

1. Tetrakis(methyldene)cyclobutane ('[4]Radialene'): Electronic States of the Molecular Ion

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Dedicated to the Memory of *Heinrich Labhart*

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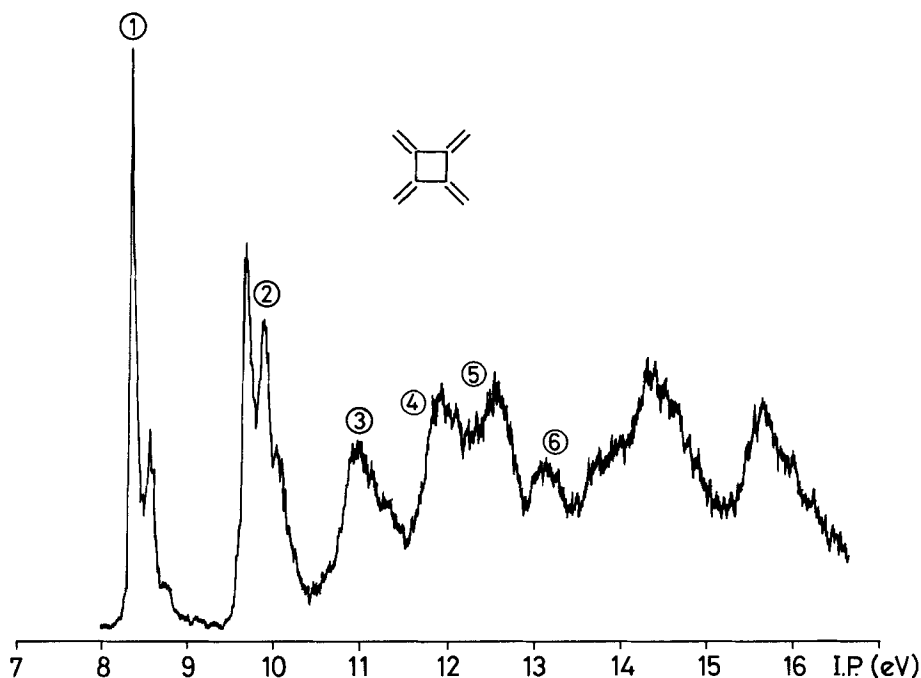
Summary

The photoelectron spectrum of tetrakis(methyldene)cyclobutane (**1**, '[4]radialene') is reported. The electronic states of **1**⁺ are assigned on the basis of model calculations and with reference to related systems. *Jahn-Teller* activity in the degenerate states is discussed. A failure of the simple LCBO-model for the $\pi(e_g)$ -orbital of **1** is noted and traced to the fact that this orbital, though having a symmetry-equivalent π^* -counterpart, does not interact with it. This feature is confined to [4n]radialenes; their total π -energies are therefore higher than those of the other members. It is shown that radialenes, in principle, do not constitute a class analogous to that of the linear polyenes as inferred earlier.

Introduction. – Tetrakis(methyldene)cyclobutane (**1**) is the second member of the family of '[n]radialenes' ($n = 3, 4, 5 \dots$). While the first member – by virtue of its isomeric relationship to benzene – has attracted some attention from both experimentalists [1] and theoreticians [2], the title compound has been dealt with only rarely since its preparation was reported [3]. A notable exception is the careful study of its vibrational features by *Miller et al.* [4], which established D_{4h} -symmetry for **1**. In the course of our studies dealing with radialenes and their radical cations, we recorded the He(I α) photoelectron spectrum (PES) of **1**. Its interpretation raises some interesting questions regarding the validity of commonly used models, such as *Dewar's* localized-bond model [5], or the simple LCBO-approximation as applied by many workers in discussing PE-spectra.

Results and Discussion. – *Figure 1* shows the He-I-PE-spectrum of **1**. *Figure 2* displays the bonding molecular orbitals of **1** pertinent to the present discussion (MINDO/3 wave-functions, MOPLOT-program [6]). The *Table* lists the results for the electronic state energies of **1**⁺ obtained from various theoretical procedures which we consider to be reliable in assisting PES-assignments.

