

very similar to those for Pd.

Summing up, the BOC model calculations project that C-O bond cleavage occurs directly on Ni to produce carbidic carbon followed by progressive hydrogenation up to the formation of CH₄. There is no way to retain the C-O bond and form CH₃OH. By contrast, the assistance of hydrogen in C-O bond cleavage is critical for Pd (and Pt). Here, the C-O bond rupture is not likely to occur before methoxide CH₃O_s is formed, after which both decomposition to CH_{3,s} + O_s and hydrogenation to CH₃OH can proceed with similar activation barriers. These projections are in agreement with the selectivities observed experimentally for CO hydrogenation over Ni, Pd, and Pt.³³⁻⁴⁰

Concluding Remarks

The analytic BOC-MP model explicitly interrelates many seemingly disparate chemisorption phenomena, including surface reactivity, which reveals the essential "elephantness" of chemisorption. Let us stress again that the BOC-MP model is based on a few well-defined assumptions and within these assumptions, the model interrelations are rigorous and (for atomic chemisorption at the zero-coverage limit) even exact. Moreover, these interrelations are expressed in terms of observa-

bles only (the heats of chemisorption and various constants), which makes comparison with experiment direct and unambiguous. The latter is critical in developing any serious theoretical model, which should be falsifiable (in the Popperian sense), and the BOC-MP model is of this kind.

The scope of the BOC-MP modeling can be further extended to embrace, in principle, any aspect of chemisorption and surface reactivity, provided the model projections retain their rigor and simplicity. The latter is naturally more difficult to achieve the more complex the ad molecules become. But this job is worth trying. The chemical appeal of the BOC-MP model is that it is a truly "back-of-the-envelope" model, which can be directly used by the practitioners in the field.

This work began during my collaboration with the late Earl L. Muetterties. He strongly believed in the comprehensible chemical order in chemisorption and kept encouraging me to look for general analytic modeling. It is hard to express the depth of my gratitude to Earl. I wish to thank Roald Hoffmann, John T. Yates, Jr., Gerhard Ertl, Michel Boudart, Alexis T. Bell, Jay B. Benziger, Robert J. Madix, and Sylvia T. Ceyer for exciting discussions and illuminating comments. My special thanks are to Roger C. Baetzold, whose parallel work on theory of chemisorption gave me much insight.

Topological Control of the Structures of Molecules and Solids

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One of the challenges that often faces chemists is the organization and understanding of the enormous wealth of molecules and solids whose structures have been determined. Oftentimes there is a clear dependence of structure on electron count, observations that have led to the famous counting rules associated with the names of Hückel,¹ Walsh,² Sidgwick, Powell, Nyholm, and Gillespie,³ Woodward and Hoffmann,⁴ and Wade.⁵ Simple one-electron orbital methods have been extremely useful in constructing such models.⁶⁻⁸ The success of Hückel's rule in polyene chemistry, the one-electron molecular orbital model behind the Woodward-Hoffmann rules, and the utility of extended-Hückel ideas to probe the properties of molecules of all types are clear evidence that imaginative use of very simple molecular orbital ideas can help us understand large tracts of chemistry. In this Account we show that there is a simple idea, drawn from the field of topology, that unifies many of these orbital problems. It ties together observations from many different areas of chemistry and provides a larger window with which to look at molecular and solid-state structure.

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Some Structural Diversity

Figure 1 shows calculated energy difference curves^{9,10} as a function of the number of relevant electrons for ten different structural problems. They have been calculated by using the simplest possible one-electron molecular orbital modes. The Hückel method was employed for homoatomic systems, the angular overlap model was used for heteroatomic systems,⁶ and the Hückel implementation of tight-binding theory was employed for solids. In all cases the results of the calculation faithfully mimic the experimental observations. The most striking feature of this figure is that the curves are all extremely similar in shape but the examples as diverse as chemistry itself.

