49. Quadricyclanes. Part I: Photoelectron Spectra and Electronic Structure

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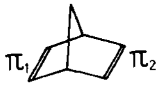
(12. XI. 73)

Summary. The photoelectron spectra of quadricyclane (**3**) and 3-methylidene quadricyclane (**4**) have been measured. The results served as a basis for the elucidation of the electronic structure of these compounds, which agreed with theoretical calculations. It is found that the symmetry of the HOMO of **3** is different when compared to that of its valence isomer norbornadiene (**1**). The results also indicate that the structure of the highest occupied orbitals cannot be derived by only considering the *Walsh*-orbitals of the two three-membered rings. In addition one of the *Walsh*-components of the four-membered ring has to be taken into account.

Introduction. – Chemical evidence suggests that in norbornadiene (**1**), a significant homoconjugation between the two localized orbitals π_1 and π_2 prevails [2], in agreement with the photoelectron (PE) spectrum of this molecule [3]. Assuming a predominant "through space" interaction of these π-bonds, the orbital sequence $b_2(\pi)$ above $a_1(\pi)$ has been proposed [3]. Support for this assignment has been subsequently obtained from the PE.spectrum of the "key compound" 7-isopropylidene-norbornadiene (**2**) [4].



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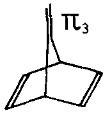

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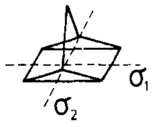
Here we report on the orbital electronic structure of quadricyclane (**3**), and on that of a "key-compound" analogous to **2**, 3-methylidene-quadricyclane (**4**).



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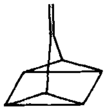

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The results are of importance in view of the valence-isomer relationship **1**$\rightleftarrows$**3** as well as for an understanding of cycloadditions involving **3** [5].

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[1] 'Small Ring Compounds', part 9. Part 8, s. [1].

Theoretical expectations. – From a MINDO/2-calculation [6] the following sequence of the four top occupied MO's of **3** is obtained²):

	AS >	SA >	AA >	SS
ε(eV)	-8.36	-9.33	-9.92	-10.62

Hence, while in **1** the highest occupied MO (HOMO) has SA-symmetry, the HOMO of **3** has AS-symmetry, the former being predicted to lie roughly 1 eV below it.

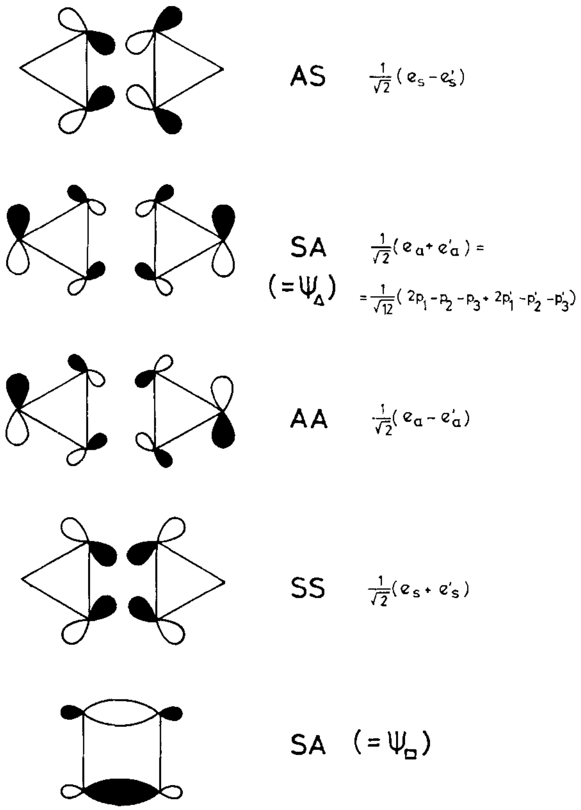

Fig. 1. *Basis-orbitals for quadricyclane* (**3**). The symmetry-adapted linear combinations of the *Walsh*-components of two cyclopropane rings and one of the *Walsh*-components of cyclobutane.

Fig. 1 shows the C_{2v}-symmetry adapted linear combinations of the outer *Walsh*-MO's e_s, e_a, e_s', e_a' of two cyclopropane moieties, which upon approach form the relevant tricyclohexane skeleton of **3**. In addition to these we also consider one of the pair of high-lying cyclobutane *Walsh*-orbitals which are degenerate in cyclobutane itself [7].

