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LINEAR COMBINATION OF WALSH ORBITALS IN TRIS-σ-HOMOBENZENES

PHOTOELECTRON SPECTROSCOPY AND MODEL CALCULATIONS

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Abstract—The applicability of the cyclopropane Walsh orbital model to a series of tris-σ-homobenzenes is investigated by means of photoelectron (PE) spectroscopy and molecular orbital (MO) theory, with particular emphasis on an understanding of the conformational dependence of the conjugative interaction between Walsh orbitals of linked 3-membered rings. The shifts of the first three PE bands in the series diademane (1), *trans*-pentacyclo[3.3.2.$0^{2,9}$.$0^{4,10}$.$0^{6,8}$]decane (2), *trans*-tris-σ-homobenzene (3) and its 3,3,6,6,9,9-hexamethyl derivative (4) are well described in terms of a "Linear Combination of Walsh Orbitals" (LCWO) model, provided "radially" oriented contributions to the cyclopropane Walsh orbitals are included. The results imply that the highest occupied MO in 2, 3 and 4 is localized in the s-cis-bicyclopropyl fragment of these species.

The interaction between Walsh orbitals of "conjugated" cyclopropane rings in diademane 1 (hexacyclo[4.4.0.$0^{2,4}$.$0^{3,9}$.$0^{5,7}$.$0^{8,10}$]decane) and *trans*-pentacyclo[3.3.2.$0^{2,9}$.$0^{4,10}$.$0^{6,8}$]decane 2 has been investigated some time ago by Heilbronner *et al.*[1] by means of photoelectron (PE) spectroscopy and simple Hückel type theory. The value of the resonance integral between linked "tangential" 2p atomic orbitals (AOs) of adjacent eclipsed cyclopropane rings was found to be − 1.73 eV.† In connection with recent studies of the rearrangement of tris-σ-homobenzenes[2–4] and PE spectroscopic investigations of homocycloheptatrienes,[5] it became of interest to extend the above mentioned investigation to *trans*-tris-σ-homobenzene 3 (*endo*, *exo*-tetracyclo[6.1.0.$0^{2,4}$.$0^{5,7}$]nonane) and its 3,3,6,6,9,9,-hexamethyl derivative 4.[6]

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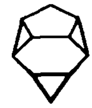

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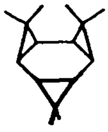
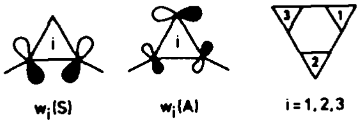


The aim of this undertaking is to estimate the applicability of the cyclopropane Walsh orbital model to systems with linked cyclopropyl groups. A recent investigation indicates that a model based on purely "tangential" 2p AOs is an oversimplification and that "radial" contributions should be considered in order to describe the measured trends.[5] As discussed below, dihedral angles between linked three-membered rings in the series 1–4 range from 0° to 120°, which provides an excellent opportunity for a sensitive test of the predictions in Ref. 5.

The LCWO model

The Walsh-type molecular orbitals (MOs) of molecules with linked 3-membered rings may be described in terms of a "Linear Combination of Walsh Orbitals" (LCWO) model introduced recently.[5] This model and its application within Koopmans' theorem ($\epsilon_{MO} = -I_v$)[7] to the PE spectra of cyclopropyl compounds have been discussed in detail;[5] only a brief outline is given here. The basis orbitals are the e′ Walsh-type orbitals of cyclopropane, w(S) and w(A).[8] In the present case of tris-σ-homobenzenes we choose the phases of the "tangentially" oriented contributions as indicated below.