- (1) Hückel, E. *Z. Phys.* 1931, 60, 204; 1932, 72, 310; 1932, 76, 628.
- (2) Walsh, A. D. *J. Chem. Soc.* 1953, 2260, 2266, 2288, 2296, 2301, 2306.
- (3) (a) Also known as the VSEPR rules. (b) Gillespie, R. J.; Nyholm, R. S. *Q. Rev., Chem. Soc.* 1957, 11, 339. (c) Gillespie, R. J. *Molecular Geometry*; Van Nostrand-Rheinhold: London, 1972.
- (4) (a) Woodward, R. B.; Hoffmann, R. *J. Am. Chem. Soc.* 1965, 87, 395, 2046, 2511, 4389. (b) Woodward, R. B.; Hoffmann, R. *Acc. Chem. Res.* 1968, 1, 17.
- (5) Wade, K. *Adv. Inorg. Chem. Radiochem.* 1976, 18, 1.
- (6) Burdett, J. K. *Molecular Shapes*; Wiley: New York, 1980.
- (7) Hoffmann, R. *Science (Washington, D.C.)* 1981, 211, 995.
- (8) See, for example: Streitwieser, A. *Molecular Orbital Theory for Organic Chemists*; Wiley: New York, 1961.
- (9) Burdett, J. K. *Struct. Bonding (Berlin)* 1987, 65, 30.
- (10) (a) Rouvray, D. H.; King, R. B., eds. *Graph Theory and Topology in Chemistry*; Plenum: New York, 1987. (b) Burdett, J. K., in ref 10a.

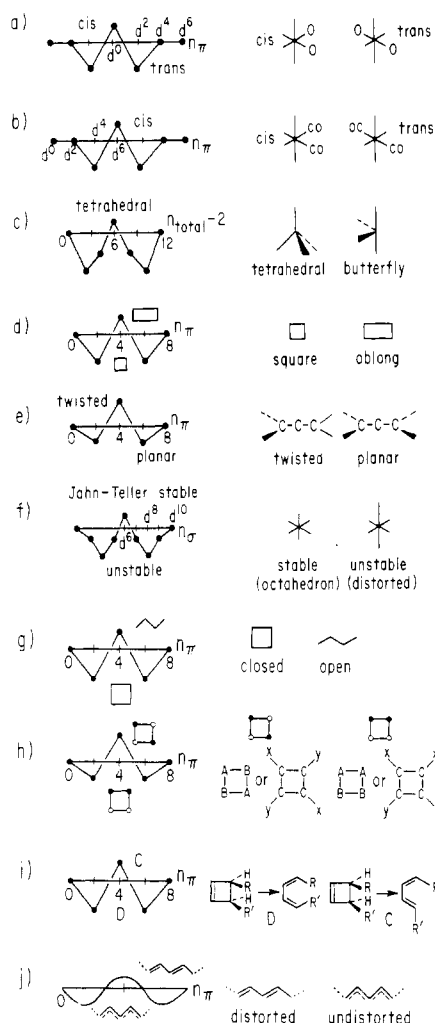


Figure 1. Energy difference diagrams as a function of electron count for ten structural problems. The units for the plots, which are not shown, are either Hückel β 's (for the homoatomic problems) or the e_λ and f_λ of the angular overlap model (for heteroatomic problems).

In Figure 1a *cis*-dioxides of transition metals are universally found for d^0 systems but the *trans* isomer is found for d^2 ; in Figure 1b *cis*-dicarbonyls are found for d^2 systems but the *trans* arrangement is found for d^4 , two results mimicked by our curves. These structural preferences are controlled by π bonding between the metal and ligands, and the electron count here is simply the number of π electrons. Since there are three metal $d\pi$ levels, for π donors the half-filled point comes at d^0 and the π manifold is full at d^6 . For π acceptors the half-filled point comes at d^6 , where all the metal-ligand π -bonding levels are full. Not all of the electron counts represented on the plots correspond to real chemical examples. In Figure 1a, for example, the lower electron counts would involve depletion of the oxide levels, and in Figure 1b electron counts higher than d^6 would populate the C–O π^* levels. However, as we shall see, it is the *shape* of the complete curve that we will find particularly interesting even though parts of it may correspond to chemically unrealistic situations.

