May, 1975]　BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN, VOL. 48 (5), 1501—1505 (1975)　1501

A General Method for Evaluating the Resonance Energies of Monocyclic Conjugated Systems and Its Application to Heteroannulenes and Annulenones

Jun-ichi Aihara
Department of Chemistry, Faculty of Science, Hokkaido University, Sapporo 060

(Received November 20, 1974)

The unit binding energy of a monocyclic conjugated system with an infinite number of the same unit structures can be employed as the reference energy in evaluating the resonance energy of a monocyclic conjugated system with a single unit structure. The latter system may be totally asymmetric in geometry. The resonance energy is then given as the difference between the π-energy of the system with the one-unit structure and the unit binding energy of the infinitely large system. This approach is justified by the proper prediction of the resonance energies for heteroannulenes and annulenones. The HMO theory was used in its simplest form.

Almost all compounds, even those which are obviously unstable, are known to have a significant HMO delocalization energy.[1,2] The lack of correlation between the calculated delocalization energy and the observed aromatic behavior has, though, been widely pointed out as a failure of the HMO method. Recently, Dewar, using the more elaborate PPP method, has for the first time obtained calculated resonance energies which correlate well with the experimental aromaticity for a wide range of conjugated hydrocarbons.[1] However, the important point turned out to be that he changed the reference structure relative to which aromatic stabilization was calculated. With the original HMO method, on the other hand, Hess *et al.* obtained resonance energies which correlate as well as Dewar's with the experimental properties for a wide variety of both conjugated hydrocarbons and heterocycles.[3-7]

In the calculation of the delocalization energy, the π-energy of a compound with n double bonds was compared to the π-energy of n isolated double bonds (ethylene). In the method of Hess *et al.*, modeled after Dewar's, the π-energy of a compound was compared to the π-energy of a reference structure with contributions from both single and double bonds. It is noteworthy that a considerable double-bond character was attached to the single bonds in the resonance structure of the conjugated system.[1,3] Hence, the π-energy of an acyclic compound was generally represented as an additive function of the individual π-bond energies. This fact indicates that any acyclic compound has essentially zero resonance energy, whereas cyclic compounds have been found to have a wide and continuous variation in resonance energies, from positive (aromatic) to negative (antiaromatic).[1-7] In this article, we attempted to refine this kind of resonance energies simply on the basis of the additivity of π-bond energies for nonaromatic species, and examined the aromaticity of less symmetric monocyclic compounds, such as heteroannulenes and annulenones, without referring to the individual π-bond energies. We used the HMO theory in its simplest form.

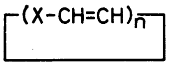
When HMO calculations are performed on conjugated compounds containing heteroatoms, appropriate corrections must be made of the Coulomb integral for each heteroatom and of the resonance integral for each carbon-heteroatom bond. A considerable amount of effort has been devoted to the determination of heteroatom parameters for such compounds.[8] Recently, Hess *et al.* evaluated the heteroatom parameters for the amine nitrogen, the ether oxygen, the thioether sulfur, and the carbonyl oxygen strictly on the basis of an experimental ground-state property, the heat of atomization.[5-7] We adopted their values, as they can be expected to be most suited to the estimation of another ground-state property, the resonance energy. They are listed in Table 1.

TABLE 1. HETEROATOM PARAMETERS

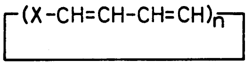
X	h_X	k_{C-X}
Amine nitrogen[5]	1.50	0.90
Ether oxygen[5]	2.00	0.34
Thioether sulfur[6]	1.00	0.68
Carbonyl oxygen[7]	0.22	0.99
sp^2-carbon	0.00	1.00

Theoretical

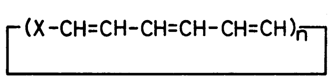
The reference energy relative to which the resonance energy of a monocyclic system is calculated is defined as follows. First, consider four hypothetical compounds of Type I-IV, in each of which n heteroatoms are periodically inserted in the cyclic chain of carbon atoms. X may be NH, O, or S. The π-energies for such systems can easily be obtained within the framework of the HMO theory.


