$$\langle\alpha\rangle_n^{\overline{E}} = \sum_\gamma \sum_a \sum_j \frac{(N_a - N_j)}{N}$$
$$\times |\langle a|m_\gamma|j\rangle|^2[(E_j - E_a) - \overline{E}]^n \quad (A5)$$

For $n = 0$ or 1, any function, $f_{aj}(E)$, symmetrical about $(E_j - E_a)$ will give eq A5. The sum over a is over all populated (ground) states and that over j is over all states contributing to the band of interest. In our case, a and j are vibronic eigenstates of H^T such as those of eq 24 and 45. Thus they are diagonal in H^T and so

$$E_a = \langle a|H^T|a\rangle$$
$$E_j = \langle j|H^T|j\rangle \quad (A6)$$

Thus from eq A5, A6, and 45 we obtain

$$\langle\alpha\rangle_0 = d_0 \sum_{\nu'} \sum_\nu {}' \frac{(N_{\nu'} - N_\nu)}{N'} \mathscr{S}_{\nu'\nu}^2$$

$$\langle\alpha\rangle_1^{\overline{E}} = 0$$

$$\overline{E} = \frac{d_0}{\langle\alpha\rangle_0} \sum_{\nu'} \sum_\nu {}' \frac{(N_{\nu'} - N_\nu)}{N'} \mathscr{S}_{\nu'\nu}^2 (E_\nu - E_{\nu'})$$

$$\langle\alpha\rangle_2^{\overline{E}} = d_0 \sum_{\nu'} \sum_\nu {}' \frac{(N_{\nu'} - N_\nu)}{N'} \mathscr{S}_{\nu'\nu}^2 (E_\nu - E_{\nu'})^2 \quad (A7)$$

where

$$N_{\nu'} = \exp(-E_{\nu'}/kT), \quad N' = \sum_{\nu'} N_{\nu'}$$

and

$$d_0 = \frac{1}{\lambda(\psi)} \sum_\gamma \sum_{\tau,\tau'} |\langle\psi_+\tau'|m_\gamma|\psi_-\tau\rangle|^2 \cong (Re/2)^2 \quad (A8)$$

The sum over ν is over all states for which $E_\nu > E_{\nu'}$. We assume that all populated vibronic states are associated with the $\lambda(\psi)$-fold degenerate states ψ_+ and ψ_-.

These zeroth, first, and second moments are related to the integrated intensity, the mean energy, and the half-width, respectively, of the absorption band.[17] Experimental moments are easily calculated by integrating the experimental dispersion using eq A3. They may then be compared as a function of temperature with theoretical moments (eq A7) based on $E_{\nu'}$, E_ν, and $\mathscr{S}_{\nu'\nu}$ factors calculated for particular ϵ, λ, and W sets. This comparison should be valid for $n = 0, 1$. For $n = 2$, it should be valid if the line width, Δ, is much less than the mixed valence bandwidth.

References and Notes

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Interaction of Walsh Orbitals in Trishomocycloheptatrienes and Related Hydrocarbons

Jens Spanget-Larsen, Rolf Gleiter,* Michael R. Detty, and Leo A. Paquette*

Contribution from the Institut für Organische Chemie der Technischen Hochschule Darmstadt, D-6100 Darmstadt, West Germany, and the Department of Chemistry, The Ohio State University, Columbus, Ohio 43210. Received July 14, 1977

Abstract: The photoelectron (PE) spectra of *syn-* and *anti-*3,5-bishomocycloheptatriene (**1** and **2**), *syn-* and *anti-*1,5-bishomocycloheptatriene (**3** and **4**), and *syn,syn-*, *anti,anti-*, and *anti,syn-*trishomocycloheptatriene (**5, 6,** and **7**) have been recorded. The first bands of their spectra have been assigned to ionization from molecular orbitals (MOs) derived from the highest occupied Walsh orbitals of the cyclopropane rings and the π orbital of the ethylenic double bond. This analysis is based on a zero differential overlap (ZDO) model and substantiated by the results of semiempirical calculations. An important feature of the ZDO model is the admixture of "radially" oriented components into the highest occupied "tangential" Walsh orbitals which is necessary to improve the description of the conformationally dependent interaction between linked cyclopropyl groups.

Introduction

The interaction between the Walsh orbitals of three cyclopropane rings has been studied recently in the case of diademane.[1] In this example, the dihedral angle between the cyclopropane units is approximately zero and the conjugative interaction between Walsh orbitals composed of "tangentially" oriented 2p atomic orbitals (AOs) is a maximum. On the basis of photoelectron (PE) spectroscopic results the resonance integral between linked 2p AOs of two adjacent eclipsed cyclopropane rings was found to be -1.73 eV.

In this paper, an evaluation is made of those hydrocarbons derived from cycloheptatriene in which the dihedral angles between the cyclopropane units deviate markedly from zero.
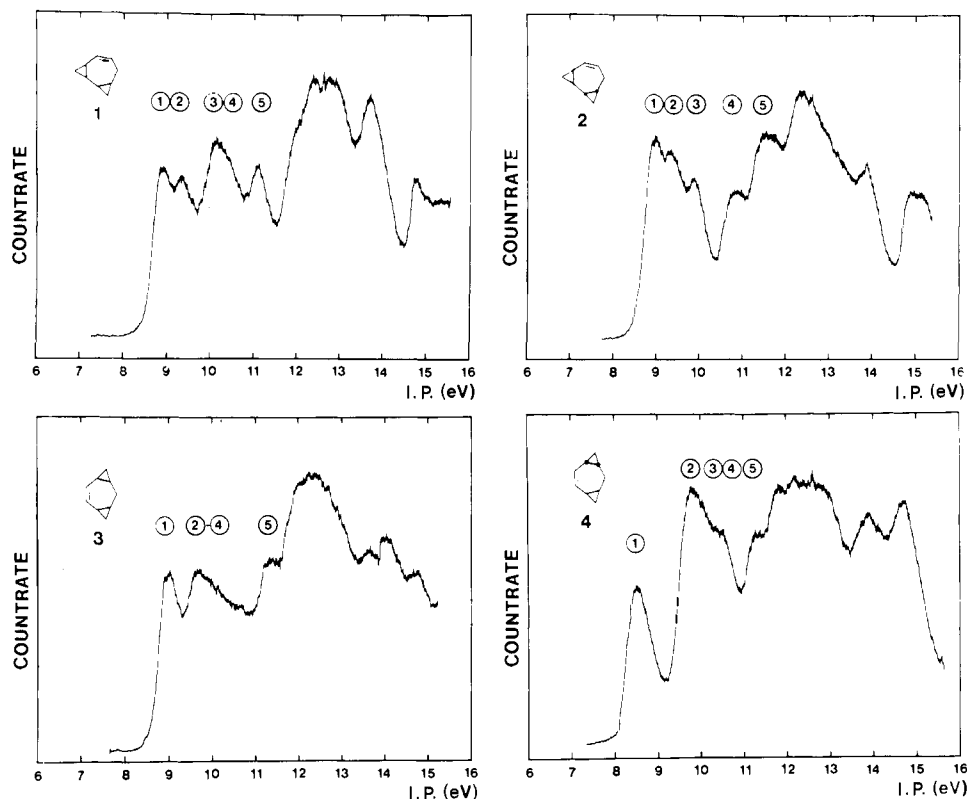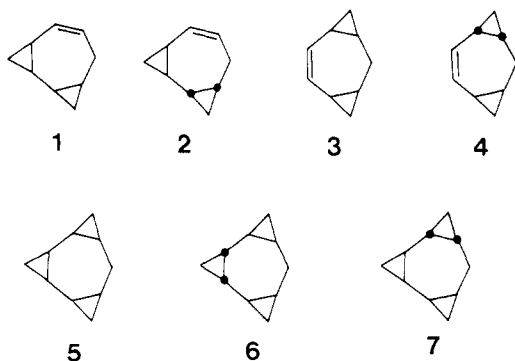
Figure 1. PE spectra of 1–4.

The hydrocarbons are *syn*- and *anti*-3,5-bishomocyclohepta-triene (**1** and **2**), *syn*- and *anti*-1,5-bishomocycloheptatriene (**3** and **4**), and *syn,syn*-, *anti,anti*-, and *anti,syn*-trishomocy-cloheptatriene (**5, 6,** and **7**).

The synthesis and the conformational features of **1–7** have been reported recently.[2] We wish to demonstrate that the in-terprctation of the PE spectra of these compounds requires a representation of the Walsh orbitals in which the "tangential" orbitals are allowed to mix with "nontangential" (e.g., "radi-al") components.

