192. Ionization Energies of Methyl-substituted [2.2]Paracyclophanes

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Summary

The photoelectron (PE.) spectra of thirteen methyl-substituted [2.2]paracyclophanes have been recorded and analyzed, to assess the influence of methyl-substitution on their ionization energies. It is shown that this influence is qualitatively and quantitatively the same as for benzenes and other π-systems. Comparison with the previous results obtained for the [2_r]cyclophanes (r = 2 to 6) strongly suggests that the hyperconjugative model for alkyl-group/π-system interactions is more appropriate than the inductive one.

Introduction. - The He(Iα) PE. spectrum of [2.2] (1,4)cyclophane (= [2.2]paracyclophane, **1**) has been studied repeatedly [1] [2]. We believe that the most satisfactory assignment of its first four bands to states of the [2.2]paracyclophane radical cation $\mathbf{1}^{+}$ is that given below (in ascending order of ionization energies).

Band	①	②	③	④
State	$^2B_{2g}$	$^3B_{3g}$	$^2B_{3u}$	$^2B_{2u}$

This assignment is based on the correlation of the PE. spectra of the complete set of all [2_r]cyclophanes (r = 2 to 6) [2], comparison with the PE. spectra of [2]paracyclo[2]naphthalenophanes, [2.2]naphthalenophanes [3] and [2.2]azulenophanes [4], as well as on ancillary experimental information [2].

For simplicity we number the π-centres of the upper and lower deck of **1** as indicated in the left-hand formula, rather than according to the cumbersome IUPAC rules shown on the right. This has the advantage of assigning the same index to 2p-atomic orbitals facing each other.

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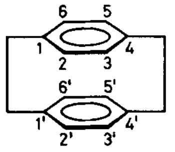

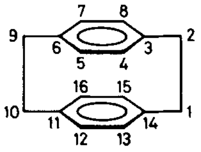

The semilocalized benzene π-orbitals of the upper (u) and lower (l) deck of **1** are $O_r \equiv a_{2u}$ and the degenerate pair $S_r, A_r \equiv e_{1g}$ (under local D_{6h} symmetry). The real components S_r, A_r of e_{1g} are symmetric and antisymmetric with respect to the plane containing the centres 1, 1', 4, 4'. The basis energies assigned to these orbitals are $\langle O_r|\mathcal{H}|O_r\rangle = -12.2$ eV, $\langle S_r|\mathcal{H}|S_r\rangle = \langle A_r|\mathcal{H}|A_r\rangle = -9.0$ eV, with $r = u$ or l [2] [3].

If we assume, in a first crude approximation that the two benzene rings in **1** are eclipsed and parallel, separated by a mean inter-deck distance D, then the overlap integrals $S_{SS} = \langle S_u|S_l\rangle$ and $S_{AA} = \langle A_u|A_l\rangle$ are equal: $S_{SS} = S_{AA}$. As shown in [3] the 'through-space' coupling parameter τ between two orbitals ψ_u, ψ_l belonging respectively to the upper and lower deck of a cyclophane is given by $(\tau/\text{eV}) = -11.52 \cdot S$, with $S = \langle \psi_u|\psi_l\rangle$. Accordingly, we find for our strongly simplified model that $\tau_{SS} = \tau_{AA}$. (Note that τ_{OO} is slightly smaller and that $\tau = 0$ for mixed indices.) As shown on the left side of *Figure 1* this results in two pairs of degenerate linear combinations $S_\pm = (S_u \pm S_l)/\sqrt{2}$, $A_\pm = (A_u \pm A_l)/\sqrt{2}$, S_+, A_+ being antisymmetric, S_-, A_- symmetric with respect to reflection at the plane passing between the two decks.

Because only S_- has the proper symmetry to interact with the bridging CH_2CH_2 groups (which provide 'through-bond' interaction between S_u and S_l, *cf.* [2]), the two highest occupied molecular orbitals b_{2g} and b_{3g} of **1** would be degenerate if our model were correct.

