same sign ($C_{2s_{N_1,7}}C_{2s_{N_2,7}} > 0$) and $J^{Fc}(7)$ is positive. Between 60 and 90° the splitting of bonding and antibonding orbital energies vanishes and the contributions of n_+ and n_- become comparable; thus, in this region the sum $J^{Fc}(6) + J^{Fc}(7)$ vanishes.

Although these qualitative arguments, based on uncoupled rather than coupled perturbation theory, that is, excluding effects of correlation energy in first order cannot furnish the exact angle at which $J^{Fc}(6) + J^{Fc}(7)$ is equal to zero, they are consistent with the angle being nearer to 90° than to 60°. Thus, the dihedral angle dependence of the Fermi contact term in hydrazine has a straightforward interpretation.

Finally, we might point out that since the dihedral angle dependence of the contact term (and therefore also the total J_{NN}) of hydrazine is due to the interaction between lone pairs which ought to vary with the cos ϕ, $J^{Fc}(\phi)$ should be of the form of a power series in cos ϕ dominated by its leading terms

$$J^{Fc} \approx a_0 + a_1 \cos \phi + a_2 \cos^2 \phi \qquad (3)$$

From the present semiempirical calculations we obtain with least-squares coefficients: $a_0 = -3.8$ Hz, $a_1 = -11.5$ Hz, and $a_2 = +3.5$ Hz. It is probable that similar functional forms will hold for other cases of *one-bond* coupling constants with two s-hybridized lone pairs.

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(14) Since the same physical arguments apply in the case of diazene, it is not surprising that the trans isomer, analogous to $\phi = 180°$ of I, has a large positive J_{NN}^{Fc}, while the cis isomer, corresponding to $\phi = 0°$, has a large negative J_{NN}^{Fc} (unpublished calculations).

(15) The n_- molecular orbital depicted in VIa and VIb for $\phi = 0$ and 180°, respectively, may be thought of as arising from rehybridization of the π^* orbital of planar hydrazine on bending.

Resonance Energies of Benzenoid Hydrocarbons

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Abstract: Resonance energies for 48 totally benzenoid hydrocarbons have been calculated by means of HMO reference polynomials previously defined by us. In many respects they are fully consonant with SCF resonance energies calculated by Dewar and de Llano. Although our resonance energies are somewhat smaller than those of Hess and Schaad, there is an excellent linear relationship between the magnitudes of the two sets of resonance energies. Among the benzenoid hydrocarbons investigated, catacondensed hydrocarbons are predicted to be less stable than pericondensed hydrocarbons with a similar hue. A new definition of partial resonance energy, which describes aromaticity in individual π-electron rings, is proposed with the use of a Sachs formula and is justified in terms of Herndon's structure-resonance theory.

In previous papers,[1-3] we succeeded in defining an HMO characteristic polynomial for a nonaromatic "localized" structure of a conjugated compound by graph-theoretically excluding from the coefficients of an HMO characteristic polynomial of the compound all contributions from cyclic structures in the π system. This kind of polynomial was termed an HMO reference polynomial, because it is thought to give a reference energy, relative to which aromatic stabilization of the compound can be calculated. Most resonance energies calculated by Hess and Schaad[4-7] were analytically reproduced by means of such reference polynomials. On this basis, aromaticity in conjugated compounds can be safely attributed to the cyclic structures in the π system, in accord with our chemical sense that aromatic stabilization must be associated with π-electron rings.[8] We present here the application of this method to a wide variety of totally benzenoid hydrocarbons. The aromatic character in these compounds has been most extensively investigated by various methods.[1,2,4,5,9-14] Hence, we can take many viewpoints to examine our criterion of aromaticity. The HMO theory is assumed in its simplest form.

