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A comparative study of bent-bond vs. Walsh model in strained systems. Bicyclo(1.1.0)butane

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Bent bond and Walsh models for the electronic structure of the highly strained bicyclo(1.1.0)butane were critically examined and compared with the available PE spectrum. It is found that the bent bond scheme is by far more superior to the widely used Walsh semilocalized molecular orbitals. Hence the local hybrid orbitals provide a useful aid in assigning and interpreting of PE spectra. Present results lend support to the hybrid model in bicyclo(1.1.0)butane proposed by Schulman.

Key words: Bent bonds—hybrid orbitals—Walsh orbitals—hybridization and PES

1. Introduction

The highly strained hydrocarbons have been the subject matter of longstanding interest due to their unusual properties. Theoretical treatments of the electronic structure of strained systems widely differ in their levels of sophistication. The advanced *ab initio* calculations have been recently reviewed by Newton [1]. The hybridization model introduced by Pauling [2] and later independently by Slater [3] proved very useful in disscussing the small ring compounds leading to the bent bond description of their electronic structure [4, 5]. Extensive calculations performed by using iterative maximum overlap method (IMOM) have shown that noninteger hybridization provides in many instances semiquantitative informations on molecular properties [6]. Although the latter were satisfactorily reproduced by hybrid orbital basis sets, the photoelectron spectra of strained systems [7, 8] were almost exclusively interpreted in terms of the Walsh model developed first on cyclopropane [9]. The widespread use of the Walsh model was based on its utmost simplicity. However, it became clear recently that the Walsh model has some inherent shortcomings. For example, its application to bicyclopropyl and related compounds required significant admixture of Walsh virtual antibonding orbitals [10]. A thorough analysis of Heilbronner et al. [11] has shown that Förster-Coulson-Moffitt (FCM) bent bond orbitals are by far more suitable for interpreting the PE spectrum of cyclopropane than Walsh (W) orbitals. True, both approaches yield the same final wavefunction if the computation is carried out far enough. However, the FCM semilocalized orbitals are so close to the final ones that the last step involving CI with the corresponding virtual MOs can be omitted. On the other hand the Walsh semilocalized MOs require massive CI if the sensible result is to be obtained at all.

In this paper we examine the simple bent-bond (BB) and Walsh (W) models for the description of the electronic structure of bicyclo(1.1.0)butane which has a number of remarkable features [12]. The early maximum overlap treatment indicated appearance of the twisted covalent bonds, i.e. bonds which exhibit out of plane bending in addition to bending in the planes of the three-membered rings [13]. This has been later confirmed by INDO and *ab initio* calculations of local hybrid orbitals performed by Schulman et al. [14, 15]. Alternative description of the C—C bonds in bicyclo(1.1.0) butane was offered by Pomerantz and Abrahamson [16] who proposed two Walsh-type models. The aim of this work is to compare the performance of the BB and W models in interpreting the properties of the bicyclo(1.1.0)butane moiety with particlar emphasis to its PE spectrum. It will appear that neither of the two Walsh models is suitable for this purpose.

2. Description of approximate models for bicyclo(1.1.0)butane. BB-basis set

The hybridization inferred from the localized orbitals obtained by the semiempirical INDO method and the minimal basis set *ab initio* calculation exhibits very low *s*-orbital participation in the C—C bridge bonding (~4% of *s*-character) [14, 15]. Concomitantly, the predicted J(C—C) spin-spin coupling constant across the central bond was small and negative (~ −6 Hz)[17, 18], which was later proved by NMR measurements [19, 20] to be correct. Hence, the hybridization model of Schulman *et al.* [15] is reasonable. We shall adopt it in a slightly idealized form of the *ab initio* hybridization assuming that the C—C bridge bond is formed by two pure *p*-orbitals inclined by 38.4° to the straight line passing through the corresponding nuclei. The peripheral (e.g. C_1—C_2) bonds are described by the $sp^{3.0}$-$sp^{5.0}$ hybridizations. Since we want to discuss only BB and W semilocalized orbitals of the carbon skeleton in bicyclo(1.1.0)butane the C—H hybrid orbitals are not of our concern. It is only assumed that the perfect orbital following holds

