43. 'Through Space' and 'Through Bond' Interactions in [2.2]Cyclophanes; the Assignment of their Photoelectron Spectra

by **Branka Kovač**[1]), **Michael Allan** and **Edgar Heilbronner**

Physikalisch-chemisches Institut der Universität Basel, Klingelbergstrasse 80, CH-4056 Basel

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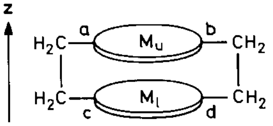
Summary

The photoelectron spectra (PE.) of ten cyclophanes (**7** to **14**, **16**, **18**) have been assigned on the basis of a simple molecular orbital model proposed recently for the cyclophanes **2** (1,4) to **6**. It is shown that the agreement between calculated and observed band positions provides strong evidence for the validity of the model.

1. Introduction. - In a recently published 'Data Bank' [1] we have reported the He(Iα) photoelectron (PE.) spectra and the ionization energies of 25 [2.2]cyclophanes (**1**), in which the upper (M_u) and lower (M_l) moieties are aromatic and/or heteroaromatic π-systems, linked in positions a, c and b, d by two CH_2CH_2 bridges.



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Based on a self-consistent interpretation of the He(Iα) PE. spectra of the complete series of nine cyclophanes from [2.2](1,4)cyclophane (= **2** (1.4) = [2.2]paracyclophane) to [2.2.2.2.2.2](1,2,3,4,5,6)cyclophane **6** (= 'superphane') [2] we now propose assignments for the PE. spectra of **7** [2]Paracyclo[2] (1,4)naphthalenophane, **8** [2]Paracyclo[2] (1,5)naphthalenophane, **9** *syn*-[2.2] (1,4)Naphthalenophane, **10** *anti*-[2.2] (1,4)Naphthalenophane, **11** [2.2] (1,5)Naphthalenophane (achiral), **12** [2.2] (1,5)-Naphthalenophane (chiral), **13** [2.2] (2,6)Naphthalenophane (chiral), and **14** [2.2] (2,6)Naphthalenophane-1,11-diene (chiral) which have been reported in [1], and the observed bandpositions of which are presented in *Table 1.* In analogy to our work on the cyclophanes **2** (1,4) to **6** [2] we rely mainly on an empirical correlation procedure [3], implemented by simple (in part qualitative) molecular orbital arguments. This model is the simplest of its kind, namely a LCMO-model (= linear combination of molecular orbitals), the basis functions of which are taken from standard *Hückel*-theory [4], whereas the orbital energies and the crossterms between these orbitals are adjusted to fit experimental data of a small set of key-compounds

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[1]) Permanent address: Department of Chemistry, 'Ruđer Bošković' Institute, Zagreb, Croatia, Yugoslavia.

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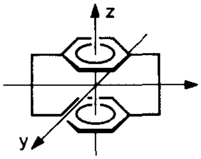
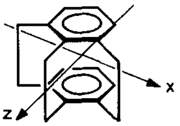
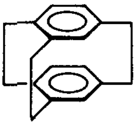


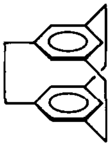
2 (1,4) D_{2h}



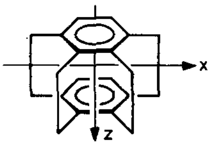
3 (1,2,3) C_{2v}



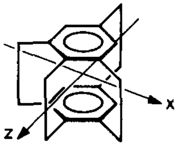
3 (1,2,4) C_s



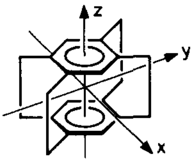
3 (1,3,5) D_{3h}



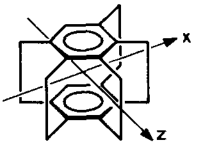
4 (1,2,3,4) C_{2v}



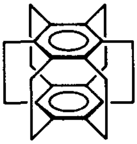
4 (1,2,3,5) C_{2v}



4 (1,2,4,5) D_{2h}

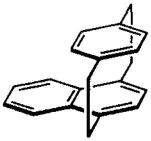


5 C_{2v}



6 D_{6h}

via Koopmans' approximation. In fact, this model, which keeps track only of the symmetry and nodal properties, is a convenient storage for the empirical correlation parameters which one would also have used implicitly in the traditional qualitative correlation diagrams.



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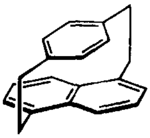

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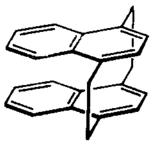

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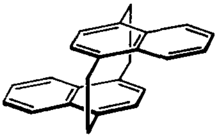

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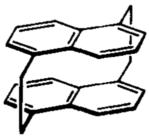

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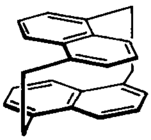

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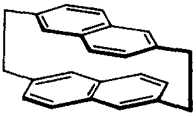

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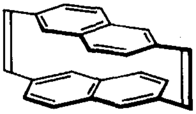

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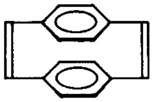

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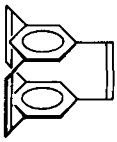

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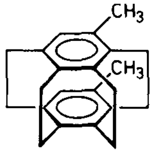

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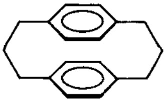


18

Table 1. *Ionization energies I_J^m in eV of cyclophanes* [1]. The I_J^m refer to the positions of the band maxima, and are thus close to the vertical ionization energies.

Compound	Maxima ①	②	③	④	⑤	⑥	⑦
7	7.6_0	8.1_5		9.2_0	9.5_0	10.0_5	
8	7.56	8.1_5	8.5_0	8.7_0	9.2_5	10.2	
9	7.2_5	7.7_5	8.0_5	8.9_0	9.5_5	10.6	
10	7.5_0	7.7_0	8.1_0	8.9_0	9.2_5	9.5_0	9.9_5
11	7.0_5	7.7_0		8.7_0	9.2_5	10.0	
12	7.2_5	7.6_0	8.3_0	8.7_0	8.9_0	9.3_0	10.0
13	7.52	8.30	8.4_0	9.2_5	9.6_5	10.3	
14	7.4_0	7.7_0	8.3_0	9.2	9.6	10.5	

Furthermore the model allows the convenient handling of 'through-space' and 'through-bond' interactions [5] and of their interplay. It will be seen that such a model is rather successful within a given set of closely related molecules for which the descriptive parameters are known to exhibit good transferability. This conclusion is also supported by *ab initio* model calculations [6] with standard STO-3G basis functions [7]. (For a general discussion of the underlying 'philosophy' see [3].)

Basis Functions and Energies. - As a start we are going to use *Hückel* molecular orbitals

$$\Phi^0_{r,J} = \sum_{\mu} c^0_{\mu J}\,\phi_{\mu} \tag{1}$$

for the π-orbitals of the lower ($r = l$) and upper ($r = u$) moieties M_r of the cyclophanes **1**. As in previous work [1] the $1a_{2u}$ π-orbital of a benzene ring is abbreviated as O^0_r and the two $1e_{1g}$ orbitals, in real representation, as A^0_r and S^0_r, the former being antisymmetric, the latter symmetric with respect to the symmetry plane passing through the centres 1 and 4. For the naphthalene systems, the five bonding π-orbitals are $N^0_{r,1}, N^0_{r,2}, N^0_{r,3}, N^0_{r,4}$ and $N^0_{r,5}$ in ascending order of energy [4]. In the simple, but adequate approximation used in [4], the two moieties M_l and M_u are

Table 2. *Distances between centres of same index μ of the upper and lower deck of cyclophanes* (in pm). D = mean inter-deck distance in pm.