Calculation of A-II Resonance Energies. An HMO reference polynomial for a benzenoid hydrocarbon $R(X)$ can be expressed simply as[1]

$$R(X) = \sum_{k=0}^{N/2} (-1)^k p(2k) X^{N-2k} \qquad (1)$$

where N is the number of sp^2-carbon atoms in the π system, and $p(2k)$ is the number of ways in which k π bonds are so chosen from the π system that no two of them are connected to each other.[15] What we call the A-II resonance energy[1] is then defined as the difference between the total π energy calculated from a characteristic polynomial $P(X)$ of the com-

Table I. Resonance Energies of 48 Benzenoid Hydrocarbons

No.	Compd	Resonance energy				REPE × 10^3,	
		A-II, β	GT, β	HS, β	SCF, eV	β^a	ϵ_{HOMO}, β^b
1	Benzene	0.273	0.278	0.39	0.869	45.4	1.000
2	Biphenyl	0.502	0.473	0.72	1.699	41.8	0.705
3	Naphthalene	0.389	0.366	0.55	1.323	38.9	0.618
4	Anthracene	0.475	0.464	0.66	1.600	33.9	0.414
5	Phenanthrene	0.546	0.499	0.77	1.933	39.0	0.605
6	Naphthacene	0.553	0.568	0.76	1.822	30.7	0.295
7	Benz[*a*]anthracene	0.643	0.599	0.90	2.291	35.7	0.452
8	Benzo[*c*]phenanthrene	0.687	0.621	0.95	2.478	38.1	0.568
9	Chrysene	0.688	0.625	0.95	2.483	38.2	0.520
10	Triphenylene	0.739	0.668	1.01	2.654	41.1	0.684
11	Pyrene	0.598	0.562	0.82	2.098	37.1	0.445
12	Pentacene	0.626	0.673	0.84	2.004	28.5	0.220
13	Benzo[*a*]naphthacene	0.725	0.703			33.0	0.327
14	Pentaphene	0.746	0.700			33.9	0.437
15	Benzo[*b*]chrysene	0.781	0.725			35.5	0.405
16	Dibenz[*a,j*]anthracene	0.806	0.733	1.12	2.948	36.7	0.492
17	Dibenz[*a,h*]anthracene	0.807	0.733	1.12	2.948	36.7	0.474
18	Dibenzo[*c,g*]phenanthrene	0.832	0.747			37.8	0.536
19	Benzo[*c*]chrysene	0.833	0.749			37.9	0.550
20	Benzo[*b*]triphenylene	0.845	0.770		3.058	38.4	0.499
21	Picene	0.835	0.752			37.9	0.502
22	Benzo[*a*]pyrene	0.725	0.692	0.98	2.584	36.2	0.371
23	Perylene	0.740	0.713	0.96	2.619	37.0	0.347
24	Benzo[*e*]pyrene	0.791	0.724	1.06	2.853	39.6	0.497
25	Hexacene	0.706	0.778			27.2	0.169
26	Benzo[*a*]pentacene	0.802	0.808			30.9	0.244
27	Hexaphene	0.829	0.804			31.9	0.336
28	Dibenzo[*b,k*]chrysene	0.873	0.826			33.6	0.348
29	Dibenzo[*a,l*]naphthacene	0.895	0.837			34.4	0.361
30	Dibenzo[*a,j*]naphthacene	0.895	0.837			34.4	0.358
31	Phenanthro[3,4-*c*]phenanthrene	0.976	0.872			37.5	0.546
32	Dibenzo[*c,l*]chrysene	0.976	0.873			37.6	0.539
33	Benzo[*c*]picene	0.980	0.879			37.7	0.471
34	Dibenzo[*a,c*]naphthacene	0.929	0.873			35.7	0.356
35	Benzo[*h*]pentaphene	0.954	0.873			36.7	0.506
36	Dibenzo[*b,g*]triphenylene	0.972	0.888			37.4	0.447
37	Dibenzo[*g,p*]chrysene	1.041	0.943			40.1	0.512
38	Dibenzo[*de,mn*]naphthacene	0.780	0.813	0.98	2.694	32.5	0.199
39	Naphtho[2,1,8-*qra*]naphthacene	0.815	0.796			33.9	0.303
40	Benzo[*a*]perylene	0.839	0.834			35.0	0.265
41	Dibenzo[*b,def*]chrysene	0.844	0.822			35.2	0.303
42	Benzo[*rst*]pentaphene	0.861	0.824			35.9	0.342
43	Benzo[*b*]perylene	0.895	0.847			37.3	0.351
44	Dibenzo[*de,qr*]naphthacene	0.898	0.825			37.4	0.505
45	Dibenzo[*fg,op*]naphthacene	0.983	0.888			41.0	0.555
46	Dibenzo[*def,mno*]chrysene	0.766	0.759			34.8	0.291
47	Benzo[*ghi*]perylene	0.853	0.788	1.12	3.128	38.8	0.439
48	Coronene	0.947	0.863	1.27	3.524	39.5	0.539
	ρ_{RE}		0.974	0.993	0.995		
	ρ_{REPE}		0.866	0.970	0.924		

[a] A-II resonance energy per π electron. [b] Energy of the HOMO.

pound and that calculated from a corresponding reference polynomial $R(X)$. A-II resonance energies thus obtained for 48 benzenoid hydrocarbons are presented in Table I.

