are closely similar to the results for two poly(L-Ala) α-helices that are identical with each other and constrained to be regular in terms of backbone dihedral angles (studied earlier[4]). This indicates that the constraints of equivalence and regularity are not severe restrictions for poly(L-Ala) model α-helices, and the conclusions obtained with the use of these restrictions can be extended to the more realistic case of poly(L-Ala) α-helices not contrained to be regular.

The introduction of bulky Leu side chains on one of the two α-helices results in slight adjustments of the relative orientation of the two helices in the low-energy packing states. The orientational torsion angles Ω_0 remain nearly the same as for poly(L-Ala). The packing is very tight, as indicated by the low values of the distance between the helix axes. In the energetically most favorable packing arrangements, the helix axes are nearly antiparallel for both the poly(Ala)/poly(Ala) and the poly(Leu)/poly(Ala) α-helix pairs. The geometrical parameters and the interhelix energies are nearly the same. Thus, the change from Ala to Leu appears to have little effect on *these* packing arrangements.

Upon comparing the results for the two kinds of pairs of α-helices, other packing arrangements can be found which are similar in terms of Ω_0. In some of these arrangements the relative energies, the values of Ω_0, or those of D are different, however. This indicates that the details of the nonantiparallel arrangements depend more sensitively on the nature of residues in contact than do those of the nearly antiparallel poly(L-Leu)/poly(L-Ala) α-helix pair. Other side chains may influence the manner of packing of α-helices differently. The packing of α-helices with actual amino acid sequences that occur in globular proteins is being investigated in more detail.[40]

The same side-chain conformation of the Leu residue is favored in an individual α-helix and in the poly(L-Leu)/poly(L-Ala) helix pair. This side-chain conformation of the bulky branched Leu side chain is sufficiently favored by intrahelix interactions (including both steric hindrance and attractive nonbonded interactions), so that added interactions with the second α-helix do not change the preferred side-chain conformation. The orientation of the side chains in this conformation does not hinder the close approach of the second α-helix, as indicated in Figures 4 and 7. The preferred side-chain conformation may change in the case of polar residues which interact with functional groups on the other α-helix.[40] Nevertheless, many basic features of the interaction and packing of α-helices in proteins can be derived and explained in terms of the interactions between pairs of poly(amino acid) α-helices. The results reported here provide further support to the principle proposed earlier,[3] viz., that it is possible to account for the main features of frequently occurring packing arrangements of regular polypeptide structures in terms of local interaction energies, without requiring the inclusion of long-range interactions.

Note Added in Proof. In a recent survey of four highly refined protein crystal structures, Blundell et al.[41] have pointed out that the mean values of the backbone dihedral angles in α-helices are close to $(\phi, \psi) = (-63°, -42°)$, with a variance of 6°, instead of the usually cited[36] reference state obtained from crystalline α-helical poly(L-Ala), viz., $(-48°, -57°)$. The observed mean values are very close to those that were obtained in this paper by energy minimization on isolated α-helices and a pair of interacting α-helices (-66 to $-68°$, -38 to $-40°$).

Acknowledgments. We thank M. Gerritsen for helpful discussions, and M. S. Pottle, S. Rumsey, and R. W. Tuttle for assistance with computer programming and for preparation of the diagrams. This work was supported by grants from the National Institute of General Medical Sciences (GM-14312) and the National Institute on Aging (Ag-00322) of the National Institutes of Health, U.S. Public Health Service, from the National Science Foundation (PCM79-20279), from the Mobile Foundation, and from the National Foundation for Cancer Research.

Registry No. CH_3CO-(L-Ala)^{10}-$NHCH_3$, 85251-49-6; CH_3CO-(L-Ala)$_{10}$-$NHCH_3$·CH_3CO-(L-Ala)^{10}-$NHCH_3$, 89399-16-6.

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(41) Blundell, T.; Barlow, D.; Borkakoti, N.; Thornton, J. *Nature (London)* **1983**, *306*, 281-283.

Bond-Deficient Molecules

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Contribution from the Department of Chemistry, University of Washington,
Seattle, Washington 98195. Received May 20, 1983

Abstract: Bond-diagrammatic molecular orbital–valence bond theory suggests that molecules comprised of an axial C_2 fragment and a set of equatorial ligands are bond deficient; i.e., they have one bond less than expected by drawing a Lewis formula satisfying the octet rule. Molecules of this type can be isolable when no significantly better geometric alternative exists.