The tetrahedral geometry of CH_4 with eight electrons is well-known, but with ten electrons the butterfly geometry of SF_4 is favored, as shown in Figure 1c, a result of course predicted by Nyholm and Gillespie's rules. (We actually plot here the variation with total number

of electrons minus two. The calculations employed only the p orbitals of the central atom and the hydrogen 1s orbitals, in the spirit of the Rundle–Pimentel approach.) In Figure 1d, cyclobutadiene with four π electrons distorts away from the square structure as expected on the basis of pseudo-Jahn–Teller ideas, but six- π -electron molecules such as Bi_4^{2-} and Se_4^{2+} are stable in this geometry. In Figure 1e the twisted geometry found for allene, $(\text{CH}_2)\text{C}(\text{CH}_2)$, with four π electrons is in accord with the van't Hoff rule, but with other electron counts the planar structure is suggested to be favored. Although there are, as yet, no molecules known with other electron counts, von Schleyer and co-workers¹¹ have shown by calculation that the planar structure is favored for the species $(\text{CH}_2)\text{C}(\text{CB}_2\text{H}_2)$ with two π electrons. The plot applies to inorganic examples too, although here the units become the e_π and f_π of the angular overlap model⁶ instead of the Hückel β . The molecule $\{[(\text{CH}_3)_3\text{Si}]_2\text{N}\}_2\text{Be}$, for example, isoelectronic with allene, has a BeN_2Si_4 skeleton that has the twisted geometry too.

Octahedral transition-metal complexes are Jahn–Teller unstable for the configurations d^7 , d^8 (low spin), and d^9 , but this geometry is stable for d^6 as reproduced by the calculation in Figure 1f. Here the orbital filling is of the metal–ligand σ orbitals. For d^8 (low spin) the effect is so large that no axial ligands are present, and all these molecules are square planar. Note that at this electronic configuration the amplitude of the plot is a maximum. In Figure 1g we show Hückel's $4n_\pi + 2$ rule applied to the four-membered ring. Relative to its open-chain analogue the square is stable for $n_\pi = 0$ (two π electrons) and $n_\pi = 1$ (six π electrons) but is unstable for four π electrons. In Figure 1h we see how to “color” the vertices of a symmetrical molecule to give *cis* and *trans* isomers. The ABAB pattern is stable at the half-filled point (as found in all known “push–pull” cyclobutadienes) but the AABB pattern is stable elsewhere. Figure 1i refers to the thermally allowed pathway for electrocyclic ring closure—the famous Woodward–Hoffmann rules. The mode of closure is predicted to depend on electron count, the result we would obtain by reworking the original ideas using orbital symmetry conservation. Finally, Figure 1j shows how a linear chain of atoms can distort via a Peierls distortion.¹² At the half-filled band the dimerization route is favored (as predicted, and found to occur in polyacetylene, $(\text{CH})_n$) but for other electron counts it is not. We have gone to some length to show a diverse collection of chemical examples whose energy difference curves with four nodes are so similar. At this point it is surely obvious that some overriding principle is at work here.

The Topological Link

The principle is in fact a topological one. All of these examples are built up from a variety of different orbitals, of s, p, and d type, involved in σ and π type interactions. The geometries of our examples are different too, which also makes them appear to have little in common. But, in terms of *how* the orbitals are linked together in the two molecules of each problem, the examples are very similar. Such considerations, associated

(11) Krogh-Jespersen, K.; Cremer, D.; Poppinger, D.; Pople, J. A.; Schleyer, P. v. R.; Chandrasekhar, J. *J. Am. Chem. Soc.* 1979, 101, 4843.

(12) Albright, T. A.; Burdett, J. K.; Whangbo, M.-H. *Orbital Interactions in Chemistry*; Wiley: New York, 1985.

