an extremely weak covalent interaction to be the dominant perturbation. CH_3F MO's 8 and 11 are both of a nature to respond most strongly to such a perturbation. But now there is no ionic repulsion to favor MO 11 for being large on F, and MO 8 enters more heavily than MO 11. Filled MO 5 is the most lost. Mixing in and out these MO's has the effect of causing charge polarization to fluorine and weakening the C–F bond. The extent of perturbation for neutral base attack at 5 Å is very much smaller than for charged base attack, consistent with the idea that covalent interactions are of shorter range than Coulombic interactions.

Discussion

When a charged base attacks along the back-side of the C–F axis in CH_3F, the major perturbing influence at 5 Å is the charge repulsion due to the base, which induces charge polarization from H_3 to F in the CH_3F substrate. Two of the empty MO's of CH_3F can effect such a polarization. Of these, the lowest in energy (MO 8) has relatively small size on the fluorine. The highest in energy (MO 11) is quite large on fluorine. As a result, MO 11 is mixed in more than MO 8. Both of these MO's (especially MO 11) are C–F antibonding. This result suggests that MO theories of reactivity which focus on only the highest filled or lowest empty MO's are of limited applicability. Inspection of eigenvalues reported in this paper indicates that orbital energies among the empty MO's are not widely different. This further argues against arbitrary neglect of higher members of this set.

When a neutral base replaces the charged base, the perturbation of CH_3F becomes very much smaller. Again, MO's 8 and 11 are of such symmetry as to interact best with the base in a covalent way. But now there is no premium in using an MO which is large on F, so here we find the lower energy MO 8 entering most heavily, followed by 11. Because MO's 8 and 11 are mixed in, some charge polarization to F results. Hence we have the interesting contrast: when a charged base induces polarization, MO's 11 and 8 mix in and the C–F bond weakens, but when a neutral base approaches, MO's 8 and 11 mix in to engage in a covalent interaction with the base, *incidently* causing charge buildup on F and weakening of the C–F bond. It appears that the neutral base must approach closer to the SN2 center than the charged base for the same extent of CH_3F distortion, C–F (leaving) charge buildup and bond weakening, and C–base bond formation.

Hückel Molecular Orbital π Resonance Energies. A New Approach

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Abstract: Single and double bonds in hydrocarbons have been classified into eight types according to the number of attached hydrogen atoms. Total HMO π energies, calculated in the usual way, have been found to be linear functions of the number of each type of bond. This allows the assignment of an empirical π-bond energy to each bond type, such that the total HMO energy of acyclic polyenes is simply a sum of these bond-energy terms. HMO π energies of cyclic hydrocarbons are not linear functions of the numbers of bonds and hence are not obtainable as a sum of bond-energy terms. Resonance energies are then defined as the difference between HMO π energy and the additive contribution obtained by summing individual bond energies. An excellent correlation between resonance energies calculated in this manner and the observed stability and chemical behavior of a wide range of cyclic polyenes is obtained. This treatment greatly extends the utility of HMO calculations.

