Photoelectron Spectra of Polynuclear Aromatics. IV. The Helicenes

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Abstract. Experimental π IP's for phenanthrene and its benzologues up to [14]helicene are reported along with the results of Hückel calculations, with resonance integrals modified so as to mimic the available X-ray geometries of these molecules. The energies of the two uppermost π levels were found to lie on two smoothly descending lines, both of which show a tendency to converge to about 6.8 eV; their energy difference decreases from 0.3 eV in phenanthrene to practically zero in the molecules beyond [7]helicene. Provisional assignments imply substantial σ–π mixing, resulting in a low-energy shift of all π bands, and lead to the conclusion that the transannular interaction term between the π AO's of superposed benzene rings is much smaller than found in the cyclophanes. The π levels overlap with the σ manifold to a similar extent as in planar aromatics, with roughly two-thirds of all π ionizations preceding the first σ band. Using empirical correlations deduced in a related paper between the first two IP's and the singlet–singlet excitation energies, the optical spectra are analyzed and the α, p, and β bands located.

The present photoelectron spectroscopic study of the helicenes synthesized in recent years by Martin et al.[1,2] in Brussels was undertaken in an attempt to detect interactions between the π orbitals of overlapping benzene rings, a question about which only tentative statements could be made on the basis of previous X-ray,[3-5] optical,[6-8] and circular dichroism[7-9] investigations. Evidence for the existence of such interactions has earlier been adduced in photoelectron studies of cyclophanes;[10,11] in the spectra of these molecules, bands originating from symmetry-equivalent, formally degenerate π orbitals of the benzene rings were found to be split due to transannular π–π overlap.

Further interest in the photoelectron spectra of the helicenes stems from the fact that the optical spectra of the higher homologs[12] are very congested and do not readily lend themselves to an experimental analysis, using, for example, fluorescence polarization, intensity criteria, and trends in band position within related series. As a consequence, little is known about the sequence and location of the α, p, β, and β' states (^1L_b, ^1L_a, $^1B_{a,b}$ in Platt's notation) in the molecules beyond [7]helicene, although this information is a prerequisite for an understanding of their chiroptical properties. Current semiempirical schemes, as typified by PPP, have not yet progressed to a stage where they can predict the main features of the optical spectra of nonplanar aromatics so that doubt attaches as to the assignments advanced so far for the higher homologs.

In unravelling diffuse optical spectra, photoelectron spectroscopy may be used to good advantage, provided that the first few IP's and the symmetries of the pertinent states can be identified.[13] As will be shown below, the photoelectron spectrum of the largest molecule studied here, [14]helicene, exhibits at least six bands, whereas the optical spectrum consists of only one broad, structureless feature, due to the merging of the individual bands and the strong geometry changes that follow electronic excitation. For obvious reasons, these geometry changes are much more pronounced in optical than in photoelectron spectroscopy so that genuinely broader bands are obtained.

Finally, by comparing the photoelectron spectra of the helicenes with those of suitable planar models we should be able to assess the extent of σ–π interaction in these nonplanar hydrocarbons, a topic of some recent interest.[6,8,22,23]

Experimental Section

All photoelectron spectra were recorded with a Perkin-Elmer PS-16 spectrometer equipped with a heatable inlet system. To avoid catalytic decomposition of the higher homologs on the hot walls of the target chamber, all copper parts were first coated with gold, then with rhodium, finally with colloidal graphite (Aquadag). Apart from increasing the sensitivity, this also improved the resolution to ca. 14 meV for the Ar doublet and to ca. 21 meV for the $^2E_{3/2}$ MeI peak. Energies were measured relative to Arα (15.76 eV), Xeα (12.13 eV), Xeβ (10.26 eV), and the first pentacene peak at 6.68 eV.

The spectrum of the least volatile compound, [14]helicene, was taken at 340°. That no decomposition took place could be confirmed from the fact that the materials recovered from the analyzer plates gave photoelectron spectra identical with those of authentic specimens; the only contaminant was vacuum pump oil.

Results and Description of the Spectra

Vertical π IP's along with the molecular orbital assignments (which will be discussed in the next section) are listed in Table I. For comparison the data for benzene (from ref 15), naphthalene (from ref 16), phenanthrene (cf. also ref 17 and 18), and 3,4-benzophenanthrene (cf. also ref 19) are given. The spectra themselves will appear in the microfilm edition.

In the molecules beyond [5]helicene, the assignments set out in Table I should be regarded as provisional, pending the results of more elaborate MO calculations of less empirical character. At this writing, no ab initio results for molecules larger than phenanthrene[20] have been published.

