Effect of Overcrowding on Mass Spectra of Polycyclic Aromatic Hydrocarbons; Co-operative Double Cyclization of Two Methyl Substituents at Overcrowded Positions

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Mass spectra of 1,10- (**2**) and 3,12-dimethyltetrabenzo[*de,hi,op,st*]pentacene (**3**), and 14-methyl-5-(2-methyl-1-naphthyl)- (**5**) and 12-methyl-5-(4-methyl-1-naphthyl)-benzo[*a*]perylene (**6**) were investigated to elucidate the effect of methyl substitution at overcrowded positions. Compound (**2**) showed a very strong $[M - 6]^{\cdot +}$ peak, whereas the spectra of (**3**), (**5**), and (**6**), which were similar to each other, showed intense $[M - 32]^{\cdot +}$ peaks. Thus, only in the case of the overcrowded compound (**2**) did a cyclization reaction occur. In the case of the analogous structure (**5**) release from overcrowding is achieved by twisting of the ring planes. This reaction also occurred on heating (**2**) in quinoline.

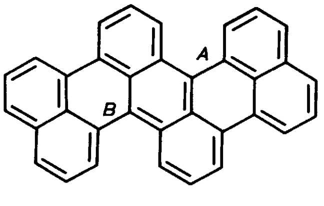
We have reported previously on the effect of overcrowding in the mass spectra of condensed polycyclic aromatic compounds.[1–3] We have established that the mass difference between a molecular ion and the most intense fragment ion in the ion-family of highest valency corresponds to the number of overcrowded hydrogen atoms detached from the parent ion, and that the mass patterns differ according to type of overcrowding (fjord-like or crab-like).[3] The high abundance of specific fragment ions at 70 eV was correlated with the lowering of their appearance energies, which provide a rough measure of the heats of formation for the reactions producing these specific fragment ions.[4]

In this paper we report the characteristic absorption spectra and mass patterns of overcrowded dimethyl derivatives, and describe a new type of aromatic cyclization reaction. A dehydrogenation reaction with co-operative double cyclization was observed not only in the mass fragmentation of multicharged ions with two methyl substituents at positions of fjord-like overcrowding, but also on heating a dilute homogeneous solution of the same molecule.

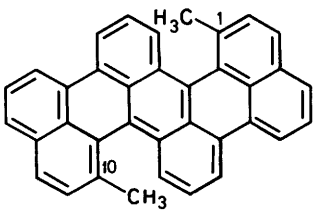
Experimental

Tetrabenzo[*de,hi,op,st*]pentacene (TBPA) (1)[1] and its 1,10-dimethyl derivative (2) were prepared by Clar's method.[5] The crude products were purified by repeated recrystallizations from xylene and column chromatography over activated alumina in xylene. 3,12-Dimethyl-TBPA (3) was synthesized and purified by a similar method. 5-(1-Naphthyl)benzo[*a*]perylene (4) and its dimethyl derivatives (5) and (6) were prepared by the action of naphthylmagnesium bromide or the corresponding methyl derivatives on 1-chloroanthraquinone, according to a similar procedure.

U.v.–visible absorption spectra were measured with a Shimadzu D-40R-W spectrophotometer. Mass spectra were measured with a Shimadzu LKB-9000 gas chromatograph–



(1)



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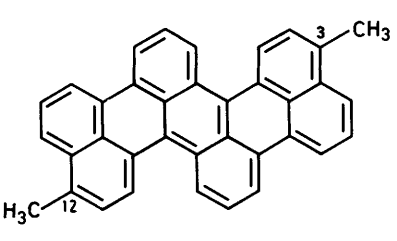

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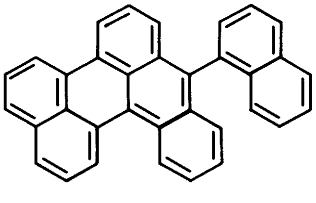

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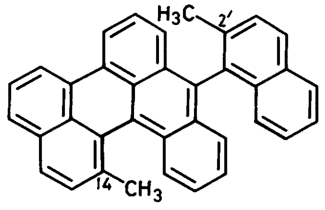

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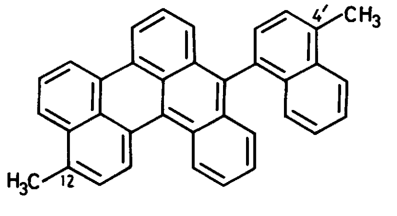


(6)

mass spectrometer using a direct inlet system. Conditions were as follows: a few micrograms of each sample dissolved in a few microlitres of the highest grade benzene (Wako Chem. Co.) were inserted into the vacuum chamber of the ionization source. The temperature of direct inlet was varied from 35 to 220 °C; temperature in the ionization source chamber was kept at 350 °C, the ionization energy was 70 eV, and the emission current was 60 μA.

