196. The Persistence of Ribbon Orbitals in Polycyclic Alkanes[1])

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Summary

Equivalent bond orbital (EBO) calculations by a procedure based on recalibrated, localized bond orbitals derived from an *ab initio* model, suggest that the two frontier 'ribbon' orbitals $\varphi_{\rm HOMO}$, $\varphi_{\rm HOMO\text{-}1}$ of polycyclic hydrocarbons consisting of all-*trans*-connected six-membered rings are well separated in energy from the remaining manifold of σ-orbitals. Assuming the validity of *Koopmans'* theorem, a PE-spectroscopic investigation of perhydroanthracenes, 2-methylperhydrophenalene and perhydroperylene have shown that this is indeed the case. According to the theoretical treatment these ribbon orbitals are evenly delocalized over the whole of the molecular frame and they conserve the characteristic phase relationship postulated by *Hoffmann et al.* [16] for cyclohexane moieties. Their behaviour under the successive introduction of centres of unsaturation, *i.e.* of double bonds is discussed.

Introduction. – 1. *The 2p Manifold of Bands in Hydrocarbon PE Spectra.* The spectra of saturated hydrocarbons C_nH_{2m} were first investigated systematically by *Potts, Price* and *Streets* [2] [3] using He(Iα) and He(IIα) radiation. They found that a hydrocarbon PE spectrum is divided into two parts, namely a congested system of bands in the ionization energy region ~ 10 eV $\leqslant I \leqslant \sim 16$ eV, and a more sparsely populated region ~ 17 eV $\leqslant I \leqslant 27$ eV. This subdivision is due to the fact that the 4n + 2m valence shell electrons of a saturated hydrocarbon C_nH_{2m} occupy 2n + m molecular orbitals of which the n + m higher-lying ones are of dominant C 2p character, whereas the n lower orbitals are mainly of C 2s parentage. In terms of *Koopmans'* approximation, electron ejection from the 2p dominated set of orbitals is associated with the ensemble of bands in the first interval, which is, therefore, called the '2p manifold', whereas ejection from the 2s-dominated set leads to the '2s manifold' at higher ionization energies [2].

There being n + m 2p-dominated molecular orbitals in a hydrocarbon C_nH_{2m}, the density of states δ(2p) within the 2p manifold is $\delta(2p) \approx (n + m)/6$ eV^{-1} or, to give an example, $\delta(2p) \sim 3$ eV^{-1} for a medium-size hydrocarbon $C_{10}H_{20}$. As the width at half

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[1]) *Part II of 'The Equivalent Bond Orbital Model Revisited'. Part I, cf.* [1].

height ($w_{1/2}$) of a typical σ-band in this region is about 0.7 to 1.0 eV, it is immediately obvious that the bands within the 2p manifold must strongly overlap with each other and will, therefore, merge to a rather undifferentiated band system which is usually beyond deconvolution. On the other hand, the state density is only $\delta(2s) \approx n/10$ eV^{-1} for the 2s manifold, or $\delta(2s) \approx 1$ eV^{-1} for the above example $C_{10}H_{20}$, leading to a better resolved band sequence notwithstanding the fact that the $w_{1/2}$ has now increased to > 1 eV. Typical examples can be found in [2] [3] and in the more recent compilations [4–6]. Note, however, that in the case of the normal alkanes C_nH_{2n+2} even the 2s manifold tends to merge into a single undifferentiated and thus unresolvable band system for $n > \sim 9$ [5].

Obviously, the above arguments hold only under the naive assumption of one state per *Koopmans'* configuration. In reality the number of states is much larger due to configuration interaction. However, it is still true that the over-all shape of the σ manifolds is due to those bands which correspond to the few states dominated by the *Koopmans'* configurations.

It should be mentioned that the task of identifying individual bands within the 2p manifold of a saturated hydrocarbon is complicated even more by the presence of different conformers in the target chamber of the PE spectrometer, so that the observed spectrum is the superposition (with largely unknown weights) of the individual PE spectra of these conformers. In addition, the deconvolution of the 2p manifold can be hampered by the fact that the radical cations $C_nH_{2m}^{+}$ may have an equilibrium structure far removed from that of the parent hydrocarbon which leads to broad and complicated band shapes, as exemplified by the PE spectra of CH_4 [4] [6] [7], C_2H_6 [5] [6] [8] or the lower cycloalkanes [9], the radical cations of which exhibit drastic *Jahn-Teller* distortions. Finally, the high density of the lower-lying states of the radical cations $C_nH_{2m}^{+}$, which is measured by $\delta(2p)$, *i.e.* their close proximity in energy, is very favourable for vibronic mixing, which almost completely invalidates the use of the *Koopmans'* approach, which consists in associating a given band with a particular canonical molecular orbital (CMO) φ_j, or, by extension, with a *Koopmans'* configuration in which φ_j is singly occupied.