In the case of the first band of [5]helicene, it is not clear whether the shoulder at 7.7 eV represents a separate ionization process or the 1–0 vibrational component of the first peak at 7.57 eV. We prefer the former assignment because vibrational spacings in the PE spectra of aromatics[14] never exceed 1400 cm^{-1} = 0.17 eV. In the higher homologs, identification of the individual vertical π IP's becomes increasingly more difficult because bands due to ionization from close-lying levels could not be resolved. We feel that in such cases a discussion of the level ordering should be reserved until further data become available. Unfortunately, the technique of photoemission from organic crystals (which would permit these materials to be studied at room temperature) is still in an infantile stage.[21]

The principal qualifications to the spectra are as follows. In the planar reference molecules, benzene and naphthalene, the first band is by far the strongest, and the 0–0 vibrational peak is extremely sharp, with a full width at half-maximum intensity comparable to that of the rare gases. In phenanthrene and 3,4-benzophenanthrene it is the second band which dominates the spectra, and the vibrational

Table I. Vertical π IP's in eV, with Molecular Orbital Assignments[a]

Hydrocarbon	Ionization potentials														
Benzene	9.24	12.25													
	$1e_{1g}$	$1a_{2u}$													
Naphthalene	8.15	8.87	10.08	10.83											
	$1a_u$	$2b_{1u}$	$1b_{2g}$	$1b_{3g}$											
Phenanthrene	7.86	8.15	9.28	9.89	10.59										
	$4b_1$	$3a_2$	$2a_2$	$3b_1$	$2b_1$										
3,4-Benzophenanthrene	7.62	8.02	8.97	9.17	9.95	10.22									
	$5b_1$	$4a_2$	$3a_2$	$4b_1$	$3b_1$	$2a_2$									
[5]Helicene	7.51	7.7	8.30	8.82	9.48	9.77	9.98	10.63							
	5a	6b	5b	4a	3a	4b	3b	2a							
[6]Helicene	7.37	7.5	8.18	8.3	8.97	9.53	9.74	9.94	10.5						
	7b	6a	6b	5a	4a	5b	3a	4b	3b						
[7]Helicene	7.25	7.4	7.73	8.13	8.65	8.75	9.45	9.74	9.9						
	8b	7a	6a	7b	6b	5a	4a	5b	4b						
[8]Helicene	7.15	7.15	7.6	7.73	8.31	8.54	9.03	9.36	9.54	9.90					
	9b	8a	8b	7a	6a	7b	6b	5a	4a	5b					
[9]Helicene	7.07	7.07	7.67	8.08	8.08	8.63	9.04	9.26	9.61	9.61	9.88				
	10b	9a	9b	8a	7a	8b	7b	6a	6b	5a	4a				
[10]Helicene	6.99	6.99	7.32	8.04	8.04	8.50	8.50	9.03	9.41	9.41	9.79	9.79			
	11b	10a	9a	10b	9b	8a	7a	8b	7b	6a	5a	6b			
[11]Helicene	6.95	6.95	7.2	7.68	7.95	8.2	8.69	8.69	9.15	9.49	9.49	9.6			
	12b	11a	10a	11b	10b	9a	9b	8a	8b	7a	7b	6a			
[12]Helicene	6.93	6.93	7.2	7.71	7.71	8.08	8.08	8.51	8.84	9.28	9.4	9.66	9.66		
	13b	12a	12b	11a	10a	11b	10b	9a	8a	9b	8b	7a	6a		
[13]Helicene	6.91	6.91	7.16	7.44	7.75	8.06	8.06	8.39	8.39	8.81	9.20	9.20	9.64	9.64	9.8
	14b	13a	13b	12a	12b	11a	10a	11b	10b	9a	8a	9b	8b	7a	6a
[14]Helicene	6.88	6.88	7.1	7.46	7.46	7.99	7.99	8.2	8.67	8.67	9.05	9.3	9.55		
	15b	14a	13a	14b	13b	12a	11a	12b	11b	10a	9a	10b	8a		

[a] Symmetry labels refer to D_{6h} in benzene, to D_{2h} in naphthalene, to C_{2v} in phenanthrene and 3,4-benzophenanthrene, and to C_2 in the homologs.

peaks in the first band show distinct broadening; concomitantly, the 1-0 peak is enhanced in intensity at the expense of the 0-0 peak. Progressive benzo annelation with consequent out-of-plane distortion has the effect of suppressing the intensity of all π bands relative to the σ band system; the π bands assume a more symmetrical shape and the vibrational structure is completely blurred, indicating substantial geometry changes upon ionization and excitation of low-frequency skeletal and torsional modes. Part of the broadening is certainly due to the fact that vibrationally excited states of the molecules are sufficiently populated at the high temperatures employed here so that hot bands precede the apparent 0-0 peak.

