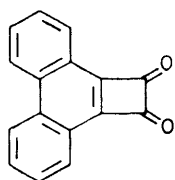


## Benzocyclobutenes. Part 7.<sup>1</sup> Synthesis and X-Ray Crystal Structure of Cyclobuta[*l*]phenanthrene-1,2-dione and the Synthesis of Hexabenzo[*a,c,g,i,m,o*]triphenylene

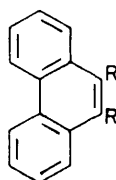
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[2 + 2] Photocycloaddition of tetrachloroethene to phenanthrene gives 1,1,2,2-tetrachloro-1,2,2a,10b-tetrahydrocyclobuta[*l*]phenanthrene. Treatment of this compound with *N*-bromosuccinimide gives the corresponding tetrachlorodihydrocyclobutaphenanthrene which can be hydrolysed to cyclobuta[*l*]phenanthrene-1,2-dione. The <sup>1</sup>H and <sup>13</sup>C n.m.r. spectra and X-ray molecular structure of the dione have been determined. Flash-vacuum pyrolysis of the dione gives a low yield of hexabenzo[*a,c,g,i,m,o*]triphenylene.

CYCLOBUTA[*l*]PHENANTHRENE-1,2-DIONE (1) was required for electrochemical reduction studies, the results of which have already been published.<sup>2</sup> This paper records the synthesis and some properties of the dione, together with an X-ray determination of its molecular structure.



(1)

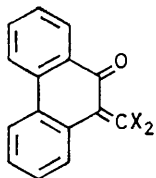
(2) R = CO<sub>2</sub>H

(3) RR = CO·O·CO

(4) RR = CO·NHNH·CO

(5) RR = CO·N(NH<sub>2</sub>)·CO

(6) RR = CO·N(N=CHPh)·CO

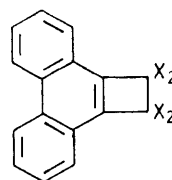
(7) RR = CO·N[N=S(O)Me<sub>2</sub>]·CO

(8) X = Br

(9) X = Cl

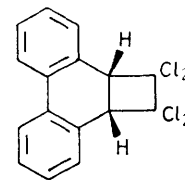
anhydride (3) which, on treatment with hydrazine, did not give the desired cyclic hydrazide (4), but gave instead the *N*-amino-imide (5), characterised as its benzylidene derivative (6). The formation of the 5-membered *N*-amino-derivative instead of the 6-membered hydrazide (4) is probably caused by steric effects, since tetrachloro- and tetrabromo-phthalic anhydrides have, similarly, given *N*-amino-imides when treated with hydrazine.<sup>3</sup> Oxidation of the *N*-amino-imide (5) with lead tetraacetate in dimethyl sulphoxide did not yield the expected sulphoximide (7) which, on flash-vacuum pyrolysis, might have given the phenanthrene-dione (1), *cf.* Rees *et al.*<sup>7</sup>

Our second approach to the dione (1) was based on a preliminary report by Sullivan *et al.*<sup>8</sup> that phenanthraquinone reacts with dibromomethylenetriphenylphosphorane (1 and 2 equiv.) to give the quinomethane (8) and the tetrabromocyclobuta[*l*]phenanthrene (10), res-

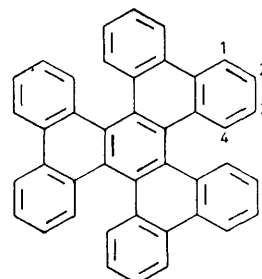


(10) X = Br

(11) X = Cl



(12)



(13)