In view of the above arguments, the *a priori* probability that anything useful could come from a PE investigation of the 2p manifold of larger hydrocarbons seems rather small, and this may be the reason why almost nothing of the sort has been attempted so far, except for some highly symmetrical, polycyclic hydrocarbons, such as adamantane [10], triasterane [11], bicyclo[2.2.2]octane [12], to give but a few examples. Indeed, what one would expect to observe, is an unresolvable 2p manifold lacking prominent features and which could, therefore, not be analyzed in a straightforward manner. Curiously enough, this is not necessarily the case, as we shall see.

2. *The EBO Model.* In the following, we rely on an equivalent bond orbital (EBO) model [13] to state the problem and to discuss the experimental results. In the particular EBO version we use [1], the valence shell CMOs $\varphi_1, \cdots \varphi_k, \cdots \varphi_{2n+m}$ of a saturated hydrocarbon C_nH_{2m} are expressed as linear combinations of localized molecular orbitals (LMO) λ_j, obtained, in principle, from the results of *ab initio* treatments of a small sample set of hydrocarbons:

$$\lambda = \varphi L. \tag{1}$$

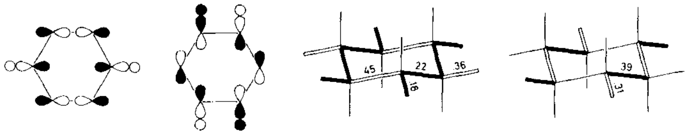
In (*1*), $\lambda = (\lambda_1 \cdots \lambda_{2n+m})$ is the row vector of the LMOs, $\varphi = (\varphi_1 \cdots \varphi_{2n+m})$ that of the CMOs, and $\boldsymbol{L}$ stands for the transformation matrix satisfying some localization criterion [14] (*e.g.* the one proposed by *Foster & Boys* [15]), as well as the condition $\boldsymbol{L}\boldsymbol{L}^t = \mathbf{1}$. Thus the LMOs λ_j form an ortho-normal set. In the case of saturated hydrocarbons only two types of LMOs are encountered: λ_{CC} and λ_{CH}, localized mainly on a C–C or C–H σ-bond, respectively. Examination of the *Fock* matrix in localized basis,

$$\boldsymbol{L}^t\boldsymbol{F}_\varphi\boldsymbol{L} = \boldsymbol{F}_\lambda = (\langle\lambda_i|\hat{\mathrm{F}}|\lambda_j\rangle), \tag{2}$$

reveals that only a limited set of matrix elements $\langle\lambda_i|\hat{\mathrm{F}}|\lambda_j\rangle$ needs to be retained in $\boldsymbol{F}_\lambda$ so that its diagonalization yields orbital energies ε_j of sufficient precision for use in the assignment of PE spectra within *Koopmans* approximation. Also, the model can be easily parametrized with respect to a given calibration set of hydrocarbons. For further details *cf.* [1].

Here we use the $A\Gamma$ version of the EBO model, which means that the *Fock* matrix $\boldsymbol{F}_\lambda$ includes *a*) the self energies A_{CC} and A_{CH} of the LMOs λ_{CC}, λ_{CH}, *b*) the geminal interaction terms B_{ij} for two LMOs λ_i, λ_j with a common C centre, and *c*) the vicinal interaction terms Γ_{ij}, for a pair of LMOs λ_i, λ_j separated by one bond. All other matrix elements of $\boldsymbol{F}_\lambda$ are set equal to zero.

3. Hoffmann's *Ribbon Orbital Concept.* It has been argued by *Hoffmann et al.* [16] that the two highest occupied CMOs φ_{HOMO}, φ_{HOMO-1} of a six-membered C ring are crucial for the interaction of such a cyclohexane moiety with other groups in a given molecule (*e.g.* groups at C(7) in a norbornane derivative). These two highest CMOs, which possess characteristic symmetry properties, have been called 'ribbon orbitals'. Their shapes and phase relationships are shown in (*3*), on the left side in terms of the dominating atomic orbitals [16] and on the right side in the form of the fully equivalent linear combination of LMOs λ_{CC} and λ_{CH}.