Cyclophane		Centres μ 1	2	3	4	5	6	D
2 (1,4)	[8]	278	309	309	278	309	309	$299._5$
3 (1,2,3)	[10]	281	256	281	382	441	382	337
3 (1,3,5)	[10]	276	283	276	283	276	283	$279._5$
4 (1,2,3,4)[a])	[10]	275	260	259	276	348	344	$293._5$
5	[10]	271	259	263	259	271	300	$270._5$
6	[10]	263	263	263	263	263	263	263
15	[9]	280	314	314	280	314	314	$302._5$
16	[11]	276	286	276	286	276	286	281

[a]) These distances are those observed for the dimethyl derivative **17** of **4** (1,2,3,4).

restricted to two hypothetical, parallel planes separated by a mean inter-deck distance D, which can be computed from known X-ray structure data in the cases of (*cf. Table 2)* **2** (1,4) [8], [2.2]paracyclophane-1,9-diene (**15**) [9] (related to **2** (1,4)), **3** (1,2,3) [10], **3** (1,3,5) [10], [2.2.2] (1,3,5)cyclophane-1,9,17-triene (**16**) [11] (related to **3** (1,3,5)), the dimethylderivative **17** of **4** (1,2,3,4) [10], **5** [10] and **6** [10] (structure data are also available for **12** [12] and for [3.3]paracyclophane **18** [13]).

In the following it will prove necessary to compute overlap integrals $S_{I,J}$ between pairs of π-orbitals $\Phi_{l,I}$ and $\Phi_{u,J}$ as a function of the inter-deck distance D, *i.e.* of, among other things, the individual inter-atomic distances according to

$$S_{IJ}=\sum_{\mu}\sum_{\nu} c_{\mu I}\, c_{\nu J}\, S_{\mu\nu} \qquad (2)$$

where $S_{\mu\nu}$ stands for the overlap integral $S_{\mu\nu}=\langle\phi_\mu|\phi_\nu\rangle$ between two $2p_z$ atomic orbitals of M_l and M_u, respectively. The latter overlap integrals $S_{\mu\nu}=S_{\mu\nu}(R_{\mu\nu},\theta_{\mu\nu})$ depend both on the distance $R_{\mu\nu}$ and on the angle $\theta_{\mu\nu}$ which the $2p_z$ orbital axes make with the line joining the centres μ and ν of the lower and upper deck, respectively. For $D=0$ we must have $S_{IJ}=\delta_{IJ}$ if the orbitals $\Phi_{r,J}$ are required to form an ortho-normal set. However, this is not the case if the coefficients $c^0_{\mu J}$ of the *Hückel* orbitals of equ. 1 are used in equ. 2, because the latter have been normalized under the assumption $S_{\mu\mu'}=\delta_{\mu\mu'}$. It is therefore necessary to renormalize them through multiplication by a factor

$$\mathcal{N}_J=\left(\sum_{\mu}\sum_{\mu'} c^0_{\mu J}\, c^0_{\mu' J}\, S_{\mu\mu'}\right)^{-1/2} \qquad (3)$$

This yields the orbitals

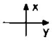
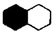
$$\Phi_{r,J}=\mathcal{N}_J\,\Phi^0_{r,J}=\sum_{\mu} c_{\mu J}\,\phi_\mu \qquad (4)$$

with $c_{\mu J}=\mathcal{N}_J\, c^0_{\mu J}$ to be inserted into the expression 2. If *Slater* 2p-orbitals with atomic orbital exponents of 1.625 are used for the computation of the $S_{\mu\nu}$, then the renormalization coefficients $\mathcal{N}_J$ given in *Table 3* are obtained.

Note that two different molecular orbitals $\Phi_{l,I}$, $\Phi_{u,J}$ belonging to the same irreducible representations within the local symmetries of M_l or M_u are no longer strictly orthogonal according to the expression 2, even if two planar, eclipsed moieties at distance D are assumed. However the S_{IJ} values will be very small and can thus be neglected.

The basis energies $A(O_r)$, $A(S_r)$ and $A(A_r)$ of the benzene π-orbitals in the cyclophanes **2** (1,4) to **8** and **15** to **18** are carried over from previous work [2] [14]. There it has been shown that it is apropriate to correct the values $A^0(S_r)=A^0(A_r)=-9.25$ eV of the frontier orbitals of benzene, derived by applying *Koopmans'* theorem in reverse to the corresponding observed ionization energy, by +0.25 eV, to absorb the neglected destabilizing effects which occur when a basis π-orbital is imbedded in the cyclophane system. In analogy, the π-orbital basis energies $A(N_2)$ to $A(N_5)$ of the naphthalene moieties in the cyclophanes **7** to **14** are postulated to be equal to the negative vertical ionization energies of the first four π-bands in the PE. spectrum of naphthalene [15] again corrected by +0.25 eV. However the position of the fifth π-band is not exactly known. Therefore the value $A(N_1)$ has been extra-

Table 3. *Basis π-orbitals, their local symmetry, renormalisation factor $\mathcal{N}_J$ and bais energies A ($\Phi_{r,J}$).* The index r refers to the lower ($r = l$) or upper ($r =$ u) moieties M_r of **1**.

Orbital		Local symm.[a])	Renorm. factor N_J	Basis energy $A(\Phi_{r,J})$/eV
S_r		$(E_{1g})\ B_{2g}$	0.9147	− 9.0
A_r		$(E_{1g})\ B_{3g}$	0.9147	− 9.0
O_r		$(A_{2u})\ B_{1u}$	0.7977	− 12.2
$N_{r,5}$		A_u	0.9599	− 7.90
$N_{r,4}$		B_{1u}	0.9209	− 8.63
$N_{r,3}$		B_{2g}	0.8830	− 9.73
$N_{r,2}$		B_{3g}	0.8399	− 10.59
$N_{r,1}$		B_{1u}	0.7714	− 12.25

[a]) Local symmetries are given with respect to the group D_{2h}. Values in brackets refer to D_{6h} local symmetry.

polated using linear regressions of $A(N_2)$ to $A(N_5)$ *vs.* the corresponding computed π-orbital energies [16] [17] and the π-orbital energy of N_1 obtained by the same theoretical procedure. The complete set of data has been collected in *Table 3*.