We tried first to prepare the dione by an extension of our general method for the synthesis of benzocyclobutene-1,2-diones.<sup>3,4</sup> This method involves the flash-vacuum pyrolysis of Diels-Alder adducts of phthalazine-1,4-diones, which are made by oxidation of the cyclic hydrazides of substituted phthalic acids in the presence of anthracene. We prepared phenanthrene-9,10-dicarboxylic acid (2) from phenanthrene by a new, convenient sequence as follows. Phenanthrene was formylated with dichloromethyl methyl ether by the method of Rieche *et al.*<sup>5</sup> and the 9-carbaldehyde was reduced and reformylated to give 10-methylphenanthrene-9-carbaldehyde, which was then oxidised to the dicarboxylic acid using aqueous sodium dichromate (Friedman *et al.*'s method<sup>6</sup>). Dehydration of the diacid then gave the

pectively. The latter would be expected to be capable of hydrolysis to give the desired dione (1). Unfortunately, no experimental details were available and, in our hands, the reaction of phenanthraquinone with the

phosphorane gave the quinomethane (8) in 2.8% yield and a tetrabromo-compound (0.4%), the m.p. ( $>255$  °C) of which differed greatly from the literature value (165–167 °C). Posner *et al.*<sup>9</sup> have noted that yields from this type of reaction are drastically affected by bulky substituents on the ketone. We then found that the reaction of phenanthraquinone with the less sterically-demanding reagent dichloromethylenetriphenylphosphorane (1 and 2 equiv.) gave the dichloroquinomethane (9) (8%) and the tetrachloro-compound (11) (19%), respectively. This tetrachloro-compound could not be separated completely from triphenylphosphine oxide so we sought an alternative route to it and this led us to the third (and successful) approach to the dione (1).

Photochemical [2 + 2] cycloaddition of tetrachloroethene gave the dihydrophenanthrene (12) (assumed to be the *cis*-isomer) in 17% yield. Treatment of this compound with *N*-bromosuccinimide followed by chromatography on alumina gave the phenanthrene (11) (71%), which, on hydrolysis with silver trifluoroacetate, gave cyclobuta[*l*]phenanthrene-1,2-dione (79%) as a stable, yellow solid.

The dione (1) forms a mono-2,4-dinitrophenylhydrazone even with an excess of the hydrazine. The reaction of the dione with *ortho*-phenylenediamine is recorded in an earlier paper.<sup>1</sup> The mass spectrum of the dione showed a weak molecular ion at  $M^+$  232 (21%) and two losses of 28 a.m.u. corresponding to successive losses of carbon monoxide to give the ions  $M^+$  204 (43%) and  $M^+$  176 (100%), which corresponds to phenanthryne. The loss of carbon oxides in the mass spectrum is well known for polycarbonyl compounds and this mode of decomposition is often paralleled in flash-vacuum pyrolysis reactions to yield biphenylenes.<sup>3,10,11</sup> Pyrolysis of the dione (1) at 700 °C gave a yellow hydrocarbon ( $M^+$ , 528), m.p.  $>360$  °C, which is clearly not the unknown tetra-

benzo[*a,c,g,i*]biphenylene but is the hexabenzotriphenylene (13). Its mass spectrum essentially consists of three groups of peaks. The molecular ion,  $M^+$  528 (relative intensity 31%) is accompanied by peaks at  $m/e$  529 (15%) and six peaks of similar intensity (*ca.* 8%) corresponding to the loss of 1–6 hydrogen atoms. This behaviour would be expected because hexabenzotriphenylene should readily lose hydrogen to form, eventually, hexabenzocoronene. The parent ion,  $m/e$  352 corresponds to a dimer of phenanthryne and the third main peak is at  $m/e$  176 (16%), corresponding to phenanthryne. The peaks at  $m/e$  352 and 176 are accompanied by other peaks with unit spacing. The <sup>1</sup>H n.m.r. spectrum of the hydrocarbon (13) consists essentially of two doublets and two triplets (ignoring further small *meta* and long-range splitting) and thus provides very strong evidence for the structure assigned to the compound.

Our hexabenzotriphenylene is probably the same as that obtained by Barton and Grinham by the oxidation of 1-amino-1*H*-phenanthro[9,10-*d*]triazole,<sup>12</sup> but it is different from the supposed hexabenzotriphenylene obtained by the action of lithium or magnesium on 9,10-dichlorophenanthrene<sup>13</sup> which has been shown recently not to possess this structure.<sup>14</sup>

*N.M.R. Spectra of Cyclobuta[*l*]phenanthrene-1,2-dione and Related Diones.*—The <sup>1</sup>H n.m.r. spectra of benzo-cyclobutene-1,2-dione<sup>15</sup> (14) and cyclobuta[*b*]naphthalene-1,2-dione<sup>3</sup> (15) have already been published; that of the phenanthrene-dione (1) is recorded in the experimental section. The <sup>1</sup>H n.m.r. spectra of these three compounds are unexceptional.