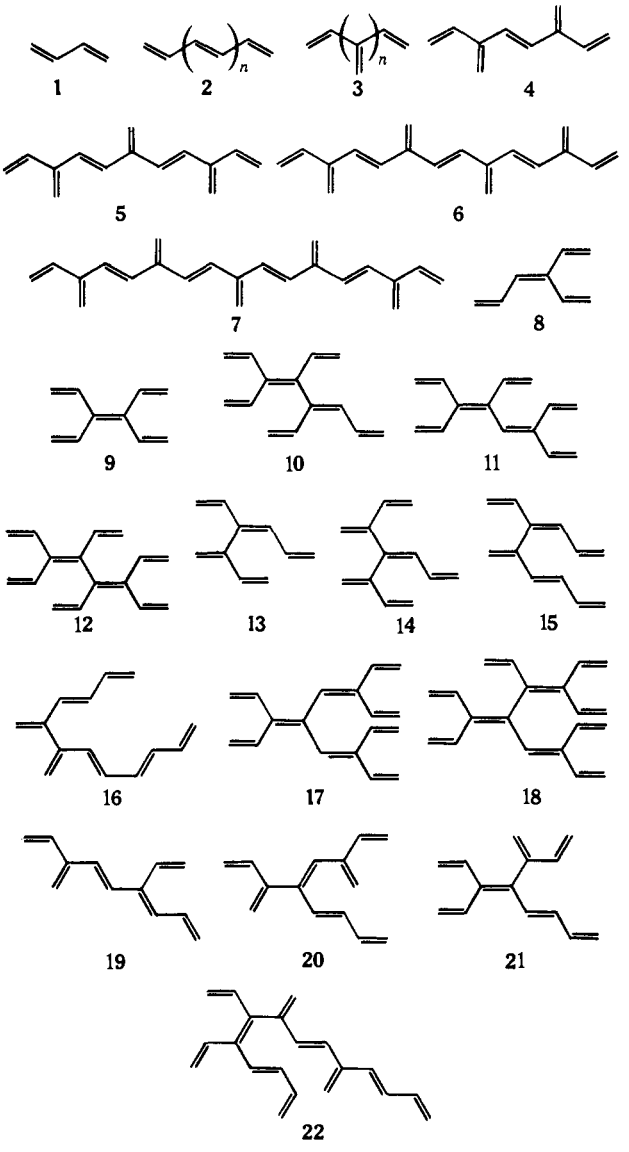
The Hückel molecular orbital theory has served for many years as a basis for the explanation of the extraordinary stability or aromaticity of benzene and related compounds.[1] HMO theory indicates that benzenoid systems should have significant delocalization energies in agreement with their high degree of stability and unusual chemical behavior. The resonance stabilization of the acyclic polyenes relative to the benzenoid systems has long been recognized experimentally to be quite small even though HMO calculations predict a significant amount of delocalization in the acyclic polyenes. In spite of this, the HMO delocalization energies of nonbenzenoid cyclic polyenes have been used as a basis for suggesting that many of them should have significant resonance stabilization. This has been largely disproved with the synthesis of compounds such as fulvene (**45**),[2] heptafulvene (**46**),[3] and fulvalene (**55**).[3] All three have large calculated delocalization energies, but none is considered to be in the least aromatic, heptafulvene and fulvalene even being too reactive to be isolated.

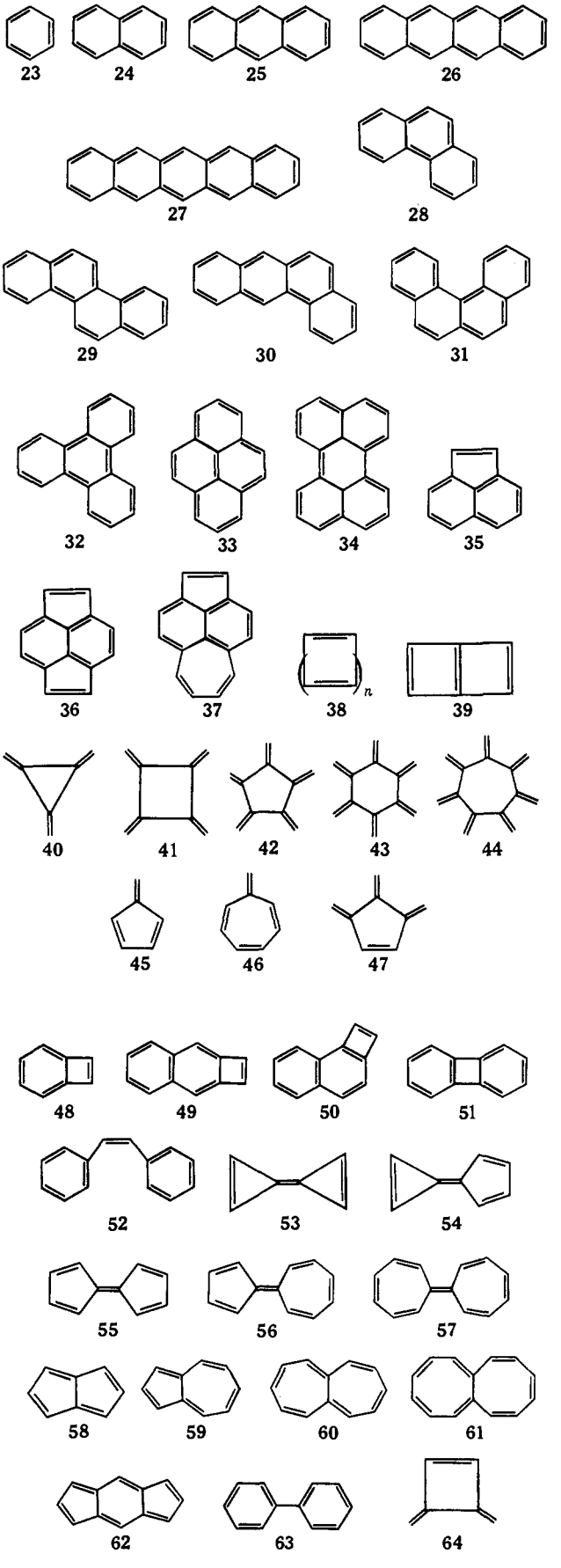
There are a number of nonbenzenoid cyclic polyenes which experimentally do appear to have significant resonance stabilization. Azulene (**59**) has stability and chemical behavior closer to those of benzene than to those of a normal acyclic polyolefin; thus it has become

