Aromaticity-Based Theory of Pericyclic Reactions

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The resonance energies of conjugated compounds in the electronically excited state were calculated on the basis of the aromaticity theory previously reported by us. The allowednesses of pericyclic reactions were predicted by means of these resonance energies. The predictions based on the resonance energy difference (RED) between the pericyclic transition state and the reactant(s) are in general agreement with the experiment.

Dewar-type resonance energy is an excellent aromaticity index for a conjugated compound.[1] It is defined as the difference between the energy of a conjugated compound and the energy of a "localized structure." Here, a "localized structure" signifies an olefinic reference structure which is hypothetically free from aromaticity. During the last three years we have been developing an analytical theory of aromaticity by means of the HMO theory, and have succeeded in formulating a characteristic polynomial for a "localized structure" of a conjugated compound.[2-5] A characteristic polynomial for the localized structure has been termed a "reference polynomial."[2] The π energy calculated from a reference polynomial can be interpreted as the π energy which a compound would possess if it were absolutely olefinic in nature.[2,3] On this basis, we could satisfactorily evaluate the aromatic resonance energy for any kind of conjugated compound and its ions.[2-5]

In this paper, we will show that the same definition of resonance energy can be applied to conjugated compounds in the excited state, and that it can be used as a new reactivity index for judging the allowedness of related pericyclic (*i.e.*, concerted) reactions.

Aromaticity in an Excited-State Species

A criterion of aromaticity in an electronically excited species is a comparison of the π energies of the compound and its localized structure (*i.e.*, its reference structure),[2] but in this case both structures must be in an equivalent excited state. We will here restrict our consideration to the lowest excited state, because, in most cases, any higher excited state will rapidly relax to the lowest excited state.[6] This means that, in most photochemical reactions, only the lowest excited state is important.

Let a characteristic polynomial for a conjugated compound and a corresponding reference polynomial be written respectively as

$$P(X) = X^N + \sum_{k=1}^{N} a_k X^{N-k} \tag{1}$$

and

$$R(X) = X^N + \sum_{k=1}^{N} b_k X^{N-k}, \tag{2}$$

where N is the number of atoms in the conjugated system. The coefficients, a_k and b_k, can be enumerated graphically with little difficulty.[2,3,7]

The roots of a secular equation, $P(X)=0$, are arranged in decreasing order as

$$X = X_1, X_2, \cdots, X_{N-1}, X_N. \tag{3}$$

The roots of a corresponding reference equation, $R(X)=0$, are arranged analogously in decreasing order as

$$X = X_1^*, X_2^*, \cdots, X_{N-1}^*, X_N^*. \tag{4}$$

The resonance energy of a conjugated system, RE, is then defined as

$$RE = \sum_{m}^{\text{occ.}} g_m (X_m - X_m^*), \tag{5}$$

where m runs over all the occupied π-molecular orbitals and where g_m is the number of electrons which occupy the m-th orbital. The resonance energy of any conjugated compound in any excited state can be calculated from this expression simply by adjusting the g_m values to its electronic configuration.

Resonance Energies of Annulenes in the Lowest Excited State

The resonance energies of ordinary annulenes (*i.e.*, Hückel annulenes) can be calculated straightforwardly from Eq. 5. The resonance energies of unrealistic Möbius annulenes (*i.e.*, singly twisted annulenes)[8] can also be calculated in the same manner. A reference polynomial for a Möbius annulene is identical with that for an ordinary annulene of the same size because the coefficients of the reference polynomials for both annulenes depend solely upon the connectivity of carbon atoms.[9] More accurately, each coefficient of a reference polynomial is a function of the bond (or heterobond) parameters squared (k^2).[3] Therefore, the coefficients of a reference polynomial are independent of the sign of any bond parameter. The π-orbital energies for the Hückel and Möbius benzenes, together with those for their reference structure, are shown in Fig. 1. Table 1 contains the resonance energies obtained for the Hückel and Möbius annulenes.