We have measured the <sup>13</sup>C n.m.r. spectra of the same three diones in order to find out if there is any correlation between the chemical shifts and the bond structure of the diones. The <sup>13</sup>C n.m.r. spectra had to be measured in

TABLE 1  
<sup>13</sup>C N.m.r. spectra of the diones (14), (15), and (1) <sup>a</sup>

Carbon	(14)			(15)		(1)
	CDCl <sub>3</sub> <sup>b</sup> (room temp.)	CD <sub>3</sub> NO <sub>2</sub> (room temp.)	CD <sub>3</sub> NO <sub>2</sub> (+100 °C)	CD <sub>3</sub> NO <sub>2</sub> (room temp.)	CD <sub>3</sub> NO <sub>2</sub> (+90 °C)	CD <sub>3</sub> NO <sub>2</sub> (+100 °C)
1	194.2	196.6	197.1		197.7	184.9
2	173.2	174.3	175.2		164.8	179.8
3	135.4	137.4	137.9	(132.5)	(132.6)	(135.1)
4	122.3	123.5	124.0		138.1	(125.8)
5				(132.5)	(132.6)	(125.8)
6				(123.0)	(123.0)	(128.8)
7						(130.7)
8						(134.4)
No. of scans		2 200	6 022	58 000	23 000	77 000

<sup>a</sup> The chemical shifts in parentheses are tentative assignments. <sup>b</sup> A. J. Jones, P. J. Garratt, and K. P. C. Vollhardt, *Angew. Chem., Int. Ed. Engl.*, 1973, **12**, 241.

CD<sub>3</sub>NO<sub>2</sub> and at elevated temperatures for the tri- and tetra-cyclic compounds because of their low solubility. However, it is clear from Table 1 that there is little solvent effect in changing from CDCl<sub>3</sub> to CD<sub>3</sub>NO<sub>2</sub> ( $\delta$  ca. 2 p.p.m.) and that the temperature dependence is even less ( $\delta$  ca. 0.5 p.p.m.). On simple resonance theory (assigning equal weight to each of the possible canonical forms) the bond orders of the bond common to the four- and the six-membered rings would be 1.33, 1.5, and 1.8 for the diones (15), (14), and (1), respectively. Table 1 shows that the <sup>13</sup>C chemical shifts for the C-2\* carbon atoms follow this sequence, *i.e.*  $\delta_C$  ca. 165, 175, and 180 p.p.m. These values may reflect, in part, the additional ring strain caused by increasing bond order in the cyclobutene ring. This spread ( $\delta$  ca. 15 p.p.m.) in chemical

$P\bar{1}$ ,  $a = 9.762(4)$ ,  $b = 9.129(4)$ ,  $c = 7.049(3)$  Å,  $\alpha = 107.71(4)$ ,  $\beta = 97.97(4)$ ,  $\gamma = 64.45^\circ$ ,  $Z = 2$ ,  $D_c = 1.429$  Mg m<sup>-3</sup>, Cu-K $\alpha$  ( $\lambda$  1.5418 Å). A four circles diffractometer Picker instrument was used with an  $\omega$ -scan of 2 $\theta_{\text{max}}$  120° and 1 595 reflections were measured of which 1 370 were observed [ $I > 2.5\sigma(I)$ ]. The structure was solved by direct methods using the program system MULTAN.<sup>18</sup> After several cycles of isotropic and anisotropic refinement of O and C atoms, the H atoms were located by a difference Fourier-synthesis and included in 3 further refinement cycles with isotropic temperature-factors. The refinement was carried out by the NRC-CRYSTALLOGRAPHIC PROGRAMS<sup>19</sup> to a final  $R$  value of 0.047 for the 1 370 observed reflections. Lists of structure factors and anisotropic thermal parameters are

