

## Synthesis and Physical Properties of Azapolycyclic Hydrocarbons. Part 1. Preparation of 1-Azabenzanthrone and its Condensation Products and their Structural Determination

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Preparation of 1-azabenz[*de*]anthrone (**27**) was carried out by making use of a German Patent reaction. An improved procedure gave (**27**) easily and rapidly. Compound (**27**) underwent self-condensation *via* a zinc-catalysed method or an alkali-fusion procedure. The zinc-catalysed condensation product was separated into four isomers; 3,12-diazatetrabenzo[*a,cd,j,lm*]perylene (**7**), 3,15-diazabenz[*rst*]phenanthro[1,10,9-*cde*]pentaphene (**4**), 5,17-diazadibenzo[*a,rs*]naphtho[8,1,2-*cde*]pentaphene (**3**), and 5,10-diazabenz[*rst*]phenaleno[1,2,3-*de*]pentaphene (**6**). The major component was (**3**). The reduced product after alkali-fusion condensation of (**27**) was separated into four isomers; (**7**), (**3**), (**6**), and 5,14-diazadinaphtho[1,2,3-*cd*:1',2',3'-*lm*]perylene (**2**). The major component was (**2**).

The structures of the isomers were assigned from their oxidation products, m.p., u.v.-visible, i.r., and mass spectra. According to our assignments, (**6**) and possibly 5,14-diazatetrabenzo[*a,cd,lm,o*]perylene (**10**) are new structural isomers of fused nanocyclic compounds whose parent aromatic hydrocarbons have not been prepared, though (**10**) has not actually been isolated.

Since 1950 some violanthrene homologues (**1**)—(**24**) and their complexes have been shown to be prototypes of organic semiconductors or photoconductors.<sup>1,2</sup> Nanocyclic and undecacyclic compounds belong to the largest molecular group of fused polycyclic aromatics, in which many isomers can be isolated as pure substances.<sup>3</sup> Therefore, they are very good model compounds for the investigation of the effects of structural differences among isomers and hetero-atom substitution on their physical and chemical properties.

One of the self-condensation products of benzanthrone (**25**), violanthrene A (**13**) (Scheme 1), has excellent photoconducting characteristics.<sup>1</sup> The self-condensation of (**25**) also afforded tetrabenzo[*a,cd,j,lm*]perylene (**19**) (Scheme 1), which has interesting photoconducting properties,<sup>2</sup> presumably because its structure is twisted.<sup>4</sup> A nitrogen atom in the skeleton might have some effect on the structures and charge distributions of 7*H*-1-azabenz[*de*]anthracen-7-one (1-azabenzanthrone) (**27**) and its condensation products and might have a significant effect on their photoconductivity. We were interested in the physical properties of aza-analogues of (**25**) and their condensation products; therefore we report here an excellent procedure for the synthesis of (**27**) and its condensation products.<sup>5</sup>

As previously reported by Aoki *et al.*,<sup>6</sup> self-condensation of (**25**) or 3-bromobenzanthrone (**26**) in a mixture of zinc chloride and zinc dust afforded mainly isoviolanthrene B (**16**) or violanthrene B (**15**) (Scheme 1), respectively. In the same suspension, the major component from (**27**) was the violanthrene B-type product (**3**).

Yokote *et al.*<sup>7</sup> reported that self-condensation of (**26**) in a mixture of potassium hydroxide and phenol yielded mainly (**14**)-like compounds. In the present work, self-condensation of (**27**) also gave mainly (**14**)-like products. These results supported the conclusion that the type of condensation from (**27**) is similar to that from (**26**).

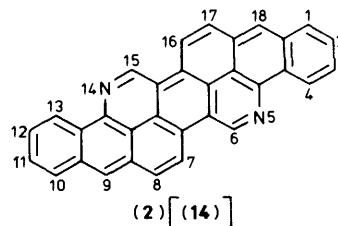
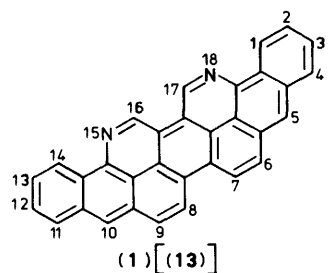
The structural identification of these polycyclic aromatics, other than by unambiguous syntheses, is not an easy problem, powerful methods of characterization being necessary.

There are at least six isomers, (**13**)—(**16**), (**19**), and (**21**), confirmed as nanocyclic hydrocarbons which might be regarded as reduced bimolecular condensation products of benzanthrone. Five of them, (**13**)—(**16**) and (**19**) have been prepared directly from benzanthrone (Scheme 1).<sup>8</sup>

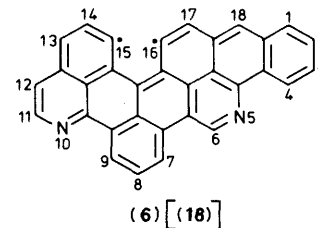
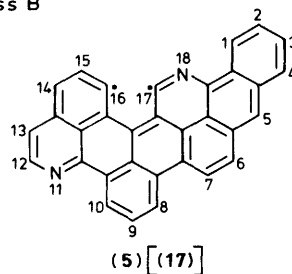
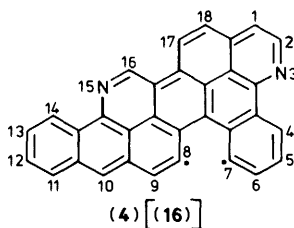
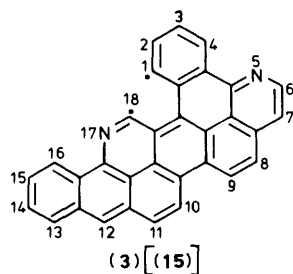
Binary condensation of benzanthrone (**25**) occurs mainly at the 3,4 positions for the reduction after alkali fusion, while it occurs at positions 6 and 7, and in higher yields for the reduction in fused zinc chloride. The possibility of condensation at the 6,7 or 7,8 positions is also increased by the substitution of more electronegative nitrogen (**27**) and (**28**) or bromine atom (**26**) and (**28**) at the X or Y position, respectively, of benzanthrone.<sup>7</sup> Thus, all combinations of the condensation at the 3,4; 6,7; and 7,8 positions give the following twelve isomers, which are grouped into classes A, B, T, and H.

Class A consists of the condensation products between the 3,4 and 3,4 positions with no noticeable overcrowding. The compounds are two almost planar isomers, anthro[9,1,2-*cde*]benzo[*rst*]pentaphene (dinaphtho[1,2,3-*cd*:3',2',1'-*lm*]perylene, violanthrene A) (**13**) and benzo[*rst*]phenanthro[10,1,2-*cde*]pentaphene (dinaphtho[1,2,3-*cd*:1',2',3'-*lm*]perylene, isoviolanthrene A) (**14**). Class B contains the condensation products between the 3,4 positions of one molecule and the 6,7 or 7,8 positions of the second with one intermediate overcrowding (designated by ● ● on the formulae). The following four isomers belong to this class; dibenzo[*a,rs*]naphtho[8,1,2-*cde*]pentaphene (violanthrene B) (**15**), benzo[*rst*]phenanthro[1,10,9-*cde*]pentaphene (isoviolanthrene B) (**16**), tribenzo[*kl,rs,vwx*]hexaphene (violanthrene C) (**17**) and benzo[*rst*]phenaleno[1,2,3-*de*]pentaphene (isoviolanthrene C) (**18**). Classes T and H are the condensation products between the 6,7 and 7,8 positions (any combination), and both have three isomers. Class T has no 7-7' bond connection and two intermediate overcrowdings, and the molecules have a twisted ring structure. Its members are tetrabenzo[*a,cd,j,lm*]perylene (**19**), dibenzo[*a,cd*]naphtho[1,8-*jk*]perylene (**20**), and tetrabenzo[*de,hi,op,si*]pentacene (**21**). Class H has a 7-7' bond connection and strong overcrowding

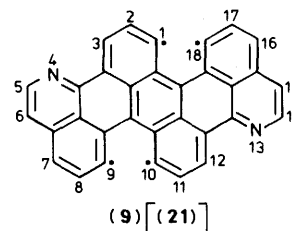
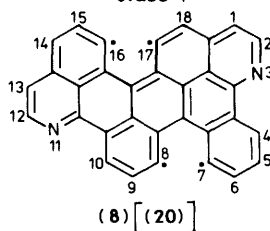
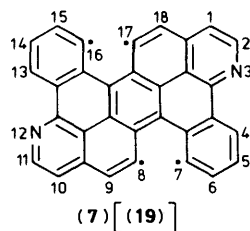
## class A