²B_{1u}(π)-state. There is hardly any doubt, that the ground state of **1**⁺ is ²B_{1u} with $I_1^0 = I_2^0 = 8.35$ eV from band ①. As the electron is ejected from a bonding π -orbital

Fig. 1. Photoelectron spectrum of **1**

strongly localized at the exocyclic double bonds, we expect vibrational excitation of the totally symmetric a_{1g} -C=C-stretching mode (ν_2 in **1**, $\tilde{\nu}=1681\text{ cm}^{-1}$ [4]). The spacing of the clearly discernible members of the progression is 1620 cm^{-1} , supporting the above assignment.

$^2E_g(\pi)$ -state. Band ② is assigned to the transition $^1A_{1g}(\mathbf{1}) \rightarrow ^2E_g(\mathbf{1}^+)$ with $I_2^0 = I_2^1 = 9.67\text{ eV}$. The ionic state is degenerate and therefore *Jahn-Teller* (*JT*) active; the degeneracy is lifted by distortion along *two non-degenerate* normal modes of b_{1g} - and b_{2g} -symmetry, leading to species with rhombic or rectangular shape, respectively. Potential minima are attained for positive and negative displacements along either of these coordinates. This contrasts to the well known cases of trigonal symmetry (*e.g.* cyclopropane [10], [3]radialene [11], hexamethyl-[3]radialene [12]) where *one degenerate* mode is capable of breaking the state degeneracy. For sizeable *JT*-stabilizations transitions to degenerate states of these systems always result in the familiar double humped band structure. However, Schwarz has pointed out for tetragonal and cubic systems [13], that this band feature (case B) is only present if distortion along *both* non degenerate coordinates leads to a significant energy lowering. If this stabilization is minute for one of the coordinates (*e.g.* XeF_4 [13]) a singly peaked band results, regardless of the magnitude of the energy gain along the other coordinate (case A).

In order to get some insight into the potential surface of $^2E_g(\mathbf{1})$ we performed MINDO/3-calculations [14], studying the relaxation along the totally symmetric

