Ruedenberg Bond Order as True Resonance-Theoretic Bond Order

Makoto ISIHARA

(Received May 31, 1996)

Abstract

This paper describes a few basic characteristics of Ruedenberg bond order from both resonance-theoretic and molecular-orbital-theoretic aspects and manifests its usefulness and validity through illustrative bond order analysis of several regular alternants containing $4n$-membered rings. Ruedenberg bond order is shown to be related with resonance structures exactly and to be regared as distributed valence which can be not only fractional but also negative or larger than unity in sharp contrast with Pauling bond order. It is pointed out that Ruedenberg bond order can reflect reactivity-stability characters of regular alternants more sensitively than Coulson bond order, having a close connection to the frontier orbital bond order. Behaviors of Ruedenberg and Pauling bond orders are compared in regular alternants containing $4n$-membered rings and Pauling bond order is concluded to be a superfluous concept.

1. Introduction

Bond orders are the most useful concept for analyzing bonding characters between sites and, therefore, often helpful for considering reactivities and stabilities of systems semiquantitatively or, at least, qualitatively. Bond order analysis can be a handy desk tool for chemists because of its great simplicity. The following three kinds of bond orders are well-known.[1)]

Let c_{jr} and λ_j be, respectively, the site-r component of the j-th eigenvector and its eigenvalue of the adjacency matrix A of a simple Hückel system. From a molecular-orbital-theoretic standpoint, Coulson has defined the bond order p_{rs} between sites r and s as [2)]

$$p_{rs} = \sum_j n_j c_{jr} c_{js} \qquad (r \neq s), \tag{1}$$

where n_j is the occupation number of the j-th eigenvector. Possible values for n_j are,

naturally, 0, 1, and 2. Coulson bond order, abbreviated to CBO below, has a clear theoretical ground and can be defined for any state of any Hückel system. CBO has been used most widely and most frequently.

On the other hand, from a resonance-theoretic standpoint, Pauling has introduced another kind of bond orders for systems having Kekulé structures. Let K be the number of Kekulé structures of a system and let $K(rs)$ be that of Kekulé structures having a bond between sites r and s. Then, Pauling bond order, abbreviated to PBO below, is defined for adjacent site pairs as [3]

$$k_{rs} = K(rs)/K \qquad (rs \text{ adjacent}). \tag{2}$$

PBO inherently assumes normal states.[4] Some correlation has been found between PBO and CBO in benzenoids empirically, though the correlation is not very tight.[5]

The third kind of bond orders, originating with Ruedenberg,[6] is again molecular-orbital-theoretic in its definition but actually resonance-theoretic in its behavior. Ruedenberg bond order, abbreviated to RBO below, is defined as

$$v_{rs} = \sum_j n_j c_{jr} c_{js} / \lambda_j \qquad (r \neq s). \tag{3}$$

This definition is valid for any state of any regular system, that is, any system having no nonbonding orbital. In particular, for normal states of regular alternants, n_j is two for each orbital j of positive λ_j and vanishes otherwise. Then, v_{rs} is simply the rs component of A^{-1}; furthermore, we have[5,7]

$$v_{rs} = k_{rs} \qquad (rs \text{ adjacent}) \tag{4}$$

for what we call benzenoids.[8] This remarkable fact seems to have led to a misleading interpretation that RBO is merely a molecular-orbital-theoretic expression of PBO. Presumably because of this and because of great success and prevalence of molecular orbital theory, RBO has drawn no practical attention in spite of its own significance.

In what follows, let us confine ourselves to normal states throughout. Exactly speaking, we have the above-mentioned equality between RBO and PBO for regular alternants containing no $4n$-membered ring, which are tentatively termed canonical alternants for convenience sake. This paper aims to clarify a few basic characteristics of RBO and to manifest its usefulness and validity by examining behaviors of RBO in noncanonical regular alternants.[9]

