33. Data Bank: The PE Spectra of Paracyclophanes with Unsaturated Bridges and of Related Molecules

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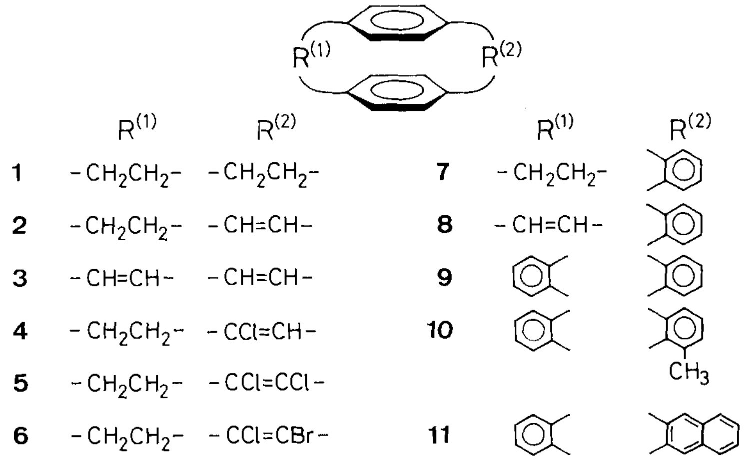
(6.1.87)

The PE spectroscopic data for a series of [2.2]paracyclophanes with olefinic and/or aromatic bridges, and of a few related molecules are reported, together with tentative assignments based on simple MO models.

Introduction. – Some time ago, we have published a data bank containing the PE spectra of a series of cyclophanes [1], and a review [2] in which those data were rationalized, using a simple MO model described previously [3]. To complement the above



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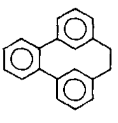

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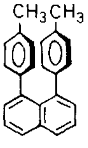

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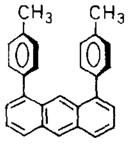

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data, we now report the PE spectra of [2.2]paracyclophanes **1–11** with olefinic and/or aromatic bridges and of the related molecules **12–14**.

Experimental Results. The He(Iα) PE spectra of the molecules **4** to **14** are shown in *Figs. 1–3*. The positions I_j^m of the band maxima, which are close to the vertical ionization energies I_j^v ($\approx I_j^m$), are given in the *Table*, together with those of **1**, **2**, and **3** [1] [2]. All spectra were recorded at higher temp. (~100°–200°), because of the low volatility of the samples. As far as we can tell, no decomposition or rearrangement occurred under these conditions (*cf.* [4]). Due to the elevated recording temp. and the size of the molecules, the PE bands lack vibrational fine structure. This and the considerable overlap between individual bands prevent in many cases a meaningful deconvolution, and, thus, a precise assessment of the I_j^m values, or of the number of bands collected in a given peak. These limiting factors should be taken into account when referring to the data in the *Table*.

Table. *PE-Band Positions* I_j^m*/eV and Tentative Assignment of the PE Spectra of the Cyclophanes* **1–12**, *of 1,8-Bis(4-methylphenyl)naphthalene* (**13**), *and of 1,8-Bis(4-methylphenyl)anthracene* (**14**)