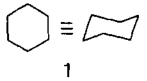
(3)

In (*3*) and in all the subsequent orbital diagrams, open and full bonds refer to LMOs λ_μ of opposite phase, and the numbers to the absolute values $|c_{\mu j}|$ of the coefficients in the linear expansion

$$\varphi_j = \Sigma_\mu c_{\mu j}\lambda_\mu. \tag{4}$$

LMOs λ_μ affected with coefficients $|c_{\mu j}| < 0.1$ have been neglected. Their position is indicated by a thin line, independent of phase, the latter being uncertain in view of the small size of $|c_{\mu j}|$.

In the particular case of cyclohexane (**1**), the ribbon orbitals φ_{HOMO}, φ_{HOMO-1} (*3*) are degenerate under D_{3d} symmetry and yield the $4e_g$ orbital pair. The corresponding double band ① ② in the PE spectrum of **1**, associated with the $4e_g^{-1}$ ionization process, is split into two maxima at 10.3 eV and 10.9 eV [6] due to the *Jahn-Teller* effect. Bands ① ② overlap band ③ (11.4 eV) which is assigned to electron ejection from the CMO $4a_{1g}$ (*cf.* [1] and ref. therein). Thus, there is an experimentally observed gap of ~ 0.5 eV between the ribbon orbitals and the remaining stack of CMOs in **1**.



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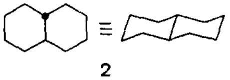

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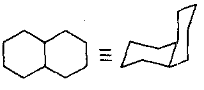

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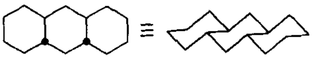

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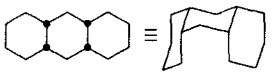

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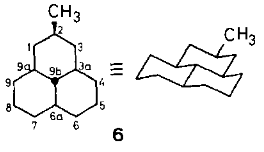

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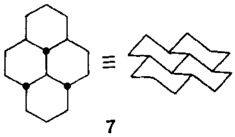

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According to the arguments presented above, we would expect that increasing the size of the hydrocarbon, *e.g.* according to **1**→decaline (**2**)→perhydroanthracene (**4**), should lead to an increased crowding of the orbitals in the 2p manifold and thus to a reduction of the gap between the CMOs φ_{HOMO}, $\varphi_{HOMO\text{-}1}$ and the remaining CMOs.

In contrast to this perhaps naive expectation, an EBO calculation of the CMOs of such polycyclic hydrocarbons strongly suggests that this should not be the case. It is

Table 1. *Orbital Energies $-\varepsilon_j$/eV of the Hydrocarbons* **1**–**7**, *Calculated by the AΓ Version of the EBO Model Proposed in* [1]. Only the top 8 occupied molecular orbitals are given.

1 (D_{3d})		**2** (C_{2h})		**3** (C_2)		**4** (C_{2h})		**5** (C_s)		**6** (C_s)		**7** (C_{2h})	
Sym.	$-\varepsilon_j$/eV	Sym.	$-\varepsilon_j$/eV	Sym.	$-\varepsilon_j$/eV	Sym.	$-\varepsilon_j$/eV	Sym.	$-\varepsilon_j$/eV	Sym.	$-\varepsilon_j$/eV	Sym.	$-\varepsilon_j$/eV
e_g	10.83	b_g	10.18	a	10.24	b_g	9.88	a″	10.09	a′	9.85	a_g	9.66
		a_g	10.27	a	10.24	a_g	10.04	a′	10.11	a″	9.86	b_g	9.71
a_{1g}	11.23	a_g	10.82	b	10.56	a_g	10.66	a′	10.32	a′	10.58	a_g	10.50
e_u	12.50	a_u	11.58	b	11.58	a_u	10.92	a″	10.82	a″	11.18	a_u	10.90
		a_u	11.80	a	11.81	b_u	11.25	a″	11.13	a′	11.33	b_u	11.08
a_{1u}	12.73	b_u	11.95	b	11.90	a_u	11.26	a′	11.43	a″	11.44	a_u	11.32
e_g	13.33	b_u	12.40	a	12.16	a_g	11.90	a′	11.92	a′	11.76	b_u	11.42
		a_u	12.45	b	12.43	b_u	12.02	a″	11.94	a″	11.95	a_u	11.84