This is the usual representation of cyclopropane Walsh orbitals which is sufficient for most qualitative applications.[8] In contrast to the case of cyclobutane,[8] it is not necessary to involve "radial" contributions in order to obtain net bonding Walsh orbitals. The admixture of "radial" components, however, is essential to the interaction between Walsh orbitals of linked 3-membered rings, particularly for torsional angles close to 90°, when the conjugative interaction between purely "tangential" Walsh orbitals is minimal. In the present model, this admixture is introduced formally as a HOMO-LUMO

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† 1 eV ≈ 96.478 kJ/mole.

mixing in cyclopropane, and the degree of admixture is specified by the parameter χ; per cent "radial" admixture = $100\chi^2$. Using the model introduced in Ref. 5, the interaction integrals between the Walsh orbitals indicated above take the following form:

$$\langle w_i(S)|\mathscr{H}|w_i(S)\rangle = \langle w_i(A)|\mathscr{H}|w_i(A)\rangle = \alpha_w$$

$$\langle w_i(S)|\mathscr{H}|w_j(S)\rangle_{j=i\pm1} = \left(\frac{1}{2}-\frac{\chi^2}{3}\right)\cos\theta_{ij}\cdot\beta$$

$$\langle w_i(A)|\mathscr{H}|w_j(A)\rangle_{j=i\pm1} = -\left(\frac{1}{6}+\frac{\chi^2}{3}\right)\cos\theta_{ij}\cdot\beta$$

$$\langle w_i(S)|\mathscr{H}|w_j(A)\rangle_{j=i\pm1} = \left[\pm\frac{1}{2\sqrt{3}}(1-2\chi^2)\cos\theta_{ij}+\frac{2}{3}\chi\sqrt{(1-\chi^2)}\sin\theta_{ij}\right]\cdot\beta \quad (1)$$

Here θ_{ij} is the dihedral angle between the rings i and j, where $\theta_{ij} = 0°$ refers to the eclipsed conformation, and β is the resonance integral between linked "tangential" 2p AOs of adjacent cyclopropane rings for $\theta = 0°$.

For $\chi = 0$ the expressions (1) refer to the interaction between purely "tangential" Walsh orbitals. As explained in detail previously,[5] the "tangential" Walsh orbital model is a good model for the eclipsed conformation of bicyclopropyl because for dihedral angles θ close to 0°, the influence of "radial" contributions tends to cancel with the effect of the interaction with σ_{cc} and σ^*_{cc} orbitals of the central bond. This is not the case for θ deviating significantly from 0°, when "radial" contributions become essential and a χ-value of $1/\sqrt{5} \approx 0.45$ corresponding to 20% admixture of "radial" components has been found appropriate.[5] These arguments can be extended to the case of three linked cyclopropyl groups as in 1–4. Consequently, we take $\chi = \chi^{cis} = 0$ for the interaction between *cis*-related and $\chi = \chi^{trans} = 1/\sqrt{5}$ for the interaction between *trans*-related cyclopropyl groups in 1–4.

In order to obtain quantitative results, it is furthermore necessary to obtain empirical estimates of the quantities θ_{ij}, α_w and β entering (1). In the case of 1, all dihedral angles θ_{ij} are equal to zero by symmetry.[1] The compounds 2–4 can be assumed to have C_s-symmetry,[1,6] which means that the dihedral angle between the *cis*-oriented cyclopropyl groups is equal to zero, i.e. $\theta^{cis} = \theta_{31} = 0°$. Inspection of molecular models indicates that the angle between *trans*-related cyclopropyl groups is close to 60° in the case of 2,[1] i.e. $\theta^{trans} = \theta_{12} = -\theta_{23} = 60°$. In the case of 3, this angle can be expected to be close to 90°, a MINDO/3[9] calculation yields[2] the value 82°; we shall consider 3 as a model compound for the case $\theta^{trans} = 90°$. The steric interaction between the geminal Me groups in 4 can be expected to increase this value to about 120°; this is consistent with the results of an X-ray diffraction investigation.[10] The dihedral angles can be summarized as follows.

