exact interpretation. Zhabotinsky and Zaikin[13] suggested that the "small-cell structure" in the Belousov-Zhabotinsky reaction arises from a diffusive instability caused by the inequalities among the diffusion coefficients of several reactants. Wintree[21] is of the opinion that oxygen transport in convective Benard cells is the cause. Our observation unambiguously supports the importance of that kind of hydrodynamic flow in the onset of macroscopic order from a homogeneous solution layer excitable to oscillation. What we actually see as a pattern is the intermediates and/or products of the reaction which exhibit macroscopic order by a slight convective motion. The oxygen mixed by this motion into the liquid layer probably plays a role also in developing the structures. In closed system, i.e., sealing the surface of the layer from an imposed parameter gradient of a convective sort, neither transient nor mosaic structures emerged. When the glass plate was removed from the top of the Petri dish, the pattern appeared. The bringing on and suppressing the structure is possible several times until the reaction proceeds to a certain extent. In light of the above interpretation the dependency of occurrence of mosaic structure on the thickness of the liquid layer can also be understood. Since the development of the mosaic patterns is accompanied in most of the cases by precipitate formation, the theory of periodic precipitation outlined by Flicker and Ross[22] may offer a further contribution to the explanation of these complex phenomena.

The results presented in this paper strongly suggest that chemical waves and/or stationary patterns can be brought about in every chemical reacting system exhibiting temporal oscillation.

Investigations are in progress in order to reveal more about these peculiar phenomena.

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(1) Part 4 of the series "Chemical Oscillation during the Uncatalyzed Reaction of Aromatic Compounds with Bromate".

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(23) $HAr(OH)_2$ stands for the aromatics in general.

Photoelectron Spectra of the Cyclophanes

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Abstract: The He(Iα) photoelectron spectra of the complete set of cyclophanes have been recorded. It is shown that the band pattern of all these spectra can be rationalized in terms of a simple molecular orbital model which takes "through-space" and "through-bond" interactions between the π orbitals of the upper and lower benzene moieties into account. The "through-space" interaction parameter $\tau(D)$ depends linearly on the mean interdeck distance D, within the range 240 pm $< D <$ 340 pm. Severe symmetry restrictions are imposed on the "through-bond" interactions. As a result the lowest ionization energies of the cyclophanes decrease little with increasing number of bridging groups. Correlation of the first four bands of the photoelectron spectra of the cyclophanes supports the previously derived assignment of the spectrum of [2.2](1,4)cyclophane (=paracyclophane): first maximum $^2B_{2g}$, $^2B_{3g}$, $^2B_{3u}$; second maximum $^2B_{2u}$. It is shown that this assignment is supported by the electronic absorption spectra of the paracyclophane radical cation and of the benzene dimer radical cation, the photoelectron spectra of 4,5,7,8-tetramethyl[2.2](1,4)cyclophane, [3.3]paracyclophane, and the Birch reduction product of [2.2.2.2](1,2,4,5)-cyclophane, and the ESR spectra of 4,5,7,8- and 4,5,15,16-tetramethyl[2.2]paracyclophane radical cations.

I. Introduction

The recently reported preparations of [2.2.2.2.2]-(1,2,3,4,5)cyclophane^{2a} and of [2.2.2.2.2.2](1,2,3,4,5,6)-cyclophane (="superphane")^{2b} terminate the series of cyclophanes shown below, so that all of them are now available for the investigation of their chemical and physical properties. For simplicity the cyclophanes have been labeled **N**(x, y, . . .), where **N** is the number of bridging ethano groups and x, y, . . . are their position, if necessary. The syntheses of the cyclophanes investigated in this work are described in the following references: [2.2](1,4)cyclophane = **2**(1,4);[3] [2.2.2](1,2,3)-cyclophane = **3**(1,2,3);[4] [2.2.2](1,2,4)cyclophane = **3**(1,2,4);[5] [2.2.2](1,3,5)cyclophane = **3**(1,3,5);[6] [2.2.2.2](1,2,3,4)cyclophane = **4**(1,2,3,4);^{7a} [2.2.2.2](1,2,3,5)cyclophane = **4**(1,2,3,5);^{7b} [2.2.2.2](1,2,4,5)cyclophane = **4**(1,2,4,5);[8] [2.2.2.2.2](1,2,3,4,5)cyclophane = **5**;^{2a} [2.2.2.2.2.2]-(1,2,3,4,5,6)cyclophane = **6**.^{2b}

In Figures 1 and 2 are presented the He(Iα) photoelectron spectra of the cyclophanes (1), with the exception of **2**(1,2) = 1,2;5,6-dibenzocyclooctane and **2**(1,3) = [2.2]metacyclophane, both of which have "open" exo structures, i.e., at variance with

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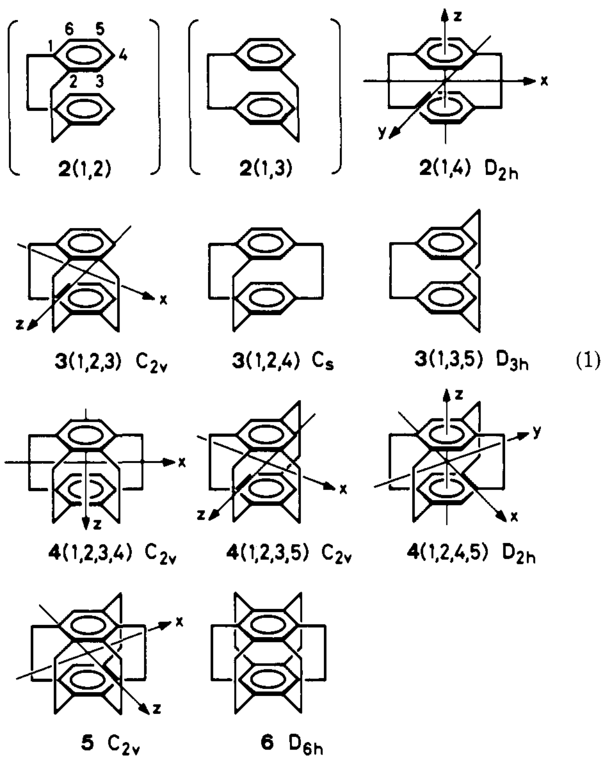
Table I. Ionization Energies of the Cyclophanes[a]

cyclophane	Figure	①	②	③	④	⑤
2(1,4)	1	8.1_0	(8.1_0)	8.4	9.6_5	10.3
3(1,2,3)	2	8.2_0			(8.7)	10.3
3(1,2,4)	2	8.0	(8.0)	8.3	9.2	10.2
3(1,3,5)	1	7.70	7.70	8.75	8.75	
4(1,2,3,4)	2	7.9	(7.9)	8.1	8.7	
4(1,2,3,5)	2	7.75	(7.75)	8.37	8.77	~10.0
4(1,2,4,5)	1	7.67	(7.67)	~8.1	8.82	9.79
5	2	7.67	(7.67)	~8.2	8.56	9.67
6	1	7.55	7.55	8.17	8.17	~9.6

[a] The ionization energies $I_j{}^m$ correspond to the positions of the band maxima and are presumably close to the vertical ionization energies: $I_j{}^v \approx I_j{}^m$. All values are in eV. Estimated precision of the data: two decimals given, ±0.02; second decimal as lower index, ±0.05 eV; one decimal given, ±0.1 eV. Values in parentheses are assumed.



(1)

the endo conformations depicted above. The ionization energies $I_j{}^m$, listed in Table I, correspond to the positions of those band maxima which can be located with confidence. Note that some bands are overlapped by other, stronger bands and appear only as shoulders, if at all. The spectra have been recorded on a Turner-type instrument incorporating a $\pi/\sqrt{2}$ cylindrical analyzer of 10-cm radius (Perkin-Elmer PS 16). The temperatures necessary to obtain sufficient sample vapor pressure were up to 200 °C and the resolution was typically ~150. Under these experimental conditions, thermal decomposition is not expected to occur. The compound **2**(1,4) is stable up to 200 °C[9] and the introduction of additional bridges has recently been shown to cause substantial further increase in thermal stability.[10]

The photoelectron spectra of **2**(1,4) (= [2.2]paracyclophane) and of **3**(1,3,5) have been published before in ref 11-14 and 6, 12, respectively (see also ref 15).

In the present paper we derive an assignment of the bands in the photoelectron spectra of the cyclophanes (1) in terms of Koopmans' approximation, relying essentially on the correlation technique, aided by qualitative molecular orbital arguments and by the rules deduced from the body of previous experience in the field of hydrocarbon photoelectron spectroscopy.[16] A somewhat more quantitative discussion will be published later, in connection with the assignment of the photoelectron spectra of a series of higher cyclophanes, e.g., naphthalenophanes, azulenophane, and related systems.[17] The latter analysis reveals that the assignment proposed below for the cyclophanes (1) can be extrapolated to the larger cyclophanes without needing any further ad hoc assumptions.