Molecule	Type of Walk	Number	Total
		6	6
		6	
		12	18
		4	
		2	6
		8	
		4	
		2	14

Figure 2. Returning walks of length two and four in open-chain and branched four-atom molecules.

with the connectivity of the orbital problem, have traditionally lain in the domain of graph theory¹³ and topology. Over the years many interesting correlations between physical properties and molecular shape have been derived.¹⁴

But how do we define shape? This question has been tackled in several ways but one answer, of interest to us here, is by the definition of topological indices of various types. One particular index (and there are indeed many others) involves the generation of the number of self-returning walks^{13,15} as shown in Figure 2. The spatial complexity of the molecule can be described by counting the number of paths that meander through the molecule along the "bonds" and eventually, after m steps, return to the atom we started on. Notice that the branched molecule has a larger number of returning four-walks than the unbranched one, even though the number of returning walks of length two are the same in the two systems. There is a nice correlation between such indices and properties such as the melting and boiling points of organic hydrocarbons using this result.¹⁵ This is all very well, but how do we relate such a foreign concept to the traditional ideas of the chemist, centered around molecular orbital diagrams and concerning not only the details of the energy level pattern but how and why they go up and down in energy on distortion or substitution.

In fact there is a very powerful technique, the method of moments, that provides a direct link between such

(13) Trinajstić, N. *Chemical Graph Theory*; CRC: Boca Raton, FL, 1983; Vols. I, II.

(14) See the series of articles in ref 10a.

(15) Bonchev, D., in ref 10a.

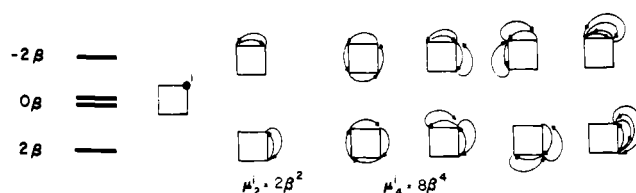


Figure 3. Generation of the fourth and eighth moments of the π -electronic density of states for cyclobutadiene by enumeration of the number of self-returning walks of length 4 and 8. Since each of the four π orbitals is equivalent by symmetry, the walks are only enumerated for one orbital (i) to give μ_n^i . The relevant moment (μ_n) is then computed by multiplying this figure by four. The Hückel π levels of cyclobutadiene are shown for completeness, referred to an α value of zero.

topological indices and the energy level patterns of molecules and solids. The method was developed¹⁶⁻¹⁹ by solid-state physicists in the late 1960s but can with profit be used in a simple fashion by chemists.²⁰⁻²² Given a set of energy levels with energies $\{\epsilon_i\}$, the m th moment for systems with discrete and continuous energy level spectra (molecules and solids, respectively) is given by $\mu_m = \sum_i \epsilon_i^m$ or $\int \rho(\epsilon) \epsilon^m d\epsilon$, where $\rho(\epsilon)$ is the energy density of states of the solid. Now, instead of studying the electronic properties of a molecular or solid-state structure in the traditional way by an analysis of the details of its set of energy levels, $\{\epsilon_i\}$ or $\rho(\epsilon)$, we use the set of moments $\{\mu_m\}$. In principle, we have not lost any information, but in fact have gained something of importance. These moments are directly related to topogeometrical features of the structure¹⁶ in the following way. In terms of a Hückel Hamiltonian the m th moment may be written as

$$\mu_m = \text{Tr} (\mathbf{H})^m \quad (1)$$

$$= \sum_j \sum H_{jk} H_{kl} \dots H_{zj} \quad (2)$$

where \mathbf{H} is the Hamiltonian matrix and the second sum in eq 2 runs over all products of order m . This means that the m th moment is simply the weighted sum of all the walks of length m that start off on orbital j and return to that orbital in m steps. The weights are simply the interaction integrals (H_{lm}) between the two orbitals l and m involved in the step, usually set proportional to the overlap integral S_{lm} . There is thus a direct connection between the moments and the topological index noted above. Electronic information, however, is coded into the walks that define the moments by their weights via the products of the H_{lm} associated with each step. Thus there is a more easily visualized relationship between the structural elements of the molecule or solid and the $\{\mu_m\}$ than between the structure and the $\{\epsilon_i\}$. Figure 3 shows how the fourth and eighth moments of the π system of square cyclobutadiene are evaluated in this way.²³ Here all the H_{lm} are of course equal to the Hückel β parameter. Notice that with these ideas, the second moment, which in-

(16) Cyrot-Lackman, F. Thèse, Orsay, 1968.