Valence bond (VB) theory[1] provides a very simple picture of the electronic structure of H_2O: Water is bent because, in this geometry, *ground-state* triplet O ($s^2p^2p^1p^1$) can be coupled to two ground-state doublet H's into an overall singlet.[2] This is no longer possible in the linear geometry. In this case, an *excited* triplet O ($s^1p^2p^2p^1$) combines with two ground-state doublet H's to produce an overall singlet species. In recent times, chemists became fascinated with molecular orbital (MO) theory and tried to reinterpret phenomena for which a VB explanation existed, as well as other trends discovered by recent experimentation, only to find themselves enmeshed in a web of confusion from which only few perceptive theoreticians could escape. Thus, for example, controversies arose as to what are "lone pairs" and "bond pairs" in H_2O, why H_2O is bent, why H_2S is more bent than H_2O, etc. Thes ambiguities have now been largely resolved by Hall[3] and Shustorovich,[4] who provided a largely correct interpretation of

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(1) (a) Heitler, W.; London, F. *Z. Phys.* **1927**, *44*, 455. (b) Slater, J. C. "Quantum Theory of Molecules and Solids"; McGraw-Hill: New York, 1963; Vol. 1.

(2) Murrell J. A.; Kettle, S. F. A.; Tedder, J. M. "Valence Theory"; 2nd ed.; Wiley: New York, 1970.

(3) (a) Hall, M. B. *J. Am. Chem. Soc.* **1978**, *100*, 633. (b) Hall, M. B. *Inorg. Chem.* **1978**, *17*, 2261.

(4) Shustorovich, E.; Dobosh, P. A. *J. Am. Chem. Soc.* **1979**, *101*, 4090.

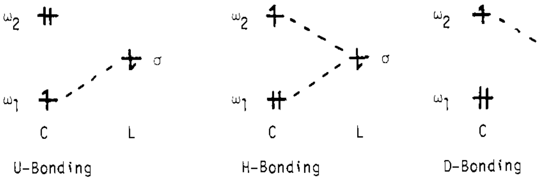
0002-7863/84/1506-3170$01.50/0

the MO's of AH_2 (A = O, S), not without significant labor. The question remains: Can we confidently use MO theory as a qualitative analytical tool when we have to go to great lengths to "understand" molecules as simple as H_2O?

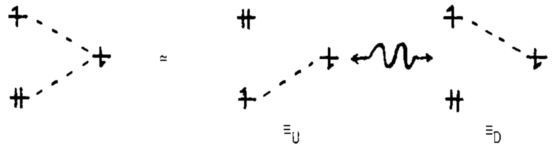
Recently, we have presented, explained, and applied a new qualitative theory of chemical bonding which is a compromise between MO and VB theory capable of pictorially depicting the electronic structure of a molecule without sacrificing formal rigor.[5-7] This new approach (MOVB theory) essentially reaffirms the basic correctness of the VB explanation of the stereochemistry of AH_2 and flashes a warning signal: MO theory may preclude a clear understanding of what are actually simple problems when applied to "large" organic molecules. This communication attempts to prevent this from happening.

Theorectical Background

According to MOVB theory, a molecule can be subdivided into a core (C) and a ligand (L) fragment, and its electronic structure can be depicted, to whatever desired degree of detail, by means of *bond diagrams* which show how the electrons are arranged in the core and ligand orbitals in order to best effect core–ligand overlap binding at the expense of the minimum amount of core and ligand excitation (with respect to the ground state of the noninteracting fragments). For example, consider a three-electron–two-orbital core ($\ddot{C}\cdot$) joined to a one-electron–one-orbital ligand (L·) by a single bond ($\ddot{C}$–L). There are three different ways by which such bonding can be effected depending on the operative orbital symmetry constraints:



Each diagram is called a *detailed bond diagram*, and the wave function depicted by it is symbolized by Ψ_M (M = U, H, D). Next, Ψ_M can be approximately expressed as a linear combination of compact bond diagrams, Ξ_N, as shown below.



We can write

$$\Psi_H \simeq \lambda_U \Xi_U + \lambda_D \Xi_D$$

The basic MOVB bond diagrammatic method is concisely outlined in the introductory section of part one of ref 6. Restricting our attention now to the H-bound $\ddot{C}$–L, we can say that, as the ω_1–σ increases relative to the ω_2–σ spatial overlap, the λ_U/λ_D ratio will increase, and vice versa. In other words, our MOVB resonance hybrid will resemble a U- or a D-bound system depending on the relative sizes of the two aforementioned overlap intergrals.