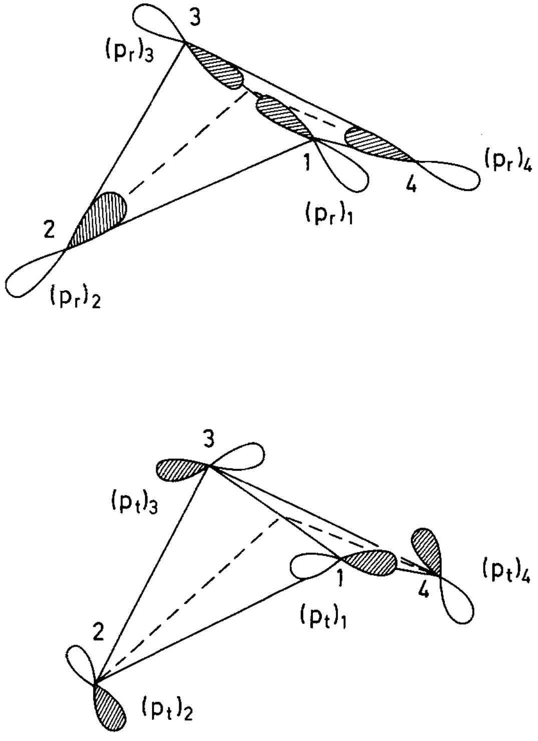


Fig. 1. Numbering in bicyclo(1.1.0)-butane and the definition of radial and tangential p-orbitals

for C—H bonds. Since the H—C—C bond angle of the bridgehead C—H bond is 128.4° [21], it follows that p-orbital bending of the central C—C bond is 38.4° as mentioned above. In order to enable the comparison between BB and W models it is convenient to define the local coordinate systems as shown in Fig. 1.

We distinguish tangential, radial and axial p-orbitals. The tangential (p_t) and radial (p_r) ones are depicted in Fig. 1. The axial (p_a) orbitals are perpendicular to the corresponding (p_t, p_r) pairs so that sequences (p_t, p_r, p_a) form the right-handed coordinate systems. Finally, the positive directions of p_t orbitals follow the right-screw orientation. Then the BB basis set of hybrid orbitals reads:

$$h_{14}=0.577(s)_1+0.707(p_t)_1+0.254(p_r)_1-0.320(p_a)_1 \tag{1a}$$

$$h_{12}=0.577(s)_1-0.707(p_t)_1+0.254(p_r)_1-0.320(p_a)_1 \tag{1b}$$

$$h_{21}=0.408(s)_2+0.707(p_t)_2+0.577(p_r)_2 \tag{1c}$$

$$h_{23}=0.408(s)_2-0.707(p_t)_2+0.577(p_r)_2 \tag{1d}$$

$$h_{13}=0.784(p_r)_1+0.621(p_a)_1 \tag{1e}$$

where h_{14} is the hybrid placed on the atom C_1 pointing toward the atom C_4 etc. The rest of hybrid orbitals is easily constructed taking into account the symmetry of the molecule.

2.1. Walsh basis set

The Walsh (W) basis set in cyclopropane consists of the three sp^2 hybrids directed from each corner to the center of the equilateral triangle. In addition, each carbon employs one tangential p_t orbital for the description of the ring bending [9, 11]. The construction of the W basis set is not unequivocal in bicyclo(1.1.0)butane. One can imagine two possible schemes [16]. The first scheme, W1, simulates the W basis in cyclopropane. Bridgehead carbons contribute two sp^2 hybrids, one for each three-membered ring. They overlap with the sp^2 hybrid emanating from the methylene group toward the center of the ring. The CH_2 group possesses the familiar tangential p_t orbitals belonging to the carbon skeleton. However, the bridgehead carbons contribute the inclined p-orbitals which describe the bonding in the central $C_1—C_3$ bond (Fig. 2). They correspond to the h_{13} orbital (1e) of the BB basis set. It is easy to see that this W basis is unacceptable. Namely, assuming that the geometry determined by microwave technique [21] is essentially correct, it follows that the two sp^2 hybrids placed on the bridgehead C_1 carbon (Fig. 2) should have the interhybrid angle smaller than 60°!

This is possible in principle if the hybrid orbitals are complex functions [22]. Unfortunately, complex hybrids have poor overlapping being thus inappropriate for the formation of strong covalent bonds [23]. The sp^2 real hybrids with mutual angle of 120° would imply that the $H—C_1—C_3$ angle is 90°. This is, however, incompatible with the experimental geometry of the bicyclo(1.1.0)butane. Hence, the W1 scheme can be safely disregarded.

The second Walsh scheme (W2) [16] is schematically given in Fig. 3. The difference to W1 is small but very important.