2. Characteristics of RBO

In even alternants consisting of m starred and m unstarred sites, we can introduce the resonance structure parity to $m!$ resonance structures having m bonds all between starred and unstarred sites by using the parity of permutations of the symmetric group of degree m.[10] Dewar structures can be defined as resonance structures that have $m-1$ adjacent bonds and one nonadjacent bond between starred and unstarred sites. It is convenient to refer to Dewar structures having a nonadjacent bond between sites r and s as rs-Dewar structures and to Kekulé structures having a bond between sites r and s as rs-Kekulé structures. Let K_η be the number of Kekulé structures of parity η and let $J_\eta(rs)$ be that of rs-Kekulé or rs-Dewar structures of parity η for pair rs of starred and unstarred sites and be zero for pair rs of starred or unstarred sites. Then, for regular alternants,[11] we can prove

$$v_{rs} = (J_+(rs) - J_-(rs)) / (K_+ - K_-). \tag{5}$$

See Appendix for some details of derivation. Note that the parity of rs-Kekulé or rs-Dewar structures in the numerator is determined on the same base as that of Kekulé structures in the denominator.[8,12] By appropriate numbering of sites, we can always set the denominator to be positive but, then, it is possible for the numerator to be negative or larger than the denominator.

If all Kekulé structures of a regular alternant have an identical parity, we can set $J_-(rs)$ for adjacent site pair rs to vanish as well as K_- and can identify v_{rs} with k_{rs}. However, even in canonical alternants, we have to take the resonance structure parity into account to calculate v_{rs} for nonadjacent pair rs of starred and unstarred sites.[13] Though the parity-dependent enumeration of Kekulé and Dewar structures provides a plain way of calculating A^{-1} for moderate systems, this is merely technical and may be secondary. It is important that RBO is related with Kekulé and Dewar structures in a simple, exact way and, in particular, that contributions from resonance structures of different parities interfere with each other in RBO.

Let N_r denote the set of sites adjacent to site r. For alternants having Kekulé structures, since we have

$$\sum_{s \in N_r} K(rs) = K, \tag{6}$$

it follows that

$$\sum_{s \in N_r} k_{rs} = 1. \tag{7}$$

Interpreting this as if the unit valence of a site is distributed to its bondings with adjacent sites, we can regard PBO as distributed valence. Naturally, PBO lies between zero and unity. On the other hand, from

$$AA^{-1} = I \tag{8}$$

it also follows for regular alternants that

$$\sum_{s \in N_r} v_{rs} = 1 \tag{9}$$

and RBO between adjacent sites can be regarded as distributed valence as PBO. However, RBO can be not only fractional but also negative or larger than unity in sharp contrast with PBO. Appearing in many noncanonical regular alternants, negative distributed valence peculiar to RBO is not exceptional at all.

In RBO the contribution $c_{jr}c_{js}$ from occupied orbital j is weighted by the factor $1/\lambda_j$, as is obvious from the original definition. Namely, RBO puts greater stress on contributions from shallower orbitals, compared with CBO. Because shallower orbitals affect chemical reactivities more strongly, RBO can reflect reactivity-stability characters of regular alternants more sensitively than CBO.[14] The roughest one-term approximation of v_{rs} is the partial RBO v'_{rs} of the highest occupied orbital h,

$$v'_{rs} = 2c_{hr}c_{hs}/\lambda_h, \tag{10}$$

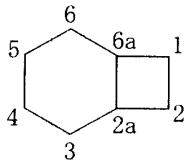
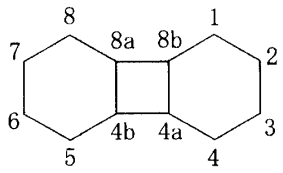
which is proportional to

$$f_{rs} = 2c_{hr}c_{hs} \tag{11}$$

in a given system. This quantity is nothing other than the partial bond order of the frontier orbital. Actually, since we can obtain v_{rs} without solving the eigenvalue problem of A and the evaluation of v_{rs} is much easier than that of v'_{rs} or f_{rs} in general, the one-term approximation has no practical value at all. It is helpful, however, for understanding a nature of RBO.

Exemplary comparisons of RBO with other bond order quantities are shown in Table 1 for cyclobutabenzene and biphenylene.[15] There exists qualitative resemblance between v_{rs}, v'_{rs}, f_{rs}, and p_{rs}, while k_{rs} is rather contrary to the others in a few respects.