Compound	$\theta^{cis} = \theta_{31}$	$\theta^{trans} = \theta_{12} = -\theta_{23}$
1	0°	0°
2	0°	60°
3	0°	90°
4	0°	120°

The energy parameters α_w and β are taken as

$$\alpha_w = -10.3\,\text{eV},$$

$$\beta = -1.73(1-\chi^2)^{-1}\,\text{eV}.$$

These values are consistent with those employed in Ref. 5. The effect of the alkyl groups in 1, 2 and 4 can be expected to destabilize $w_i(A)$ relative to $w_i(S)$ for each substituted ring[1] because of the large difference in amplitude in the substituted position. We shall adopt a crude scheme for the approximation of this effect: the substitution of an alkyl group is assumed to destabilize $w_i(A)$ by 0.5 eV, leaving $w_i(S)$ unaffected. In the case of 1, α_w is thus taken as −9.8 eV for the three $w_i(A)$ orbitals, and as −10.3 eV for the three $w_i(S)$ orbitals. In the case of 2 we have $\alpha_w = -9.8$ eV for $w_1(A)$ and $w_3(A)$, and $\alpha_w = -10.3$ eV for the remaining basis orbitals. The effect of two alkyl groups as in 4 is taken as twice the effect of one, i.e. $\alpha_w = -9.3$ eV for $w_i(A)$ and $\alpha_w = -10.3$ eV for $w_i(S)$. The simplicity of this scheme is in keeping with the basic simplicity of the LCWO model and keeps the number of disposable parameters at a minimum.

In this section the general features and parametrization of the model have been presented. It is now straightforward to set up and solve the 6 × 6 secular problem and obtain the LCWO MOs and their energies ϵ for 1–4. The application to the PE spectra of these compounds is discussed in the following section.

RESULTS AND DISCUSSION

The PE spectra of 3 and 4 are shown in Fig. 1 and measured vertical ionization energies I_v for the series 1–4 are given in Table 1 together with calculated MO energies.

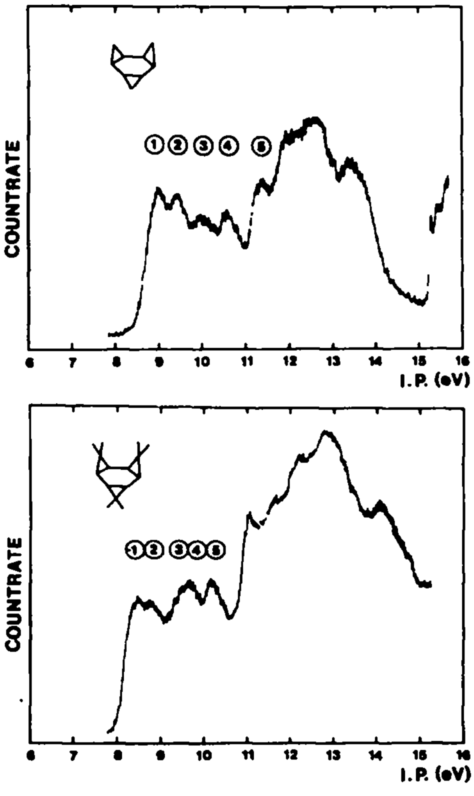

Fig. 1. Photoelectron spectra of 3 and 4.

Table 1. Measured ionization energies I_v and calculated MO energies ϵ for 1–4. I_v for 3 and 2 are taken from Ref. 1

Compound	Band	I_v	$-\epsilon$		
			LCWO(a)	LCWO(b)	MINDO/3
1(D_{3h})	①	8.5	8.84(e)		8.74(8e)
	②	9.0			
	③	9.4	9.22(a_2)		8.80($2a_2$)
	④	10.6	10.69(e)		10.18(7e)
	⑤	11.1			
	⑥	11.4			10.87(6e)
			12.03(a_1)		10.98($7a_1$)
2(C_s)	①	8.8	8.96(a")	8.73(a")	
	②	9.2	9.47(a')	9.39(a")	
	③	9.6	9.72(a")	9.74(a')	
	④	10.4	10.54(a')	10.04(a')	
	⑤	10.9	10.57(a")	11.13(a")	
	⑥	11.2	11.54(a')	11.78(a')	
3(C_s)	①	9.0	9.15(a")	8.79(a")	8.83(10a")
	②	9.4	10.30(a')	9.55(a')	9.48(9a")
	③	9.9	10.30(a")	10.08(a")	9.48(14a')
	④	10.5	10.30(a")	10.88(a')	9.97(13a')
	⑤	11.3	10.30(a')	10.88(a")	10.86(8a")
			11.45(a')	11.63(a')	11.08(12a')
4(C_s)	①	8.5	8.68(a")	8.36(a")	
	②	8.8	9.07(a")	8.66(a')	
	③	9.6	9.18(a')	9.53(a")	
	④	9.8	10.00(a")	9.86(a")	
	⑤	10.3	10.34(a')	10.87(a')	
			11.53(a')	11.52(a')	

(a) $\chi^{cis} = \chi^{trans} = 0$.