It is noteworthy that the aromaticity of a Möbius annulene in the ground state is determined by the converse of the Hückel (4n+2) rule, in agreement with a conclusion by Heilbronner.[8] The sign and the magnitude of the resonance energy for any ground-state annulene are essentially the same as those previously reported by us.[10] On the other hand, either conformation of any annulene in the excited state can be predicted to have an aromatic character opposite to that in the ground state. For example, a Hückel benzene (*i.e.*, an ordinary benzene) is the most stable annulene in the ground state, but the resonance energy becomes greatly negative when it is electronically excited. Such a situation is best represented by a high reactivity of

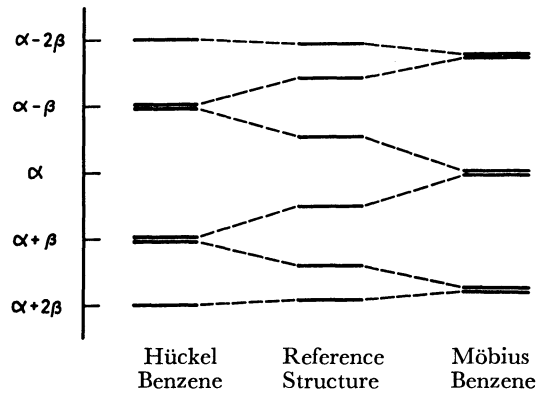


Fig. 1. Orbital correlations between benzenes and their reference structure.
Dashed lines indicate orbital correlations, which are drawn according to the principle described in J. Aihara, *Bull. Chem. Soc. Jpn.*, **50**, 2010 (1977). However, another definition of resonance energy given therein is not used in this paper, because the original definition (Ref. 2) is more practical and physically meaningful. Note that the reference energy in Ref. 2 defines the lowest energy of the reference structure.

Table 1. Resonance energies of annulenes

Species	Resonance energy (β)	
	Ground state	Excited state
Hückel cyclobutadiene	−1.226	0.305
Möbius cyclobutadiene	0.431	−0.867
Hückel benzene	0.273	−0.692
Möbius benzene	−0.799	0.236
Hückel cyclooctatetraene	−0.595	0.186
Möbius cyclooctatetraene	0.201	−0.550
Hückel[10]annulene	0.159	−0.451
Möbius[10]annulene	−0.474	0.152

this compound in the excited state. Benzene often forms benzvalene, Dewar benzene, and prismane when it is irradiated by ultraviolet light.[11]

Pericyclic Reactions with a Monocyclic Transition State

The above aspect of the aromaticity of annulene reminds us of the stereoselectivity of pericyclic reactions. Thus far, two principal approaches, the frontier orbital method[12] and the correlation diagram method,[13] have been widely employed to explain a number of pericyclic reactions. An alternative approach was made by Dewar[14] and Zimmerman,[15] who independently considered an aromatic property of a transition state as a determinant for the allowedness of pericyclic reactions.

Since, at any point along the reaction coordinate, a set of electrons are cyclically delocalized over the reacting centers, a transition state of the pericyclic reaction can be considered as a kind of cyclic conjugated system. For example, a transition state of a $[4_s+2_s]$ Diels-Alder reaction is isoconjugate with a Hückel benzene. According to an aromaticity-based theory of pericyclic reactions,[14,15] this reaction is thermally allowed because benzene is aromatic in the ground state. Dewar and Zimmerman thus showed that the problem of pericyclic reactions is identical in principle with that of aromaticity. The utility of this approach depends on the facility with which one can predict whether or not a given pericyclic transition state is aromatic. However, there has been no satisfactory theory of aromaticity for conjugated systems in the excited state. Their account of photochemical pericyclic reactions hence appeared less persuasive than that of thermal pericyclic reactions.

Now, we have an analytical theory of aromaticity[2-5] applicable to the excited-state species. By correlating the present resonance energies of annulenes (Table 1) with the pericyclic reactions whose transition states are monocyclic, we can safely predict that, if a pericyclic transition state is electronically equivalent to an annulene in an aromatic state, the reaction is allowed, while if it is not, the reaction is forbidden. Here, an aromatic state signifies a state in which the compound has a positive resonance energy, whether or not it is a ground-state species. On this basis, it can be predicted that a $[4_s+2_s]$ Diels-Alder reaction is photochemically forbidden, since a corresponding Hückel benzene has a negative resonance energy in the excited state. This is, of course, in harmony with the fact that such a reaction has not been reported.

