Photoelectron Spectra of Polynuclear Aromatics. 6. Applications to Structural Elucidation: "Circumanthracene"[1a†]

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Abstract: From the PE spectrum of an aromatic hydrocarbon with N carbon atoms, $N/3$ π-IP's are accessible which can be measured within ± 0.01–0.02 eV. The PE spectrum thus contains more information than the UV and mass spectra which yield four and one characteristic quantities, respectively. The π-IP's are a sensitive function of size and shape of the hydrocarbons and can be predicted with a suitably parametrized Hückel procedure within ± 0.10 eV. Thus, comparison of the observed and calculated IP's allows one to unambiguously confirm or reject the assumed molecular constitution. If nothing is known about the hydrocarbon in question, the occurrence of characteristic PE key bands reveals the basic chromophores (e.g., anthracene, tetracene, pyrene, coronene, etc.). Whether the hydrocarbon is alternant or nonalternant follows from a comparison of the PE and UV spectra: while in the alternant series the excitation energies and IP's move in parallel, this is not the case with the nonalternant hydrocarbons which absorb at significantly longer wavelengths than expected on the basis of the IP's. These regularities, which are exemplified with many examples, are used to deduce the true molecular structure of "circumanthracene", a hydrocarbon remarkable because of its pronounced photoconduction. The X-ray structure is shown to be incorrect because the crystals are strongly disordered.

Introduction

Organic chemists are accustomed to deduce the constitution of a newly synthesized compound from the combustion analysis and the NMR, IR, and mass spectra. Final comfirmation is sought from the X-ray analysis if the effort is deemed to be worthwile.

Unfortunately, none of these techniques is particularly helpful in the field of polycyclic aromatic hydrocarbons, for a number of reasons. (1) Irrespective of size and shape of the hydrocarbons, the combustion analysis invariably yields ≈95% C and ≈5% H. (2) The mass spectrum, while giving the accurate molecular weight and thus the exact elemental composition, does not provide further structural information because aromatic hydrocarbons do not fragment in the ion source; in particular, isomers cannot be distinguished. (3) NMR is only of limited value because no suitable solvent exists for hydrocarbons with more than five condensed rings; also, due to strong spin–spin coupling of the peripheral protons, the ¹H spectra would be interpretable only for compounds with trigonal or hexagonal symmetry. (4) Due to the difficulty in obtaining suitable single crystals, it is often impossible to characterize aromatic hydrocarbons by X-ray diffraction. It is also unfortunate that most hydrocarbons belong to the monoclinic and triclinic system where data refinement is cumbersome. (5) The only attempt to utilize the IR spectra is that due to Groenewege,[2] who showed that the γ vibrations occur at different wavelengths depending on the number of adjacent C–H bonds ("solo", "duo", "trio", "quartet") on a given ring. However, these wavelength regions overlap in part and depend to some extent on the size of the hydrocarbons so that no unambiguous structural information can be extracted.

Structural proof thus rests largely on UV spectroscopy which, owing to its sensitivity and versatility, is still the method of choice for purposes of structural identification and purity control. Clar[3–7] has devised a powerful scheme to relate the positions of the α, ρ, β, and β' bands to the molecular topology ("annelation principle"). Within homologuous series, this scheme allows the wavelengths of these bands to be predicted with surprising accuracy. However, application of Clar's theory is often hampered by the diffuseness of the spectra, in particular, of the larger hydrocarbons, and by the appearance of additional bands[8] which do not fit in the α, ρ, β, and β' scheme so that band assignments are somewhat uncertain.

As a consequence of this unsatisfactory state of affairs, the constitution of about one-fifth of all aromatic hydrocarbons mentioned in the literature (taken to include dissertations and patents) is uncertain or unknown and many more are at least suspect because the synthetic methods employed are ambiguous. That the Elbs pyrolysis often results in partial or complete skeletal rearrangement is long known. Evidence has accumulated over the last few years that some other established synthetic techniques such as the Lewis acid-catalyzed cyclodehydrogenation,[9] the photocyclodehydrogenation,[10] or the sodalime sublimation may also lead to unexpected rearrangement, splitting, or oxidative C–C coupling.

A classical example is 1,2:3,4-dibenzopyrene (I), whose con-

I   II
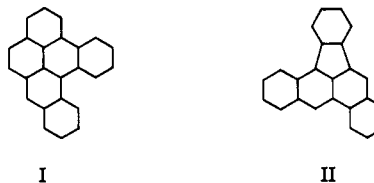
stitution was unchallenged for almost 40 years, although its UV spectrum, if critically examined in the light of Clar's rules, did by no means support the presumed structure. Three independent syntheses have been worked out for this important hydrocarbon, all of which rely however on an AlCl₃-catalyzed cyclodehydrogenation, in the final step.[11] On chemical grounds and by comparison with a sample prepared in an unambiguous manner, its true constitution was shown to be that of a dibenzofluoranthene (II).[12]

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(2) (a) M. P. Groenewege, Colloquium Spectroscopicum Internationale VI, Amsterdam, 1956, p 579; London, 1956. (b) M. Zander, *Erdoel Kohle*, **15**, 362 (1962).

(3) E. Clar, *Ber. Dtsch. Chem. Ges.*, **69**, 607 (1936).

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(6) E. Clar, "Polycyclic Hydrocarbons", Academic Press, New York, 1964.

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This paper describes a novel method which permits structural assignment even if nothing is known beforehand about the hydrocarbon in question. The method is based on a comparison of the experimental gas-phase IP's with those calculated by Hückel (or some other) theory and correlation of the IP's with the UV spectral data. Experience over the last 3 years showed that the method yields unambiguous results and furthermore provides information about the purity of the hydrocarbons.

Photoelectron Spectra

Now that the high-resolution PE spectra of practically all hydrocarbons with known structures are available,[8,13-24] the next step is to turn to those hydrocarbons whose constitution is unknown or uncertain. For the following reasons, the PE spectra are an ideal source of information in this respect.

(a) Unlike the UV spectra, the PE spectra are clear and simple, even in the case of nonplanar, overcrowded hydrocarbons. Band overlap is the exception rather than the rule and is in any case readily recognized because all π ionizations have the same transition probability. The clarity of the PE spectra is due to the fact that the energy levels of aromatic hydrocarbons spread over a considerable energy range, while the excited singlet states bunch closely; furthermore, ionization influences the equilibrium geometries much less than excitation so that most of the intensity of the PE bands is in the 0–0 transitions. The first few PE bands can usually be located within ±0.01 eV, the higher within ±0.02 eV.

(b) Since the spectra are taken in the gas phase, the IP's are an intrinsic property of the molecules, unperturbed by the medium. For instance, it is possible to record the PE spectra of hydrocarbons whose UV spectra could never be obtained because of extreme air sensitivity or insolubility.

(c) Of the $N/2$ π-IP's expected for a hydrocarbon with N carbon atoms, $N/3$ can be observed in the 6–10.5-eV range, the remaining π-IP's being obscured by σ ionization. The PE spectra thus contain more information than both the UV and mass spectra. This is an important consideration because there exist families of hydrocarbons with different shape but almost identical UV spectra ("isotopic hydrocarbons"[23]).

(d) Impurities, a frequent cause of confusion in UV spectroscopy, are readily recognized by recording the spectra at different temperatures and monitoring the relative band intensities.