Photoelectron Spectra

The PE spectra of **1–7** are shown in Figures 1 and 2 and the relevant data are listed in Tables I and II together with results of molecular orbital calculations. For the interpretation of the PE spectra of **1–7**, Koopmans' theorem[3] is used. In this ap-proximation the orbital energy E_J is set equal to minus the vertical ionization energy $I_{V,J}$:

$$E_J = -I_{V,J}$$

This enables correlation of the PE band positions with the or-bital energies obtained from model calculations. A ZDO model and the extended Hückel (EH)[4] method have been utilized for interpretation of the PE spectra.
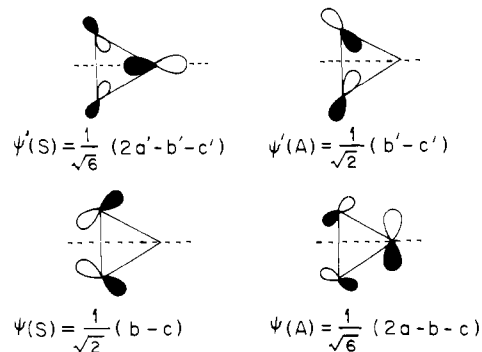
ZDO Model

In this section, a zero differential overlap (ZDO) model involving the highest occupied Walsh orbitals of the cyclo-propane rings and the π orbital of the double bond is developed for these compounds. The only structural parameters which enter this model are the angles of twist around the σ bonds connecting these units. The main emphasis is thus put on an analysis of the conformational dependence of the resulting orbital energies.

A. Walsh Orbitals. The molecular orbitals (MOs) of cy-clopropane are best described in terms of the so-called Walsh orbitals.[5,6] Consider the AO basis set consisting of the three tangentially and the three radially oriented carbon 2p orbitals, as indicated. Approximations to the frontier orbitals of cy-

clopropane, 3e' and 4e', can be obtained by constructing the following linear combinations (ZDO).[5,6] $\varphi(S)$ and $\varphi(A)$ rep-

$$\psi'(S) = \frac{1}{\sqrt{6}}(2a'-b'-c')$$

$$\psi'(A) = \frac{1}{\sqrt{2}}(b'-c')$$

$$\psi(S) = \frac{1}{\sqrt{2}}(b-c)$$

$$\psi(A) = \frac{1}{\sqrt{6}}(2a-b-c)$$

Table I. Observed Vertical Ionization Energies $I_{V,J}$ and Calculated ZDO Orbital Energies E_J for Different Values of the Mixing Parameter χ (eV)[a]

| Compd (θ_1, θ_2)[b]	$I_{V,J}$	Assignment	E_J $\chi = 0$	E_J $\chi = 1/\sqrt{5}$
1[c] (80°, −50°)	8.90	π	−9.16	−8.80[d]
	9.34	w_a	−9.47	−9.52
	10.1	w_b	−10.20	−10.05
	10.4	w_a	−10.23	−10.40
	11.1	w_b	−10.94	−11.22
2[c] (80°, −130°)	8.96	π	−9.16	−8.88[d]
	9.37	w_b	−9.47	−9.34
	9.88	w_a	−10.20	−9.83
	10.9	w_b	−10.23	−10.84
	11.4	w_a	−10.94	−11.11
3[e] (90°, −90°)	9.0	π	−9.20	−8.78
	9.56		−10.20	−10.20
	10.0	w', w'', w''	−10.20	−10.20
	10.3		−10.20	−10.20
	11.4	w'	−10.20	−10.62
4 (70°, 0°)	8.5	π	−8.44	−8.34
	9.8	w	−10.20	−10.20
	10.2	w	−10.20	−10.20
	10.5	w	−10.20	−10.20
	11.3	w	−10.96	−11.06
5[e] (−45°, 45°)	8.8	w'	−9.20	−8.87
	9.5	w''	−9.62	−9.66
	10.0		−10.20	−10.20
	10.4	w', w''	−10.20	−10.20
	10.75	w''	−10.78	−10.74
	11.4	w'	−11.20	−11.53
6[e] (120°, −120°)	9.0	w'	−9.49	−9.03
	9.3	w''	−9.79	−9.63
	10.0		−10.20	−10.20
	10.5	w', w''	−10.20	−10.20
	10.9	w''	−10.61	−10.77
	11.3	w'	−10.91	−11.37
7 (45°, −120°)	8.88	w	−9.31	−9.03
	9.45	w	−9.74	−9.48
	10.0	w	−10.20	−10.20
	10.4	w	−10.20	−10.20
	10.85	w	−10.66	−10.92
	11.55	w	−11.09	−11.37

[a] For details of the calculation see the text. [b] Twist angles θ_1 and θ_2 are defined in the text. [c] The orbitals localized predominantly on the bicyclopropyl fragment are labeled according to a local approximate C_2 symmetry. [d] $k = \beta_{ww}/10$; see the text. [e] The orbitals are labeled according to C_s symmetry.

Table II. Observed Ionization Energies[9] and Calculated ZDO Orbital Energies for Bicyclopropane (eV)

Obsd	Calcd[a] Gauche ($\theta = 45°$)	s-Trans ($\theta = 180°$)
9.6–9.7₅	−9.73 (a)	−9.57 (b_g)
10.1–10.4	−10.54 (b)	−10.21 (a_g)
11.0	−10.86 (a)	−11.19 (b_u)
11.75–11.9	−11.67 (b)	−11.83 (a_u)

[a] The orbitals are labeled according to the irreducible representations of the C_2 (gauche) and the C_{2h} (s-trans) point groups. For details of the calculation see the text.

resent the two degenerate highest occupied MOs (HOMOs) of cyclopropane, and $\varphi'(S)$ and $\varphi'(A)$ correspond to the two degenerate lowest unoccupied MOs (LUMOs). S and A designate the symmetry, symmetric and antisymmetric, respectively, with respect to the vertical plane of symmetry indicated by the broken line in each diagram. The representation of the
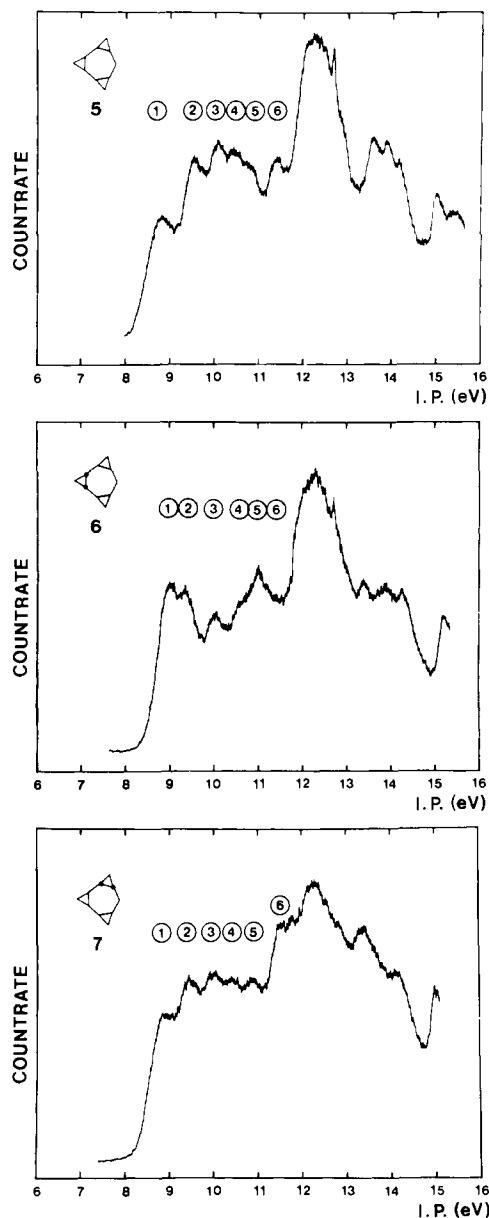
Figure 2. PE spectra of **5–7**.

HOMOs of cyclopropane given above was introduced by Walsh[5] and the orbitals are known as "Walsh orbitals". A more adequate description of the LUMOs of cyclopropane would be obtained by constructing them from carbon s–p hybrids,[5,6] but the representation given above is sufficient for our purpose since we are only interested in the p contribution to these orbitals (see later).