However, the x-ray structure analysis of **1** shows [5] that the distances $R_{1,1'} = R_{4,4'} = 278$ pm between the bridged centres are smaller than the distances $R_{\mu,\mu'} = 309$ pm

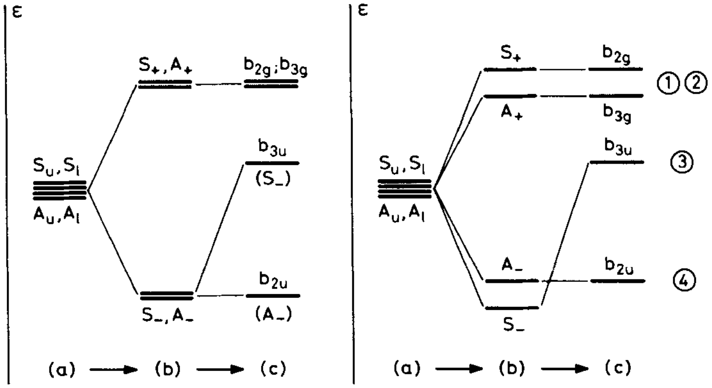

Fig. 1. *Influence of non-planarity of the benzene rings on orbital energies of [2.2]paracyclophane* **1**. Left diagram: Model with two planar eclipsed benzene rings separated by a mean interdeck distance D. Right diagram: Model with bent benzene rings, with distances $R_{\mu\mu'}$ according to [5]. Step (a)→(b): 'through-space' interaction, step (b)→(c): 'through-bond' interaction.

between the others ($\mu = 2$, 3, 5 and 6). Consequently $S_{SS} = \langle S_u | S_l \rangle$ is larger in absolute value than $S_{AA} = \langle A_u | A_l \rangle$ (both S_{SS} and S_{AA} are negative!) so that $\tau_{SS} > \tau_{AA}$. This lifts the former degeneracy of S_+ and A_+, placing S_+ above A_+ and thus, finally, b_{2g} above b_{3g} as shown in the right-hand side of *Figure 1*. The resulting orbital sequence, taking 'through-bond' interaction into account, is in complete agreement with the state sequence of $\mathbf{1}^+$ presented above.

In this contribution we investigate the influence of methyl substitution on the ionization energies of **1**. This allows a direct comparison of the influence of the bridging CH_2CH_2 groups on ionization energies, which is severely restricted by symmetry, with that of the methyl groups which lack such restrictions.