(e) Despite intense efforts at the SCF–CI level,[25] the energies of the excited singlet states of the larger hydrocarbons still cannot be calculated reliably. On the other hand, even simple MO procedures such as a suitably parametrized Hückel theory are quite successful in reproducing the observed π-IP's of any hydrocarbon. Comparison of the observed IP's with those calculated for the structural alternatives in question permits a straightforward decision which is the correct one.

(f) Even if nothing is known about the constitution of the hydrocarbon in question, it can often be deduced from the PE spectrum by inspection, using the following regularities. Catacondensed hydrocarbons differ from the pericondensed ones in
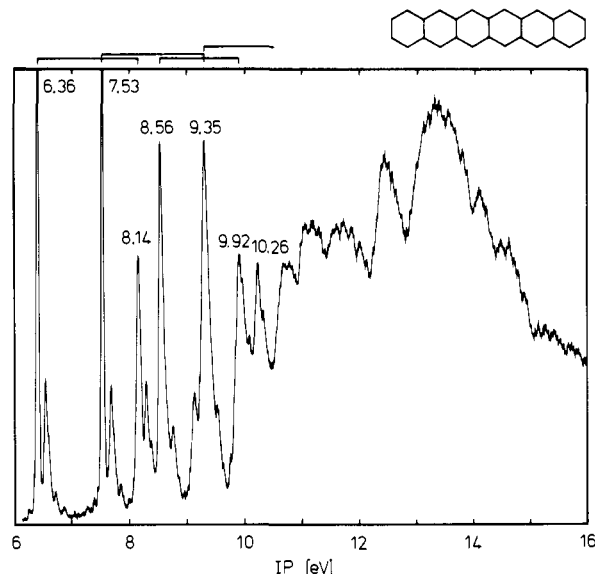
(12) (a) D. Lavit-Lamy and N. P. Buu-Hoi, *Chem. Commun.*, 92 (1966); (b) F. A. Vingiello, J. Yanez, and E. J. Greenwood, *ibid.* 375 (1966); (c) W. Carruthers, *ibid.*, 548 (1966).

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(22) E. Clar and W. Schmidt, *Tetrahedron*, 35, 1027 (1979).

(23) E. Clar and W. Schmidt, *Tetrahedron*, 35, 2673 (1979).

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Figure 1. Gas-phase PE spectrum of hexacene (Perkin-Elmer PS-18 spectrometer with Helectros Developments photon source). IP's relating to orbitals with the same angular quantum number are connected by brackets.

that the latter have additional PE bands originating from the orbitals of the insular structures. For example, all coronenes (in which an inner benzene nucleus is surrounded by an outer (4n + 2) perimeter) show a double band at about 8.6 and 9.0 eV, in addition to the more or less regularly spaced bands coming from the orbitals of the peripheral ring; similarly, most pyrenes show a band at about 9.1 eV which is due to the ethylene insula. Furthermore, even in large polycyclic hydrocarbons, the IP's of smaller fragment molecules (e.g., naphthalene, phenanthrene, anthracene, tetracene, pyrene, perylene, coronene, etc.) can frequently be encountered ("subspectrality"[23]). Thus, by looking for the IP's of these basic chromophores, we can often write down the correct structure of the hydrocarbon in question immediately.

(g) In sufficiently well-resolved PE spectra (i.e., planar hydrocarbons), the bands can be classified into two types: "sharp" bands with intense 0–0 transition and a well-developed vibrational structure and "diffuse" bands with weak 0–0 transition and a poorly resolved or missing structure. As has been discussed in ref 8 and 26, pairs of sharp and diffuse bands correspond to orbitals which, in the pertinent (4n + 2) annulene, are degenerate and have the same angular quantum number λ. Thus, by correlating the orbitals of the hydrocarbon with those of the pertinent (4n + 2) annulene, we can predict the band shapes and compare them to the experimental band shapes thereby providing a further criterion for checking the assumed constitution (in addition to the agreement of the IP's).

(h) In the alternant hydrocarbon series, the energies of the α, p, β, and β' bands correlate linearly with the IP's of the occupied orbitals of highest λ; these IP's are usually IP$_1$ and IP$_2$, in rare cases IP$_1$ and IP$_3$.[8] On the other hand, in the nonalternant series, there is no relation between excitation energies and IP's; the UV bands are uniformly displaced to longer wavelengths. Comparison of the PE and UV spectra of the hydrocarbon in question thus gives a clear-cut answer whether it is alternant or nonalternant.

The features a, b, c, d, and g are best illustrated by a specific example, namely, hexacene. This is a most sensitive hydrocarbon, almost insoluble in the usual solvents and difficult to obtain in a pure state so that its UV spectrum is unknown.[6] The PE spectrum (Figure 1) could readily be obtained at 300 °C. Of the 13 π-IP's expected for a $C_{26}H_{16}$ hydrocarbon, 8 are clearly seen in the 6–10.5-eV region; note that the 9.35-eV band is due to two ionization processes. Bands relating to orbitals of the same λ are connected by brackets. The first sharp and first diffuse bands, at 6.36 and 8.14 eV, relate to $\lambda = 6$; the second sharp and second diffuse bands (7.53 and 9.35 eV) to $\lambda = 5$ and so on. A noteworthy feature, which distinguishes catacondensed from pericondensed

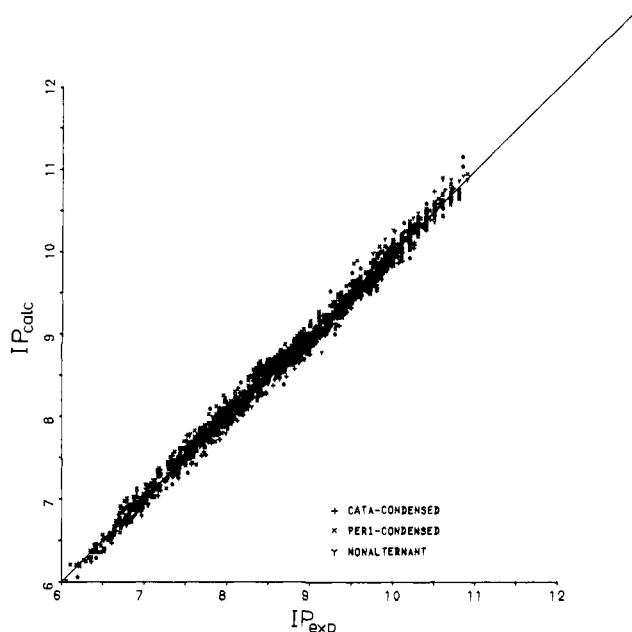1322 *J. Am. Chem. Soc., Vol. 103, No. 6, 1981*

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Figure 2. Linear regression of the π-IP's calculated by a parametrized Hückel theory (eq 1) on those taken from the photoelectron spectra (2500 data points).
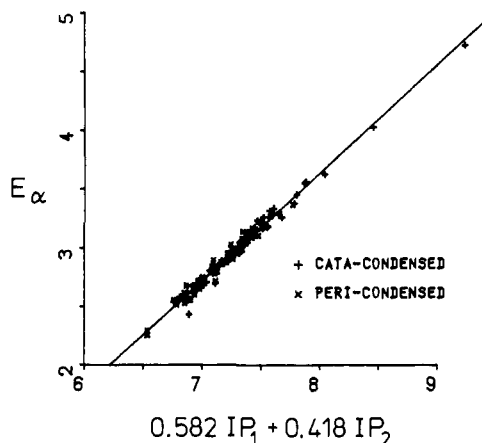

Figure 3. Linear regression of the α-band energies (0–0 transitions) on the first two IP's of alternant hydrocarbons (115 data points).

hydrocarbons, lies in the fact that the means of IP's relating to orbitals of the same λ (7.25, 8.44, 9.24, and $\approx$10.0 eV for hexacene) form a slowly convergent series; there are no extra bands as in the pericondensed series.