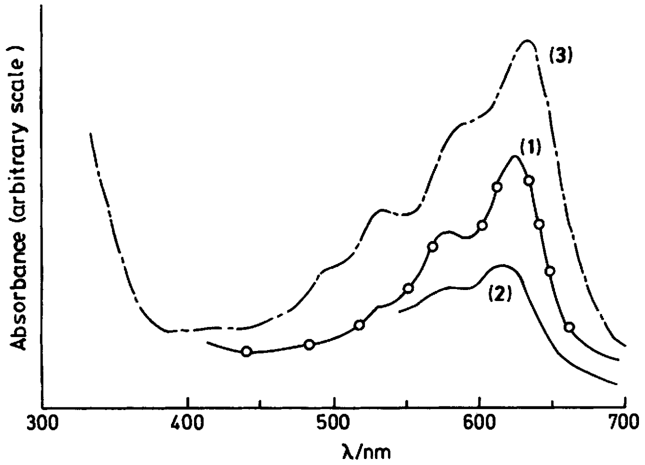


Figure 1. Visible absorption spectra of tetrabenzopentacenes (1)—(3). The spectrum of (2) was overlapped by impurity absorptions; only the part of longer wavelength was thought to be reliable and is given here

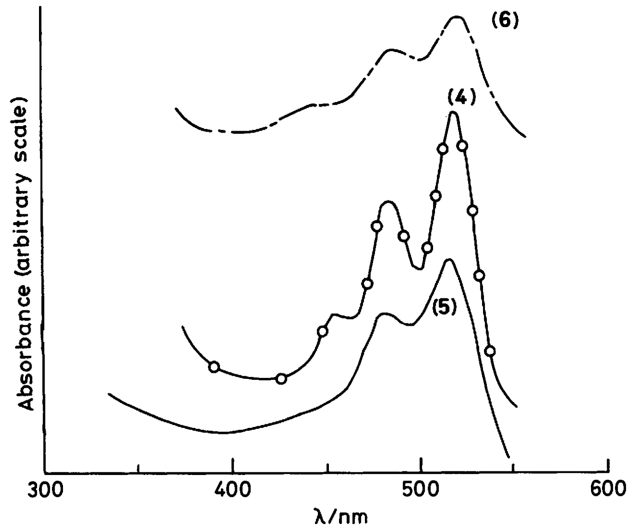


Figure 2. Visible absorption spectra of 5-naphthylbenzo[*a*]perylenes (4)—(6)

Results and Discussion

Visible absorption spectra were used for identification and purity checks. As shown in Figures 1 and 2, the spectra of (1)—(3) and (4)—(6) were similar within each group, reflecting the presence of the same conjugated ring system. While the *p*-bands of the former group appeared around 630 nm, those of the latter appeared at lower wavelength (about 520 nm) owing to the breakdown of the pentacene skeleton and the twisting of the ring planes. Generally, methyl substitution causes a red shift because of hyperconjugation; indeed this applies to the substitution at uncrowded positions in the molecules (3) and (6). However, substitution at the overcrowded positions in (2) and (5) brought about a blue shift, resulting from decreased conjugation. In order to confirm these speculations, HOMO and LUMO energy levels of Hückel molecular orbitals were calculated. Overcrowding was taken into consideration as a decrease in the resonance integral about the bonds *A* and *B* [see (1)] in the pentacene skeleton; this was assumed to be proportional to the overlap integral and to follow a cosine function of the torsion angle. This type of approximation has been used, for example, in the calculations by the PPP method for overcrowded molecules.[6,7] As seen in Table 1, the coincidence with observed values was qualitatively good and several torsion angles were evaluated. The naphthalene plane was shown to be considerably twisted from the plane of the benzo[*a*]perylene for compound (4)—(6).

Mass spectra of the molecules (2), (3), (5), and (6) are shown in Table 2 and Figure 3. In the spectrum of 1,10-dimethyltetrabenzo[*de,hi,op,st*]pentacene (2), $[M - 6]^{i+}$ was the highest peak for both doubly and triply charged ions. Even for singly charged ions, $[M - 6]^{+\bullet}$ was the second highest except for the isotope molecular ion $[M + 1]^{+}$. However, $[M - 3]^{i+}$ was notably weak. The ion families $[M - 18]^{i+}$ and $[M - 30]^{i+}$ also showed high intensity, though not the highest.