(1) K. Hückel, *Z. Electrochem.*, **43**, 752 (1937).

(2) J. Thiec and J. Wiemann, *Bull. Soc. Chim. Fr.*, 177 (1956).

(3) W. von E. Doering, *Theor. Org. Chem., Pap. Kekulé Symp., 1958*, 35 (1959).





apparent that HMO delocalization energies are not useful in the prediction of stability or aromaticity of cyclic polyenes. Theoreticians have therefore turned to other types of calculations which in virtually all cases are much more complex and expensive. Dewar has recently shown that an interpretation of his semi-empirical SCF MO calculations fairly successfully predicts the aromaticity or lack of aromaticity in a large number of polyolefins.[4] A notable exception is azulene, which is calculated to have very little resonance stabilization. It is our purpose to describe a new treatment of the results of HMO calculations which allows the calculation of meaningful resonance energies for benzenoid as well as nonbenzenoid hydrocarbons.

Results

Dewar, using the Pariser–Parr–Pople method, has found that the bond energies of acyclic polyenes are additive. Therefore, one can readily calculate the total energy of any acyclic polyene merely by summing energies of all its bonds.[4] Using these bond energies, one can also calculate energies of "localized" structures of cyclic polyenes and hence readily obtain their resonance energies. We felt that a similar treatment of Hückel π energies allow the calculation of π resonance energies in a much simpler way.

(4) (a) M. J. S. Dewar and C. de Llano, *J. Amer. Chem. Soc.*, **91**, 789 (1969); (b) M. J. S. Dewar, "The Molecular Orbital Theory of Organic Chemistry," McGraw-Hill, New York, N. Y., 1969.

A plot of total HMO π energies of linear polyenes (see Figure 1) *vs.* the number of carbon–carbon single bonds (m) indicates that their bond energies are indeed additive (eq 1). Examination of a similar plot and eq 2 of compounds **3** (n = 1–10) again indicates

$$m(E_{C=C}{}^{\pi} + E_{C-C}{}^{\pi}) + E_{C=C}{}^{\pi} = \text{total } \pi \text{ energy} \quad (1)$$

$$m(E_{C=C}{}^{\pi} + E_{C-C}{}^{\pi}) + 2E_{C=C}{}^{\pi} + E_{C-C}{}^{\pi} = \text{total } \pi \text{ energy} \quad (2)$$

additivity of bond energies. The π-double- and π-single-bond energies may be obtained from the slopes and the intercepts of the lines in Figure 1. They are 1.910 and 0.628 for $E_{C=C}{}^{\pi}$ and $E_{C-C}{}^{\pi}$, respectively, for the linear polyenes and 2.036 and 0.396 for compounds **3** (n = 1–10). Thus, the π-bond energies of polyenes appear to be additive only for polyenes of similar structure. These results suggested that not just two types of bonds, double and single, should be considered, but rather a number of different types of both carbon–carbon single and double bonds.