Accordingly, an aromaticity-based theory of pericyclic reactions can be generalized into a single definitive rule: pericyclic reactions, both thermal and photochemical, take place *via* aromatic transition states. Since there are no exceptions to the Woodward-Hoffmann rules, there are no exceptions to this rule, either.

Pericyclic Reactions with a Polycyclic Transition State

Even though a pericyclic reaction has a polycyclic transition state, we can expect that an analogous consideration can be applied to it. In this case, the reactants are often cyclic conjugated compounds, and they may have an aromatic character. In order to take this new factor into account, we propose a new quantity, defined as the resonance energy difference (RED) between the pericyclic transition state and the reactants. This quantity reflects the relative aromatic stabilization of the transition state as compared with that of the reactants in an equivalent electronic state.

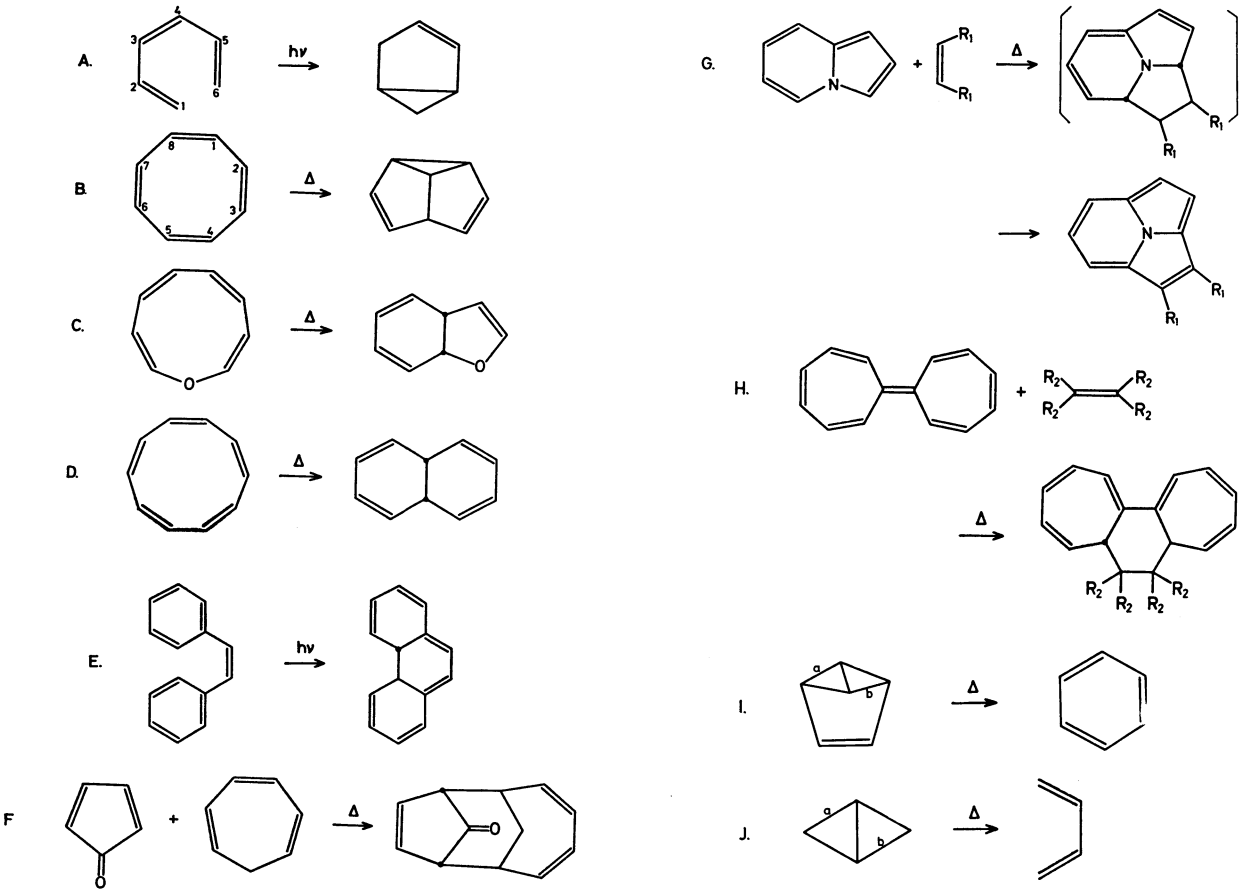
After extensive numerical analysis, the RED was found to give an excellent reactivity index for pericyclic reactions of any type. In Table 2 some typical pericyclic reactions with a polycyclic transition state are listed, together with their RED values. In calculating these RED values, some substituents, denoted therein as R_1 and R_2, were ignored for the sake of simplicity. As is shown in this table, the RED must be positive in order for the reaction to be allowed. The reaction is predicted to be allowed *via* a transition state with the largest RED value. When the RED is smaller than that, the reaction cannot be expected to occur, in accord with the experimental results.