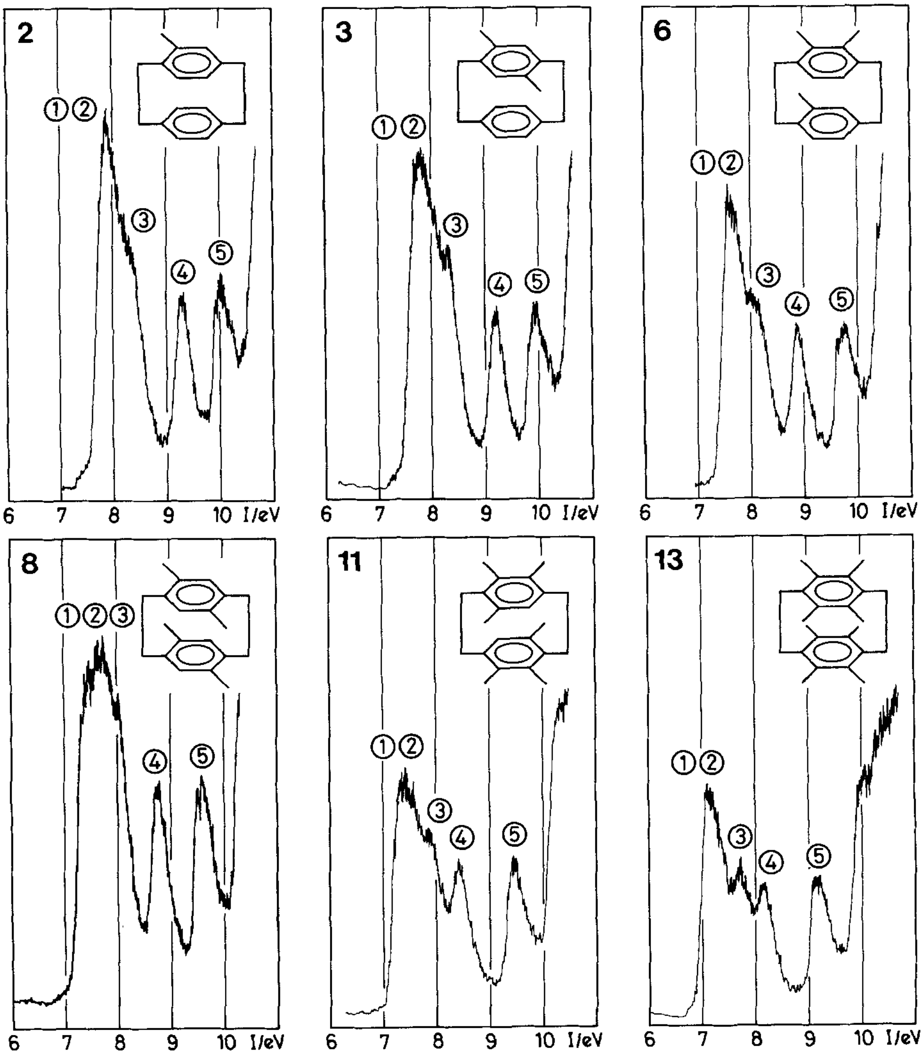

Fig. 2. *He(Ia) PE. spectra of selected, methyl-substituted [2.2]paracyclophanes*

Experimental Data and Qualitative Survey. - In *Table 1* are given the ionization energies I_j^m for the first five bands in the PE. spectra of **1** and of twelve methyl-substituted [2.2]paracyclophanes **2** to **13**. The I_j^m correspond to the positions of the band maxima and are thus close to the corresponding vertical ionization energies I_j^v. In the second column of *Table 1* the number n of methyl substituents and their positions $\mu, \nu, \ldots; \kappa', \lambda', \ldots$ are represented by the abbreviation $n(\mu, \nu, \ldots; \kappa', \lambda' \ldots)$.

In *Figure 2* are shown some typical spectra. As can be seen, the over-all features of the spectrum of **1** are largely preserved under methyl substitution: The first two bands ① ② are always so close to each other that they form a single, prominent maximum, the position of which (given in *Table 1* under the label ① ②) is the mean of the two positions I_1^m and I_2^m, at least in a first approximation. Band ③ always appears as a shoulder, so that the values I_3^m of *Table 1* are affected with larger limits of error ($\sim \pm 0.1$ to ± 0.2 eV).

For ease of comparison the experimental data are displayed in the correlation diagram of *Figure 3* which draws attention to the rather regular evolution of the band positions as a function of the number n of methyl substituents. This is especially evident if the methyl groups are evenly distributed over the two rings, *i.e.* n/2 per benzene moiety, as shown in *Figure 4*, in which the means of the ionization energies listed in the legend are plotted against the number n/2 of methyl groups in each ring. The corresponding linear regressions are:

$$\bar{I}^m[\text{① ②}] = [(8.09 \pm 0.03) - (0.24 \pm 0.01)\,n/2]\ \text{eV} \tag{1}$$

$$\bar{I}^m[\text{③}] = [(8.37 \pm 0.03) - (0.17 \pm 0.01)\,n/2]\ \text{eV} \tag{2}$$

$$\bar{I}^m[\text{④}] = [(9.58 \pm 0.07) - (0.38 \pm 0.03)\,n/2]\ \text{eV} \tag{3}$$

The uncertainties indicated correspond to the standard error of the intercept and of the slope. It will be noticed that these standard errors are much larger in regression 3 than in 1 and 2. The reason is that inclusion of a quadratic term reduces the remainder variance significantly, as is evident from *Figure 4*.