'Through-Space' Interactions of the Cyclophane π-Systems. - The orbital interaction pattern in **2** (1,4) was first analyzed in terms of 'through-space' and 'through-bond' interactions [5] by *Gleiter* [18]. Later *Boschi & Schmidt* [19] provided a semi-quantitative assessment of the magnitude of the 'through-space' coupling parameter τ, using PE. spectroscopic data. Although the theoretical procedure used for the computation of the parameter τ and, thus, its exact meaning remained undefined (*cf.* footnote 11 in [19]), the results clearly demonstrated that τ decreases with increasing mean interdeck distance D between the two benzene moieties M_l and M_u. This is supported by the more detailed analysis of the PE. spectra of compounds **2** (1,4), **3** (1,2,3), **3** (1,3,5), **4** (1,2,3,4), **5** and **6** reported in [2] which yielded the linear regression

$$\left(\frac{\tau(\mathrm{D})}{\mathrm{eV}}\right) = 4.9 - 0.0132\left(\frac{\mathrm{D}}{\mathrm{pm}}\right) \tag{6}$$

valid for the interval 260 pm < D < 350 pm.

In the following paragraphs we shall assume that the 'through space' interaction parameter

$$\tau_{IJ} = \langle \Phi_{l,I} | \mathcal{H} | \Phi_{u,J} \rangle \tag{7}$$

is proportional to the overlap S_{IJ} between the two basis orbitals, *i.e.*

$$\tau_{IJ} = -\tau_0 \cdot S_{IJ} = -\tau_0\, \mathcal{N}_I\, \mathcal{N}_J\, S^0_{IJ} \tag{8}$$

Table 4. *Values of the overlap integrals and the interaction parameters*

Compound	$S_{SS} = S_{AA}$	S_{OO}	τ_{SS}/eV
6	−0.1343	−0.1107	1.45
5	−0.1207	−0.0984	1.33
3 (1,3,5)	−0.1057	−0.0850	1.30
4 (1,2,3,4)	−0.0852	−0.0671	1.10
2 (1,2)	−0.0775	−0.0460	0.90
3 (1,2,3)	−0.0411	−0.0303	0.50

so that τ_{IJ} becomes a function of the distance between the two moieties M_l and M_u, and in the compounds **7** to **14** of their relative orientations and/or shifts in the x- and/or y-directions. If the z-axis is oriented as shown in **1** and if the $2p_z$ atomic orbitals ϕ_μ of the π-orbitals (1) are defined with respect to this orientation, then the overlap integrals S_{II} (*i.e.* between two orbitals $\Phi_{l,I}$ and $\Phi_{u,I}$ of same type) will be negative for distances in the interval 260 pm $< D <$ 350 pm. Consequently, because of the negative sign in (8), the τ_{II} are positive.

If for the six cyclophanes underlying regression 6, we calculate the overlaps S_{AA}, S_{SS} and S_{OO} assuming that M_l and M_u are planar, fully eclipsed (*i.e.* with common sixfold axis), parallel and separated by the mean inter-deck distance D given in *Table 1*, the values of *Table 4* are obtained. Under the assumptions implicit in our model the overlaps S_{SS} and S_{AA} must be equal, and we should also have (according to equ. 8) that $\tau_{SS} = \tau_{AA}$. The values given in the last column of *Table 4* are taken from [1]. The data of *Table 4* (τ_{SS} *vs.* S_{SS}) yield the regression

$$\left(\frac{\tau}{\mathrm{eV}}\right) = (0.13 \pm 0.10) - (10.25 \pm 1.04) \cdot S(D), \tag{9}$$

where the first term is not significantly different from zero. If the regression is forced through the origin $S(\infty) = 0$, $\tau = 0$, then a least squares treatment yields

$$\left(\frac{\tau}{\mathrm{eV}}\right) = -(11.52 \pm 0.34) \cdot S(D) \tag{10}$$

which has been used subsequently. Both equ. 9 and 10 are displayed graphically in *Figure 1*.

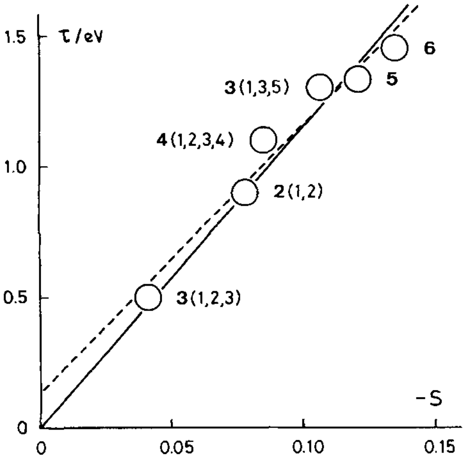


Fig. 1. *Dependence of the 'through-space' coupling parameter τ on the overlaps S between the lower and upper benzene π-orbitals, according to equ. 9, dotted line and equ. 10, full line*

Table 5. *Interaction parameters from [21] and from equ. 10*

D/pm	τ/eV from	
	[21]	(10)
260	1.17	1.34
270	1.02	1.14
280	0.89	0.97
290	0.77	0.82
300	0.67	0.69
310	0.57	0.58

It is of interest to compare the τ-values derived from equ. 10 with those obtained by *Koutecky & Paldus* [20] by a completely independent, purely theoretical assessment of the transannular 'through-space' interaction matrix element (see *Table 5*). Within the limits of significance both sets are in pleasing agreement, especially for the relevant distances $D > 280$ pm.

A simplification introduced in our treatment consists in the neglect of 'through-space' interactions between the σ orbitals of one benzene moiety and the π orbitals of the other. This is a reasonable approximation because of the energy difference between such pairs and because of the small value of the overlap of these orbitals for mean inter-deck distances of the order of $D \approx 300$ pm.

'Through-Bond' Interactions of the Cyclophane π-Systems. - The treatment of 'through-bond' interactions [5] follows closely from the one proposed previously for the cyclophanes **2** (1,4) to **6** [2] [14], where it has been shown that only one of the σ-orbitals of the linking C_2H_4-bridges has the proper symmetry and shape to interact appreciably with the relevant linear combinations of $\Phi_{l,\mathrm{I}}$ and $\Phi_{\mathrm{u,I}}$. (For a detailed discussion see [2].)

The relay orbital bridging the centres μ of M_l and ν of M_u is named $\varphi_{\mu\nu}$. Its interaction cross term with the π-orbital $\Phi_{\mathrm{r,I}}$ (r = l or u) is postulated to be well represented by equ. 11:

$$\begin{aligned}\kappa_{\mathrm{I},\mu} &= \langle \Phi_{l,\mathrm{I}} | \mathscr{H} | \varphi_{\mu\nu} \rangle = \pm c^0_{\mu\mathrm{I}} \cdot \mathrm{B} \\ \kappa_{\mathrm{I},\nu} &= \langle \Phi_{\mathrm{u,I}} | \mathscr{H} | \varphi_{\mu\nu} \rangle = \pm c^0_{\nu\mathrm{I}} \cdot \mathrm{B}\end{aligned} \tag{11}$$

where $c^0_{\mu\mathrm{I}}$ is the LCAO coefficient of ϕ_μ in the *Hückel* molecular orbital (1), that is at the point of attachment of the bridge orbital $\varphi_{\mu\nu}$. The sign of $\kappa_{\mathrm{I}\rho}$ depends on the local phase relationship of $\Phi_{\mathrm{r,I}}$ and $\varphi_{\mu\nu}$, and B is a resonance integral assumed to be a transferable parameter. Previous experience has shown [2] [14] that $\mathrm{B} = -2.4$ eV is appropriate, a value in keeping with that describing the conjugative interaction of a π-center with the pseudo-π-orbital of a substituting methyl-group, *i.e.* hyperconjugation [3] [21].