The isomeric dimethyl derivative (3) did not show a very strong $[M - 6]^{i+}$ peak; the most intense peaks were at $[M - 19]^{2+\bullet}$ and $[M - 30]^{3+\bullet}$ for the multi-charged ions. The mass spectra of the dimethyl derivatives (5) and (6) differed considerably from that of (2) but were similar to each other and to that of (3). The intensity of the $[M - 141]^{+}$ ion of (5) was twice as large as that of (6), although both were of low intensity. Since this ion may be considered to be formed by elimination of the methylnaphthyl group, this observation can be understood as the effect of overcrowding in (5).

The mass spectra of (5) and (6) had strong peaks

Table 1. Calculated and observed wavelengths of *p*-bands

Molecule	λ_p (obs.)/nm	Torsion angles[a]		$\Delta E/\beta$[b]	λ_p (calc.)/nm[c]
		Bond *A*	Bond *B*		
(3)	635	15	15	0.385	601
(1)	627.6	15	15	0.392	595
(2)	620	27	27	0.402	588
(6)	522	60	15	0.503	520
(4)	520	60	15	0.508	517
(5)	517.6	65	27	0.522	509

[a] Resonance integrals about bonds *A* and *B* in the pentacene skeleton [see (1)] were assumed to follow $\beta \cos \theta$ according to Mulliken's approximation.[6] The heteroatom model was used for the methyl parameters [$\alpha(CH_3) = \alpha + 2\beta$, $\beta(CH_3\text{-}C) = 0.7\beta$]. [b] The difference between LUMO and HOMO energy levels. [c] Calculated by the approximation $\lambda/\text{nm} = 10^7/(8\,196 + 21\,940\Delta E/\beta)$ (E. Heilbronner and J. N. Murrell, *J. Chem. Soc.*, 1962, 2611).

Table 2. Mass spectra (relative intensities) for the dimethyl derivatives (**2**), (**3**), (**5**), and (**6**) [molecular weights 454 for (**2**) and (**3**); 456 for (**5**) and (**6**)]

	Monovalent			
m/z	(**2**)	(**3**)	(**5**)	(**6**)
459			5.2	2.7
458			20.6	14.8
457			47.7	46.3
456	5.8	12.9	100	100
455	42.5	40.6	5.5	5.4
454	100	100	4.5	5.2
453	17.0	14.3	3.1	3.7
452	19.8	6.1	1.8	1.9
451	11.3	6.0	1.9	2.0
450	10.1	4.7	1.7	1.5
449	15.8	3.3		
448	26.7	5.0	1.9	1.7
446	5.9	1.3		
443			4.4	2.7
442	1.0	1.2	11.0	8.2
441	7.9	1.6	8.9	8.0
440	12.9	5.6	15.5	14.6
439	8.1	4.6	9.2	9.3
438	18.7	9.2	5.9	5.8
437	15.0	10.4	7.4	6.4
436	8.4	2.3	2.1	2.1
435	9.4	4.2	2.8	2.5
433	3.8	1.1		
428	3.2	0.6	3.2	2.5
427	1.6	1.0	8.1	7.0
426	1.6	1.7	12.5	9.8
425	3.7	2.1	7.0	6.2
424	6.7	4.5	8.1	6.6
423	2.0	1.0	1.7	1.2
422	4.0	1.7	1.7	1.0
414			1.1	
413	1.5	0.3	2.6	2.3
412	2.0	0.6	1.2	
411	2.4	1.4	3.0	2.5
Naphthyl loss				
316			2.7	1.9
315			2.7	1.7
314			1.6	1.2
313			3.8	3.0
300			2.4	1.8