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²) ε is the energy of the orbitals in question. The symbols S, A refer to the symmetry behaviour – Symmetric, Antisymmetric – of the orbitals with respect to the mirror planes σ_1, σ_2, indicated in the figure above.

The PE. spectrum of 3. – In Fig. 2a, the PE. spectrum of **3** is shown which exhibits four distinct bands in the 8–11 eV energy range. It is useful to get a rough estimate of these band positions using previously obtained data for similar molecules.

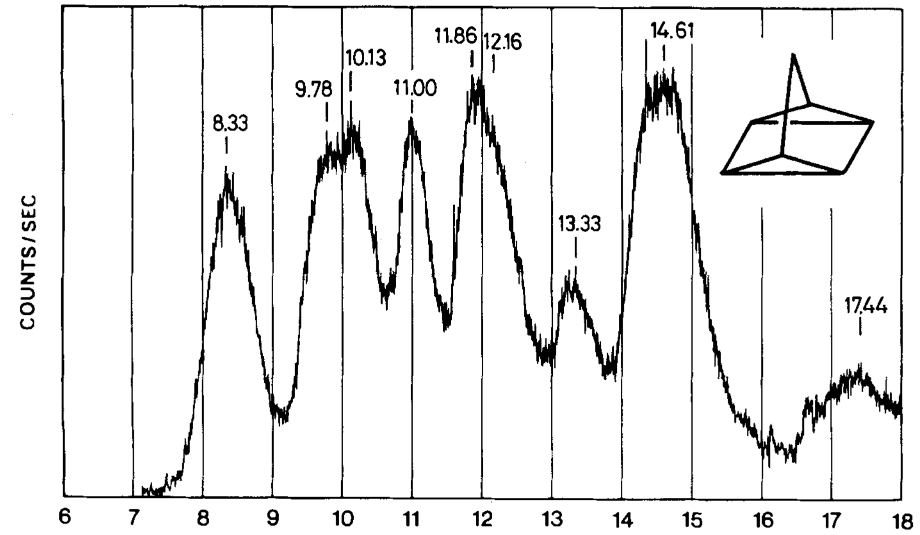


Fig. 2a. *Photoelectron spectrum of quadricyclane* (**3**) (IP's in eV)

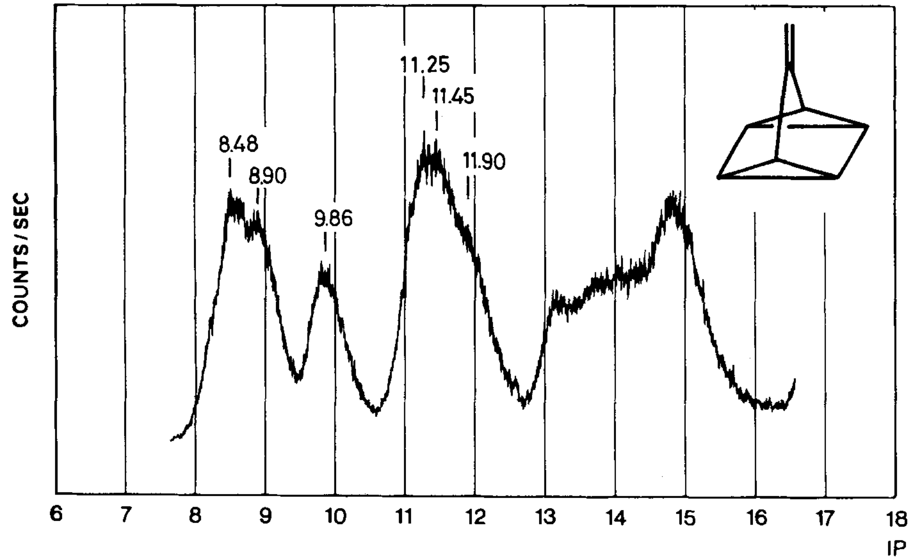
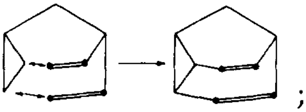


Fig. 2b. *Photoelectron spectrum of 3-methylidenequadricyclane* (**4**) (IP's in eV)

The basis orbital energy (ε') of the *Walsh*-orbitals in barbaralane (**5**) has been determined to be about $\varepsilon'(\mathbf{5}) = -10.2$ eV [8]. A linear relationship between ε' of a three-membered ring and the number of attached double bonds has been found, the



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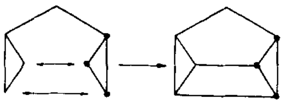

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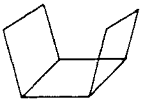
slope being -0.3 eV/double bond [9]. Given that in **3** only three "sp²"-type centres are connected to a cyclopropane ring, the foregoing suggests that:

$$\varepsilon' (\mathbf{3}) = -10.20 \text{ eV} + 0.5 \times 0.3 \text{ eV} = -10.05 \text{ eV}.$$

This value is used in Fig. 3.