Table 1. Bond Order Quantities in Noncanonical Regular Alternants

System Numbering	r s	v_{rs}	v'_{rs}	f_{rs}	p_{rs}	k_{rs}
Cyclobutabenzene	1 2	2	0.8931	0.2343	0.8975	2/3
	2 2a	−1	−0.6588	−0.1728	0.2149	1/3
	2a3	1	0.3003	0.0788	0.7285	1/3
	3 4	0	−0.2516	−0.0660	0.5626	2/3
	4 5	1	0.3411	0.0895	0.7315	1/3
	6a2a	1	0.4859	0.1275	0.5498	1/3
Biphenylene	1 2	1/3	−0.1089	−0.0485	0.6208	3/5
	2 3	2/3	0.1962	0.0873	0.6907	2/5
	4 4a	2/3	0.1358	0.0604	0.6830	2/5
	4a4b	−1/3	−0.3051	−0.1358	0.2634	1/5
	8b4a	2/3	0.3051	0.1358	0.5648	2/5

3. RBO Analysis of Noncanonical Regular Alternants

This section provides a few examples of applications of RBO analysis. The examples deal mostly with noncanonical regular alternants, where RBO differs from PBO necessarily and comparison between them is possible.

The first example concerns electronic structures of two-ring ortho-condensed systems composed of 4- and 8-membered rings, cyclobutacyclobutene, cyclobutacyclooctene, and cyclooctacyclooctene. These systems have RBOs quite different from PBOs as shown in Fig. 1. The most remarkable fact is that negative RBOs appear on the bridging σ-bonds. This fact seems to be related with Hückel's rule. The three systems have $4n$+2 sites in their perimeters and it is reasonable to infer that the systems tend to resemble the corresponding cyclic systems of $4n$+2 sites in electronic structure.[16] The degree of delocalization in the perimeters is not so complete as that in [$4n$+2]-annulenes but similar to that in linear polyenes. On the other hand, PBO analysis suggests greatly

delocalized electronic structures, the degree of delocalization being as large as that in naphthalene. This clearly contradicts real instabilities of the systems. For reference, Fig. 2 shows RBOs of linear polyenes, [4*n*+2]-annulenes, and naphthalene.

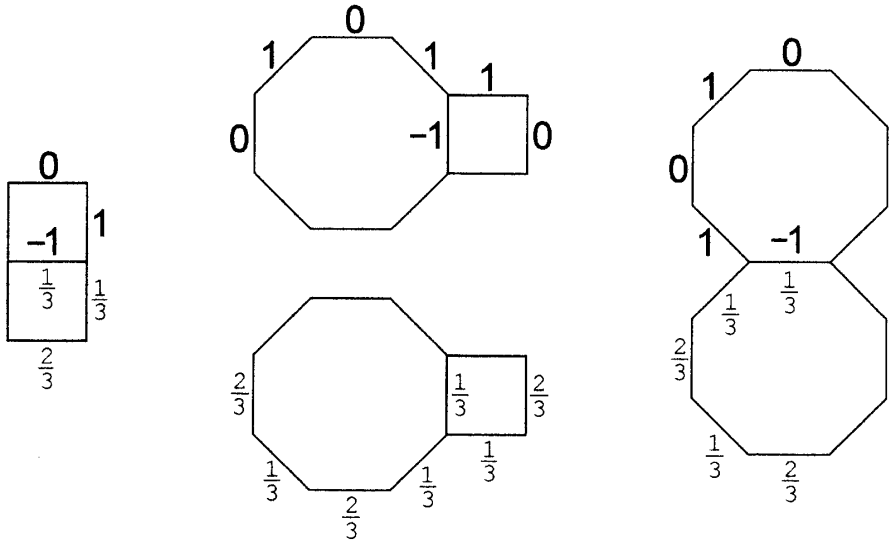


Fig. 1. RBOs and PBOs of ortho-condensed 4- and 8-membered rings. RBOs are bold-faced.

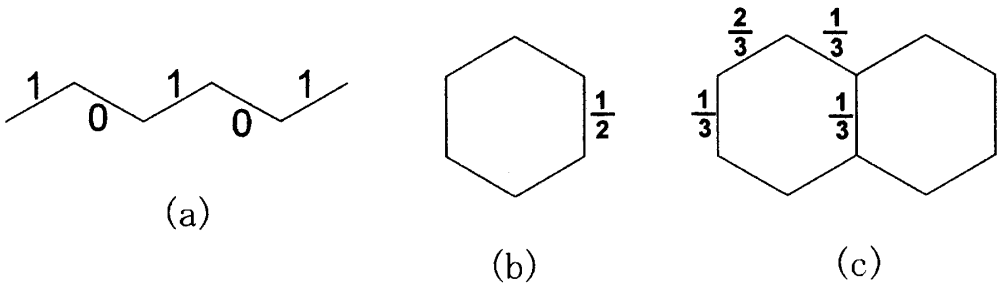


Fig. 2. RBOs of (a) linear polyenes, (b) [4*n*+2]-annulenes, and (c) naphthalene.