	Divalent			
m/z	(**2**)	(**3**)	(**5**)	(**6**)
229			2.3	1.7
228.5			4.2	5.4
228		1.7	9.2	13.4
227.5		7.3	0.3	0.7
227	19.6	17.0	1.5	2.1
226.5		3.2	0.4	1.0
226	6.8	3.0	0.5	1.0
225.5	5.7	3.9	1.3	1.4
225	7.8	4.3	1.9	2.1
224.5	17.0	6.6	2.1	2.2
224	23.9	11.5	3.5	4.1
223	13.8	4.4	1.6	1.9
222	6.1	1.5		
221.5			3.0	2.3
221			8.3	6.8
220.5		1.4	11.1	12.8
220	2.4	5.0	14.7	17.7
219.5	7.5	11.1	5.8	7.2
219	17.4	16.3	10.1	10.9
218.5	17.1	15.6	13.3	14.2
218	18.0	12.8	8.0	9.7
217.5	21.1	18.8	11.2	13.6
217	6.5	3.3	2.5	2.5
216.5	6.0	4.7	2.3	2.7
214			6.2	6.2
213.5		1.3	13.3	12.7
213		3.7	24.8	27.4
212.5	5.6	7.6	16.3	17.5
212	14.4	16.2	27.0	31.8
211.5	4.4	5.2	6.1	6.6
211	9.5	9.1	9.0	9.5
210.5	2.4	1.8	0.8	1.2
210	4.2	3.5	1.0	1.7
208	1.4		2.8	2.5
207	1.9	1.5	4.8	4.3
206.5		1.2	6.9	6.2
206	2.8	2.8	7.9	8.3
205.5	8.2	6.2	12.9	14.6
205	1.9	1.9	2.8	3.1
204.5	4.7	3.5	4.0	4.1
204	3.0			
203.5		1.6		
200.5			2.3	2.0
200	1.9		4.7	4.1
199.5		1.3	2.6	2.5
199	1.1	2.9	5.8	5.4
198	3.9	1.2	1.6	2.1
193.5			2.1	2.3
193	2.3			
192.5			2.5	2.1
187.5			0.7	0.8
187			2.0	2.1
186.5			0.5	0.3
186			0.9	1.2

	Trivalent			
m/z	(**2**)	(**3**)	(**5**)	(**6**)
152			0.3	0.4
151.3	0.8	0.4		
151		0.2	0.3	0.3
150.7	0.6			
150.3	0.8	0.3		
150	1.3	0.5	0.5	0.5
149.7	1.6	0.3		
149.3	2.5	0.9	0.2	0.2
148.7	0.6	0.3		
147.7			0.2	
147.3			0.2	
147	0.4		0.4	0.6
146.7		0.2	0.3	0.5
146.3		0.3	0.8	1.0
146	0.7	0.7	0.6	1.0
145.7	1.0	1.2	1.0	1.2
145.3	2.0	1.0	0.5	0.7
145	1.1	1.0	0.9	1.3
144.7	0.2	0.5		
142.3			0.6	0.6
142		0.5	1.1	1.8
141.7	0.3	0.6	1.2	1.7
141.3	1.3	1.2	2.0	1.9
141	0.8	1.0	1.0	0.6
140.7	0.9	1.0	0.7	0.9
138	0.3		0.3	0.6
137.7		0.2	0.6	0.8
137.3	0.3	0.4	0.6	0.7
137	0.9	1.0	1.2	1.8
136.7			0.3	
136.3	0.9	0.5	0.4	
133.7			0.2	
133.3	0.2		0.3	0.4
133	0.5	0.4	0.3	0.4
132.7		0.3	0.6	0.6
132	0.8	0.3		

corresponding to $[M - 32]^{i+}$ and $[M - 16]^{i+}$, especially for the multi-charged ions. These species may be interpreted on the basis of elimination of one or two methane (or CH_3 + H) units. In cases where two condensed-ring planes are twisted with respect to each other and their conjugation is considerably decreased, methyl elimination and formation of a five-membered ring is considered to be much easier than co-operative formation of six-membered conjugated rings, with elimination of two sets of three hydrogen atoms. The $[M - 3]^{i+}$ peaks were very weak for both (**5**) and (**6**).

In view of the observation of strong $[M - 6]^{i+}$ and weak $[M - 3]^{i+}$ peaks for (**2**), in contrast to (**3**), (**5**), and (**6**), we suggest that two new six-membered fused rings are added to the parent skeleton of (**2**) at the sites of the crowded methyl groups, to give dinaphtho[1,8,7-*abc*:1′,8′,7′-*jkl*]coronene (**7**).