We have classified the bonds of acyclic polyenes into eight different types: five types of carbon–carbon double bonds and three types of carbon–carbon single bonds, depending upon the number of attached hydrogens (see Table I). Any acyclic (or cyclic) polyene

Table I. Calculated Hückel π-Bond Energies of Carbon–Carbon Double Bonds and Carbon–Carbon Single Bonds of Acyclic Polyenes

Designation[a]	Type of bond	Calculated π-bond energy, β
23	$H_2C{=}CH$	2.0000[b]
22	$HC{=}CH$	2.0699
22′	$H_2C{=}C$	2.0000[b]
21	$HC{=}C$	2.1083
20	$C{=}C$	2.1716
12	$HC{-}CH$	0.4660
11	$HC{-}C$	0.4362
10	$C{-}C$	0.4358

[a] The first index gives the bond order, the second the number of attached hydrogens. [b] Arbitrarily assigned.

can be constructed by various combinations of these eight types of bonds. If one could obtain the π energy for each, one might be able to calculate the π energy of any conjugated acyclic polyolefin in an additive fashion. The success of such a calculation depends on whether or not the values of the π-bond energies remain constant for each type of bond in all acyclic polyolefins (see below). For example, the π energy of **5** might be calculated as

$$\pi \text{ energy} = 2E_{23}{}^{\pi} + 2E_{22}{}^{\pi} + 3E_{22'}{}^{\pi} + 6E_{11}{}^{\pi} \quad (3)$$

where $E_{ij}{}^{\pi}$ is the π-bond energy in units of β for an ij bond.

To determine the eight bond energies, one might choose eight acyclic compounds and equate computed Hückel energies to a sum of additive terms, as in eq 3. Solutions of the resulting eight equations would be expected to give the eight unknown bond energies. Somewhat better parameter values could be obtained by choosing more than eight acyclic compounds and fitting the eight π-bond energies by least squares. A

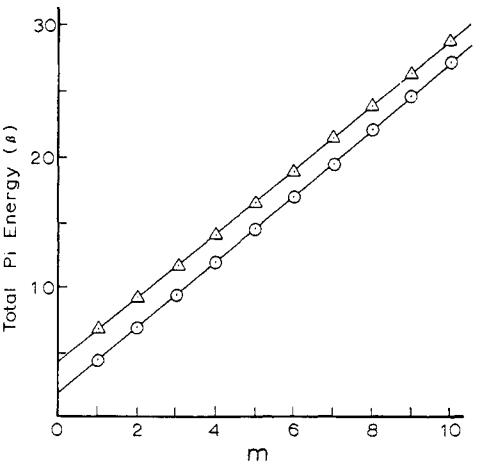


Figure 1. Plot of total π-bond energy *vs.* the number of carbon–carbon single bonds in **2** and **3**, where m is the number of carbon–carbon single bonds in **2** and (m + 1) is the number of carbon–carbon single bonds in **3**: ⊙, compounds **2** (n = 1, 2, ..., 10); ◬, compounds **3** (n = 1, 2, ..., 10).

problem arises in either case. No matter how many different acyclic polyenes for which one chooses to write π-bond summation equations (eq 3), the equations will always be reducible to a set of six. Hence, we will have a set of six linear equations with eight unknowns (the eight π-bond energies in Table I) for which no unique solution can be obtained. This implies that it is not possible to construct acyclic conjugated hydrocarbons with arbitrary numbers of more than six of the bond types. The two linear relations connecting the numbers of the eight bond types are derived in the Computational Details section (eq 17 and 20). However, this in no way prevents us from obtaining usable values of the π-bond energies. For one need only arbitrarily assign a value to two of the bond energies.

We arbitrarily assigned a value of 2.0 to $E_{23}{}^{\pi}$ and $E_{22'}{}^{\pi}$ and proceeded to write the π-bond energy summation equations for 40 acyclic polyenes (see Table II) of the form of eq 4, where the coefficients (n_{ij}) are the

$$n_{23}E_{23}{}^{\pi} + n_{22}E_{22}{}^{\pi} + n_{22'}E_{22'}{}^{\pi} + n_{21}E_{21}{}^{\pi} + n_{20}E_{20}{}^{\pi} + n_{12}E_{12}{}^{\pi} + n_{11}E_{11}{}^{\pi} + n_{10}E_{10}{}^{\pi} = \text{HMO } \pi \text{ energy} \quad (4)$$

numbers of bonds of a given type in a molecule. Applying the least-squares method to the equations for compounds **1**–**22** we obtained the other six π-bond energies (those not arbitrarily assigned; see Table I). The additive π-bond energies (eq 4) of **1**–**22**, the differences between the Hückel total π energies and the additive π-bond energies, and the difference per carbon atom (dif/C) are given in Table II. It is apparent from Table II that the Hückel π energies of acyclic polyenes can be calculated with a high degree of accuracy in an additive manner, using the eight values given in Table I. In addition, we found that a least-squares treatment of **1**–**22**, assuming all single bonds to be of the same π energy and all double bonds to be of the same π energy, gave a far less satisfactory result in that the difference between the HMO π energy and the additive π energy (using the two values of $E_{C=C}{}^{\pi}$ and $E_{C-C}{}^{\pi}$ obtained) divided by the number of carbon atoms ranged from 0.023 to -0.021β.