The detailed bond diagram of bent H_2O (viewed as O core plus H_2 ligand), Ψ, is shown in Figure 1b and it can be expressed as a linear combination of Ξ_D and Ξ_U, as shown in Figure 1a. Because $2p_y$ and $2p_x$ overlap appreciably with σ and σ^*, respectively, and because the energy gap separating 2s and 2p in oxygen is very large, we predict that $\lambda_U/\lambda_D \ll 1$, i.e., H_2O is essentially ground triplet O plus triplet H_2. This description now makes abundantly clear what is a "lone pair" and what is a "bond pair" in H_2O and also renders the H_2O stereochemical problem (i.e., why H_2O is bent and not linear) transparent (compare the detailed bond diagrams of $D_{\infty h}$ and C_{2v} H_2O in Figure 1).[8]

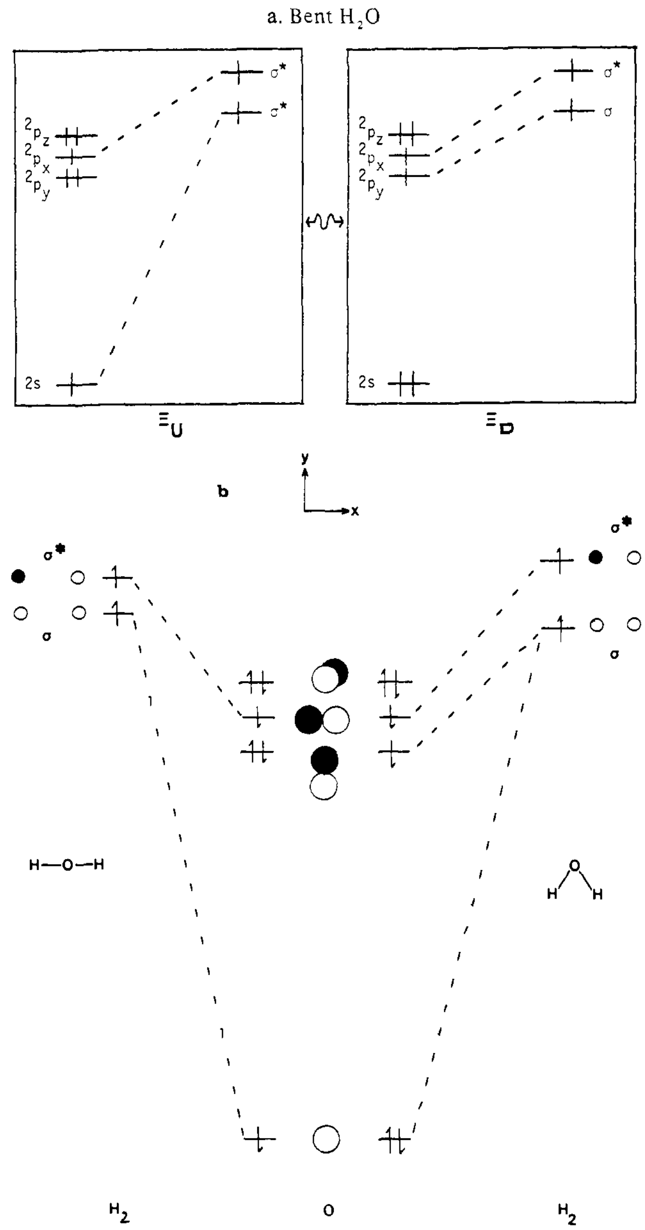


Figure 1.

When a new approach to molecular electronics is submitted for publication, it is especially true that the remarks of the reviewers reflect non only reasonable questions which may arise in the mind of the average reader, now asked to think in ways different from what he has been used to, but, also, the skepticism and bias with which anything challenging the status quo is viewed in science. Thus, before we proceed any further, it is instructive to consider some specific, scientific points raised by a referee with regard to the MOVB depiction of the electronic structure of water. This is necessary because the H_2O problem is the simplest illustrator of MOVB theoretical conventions and concepts. Hence,

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[5] Epiotis, N. D.; Larson, J. R.; Eaton, H. *Lect. Notes Chem.* **1982**, *29*, 1.

[6] Epiotis, N. D. *Lect. Notes Chem.* **1983**, *34*, 1.

[7] Parts of the MOVB theory of chemistry and illustrative applications have been presented in conferences: (a) NATO Advanced Study Institute on Topics on Theoretical Organic Chemistry, Gargnano, Italy, 1979. (b) International Symposium on Stereoelectronic Effects in Organic Chemistry, St. Andews, Scotland, 1980. (c) Symposium on Theoretical Aspects of Fluorinocarbon Chemistry, 183rd National Meeting of the American Chemical Society, Las Vegas, NV, March 1982; American Chemical Society: Washington, DC; FLUO 11. (d) International Symposium on Theoretical Organic Chemistry, Dubrovnik, Yugoslavia, 1982. For applications, see also: (e) Epiotis, N. D. *Pure Appl. Chem.* **1983**, *55*, 229. (f) Epiotis, N. D.; Larson, J. R. *Isr. J. Chem.* **1983**, *23*, 53.