The second example makes a comparison of biphenyl, biphenylene, and triphenylene. These systems can be regarded as composite systems of interacting benzene subsystems. The bond order on the σ-bond connecting benzene subsystems is considered to represent a feature of intersubsystem interaction. From RBOs shown in Fig. 3, we can infer that the order of strength of intersubsystem interaction is triphenylene > biphenylene > biphenyl but that benzene subsystems interact antibondingly in biphenylene. This accords with the fact that the stabilization energy of biphenylene is small.[17] Moreover,

RBO analysis suggests that the delocalization in the benzene subsystems of biphenylene is rather opposite to that of naphthalene. This is consistent with the well-known experimental fact that the most reactive is position 1 in naphthalene but position 2 in biphenylene.[18] Though PBO analysis leads to the same order of strength of intersubsystem interaction as RBO analysis, PBO of biphenylene suggests a naphthalene-like electronic structure, which clearly contradicts the experimental facts mentioned above.

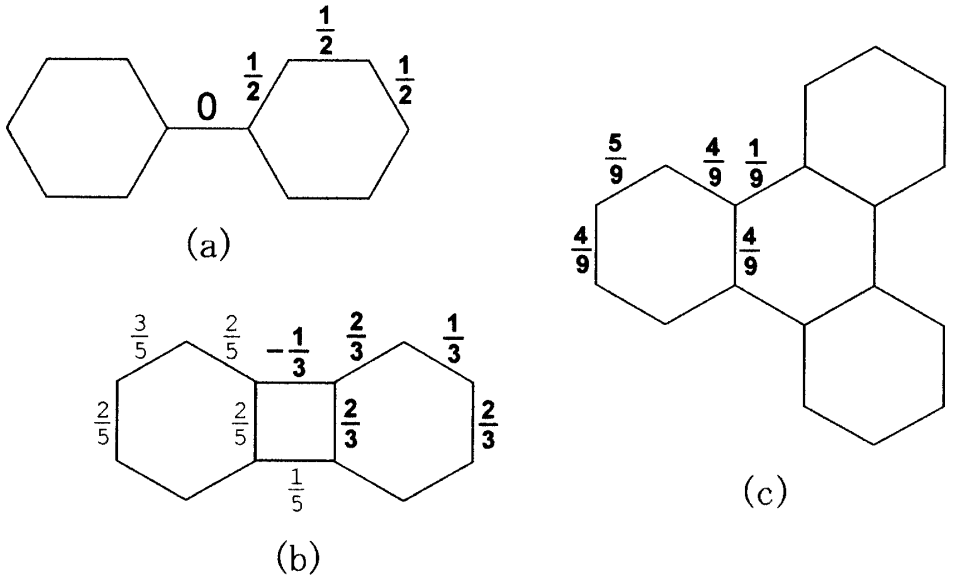


Fig. 3. RBOs and PBOs of (a) biphenyl, (b) biphenylene, and (c) triphenylene. RBOs are bold-faced; PBO is identical with RBO for (a) and (c).

As the last example, let us treat the problem on stabilities of biphenylene and its isomers, cyclobuta[a]naphthalene and cyclobuta[b]naphthalene. This problem has been taken first by Coulson and Poole [19] and next by Wilcox.[20] The correct order of stability, biphenylene > cyclobuta[b]naphthalene > cyclobuta[a]naphthalene, can be obtained by the comparison of the algebraic structure count and by Hückel orbital theory but cannot by the comparison of the number of Kekulé structures.[19-21] Figure 4 shows RBOs and PBOs of cyclobutanaphthalenes. For biphenylene see Fig. 3(b) again. What should be noted is the negative RBOs and the large positive RBO on the cyclobutadiene rings. From the degree of antibonding interaction and that of bond fixation indicated by these RBOs, we can clearly obtain the correct order of stability. PBO analysis provides

spurious smooth delocalizations for all and fails as the comparison of the number of Kekulé structures. Although comparisons of the algebraic structure count may succeed to predict the order of stability, it is possible or rather probable for RBO analysis to elucidate some "reason" for it.

