [12]- (Refs. 67 & 68), and [16]annulene (Ref. 69) have all been formed in solution. Furthermore, Stevenson (Ref. 70) has found experimentally the dianion of [8]annulene to be aromatic. The dianions of two bridged [14]annulenes have also been observed (Ref. 71). Note that even though the dianion of [14]annulene is a 4N system we calculate its REPA to be 0.027.

Several polycyclic dianions (16, 17 and 18) have been isolated as stable salts (Refs. 72-74) and they have large positive REPA's. The dianion 19 has a large positive REPA (0.092). It has not only been formed in solution but in the crystalline state at -10°C as well (Ref. 75). Heptalenyl dianion has been observed by nmr at temperatures ranging from -80°to +140°C (Ref. 76). The dianions of acenaphthene (21), dibenz[b,f]pentalene (22) and heptafulvene (23) have also been observed in solution (Refs. 77, 50 & 78).

Radicals. Again the bond energy terms given in Table II can be used in computing the reference energy of any acyclic or cyclic conjugated radical. In Fig. 5 and Table VIII are given the REPA's of the monocyclic annulenyl radicals. Unlike the corresponding cations

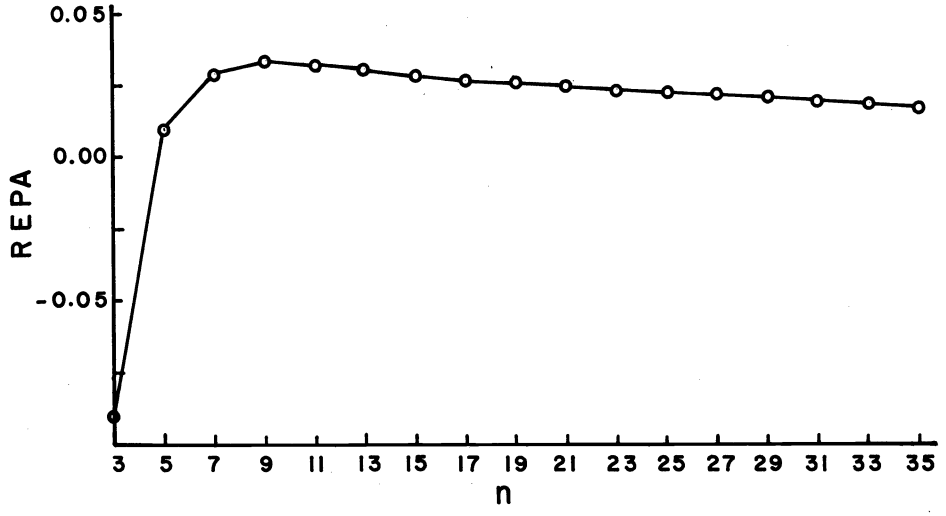


Fig. 5. A plot of REPA (β) vs. number of carbon atoms (n) of the monocyclic radicals.

and anions no alternation between antiaromatic and aromatic is found. Rather there is an initial large increase from strongly antiaromatic to somewhat aromatic with a subsequent slow decrease in REPA as the ring size is increased. The relatively high antiaromaticity

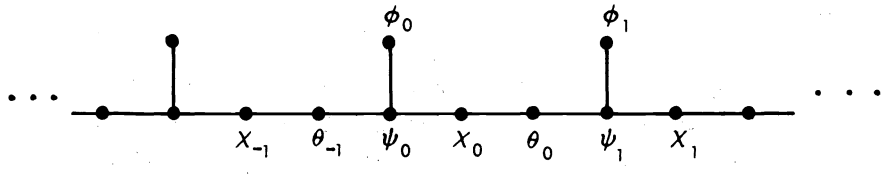
Table VIII. Resonance energies of monocyclic radicals

ring size	HMO energy	reference energy	RE	REPA
3	3.000	3.269	-0.269	-0.090
5	5.854	5.805	0.049	0.010
7	8.543	8.341	0.202	0.029
9	11.170	10.877	0.293	0.033
11	13.769	13.413	0.356	0.032
13	16.351	15.949	0.403	0.031
15	18.924	18.485	0.440	0.029
17	21.491	21.020	0.471	0.028
19	24.054	23.556	0.498	0.026
21	26.614	26.092	0.521	0.025
23	29.171	28.628	0.543	0.024
25	31.726	31.164	0.562	0.022
27	34.281	33.700	0.581	0.022
29	36.834	36.236	0.598	0.021
31	39.386	38.772	0.614	0.020
33	41.938	41.308	0.630	0.019
35	44.489	43.844	0.645	0.018

of the cyclopropenyl radical (REPA = -0.090) is an interesting result and appears to have experimental support. By comparing esr data of a phenylcyclopropenyl radical with that of phenyl allyl radical Schreiner (Ref. 79) has concluded that the cyclopropenyl radical is antiaromatic. Breslow had also suggested that the cyclopropenyl radical might be antiaromatic (Ref. 80).