	①	②	③	④	⑤	⑥	⑦	⑧	⑨
1	8.1_0	8.1_0	8.4	9.6_5	10.3				
	$S_+(b_{2g})$	$A_+(b_{3g})$	$S_-(b_{3u})$	$A_-(b_{2u})$	σ				
2	8.1_0	8.1_0	8.6_5	9.3	9.7_0	10.2			
	$S_+(b_2)$	$A_+(a_2)$	$S_-(a_1)$	π	$A_-(b_1)$	σ			
3	8.1_0	8.1_0	8.9_5	9.4_0	9.8_5	10.3			
	$S_+(b_{2g})$	$A_+(b_{3g})$	$S_-(b_{3u})$	π_+, π_-	$A_-(b_{2u})$	σ			
4	8.3	8.4	9.1	9.1	9.8_5	10.4	10.9_5		
	$A_+(a'')$	$S_+(a')$	$S_-(a')$	$\pi - n(\pi)$	$A_-(a'')$	σ			
5	8.4 ——	——	8.8 ——	9.2	9.9_0	10.5	11.2		
	$A_+(a_2)$	$S_+(b_2)$	$\pi - n_+(\pi)$	$S_-(a_1)$	$A_-(b_1)$	σ			
6	(8.4) ——	——	8.7_5 ——	9.1	9.9	10.2_5	10.6_5		
	$A_+(a'')$	$S_+(a')$	$\pi - n_+(\pi)$	$S_-(a')$	$A_-(a'')$	$n(\sigma)$	σ		
7	8.0 ——	8.3	8.7 ——	9.0	9.1_5	9.6_5	10.3_0		
	$S_+(b_2)$	$A_+(a_2)$	$P_A(b_1)$	$S_-(a_1)$	$P_S(a_2)$	$A_-(b_1)$	σ		
8	8.0 ——	8.4	8.8 ——	8.9	9.3 ——	9.4	9.8	10.2_5	
	$S_+(b_2)$	$A_+(a_2)$	$P_A(b_1)$	$S_-(a_1)$	$P_S(a_2)$	$\pi(b_1)$	$A_1(b_1)$	σ	
9	8.1 ——	8.4	8.8 ——	——	——	——	9.3	9.7	10.3
	$S_+(b_{2g})$	$A_+(b_{3g})$	$P_{A+}(b_{2u})$	$P_{A-}(b_{1g})$	$S_-(b_{3u})$	$P_{S+}(b_{3g})$	$P_{S-}(a_u)$	$A_-(b_{2u})$	σ
10	7.8 ——	8.2	8.5 ——	——	——	——	9.2	9.7	10.2_0
	$S_+(a')$	$A_+(a'')$	$P_{A+}(a'')$	$P_{A-}(a'')$	$S_-(a')$	$P_{S+}(a'')$	$P_{S-}(a'')$	$A_-(a'')$	σ
11	8.0	8.2	8.5	8.7	8.8	9.0	9.8	10.0	10.4
	$\psi_5(a_2)$	$S_+(b_2)$	$A_+(a_2)$	$\psi_4(b_1)$	$P_A(b_1)$	$S_-(a_1)$	$A_-(b_1)$	$\psi_3(a_2)$	σ
12	7.8_5	8.4_5	8.4_5	9.0_0	9.5_0	9.5_0			
	b	a	b	b	a	b			
13	7.7	7.9_0	8.5_5	8.5_5	9.1	9.6	9.6		
	$S_+(b_2)$	$\psi_5(a_2)$	$A_+(a_2)$	$\psi_4(b_1)$	$S_-(a_1)$	$A_-(b_1)$	$\psi_3(b_1)$		
14	7.0_5	8.2_5 ——	——	8.4_5	9.0_0	9.0_0	9.8_0		
	$\psi_7(b)$	$\psi_6, S_-(a)$	$S_+(b)$	$A_+(a)$	$A_-(b)$	$\psi_5(a)$	$\psi_4, S_-(a)$		