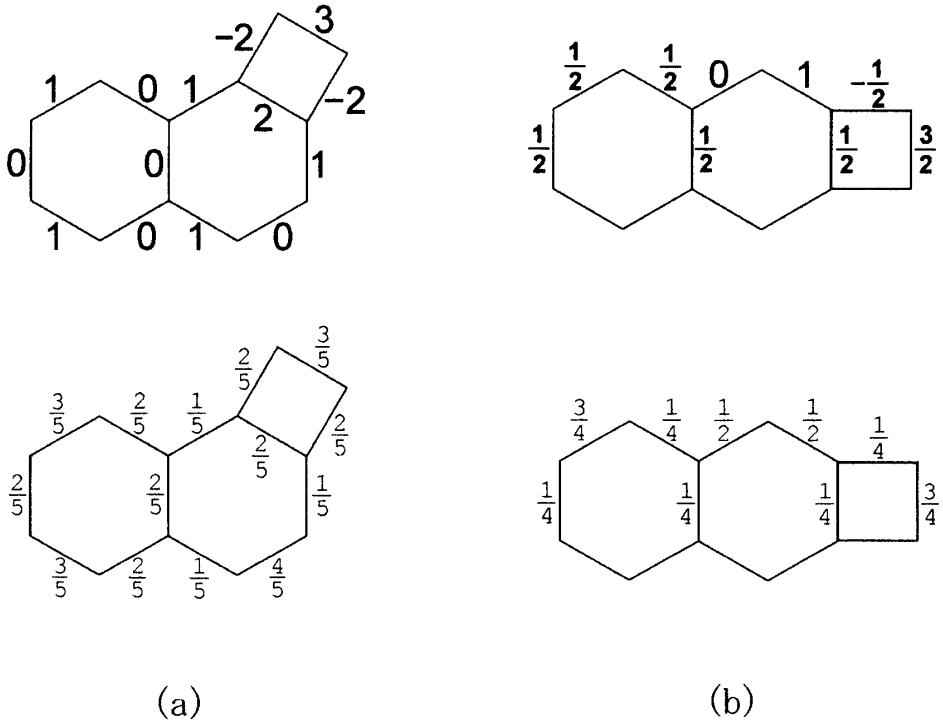


Fig. 4. RBOs and PBOs of (a) cyclobuta[a]naphthalene and (b) cyclobuta[b]naphthalene. RBOs are bold-faced.

4. Concluding Remarks

RBO for normal states is a simple quantity related directly to adjacency of sites and can be evaluated quite easily. Still, it has sound characteristics appropriate for analyzing bonding characters between sites. In particular, RBO analysis is expected to provide some essential information on peculiar electronic structures of noncanonical regular alternants, as illustrated in the preceding section.

It is now evident that PBO cannot represent any real situation of electronic structures at all in noncanonical regular alternants. Delocalized electronic structures suggested by PBO in noncanonical regular alternants are a consequence of neglecting the parity of

Kekulé structures and are necessarily spurious. PBO works well only when it coincides with RBO. We have to say that it was purely fortunate for PBO that all Kekuké structures have an identical parity in benzenoids. Even for benzenoids, of course, we must introduce the resonance structure parity for extending "PBO" to nonadjacent site pairs. Thus the concept of PBO is concluded to be superfluous. RBO is true resonance-theoretic bond order.

Appendix

Consider a regular alternant of $2m$ sites. Numbering the starred and the unstarred sites from 1 to m and from m+1 to $2m$, respectively, we can write A and A^{-1} as

$$A = \begin{pmatrix} 0 & B \\ {}^{t}B & 0 \end{pmatrix} \tag{A1}$$

and

$$A^{-1} = \begin{pmatrix} 0 & {}^{t}B^{-1} \\ B^{-1} & 0 \end{pmatrix} \tag{A2}$$

with the half-size submatrix B whose rs component b_{rs} is the r, s+m component of A. Obviously, v_{rs} vanishes for pair rs of starred or unstarred sites. Denote the set $\{1, \cdots, m\}$ and $\{m+1, \cdots, 2m\}$ of natural numbers by M and L, respectively, and designate s–m as $\tilde{s}$ for $s \in L$. Then, since A^{-1} is real-symmetric, we have

$$v_{rs} = \mathrm{cof}\,|\,B(r\tilde{s})\,|\,/\det|\,B\,| \qquad (r \in M, s \in L), \tag{A3}$$

where $\mathrm{cof}\,|\,B(r\tilde{s})\,|$ stands for the cofactor of $b_{r\tilde{s}}$ in B.