Table 1. *Ionization energies I_j^m of [2.2]paracyclophane* **1** *and of twelve methyl-substituted [2.2]paracyclophanes* **2** *to* **13** (*cf.* formulae in *Fig. 3*). Estimated errors: ± 0.05 eV if the second decimal is given as a lower index; ± 0.1 eV or more, if only one decimal is given..

Compound No.	Number (n) and positions of Me-groups	Bands			
		① ②	③	④	⑤
1	0	8.1_0	8.4	9.6_5	10.3
2	1	7.9_0	8.2	9.3_5	10.0_5
3	2 (2,5)	7.7_5	8.3	9.1_5	9.9_0
4	2 (2; 5′)	7.8_5	8.2	9.2_0	9.9_5
5	2 (2; 6′)	7.8_5	8.1	9.1_5	10.0_0
6	3 (2,3; 2′)	7.7_0	8.1	8.9_5	9.8_0
7	4 (2,3; 5′,6′)	7.6_0	8.1	8.7_0	9.8_0
8	4 (2,5; 2′,5′)	7.7_5	8.1	8.8_0	9.6_0
9	4 (2,5; 3′,6′)	7.5_5	8.2	8.8_0	9.8_0
10	5 (2,3,6; 5′,6′)	7.5_5	8.1	8.5_5	9.6_5
11	6 (2,3,6; 3′,5′,6′)	7.4_5	7.9	8.4_0	9.4_5
12	7	7.4_0	7.8	8.3_5	9.4_0
13	8	7.1_5	7.7	8.1_0	9.2_0

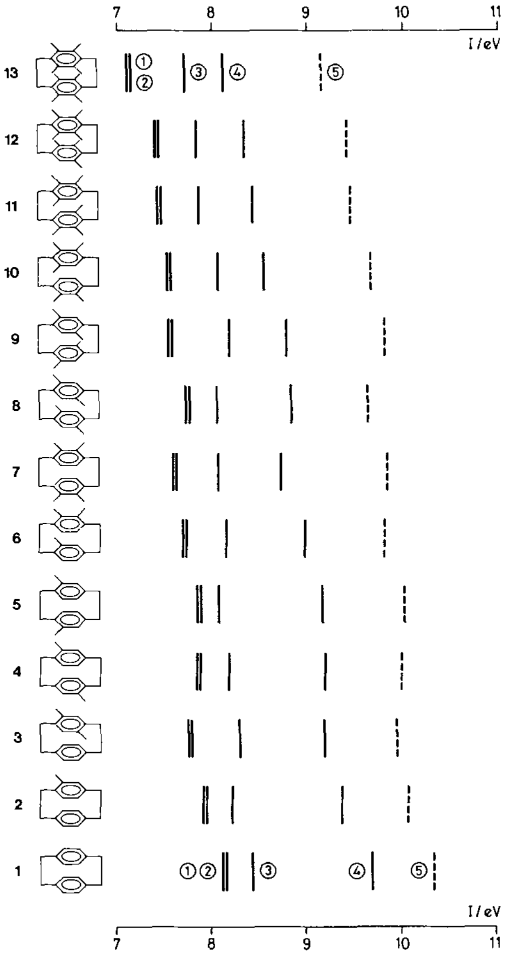

Fig. 3. *Correlation diagram of the observed band positions* I_j^m *in the PE. spectra of compounds* **1** *to* **13**. The solid lines refer to those bands, the assignment of which is given in (1). The broken lines (⑤) correspond to the position of a band which is due, presumably, to ejection of an electron from a σ-orbital (*cf.* [2]).