The representation of the Walsh orbitals given above is sufficient for most qualitative applications. This description, however, neglects the interaction between the HOMOs and the LUMOs. The results of more accurate models show that e.g., the HOMOs contain small admixtures of radially oriented components (e.g., ref 6a). For reasons which will become apparent in the following, this type of mixing plays an important role in the conformational dependence of the orbital pattern in compounds like **1–7**. We will thus allow for a mixing of $\varphi'(S)$ and $\varphi'(A)$ into $\varphi(S)$ and $\varphi(A)$:

$$w(S) = \sqrt{1 - \chi^2}\, \varphi(S) + \chi\varphi'(S)$$

$$w(A) = \sqrt{1 - \chi^2}\, \varphi(A) - \chi\varphi'(A) \tag{1}$$

The mixing parameter χ is a small positive quantity. The re-

sulting orbitals w(S) and w(A) represent the two HOMOs (Walsh orbitals) of cyclopropane, and are the essential building blocks in the present formulation.
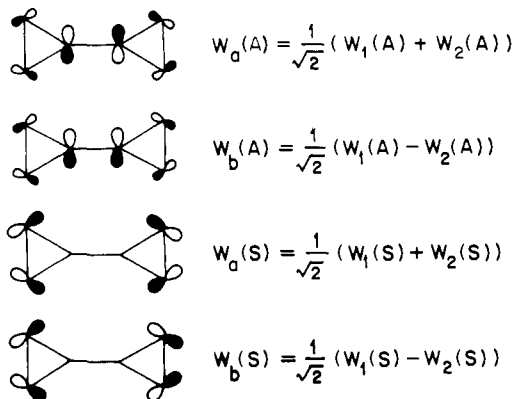
B. Bicyclopropyl. This species will serve as a simple example of the application of the ZDO model, and the results will furthermore be useful in the treatment of **1** and **2**. The tangential and radial p orbitals are labeled in the following way. The
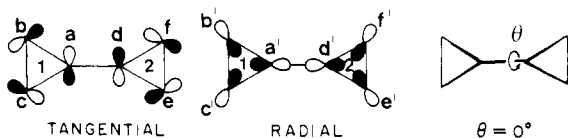
relative phases indicated above correspond to the eclipsed conformation, corresponding to a twist angle $\theta = 0°$. All overlaps between neighboring tangential p orbitals are thus defined to be negative[1] and overlaps between neighboring radial p orbitals are defined to be positive in the eclipsed s-cis conformation. From this set of p orbitals, the following four Walsh orbitals (**1**) are constructed. The small components
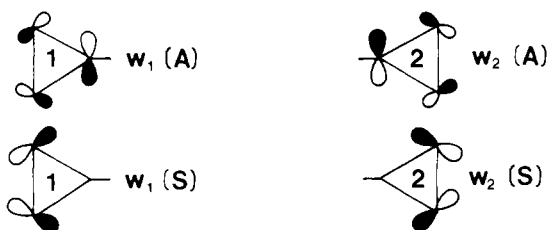
corresponding to the admixture of $\varphi'(S)$ and $\varphi'(A)$, see eq 1, are not drawn in this diagram. For all conformations of bicyclopropane, i.e., for all values of θ, a C_2 axis of symmetry is maintained. We may thus construct the following symmetry-adapted combinations. The subscripts a and b indicate the ir-

$$W_a(A) = \frac{1}{\sqrt{2}} (W_1(A) + W_2(A))$$

$$W_b(A) = \frac{1}{\sqrt{2}} (W_1(A) - W_2(A))$$

$$W_a(S) = \frac{1}{\sqrt{2}} (W_1(S) + W_2(S))$$

$$W_b(S) = \frac{1}{\sqrt{2}} (W_1(S) - W_2(S))$$

reducible representation of the C_2 point group.

The next step is to estimate the matrix elements of the Hamiltonian energy operator. The energy of the Walsh orbitals of cyclopropane is taken as our reference point, i.e.,

$$\langle w(S)|\mathcal{H}|w(S)\rangle = \langle w(A)|\mathcal{H}|w(A)\rangle = \alpha_w$$

We then need to estimate the interaction of the p orbitals a and a' with the p orbitals d and d' (see above). The value of the resonance integral $\langle a|H|d \rangle$ has been estimated by PE spectroscopy to be 1.73 eV for $\theta = 0°$.[1] This quantity is parametrized by means of the parameter β_{ww}

$$\langle a|\mathcal{H}|d\rangle = -\cos\theta \cdot \beta_{ww} \qquad (3)$$

and the usual overlap dependence of the resonance integral is assumed (note that a and d are out of phase for $\theta = 0°$). The remaining resonance integrals involving a' and d' are slightly more complicated because the radial p orbitals are not oriented perpendicular to the central bond axis. The dependence of the results on the deviation from the perpendicular orientation has

been investigated using proper expressions for the rotational dependence of the overlap integrals. A deviation of, for example, 30° has been found not to seriously affect the predicted trends. More importantly, the effect appears to be overridden by the interaction with the remaining σ frame of bicyclopropane (see later). We thus present here only the results obtained for the assumption that the radial p orbitals a' and d' are oriented perpendicular to the central C–C bond. The following simple expressions are thereby obtained:

$$\langle a'|\mathcal{H}|d'\rangle = \cos\theta \cdot \beta_{ww}$$

$$\langle a|\mathcal{H}|d'\rangle = -\sin\theta \cdot \beta_{ww} \qquad (4)$$

$$\langle a'|\mathcal{H}|d\rangle = -\sin\theta \cdot \beta_{ww}$$

These permit construction of the expressions for the elements of the Hamiltonian matrix. The results for the basis orbitals $w_1(A)$, $w_2(A)$, $w_1(S)$, and $w_2(S)$ are given in the Appendix (eq A1), where computation of the element $\langle w_1(A)|\mathcal{H}|w_2(S)\rangle$ is given as an example. The matrix elements for the symmetry-adapted basis orbitals $w_a(A)$, $w_a(S)$, $w_b(A)$, and $w_b(S)$ are similarly given in the Appendix. For reasons of symmetry, $w_a(A)$ and $w_a(S)$ will only interact with each other; the integrals are given in eq A2. The solutions to the 2 × 2 eigenvalue problem are

$$E_a^\pm = \alpha_w + [\tfrac{1}{3}(2\chi^2 - 1)\cos\theta \\ \pm \tfrac{1}{3}\sqrt{\cos^2\theta + 4\chi^2(1 - \chi^2)\sin^2\theta}]\beta_{ww} \quad (5)$$

In the case of $w_b(A)$ and $w_b(S)$ the results are similar except for a change of sign (eq A3):

$$E_b^\mp = \alpha_w - [\tfrac{1}{3}(2\chi^2 - 1)\cos\theta \\ \pm \tfrac{1}{3}\sqrt{\cos^2\theta + 4\chi^2(1 - \chi^2)\sin^2\theta}]\beta_{ww} \quad (6)$$

It is recalled that the parameter χ is a measure of the mixing of the simple Walsh orbitals $\varphi(S)$ and $\varphi(A)$ with their radial counterparts (see eq 1). For $\chi = 0$, the results (eq 5 and 6) take the simple form

$$E_a = \begin{cases} \alpha_w + \tfrac{2}{3}\cos\theta \cdot \beta_{ww} \\ \alpha_w \end{cases} \quad E_b = \begin{cases} \alpha_w \\ \alpha_w - \tfrac{2}{3}\cos\theta \cdot \beta_{ww} \end{cases} \quad (7)$$

The dependence of the orbital energies on the twist angle θ for $\chi = 0$ is shown in the top of Figure 3. All four curves are seen to cross at the same point for $\theta = 90°$. This situation is clearly unrealistic and results because $w_a(S)$ and $w_b(S)$ have no amplitude on the joined centers (see eq 2) and are thus unable to interact at all. The admixture of radial components enables these orbitals to interact through the resonance integrals listed in eq 4. It is seen in Figure 3 how the symmetry-forbidden crossings are avoided for nonzero values of χ, weakly for $\chi = \frac{1}{10}$ and quite strongly for $\chi = 1/\sqrt{5}$. The latter value of χ corresponds to 20% admixture of radial components. The appropriate value of χ is not necessarily the same in cyclopropane and bicyclopropane. Furthermore, owing to the lower symmetry of bicyclopropane it is possible to mix in more components of radial or related character than in the case of cyclopropane. This may be simulated by an appropriate choice of the parameter χ. It will appear in the following that $\chi = 1/\sqrt{5}$ is a reasonably adequate value.