$(\text{X-CH=CH})_n$

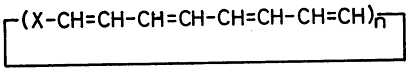
(I)


$(\text{X-CH=CH-CH=CH})_n$

(II)


$(\text{X-CH=CH-CH=CH-CH=CH})_n$

(III)


$(\text{X-CH=CH-CH=CH-CH=CH-CH=CH})_n$

(IV)

For example, the π-energy of a compound of Type II can be obtained by solving the following secular equations:

$$\begin{aligned} a_i(\chi+h)+ke_{i-1}+kb_i &= 0\\ b_i\chi+ka_i+c_i &= 0\\ c_i\chi+b_i+d_i &= 0\\ d_i\chi+c_i+e_i &= 0\\ e_i\chi+d_i+ka_{i+1} &= 0 \qquad i=1,2,\cdots,n \end{aligned} \tag{1}$$

where $\chi=(\alpha-\mathrm{E})/\beta$ and where a_i, b_i, c_i, d_i, and e_i are the Hückel coefficients of the atomic orbitals concerned on the atoms arranged in this manner:

$$\begin{array}{cccccccccc} \text{—CH=} & \text{CH—} & \text{X—} & \text{CH=} & \text{CH—} & \text{CH=} & \text{CH—} & \text{X—} & \text{CH=} & \text{CH—}\\ d_{i-1} & e_{i-1} & a_i & b_i & c_i & d_i & e_i & a_{i+1} & b_{i+1} & c_{i+1} \end{array}$$

These equations must be solved together with the boundary conditions:[3)]

$$a_{n+1}=a_1,\quad b_{n+1}=b_1,\quad c_{n+1}=c_1,\quad d_{n+1}=d_1,\quad \text{and}\quad e_{n+1}=e_1 \tag{2}$$

The function

$$a_i=\sin i\lambda \tag{3}$$

automatically satisfies Eq. (2) for $i=n+1$ if

$$\lambda=\lambda_{nm}=\frac{2m\pi}{n} \qquad m=0,1,\cdots,(n-1) \tag{4}$$

The elimination of b_i, c_i, d_i, e_i, and e_{i-1} in Eq. (1), followed by the substitution of Eqs. (3) and (4), gives n algebraic equations of degree five:

$$\chi^5+h\chi^4-(2k^2+3)\chi^3-3h\chi^2+(1+4k^2)\chi + (h+2k^2\cos\lambda_{nm})=0 \qquad m=0,1,\cdots,(n-1) \tag{5}$$

Each of these equations possesses five real roots:

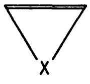
$$\chi=\chi_1(\lambda_{nm})\leq\chi_2(\lambda_{nm})\leq\chi_3(\lambda_{nm})\leq\chi_4(\lambda_{nm})\leq\chi_5(\lambda_{nm}) \tag{6}$$

Among them, the smaller three roots correspond to the π-energies of the occupied orbitals in the heterocycle in quetion. Accordingly, the π-energy of a compound of Type II can be obtained by summing the smaller three roots for every λ_{nm} over all the m's.

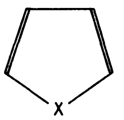
As may easily be seen, the unit structure of the periodic compound of Type II is composed of the two CH=CH, one CH–CH, and two CH–X bonds when the classical resonance structure is written for it. The unit binding energy corresponding to the unit structure is obtained by dividing the π-energy of the whole system by the number of the unit structures (n). It is a function of the number of the unit structures, as the π-energy might be influenced by the possible aromatic character of the smaller systems. When the n is large enough, the system can, however, be considered without difficulty as a nonaromatic species, regardless of the X. The unit binding energy of any infinitely large system should, therefore, be free from aromaticity. The unit binding energy (E_u) of an infinitely large system of Type II can be expressed in units of β as:

$$\begin{aligned} E_\mathrm{u}(\mathrm{X}) &= -\lim_{n\to\infty}\frac{2}{n}\sum_{m=0}^{n-1}\left\{\chi_1(\lambda_{nm})+\chi_2(\lambda_{nm})+\chi_3(\lambda_{nm})\right\}-2h_\mathrm{x}\\ &= -2\int_0^1\{\chi_1(2\pi x)+\chi_2(2\pi x)+\chi_3(2\pi x)\}\mathrm{d}x-2h_\mathrm{x} \end{aligned} \tag{7}$$