In a previous paper,[2] we pointed out that the A-II resonance energy can be approximated well in terms of the coefficients of both $P(X)$ and $R(X)$ in the following manner:

$$\mathrm{RE}_{\text{A-II}} \approx \mathrm{RE}_{\mathrm{GT}} = 6.0846\{\log |P(i)| - \log |R(i)|\} \quad (2)$$

where RE signifies the resonance energy specified by a subscript (A-II or GT), and $i = (-1)^{1/2}$. The approximate resonance energy, derived from this expression, is termed the GT resonance energy because the coefficients of the two polynomials are enumerated graph-theoretically.[1,2,15,16] A correlation coefficient (ρ_{RE}) between A-II and GT resonance energies is calculated to be 0.974, which gives a fairly good evidence for the validity of eq 2.

Comparison with Hess–Schaad Resonance Energies. As previously stated,[1] the first and best way of judging the reasonableness of A-II resonance energies is a comparison with the corresponding ones calculated by Hess and Schaad (HS resonance energies).[4,5] Both sets of resonance energies are favorably based on the simplest HMO model. Table I contains HS resonance energies for 20 typical benzenoid hydrocarbons. An excellent correlation found between A-II and HS resonance energies ($\rho_{RE} = 0.993$) shows that both types of resonance energies are quite consistent with each other. By a least-squares analysis, we obtain the following proportionality:

$$\mathrm{RE}_{\text{A-II}} \approx 0.7365\mathrm{RE}_{\mathrm{HS}} \quad (3)$$

From this expression, one finds that the A-II resonance energy, on the average, is about 26% smaller than the HS resonance energy for these benzenoid hydrocarbons. However, an ex-

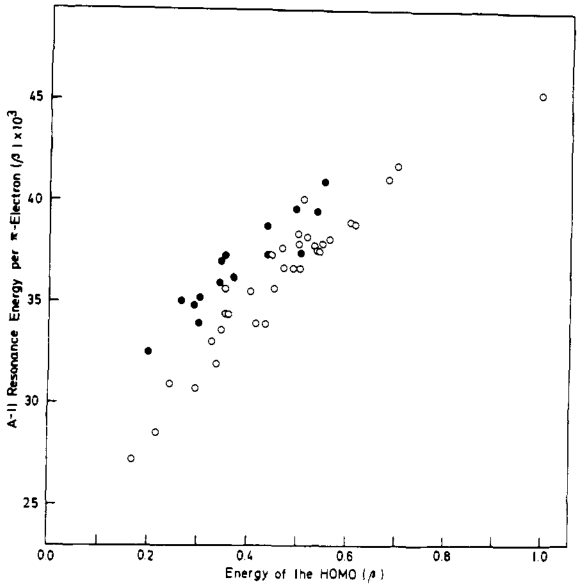


Figure 1. Plot of A-II resonance energy per π electron vs. the energy of the HOMO for benzenoid hydrocarbons. Open and closed circles show catacondensed and pericondensed hydrocarbons, respectively.

cellent correlation between them supports the view that HS resonance energies are as useful as our A-II resonance energies although the additive π-bond energies determined by Hess and Schaad[4] may be slightly smaller than they should be.

Comparison with SCF Resonance Energies. For a better comprehension of our resonance energies, it is instructive to compare them with those calculated by Dewar and de Llano.[11] Their resonance energies are based on the Pariser-Parr-Pople method and are hence referred to as SCF resonance energies. SCF resonance energies for 21 of the 48 benzenoid hydrocarbons are now available.[11] They are added for comparison in Table I. As indicated by a correlation coefficient (ρ_{RE} = 0.995), the A-II resonance energies are highly correlated with the SCF resonance energies. Such a nice correlation is also gratifying enough to justify our A-II resonance energies for benzenoid hydrocarbons. By a least-squares analysis, we obtain the following equality:

$$\mathrm{RE}_{\mathrm{SCF}} \approx 3.562\mathrm{RE}_{\mathrm{A\text{-}II}} \tag{4}$$

Here, the SCF and A-II resonance energies are given in units of eV and β, respectively. From an opposite viewpoint, the same correlation can be considered as logical evidence to justify the SCF resonance energies, because the correlative A-II resonance energies have been derived analytically.

