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250. The Ionization Energies of Bridged [14]Annulenes and of Dicyclohepta[*cd*, *gh*]pentalene¹)

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Dedicated to Prof. Dr. *Hermann Hartmann* on the occasion of his sixtieth birthday

(2. IX. 74)

Summary. The ionization energies I_J of 1,6;8,13-alkanediylidene-[14]annulenes (**2** to **5**) and of dicyclohepta[*cd,gh*]pentalene (**1**) have been determined by photoelectron spectroscopy, using HeI radiation. The data are interpreted in terms of *Koopmans'* theorem ($I_J = -\varepsilon_J$) on the basis of correlation diagrams and with the help of simple molecular orbital models.

If the bridge is an ethane-, propane- or butane-diylidene group, the π-orbital sequence, in descending order of orbital energies, is (in C_{2v}): b_1, b_2, a_2, a_1. The sequence is due to a complicated

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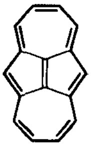
¹) On occasion of the 2nd International Symposium on the Chemistry of Nonbenzenoid Aromatic Compounds in Lindau (September 23–27, 1974) it was found that the PE. spectra of the compounds **3**, **4** and **5** had been investigated independently and unknown to us by *J. F. M. Oth, J.-C. Bünzli, H. Baumann & J.-C. Gfeller* (Organisch-chemisches Laboratorium, ETH-Z, Zürich) as part of the thesis of *J.-C. Gfeller*. The results obtained by both groups were presented in plenary lectures at the Symposium mentioned above and are referred to in the corresponding manuscripts submitted for the Symposium Volume to the Journal of Pure an Applied Chemistry. Therefore the present publication does ndt involve and priority claim.

and not uniquely definable interplay of inductive, conjugative and homoconjugative effects. A detailed analysis of these effects suggests that the effective angle of twist between two consecutive basis-AOs $2p_\mu$, $2p_\nu$ of the peripheral π-system should be smaller than the twist angles $\theta_{\mu\nu}$ determined by X-ray analysis, *i.e.* that the π-ribbon adjusts elastically and is no longer locally orthogonal to the σ-frame.

In the non-alternant hydrocarbon **1** of symmetry D_{2h}, the sequence is $2b_{2g}$, $3b_{1u}$, $2b_{3g}$, $1a_u$, $2b_{1u}$. The sequence $3b_{1u}$ above $2b_{3g}$, *i.e.* the reverse of b_2 above a_1 in the bridged [14]annulenes, is explained as being due to the interaction of the semilocalized perimeter orbitals b_{1u} and b_{3g} with the bonding ($\pi(B_{1u})$) and antibonding ($\pi^*(B_{3g})$) orbital of the central double bond. In **2** the replacement of the two latter orbitals by the *Walsh*-orbitals of the cyclopropane moiety leads to the sequence b_1, b_2, a_1, a_2.

From the data observed for **1** to **5** and for 1,6-methano-[10]annulene [11], a crude estimate for the orbital energies of the hypothetical *all-cis* D_{10h}-[10]- and D_{14h}-[14]annulenes can be derived.

Vogel et al. have synthesized bridged 1,6;8,13-alkanediylidene-[14]annulenes in which the alkane moieties are cyclopropane (**2**) [1], ethane (**3**) [2], propane (**4**) [3] or butane (**5**) [4]. Their physico-chemical properties have been the subject of extensive investigation (*e.g.* [5] and references given therein). We now report the ionization energies I_J of **2** to **5** and those of the non-alternant hydrocarbon dicyclohepta[*cd,gh*]-pentalene ('dipleia-pentalene') (**1**) [6], as determined by photoelectron-spectroscopy (PE. spectroscopy).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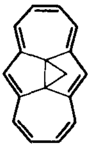
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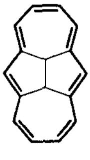
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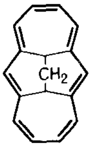

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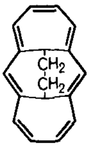

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The PE. spectra have been recorded on an instrument built according to the specifications given by *Turner* [7], using HeI radiation. The ionization energies I_J listed in Tab. 1 and displayed in the correlation diagram of Fig. 1 refer to the maxima of the *Franck-Condon* envelopes of the individual bands. Therefore the I_J are close to the vertical ionization energies: $I_J \approx I_{v,J}$. The corrections necessary to convert I_J into $I_{v,J}$ should be smaller than approx. 0.03 eV, the limits of error which affect the I_J-values.

To interpret the data of Tab. 1 we make use of *Koopmans'* theorem [8], *i.e.* we identify the negative ionization energies with 'observed' orbital energies $\varepsilon_J = -I_{v,J} \approx -I_J$. The known shortcomings of this approximation should always be kept in mind. In particular it must be emphasized once more that the experimental results relate to the electronic states of the radical cations 1^+ to 5^+, so that their interpretation, in terms of the energies ε_J of the canonical orbitals of the neutral parent molecules **1** to **5**, must be taken with a grain of salt [9].

The π-systems of the hydrocarbons **2** to **5** and, in a certain sense, also that of **1** can be considered as deformed and perturbed π-perimeters, originally of D_{14h}-symmetry, extending over the 14 peripheral 2p-centres. Therefore it is convenient to begin our analysis with a discussion of the perimeter π-orbitals of a hypothetical *all-cis*-D_{14h}-[14]annulene (**6**). For the sake of comparison we include *all-cis*-D_{10h}-

Table 1. *Ionization Energies I_J in eV*

The assignment of the individual bands is that derived in this work. Estimated error of the I_J values, approx. ±0.03 eV for values given with two decimals, otherwise ±0.05 or ±0.1 eV. σ-Ons. = Onset of the σ-band system.

	1		**2**		**3**		**4**		**5**	
Band	I_J	ψ_J	I_J	φ_J	I_J	φ_J	I_J	φ_J	I_J	φ_J
①	7.14^a	$2b_{2g}$ ψ_8	7.15^c	$14b_1$ φ_6	7.33	$13b_1$ φ_6	7.37	$14b_1$ φ_6	7.4_0	$14b_1$ φ_6
②	7.64^b	$3b_{1u}$ ψ_7	7.5^d	$14b_2$ φ_7	7.58	$14b_2$ φ_7	7.6_0^d	$15b_2$ φ_7	7.6_5^d	$17b_2$ φ_7
③	8.31	$2b_{3g}$ ψ_6	8.63	$19a_1$ φ_4	8.83	$10a_2$ φ_5	8.66	$10a_2$ φ_5	8.57	$11a_2$ φ_5
④	9.58	$1a_u$ ψ_5	9.01	$10a_2$ φ_5	9.4_5	$17a_1$ φ_4	9.47	$19a_1$ φ_4	9.5_0	$20a_1$ φ_4
⑤	10.3	$2b_{1u}$ ψ_4	9.7_5	?	9.7^e	?	9.6	?	9.6	?
⑥	10.8	σ-Ons.	10.4	σ-Ons.	10.3	σ-Ons.	10.4	σ-Ons.	10.4	σ-Ons.

[a] Dominating vibrational fine-structure: $\tilde{\nu} \approx 800$ cm^{-1}.

[b] Dominating vibrational fine-structure: $\tilde{\nu} \approx 1200$ cm^{-1}.

[c] I_J perhaps higher by one vibrational quantum: $\tilde{\nu} \approx 1300$ cm^{-1} *i.e.* $\approx 0.1_5$ eV.