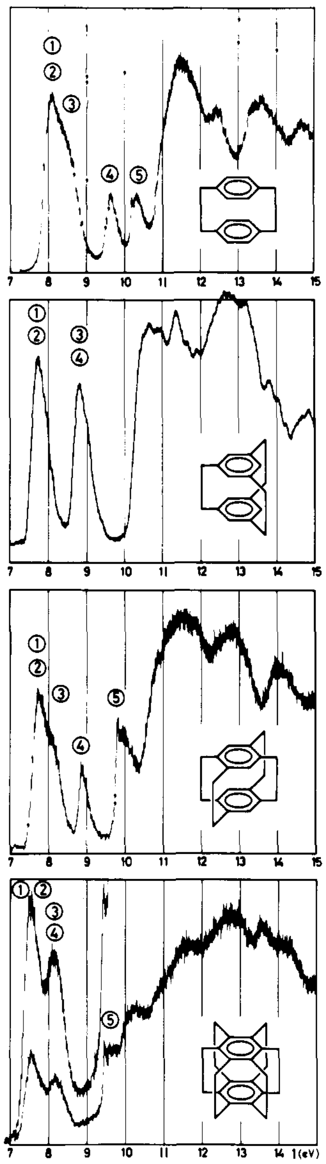


Figure 1. He(Iα) photoelectron spectra of the cyclophanes of higher symmetry: D_{2h} (**2**(1,4), **4**(1,2,4,5)), D_{3h} (**3**(1,3,5)), and D_{6h} (**6**).

As far as **2**(1,4) and **3**(1,3,5) are concerned, the new results confirm the previously proposed interpretation of their photoelectron spectra.[6,12,13] On the other hand, they disprove the assignment due to Duke et al. on the basis of a semiempirical CNDO/S3 calculation.[18]

II. Qualitative Survey and Orbital Labels

The complete set of photoelectron spectra of the cyclophanes (1) presents a unique opportunity for the application of the correlation technique,[16] i.e., to let the experimental data speak for themselves without the need for more or less involved quantum-chemical calculations. To this end, only elementary rules involving the symmetry behavior and/or nodal properties of the relevant wave functions are borrowed from quantum mechanics.

The reader is reminded that strictly speaking the photoelectron spectrum of a neutral, closed-shell molecule M yields

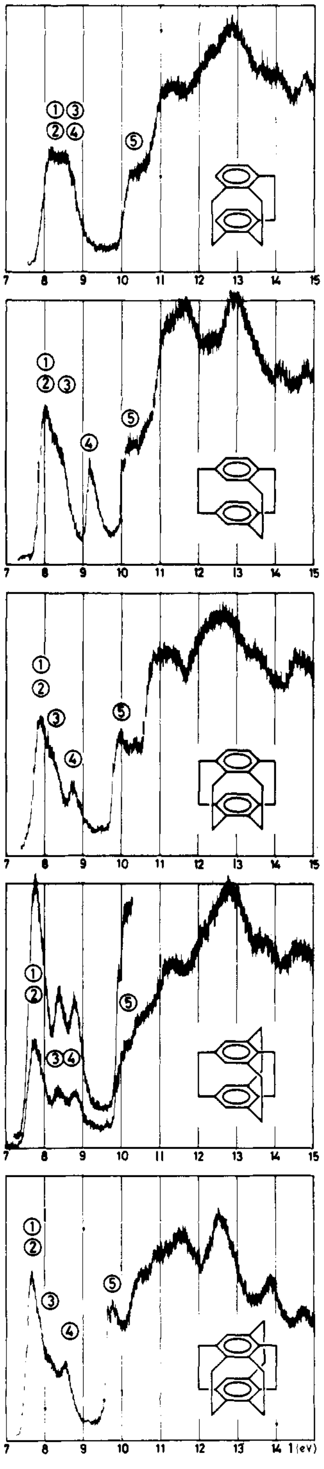


Figure 2. He(Iα) photoelectron spectra of the cyclophanes possessing only C_{2v} or C_s symmetry.

information concerning the doublet electronic states $^2\Psi_j$ of the radical cation M^+. However, we shall follow the custom of discussing these radical cation states in terms of Koopmans' approximation by associating each state $^2\Psi_j$ with the molecular orbital ψ_j of M from which the electron has been ejected. Note that the correlation procedure corrects for most of the deficiencies of this simplifying assumption (e.g., neglect of electron reorganization and correlation) because observed band positions are used.

In this work, we are only concerned with the low ionization energy part of the photoelectron spectra of Figures 1 and 2, which spans the region from 7 to 10 eV. The first four bands (labeled ①-④) found in this interval are due to π^{-1} ionization processes; i.e., they correspond to the removal of an electron from orbitals $\psi_j(\pi)$ which are dominantly of π parentage, albeit mixed to some extent with σ orbitals of the bridging ethano groups. Thus, the parent orbitals of $\psi_j(\pi)$ are largely those of the two benzene moieties, i.e., the HOMO $e_{1g}(\pi)$ and the $a_{2u}(\pi)$ orbitals of benzene. Combining these orbitals by pairs $((e^u{}_{1g} \pm e^l{}_{1g})/\sqrt{2}$; $(a^u{}_{2u} \pm a^l{}_{2u})/\sqrt{2}$; u(l) = upper (lower) benzene ring) yields six molecular basis π orbitals which will dominate the molecular orbitals $\psi_j(\pi)$. Note that the symbol π (as used in this work) refers to the local symmetry behavior of the parent orbitals $e_{1g}(\pi)$, $a_{2u}(\pi)$ within each ring and not to that of $\psi_j(\pi)$ with respect to the global symmetry of the molecule. To label the symmetry behavior of the $\psi_j(\pi)$ we define for each molecule a coordinate system, as shown in (1). For convenience the xy plane in D_{2h}, D_{3h}, and D_{6h} ($=\sigma_h$ in the latter two) and the discriminating zx plane ($=\sigma$) in C_{2v} and C_s have been chosen in such a way that they coincide with the interdeck mirror plane. The symbols s and a refer in all molecules to those molecular orbitals or linear combinations which are symmetric or antisymmetric with respect to this plane. With these definitions the following descent in symmetry labels (assuming idealized geometries) is obtained (2).

Behaviour of $\psi_j(\pi)$ relative to the inter-deck symmetry plane:		Parent orbitals:			
		$e_{1g}(\pi)$		$a_{2u}(\pi)$	
		s	a	s	a
Symmetry	Compd.				
D_{6h}	**6**	e_{1u}	e_{1g}	a_{1g}	a_{2u}
D_{3h}	**3** (1, 3, 5)	e'	e''	a'_1	a''_2
D_{2h}	**2**(1, 4) **4**(1, 2, 4, 5)	b_{2u} b_{3u}	b_{3g} b_{2g}	a_g	b_{1u}
C_{2v}	**3**(1, 2, 3) **4**(1, 2, 3, 5) **5**	b_1 a_1	a_2 b_2	a_1	b_2
	4(1, 2, 3, 4)	a_1 b_1	b_2 a_2	a_1	b_2
C_s	**3**(1, 2, 4)	a' b'	a'' a''	a'	a''

(2)

From (2) it is obvious that within D_{6h}, D_{3h}, and D_{2h} each π orbital (or pair of π orbitals) belongs to a different irreducible representation of the group. Consequently, they cannot mix with each other, but only with σ orbitals of the same symmetry. It is therefore expected (and, as we shall see, indeed observed) that the interpretation of the π^{-1} part of the photoelectron spectra of the corresponding molecules **6**, **3**(1,3,5), **4**(1,2,4,5), and **2**(1,4) is relatively simple (cf. Figure 1). On the other hand, under C_{2v} or C_s symmetry, orbitals of $e_{1g}(\pi)$ and $a_{2u}(\pi)$ parentage will mix with each other and also with the corresponding σ orbitals of the same symmetry. This leads to a somewhat more complicated situation (cf. Figure 2). However, its analysis will prove to be rather straightforward, because of the simplifications introduced by local symmetry conditions. These restrict hyperconjugative interactions between the benzene π orbitals of each deck and the σ orbitals of the alkyl bridges.

The $e_{1g}(\pi)^{-1}$ band in the photoelectron spectrum of benzene and the corresponding band in the spectrum of hexamethylbenzene are found at 9.2₅ and 7.9 eV, respectively. In methyl-substituted benzenes of lower than D_{3h} symmetry the degeneracy of the $e_{1g}(\pi)$ orbitals is lifted and the two separated bands ①② are observed at positions $I_1{}^m(\pi)$ and $I_2{}^m(\pi)$. It has been shown that the mean ionization energy $\bar{I}^m(\pi) = (I_1{}^m(\pi) + I_2{}^m(\pi))/2$ is a strictly linear function of the number of substituting methyl groups.[13]

The $a_{2u}(\pi)^{-1}$ band of benzene is found at 12.2 eV and we expect that in the case of methyl-substituted benzenes its position will also shift linearly with the number of substituting groups, to reach a value somewhere between 11.0 and 10.5 eV in the photoelectron spectrum of hexamethylbenzene. Consequently the band(s) in the photoelectron spectra of methyl-substituted benzenes following the first two π bands must be of σ^{-1} character. It is found that in all cases they occur above ~10 eV.