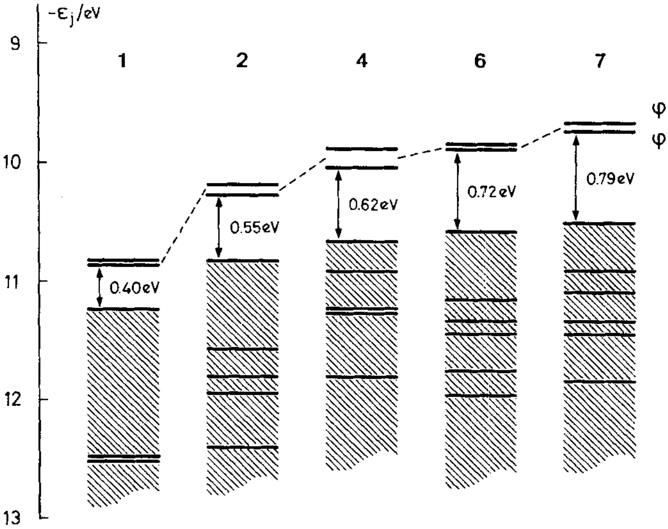


Fig. 1. *Orbital diagram of the canonical orbitals of the hydrocarbons* **1**, **2**, **4**, **6** *and* **7** (*cf.* *Table 1*)

predicted that φ_{HOMO} and $\varphi_{\mathrm{HOMO\text{-}1}}$ conserve their characteristic phase relationship and that they tend to float above the sea of the lower-lying CMOs. This is shown in *Table 1* (and *Fig. 1*), where the orbital energies ε_j derived from the AΓ version of the EBO model [1] are presented for **1** and the polycyclic hydrocarbons *trans*-decaline (**2**), *cis*-decaline (**3**), *trans-cisoid-trans*-perhydroanthracene (**4**), *cis-cisoid-cis*-perhydroanthracene (**5**), 2-methylperhydrophenalene (**6**), perhydropyrene (**7**), the latter two in the configurations depicted. (Concerning the configuration of **6**, see below.) According to *Fig. 1*, the calculated energy gap Δ between the two highest occupied CMOs and the rest, increases from $\Delta = 0.40$ eV for **1** to $\Delta = 0.79$ eV for **7** *i.e.* with increasing number of *transoid*-connected cyclohexane rings. However, it should be noted that this predicted increase in Δ does not, by itself, guarantee that a corresponding gap can be observed in the PE spectrum between the first two bands ① ② and the remaining band system. This will only be the case if the two bands ① ② associated with the $\varphi^{-1}_{\mathrm{HOMO}}$ and $\varphi^{-1}_{\mathrm{HOMO\text{-}1}}$ ionization processes have relatively small $w_{1/2}$-values, which requires that these two processes occur with only minor changes in molecular geometry.

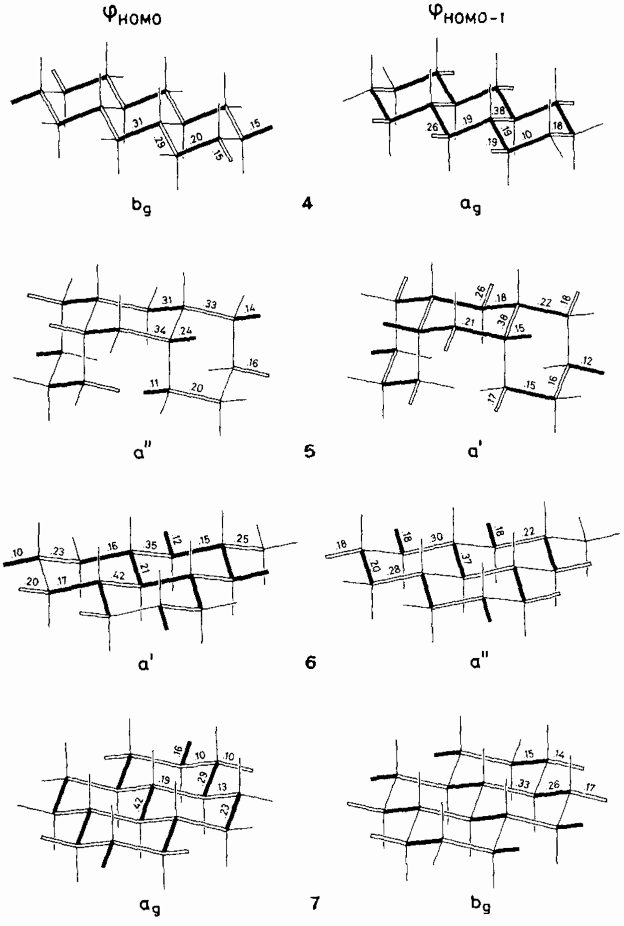
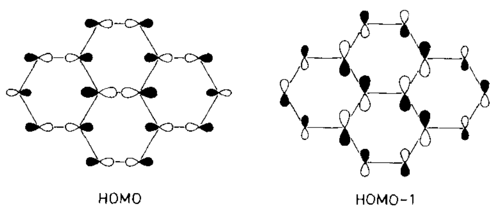