[d] Badly resolved *Franck-Condon* envelope. I_J of second component of double band uncertain (±0.1 or ±0.05 eV).

[e] Fifth band near 9.7 eV. This band is rather broad and ill-defined.

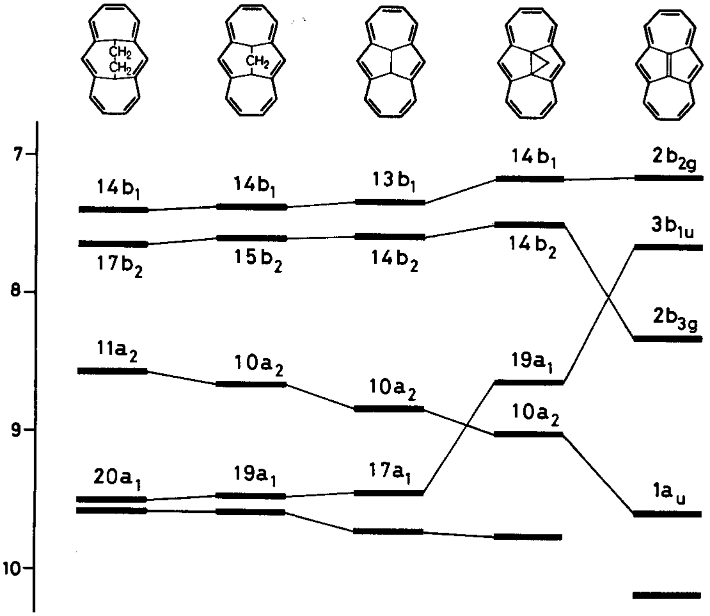
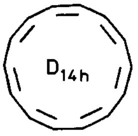


Fig. 1. *Orbital correlation diagram for the hydrocarbons* **1** *to* **5**. The assignment is that suggested by the analysis presented in this work

[10]annulene (**7**), the parent system of 1,6-methano-[10]annulene (**8**) [10], the PE. spectrum of which has been investigated by *Boschi, Schmidt & Gfeller* [11].



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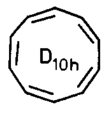

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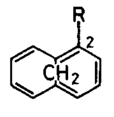
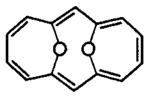


R = H **8**
= COOH **9**



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D_{41h}-[14]- and D_{10h}-[10]-Annulene. – The two pairs of highest occupied π-orbitals of *all-cis*-D_{14h}-[14]annulene (**6**) are the $1e_{3g} = (\varphi_6, \varphi_7)$ (HOMO) and $1e_{2u} = (\varphi_4, \varphi_5)$ orbitals with HMO orbital energies $\varepsilon_J^0 = \alpha + x_J\beta^0$ given by $x_6 = x_7 = 0.445$ and $x_4 = x_5 = 1.247$. The corresponding quantities for *all-cis*-D_{10h}-[10]annulene (**7**) are: $1e_{2u} = (\varphi_4', \varphi_5')$; $1e_{1g} = (\varphi_2, \varphi_3)$; $x_4 = x_5 = 0.618$; $x_2 = x_3 = 1.618$. Qualitative representations of these orbitals (after having deformed the D_{nh}-[n]annulene into a system of D_{2h}-symmetry) are given in Fig. 2. In the framework of the usual HMO approximation, such a topological in-plane deformation leaves the orbital energies ε_J^0 invariant.

A first estimate of the vertical ionization energies $I_{v,J}$, and thus (in *Koopmans'* approximation) of the 'observed' orbital energies $\varepsilon_J = -I_{v,J}$, can be obtained by a calibrated perturbation treatment described previously [12]. This takes into account

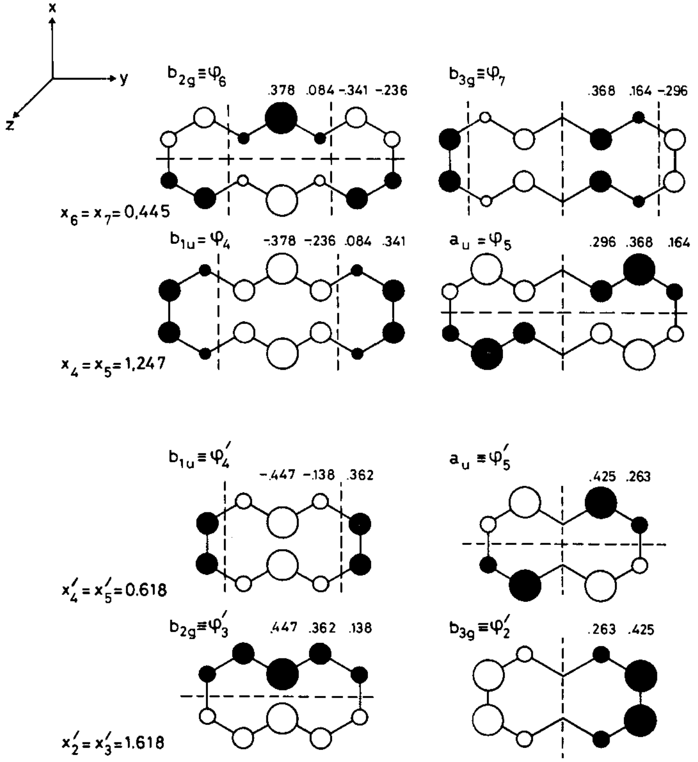


Fig. 2. *Qualitative orbital diagrams for the four highest occupied π-orbitals of [14]annulene* (**6**) *and [10]annulene* (**7**) *deformed to D_{2h} symmetry.* The diagrams show qualitatively the phase relationship of the AOs in the linear combinations $\varphi_J = \sum_\mu c_{J\mu}\varphi_\mu$. The values of the $c_{J\mu}$ are given above each diagram

first-order bond localization in the neutral parent compound [13] and the changes in bond orders which accompany the ejection of the photoelectron from orbital φ_J. The relevant formula is:

$$\varepsilon_J = (\alpha + \beta x_J) - b \sum_{\mu\nu} (p^{+}_{\mu\nu,J} - p_{\mu\nu})\,(p_0 - p_{\mu\nu}), \qquad (1)$$

where

a) $\alpha + \beta x_J$ is the orbital energy as defined in the usual *Hückel* approximation;

b) $p_{\mu\nu}$ the bond order between bonded centres μ, ν of the neutral parent molecule;

c) $p^{+}_{\mu\nu,J} = p_{\mu\nu} - c_{J\mu}\, c_{J\nu}$, the corresponding bond order of the radical cation in the electronic state in which φ_J is only singly occupied;

d) $p_0 = 2/3$, the standard bond order in benzene;

e) b, a factor dependent upon the force constants of the π and σ bonds and upon the derivative $\mathrm{d}\beta/\mathrm{d}R$ of the resonance integral β with respect to the length of the π-bond.

Summation is performed over all bonds.

Strictly speaking formula (1) yields estimates of $-I_{v,J}$ rather than orbital energies. However, it is convenient for the analysis presented in this paper to treat the results as orbital energies ε_J, obtained by applying *Koopmans'* theorem in reverse.