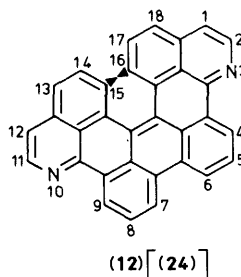
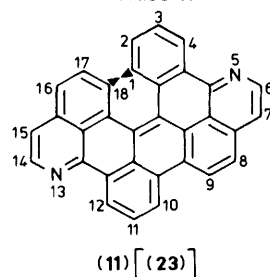
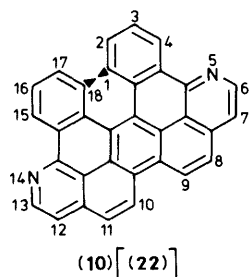
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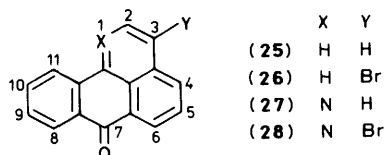
## class T



## class H



The number in brackets corresponds to the parent hydrocarbon isomer



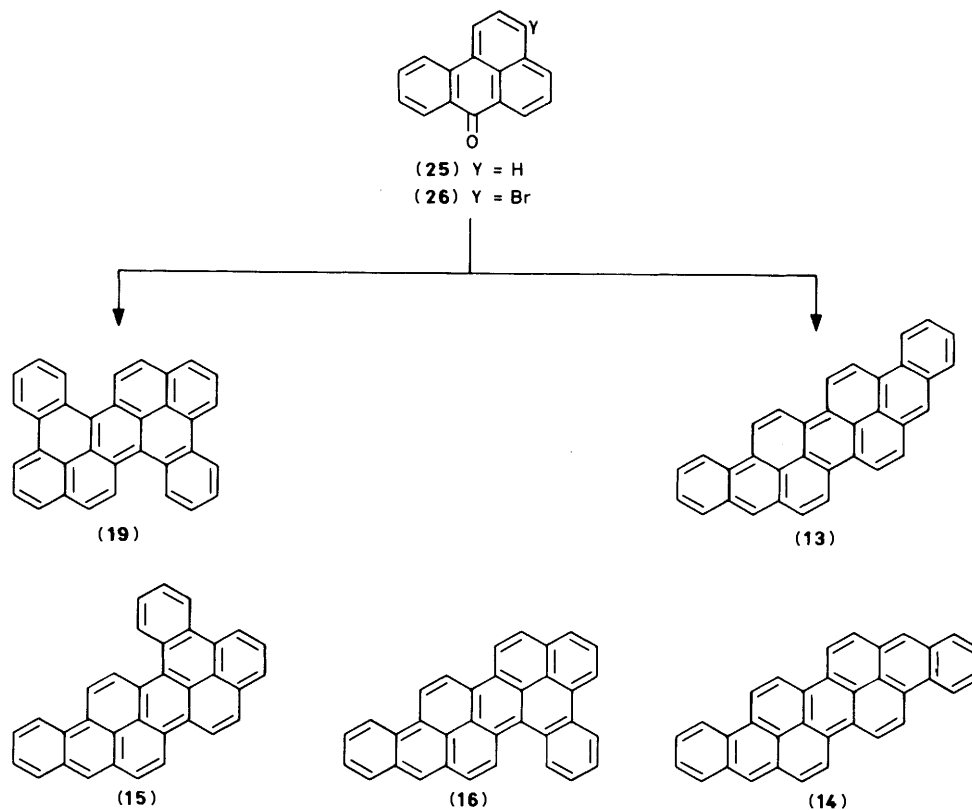
(designated by  $\blacktriangle$   $\blacktriangle$ ), and the compounds have a helical ring structure, and thus two optically active isomers may be separated for each member. The three members of this class are tetrabenzo[*a,cd,lm,o*]perylene (22), dibenzo[*a,cd*]naphtho[1,8-*no*]perylene (23), and tetrabenzo[*fg,ij,pq,uv*]pentaphene (24).

With regard to the homologous diaza series of compounds, two new-type isomers (6) and possibly (10) were studied in addition to four known isomers (2)–(4) and (7). These isomers of 1-azaviolanthrenes, compounds (1)–(12), are considered to be reduced binary condensation products of the 1-aza-

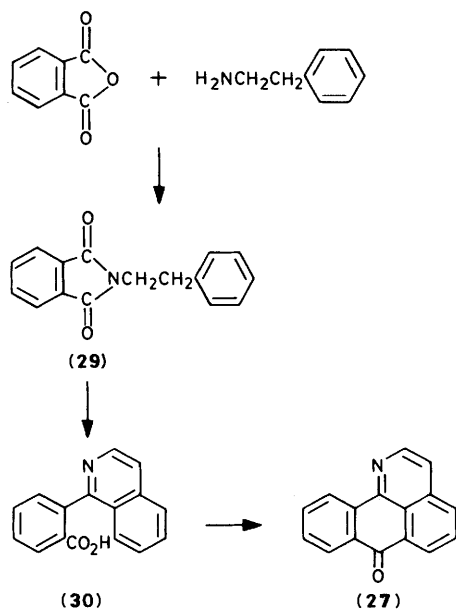
benzanthrone (27). The yields of the diazahomologues are significantly different from those for the hydrocarbons, and new isomers were prepared by specific nitrogen substitution methods.

## Results and Discussion

**Characterization of Condensation.**—In the present work, acylation of  $\beta$ -phenylethylamine with phthalic anhydride gave phenylethylphthalimide (29) in 88.2% yield (m.p. 124–126 °C) (see Scheme 2). Compound (29) was heated in sodium chloride and anhydrous aluminium chloride (1:5) at 220 °C for 2 h to yield *o*-isoquinolin-2-ylbenzoic acid (30). Cyclisation of (30) in concentrated sulphuric acid at 230 °C for 2 h afforded (27) in 14.1% overall yield, which was evaluated from the starting quantities of  $\beta$ -phenylethylamine and phthalic anhydride. This procedure, isolating two intermediates (29) and (30), offered a



Scheme 1.



Scheme 2.

three-step synthesis of (27) (Scheme 2). A one-step procedure, without isolation of any intermediate, gave (27) in 26.6% yield. A two-step procedure, isolating only one intermediate, (29), afforded (27) in 38.6% overall yield. This two-step procedure gave the highest yield and is easy to perform and is recommended by us. Comparison of u.v.-visible spectral data of (27) (see Figure 1) with those of the corresponding benzanthrone (25) supported the structure of compound (27).

Binary condensation of (27) was carried out mainly by two

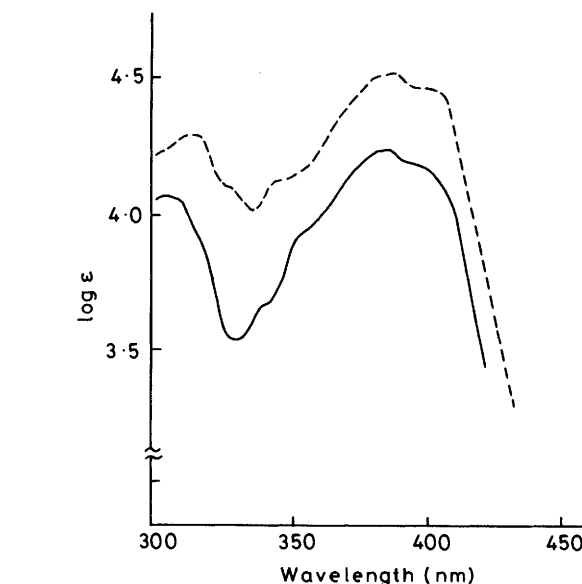
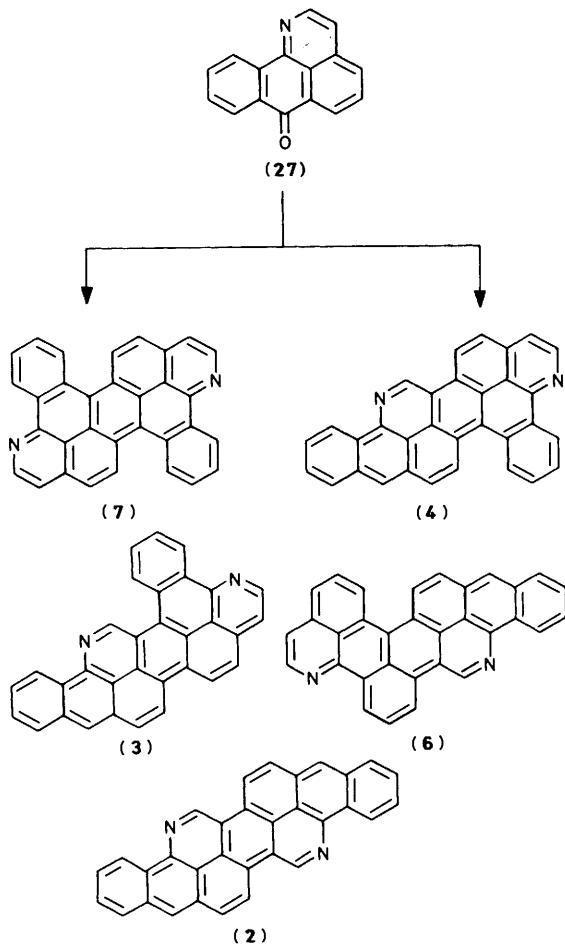