Let S be the symmetric group of degree m and indicate the parity of permutation x by sign η_x. Because each permutation of S corresponds uniquely to a resonance structure having m bonds all between starred and unstarred sites, we can define the parity of such a resonance structure by the sign of the corresponding permutation. Let T be the subset of all permutations corresponding to Kekulé structures in S. Each summand in the right-hand side of

$$\det|\,B\,| = \sum_{x \in S} \eta_x \prod_{t \in M} b_{t,xt} \tag{A4}$$

survives only when all $b_{t,xt}$ for given x are equal to unity, so that we have

$$\det|\,B\,| = \sum_{x \in T} \eta_x = K_+ - K_-. \tag{A5}$$

The numerator can be treated likewise. Let $S(r\tilde{s})$ be the subset of all permutations mapping r to $\tilde{s}$ in S and let $T(r\tilde{s})$ be the subset of all permutations corresponding to rs-Kekulé or rs-Dewar structures in $S(r\tilde{s})$. Since $\mathrm{cof}\,|\,B(r\tilde{s})\,|$ is the coefficient of $b_{r\tilde{s}}$ in the expansion of $\det|\,B\,|$, namely,

$$\mathrm{cof}\,|B(r\tilde{s})| = \sum_{x \in S(r\tilde{s})} \eta_x \prod_{\substack{t \in M \\ t \neq r}} b_{t,xt}, \tag{A6}$$

it follows that

$$\mathrm{cof}\,|B(r\tilde{s})| = \sum_{x \in T(r\tilde{s})} \eta_x = J_+(rs) - J_-(rs). \tag{A7}$$

References and Notes

1) Besides the three, for example, we have the topological bond order, which is strongly correlated with Coulson bond order; R. E. Merrifield and H. E. Simons, "Topological Methods in Chemistry," John Wiley and Sons, Inc., New York (1989), pp.112, 136.
2) C. A. Coulson, *Proc. R. Soc. London Ser. A*, **169**, 413 (1939).
3) L. Pauling, "The Nature of the Chemical Bond," Cornell University Press, Ithaca, New York (1940), p. 142.
4) Normal states mean m-electron ground states of m-site systems.
5) N. S. Ham and K. Ruedenberg, *J. Chem. Phys.*, **29**, 1215 (1958).
6) K. Ruedenberg, *J. Chem. Phys.*, **22**, 1878 (1954).
7) N. S. Ham, *J. Chem. Phys.*, **29**, 1229 (1958).
8) D. Cvetković, I. Gutman, and N. Trinajstić, *J. Chem. Phys.*, **61**, 2700 (1974).
9) Ham has mentioned to even alternant nonbenzenoids as an example of nonregular (K_+=K_-) systems in Ref. 7. He seems to have paid no attention to regular nonbenzenoids.
10) M. J. S. Dewar and H. C. Longuet-Higgins, *Proc. R. Soc. London Ser. A*, **214**, 482 (1952).
11) The number of starred sites and that of unstarred are necessarily identical in regular alternants.
12) If one proceeds to the Kekulé structure enumeration within subsystems obtained by deleting a pair of starred and unstarred sites, the sign determination becomes rather complicated.
13) E. Heilbronner, *Helv. Chem. Acta*, **45**, 1722 (1962).
14) RBO is closely connected to superdelocalizability conceptually and can be regarded as bond superdelocalizability; K. Fukui, A. Imamura, T. Yonezawa, and C. Nagata, *Bull. Chem. Soc. Jpn.*, **34**, 1076 (1961).
15) C. A. Coulson and A. Streitwieser Jr., "Dictionary of π-Electron Calculations," Pergamon, Oxford (1965), pp. 88-89.
16) Not that the systems are sufficiently stabilized by this tendency; J. D. Roberts, A. Streitwieser Jr., and C. M. Regan, *J. Amer. Chem. Soc.*, **74**, 4579 (1952).
17) The stabilization energy of biphenylene is almost ascribable to that of the two benzene parts.
18) W. Baker, J. W. Barton, and J. F. W. McOmie, *J. Chem. Soc.*, **1958**, 2666.
19) C. A. Coulson and M. D. Poole, *Tetrahedron*, **20**, 1859 (1964).
20) C. F. Wilcox Jr., *Tetrahedron Lett.*, **1968**, 795.
21) N. Trinajstić, "Chemical Graph Theory," CRC Press, Boca Raton, Florida (1983), Vol. 2, pp. 36-38.