[8] This problem is analogous to the problem of why singlet CH_2 is bent discussed in ref 5.

[9] Actually, formula **2** is the pictorial description of the total MOVB wave function (Θ) which is a linear combination of detailed bond diagrams (Ψ_i), the most important of which is that shown in Figure 2.

it is directly relevant to what follows. Furthermore, if H_2O is unconvincing, then all the rest should be unconvincing too. For, after all, what I say is that understanding properly the bonding of H_2O allows one to easily deal with many other apparently different and seemingly more complicated problems: The MOVB analysis of the stereochemistry of H_2O permits extensive "bridge-building", and this is discussed in detail in a paper to be published shortly.[19]

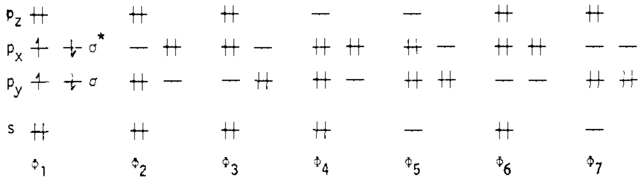
The specific queries of the referee are as follows: (i) Isn't $2s^1$–$2p^1$ hybridization necessary to infer a linear structure for Ξ_U? (ii) If (i) is used, why not s^1p^3 tetrahedral hybridization and an HOH angle of 109°? (iii) Does not Ξ_D infer a 90° angle? (iv) While the author suggests $H_2O(^1A)[H_2(^3\Sigma); O(^3P)]$, why not $H_2O(^1A)[H_2(^1\Sigma); O(^1D)]$? (v) The H_2O analysis is further complicated by the fact that C_{2v} dissociation requires the curve crossing of $H_2O(^1A)[H_2(^1\Sigma); O(^1D)]$ and $H_2O(^3B)[H_2(^1\Sigma); O(^3P)]$.

The MOVB explanation of why H_2O is bent is straightforward. As the linear is transformed to the bent form, ligand overlap nonbonded repulsion (brought into play by the perfect pairing CW's which are probably the dominant contributors to Ξ_D and Ξ_U) increases and $2p_x$–σ^* core–ligand overlap decreases. On the other hand 2p → 2s deexcitation is progressively permited to occur. There is plenty and diverse computational data in support of the proposition that H_2O bending is driven by deexcitation (i.e., lone pair accommodation by the 2s AO of oxygen), and I point out the careful work of Hall (ref 3). More references can be found in ref 19. H_2O and CH_2 are bent for the same reasons and CH_2 has been discussed in part II, ref 5.

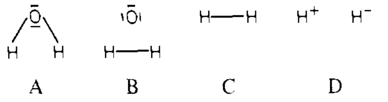
The answers to the referee's questions are as follows: (i, ii) As bending occurs, the Ξ_U/Ξ_D ratio gradually chaanges and the molecule samples hybridizations ranging from sp to sp^2 to sp^3 to pure p, in Pauling VB language. The exact form of hybrid oxygen orbitals can only be determined by explicit calculations, but this is not what qualitative theory seeks to accomplish.

(iii) Since Ξ_D and Ξ_U can interact and since nonbonded overlap repulsion exists in both, one can hardly expect a 90° angle even if Ξ_D were almost the exclusive contributor. Nonbonded overlap respulsion is discussed in Chapter 5 of ref 6.

(iv)



Firstly, all above shown CW's are nondegenerate. Φ_1–Φ_3 are contained in the lowest energy bond diagram of Figure 1. By contrast, Φ_4–Φ_7 belong to higher energy bond diagrams. The reason is that each contains a four-electron core–ligand antibond. Secondly, if we compare Φ_1 to Φ_2 and Φ_3, as actually implied by the referee, it is easy to determine that, because of the fact that σ and σ^* tend to be degenerate, the "classical" energies of Φ_1 and Φ_2 are comparable. On the other hand, exchange stabilization ("nonclassical" energy term) is present only in Φ_1 (the two core–ligand bonds). To put it crudely, MOVB "resonance structure" A has much lower energy than B much like, in H_2, C has much lower energy than D.



A B C D

At this point, I add that in most problems of interest, the identification of the dominant CW is immaterial to the main argument as this is typically based on consideration of *collections* of CW's projected by the bond diagrams. Of course, in many problems of interest, such an identification can be made without the need of explicit computations.

(iv) This is totally irrevlevant.