The pair of sp^2 hybrids at the bridgehead carbon (e.g. C_1) is replaced by the sp hybrid and the tangential p_t orbital. The rest of the W1 scheme is left untouched. Although the use of the sp hybrid is somewhat arbitrary, we shall see that the W2 scheme is close to the BB basis set discussed in the previous section. For

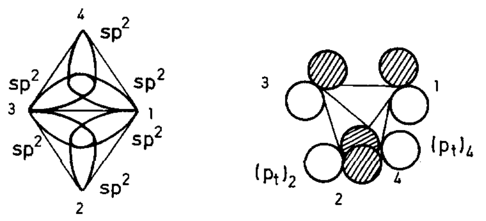


Fig. 2. Walsh sp^2 model for bicyclo(1.1.0)butane

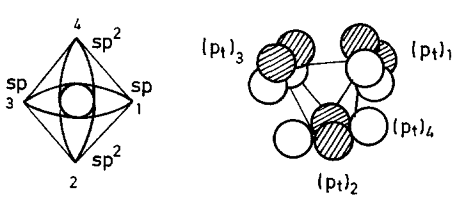


Fig. 3. Walsh sp-sp^2 model for bicyclo(1.1.0)-butane

this purpose it is useful to observe that the Walsh and bent-bond basis sets are related in a very simple fashion, if the carbon atoms keep their hybridization states unchanged. For instance, denoting the sp^2 hybrid at the C_2 center by ρ_2, it immediately follows that

$$h_{21}=\frac{1}{\sqrt{2}}[\rho_2+(p_t)_2], \qquad h_{23}=\frac{1}{\sqrt{2}}[\rho_2-(p_t)_2] \tag{2a}$$

and conversely

$$\rho_2=\frac{1}{\sqrt{2}}[h_{21}+h_{23}], \qquad (p_t)_2=\frac{1}{\sqrt{2}}[h_{21}-h_{23}]. \tag{2b}$$

Analogous expressions hold for the C_1 center. Adopting the *ab initio* hybridization parameters of Schulman et al. [14, 15] as in the case of the BB basis, one finds out that the ρ_1 hybrid is directed in the region between the wings of the molecule making an angle of 51.6° with the C_1—C_3 bond. In addition, the hybrid ρ_1 is of the $sp^{0.5}$ composition which can be compared with the *sp* suggestion of Pomerantz and Abrahamson [16].

2.2. *Construction of semilocalized molecular orbitals* (SLMO)

Having defined BB and W basis sets, which are completely equivalent (cf. (2)), we can proceed to the formation of semilocalized MOs (SLMOs). The latter should reflect the main features of the carbon skeleton in bicyclo(1.1.0)butane. The molecule has C_{2v} symmetry and the reducible representation generated by the hybrid AOs can be decomposed to the irreducible components as follows:

$$\Gamma_h=3A_1\oplus 2A_2\oplus 3B_1\oplus 2B_2.$$

The same result is obtained of course if the W basis set is employed. By using the BB set and neglecting overlap in the normalization one can construct approximate SLMOs possessing desired symmetry properties. The bonding BB-SLMOs are:

$$\varphi'(2a_1)=(1/\sqrt{2})[h_{13}+h_{31}] \tag{3a}$$

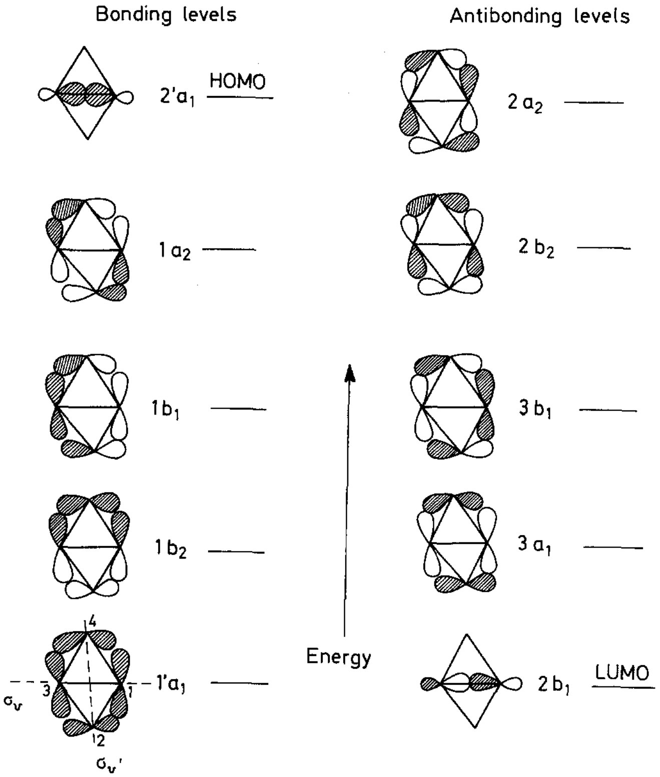
$$\varphi(1a_2)=(1/\sqrt{8})[-h_{14}-h_{41}+h_{43}+h_{34}-h_{32}-h_{23}+h_{21}+h_{12}] \tag{3b}$$