With this background a first survey of the experimental evidence yields the following facts:

(a) In the photoelectron spectra of **3**(1,3,5) (D_{3h}) and **6** (D_{6h}) the first two maxima at 7.7, 8.7₅ and 7.5₅, 8.1₅ eV (respectively) can only be due to $[e'(\pi)^{-1}, e''(\pi)^{-1}]$ and $[e_{1u}(\pi)^{-1}, e_{1g}(\pi)^{-1}]$ ionization processes, the sequence within the brackets remaining for the moment unspecified.

(b) Although in all other lower symmetry cyclophanes the degeneracy of the e-type orbitals is lifted (cf. (2)), it is a remarkable observation that for the orbitals associated with the first two bands ①② the split must be extremely small. This is evident from the fact that in *all* photoelectron spectra presented in Figures 1 and 2 the first two bands ①② merge to yield a maximum of double intensity, compared to the bands labeled ③ and ④, of which the former is discernible only as a shoulder on the high-energy flank of the maximum ①②.

(c) A second surprising fact is that the position of this maximum ①② shifts by only −0.5 eV when the number of bridging ethano groups is increased from two to six. This is only half the size of what one would have expected on the basis of the observed mean shifts $\overline{I^m}(\pi)$ of the bands ①,② in the photoelectron spectra of the methyl-substituted benzenes.

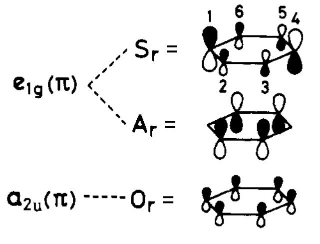
(d) In the photoelectron spectra of the lower symmetry cyclophanes (symmetry D_{2h}, C_{2v}, and C_s), the bands ③④ to be correlated with the second maximum in the spectra of **3**(1,3,5) and **6** are split considerably more and in a way which depends uniquely on the positions of the bridging groups.

(e) Finally, even a superficial correlation of the above type reveals that all the bands in the interval 7 to ~10 eV, i.e., the bands labeled ①-④ in the spectra of Figures 1 and 2, must be due to π^{-1} ionization processes.

III. Heuristic Model of Orbital Interactions in Cyclophanes

To establish the orbital sequence in cyclophanes, we apply, following the example of Gleiter,[19] the concepts of "through-space" and "through-bond" interaction (introduced by Hoffmann[20]) to a set of conveniently defined basis orbitals. Such a procedure has proved to be rather successful in coordinating a large body of photoelectron spectroscopic results[16,21] and has been shown to allow the transfer of information from one set of compounds to another.[22] It has been used in previous work dealing with cyclophanes.[6,12,13]

The ensuing arguments being based essentially on orbital symmetry and phase relationships, we may use without loss of relevance simple Hückel π orbitals for the description of the π systems of the upper (u) and lower (l) benzene moieties. For convenience the $e_{1g}(\pi)$ orbitals are written in their usual, real form. The symbols in (3) will be used (r = u, or l). The basis orbital S_r is symmetric and A_r is antisymmetric with respect to the plane of the paper. To characterize the parentage of the π orbitals $\psi_j(\pi)$ of the cyclophanes it is of advantage to form linear combinations of the pairs (S_u,S_l), (A_u,A_l), and (O_u,O_l), which are symmetric (s) or antisymmetric (a) with respect to the interdeck mirror plane:



(3)

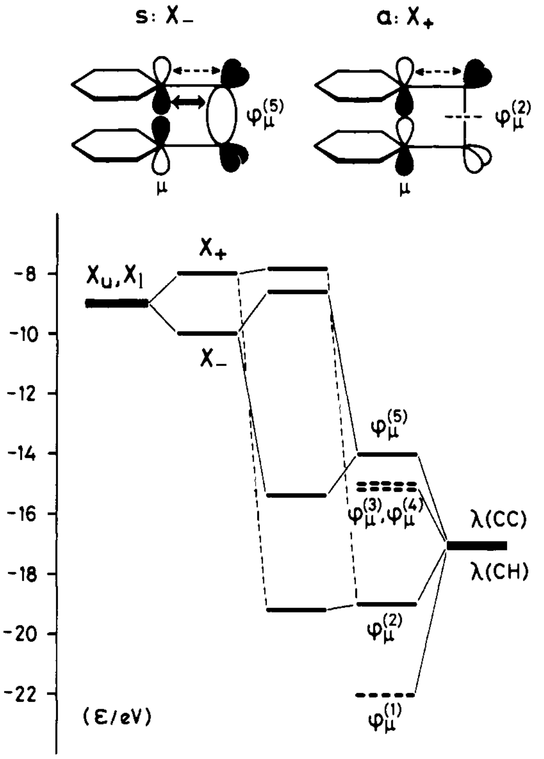


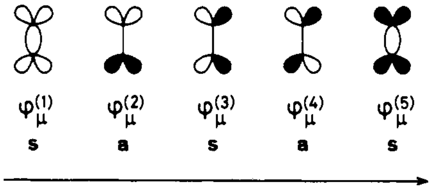
Figure 3. Orbital diagram for the "through-bond" interaction between the linear combinations X+ and X− of the upper (X_u) and lower (X_l) benzene basis orbitals (4) with the ethano-bridge orbitals $\varphi_\mu^{(i)}$ (5). The parameters implied are τ = 1.0 eV; self energy of λ(CC) and λ(CH) = −17 eV; geminal interaction parameter B = −2 eV.

$$S_\pm = (S_u \pm S_l)/\sqrt{2}$$
$$A_\pm = (A_u \pm A_l)/\sqrt{2} \qquad (4)$$
$$O_\pm = (O_u \pm O_l)/\sqrt{2}$$

Because the atomic orbital signs (shown in (3)) are the same for the π orbitals of the upper and the lower benzene ring, the (+) combinations are antisymmetric (a) and the (−) combinations are symmetric (s) relative to the mirror plane passing between the two decks; e.g., S_- is s and S_+ is a.

The second set of basis orbitals needed are those of the ethano groups bridging the positions μ of both decks.

The five doubly occupied semilocalized orbitals of each ethano group (discounting the two σ bonds which link it to the benzene moieties) can be represented in equivalent orbital diagrams as in (5) (μ = position of attachment), with ascending orbital energy in the direction of the arrow.



(5)

A crude estimate of these orbital energies is obtained by applying the Hückel-type model proposed recently.[22b] This model uses bond orbitals λ_{CC} and λ_{CH}, and takes only geminal interactions into account. With the basis energies $A_{CC} \approx A_{CH} \approx -17$ eV and $B_{gem} \approx -2$ eV the eigenvalues $\epsilon_1 \approx -22$, $\epsilon_2 \approx -19$, $\epsilon_3 = \epsilon_4 \approx -15$, and $\epsilon_5 \approx -14$ eV are calculated (cf. Figure 3).

It is obvious by inspection that $\varphi_\mu^{(3)}$ and $\varphi_\mu^{(4)}$ are locally orthogonal to the atomic orbitals p_μ of the benzene π orbitals (3) and that $\varphi_\mu^{(1)}$ is almost orthogonal to them. On the other hand, the $\varphi_\mu^{(2)}$ orbitals can interact in principle only with a-type linear combinations S_+, A_+, O_+ (cf. (4)), the $\varphi_\mu^{(5)}$ orbitals

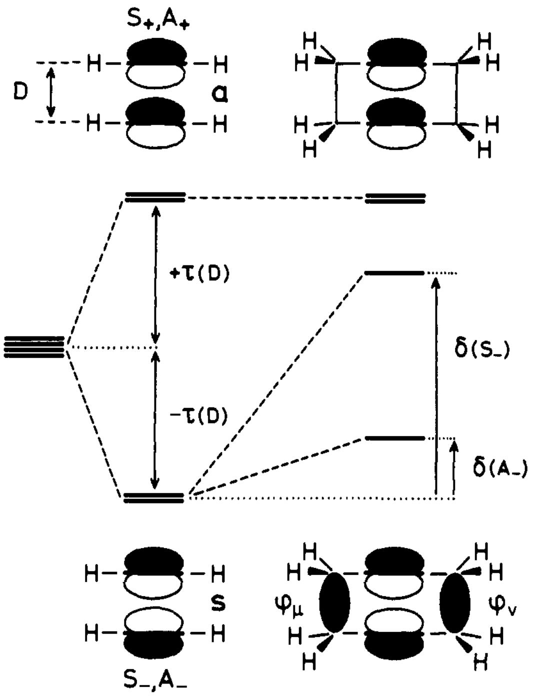


Figure 4. Orbital diagram for "through-space" and "through-bond" interaction in the cyclophanes of D_{6h}, D_{3h}, and D_{2h} symmetry (cf. Figure 1).

with S_-, A_-, O_- which exhibit s symmetry behavior. This is shown diagrammatically in the upper part of Figure 3, in which X_+ and X_- stand for linear combinations (4), i.e., $X_\pm = (X_u \pm X_l)/\sqrt{2}$.