To illustrate feature e, Figure 2 shows a plot of 2500 π-IP's calculated by a parametrized Hückel procedure[24] on those taken from the PE spectra of some 250 alternant and nonalternant hydrocarbons of known structure. The only group of hydrocarbons, which does not fit this regression (standard deviation 0.100 eV), are the helicenes whose IP's are uniformly too low due to the effect of overcrowding. The IP's were calculated from the zero-order Hückel eigenvalue coefficients x_i^0 according to eq 1.

$$IP_i^{calcd} =$$
$$5.391 + 5.549/N + 3.215(x_i^0 + 0.788\sum 2c_{\mu i}c_{\nu i}(P_{\mu\nu} - \frac{2}{3})) \quad (1)$$

The constants, 5.391 and 3.215, are the experimental values of $-\alpha$ and $-\beta$, respectively, in Hückel theory. The $1/N$ term describes in a crude, empirical manner the effect of electronic relaxation in the radical cations; this correction proved necessary because IP's that relate to the same eigenvalue coefficients may vary by up to 1 eV, depending on the size of the hydrocarbons.[23] For instance, while the $x_i^0 = 1$ orbitals in benzene ($N = 6$) are found at 9.24 eV, the same orbitals in hexabenzocoronene (13 condensed rings, $N = 48$) are in the 8.17–8.83-eV range. The effect of
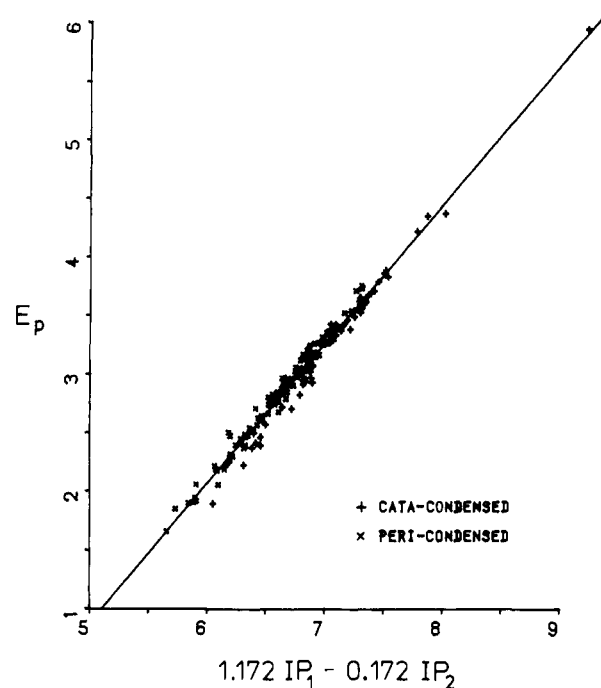

Figure 4. Same as Figure 3, but for ρ bands (189 data points).
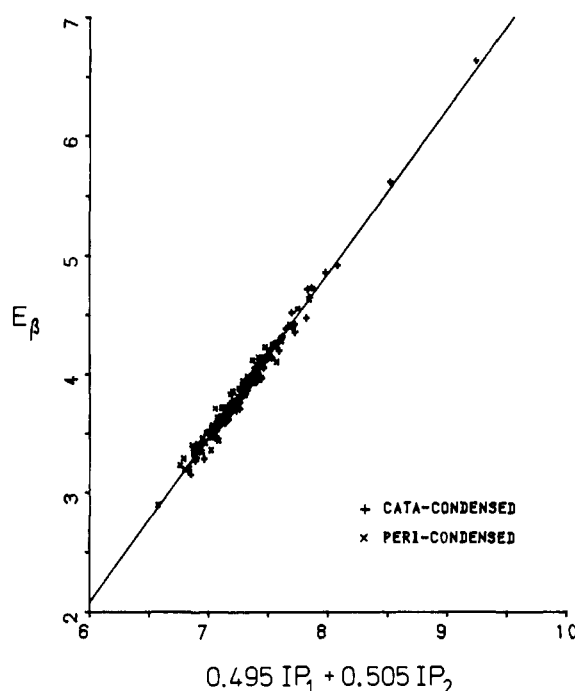
Figure 5. Same as Figure 3, but for β bands (184 data points).

first-order double-bond fixation[13,14] is taken into account by the summation term in eq 1. All constants were obtained by least-squares minimization of the differences between calculated and observed IP's.

The relations between the PE and UV spectra (feature h) have been discussed in detail in ref 8. As expected on theoretical grounds, the ρ- and β'-band energies were found to correlate linearly with IP_1 and IP_2, respectively, the α- and β-band energies both with $\overline{IP} = 1/2(IP_1 + IP_2)$; note that for some hydrocarbons, the so-called "inversion" cases,[26] IP_2 has to be replaced by IP_3. These correlations have, in the meantime, been refined and extended to all hydrocarbons of known structure. The regressions of the α, ρ, and β band energies (0–0 components, corrected to

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the gas phase[6,19]) on a function of the type $aIP_1 + bIP_2$ are shown in eq 2–4. As is evident from Figures 3–5, these correlations are

$$E_\alpha = -3.750 + 0.924(0.582IP_1 + 0.418IP_2) \quad (2)$$

$$E_\rho = -5.015 + 1.190(1.172IP_1 - 0.172IP_2) \quad (3)$$

$$E_\beta = -6.232 + 1.386(0.495IP_1 + 0.505IP_2) \quad (4)$$

highly significant, having standard deviations of 0.047, 0.080, and 0.059 eV, respectively, and are valid for planar as well as nonplanar *alternant* hydrocarbons, irrespective of size, shape, and symmetry.

Feature f, namely, the appearance of the IP's of smaller fragments in large hydrocarbons, is exemplified by the series of perylenes III–VII. These can be formally considered to be built

III	IV	V	VI	VII
-	7.94	7.86	7.84/8.07	7.81/8.08 eV
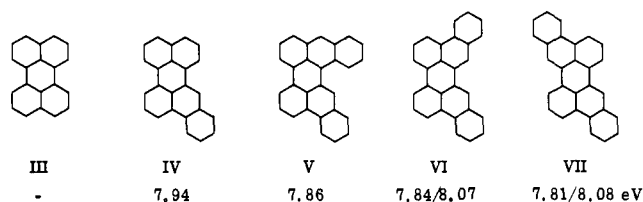
up from naphthalene ($IP_1 = 8.15$ eV), anthracene ($IP_1 = 7.41$ eV), and phenanthrene ($IP_1 = 7.86$ eV) units. Although interaction takes place between the fragment orbitals, at least the IP_1 values of the phenanthrene units are clearly recognizable in the PE spectra; see the experimental values above. This allows IV with one phenanthrene band to be distinguished from VI and VII with two each. It should be pointed out that the UV spectra of these three compounds are practically identical.