In a D_{nh}-[n]annulene the bond order between bonded centres μ, ν is

$$p_{\mu\nu} = 2\left(n \sin \frac{\pi}{n}\right)^{-1}. \tag{2}$$

Furthermore, because of $x_J = 2 \sum_{\mu\nu} c_{J\mu} c_{J\nu}$ (over all bonds) we have

$$p^{+}_{\mu\nu,J} = p_{\mu\nu} - x_J/2n. \tag{3}$$

Inserting (2) and (3) into (1) yields:

$$\varepsilon_J = \alpha + \left(\beta + \frac{b}{2}(p_0 - 2(n \sin \frac{\pi}{n})^{-1})\right) x_J. \tag{4}$$

Using a mixed set of unsubstituted, unsaturated benzenoid and non-benzenoid hydrocarbons, the following parameters for (4) have been determined: $\alpha = -5.847 \pm 0.163$ eV; $\beta = -3.326 \pm 0.152$ eV; $b = 7.733 \pm 1.009$ eV [12]. Slightly different, but equivalent values have been obtained on the basis of the five benzenoid $C_{18}H_{12}$ hydrocarbons [14], the acenes from benzene to pentacene [15] or a larger set of benzenoid hydrocarbons [16]. For n = 14 or n = 10 and with the parameters mentioned above, formula (4) reduces to:

$$\begin{aligned} n = 14: &\quad \varepsilon_J = (-5.847 - 3.231 x_J)\ \text{eV} \\ n = 10: &\quad \varepsilon'_J = (-5.847 - 3.251 x'_J)\ \text{eV}. \end{aligned} \tag{5}$$

Thus the orbital energies predicted for *all-cis-*D_{14h}-[14]annulene (**6**) are

$$\mathbf{6} \quad \begin{aligned} 1e_{3g} &= (\varphi_6, \varphi_7);\ \varepsilon_6 = \varepsilon_7 = -7.28\ \text{eV} \\ 1e_{2u} &= (\varphi_4, \varphi_5);\ \varepsilon_4 = \varepsilon_5 = -9.88\ \text{eV}, \end{aligned} \tag{6}$$

and for *all-cis-*D_{10h}-[10]annulene (**7**):

$$\mathbf{7} \quad \begin{aligned} 1e_{2u} &= (\varphi'_4, \varphi'_5);\ \varepsilon'_4 = \varepsilon'_5 = -7.86\ \text{eV} \\ 1e_{1g} &= (\varphi'_2, \varphi'_3);\ \varepsilon'_2 = \varepsilon'_3 = -11.11\ \text{eV}. \end{aligned} \tag{7}$$

For benzene (= 'D_{6h}-[6]annulene') the orbital energies derived from (4) were: $1e_{1g} = (\varphi''_2, \varphi''_3)$; $1a_{1u} = (\varphi''_1)$; $x''_2 = x''_3 = 1.000$; $x''_1 = 2.000$; $\varepsilon''_2 = \varepsilon''_3 = -9.17$ eV; $\varepsilon''_1 = -12.50$ eV [12] (experimental values from PE. spectra: $\varepsilon''_2 = \varepsilon''_3 = -9.24$ eV; $\varepsilon''_1 = -12.25$ eV [17]).

The calibration of formula (1) is based on π-systems which contain only small, mainly six-membered rings. Therefore the sizeable 1,3 and 1,4 interactions, which are present in such systems, have been absorbed into the parameters α, β and b of (1) and (4). Because such interactions are presumably smaller in **6** and **7**, it will not be surprising, if the estimates of ε_J and ε'_J given in (6) and in (7) each deviate more from values obtained by other means (see below) than is the case for benzene.

1,6;8,13-Alkanediylidene-[14]annulenes. – The bridged [14]annulenes **3** to **5** and 1,6-methano-[10]annulene **8** each present a deformed perimeter π-system of symmetry C_{2v}. (We prefer to deal with compound **2** at a later stage.) The relationship between the different symmetry labels for the four highest occupied π-orbitals is (leaving out the main quantum numbers):

$$\begin{array}{lcccl}
\text{Symmetry:} & D_{nh} \longrightarrow & D_{2h} \longrightarrow & C_{2v} & \text{Fig. 2}\\
 & & & & \quad\mathbf{6} \quad\; \mathbf{7}\\
 & \nearrow & b_{3g} \longrightarrow & b_2 & (\varphi_7 \text{ or } \varphi_2')\\
e_{1g} \text{ or } e_{3g} & & & & \\
 & \searrow & b_{2g} \longrightarrow & b_1 & (\varphi_6 \text{ or } \varphi_3')\\
 & \nearrow & a_u \longrightarrow & a_2 & (\varphi_5 \text{ or } \varphi_5')\\
e_{2u} & & & & \\
 & \searrow & b_{1u} \longrightarrow & a_1 & (\varphi_4 \text{ or } \varphi_4').
\end{array} \tag{8}$$

X-ray structure analyses of **4** [18] and **5** [19] show that the π-systems are not planar. Nevertheless, the peripheral CC-bonds deviate only little from the value 1.39 Å expected for a pure 'aromatic' π-bond: in **4** (**5**): $R_{1,2} = 1.40$ (1.40); $R_{2,3} = 1.38$ (1.36); $R_{3,4} = 1.41$ (1.42); $R_{1,14} = 1.38$ (1.40) Å. We may therefore safely neglect the effect of first-order bond localization. This is in agreement with the HMO picture discussed above: The factors of x_J and x_J' in (5) differ only very little from $\beta = -3.326$ eV, the value for a bond of bond-order p_0 (see (1)). On the other hand, the lack of planarity leads to sizeable twist angles $\theta_{\mu\nu}$. (We list here the absolute mean values of these angles, or of their complement to 180°.) For comparison the corresponding values of $\theta_{\mu\nu}$ found for 1,6;8,13-bis-epoxy-[14]annulene (**10**) [20] and 1,6-methano-[10]annulene-2-carboxylic acid (**9**) [21] are included.

$\theta_{\mu\nu}$; $\mu, \nu =$		1,14 (1,10 in **9**)	1,2	2,3	3,4
n = 14	**4**	15°	29°	21°	0°
	5	23,4°	35,6°	18,6°	0°
	10	13,4°	23,7°	19,2°	1,8°
n = 10	**9**	34,0°	19,7°	0°	–

(9)

To correlate the 'observed' orbital energies ε_J, derived from the PE. spectroscopic data of **3**, **4**, **5**, with the expectation values (6) of **6** and those of **8** with those of **7** (see (7)) we take into consideration three types of perturbations, which suggest themselves as being the main contributors to $\delta\varepsilon_J$:

A) *'Inductive' destabilization* $\delta\varepsilon_J^{\text{ind.}}$. The so called 'inductive effect' of an alkyl group R is due, in the last analysis, to a conjugative interaction between its σ-orbitals (of appropriate symmetry) and the π-orbitals in the substituted system S–R (see *e.g.* [22] and the literature survey given therein). Nevertheless it is possible to parametrize it in the framework of a simple *Hückel* model [23], in terms of a destabilization $\delta\alpha$ of the 2p-*Coulomb* integral α_μ at the substitution centre μ and of $m\delta\alpha$

at the neighbouring centres ϱ. For the transmission factor m, originally introduced by *Wheland & Pauling* [24], we have $0 \leqslant m < 1$. (For a notable exception see [25].)