TABLE 2

Atomic co-ordinates ( $\times 10^4$ ) and thermal parameters ( $\times 10^3$  for  $B_{ij}$  in Å<sup>2</sup> for  $B$  of hydrogen atoms) for compound (1). The anisotropic temperature factor is expressed in the form:

$$B = \exp[-(B_{11}h^2 + B_{22}k^2 + B_{33}l^2 + B_{23}kl + B_{13}hl + B_{12}hk)]$$

	<i>x</i>	<i>y</i>	<i>z</i>	$B_{11}$	$B_{22}$	$B_{33}$	$B_{23}$	$B_{13}$	$B_{12}$
O(1)	4 128(2)	9 448(1)	2 755(2)	180	107	385	151	6	-80
O(2)	7 867(1)	7 609(2)	3 418(2)	156	193	375	95	7	-247
C(3)	5 047(2)	8 092(2)	2 868(2)	139	115	197	75	22	-108
C(4)	6 823(2)	7 220(2)	3 176(2)	132	134	205	76	10	-146
C(5)	6 596(2)	5 664(2)	2 944(2)	103	119	157	72	17	-106
C(6)	5 064(2)	6 416(2)	2 695(2)	101	103	149	69	16	-7 $\ddagger$
C(7)	4 111(2)	5 541(2)	2 343(2)	93	108	155	75	23	-66
C(8)	4 862(2)	3 795(2)	2 264(2)	96	117	149	86	11	-98
C(9)	6 517(2)	2 986(2)	2 523(2)	96	113	164	100	1	-81
C(10)	7 405(2)	3 928(2)	2 876(2)	89	123	172	93	3	-89
C(11)	8 983(2)	3 164(2)	3 127(3)	86	170	253	139	-11	-97
C(12)	9 686(2)	1 482(2)	3 013(3)	93	170	321	161	-14	-35
C(13)	8 827(2)	553(2)	2 694(3)	129	126	383	162	-21	-46
C(14)	7 275(2)	1 275(2)	2 456(3)	119	112	311	145	-14	-76
C(15)	3 951(2)	2 897(2)	1 924(2)	124	148	212	105	9	-157
C(16)	2 404(2)	3 679(2)	1 670(3)	115	207	261	118	23	-189
C(17)	1 690(2)	5 385(2)	1 750(3)	92	204	248	110	11	-114
C(18)	2 538(2)	6 304(2)	2 082(2)	90	140	197	93	-13	-69
H(19)	9 585(24)	3 859(27)	3 437(31)	<i>B</i> 3.8					
H(20)	10 755(23)	1 001(25)	3 263(30)	3.2					
H(21)	9 316(22)	-644(25)	2 708(28)	3.1					
H(22)	6 716(23)	530(25)	2 220(30)	3.1					
H(23)	4 357(22)	1 741(24)	1 890(29)	2.9					
H(24)	1 778(23)	3 053(25)	1 496(29)	3.3					
H(25)	578(24)	5 893(26)	1 538(31)	3.6					
H(26)	2 086(20)	7 516(23)	2 202(27)	2.5					

shift is not observed in the systems without the cyclobutene ring, thus the corresponding carbon atoms in naphthalene, benzene, and phenanthrene have <sup>13</sup>C chemical shifts of 126.1, 128.5, and 127.3,<sup>16</sup> *i.e.* close to 127  $\pm$  1 p.p.m. It is known that <sup>13</sup>C chemical shifts are relatively insensitive to ring-currents, but are very sensitive to structural and substituent changes.<sup>16</sup>

The X-ray crystal structure of benzocyclobutene-1,2-dione (14) has already been published.<sup>17</sup> We have determined that of the phenanthredione (1), but we were unable to grow crystals of the naphthalenedione (15) suitable for X-ray studies.

*Crystal and Molecular Structure of Cyclobuta[1]phenanthrene-1,2-dione (1).*—*Crystal data:* C<sub>16</sub>H<sub>8</sub>O<sub>2</sub>, triclinic,

\* The numbering used to discuss n.m.r. data is not that of the IUPAC systematic name and is shown in Table 1.