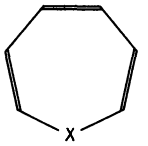
Note that it is not difficult to regard such unit binding energy as the reference energy in evaluating the aromaticity of a five-membered heterocycle of Type VI. The five-membered ring of Type VI is a special case of the compound of Type II, in which only one unit structure is present. If any compound of Type II is assumed to be absolutely nonaromatic, it should possess the same unit binding energy as the compound of Type II with $n=\infty$. Therefore, as long as the additivity of π-bond energies is assumed for the like nonaromatic systems, the unit binding energy derived from Eq. (7) can be considered as the reference energy of the five-membered heterocycle of Type VI.



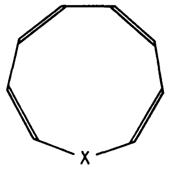
(V)



(VI)



(VII)



(VIII)

In other words, the five-membered heterocycle of Type VI has the same numbers of the CH=CH, CH–CH, and CH–X bonds as the unit structure of the compound of Type II containing the same heteroatom. Furthermore, the positions of the carbon atoms relative to the position of the heteroatom in the five-membered heterocycle are exactly equivalent to those in the unit structure. The effect of the electronegative heteroatom on the nearby π-bonds in the heterocycle of Type VI is necessarily taken into account in the unit binding energy derived from Eq. (7). This explain well how that the unit binding energy of an infinitely large system represents the reference energy of the corresponding five-membered heterocycle. The resonance energy of a given heterocycle of Type VI is, then, the difference between the π-energy of the compound and the unit binding energy of the infinitely large system of Type II.

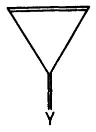
The resonance energies of the three-, seven-, and nine-membered heteroannulenes containing single heteroatoms (V, VII, and VIII) are calculated in the same manner by comparing their π-energies with the unit binding energies of the infinitely large systems of Type I, III, and IV respectively. The secular equations for these systems are analogously reduced to the following algebraic equations:

$$\chi^3+h\chi^2-(2k^2+1)\chi+(2k^2\cos\lambda_{nm}-h)=0 \quad \text{for I} \tag{8}$$

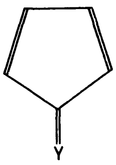
$$\chi^7+h\chi^6-(2k^2+5)\chi^5-5h\chi^4+(8k^2+6)\chi^3+6h\chi^2 -(6k^2+1)\chi+(2k^2\cos\lambda_{nm}-h)=0 \quad \text{for III} \tag{9}$$

$$\chi^9+h\chi^8-(2k^2+7)\chi^7-7h\chi^6+(12k^2+15)\chi^5+15\chi^4 -(20k^2+10)\chi^3-10h\chi^2+(8k^2+1)\chi +(2k^2\cos\lambda_{nm}+h)=0 \quad \text{for IV} \tag{10}$$

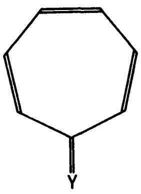
The unit binding energies are numerically computed



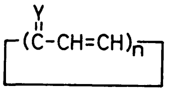
(IX)



(X)

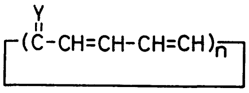


(XI)



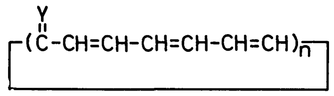
$\left(\overset{\overset{\mathrm{Y}}{\|}}{\mathrm{C}}\mathrm{-CH{=}CH}\right)_n$

(XII)



$\left(\overset{\overset{\mathrm{Y}}{\|}}{\mathrm{C}}\mathrm{-CH{=}CH{-}CH{=}CH}\right)_n$

(XIII)



$\left(\overset{\overset{\mathrm{Y}}{\|}}{\mathrm{C}}\mathrm{-CH{=}CH{-}CH{=}CH{-}CH{=}CH}\right)_n$

(XIV)

with these equations as in Eq. (7) for the five-membered heteroannulenes.