Table II. π Energy in Units of β of Acyclic Polyenes

Compound	Hückel	Additive[a]	Dif	Dif/C
1	4.472	4.466	0.006	0.002
2 (n = 1)	6.988	7.002	−0.014	−0.002
2 (n = 2)	9.518	9.538	−0.020	−0.002
2 (n = 3)	12.053	12.074	−0.021	−0.002
2 (n = 4)	14.592	14.609	−0.017	−0.001
2 (n = 5)	17.134	17.145	−0.011	−0.001
2 (n = 6)	19.676	19.681	−0.005	0.000
2 (n = 7)	22.219	22.217	−0.002	0.000
2 (n = 8)	24.763	24.753	0.010	0.001
2 (n = 9)	27.307	27.289	0.018	0.001
2 (n = 10)	29.852	29.825	0.027	0.001
3 (n = 1)	6.899	6.873	0.026	0.004
3 (n = 2)	9.332	9.308	0.024	0.003
3 (n = 3)	11.764	11.744	0.020	0.002
3 (n = 4)	14.196	14.180	0.016	0.001
3 (n = 5)	16.628	16.615	0.013	0.001
3 (n = 6)	19.060	19.051	0.009	0.001
3 (n = 7)	21.492	21.487	0.005	0.000
3 (n = 8)	23.924	23.923	−0.001	0.000
3 (n = 9)	26.356	26.359	−0.003	0.000
3 (n = 10)	28.788	28.794	−0.006	0.000
4	11.831	11.815	0.016	0.002
5	16.763	16.757	0.006	0.000
6	21.694	21.699	−0.005	0.000
7	26.625	26.642	−0.016	−0.001
8	9.446	9.447	−0.001	0.000
9	11.925	11.916	0.009	0.001
10	16.908	16.926	−0.018	−0.001
11	16.920	16.897	0.023	0.002
12	19.394	19.396	−0.002	0.000
13	11.875	11.882	−0.007	−0.001
14	14.302	14.318	−0.016	−0.001
15	14.385	14.418	−0.033	−0.003
16	16.913	16.916	−0.003	0.000
17	21.906	21.878	0.028	0.002
18	24.385	24.377	0.008	0.000
19	14.388	14.389	0.001	0.000
20	16.814	16.825	−0.011	−0.001
21	16.881	16.888	−0.007	−0.001
22	24.319	24.366	−0.047	−0.002

[a] π energy calculated in an additive manner using the eight values in Table I.

The ability to calculate accurately in an additive manner the total π energies of acyclic polyenes allows one to calculate the π energies of "localized" structures (E_{loc}^{π}) of cyclic polyenes, and hence to obtain calculated π resonance energies (RE). For example, the RE of benzene is easily obtained by use of eq 5–7.[5]

$$E_{loc} = 3E_{22} + 3E_{12} = 7.61\beta \quad (5)$$

$$RE = E_{HMO} - E_{loc} \quad (6)$$

$$RE = (8.00 - 7.61)\beta = 0.39\beta \quad (7)$$

In Table III the π resonance energies for a number of compounds (**23–63**) are listed. The resonance energy per π electron (REPE) is also given for each compound. Owing to the wide variation in the size of molecules usually compared, we feel that REPE is a better way of comparing resonance energies than using the total resonance energies (RE).

Compounds with a high REPE are predicted to be of high stability and hence aromatic. Those with essentially no REPE should be similar in stability to acyclic polyenes. Those with a large negative REPE should be quite unstable or "antiaromatic" and not isolable.

(5) If more than one localized structure can be written for a molecule, as in naphthalene, the E_{loc} is calculated for each structure and an average of all of them is taken. In no case are the energy differences between various localized structures of the same molecule significant.