(17) Cyrot-Lackman, F. *J. Phys. Chem. Solids* 1968, 29, 1235.

(18) Cyrot-Lackman, F. *Surf. Sci.* 1969, 15, 535.

(19) Ducastelle, F.; Cyrot-Lackman, F. *J. Phys. Chem. Solids* 1970, 31, 1295; 1971, 32, 285.

(20) Burdett, J. K.; Lee, S. *J. Am. Chem. Soc.* 1985, 107, 3050.

(21) Burdett, J. K.; Lee, S. *J. Am. Chem. Soc.* 1985, 107, 3063.

(22) Burdett, J. K.; Lee, S.; McLarnan, T. *J. Am. Chem. Soc.* 1985, 107, 3083.

(23) Burdett, J. K.; Lee, S. *Croat. Chim. Acta* 1984, 57, 1193.

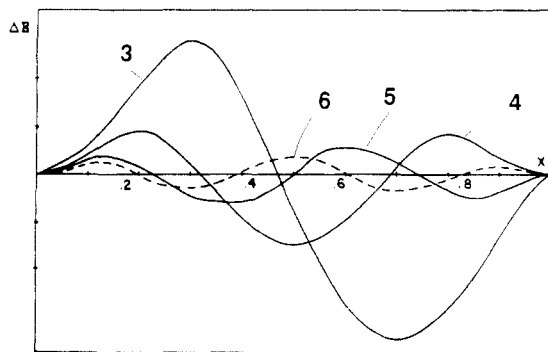


Figure 4. Energy difference curves as a function of fractional orbital (or band) filling expected for pairs of structural problems whose energy density of states differ at the m th moment. In practice, it is often found that although the number of nodes is given correctly, the crossing points of the curves are system dependent. One of the curves, that describing the sixth-moment behavior, is dashed for clarity.

involves only walks to first nearest neighbors and back, is a measure of the coordination number or strength. In Figure 1 all of the pairs of systems we compared each used the same second moment. In some cases this is clear to see (e.g., Figure 1a), but in others (e.g., Figure 1d) it is built into the parameters of the distorted molecule.

At this stage it is important to know when ideas based on such a one-electron orbital model (and strictly speaking its simplest, Hückel-type implementation) can be useful. In fact such simple models have permeated much of chemistry, but we will not dare to use the moments method in those areas where, from experience, the use of high-quality numerical calculations is essential. This excludes from consideration many problems where there is a change in coordination number, where soft distortion modes exist, or where the major interest is in the numerical values of reaction rates or bond energies and lengths.

Energy Difference Curves

The power of the moments approach lies in the following observation. If two structures differ first at the m th moment, then the energy difference curve between them as a function of orbital filling often has a very characteristic shape set by the value of m . In fact the energy difference curve as a function of fractional orbital occupancy will have m nodes, with the structure most stable at the lowest band fillings being the one with the largest m th moment.^{16-20,24} Figure 4 shows the form of the curves we expect to see. Here we introduce x , the fractional orbital occupancy, or for solids the band filling, as empty; $0 < x < 1$; full. The amplitude of the energy differences decreases with increasing m , a feature readily understood in terms of the self-returning-walk picture. If two systems differ at the second nearest neighbor (a walk of at least length four), then their energy difference will be smaller than for two similar systems that differ at the first nearest neighbor with a walk of at least length two.

The examples of Figure 1 are thus fourth-moment problems in this new language. In order to understand the structural preferences as a function of electron count, we need to look at the walks of length four in the two systems. The allene example of Figure 1e can be

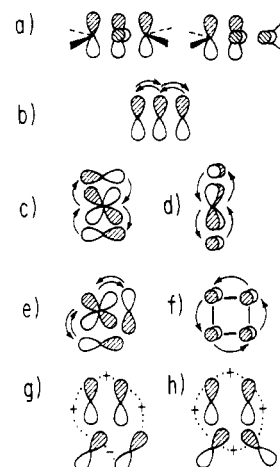


Figure 5. Important walks of length four between the orbitals important in the structural problems of Figure 1. See text for details.