So far, interaction of the Walsh orbitals in eq 2 with the remaining σ orbitals of bicyclopropane has not been introduced explicitly. In this connection, interaction with the σ_{CC} and σ^*_{CC} type orbitals of the central bond is of particular importance, since similar interactions are not present in the case of cyclopropane. Inspection of the orbitals $w_a(A)$ and $w_b(A)$ (see eq 2) shows that they have a node on the central bond axis, and the interaction with σ_{CC} and σ^*_{CC} can be expected to be small. $w_a(S)$ may interact with the lower lying σ_{CC} orbital and become destabilized, while $w_b(S)$ may be stabilized by interaction with the higher lying σ^*_{CC} orbital. This can be represented in
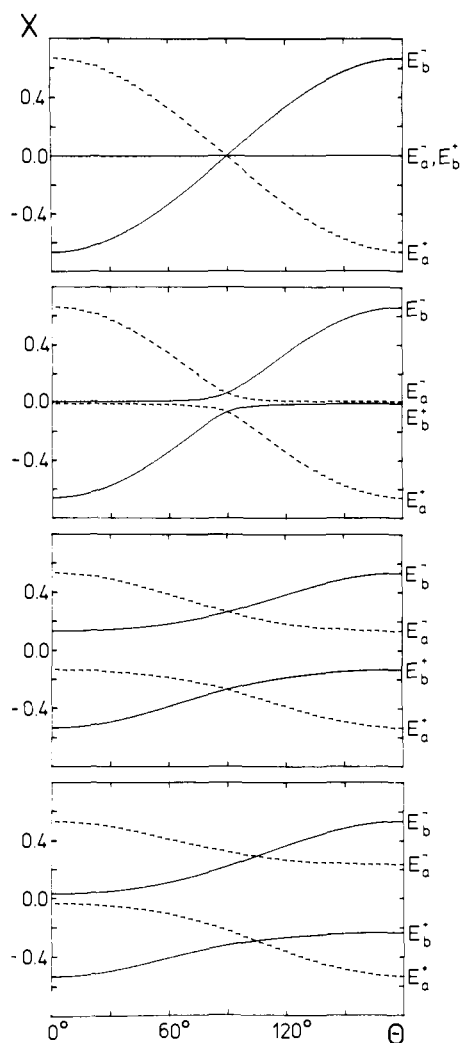
Figure 3. Orbital energies $x = (\alpha_w - E)/\beta_{ww}$ obtained by the ZDO model for bicyclopropane as a function of the twist angle θ. Top to bottom: (i) $\chi = 0, k = 0$; (ii) $\chi = \frac{1}{10}, k = 0$; (iii) $\chi = 1/\sqrt{5}, k = 0$; (iv) $\chi = 1/\sqrt{5}$, $k = \beta_{ww}/10$. Cf. eq 5, 6, and 8.
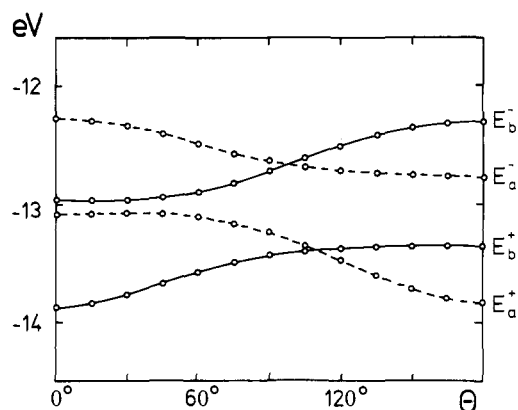

Figure 4. The four highest occupied orbital energies of bicyclopropane obtained by the EH method as a function of the twist angle θ.

a qualitative way by raising the energy of the $w_a(S)$ orbital and lowering the energy of the $w_b(S)$ orbital by a constant amount k (units of β_{ww}; note that $\beta_{ww} < 0$). The results (eq 5 and 6) then take the form

$$E_a^{\pm} = \alpha_w + [\frac{1}{3}(2\chi^2 - 1) \cos \theta - \frac{1}{2}k$$
$$\pm \frac{1}{3}\sqrt{(\cos \theta - \frac{3}{2}k)^2 + 4\chi^2(1 - \chi^2) \sin \theta}]\beta_{ww}$$

$$E_b^{\pm} = \alpha_w - [\frac{1}{3}(2\chi^2 - 1) \cos \theta - \frac{1}{2}k \tag{8}$$
$$\pm \frac{1}{3}\sqrt{(\cos \theta - \frac{3}{2}k)^2 + 4\chi^2(1 - \chi^2) \sin \theta}]\beta_{ww}$$

In the bottom of Figure 3 are shown the results for $\chi = 1/\sqrt{5}$ and $k = \beta_{ww}/10$. The most important trend is the asymmetry of the plot: different orbital energy patterns are now obtained for the s-cis ($\theta = 0°$) and the s-trans ($\theta = 180°$) conformation. In particular, the difference in energy between the second and the third level, Δ_{23}, is predicted to be smaller for the s-cis than for the s-trans conformation. An important observation is the finding that a simple, purely tangential Walsh orbital model can be expected to be a good model for twist angles close to $0°$, but not for appreciately larger values; this is apparent from a comparison of the results for $\chi = 0$ and $k = 0$ (Figure 3, top) with those for $\chi = 1/\sqrt{5}$ and $k = \beta_{ww}/10$ (Figure 3, bottom). This can be explained by the fact that the contributions introduced by increasing χ and k tend to cancel for small twist angles, but add for larger values (cf. eq 8).

The results in Figure 3 may be compared with the results

of an extended Hückel (EH)[4] calculation shown in Figure 4. This figure shows the dependence of the four highest occupied orbital energies on the twist angle θ if an otherwise rigid structure is assumed.[7] The similarity of the results of the ZDO model in Figure 3 (bottom) and the EH results in Figure 4 is striking, and indicates that the most significant terms have been included in the ZDO model. The analysis carried through in this paragraph may thus serve as a rationalization of the results of the EH method. The minor discrepancies are probably mainly due to the simplified representation of the interaction with non-Walsh orbitals in the ZDO model. The simple model, moreover, does not include interaction with the antibonding Walsh orbitals;[1] one could say that this contribution has been sacrificed in favor of the interaction with radial or related orbitals, in order to improve the description for twist angles close to $90°$.
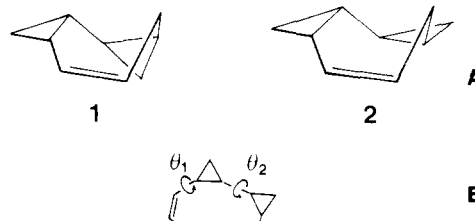
The PE spectrum of bicyclopropane has been measured by Bodor, Dewar, and Worley,[8] and by Asmus and Klessinger.[9] The interpretation is not straightforward since bicyclopropane is not rigid.[7,10] The PE spectra of the bicyclopropane derivatives cis- and trans-tricyclo[5.1.0.0^{3,5}]octane (**8** and **9**) have
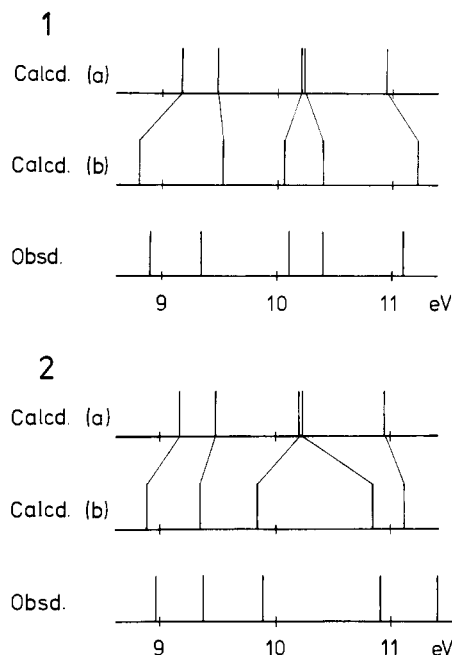

8   **9**
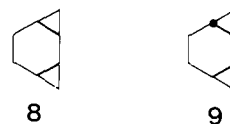
been measured by Heilbronner et al.[1] The twist angle has been estimated to be $20°$ in the case of **8** and $40°$ for the most stable conformation of **9**.[1] The rather small difference between these two θ values does not allow a sensitive test of the predicted conformation dependence of the energy level picture; the measured results[1] correspond roughly to the situation in the left half of Figure 3, bottom, but the correspondence is not clear cut. In the following section we test the present model on the systems **1** and **2**, and shall then reconsider the case of bicyclopropane.

syn- and *anti-*3,5-Bishomocycloheptatrienes (1 and 2)

Investigation of the conformational features[2] of the bicyclopropane derivatives **1** and **2** indicates that the most stable conformations are the ones shown. The conformations can be

1   **2**   **A**

B

1

Calcd. (a)

Calcd. (b)

Obsd.

       9   10   11   eV

2

Calcd. (a)

Calcd. (b)

Obsd.