The Circumanthracene Problem

In 1956, Clar, Kelly, Robertson, and Rossmann[27] reported on the decarboxylation of the bis adduct IX, obtained from di-*peri*-naphthyleneanthracene (VIII) and maleic anhydride (MA)
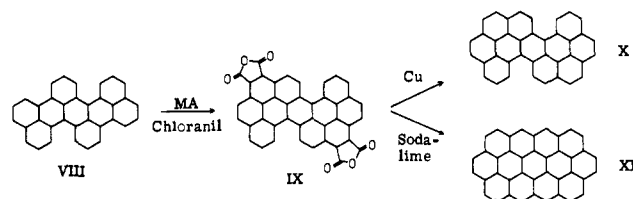
in the presence of chloranil. Depending on whether the decarboxylation is carried out with copper in boiling quinoline or with sodalime at 400 °C, different products are formed.

The hydrocarbon of mp 338–339 °C obtained with copper was identified as dinaphthoperopyrene (X), both by analogy with similar decarboxylations[6] and on the basis of its UV spectrum which showed the expected violet shift of the ρ band relative to VIII (X has five aromatic sextets while VIII has only three). This structural assignment is borne out by the satisfactory agreement between observed and calculated IP's (see Table I).

If the decarboxylation is carried out with sodalime, there is obtained, in addition to X, a new hydrocarbon of mp 480 °C which sublimes in almost black needles. This was formulated as circumanthracene (XI) because the ρ band in its UV spectrum fitted the homologous series pyrene, coronene, and ovalene. Further support came from an X-ray investigation which showed the crystals to be monoclinic, with lattice constants which also fitted the above series. The molecular weight determined from the dimensions of the unit cell and the density of the crystals (492 ± 5) was also in accord with the composition $C_{40}H_{16}$ (496.6). A Fourier synthesis, which could be refined to an R value of 19%, revealed the two carbon atoms which are absent in X. These results lead to the conclusion that these carbon atoms came from the carbonyl groups of the adduct IX or from the breakdown of another part of the adduct, a process for which the term "controlled graphitization" was introduced.

The synthesis and successful structural characterization of circumanthracene received considerable attention,[28] in particular, when Clar, Inokuchi, and co-workers discovered its strong photoconduction.[29] On the basis of the structural parameters of the X-ray work, Inokuchi and co-workers[30] carried out band structure calculations, aimed at understanding the carrier mechanism and the relations between molecular topology and electrical properties. The results of these calculations were not unambiguous, as were attempts to prepare the hydrocarbon on a larger scale: Clar and co-workers[31] added carbene precursors and similar reagents to the adduct IX in order to introduce the two carbon atoms; however, only spectroscopic quantities of circumanthracene were formed.

New Experimental Data

Although we had little hope to obtain the gas-phase PE spectrum of circumanthracene, this proved possible already at 370 °C. (For comparison, other planar, rigid, highly symmetrical hydrocarbons of similar size such as hexa-*peri*-benzocoronene and quaterrylene required temperatures of almost 500 °C.) This unexpected volatility raised the first doubts as to the correctness of the circumanthracene structure. Also, this structure does not account for the low melting point of 480 °C (ovalene melts at 473 °C, hexa-*peri*-benzocoronene and quaterrylene melt above 700 °C) and the good solubility in 1,2,4-trichlorobenzene and even in dioxane.

Figure 6 shows the PE spectra of pyrene, coronene, and ovalene. For comparison with future experiments, the spectrum of circumanthracene predicted by Hückel theory is also given; the numerical data and MO assignments are gathered in Table I. In estimating the band shapes (sharp, diffuse), we used the method outlined in ref 8 and 24. This procedure predicts the shapes of the first three bands to be sharp, sharp, and diffuse; i.e., we are dealing with an "inversion" case.

The PE spectrum of Clar's compound, shown in Figure 7a, bears no resemblence to the calculated one, thus definitively ruling out the circumanthracene structure. First, the spectrum is too diffuse, with little vibrational structure, as is typical of nonplanar hydrocarbons. Second, the first three bands are of sharp, diffuse, and sharp types, in conflict with the theoretical prediction for circumanthracene. Third while $40/3 \approx 13$, π-IP's are expected out to 10.5 eV and only 12 IP's are found, indicating that Clar's hydrocarbon contains less than 40 carbon atoms. Fourth and most important, the observed first IP of 6.69 eV is almost 0.4 eV higher than the expected one; this is 4 times the standard deviation of the Hückel regression.

That Clar's hydrocarbon is not a homologue of pyrene, coronene, and ovalene is also evident from the UV spectra (Figure 8). The first three spectra are nicely structured, and the α-, ρ-, and β-band positions are as expected on the basis of the UV/PE regressions (eq 2–4). The UV spectrum of circumanthracene predicted by this scheme, using $IP_1 = 6.31$ and $IP_3 = 7.55$ eV, is also pictured[32] in Figure 8, while that observed for Clar's compound is shown in Figure 7b. Again, there is no correspondence, neither in general type nor in band positions. The tailing of the long wavelength band and the blurred vibrational structure are reminiscent of a nonplanar or nonalternant hydrocarbon.

The correlation diagram (Figure 9) summarizes again the trends in the first two IP's and the E_α, E_ρ, and E_β values. One of the

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(27) E. Clar, W. Kelly, J. M. Robertson, and M. G. Rossmann, *J. Chem. Soc.*, 3878 (1956).

(28) (a) H. Meier, "Organic Semiconductors", Verlag Chemie, Weinheim, 1974, pp 122 and 390; (b) *Faraday Discuss. Chem. Soc.*, **51**, 24 and 67 (1971); (c) Y. Kamura, H. Inokuchi, J. Aoki and S. Fujisawa, *Chem. Phys. Lett.*, **46**, 356 (1977).

(29) H. Inokuchi, N. Matsubara, Y. Maruyama, and E. Clar, *Nature (London)*, **205**, 64 (1965). Also unpublished experiments by the same authors.

(30) Y. Harada, Y. Maruyama, H. Inokuchi, and N. Matsubara, *Bull. Chem. Soc. Jpn.*, **38**, 129 (1965).

(31) (a) McLaughlin, Ph.D. Thesis, University of Glasgow, 1956. (b) C. T. Ironside, Ph.D. Thesis, University of Glasgow, 1959.

(32) In predicting the shapes of the ρ and β bands, we assumed the ϵ_{max} values and Franck–Condon envelopes to be similar to those found for ovalene and related hydrocarbons. The vibrational spacing used was 1400 cm^{-1}, as commonly found in the ρ and β bands. The α band is hidden.