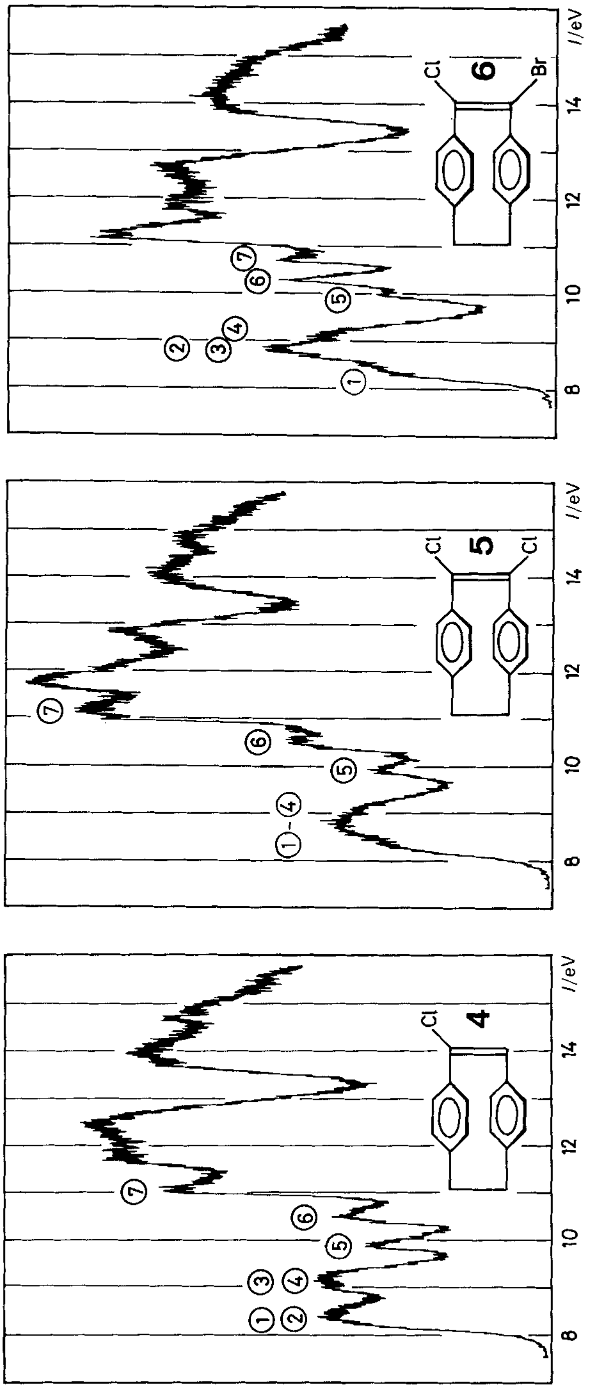


Fig. 1. *He(Iα) PE spectra of* 4–6

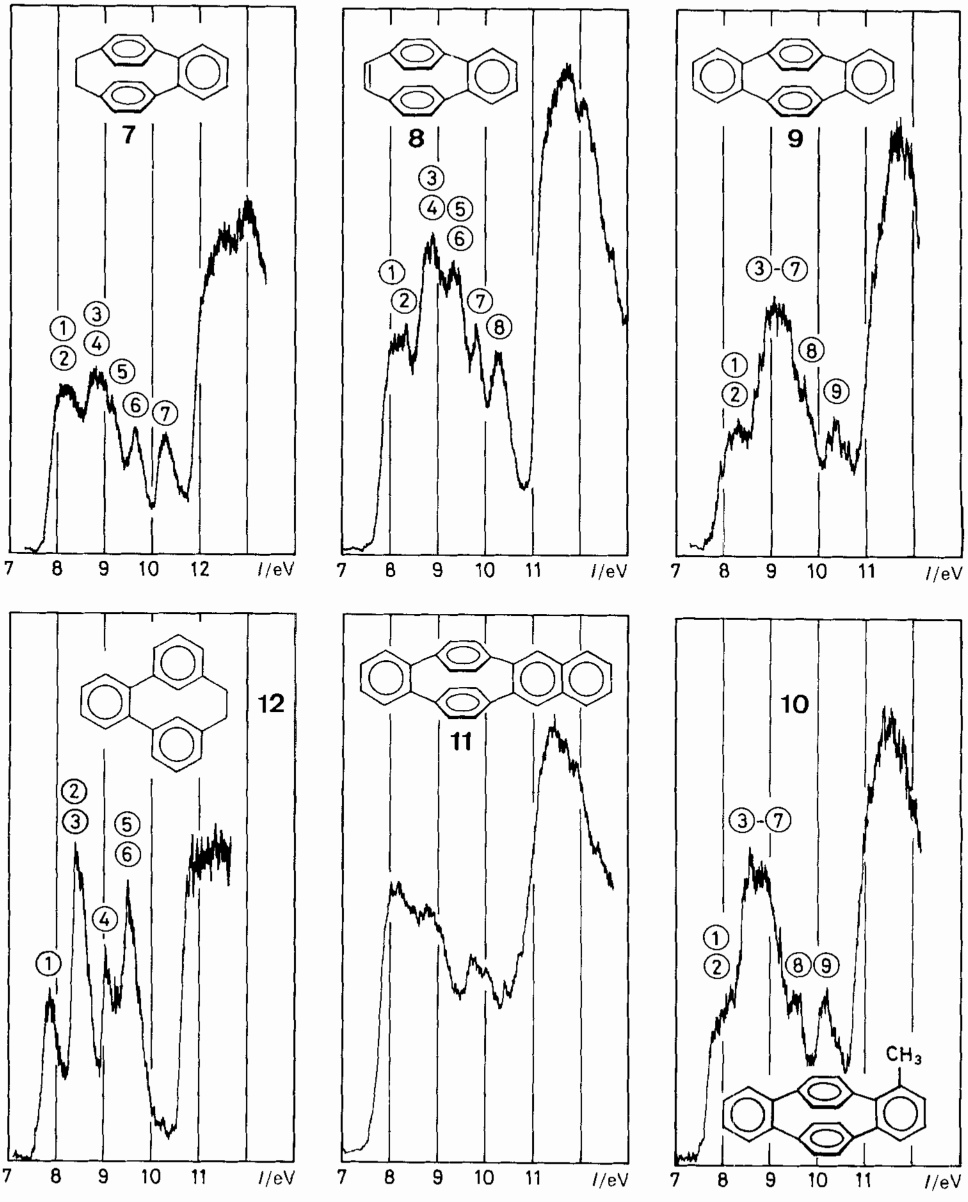