Analysis of the Spectra

The question of σ-π mixing in the helicenes is a longstanding, much debated problem, discussed by Moscowitz,[22] El-Sayed,[6] and, more recently, Wagnière[23] and Mason.[8] With the advent of semiempirical all-electron procedures of the EHT, CNDO, and MINDO type, there is, in principle, no need to introduce assumptions as regards σ-π separability in overcrowded hydrocarbons. Experience has shown,[16,14] however, that these schemes suffer from a number of shortcomings, notably the presence of spurious high-lying σ levels so that grossly exaggerated σ-π interaction is anticipated. It is therefore only hoped that the analysis given below will be considered as a basis for future work, in particular for better calculations of less empirical character.

Four simple π electron models, all of which follow the usual Hückel conventions, have been examined. The first disregards all complications due to breakdown of σ-π separability, bond shortening, stretching, and torsion. In the second model the effect of double-bond fixation on the π levels is investigated, and in the third all these factors are simultaneously taken into account. In the fourth model, the transannular (through-space) interaction between the π levels of overlapping benzene rings is accounted for by means of a first-order perturbation treatment, in addition to the above factors.

Band assignments were made by minimizing the differences between calculated and observed vertical π IP's, the band intensities being used to assess the number of MO's to be assigned to a given band.

Model A. Zero-Order Hückel. The regression of the observed band positions on the Hückel eigenvalue coefficients x_i, calculated with all $\beta_{\mu\nu} = 1$, is shown in Figure 1. The eigenvalue coefficients have been scaled according to: $\mathrm{IP}_i(\mathrm{eV}) = (5.605 \pm 0.092) + (3.001 \pm 0.091)x_i$; $\mathrm{SE(IP)} = 0.160$ eV, where the 95% confidence limits refer to 110 degrees of freedom (Student's t test). Given the crudeness of the theory and the many approximations involved in applying it to nonplanar aromatics, the least-squares fit is surprisingly good. The standard deviation, SE(IP), is comparable to that obtained in an earlier[14] photoelectron study of planar aromatics, where the following regression parameters and 95% confidence limits, for 434 degrees of freedom, have been found: $\mathrm{IP}_i(\mathrm{eV}) = (5.925 \pm 0.048) + (2.880 \pm 0.046)x_i$; $\mathrm{SE(IP)} = 0.171$ eV. In accord with expectation, the intercept (minus Hückel's α) has a different value in the two classes of aromatics. (Note, that the difference in the slope, which corresponds to minus Hückel's β, is not significant at the 95% security level.)

Model B. Hückel with First-Order Double Bond Fixation. In earlier studies of planar aromatics[14,16,19] it was found that an improved correlation with experiment can be obtained if the Hückel resonance integrals are made self-consistent with respect to bond orders. The improvement was particularly striking in the acene series, but less pronounced in angular annelated aromatics, as typified by the phenes. Applying this scheme to the helicenes yields: $\mathrm{IP}_i(\mathrm{eV}) = (5.303 \pm 0.094) + (3.396 \pm 0.097)x_i$; $\mathrm{SE(IP)} = 0.150$ eV. The corresponding least-squares regression for the planar aromatics was as follows:[14] $\mathrm{IP}_i(\mathrm{eV}) = (5.686 \pm 0.040) + (3.218 \pm 0.039)x_i$; $\mathrm{SE(IP)} = 0.133$ eV. Thus, double-bond fixation in the helicene series can hardly be said to improve the correlation. This is not surprising, considering the con-

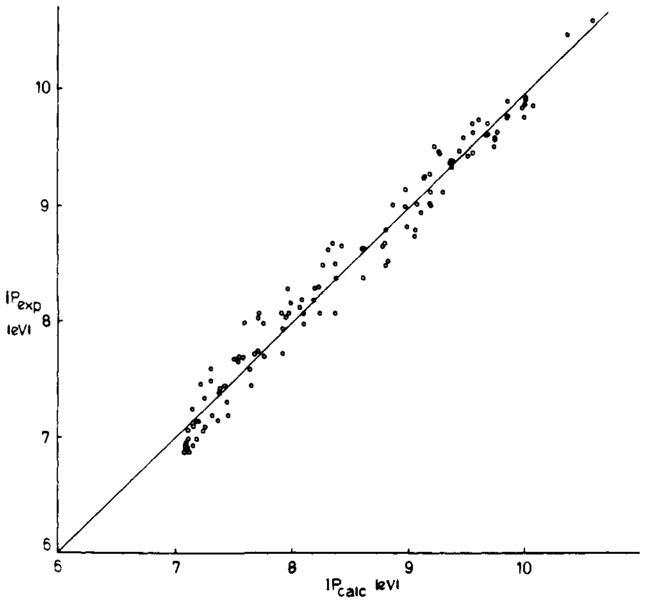


Figure 1. Least-squares regression of the observed vertical π IP's of [5]- to [14]helicene on the calculated π IP's according to model A.