       9   10   11   eV

Figure 5. Calculated and observed ionization energies of **1** and **2**. (a) $\chi = 0$, $k = 0$; (b) $\chi = 1/\sqrt{5}$, $k = \beta_{ww}/10$.

characterized by twist angles for the bonds connecting the ethylene and the cyclopropane moieties. The conformation characterized by $(\theta_1, \theta_2) = (0°, 0°)$ may be taken as the one where the double bond is cis-"bisecting" the adjacent cyclopropane ring and the two cyclopropane rings are eclipsed. Plausible twist angles in the case of **1** are then $(80°, -50°)$ and in the case of **2** $(80°, -130°)$.

The circumstance that the θ_1 values for **1** and **2** are close to 90° indicates that the interaction between the olefinic linkage and the bicyclopropane moiety is small; $\theta_1 = 90°$ corresponds to minimum conjugation between the ethylenic π orbital and the tangential components of the adjacent Walsh orbitals. In the application of the ZDO model, it is assumed that the symmetry-adapted basis orbitals $w_a(A)$, $w_b(A)$, $w_a(S)$, and $w_b(S)$ (eq 2) and their matrix elements (eq A2 and A3) used for bicyclopropane are appropriate also for the bicyclopropane moieties in **1** and **2**. The matrix elements between these Walsh-type orbitals and the π orbital of the double bond are readily derived; the results are given in the Appendix (eq A4). Here $\beta_{w\pi}$ is the resonance integral for the linkage between a $2p\pi$ AO of the ethylene fragment and a tangential $2p$ AO of the cyclopropane ring for $\theta_1 = 0°$ (maximum conjugation).

In order to obtain quantitative results, values must be estimated for the basis orbital energies α_w and α_π and the resonance integrals β_{ww} and $\beta_{w\pi}$. The effective value of α_w can be expected to vary slightly through the series **1–7** owing to the different inductive effects. For simplicity we shall use the same value for all compounds, namely, the mean value of the first six ionization potentials of the trishomocycloheptatrienes **5**, **6**, and **7**:

$$\alpha_w = -10.2 \text{ eV} \tag{9}$$

This value is reasonably consistent with an extrapolation from the corresponding centers of gravity, $\bar{I}_w$, for bicyclo[4.1.0]-heptane (**10**, $\bar{I}_w = 9.7$ eV), **8** ($\bar{I}_w = 10.0$ eV), and **9** ($\bar{I}_w = 10.1$

10   **11**

eV).[1] The value for α_π we take from the estimated basis orbital energy for bicyclo[4.1.0]heptane-2 (**11**).[1]

$$\alpha_\pi = -9.2 \text{ eV} \tag{10}$$

Values for the resonance integrals can similarly be taken from the literature. Under the assumption of purely tangential Walsh orbitals ($\chi = 0$), the values -1.73[1] and -1.9 eV[11] have been obtained for β_{ww} and $\beta_{w\pi}$, respectively. In the present model we must correct these values for the mixed character of the Walsh-type orbitals:

$$\beta_{ww} = -1.73/(1 - \chi^2) \text{ eV}$$

$$\beta_{w\pi} = -1.9/\sqrt{1 - \chi^2} \text{ eV} \tag{11}$$

The 5×5 secular problem based on the four Walsh-type orbitals and the ethylenic π orbital can now be formulated, using eq A2, A3, and A4, and solved for the parameter values given in eq 9, 10, and 11. Let us first consider the results for $\chi = 0$ and $k = 0$.

Because θ_1 is identical for **1** and **2** and the two θ_2 values are supplementary (see above), the ZDO model predicts identical orbital energies for **1** and **2** in the case of $\chi = 0$. The calculated results are included in Table I and are furthermore shown in Figure 5 where the observed ionization energies for **1** and **2** are also indicated. The comparison between the results obtained for $\chi = 0$ and the observed energies indicates that agreement is reasonably good in the case of **1**, but not in the case of **2**; in particular, the large gap between the third and fourth ionization energy of **2** is not reproduced by the model. This is consistent with the observation made in the previous section that the simple tangential Walsh orbital model characterized by $\chi = 0$ is a good model for bicyclopropane only for small twist angles; the results should thus be better for syn isomer **1** than for anti isomer **2**.

The results of the improved model with admixture of radial p orbitals and consideration of the interaction with σ and σ^* orbitals ($\chi = 1/\sqrt{5}$, $k = \beta_{ww}/10$; see the previous section) are included in Table I and shown in Figure 5. The improvement in results is considerable. The different spacing of the PE bands of **1** and **2** is now well reproduced by the model, and a convincing numerical agreement is obtained. The first ionization energy corresponds in both cases to ejection of an electron from an orbital well described by the π orbital of the double bond, and the next four ionization energies can be assigned to ejections from slightly perturbed bicyclopropane orbitals. The pattern described by the second to the fifth ionization energy of **1** and **2** can thus be directly compared with the theoretical diagram in the bottom of Figure 3 for $\theta \sim 50°$ (**1**) and $\theta \sim 130°$ (**2**). The good agreement realized may be considered as an experimental verification of the trends of this diagram and supports the analysis behind it (see the previous section).

In view of the satisfactory results obtained for the bicyclopropane derivatives **1** and **2** it may be of interest to again consider the results for bicyclopropane itself. The PE spectrum of bicyclopropane shows four main peaks in the region 9–12 eV with a mean value of 10.7 eV,[9] close to the corresponding value for cyclopropane, 10.9 eV.[12] The results of the model for $\chi = 1/\sqrt{5}$, $k = \beta_{ww}/10$, $\alpha = -10.7$ eV, and β_{ww} given in eq 11 are listed in Table II for the gauche ($\theta = 45°$) and the s-trans conformation ($\theta = 180°$). These conformations are expected to be present in the gas phase with the ratio gauche/s-trans ≈ 60:40.[10] Comparison of the calculated levels with the measured ones (see Table II) shows a very satisfactory agreement. The assignment indicated in Table II is at variance with the one suggested by Asmus and Klessinger on the basis of MINDO/2 calculations.[9] In consideration of the success of the ZDO model in the case of **1** and **2** we feel that the assignment obtained for bicyclopropane is at least plausible.

syn- and anti-1,5-Bishomocycloheptatrienes (3 and 4)

The most stable conformations of **3** and **4** are the ones indicated.[2] Hydrocarbon **4**, however, undergoes rapid ring in-

3   **4**

version at room temperature. The process is degenerate and gives rise to an identical molecule.[2] If the conformations are characterized by the twist angles θ_1 and θ_2, and that having (θ_1,
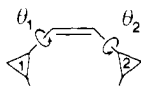
θ_2) = (0°, 0°) as the one where the double bond is cis bisecting both cyclopropane rings, the most stable structural arrangements can be defined as (90°, −90°) in the case of **3** and as ~ (70°, 0°) ⇌ (0°, 70°) for **4**. The transition state of the ring inversion in **4** can be represented approximately as (40°, 40°).

Application of the ZDO model now becomes straightforward. The basis orbitals indicated below have been adopted.
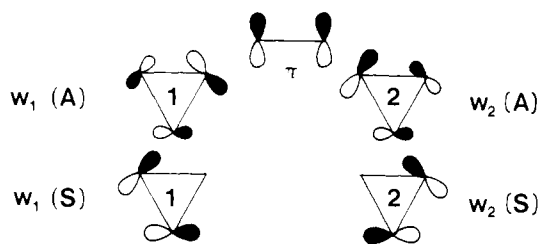
The nonzero out-of-diagonal matrix elements are given in the Appendix (eq A5). Using the α_w, α_π, and $\beta_{w\pi}$ values given in eq 9, 10, and 11 the secular problem can be solved. The solution can be obtained in analytical form by a simple linear transformation of the Walsh orbitals. Consider the linear combination

$$w = N \sum_i |w_i\rangle \langle w_i | \mathcal{H} | \pi \rangle$$

where the summation is over the four degenerate Walsh orbitals and N is a normalization factor:

$$N = \left(\sum_i |\langle w_i | \mathcal{H} | \pi \rangle|^2 \right)^{-1/2}$$

The linear combination w interacts with the π orbital with the matrix element

$$\langle \pi | \mathcal{H} | w \rangle = \left(\sum_i |\langle w_i | \mathcal{H} | \pi \rangle|^2 \right)^{1/2}$$

$$= \frac{1}{\sqrt{3}} [(1 - \chi^2)(\cos^2 \theta_1 + \cos^2 \theta_2)$$

$$+ \chi (\sin^2 \theta_1 + \sin^2 \theta_2)]^{1/2} \beta_{w\pi}$$

The remaining three of the four linear Walsh orbital combinations which can be constructed will not interact with the π orbital if they are orthogonal to w. Rather, they remain degenerate with a common energy α_w. The secular problem can thus be reduced to a 2 × 2 problem involving w and π with the eigenvalues