The set of alkyl bridge orbitals to which $\varphi_{\mu\nu}$ belongs has been derived from an equivalent bond orbital model using localized λ_{CH} and λ_{CC} bond orbitals [22]. Such a calculation yields a self energy $A_\varphi = \langle \varphi_{\mu\nu} | \mathscr{H} | \varphi_{\mu\nu} \rangle = -14$ eV [2]. This value is not very critical because of the large energy gap which separates A_φ from the π-orbital basis energies listed in *Table 3*.

[2]Paracyclo[2]naphthalenophanes. - In *Figure 2* (top) are shown: a) the observed vertical ionization energies (I_j) of the first four bands of naphthalene and

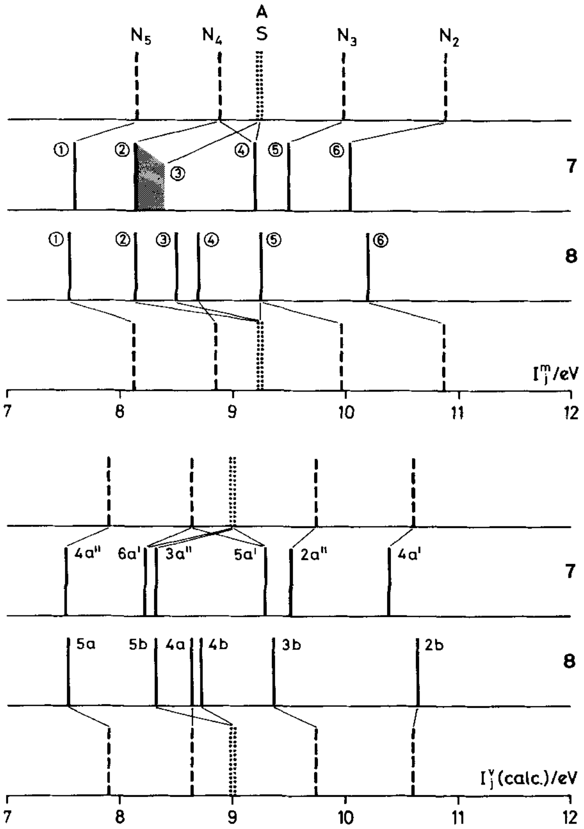
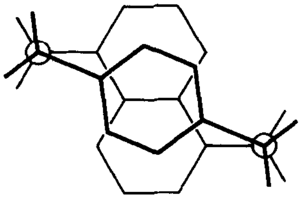


Fig. 2. *Comparison of observed (I_j^m) and calculated (I_j^v(calc.)) band positions of the photoelectron spectra of* **7** *(=[2]paracyclo[2] (1,4)-) and* **8** *(=[2]paracyclo[2] (1,5)naphthalene).* The dotted and broken lines above and below the bar-diagrams correspond to the negative basis energies of the naphthalene (broken) and benzene (dotted) π-orbitals. For details, see text.

of the first (double) band of benzene, corresponding to electron ejection from the naphthalene π-orbitals N_5 to N_2 and the benzene $1e_{1g}$ π-orbitals (*i.e.* S and A), respectively; b) the observed band position I_j^m of the first six bands in the PE. spectra of [2]paracyclo[2] (1,4)naphthalenophane (**7**) and of [2]paracyclo[2] (1,5)-naphthalenophane (**8**).

For neither of these two molecules are experimentally determined structure parameters available. Therefore we have assumed that the two moieties M_l = naphthalene system and M_u = benzene system are planar and parallel to each other at a mean interdeck distance of $D \approx 300$ pm. Furthermore, in the model of **7**, the benzene ring is supposed to eclipse one of the six-membered rings of the naphthalene nucleus, and in the model of **8** its six-fold axis is postulated to pass through the centre of the 9,10-bond of the naphthalene moiety, the two parts being rotated by $\alpha \approx 25°$ relative to each other, as shown by the topview of **8** in the following diagram:



The non-zero overlap integrals S_{IJ} obtained under these premises are collected in the *Table 6,* the first index I referring to the naphthalene orbital N_I, the second index J (= 1, 2, 3) to the benzene orbitals O, A, S respectively:

Table 6. *Overlap-integrals values for compound* 7 *and* **8**

7	**8**
$S_{11} = -0.1091$	$S_{11} = -0.1204$
$S_{12} = -0.0277$	$S_{22} = -0.0570$
$S_{21} = -0.0563$	$S_{23} = +0.0266$
$S_{22} = -0.0423$	$S_{32} = -0.0297$
$S_{33} = -0.0619$	$S_{33} = -0.0634$
$S_{41} = -0.0033$	$S_{41} = +0.0136$
$S_{42} = -0.0548$	
$S_{53} = -0.0380$	

The ten orbitals of the molecules **7** and **8** which are of π parentage, span the following irreducible representations:

$$\begin{array}{l} \mathbf{7}\ (\text{Symmetry } C_s)\text{: } 6\times A' + 4\times A'' \\ \mathbf{8}\ (\text{Symmetry } C_2)\text{: } 5\times A + 5\times B \end{array} \qquad (12)$$

For simplicity only the ten outer orbitals are prefixed by numbers, *e.g.* 1a′ to 6a′ and 1a″ to 4a″ in **7** *(cf. Fig. 2* and *Table 7).*

The necessary 'through-space' cross terms are calculated from the overlap integrals (see *Table 6*) according to equ. 10 and the 'through-bond' interaction parameters are obtained from expression 11. These, and the basis energies $A(N_I)$, A(S), A(A), A(O) and A_φ define a 10×10 matrix, the diagonalization of which yields the orbital energies ε_j and, applying *Koopmans'* approximation, the vertical ionization energies I_j^v (calc.) listed in *Table 7* and graphically displayed in *Figure 2.* In view of the approximations involved, the agreement is remarkably good and leaves little doubt that the resulting assignment is trustworthy, except for a possible reversal of the labels 6a′, 3a″ in the PE. spectrum of **7** or of 4a, 4b in that of **8**.

The linear combination ψ_j belonging to $\varepsilon_j = -I_j^v$ (calc.) is

$$\psi_j = \sum_{r,I} C_{r,I;j}\,\Phi_{r,I} + C_{\mu\nu,j}\,\varphi_{\mu\nu} + C_{\rho\sigma,j}\,\varphi_{\rho\sigma} \qquad (13)$$

with r = *l* and r = u depending on $\Phi_{r,I}$ belonging to the lower or upper deck of the molecule. In *Table 7* are listed the basis orbital contributions in percent, *i.e.* $C^2_{r,I;j}\cdot 100$ and $(C^2_{\mu\nu,j}+C^2_{\rho\sigma,j})\cdot 100$, which allow the orbital parentage of the linear combination ψ_j to be assessed.

Table 7. *Comparison of observed and calculated band positions.* The numbers in the orbitals labels count only the ten orbitals which are of π-parentage (*cf.* text). The basis orbital contributions (in percent) correspond to the rounded values of $c_{Ij}^2 \cdot 100$, c_{Ij} being the coefficient of basis orbital Φ_I in the linear combination ψ_j.