used to illustrate the approach. Figure 5a shows the π orbitals of the planar and twisted forms. It is easy to see that in the planar form, there exist walks (shown schematically in Figure 5b) of length four that connect the two ends of the molecule. (In fact this diagram represents more than one walk, since it may originate on either of the three orbitals of the problem.) In the twisted form this set of walks does not exist since one end orbital is orthogonal to the other. So planar allene has the larger number of four-walks and thus the higher fourth moment. It is then the structure favored at low electron counts. The twisted form with the smaller fourth moment will be the stable isomer at the half-filled point. A similar situation holds for the cis and trans transition-metal complexes of Figure 1a,b. Here the problem is also controlled by π bonding. In the trans form the two four-walks of Figure 5c,d are possible, but in the cis form only that of Figure 5e is possible. The cis arrangement, with the smaller fourth moment, is thus the structure stable at the half-filled point. This is where all the M-O π -bonding orbitals are full. For the dioxo compounds, this occurs at d^0 and for the carbonyls, at d^6 . In Figure 1g it is obvious that the cyclic structure possesses a set of walks around the ring (Figure 5f) not available for the open-chain system. The cyclic structure is therefore the one unstable at the half-filled position, in accord with Hückel's rule.

Some of the other problems need a little bit of algebra to sort out. The Jahn-Teller and Peierls problems of Figure 1d,f,j are cases in point.^{9,10} Here, if the average "coordination number" (the second moment) remains constant, then it is the fourth moment that is the first to differ on distortion, and we can readily show that it is the undistorted structure that has the higher fourth moment. Notice that the treatment is independent of whether we are considering a σ -orbital problem (in transition-metal complexes), a π -orbital problem (in cyclobutadiene) or the Peierls distortion, which may be either of σ type (recall that a linear chain of hydrogen atoms under ambient conditions distorts to H_2 units) of π type (polyacetylene).

Hückel and Möbius Rings

All of the structural problems of Figure 1 are fourth-moment ones and may be understood in a similar way. Other systems will have energy difference

curves with a different number of nodes. For example, with reference to our comments concerning Hückel's rule for the four-membered ring, it is interesting to find that, in general, the stable regions of the plots of Figure 4 come at the positions expected on the basis of the rule.²¹ If we wish to compare the stability of an m -membered ring relative to its open-chain analogue, then the first moment that will be different will be the m th, associated with the two sets of complete walks around the ring (clockwise and counterclockwise) of length m and absent in the open chain. So the ring has the larger m th moment. Thus the three-membered ring is stable for $x = 1/3$ (Hückel's $n_\pi = 0$), but there are three maxima (at $1/6$, $1/2$, and $5/6$, which correspond to Hückel's $n_\pi = 0, 1$, and 2) for the six-membered ring. As a result cyclopropenium is stable as its cation but benzene is stable as a neutral molecule. We have known for a long time that Hückel's rule has a strong topological component. Here we have shown a link to other structural problems. From our approach there is nothing special about the orbitals of the problem of π type. Similar observations should be observed for the σ manifold. Indeed ideas related to these have been used in organic chemistry for some years under the title of σ aromaticity.²⁵

Sometimes the situation is a little more complex. Instead of the first disparate moment (the m th say) controlling the energetics, sometimes the $(m + 1)$ th or $(m + 2)$ th is important too. For example, the computed energy difference curve²¹ as a function of x which separates the graphite structure (which is made up of six-rings fused together) and that of the nonmetal net in ScB_2C_2 (made up of equal numbers of fused five and seven rings) is a weighted sum of the relevant fifth- and sixth-moment curves of Figure 4. The seventh-moment curve, being of smaller amplitude, makes a much smaller contribution to the overall energy difference curve.