On the other hand, the reference energies of the first three members of annulenones (IX, X, and XI; Y=O) and fulvenes (IX, X, and XI; $Y=CH_2$) are obtained on the basis of the following equations, which are the algebraic versions of the secular equations for the systems of Types XII, XIII, and XIV:

$$\chi^4 + h\chi^3 - (k^2+3)\chi^2 - (3h-2\cos\lambda_{nm})\chi + (k^2+2h\cos\lambda_{nm}) = 0 \quad \text{for XII} \tag{11}$$

$$\chi^6 + h\chi^5 - (k^2+5)\chi^4 - 5h\chi^3 + (3k^2+5)\chi^2 + (5h+2\cos\lambda_{nm})\chi - (k^2-2h\cos\lambda_{nm}) = 0 \quad \text{for XIII} \tag{12}$$

$$\chi^8 + h\chi^7 - (k^2+7)\chi^6 - 7h\chi^5 + (5k^2+14)\chi^4 + 14h\chi^3 - (6k^2+7)\chi^2 - (7h-2\cos\lambda_{nm})\chi + (k^2+2h\cos\lambda_{nm}) = 0 \quad \text{for XIV} \tag{13}$$

The resonance energy of a given annulenone or fulvene is the difference between the π-energy of the compound and the unit binding energy of an infinitely large system composed of like unit structures.

Results and Discussion

The resonance energies of the heteroannulenes calculated according to the above-mentioned procedure are all listed in Table 2. The most striking aspect of these resonance energies is the strong alternation between aromaticity and antiaromaticity. The alternation decreases as the ring size increases. When the heteroannulenes are $(4r+2)\pi$-electron systems, they are predicted to be aromatic, with positive resonance energies. Conversely, when they are $4r$ π-electron systems, they are predicted to be antiaromatic, with negative resonance energies. Here, r is an integer. Such a trend in the aromatic character is clearly common to all the heteroannulenes containing single heteroatoms. This fact indicates that the Hückel $(4r+2)\pi$ rule of aromaticity can still be applied to such heterocyclic systems as heteroannulenes.

It should, then, be emphasized that their chemistry is in good accord with these predictions. The three-membered rings are predicted to be strongly antiaromatic, probably because of their four π-electron systems. These compounds are correspondingly unknown as yet. On the other hand, the five-membered rings, each of which forms an aromatic sextet, are predicted to be aromatic, in line with their well-known properties.[9,10] Among them, furan is predicted to be only slightly aromatic, as is indicated by its chemistry. Furan undergoes Diels-Alder reactions readily, while pyrrole and thiophene do not.

Table 2. Calculated resonance energies of heteroannulenes

Species	n	Hückel MO π-energy (β)	Reference energy (β)	Resonance energy (β)	Resonance energy (kcal/mol)
		Aza[n]annulenes			
C_2H_2NH	3	2.0000	2.6590	−0.6590 (−0.666)	−20.224
C_4H_4NH	5	5.4351	5.1557	0.2794 (0.233)	8.574
C_6H_6NH	7	7.4469	7.7077	−0.2607 (−0.291)	−8.003
C_8H_8NH	9	10.4126	10.2573	0.1552 (0.139)	4.764
		Oxa[n]annulenes			
C_2H_2O	3	2.0000	2.2210	−0.2210 (−0.018)	−6.783
C_4H_4O	5	4.5982	4.5539	0.0443 (0.044)	1.361
C_6H_6O	7	7.0385	7.0714	−0.0329 (−0.051)	−1.009
C_8H_8O	9	9.6266	9.6018	0.0247 (0.001)	0.759
		Thia[n]annulenes			
C_2H_2S	3	2.0000	2.6052	−0.6052 (−0.457)	−18.575
C_4H_4S	5	5.1855	4.9607	0.2248 (0.193)	6.900
C_6H_6S	7	7.2959	7.5044	−0.2085 (−0.232)	−6.400
C_8H_8S	9	10.1819	10.0497	0.1322 (0.118)	4.057