Figure 1. Absorption spectra of benz[de]anthrone (25) and 1-aza-benz[de]anthrone (27) in benzene; — (25), ---- (27)

procedures (Scheme 3), the zinc-catalysed method and the alkali-fusion procedure. Table 1 shows, for the two procedures, relative yields of condensation products which were prepared from three kinds of benzanthrone (25)—(27), and their absorption maxima and melting points. The use of zinc dust gave a larger amount of self-condensation product than the use of copper powder as a catalyst.

The absorption spectra of four fractions eluted from the separation column are shown in Figures 2 and 3. Comparison of



Scheme 3.

u.v.-visible spectral data of the first fraction with those of compound (7) suggested the structural assignment of the 439 nm absorption to (7). Its structure followed from the elemental analysis (see Experimental section) and by the absence of any oxidation product. This fraction probably contains compound (10) as discussed later, but the term '3,12-diazaTBP' is used to denote the 439 nm-type product for convenience's sake except in the section headed Structural Determination.

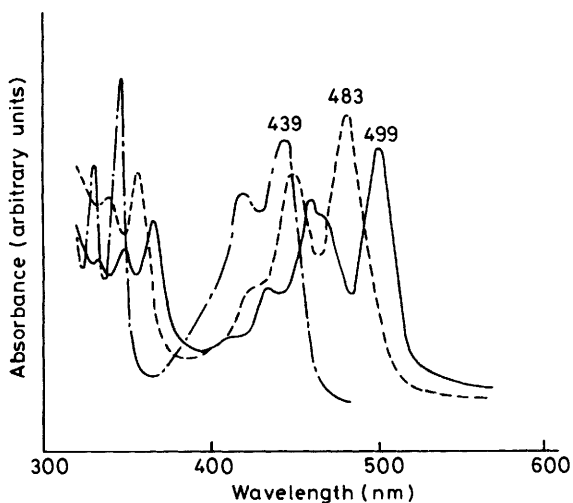


Figure 2. Absorption spectra of compounds (7), (3), and (6) in toluene; ----- (7), -.-.- (3), — (6)

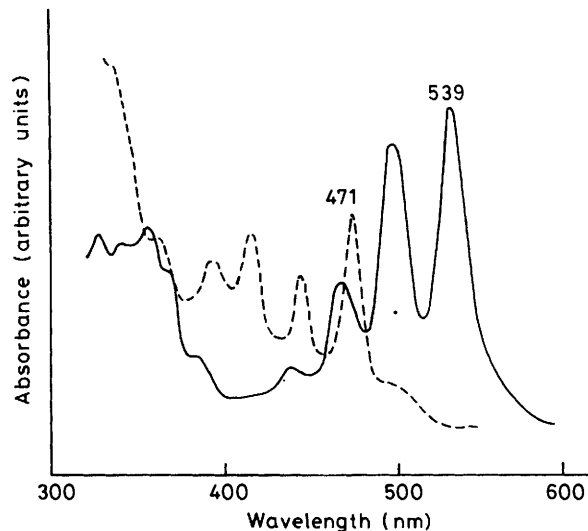


Figure 3. Absorption spectra of (2) and (4) in *o*-dichlorobenzene and toluene, respectively; — (2), ----- (4)

The second fraction showed a maximum at 499 nm and was assigned to a new isomer, (6), as described later.

The absorption spectrum of the third fraction, with a maximum at 483 nm, was nearly identical with that of violanthrene B (15). Oxidation and reduction of (3) gave a product with a 483 nm-type spectrum, and which could be vatted at 80–90 °C. From these results, together with its m.p. [(15) 339.4 °C; product 320–325 °C], the third fraction was assigned structure (3). Other fractions were also identified in this way as discussed in the structural determination section.

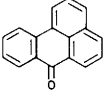
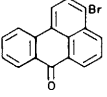
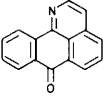
As previously reported,<sup>9</sup> self-condensation of (25) in a mixture of zinc chloride and copper powder afforded (19), (16), and (15) in the proportions 34:54:12. The major component was (16). On the other hand, self-condensation of (26) in a mixture of zinc chloride and zinc dust gave (19), (16), and (15) in the proportions 8:18:74.<sup>6</sup> In our hands, self-condensation of (27) under the same conditions gave (7), (3), and (6) in the proportions 29:68:3. A trace amount of (4) was also obtained. These results led to the conclusion that the type of condensation from (27) is not like that from (25) but is similar to that from (26).

Similar condensation products were obtained in 94.2% yield by alkali fusion of (27) in a mixture of phenol and potassium hydroxide at  $230 \pm 5$  °C for 30 min. The reaction products were reduced in a mixture of zinc chloride and zinc dust and the product was vatted. By column chromatography of the vatted products a large amount of a product with  $\lambda_{\max}$  539 nm was isolated, along with 439 nm, 483 nm, and 499 nm products. Oxidation of the 539 nm-type compound afforded 5,14-diazaisoviolanthrone A (31) which had already been prepared by different routes by King and his co-workers<sup>10</sup> and Yokote.<sup>7</sup> Furthermore, the 539 nm-product was a reduction product of (31) (see Figure 4), and thus it was assigned structure (2). The relative proportions of (7), (3), (6), and (2) were 3:14:23:60. The major component was (2).

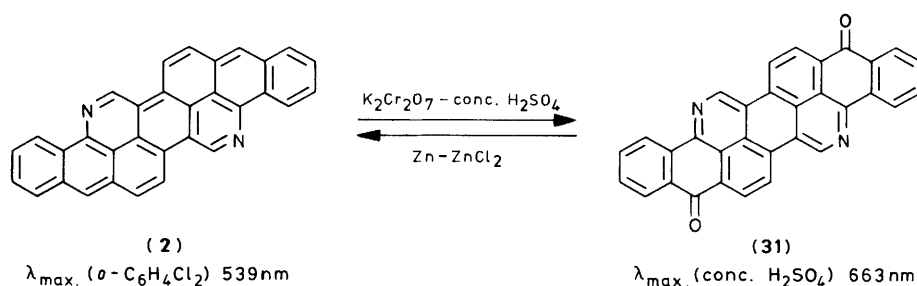
Alkali fusion of (27) was examined also in a mixture of potassium hydroxide and ethanol at 110 °C for 1 h and then in a mixture of potassium acetate and potassium hydroxide at 270–290 °C for 1 h. The products were reduced and vatted to give (7), (3), (6), and (2) in the proportions 3:6:26:66.

Alkali fusion of (25) yielded violanthrene B, violanthrene A, and isoviolanthrone A in the proportions 37:59:4.<sup>11</sup> Alkali fusion of (26) gave isoviolanthrone B, violanthrene A, and isoviolanthrone A (24:8:68).<sup>12</sup> In the present work, alkali

**Table 1.** Relative yields and physico-chemical properties of self-condensation products prepared from the benz[de]anthrones (25), (26), and (27)

Kekulé structure counts		(19)-type	(16)-type	(15)-type	(18)-type	(13)-type	(14)-type
	$\lambda_{\max.}$ (nm)	444	471	482		490	521
	m.p. ( $^{\circ}\text{C}$ )	340.8	318.3	339.4		506.5	526.5
	<i>a</i> (%)			37		59	4
	<i>b</i> (%)	34	54	12			
	$\lambda_{\max.}$ (nm)	444	471	482		490	521
	m.p. ( $^{\circ}\text{C}$ )	340.8	318.3	339.4		506.5	526.5
	<i>a</i> (%)		24			8	68
	<i>b</i> (%)	8	18	74			
	$\lambda_{\max.}$ (nm)	439	471	483	499		539
	m.p. ( $^{\circ}\text{C}$ )	342—345		320—325	346—348		500 <
	<i>a</i> (%)	3	trace	14	23		60
	<i>b</i> (%)	29	trace	68	3		

<sup>a</sup> Alkali fusion yield. <sup>b</sup> Zn-ZnCl<sub>2</sub> reduction yield. ○ = N Atom.