Fig. 2. *Diagrams of the two highest occupied canonical orbitals* φ_{HOMO}, $\varphi_{HOMO\text{-}1}$ (ribbon orbitals) *of the hydrocarbons* **4**–**7**, *given as linear combinations of the C–C and C–H LMOs*. Open and full bonds refer to LMOs of opposite phase. The numbers given are the absolute values $|c_{\mu j}|$ of the expansion coefficients, if $|c_{\mu j}| > 0.1$. LMOs affected with coefficients $|c_{\mu j}| < 0.1$ are indicated by thin lines, irrespective of sign.

The frontier orbitals φ_{HOMO}, $\varphi_{\mathrm{HOMO\text{-}1}}$ of **4**–**7** are shown in *Fig. 2*, the meaning of the bond types and numbers being the same as in (*3*). Two observations are relevant for our discussion. First, we note that the typical ribbon orbital pattern shown in (*3*) for **1** is maintained practically unchanged for each individual cyclohexane moiety of the polycyclic systems **2**—**7**. This becomes even more obvious if, for example, the $\varphi_{\mathrm{HOMO}}(a_g)$ and $\varphi_{\mathrm{HOMO\text{-}1}}(b_g)$ of **7** are redrawn schematically in the equivalent, but perhaps more familiar form shown in (*5*). Secondly, the orbitals φ_{HOMO}, $\varphi_{\mathrm{HOMO\text{-}1}}$, and consequently the positive hole of the radical cations produced by a $\varphi^{-1}_{\mathrm{HOMO}}$, $\varphi^{-1}_{\mathrm{HOMO\text{-}1}}$ ionization process is smoothly delocalized over the molecular frame. Therefore, removal of an electron from one or the other of the ribbon orbitals will lead to only small changes in bond population and, therefore, to small differences between the equilibrium geometries of the neutral hydrocarbon and the radical cation. Thus, in the absence of symmetry conditioned *Jahn-Teller* effects (*e.g.* **1**) the adiabatic vertical ionization processes will be close in energy to the vertical ones and the $w_{1/2}$-values of the bands ① ② are expected to be smaller than usual for hydrocarbons. Under these conditions it should be possible to observe the predicted gap Δ in the PE spectra of such molecules as **4**, **6** or **7**.



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The He(Iα) PE Spectra of Some Polycyclic Hydrocarbons. – The He(Iα) PE spectra of the hydrocarbons **4**–**7** are shown in *Fig. 3* (recording temperatures ~ 30° to 40°). He(Iα) and He(IIα) PE spectra of **1**–**3** have been published previously [4].

cis-cisoid-cis-Perhydroanthracene (**5**) was obtained by catalytic hydrogenation of either anthracene or 1,4,5,8,9,10-hexahydroanthracene. From **5**, the *trans-cisoid-trans*-isomer **4** was prepared according to procedures described in [17]. Their structure was confirmed by comparison with the data in [17], in particular their ^{13}C-NMR spectra [18]. The sample of 2-methylperhydrophenalene (**6**) was unintentionally obtained by treating **5** at room temperature with $AlCl_3$ in hexane solution for 7 days. Its structure has been established by ^{13}C-NMR spectroscopy on the basis of the number of observed signals and their relative intensities. Further support comes from the multiplicities obtained in the ^{1}H-coupled spectrum and the increment scheme developed for ^{13}C chemical shifts of polycyclic perhydro aromatics by *Dalling & Grant* [18]. The latter comparison also establishes the thermodynamically favoured all-*trans*-configuration with an equatorial Me-group. Accordingly, the linewidths of the ^{13}C signals of **6** were found temperature-independent down to –60°. The relevant data are collected in *Table 2*.