Such a trend in reactivity strongly suggests that an

TABLE 2. RED VALUES FOR TYPICAL PERICYCLIC REACTIONS

Type of reaction	Stereochemistry	RED (β)	Allowedness	Type of reaction	Stereochemistry	RED (β)	Allowedness
A	(4_s+2_a) or (4_a+2_s)	0.02	Yes[a]	F	(6_s+4_s)	0.16	Yes[f]
	(4_s+2_s)[k] or (4_a+2_a)	−0.26	No		(6_s+4_a)[k] or (6_a+4_s)[k]	−0.29	No
B	(4_a+2_a)	0.80	Yes[b]	G	(8_s+2_s)	0.19	Yes[g]
	(4_s+2_a)[k] or (4_a+2_s)[k]	−0.28	No		(8_s+2_a) or (8_a+2_s)	−0.30	No
C	Disrotatory	0.25	Yes[c]	H	(14_a+2_s)	0.08	Yes[h]
	Conrotatory	−0.71	No		(14_a+2_a) or (14_s+2_s)	0.00	No
D	Disrotatory	0.23	Yes[d]	I	Disrotatory-disrotatory	0.25	Yes[i]
	Conrotatory	−0.52	No		Conrotatory-disrotatory[k]	0.28	No
E	Conrotatory	0.06	Yes[e]	J	Conrotatory-disrotatory	0.40	Yes[j]
	Disrotatory	−0.18	No		Disrotatory-disrotatory	−0.47	No

a) During the reaction two bonds are simultaneously formed, one bond between C_1 and C_3, and the other bond between C_2 and C_6: G. S. Hammond, N. J. Turro, and R. S. H. Liu, *J. Org. Chem.*, **28**, 3297 (1963); G. S. Hammond and R. S. H. Liu, *J. Am. Chem. Soc.*, **85**, 477 (1963). b) During the reaction two bonds are simultaneously formed, one bond between C_1 and C_5 and the other bond between C_2 and C_8: R. Criegee and R. Askani, *Angew. Chem., Int. Ed. Engl.*, **7**, 537 (1968). c) S. Masamune, S. Tanaka, and R. T. Seidner, *J. Am. Chem. Soc.*, **91**, 7769 (1969). d) S. Masamune and R. T. Seidner, *J. Chem. Soc., Chem. Commun.*, **1969**, 542. e) K. A. Muszkat and E. Fisher, *J. Chem. Soc. B*, **1967**, 662; F. B. Mallory, C. S. Wood, and J. T. Gordon, *J. Am. Chem. Soc.*, **86**, 3094 (1964). f) K. Houk, Dissertation, Harvard University (1968). See also Ref. 13. g) R_1=—$COOCH_3$: A. Galbraith, T. Small, R. A. Barnes, and V. Boekelheide, *J. Am. Chem. Soc.*, **83**, 453 (1961). h) R_2=—CN: W. von E. Doering, cited in Ref. 13. i) During the reaction two bonds, a and b, are simultaneously broken: T. J. Katz, E. J.Wang, and N. Acton, *J. Am. Chem. Soc.*, **93**, 3782 (1971); Ref. 16. j) During the reaction two bonds, a and b, are simultaneously broken: G. L. Closs and P. E. Pfeiffer, *J. Am. Chem. Soc.*, **90**, 2452 (1958); H. M. Frey and I. D. R. Stevens, *Trans. Faraday Soc.*, **61**, 90 (1969); R. Srinivasan, A. A. Levi, and I. Haller, *J. Phys Chem.*, **69**, 1775 (1965); Ref. 16. k) Heavy steric hindrance does not allow this reaction path, either.