$$E = \frac{1}{2}(\alpha_w + \alpha_\pi \pm \sqrt{(\alpha_w - \alpha_\pi)^2 + 4\langle \pi | \mathcal{H} | w \rangle})$$

where $\langle \pi | \mathcal{H} | w \rangle$ is given above. The degeneracy of the three Walsh-type combinations is lifted when long-range interactions or interaction with other orbitals, such as σ, σ^*, and π^*, are included in the model. The influence of the π^* orbital can be estimated to stabilize one of the three orbitals in question by less than 0.1 eV. The effect of the interaction with σ and σ^* cannot be simply represented as in the case of bicyclopropane (i.e., through the parameter k, see eq 8); we shall neglect these
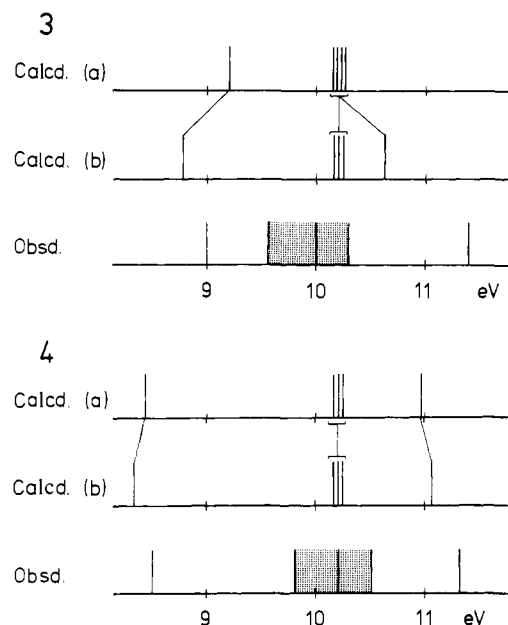

Figure 6. Calculated and observed ionization energies of **3** and **4**. (a) χ = 0; (b) $\chi = 1/\sqrt{5}$.

contributions in the case of **3** and **4** (**5**, **6**, and **7** are treated similarly).

The results of the ZDO model for $\chi = 0$ and $\chi = \frac{1}{5}$ are included in Table I and shown in Figure 6. The agreement with experiment is reasonably good; the results for $\chi = 1/\sqrt{5}$ are only slightly better than the results for $\chi = 0$. The first ionization energy of **3** and **4** corresponds to ejection of an electron from an orbital with predominantly π character. The ionization energy is 0.5 eV lower for **4** than for **3**, which is easily understood in view of the different twist angles. The strongly overlapping bands close to 10 eV in both PE spectra can be assigned to the three accidentally degenerate Walsh-type combinations. The fifth band at 11.3–11.4 eV can probably be assigned to the remaining Walsh-type orbital w, stabilized by interaction with the π orbital, although the ZDO model appears to underestimate the stabilization of this level (see Figure 6). In the case of **3** the calculated results suggest that the ionization corresponding to this level may be hidden by the tail of the broad band close to 10 eV.

The fact that **4** is not rigid does not affect the appearance of the PE spectrum; i.e., no band broadening or related effects are observed (see Figure 1). A reasonable explanation is that ring flipping produces an identical species with an identical PE spectrum. Furthermore, intermediate conformations can be expected to give rise to very similar PE spectra; the ZDO results for the (70°, 0°) conformation and the estimated transition state of (40°, 40°) are identical within a few hundredths of an eV.

syn,syn-, anti,anti-, and anti,syn-Trishomocycloheptatrienes (5, 6, and 7)

The stable conformations of the trishomocycloheptatrienes **5**, **6**, and **7** are represented.[2] The conformations can be char-

5   **6**   **7**
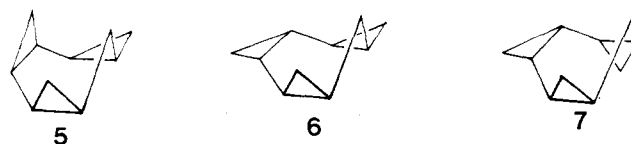
acterized by the usual twist angles θ_1 and θ_2. If (θ_1, θ_2) = (0°, 0°) relates to the all-eclipsed cis, cis conformation, plausible values in the case of **5**, **6**, and **7** are (−45°, 45°), (120°, −120°), and (120°, −45°), respectively. The severe nonbonded
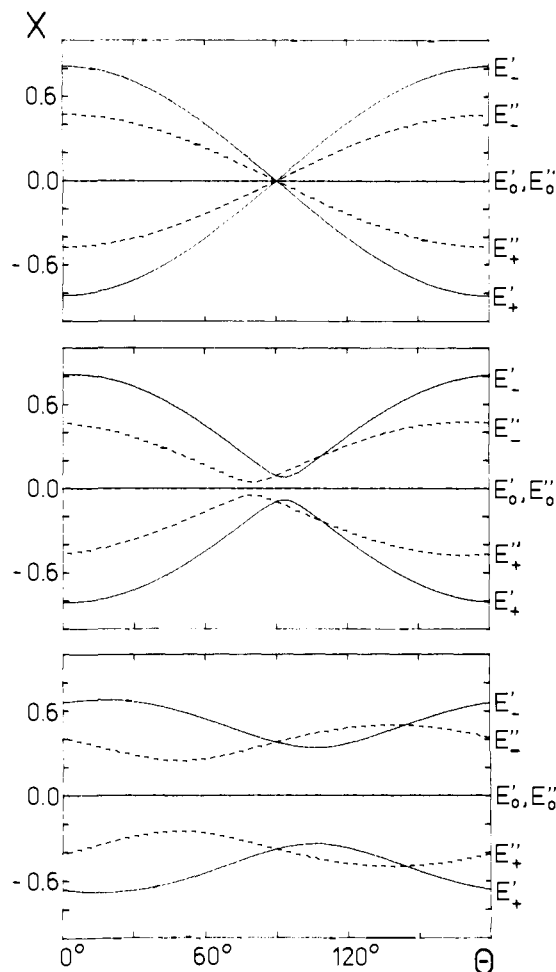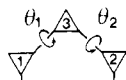
Figure 7. Orbital energies $x = (\alpha_w - E)/\beta_{ww}$ obtained by the ZDO model for C_s conformations of trishomocycloheptatriene as a function of the twist angle $\theta = -\theta_1 = \theta_2$. Top to bottom: (i) $\chi = 0$; (ii) $\chi = 1/10$; (iii) $\chi = 1/\sqrt{5}$.

interactions in the case of **5** make the twist angles difficult to estimate from usual molecular models, and the suggested values should be considered as rather tentative in this instance.

Application of the ZDO model to these species is similar to that employed for **3** and **4**, except that the central π orbital is replaced by a symmetric and an antisymmetric Walsh orbital.
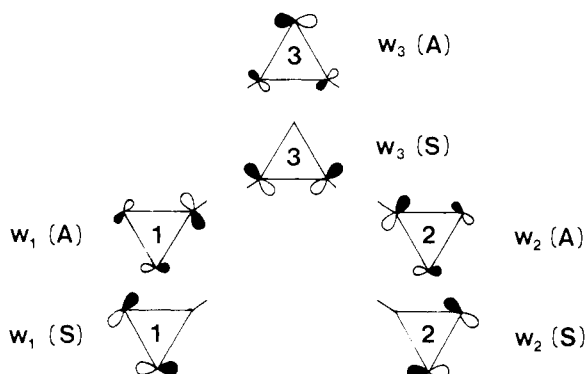
The nonzero off-diagonal matrix elements are listed in the Appendix (eq A6). The solutions to the 6 × 6 secular problem based on the six degenerate Walsh-type basis orbitals can be
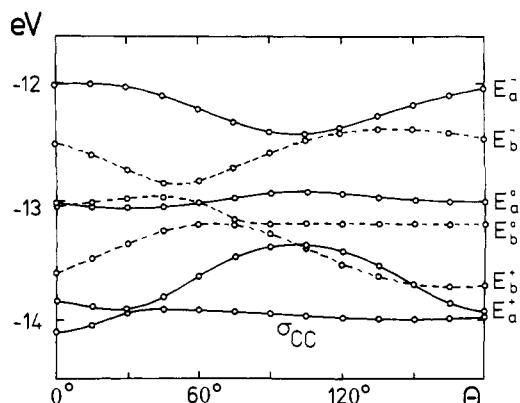

Figure 8. Orbital energies for C_2 conformations of *endo,exo*-trishomohexatriene obtained by the EH method as a function of the twist angle θ.