APPENDIX

Energy levels of the six infinite chains a) to e) in Eqs. (5)-(10) were computed using the standard tight-binding approximation. Compound d) will illustrate the method



Atomic $2p\pi$ orbitals on each atom were labeled as indicated. Applying the Born-von Kármán cyclic boundary conditions and projection operators of the translational group gives the symmetry-adapted basis functions

$$\Phi_m = \frac{1}{\sqrt{U}} \sum_{j=-u}^{+u} \phi_j \exp 2\pi i\left(\frac{jm}{U}\right)$$

$$\Psi_m = \frac{1}{\sqrt{U}} \sum_{k=-u}^{+u} \psi_k \exp 2\pi i\left(\frac{km}{U}\right)$$

$$X_m = \frac{1}{\sqrt{U}} \sum_{\ell=-u}^{+u} X_\ell \exp 2\pi i\left(\frac{\ell m}{U}\right)$$

$$\Theta_m = \frac{1}{\sqrt{U}} \sum_{n=-u}^{+u} \theta_n \exp 2\pi i\left(\frac{nm}{U}\right) .$$

There is a total of $2u + 1 = U$ four-atom unit cells, and the index m goes from $-u$ to $+u$. Basis functions with different values of m do not interact, so that the only matrix elements needed are

$$\langle \Phi_m|H|\Phi_m\rangle = \langle \Psi_m|H|\Psi_m\rangle = \langle X_m|H|X_m\rangle = \langle \Theta_m|H|\Theta_m\rangle = \alpha$$

$$\langle \Phi_m|H|\Psi_m\rangle = \langle \Psi_m|H|X_m\rangle = \langle X_m|H|\Theta_m\rangle = \beta$$

$$\langle \Phi_m|H|X_m\rangle = \langle \Phi_m|H|\Theta_m\rangle = 0$$

$$\langle \Psi_m|H|\Theta_m\rangle^* = \beta \exp(2\pi i m/U) .$$

These give the secular equation

$$\begin{vmatrix} x & 1 & 0 & 0 \\ 1 & x & 1 & f^* \\ 0 & 1 & x & 1 \\ 0 & f & 1 & x \end{vmatrix} = x^4 - 4x^2 + (2\cos\vartheta)x + 1 = 0,$$

where $f = \exp(2\pi i m/U)$ and the variable $\vartheta = 2\pi m/U$ ranges from $-\pi$ to $+\pi$. The secular equation was solved in closed form using the usual trigonometric substitution to solve the cubic which gives the quadratic factors of the quartic (Ref. 81). All values of the lowest two roots, x_1 and x_2, for varying ϑ lie below all values of the highest two, x_3 and x_4. Hence, since the lowest two levels are doubly filled and since they are even functions of ϑ, the average energy per electron is given by

$$\bar{E} = \alpha - 4\beta \left[\int_0^{\pi} [x_1(\vartheta) + x_2(\vartheta)]\, d\vartheta \Big/ 8 \int_0^{\pi} d\vartheta \right] .$$

The integral in the numerator was evaluated numerically by the 3-point Simpson's rule. Ten intervals gave 5-decimal accuracy (though up to 999 intervals were used as a check), and resulted in