Band		I_j^m/eV obs.	I_j^v/eV calc.	Orb.	Basis orbital contributions in percent:								
					N_5	N_4	N_3	N_2	N_1	S	A	O	φ
7	1	7.6_0	7.52	4a″	91		2	1					6
	2	8.1_5	8.23	6a′		63					36		
	3	(8.4)	8.31	3a″	1		1			90			8
	4	9.2_0	9.29	5a′		37		6			57		
	5	9.5_0	9.42	2a″	5		90						6
	6	10.0_5	10.39	4a′		1		82	4		6	2	6
8	1	7.56	7.54	5a	94								6
	2	8.1_5	8.31	5b						25	65		10
	3	8.5_0	8.63	4a		100							
	4	8.7_0	8.73	4b			19	3		56	21		1
	5	9.2_5	9.37	3b			65	13		8	5		8
	6	10.2	10.64	2b			9	80		9	2		1
9	1	7.2_5	7.27	$2a_2$	100+								
(C_{2v})	2	7.7_5	7.66	$3b_1$	80−		6−						14−
	3	8.0_5	7.96	$3b_2$		100+							
	4	8.9_0	9.01	$1a_2$			100+						
	5	9.5_5	9.30	$4a_1$		100−							
			9.79	$2b_2$				100+					
			9.92	$2b_1$	13−		81−						6−
10	1	7.5_0	7.38	$3a_u$	89+		1−						10−
(C_{2h})	2	7.7_0	7.67	$2b_g$	95−		5+						
	3	8.1_0	8.18	$4a_g$		98−		2+					
	4	8.9_0	8.98	$3b_u$		97+		2−					
	5	9.2_5	9.37	$1b_g$	5−		95+						
	6	9.5_0	9.46	$2a_u$	4+		87−						9−
	7	9.9_5	10.20	$3a_g$		2−		88+					10+
11	1	7.0_5	7.27	$3a_u$	100+								
(C_{2h})	2	7.7_0	7.80	$4a_g$	88−				1−				11+
	3	(7.8)	7.96	$2a_u$		100+							
	4	8.7_0	9.01	$2b_g$			100+						
			9.30	$3a_g$		100−							
	5	9.2_5	9.44	$3b_u$			72−	8−					20−
	6	10.0	9.79	$1b_g$				100+					
12	1	7.2_5	7.34	4a	85+	5−			1−				9+
(D_2)	2	7.5_0	7.52	$3b_1$	84−	16+							
	3	8.3_0	8.54	$2b_1$	16−	84+							
	4	8.7_0	8.96	3a	4+	95−							1+
	5	8.9_0	9.23	$2b_2$			86−						14−
	6	9.3_0	9.28	$3b_3$			92+	8−					
	7	10.0	9.78	$1b_2$			1−	93+					6−
13	1	7.52	7.55	4a	95+								4+
(D_2)	2	(7.7)	7.69	$3b_1$	65−	35+							
	3	8.30	8.31	3a	1+	87−			1−				11+
	4	8.4_0	8.53	$2b_1$	35−	65+							
	5	9.2_5	9.13	$3b_3$			97+						3−
	6	9.6_5	9.66	$2b_2$			40−	60+					
	7	10.3	10.09	$2b_3$				77−					23−

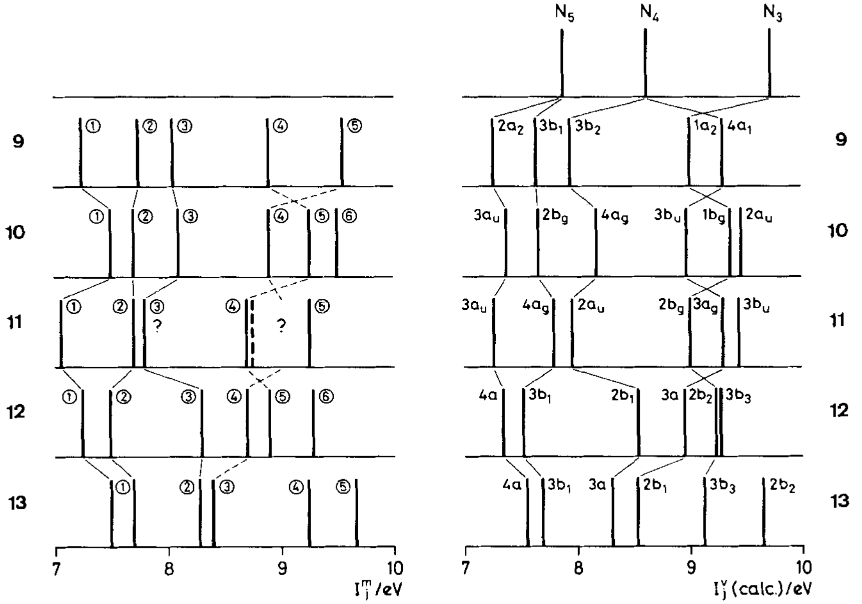


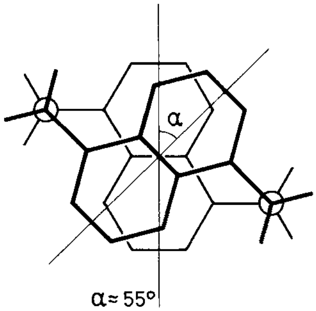
Fig. 3. *Comparison of the observed (I_j^m) and calculated (I_j^v(calc.)) band positions of the PE. spectra of the [2.2]naphthalenophanes* **9** *to* **13**. The vertical bars, labeled N_5, N_4 and N_3 correspond to the negative orbital energies of the naphthalene basis π-orbitals. For details, see text.

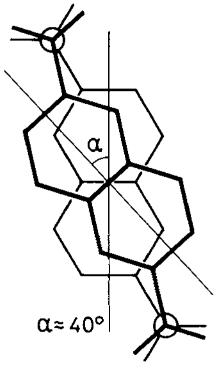
[2.2]Naphthalenophanes. - *Figure 3* shows the observed ionization energies I_j^m, *i.e.* the positions of the maxima in the PE. spectra of the five [2.2]naphthalenophanes **9** to **13** [1], which are also listed in *Table 1*. As we shall see, some of the labeled maxima refer to features which are due to the superposition of two bands belonging to different states of the radical cation. However, for the sake of consistency, we have preferred to conserve the numbering proposed in [1], rather than changing it in accordance with the assignment resulting from the present analysis.

In view of the simplifications that have to be necessarily used, in particular because of the lack of structural information, we believe that only the first four or five bands of the PE. spectra of **9** to **13** can be assigned with some confidence. The assignment of the higher energy bands proposed in *Table 8* is much less certain and the labels should be considered, at best, only as a working hypothesis.