Table III. Hückel π Energies and Resonance Energies of Cyclic Polyenes[a]

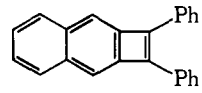
Compound	Hückel	Additive[b]	RE	REPE
23	8.00	7.61	0.39	0.065
24	13.68	13.13	0.55	0.055
25	19.31	18.65	0.66	0.047
26	24.93	24.18	0.75	0.042
27	30.54	29.70	0.84	0.038
28	19.45	18.68	0.77	0.055
29	25.19	24.23	0.96	0.053
30	25.10	24.21	0.89	0.050
31	25.19	24.23	0.96	0.053
32	25.27	24.26	1.01	0.056
33	22.51	21.70	0.81	0.051
34	28.25	27.28	0.97	0.048
35	16.62	16.15	0.47	0.039
36	19.42	19.16	0.26	0.019
37	22.25	21.70	0.55	0.034
38 (n = 1)	4.00	5.07	−1.07	−0.268
38 (n = 3)	9.66	10.14	−0.48	−0.060
38 (n = 4)	12.94	12.68	0.26	0.026
38 (n = 5)	14.93	15.22	−0.29	−0.024
38 (n = 6)	17.98	17.75	0.23	0.016
38 (n = 7)	20.11	20.29	−0.18	−0.011
38 (n = 8)	23.04	22.82	0.22	0.012
38 (n = 9)	25.25	25.36	−0.11	−0.006
38 (n = 10)	28.11	27.89	0.22	0.010
39	7.66	8.06	−0.40	−0.067
40	7.30	7.31	−0.01	−0.002
41	9.66	9.74	−0.08	−0.010
42	12.16	12.18	−0.02	−0.002
43	14.60	14.61	−0.01	−0.001
44	17.02	17.05	−0.03	−0.002
45	7.47	7.48	−0.01	−0.002
46	9.99	10.01	−0.02	−0.002
47	9.80	9.81	−0.01	−0.002
48	10.38	10.60	−0.22	−0.027
49	16.20	16.12	0.08	0.007
50	16.00	16.15	−0.15	−0.012
51	16.51	16.18	0.33	0.027
52	18.88	18.17	0.71	0.051
53	7.46	8.06	−0.60	−0.100
54	10.94	10.59	0.35	0.043
55	12.80	13.13	−0.33	−0.033
56	15.93	15.66	0.27	0.022
57	18.00	18.20	−0.20	−0.014
58	10.46	10.60	−0.14	−0.018
59	13.36	13.13	0.23	0.023
60	15.62	15.67	−0.05	−0.004
61	18.30	18.20	0.10	0.007
62	16.23	16.12	0.11	0.009
63	16.38	15.66	0.72	0.060
64	7.21	7.38	−0.17	−0.028

[a] All energies are in units of β. [b] Calculated in an additive manner using the eight π-bond energies given in Table I.

Discussion

Benzenoid Hydrocarbons. As seen from Table III, compounds **23–34** are all predicted to have reasonably high resonance energies. Note that the REPE is not the same for **23–34** but varies from 0.065 for benzene to as low as 0.038 for pentacene. This is in agreement to a large extent with the observed reactivities of the various compounds. Phenanthrene is known to undergo addition reactions readily at the 9 and 10 positions, whereas benzene undergoes addition reactions only under forcing conditions. The important point is that all of the benzenoid compounds listed have a total π energy which is more negative than one would predict using a "localized" model, and hence should have significant resonance stabilization relative to the acyclic polyenes.

Cyclobutadiene and Its Derivatives. The REPE of cyclobutane is calculated to be −0.268. The instability of cyclobutadiene is well known, as it has defied all attempts of isolation.[6] Furthermore, it is apparently of such high reactivity that not even dilute solutions of it are attainable, as is the case for a number of other reactive hydrocarbons (see below). Even when cyclobutadiene is fused to a benzene ring as in **48**, it is predicted to be antiaromatic (REPE = −0.027). All attempts to prepare and isolate **48** have met with failure.[6,7] When cyclobutadiene is fused to the naphthalene system at the 3,4 positions, its REPE is +0.007, which suggests the **49** should not be aromatic, but at least might be isolable. In agreement with this prediction, a derivative of **49** (**65**) has recently been synthesized.[8] We may also predict that the 1,2-fused



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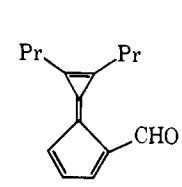
derivative of naphthalene (**50**) might be more reactive than **49** and perhaps not be isolable. Finally, biphenylene (**51**), which has an appreciable REPE (0.027), is a stable isolable compound which is aromatic in its chemical behavior.