Clar reported[8,9] that compound (**7**) was obtained along with (**2**) when 9,10-bis-(2-methyl-1-naphthyl)anthracene was heated with potassium hydroxide in quinoline. Compound (**2**) was considered to be an intermediate in the formation of (**7**). We have confirmed that the isolated substance (**2**) can be converted

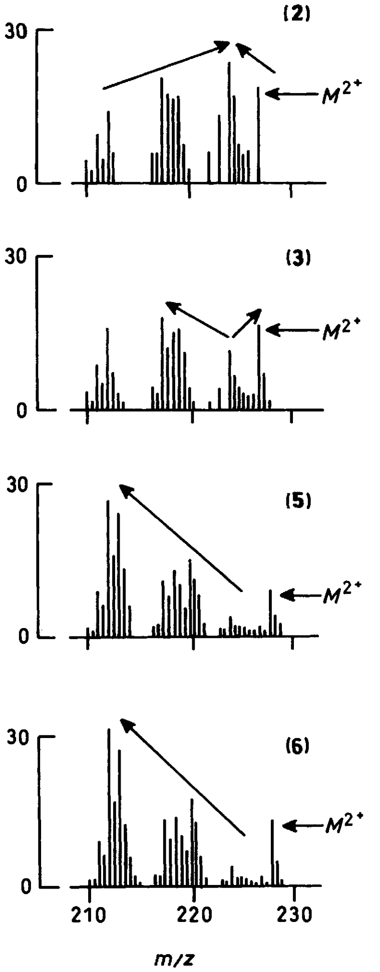
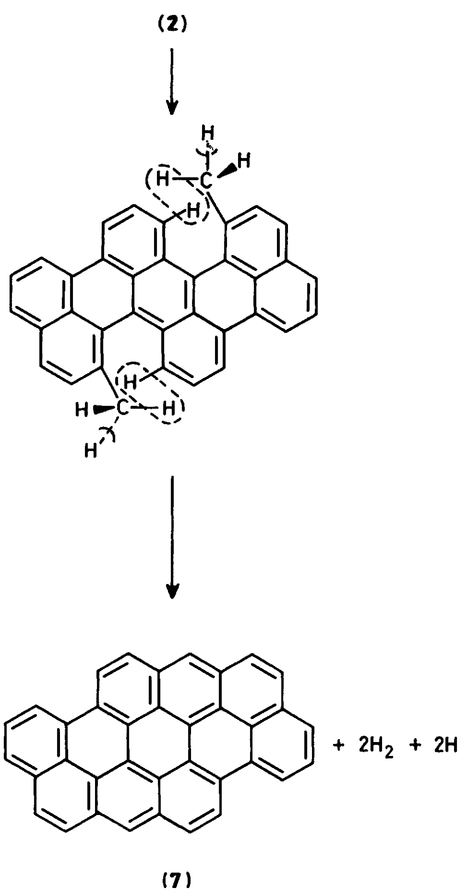


Figure 3. Mass spectra of doubly charged ions for the dimethyl derivatives (**2**), (**3**), (**5**), and (**6**); arrows indicate the highest peaks in the groups

into (**7**) simply by heating in quinoline.* The product (**7**) was identified by its absorption spectrum. This pyrolytic cyclization may be compared with the well known Elbs pyrolysis reaction.[9] Elbs pyrolysis occurs with *o*-methyl aromatic ketones and may give two isomers with elimination of one water molecule. Our pyrolysis occurs with a system containing methyl substituents at two positions of fjord-like overcrowding, and gives one product with elimination of three hydrogen molecules.

It might be expected that heating compound (**2**) in the direct inlet would also give compound (**7**). In fact, we observed the mass spectrum of (**7**) as the last component when (**2**) was heated for an extended period in the direct inlet. Its mass pattern showed the highest molecular-ion peak $[M]^{+\bullet}$ at *m*/*z* 448 and no discernible signal for $[M + 6]^{+\bullet}$ at 454 {corresponding to $[M - 6]^{+\bullet}$ and $[M]^{+\bullet}$, respectively, of (**2**)}. We thus confirmed that a relatively strong $[M - 6]^{+\bullet}$ peak and all other peaks in the preceding discussion belonged to the molecule (**2**) and not to the pyrolysis product (**7**).

In conclusion, we observed unusually high intensity $[M - 6]^{i+}$ fragments for the molecule (**2**). The ions $[M - 6]^{2+}$ and $[M - 6]^{3+\bullet}$ were the strongest among the doubly and triply charged ions, respectively. This observation is interpreted as another effect of overcrowding,[1,3] resulting from co-operative elimination of six hydrogen atoms at the overcrowded positions and the addition of two six-membered fused rings to the parent skeleton. This new type of co-operative double cyclization is also an easy thermolytic reaction and might be applied to the synthesis of large fused-ring aromatic compounds.



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Received 1st April 1987; *Paper* 7/711

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* Details to be reported in a later paper.