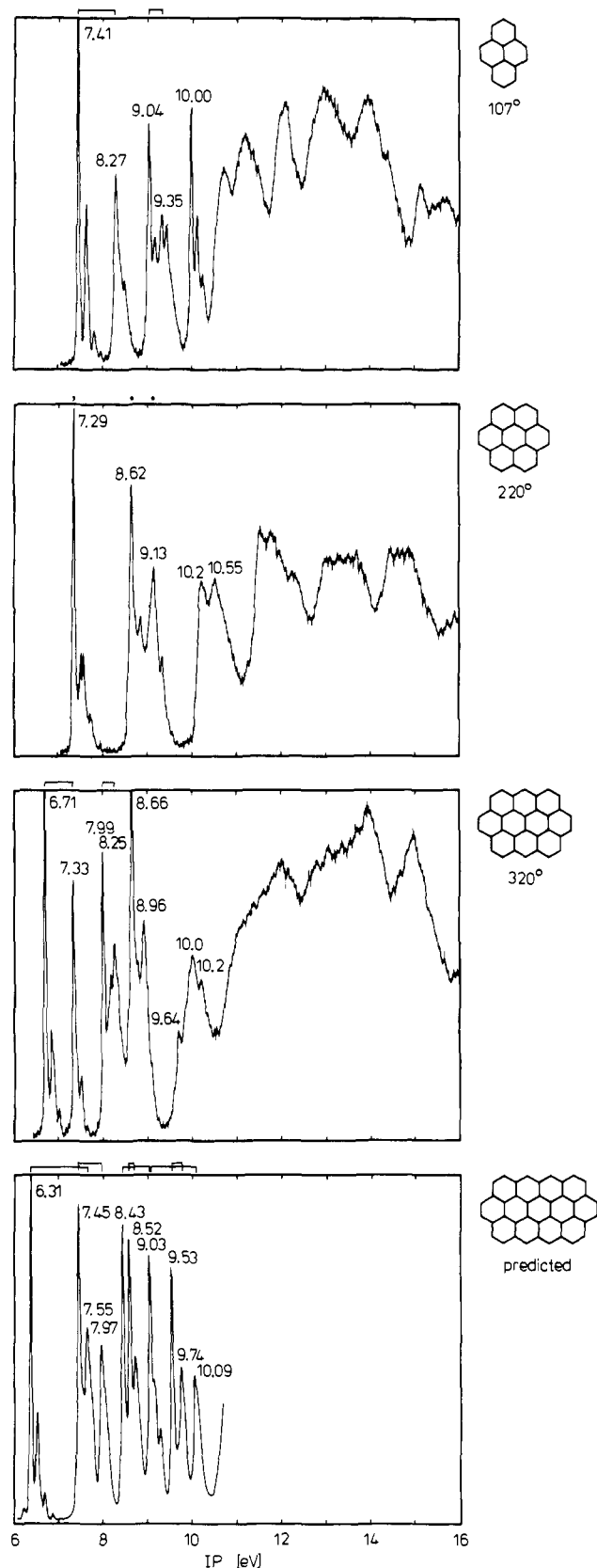1324   *J. Am. Chem. Soc., Vol. 103, No. 6, 1981*

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Figure 6. Gas-phase PE spectra of pyrene, coronene, and ovalene. The spectrum of circumanthracene is extrapolated; see text. IP's relating to orbitals with the same angular quantum number are connected by brackets.

IP's remains stationary between 7.3 and 7.5 eV (the corresponding orbital transforms as b_1 within the reduced point group C_{2v}), whereas the other one responds strongly to the extension of the conjugation system (the orbital is a_2 within C_{2v}); this explains the
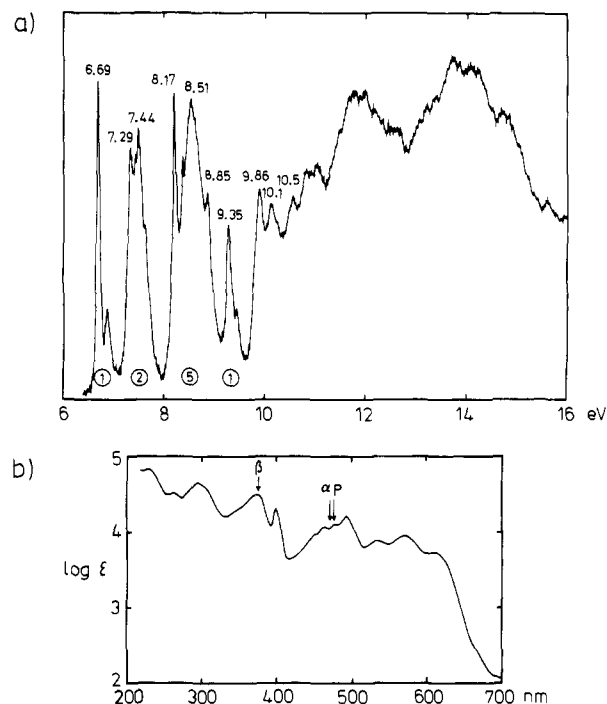

Figure 7. (a) PE and (b) UV spectra of Clar's hydrocarbon. Encircled figures in the PE spectrum indicate the number of orbitals to be allotted to the various bands. UV spectrum recorded in trichlorobenzene, below 300 nm in dioxane. The arrows denote the α-, ρ-, and β-band positions expected for an alternant hydrocarbon with $IP_1 = 6.69$ and $IP_2 = 7.29$ eV.

exceptionally low first IP predicted for circumanthracene. Due to the decrease of $\overline{IP}$ with increasing molecular size, the α- and β-band energies are steadily lowered within the series. The ρ band energy, which depends in the first place on IP_1, changes first only marginally (the IP_1 values of pyrene and coronene differ little) and is then lowered to 2.24 eV for circumanthracene; in trichlorobenzene, this corresponds to $\lambda_p = 601$ nm. For comparison, Clar's hydrocarbon has about 670 nm, as estimated from the onset of absorption.

In order to elucidate the structure of Clar's hydrocarbon, a comparison of the PE and UV spectra (Figure 7) was revealing. If we calculate the α-, ρ-, and β-band positions according to eq 2–4, using $IP_1 = 6.69$ eV and $IP_2 = 7.29$ eV, we arrive at the results indicated by arrows in Figure 7b. The lack of agreement between observed and predicted band positions is striking; i.e., we are dealing with a nonalternant hydrocarbon! Based on this information and taking into account that the compound presumably contains less than 40 carbon atoms, we have examined the trial structures XII and XIII. These may be formed from IX or X by oxidative C–C coupling due to residual oxygen in the decarboxylation step.
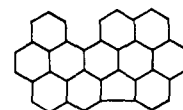
$C_{38}H_{16}$, M = 472 $C_{38}H_{14}$, M = 470
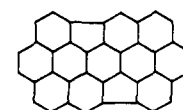
XII   XIII

The IP's calculated for 2',12-dehydrodinaphthoperopyrene (XII) correlate well with those of Clar's hydrocarbon, whereas serious discrepancies arise for the bis-dehydro structure XIII (see Table II). The overcrowded structure XII also explains the diffuseness of the PE and UV spectra, the unexpected solubility and volatility, and the rather low melting point.