Fig. 2. *He(Iα) PE spectra of* **7**–**12**

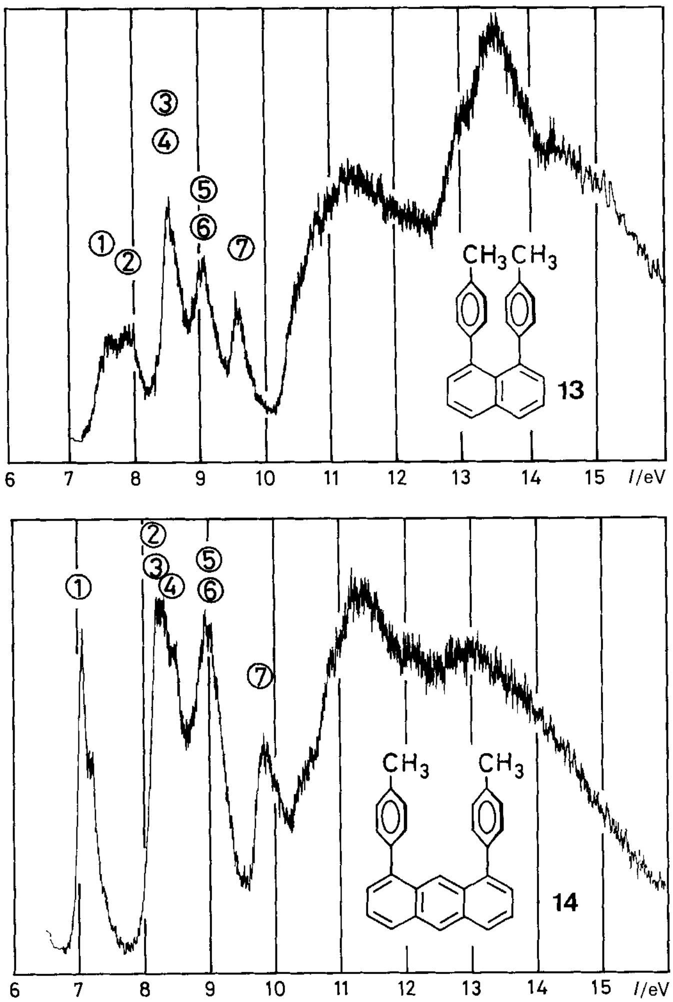
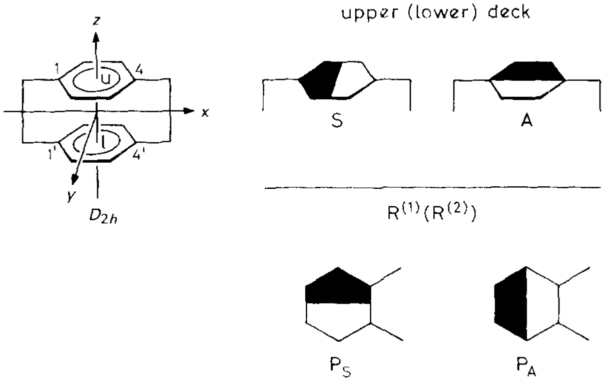