† For details of Supplementary Publications see Notice to Authors No. 7 in *J. Chem. Soc., Perkin Trans. 1*, 1980, Index issue.

given in Supplementary Publication No. SUP 23173 (10 pp).† The positional and thermal parameters are listed in Table 2 and the bond lengths and angles in

TABLE 3

Bond lengths (Å) and angles (°) for compound (1)

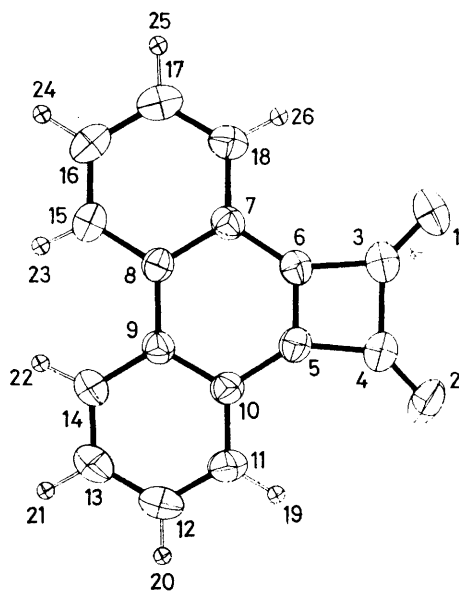
C(3)—O(1)	1.195(2)	C(9)—C(14)	1.399(2)
C(4)—O(2)	1.193(2)	C(8)—C(15)	1.404(3)
C(3)—C(4)	1.580(3)	C(15)—C(16)	1.376(3)
C(4)—C(5)	1.487(3)	C(16)—C(17)	1.391(3)
C(3)—C(6)	1.491(2)	C(17)—C(18)	1.368(3)
C(5)—C(6)	1.362(2)	C(7)—C(18)	1.398(2)
C(6)—C(7)	1.422(2)	C(11)—H(19)	1.00(3)
C(7)—C(8)	1.425(2)	C(12)—H(20)	0.96(2)
C(8)—C(9)	1.469(2)	C(13)—H(21)	0.99(2)
C(9)—C(10)	1.417(2)	C(14)—H(22)	1.01(2)
C(5)—C(10)	1.423(2)	C(15)—H(23)	0.95(2)
C(10)—C(11)	1.401(3)	C(16)—H(24)	0.98(2)
C(11)—C(12)	1.365(3)	C(17)—H(25)	0.99(3)
C(12)—C(13)	1.386(3)	C(18)—H(26)	0.98(2)
C(13)—C(14)	1.376(3)		

TABLE 3 (continued)

O(1)—C(3)—C(4)	137.0(2)	O(2)—C(4)—C(3)	137.2(2)
O(1)—C(3)—C(6)	137.1(2)	O(2)—C(4)—C(5)	137.0(2)
C(4)—C(3)—C(6)	85.9(1)	C(3)—C(4)—C(5)	85.7(1)
C(3)—C(6)—C(5)	94.0(1)	C(4)—C(5)—C(6)	94.4(1)
C(5)—C(6)—C(7)	123.3(1)	C(6)—C(5)—C(10)	123.6(2)
C(6)—C(7)—C(8)	115.6(1)	C(5)—C(10)—C(9)	115.8(1)
C(7)—C(8)—C(9)	121.0(1)	C(10)—C(9)—C(8)	120.8(1)
C(7)—C(8)—C(15)	117.0(1)	C(10)—C(9)—C(14)	117.4(2)
C(8)—C(15)—C(16)	121.0(2)	C(9)—C(14)—C(13)	120.4(2)
C(15)—C(16)—C(17)	121.3(2)	C(14)—C(13)—C(12)	121.6(2)
C(16)—C(17)—C(18)	119.5(2)	C(13)—C(12)—C(11)	119.6(2)
C(17)—C(18)—C(7)	120.4(2)	C(12)—C(11)—C(10)	119.9(2)
C(8)—C(7)—C(18)	120.8(1)	C(11)—C(10)—C(9)	121.0(2)
C(3)—C(6)—C(7)	142.7(2)	C(4)—C(5)—C(10)	142.0(2)
C(6)—C(7)—C(18)	123.5(1)	C(5)—C(10)—C(11)	123.2(2)
C(9)—C(8)—C(15)	122.1(1)	C(8)—C(9)—C(14)	121.8(2)

Table 3. The atomic numbering (which is not that of the IUPAC systematic name) is explained in the Figure.