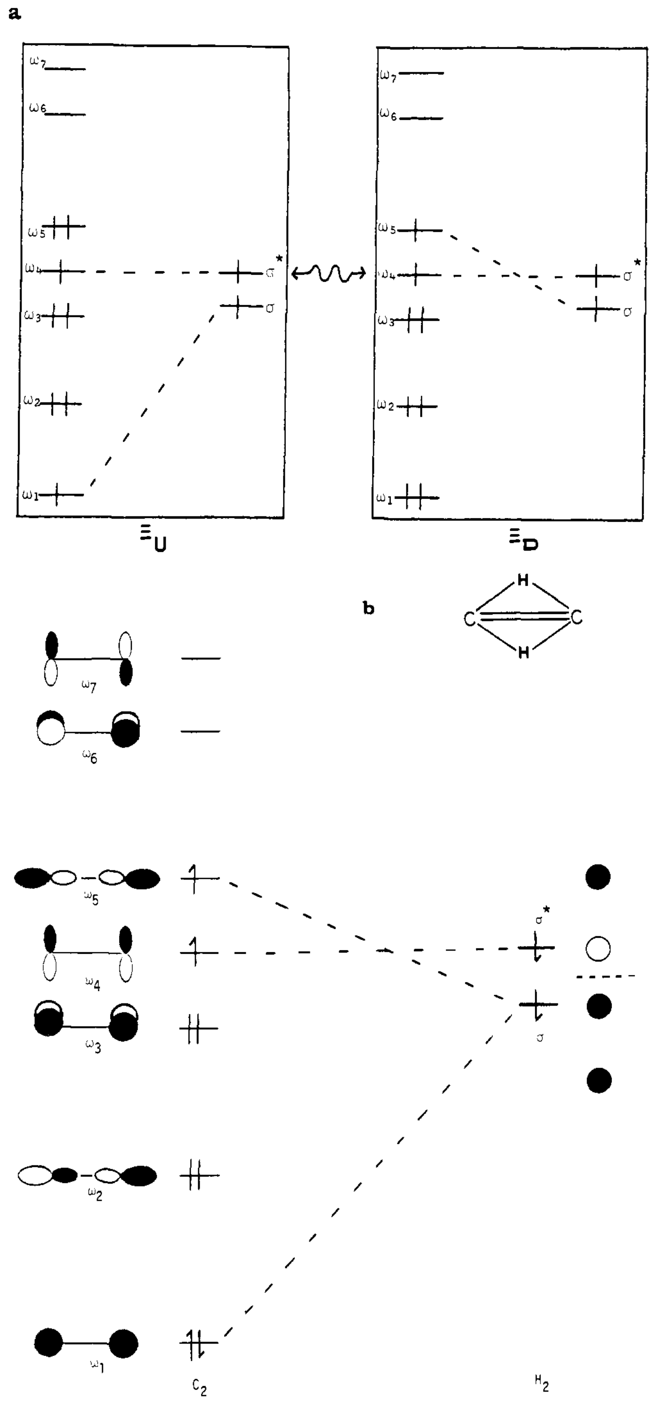
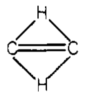


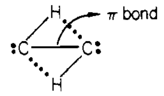
Figure 2.

σ-Bond Deficient Molecules

The detailed bond diagram of rhomboidal (D_{2h}) C_2H_2 (viewed as C_2 core plus H_2 ligand) is shown in Figure 2b. The high energy ω_8 (σ_{CC}^*) core MO has been purposely omitted, for simplicity. Working as before, we can express it as a linear combination of Ξ_D and Ξ_U, as shown in Figure 2a. Now, ω_5 is a core *nonbonding* MO, and it can overlap only minimally with σ. Hence we predict that the λ_U/λ_D ratio will either be close to, or, in fact, greater than unity. As a result, the line drawing (no electronic structure implied) of D_{2h} C_2H_2 will be **1** but the "best" electronic formula could be **2**.



1



2

C–C σ-bond deficient

Let us spell out explicity why **2** will be an apt respresentation of D_{2h} C_2H_2 if indeed $\lambda_U/\lambda_D > 1$. Inspection of Ξ_U reveals that there is *one* doubly occupied bonding core MO (ω_3) and *two* doubly occupied nonbonding core MO's (ω_2 and ω_5). Hence, D_{2h} C_2H_2 will tend to look like a "screwed up" singlet dicarbene generated by the union of two "screwed up" carbynes. We say then that D_{2h} C_2H_2 is *bond deficient*, compared to $D_{\infty h}$ C_2H_2, since in order to maintain two C–H bonds it must sacrifice a strong C–C bond.