**Figure 4.** Redox reaction between (2) and (31)

fusion of (27) followed by reduction afforded (7), (3), (6), and (2) (3:14:23:60). These results supported the conclusion that the type of self-condensation of (27) in a mixture of potassium hydroxide and phenol is again similar to that of (26).

**Structural Determination.**—Structural isomers of polycyclic aromatic compounds are in general very similar to each other, and so their separation and purification are very difficult and their structural determination is not so easy. We are trying to make the structural determination for these compounds easier, faster, and more certain by examining the correlation between the isomers' structures and their physical properties such as u.v.-visible, i.r., and mass spectra<sup>13</sup> and m.p.s.

Electronic spectra for violanthrene homologues consist of two kinds of absorption bands; a  $\beta$  band below 350 nm and a  $p$  band above 400 nm.<sup>3</sup> Both of them have vibrational fine structures. In Figures 2 and 3 are shown the spectra for five components of diazaviolanthrenes, which were separated on an alumina column. Each isomer has different wavelengths of absorption maxima for  $p$  and  $\beta$  bands, and the intensity ratio of the two bands is different, as is true also for the parent hydrocarbons. These features suggest the future possibility for isomer discrimination simply by more accurate theoretical calculation of electronic spectra. In Table 2 are shown the structure counts of Kekulé resonance formulae for twelve isomers of violanthrene homologues and the observed and calculated wavelengths of the  $p$  bands, which are assigned to a

transition between the LUMO and HOMO levels. It is well known<sup>14</sup> that the  $p$  band shifts to shorter wavelength as the structure counts increase in a series of compounds with the same number of condensed rings. This empirical rule was reconfirmed for six identified isomers of parent hydrocarbons.<sup>8,13</sup> The calculated values were based on the simple Hückel molecular orbital method and corrected by an empirical formula of Heilbronner and Murrell.<sup>15</sup> Though the Hückel method is recognized as having a weak point in completely neglecting electronic repulsions, our values are in a fairly good agreement with the observed ones. The wavelengths of visible absorption bands for diazaviolanthrenes are not so different from those for the parent hydrocarbons (Table 2). An isomer with the band at 499 nm is assigned structure (6) for the following reasons. All isomers with their  $p$  band between 483 and 539 nm are confined, by structure counts between 49 and 40, to the four structures (1), (6), (8), and (12). Among them the isomer with a 499 nm band cannot belong to class A because of the low m.p., but must belong to class B from the pattern of its mass spectrum and its properties under the vatting conditions as explained later. This 499 nm band also has an abnormal splitting for the second vibronic branch. We notice that the  $p$  band of the diazaviolanthrene homologue at 439 nm shows a blue shift compared with that of (19) at 444 nm. The former substance might contain some (10) as well as (7), because it shows two different mass patterns and two m.p.s by DSC (differential scanning calorimetry). The structure count of (10) is

**Table 2.** Visible absorption maxima ( $\lambda_p$ /nm) of violanthrene homologues

Class	Violanthrenes			Diazviolanthrenes			Kekulé structure count
	Isomer	$\lambda_{\text{obs.}}$	$\lambda_{\text{calc.}}^{a,b}$	Isomer	$\lambda_{\text{obs.}}$	$\lambda_{\text{calc.}}^{a,b}$	
A	(13)	490	540	(1)			41
	(14)	521 <sup>c</sup>	552	(2)	539 <sup>d</sup>	562	40
B	(15)	482	495	(3)	483	503	49
	(16)	471	487	(4)	471	495	50
	(17)			(5)			39
T	(18)			(6)	499	545	42
	(19)	444	429	(7)	439?	435	60
	(20)			(8)			48
H	(21)	627	603	(9)			36
	(22)			(10)	439?	431	61
	(23)			(11)			51
	(24)			(12)			45

<sup>a</sup> Calculated by the simple Hückel molecular orbital method and corrected by a recurrent formula  $\lambda/\text{nm} = 10^7 (8196 + 21940 \Delta E/\beta)^{-1}$ .<sup>8</sup> <sup>b</sup> Core integrals associated with nitrogen are  $\alpha_N = \alpha + 0.6 \beta$ ,  $\alpha_{\text{adj}}^N = \alpha + 0.1 \beta$ , and  $\beta_{\text{CN}} = \beta$ . <sup>c,d</sup> Values measured in 1,2,4-trichlorobenzene and *o*-dichlorobenzene solution, respectively, for *c* and *d*, which show a red shift of 5–8 nm as compared with those measured in benzene, toluene, and xylene solution.

**Table 3.** Mass spectra (relative intensities) for diazviolanthrenes: a, (2); b, (3); c, (6); d, (7); and e, possibly (10)

<i>m/z</i>	Monovalent					<i>m/z</i>	Divalent					<i>m/z</i>	Trivalent				
	a	b	c	d	e		a	b	c	d	e		a	b	c	d	e
431	1.2																
430	7.1	6.6	6.6	6.2	5.7	215	3.3	2.2	2.1	2.3	2.2						
429	36.2	35.6	36.3	35.7	30.9	214.5	14.6	11.7	8.6	12.6	11.9	143	1.0				
428	100	100	100	100	100	214	43.6	35.1	27.4	36.4	36.6	142.7	2.8	2.3	1.5	1.2	1.8
427	6.8	13.1	14.6	21.2	76.6	213.5	11.8	20.7	18.5	9.3	25.6	142.3	1.5	1.3	1.5		1.0
426	8.2	12.9	14.4	11.3	21.6	213	10.1	13.6	13.6	16.2	13.8	142	1.5	2.1	1.8	3.1	2.4
425	3.4	4.2	5.6	6.8	8.6	212.5	4.9	8.3	8.5	11.0	13.8	141.7			1.0		1.0
424	2.1	3.7	3.6	5.5	7.9	212	3.1	4.4	3.9	6.8	7.1						
423		1.1	1.8	1.6	3.1	211.5	1.3	1.8	2.0	2.5	2.8						
422		1.0	1.1	1.7	2.2	211		1.0		1.0	1.7						
						207		1.6									
						201.5		1.1									
402	1.7					201		3.8	1.7	1.3	1.0	1.0					
401	1.6	1.3	1.0			200.5	3.9	4.8	2.5	3.0	3.1	133.7					1.2
400	2.3	2.7	2.0	1.9		200	5.4	9.6	4.1	7.3	7.6	133.3	1.0	1.7			1.6
399	2.7	3.5	2.4	2.9	3.3	199.5	6.2	8.4	5.2	7.4	10.0	133		1.0	1.1		2.0
398	1.3	1.8	1.7	2.0	2.7	199	3.8	6.7	4.6	7.4	9.0	132.7		1.2	1.2	1.7	
397	1.2	1.7	1.5	2.5	3.3	198.5	2.0	5.5	4.3	7.2	9.8						
396				1.0	1.4	198	1.3	2.2	2.1	2.7	4.5						
395				1.0	1.4	197.5	1.0	1.6	1.2	1.9	3.2						
						188		1.6	1.2								
						187.5		2.2		1.4	1.2	1.6					
						187		3.1	3.0	2.2	2.2	2.8					
373	1.2			1.0	1.2	186.5	3.8	4.1	3.2	4.2	4.3						
372					1.2	186	3.1	4.7	3.1	4.9	6.6	124		1.2		1.1	1.4
371					1.0	185.5	2.3	3.6	2.7	5.1	6.0						
370					1.0	185	2.1	4.1	2.7	4.8	7.4	123.3					1.1
						184.5	1.1	1.7	1.2	2.0	3.1						
						184		1.4		1.7	2.5						
						183.5					1.0						
						179.5					1.0						
						174.5	1.3	1.2									
						174	1.8	1.4	1.2	1.1	1.8						
						173.5	1.8	2.1	1.5	1.5	1.8						
						173	2.1	2.7	1.8	3.1	3.5						
						172.5	1.3	1.6	1.3	1.8	2.2						
						172	1.5	2.1	1.5		2.8						
						161	1.3	1.0	1.2	1.0							
						160.5	1.0	1.0			1.0						
						160	1.3	1.4	1.1	1.1	1.4						

61 and so the *p* band is expected to be seen at shorter wavelength than that for (7) which has a structure count of 60.