The bond lengths, C—C and C—O, in the cyclobutene ring agree well with results for the dione (14).<sup>17</sup> However, the distance C(5)—C(6) [1.362(2) Å] is intermediate



Crystallographic numbering for compound (1)

between that of the corresponding bond in the dione (14) [1.384(11) Å] and in phenanthrene [1.341(7) Å];<sup>20</sup> it corresponds to a bond order of 1.65 calculated according to Pauling's equation.<sup>21</sup>

## EXPERIMENTAL

General directions are given in ref. 3. <sup>1</sup>H N.m.r. spectra were recorded on a Varian HA-100 spectrometer for solutions in deuteriochloroform. <sup>13</sup>C N.m.r. spectra were recorded on a Jeol JNM-PS-100 spectrometer for solutions in deuteriochloroform and in nitromethane. Tetramethylsilane ( $\delta$  0.00) was used as an internal standard.

**Phenanthrene-9,10-dicarboxylic Anhydride (3).**—Dichloromethyl methyl ether (18 g) was added as drops to a vigorously stirred, ice-cold mixture of phenanthrene (17.8 g) and stannic chloride (39.1 g). The mixture was allowed to warm to room temperature while being stirred for 24 h, after which it was poured into ice-cold 3M hydrochloric acid

and stirred for 30 min. The organic layer was collected and the aqueous layer extracted with dichloromethane. The organic layers were combined and evaporated, and the residue was chromatographed in benzene on a dry column of alumina (40 × 2 in). The material from the yellow band consisted of phenanthrene-9-carbaldehyde (8.3 g, 43%), m.p. 88—95 °C (lit.,<sup>22</sup> 100—101 °C).

The crude aldehyde (5 g), potassium hydroxide (5 g), and hydrazine hydrate (10 ml) were heated in digol (100 ml). Water and hydrazine were distilled off until the temperature reached 180 °C. The mixture was then refluxed for 3 h, cooled, diluted with water, acidified, and the precipitate collected to give 9-methylphenanthrene (4.5 g, 95%), m.p. 75—80 °C (lit.,<sup>23</sup> 90—91 °C).

Stannic chloride (12 ml) was added at 0 °C to a stirred mixture of 9-methylphenanthrene (0.8 g), 1,2-dichloroethane (15 ml), and dichloromethyl methyl ether (3 ml). The mixture was stirred for 24 h and then poured into ice-cold 3M hydrochloric acid (40 ml) (**CAUTION:** the temperature must be kept below 25 °C). The product, collected in dichloromethane, was recrystallised from ethanol-water to give 10-methylphenanthrene-9-carbaldehyde (0.58 g, 63%), m.p. 115—120 °C (lit.,<sup>24</sup> 130—131 °C).

The methyl-aldehyde (2 g), sodium dichromate (7 g), and water (20 ml) were heated in a rocking autoclave at 250 °C for 18 h. The mixture was filtered and the filtrate was acidified, thereby giving phenanthrene-9,10-dicarboxylic acid (2). This acid was heated with acetic anhydride to give phenanthrene-9,10-dicarboxylic anhydride (3) (1.7 g, 83%), m.p. 317 °C (lit.,<sup>6</sup> 317—318 °C).

