Stability of Multi-center Bonds in Inorganic Cluster Compounds

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An ideal multi-center bond is a bond in which three or more atomic orbitals of the same kind, each from a different atom, interact equally with each other. Since such a multi-center bond can be regarded as a cyclic conjugated system, the graph theory of aromaticity can be applied to it. It was then found that multi-center bonds are aromatically stabilized to a great extent. Most inorganic cluster compounds are polyhedral in shape. This might be rationalized by the fact that polyhedrons are favorable to a formation of a multi-center bond or the like at the core.

Boranes and metal carbonyl clusters were once regarded as obscure chemical rule-breakers because of their unfamiliar bonding patterns. During the last decade a great deal of effort has been devoted to an understanding of chemical bonds in such non-classical cluster compounds.1) The present-day situation can adequately be expressed by the following sentence: Gather any large group of inorganic chemists and they will start talking about metal clusters.2) Pauling also pointed out that the bonding principle of metal carbonyl clusters is one of the most important problems yet to be solved.3) In line with this, several skeletal electron-counting rules have been proposed as a theoretical basis for rationalizing the bonding pattern of cluster compounds.4–8) However, these rules rarely provide explicitly for a measure of stabilization of the molecular clusters. In this paper, I would like to stress that a multi-center bond formation might often play a significant role in stabilizing non-classical molecular clusters.

Theoretical

Consider a multi-center bonding system in which three or more atomic orbitals of the same kind, each belonging to a different atom, interact equally with each other. The simplest multi-center bond is a central three-center BBB bond, in which each of the three boron atoms interacts equally with the other two.9) When ten atomic orbitals interact in this manner to form a ten-center bond, its bonding pattern can be expressed as in Fig. 1. This is identical with a complete graph of degree ten, K_{10}, where the vertices indicate the atomic orbitals concerned. In general, a complete graph of degree n, K_n, is a graph in which each of the n vertices is connected to all the other vertices.10) A conjugated system of the type K_n gives only one bonding molecular orbital,8) the energy of which is equal to $(n-1)\beta$. All the other molecular orbitals are antibonding, and the energies are equal to $-\beta$. Therefore, any ideal multi-center bond has two bonding electrons with the bonding energy of $2(n-1)\beta$.

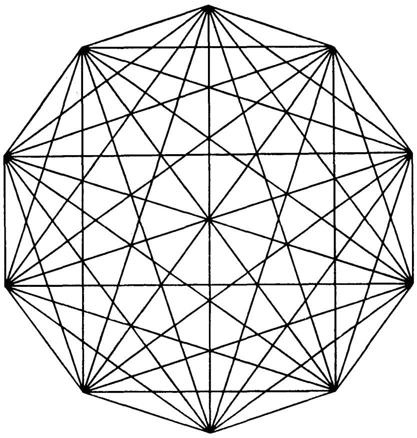


Fig. 1. A complete graph of degree ten, K_{10}.

TABLE 1. RESONANCE ENERGIES OF K_n-TYPE BONDING SYSTEMS

n	SC	RE/β	$\%RE$
3	3	0.536	15.5
4	3	1.331	28.5
5	15	2.286	39.6
6	15	3.351	50.4
7	105	4.499	60.0
8	105	5.711	68.9
9	945	6.975	77.3
10	945	8.281	85.2
11	10395	9.624	92.8
12	10395	10.998	100.0

In order to estimate stabilities of such multi-center bonding systems, it is instructive to examine the resonance energies calculated by means of the graph theory of aromaticity.11) Resonance energies calculated for a series of K_n-type conjugated systems12) are listed in Table 1. This type of resonance energy has been interpreted as an extra stabilization energy due to aromaticity.11)

Results and Discussion

First of all, it is noteworthy that the resonance energy of any K_n-type bonding system is positive, indicating its aromaticity. The resonance energy (RE) is proportional to the logarithm of the Kekulé structure count (SC), *i.e.*, the number of Kekulé structures allowed for K_n. An analogous feature of resonance energies has already been reported for benzenoid hydrocarbons13) and polyhedral boranes.14) However, the situation is somewhat different from that for these compounds. As shown in Fig. 2, a correlation line for K_n with $n=2m-1$ obviously deviates downward from that for K_n with $n=2m$. Here, m is an arbitrary integer. For K_{2m}-type bonding systems