A molecule of an anthraquinone-type substance can be vatted easily by air oxidation after reduction by alkaline sodium

hydrosulphite. Violanthrene homologues have also the same kind of oxidizable carbons (C-7 in benzanthrene skeleton) as the quinone. Classes A, B, T, and H have two, one, zero, and zero such free carbons, respectively. Therefore, class A

compounds were vatted easily at 60 °C and those in class B, e.g. (6), was vatted at 80–90 °C. Neither class T nor class H compounds could be vatted even at >90 °C.

Elution order in column chromatography might also be correlated with the isomer class, though the reason is not clear. Parent hydrocarbons (13)–(16) and (19) were eluted in the order of classes T, B, and A. Diazaviolanthrenes were also eluted in the same order: (7) [(10)], (6), (3), and (2).

The pattern of mass spectra for polycyclic aromatic compounds reflects sharply the overcrowding, as reported previously.<sup>13</sup> The electron-impact mass spectra are shown in Table 3 for five almost pure isomeric diazaviolanthrenes. The peak of the monovalent molecular ion  $[M]^{+}$  is largest in the spectra of the diaza homologues and those of the parent hydrocarbons. The charges of three groups, one composed mainly of a singly charged molecular ion peak at  $m/z$  428, the second containing a doubly charged ion  $m/z$  214, and the last containing a triply charged ion  $m/z$  142.7, are verified by the intervals of the  $m/z$  values for successive peaks within these groups: one, one-half, and one-third, respectively.

Atoms of the ring skeleton are eliminated two by two, and two CN groups are eliminated first, because the weighted average  $m/z$  value of fragment ion families  $[M - 26n]^{i+}$  ( $n > 2$ ) is almost the same as that of the corresponding hydrocarbon isomer.<sup>13</sup> These fragment families for diaza homologues have already lost the two CN groups and the residual ions must be similar to those for the hydrocarbons.

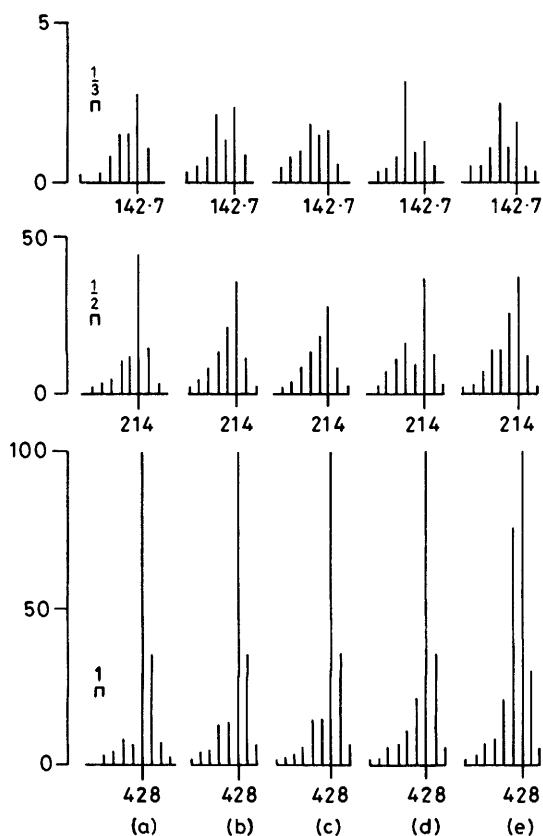


Figure 5. Mass spectra of molecular ion families for five isomers of diazaviolanthrenes: (a) (2), (b) (3), (c) (6), (d) (7), and (e) probably (10)

The  $\lambda_{\max}$  439 nm sample showed a mass pattern (e) at first, and this then changed to pattern (d) as shown in Figure 5. Both of them have the same molecular weight (428) but should be assigned to two different isomers, because their patterns are completely different. The mass spectrum of (e) has an

abnormally intense peak of  $m/z$  427 which suggests a heavy overcrowding for the molecule. The result of DSC measurements showed that this sample has a sharp peak at 338.8 °C and another broad peak at 347 °C. The sample used was a clean yellow crystal, though still not isolated. The spectra of fractions (d) and (e) are assigned to (7) and (possibly) (10), respectively.

Let us examine mass patterns of the molecular family with singly, doubly, and triply charged ions. Those for six hydrocarbon isomers are shown in Figure 6.<sup>13</sup> Ions with the same mass but different charge are arranged vertically for each isomer, and the intensity scale of trivalent ions is expanded ten times. As seen from Figure 6, the six isomers can be grouped

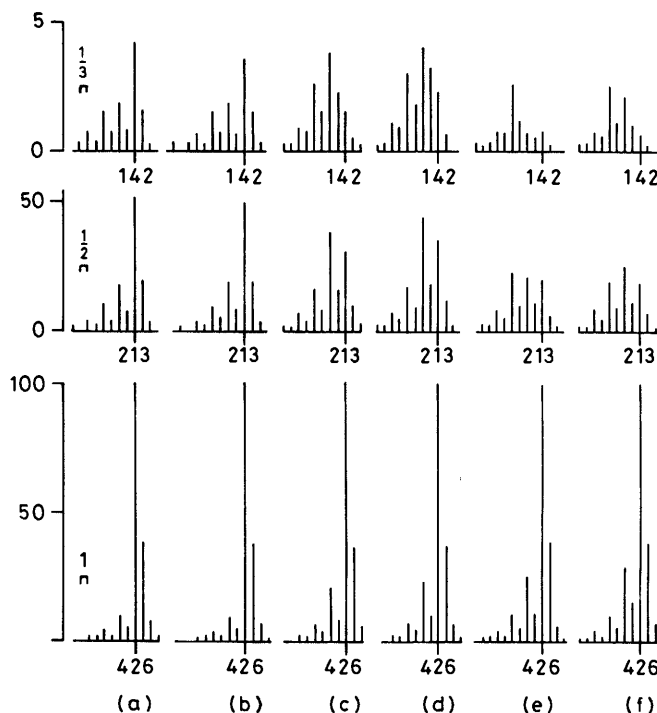


Figure 6. Mass spectra of molecular ion families for six violanthrene isomers: (a) (13), (b) (14), (c) (15), (d) (16), (e) (19), and (f) (21). The part of trivalent ions is expanded ten times

into three classes A, B, and T, and the two isomers in the same class are very similar to each other. Each family has lines in the order strong, weak, strong, weak . . . , and the intensity ratios of the weaker peaks to the stronger ones are almost compatible with the theoretical values of 0.38 for a  $C_{34}$  system and the hydrogen atoms are lost mainly two by two. The intensities of  $[M - 2]^{+}$  ions, which have lost one hydrogen pair, are over twice as high for classes B and T as those for class A. The intensities of  $[M - 4]^{+}$  ions, which have lost two hydrogen pairs, are lowest for class A, double for class B, and double again for class T. This tendency is enhanced in the order singly < doubly < triply charged ions, and the largest peak of the trivalent ions is  $[M]^{3+}$  for class A,  $[M - 2]^{3+}$  for class B, and  $[M - 4]^{3+}$  for class T. We concluded for the hydrocarbon case that the number of hydrogen pairs which is easily eliminated from the parent ions is zero for class A, one for class B, and two for class T, and this corresponds to the number of overcrowded hydrogen-atom pairs (● ●) in the structural formulae.

The mass patterns of molecular ion families are shown in Figure 5 for five isomeric diazaviolanthrenes. These patterns are not so regular as those for the hydrocarbons. However, we do see something of their features. The intensity of the

molecular ions is strengthened by the substitution of two nitrogens and it is still higher in the divalent ions, because two positive charges can be stabilized locally on two nitrogens. Hydrogens seem to be eliminated not only in pairs but also as atoms, in contrast with the parent hydrocarbons, probably because nitrogen substitution has an asymmetric effect on the overcrowded hydrogen pairs.