**N-Aminophenanthrene-9,10-dicarboximide (5)**—(With M. E. CRACKNELL).—Phenanthrene-9,10-dicarboxylic anhydride (97 mg) and hydrazine hydrate (0.15 ml) in ethanol (5 ml) was boiled under reflux for 6 h. The mixture was cooled and the solid was collected, washed successively with ethanol and light petroleum to give the *N*-amino-imide (5) (67 mg, 65%) as yellow, fluffy needles (from ethanol) which melted at ca. 285—290 °C (Found: C, 10.6; H, 72.9; N, 3.8. C<sub>16</sub>H<sub>10</sub>N<sub>2</sub>O<sub>2</sub> requires C, 10.7; H, 73.3; N, 3.8%);  $\nu_{\max}$ . 3 350, 3 250(NH), 1 770, and 1 720 (C=O) cm<sup>-1</sup>.

**N-Benzylideneaminophenanthrene-9,10-dicarboximide (6).**—The *N*-amino-imide (5) (200 mg), benzaldehyde (100 mg), acetic acid (2 drops), and ethanol (50 ml) were boiled under reflux for 1 h. The mixture, when cooled, gave the *N*-benzylidene-derivative (6) (180 mg, 67%) as yellow plates (from ethanol), which decomposed at ca. 300 °C, but did not melt up to 360 °C (Found: C, 78.5; H, 4.2; N, 8.0. C<sub>23</sub>H<sub>14</sub>N<sub>2</sub>O<sub>2</sub> requires C, 78.8; H, 4.0; N, 8.0%).

**Reactions of 9,10-Phenanthraquinone with Dibromomethyl-triphenylphosphorane.**—Phenanthraquinone (5.2 g) in dichloromethane (100 ml) was added, under nitrogen, to a solution of carbon tetrabromide (33 g) and triphenylphosphine (53.4 g) in dichloromethane (250 ml) at 0 °C. The mixture was allowed to warm to room temperature and was then stirred for 2 h. The solvent was removed under reduced pressure and the oily residue filtered. The filtrate, when added to light petroleum, gave a solid which was extracted with light petroleum (2 l). Evaporation of the solvent left a yellow residue which was chromatographed in light petroleum on a column of dry alumina (40 cm long). The first eluate was evaporated and the residue (250 mg) was purified on thick silica-gel plates to give, presumably, the tetrabromo-compound (10) (50 mg, 0.39%), m.p. 255 °C (lit.,<sup>8</sup> 165—167 °C) (Found: *M*<sup>+</sup>, 516. Calc. for

$C_{16}H_8^{79}Br_4$ :  $M$ , 516);  $\nu_{max}$ , 3 070, 875, 800, 760, 735, and 725  $cm^{-1}$ .

Further elution of the alumina column yielded the yellow ketone (8) (250 mg, 2.8%), m.p. 120–130 °C (lit.,<sup>8</sup> 135 °C);  $\nu_{max}$ , 3 050, 1 725, 1 600, 805, 800, 750, 720, 695, and 655  $cm^{-1}$ .

1,1,2,2-Tetrachloro-1,2,2a,10b-tetrahydrocyclobuta[1]phenanthrene (12).—A solution of phenanthrene (recrystallised from ethanol) (5 g) in freshly distilled tetrachloroethane (100 ml) and hexane (850 ml) was purged with nitrogen and then irradiated for 72 h with a 450-W Hanovia medium-pressure mercury lamp. The reaction mixture was chromatographed on a dry column of alumina (25 × 3.5 cm) using pentane as eluant; 50-ml fractions were collected and groups of these were then united. The eluate, in order of elution, consisted of fractions 1–4, phenanthrene (ca. 2 g, 40% recovery), and 5–15, phenanthrene plus the cycloadduct. Fractions 5–15 were rechromatographed as before on the same column to give fractions 1–7, phenanthrene (1.0 g, 20%) and fractions 8–15 which contained 1,1,2,2-tetrachloro-1,2,2a,10b-tetrahydrocyclobuta[1]phenanthrene (12) (1.7 g, 17.5%) as needles (from ethanol), m.p. 166–168 °C (Found: C, 56.1; H, 2.9; Cl, 41.2.  $C_{16}H_{10}Cl_4$  requires C, 55.8; H, 2.9; Cl, 41.2%);  $\nu_{max}$ , 3 100, 3 050, 3 010, 895, 870, 800, 775, 750, 715, 700, and 675  $cm^{-1}$ ;  $\lambda_{max}$  ( $CH_2Cl_2$ ) 234, 242sh, 269sh, 279, 288sh, and 360 nm (log  $\epsilon$  4.49, 4.28, 4.45, 4.55, 4.40, and 3.20, respectively);  $\delta$  4.63 (2 H, s, 2a- and 10b-H), 7.36 (6 H, m, 3-, 4-, 5-, 8-, 9-, and 10-H), and 7.99 (2 H, m, 6- and 7-H).