The basis orbital energy (ε'') of the *Walsh*-cyclobutane SA-orbital in **3** can be estimated by comparison with the HOMO of **6**.



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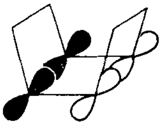

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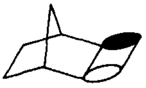
This orbital is strongly localized in the inner cyclobutane ring of **6** and has the shape and the symmetry depicted in **7** [10]. Inspection of the first IP. of cyclobutane (11.0 eV [7]) and that of **6** (9.18 eV [10]) shows that the "tetraalkyl"-substitution present in **6** results in an upward shift of 1.82 eV. Only half of this inductive perturbation does operate in **3**, leading to $\varepsilon'' = -10.1$ eV. However, the introduction of two cyclopropane rings not only brings about a destabilizing "alkyl effect" but also a stabilizing effect similar to that observed upon introduction of three double bonds, *e.g.* six sp²-centres. This reduces the above value to

$$\varepsilon'' (\mathbf{3}) = -10.1 \text{ eV} - 3 \times 0.4 \text{ eV} = -11.3 \text{ eV},$$

the increment: $-0{,}4$ eV/double bond being obtained from the discussion of the PE. spectra of **6** and related systems [10].

A more reliable value for ε'' (**3**) is obtained from the (S)A-*Walsh*-orbitals of the polycyclic hydrocarbons shown below.



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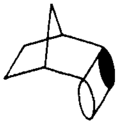

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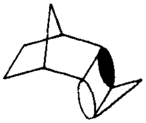

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From the PE.spectra and theoretical calculations $\varepsilon'' = -10.1$ eV has been derived for both **8** and **9** [11] [12]. For **10**, $\varepsilon'' = -10.5$ eV was observed, suggesting a "negative" inductive effect of -0.4 eV for the additional three-membered ring³) in **10**. The

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³) This 'negative' inductive effect has first been observed for benzocyclopropene, albeit to a lesser extent [14].

same value is obtained by MINDO/2-calculations for cyclobutane and bicyclo [2.1.0] pentane [13]. Taking twice the above substituent effect and adding it to $\varepsilon'' = -11.0$ eV observed for cyclobutane leads to $\varepsilon'' = -11.8$ eV for **3**.

On the basis of the above two estimates we take for ε'' in Fig. 3 the energy range -11.3 to -11.8 eV. (mean value: $\overline{\varepsilon''} = -11.55$ eV).

The interaction of the separated cyclopropane moieties shall now first be considered. In view of the phase properties of the corresponding symmetry adapted orbitals (Fig. 1), the SS-MO is strongly stabilized and the AS-MO strongly destabilized by roughly the same amounts. (A displacement of the SA- and AA-MO's is neglected in view of the small coefficients at the interacting centers (*cf.* Fig. 1)). This first-order picture is now modified due to the second-order interaction between the three-ring and the four-ring SA-levels (Fig. 3), leading to an orbital scheme compatible with the PE.spectrum of **3** as well as with the calculated sequence.