The qualitative picture suggested by *Figures 3* and *4* seems straightforward. However, we believe that there is no simple and unique rationalization for it, and that, in fact, the trends displayed are the resultants of conflicting effects, as will be discussed in the next section.

Discussion. - The ionization energy reducing influence of methyl groups in substituted π-systems, in particular in benzene [6] is dealt with in simple *Hückel*-type approximations by either of two models:

a) the inductive model which assumes positive perturbations δa_p of the *Coulomb* integral a_p at the methyl-substituted positions p (and perhaps secondary perturbations $m\delta a_p$ in the positions *ortho* to p, with $m \sim 1/3$);

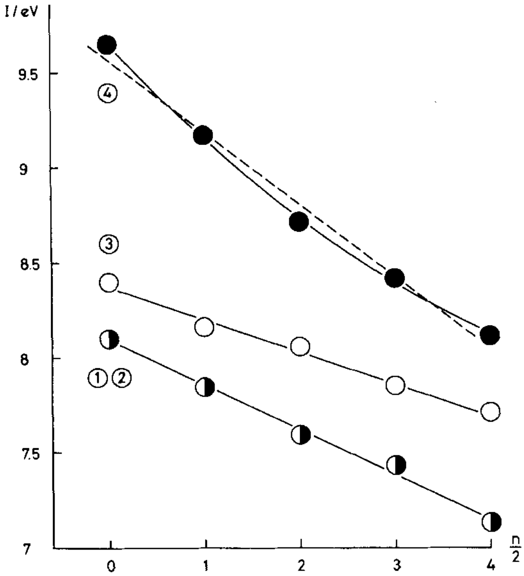

Fig. 4. *Regressions of mean ionization energies $\bar{I}^m$ as a function of n/2, the number of methyl groups per ring.* The data of the following molecules have been used: n/2=0, **1**; n/2=1, **4**, **5**; n/2=2, **7**, **8**, **9**; n/2=3, **11**; n/2=4, **13**. The solid lines labeled ①, ② and ③ correspond to expressions (2) (3). The broken line ④ corresponds to the linear regression (4), the solid one to a quadratic regression.

b) the hyperconjugative model which assumes the existence of a resonance integral β' between the pseudo-π orbital of the substituting methyl group and the atomic 2p orbital in position p.

The analysis of the mean e_{1g}^{-1} ionization energies of the set of methyl-substituted benzenes from toluene to hexamethylbenzene [7] yields the result that $\bar{I}^m(e_{1g})$ is a strictly linear function of the number N of substituting methyl groups, namely:

$$\bar{I}^m(e_{1g}) = [(9.24 \pm 0.03) - (0.23 \pm 0.01)N]\ \mathrm{eV} \qquad (4)$$

From this we deduce that $\delta a_p = 1.4$ eV within model *a* if m=0 (*i.e.* no transmission), or $\delta a_p = 0.8$ eV if m=1/3. According to model *b*, the same regression 4 would be obtained with $\beta' = -2.6$ eV for the resonance integral between the methyl pseudo-π-orbital ($a_{Me} = -14$ eV) and the atomic 2p orbital at the substituted position.

Applying the molecular orbital model proposed in [2-4] to the parent compound **1**, but taking into account the interatomic distances revealed by the x-ray structure analyses [5], the following absolute values of the atomic orbital coefficients $|c_{\mu J}| = |c_{\mu' J}|$ are obtained:

Table 2

Orbital	μ=1,4	μ=2,3,5,6
$b_{2g}(\pi)$	0.403	0.209
$b_{3g}(\pi)$	0	0.354
$b_{3u}(\pi)$	0.343	0.206
$b_{2u}(\pi)$	0	0.354

Using model *a*, the δa_ρ values calibrated on the ionization energies of the methyl-substituted benzenes and the values of the atomic orbital coefficients given in *Table 2*, the following slopes are predicted for the linear regressions 1, 2 and 3:

Table 3

	$\delta a_\rho = 1.4$ eV m = 0	$\delta a_\rho = 0.8$ eV m = 1/3	Observed values
$\frac{\partial \bar{I}^{m}[\text{①②}]}{\partial(n/2)}$	0.24 eV	0.22 eV	0.24 eV
$\frac{\partial \bar{I}^{m}[\text{③}]}{\partial(n/2)}$	0.12 eV	0.15 eV	0.17 eV
$\frac{\partial \bar{I}^{m}[\text{④}]}{\partial(n/2)}$	0.35 eV	0.27 eV	0.38 eV

Comparing these with the observed values (last column of *Table 3*) we note that the agreement is as good as can reasonably be expected in view of the crude treatment. We are forced to conclude that in a first approximation the influence of substitution by methyl groups on the ionization energies of **1** is both qualitatively and quantitatively the same as on benzene.

The same result, and thus the same conclusions would have been reached if we had used model *b*. As has been pointed out before [7], both treatments must necessarily lead to very similar predictions and it is usually not possible to discriminate between the two models, within the limits of error of the experimental method.

If the molecular model used previously [2-4] is applied directly to the molecules **1** to **13** under the assumption that the [2.2]cyclophane framework of all compounds is identical to that of **1** [5], and if the local perturbation by the methyl groups is taken care of according to model *a*, then the ionization energies displayed in the correlation diagram of *Figure 5* are obtained. Over all, this diagram is a rather fair reproduction of the one shown in *Figure 3*.

Nevertheless, a few critical remarks are in order:

1) As indicated in *Figure 5*, our model yields two first ionization energies which are separated in the mean by $\sim 0.2_5$ eV. (Concerning the large gap of 0.4 eV obtained for **8**, see below). This separation is the resultant of two opposing effects: Firstly, as discussed above for **1** *(cf. Fig. 1)*, the 'through-space' coupling parameter τ_{SS} is larger than τ_{AA}, thus placing the orbital b_{2g} above b_{3g} as long as the centres 1, 1' and 4, 4' are closer together than the unbridged ones. Secondly, in the methyl-substituted compounds **2** to **13**, the destabilizing influence of the substituents is larger for the b_{3g} than the b_{2g} orbital because A_u and A_l have big coefficients $|c_{\mu A}| = 1/2$ in positions $\mu, \mu' = 2, 3, 5$ and 6, compared to the small ones $|c_{\mu S}| = 1/\sqrt{12}$ for S_u, S_l. Thus, in the octamethyl derivative **13**, the eight methyl groups have raised b_{3g} above b_{2g}, as shown diagramatically in *Figure 6*, step (c) → (d).

2) In contrast to what a simple perturbation treatment based on the molecular orbitals of **1** would lead us to expect, the calculated trend shown in *Figure 5* is a bit more complicated. The reason is, that in those cases where the molecule departs