obtained in analytical form by means of an extension of the procedure applied in the previous section in the case of **3** and **4**. Independent of the twist angles and the choice of χ value, two Walsh orbital combinations localized on the rings **1** and **2** (see above) will remain degenerate with a common energy α_w (this is similar to the case of **3** and **4** if the π^* orbital is included in the basis set). The remaining four molecular orbital energies will be positioned symmetrically with respect to α_w, two above and two below. For simplicity we give only the results for conformations with a plane of symmetry bisecting the central cyclopropane ring, i.e., $\theta_2 = -\theta_1 = \theta$:

a′: $$E_0' = \alpha_w$$

$$E_{\pm}' = \alpha_w \pm 2\sqrt{a^2 + b^2}\beta_{ww}$$

$$a = \frac{1}{\sqrt{6}}(1 - \chi^2)\cos\theta + \frac{1}{3\sqrt{2}}\chi\sqrt{1 - \chi^2}\sin\theta$$

$$b = \frac{1}{3\sqrt{2}}\chi^2\cos\theta - \frac{1}{\sqrt{6}}\chi\sqrt{1 - \chi^2}\sin\theta$$

a″: $$E_0'' = \alpha_w$$

$$E_{\pm}'' = \alpha_w \pm 2\sqrt{c^2 + d^2}\beta_{ww}$$

$$c = \frac{1}{3\sqrt{2}}(1 - \chi^2)\cos\theta - \frac{1}{\sqrt{6}}\chi\sqrt{1 - \chi^2}\sin\theta$$

$$d = \frac{1}{\sqrt{6}}\chi^2\cos\theta + \frac{1}{3\sqrt{2}}\chi\sqrt{1 - \chi^2}\sin\theta$$

Prime and double prime label the levels according to the irreducible representations of the C_s point group, a′ and a″, respectively. It is quickly seen that in the case of $\chi = 0$ the splitting of the nondegenerate levels is described by simple cosine relationships,

$$E_{\pm}' = \alpha_w \pm \frac{2}{\sqrt{b}}\cos\theta\,\beta_{ww}$$

$$E_{\pm}' = \alpha_w \pm \frac{2}{3\sqrt{2}}\cos\theta\,\beta_{ww}$$

reminiscent of the case of bicyclopropane (eq 7). The conformational dependence of the levels for $\chi = 0$ is shown in the top of Figure 7; as in the case of bicyclopropane all levels cross for $\theta = 90°$. The subsequent plots in Figure 7 show how the symmetry-forbidden crossings are avoided for nonzero values of χ. It is characteristic that the oscillations of the E' and E'' curves become increasingly out of phase as χ is increased, leading to a strong conformational dependence of the difference $E_-' - E_-'' = E_+'' - E_+'$. The results in Figure 7 can be compared with the results of an EH calculation on trishomohexatriene in Figure 8. To avoid the interaction between the terminal cyclopropane rings in the endo,endo configuration

the calculation was carried out for the endo,exo isomer. The conformational dependence was then investigated for conformations with a C_2 axis of symmetry. For the sake of comparison with the results of the ZDO model, this procedure is adequate since the simple model does not distinguish between an endo,endo conformation of C_s symmetry and the corresponding endo,exo conformation of C_2 symmetry. Comparison of the plot in the bottom of Figure 7 with the EH results in Figure 8 indicates that a number of significant trends are well reproduced by the ZDO model. In particular, the oscillatory behavior of the curves is well described. The degeneracy of the third and fourth level is lifted in the EH approximation, but the levels are still close together, particularly for $\theta < 70°$. The dependence of these levels on θ is not simple, particularly not in the region below 90° where the crossings of the E_b curves in Figure 8 (corresponding to the E'' curves in Figure 7) are only weakly avoided. The region of interest in the present investigation is the region ~30-75°; the ordering of the two highest and the two lowest levels obtained by the ZDO model in this region is confirmed by the results of the EH calculations.

The highest occupied non-Walsh orbital obtained by the EH method, labeled σ_{CC} in Figure 8, is totally symmetric and has σ character with respect to the connecting bonds; this is indicated by the independence of θ of the orbital energy. The interaction of this orbital with the Walsh-type orbitals is small, as shown by the very weakly avoided crossing with the E_a^+ orbital (see Figure 8).

The compounds 5 and 6 can be considered as symmetric, with a plane of symmetry perpendicular to the central cyclopropane ring through the methylene group.[2] The estimated values of the twist angle $\theta = -\theta_1 = \theta_2$ are 45 and −120°, respectively; the results of the ZDO model are periodic with a frequency of 180°, i.e., a value of $\theta = -120°$ is equivalent to $\theta = 60°$. The ZDO results relevant for 5 and 6 are thus found in Figure 7 for $\theta = 45°$ and $\theta = 60°$, respectively. The results obtained for $\chi = 0$ and $\chi = 1/\sqrt{5}$ with the α_w and β_{ww} values given in eq 9 and 11 are furthermore included in Table I and Figure 9.

Comparison of the calculated results with the measured ionization energies draws attention to two points of interest. Firstly, when passing from 5 to 6 the first ionization energy is increased while the second is decreased (see Table I); a similar situation applies to the fifth and sixth level. This is inconsistent with the results of the ZDO model for $\chi = 0$, where any shift in θ is accompanied by parallel shifts of the two highest, as well as of the two lowest, levels. However, allowing for admixture of radially oriented components by increasing the value of χ leads to a prediction in agreement with the measured trend. This is due to the different phase shifts as shown in Figure 7. Opposite shifts of the first and the second level, and of the fifth and the sixth level, under a change of θ from 45 to 60° are predicted by the model for $\chi = 1/\sqrt{5}$, although the predicted shifts of the second and the fifth level are smaller than measured. The second point of interest is the "total width" of the spectrum as measured by the distance between the first and the sixth level. The widths predicted in the case of 5 and 6 for $\chi = 0$ are 2.00 and 1.42 eV, respectively, significantly smaller than the measured values (2.6 and 2.3 eV). The results for $\chi = 1/\sqrt{5}$ are 2.66 and 2.34 eV, respectively; these values are obviously in much better agreement with experiment (see Figure 9). Finally, one could note again the overall good numerical agreement between calculated and observed levels of the unsymmetrical anti,syn isomer 7 (see Table I). A significant improvement is observed when χ is increased from zero. All things considered, we believe that the ZDO model for interacting Walsh orbitals developed in this paper is a significant and relevant extension of the simple tangential picture for systems with nonzero twist angles.
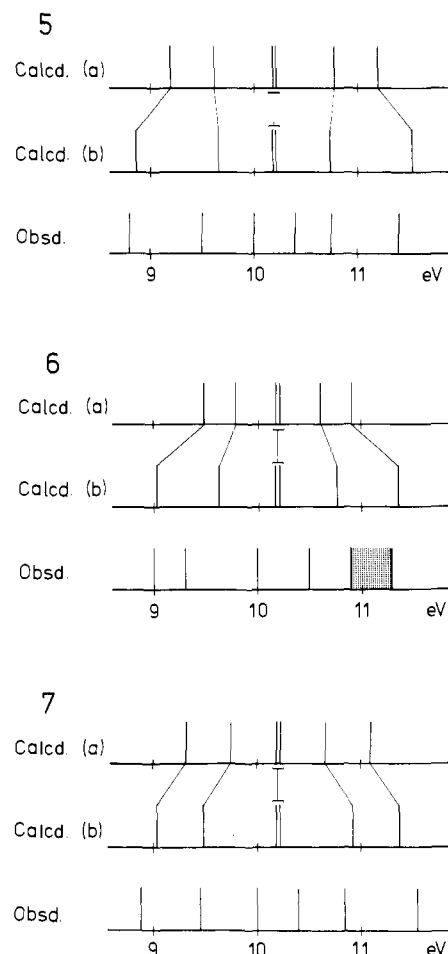

Figure 9. Calculated and observed ionization energies of 5, 6, and 7. (a) $\chi = 0$; (b) $\chi = 1/\sqrt{5}$.

Conclusion

The aim of this study has been to elucidate the orbital interactions present between two and three linked cyclopropane rings as a function of the dihedral angles. Good agreement between PE measurements and model calculations can only be achieved if admixture of nontangential components into the highest occupied Walsh orbitals of the cyclopropane ring is considered. This leads to a refinement of the simple Walsh orbital picture.