Since the SCF resonance energies were calculated from the calculated heats of atomization which nicely duplicate the experimental values,[11] they can be considered as the best estimates for the resonance energies available at present. An effect of actual bond alternation on the π system was empirically taken into account in the SCF resonance energies, whereas it was completely neglected in the A-II resonance energies. We suspect that the π bonds strongly alternate in the localized structure of Dewar and de Llano[11] as in acyclic polyenes.

However, a nice correlation in the form of eq 4 suggests that we can apparently ignore the effect of bond alternation on the A-II resonance energies, at least for benzenoid hydrocarbons. This may be due to the fact that π bonds do not strongly alternate in these compounds.[10] Variable β SCF-MO calculations[17] support this view. For this reason, the coefficient of eq 4 can be regarded as a kind of conversion factor. We may identify it with an effective β value, applicable only to the estimation of resonance energies. It means that, by taking β = −3.562 eV, the SCF resonance energies can be formally reproduced from the A-II resonance energies. Owing to a somewhat vague notion of this value, it cannot be directly compared with a thermochemical β value estimated by Schaad and Hess (−1.420 eV).[18] Furthermore, our A-II resonance energies are in harmony with Herndon's resonance-theoretical resonance energies.[19]

A-II Resonance Energies per π Electron. As has been seen above, we could firmly establish that the A-II resonance energies are fully consonant with the HS and SCF resonance energies for benzenoid hydrocarbons. Now, we can examine aromaticities of individual hydrocarbons, in relation to their A-II resonance energies. Clar has long suggested that the stability of a benzenoid hydrocarbon is closely related to its color.[10] It is based on the observation that, the deeper the color of the compound is, the less stable does it appear. This effect was first ascertained by Hess and Schaad by means of their HS resonance energies.[5]

In order to reexamine the color-stability relationship, the A-II resonance energy per π electron (REPE) was plotted against the energy of the highest occupied molecular orbital (HOMO) for the 48 benzenoid hydrocarbons in Figure 1. REPE has been acknowledged as an excellent index for the stability of a conjugated system.[4-7,20] In the simplest HMO model, the transition energy of the first allowed absorption band (p band)[10] is proportional to the energy of the HOMO for these alternant hydrocarbons.

As shown in Figure 1, there is a fairly good correlation between the two quantities although it is not as good as that found by Hess and Schaad.[5] This fact indicates that, as a p band moves toward a low-energy side, the REPE gradually decreases. In other words, a compound with a p band on a long-wavelength side is predicted to be less stable. This prediction is in general agreement with the conclusion of Hess and Schaad[5] and also with Clar's inference concerning the color-stability relationship.[10]

However, if Figure 1 is examined in more detail, one finds that pericondensed hydrocarbons generally appear more stable than catacondensed hydrocarbons with a similar HOMO energy. A pericondensed hydrocarbon in which some sp²-carbon atoms are shared among adjacent three rings is predicted to be somewhat more stable than a catacondensed one of a similar hue in which all sp²-carbon atoms are arranged along a periphery of the π system. A relative stability of the pericondensed hydrocarbon is apparently related to its molecular geometry, in which there are fewer K or L regions as compared with a catacondensed hydrocarbon.[21] This might be a plausible reason for the stability of pericondensed hydrocarbons.

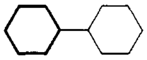
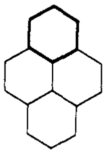
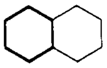
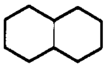
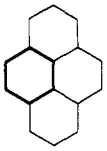
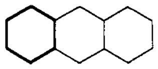
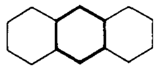
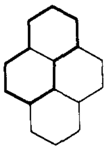
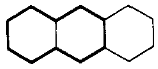
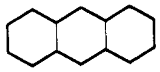
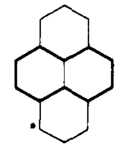
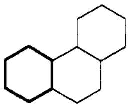
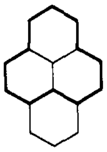
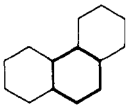
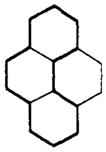
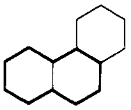
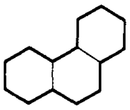
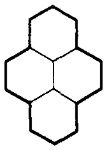
In general, a correlation coefficient between A-II and other resonance energies per π electron (ρ_{REPE}) is slightly smaller than that between the same two sets of resonance energies (ρ_{RE}). For numerical values for ρ_{REPE}, see Table I. However, it seems that these values should not be taken seriously, since the REPE are all distributed within a relatively narrow energy range.