Table 2. *Calculated and Observed $\delta(^{13}C)$ Values*[a]*, ^1H Multiplicities*[b]*, and Relative Intensities for 2-Methylperhydrophenalene* (**6**)

	CH_3	C(5, 8)	C(2)	C(4, 9) C(6, 7)	C(9a, 3a)	C(6a)	C(1, 3)	C(9b)
δ_{exp}	22.80	26.09	32.05	$\overbrace{34.36,\ 34.42}$	41.39	41.57	43.25	53.31
δ_{calc}	24.56	27.23	33.95	35.25, 35.25	43.23	43.23	43.27	52.51
Multiplicity	*q*	*t*	*d*	*t,t*	*d*	*d*	*t*	*d*
Rel. intensity	1	2	1	2,2	2	1	2	1

[a] In ppm, rel. to int. TMS. [b] *d* = doublet, *t* = triplet, *q* = quadruplet.

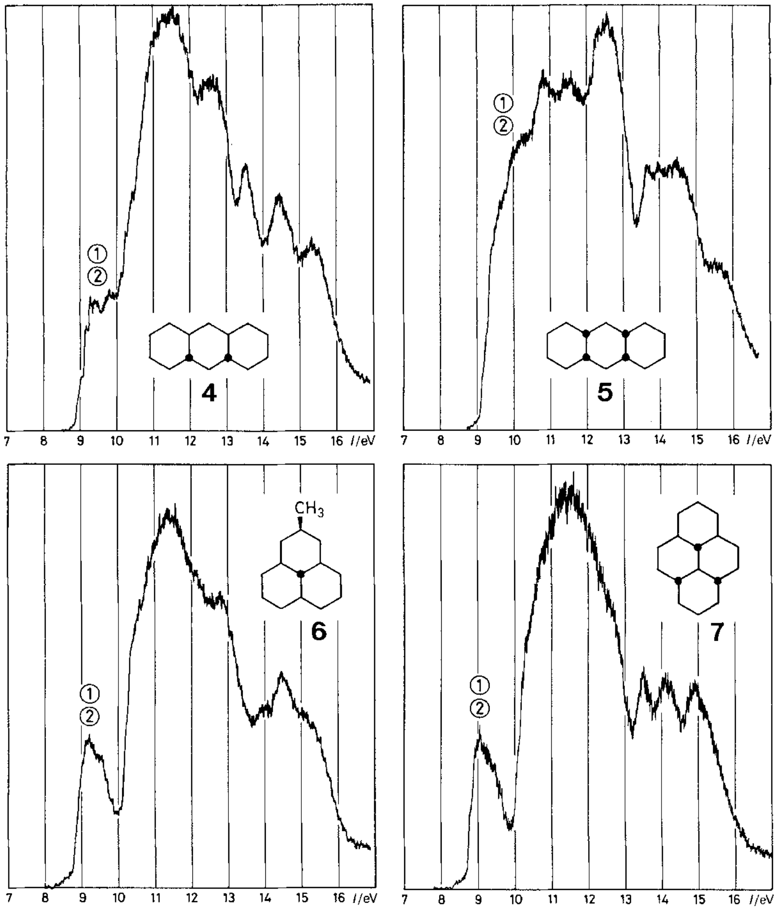

Fig. 3. *He(Iα) PE spectra of the polycyclic hydrocarbons* **4**–**7**

A definite proof of structure **6** by X-ray analysis was not possible because of the poor quality of the crystals (m.p. 31–34°). However, the PE evidence to be discussed below fully supports the conclusions drawn from the ^{13}C-NMR data in favour of the postulated configuration.

Discussion. – The obvious result of our experiment is that the predicted gap Δ between the positions I_1^m, I_2^m of the φ_{HOMO}^{-1}, φ_{HOMO-1}^{-1} bands ① ② and the I_j^m of the remaining σ^{-1}-bands can indeed be observed in the PE spectra of hydrocarbons such as **4**, **6** or **7** in which all rings are *trans*-fused, Δ increasing with increasing size of the molecules. Changing the configuration at a ring junction from *trans* to *cis*, *e.g.* going from **4** to **5**, will lead to a substantial reduction of Δ *(cf. Fig. 3)*, in accord with the theoretical calculations *(cf. Table 1)* where a reduction from Δ(**4**) = 0.62 eV to Δ(**5**) = 0.21 eV is predicted.