If the symmetry of Clar's compound is C_s rather than D_{2h}, this should also show up in the IR spectra. This is the case, indeed. As seen from Figure 10, the IR spectra of pyrene, coronene, and
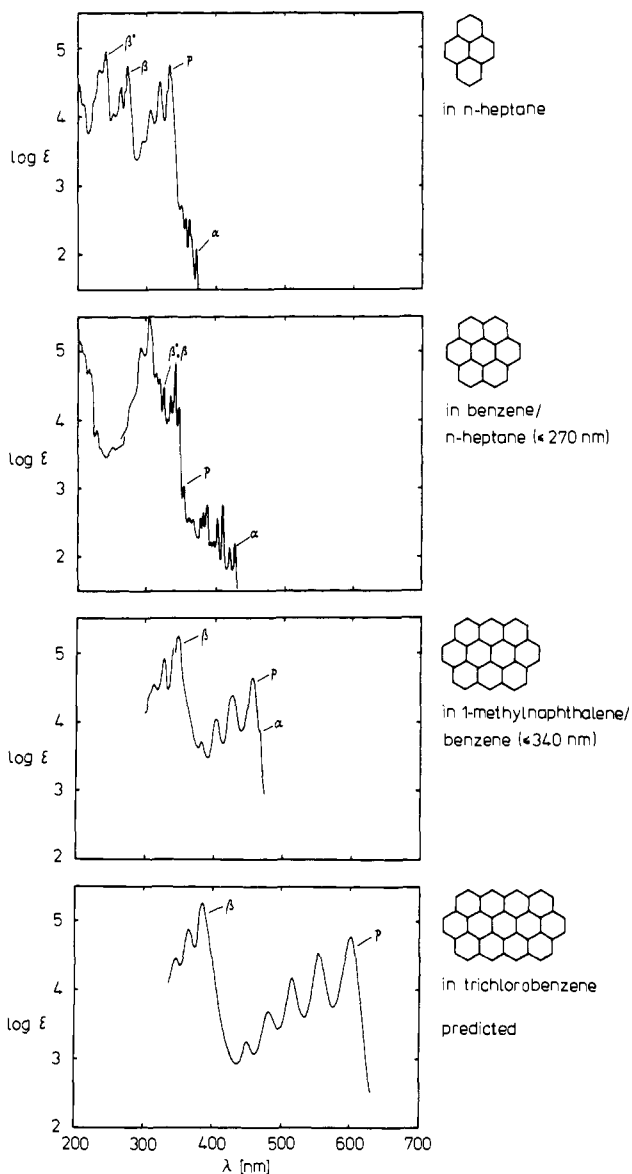
Figure 8. UV spectra of pyrene, coronene, and ovalene. The spectrum of circumanthracene is extrapolated; see text.
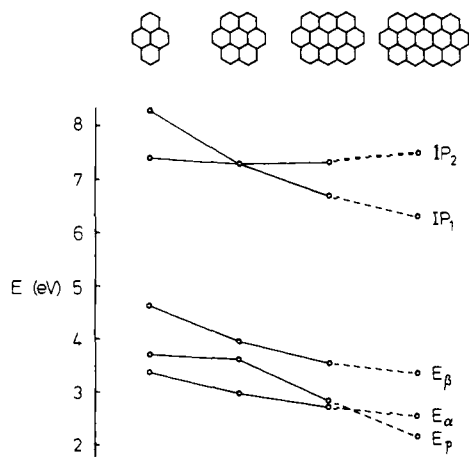
Figure 9. Correlation diagram, showing the effect of the extension of the conjugation system on the first two IP's and the α-, ρ-, and β-band energies. Values for circumanthracene extrapolated by Hückel theory (eq 1–4).

Figure 10. IR spectra of pyrene, coronene, ovalene, and Clar's hydrocarbon in KBr (Perkin-Elmer spectrophotometers; first three spectra Model 125 and last spectrum Model 683).

approximately analyzed in terms of Groenewege's scheme.[2] Thus, pyrene with four duo and six trio C–H bonds shows the two expected bands in the duo (800–860-cm^{-1}) and trio (750–810-cm^{-1}) regions. Coronene with 12 duo C–H bonds has only one strong band in the duo range. Ovalene with 12 duo and two solo bonds shows, in addition to the duo band, a solo band in the solo region (860–910 cm^{-1}). The spectrum of circumanthracene should be similar to that of ovalene, with the solo band being more intense because there are now four solo bonds. Clar's hydrocarbon shows, besides the intense duo band, a very weak solo band and a medium-intensity band at 745 cm^{-1} which is interpreted as being due to the three trio C–H bonds in XII. Thus, while not definitively proving XII, the IR data exclude beyond doubt the circumanthracene structure.

As a final piece of evidence in favor of XII, the mass spectrum would of course be welcome. Satisfactory spectra were obtained long after the true structure of "circumanthracene" was deduced from the PE and UV spectra and communicated at various occasions.[33] The compound proved to be uniform, and at 300 °C

ovalene are relatively simple, while that of Clar's hydrocarbon contains many additional bands. Furthermore, the 735–910-cm^{-1} region, which is due to the out-of-plane C–H vibrations, can be

Table I. Comparison between Observed and Calculated π-IP's with Molecular Orbital Assignments[a]

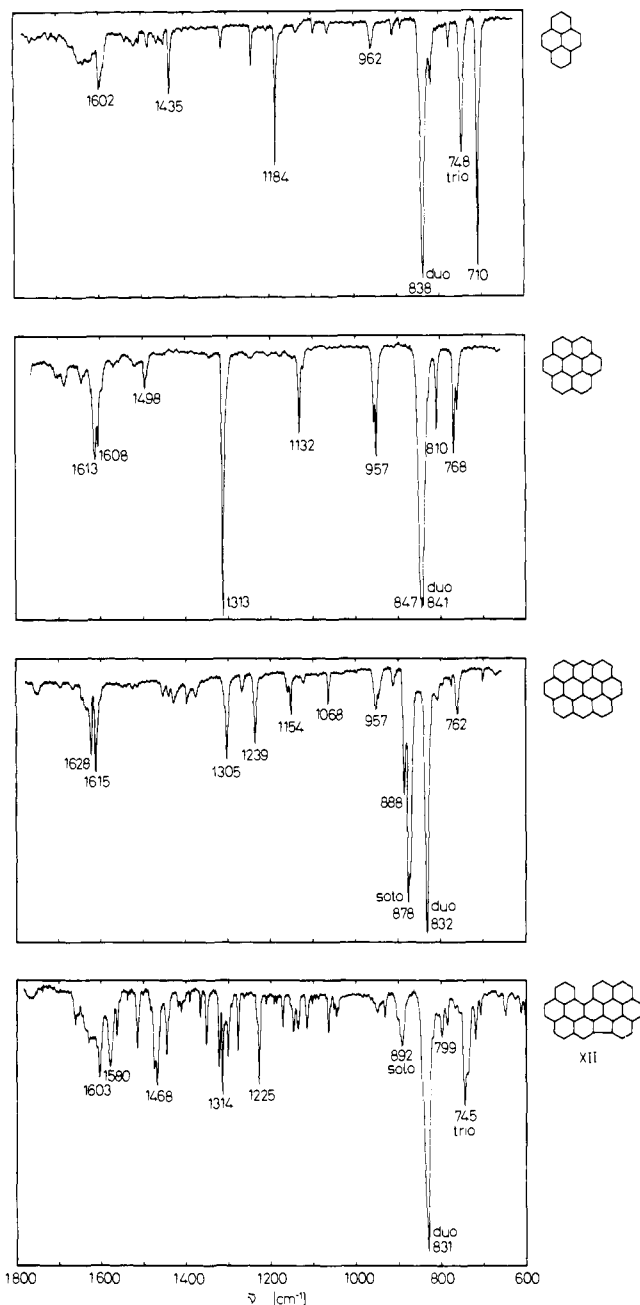| hydrocarbon			π-IP's, eV										
X	C_{2h}	obsd	6.50	7.37	7.65	8.04	8.48	8.60	8.60	8.72	9.28	9.77	9.77	10.3
		calcd	6.58	7.58	7.66	8.11	8.60	8.63	8.65	8.79	9.35	9.84	9.88	10.24
			B_g	B_g	A_u	A_u	B_g	A_u	B_g	B_g	A_u	B_g	A_u	A_u
	D_{2h}	obsd	7.41	8.27	9.04	9.35	10.00							
		calcd	7.34	8.34	9.03	9.36	10.03							
			B_{3g}	B_{2g}	B_{1u}	A_u	B_{1u}							
	D_{6h}	obsd	7.29	7.29	8.62	8.62	9.13	9.13	10.2	10.55	10.55			
		calcd	7.39	7.39	8.70	8.70	8.99	9.04	10.32	10.65	10.65			
			E_{2u}		E_{1g}		B_{2g}	B_{1g}	A_{2u}	E_{2u}				
	D_{2h}	obsd	6.71	7.33	7.99	8.25	8.66	8.66	8.96	9.64	10.0	10.0		
		calcd	6.74	7.47	8.03	8.34	8.61	8.71	8.99	9.62	9.96	10.09		
			B_{2g}	B_{3g}	A_u	B_{1u}	B_{1u}	A_u	B_{2g}	B_{3g}	B_{2g}	B_{3g}		
	D_{2h}	obsd	...	...	...	...	...	...	...	...	...	...	...	...
		calcd	6.31	7.45	7.55	7.97	8.43	8.52	8.59	9.03	9.04	9.53	9.74	10.09
			A_u	B_{2g}	B_{1u}	B_{3g}	A_u	B_{3g}	B_{2g}	B_{1u}	B_{2g}	A_u	B_{1u}	B_{3g}
XII	C_s	obsd	6.69	7.29	7.44	8.17	8.51	8.51	8.51	8.85	9.35	9.86	10.1	10.5
		calcd	6.79	7.30	7.62	8.20	8.44	8.60	8.67	8.87	9.33	9.66	9.92	10.37
			A"	A"	A"	A"	A"	A"	A"	A"	A"	A"	A"	A"
XIII	C_{2h}	obsd	...	...	...	...	...	...	...	...	...	...	...	...
		calcd	7.01	7.16	7.56	8.13	8.25	8.60	8.80	8.84	9.37	9.55	9.90	10.53
			B_g	A_u	B_g	B_g	A_u	B_g	A_u	B_g	A_u	A_u	B_g	B_g