If the π-orbitals φ_J of the parent systems S = **6** or **7** are given as linear combinations over 2p-AOs, then the inductive perturbations $\delta\varepsilon_J^{\text{ind.}}$ due to the bridging alkyl moieties in **2** to **5** and in **8** are given by first-order perturbation theory as

$$\text{n} = 14:\ \delta\varepsilon_J^{\text{ind.}} = (4c_{J1}^2 + 4m(c_{J2}^2 + c_{J14}^2))\,\delta\alpha = a_J\delta\alpha \tag{10}$$

$$\text{n} = 10:\ \delta\varepsilon_J'^{\text{ind.}} = (2c_{J1}^2 + 4m\ c_{J2}^2)\,\delta\alpha = a_J'\delta\alpha \tag{11}$$

Calibration of $\delta\alpha$ and m, using the PE. spectroscopic data of alkylsubstituted benzenes and pyridines [26], butadienes and hexatrienes [27] and other unsaturated hydrocarbons [28], yields $\delta\alpha = 1.0$ to 1.4 eV (depending on the size of R) and $m = 1/3$.

B) *Homoconjugative effect* $\delta\varepsilon_J^{\text{homo.}}$. It has been recognized for some time (see [1] to [5]) that an important feature of the electronic structure of the bridged annulenes is the homoconjugative 'through-space' [29] interaction between the opposing 2p-AOs at the bridgeheads *i.e.* those in positions 1,6 and 8,13 in **2** to **5** or 1,6 in **8**. Relative to the orbital energies ε_J and ε_J' of **6** and **7**, the expected change due to homoconjugation is in a first approximation given by:

$$\text{n} = 14:\ \delta\varepsilon_J^{\text{homo.}} = (4c_{J1}c_{J6})\,\beta_{\text{homo.}} = h_J\beta_{\text{homo.}} \tag{12}$$

$$\text{n} = 10:\ \delta\varepsilon_J'^{\text{homo.}} = (2c_{J1}c_{J6})\,\beta_{\text{homo.}} = h_J'\beta_{\text{homo.}} \tag{13}$$

The resonance integral $\beta_{\text{homo.}}$ will not be constant for all our compounds, but will depend on the distance and relative orientation of the two interacting 2p-AOs *i.e.* on the CCC-angle at the bridging carbon atom(s).

C) *Destabilization* $\delta\varepsilon_J^{\text{twist}}$ *due to lack of planarity.* A third perturbation of ε_J or ε_J', which seems to be an obvious one to take into consideration, is that due to the deviation from coplanarity. The destabilization $\delta\varepsilon_J^{\text{twist}}$ to be expected on the basis of a traditional HMO treatment can again be computed by first order perturbation theory, if one assumes that the individual resonance integrals $\beta_{\mu\nu}$ between bonded centres μ, ν depend on the twist angles given in (9) according to $\beta_{\mu\nu} = \beta^0 \cos\theta_{\mu\nu}$, where β^0 is the standard resonance integral for a planar π-bond. The resulting perturbation is

$$\delta\varepsilon_J^{\text{twist}} = (2\sum_{\mu\nu} c_{J\mu}c_{J\nu}(\cos\theta_{\mu\nu} - 1))\,\beta^0 = t_J\beta^0, \tag{14}$$

where summation extends over all bonds.

In Tab. 2 are given the perturbations (10) to (14) calculated by using the HMO coefficients $c_{J\mu}$ given in Fig. 2 and the twist angles $\theta_{\mu\nu}$ listed in (9).

The naive and rather crude first-order treatment embodied in the formulae (10) to (14) is only relevant, at best, for the four highest occupied molecular orbitals of the molecules **2** to **5**. The energies of the lower lying perimeter π-orbitals of the reference systems **6** and **7** fall into the energy range of the σ-orbitals of the bridged systems and will therefore mix with them to such an extent that our perturbation calculation becomes unrealistic. Even for the upper four occupied orbitals, to which we limit our discussion, the results derived from (10) to (14) should be regarded with suspicion, although they do yield a pleasing and heuristically useful interpretation of the observed data.

Table 2. *Factors a_J, h_J and t_J of the perturbations $\delta\varepsilon_J^{\text{ind.}}$, $\delta\varepsilon_J^{\text{homo.}}$ and $\delta\varepsilon_J^{\text{twist}}$ for* **4**, **5** *and* **8**, *calculated according to formulae (10) to (14)*

			φ_7	φ_7	φ_5	φ_5
			b_{3g}, b_2	b_{2g}, b_1	a_u, a_2	b_{1u}, a_1
a_J	**4, 5**	m = 0	0.542	0.028	0.350	0.223
		m = 1/3	0.578	0.374	0.531	0.423
h_J	**4, 5**		0.542	-0.028	-0.350	0.223
t_J	**4**		-0.035	-0.023	-0.141	-0.020
	5		-0.070	-0.012	-0.188	-0.041

			φ'_5	φ'_4	φ'_3	φ'_2
			a_u, a_2	b_{1u}, a_1	b_{2g}, b_1	b_{3g}, b_2
a'_J	**8**	m = 0	0.000	0.400	0.400	0.000
		m = 1/3	0.241	0.425	0.574	0.092
h'_J	**8**		0.000	0.400	-0.400	0.000
t'_J	**8**		-0.052	-0.061	-0.245	-0.052

Boschi, Schmidt & Gfeller [11] analysed the PE. spectrum of **8** in terms of the perturbations (11) and (13) only, assuming $m = 0$ *i.e.* zero transmission of the inductive effect (*cf.* Tab. 2). This yielded the following assignment:

	Band	I_J [11]	Orbital [11]	
	①	7.90 eV	$7a_2$ (φ'_5)	
8	②	8.38	$13a_1$ (φ'_4)	(15)
	③	9.24	$9b_1$ (φ'_3)	
	④	10.36	$9b_2$ (φ'_2).	

The observed I_J are reproduced under the above assumptions, if one uses $\alpha = -6.38$ eV, $\beta' = -2.46$ eV for the HMO orbital energies of **7** (see Fig. 2), $\delta\alpha = 0.80$ eV (with $m = 0$) in (11) and $\beta_{\text{homo.}} = -2.00$ eV in (13). We agree completely with the assignment (15). Nevertheless a few comments are desirable:

a) Previous experience clearly indicates that the assumption $m = 0$, *i.e.* zero transmission of the 'inductive' effect, is not appropriate, especially when the centre μ of substitution lies on a node (*e.g.* in **8**) of orbital φ'_J, which leads to $c_{J\mu} = 0$. As mentioned before, a least squares calibration of m suggests a value of $m = 1/3$ [26] [28]. If this value is inserted into (11) (see Tab. 2), then the data recorded by *Boschi, Schmidt & Gfeller* lead to $\alpha = -6.70$ eV, $\beta' = -2.32$ eV, $\delta\alpha = 0.96$ eV, $\beta_{\text{homo.}} = -1.64$ eV, and therefore to $\varepsilon(e_{2u}) = -8.13$ eV, $\varepsilon(e_{1g}) = -10.45$ eV for **7**.

b) The above authors have drawn attention to the relatively small value of $\beta' = -2.46$ eV derived from the data of **8**, if compared to $\beta^0 = -2.7$ to -3.1 eV found for other 'aromatic' hydrocarbons (least squares value $\beta^0 = -2.734$ eV [12]; $\beta'' = -3.0$ eV for benzene from $I_1 = 9.24$ eV; $I_2 = 12.25$ eV). This decrease was attributed to the lack of coplanarity of the perimeter π-system in **8**. However there is a slight difficulty. The influence of the deviations of $\theta_{\mu\nu}$ from zero (see (9)) cannot be absorbed simply in a mean β', because they affect the individual orbital energies ε_J' not proportionally to x_J but to the t_J given in Tab. 2. In fact only the orbital $\varphi_3 = 9b_1$ would suffer a sizeable destabilization, whereas the others remain relatively unaffected. Including the t_J values of Tab. 2 in the calculation, the data (15) are fitted by the new set of parameters $\alpha = -6.58$ eV, $\beta' = -2.43$ eV, $\delta\alpha = 0.23$ eV and $\beta_{\text{homo.}} = -1.36$ eV. Except for the smallness of $\delta\alpha$, these values are not unreasonable. If nothing else, this analysis shows that simple models, such as the one under discussion, have to be handled with caution. We shall come back to this point in connection with the PE. spectra of the bridged [14]annulenes.