Many of the arguments we used above for Hückel's rule are applicable to the Woodward-Hoffmann rules,⁹ phrased initially by these authors⁴ in terms of orbital symmetry conservation. Zimmerman²⁶ used the Hückel-Möbius concept to demonstrate the strong topological control of the reaction pathway. Möbius rings are ones where there is always an orbital phase change on making a circuit a round the ring as shown in Figure 5g for the four-membered cyclization example of Figure 1i. Hückel rings contain no such inversion (Figure 5h). The energy level patterns^{26,27} for Hückel and Möbius systems are quite different, a result that may also be seen via the moments method.²³ The weight of the Hückel walk around the ring in Figure 5h is positive, since all the overlap integrals (and hence all the H_{lm}) are of the same sign. However, in the analogous Möbius walk, since there is a single sign change in the set of H_{lm} on moving around the ring, there is a sign change in the relevant product of eq 2. Thus the absolute value of the m th moment for the Hückel walk is always larger than that for the Möbius walk. From the curves of Figure 4, at the half-filled point ($x = 1/2$) notice that it is the system with the smaller fourth moment that is more stable for four-rings, but the system with the

Table I

	element			
	Tl	Pb	Bi	Po
crystal structure	hcp	fcc	α -bismuth	simple cubic
electronic configuration	s^2p^1	s^2p^2	s^2p^3	s^2p^4
x (p-only model)	0.17	0.33	0.5	0.67
predominant ring type	3	3	6	4

larger sixth moment that is stable for six-rings. Since carbon chemistry is the chemistry of the half-filled band (there are four orbitals and four electrons involved in the butadiene cyclization), this implies that the lower energy pathway for cyclizations involving four-rings will be via the Möbius route (conrotatory), but that for the six-rings will be via the Hückel route (disrotatory). These results are in agreement with experiment of course. Zimmerman²⁶ used similar arguments to understand the origin of the twisted structure of allene, which we described earlier.

Notice that in all of these examples the emphasis is somewhat different from the traditional molecular orbital approach, which relies heavily on symmetry ideas for their interpretation. The Jahn-Teller theorem applied to the transition-metal species of Figure 1f, for example, is a case in point. There will only be an orbitally degenerate state for octahedral Cu^{II} if all of the ligands are identical (such that the point symmetry is O_h), and, strictly speaking, a first-order Jahn-Teller distortion is only possible under these conditions. The viewpoint presented here tells us that as long as there are walks of a given type, the actual nature of the ligands attached to the metal is of somewhat secondary importance. It is well-known that there are an enormous number of "Jahn-Teller" distorted systems where one or more of the ligands are different from the rest, an observation that emphasizes the merits of the broader approach to this problem. Thus *symmetry* appears not to be as important as *connectivity*.²⁸ A further illustration of this important aspect of the topological approach is also apparent of course in our discussion of the Woodward-Hoffmann rules. In contrast to the original formulation of the rules in terms of orbital symmetry conservation, molecules do not have to possess elements of symmetry for the schemes to be applicable. The rules work, for example, irrespective of whether the two substituents R and R' of Figure 1i are the same or different. It is the *connectivity* of the transition state that is important, a point noted by Zimmerman.²⁶

Solids

Our approach is just as applicable to the solid state, which is where it originated.¹⁶⁻¹⁹ For example, just as Figure 1h showed us how to color the vertices of cyclobutadiene to produce the more stable isomer (ABAB or AABB) as a function of electron count, exactly analogous plots dictate²⁹ the stable patterns for the so-called ordering problem in solids. A particularly nice example of the topological control of geometry is exhibited by the structures²¹ of the heavy p-block elements at the bottom right-hand side of the periodic

(25) Dewar, M. J. S. *Bull. Soc. Chim. Belg.* 1979, 88, 957.

(26) Zimmerman, H. E. *Acc. Chem. Res.* 1971, 4, 272.

(27) Yates, K. *Hückel Molecular Orbital Theory*; Academic: New York, 1978.

(28) We have pointed this out before. For a similar argument but from a different point of view see the discussion in: Burdett, J. K. *Inorg. Chem.* 1977, 20, 1959.

(29) Burdett, J. K.; Kulkarni, R. *J. Am. Chem. Soc.*, in press.