Definition of Partial Resonance Energy. With a view to clarifying further the origin of aromaticity, we estimated aromaticity assignable to each π-electron ring in a polycyclic hydrocarbon as follows. We consider a given ring in a condensed hydrocarbon as the only cyclic component of Sachs graphs.[16] Let all the Sachs graphs which have cyclic components other than the ring under consideration be ignored. We then construct a modified characteristic polynomial $P^*(X)$ with the use of the remaining set of Sachs graphs and a Sachs formula presented by Graovac et al.[16] It is expressed in the following form:

$$P^*(X) = \sum_{k=0}^{N} C_k{}^* X^{N-k} \tag{5}$$

where

Table II. Partial Resonance Energies of Individual Rings in Benzenoid Hydrocarbons

Ring[a]	Partial resonance energy		Ring[a]	Partial resonance energy	
	A-II, β	RT, β		A-II, β	RT, β
	0.273	0.273			
	0.248	0.273		0.156	0.182
	0.179	0.182			
	0.122	0.159		0.109	0.091
	0.151	0.136			
	0.120	0.136		0.059	0.053
	0.083	0.080			
	0.069	0.057		0.012	0.000
	0.196	0.218		-0.005	0.000
	0.108	0.109		0.046	0.034
	0.073	0.064			
	0.060	0.045		0.046	0.034

[a] The ring concerned is boldly outlined in each structural formula.

$$C_k^* = \sum_{s \in S_k^*} (-1)^{c(s)} 2^{r(s)} \qquad (6)$$

Here, every prime signifies that the quantity concerned is associated with Sachs graphs which do not have cyclic components except for the ring under consideration, $c(s)$ is the number of components of Sachs graph s, $r(s)$ is the number of cyclic components of the same Sachs graph, and s runs over a set of possible Sachs graphs which have k carbon atoms S_k^*. Since at most one cyclic component is allowed for any Sachs graph, $r(s)$ is always zero or unity.

By analogy with a characteristic polynomial for the entire π system,[1-3] this type of polynomial can be supposed to give a characteristic polynomial which describes the same π system with aromaticity in the ring concerned only. The A-II resonance energy ascribable to the single ring is then defined as the difference between the total π energy calculated from $P^*(X)$ and that calculated from the reference polynomial $R(X)$. It is termed an A-II partial resonance energy. Table II contains several examples of A-II partial resonance energies thus obtained for familiar benzenoid hydrocarbons.

In this connection, accumulated evidence supports the idea, introduced by Clar,[10] that individual rings in the same benzenoid hydrocarbon may have different aromaticity.[11,13,22,23] However, it should be noted that, even though a certain benzene character is mostly preserved in a given six-membered ring, it does not warrant the ring to be as aromatic as benzene. Since the A-II resonance energy of benzene amounts to only 3.4% of the total π energy, even the retention of most π energy of benzene in the ring under consideration is not a sufficient condition for the presence of most resonance energy of benzene in it. In this sense, Herndon's structure-resonance theory[13] has been the only one which is purely concerned with aromatic character in a local structure of a π system. Randić's simplified model for local aromaticity[23] is closely related to this theory.

Herndon's resonance-theoretical concept of aromaticity is hence adopted to examine the validity of our A-II partial resonance energies. According to his theory,[13] the partial resonance energy (PRE) which arises from a given π-electron ring x in a polycyclic hydrocarbon is expressed as

$$\mathrm{PRE}_{\mathrm{RT}} = \frac{2N_x\gamma_x}{\mathrm{SC}} \qquad (7)$$

Here, a subscript RT signifies that the partial resonance energy has a resonance-theoretical origin, N_x is the Kekulé structure count of the residual π system, obtained by excision of the ring

Table III. A-II Resonance Energies of Annulenes

Compd	A-II resonance energy, β[a]
Cyclobutadiene	−1.226
Benzene	0.273
Cyclooctatetraene	−0.595
[10]Annulene	0.159
[12]Annulene	−0.394
[14]Annulene	0.113

[a] Reference 1.

x, γ_x is the resonance integral related by a permutation of all double bonds within a periphery of the ring x, and SC is the Kekulé structure count of the entire π system. The γ_x might be very close to the resonance energy of an annulene of the same size.