The conformation of the product shown in each of these chemical equations is the one obtained from the allowed reaction path.

actual transition state of a pericyclic reaction must be more aromatic, or less antiaromatic, than the reactants and any other transition state imaginable in an equivalent electronic state. This trend appears to be justified by the view that a more aromatic state might more easily be reached in the course of the reaction. All the pericyclic reactions investigated can be explained in this manner.

Therefore, the definitive rule found above for pericyclic reactions with a monocyclic transition state must neccessarily be modified to include all kinds of pericyclic reactions as follows: Pericyclic reactions, both thermal and photochemical, take place *via* more aromatic transition states than the reactants. In the case of pericyclic reactions with a monocyclic transition state, the RED agrees exactly with the resonance energy of the transition state.

Above all, it should be noted that, on the basis of the present approach, we can avoid a certain ambiguity encountered in applying the Woodward-Hoffmann rules to pericyclic reactions with a polycyclic transition state. For example, the fact that the conversion of benzvalene to benzene is thermally allowed in a disrotatory-disrotatory manner (Reaction I in Table 2), whereas the same stereochemical conversion of bicyclobutane to butadiene is thermally forbidden (Reaction J in Table 2), cannot be explained in terms of orbital correlations between reactants and products.[16]

This problem can, in principle, be solved by means of the present aromaticity-based theory. The reason for the occurrence of the former reaction is that the resonance energy of the transition state, which is something like tricyclo[3.1.0.$0^{4,6}$]hexatriene, is positive. On the contray, the resonance energy of a transition state for the latter reaction, which is something like propalene, is negative. They are 0.253 and -0.473 respectively in units of β. Since the reactants for both reactions are nonaromatic, the RED for only the former reaction is positive. In agreement with a suggestion of Dewar and Kirschner,[16] a double bond in benzvalene obviously plays a significant role in determining both the aromaticity of the transition state and the allowedness of this reaction.

In this context, one comment must be made here. A thermal conrotatory-disrotatory conversion of benzvalene to benzene (Ia) can also be predicted to have a positive RED value (see Table 2). Unfortunately, this value is considerably larger than that for a thermal disrotatory-disrotatory conversion of the same compound (Ib). However, heavy steric hindrance forbids the occurrence of the former reaction (*i.e.*, Ia). It goes without saying that the steric effect is one of the crucial factors in determining the allowedness of any pericyclic reaction.

Apart from the steric effect, the suspicion that an actual reaction may not follow a reaction path with the maximum RED value seems to be related to a fault in the HMO model, rather than to one in the present approach to pericyclic reactions. According to our simplest HMO model, the energy of the transition state for Ia is estimated to be larger than that for Ib. This difficulty can be overcome simply by improving the HMO model so as to reproduce the actual transition states for both reactions (*i.e.*, Ia and Ib). Because any actual reaction occurs along the lowest-energy path, an actual transition state for Ib should be energetically lower than that for Ia. Logically, the RED for Ib is larger than that for Ia. For such a reason, the slight inconsistency found in Table 2 should be ascribed to a rather incomplete HMO model, in which bond alternation and the like are not taken into consideration.

Concluding Remarks

We now feel confident that the degree of aromaticity in a conjugated transition state is an important factor in determining the allowedness of pericyclic reactions. We might safely conclude that pericyclic reactions with the largest RED occur only thermally or photochemically, depending upon the electronic state concerned. It goes without saying that a heavy steric hindrance may forbid an electronically-allowed reaction. It is clear that the present approach complements and completes the aromaticity-based theory of pericyclic reactions, originally proposed by Dewar[14] and Zimmerman.[15] From this standpoint, the new concept of the aromaticity of the excited-state species also seems to have been explained fairly well, although it is not easy to estimate this aromaticity experimentally. The introduction of actual bond alternation would obviously improve the value of the RED as a reactivity index.[3]

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