Let us consider  $[M - 1]$  and  $[M - 2]^{3++}$  ions for diazaviolanthrenes instead of  $[M - 2]^{i+}$  and  $[M - 4]^{i+}$  ions for the hydrocarbons. The intensity of the  $[M - 1]^+$  ion is weakest for (a) of (2) and that for (c) is same as that for (b) of (3). The same intensity suggests that both of them belong to class B. The ion intensity for (d) of (7) is stronger and that for (e) is by far the strongest. The last isomer is thought to be a member of class H, since this has a very strong  $[M - 1]^+$  peak. The intensity ratios of  $[M - 2]^{3++}$  to  $[M]^{3++}$  are less than one, nearly equal to one, and larger than one for classes A, B, and T or H, respectively.

I.r. absorption spectra of condensed polycyclic aromatic compounds are expected to show characteristic frequencies of each isomer both for C-H out-of-plane (o.o.p.) bending vibrations and the vibrations of the ring skeleton. C-H o.o.p. bending vibrations have group frequencies characteristic of the number of adjacent CH units, and are observed in the region  $900-700\text{ cm}^{-1}$ .<sup>16</sup> Ring deformation vibrations in the far-i.r. region probably depend on the benzanthrene skeleton and the condensation site. The composition of adjacent CH units and the condensation site (3,4;6,7;7,8) of the benzanthrene skeleton for violanthrene isomers are shown below, where  $\bar{2}$  means, for example, that the local structure of two adjacent CH units exists near the central bridged ring ( $\bar{\quad}$ ) and each couples easily with the other;

(13), (14)	(1- $\bar{2}$ -4) <sub>2</sub>	(3,4) <sub>2</sub>
(15), (16)	1-2 $\bar{2}$ -3-4 $\bar{4}$	3,4-6,7
(19)	( $\bar{2}$ -3- $\bar{4}$ ) <sub>2</sub>	(6,7) <sub>2</sub>
(21)	( $\bar{3}$ $\bar{3}$ ) <sub>2</sub>	(7,8) <sub>2</sub>

I.r. spectra of six isomers for wavenumbers  $< 1000\text{ cm}^{-1}$  are shown in Figure 7. The spectrum of (13) gives the same pattern as that of (14), but the intensity of the former is five times that of the latter. The latter isomer has a centre of symmetry and too weak an interaction between molecules to affect the i.r. intensity. Tentative assignments for C-H bending modes are given in Figure 7.

In regard to diazaviolanthrenes, several bands other than C-H o.o.p. modes are enhanced by nitrogen substitution and the frequencies of C-H o.o.p. bending modes of carbons neighbouring a nitrogen atom may be different from those of the corresponding violanthrene carbons. The frequency of the C-H o.o.p. mode for an isolated CH unit can be assigned by the disappearance of the band when the compounds are vatted to give the diazaviolanthrenes. The compositions for diazaviolanthrenes, where IN means an isolated CH adjacent to N and 2N means two consecutive CH's adjacent to N, are:

(2)	(1-IN $\bar{2}$ -4) <sub>2</sub>	(3,4) <sub>2</sub>
(3)	1-IN $\bar{2}$ $\bar{2}$ N-4 $\bar{4}$	3,4-7,6
(6)	1-IN $\bar{2}$ $\bar{2}$ N-3 $\bar{3}$ -4	3,4-8,7
(7), (10)	( $\bar{2}$ -2N- $\bar{4}$ ) <sub>2</sub>	(6,7) <sub>2</sub>

The i.r. spectra for the above four samples are shown in Figures 8 and 9. The spectrum for each isomeric diazaviolanthrene in Figure 8 resembles that for the corresponding hydrocarbon isomer in Figure 7. In regard to skeletal deformation vibrations, an intense band at  $608\text{ cm}^{-1}$  for (d) [(7)] is also seen for (b) [(3)] at  $597\text{ cm}^{-1}$  and these wavenumbers are higher than that for (a) [(2)] at  $571\text{ cm}^{-1}$ . Medium bands for (d) in the region of  $530\text{ cm}^{-1}$  may be due to [(10)] because of a lack of correspondence with (7) [(e) in

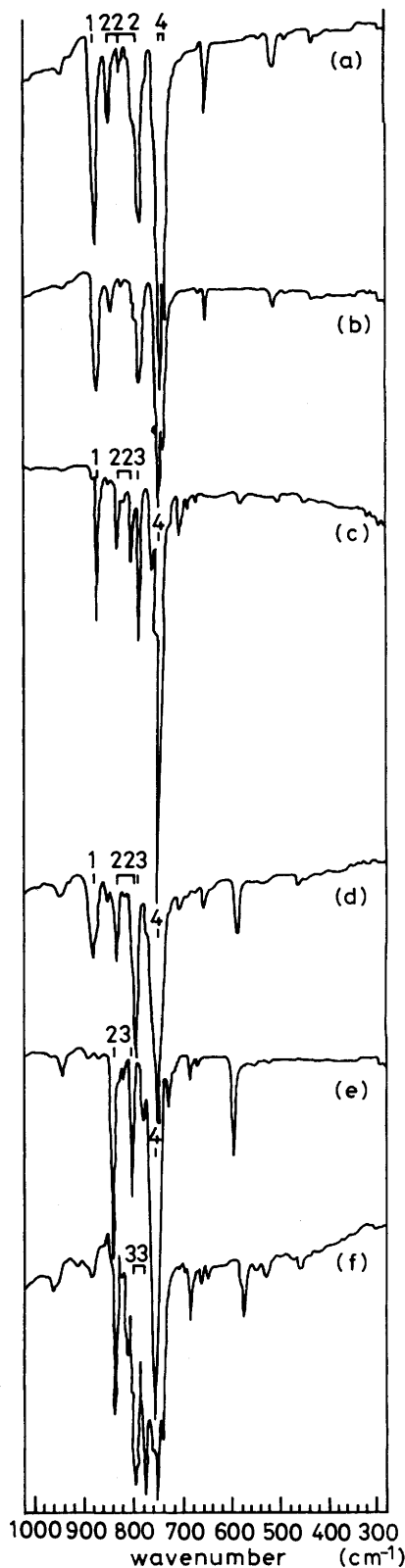


Figure 7. I.r. spectra below  $1000\text{ cm}^{-1}$  of six violanthrene isomers. (a) (13), (b) (14), (c) (15), (d) (16), (e) (19), and (f) (21). Each band in the region of C-H o.o.p. bending mode is correlated with the number of adjacent CH units as shown in the spectra

Figure 7]. Two bands for (c) [(6)] at  $535$  and  $507\text{ cm}^{-1}$  are rather different from those for other isomers.

The m.p.s for class A violanthrenes are  $> 500^\circ\text{C}$ ; i.e.  $506.5^\circ\text{C}$



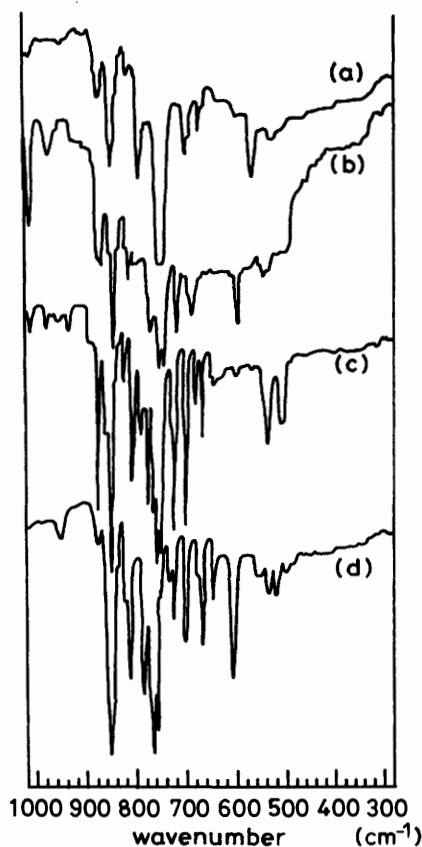


Figure 8. I.r. spectra of (a) (2), (b) (3), (c) (6), and (d) a mixture of (7) and probably (10)