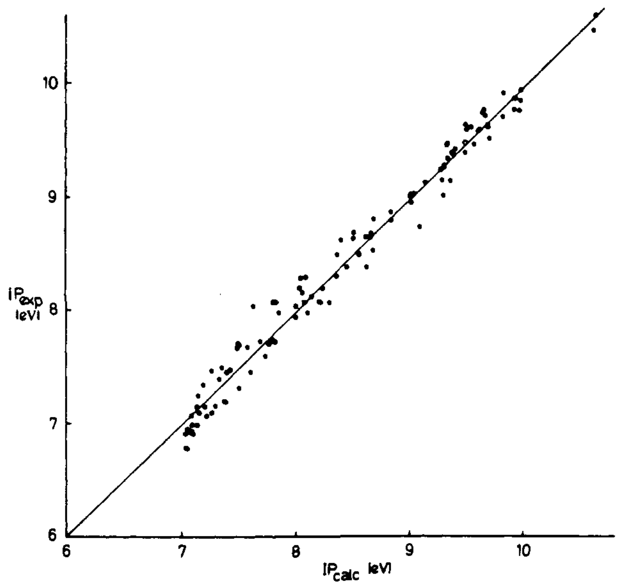


Figure 2. Least-squares regression of the observed vertical π IP's of [5]- to [14]helicene on the calculated π IP's according to model D.

straints imposed upon the geometry (and consequently, the bond orders) of these molecules due to their helical structure. Note, again, that the α and β parameters differ in the two classes of compounds.

Model C. Refined Scheme. In order to investigate the effect of bond shortening, stretching, and torsion, Hückel calculations have been carried out with π resonance integrals modified so that they mimic the distorted geometries of these molecules. A consistent feature of the X-ray structure determinations published so far[4] is the stretching of the inner-core CC bond lengths and the shortening of the peripheral CC bond lengths; in [6]helicene, these two bond lengths measure 1.437 and 1.334 Å, respectively. We have assumed that these features persist in the higher homologs (for which no X-ray data are available to date), and have adjusted the π resonance integrals according to $\beta_{\mu\nu} = \beta_{\mu\nu}{}^0 S_{\mu\nu}/S^0$, employing Slater-type orbitals and an orbital exponent of 1.625, S^0 being the π-π overlap in benzene. The same correction has been applied with respect to the "spokes" connecting the inner core with the outer perimeter since their lengths in [6]helicene differ appreciably from the normal benzene value; their distances were obtained with the aid of the following bond-order/bond-length relationship:[14] $R_{\mu\nu} = 1.5419 - 0.2196 P_{\mu\nu}$. The effect of torsion has been accounted for by means of the familiar cosine relationship, using a torsional angle of 22° (estimated from molecular models) for the inner core π bonds. (A complete list of the resonance integrals may be obtained upon request.) The resulting least-squares regression, $\mathrm{IP}_i(\mathrm{eV}) = (5.615 \pm 0.082) + (2.885 \pm 0.079)x_i$; $\mathrm{SE(IP)} = 0.143$ eV, shows a slight improvement over models A and B which is however not significant at the 95% security level, according to an F test.

Model D. Transannular Effect. In [6]helicene, there is one nonbonded CC distance (C1-C16 in Newman's numbering scheme) which is shorter than the sum of the van der Waals radii, thereby opening the possibility for three-dimensional π electron delocalization. In order to assess the importance of this effect, first-order perturbation calculations have been carried out, using the orbitals of model C as a starting point, and considering only interactions between superposed π centers of the inner core, of which there are $2(n - 5)$ in an [n]helicene. This amounts to adding the term $\delta\epsilon_i = \Sigma_{\mu\nu} 2c_{\mu i}c_{\nu i}\beta_{\mu\nu}{}^{\mathrm{trans}}$ to the Hückel energies ϵ_i, where $\beta_{\mu\nu}{}^{\mathrm{trans}}$ represents the transannular interaction term. Assuming $\beta_{\mu\nu}{}^{\mathrm{trans}}$ to be the same for all pairs of superposed π AO's, and treating it as an adjustable parameter, the following least-squares results, for 109 degrees of freedom, have been obtained (cf. also Figure 2): $\mathrm{IP}_i(\mathrm{eV}) = (5.612 \pm 0.080) + (2.889 \pm 0.077)x_i$; $\mathrm{SE(IP)} = 0.139$ eV. From the feeble improvement it is obvious that $\beta_{\mu\nu}{}^{\mathrm{trans}}$ does not differ significantly from zero.