As in the previous examples **7** and **8**, we have assumed that the two decks M_l and M_u are parallel and separated by a distance D = 300 pm in all five [2.2]naphthalenophanes **9** to **13**. This is probably an acceptable approximation for all but the first molecule **9**, because in this case the two naphthalene nuclei must certainly assume a V-shaped structure. This decreases the 'through-space' interaction, relative to the one calculated under the above assumptions. In the model of **9** and **11** the two naphthalene moieties are supposed to be fully eclipsed, which means that the same 'through-space' coupling parameters τ_{IJ} are obtained for both molecules. In the model of **10** the upper deck M_u is shifted along the y-axis by 242 pm relative to M_l, *i.e.* by the width of a benzene ring, and in the models of **12** and **13** the upper deck

M_u is rotated relative to M_l by an angle $\alpha = 55°$ and 40°, respectively, as shown in the following projections:





The twelve molecular orbitals for **9** to **13** which are obtained by combining the ten naphthalene π-orbitals N of M_l and M_u with the two bridge orbitals $\varphi_{\mu\nu}$, $\varphi_{\rho\sigma}$, span the following irreducible representations of the respective groups:

$$\begin{array}{rll} \mathbf{9} & (\text{Symm. } C_{2v}): & 4\times A_1+2\times A_2+3\times B_1+3\times B_2 \\ \mathbf{10, 11} & (\text{Symm. } C_{2h}): & 4\times A_g+3\times A_u+2\times B_g+3\times B_u \\ \mathbf{12, 13} & (\text{Symm. } D_2): & 4\times A+3\times B_1+2\times B_2+3\times B_1 \end{array} \qquad (14)$$

The two decks M_l and M_u are symmetry equivalent in all cases, so that the molecular orbitals belonging to the irreducible representations (14) contain either the in-phase or the out-of-phase linear combination(s)

$$\begin{aligned} N_{I,+} &= (N_{l,I}+N_{u,I})/\sqrt{2} \\ N_{I,-} &= (N_{l,I}-N_{u,I})/\sqrt{2} \end{aligned} \qquad (15)$$

of the naphthalene π-orbitals of same quantum number I. Because the definition given in equ. 4 is the same for $N_{l,I}$ and $N_{u,I}$, one finds that in the models of **9** and **11** $N_{I,+}$ is antisymmetric and $N_{I,-}$ symmetric with respect to reflection in the plane passing between the two decks. For the same reason all overlap integrals S_{II} are negative in **9** and **11**, which yields positive interaction parameters according to expression 10. Consequently, if the two naphthalene systems are exactly on top of each other, as in the compounds **9** and **11**, 'through-space' interaction will place $N_{I,+}$ above $N_{I,-}$ in energy. In all the other molecules the situation is a bit more complicated due, for example, to the shift of M_l relative to M_u (as in **10**) or to the relative rotation of M_l with respect to M_u about their common z-axis (as in **12** and **13**). For the latter case, the dependence of the overlap integrals S_{IJ} on the angle of rotation α is displayed graphically in *Figure 4.*

The computation of I_J^v(calc.) proceeds as in the case of the [2]paracyclo[2]-naphthalenes, except that a 12×12 matrix has to be diagonalized. The results for the top seven orbitals are given in *Table 7* and are partially displayed in the right-hand part of *Figure 4.* The + and − signs affixed to the percentage basis orbital

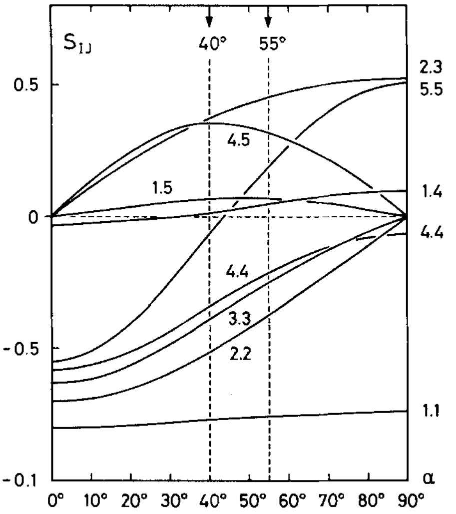


Fig. 4. *Dependence of the overlap integrals S_{IJ} on the relative angle of rotation α of the lower and upper deck in [2.2]naphthalenophanes such as* **11**, **12**, **13** *and* **14**. The labels I,J of each line correspond to the lower indices of S_{IJ}.

contributions listed for **9** to **13** in *Table 7* refer to the sign of the particular linear combination 15 to which the corresponding number belongs.

In view of the arbitrariness of some of the assumptions that had to be made in setting up our simple model, the agreement between the observed and calculated

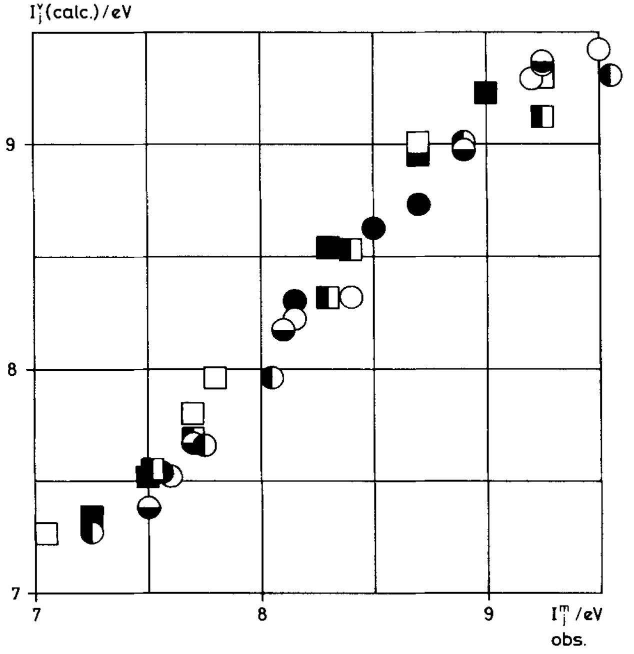


Fig. 5. *Plot of the calculated ionization energies I_j^v(calc.) vs. the observed ones, I_j^m, for the [2.2]cyclophanes* **7** *to* **13**. The numerical data are given in Table 7. Symbol/Compound: ○/**7**, ●/**8**, ◐/**9**, ⊖/**10**, □/**11**, ■/**12**, ◧/**13**.

values is rather good. Obviously the calculated label sequences of bands separated by less than 0.3 eV are unreliable, but there is hardly any doubt that the over-all features of the PE. spectra are well reproduced. This is evident from *Figure 5* in which the calculated band positions I_j^v(calc.) of the bands in the ionization energy interval from 7 to $\sim$9.5 eV are plotted *vs.* the observed values I_j^m for the set of compounds **7** to **13**. Although this type of plot can be very misleading [22], the present example does illustrate the degree of correspondence between model calculation and experiment.

[2.2]Cyclophanes with Unsaturated Bridges. - Of the three [2.2]cyclophanes with unsaturated bridges (**14**, **15**, **16**) only the PE. spectra of **14** [1] and of **16** [23] are known. Because of their high D_{3h}-symmetry, the pair **3** (1,3,5) and **16** are ideal for a discussion of the changes which occur in the PE. spectrum of a [2.2]cyclophane when the CH_2CH_2 bridges are replaced by CH=CH groups.