We shall now subject the data for **4** and **5**, given in Tab. 1, to the same type of analysis. Before doing so, it is important to realize that whereas the orbital sequence in **8** is uniquely determined according to qualitative arguments [11], the situation in **3**, **4** and **5** seems to be not as clear-cut, in particular with reference to the relative ordering of φ_6 and φ_7 (b_1 and b_2). The reason is immediately obvious from Tab. 2. For φ_7 the inductive and homoconjugative effects tend to compensate each other, and for φ_6 they are rather small, if $m = 0$. For this reason we have carried out our analysis under both assumptions: φ_7 above φ_6 and φ_7 below φ_6. It is found, that for all modifications of the model taken into consideration (*i.e.* those listed in Tab. 2), only the latter sequence yields parameters which make sense in the framework of our approximation. We interpret this result in the sense that the two highest occupied orbitals in **3**, **4** and **5** are φ_6 (b_1, HOMO) above φ_7 (b_2). Under this condition, the following parameters are obtained from the first four ionization energies I_1 to I_4:

t_J excluded		α	β	$\delta\alpha$	$\beta_{\text{homo.}}$
4	$m = 0$	−6.34	−2.46	0.90	−1.21
	$m = 1/3$	−7.02	−2.40	1.85	−1.07
5	$m = 0$	−6.38	−2.44	1.05	−1.39
	$m = 1/3$	−7.19	−2.37	2.17	−1.21
t_J included					
4	$m = 1/3$	−6.67	−2.43	0.82	−0.75
5	$m = 1/3$	−6.67	−2.46	0.55	−0.89

(16)

It is immediately apparent that the *Boschi-Schmidt-Gfeller* approximation ($m = 0$; t_J excluded) yields parameters in complete agreement with those derived from **8** [11]. The larger values of $\delta\alpha$ and the smaller absolute values of $\beta_{\text{homo.}}$ (both increasing from **4** to **5**) are as expected. The transferability of parameters becomes worse if we assume $m = 1/3$; in particular $\delta\alpha$ is now much too large. Inclusion of the corrections t_J, which take into account the non-planarity of the perimeter, tends to overcompensate this effect: $\delta\alpha$ has become too small and decreases in going from **4** to **5**. Thus, improving the model by including effects which must be present, in view of previous experience with other unsaturated systems, carries the model beyond the '*Pauling* point', *i.e.* the point at which increased sophistication leads to worse agreement with experiment.

However, if the model is taken at its face value, there is a perfectly good reason for this observation. To assume that the observed twist angles $\theta_{\mu\nu}$ are those to be used in formula (14) is probably wrong. It implies that the 2p-AOs at centres μ, ν are strictly perpendicular to the local σ-plane, a hypothesis which seems to be supported by the results of PE.-spectroscopic investigations of loosely coupled π-systems R–S such as sterically hindered butadienes [30], styrenes [31] and biphenyls [32]. In all these cases the change in π-orbital interaction 'measured' by PE.-spectroscopy is well represented by $\beta_{\mathrm{RS}} = \beta_0 \cos \theta_{\mathrm{RS}}$, where θ_{RS} is the twist angle between the planes of the two partial systems R and S, connected in R–S by a sp^2-sp^2 single bond. However, in these systems the 2p-AOs at the linked centres are strongly coupled to other 2p-AOs within each partial system and are thus locked in orientations perpendicular to the planes of R and S respectively. On the other hand, this is no longer true in molecules such as **4**, **5** or **8** ,where the neighbouring 2p-AOs of the twisted bond are strongly coupled. They will polarize in such a way as to yield optimum overlap within the constraints imposed by the σ-frame. The resulting π-ribbon stretches 'elastically' around the periphery and will not necessarily be locally perpendicular to the σ-bonds, as long as such deviations optimize the total energy of the system. A similar type of adjustment has been predicted by *Mock, Radom & Pople* [33] for the distorted π-orbital of a deformed ethylene. PE.-spectroscopic evidence for hydrocarbons containing such bonds [34] seems to support such a view.

Therefore it is reasonable to assume that the observed twist angles $\theta_{\mu\nu}$ given in (9) exaggerate the true angles between linked AOs $2p_\mu$, $2p_\nu$ participating in the perimeter orbitals of **4**, **5** and **8**, or other bridged [n]annulenes. In turn, this implies that the t_J computed on the basis of the $\theta_{\mu\nu}$ given in (9) are definitely too large. If they are reduced, *e.g.* to half their size, a consistent and reasonable set of parameters is obtained in the framework of a more realistic model, which is also valid for other π-systems.

Assuming that t_J is indeed only half as large as given in Tab. 2, we obtain the following set of parameters with $m = 1/3$ and $t_J/2$ instead of t_J:

	α	β	$\delta\alpha$	$\beta_{\mathrm{homo.}}$
8	−6.64	−2.37	0.60	−1.50
4	−6.85	−2.41	1.34	−0.91
5	−6.88	−2.42	1.38	−1.05

(17)

It is worth mentioning that the usual semi-empirical models do not allow for such deformations of the 2p-AOs. Because of the restricted basis, consisting of 2s and 2p-AOs only, the π-orbitals are by necessity locally perpendicular to the plane of the strongly bonding σ-orbitals. Obviously it would be necessary to include polarization functions (*e.g.* fictitious 2d-orbitals) to obtain a realistic model for bridged annulenes. It may well be that the poor performance of the traditional semi-

Table 3. *Extrapolated orbital energies for all-*cis-D_{nh}-[*n*]*annulenes* (*in eV*)

HMO-P: Calculated according to the HMO perturbation treatment (1), (4) from formulae (5) for n = 10 and 14. For n = 6 see [12]. – A: Extrapolated values using the scheme proposed by *Boschi, Schmidt & Gfeller* [11]: $m = 0$ (no transmission), $t_J = 0$ (no influence of twist angles $\theta_{\mu\nu}$). – B: Extrapolated values assuming a transmission coefficient $m = 1/3$ and including the corrections t_J for the twist-induced displacement in **4**, **5** and **8**. – C: Extrapolated values assuming a transmission coefficient $m = 1/3$ and a reduced correction of $t_J/2$ for the twist-induced displacements in **4**, **5** and **8**

n	Orb.	HMO-P	A $m = 0$ $t_J = 0$	B $m = 1/3$ t_J	C $m = 1/3$ $t_{J/2}$
6	$1e_{1g}$	-9.17	(-9.24)[a]	(-9.24)[a]	(-9.24)[a]
	$1a_{1u}$	-12.50	(-12.25)[a]	(-12.25)[a]	(-12.25)[a]
10	$1e_{2u}$	-7.86	-7.90[b]	-8.08[d]	-8.11[f]
	$1e_{1g}$	-11.11	-10.36[b]	-10.51[d]	-10.48[f]
14	$1e_{3g}$	-7.28	-7.45[c]	-7.70[e]	-7.94[g]
	$1e_{2u}$	-9.88	-9.42[c]	-9.73[e]	-9.88[g]

[a] Experimental values – I_J taken from the PE. spectrum of benzene [17].