3,4-Dimethylenecyclobutene (**64**), although not a cyclobutadiene derivative, is similar in structure to cyclobutadiene. Its large negative REPE predicts that it should not be isolable. It constitutes the most serious failure we have yet noted of the predictive power of our method in that it has been isolated,[9] although it does polymerize readily in the presence of air. However, its physical and chemical properties[9] appear to be extraordinary, *e.g.*, its large dipole moment (0.68 D).

Nonalternant Hydrocarbons. The present treatment indicates that the majority of the nonalternant hydrocarbons should be polyolefinic or antiaromatic in nature. Fulvalene (**55**) and pentalene (**58**) should be highly unstable or antiaromatic due to their large negative REPE's. Pentalene has never been prepared despite many attempts.[7] Fulvalene has been prepared in dilute solution, but all attempts to isolate it have led to polymer, attesting to its high degree of instability.[3]

Fulvene (**45**) and heptafulvene (**46**) are predicted to be essentially polyolefinic in nature. Fulvene has been isolated but undergoes polymerization readily.[2] Heptafulvene has also been prepared but it is too reactive to be isolated.[3] Hence, neither is in the least aromatic in its chemical behavior. *s*-Indacene (**62**) should behave essentially as a polyolefin and this has been verified experimentally by Hafner, who has reported its isolation but has noted its low thermal stability.[10]

Both calicene (**54**) and sesquifulvalene (**56**) have significant REPE's, but neither has been isolated.



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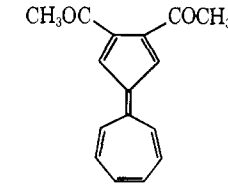

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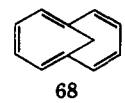
However, simple derivatives of both (**66** and **67**) have been isolated and appear to possess a high degree of stability.[11,12] Furthermore, simple derivatives of calicene are known to undergo a number of electrophilic substitution reactions,[11b] a long-standing criterion of aromaticity. The chemical behavior of derivatives of sesquifulvalene has not as yet been reported. Azulene has a calculated REPE of 0.022, and in agreement with this is its high degree of stability and its ability to undergo many varied electrophilic substitution reactions. A comparison of the RE of azulene with that of naphthalene indicates that azulene has about *one-half* the RE of naphthalene. Dewar's calculations[4] show azulene to have only *one-eight* the RE of naphthalene. We feel our value for azulene is much more in line with its chemical behavior.

The Annulenes. Note that [10]annulene and [14]annulene have a significant degree of resonance stabilization. A number of bridged derivatives (*e.g.*, **68** and **69**) of these two annulenes have been prepared which exhibit not only a high degree of stability, but also undergo electrophilic substitutions under mild conditions.[13,14]



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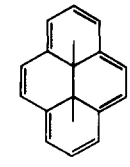

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Conclusions

The use of the π-bond energies listed in Table I allows one to calculate total π energies of the localized structures of cyclic polyenes; HMO resonance energies are calculated as the difference between the total HMO energy and the energy of the localized structure. In view of the excellent correlation between calculated HMO REPE's and chemical behavior of a large number of compounds, we suggest that HMO calculations are still of great utility, contrary to Dewar's suggestion that "... there no longer seems any point at all in carrying out calculations by less refined procedures, in particular the HMO method or variants of it."[4]

We are currently investigating the application of our treatment of the HMO calculations to conjugated carbonium ions, carbanions, and to polyolefins containing heteroatoms.

Computational Details

Total π energies were calculated using the simple Hückel molecular orbital (HMO) method with overlap integrals set equal to

(6) M. P. Cava and M. J. Mitchell, "Cyclobutadiene and Related Compounds," Academic Press, New York, N. Y., 1967.
(7) G. M. Badger, "Aromatic Character and Aromaticity," Cambridge University Press, New York, N. Y., 1969.
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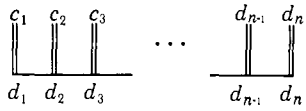
zero. A number of energies were taken from the compilations in ref 15.