Fig. 3. *He(Iα) PE spectra of* **13** *and* **14**

Assignments. The proposed assignments are based on correlation [5] and on the results of model calculations (see below). Notwithstanding the fact that they are both reasonable and in good agreement with previous results [2], they are subject to the limitations imposed by the experimental data (PE-band overlap) and the crudeness of the theoretical treatment [3]. The individual bands, or groups of overlapping bands are characterized by the basis orbitals or their symmetry-adapted linear combinations which dominate the particular molecular orbital from which the electron is ejected. The basis is defined as follows:



(1)

a) The $1e_{1g}$ orbitals of the benzene moieties of the upper (u) and lower (l) deck of **1** are designated by S_u, A_u, and S_l, A_l, respectively (*cf.* (*1*)), being symmetric (S) or antisymmetric (A) with respect to the x,z-plane containing the centres 1,4, 1', 4'. The symmetry-adapted linear combinations (under D_{2h}) are: S_+ (b_{2g}), A_+ (b_{3g}), S_- (b_{3u}), and A_- (b_{2u}). Note that S_+ and A_+ are antisymmetric, S_- and A_- symmetric with respect to the x,y-plane.

b) The two-centre π-orbital of a bridging double bond (*e.g.* in **2**, **3** *etc.*) is labeled π. The symmetry-adapted linear combinations in **3** are π_+ (b_{2u}) and π_- (b_{1g}).

c) The $1e_{1g}$ orbitals of the *o*-phenylene groups (*e.g.* in **7**, **8** *etc.*) are labeled P_S and P_A, as shown in (*1*). The symmetry-adapted linear combinations (under D_{2h}) in **9** and **10** (disregarding the symmetry-breaking CH_3 group) are: P_{S+} (b_{3g}), P_{A+} (b_{2u}), P_{S-} (a_u), and P_{A-} (b_{1g}).

d) Finally, the σ-type lone-pair orbitals of the halogen atoms are designated by n(X), the σ orbitals of the cyclophane framework by σ, and the molecular π orbitals of the naphthalene and anthracene moieties in **11** and **13**, or in **14** by ψ_j, numbered in ascending order of orbital energy.