We hence calculated the RT partial resonance energies for several benzenoid hydrocarbons, using A-II resonance energies of annulenes (Table III) as the values for a resonance integral in eq 7. As shown in Table II, the RT partial resonance energy thus obtained is in satisfactory accord with the A-II partial resonance energy for all the rings investigated. It is noteworthy that when any Kekulé structures cannot be written for the residual π system, aromaticity in the ring concerned is negligible. We might say that our A-II partial resonance energies have been justified in terms of Herndon's structure-resonance theory.[13] As long as both sets of partial resonance energies agree well, the validity of his structure-resonance theory also seems to have been intensified at the same time.

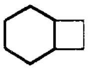
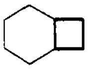
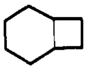
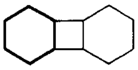
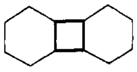
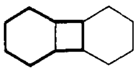
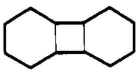
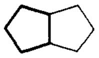
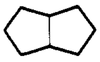
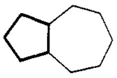
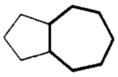
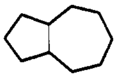
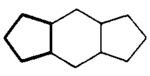
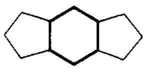
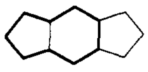
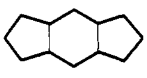
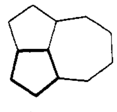
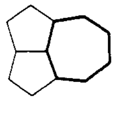
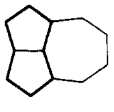
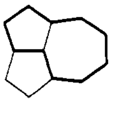
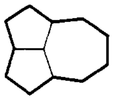
Some Comments on Resonance Energies of Nonbenzenoid Hydrocarbons. A-II resonance energies of many nonbenzenoid hydrocarbons have already been published.[1,2] Nothing especially novel has since been found concerning overall resonance energies of the nonbenzenoid systems. However, when the above concept of A-II partial resonance energy was applied to these π systems, somewhat different results were obtained. In order to clarify this situation, A-II and RT partial resonance energies were calculated for typical nonbenzenoid hydrocarbons. They are listed in Table IV.

One can note therein a general parallelism between the two sets of partial resonance energies for these compounds, although the correlation is not as exact as that for benzenoid hydrocarbons. One marked trend is that A-II resonance energies assigned to $(4n)$-membered rings are poorly reproduced by means of eq 7. When a ring under consideration is a four-membered ring, a discrepancy between the two partial resonance energies is particularly large. Compare, for example, two partial resonance energies of a central four-membered ring in biphenylene.

The variance between the two sets of results can formally be diminished by increasing the γ_x values for $(4n)$-membered rings. Such a process appears more or less responsible for a fairly good correlation found between RT and SCF overall resonance energies for nonbenzenoid hydrocarbons.[13b] However, at least a part of the difference between the A-II and RT partial resonance energies should be related to the fact that still Herndon and Ellzey could not reproduce SCF resonance energies of the nonbenzenoid hydrocarbons as accurately as those of benzenoid hydrocarbons.[13b] Our A-II partial resonance energies show that $(4n)$-membered rings are greatly stabilized in a polycyclic nonbenzenoid system, out of line with the prediction based on eq 7. On the other hand, every $(4n + 2)$-membered ring in it appears as stable as an annulene of the same size, as in the case of a polycyclic benzenoid hydrocarbon. Herndon's structure-resonance theory thus seems to be of limited utility to nonbenzenoid hydrocarbons.