Experimental Section

Appendix

As an example of the derivation of the matrix elements between the Walsh orbitals $w_1(A)$, $w_2(A)$, $w_1(S)$, and $w_2(S)$ in the case of bicyclopropane we compute the element $\langle w_1(A) \cdot |\mathcal{H}|w_2(S)\rangle$:

$\langle w_1(A) | \mathcal{H} | w_2(S) \rangle =$
$\langle \sqrt{1 - \chi^2} \, \varphi_1(A) - \chi\varphi_1'(A) | \mathcal{H} | \sqrt{1 - \chi^2} \, \varphi_2(S) + \chi\varphi_2'(S) \rangle$

$= (1 - \chi^2) \langle \varphi_1(A) | \mathcal{H} | \varphi_2(S) \rangle$
$+ \chi\sqrt{1 - \chi^2} \, \langle \varphi_1(A) | \mathcal{H} | \varphi_2'(S) \rangle$
$+ \chi\sqrt{1 - \chi^2} \, \langle \varphi_1'(A) | \mathcal{H} | \varphi_2(S) \rangle$
$- \chi^2 \langle \varphi_1'(A) | \mathcal{H} | \varphi_2'(S) \rangle$

$= (1 - \chi^2) \dfrac{1}{\sqrt{6}} \dfrac{1}{\sqrt{2}} \langle 2a - b - c | \mathcal{H} | e - f \rangle$

$+ \chi\sqrt{1 - \chi^2} \dfrac{1}{\sqrt{6}} \dfrac{1}{\sqrt{6}} \langle 2a - b - c | \mathcal{H} | 2d' - e' - f' \rangle$

$+ \chi\sqrt{1 - \chi^2} \dfrac{1}{\sqrt{2}} \dfrac{1}{\sqrt{2}} \langle b' - c' | \mathcal{H} | e - f \rangle$

$- \chi^2 \dfrac{1}{\sqrt{2}} \dfrac{1}{\sqrt{6}} \langle b' - c' | \mathcal{H} | 2d' - e' - f' \rangle$

$= \chi\sqrt{1 - \chi^2} \, \tfrac{2}{3} \langle a | \mathcal{H} | d' \rangle = -\tfrac{2}{3} \chi\sqrt{1 - \chi^2} \sin \theta \cdot \beta_{ww}$

The remaining nonzero out-of-diagonal elements are given by

$$\langle w_1(A) | \mathcal{H} | w_2(A) \rangle = -\frac{2}{3}(1 - \chi^2) \cos \theta \cdot \beta_{ww}$$

$$\langle w_1(S) | \mathcal{H} | w_2(S) \rangle = \frac{2}{3} \chi^2 \cos\theta \cdot \beta_{ww}$$

$\langle w_1(S) | \mathcal{H} | w_2(A) \rangle$

$$= \langle w_1(A) | \mathcal{H} | w_2(S) \rangle = -\frac{2}{3} \chi\sqrt{1 - \chi^2} \sin \theta \cdot \beta_{ww} \quad (A1)$$

The matrix elements over the symmetry-adapted Walsh orbitals of bicyclopropane $w_a(A)$, $w_a(S)$, $w_b(A)$, $w_b(S)$ (eq 2) are given as follows:

$$\langle w_a(A) | \mathcal{H} | w_a(A) \rangle = \alpha_w - \tfrac{2}{3}(1 - \chi^2) \cos \theta \cdot \beta_{ww}$$

$$\langle w_a(S) | \mathcal{H} | w_a(S) \rangle = \alpha_w + \tfrac{2}{3} \chi^2 \cos \theta \cdot \beta_{ww} \quad (A2)$$

$$\langle w_a(A) | \mathcal{H} | w_a(S) \rangle = -\tfrac{2}{3} \chi\sqrt{1 - \chi^2} \sin \theta \cdot \beta_{ww}$$

$$\langle w_b(A) | \mathcal{H} | w_b(A) \rangle = \alpha_w + \tfrac{2}{3}(1 - \chi^2) \cos \theta \cdot \beta_{ww}$$

$$\langle w_b(S) | \mathcal{H} | w_b(S) \rangle = \alpha_w - \tfrac{2}{3} \chi^2 \cos \theta \cdot \beta_{ww} \quad (A3)$$

$$\langle w_b(A) | \mathcal{H} | w_b(S) \rangle = +\tfrac{2}{3} \chi\sqrt{1 - \chi^2} \sin \theta \cdot \beta_{ww}$$

The matrix elements between these orbitals and an ethylenic orbital $1/\sqrt{2} \, (\pi_1 + \pi_2)$ as in the case of **1** and **2** are given by

$\langle w_a(A) | \mathcal{H} | \pi \rangle = \langle w_b(A) | \mathcal{H} | \pi \rangle$

$$= \tfrac{1}{2} \left[\frac{1}{\sqrt{6}} \sqrt{1 - \chi^2} \cos \theta_1 - \frac{1}{\sqrt{2}} \chi \sin \theta_1 \right] \beta_{w\pi}$$

$\langle w_a(S) | \mathcal{H} | \pi \rangle = \langle w_b(S) | \mathcal{H} | \pi \rangle$

$$= \tfrac{1}{2} \left[\frac{1}{\sqrt{2}} \sqrt{1 - \chi^2} \cos \theta_1 + \frac{1}{\sqrt{6}} \chi \sin \theta_1 \right] \beta_{w\pi} \quad (A4)$$

The nonzero out-of-diagonal matrix elements between the Walsh orbitals $w_1(A)$, $w_2(A)$, $w_1(S)$, and $w_2(S)$ and the π orbital $1/\sqrt{2} \, (\pi_1 + \pi_2)$ as defined in the case of **3** and **4** are given below:

$$\langle w_1(A) | \mathcal{H} | \pi \rangle = -\frac{1}{\sqrt{3}} \sqrt{1 - \chi^2} \cos \theta_1 \cdot \beta_{w\pi}$$

$$\langle w_2(A) | \mathcal{H} | \pi \rangle = +\frac{1}{\sqrt{3}} \sqrt{1 - \chi^2} \cos \theta_2 \cdot \beta_{w\pi}$$

$$\langle w_1(S) | \mathcal{H} | \pi \rangle = -\frac{1}{\sqrt{3}} \chi \sin \theta_1 \cdot \beta_{w\pi}$$

$$\langle w_2(S) | \mathcal{H} | \pi \rangle = +\frac{1}{\sqrt{3}} \chi \sin \theta_2 \cdot \beta_{w\pi} \quad (A5)$$

The corresponding elements between the six Walsh orbitals in the case of **5, 6,** and **7** are the following:

$\langle w_1(A) | \mathcal{H} | w_3(A) \rangle$

$$= \left[-\frac{1}{3}(1 - \chi^2) \cos \theta_1 - \frac{1}{\sqrt{3}} \chi\sqrt{1 - \chi^2} \sin \theta_1 \right] \beta_{ww}$$

$\langle w_1(A) | \mathcal{H} | w_3(S) \rangle$

$$= \left[-\frac{1}{\sqrt{3}}(1 - \chi^2) \cos \theta_1 + \frac{1}{3} \chi\sqrt{1 - \chi^2} \sin \theta_1 \right] \beta_{ww}$$

$\langle w_2(A) | \mathcal{H} | w_3(A) \rangle$

$$= \left[-\frac{1}{3}(1 - \chi^2) \cos \theta_2 + \frac{1}{\sqrt{3}} \chi\sqrt{1 - \chi^2} \sin \theta_2 \right] \beta_{ww}$$

$\langle w_2(A) | \mathcal{H} | w_3(S) \rangle$

$$= \left[+\frac{1}{\sqrt{3}}(1 - \chi^2) \cos \theta_2 + \frac{1}{3} \chi\sqrt{1 - \chi^2} \sin \theta_2 \right] \beta_{ww}$$

$\langle w_1(S) | \mathcal{H} | w_3(A) \rangle$

$$= \left[-\frac{1}{3} \chi\sqrt{1 - \chi^2} \sin \theta_1 + \frac{1}{\sqrt{3}} \chi^2 \cos \theta_1 \right] \beta_{ww}$$

$\langle w_1(S) | \mathcal{H} | w_3(S) \rangle$

$$= \left[-\frac{1}{\sqrt{3}} \chi\sqrt{1 - \chi^2} \sin \theta_1 - \frac{1}{3} \chi^2 \cos \theta_1 \right] \beta_{ww}$$

$\langle w_2(S) | \mathcal{H} | w_3(A) \rangle$

$$= \left[-\frac{1}{3} \chi\sqrt{1 - \chi^2} \sin \theta_2 - \frac{1}{\sqrt{3}} \chi^2 \cos \theta_2 \right] \beta_{ww}$$

$\langle w_2(S) | \mathcal{H} | w_3(S) \rangle$

$$= \left[+\frac{1}{\sqrt{3}} \chi\sqrt{1 - \chi^2} \sin \theta_2 - \frac{1}{3} \chi^2 \cos \theta_2 \right] \beta_{ww} \quad (A6)$$

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