$$\varphi(1b_1)=(1/\sqrt{8})[-h_{14}-h_{41}+h_{43}+h_{34}+h_{32}+h_{23}-h_{21}-h_{12}] \tag{3c}$$

$$\varphi(1b_2)=(1/\sqrt{8})[h_{14}+h_{41}+h_{43}+h_{34}-h_{32}-h_{23}-h_{21}-h_{12}] \tag{3d}$$

$$\varphi'(1a_1)=(1/\sqrt{8})[h_{14}+h_{41}+h_{43}+h_{34}+h_{32}+h_{23}+h_{21}+h_{12}]. \tag{3e}$$

The BB-SLMOs (3) and (4) are shown on Scheme 1. The most stable and the highest occupied molecular orbitals are denoted by $\varphi'(1a_1)$ and $\varphi'(2a_1)$, respectively. Here, the peripheral and central bond orbitals are quite arbitrarily separated. The SLMOs $\varphi'(1a_1)$ and $\varphi'(2a_1)$ are of the same symmetry and should be mixed together (inner CI). This, however, requires the parametrization of the model which will be made at the later stage. One observes (Scheme 1) that the



Scheme 1. Bent-bond SLMO energy levels in bicyclo(1.1.0)butane

four most stable occupied SLMOs have 4 positive bond overlaps. The HOMO has only one bonding overlap which should be relatively low, because the central bond is formed by two pure (and bent) p-orbitals. The ordering of $\varphi(1a_1)$, $\varphi(1b_2)$, $\varphi(1b_1)$ and $\varphi(1a_2)$ is made on the basis of the overlap criterion. It was supposed that the positive overlap within a ring (e.g. $\langle h_{14}|h_{43}\rangle$ and $\langle h_{14}|h_{34}\rangle$) is more important than the positive overlapping between the two wings (like $\langle h_{21}|h_{41}\rangle$ and $\langle h_{21}|h_{43}\rangle$), which is a plausible assumption. We shall see that ordering of occupied levels is correct even after the CI with virtual orbitals of the appropriate symmetry (vide infra).

Let us focus our attention now to W-SLMOs. They are given by the following formulas:

$$\psi(1b_1) = (1/2)[(p_t)_2 - (p_t)_4 - h_{13} + h_{31}] \tag{4a}$$

$$\psi'(2a_1) = (1/\sqrt{2})[h_{13} + h_{31}] \tag{4b}$$

$$\psi(1b_2) = (1/\sqrt{2})[(p_t)_1 - (p_t)_3] \tag{4c}$$

$$\psi(1a_2) = (1/2)[(p_t)_2 + (p_t)_4 - (p_t)_1 - (p_t)_3] \tag{4d}$$

$$\psi'(1a_1) = (1/2)[\rho_1 + \rho_2 + \rho_3 + \rho_4] \tag{4e}$$

and

$$\psi^*(2a_2) = (1/2)[(p_t)_2 + (p_t)_4 + (p_t)_1 + (p_t)_3] \tag{5a}$$

$$\psi^*(3a_1) = (1/2)[\rho_1 + \rho_3 - (\rho_2 + \rho_4)] \tag{5b}$$

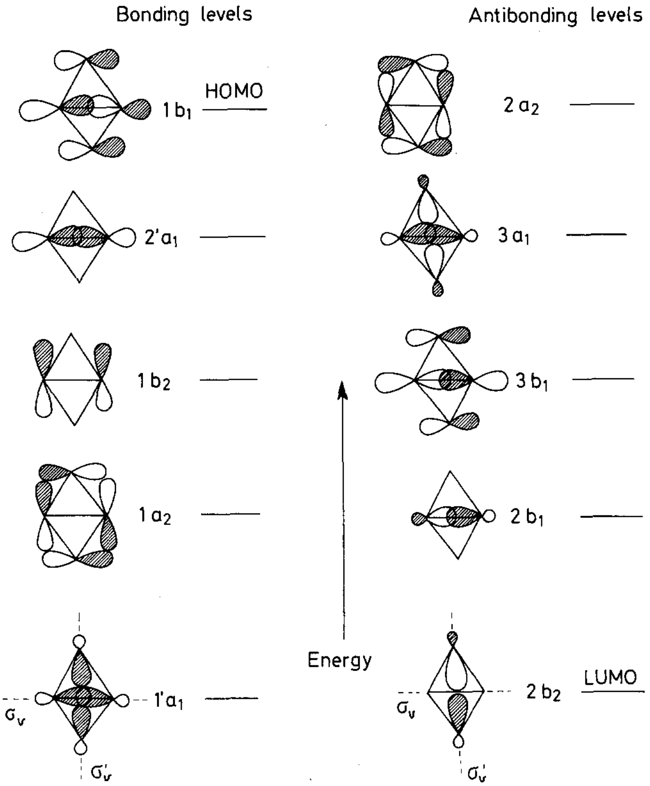
$$\psi^*(3b_1) = (1/2)[(p_t)_2 - (p_t)_4 + h_{13} - h_{31}] \tag{5c}$$