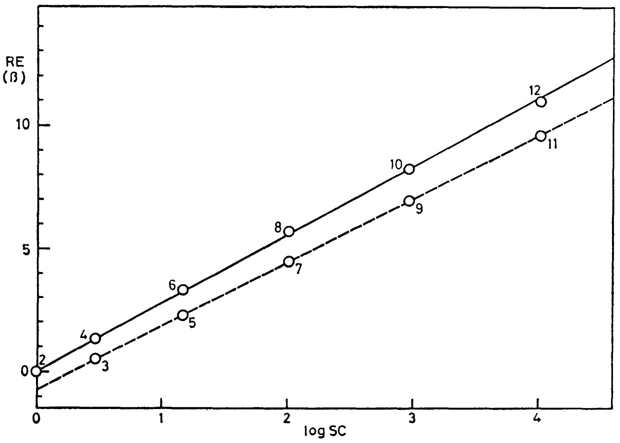


Fig. 2. *SC* Dependence of resonance energy for a series of K_n-type bonding systems.

$$RE = 2.768 \log SC, \tag{1}$$

and for K_{2m-1}-type bonding systems

$$RE = 2.573 \log SC - 0.710. \tag{2}$$

These relations hold well at least up to $m=6$.

One of the characteristics of such a multi-center bonding system is that its resonance energy is unusually large as compared with the energy of its olefinic reference structure, *i.e.*, the reference energy,[11] In order to see this aspect, a new quantity is defined as 100 times the resonance energy, divided by the reference energy, and it will be called the percent resonance energy (%*RE*). The %*RE* can be regarded as a practical index suitable for estimating aromatic stabilization of a conjugated system. The two largest %*RE*'s so far known among familiar compounds are 15.5 for a cyclopropenyl cation and 3.5 for benzene.[11] Note that a conjugated system of a cyclopropenyl cation is another example of a three-center bonding system.

In contrast to them, even for the next smallest multi-center bond, K_4, the %*RE* amounts to 28.5. The %*RE* increases as the degree of a complete graph increases. Such large %*RE* values cannot be imagined for any other kind of conjugated system. This means that a larger multi-center bonding system fixes itself more tightly, as long as the resonance integrals between the atomic orbitals remain almost unchanged.

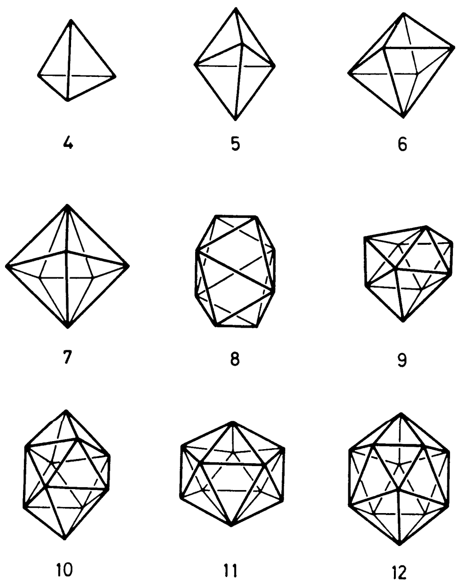
From the above energy consideration, we can fully expect the formation of bonding systems analogous to multi-center bonds in some way or other. When atoms M, each with an s-type atomic orbital, are employed for simplicity, molecular clusters with a general formula of $M_n{}^{n-2}$ can be constructed so as to form K_n-type conjugated systems. The simplest example is a triangular $H_3{}^+$ ion.[15] When the size of such a cluster increases, an increased excess ($n-2$) charge must be overcome either by some intramolecular balance or by the environment. In this sence, the realistic clusters of this type must be relatively small. The next promising species is of the type $M_4{}^{2+}$, where M is either an alkali or a coinage metal atom.