Concluding Remarks. The above comparative studies of A-II resonance energies have established the usefulness of an HMO

Table IV. Partial Resonance Energies of Individual Rings in Nonbenzenoid Hydrocarbons

Ring[a]	Partial resonance energy	
	A-II, β	RT, β
	0.186	0.182
	-0.444	-0.818
	-0.246	-0.397
	0.204	0.218
	-0.231	-0.491
	-0.119	-0.238
	-0.092	-0.158
	0.016	0.000
	-0.542	-0.595
	0.022	0.000
	0.008	0.000
	0.148	0.159
	0.023	0.000
	0.054	0.000
	0.003	0.000
	-0.336	-0.394
	0.015	0.000
	0.006	0.000
	-0.183	-0.397
	0.101	0.106
	0.001	0.000

[a] The ring concerned is boldly outlined in each structural formula.

reference polynomial in analyzing aromaticity even in such large conjugated systems as polycyclic benzenoid hydrocarbons. Several energetic relationships found in comparisons with other aromaticity theories have provided a wide basis for further understanding the physical and topological aspect of A-II resonance energies. At the same time, the related theories of aromaticity for benzenoid hydrocarbons have been more strongly supported by these relationships.

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(19) According to the resonance-theoretical considerations of Herndon et al.,[13,14] the A-II resonance energy of a benzenoid hydrocarbon can be formally expressed as $RE_{A\text{-}II} \approx 2(0.2174N_1 + 0.1241N_2)/SC$ [$\rho_{RE} = 0.984$] and $RE_{A\text{-}II} \approx 0.6883 \log SC + 0.0735$ [$\rho_{RE} = 0.996$], where N_1 is the number of resonance integrals related by a permutation of three double bonds within a six-membered ring, N_2 is the number of resonance integrals related by a permutation of five double bonds within two annelated rings, and SC is the Kekulé structure count of the entire π system.
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Some Aspects of the Potential Surface for Singlet Trimethylenemethane

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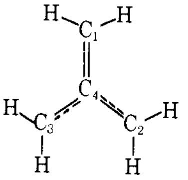
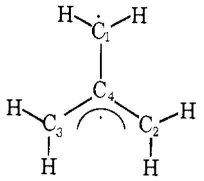
Abstract: The potential surface for bond length variations in singlet trimethylenemethane has been explored by ab initio calculations, employing an STO-3G basis set and including full π space CI. The effects of angle distortions at the central carbon atom, methyl substitution, and twisting of a methylene group by 90° to the orthogonal geometry have also been determined. The design of a trimethylenemethane derivative, in which a planar geometry would be lower in energy than an orthogonal one for the singlet, is discussed.

In previous papers we have discussed the wave functions for the $^1E'$ state of D_{3h} (planar, all C–C bond lengths and bond angles equal) trimethylenemethane.[1,2] We showed that while the π bonding in the $^3A_2'$ ground state is necessarily fully delocalized, as represented in **1**, the bonding in the two components of the $^1E'$ state is more localized,[1,3] as represented in **2** and **3**. The particular choice[4] of $^1E'$ wave functions implicit in **2** and **3** allows the wave functions to be classified according to their symmetry in the C_{2v} point group, and we will refer to the wave functions by the representation of C_{2v} to which they belong. Thus, the wave function of **2**, which is essentially that of an allyl radical plus an electron localized in a p orbital, we call the $^1B_2$ wave function. The wave function of **3**, which can be crudely described as an ethylene interacting *weakly*[5] with a diradical, we denote as $^1A_1$.



1



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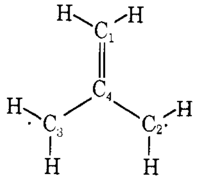

3

It is clear from inspection of the bonding in **1–3** that, while the $^3A_2'$ ground state of trimethylenemethane may prefer a D_{3h} geometry, the two components of the $^1E'$ state will not. The $^1B_2$ component will have its energy minimum at a geometry in which the C_1–C_4 bond is longer than the $C_{2(3)}$–C_4 bonds. In contrast, the $^1A_1$ wave function will prefer a geometry in which the C_1–C_4 bond is shorter than the $C_{2(3)}$–C_4 bonds. In this paper we report the results of ab initio calculations on the optimum geometries and relative energies of the $^1B_2$ and $^1A_1$ wave functions, and we discuss pseudorotation in planar singlet trimethylenemethane, the process by which, for instance, C_2 replaces C_1 as the unique peripheral carbon atom. We also report the results of calculations on the effect of substituents on the relative energies of the $^1B_2$ and $^1A_1$ wave functions and the consequences of twisting one methylene group 90°, so that its p orbital is orthogonal to the rest of the π system of trimethylenemethane.