$$\bar{E} = \alpha + 1.23281\beta .$$

REFERENCES AND NOTES

1. B. A. Hess, Jr., and L. J. Schaad, J. Am. Chem. Soc., 93, 305 (1971).
2. B. A. Hess, Jr., and L. J. Schaad, J. Am. Chem. Soc., 93, 2413 (1971).
3. B. A. Hess, Jr. and L. J. Schaad, J. Org. Chem., 36, 3418 (1971).
4. L. J. Schaad and B. A. Hess, Jr., J. Am. Chem. Soc., 94, 3068 (1972).
5. L. J. Schaad and B. A. Hess, Jr., J. Chem. Educ., 51, 640 (1974).
6. B. A. Hess, Jr., and L. J. Schaad, J. Chem. Soc., Chem. Commun., 243 (1977).
7. B. A. Hess, Jr., L. J. Schaad and I. Agranat, J. Am. Chem. Soc., 100, 5268 (1978).
8. In this paper we shall use the word "molecules" to distinguish electrically neutral, diamagnetic systems from ions and radicals
9. M. J. S. Dewar and C. deLlano, J. Am. Chem. Soc., 91, 789 (1969).
10. I. Gutman, M. Milun, and N. Trinajstić, MATCH, 1, 171 (1975).
11. I. Gutman, M. Milun, and N. Trinajstić, J. Am. Chem. Soc., 99, 1692 (1977).
12. J. Aihara, J. Am. Chem. Soc., 98, 2750 (1976); 99, 2048 (1977).
13. H. Sachs, Publ. Math. (Debrecen), 11, 119 (1964).
14. J. McKelvey and W. J. Hehre, Mol. Phys., 25, 984 (1973).
15. R. W. Fessenden and R. H. Schuler, J. Chem. Phys., 39, 2147 (1963).
16. R. B. Bates, W. A. Bevers, M. G. Greene and J. H. Klein, J. Am. Chem. Soc., 96, 5640 (1974).
17. R. B. Bates in "Comprehensive Carbanion Chemisty", E. Buncel, Ed., Elsevier, New York, N.Y. (in press).
18. B. A. Hess, Jr., L. J. Schaad and C. W. Holyoke, Jr., Tetrahedron, 28, 5299 (1972).
19. B. A. Hess, Jr., L. J. Schaad and C. W. Holyoke, Jr., Tetrahedron, 28, 3657 (1972).
20. R. S. Mulliken and R. G. Parr, J. Chem. Phys., 19, 1271 (1951).
21. M. Wolfsberg and L. Helmholtz, J. Chem. Phys., 20, 837 (1952).
22. J. C. Slater, Phys. Rev., 36, 57 (1930).
23. C. A. Coulson and A. Golebiewski, Proc. Phys. Soc., (London) 78, 1310, (1961).
24. L. Salem, "Molecular Orbital Theory of Conjugated Systems", W. A. Benjamin, New York, 1966, p. 138.
25. Resonance energies and resonance energies per electron or per atom will all be given in units of β_o from this point on; i.e., we shall write REPE = 0.002 instead of REPE = 0.002 β_o.

26. C. A. Coulson and G. S. Rushbrooke, Proc. Cambridge Phil. Soc., 36, 193 (1940).
27. H. C. Longuet-Higgins, J. Chem. Phys., 18, 265 (1950).
28. R. Zahradník, J. Michl and J. Pancíř, Tetrahedron, 22, 1356 (1966).
29. J. Aihara, Bull. Chem. Soc. Japan, 50, 3057 (1977).
30. J. Aihara, J. Am. Chem. Soc., 100, 3339 (1978).
31. P. Ilić, B. Jerman-Blažič-Džonova, B. Mokar and N. Trinajstić, Croat. Chem. Acta, 52, 35 (1979).
32. D. Lewis and D. Peters, "Facts and Theories of Aromaticity", Macmillan, London, 1975, p. 53.
33. R. Breslow, Pure and Appl. Chem., 28, 111 (1971).
34. R. Breslow and J. T. Groves, J. Am. Chem. Soc., 92, 984 (1970).
35. R. Breslow and J. M. Hoffman, J. Am. Chem. Soc., 94, 2110 (1972).
36. F. P. Lossing and J. C. Traeger, J. Am. Chem. Soc., 97, 1579 (1975).
37. W. von E. Doering and L. H. Knox, J. Am. Chem. Soc., 76, 3203 (1954).
38. J. C. Barborak, T. M. Su, P. von R. Schleyer, G. Boche and G. Schneider, J. Am. Chem. Soc., 93, 279 (1971).
39. A. G. Anastassiou and E. Yakali, J. Chem. Soc., Chem. Commun., 92 (1972).
40. E. Vogel, R. Feldman and H. Düwel, Tetrahedron Lett., 1941 (1970).
41. R. Destro, T. Pilati and M. Simonetta, J. Am. Chem. Soc., 98, 1999 (1976).
42. R. Pettit, J. Am. Chem. Soc., 82, 1972 (1960).
43. K. Yamamoto, Y. Kayane and I. Murata, Bull. Chem. Soc. Jap., 50, 1964 (1977).
44. (a) T. J. Katz and E. G. Gold, J. Am. Chem. Soc., 86, 1600 (1964); (b) T. J. Katz, J. R. Hall and W. C. Neikam, J. Am. Chem. Soc., 84, 3199 (1962).
45. G. A. Olah, J. S. Staral and L. A. Paquette, J. Am. Chem. Soc., 98, 6290 (1976).
46. K. Krogh-Jespersen, P. von R. Schleyer and J. A. Pople, J. Am. Chem. Soc., 100, 4301 (1978).
47. G. A. Olah, J. S. Staral and L. A. Paquette, J. Am. Chem. Soc., 98, 1267 (1976).
48. J. F. M. Oth, D. M. Smith, U. Prange and G. Schröder, Angew. Chem. Int. Ed. Engl., 12, 327 (1973).
49. R. W. Johnson, J. Am. Chem. Soc., 99, 1461 (1977).
50. I. Willner and M. Rabinovitz, J. Am. Chem. Soc., 100, 337 (1978).
51. R. Breslow and W. Chu, J. Am. Chem. Soc., 95, 411 (1973).
52. T. J. Katz and P. J. Garratt, J. Am. Chem. Soc., 86, 5194 (1964).
53. E. A. LaLancette and R. E. Benson, J. Am. Chem. Soc., 87, 1941 (1965).
54. G. Boche, H. Weber, D. Martens and A. Bieberbach, Chem. Ber., 111, 2480 (1978).
55. (a) G. Boche, H. Weber and A. Bieberbach, Chem. Ber., 111, 2833 (1978); (b) G. Boche and A. Bieberbach, Chem. Ber., 111 2850 (1978).
56. S. W. Staley and A. Orvedal, J. Am. Chem. Soc., 95, 3384 (1973).
57. G. Schröder, G. Plinke, D. M. Smith and J. F. M. Oth, Angew. Chem. Int. Ed. Engl., 12, 325 (1973).
58. P. Hildebrand, G. Plinke, J. F. M. Oth and G. Schröder, Chem. Ber., 111, 107 (1978).
59. S. W. Staley and A. W. Orvedal, J. Am. Chem. Soc., 95, 3382 (1973).
60. P. J. Garrett and K. A. Knapp, J. Chem. Soc., Chem. Commun., 1215 (1970).
61. A. G. Anastassiou and R. C. Griffith, J. Am. Chem. Soc., 96, 611 (1974).
62. I. Willner and M. Rabinovitz, Tetrahedron Lett., 1223 (1976).
63. S. W. Staley, F. Heinrich and A. W. Orvedal, J. Am. Chem. Soc., 98, 2681 (1976).
64. J. S. McKennis, L. Brener, J. R. Schweiger and R. Pettit, J. Chem. Soc., Chem. Commun., 365 (1972).