As we shall see, overlap controlled "through-space" interaction between X_u and X_l will split the orbital energies of X_+ and X_- symmetrically with respect to the energies of the basis functions (3), X_- being the more stable linear combination. Because the orbital energies of $\varphi_\mu^{(5)}$'s are much closer in energy to X_- and because the cross terms between them are large, they will provide the dominant σ/π interactions in the cyclophanes. By comparison the $\varphi_\mu^{(2)}$ orbitals play only a minor role, as shown in Figure 3, and the small energy shift induced in the X_+-dominated linear combinations can be neglected. Consequently, to a first, and admittedly crude, approximation we are going to take into consideration only the interaction of the benzene π orbitals with the orbitals $\varphi_\mu^{(5)}$, which we abbreviate as φ_μ from here on.

We are now in a position to discuss and rationalize in more detail the observations (a)–(e) mentioned in section II. To this end we make the following assumptions:

(1) All electronic effects operative in the cyclophanes are of same type and same size as those deduced from photoelectron spectroscopic studies of other hydrocarbons. In particular no ad hoc "cyclophane effect" should be introduced.

(2) As in previous cases,[16] the dominating electronic effects are classified as "through-space" and "through-bond" interactions. It has been shown that[22a] this is always possible and that such a classification yields a complete description of the electronic structure of a given molecule, i.e., complete within the framework of any SCF model.

(3) The geometry of the models on which we base our discussion corresponds to idealized structures, as depicted in the formulas **2**(1,4) to **6** shown in (1). Thus the two benzene moieties are assumed to be planar, exactly parallel, and eclipsed with respect to the common sixfold axis. Their distance depends on the number of bridging groups and will be characterized by a mean interdeck distance D which can be calculated directly in those cases where structural data are available from an X-ray analysis.

For consistency, we use for the orbitals S_r, A_r, O_r, and φ_μ the same basis energies as in a former communication,[13] namely

$$\begin{aligned}\langle S_r|H|S_r\rangle = \langle A_r|H|A_r\rangle &= -9.0\ \text{eV}\\ \langle O_r|H|O_r\rangle &= -12.2\ \text{eV}\\ \langle \varphi_\mu|H|\varphi_\mu\rangle &= -14.0\ \text{eV}\end{aligned} \qquad (6)$$

where r = u or l.

Under the assumption (3), concerning the geometry of our model, through-space interaction between the π orbitals S_r, A_r, and O_r of the upper and lower deck can occur only between those of same local symmetry. The through-space cross term τ is assumed to be the same for all pairs (4) (which in fact is not quite true; cf. ref 17), and a function of the mean interdeck distance D; i.e., $\tau = \tau(D)$. Hyperconjugation of the basis π orbitals (3) with φ_μ is governed by a resonance integral $\mathbf{B}$ and by the coefficients $\mathbf{c}_{\mu X}$ (X = S, A, or O) of the Hückel π orbital at position μ. This yields the following interaction matrix elements:

$$\begin{aligned}\langle S_u|H|S_l\rangle = \langle A_u|H|A_l\rangle = \langle O_u|H|O_l\rangle &= \tau(D)\\ \langle X_u|H|\varphi_\mu\rangle &= \mathbf{c}_{\mu X}\cdot\mathbf{B}\\ \langle X_l|H|\varphi_\mu\rangle &= -\mathbf{c}_{\mu X}\cdot\mathbf{B}\end{aligned} \qquad (7)$$

The sign reversal for the hyperconjugative interaction matrix element of φ_μ with the lower orbitals X_l is due to the way in which the phases of X_u and X_l have been defined (see (3)). Another consequence of this phase definition is that $\tau(D)$ will always be a positive quantity. For the resonance integral $\mathbf{B}$ we are going to use the value $\mathbf{B} = -2.4$ eV, which has been derived previously.[13]

It should be noted that the precise values of the matrix elements defined above are not critical, as long as a qualitative analysis is aimed at. The availability of a complete set of correlatable photoelectron spectra more than compensates this lack of precision. In fact our conclusions remain unchanged if the matrix elements are altered within acceptable limits.

IV. Assignment of the Photoelectron Spectra

We discuss first the spectra of the cyclophanes **2**(1,4), **3**(1,3,5), **4**(1,2,4,5), and **6** shown in Figure 1. Because of their high symmetry the six linear combinations (4) of each belong to four (six) different irreducible representations (cf. (2)) and cannot therefore mix under the influence of "through-bond" interaction via the relay orbitals φ_μ. As a consequence, the low-energy part of their photoelectron spectra can be assigned by taking only the four π orbitals S_r, A_r of e_{1g} parentage and the corresponding symmetry-adapted linear combinations of the φ_μ into account, as shown qualitatively in Figure 4.

The π orbitals X_r (X = S, A; r = u, l), which are locally antisymmetric, combine under the influence of through-space interaction to yield (cf. (4)) linear combinations of energy

$$\begin{aligned}\langle X_-|H|X_-\rangle &= \langle X_r|H|X_r\rangle - \tau(D);\ \text{s}\\ \langle X_+|H|X_+\rangle &= \langle X_r|H|X_r\rangle + \tau(D);\ \text{a}\end{aligned} \qquad (8)$$

The combinations X_- are symmetric (s) and X_+ are antisymmetric (a) with respect to the interdeck xy plane. The simplifying assumption that only the orbitals $\varphi_\mu \equiv \varphi_\mu^{(5)}$ (cf. (5)) act as relay orbitals for "through-bond" interaction between X_u and X_l has the consequence that only the X_- combinations will be shifted by mixing with the φ_μ. Being antisymmetric (a) with respect to the xy plane, the X_+ combinations remain unaffected by "through-bond" interaction. Note that the value $A = -9.0$ eV assumed for the basis energies of S_r and A_r (cf. (6)) takes into account the neglected "through-bond" interaction with other orbitals of the set (5).[13] The destabilization $\delta(S_-)$ and $\delta(A_-)$ (see Figure 4) depends on the cross terms of

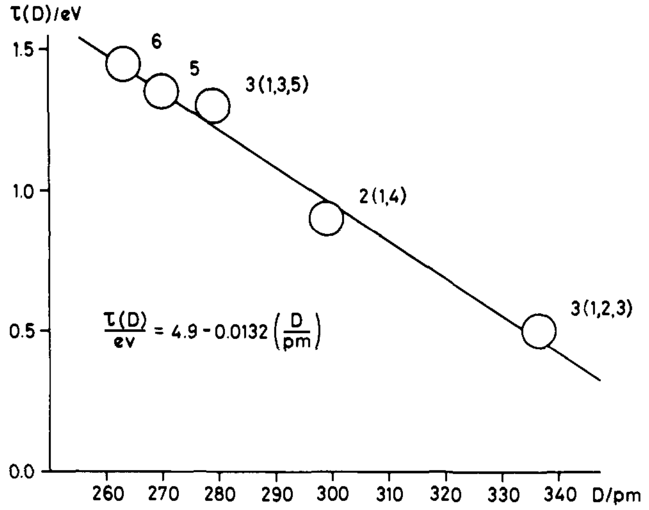


Figure 5. Dependence of the "through-space" parameter τ, calculated according to (10), on the experimentally determined mean interdeck distance D.

the X_- orbitals with those linear combinations of the φ_μ which belong to the same irreducible representation and on the energy gap $\langle X_-|H|X_-\rangle - \langle\varphi_\mu|H|\varphi_\mu\rangle$ between the orbital energies of X_- and of the φ_μ. The cross terms for the four cyclophanes, calculated according to (4) and (7) are given in (9).

$$\begin{array}{lcc}
 & \multicolumn{2}{c}{\text{cross term of symmetry-adapted linear combination of the } \varphi_\mu \text{ with}} \\
 & S_- & A_- \\
\mathbf{2}(1,4) & (2/\sqrt{3})B & 0 \\
\mathbf{3}(1,3,5) & B & B \\
\mathbf{4}(1,2,4,5) & (\sqrt{2/3})B & (\sqrt{2})B \\
\mathbf{6} & (\sqrt{2})B & (\sqrt{2})B
\end{array} \qquad (9)$$

It is immediately obvious that the molecular orbitals $\psi_j(\pi)$ derived from the linear combinations S_- and A_- must have different energies in **2**(1,4) and **4**(1,2,4,5), and a fortiori in all the cyclophanes of lower symmetry, collected in Figure 2. On the other hand, the orbitals $\psi_j(\pi)$ dominated by S_+ and A_+ should have very close energies in *all* cyclophanes. Thus we conclude that the high-intensity maximum (labeled ①② in Figures 1 and 2) which is present in all cyclophane photoelectron spectra (see observation II,b) has to be correlated with the pair of a-type molecular orbitals S_+ and A_+ which have the same energy in our crude model, as shown in Figure 4.

This allows a very simple calibration of the "through-space" interaction parameter

$$\tau(D) = -\langle X_r|H|X_r\rangle - I_1{}^m \qquad (10)$$

which should decrease with increasing interdeck distance D.