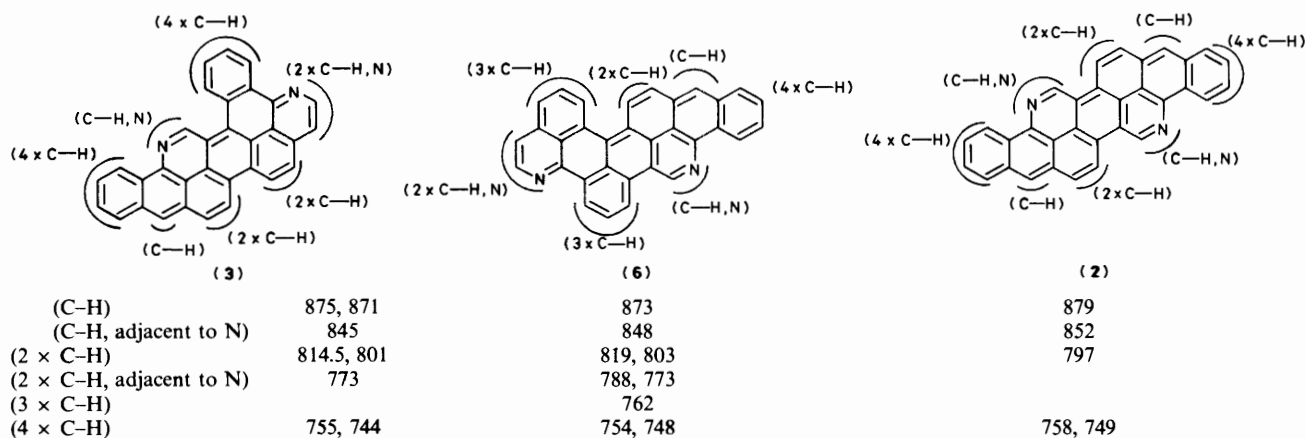


Figure 9. C-H o.o.p. deformation vibrations in i.r. spectra of (3), (6), and (2). There is one possibility of a very tentative assignment

for (13) and 526.5 °C for (14), while those for other classes are lower by about 200 °C; *i.e.* 339.4 °C for (15), 318.3 °C for (16), 340.8 °C for (19), and 334 °C for (21) (see Table 1). In general, the m.p. is thermodynamically expressed by the equation  $T_m = \Delta H/\Delta S$ . The large lowering of the m.p. for classes other than class A may be explained mainly by a rather large increase in entropy due to overcrowding; that is, the release of large-amplitude motion between two non-planar structures at the transition from the solid to the liquid phase.

The m.p. for (2) is > 500 °C, while those for (3), (6), (7), and probably (10) are 320–325, 346–348, 347, and 338.8 °C, respectively, and so the last four isomers cannot be ascribed to class A.

In conclusion we have tried to obtain a method of structural elucidation for polycyclic isomers from their mass, u.v.–visible, and i.r. spectra, their m.p.s, and vating conditions. By combining these results we have made our structural assignments. As a result, two new types of isomer, (6) and probably (10), have been identified. Refinement of the analytical method described should allow a more precise theoretical treatment of future results and lead to quantitative agreement for various physical properties. We are now trying to isolate compound (10) and to identify its isomers by unambiguous syntheses.

### Experimental

U.v.–visible absorption were measured in xylene (except where stated) on a Shimadzu D-40R-W spectrophotometer with a slit width of 0.25 nm. Mass spectra were measured with a Shimadzu LKB-9000 gas chromatograph–mass spectrometer using a direct inlet system. Measurement conditions were as follows: about 0.2 mg of each sample were used; temperature of direct inlet varied from 115 to 220 °C; temperature in ionization source chamber 290 °C; ionization voltage 70 eV; emission current 60  $\mu$ A.

I.r. absorption spectra were recorded over the range 4 000–200  $\text{cm}^{-1}$  with a KBr disc using a Shimadzu IR-450S spectrophotometer.

*Syntheses of the 1-Azabenzanthrone (27) (Scheme 2).*—(a) 7H-1-Azabenz[de]anthracen-7-one (27) from  $\beta$ -phenylethylamine and phthalic anhydride. To a mixture of phthalic anhydride (30 g, 0.2 mol) and  $\beta$ -phenylethylamine (26 g, 0.2 mol) was added anhydrous aluminium chloride (40 g, 0.3 mol) at 140 °C during 30 min. The reaction was allowed to continue at 180  $\pm$  5 °C for 30 min. To the reaction product was added

sodium chloride (8 g, 0.14 mol) at 220 °C, followed by anhydrous aluminium chloride (40 g, 0.3 mol) at 230–240 °C during 30 min. The mixture was kept at 230–240 °C for 2 h. After the mixture had cooled, the product was finely ground, and poured slowly into concentrated sulphuric acid (1 l) at 90 °C. After being kept at 220–230 °C for 2 h, the suspension was cooled and poured into a large amount of ice. Sodium hydroxide was added until pH 3 was obtained and the resultant precipitate was filtered off and washed in turn with dilute aqueous sodium hydroxide and water to give the crude product (187 g) which was extracted with acetic acid. The extract was condensed under reduced pressure and the resultant precipitate was filtered off, dried, and sublimed at 140 °C at a pressure of

$10^{-3}$  Torr to give the product (27) (12.5 g, 26.6%) as light yellow needles, m.p. 181–183 °C.

(b) 7H-1-Azabenz[de]anthracen-7-one (27) from phenylethylphthalimide (29). To a mixture of anhydrous aluminium chloride (100 g, 0.75 mol) and sodium chloride (20 g, 0.34 mol) was slowly added phenylethylphthalimide (53 g, 0.2 mol) at 180 °C during 30 min. The reaction was allowed to continue at 220 °C for 2 h. The product was cooled, finely ground and poured slowly into concentrated sulphuric acid (700 cm<sup>3</sup>) at 90 °C. The mixture was stirred and heated at 220–230 °C for 2 h. After being cooled, the solution was poured into ice, and the resultant precipitate was treated in a similar way to that described in (a) above to give the product (27) (20.4 g, 43.8%) as light yellow needles, m.p. 181–183 °C (in 38.6% overall yield from phthalic anhydride and  $\beta$ -phenylethylamine).

(c) 7H-1-Azabenz[de]anthracen-7-one (27) from *o*-isquinolin-2-ylbenzoic acid (30). To concentrated sulphuric acid (200 cm<sup>3</sup>) was slowly added crude (30) (20 g, 0.08 mol) at 90 °C during 30 min. The mixture was stirred and heated at 220–230 °C for 2 h. The solution was cooled and poured into ice, and the resultant precipitate was treated in a similar way to that shown in section (a) above to give the product (27) (2.0 g, 10.8%) (14.1% overall yield from phthalic anhydride and  $\beta$ -phenylethylamine).

**Condensation of Compound (27) (Scheme 3).—Copper powder-catalysed condensation.** To a mixture of zinc chloride (50 g) and sodium chloride (10 g) were added copper powder (2.5 g) and then compound (27) (2.5 g). The mixture was kept at  $280 \pm 5$  °C for 1 h. The product was poured into water, the mixture was filtered, and the product was washed in turn with dilute hydrochloric acid and water, and dried. Starting material was removed by sublimation at 140 °C at a pressure of  $10^{-3}$  Torr. The residue was extracted with xylene and the extract was chromatographed over activated alumina using xylene as eluant. First, elution with xylene yielded compound (7) (0.22 g, 37.29% of condensed products) as yellow needles, m.p. 342–345 °C;  $\lambda_{\max}$ . 439 nm,  $\nu_{\max}$ . 816 (C–H), 788, 771 (C–H adjacent to N), and 746 cm<sup>-1</sup> (C–H) (Found: C, 89.7; H, 3.55; N, 6.4. C<sub>32</sub>H<sub>16</sub>N<sub>2</sub> requires C, 89.78; H, 3.7; N, 6.5%); *m/z* 428.

Further elution with xylene yielded compound (6) (0.03 g, 5.08%) as red needles, m.p. 346–348 °C;  $\lambda_{\max}$ . 499 nm;  $\nu_{\max}$ . 873 (C–H), 848 (C–H adjacent to N), 819, 803 (C–H), 788, 733 (C–H adjacent to N), 762 (C–H), 754, 748 cm<sup>-1</sup> (C–H) (Found: C, 89.6; H, 3.9; N, 6.45%); *m/z* 428.

The third product eluted with xylene was compound (3) (0.34 g, 57.63%) as dark orange crystals, m.p. 320–325 °C;  $\lambda_{\max}$ . 483 nm;  $\nu_{\max}$ . 875, 871 (C–H), 845 (C–H and N), 814.5, 801 (C–H), 773 (C–H adjacent to N), 754, and 744 cm<sup>-1</sup> (C–H) (Found: C, 89.8; H, 3.65; N, 6.4%); *m/z* 428. Total yield of condensation products was 25.43% overall from (27).