(b) $\chi^{cis} = 0, \chi^{trans} = 1/\sqrt{5}$; in the case of **1**, the results are identical to those under (a) because no trans interactions are present.

Before turning to the results for the individual species 1–4, it is instructive to consider some general results for tris-σ-homobenzenes. In Fig. 2 are shown the results of the LCWO model for C_s conformations as a function of θ^{trans} under the assumption of purely "tangential" Walsh orbitals, i.e. $\chi = 0$. It is seen that for $\theta^{trans} = 90°$, the four intermediate levels are accidentally degenerate with a common energy α_w. This situation occurs because the conjugative interaction between the *exo*, *exo* bicyclopropyl fragment and the *endo* cyclopropyl group vanishes for $\theta^{trans} = 90°$ and the MOs correspond to those of s-*cis*-bicyclopropyl and cyclopropane (see Fig. 3). For θ^{trans} deviating slightly from 90°, the levels are split according to the interaction diagram in Fig. 3. However, this picture is changed when the influence of "radial" contributions is considered. Fig. 4 shows the LCWO results for $\theta^{trans} = 80°$ as a function of χ, i.e. as a function of the admixture of "radial " components. The ordering and relative spacing of the four intermediate levels depend strongly on χ, particularly for small values of χ. It is evident that a proper representation of "radial" and related contributions is critical in this region.

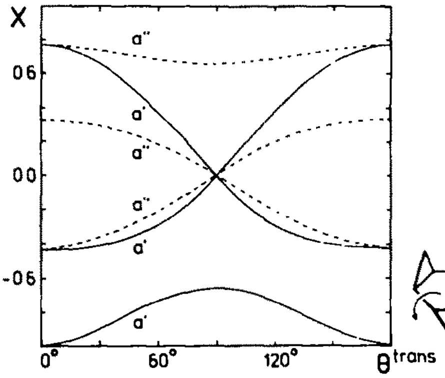

Fig. 2. Orbital energies $X = (\alpha_w - \epsilon)/\beta$ obtained by the LCWO model for C_s conformations of tris-σ-homobenzene as a function of θ^{trans}. The results refer to the interaction between purely "tangential" Walsh orbitals ($\chi = 0$, see text).

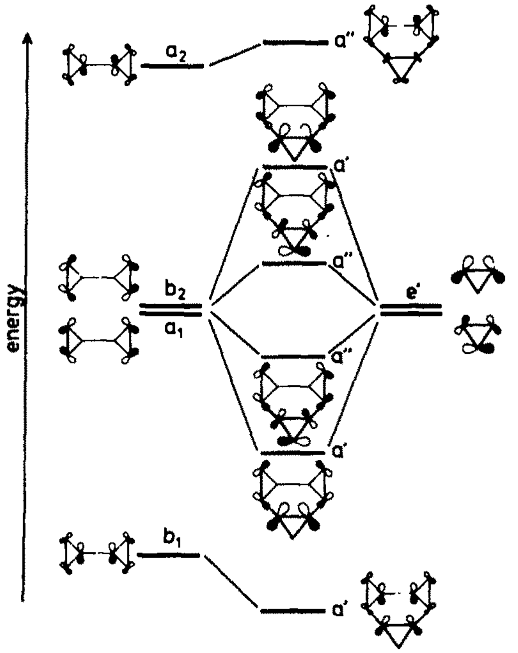

Fig. 3. Qualitative first order interaction diagram of the "tangential" Walsh orbitals of s-*cis*-bicyclopropyl and cyclopropane yielding the Walsh orbitals of tris-σ-homobenzene for θ^{trans} somewhat less than 90°.