Concerning the assignment of the PE spectra of **1**, **2**, and **3**, the reader is referred to [2]. From the PE-spectroscopic investigations of Cl- and Br-substituted ethylenes by *Wittel* and *Bock* [6] [7], it is known that the $(\pi - n(\pi))^{-1}$ band of chloroethylene (**15**) and the $(\pi - n_+(\pi))^{-1}$ band of (*Z*)-1,2-dichloroethylene (**16**) are shifted by − 0.35 eV and − 0.63 eV, respectively, relative to the π^{-1} band of ethylene. The lone-pair bands occur at 11.61 eV ($n(\sigma)^{-1}$ of **15**) and at 11.85, 12.09 eV ($n_\pm(\sigma)^{-1}$ of **16**). For (*Z*)-1,2-dibromoethylene (**17**), a shift of − 0.87 eV for the $(\pi - n_+(\pi))^{-1}$ band is observed, and ionization energies of 10.74 eV and 11.23, 11.53 eV (spin-orbit coupling) for the $n_+(\sigma)^{-1}$ bands. From these data, we deduce that the π^{-1} band of **2** shifts towards smaller ionization energies along the series **2**→**4**→**5**→**6**, as indicated qualitatively in *Fig. 4*. Because of the additional substitution at the double bond, the shifts are expected to be smaller than those observed for **15**, **16**, and **17** [6] [7]. *Schmidt* and *Schweig* have shown [8] that in benzylchloride (**18**) and benzylbromide (**19**), the benzene A orbitals are marginally shifted with respect to the benzene π-orbital energy of − 9.25 eV, whereas the S orbitals are lowered by about − 0.35 eV, or by about − 0.7 eV relative to the S-orbital energy of toluene. These results are supported by similar observations on allylhalides [9]. The same S_+- and S_--orbital-energy lowering effect of the out-of-plane halogen atoms can be observed in the PE spectra of **4**, **5**, and **6**, as shown qualitatively in *Fig. 4*. On the other hand, the A_+ and A_- orbitals are only little affected. Finally, one can extrapolate the lone-pair ionization energies of the above reference compounds **15–19** to our molecules. The result is that the $n(\sigma)^{-1}$ bands of the Cl-atoms in **4**, **5**, and **6** are expected to be part of the band systems above 11 eV, whereas band ⑥ of **6** should be ascribed to the $n(\sigma)$ lone-pair (symmetry a') of the Br-atom.

The assignment of the PE spectra of **3**→**8**→**9** given in the *Table* (*cf. Fig. 5*) rests on those of the spectra of **3** [2] and of **7**. The latter assignment has been obtained by applying the MO model presented in [2] [3], using the structure parameters of [10]. This yields the orbital energies $\varepsilon(P_A) \approx -8.7$ eV and $\varepsilon(P_S) \approx -9.1$ eV for the orbitals P_A and P_S shifted by interaction with the σ-orbitals of the upper- and lower-deck benzene rings. Because of the negligible 'through-space' interaction between the left and right P_A and P_S orbitals in