[a] D_{2h} molecules oriented in the x,y plane, with x vertical and y horizontal.

Table II. Comparison between Observed and Calculated π-IP's with Molecular Orbital Assignments

| hydrocarbon			π-IP's, eV										
XV	C_s	obsd	6.58	7.38	7.84	7.84	8.31	8.64	8.89	8.89	9.44	9.8	9.8	10.2
		calcd	6.59	7.30	7.81	7.91	8.31	8.69	8.89	9.03	9.43	9.67	9.84	10.18
			A"	A"	A"	A"	A"	A"	A"	A"	A"	A"	A"	A"
XVI	D_{2h}	obsd	6.90	7.73	7.92	8.28	8.70	8.93	9.58	9.58	9.72	10.26		
		calcd	6.91	7.64	7.90	8.33	8.74	8.96	9.51	9.62	9.88	10.31		
			B_{1u}	B_{3g}	A_u	B_{2g}	B_{1u}	A_u	B_{2g}	B_{3g}	B_{1u}	B_{3g}		
XVII	C_{2v}	obsd	7.11	7.34	7.89	8.46	8.71	8.71	9.53	9.53	10.1	10.1		
		calcd	7.23	7.27	7.93	8.55	8.61	8.66	9.59	9.63	10.08	10.15		
			A_2	B_1	A_2	B_1	A_2	B_1	A_2	B_1	A_2	B_1		

the molecular ion was found at m/e 472, with the doubly and triply charged ions coming at 236 and 157.3, respectively. Increasing the probe temperature to 395 °C produced no new signals. At this temperature, even traces of circumanthracene should be easily detectable since hexa-*peri*-benzocoronene and quaterrylene gave intense signals in the 370–395 °C range.

In order to settle the discrepancy between the 1956 X-ray structure and the present spectroscopic findings, we made an attempt to repeat the single-crystal X-ray work. The crystal selected for this purpose gave approximately the same lattice constants as in the earlier study, but the quality of the X-ray photographs was so poor that further refinement proved impossible; in particular, the higher order reflections faded away too rapidly. As it stands, structure XII fitted the data almost equally well as XI and XIII. The reason for this became immediately evident when the crystals were examined under the optical and scanning electron microscope: they had a most complicated morphology and were obviously unsuited for single-crystal work. Since the present spectroscopic evidence in favor of XII is conclusive, attempts to grow better crystals were not deemed to be worthwhile and therefore abandoned.

Related Structural Problems

Regarding the mode of formation of Clar's hydrocarbon, it is worth noting that the decarboxylation was carried out at 1 torr. Lack of material so far prevented us from testing whether XII is formed from IX or from X and whether residual oxygen is essential for C–C coupling. As long as information on these questions is lacking, the possibility of C–C coupling in pyrolytic processes should always be considered for compounds comprising the 3,4-benzophenanthrene skeleton.

We report here on yet another case where an otherwise well-understood reaction yielded an unexpected product. Elbs pyrolysis of the ketone XIV[34] under CO_2 gave, besides the expected naphthopyrenopyrene (XV), approximately the same amount of pyrenopyrene (XVI) which is formed as a splitting product. Both
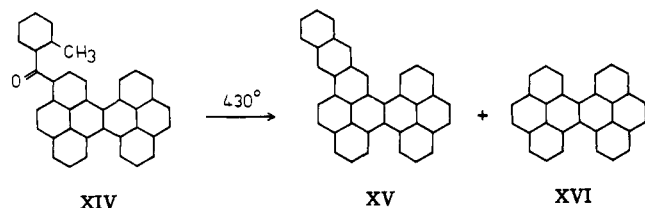
could be separated by chromatography, and XV crystallized in the form of orange-red needles of mp 309–310 °C. We became interested in XV because of its intense red crystal luminiscence. Examination by temperature-programmed PE spectroscopy showed that the compound contained about 35% of a new hydrocarbon whose PE spectrum could be measured at 260 °C; for the IP's see Table II. Analysis of the spectrum shows the hydrocarbon to be 3,3′-dehydropyrenopyrene (XVII), apparently

XVII

formed by oxidative C–C coupling from XIV or XVI. This assignment is confirmed by the appearance of the molecular ion at m/e 374 in the mass spectrum of the mixture. When the probe temperature was increased to 275 °C, the PE spectrum of XVII faded completely and was replaced by that of XV whose con-
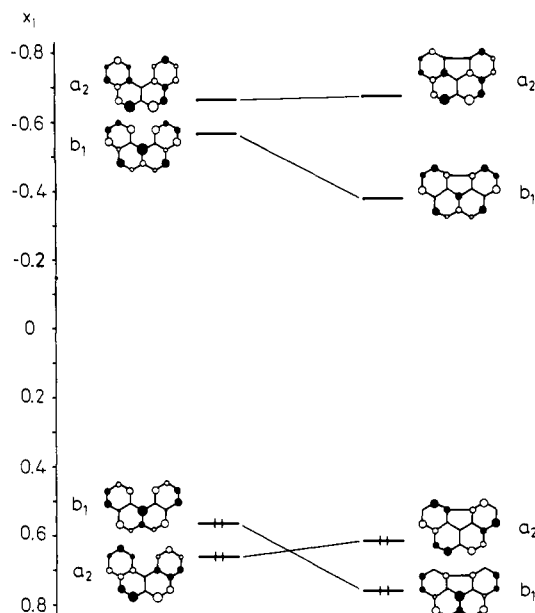
Figure 11. Hückel correlation diagram, showing the increase in IP_1 and the decrease in the HOMO–LUMO excitation energy in going from an alternant to a nonalternant hydrocarbon. Bonding occurs between AO's of the same (starred or unstarred) set: left, 3,4-benzophenanthrene; right, 2,13-benzofluoranthene.

stitution is proven by the agreement between observed and calculated IP's (cf. Table II) and by the mass spectrum.