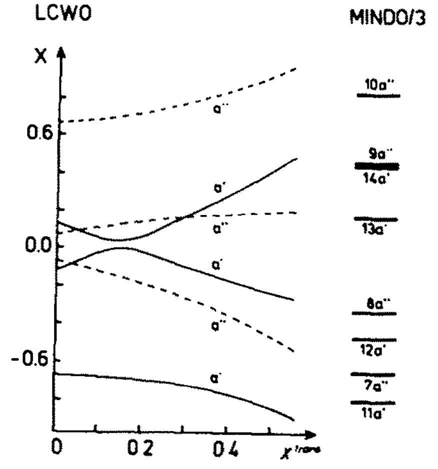

Fig. 4. LCWO energies $X = (\alpha_w - \epsilon)/\beta$ of tris-σ-homobenzene for $\theta^{trans} = 80°$ as a function of the admixture of "radial" components (see text). MINDO/3 results for 1 ($\theta^{trans} = 82°$)[2] are shown to the right.

The trends of Fig. 4 can be rationalized by a consideration of the shape of the orbitals in Fig. 3, but we shall not further discuss this point. It should be noted, however, that the approximate representation of "radial" terms in the LCWO model leads to general consistency with the ordering of the highest occupied MOs obtained by a MINDO/3 calculation, as shown in Fig. 4. Inspection of the wavefunctions indicates that the LCWO and MINDO/3 results are quite similar with respect to the shape of the three to four highest occupied MOs, which are reasonably well represented by the diagram in Fig. 3. Unfortunately, this does not appear to be the case for the lower lying MOs which are predicted by MINDO/3 to be so mixed with other contributions that their classification as Walsh orbitals becomes problematic. This observation is probably significant; a similar situation applies to the case of 1 (Table 1), and the existence of "σ-type" orbitals in the region of the most bonding Walsh orbitals has been indicated in the case of trishomocycloheptatrienes.[5] As a consequence, the following application of the LCWO model concerns primarily the three highest MOs of 1–4 which can be expected to be of predominantly Walsh orbital character.

The conformational dependence of the results of the LCWO model with inclusion of "radial" contributions ($\chi^{trans} = 1/\sqrt{5}$) for conformations close to the one described by $\theta^{trans} = 90°$ is shown in Fig. 5. As anticipated, the results deviate strongly from those in Fig. 2. The symmetry of the diagram in Fig. 2 is completely lost in Fig. 5, and this is mainly due to the fact that the "avoided crossing" of the a'-curves takes place for a θ^{trans}-value *below* 90°, while the corresponding event for the a''-curves occurs for a θ^{trans}-value *above* 90°. The ordering of the four intermediate levels is thus a'', a', a', a'' for $\theta^{trans} \approx 60°$, and a', a'', a'', a' for $\theta^{trans} \approx 120°$. Apart from the conjugative conformational dependence, the MOs of 1, 2 and 4 are further influenced by the inductive effects of the alkyl moieties, which are not considered in the results in Figs. 2 and 5. Results with inclusion of this effect as discussed in the previous section are given in

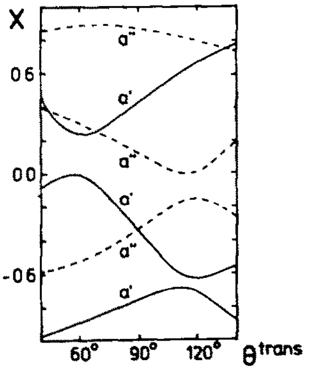

Fig. 5. LCWO energies $X = (\alpha_w - \epsilon)/\beta$ of tris-σ-homobenzene with inclusion of "radial" contributions ($\chi^{trans} = 1\sqrt{5}$, see text) as a function of θ^{trans}.