(b) **Zinc dust-catalysed condensation.** The reaction conditions were the same as for the copper-catalysed condensation, but with a lower reaction temperature at  $260 \pm 5$  °C. The products were separated and purified by column chromatography using xylene as eluant. First, elution with xylene gave compound (7) (0.39 g, 28.5% of total products) as yellow needles, m.p. 342–345 °C;  $\lambda_{\max}$ . 439 nm.

Further elution with xylene yielded compound (6) (0.04 g, 2.9%) as red needles, m.p. 346–348 °C;  $\lambda_{\max}$ . 499 nm. Lastly, further elution with xylene afforded the compound (3) (0.94 g, 68.6%) as dark orange needles, m.p. 320–325 °C;  $\lambda_{\max}$ . 483 nm. Total yield of condensation products was 1.37 g, 59.05%.

(c) **Phenol-potassium hydroxide fusion.** To a suspension of potassium hydroxide (20 g, 85%) and phenol (5 g) was added compound (27) (5 g). The mixture was kept at  $230 \pm 5$  °C for 30 min, then poured into water, oxidized by air overnight, filtered, and the residue was washed with water and dried to give the

crude product (4.73 g). The crude product was sublimed at 140 °C at a pressure of  $10^{-3}$  Torr to give a pure product (4.55 g, 94.2%) as dark violet crystals which were used in the next step.

(c') **Separation of phenol-potassium hydroxide fusion products into compounds (2), (3), (6), and (7).** To a mixture of zinc chloride (100 g) and sodium chloride (10 g) was added zinc dust (4.55 g) at 220 °C. To the mixture was added the aforementioned phenol-potassium hydroxide fusion product (4.5 g) at 220 °C. The mixture was kept at  $230 \pm 5$  °C for 30 min and was then poured into water, filtered, and the residue was washed in turn with dilute hydrochloric acid and water and dried. To remove starting material, the reduced product was added to aqueous alkaline 5% sodium hydrosulphite (300 cm<sup>3</sup>) and the mixture was kept at 80 °C for 30 min and the resultant precipitate was filtered off at 80 °C. The vat operation was repeated several times to give a crude product (5.15 g) which was extracted with toluene and then with *o*-dichlorobenzene. The toluene extract was evaporated to give a mixture which was chromatographed on activated alumina giving, on elution with toluene successively compounds (7) (0.04 g, 3.1%), (6) (0.29 g, 22.5%), and (3) (0.18 g, 14.0%). The *o*-dichlorobenzene extract was evaporated to give a mixture which was chromatographed on activated alumina (eluant *o*-dichlorobenzene), to give compound (2) (0.77 g, 60.1%) as dark violet crystals, m.p. 500 °C;  $\lambda_{\max}$ . (1,2,4-trichlorobenzene) 539 nm;  $\nu_{\max}$ . 879 (C–H), 852 (C–H adjacent to N), 797 (C–H), 758, and 739 cm<sup>-1</sup> (C–H); *m/z* 428. The overall yield of condensation products was 1.28 g, 27.64%.

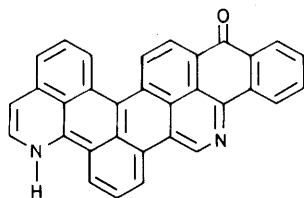
(d) **Ethanol-potassium hydroxide fusion.** To a solution of potassium hydroxide (24.4 g) in ethanol (400 cm<sup>3</sup>) was added compound (27) (2.4 g) at 110 °C. To the suspension was added a mixture of potassium acetate (5.6 g) and potassium hydroxide (26.8 g). The mixture was gradually heated to 270–290 °C and kept within this temperature range for 1 h. The crude alkali fusion product was then treated in a similar way as shown above to give a product (1.90 g, 81.9%) as dark violet crystals, used immediately in the next step.

(d') **Separation of ethanol-potassium hydroxide fusion products into compounds (2), (3), (6), and (7).** To a mixture of zinc chloride (80 g) and sodium chloride (8 g) was added zinc dust (2.0 g) at 220 °C. To the suspension was added the ethanol-potassium hydroxide fusion mixture (1.90 g). The mixture was kept at  $230 \pm 5$  °C for 30 min and was then treated in a similar way to that described in section (a). The vat operation was repeated several times to give total crude product (1.54 g). The crude product was extracted with toluene and then with *o*-dichlorobenzene. The toluene extract was evaporated to give a mixture which was chromatographed on activated alumina, eluant toluene, giving successively compounds (7) (0.01 g, 2.9%), (6) (0.09 g, 25.7%), and (3) (0.02 g, 5.7%). The *o*-dichlorobenzene extract was evaporated to give a mixture which was chromatographed on activated alumina, eluant *o*-dichlorobenzene, giving the compound (2) (0.23 g, 65.6%) as dark violet crystals. The overall yield of condensation products was 0.35 g (15.8%).

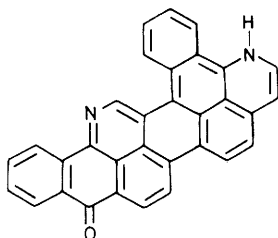
**Conversion into Violanthrones.**—(a) **Conversion of (2) into (31).** To a solution of compound (2) (0.7 g) in concentrated sulphuric acid (35 cm<sup>3</sup>) and water (140 cm<sup>3</sup>) was added dropwise a solution of sodium dichromate (0.1 g) in water (14.0 cm<sup>3</sup>) at 50 °C. The mixture was stirred at 60 °C for 2 h and the resultant precipitate was filtered off, washed with water, and poured into 5% aqueous sodium hydrosulphite (300 cm<sup>3</sup>). The suspension was kept at 55–60 °C for 30 min and the resultant precipitate was filtered off. The filtrate was oxidized by air for several hours. The oxidized product was filtered off and dried. The vat operation was repeated several times to give 5,14-diazaisoviolanthrene-9,18-dione (31) (0.21 g, 28.0%) as dark

blue-violet crystals, m.p. 489–492 °C (decomp.);  $\lambda_{\max}$ . (sulphuric acid) 663 nm ( $\log \epsilon$  4.43).

(b) *Oxidation of (6)*. To a solution of compound (6) (0.1 g) in concentrated sulphuric acid (5 cm<sup>3</sup>) and water (20 cm<sup>3</sup>) was added dropwise a solution of sodium dichromate (0.1 g) in water (20 cm<sup>3</sup>) at 60 °C. The mixture was stirred at 60 °C for 2 h and the resultant precipitate was filtered off, washed with water, and poured into 5% aqueous sodium hydroxide (300 cm<sup>3</sup>) containing sodium hydrosulphite (10 g). After the mixture had been kept at 85–90 °C for 30 min, ethanol (50 cm<sup>3</sup>) was added. The vat operation was repeated several times and the combined filtrates were oxidized by air to give 5,10-diazaisoviolanthrone C (32) (0.11 g, 10.3%) as dark green-brown crystals, m.p. 470–484 °C (decomp.);  $\lambda_{\max}$ . (sulphuric acid) 522 (4.30) and 628 nm (4.07).



(32)



(33)

(c) *Conversion of (3) into (33)*. To a solution of the condensation product of (27) (0.33 g) in concentrated sulphuric acid (16.5 cm<sup>3</sup>) was added water (66 cm<sup>3</sup>) at 50 °C. To the solution was added dropwise a solution of sodium dichromate (0.228 g) in water (66 cm<sup>3</sup>). The mixture was stirred at 60 °C for 2 h and the resultant precipitate was filtered off at that temperature and poured into 5% aqueous sodium hydroxide

(300 cm<sup>3</sup>) containing sodium hydrosulphite (10 g). After the solution had been vatted at 85–90 °C for 30 min, ethanol (50 cm<sup>3</sup>) was added to the solution. The precipitate was filtered off at 80–90 °C. The vat operation was repeated several times and the combined filtrates were oxidized by air to give 5,17-diazaviolanthrone B (33) (0.018 g, 5.3%) as dark purple-black crystals, m.p. 500 °C;  $\lambda_{\max}$ . 653 nm (4.38).

(d) *Attempted oxidation of (7)*. Condensation product (7) was not oxidized and the absorption spectrum of the product was identical with that of the starting material.

### Acknowledgements

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