Resonance energies given in kcal/mol were calculated with $\beta = -1.33077$ eV.[5]

The seven-membered ring systems, azepine, oxepin, and thiepin, are characterized by a cyclic array of eight π-electrons, and are predicted to be antiaromatic. Though planarity is feasible in such compounds, the maintenance of such a conformation would not be energetically preferable. X-ray studies suggest that 1H-azepines are nonplanar in the crystalline state and also, probably, in solution, so as to be liberated from antiaromaticity.[11] Azepine and oxepin are very reactive, in agreement with their calculated resonance energies.[11] Unsubstituted thiepin and the higher members of the thiaannulenes have not been reported on.

One of the nine-membered ring systems, azonine, has a positive resonance energy, which suggests that it is probably aromatic, while oxonin has a negligible resonance energy, and therefore is probably olefinic in nature. According to the experimental studies by Anastassiou *et al.*,[12] these nine-membered heterocycles are characterized in an analogous way, as azonine is considerably more stable than oxonin.

The calculated resonance energies for some annulenones and fulvenes are given in Table 3. Cyclopropenone and tropone are predicted to be aromatic, with positive resonance energies, whereas cyclopentadienone is predicted to be antiaromatic, with a negative resonance energy. The fulvenes are all predicted to be substantially

TABLE 3. CALCULATED RESONANCE ENERGIES OF SOME ANNULENONES AND FULVENES

Species	Hückel MO π-energy (β)	Reference energy (β)	Resonance energy (β)	Resonance energy (kcal/mol)
Cyclopropenone	5.0648	4.9292	0.1356 (0.126)	4.161
Cyclopentadienone	7.3811	7.4578	−0.0767 (−0.094)	−2.355
Tropone	10.0638	9.9941	0.0696 (0.053)	2.137
Methylenecyclopropene	4.9624	4.9312	0.0312	0.956
Fulvene	7.4659	7.4560	0.0099	0.304
Heptafulvene	9.9944	9.9898	0.0045	0.139

Resonance energies given in kcal/mol were calculated with $\beta = -1.33077$ eV.[5)]

nonaromatic, with slight resonance energies. As was stated by Hess *et al.*,[7)] their chemistry also appears to be in good accord with these predictions.

Recently, Machiguchi *et al.*[13)] reported on the aromaticity of tropothione (cycloheptatrienethione), suggesting, from the carbon-13 chemical shifts, that this compound is considerably less aromatic than tropone. As the electronegativity of sulfur is presumably close to that of carbon,[8)] the Coulomb integral on the thionyl sulfur might be approximated by that on the carbon atom—that is, $h \sim 0$. Consequently, the electronic structure of tropothione is likely to resemble that of heptafulvene rather than that of tropone.

On the other hand, chemical evidence of aromatic character is much easier to find in the case of tropolone (2-hydroxytropone).[14)] Interaction between the neighboring hydroxy and ketone groups due to the intramolecular hydrogen bonding has been seen as a source of difference between tropone and tropolone, since the isomers of tropolone, 3- and 4-hydroxytropones, resemble tropone in their chemical properties. One of the most prominent effects arising from the intramolecular hydrogen bonding is probably that the attached proton tends to increase the effective Coulomb integral on the carbonyl oxygen within the Hückel approximation. Chemically speaking, the hydrogen bonding may be said to stabilize the classical ionic structure of tropone.