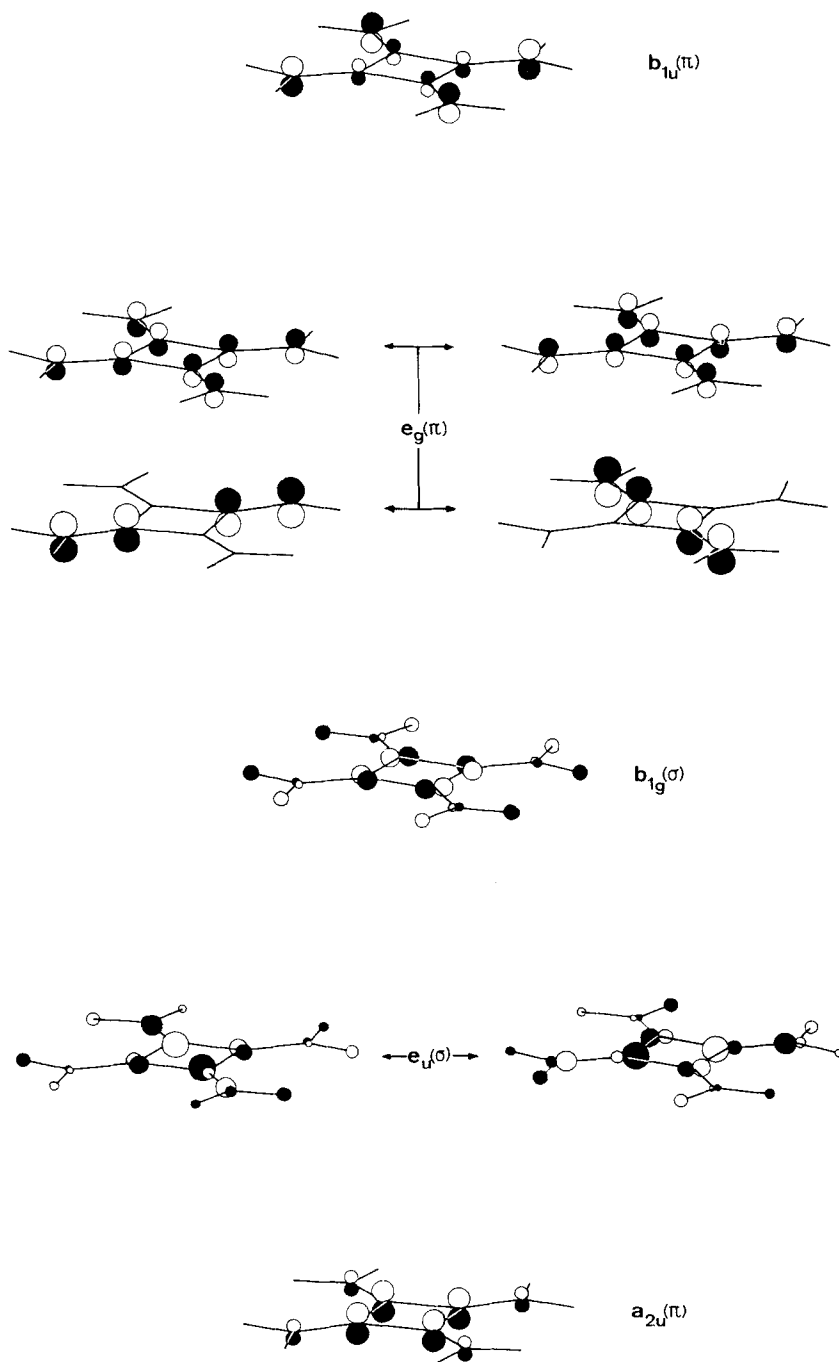
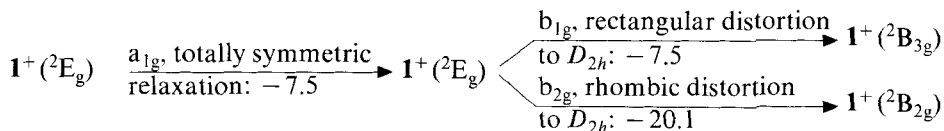


Fig. 2. Pictorial representation of the highest five occupied orbitals of **1**

coordinate a_{1g} as well as along the two JT -modes, b_{1g} and b_{2g} (energies in $\text{kJ} \cdot \text{mol}^{-1}$).



The totally symmetric relaxation of the vertically produced ion is minute ($7.5 \text{ kJ} \cdot \text{mol}^{-1}$); excitation of the corresponding fundamental is therefore not expected to complicate the spectrum. From the two motions leading to removal of degeneracy, the b_{2g} -coordinate is clearly more effective, as it renders the ion $12.6 \text{ kJ} \cdot \text{mol}^{-1}$ more stable than for the b_{1g} -distortion. In any case the total JT -stabilization for $^2E_g(1)$ is small enough that the band associated with $^1A_{1g} \rightarrow ^2E_g$ is expected to exhibit a prominent 0–0 transition. The molecular shape is strongly determined by the stiff σ -electron framework; removal of a π -electron (leaving still five of them) is not expected to significantly distort the molecule. Note, however, that even in this case transitions to the non-totally symmetric vibrational levels are allowed in all quanta (*cf.* $^2E''(\pi)$ -state of [3]radialene [11]).

Band ② displays vibrational quanta of 1610 cm^{-1} which may be associated with the b_{2g} -C=C-stretching motion in 1^+ with $\tilde{\nu} = 1662 \text{ cm}^{-1}$ (ν_{12}) in **1** [4]. Note that for a distortion along the b_{1g} -coordinate we ought to observe a much smaller frequency, as the b_{1g} -ring-deformation mode (ν_{17}) in **1** has $\tilde{\nu} = 1195 \text{ cm}^{-1}$ [4]. We conclude that $1^+(^2E_g)$ most probably assumes a rhombic shape through distortion along the b_{2g} -symmetry coordinate, thus lifting its degeneracy.