$$\psi^*(2b_1) = (1/\sqrt{2})[\rho_1 - \rho_3] \tag{5d}$$

$$\psi^*(2b_2) = (1/\sqrt{2})[\rho_2 - \rho_4] \tag{5e}$$

where the nonbonding SLMOs are denoted by asterisk. They are depicted in Scheme 2, where the ordering is obtained anticipating the later calculation of orbital energies. However, inspection reveals that the $\psi(1b_2)$ and $\psi(1b_1)$ SLMOs have poor overlaps. On the other hand $\psi'(1a_1)$, $\psi(1a_2)$ and $\psi'(2a_1)$ have favorable overlaps. In fact, it can be shown that they are identically equal to the corresponding BB-SLMOs $\varphi'(1a_1)$, $\varphi(1a_2)$ and $\varphi'(2a_1)$, respectively. Since the relations between the BB and W-SLMOs are of some interest, we give them here. They are obtained by the simple algebra:

$$\varphi'(2a_1) = \psi'(2a_1) \tag{6a}$$



Scheme 2. Walsh SLMO energy levels in bicyclo(1.1.0)butane

$$\varphi(1a_2)=\psi(1a_2) \tag{6b}$$

$$\varphi(1b_1)=(1/2)[\psi(1b_1)+\sqrt{2}\psi^*(2b_1)+\psi^*(3b_1)] \tag{6c}$$

$$\varphi(1b_2)=(1/\sqrt{2})[\psi(1b_2)+\psi^*(2b_2)] \tag{6d}$$

$$\varphi'(1a_1)=\psi'(1a_1). \tag{6e}$$

One observes that in order to reproduce BB-SLMOs $\varphi(1b_1)$ and $\varphi(1b_2)$, which have good overlap features, it is necessary to mix-in 75% and 50% of the corresponding virtual Walsh SLMOs, respectively. It is already obvious that the use of W-SLMOs requires massive CI if the satisfactory results are desired.

2.3. Parametrization of the BB *and* W-SLMO *models*

In order to put our arguments in more quantitative terms, we need some parametrization. The linear combination of hybrid orbitals (LCHO) was used extensively by Meyer and coworkers [24] within the CNDO framework in discussing the spectra of some alkanes and cycloalkanes. Instead, we shall keep our models as simple as possible particularly because the use of the CNDO scheme requires symmetric orthogonalization of the hybrid orbital basis set [25, 26]. This would lead to somewhat less transparent approach. The simplest semiempirical scheme is offered by the Hückel approximation which should be slightly generalized since we are dealing with the hybrid AOs instead of π-orbitals. We shall illustrate the actual calculations by the explicit consideration of the BB-SMLOs. The compact expressions for orbital energies are obtained if the two-center localized bonding and antibonding orbitals are used

$$\lambda_{ij}=(1/\sqrt{2})[h_{ij}+h_{ji}] \quad \text{and} \quad \lambda^*_{ij}=(1/\sqrt{2})[h_{ij}-h_{ji}]. \tag{7}$$

The orbital energies of the BB-SLMOs are easily expressed in terms of the Hückel Hamiltonian. This scheme is based on the effective Hamiltonian where it is tacitly assumed that molecular energy is a sum of one-electron orbital energies. The latter can be expressed in terms of the s-characters a_1^2 and a_4^2 of the hybrid orbitals h_{14} and h_{41}, respectively, and the effective average energies of s and p-orbitals

$$\alpha_s=\langle s_i|\hat{H}|s_i\rangle \tag{8}$$

and

$$\alpha_p=\langle (p_t)_i|\hat{H}|(p_t)_i\rangle=\langle (p_r)_i|\hat{H}|(p_r)_i\rangle=\langle (p_a)_i|\hat{H}|(p_a)_i\rangle \tag{9}$$

where $i=1, 2, 3, 4$. In other words, it is supposed that α_s and α_p matrix elements do not depend on the position of the carbon atom in a molecule. In addition, the spherical invariance of the p-subshell is assumed to hold. Further, the resonance integrals are expressed by the corresponding overlap integrals.