All four models are remarkably similar in their predicted order of the π levels, thus lending credit to the assignments set out in Table I. Minor discrepancies concern the order of some close-lying levels in the lower homologs; in such cases model D was considered to be the most reliable. In opposition to all four calculations, however, the 7.37 eV peak in [6]helicene was assigned to 7b rather than to 6a because the steep onset of this peak points to an MO with nodal properties similar to those of the highest occupied level in 3,4-benzophenanthrene ($5b_1$).

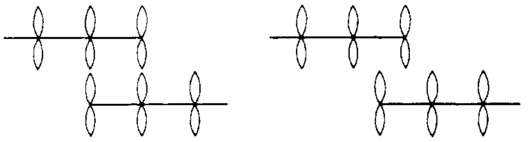
The onset of the first σ band (judging from the onset of continuous absorption) is found at 10.5 eV in 3,4-benzophenanthrene, at 10.4 eV in [5]helicene, and between 10.2 and 10.0 eV in the higher homologs. These figures compare reasonably well to those found in planar aromatics comprising a similar number of benzene rings, and indicate that it is still legitimate to speak of π and σ levels.

The σ region in the present spectra shows some regularities which are also evident in other series of polynuclear aromatics. Comparison with the benzene spectrum,[15] which has been fully assigned, suggests that the 12 eV band may correlate with CC levels, the prominent 14 eV band with CH levels.

Discussion and Conclusions

Transannular Interaction. Although the overall agreement between calculated and observed π IP's was pleasing, the search for transannular effects seems frustrated so far. Considering the 1.1 eV splitting between the benzene e_{1g} levels in tris-bridged cyclophanes,[10] our failure to demonstrate analogous effects in the helicenes clearly demands an explanation.

If transannular interaction in the helicenes is of the Möbius type,[8,24] it is likely to increase the total energy of the molecules. Their stability may therefore be increased by minimizing transannular overlap. Where geometry allows it, a very efficient means for accomplishing this consists in a rehybridization of the sp^2 carbon atoms (resulting in diminished π electron density in the overlap region) and, to a lesser extent, in a displacement of superposed π AO's of the inner core by one-half of a CC bond length. The topological equivalent of two carbon ribbons overlapping in σ fashion through space is shown below: on the left the overlap is optimal, whereas on the right it is conceivably reduced, depending on the nodal properties of the MO concerned.



That these suggestions are not too far fetched is indicated by two recent, highly refined X-ray studies of [2.2]paracyclophane[25] and [2.2.2](1,3,5)cyclophane-1,9,17-triene.[26] In the first of these, the two benzene rings were found to oscillate rapidly in opposite directions about their common normal, with a small barrier to interconversion between the two enantiomers. Corresponding hydrogen atoms of opposing benzene rings are bent inwards, implying a departure from sp^2 hybridization at the carbon atoms and accumulation of π electron density outside the cavity of the molecule. Such a displacement of the hydrogen atoms has also been observed in the tris-bridged cyclophanetriene[26] and in [2.2]paracyclophane-1,9-diene, and Cram[27] has made the suggestion that these structural abnormalities reflect the need for minimizing transannular overlap. Since the helicenes may be considered to be more flexible than the cyclophanes, this goal can be achieved easier.

That the helicenes are conformationally much more flexible than believed hitherto has recently been demonstrated by the unusual ease with which optically active helicenes racemize; Arrhenius activation energies vary from 23.5 kcal/mol for [5]helicene to 42.3 kcal/mol for [9]helicene.[28] Martin and coworkers proposed a racemization mechanism based on in-plane and out-of-plane stretching and bending of the benzene rings, and attributed the low activation energies to the fact that the necessary molecular deformations are spread over a large number of bonds. In accord with this, Wynberg et al.[29] showed, by means of ab initio calculations, that the potential curves for bending of the benzene rings in aromatics are flatter than usually assumed. The implication for the photoelectron spectra is that the transannular effect is averaged out because the helix radii and the distances between opposing benzene rings adopt no fixed values.

σ–π Interaction. In Table II the π self-energies, α, and the nearest-neighbor π resonance integrals, β, obtained by fitting the measured π IP's of each molecule separately to the calculated orbital energies, are contrasted with the corresponding data for the planar aromatics. [5]Helicene is seen to behave "normal" in that its α value does not differ significantly from that of the planar reference molecules. For the homologs a trend to higher energies is noted, the mean increment per additional benzo ring being 0.05 eV in model A and 0.06 eV in model C. The congruence between these figures lends support to the supposition that the increase in the self-energies is not an artifact of the method chosen to fit the experimental data, but rather reflects progressive σ–π interaction, as the series is descended. The corresponding changes in the resonance integrals are less pronounced (at least in model A), indicating that π electron delocalization is not significantly impeded due to the lack of planarity. This conclusion is supported by the optical spectra discussed in the next paragraph.