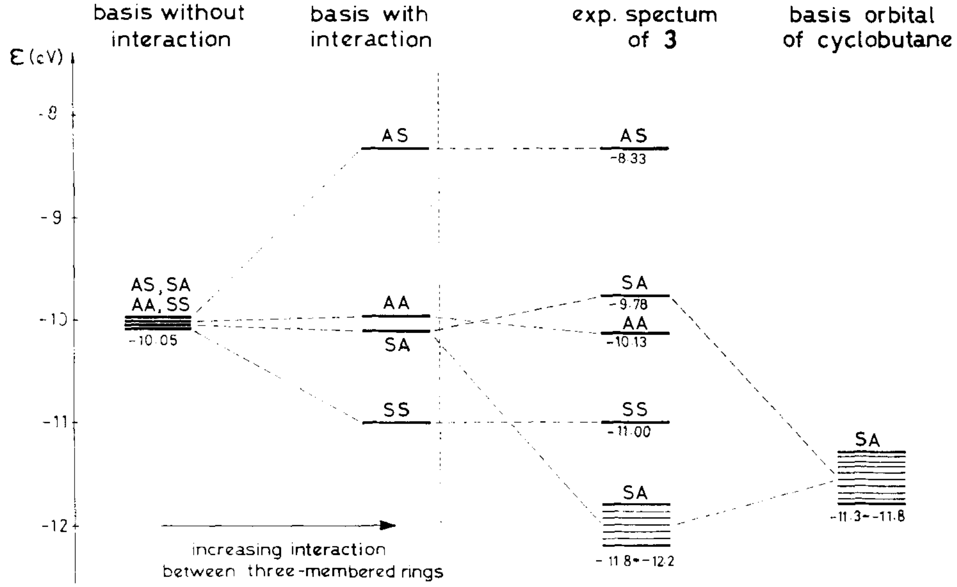


Fig. 3. *Correlationdiagram for the construction of the valence orbitals of quadricyclane* (**3**)

The interaction between the SA-levels enables us to derive an interaction parameter χ and also to get insight into the shape of the upper SA-component. Using the basis and the experimental SA-orbital energies given in Fig. 3 one finds

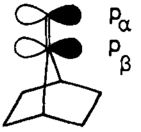
$$\chi = \langle \psi'_{\mathrm{SA}} | \mathcal{H} | \psi''_{\mathrm{SA}} \rangle = -0.72 \text{ eV}.$$

With this the upper SA-component at -9.78 eV is obtained as

$$\psi_{\mathrm{SA}} = 0.9\, \psi'_{\mathrm{SA}} - 0.43\, \psi''_{\mathrm{SA}}.$$

Thus ψ_{SA} is predominantly the in-phase linear combination of the antisymmetric e_a and e'_a *Walsh*-components of the three-membered rings, contaminated however with a considerable fraction of the four-ring SA *Walsh*-component. (See Fig. 5 for the shape of this MO).

The PE. spectrum of 4. – In Fig. 2b the PE. spectrum of the "key compound" **4** is shown. We first estimate the basis orbital energies the relevant entities in **4**. The π-IP of the exocyclic double bond (SA-symmetry) in 7-methylidene norbornadiene (**6**) is at 9.40 eV [15].



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In **4**, the corresponding orbital is stabilized due to the inductive effect of six additional *Walsh* "sp²"-centres, being roughly equivalent to three double bonds. According to the above discussion this leads to

$$\varepsilon_\pi(\mathbf{4}) = -9.40 \text{ eV} - 3 \times 0.3 \text{ eV} = -10.3 \text{ eV}.$$

The *Walsh*-orbitals of the quadricyclane moiety in **4** is also stabilized by the inductive effect of this double bond. This increased unsaturation of **4** with respect to **3** has been

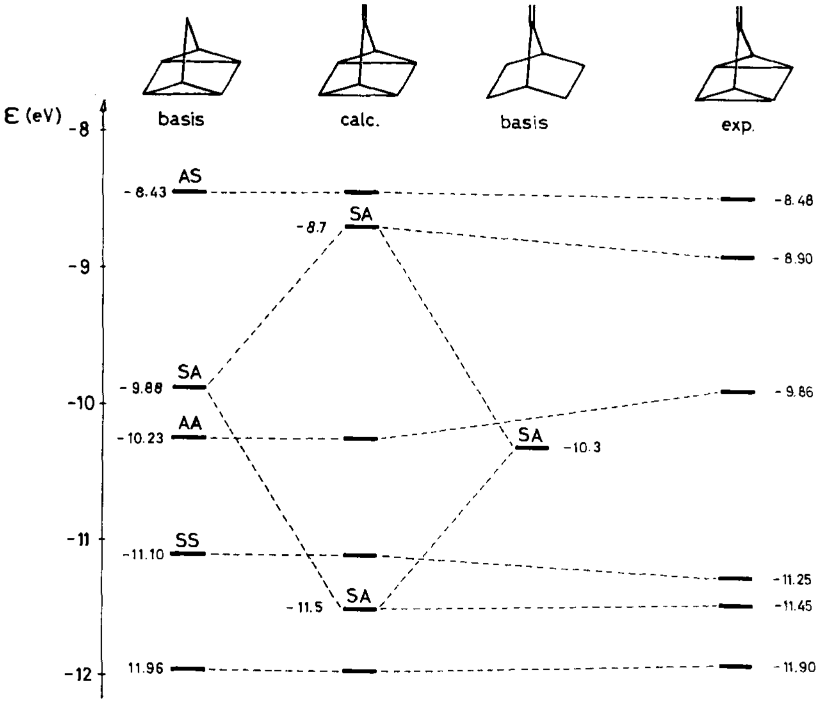

Fig. 4. *Correlationdiagram for the construction of the valence-orbitals of 3-methylidenequadricyclane* (**4**) and comparison with the experimental data