[b] From [11].

[c] Using $\alpha = -6.36$ eV, $\beta = -2.45$ eV, *i.e.* mean of values obtained for **4** and **5** with $m = 0$, $t_J = 0$ (see (16)).

[d] Using $\alpha = -6.58$ eV, $\beta = -2.43$ eV derived from the data given in [11] with $m = 1/3$ and the values of t_J given in Tab. 2.

[e] Using $\alpha = -6.67$ eV, $\beta = -2.445$ eV (mean value) derived from data for **4** and **5** with $m = 1/3$ and t_J as given in Tab. 2.

[f] Using α and β given in (17) for **8**.

[g] Using the mean of the α- and β-values given in (17) for **4** and **5**.

empirical SCF models in predicting ESR. coupling constants [35] is intimately linked to this shortcoming.

In spite of the range of values for the individual parameters, all these models extrapolate to roughly the same orbital energies for the hypothetical *all-cis* D_{nh}-[n]annulenes with n = 10 and 14 (see Tab. 3). As shown in Fig. 3, these orbital energies fall on a straight line, if plotted *vs.* the standard HMO x_J^0-values. Taking the orbital energies of the last column of Tab. 3 as a typical example, the regression line is:

$$\varepsilon_J = [-(6.550 \pm 0.276) - (2.685 \pm 0.217)\, x_J]\ \text{eV} \qquad (18)$$

$$\text{corr. coeff.} = 0.9872$$

Regression lines of the same quality are obtained, if the extrapolated ε_J of the other models are used as the dependent variable.

Independent of the model used, the predicted sequence of orbitals in **8**, **4** and **5** (and thus in **3**) is the same, *i.e.* that given in Tab. 1 and Fig. 1. In contrast, the different ways in which the inductive, conjugative and homo-conjugative effects have been handled lead to a significant ambiguity in the parameters (16), (17). Therefore we do not believe that any reliable conclusions can be drawn from them concerning

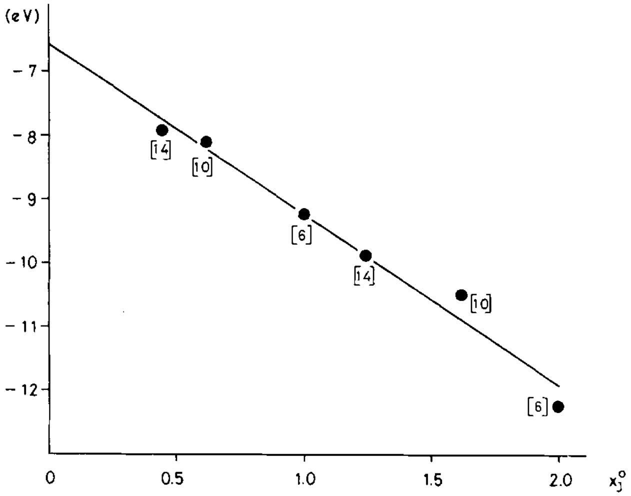


Fig. 3. *Correlation of the extrapolated orbital energies* ε_J *for an* all-cis-[*10*]- *and* -[*14*]*annulene with the* Hückel *parameters* x_J. Values ε_J from Tab. 3, last column. ([6]Annulene = benzene). Regression line, see (18)

the 'aromaticity' of such molecules, whatever the connotation of this term may be [36].

No structural data are as yet available for **3**. However, molecular models suggest that its perimeter should be flatter than those of **4** and **5** (*cf.* [5]). This is supported by the experimental results given in Fig. 1 and Tab. 1. In view of what has been said above, however, it is not possible to derive estimates of the twist angles $\theta_{\mu\nu}$, beyond the qualitative statement that they must be smaller than those of **4**.

Before analysing the PE. spectrum of **2**, it is of advantage to discuss first the planar, non-alternant hydrocarbon **1**.

Dicyclohepta[*cd,gh*]pentalene (1). – Some time ago it has been suggested [37] that **1** [6] is best regarded as a [14]annulene perturbed by a central double bond. This view is supported by semi-empirical calculations [38] and by the ESR. investigation due to *Müllen & Reel* [39]. All results suggest that the peripheral bond orders $p_{\mu\nu}$ are close to the value found for benzene and that the charge orders q_μ do not differ significantly from unity, although the system is a non-alternant one.

In Tab. 4 are given the orbital energies obtained according to the standard HMO treatment (x_J values from [40]), the perturbation HMO treatment discussed before [12] (see formula (1)) and PPP-calculations [41] using the original approximation of *Pariser & Parr* [42] or that proposed by *Mataga & Nishimoto* [43]. For the PPP-calculation we have assumed all bond lenths equal to 1.40 Å and bond angles as close to 108° and 128.6° as compatible with this assumption. All models agree in predicting the sequence of occupied orbitals shown in Fig. 1 and listed in Tabs. 1 and 4. Qualitative orbital diagrams based on the standard HMO treatment [40] are displayed in Fig. 4. It is noteworthy that for symmetry reasons the orbitals $\psi_8 \equiv 2b_{2g}$ (HOMO) and $\psi_5 \equiv 1a_u$ are strictly confined to the periphery of the molecule **1**. There-

Table 4. *Orbital energies ε_J for dicyclohepta*[cd, gh]*pentalene* **1** (*in eV*), *calculated in the HMO and PPP approximation*

Orb.		x_J[40]	HMO (a)	(b)	(c)	(d)	(e)	(f)
ψ_8	b_{2g}	0.445	-7.77	-7.54	2.259	-7.05	2.735	-7.14
ψ_7	b_{1u}	0.494	-7.90	-7.64	1.970	-7.33	2.613	-7.27
ψ_6	b_{3g}	1.000	-9.29	-8.42	0.767	-8.54	1.299	-8.58
ψ_5	a_u	1.247	-9.96	-9.68	-0.448	-9.75	0.195	-9.68

[a] Calculated according to $\varepsilon_J = \alpha + x_J\beta$ with $\alpha = -6.553$ eV, $\beta = -2.734$ eV [12].

[b] Calculated according to the perturbation treatment (1) with $\alpha = -5.847$, $\beta = -3.326$, $b = 7.733$ eV [12].

[c] Orbital energies calculated according to the original *Pariser-Parr-Pople* procedure [41]. The two-centre integrals were calculated by the uniform-charged-sphere approximation [42]. Parameters: $\beta_{\mu\nu} = -2.371$ eV (bonded centres) and zero otherwise; $\gamma_{\mu\mu} = 10.959$ eV; $\gamma_{\mu\nu} = (328.77 + R_{\mu\nu})/(30.0 + 12.341\ R_{\mu\nu} + R^2_{\mu\nu})$ for $R_{\mu\nu} \leq 6$ Å; $\gamma_{\mu\nu} = 14.395/R_{\mu\nu}$ for $R_{\mu\nu} > 6$ Å.

[d] Orbital energies calculated from those given under c) by adding -9.304 eV.

[e] Orbital energies calculated as under c) except for a change in parameters, which are computed in the *Mataga-Nishimoto* approximation [43]: $\beta_{\mu\nu} = -2.318$ eV; $\gamma_{\mu\mu} = 10.84$ eV; $\gamma_{\mu\nu} = 14.399/(1.328 + R_{\mu\nu})$ eV.