What happens when we replace H by Li? As discussed before,[6] Li is a much weaker *overlap binder* than H. Hence, upon replacement of H by Li, core–ligand bonding is deemphasized in favor of reduced core excitation. This means that the λ_U/λ_D ratio tends to 0. At this limit, not ony is there a restored C–C bond in D_{2h} C_2Li_2 but this species becomes more stable than $D_{\infty h}$ C_2Li_2 on account of lower core excitation! This amazing stereochemical switchover has been discussed in greater detail elsewhere.[6]

What is the message of broad significance delivered by this analysis? MOVB theory allows us to define (core and/or ligand) nonbonding and bonding "lone" electron pairs as well as (core–ligand) "bond" pairs. In turn, this allows us to monitor electronic reorganization brought about by perturbation (e.g., atomic substitution) in a very direct and clear way. This is not possible at the level of any theory which does not contain the concept of "lone" and "bond" electron pairs.

Our treatment can be easily extended to large systems. Specifically, it can be easily shown that every molecule with an "axial" C_2 fragment surrounded by "equatorial" ligands will also tend to be a *bond-deficient molecule* because *there exists only one C_2 bonding orbital capable of strongly overlapping with the lowest energy* (*totally symmetric*) *ligand MO*, something which necessitates the presence of a nonbonding core electron pair. Examples are Ia/Ic (dotted lines indicate the "missing" bond). For illustrative purposes, the detailed bond diagram of Ia (viewed a C_2 core plus $(CH_2)_3$ ligand) is shown in Figure 3.[10] All Ia, IIa, and IIIa tend to be *bond deficient*.

Does bond deficiency imply *relative* instability? As implied above (C_2Li_2 case), the answer is a resounding NO! In comparing two isomers, each of which can be viewed as a composite of a core and ligand fragment, one should always remember that one may have more bonds but high fragment excitation and the second exactly the opposite. Depending on which of the two factors is more important for the species at hand, either the bond-efficient or the bond-deficient isomer can be more stable. With this in mind, we can compare isomers a and b shown in Figure 3a (each viewed as C_2 core plus X_m ligand) cognizant of their fundamental differences according to MOVB theory. This leads us to anticipate that the a *could* turn out to be more stable than the corresponding b isomers much like linear turns out to be more stable than trans-bent C_2H_2.[11,12] The labels "superaromatic" and "nonsuperaromatic" should be taken to mean "better" and "worse" core-ligand overlap in bond making, respectively. These expectations are in consonance with various computational and experimental results:

(a) IIa is computed to have a side bond which is *longer* than the central (C_1–C_3) bond. Furthermore, IIa and IIb lie very close in energy with IIa being predicted to be a global minimum.[13]

(b) Ia is isolable,[14] and computations[14,15] suggest that there is actually no central (C_1–C_3) bond.

Are there derivatives of Ia, IIa, and IIIa in which the central C_1–C_3 bond "reappears"? That is to say, can we construct *bond-efficient* derivatives of Ia, etc.? By following the analysis presented in Chapters 1 and 2 of ref 6, we predict that replacement of the bridging groups (CH_2 in Ia and IIIa and $\ddot{C}$ in IIa) by weak overlap binders, –X–, will change the λ_U/λ_D ratio from greater to less than unity, and the molecule will now tend to have a true C_1–C_3 bond. Finally, it is predicted that, as X varies in the order $H_2C \rightarrow H_2Si \rightarrow Be$ (i.e., as its overlap binding ability decreases), the most stable singlet should be a → b → a, i.e., both *very strong* and *very weak* X's should favor a.