This mean distance D can be calculated from the known structure parameters in those cases where an X-ray analysis has been performed. Thus one finds D = 263 pm for **6**,[23] D = 270 pm for **5**,[23] D = 299 pm for **2**(1,4),[24] D = 279 pm for **3**(1,3,5),[23] and D = 337 pm for **3**(1,2,3).[23] In the last-named molecule, the structure of which looks like an open clam, the two benzene moieties form a dihedral angle of approximately 40°. Nevertheless, the mean distance D is, to a first approximation, an acceptable parameter, because the individual overlap integrals between the 2p orbitals of the upper and lower deck depend almost linearly on their distance in the interval 260-350 pm. If the $\tau(D)$ values calculated according to (10) are now plotted vs. D, the excellent linear correlation shown in Figure 5 is obtained.

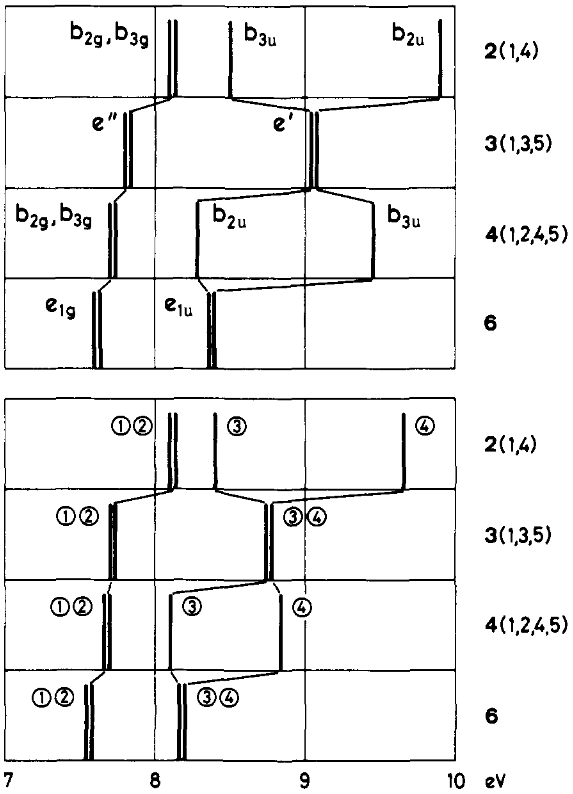


Figure 6. Correlation of calculated (upper diagram) and observed (lower diagram) band positions in the photoelectron spectra of the higher symmetric cyclophanes shown in Figure 1.

Using the basis energies (6), the cross terms (9) (with $B = -2.4$ eV), and the $\tau(D)$ values of Figure 5, we can now compute the model π-orbital energies for the four cyclophanes of Figure 1. The results are presented in the upper half of Figure 6 and should be compared to the experimental data displayed in the lower half of the same figure. (For numerical values see Table II.) In view of the simplicity of our model, the correspondence is surprisingly good, insofar as the sign and the order of magnitude of relative band shifts are correctly represented throughout.

A rather conclusive test of our assignment is provided by the remaining set of five lower symmetry cyclophanes, the photoelectron spectra of which are shown in Figure 2. With the exceptions of **3**(1,2,3) and **5**, for which structural parameters are available,[23] the mean interdeck distances D, and thus the through-space parameter $\tau(D)$, have to be interpolated using the regression of Figure 5. The following values have been used: **3**(1,2,4), $\tau(D)$ = 1.0 eV; **4**(1,2,3,4), $\tau(D)$ = 1.0 eV; **4**(1,2,3,5), $\tau(D)$ = 1.3 eV. Otherwise, all parameters are the same as before. The results of the calculation are shown in the upper half of Figure 7 and in Table II.

The comparison with the experimental ionization energies, presented in the lower half of Figure 7, clearly demonstrates that the overall agreement is as good as can reasonably be expected in view of such a simple model. The relative positions and intensities (i.e., maxima with areas 2:1:1) are faithfully reproduced even in those cases where π basis orbitals O_- of a_{2u} parentage mix with S_- and A_-.

The orbital labels corresponding to the bands ①-④ and the dominant basis orbitals are given in Table II. Obviously the sequence of the two orbitals correlated with the maximum ①② is arbitrary, but there are indications (see below) that the HOMO is the one associated with the linear combination S_+.

In the preceding discussion we have neglected changes in the basis energy A (cf. (6)) due to the bending of the benzene

Table II. Computed Ionization Energies, Derived by Applying Koopmans' Approximation to the Orbital Energies Obtained from the Model Described in the Text

	①	②	③	④
2(1,4)	b_{2g} (S_+) 8.10	b_{3g} (A_+) 8.10	b_{3u} (S_-) 8.50	b_{2u} (A_-) 9.90
3(1,2,3)[a]	a_1 (S_-) 8.24	b_1 (A_-) 8.46	b_2 (S_+) 8.50	a_2 (A_+) 8.50
3(1,2,4)	a'' (S_+) 8.00	a'' (A_+) 8.00	a' (S_-) 8.36	a' (A_-) 9.41
3(1,3,5)	e'' (S_+, A_+) 7.80		e' (S_-, A_-) 9.04	
4(1,2,3,4)	a_2 (S_+) 8.00	b_2 (A_+) 8.00	b_1 (S_-) 8.31	a_1 (A_-) 8.67
4(1,2,3,5)[b]	b_2 (S_+) 7.70	a_2 (A_+) 7.70	a_1 (S_-) 8.49	b_1 (A_-) 9.12
4(1,2,4,5)[c]	b_{2g} (S_+) 7.70	b_{3g} (A_+) 7.70	b_{2u} (A_-) 8.28	b_{3u} (S_-) 9.46
5[d]	b_2 (S_+) 7.70	a_2 (A_+) 7.70	b_1 (A_-) 8.28	a_1 (S_-) 8.75
6	e_{1g}(S_+, A_+) 7.60		e_{1u}(S_-, A_-) 8.36	

To make optimal use of the symmetries of the basis π orbitals $S_\pm$ and $O_\pm$, the calculated models carry the bridging groups in the following positions: [a] **3**(1,2,6); [b] **4**(1,2,4,6); [c] **4**(2,3,5,6); [d] **5**(1,2,3,5,6).

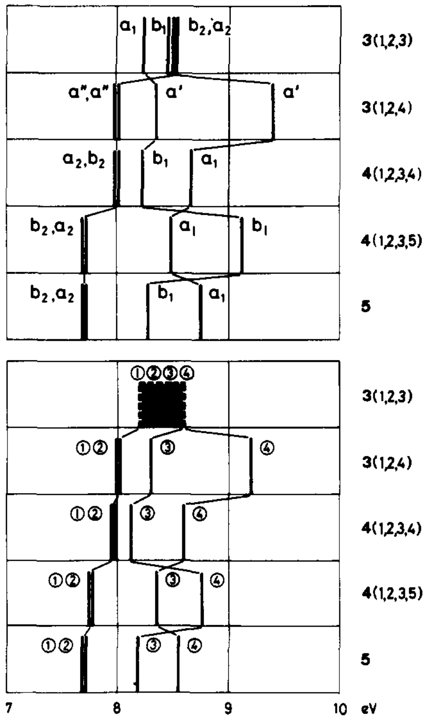


Figure 7. Correlation of calculated (upper diagram) and observed (lower diagram) band positions of the lower symmetric cyclophanes shown in Figure 2.

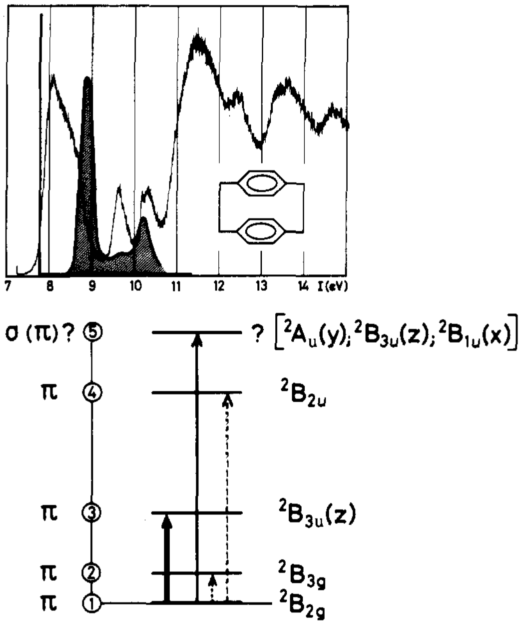


Figure 8. Electronic absorption spectrum (shaded) of the radical cation **2**(1,4)$^+$, redrawn from ref 29 and superposed on the photoelectron spectrum of **2**(1,4). The lower state diagram of **2**(1.4)$^+$ is explained in the text: solid arrows = electronically allowed transitions; dotted arrows = electronically forbidden transitions. The labels *x*, *y*, *z* in parentheses indicate the direction of polarization for the transition from the electronic ground state $^2B_{2g}$ of **2**(1,4)$^+$.

π systems. According to traditional views such a departure from planarity should entail loss of "aromaticity". However, at this level it would be an open question whether this will raise the basis energy A (i.e., bent π system less "stable") or lower it (i.e., tendency of bent system to localize double bonds). In fact, previous experience with bent π systems (double bonds,[25,26] triple bonds,[25,27] cyclic π systems[28]) shows that out-of-plane (or out-of-line) deformations of the size encountered in the cyclophanes will not change the ionization energies by significant amounts, relative to the values for the corresponding planar (or linear) system.