[f] Orbital energies calculated from those given under e) by adding -9.879 eV.

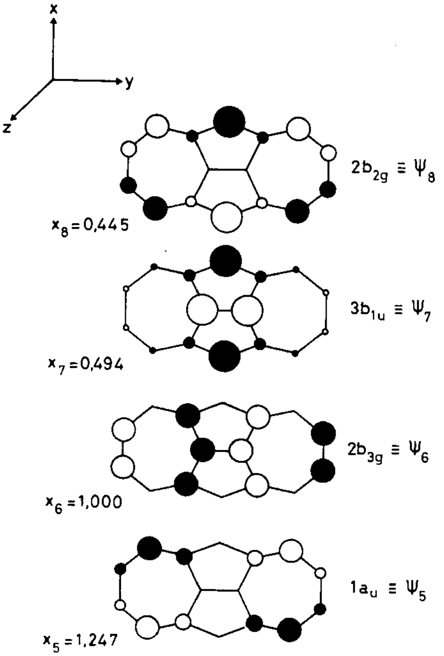


Fig. 4. *Qualitative orbital diagram for the four highest occupied π-orbitals of dicyclohepta*[cd, gh]*-pentalene* (**1**)

fore one might expect that, in a first approximation, the 'observed' orbital energies ε_8 and ε_5 should be close to, if not identical with, those derived for an *all-cis* D_{14h}-[14]annulene. A look at Tab. 3 (n = 14) reveals that for the HOMO ψ_8 this is not quite the case: $\varepsilon_8 = 7.14$ eV *vs.* $\varepsilon(e_{3g}) = -7.5$ to -7.9 eV; $\varepsilon_5 = -9.58$ eV *vs.* $\varepsilon(e_{2u}) = -9.4$ to -9.9 eV. However, there is an obvious reason for the discrepancy. In **1** the bond orders $p_{\mu\nu}$ of the peripheral bonds are not all equal (zero order HMO approximation [40]: $p_{12} = 0.543$, $p_{23} = 0.707$, $p_{34} = 0.590$, $p_{1,14} = 0.602$) in contrast to **6** where (2) yields $p_{\mu\nu} = 0.642$ for all bonds. If an electron is removed from orbital φ_J of **6**, the resulting bond orders $p^{+}_{\mu\nu,J}$ of **6**$^+$ are still all equal, for reasons of symmetry, and close to $p_{\mu\nu}$. (This is of course not apparent from the orbital diagrams for D_{2h} symmetry given in Fig. 2. For D_{14h} the corresponding complex orbitals have to be used.) In the case of **1** the $p^{+}_{\mu\nu,J}$ of **1**, obtained by ejecting an electron from ψ_J (see Fig. 4), differ significantly from the $p_{\mu\nu}$. Although the $p_{\mu\nu}$ of **1** do not provide for large bond alternations in the ground state of this molecule, they have nevertheless a significant effect on the orbital energies, if inserted into (**1**) together with the $p^{+}_{\mu\nu,J}$ of **1**$^+$. As shown in Tab. 4 (columns (a) and (b)), the computed corrections are $+\,0.23$ eV for ε_8 and $+\,0.28$ eV for ε_5. If subtracted from the 'observed' ε_8 and ε_5 of **1**, they yield $-\,7.41$ eV for $\varepsilon(1e_{3g})$ of **6** and $-\,9.86$ eV for $\varepsilon(1e_{2u})$ of **6**, in excellent agreement with the values given in Tab. 4. This confirms that our extrapolated orbital energies for **6** are presumably not far off the mark.

The orbital energies ε_8 to ε_5 computed by the HMO perturbation procedure (1), using the parameters obtained previously [12], account nicely for the observed PE. spectrum of **1** (see Tab. 1 and Tab. 4, column (b)). In addition, the relative spacings of the bands ① to ④ are well accounted for by the PPP-treatments. To force agreement with the absolute values of $I_J = -\,\varepsilon_J$, a value of $V_{\mu\mu} = -\,9.3$ eV or $-\,9.9$ eV has to be chosen, depending on the approximation used (*i.e.* [42] or [43]).

If looked at from the point of view of their symmetry behaviour, the orbitals ψ_J of **1** are stacked quite differently from their counterparts φ_J in **3**, **4** or **5**. This is shown qualitatively in columns I, II, III of the correlation diagram of Fig. 5. The main reason for this situation is obvious from the orbital pictures of Figs. 2 and 4. The perimeter orbitals $\psi_4 \equiv b_{1u}$ and $\varphi_7 \equiv b_{3g}$ (in D_{2h}) can mix with the bonding

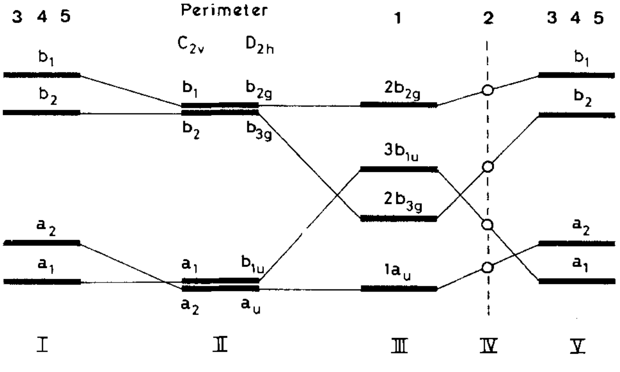


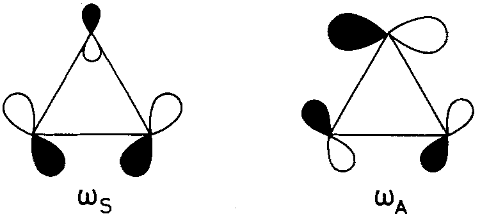
Fig. 5. *Orbital correlation diagram showing qualitatively the relative order of the four highest occupied π-orbitals in compounds* **1** *to* **5**

($\pi(B_{1u})$) or antibonding ($\pi^*(B_{3g})$) π-orbital of the central double bond in **1**, yielding $\psi_7 \equiv 3b_{1u}$ and $\psi_6 \equiv 2b_{3g}$ respectively (see Fig. 5). The orbital energies of $\pi(B_{1u})$ and $\varphi_4 \equiv$ are close together, so that the interaction of these two semi-localized orbitals leads to a destabilization of $\psi_7 \equiv 3b_{1u}$ relative to $\varphi_4 \equiv b_{1u}$. On the other hand $\pi^*(B_{3g})$ is a virtual orbital which has markedly higher energy with respect to $\varphi_7 \equiv b_{3g}$. As a consequence, interaction of $\pi^*(B_{3g})$ with the latter will yield $\psi_6 \equiv 2b_{3g}$, stabilized with respect to $\varphi_7 \equiv b_{3g}$. As we have seen, the reason for the ordering of the orbitals in **3**, **4**, and **5** is more complex, due to the interplay of various perturbations.

First ionization potentials have been calculated by *DasGupta & DasGupta* [38] using various modifications of the PPP-treatment. Their values range from 7.40 to 8.76 eV, *i.e.* are too high by 0.3 to 1.6 eV. *Müllen & Reel* [39] have given an orbital scheme for **1** which suggests the sequence (starting from HOMO) b_{3g}, b_{2g}, b_{1u}, a_u, *i.e.* at variance with that obtained in this paper.