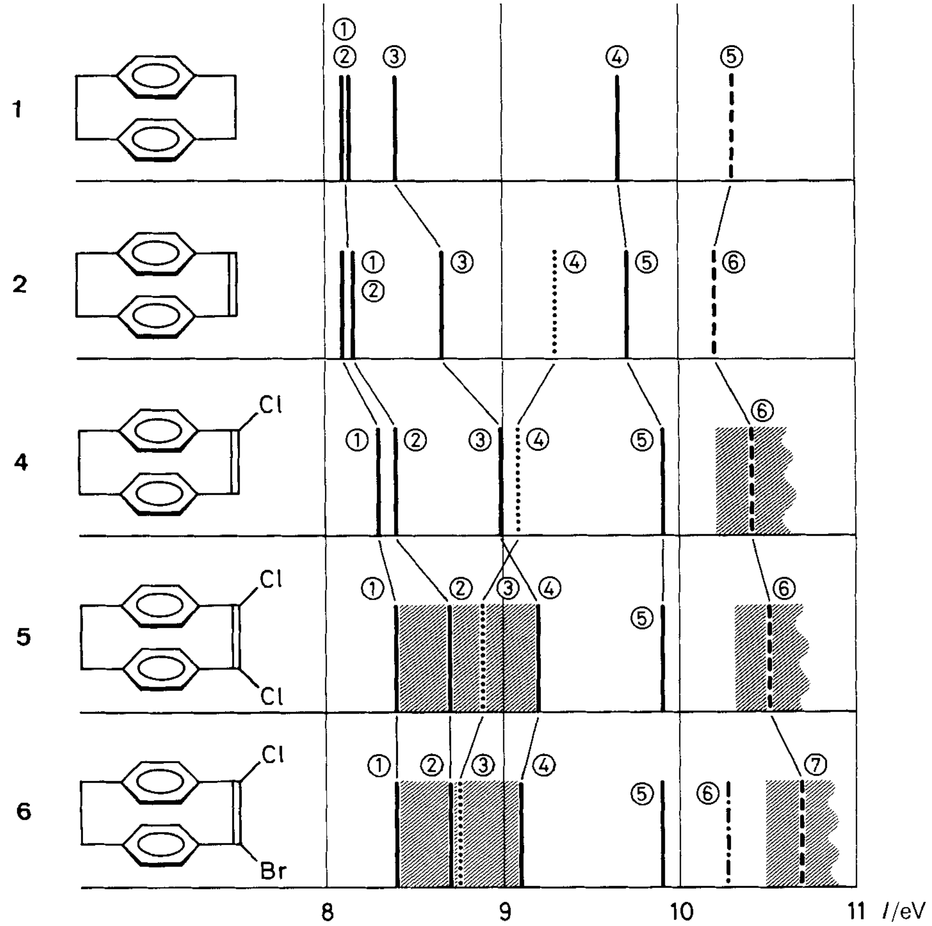


Fig. 4. *Correlation diagram.* The solid vertical bars refer to bands associated with orbitals dominated by the benzene-moiety π orbitals, the dotted lines and the broken lines to bands associated with the double-bond π and the σ-frame orbitals, respectively. Band ⑥ of **6** is due to ejection of an electron from a Br lone-pair orbital. Band positions within the shaded regions are uncertain.

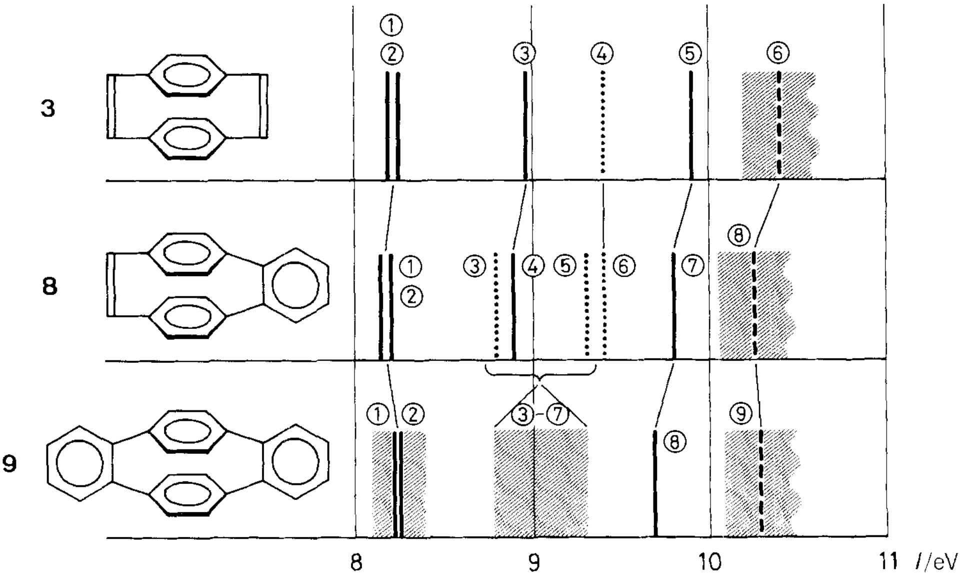


Fig. 5. *Correlation diagram.* Concerning the meaning of the vertical bars, see legend to *Fig. 4*. Note that the dotted lines now also refer to bands associated with the π orbital of the bridging *o*-phenylene groups.

9, the P_{A+}^{-1}, P_{A-}^{-1}, and P_{S+}^{-1}, P_{S-}^{-1} bands in the PE spectrum are expected to merge into two double bands, respectively, according to our MO model [2] [3] based on the structure [11]. The resulting assignment is supported by the experimental results for the methyl derivative **10**.

Again, the orbital labels proposed for the bands in the PE spectra of **11**, **13**, and **14** are obtained by the MO model defined in [2] [3], using the π orbitals ψ_j of the naphthalene or anthracene moieties [12] as basis orbitals. For the 'through-space' interaction between the two peripositioned benzene π orbitals of **13**, a coupling parameter of $\tau \approx 0.9$ eV has been assumed, whereas $\tau = 0$ eV is postulated for **14**.

The orbital sequence in **12** is rather uncertain and should be used only with caution.

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