$$\langle h_{ij}|\hat{H}|h_{kl}\rangle=K\langle h_{ij}|h_{kl}\rangle \tag{10}$$

by using only one universal constant of proportionality. The parameters α_s, α_p and K could be in principle determined by fitting the experimental PE spectrum of bicyclo(1.1.0)butane. This would be inappropriate for several reasons. Firstly, we would in this case put in the model what should in principle come out as a result, if the model is adequate. Secondly, the main goal is not the reproduction of the PE-data but a comparison between the bent-bond and Walsh schemes in the description of the highly strained carbon skeleton. The former would require the inclusion of C—H bond orbitals which are left out of the present treatment. Therefore we shall rely on some *ab initio* (STO-3G) calculations performed on cyclopropane [11]. In particular, the integral $\alpha_p = -8.1$ eV is adopted. Further, the proportionality parameter K is deduced from the relation $\beta_{12} = KS_{12}$ where the subscripts refer to the C_1—C_2 bond in cyclopropane. Then the constant K assumes the value of -10.9 eV. Finally, the difference between α_s and α_p levels is taken to be the same as in the free atom $\alpha_s - \alpha_p = -9$ eV [27]. We shall employ also the Slater AOs in the rest of calculations to be consistent with this parametrization. Our extensive investigation of hybridization in a large number of hydrocarbons has shown that the use of Clementi DZ AOs [28] is advantageous [6]. However, the whole scheme is highly approximate. What matters is that the applied set of approximations is the same for both BB and Walsh models. Hence the use of Slater AOs is justified. More accurate and better approach will give somewhat different numbers but we feel confident that it will not change the main conclusions.

3. Results and discussion

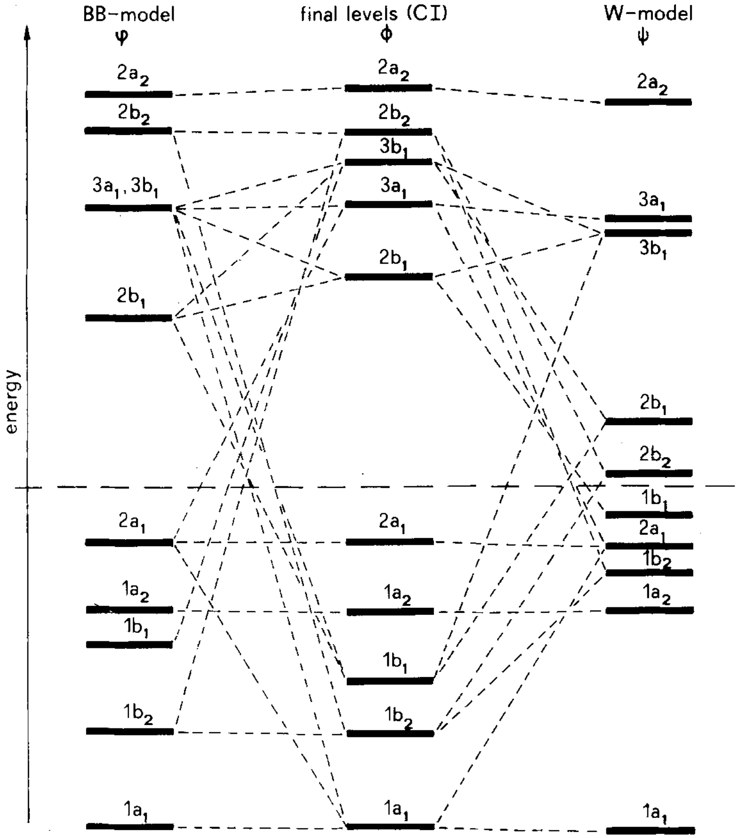
The orbital energies for the BB and W-SLMO models obtained with the parametrization described above are displayed in Table 1 and Scheme 3.