In terms of *Koopmans'* approximation the two ribbon orbitals φ_{HOMO}, φ_{HOMO-1} are, therefore, a pair of rather individualistic orbitals, well separated from the remaining, closely spaced stack of σ-orbitals and giving rise to bands at rather low ionization energies. For instance, we find for **7** $I_1^m \approx 9.0$ eV, which is smaller than, *e.g.*, the first π^{-1} ionization energy of benzene. This suggests that the ribbon orbitals are good donator orbitals and that they must play an important, if not dominant role in intramolecular charge transfer (CT) processes, as was indeed assumed previously by *Hoffmann et al.* [16]. Intermolecular charge transfer, involving an appropriate acceptor molecule, is of course strongly hampered by the axial C–H bonds of the hydrocarbon molecule, which keep potential acceptors at such distances from the C–C σ-frame of the hydrocarbon that the relevant donator-/acceptor-orbital overlap remains negligibly small and that the CT *Coulomb* term becomes rather large. Both these effects prevent substantial CT interaction [19]. For example no trace of a CT absorption band in the UV/VIS region could be observed for the donator/acceptor pairs **7**/tetrakis(perfluorocyclobuta) cyclooctatetraene or **7**/tetracyanoethylene, even if the compounds were mixed neat [20].

There is little doubt that the high-lying ribbon orbitals φ_{HOMO}, $\varphi_{\mathrm{HOMO\text{-}1}}$ play an important role for the 'through bond' interaction [21] of two (semi)localized orbitals imbedded in a large σ-frame (for striking examples see [22]) because they are *a*) close in energy to the usual target orbitals (double bond π- or lone-pair orbitals), and *b*) because they are ideally delocalized over the whole of the connecting σ-frame. This makes them ideal 'relay orbitals' [23], provided that they yield significant cross terms with the target orbitals.

In this connection, an observation by *Veszprémi* [24] is of interest. Analyzing the PE data of aromatic hydrocarbons [25] with the help of modified CNDO/S calculations [26], he found that the positions of the σ-bands in the acene PE spectra, which can also be identified by *Penning* ionization electron spectroscopy [27], fall into a simple pattern if plotted as a function of the number of catacondensed rings. In fact, this pattern is rather similar to the one obtained for the π-bands [28], albeit shifted towards higher ionization energies by about 4 eV. According to this analysis the first σ-band of naphthalene (b_{1g}^{-1}) occurs near 11 eV, that of anthracene (b_{1g}^{-1}) near 10.8 eV [27]. In other words, applying *Koopmans'* theorem in reverse, the original ribbon orbitals of the saturated hydrocarbons **2** and **4** have been shifted in naphthalene and anthracene by roughly –1 ½ to –2 eV. This raises the question if this 'sinking' of the ribbon orbitals φ_{HOMO}, $\varphi_{\mathrm{HOMO\text{-}1}}$ can be followed quantitatively, *e.g.* as a function of the number of double bonds introduced into the hydrocarbon and whether these orbitals keep their individuality.

A complete series of hydrocarbons for which the experimental data are known is presented in *Fig. 4*. The removal of an electron from the $4e_g$ ribbon orbitals (*3*) of **1** leads to a *Jahn-Teller* unstable state of the radical cation $\mathbf{1}^+$ and thus to the typical double band ① ② at $I_1^m = 10.3$ eV, $I_2^m = 10.9$ eV [4] [6]. The negative mean value –10.6 eV is assumed to be representative for the orbital energy of the $4e_g$ pair. Introducing a double bond into **1** to yield cyclohexene **8** shifts the first two σ-bands in the PE spectrum to 10.7 and 11.3 eV [4] [29], suggesting a mean ribbon orbital energy of –11.0 eV. The corresponding bands in the PE spectra of the isomers 1,3-cyclohexadiene (**9**) and 1,4-cyclohexadiene (**10**) are found at 11.3 eV, 11.8 eV [4] and 11.0 eV, 12.0 eV [29] [30], respectively. Although the split between the two bands is twice as large for **10** than for **9**, their mean values 11.5_5 eV, 11.5_0 eV agree within the limits of error. Finally, in '1,3,5-cyclohexatriene' (**11**), the ribbon orbitals are degenerate, *i.e.* they form the e_{2g} σ-orbitals of benzene. Electron ejection from this pair of orbitals yields the *Jahn-Teller*-broadened band at 11.5 eV to ~ 12.3 eV in the PE spectrum of benzene [6] [31],