On the other hand, the assumption that the "through-space" coupling parameter τ is the same for all linear combinations (4) (see also (8) and (10)), depending only on the mean interdeck distance D, is of course only true if the benzene moieties are strictly planar, parallel, and eclipsed. A more precise estimate of individual τ values involves the computation of the overlap integral between upper and lower benzene π orbitals.[17] One of the consequences will be that the accidental degeneracy of the orbitals S_+ and A_+ suggested by our simple model (cf. Figure 4) is slightly lifted. In particular, in the case of **2**(1,4) the distance between the bridged centers is only 275 pm, between the other 309 pm.[24] As a consequence the overlap integral (and thus the parameter τ) between S_u and S_l is necessarily larger than between A_u and A_l, as can be seen from the diagrams (3). This means that the HOMO of **2**(1,4) must be $b_{2g}(\pi)$, followed by $b_{3g}(\pi)$. This yields for the sequence of states of the [2.2](1,4)cyclophane radical cation

$$\begin{array}{lcccc} \text{band} & ① & ② & ③ & ④ \\ \mathbf{2}(1,4)^+ & {}^2B_{2g} & {}^2B_{3g} & {}^2B_{3u} & {}^2B_{2u} \end{array} \qquad (11)$$

V. Ancillary Support for the Proposed Assignment

In this section we are going to present ancillary information which we believe supports the proposed assignment.

(1) The Electronic Spectrum of 2(1,4)$^+$. The electronic (absorption) spectrum of the radical cation **2**(1,4)$^+$ has been recorded[29] and discussed[30] by Badger and Brocklehurst. The spectrum of **2**(1,4)$^+$ dissolved in a solid matrix of *n*-butyl chloride/isopentane at 77 K shows a first intense band with onset ~0.7 eV (maximum ~1.0 eV) and a second weaker band with onset ~2.1–2.2 eV (maximum ~2.4 eV). This spectrum has been redrawn from ref 29 and superposed on the photoelectron spectrum of **2**(1,4) in Figure 8. The coordinate system has been chosen in such a way that its origin coincides with the first adiabatic ionization energy $I_1{}^a$ = 7.8 eV. According to previous experience[31] it is not to be expected that the gas-phase absorption spectrum will be shifted by a significant amount relative to the one recorded in the *n*-butyl chloride/isopentane matrix.

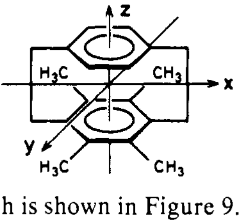
All previous experimental and theoretical evidence suggests that the fourth (Koopmans) state of $\mathbf{2}(1,4)^+$ is $^2B_{2u}$; i.e., that it is due to ejection of an electron from orbital $b_{2u}(\pi)$, in agreement with our own assignment. Consequently the three lower states must be $^2B_{3u}$, $^2B_{3g}$, and $^2B_{2g}$. Among these, the only allowed transition (assuming strict D_{2h} symmetry) is between $^2B_{3u}$ and $^2B_{2g}$ (*z*-polarized), which must therefore correspond to the intense band with onset 0.7 eV and maximum at 1.0 eV in the electronic spectrum of $\mathbf{2}(1,4)^+$. This leaves only the choice of $^2B_{3u}$ or $^2B_{2g}$ for the electronic ground state of $\mathbf{2}(1,4)^+$. According to our assignment the maximum ①② in the photoelectron spectrum of **2**(1,4) must correspond to the $^2B_{3g}$ and $^2B_{2g}$ states. This yields necessarily $^2B_{2g}$ for the electronic ground state of $\mathbf{2}(1,4)^+$, or in Koopmans' approximation that the HOMO of **2**(1,4) is $b_{2g}(\pi)$. This agrees with Badger and Brocklehurst's conclusions,[29,30] which assign this $^2B_{3u} \leftarrow {}^2B_{2g}$ band to a charge resonance transition polarized in the *z* direction. The resulting, qualitative state diagram for $\mathbf{2}(1,4)^+$ is shown in the lower part of Figure 8, which is exactly the one proposed in (11).

According to this diagram the transition from the ground state $^2B_{2g}$ to the fourth state $^2B_{2u}$ is forbidden, which explains why no band is observed in the electronic spectrum of $\mathbf{2}(1,4)^+$ around 1.8 eV, i.e., corresponding to band ④ in the photoelectron spectrum. (It is an open question whether the small hump in this region of the electronic spectrum is real or not.) The second band at 2.4 eV must correspond again to an allowed transition, which leaves us the choice of assigning to the band ⑤ in the photoelectron spectrum a state labeled either ^2A_u, $^2B_{3u}$, or $^2B_{1u}$. If this state is related to the highest occupied σ orbital $3e_{2g}$ of benzene, then either ^2A_u or $^2B_{1u}$ would be acceptable, and the observed transition would be *y* or *x* polarized.

Thus our assignment of the photoelectron spectrum of **2**(1,4) can be easily reconciled, and is in rather good agreement with the electronic (absorption) spectrum of $\mathbf{2}(1,4)^+$.

(2) Photoelectron Spectra of 4,5,7,8-Tetramethyl[2.2]paracyclophane (7) and of [3.3]Paracyclophane (8). The most important difference between our assignment of the photoelectron spectrum of **2**(1,4) and that of Duke et al.[18] is that the latter group of authors associates four bands with the first maximum (between 8 and 9 eV), instead of only three. This accumulation of four states for $\mathbf{2}(1,4)^+$ within a small energy interval was difficult to reconcile with experimental evidence on **2**(1,4) and other cyclophanes available at the time, and it is certainly contradicted by the body of information summarized in Figures 1 and 2.

A simple way to decide the question of how many bands contribute to the maximum at 8 eV in the photoelectron spectrum of **2**(1,4) is to cause a larger splitting between the bands by a one-sided substitution which lowers the symmetry from D_{2h} to C_{2v}. The compound of choice is 4,5,7,8-tetramethyl[2.2]paracyclophane (**7**), the He(Iα) photoelectron spectrum of which is shown in Figure 9.



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It is obvious that the first maximum in the photoelectron spectrum of **2**(1,4) has been split into two maxima with intensity ratio 2:1, and not into a pattern which would accommodate four bands, e.g., two maxima of equal intensity.

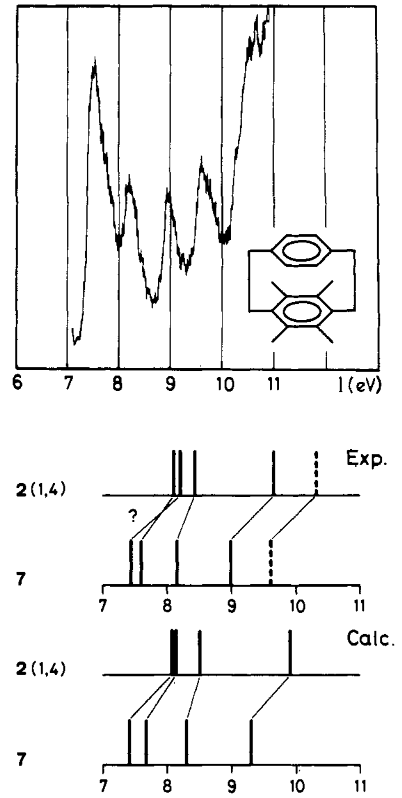


Figure 9. He(Iα) photoelectron spectrum of **7**. The bar diagrams show the correlation between the experimentally observed (exp) and the calculated (calcd; cf. (12)) band positions of **2**(1.4) and its tetramethyl derivative **7**.

To apply our model, all that has to be done is to change the basis energies of S_l, A_l, and O_l to account for the four methyl substituents. From the photoelectron spectrum of 1,2,4,5-tetramethylbenzene one deduces that the basis energy of S_l should be shifted by 0.5 eV, that of A_l by 1.0 eV, and that of O_l presumably by 0.7₅ eV. However, the latter value is irrelevant because the orbitals O_r (a_1) cannot mix with S_r (b_1) and A_r (b_2). Using $\langle S_l|H|S_l\rangle = -8.5$ eV and $\langle A_l|H|A_l\rangle = -8.0$ eV and keeping all other parameters unchanged yields for the first four π orbitals of **7**:

band	I_j	orbital $\psi_j(\pi)$	
1	7.47	$b_2(\pi) = 0.51A_u + 0.86A_l$	
2	7.76	$b_1(\pi) = 0.41S_u + 0.90S_l + 0.11(\varphi_1 - \varphi_4)$	(12)
3	8.40	$b_1(\pi) = 0.86S_u - 0.32S_l - 0.29(\varphi_1 - \varphi_4)$	
4	9.53	$b_2(\pi) = 0.86A_u - 0.51A_l$	

Within the limits of our model this is a faithful representation of the pattern observed for the first four bands of the photoelectron spectrum of **7**, compared to that of **2**(1,4), as can be seen from the bottom part of Figure 9. The agreement between experiment and model calculation is not impaired by assuming that the mean interdeck distance *D* is perhaps slightly larger in **7** than in **2**(1,4) for steric reasons, or that the basis energy shifts are somewhat different from those used above.