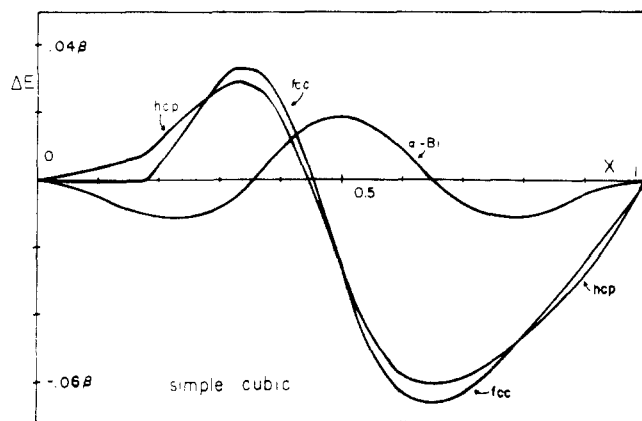


Figure 6. Calculated energy difference curves for the α -bismuth and cubic and hexagonal close-packed structures relative to that of simple cubic. Notice the strong similarity to the curves of Figure 4 for $m = 3$ and 6.

table (Table I). Figure 6 shows the calculated energy difference²¹ curve between the different structures as a function of p electron count from a band structure calculation. (Here we have ignored the $6s^2$ pair and used a p -orbital-only model.) Notice the very characteristic shapes of these curves, which accurately reflect the correct stable structure and are understandable using the moments method. The dominant moment of the close-packed structures is the third. With a coordination number of 12, three-walks involving neighbors in the first coordination shell are important. In the simple-cubic structure, it is obviously the fourth moment that is important, and in the α -bismuth structure, a puckered graphite sheet, it is the sixth. Remembering that the energetic importance of the moments decreases with their order, we can understand why the curves of Figure 6 are those for third- and fourth-moment problems. (The separation of hcp and fcc structures is more difficult. It turns out²¹ to be a fifth-moment problem.)

Of general interest from Figure 6 is the stability of arrangements with three-rings at low electron counts and of structures with six-rings at the half-filled point. A similar third-moment problem is apparent when we compare²¹ the rhombohedral boron structure (containing linked icosahedra with many three-membered rings) to that of cubic diamond (where the smallest ring size is six). The boron structure is stable for lower electron counts (boron has a $3/8$ -full s/p band), and the diamond structure stable at the half-filled point (carbon has a half-full s/p band). We find similar control of the molecular structure. Three-membered rings are found

in species with low electron counts (sometimes called "electron deficient") as typified by the boranes, transition-metal cluster compounds, and dihydrogen complexes.³⁰ Six-membered rings are the norm in "electron-precise" carbon chemistry.

A Universal Panacea?

Although two structural problems may appear to be completely different from the geometrical point of view and contain elements that come from very different parts of the periodic table, in topological terms they may sometimes be very similar indeed. The areas where the use of the energy difference curves of Figure 4 becomes more complex, and rapidly not so useful, are obviously where the orbital picture itself becomes more complex. These problems are invariably difficult to understand from the conventional standpoint too. Sometimes energy levels from different parts of the structural problem overlap. For example, Hückel's ideas applied to the benzene(4+) ion (which should be aromatic) are in practice not valid at all. At this electron count σ rather than π electrons have been removed from the neutral molecule. In solids this orbital (or band) overlap problem is sometimes especially acute.

We have for a long time known about the importance of that eternal triangle, symmetry, overlap, and electronegativity, in controlling much of chemistry. Of these, symmetry is perhaps the most elusive to pin down. In our discussions of the Jahn-Teller theorem and the Woodward-Hoffmann rules we have shown that it is not really the presence of bona fide symmetry elements that are important in controlling the underlying chemistry of the problem, but the connectivity of the orbital picture. (There is more evidence for this view from the study of systems with "accidental degeneracies", degeneracies that are of a higher order than the maximum permitted by the point group.³¹) Since the definition of the orbital connections of a problem includes all the geometrical information, the symmetry defined by the atomic positions is then superseded by a more powerful concept. A much broader view of structural chemistry is the result.

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(30) Burdett, J. K.; Lee, S. *J. Solid State Chem.* **1984**, *56*, 211.

(31) Burdett, J. K.; Lee, S.; Sha, W. C. *Nouv. J. Chim.* **1985**, *9*, 757.