According to this scheme, we tentatively increased the Coulomb integral on the carbonyl oxygen as an effect of hydrogen bonding; we thus found that the resonance energy of tropone is a function of the Coulomb integral on the carbonyl oxygen—it increases rapidly with an increase in the h-value for the carbonyl oxygen. For example, the resonance energy amounts to 0.2108β or 6.471 kcal/mol with this set of parameters; $h=1.00$ and $k=1.00$. Such a trend in aromaticity strongly suggests that, as has long been expected, the aromatic character of troponoid compounds is attributable to the formation of an aromatic sextet in the tropenylium structure. At present, we can not determine the amount of change in the effective Coulomb integral due to the hydrogen bonding. Nevertheless, the above idea appears to give quite a possible explanation of the enhanced aromaticity of tropolone within the HMO theory.

The resonance energies presented in Tables 2 and 3 parallel fairly well those determined by Hess *et al.*,[3–7)] which are placed within parentheses in the tables. In estimating these resonance energies, they classified the π-bonds according to the number of attached hydrogens, and assigned a π-energy to every π-bond type. The reference energy of a given conjugated compound is a combination of such π-bond energy terms. Therefore, the slight differences between the resonance energies determined by Hess *et al.* and those determined by us are probably due to the fact that they applied the fixed π-bond energies of carbon-carbon bonds to the conjugated hydrocarbons and to the heterocycles as well.

If the π-bond energies are universally additive in the nonaromatic compounds, the increase in the reference energy on going from a given heteroannulene to the next member of the same series must be the same as the unit binding energy of an infinitely large annulene. Both should correspond to the sum of the π-energies of the CH=CH bond and the CH–CH bond in the classical resonance structure. However, the actual increases in the reference energies, for example, for the azaannulene series (2.4967β, 2.5520β, and 2.5496β) are somewhat different from the unit binding energy of an infinitely large annulene (2.5465β).[15)] The situation is the same for the other cyclic systems considered. As was suggested before, such a discrepancy should be ascribed to the electronegativity of the heteroatom or to the polarity of the carbon-heteroatom bonds. It is, hence, noteworthy that the present approach skillfully avoids this kind of difficulty by evaluating the π-energy of a group of π-bonds.

As may be seen from the above discussion, the present approach assumes, for the sake of simplicity, the planarity of the compound, and it does not take into consideration the effects of the bond alternation and the ring strain on the π-energy of the compound. Since the geometry of the reference structure is necessarily assumed to be the same as that of the compound under consideration, the rsonance energy defined by us should be regarded as a kind of vertical resonance energy. Such assumptions are analogous to those made in calculating the delocalization energy. As far as the vertical resonance energy is concerned, the distortion energy brought about in the flattened molecule is retained in the reference structure.

When there is a bond alternation in the actual conjugated compound, the same bond alternation must be present in the reference structure for the vertical resonance energy to be evaluated. Though the introduction of bond alternation is often preferable,[16–18)] it can not easily be carried out, and it might cause a considerable amount of ambiguity in the obtained resonance energy. In general, the resonance energy is a very small quantity as compared to the total π-energy of the compound. To make matters worse, when the bond alternation is considered, some other comparable terms, such as the strain energy and the σ-compression energy, must be considered at the same time.

However, the good correlation found between the calculated resonance energies and the experimental properties for various monocyclic systems definitely shows that these resonance energies are still excellent indices, much better than the delocalization energies, in predicting the stability of the compounds in the ground state.

With this aspect of the present results in mind, the stability of the actual compounds should be understood in the following manner. If the calculated resonance energy is large enough, a large portion of it will be preserved in the actual compound. On the other hand, if the calculated resonance energy is small or negative, the bond alternation will be significant in the actual system and will lower the π-energy of the compound. Especially, when the compound is predicted to be markedly antiaromatic, the bond alternation is assuredly introduced in the system, and even the planarity of the compound might be broken so as to be relieved from antiaromaticity, as in the case of azepines. The bond alternation is thus necessary to lower the absolute value of the resonance energy as well as the π-energy of the antiaromatic system. However, the sign of the resonance energy always remains unchanged upon the introduction of bond alternation. The resonance energy obtained on the assumption of constant resonance integrals hence denotes the upper limit of the absolute value of the resonance energy.