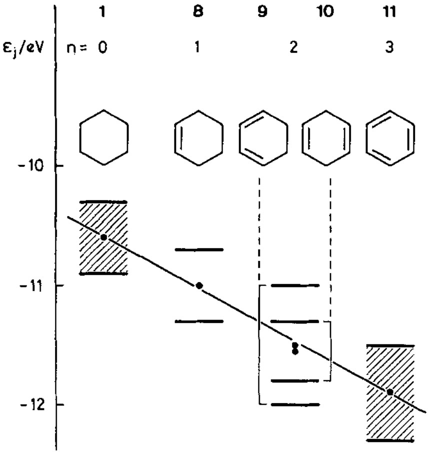

Fig. 4. *Dependence of the mean ribbon-orbital energy on the number n of double bonds in the series cyclohexane* (**1**) *to '1,3,5-cyclohexatriene'*

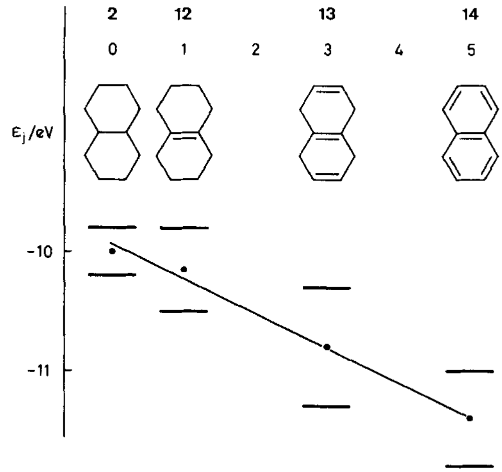

Fig. 5. *Dependence of the mean ribbon-orbital energy on the number n of double bonds in the series* trans-*decaline* (**2**) *to naphthalene* (**14**)

with a mean value of ~ 11.9 eV. As can be seen from *Fig. 4*, the mean ribbon orbital energies depend linearly on the number n of double bonds in the 6C-molecules **1**, and **8** to **11**. The observation that the e_{2g} orbital energy of **11** does not deviate significantly from the linear regression shown in *Fig. 4* is explained by the fact that the LMO self-energies A_{CC} of C–C bond orbitals λ_{CC} which are derived from *ab initio* treatments are practically linear functions of the C–C-bond lengths in the interval 133 pm to 154 pm [32]. From *Fig. 4* one deduces that replacing three of the six C–C bonds of **1** by double bonds, lowers the (mean) ribbon orbital energy by −1.3 eV, or expressed differently, shortening a C–C σ-bond from 154 pm ($sp^3 - sp^3$) to 133 pm ($sp^2 - sp^2$) seems to lower the self energy A_{CC} by −2.6 eV. In fact, the problem is slightly more complicated because of the concommitant changes of the cross-terms between pairs of LMOs [32].

As a control we show in *Fig. 5* the analogous, albeit incomplete series of hydrocarbons from *trans*-decaline (**2**) to naphthalene (**14**). The mean positions of the first two σ-bands in the PE spectra of the monoene **12** (9.8 eV; 10.5 eV), of the triene **13** (10.3 eV; 11.3 eV) [30] and of naphthalene **14** (b_{1g}: 11.0 eV; a_g: 11.8 eV) [24] [25] interpreted as negative orbital energies again fall on a straight line if plotted as a function of the number n of double bonds. The lowering of the ribbon orbital energy, going from **2** to **14**, is found to be −1.4 eV, in excellent agreement with the previous value of −1.3 eV. The PE bands corresponding to the two highest occupied σ-orbitals of anthracene are observed at 10.8 eV (b_{1g}) and 11.2 eV (a_g) [24], yielding an estimate of −11.0 eV for the mean ribbon orbital energy. On the other hand bands ① ② of **4** cluster around 9.6 eV (*cf. Fig. 2*), which leads again to a lowering of −1.4 eV of the ribbon orbital energy when half of the C–C σ-bonds of **4** are replaced by shorter double bonds. The observation that this shift is independent (within the limits of error of the method) of the size of the parent compound **1**, **2**, **4**, is an indication that the ribbon orbitals are rather evenly delocalized over the molecules as shown in *Fig. 3*.

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