Table. Summary of calculated and observed electronic state energies of 1^+ (in eV)

	mod. HMO [7]	PPP-CI [8] ^{a)}	SPINDO [9]	exp. (this work)
$^2B_{1u}(\pi)$	8.13 ± 0.34	(8.35) (95)	8.92	8.35
$^2E_g(\pi)$	9.97 ± 0.41	9.77 (80)	10.12	9.67
$^2A_{2u}(\pi)$		10.18 (2)		
$^2B_{1g}(\sigma)$			11.31	11.0
$^2E_g(\pi)$		11.96 (18)		(11.4?)
$^2E_u(\sigma)$			12.35	11.9, 12.6
$^2B_{1u}(\pi)$		13.41 (4)		
$^2A_{2u}(\pi)$	12.44 ± 0.73	13.92 (96)	12.90	13.1

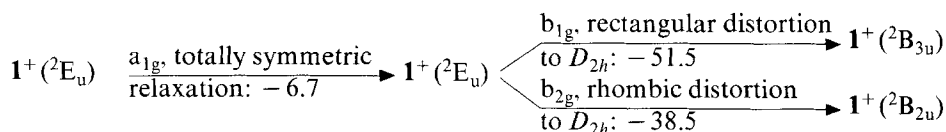
^{a)} Values are sum of exp. $I_1^+ = 8.35 \text{ eV}$ and calculated transition energies; (values) indicate weight (%) of Koopmans configuration(s) in CI-expansion.

$^2B_{1g}(\sigma)$ -state. Based on the SPINDO-result (see the Table) we propose band ③ to originate from $^1A_{1g} \rightarrow ^2B_{1g}$ with $I_3^+ = 11.0 \text{ eV}$. There is no well developed fine structure discernible. We note, however, the additional maximum occurring at the high energy tail of the band (11.4 eV). The rather reliable [8] PPP-CI calculations predict a $^2E_g(\pi)$ shake-up state in this region which contains 18% admixture of a

Koopmans type configuration and may thus show up weakly in the PE-spectrum. (Note that these calculations also predict a ${}^2A_{2u}(\pi)$ and a ${}^2B_{1u}(\pi)$ state at 10.18 and 13.41 eV, which, however, are of almost pure shake-up nature.)

${}^2E_u(\sigma)$ -state. The SPINDO-calculations predict this state at 12.35 eV. As it is of degenerate σ -nature, we expect a strong *JT*-distortion resulting either in a broadened singly peaked or a double humped band (cases A or B, respectively, see discussion of ${}^2E_g(\pi)$ -state). In addition the area of the band system ought to be roughly twice as large as that found for band ③ or ①, and comparable to that of ②. Accounting roughly for the rise in base line we tentatively propose bands ④ and ⑤ to originate from ${}^1A_{1g} \rightarrow {}^2E_u$, hence implying case B to prevail. Support for this proposal is obtained from the following consideration:

a) MINDO/3-calculations for rectangular and rhombic distortion yield (in kJ mol⁻¹):



The *JT*-stabilizations experienced by the σ -state are both large, in fact much larger than for the above discussed π -state 2E_g . This finding is compatible with a double humped band structure (case B).

b) The splitting between bands ④ and ⑤ is 0.7 eV, which is about equal to that observed for the *JT*-active σ -states of cyclobutane [15] or systems embodying a three-membered ring: cyclopropane [10], [3]radialene [11] and its hexamethyl derivative [12]. Note that the *JT*-stabilization energies calculated for these states are very similar in magnitude to those for 1^+ given above.

${}^2A_u(\pi)$ -state. We propose this state to be associated with band ⑥, $I_5^v = 13.1$ eV. This figure lies within the predictions given by PPP-CI (96% *Koopmans* configuration) and SPINDO, and also within the error range given by the modified HMO-approach. We sought further support for our assignment from a simple LCBO-model, considering only bonding π -basis functions. The interaction parameters $B = \langle \pi_i | \times | \pi_j \rangle$ for appropriate reference systems are: 1.215 eV for *trans*-butadiene [16], and 1.35 eV for [3]radialene [11], yielding the mean $B = 1.28$ eV. The LBCO-splitting for **1** between the highest and lowest occupied π -MO's of b_{1u} - and a_{2u} -symmetry, respectively, is easily calculated to be $4B$. Hence, with $\varepsilon(\pi, b_{1u}) = -8.35$ eV (band ①) we arrive at the estimate $\varepsilon(\pi, a_{2u}) = -13.47$ eV, which strongly supports our assignment.