Table II. Self-Energies, α, of the Isolated π AO's, and Nearest-Neighbor π Resonance Integrals, β, in the Helicenes[a]

	Model A		Model C	
Hydrocarbon	α	β	α	β
Planar aromatics[14]	−5.93	−2.89	−5.69	−3.22
[5]Helicene	−5.94	−2.82	−5.79	−3.01
[6]Helicene	−5.82	−2.90	−5.57	−3.22
[7]Helicene	−5.78	−2.82	−5.28	−3.47
[8]Helicene	−5.61	−2.90	−5.29	−3.32
[9]Helicene	−5.72	−2.93	−5.72	−2.93
[10]Helicene	−5.60	−3.01	−5.43	−3.24
[11]Helicene	−5.57	−3.05	−5.19	−3.55
[12]Helicene	−5.46	−3.14	−5.46	−3.14
[13]Helicene	−5.56	−2.96	−5.34	−3.25
[14]Helicene	−5.38	−3.24	−4.92	−3.85

[a] All energies in eV.

Optical Spectra. From the fact that no σ ionizations are found below 10 eV in the photoelectron spectra, we can dismiss the possibility (discussed by Mason[8]) that $\pi^* \leftarrow \sigma$ or $\sigma^* \leftarrow \pi$ transitions intrude into the $\pi^* \leftarrow \pi$ manifold. Transitions involving σ levels require an additional 3 eV in energy and should thus take place in the far-uv, as in planar aromatics.

For [5]helicene, the sequence of states in the visible and near-uv region has been deduced as α, p, β, and β', in order of increasing energy.[8a,30] It is now generally agreed that this is also the ordering in [6]- and [7]helicene;[7,8b,12] however, the spectrum of the latter molecule exhibits more maxima than states expected so that it is by no means trivial to locate these four transitions. For example, the assignments given by Mason[8b] would imply that the p and β bands shift hypsochromically, on passing from [6]- to [7]helicene. This is contrary to expectation and in disagreement with the photoelectron data, as shown below. Up to now no attempt has been made to interpret the generally very diffuse spectra of the higher homologs, but Birks et al.[12] were able to locate the α band in the long-wavelength wing of the spectrum of [8]helicene.

It is in situations such as this that the photoelectron data may be used to good advantage. In a comparative study of the optical and photoelectron spectra of planar cata-condensed aromatics,[13b] we noticed that the position of the α band relative to the p band can be predicted from the first two IP's. If their difference, $\Delta IP = IP_2 - IP_1$, exceeds the critical value of ca. 0.7 eV, then the p band is the first band in the optical spectrum, whereas for $\Delta IP \leqslant 0.5$ eV the α band is the first one. Inspection of Table I shows that (with the exception of naphthalene) ΔIP is quite small so that the α band is expected to precede the p band. As far as benzene to [8]helicene are concerned, this is in accord with the assignments given in the literature.

In the above-mentioned study of cata-condensed aromatics,[13b] it was shown that the p-band energies, E_p, correlate linearly with the first IP's, whereas for the α- and β-band energies, E_α and E_β, respectively, a linear correlation with the mean of the first two IP's, $\overline{IP}$, was established: $E_p(eV) = (-7.576 \pm 0.851) + (1.503 \pm 0.116)IP_1$; $SE(E_p) = 0.162$ eV, $E_\alpha(eV) = (-3.047 \pm 1.056) + (0.829 \pm 0.134)\overline{IP}$; $SE(E_\alpha) = 0.109$ eV, $E_\beta(eV) = (-7.683 \pm 0.796) + (1.580 \pm 0.104)\overline{IP}$; $SE(E_\beta) = 0.111$ eV; (for $\phi = 24$, 12, and 23, respectively) In Table III the transition energies calculated according to these relations are compared with the experimental quantities when available. The ratio of the E_β and E_α values, which has been shown by Clar[30] to be 1.35 for medium-sized hydrocarbons, is also given. All experimental energies have been corrected for the gas phase according to ref 30, and refer to the 0-0 vibrational transi-

Table III. Calculated and Experimental[a] Transition Energies of the α, p, and β Bands[j]