An alternative way of inducing different splittings of the π bands consists in changing the bridging groups, e.g., in [3.3]paracyclophane[3] (**8**), the photoelectron spectrum of which is presented in Figure 10. In the crystal, the molecule assumes a chair conformation **8a**[32] in which the two benzene moieties are separated by a mean interdeck distance *D* = 325 pm and are no longer on top of each other. In solution a conformational

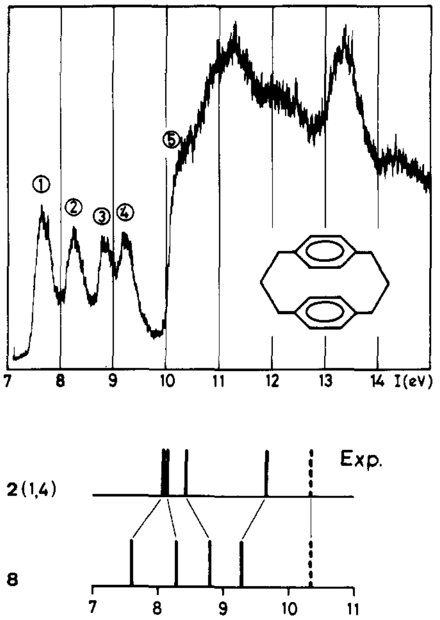
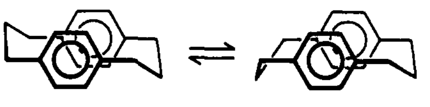


Figure 10. He(Iα) photoelectron spectrum of **8**. The bar diagram shows the proposed correlation between the observed band positions in the photoelectron spectra of **2**(1,4) and of **8**.



8a 8b

equilibrium **8a** $\rightleftharpoons$ **8b** (ratio 1:2) has been demonstrated to exist[33] and the same is probably true in the gas phase. For these reasons it is not possible to apply our strongly simplified model and a somewhat more sophisticated treatment is necessary as will be discussed elsewhere.[17]

The main difference between **2**(1,4) and **8** is that high-lying bridge orbitals φ_μ are now available in the latter molecule, which have the proper symmetry to interact with the linear combination S_+ (cf. (4)). As a consequence the near degeneracy of the two highest occupied molecular orbitals ($b_{2g}(\pi)$ and $b_{3g}(\pi)$ in **2**(1,4)) is lifted and four separate bands are expected in the spectrum of **8**. As can be seen from Figure 10, this is indeed the case. Correlation with the spectrum of **2**(1,4) strongly supports the assumption that the first broad maximum in the latter corresponds to three radical cation states only, as indicated in (11) and in the bottom part of Figure 9. In particular, this result excludes the assignment of the band at 9.9 eV in the spectrum of **2**(1,4) (band ④ in our nomenclature) to a σ^{-1} ionization process,[18] because this would mean that the corresponding band in the photoelectron spectrum of **8** would have been shifted toward higher ionization energies, which is impossible.

(3) **The Photoelectron Spectrum of the Birch Reduction Product of [2.2.2.2](1,2,4,5)Cyclophane (9).** A further, amusing addendum to our assignment, which again confirms that the bands labeled ④ in the photoelectron spectra of the cyclophanes are indeed due to an ionization process of predominantly π^{-1} character, is provided by the analysis of the photoelectron spectrum of the tetraene **9**[8] shown in Figure 11. For correlation this hydrocarbon, related to the cyclophane **4**(1,2,4,5), can be regarded either as two 1,4-cyclohexadiene moieties (**10**) linked in [2.2.2.2](1,2,4,5)cyclophane fashion **9a**, or as two 1,5-cyclooctadiene moieties (**11**) joined by four methylene groups as indicated in formula **9b**.

The photoelectron spectrum of **10** (D_{2h} symmetry)[34] exhibits two bands at positions $I_1^m = 8.8$ and $I_2^m = 9.8$ eV,[35] which correspond to the ejection of an electron from the in-phase linear combination $\pi_+ \simeq (\pi_a + \pi_b)/\sqrt{2}$ and the out-of-phase combination $\pi_- \simeq (\pi_a - \pi_b)/\sqrt{2}$, respectively. This "inverted" sequence[36] π_+ above π_- (as compared to the normal one of π_+ below π_-, e.g., in norbornadiene[37] and similar systems)[38] is the consequence of the dominant hyperconjugative interaction of π_+ with the pseudo-π orbitals of the methylene groups in positions 3 and 6.

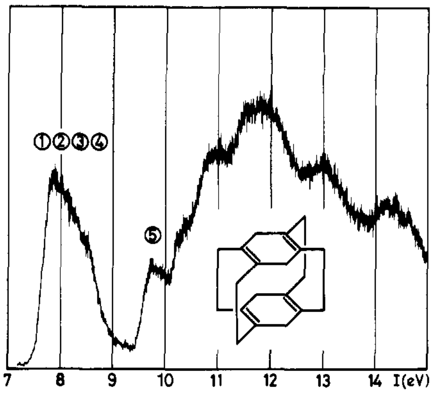
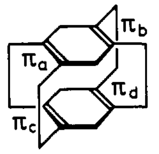


Figure 11. He(Iα) photoelectron spectrum of the tetraene **9**.



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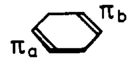

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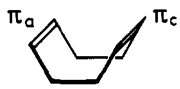

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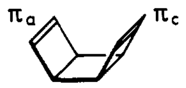

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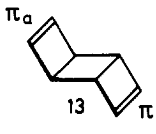

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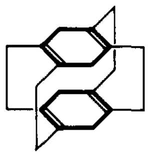
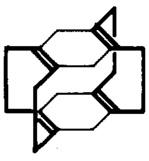


9a



9b

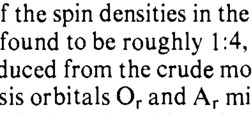
The photoelectron spectrum of **11** (which assumes predominantly the tub conformation (C_{2v}) depicted in formula **10**) shows a maximum at position $I_1^m \approx I_2^m \approx 9.1$ eV,[39] due to the superposition of the two bands corresponding to electron ejection from $\pi_+' \simeq (\pi_a + \pi_c)/\sqrt{2}$ and $\pi_-' \simeq (\pi_a - \pi_c)/\sqrt{2}$, respectively. The reason for this near degeneracy is the fortuitous cancellation of the shifts due to "through-space" and "through-bond" interaction of π_a and π_c. Apart from theoretical considerations, this can be shown by comparison with the photoelectron spectra of **12** ($I_1^m = 9.1$ (π_+^{-1}), $I_2^m = 9.4_5$ eV (π_-^{-1})) and **13** ($I_1^m = 8.9_5$ (π_+^{-1}), $I_2^m = 9.9_5$ eV (π_-^{-1}))[40] and of related systems.[41]

In contrast to the cyclophanes it is possible to construct a "strain-free" Dreiding model of **9**, without significant departure from standard bond lengths and bond angles. However, the distance between the CC axes of π_a and π_c is then only ~250 pm, and it is expected that in the real molecule this is increased to ~300 pm. As a consequence, each cyclohexadiene moiety is folded along the line joining the methylene groups, yielding a dihedral angle of 140–150°. It has been shown experimentally, and theoretically, that the difference $\Delta I = I_2^m - I_1^m$ of the π ionization energies of **10** is a function of the dihedral angle ω.[36,41] From Figure 2 of ref 41, in which the dependences $I_2{}^m(\omega)$ and $I_1{}^m(\omega)$ are shown, it follows that ΔI ($\sim$145 ± 5°) = $\sim$0.3–0.4 eV. Thus, the cross terms between π_a and π_b, or π_c and π_d, are only 0.3–0.4 eV, and those between π_a and π_c, or π_b and π_d, are almost zero, as deduced from the experimental results obtained for **11** (and **12**). From the ionization energies of **10** and **11**, and by comparing $I_1{}^m$(2-butene) = 9.13 eV to $I_1{}^m$(2,3-dimethyl-2-butene) = 8.30 eV, we obtain an expectation value for the mean π-ionization energy of **9** of $\sim$8.4–8.5 eV. Consequently all four bands due to predominantly π^{-1} ionization processes are expected in the narrow interval from $\sim$7.9 to $\sim$8.9 eV, which is in complete agreement with the photoelectron spectrum shown in Figure 11.

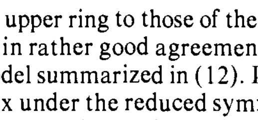
Thus we are led to the conclusion that band ⑤ (at $I_5{}^m = 9.7_5$ eV) in the photoelectron spectrum of **9** (cf. Figure 10) is necessarily associated with an ionization process of predominant σ^{-1} character. On the other hand, the σ frame of **9** is essentially the same as that of **4**(1,2,4,5). The only difference is that the latter contains eight sp^2–sp^2 CC bonds instead of the sp^2–sp^3 bonds in **9** and that four sp^3–1s bonds have disappeared. It is a consistent rule, derived from a large body of experimental evidence, that the higher the 2s character of an outer valence shell σ orbital, the higher the corresponding ionization energy. A necessary consequence is that the value $I_5{}^m = 9.7_5$ eV in the spectrum of **9** is a lowest limit for the first σ^{-1} band in the spectrum of **4**(1,2,4,5). Once more this excludes that band ④ in the latter spectrum at $I_4{}^m = 8.8$ eV could be due to removal of an electron from a σ orbital.