Solution of the Secular Equations by Difference Methods. Several of the systems studied gave secular equations which were most easily solved by finite difference methods.[16] Results of such a treatment have been published for linear and cyclic polyenes and for linear polyacenes.[15] Consider the series of molecules (**3** in the list above) where c_i and d_i are Hückel coefficients of the $2p\pi$



AO's on the indicated atom. The secular equations for this system are

$$xc_i + d_i = 0$$

$$xd_i + d_{i+1} + d_{i-1} + c_i = 0 \qquad i = 1, 2, \ldots, n \quad (8)$$

where $x = (\alpha - E)/\beta$. Equation 8 must be solved together with the boundary conditions

$$d_0 = d_{n+1} = c_0 = c_{n+1} = 0 \quad (9)$$

The function

$$d_i = \sin i\lambda \quad (10)$$

automatically satisfies eq 9 for $i = 0$. The boundary condition at $i = n + 1$ will also be satisfied if

$$\lambda = \frac{m\pi}{n+1} \qquad m = 1, 2, \ldots, n \quad (11)$$

Elimination of c_i in eq 8 followed by substitution of (10) and (11) gives the $2n$ energy levels

$$E = \alpha + [\cos\lambda \pm (\cos^2\lambda + 1)^{1/2}]\beta \quad (12)$$

The radialenes (molecules **40–44** in the list above) also satisfy secular eq 8, but the appropriate boundary conditions are

$$c_{n+1} = c_i \qquad d_{n+1} = d_i \quad (13)$$

Equation 12 is then found to hold for the energy levels of the radialenes, except that λ does not satisfy eq 11, but rather

$$\lambda = \frac{2m\pi}{n} \qquad m = 0, 1, \ldots, (n-1) \quad (14)$$

Linear Dependence of Bond Types. As described above, an attempt to fix bond energies by least squares for all eight types of bonds encountered led to singular equations. For acyclic conjugated hydrocarbons there turn out to be two linear relations connecting the numbers of the eight bond types in any given molecule. These relations may be displayed as follows.

In any completely conjugated hydrocarbon, acyclic or otherwise, each H atom is attached to a C–C double bond. No two double bonds share a common C atom. Therefore, no H atom is connected to two double bonds. The total number of H atoms N_H in a molecule is thus obtained by multiplying each type of double bond by the number of H's attached to it and summing over all double bonds. In the notation of Table I

$$N_H = n_{21} + 2n_{22} + 2n_{22'} + 3n_{23} \quad (15)$$

In a similar way each H, except the terminal pair on 22′ and 23 double bonds, is attached to a C–C single bond. Two single bonds can terminate on the same carbon atom, but there can be no H on that carbon. Therefore, no H is shared between two single bonds, and hence

$$N_H = 2n_{12} + n_{11} + 2n_{22'} + 2n_{23} \quad (16)$$

Equating (15) and (16) gives one linear relation among the n_{ij}

$$n_{11} + 2n_{12} = n_{21} + 2n_{22} + n_{23} \quad (17)$$

Equation 17 holds for all completely conjugated hydrocarbons. A second relation, valid only for acyclic conjugated hydrocarbons, can be obtained from the empirical formula for such systems. Any acyclic conjugated hydrocarbon may be formed from ethylene (C_2H_4) by successive substitutions of an H atom by a $-CH{=}CH_2$ group. Each substitution adds C_2H_2 to the empirical formula, which must therefore be C_NH_{N+2}. Or in the notation above

$$N_H = N_C + 2 \quad (18)$$

The total number of double bonds is one greater than the total single bonds. The number of carbon atoms equals twice the total number of double bonds. Combining these statements with eq 18 gives

$$N_H = 4(n_{20} + n_{21} + n_{22} + n_{22'} + n_{23}) - 2(n_{10} + n_{11} + n_{12}) \quad (19)$$

which when equated to (15) gives the second linear relation

$$2n_{10} + 2n_{11} + 2n_{12} = 4n_{20} + 3n_{21} + 2n_{22} + 2n_{22'} + n_{23} \quad (20)$$

In arbitrarily assigning two of the E_{ij}^{π}'s not any two may be picked. For example, choosing E_{22}^{π} and E_{12}^{π} would arbitrarily fix energies of all the annulenes. More generally, one may not fix energies of bonds ij and $i'j'$ if

$$\begin{vmatrix} c_1(ij) & c_1(i'j') \\ c_2(ij) & c_2(i'j') \end{vmatrix} = 0 \quad (21)$$

where $c_1(ij)$ is the coefficient of n_{ij} in eq 17 and $c_2(ij)$ is the corresponding coefficient in eq 20.

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