Finally we note that all [n]radialenes have a HMO-energy for the lowest occupied orbital of $\alpha + 2.414\beta$. Hence, the energies for ejection of an electron from this orbital should be rather independent of n . For $\varepsilon(\pi, a_2')$ of [3]radialene we found -13.0 eV [11] which is indeed very similar to the value deduced for **1**.

Corollaries. – *Failure of the LCBO-model for the ${}^2E_g(\pi)$ -state.* Failure of the simple and widely used LCBO-model, i.e. the necessity to include antibonding π^* -orbitals in the basis set was previously noted from:

- a) unsatisfactory agreement between predicted and observed orbital energies (applying *Koopmans* theorem) in certain polyenes [17], annulenes [18] and polyynes [19];
- b) unsatisfactory prediction of wavefunctions to be used in the simulation of experimentally determined spin-orbit coupling constants [20].

We wish to present a further intriguing failure of the simple LCBO-model. It predicts the π -orbitals in **1** of b_{1u} -, e_g - and a_{2u} -symmetry to be equally spaced by an energy amount of 2B. Given $\varepsilon(\pi, b_{1u}) = -8.35$ eV and $\varepsilon(\pi, a_{2u}) = -13.1$ eV it thus predicts $\varepsilon(\pi, e_g) = -10.78$ eV, which is more than 1 eV too low (exp. -9.67 eV, band ②)!

Wirz has traced an analogous failure of the simple LCBO-model for a particular orbital in a $[4n]$ annulene [18] to the fact, that this orbital has no symmetry-equivalent counterpart in the antibonding manifold. As depression of bonding orbitals by antibonding ones is somehow absorbed in the parameters of the simple LCBO-model, orbitals which lack such a congruency are necessarily predicted to lie at too low energies. While this conclusion is definitely valid and worth noting, it needs generalization as shown by the present example: the $\pi(e_g)$ -orbital of **1**, though predicted to lie too low, has a symmetry-matching counterpart in the π^* -manifold. This orbital is readily visualized by switching the signs of the outer lobes in the lower real representation of $\pi(e_g)$ in *Figure 2*. It is immediately evident that these π - and π^* -orbitals are defined by topology as long as 1,3 cross-ring interaction is neglected: They involve (apart from a normalization factor) mutually unperturbed pairs of π - and of π^* -orbitals, respectively, of ethylene, which are free of interaction in any approximation. Hence, despite the fact that $\pi(e_g)$ and $\pi^*(e_g)$ of **1** belong to the same irreducible representation they are unable to interact. Note that this feature is unique for this orbital couple; the LCBO-orbitals $\pi(b_{1u})$ and $\pi(a_{2u})$ of **1** have symmetry equivalent counterparts in the π^* -manifold with which they *do* interact. We were therefore entitled to apply above the simple LCBO-model to corroborate the orbital energy $\varepsilon(\pi, a_{2u})$.