1,6; 8,13-Cyclopropanediylidene-[14]annulene (2). – The last PE. spectrum to be discussed is that of the bridged [14]annulene **2**. The twist angles $\theta_{\mu\nu}$ of the perimeter of this hydrocarbon are presumably close to those of **3** and one might expect that the inductive and homoconjugative effects are similar in both molecules. In spite of this, their PE. spectra differ significantly, the spectrum of **2** showing features intermediate between those of the spectrum of **1** and of the spectra of **3**, **4** or **5**.

The reason is that the central cyclopropane moiety possesses high-lying *Walsh*-orbitals [44] which, to a certain extent, play the same role in **2** as the π-orbitals of the central double bond in **1**, in agreement with previous PE.-spectroscopic evidence obtained for other molecules containing three-membered rings, *e.g.* [45]. Semi-empirical and *ab-initio* calculations [44] [46] [47] indicate that these *Walsh*-orbitals can be represented qualitatively as follows:



(19)

Therefore $\omega_S(A_1)$ can interact with the perimeter orbital $\varphi_4 \equiv b_{1u}(D_{2h}) \equiv a_1(C_{2v})$ exactly like $\pi(B_{1u})$ did in **1** under D_{2h} symmetry, although to a lesser degree. The orbital $\omega_A(B_1)$ will mix with $\varphi_7 \equiv b_{3g}(D_{2h}) \equiv b_1(C_{2v})$. Because of the smallness of the coefficients of the 2p-basis orbitals at the points of attachment of the cyclopropane-moiety, the interaction of φ_7 and $\omega_A(B_1)$ will not be very important. Also, the analogy to the interaction of $\pi^*(B_{3g})$ with φ_7 in **1** breaks down, because $\omega_A(B_1)$ is a bonding orbital of roughly the same orbital energy as $\omega_S(A_1)$, whereas $\pi^*(B_{3g})$ is an antibonding one. (In cyclopropane ω_S and ω_A are degenerate, belonging to the irreducible representation E'.)

If these interactions are taken into account, then the 'observed' orbital energies of **2** can be interpolated nicely between the data for **1** and **3**, as indicated in the correlation diagram of Fig. 5 (columns III, IV, V) and also in Fig. 1:

a) The perimeter orbital $\varphi_6 \equiv b_1$ (corresponding to b_{2g} HOMO in **1**) will be still free of interaction with the high lying semi-localized orbitals of the inner island *i.e.* $\omega_S(A_1)$ or $\omega_A(B_2)$. The twist angles $\theta_{\mu\nu}$ induced by the bridging group are close to those expected for **3**, and we would therefore predict that in energy the b_1-orbital of **2** should lie close to the orbital b_1 of **3**.

b) The same reasoning applies to the perimeter orbital φ_5 which becomes $1a_u$ of **1** and a_2 in **2**, **3**, **4** and **5**. However, this is the orbital for which the energy is most sensitive to a homo-conjugative interaction between the pairs of centres 1,6 and 8,13. The resulting destabilization, which should be of roughly the same size in **2** as in **3** (perhaps slightly less), moves the energy of what was the a_u orbital in **1** into the vicinity of a_2 of **3**.

c) As discussed above, replacing the central π-orbital $\pi(B_{1u})$ of **1** by $\omega_S(A_1)$ must lead to a significant lowering of the orbital energy of what was the $3b_{1u}$ orbital in **1** for two reasons: First of all there is a net decrease in the size of the resonance integrals β which link $\omega_S(A_1)$ to the perimeter orbital $\varphi_7 \equiv a_1$ in **2**, compared to the size of the βs between the coplanar basis orbitals $\pi(B_{1u})$ and φ_7 in **1**. The reason is the tilt of the 2p-like AOs in $\omega_S(A_1)$ (see (19)). Secondly it is known from PE.-spectroscopic evidence [45] [47] that the basis energy of $\omega_S(A_1)$ is lower (*i.e.* shifted towards more negative orbital energies) than that of $\pi(B_{1u})$. This will lead to a smaller destabilization of a_1 in **2** than of $3b_{1u}$ in **1** relative to φ_7 of the unperturbed perimeter.

d) In **2** there will be less interaction, if any, between the perimeter orbital $\varphi_7 \equiv b_1(C_{2v}) \equiv b_{3g}(D_{2h})$ with the virtual antibonding *Walsh*-orbital $\omega_A^*(B_1)$, which in **2** takes the place of $\pi^*(B_{3g})$ in **1**. As a consequence, the downwards shift observed for $\psi_6 = 2b_{3g}$ in the latter molecule, relative to $\varphi_7 \equiv b_{3g}(D_{2h})$ of the perimeter, will be missing in **2**. In contrast one might expect a small destabilization of φ_7, due to the interaction with the bonding *Walsh*-orbital $\omega_A(B_1)$, which has no counterpart in **1**. However, as mentioned above, this shift is presumably rather small.

If we take these effects into account, the orbital scheme of **2** can be obtained simply by interpolation between the schemes of **1** and **3**, as shown in columns III, IV and V of Fig. 5. Comparison of this prediction with the level scheme of Fig. 1, deduced from the PE. spectra, provides convincing evidence for such an interpretation.

We believe that the rationalization of the PE.-spectroscopic data of **1** to **5** given here is at least a sound working hypothesis. Except for the unavoidable uncertainties due to the use of rather crude models, the resulting correlation is self-consistent and also in agreement with the behaviour of other 'aromatic' systems, if treated in the framework of the same set of approximations.

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251. Synthesen der Nonactinsäure

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(2. IX. 74)

Summary. Two stereoselective syntheses of nonactic acid I, the building block of the macrotetrolide antibiotic nonactin are described. The characteristic *cis*-configuration of the 2,5-substituents on the tetrahydrofuran ring of I is obtained in the first synthesis by catalytic hydrogenation of the furan derivative X. This key intermediate possesses the carbon skeleton and correct distribution of oxygen functions for conversion into nonactic acid. It is synthesized by an electrophilic substitution of 2-acetonylfuran (VI) with the N-cyclohexyl-N-propenyl nitrosonium ion (V) generated from the corresponding α-chloronitrone (VII) and silver fluoroborate, followed by hydrolysis and oxidation of the aldehyde group.

The second synthesis starts with a diol already having the correct configuration of the side chain that contains the hydroxyl group. For this purpose *threo*-1-octen-5,7-diol (XV) is synthesized from acetylacetone in two steps. Oxidative cleavage of the terminal double bond of this *threo*-diol yields an aldehyde which is converted by a Wittig reaction, with the carbanion, obtained from diethyl α-methoxycarbonylethyl phosphonate, into the open chain intermediate, 2-methyl-6,8-dihydroxy-2-nonenoic acid methylester (XVIII). Base-catalyzed cyclisation of this α,β-unsaturated dihydroxy ester yields the methyl ester of nonactic acid (I) as the main product.

In dieser Arbeit soll über zwei Synthesen der racemischen Nonactinsäure (I) berichtet werden. Diese Säure ist ein Baustein der Makrotetrolide Nonactin, Monactin, Dinactin, Trinactin, Tetranactin [1a]. Die Makrotetrolide sind mikrobielle Stoffwechselprodukte und weisen eine hohe biologische Aktivität auf, welche auf eine spezifische Komplexbildung mit Kalium-Ionen zurückgeführt wurde [1b]. Durch die Bildung der lipophilen Komplexe wird der Transport von Kalium durch Lipoid-