Hydrocarbon	$E\alpha$ Calcd	$E\alpha$ Exptl	Ep Calcd	Ep Exptl	$E\beta$ Calcd	$E\beta$ Exptl	$E\beta/E\alpha$ Calcd	$E\beta/E\alpha$ Exptl
Benzene	4.61	4.65[b]	6.32	6.08[b]	6.92	6.93[b]	1.50	1.49
Naphthalene	4.01	3.91[b]	4.68	4.46[b]	5.76	5.72[b]	1.44	1.46
Phenanthrene	3.59	3.62[b]	4.24	4.35[b]	4.97	5.05[b]	1.38	1.40
3,4-Benzophenanthrene	3.44	3.36[b]	3.88	3.92[b]	4.67	4.52[b]	1.36	1.35
[5] Helicene	3.26	3.17[b]	3.72	3.88[b]	4.33	4.11[b]	1.33	1.30
[6] Helicene	3.12	3.04[c]	3.51	3.68[c]	4.06	3.93[c]	1.30	1.29
[7] Helicene	3.03	2.96[d]	3.32	3.49[e]	3.89	3.86[f]	1.29	1.30
[8] Helicene	2.88	2.88[d]	3.17	3.42[g]	3.61	3.67[g]	1.25	1.28
[9] Helicene	2.81	2.81[h]	3.05	3.27[g]	3.49	3.53[g]	1.24	1.26
[10] Helicene	2.75		2.93		3.36		1.22	
[11] Helicene	2.72		2.87		3.30		1.22	
[12] Helicene	2.70		2.84		3.27		1.21	
[13] Helicene	2.68		2.81	2.99[i]	3.24	3.16[i]	1.21	
[14] Helicene	2.66		2.77		3.19		1.20	

[a] All energies corrected for the gaseous state according to Clar.[30] [b] From ref 30, solvent MeOH or EtOH. [c] From ref 8b, solvent 2-propanol–ether. [d] From ref 12, solvent dioxane. [e] From ref 31, solvent EtOH. [f] From ref 8b, solvent EtOH. [g] From ref 32, solvent $CHCl_3$. [h] From ref 12, extrapolated from the fluorescence spectra, solvent dioxane. [i] From ref 2b, solvent dioxane. [j] For the assignment of the optical spectra see text. All energies in eV.

tions (as do the IP's) when resolved, otherwise to the first discernible maximum or shoulder. A plot of E_α, E_p, E_β, and $E_{\beta'}$ vs. the number of benzene rings is shown in Figure 3; for comparison the first two IP's are also plotted.

Since both the IP_1 and IP_2 values lie on smoothly descending lines, this must also hold for the E_α, E_p, and E_β data. On this basis the identification of the transitions in the spectra of the higher helicenes is straightforward. For [7]helicene our assignments differ from those given by Mason[8b] in that we locate the p band at 367 nm and assign the 331-nm peak to the β band. As seen from Table III, these assignments fit the respective E_p/IP_1 and $E_\beta/\overline{IP}$ correlations very well, and no discontinuities are apparent from Figure 3; furthermore, the E_β/E_α ratio of 1.30 is perfectly in line with that expected for a hydrocarbon of the size of [7]helicene (1.29). For the lower homologs we have adopted the assignments given in the literature.

The E_α values calculated by these empirical relations for [7]- and [8]helicene compare favorably with those reported by Birks.[12] In the higher helicenes, the α band is masked by the adjacent intense p band, but Birks showed that the first discernible maximum in the fluorescence spectra is shifted to the red by 0.07 eV, on going from [8]- to [9]helicene. The resulting E_α value of 2.81 agrees with the calculated one.

In the molecules beginning with [5]helicene, the 0-0 vibrational transitions of the p bands are not perceptible; the E_p data quoted in Table III refer therefore to the first resolved maximum or shoulder and are for this reason too high by one or two vibrational quanta $\Delta\nu$ in the CC stretching mode which is activated in the p bands (planar aromatics:[30] $\Delta\nu \approx 1400\ \mathrm{cm}^{-1} = 0.17$ eV). If 0.17 eV is subtracted from the experimental E_p data, almost perfect agreement with the calculated values is obtained, giving confidence in our assignments.[33]

The excellent agreement between calculated and observed transition energies extends also to the β bands (cf. also the E_β/E_α ratios).

There is some ambiguity as to the identification of the β' bands. In planar aromatics, their energies correlate[13b] roughly with the second IP's. Furthermore, in molecules whose first two IP's lie close together, the $E_{\beta'}/E_p$ separation is to first order twice the Hamiltonian matrix element $\langle \chi_j^k | H | \chi_i^l \rangle$ (i and j are the labels of the second-highest and highest occupied levels and k and l those of the lowest and second-lowest unoccupied levels). Since this matrix element can be shown to diminish with increasing molecular size, we would expect the $E_{\beta'}/E_p$ separation in the higher helicenes (where $IP_2 \approx IP_1$) to be smaller than in benzene where it amounts to 0.85 eV. Using this argument, we have tentatively assigned the β' band in [6]- to [9]helicene to the peaks at 290, 302, 313, and 330 nm, respectively. This yields $E_{\beta'}/E_p$ separations of 0.71, 0.72, 0.65, and 0.60 eV which are reasonable figures for molecules of the present size. For the lower homologs literature assignments have been adopted in Figure 3, although it is seen that the value for 3,4-benzophenanthrene does not fit the $E_{\beta'}/IP_2$ correlation. This point will have to be investigated further, preferably with the aid of low-temperature optical data.