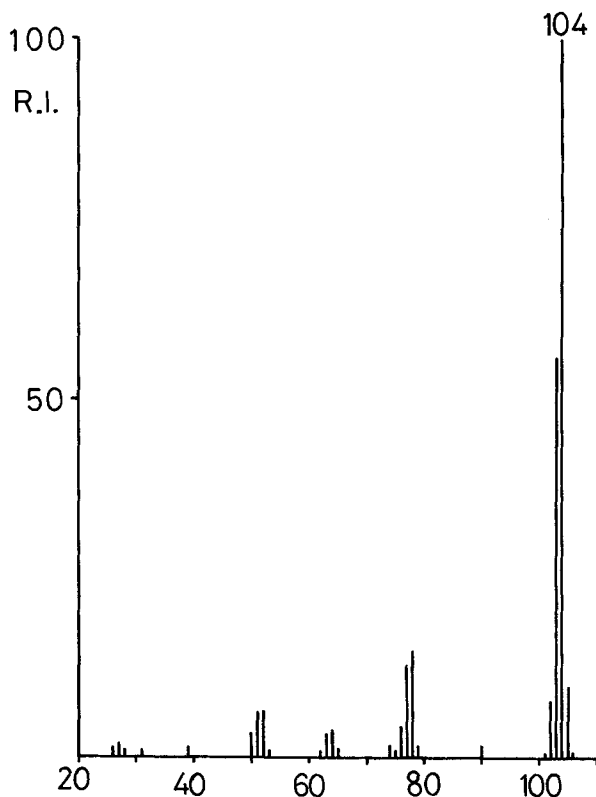
[4n]radialenes: 'antiaromatic' radialenes? Analysis shows that the peculiarity discussed above is uniquely confined to $[4n]$ radialenes. For all other members the LCBO π - and π^* -orbitals occur in symmetry equivalent pairs experiencing finite interaction. This difference in one-electron properties is likely to reflect on all-electron properties: The absence of depression of certain bonding LCBO-orbitals by antibonding ones is expected to result in significantly lower π -energies per double bond for the $[4n]$ radialenes with respect to the rest of the family. This is indeed the case as shown by the HMO- E_π -values quoted in [21]. Similarly, we are now able to rationalize the slightly negative resonance energies (E_R) of the $[4n]$ radialenes, which contrast to the slightly positive ones found for the other members by *Aihara* [22]. Admittedly, since the E_R -values are rather small and their oscillation falls off much faster than for annulenes, the only member for which this finding may have some observable consequences is, in fact, the title compound **1**. Calibration of *Aihara's* E_R -values with $E_R(\text{benzene}) = 0.3606\beta = 83.7$ kJ mol⁻¹ [5] leads us to predict that **1** is conjugatively destabilized with respect to [3]- or [5]radialene by about 17.6 or 16.7 kJ mol⁻¹, respectively. Thermochemical data for [3]-, [4]- and

[5]radialene¹⁾ are clearly desirable to test this prediction, though we are aware of the problems associated with disentangling strain and π -energy.

One final remark is appropriate: Radialenes have commonly been assumed to constitute an analogous class of compounds to that of the linear polyenes; *Dewar's* localized bond model was thought to apply equally well to both families [5]. The present discussion suggests that this, in principle, is not the case. With respect to *Aihara's* reference systems [22] there is a clear distinction between the $[4n]$ members ('anti-aromatic?') and those with $[n + \text{int}((n-1)/3)]$ double bonds ('aromatic?'), as it exists for the $[2n]$ members and the $[2n+2]$ members of the annulenes, respectively. Both series, annulenes and radialenes, show non-monotonic features by virtue of the cyclic topology. We are aware of the fact that for the radialenes this is of minor practical importance except perhaps for the present substrate **1**.

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Experimental Part. - **1** [3] was synthesized starting from tetrakis(bromomethyl)cyclobutane [24]. Dehydrobromination was effected by passing the gaseous precursor at low pressure over dry KOH at



¹⁾ We have recently determined $\Delta H_f^\circ = 398 \pm 10 \text{ kJ mol}^{-1}$ for [3]radialene from various fragmentation processes undergone by its molecular ion on impact of synchrotron radiation [23].

150°. (for details of the experimental set up see [25]). The purity of **1** was monitored by mass spectrometry. Above we depict the mass spectrum of **1** as obtained by the described procedure. It shows no signals that cannot be attributed to reasonable fragments of **1**⁺.

The He(I)PE-spectrum was recorded on a modified *Perkin-Elmer* PS15 instrument equipped with an inlet system for gaseous samples. IP's were *in situ* calibrated by benzene, water and rare gases.

Details of the technique employed in the MINDO/3-calculations of the excited states of **1**⁺ (which could not be effected using the standard method) will be described in a forthcoming paper [26]. Geometries were optimized with a routine based on the gradient algorithm of *Fletcher & Powell* [27]. Details of the calculated molecular constants are available on request (see also [25]).

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