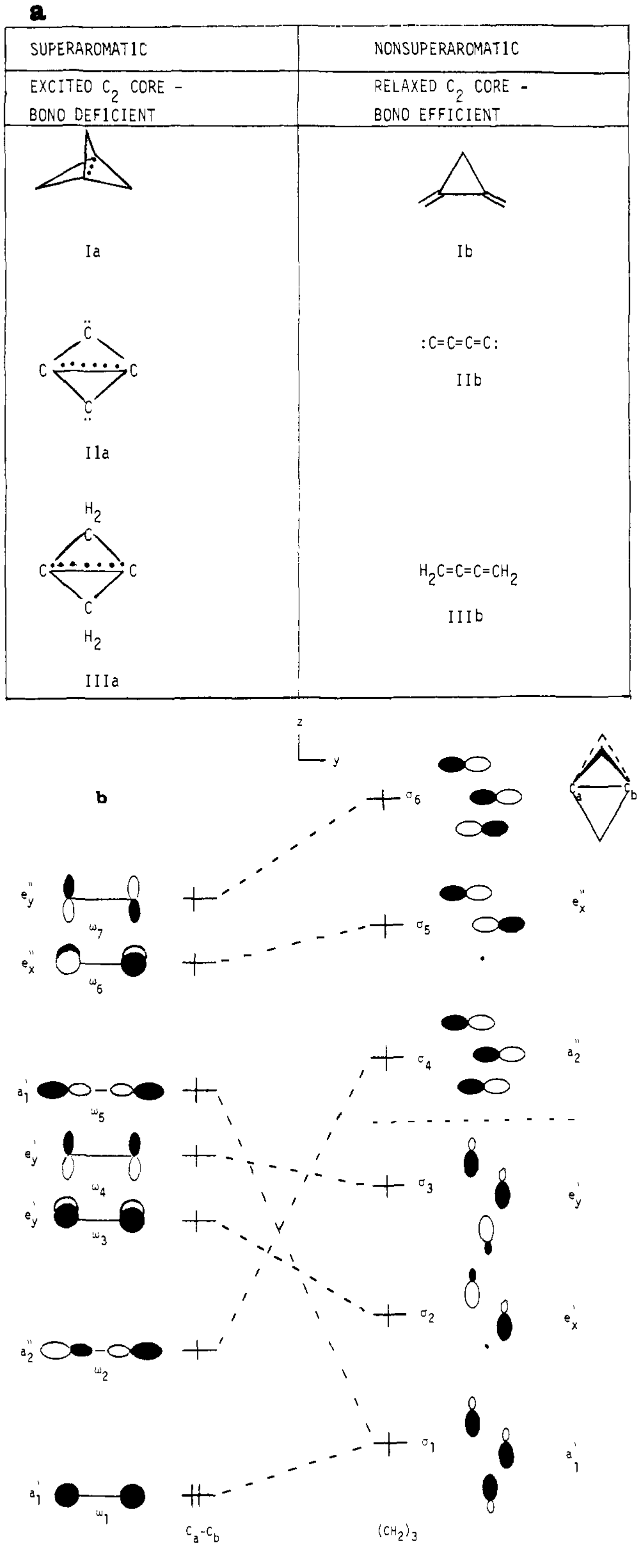


Figure 3.

Qualitative theory does not predict absolute magnitudes, only trends. Thus, we can say that $D_{\infty h}$ differs from D_{2h}, Ib differs from Ia, etc., to the extent that the first has a *much smaller* λ_U/λ_D ratio than the second which thus tends to be bond deficient. A *proper* analysis of the data contained in a computer output (overlap populations, AO occupation numbers, etc.) can actually reveal

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[10] See Chapter 13 of ref 6.

[11] See pages 280–284 of ref 5 and also ref 7f.

[12] Note that rhomboidal (D_{2h}) C_2H_2 and Ia–IIIa tend to be bond deficient, i.e., "C_2 core excited", much like linear H_2O is "O core excited". By the same token $[Fe(CO)_3]_2(CO)_3$ is bond deficient much like $C_2(CH_2)_3$!

[13] Whiteside, R. A.; Raghavachari, K.; DeFrees, D. J.; Pople, J. A.; Schleyer, P. v. R. *Chem. Phys. Lett.* **1981**, *78*, 538.

[14] Wiberg, K. B.; Walker, F. H. *J. Am. Chem. Soc.* **1982**, *104*, 5239.

[15] Newton, M. D.; Schulman, J. M. *J. Am. Chem. Soc.* **1972**, *94*, 773.

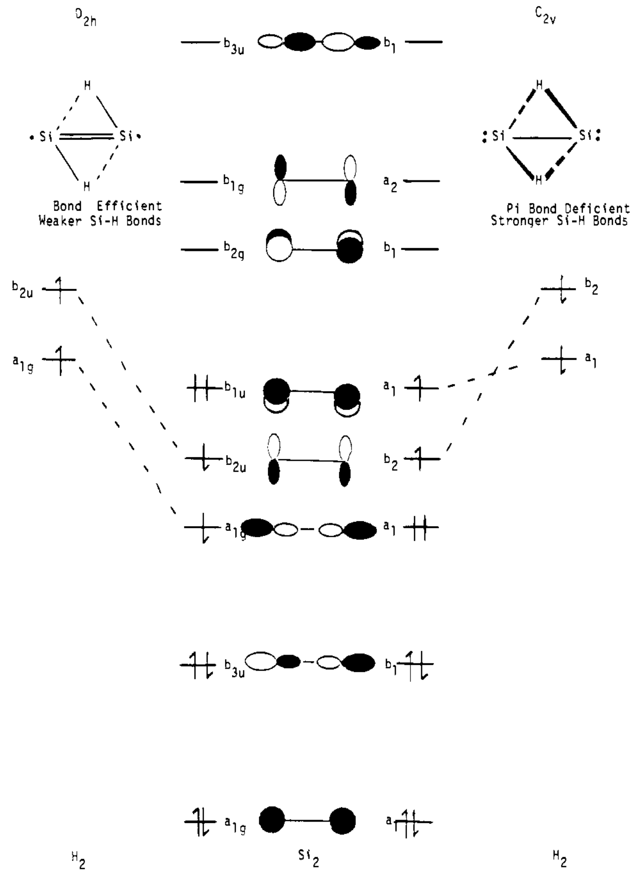

Figure 4.