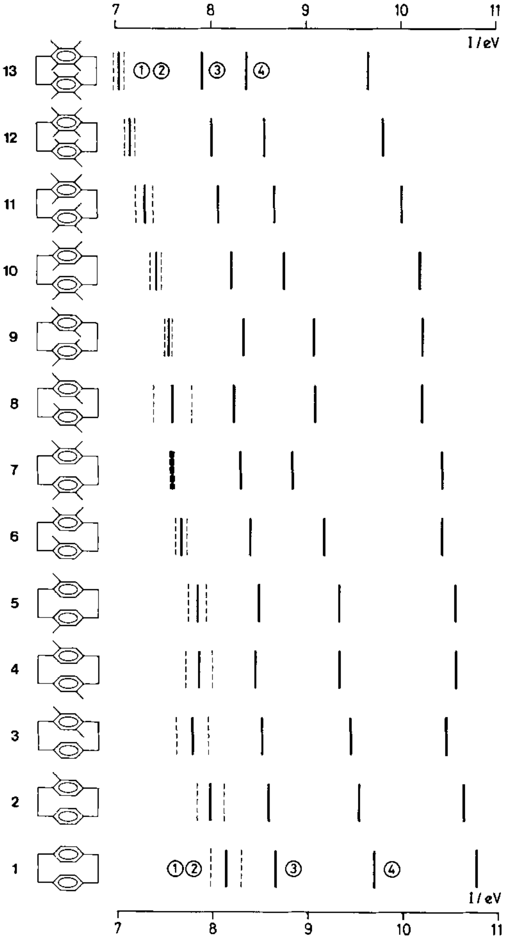

Fig. 5. *Correlation diagram of the calculated band positions* $I_j^v = -\varepsilon_j$ *for the compounds* **1** *to* **13**. The broken vertical bars refer to $I^v(b_{2g})$ and $I^v(b_{3g})$ corresponding to the two highest occupied molecular orbitals, the solid bar between them to their mean value. Note that the highest energy band position (around 10 eV) does *not* correspond to the position of band ⑤, *i.e.* the broken lines in *Figure 3*.

strongly from an idealized D_{2h} symmetry, we can get considerable mixing of the formerly orthogonal $A_{\pm}$ and $S_{\pm}$ linear combinations. This is especially evident in the case of **8**, where the resultant molecular orbitals are best described by combinations of $A_{\pm}$ and $S_{\pm}$ orbitals which are rotated by ~60° with respect to their orientation in the D_{2h} systems **1** or **13**. This rotation, induced by the four methyl groups in positions 2, 2′, 5 and 5′, leads to a large predicted split of 0.4 eV between the first two ionization energies as shown in *Figure 5*. It is perhaps more than a simple coincidence, that the shape of the first feature in the PE. spectrum of **8** (see *Fig. 2*) departs significantly from the shapes observed in the spectra of the other cyclophanes. Similar effects are responsible for the absence of a significant split in **7** and the other, irregular variations shown in *Figure 5*.

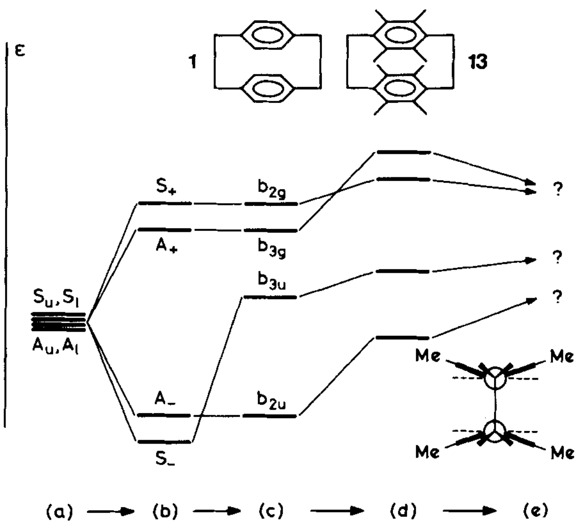

Fig. 6. *Qualitative diagram showing the influence of methyl-substitution and of the bending of the benzene nuclei on the spacing and sequence of the [2.2]cyclophane π-orbitals*