achieved by enlargement of the molecular skeleton. Following previous experience with cases of this kind [4] we assume that in the process **3**→**4** all four measured orbital energies of **3** are stabilized by about 0.1 eV, leading to the basis orbital energies for **4** depicted in Fig. 4. The major change in the PE.spectrum of **4** with respect to **3** is due to the interaction between the symmetry equivalent SA-basis orbitals

$$\psi_\pi = \frac{1}{\sqrt{2}}(p_\alpha + p_\beta) \quad \text{at} \quad \varepsilon_\pi = -10.3\ \text{eV}$$

and (see previous paragraph and Fig. 1)

$$\psi_{SA} = 0.9\,\psi'_{SA} - 0.43\,\psi''_{SA} \quad \text{at} \quad \varepsilon_{SA} = -9.88\ \text{eV},$$

the interaction element being given by

$$\langle\psi_{SA}|\mathcal{H}|\psi_\pi\rangle = 0.9\sqrt{\frac{2}{3}}\,\beta.$$

Using a value of $\beta = -1.9$ eV [9], solution of the secular problem yields the roots

$$\varepsilon_1 = -8.7\ \text{eV}, \quad \varepsilon_2 = -11.5\ \text{eV},$$

in agreement with the measured position of the second and fifth band in the PE.spectrum of **4**. This treatment also predicts similar positions for the first, third and fourth band of **3** and **4**, again in agreement with the observation.

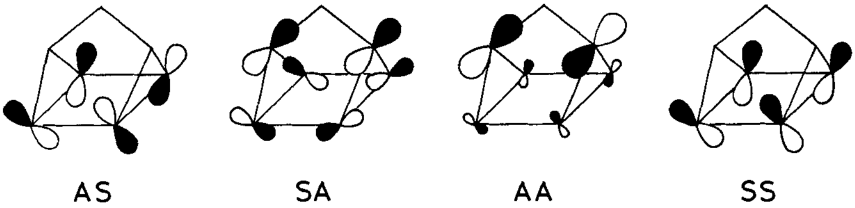

Fig. 5. *The four highest occupied MO's of quadricyclane* (**3**)

In Fig. 5 the four highest occupied MO's of **3** are displayed as deduced from the above treatment. (Only those basis functions are drawn which contribute predominantly to the respective MO). Thus π-donors or π-acceptors at the 3-position are expected to influence the three-membered rings in **3** in quite a different way than usually encoutered [16]. This may be visualized by inspection of the SA-MO in Fig. 5. In the following paper [17] the chemistry of quadricyclanes is discussed in view of these findings.

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50. Quadricyclanes. Part II: Electronic Structure and Chemical Reactivity

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Summary. The electronic structure of quadricyclane and 3-methylidenequadricyclane obtained by photoelectron spectroscopy, is used as a basis for the discussion of cycloadditions to these systems. The electronic structure of 3-heteroquadricyclanes, arrived at by theoretical calculations, agrees well with that expected from the above measured systems. A surprising outcome is that the orbital most responsible for the observed 2,4-cycloadditions to these heterosystems is *not* the HOMO but the third highest orbital which lies well below the former. This strongly suggests that these 2,4-cycloadditions proceed not in a concerted fashion but presumably involve as rate-determining step the formation of a resonance-stabilized zwitterionic intermediate. The nature of this intermediate is discussed and the feasability of its formation investigated on the basis of thermochemical considerations.

Introduction. – In the preceeding paper [1] the electronic structure of quadricyclane (**1**) and 3-methylidenequadricyclane (**2**) has been investigated by means of photoelectron spectroscopy. The present work describes some consequences concerning the interpretation of the chemical reactivity of quadricyclane systems which derive from these results.

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[1] 'Small Ring Compounds' part 10. Part 9 [1].