whether the species in question is bond efficient ($\lambda_U/\lambda_D << 1$), intermediate ($\lambda_U/\lambda_D \simeq 1$), or truly bond deficient ($\lambda_U/\lambda_D >> 1$).[16] In any event, the fact remains that there are isolable molecules (such as Ia) which are serious candidates for the title "bond-deficient molecule". Furthermore, MOVB theory allows one to "dig" into the total MOVB wavefunction, Θ, and find physical meaning in Ξ_M. By contrast, one must expend considerably labor before he understands the problem discussed here *in an MO frame* simply because the total SCF-MO-CI wavefunction, Θ', is equivalent to Ξ, and chemists have not yet devised any MO methodology for reducing Θ' to Ξ_M like we have for reducing Θ to Ξ_M (*MOVB frame*).

Closing Remarks

While this manuscript was being reviewed, a paper by Lischka and Köhler[17] appears reporting ab initio computations of the Si_2H_2 hypersurface. In full agreement with the implications of the MOVB analysis, the bridged D_{2h} form is found to have lower energy than other conventional nonbridged structures, *much like* C_2Li_2! However, the global minimum turns out to be a C_{2v} form, i.e., a distorted bridged D_{2h} form. The reason C_{2v} is favored over D_{2h} is immediately made apparent by construction of the likely principal compact bond diagrams (Figure 4). It is evident that, *with the benefit of small core deexcitation*, the very weak a_{1g} can be converted to the much stronger a_1 core-ligand bond. This transformation is tantamount to simply strengthening the Si-H bonds since the a_{1g} bond gets stronger more than the b_{2u} bond gets weaker upon symmetry reduction. For the same reasons, we expect that the global minimum of C_2Li_2 could also be not D_{2h} but C_{2v}. In any event, the important message for the reader is that Si and Li are weak overlap binders[18,19] and C_2Li_2 and Si_2H_2 have similar "strange" structures for entirely the same reasons. Indeed, the forecast made at the end of Chapter 1 of ref 6 seems to hold.

Acknowledgment. I thank Professors Allen, Lischka, Michl, Schleyer, West, and Wiberg and Dr. G. Frenking for preprints, information, and comments.

Registry No. IIIc, 2873-50-9; C_2H_2, 74-86-2; H_2O, 7732-18-5; C_2Li_2, 1070-75-3; Si_2H_2, 36835-58-2.

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(16) In our original work (ref 6), we tacitly assumed that $\lambda_U/\lambda_D \simeq 1$ in D_{2h} C_2H_2 and used the Ξ_D bond diagram in our analysis of the stereochemistry of C_2H_2. It is very likely that this species, as well as Ia, IIa, and III, all lie in the $\lambda_U/\lambda_D >> 1$ regime. A more definitive pronouncement must await the analysis of high level SCF-MO-CI (or VB) computations.

(17) Lischka, H.; Köhler, H-J. *J. Am. Chem. Soc.* **1983**, *105*, 6646.

(18) Li is a weaker overlap binder than H because of its greater electropositivity (and the resulting difference in the shapes of the valence AO's). Si is a weaker overlap binder than C because the 3s AO of the former binds much less strongly than the 2s AO of the latter through overlap while the overlap binding abilities of 2p and 3p are nearly constant. This is true for every comparison of first and second row atoms. Hence, one may say that Si and Si_2 will bind H_2 via the 3p and π orbitals, respectively, while C and C_2 will become excited in order to take advantage of the much greater overlap binding ability of 2s and σ_u orbitals, respectively (see Chapter 1 of ref 6). The broad utility of the induced deexcitation model (see Chapter 2 of ref 6) is due to the fact that it is constructed so that its applicability does not depend on the precise origin of the differential overlap binding ability of atoms. Thus, SiH_2 differs in spin state and geometry from CH_2 for the same reasons that C_2H_2 has a geometry different from Si_2H_2, and the similarity of C_2Li_2 and Si_2H_2 is traceable to different atomic origins which, nonetheless, have identical stereochemical consequences!

(19) Epiotis, N. *Croat. Chem. Acta*, in press.

(20) For an interesting MO study of [1.1.1]propellane, see: Jackson, J. E.; Allen, L. C. *J. Am. Chem. Soc.* **1984**, *106*, 591.