The energies of the $1'a_1$ and $2'a_1$, levels are -28.8 eV and -11.2 eV, respectively. Their mutual interaction $\langle\varphi'(1a_1)|\hat{H}|\varphi'(2a_1)\rangle = -4.2$ eV leads to the repulsion and shifts the levels by ~0.9 eV to the values -29.7 eV and -10.3 eV. The corresponding linear combinations are:

$$\varphi(1a_1) = 0.977\varphi'(1a_1) + 0.212\varphi'(2a_1) \tag{11a}$$

Table 1. Comparison of calculated orbital energies (eV) for bent-bond (BB) model, Walsh (W) model and final levels of bicyclo(1.1.0)butane with measured ionization energies (eV)

BB Model	W Model	Final Levels	I_v[7]
$e(\varphi^*_{2a_2}) = -2.3$	$e(\psi^*_{2a_2}) = -2.3$	$\varepsilon(\Phi^*_{2a_2}) = -2.1$	
$e(\varphi^*_{2b_2}) = -2.7$	$e(\psi^*_{3a_1}) = -3.7$	$\varepsilon(\Phi^*_{2b_2}) = -2.7$	
$e(\varphi^*_{3a_1}) \cong e(\varphi^*_{3b_1}) = 3.7$	$2(\Psi^*_{3b_1}) = -4.0$	$\varepsilon(\Phi^*_{3b_1}) = -2.5$	
$e(\varphi^*_{2b_1}) = -5.0$	$e(\Psi^*_{2b_1}) = -6.6$	$\varepsilon(\Phi^*_{3a_1}) = -3.5$	
	$e(\Psi^*_{2b_2}) = -8.3$	$\varepsilon(\Phi^*_{2b_1}) = -4.1$	
$e(\varphi_{2a_1}) = -10.3$	$e(\Psi_{1b_1}) = -9.6$	$\varepsilon(\Phi_{2a_1}) = -10.3$	9.4
$e(\varphi_{1a_2}) = -11.2$	$e(\Psi_{2a_1}) = -10.3$	$\varepsilon(\Phi_{1a_2}) = -11.3$	11.3
$e(\varphi_{1b_1}) = -11.6$	$e(\Psi_{1b_2}) = -10.4$	$\varepsilon(\Phi_{1b_1}) = -13.7$	11.7
$e(\varphi_{1b_2}) = -16.1$	$e(\Psi_{1a_2}) = -11.2$	$\varepsilon(\Phi_{1b_2}) = -16.1$	13.0
$e(\varphi_{1a_1}) = -29.7$	$e(\Psi_{1a_1}) = -29.7$	$\varepsilon(\Phi_{1a_1}) = -29.9$	



Scheme 3. Correlation diagram between the final levels of bicyclo(1.1.0)butane and those of the bent-bond (BB) and Walsh (W) model

$$\varphi(2a_1) = -0.212\varphi'(1a_1) + 0.977\varphi'(2a_1). \tag{11b}$$

The same relations hold for the $\psi(1a_1)$ and $\psi(2a_1)$ W-SLMOs. The energies of the first four occupied BB-SLMOs $\varphi(2a_1)$, $\varphi(1a_2)$, $\varphi(1b_1)$ and $\varphi(1b_2)$ can be compared with the first four ionization potentials of the bicyclo(1.1.0)butane [7, 17]. It appears that the ordering of the orbitals is well reproduced even without inner-outer CI between bonding and virtual orbitals. The quantitative agreement with the experimental data is moderate. However, better accordance could not be expected in view of the rough calibration of the model against the STO-3G results on cyclopropane and omission of C—H orbitals. On the other hand, a good qualitative agreement with the experimental PE spectrum lends support to the employed hybridization model of Schulman et al. [14, 15], because the orbital energies (A1-10) depend explicitly on the *s*-characters and/or implicitly through the overlap integrals. The W-SLMOs fail to reproduce the experimental ordering of highest occupied orbitals.

While the $\psi(2a_1)$ and $\psi(1a_2)$ levels are correctly placed since they are equivalent to the corresponding bent-bond orbitals, the levels of B symmetry are substantially destabilized. Thus, the HOMO is of the B_1 symmetry which is contrary to experiment. The $\psi(1b_2)$ level is also shifted up considerably in disagreement with ionization potentials. In addition, the $\psi(2a_1)$ and $\psi(1b_2)$ levels are practically degenerated which is not observed in the PE spectrum. Although the sum of orbital energies is not a very good measure of the total molecular energy [29], it gives a rough idea of molecular stability. Comparison of the BB and W-SLMOs orbital energies indicates that the former scheme is by 14.5 eV more stable. Concomitantly, the virtual levels of the B symmetries in the Walsh model are very low indicating strong mixing (vide infra). The poor performance of the W-model is not surprising because only the most stable C—C valence SLMO is built from hybrid orbitals possessing high s-content (4a–e). The rest of the s-character is shifted to excited state orbitals (5a–e). This explains the fact that the $\psi(1b_1)$ and $\psi(1b_2)$ orbitals are too high while the corresponding virtual orbitals are too low. Let us concentrate on the CI between the occupied and unoccupied orbitals. The BB-SLMOs are left practically untouched with exception of $\varphi(1b_1)$ level which is stabilized by 2.1 eV. The final molecular orbitals for a_1 and b_1 species are:

$$\Phi(1a_1)=0.997\varphi(1a_1)-0.001\varphi(2a_1)-0.076\varphi^*(3a_1) \tag{12a}$$

$$\Phi(2a_1)=0.005\varphi(1a_1)+0.999\varphi(2a_1)+0.044\varphi^*(3a_1) \tag{12b}$$

$$\Phi(3a_1)=-0.076\varphi(1a_1)+0.044\varphi(2a_1)-0.996\varphi^*(3a_1) \tag{12c}$$

$$\Phi(1b_1)=0.899\varphi(1b_1)+0.421\varphi^*(2b_1)+0.117\varphi^*(3b_1) \tag{12d}$$

$$\Phi(2b_1)=0.161\varphi(1b_1)-0.569\varphi^*(2b_1)+0.806\varphi^*(3b_1) \tag{12e}$$

$$\Phi(3b_1)=-0.406\varphi(1b_1)+0.706\varphi^*(2b_1)+0.580\varphi^*(3b_1). \tag{12f}$$

It appears that the first three MOs are quite well represented by approximate relations $\Phi(1a_1)\cong\varphi(1a_1)$,$\Phi(2a_1)\cong\varphi(2a_1)$ and $\Phi^*(3a_1)\cong\varphi^*(3a_1)$. Analogously, we can write: $\Phi(1a_2)\cong\varphi(1a_2)$, $\Phi(1b_2)=\varphi(1b_2)$, $\Phi^*(2b_2)=\varphi^*(2b_2)$ and $\Phi^*(2a_2)\cong\varphi^*(2a_2)$.

The main difference (and drawback) in the W-SLMO scheme lies in the orbitals of B_1 and B_2 symmetry as discussed above.

Hence we shall give only their linear combination after CI. The $\Phi(1b_2)$ and $\Phi(2b_2)$ wavefunctions are:

$$\Phi(1b_2)=0.762\psi(1b_2)+0.648\psi^*(2b_2) \tag{13a}$$

$$\Phi(2b_2)=-0.648\psi(1b_2)+0.762\psi^*(2b_2). \tag{13b}$$

The b_1 levels are described by the W-SLMOs:

$$\Phi(1b_1)=0.794\psi(1b_1)+0.577\psi^*(2b_1)+0.188\psi^*(3b_1) \tag{14a}$$

$$\Phi(2b_1)=0.149\psi(1b_1)-0.486\psi^*(2b_1)+0.861\psi^*(3b_1) \tag{14b}$$

$$\Phi(3b_1) = 0.588\psi(1b_1) - 0.657\psi^*(2b_1) - 0.472\psi^*(3b_1). \qquad (14c)$$

The final molecular orbitals Φ and their orbital energies are identical for both BB and W basis set. This is of course expected because BB and W basis are orthonormal and can be related by an orthogonal transformation. There is, however, a significant difference between them. The bent-bond hybrid orbitals provide a more natural choice. They can be combined in a favorable bonding fashion when the symmetry adapted SLMOs are formed. They are qualitatively in agreement with measured ionization potentials even without CI. Hence, the linear combinations of hybrid orbitals with some educated guess or actual calculation of overlap integrals might be useful in interpreting PE spectra. On the contrary, Walsh basis and corresponding symmetry adapted SLMOs have sometimes very poor energetic properties and only the proper CI can put the ordering of orbitals in line with experiment.

Our studies of hybridization have shown that hybrid orbitals have very high chemical information content. They give quite reliable heats of formation and strain energies [30], spin-spin coupling constants across one-bond [31], structural parameters of hydrocarbons [32], thermodynamic acidity of C—H bonds [33] etc. The present analysis and the earlier results of Heilbronner et al. [11] and Meyer et al. [24] provide conclusive evidence that local hybrid orbitals offer a transparent and powerful tool for assigning and interpreting PE spectra.

To conclude, we found that one of the two Walsh schemes for bicyclo(1.1.0)butane (W2) proposed by Pomerantz and Abrahamson [16] is physically acceptable. The corresponding Walsh basis set can be made, after some adjustments, identical to the hybrid basis suggested by Schulman et al. [14, 15]. In spite of this identity, the Walsh basis is less suitable for the formation of SLMOs. The local hybrid orbital basis is intuitively more appealing and leads to the final result in a smooth and direct fashion. A good agreement of the BB-SLMOs with ionization potential supports the hybridization description of bicyclo(1.1.0)butane advocated by Schulman et al. [14, 15].

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