(4) ESR Spectra of 4,5,7,8-Tetramethyl- and 4,5,15,16-Tetramethyl[2.2]paracyclophane Radical Cation (7^+ and 14^+). The ESR spectra of 7^+ and 14^+ have been studied by Gerson et al.[42,43] The absolute values of the spin densities at the π centers of 7^+ and 14^+ [43] are as follows:

7^+



14^+

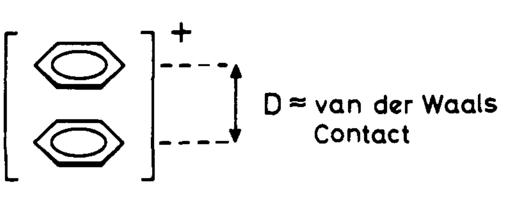


These results suggest that the singly occupied orbital in 7^+ and 14^+ (and thus the HOMO of the parent hydrocarbons within a naive orbital picture) is dominated in both cases by a linear combination of the A_l and A_u basis orbitals. In view of our analysis of the photoelectron spectra, this would have to be essentially the A_+ combination. As far as 7^+ is concerned the ratio of the spin densities in the upper ring to those of the lower one is found to be roughly 1:4, in rather good agreement with 1:3 deduced from the crude model summarized in (12). In 14^+ the basis orbitals O_r and A_r mix under the reduced symmetry of **14** (C_{2h}), as is evident from the observed spin densities. However, A_+ is again the dominating linear combination of the orbital from which the electron has been removed.

Although these results are nicely compatible with our assignments, they carry little weight as far as the assignment (11) of **2**(1,4) is concerned, because of the large orbital energy shifts induced by the methyl groups. Also, the influence of the solvent in which the ESR spectra have been recorded cannot be neglected. For further details the reader is referred to ref 42.

(5) The Electronic Spectrum of the Benzene Dimer Radical Cation (15^+). In Figure 5 is shown the dependence of the "through-space" parameter τ on the mean interdeck distance D. A nice verification of this relationship is provided by the first electronic transition[29,30,44] of the benzene dimer radical cation 15^+, which may be viewed as "zerophane" (="[0](0)cyclophane"). In **15** the two benzene moieties are in van der Waals contact, which is presumably equal or slightly shorter than for two neutral benzene molecules, i.e., $D \approx$ 320–330 pm. According to Figure 5 this yields τ = 0.7–0.5$_5$ eV. Under D_{6h} (D_{6d}) symmetry (cf. (2) and Figure 4) we predict that the electronic ground state of 15^+ is $^2E_{1g}$ ($^2E_1$) and the first electronically excited one is $^2E_{1u}$ ($^2E_5$). The two states are separated by 2τ = 1.4–1.1 eV according to our model and the transition from one to the other is electronically allowed (z polarized). The value observed by Bühler and Funk[44] is 1.33 eV, in complete agreement with the one derived from our simple model. If the latter were taken at face value, a mean interdeck distance of D = 322 pm would be predicted.

15^+



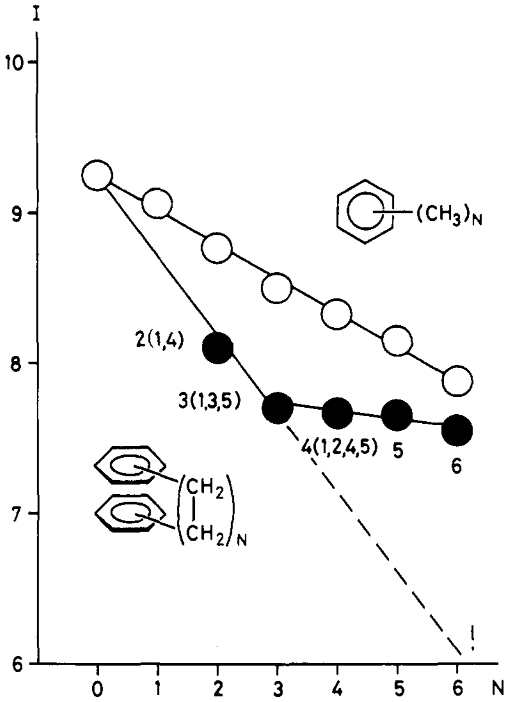


Figure 12. Correlation diagram of the mean first ionization energies of methyl-substituted benzenes (open circles) and of the correspondingly substituted cyclophanes (full circles).

VI. Discussion of Results

At first sight, the most surprising result is probably the fact that "superphane" **6** does not have as low an ionization energy as one might have expected. Indeed two effects could have been invoked in predicting that **6** should be, for its size, one of the hydrocarbons with lowest first ionization energy:

(a) It is known that the mean ionization energy $\overline{I^m}(\pi)$ of methyl-substituted benzenes (as defined in section II) decreases linearly with increasing number N of methyl groups,[16,45] as shown in Figure 12. The same effect could be expected to operate in the cyclophane series and it could even be argued that the shift dependence on N should be a bit steeper than in the benzene case.

(b) In addition squeezing the two benzene moieties against each other to distances considerably shorter than the usual van der Waals contact ($\sim$340 pm) should result in a sort of "toothpaste-tube effect", i.e., the closer the mean interdeck distance D, the easier should be the removal of a π electron.

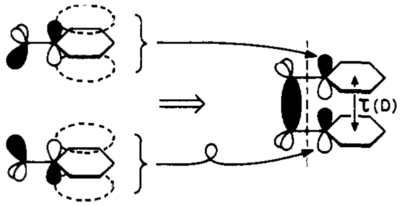
As shown in Figure 12, such an argumentation seems to be supported by the results that had previously been observed for **2**(1,4) and **3**(1,3,5). Indeed I_1 = 8.1 eV for **2**(1,4) and I_1 = 7.7

eV for 3(1,3,5) are ~0.6–0.7 and ~0.8 eV lower than the $\overline{I^m}(\pi)$ for the xylenes and for trimethylbenzenes, respectively. Assuming that the hyperconjugative destabilization of the highest occupied π orbitals increases with increasing number N of ethano bridges and that D decreases roughly in proportion to the same number N of bridging groups, one would have predicted by a rather naive linear extrapolation that the photoelectron spectrum of superphane **6** should have its first maximum close to 6 eV (cf. Figure 12). Quite obviously such an expectation is widely off the mark.

It is a pleasing feature of our assignment and its underlying model that it permits a straightforward rationalization of the observed trend in the first ionization potentials ($I_1{}^m \approx I_2{}^m$) of the cyclophanes.

According to the analysis of the photoelectron spectra of Figures 1 and 2 and to the supporting arguments presented in the previous sections the two highest occupied molecular orbitals of the cyclophanes correspond mainly (in our crude model exclusively) to the linear combinations S_+ and A_+ (see (4) and Figure 4). Because S_+ and A_+ are antisymmetric with respect to the xy plane and because of the local symmetry of the atomic 2p orbitals at the centers μ, the only bridge orbital which could interact with S_+ or A_+ is $\varphi_\mu{}^{(2)}$ (cf. Figure 3). However, this is a very low-lying orbital and its cross terms with S_+ and A_+ are small. In fact we have neglected it in our model, and the observation that the split between the bands ① and ② is too small to be detectable justified this simplification. As a result we are in the presence of a case of symmetry-forbidden hyperconjugation, as far as the S_+ and A_+ orbitals are concerned. Such restrictions conditioned by symmetry are nothing new, and have been observed and discussed before, e.g., in ref 20 and 46.

It is perhaps worthwhile to discuss the situation in slightly more detail. In the case of a methyl-substituted benzene, two pseudo-π orbitals can be formed by combining the CH σ orbitals of a methyl group, one of which is available for hyperconjugation with the benzene π orbitals. If more than one position is substituted, the effects are additive because of the very weak coupling between the methyl groups. In the cyclophane the two pseudo-π orbitals of the original methyl groups are now solidly linked in phase by the newly formed CC σ bond, whereas the rather large positive through-space matrix element between the upper and lower π orbitals S_u, S_l and A_u, A_l demands that the highest occupied orbitals S_+, A_+ in the cyclophane are antisymmetric with respect to the x,y plane. This decouples the hyperconjugation, as far as these orbitals are concerned. With respect to Figure 12, a prediction of the first ionization energy cannot therefore be obtained by referring to the regression line of the methylbenzenes and by adding the through-space contribution, but only by taking the latter into account, relative to a fixed basis value. As has already been shown in Figure 5, $\tau(D)$ depends almost linearly on D in the interval spanned by the cyclophanes and thus explains the observed trend shown in Figure 12.



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