In this connection, it must be noticed that the experimental resonance energies so far published are all related to the delocalization energies; they should rather be called the "conjugation energies" in the sense that any conjugation among the formal double bonds contributes to the increase in the delocalization energy. In general, the delocalization energy is large for the large conjugated compounds, as they contain many formal single bonds. Therefore, the experimental conjugation energies should not be correlated with the present results.

In a previous paper,[15] we examined the aromaticity of some monocyclic systems, such as annulenes and radialenes, for which analytical solutions of the HMO secular equations are available. The present approach is an extension of the same procedure to less symmetric systems. In general, the unit binding energy of a monocyclic conjugated system with an infinite number of unit structures can be employed as the reference energy in evaluating the resonance energy of a monocyclic conjugated system with a single-unit structure. It should be emphasized that this approach is applicable to almost all kinds of monocyclic conjugated systems, even to those totally asymmetric in geometry. As for heteroannulenes and annulenones, the present approach gives proper values for the resonance energies which are consistent with their chemical properties. It goes without saying that the estimation of these resonance energies was made possible by the accurate heteroatom parameters determined by Hess *et al.* All the simplicity and elegance of the HMO theory remain in the present approach.

We are grateful to the Hokkaido University Computing Center for the use of their FACOM 230-60, on which all the calculations were performed.

References

1) M. J. S. Dewar, "The Molecular Orbital Theory of Organic Chemistry," McGraw-Hill, New York, N. Y. (1969), Ch. 5.

2) L. J. Schaad and B. A. Hess, Jr., *J. Amer. Chem. Soc.*, **94**, 3068 (1972).

3) B. A. Hess, Jr. and L. J. Schaad, *ibid.*, **93**, 305 (1971).

4) B. A. Hess, Jr. and L. J. Schaad, *ibid.*, **93**, 2413 (1971).

5) B. A. Hess, Jr., L. J. Schaad, and C. W. Holyoke, Jr., *Tetrahedron*, **28**, 3657 (1972).

6) B. A. Hess, Jr. and L. J. Schaad, *J. Amer. Chem. Soc.*, **95**, 3907 (1973).

7) B. A. Hess, Jr., L. J. Schaad, and C. W. Holyoke, Jr., *Tetrahedron*, **28**, 5299 (1972).

8) A. Streitwieser, Jr., "Molecular Orbital Theory for Organic Chemists," John Wiley & Sons, New York, N. Y. (1961), Ch. 4.

9) G. Marino, "Advances in Heterocyclic Chemistry," Vol. XIII, edited by A. R. Katritzky and A. J. Boulton, Academic Press, New York, N. Y. (1971), pp. 235—314.

10) L. A. Paquette, "Principles of Modern Heterocyclic Chemistry," Benjamin, New York, N. Y. (1968).

11) L. A. Paquette, "Nonbenzenoid Aromatics," Vol. I, edited by J. P. Snyder, Academic Press, New York, N. Y. (1969), Ch. 5.

12) A. G. Anastassiou, S. W. Eachus, R. P. Cellura, and J. H. Gebrian, *Chem. Commun.*, **1970**, 1133.

13) T. Machiguchi, Y. Inagaki, M. Hoshino, and Y. Kitahara, *Chem. Lett.*, **1974**, 497.

14) D. Lloyd, "Carbocyclic Non-Benzenoid Aromatic Compounds," Elsevier, Amsterdam (1966), Ch. 6.

15) J. Aihara, This Bulletin, **48**, 517 (1975).

16) T. Nakajima and S. Katagiri, *Mol. Phys.*, **6**, 149 (1963).

17) M. J. S. Dewar and C. de Llano, *J. Amer. Chem. Soc.*, **91**, 789 (1969).

18) G. J. Gleicher, D. D. Newkirk, and J. C. Arnold, *ibid.*, **95**, 2526 (1973).