3) One might have expected that the calculated differences $(I_2 - I_1)_{calc.}$ correlate, at least roughly, with the halfwidth of the first double band in the PE. spectra of the cyclophanes **1** to **13**. However, this does not seem to be the case (with the exception of **8**), even if one takes into account that this half-width is rather difficult to assess because of the presence of the shoulder ③. One of the possible rationalizations is the following: The discussion in the two preceeding paragraphs refers exclusively to the model we have used, *i.e.*, to a model which assumes that the [2.2]paracyclophane moieties, disregarding the methyl substituents, have exactly the same geometry in all compounds, as experimentally observed for **1**. This is highly improbable. From the structure analysis of **1** [5] it is known that two opposed C,H-bonds in positions μ, μ' of the benzene rings point slightly towards each other. Thus the distance of two H-atoms is less than 309 pm and this would lead *a fortiori* to an even shorter distance between two methyl group C-atoms in **13**, if the same bond angles prevailed. However, this is considerably shorter than the sum of the *van der Waals* radii of two opposed methyl groups, which must be of the order of $\sim$400 pm. Consequently we expect that for instance in **13** or in all cases where pairs of methyl groups occupy positions of same index μ, μ' in the two rings, the substituted centres are bent away from each other, as shown by the *Newman* projection in the bottom right corner of *Figure 6*. The consequence of such a distortion would be to reduce τ_{AA} more than τ_{SS}, thus closing up the gap between b_{3g} and b_{2g}, as indicated by the arrows in *Figure 6*, step (d)→(e). This could be an explanation for the observed fact, that the double peak ① ② does not exhibit an observable split in any of the recorded PE. spectra with the possible exception of the spectrum of **8**. A more detailed analysis can only be presented when reliable structural data are available for at least some of the compounds **2** to **13**.

The present results show that the orbital-destabilizing and thus ionization energy reducing effect of methyl groups is exactly the same for cyclophanes as for other unsaturated and/or aromatic hydrocarbons. We are forced to conclude that the benzene moieties in these compounds do not differ significantly in their electronic build-up from benzene itself. It is equally improbable that the bridging CH_2CH_2 groups should exhibit an electronic structure fundamentally at variance with the one postulated for the corresponding parafins (*e.g.* ethane) or alkyl groups. Consequently the observation [2-4] that the bridging CH_2CH_2 groups in the series of $[2_r]$cyclophanes (r = 2 to 6) do not affect the two lowest ionization energies $I^m(b_{2g}^{-1})$, $I^m(b_{3g}^{-1})$ (see (1)) must have some other cause. The only one, peculiar to $[2_r]$cyclophanes which suggests itself is the symmetry behaviour of the interacting semi-localized orbitals of the two benzene moieties and of the bridging groups, as has been suggested previously by *Gleiter* [8] (see also [2]). In fact the present results, taken in conjunction with those previously reported in [2-4] strongly support this assumption.

A rather interesting conclusion that can be drawn from the present results is that the hyperconjugative model *b* discussed above is to be preferred over the inductive model *a* because the symmetry argument presented can only be applied to the former. Whereas hyperconjugation can be allowed or forbidden, depending on the symmetry behaviour of the semilocalized (pseudo-π) orbitals of the alkyl groups and the linear combinations of the benzene π-orbitals (*cf.* the discussion in [2]), the inductive effect, if treated according to model *a* is always allowed. This does not seem to be compatible with the results presented here and previously [2] [3].

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Experimental Part. - [2.2]Paracyclophane (**1**) was purchased from *Aldrich* and sublimed under high vacuum for purification; the preparation of **7** as well as **10-13** has already been described [9]. The methodology developed there, namely formylation by dichloromethyl methyl ether/$TiCl_4$ according to *Rieche et al.* [10], followed by reduction of the resulting aldehyde with $LiAlH_4$ and conversion of the alcohol to the corresponding bromide by treatment with PBr_3/CH_2Cl_2 and final reduction of the bromomethyl to the methyl substituent with $LiAlH_4$/THF was then applied to **1** (providing **2**) and **2** (providing **3**). Twofold repetition of the sequence on **3** yields **8**, whose isomer **9** was obtained by $TiCl_4$/HCl-catalyzed isomerization of **7** [11]. The remaining three methyl derivatives **4**, **5** and **6** were obtained by reducing the corresponding di- [13] and triesters [12], respectively, with $LiAlH_4$ and converting the hydroxymethyl derivatives into the hydrocarbons according to the procedure described above.

All new compounds were characterized by the usual spectroscopic methods as well as their elemental analyses.

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