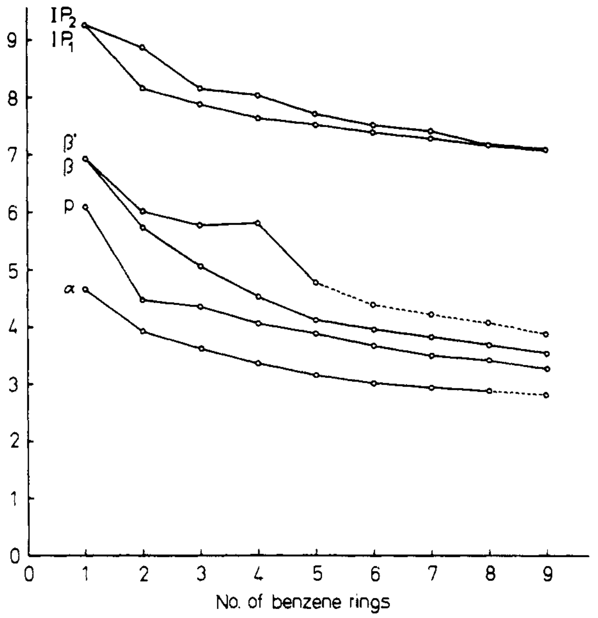


Figure 3. Correlation diagram for the four low-energy optical transitions and the first two IP's. Correlations with uncertain or extrapolated states are indicated by broken lines. All energies in eV.

In conclusion, the optical spectra of the helicenes show no abnormalities, compared to planar aromatics; all effects due to the helicity of these molecules are absorbed in the IP's. The discrepancies noted by previous workers between the transition energies calculated by the PPP method[8,23] and the observed ones have therefore to be ascribed to limitations of this method and to incorrect assignments of the optical spectra. The empirical correlation scheme based on the photoelectron data offers definite advantages.

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Supplementary Material Available. Spectra for benzene, naphthalene, phenanthrene, 3,4-benzophenanthrene, and the higher homologs will appear following these pages in the microfilm edition of this volume of the journal. Photocopies of the supplementary material from this paper only or microfiche (105 × 148 mm, 24× reduction, negatives) containing all of the supplementary material for the papers in this issue may be obtained from the Business Office, Books and Journals Division, American Chemical Society, 1155 16th St., N.W., Washington, D.C. 20036. Remit check or money order for $4.00 for photocopy or $2.50 for microfiche, referring to code number JACS-75-6633.

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(33) NOTE ADDED IN PROOF. The optical spectra of [10]- to [14]helicene are at present under investigation in the laboratories of J. B. Birks (The University, Manchester) and E. VanDer Donckt (Université Libre de Bruxelles). The energies of the p bands (from the absorption spectra) and α bands (measured on the fluorescence spectra and increased by 0.12 eV in order to compensate for the Stokes shift between the absorption and emission spectra) are, after correcting for the gas phase:

	E_α	E_p
[10]Helicene	2.73	3.26 ± 0.06
[11]Helicene	2.67	3.16 ± 0.06
[12]Helicene	2.61	3.07 ± 0.06
[13]Helicene	2.57	3.03 ± 0.06
[14]Helicene	2.57	3.03 ± 0.06

Thus, the α band is the first transition in the optical spectra. Comparison with the calculated transition energies in Table III shows good agreement for the α bands; the experimental E_p values quoted above are again too high by one or two quanta in the CC stretching mode. We thank Professors Birks and VanDer Donckt for communicating their data to us in advance of publication.

Microwave Spectrum, Molecular Structure, and Dipole Moment of Oxaspiro[2.2]pentane

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Abstract: The assignment of microwave spectrum of oxaspiro[2.2]pentane, **1**, and its ^{13}C and monodeuterio isotopically substituted derivatives is reported. These data are sufficient to permit the determination of the complete molecular structure. Measurement of a large number of microwave transitions allowed the quartic centrifugal distortion parameters to be calculated for the parent and each of the isotopic species. The Stark effect was used to obtain the two components of the electric dipole moment, giving $\mu_a = 0.840 \pm 0.012$ D, $\mu_c = 1.721 \pm 0.004$ D, and $\mu_{\text{total}} = 1.915 \pm 0.009$ D.

Oxaspiro[2.2]pentane, **1**, and its derivatives have only recently been prepared; their chemistry has received increasing attention in recent years[2] because of interest in the unusually strained bonding, hybridization, and reactivity of this ring system and because of their potential as synthetic intermediates.[2a,c]

The structure and dipole moment of oxaspiro[2.2]pentane is of interest in relation to the related oxirane,[3] cyclo-