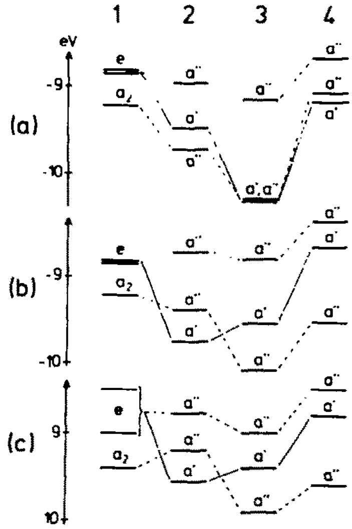

Fig. 6. Correlation of the three highest occupied levels in the series 1–4: (a) LCWO energies for purely "tangential" Walsh orbitals. (b) LCWO results with inclusion of "radial" contributions. (c) Ionization energies assigned according to results (b).

Table 1 and displayed in Fig. 6, without (a) as well as with (b) consideration of "radial" contributions. The results for 1 and 2 without "radial" contributions (a) are consistent with those obtained by Heilbronner *et al.*[1] on the basis of simple Hückel-type theory, when it is recognized that in Ref. 1 symmetry designations for 2 are in error by a reversal of a' and a". However, the correlation of results in Fig. 6 clearly indicates that experimental trends in the series 1–4 are not well described unless "radial" contributions are considered. In particular, the variation and relative spacing of the second and the third ionization energy are not well predicted by results (a), while results (b) are in excellent agreement with the observed trends. Reversal of the order of these levels is predicted when passing from 1 to 2 and from 2 to 3; the origin of these crossings is apparent from inspection of Fig. 5.

The general agreement between calculated and measured results obtained by inclusion of "radial" terms in the Walsh orbital model appears convincing. Only the highest occupied a" level is about equally well described by both sets of results (a) and (b). This can be explained by the tendency of this orbital to localize in the s-*cis*-bicyclopropyl fragment (Fig. 3), which means that the conformational dependence is small (Figs. 2 and 5) and that the energy shifts in the series 1–4 are due largely to the variation of the inductive effects of the alkyl groups. This fact may be taken to indicate, that the lower activation energy for the thermal isomerization of 4 with respect to that of 3 is mainly due to the inductive effect of the six Me groups rather than the conformational differences between 3 and 4.[3] The LCWO model predicts that about 80% of the density of the highest occupied MO in 2, 3 and 4 is localized in the s-*cis* fragment; the MINDO/3 calculation on 3 predicts a localization of more than 90% with almost 40% on the central bridgehead atoms, in agreement with the shape indicated in Fig. 3. These results are consistent with the observation that the first ionization energy of 3 is identical to that of *cis*-tricyclo[5.1.0.0^{2,4}]octane 5,[1] in agreement with the assumption that in both cases the highest occupied MO is essentially an s-*cis*-bicyclopropyl orbital (the bicyclopropyl unit in 5 has a torsional angle of 18°[11]).

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CONCLUDING REMARKS

The results of this and the previous[5] investigation show that the highest occupied MOs of linked cyclopropyl groups can be described in terms of the LCWO model. This means that the simple Walsh orbital picture is applicable to these systems (provided "radial" contributions are not neglected) and that the nature of these MOs can be discussed in relatively simple terms.

The MO description in this study can be considered as an adaptation of Hall's *Linear Combination of Bond Orbitals* scheme.[12,13] One may argue that the investigation could just as well have been based on one of the standard all-valence MO procedures such as the extended Hückel method, etc. However, the drawback of these methods is that they give almost too much information for our purpose and details may easily obscure the essential message. By constructing a simplified model we are able to concentrate on a few basic principles, leading to explanation of observed facts in terms of individual "effects" in the way which has been found so useful in organic chemistry.

EXPERIMENTAL

The PE spectra of 1 and 2 have been reported previously.[1] The compounds 3 and 4 were synthesized according to directions in the literature[3,4] and their He(I) PE spectra were recorded at room temp. on a PS 18 instrument (Perkin Elmer Ltd.). The PE spectra were calibrated with argon; a resolution of about 20 meV on the argon line was obtained. Each spectrum was recorded several times to ensure the reproducibility of the results.

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