A similar cyclodehydrogenation process may have occurred in Jenny and Peter's attempted synthesis of [10]coronaphene.[35] Dehydrogenation of the cyclophane XVIII with $AlCl_3$ and Pd/C yielded a hydrocarbon which, judging from its intense yellow-green fluorescence, may be the fluoranthene derivative XIX or XX.
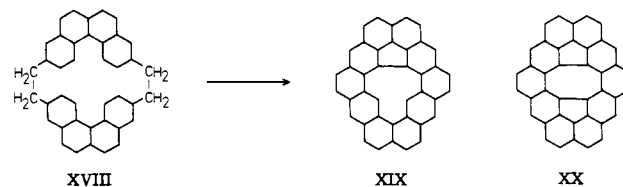
Concluding Remarks

The most important achievement of this work lies in the fact that it permits a straightforward and unambiguous distinction between alternant and nonalternant hydrocarbons. Earlier workers utilized fluorescence quenching to this end, the rate constants for quenching by electron acceptors usually being larger for alternant than for nonalternant hydrocarbons; the reverse holds for electron donors.[36] This is a tedious procedure, necessitating Stern–Volmer plots and lifetime measurements, and therefore prone to experimental errors due to trace impurities. Furthermore, among the 22 hydrocarbons studied in ref 36, several borderline cases and even exceptions are apparent. A more satisfactory but not yet systematically explored method would be ESR since the spectra of the radical cations and anions differ appreciably for nonalternant hydrocarbons, while they are very similar for the alternant ones.[37]

The present method, relying on the combined use of PE and UV spectroscopy, is readily applied and does not require highly purified substances, as the results for naphthopyrenopyrene show. Compared with alternant hydrocarbons of the same IP_1 and IP_2 values, the absorption bands of nonalternant compounds are always shifted to the red, never to the violet. This is most impressively

(33) The results were presented in seminars (Ruder Boskovic Institute, Zagreb, April 1979; Physik.-Chem. Institut Universität Zürich, June 1979; Chemiedozententagung, Erlangen, March 1980) and communicated to colleagues (e.g., Professor H. Inokuchi, Tokyo, Dec 1978).

(34) E. Clar, J. F. Guye-Vuillème, and J. F. Stephen, *Tetrahedron*, **20**, 2107 (1964).

(35) W. Jenny and R. Peter, *Angew. Chem., Int. Ed. Engl.*, **4**, 979 (1965). Private communication from W. Jenny to E. Clar.

(36) U. Breymann, H. Dreeskamp, E. Koch, and M. Zander, *Chem. Phys. Lett.*, **59**, 68 (1978).

(37) (a) F. Gerson, "Hochauflösende ESR-Spektroskopie", Verlag Chemie, Weinheim, 1967, p 107. (b) F. Gerson and J. Heinzer, *Helv. Chim. Acta*, **49**, 7 (1966).

Chart I

−0.381	−0.503	−0.668
−0.371	−0.445	−0.388
0.298 (6.74)	0.445 (7.17)	0.323 (7.05)
0.618 (7.53)	0.669 (7.87)	0.842 (8.20)

seen from Figure 7 where the observed band positions for Clar's hydrocarbon are compared with those calculated by eq 2–4. Conversely, among hydrocarbons with the same ρ band position,[38] the nonalternant ones have always higher IP_1 values.

At the most naive level, this seemingly paradox behavior is due to the fact that in alternant hydrocarbons (for which the pairing theorem holds) the partial bond orders between AO's of the same—starred or unstarred—set are positive for HOMO and LUMO, while they are negative for the second highest occupied and second lowest unoccupied orbitals. Introduction of a new bond to give a five-membered ring will thus lower the HOMO and LUMO energies, while the second highest occupied and second lowest unoccupied levels are raised. This results in a decrease

of the HOMO–LUMO gap, as shown in the Hückel correlation diagram (Figure 11) for the simplest case of interest, namely, 3,4-benzophenanthrene and 2,13-benzofluoranthene. Although the latter has the higher IP_1 value (7.90 vs. 7.61 eV), it absorbs at longer wavelengths.

Hückel calculations for a large number of known as well as unknown nonalternant hydrocarbons show that the lowering of the HOMO and LUMO energies is a quite general result. Among the known compounds, for which PE spectra are available, only three exceptions were found; their eigenvalue coefficients for the two lowest unoccupied and highest occupied levels, with measured IP's in brackets, are shown in Chart I. Yet their absorption bands are at longer wavelengths than expected on the basis of eq 2–4. This applied also to acepleiadylene which, judging from its level scheme, might be considered as quasi-alternant. Its ρ band in benzene as solvent is expected at 385 nm, while it is found at about 570 nm.

A forthcoming paper in this series will describe application of our scheme to some long-standing structural problems, for instance, the hydrocarbon obtained from naphthalene and fumaryl chloride[39] and the compounds formed in the attempted syntheses of terrylene and quaterrylene.[40]

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(38) The ρ band corresponds in a good approximation (see eq 3) to the HOMO–LUMO transition.

(39) (a) E. Clar, "Aromatische Kohlenwasserstoffe", Springer-Verlag, Berlin, 1952. (b) D. G. Stewart, Ph.D. Thesis, University of Glasgow, 1953. (c) W. Kemp, Ph.D. Thesis, University of Glasgow, 1956. (d) G. S. Fell, Ph.D. Thesis, University of Glasgow, 1959.
(40) (a) E. Clar, Chem. Ber., 81, 52 (1948); (b) E. Clar, W. Kelly, and R. M. Laird, Monatsh. Chem., 87, 391 (1956).

A Molecular Orbital Study of Hydrogen, Methyl, and Phenyl Bridging in Beryllium Compounds

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Abstract: A detailed molecular orbital study of molecules of the type $R^t BeR^b_2 BeR^t$ and the corresponding monomers $R^t BeR^b$ is presented for R^t = H, CH_3, F, BH_4, C_5H_5, and phenyl and R^b = H, CH_3, or phenyl. The effect of a substituent in the R^t position is measured by calculating ΔE's for dimerization and comparing them to that for R^t = H. Cyclopentadiene groups are shown to *strongly* disfavor dimerization, while CH_3 or F substituents in the R^t position slightly destabilize the dimers. BH_4 substituents provide a small dimer stabilization. Phenyl bridging is shown to be highly favored relative to methyl bridging. These effects are rationalized by examining orbital interactions, particularly π-bonding effects involving formally vacant orbitals on beryllium.

Introduction

While the phenomenon of hydrogen bridging has been well studied in the boron hydrides, carboranes, and related molecules,[1] significantly less is known about bridge formation in molecules containing beryllium. Of particular interest is the fact that unlike boron, beryllium-containing molecules are known to form bridges with methyl[2] and phenyl[3] groups, in addition to hydrogen bridges.

The simplest system in which a Be–H–Be bond occurs is the beryllium hydride dimer. Although I has not been observed

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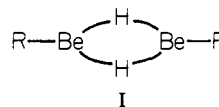
experimentally, it has been thoroughly studied by accurate SCF-CI calculations,[4] which have placed the dimerization energy at ~30 kcal/mol. This value is comparable to the borane dimerization energy, which is thought to be ~35 kcal/mol.[5] Other examples of bridge hydrogens involving beryllium include solid BeH_2, $EtBeH_2BeEt_2{}^{2-}$, beryllium borohydride, and methylberyllium borohydride,[6–9] the latter two examples having Be–H–B bridges.

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