On the other hand, King and Rouvray presented a new bonding model of polyhedral systems, such as boranes $B_nH_n{}^{2-}$ and carboranes $B_{n-2}C_2H_n$.[8] According to it, the skeletal boron (or carbon) atom can be regarded as sp hybridized. The remaining two p orbitals, which are tangentially oriented with respect to the pseudo-polyhedron surface, are used for surface bonding. One sp hybrid orbital is used to bond the terminal hydrogen. The other sp hybrid orbital points radially in toward the center of the cluster. Such inward pointing sp hybrid orbitals emanating from all vertex atoms interact at the core of the polyhedral cluster. King and Rouvray assumed that the bonding pattern of these sp hybrid orbitals can roughly be represented by a complete graph.[8] In other words, all the inward pointing sp hybrid orbitals form a single multi-center bonding orbital with two electrons.

In a previous paper,[14] I calculated resonance energies of polyhedral boranes on the basis of the Kettle-Tomlinson bonding model,[16] in which borane molecular orbitals are depicted as a linear combination of localized three-center BBB bonding orbitals. The resonance energy obtained for every borane correlated well with the energy separation between the lowest unoccupied molecular orbital (LUMO) and the highest occupied molecular orbital (HOMO). We must, however, say that these resonance energies reflect primarily the stability of the surface bonding of the cluster because both LUMO and HOMO belong mostly to the surface bonding[1] and because the Kettle-Tomlinson model cannot fully express the multi-center bonding at the core of the cluster.[16] The weight of a core bonding system is obviously underestimated in this model.

On the contrary, the most distinct aspect of the King-Rouvray model is that a K_n-type core bonding system is factored out from an entire molecular cluster.[8] In accord with this, it has been shown that the core bonding can be factored out with some precautions to obtain an approximate picture of the valence structure.[17] Therefore, this model can be considered as a complement to the Kettle-Tomlinson model. The core bonding system is totally symmetric, and hence constitutes the lowest molecular orbital in a molecular cluster. It is often much lower in energy than the second lowest orbital.[18] Consequently, it naturally follows that, even if an actual core bonding system deviates more or less from a complete graph,[19] it should still contribute much to the stability of an entire cluster compound because an ideal multi-center core bonding orbital has both the largest bonding energy in the cluster and quite a large %*RE* value. This view is consistent, at least, with synthetic accessibility to many polyhedral boranes and metal carbonyl clusters and their stability. In these compounds, the overall charge which a cluster bears is generally small because most of the excess ($n-2$) charge due to the K_n-type core bonding is cancelled by the polyhedral surface bonding.[8]

Conversely, we might safely say that an inorganic compound often tends to become polyhedral in shape so as to form a K_n-like core bonding system. This gives the major reason why shapes of most inorganic cage compounds are polyhedrons or polyhedral fragments. A multi-center bond formation thus appears to be one of the most workable ways to stability. Figure 3 shows typical shapes of polyhedral compounds (*e.g.*, closo-



iFg. 3. Shapes of typical polyhedral compounds.

boranes) which contain such multi-center core bonding systems. The number given below each polyhedron indicates the degree of a complete graph related to the core bonding,[19] and this is equal to the number of vertices of the polyhedron.

The present approach thus provides a convenient rationale for the existence and stability of polyhedral non-classical compounds, although it is simple and based on approximate bonding models. It goes without saying that the surface bonding may modify the degree of stability of an entire conjugated system to some extent. Considering that a surface bonding system is often a network of three-center bonds,[16] I feel confident that the concept of a multi-center bond is in some way essential to the stability consideration of not only homopolyatomic clusters formed by the s-like atomic orbitals but also general inorganic cage compounds including mixed clusters.[1]

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19) When the size of a molecular cluster increases, the geometry of the core bonding system will necessarily deviate from that of a complete graph. The β values in it will then be diversified, the absolute values being decreased to a varying extent. Such modification of the core bonding system will somewhat diminish both the resonance energy and the %*RE*. This might be partially responsible for the fact that there are few polyhedral compounds which have more than eleven vertex atoms.[1]