65. T. J. Katz, J. Am. Chem. Soc., 96, 1348 (1974).
66. S. Z. Goldberg, K. N. Raymond, C. A. Harmon and D. H. Templeton, J. Am. Chem. Soc., 96, 1348 (1974).
67. J. F. M. Oth and G. Schröder, J. Chem. Soc. (B), 904 (1971).
68. J. F. M. Oth, K. Müllen, H. Königshofen, M. Mann, Y. Sakata and E. Vogel, Angew. Chem. Int. Ed. Engl., 17, 456 (1972).
69. J. F. M. Oth, H. Bauman, J. M. Gilles and G. Schröder, J. Am. Chem. Soc., 94 3498 (1972).
70. G. R. Stevenson, I. Ocasio and A. Bonilla, J. Am. Chem. Soc., 98, 5469 (1976).
71. (a) R. H. Mitchell, C. E. Klopfenstein and V. Boekelheide, J. Am. Chem. Soc., 91, 4931 (1971); (b) F. Gerson, K. Müllen and E. Vogel, Angew. Chem. Int. Ed. Engl., 10, 920 (1971).
72. T. J. Katz and M. Rosenberger, J. Am. Chem. Soc., 84, 865 (1962).
73. K. Hafner, Angew. Chem. Int. Ed. Engl., 3, 165 (1964).
74. K. Hafner, S. Braun, T. Nakazawa and H. Tappe, Tetrahedron Lett., 5507 (1975).
75. B. M. Trost and P. L. Kinson, J. Am. Chem. Soc., 97, 2438 (1975).
76. J. F. M. Oth, K. Müllen, H. Königshofen, J. Wassen, and E. Vogel, Helv. Chim. Acta, 57, 2387 (1974).
77. L. D. Kershner, J. M. Gaidis and H. H. Freedman, J. Am. Chem. Soc., 94, 985 (1972).
78. T. Clark and P. von R. Schleyer, J. Chem. Soc., Chem. Commun., 798 (1976).
79. K. Schreiner, W. Ahrens and A. Berndt, Angew. Chem. Int. Ed. Engl., 14, 550 (1975).
80. M. R. Wasielewski and R. Breslow, J. Am. Chem. Soc., 98, 4222 (1976).
81. C. C. MacDuffee, "Theory of Equations", Wiley and Sons, New York, 1954, p 76-80.