In *Figure 6* are shown bar diagrams of the PE. spectra of **3** (1,3,5) and **16**, as well as the assignment proposed by *Boekelheide & Schmidt* [23]. Although this

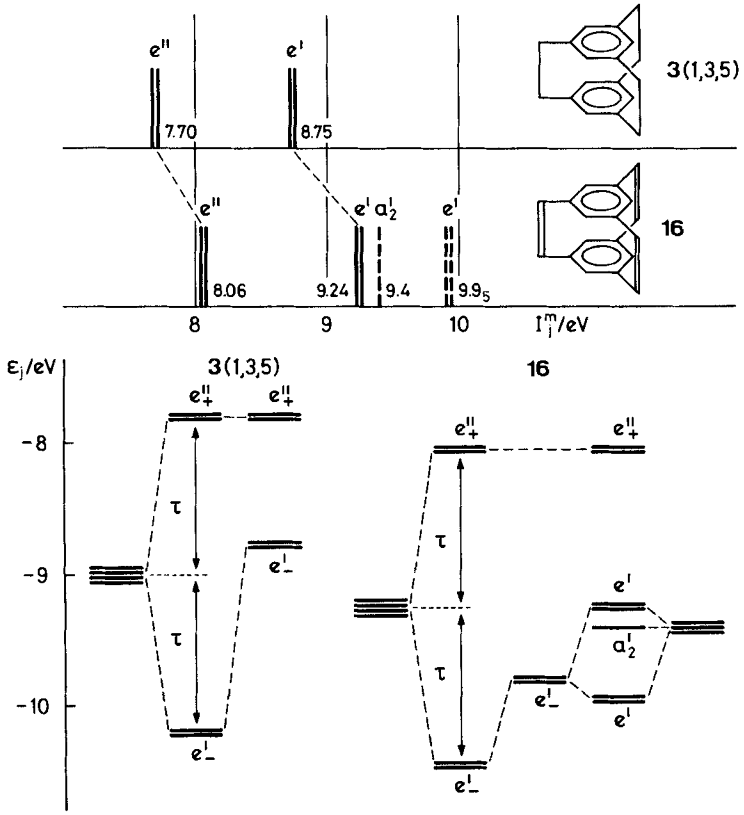


Fig. 6. *Observed band positions in the PE. spectra of* **3** (1, 3, 5) *and* **16** [23], *and orbital-correlation diagram leading to the proposed assignment.* The lower indices + and − of the e-type orbitals refer to the out-of-phase and in-phase combinations of the basis e_{1g} orbitals respectively. For the sign convention see text and [2]. The orbitals marked π in the lower.right-hand diagram refer to the three two-centre π-orbitals of the bridging CHCH groups.

assignment is certainly correct (*cf.* [2]), its rationalization, as given by the above authors, needs some modification in view of more recent results.

According to the data listed in *Table 2*, the mean interdeck distance D is the same in **3** and **16**, namely 279.5 pm and 281 pm respectively. Thus, according to equ. 6, the 'through space' coupling parameters τ is the same in both molecules, *i.e.* $\tau = 1.2$ eV. It follows that position differences of corresponding bands in the PE. spectra of **3** (1,3,5) and **16** must necessarily be due to changes in basis energies and/or 'through-bond' coupling.

In a previous discussion of the PE. spectra of the cyclophanes **2** (1,4) to **6** we have assumed a basis energy $A(e_{1g}) = -9.0$ eV for the degenerate pair of the benzene π-orbitals, to take into account neglected interactions with low lying bridge orbitals. These interactions are practically nil in **16** because of the sp^2-character of the bridge C-centres. Therefore $A(e_{1g}) = -9.25$ eV, *i.e.* the negative first ionization energy of benzene seems to be an appropriate choice. Combining these basis energies and the 'through-space' coupling term, yields the orbital energies $A(e_{1g}) \pm \tau$ for the out-of-phase and in-phase linear combinations (symmetry E″ and E′) of the e_{1g} orbitals of M_l and M_u of **3** (1,3,5) and **16**. This is shown in the correlation diagrams of the lower part of *Figure 6.*

In the case of **3** (1,3,5) only the in-phase linear combination e'_{-} can interact with the σ-orbitals of the bridging CH_2CH_2-groups, which shifts the e'_{-} orbital to the 'observed' value $\varepsilon(e'_{-}) = -8.75$ eV. This has been discussed in detail in [2]. Accordingly the 'through-bond' shift experienced by the e'_{-} linear combination is found to be 1.45 eV.

The situation is a bit more involved in the triene **16**. Although the ionization energy of ethylene is 10.5 eV, we expect that the basis π-orbital energy of the three bridging double-bond orbitals must lie well above -10.5 eV, because of interaction with the σ-orbitals of the two benzene moieties. The symmetry correct linear combinations of the three double-bond orbitals of **16** are of E' and A'_2 symmetry. Out of the 27 valence shell σ-orbitals only one has A'_2 and five E' symmetry. The former is the out-of-phase linear combination of the two benzene $1b_{2u}$ orbitals, which have approximately -15 eV as an orbital energy and only two pairs of the E' orbitals are localized within the two benzene rings and thus available for interaction with the double-bond π-orbitals. The size of the shift induced is uncertain but the value ~ 1.1 eV is suggested by the subsequent analysis of the PE. spectrum of **16** is a very reasonable one. This places the basis energies of the π-orbitals of the three double bonds at -9.4 eV. (Note that the π-orbital energy in *cis*- and *trans*-2-butene is -9.1 eV.) Because of the large distance between the double bonds (~ 500 pm), their 'through-space' interaction must be practically zero and for simplicity we have assumed that all three linear combinations have approximately the same energy, as indicated on the right-hand side of *Figure 6.*

The two bands at 9.24 eV and 9.95 eV in the PE. spectrum of **16** must necessarily belong to the removal of an electron from one or the other of the two pairs of e′ orbitals. Consequently the in-phase combination of the benzene e_{1g} orbitals after 'through-bond' interaction with the e′ linear combination of the bridge σ-orbitals must be close to -9.8 eV, as shown in *Figure 6.* From this we deduce that the 'through-bond' interaction is only 0.65 eV, as compared to 1.45 eV in **3** (1,3,5).

Such a reduction was to be expected, because the bridge σ-orbitals lie at much lower energies in **16** than in **3** (1,3,5) due to their high 2s-character and because the conjugation parameter is somewhat smaller.

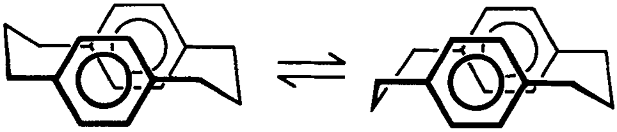
The correlation diagram of *Figure 6*, which is selfexplanatory, shows that the assignment proposed by *Boekelheide & Schmidt* [23] is consistent, and indeed supports the simple model for the electronic structure of the cyclophanes used in this and previous works [2] [14].

The information derived from the pair of compounds **3** (1,3,5) and **16** yields instant insight into the relationship between the PE. spectra of **13** and **14**. It is presumably reasonable to assume that the mean inter-deck distance D is about the same in both compounds, in analogy to the pairs **2** (1,4), **15** and **3** (1,3,5), **16** *(cf. Table 2)*, and that the same 'through-space' coupling constant applies in both cases. Because of the size of the naphthalene moieties, the importance of 'through-bond' interaction is less than in the cyclophanes **2** (1,4) to **6**, as evidenced by the size of the contributions of the bridge σ-orbitals listed in *Table 7*. Consequently little change is expected as far as the positions of the π-bands in the PE. spectra of **13** and **14** are concerned.

The only notable difference in these spectra is due to the presence of two additional bands in the PE. spectrum of **14** close to the region of ~ 9.5 eV. These are due to ejection of an electron from the orbitals associated mainly with the two double-bond π-orbitals, destabilized by interaction with the naphthalene σ-orbitals. These expectations are nicely borne out by the experiment, as is evident from the data in *Table 1*, and the corresponding spectra presented in *Figures 4* and *5* of [1].

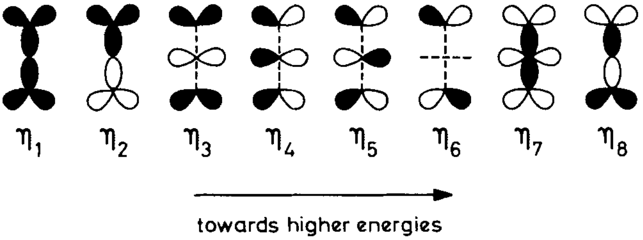
[3.3]Paracyclophane. - The structure of [3.3]paracyclophane (**18**) is known from an X-ray structure analysis by *Gantzel & Trueblood* [13]. The mean inter-deck distance D is 325 pm and the two benzene rings are shifted by 19 pm along the x- and by 44 pm along the y-axis with respect to each other. Using these parameters and assuming that the mean planes of the two rings are parallel, the following 'through-space' coupling parameters τ_{IJ} are calculated according to the procedure outlined above: $\tau_{11} = 0.56$ eV, $\tau_{22} = \tau_{33} = 0.39$ eV. All other τ-values were smaller than 0.1 eV and have been neglected.

The major problem consists in the assessment of the 'through-bond' interaction, which is made difficult because it is not known which of the conformations of **18** is present in the gas phase. In the crystal [13] only the conformer **18a** is observed but in solution an equilibrium **18a** $\rightleftharpoons$ **18b** has been postulated on the basis of NMR. studies [24].



18a **18b**

Using the *Hückel*-type treatment of hydrocarbon σ-orbitals proposed some time ago [25] we can derive the nodal properties and rough approximations for the orbital energies of the $CH_2CH_2CH_2$ bridge orbitals which can serve as a relay for the 'through-bond' interaction between the π-orbitals of M_l and M_u in **18**. The 8 orbitals so obtained are:



(16)

These orbitals η_μ should be compared to the CH_2CH_2 bridge orbitals depicted in [2]. In particular it will be observed that η_8, η_7 and φ_5 [2] have the same local symmetry at the point of attachment to the benzene ring which allows them to conjugate effectively with the benzene orbitals $S_r(r=u,l)$. In addition the orbital energies $\varepsilon(\eta_8) \approx -13.5$ eV, $\varepsilon(\eta_7) \approx -14$ eV, are obtained by using the calibrated *Coulomb* and resonance integrals given in [2]. The orbitals η_1 to η_6 can not serve as relay orbitals for symmetry reasons, or because their orbital energies are too low and their coupling with the benzene π-orbitals too small.

This leaves η_8 and η_7 as potential relay orbitals. An important difference to the [2.2]cyclophanes is that η_8 provides 'through-bond' coupling to the out-of-phase linear combination, leading to a splitting of the first two bands ①, ② in the PE. spectrum of **18**, in addition to the splitting of bands ③ and ④ which was the only one observed in the cyclophanes **2** (1,4) to **6**. The magnitude of the splits between ①, ② and ③, ④ is difficult to predict in the absence of detailed information about the conformation of **18**, but qualitatively we expect to find four well separated bands spanning the interval from 7.5 to 9.5 eV. This is borne out by the experimental results presented in [2], which are summarized in *Figure 7*, together with a rationalization. Because of the size of the alkyl-bridges, corresponding *cum grano salis* to propyl groups, a basis orbital energy of $A(e_{1g}) = -8.7$ eV seems appropriate to account for

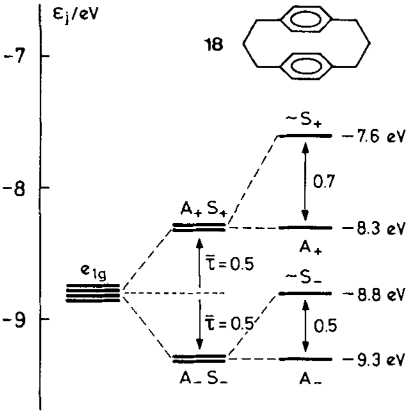


Fig. 7. *Orbital correlation diagram for the [3.3]paracyclophane* (**18**). The values given on the right-hand side correspond to the observed band positions, implying *Koopmans'* approximation.

the destabilizing influence of the bridge orbitals η_1 to η_6 which we have neglected in the ensuing discussion. This value should be compared to $A(e_{1g}) = -9.0$ eV used previously for the cyclophanes **2** (1,4) to **6** [2] [14]. The experimentally observed positions of bands ② and ④ in the PE. spectrum of **18** suggest that a mean 'through-space' interaction parameter $\bar{\tau} = 0.5$ eV is appropriate, which differs by only 0.1 eV from the values $\tau_{22} = \tau_{33} = 0.4$ eV computed above for the conformation present in the crystal. This leads to a 'through-space' split of 1.0 eV between the in-phase (A_-, S_-) and out-of-phase (A_+, S_+) linear combinations. In contrast to **2** (1,4), *both* S_+ and S_- are now subject to 'through-bond' interaction, the relay orbitals being η_8 and η_7, respectively. It is found that the destabilization of S_+ (0.7 eV) is larger than that of S_- (0.5 eV), within the simple scheme we are using *(cf. Fig. 7)*. Because the energy separation of the interacting orbitals is roughly the same, namely $\varepsilon(S_+) - \varepsilon(\eta_8) \approx 5.1$ eV, $\varepsilon(S_-) - \varepsilon(\eta_7) \approx 4.7$ eV the reason for the observed difference must be due to the interaction matrix elements. This view is supported by the LCBO model underlying the bridge orbitals (17), which yields

$$\langle \eta_8 | \mathcal{H} | S_r \rangle^2 / \langle \eta_7 | \mathcal{H} | S_r \rangle^2 \approx 1.4 \qquad (17)$$

in perfect agreement with the shift ratio 0.7 eV/0.5 eV.

Lack of structural information prevents more detailed calculations. On the other hand there is no doubt that the qualitative rationalization presented is in complete agreement with observation and therefore supports the picture of the electronic structure of cyclophanes developed so far.

Concluding Remarks. - It is rather satisfactory that a large body of experimental evidence can be explained and systematized in terms of a simple model which accounts for the essential features observed.

The most drastic simplification incorporated into the model is to assume a mean inter-deck distance D between two parallel decks M_l and M_u. To check the influence of this assumption we have carried out calculations of the 'through-space' interaction parameters τ_{IJ} according to equ. 8, using overlap integrals S_{IJ} derived from equ. 2 but taking into account the observed interatomic distances listed in *Table 2* for **2** (1,4), **3** (1,2,3) and **4** (1,2,3,4). As a result the degeneracy of S_+, A_+ and of S_-, A_- is lifted but the splits in energy are too small to lead to significant changes, within the rather wide limits of error imposed by the broad and almost structureless bands.

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