1,1,2,2-Tetrachloro-1,2-dihydrocyclobuta[1]phenanthrene (11).—A mixture of the tetrachloro-compound (12) (2.1 g), *N*-bromosuccinimide (2.1 g), and dibenzoyl peroxide (ca. 25 mg) in carbon tetrachloride (15 ml) was refluxed for 2 h. The hot mixture was filtered and the filtrate was cooled, washed with 0.1M sodium thiosulphate (100 ml), then dried and evaporated. The residue was dissolved in light petroleum and chromatographed on a column of dry alumina with the same solvent as eluant. The eluate yielded the phenanthrene (11) (1.5 g, 71%) as plates (from ethanol), m.p. 229–230 °C (Found: C, 56.5; H, 2.5.  $C_{16}H_8Cl_4$  requires C, 56.2; H, 2.4%);  $\nu_{max}$ , 3 070, 3 050, 3 020, 845, 805, 790, 760, 750, 735, 720, and 695  $cm^{-1}$ ;  $\lambda_{max}$  ( $CH_2Cl_2$ ) 235, 250sh, 257, 265sh, 276sh, 281, 292, and 305 nm (log  $\epsilon$  4.54, 4.76, 4.81, 4.42, 4.18, 4.05, 3.99, and 4.01, respectively);  $\delta$  7.78 (4 H, m, 4-, 5-, 8-, and 9-H), 8.18 (2 H, m, 3- and 10-H), and 8.70 (2 H, m, 6- and 7-H).

Cyclobuta[1]phenanthrene-1,2-dione (1).—Silver trifluoroacetate (1.7 g), distilled water (0.5 ml), and 1,1,2,2-tetrachloro-1,2-dihydrocyclobuta[1]phenanthrene (11) (0.5 g) in acetonitrile (35 ml) were refluxed for 24 h whilst protected from light. The hot mixture was filtered and the filtrate evaporated off. The residue was dissolved in dichloromethane (250 ml) and washed successively with water (2 × 75 ml) and saturated sodium chloride (2 × 75 ml). The solution (dried over sodium sulphate) was evaporated to give cyclobuta[1]phenanthrene-1,2-dione (1) (0.27 g, 79%) as yellow needles, m.p. 285–286 °C (Found: C, 82.6; H, 3.4.  $C_{16}H_8O_2$  requires C, 82.8; H, 3.5%);  $\nu_{max}$ , 3 090, 3 050, 1 835, 1 775, 1 700, 1 610, 945, 765, 750, 725, and 715  $cm^{-1}$ ;  $\lambda_{max}$  ( $CH_2Cl_2$ ) 262, 298, 315sh, and 346sh (log  $\epsilon$  4.65, 4.66, 4.23, and 3.46, respectively);  $\delta$  7.92 (4 H, m, 4-, 5-, 9-, and 10-H), 8.54 (2 H, m, 3- and 10- or 6- and 7-H), and 8.75 (2 H, m, 6- and 7- or 3- and 10-H).

The dione gave the *mono*-2,4-dinitrophenylhydrazone as orange needles (from aqueous dimethyl sulphoxide), m.p. >360 °C (Found: C, 63.5; H, 3.0; N, 13.2.  $C_{22}H_{12}N_4O_5$  requires C, 64.1; H, 2.9; N, 13.6%);  $m/e$  412 ( $M^+$ ).

Pyrolysis of the Dione (1).—The dione (50 mg) was pyrolysed at 700 °C and 0.01 mmHg by passage through a silica tube (45 × 1 cm i.d.).<sup>3</sup> The pyrolysate was chromatographed on silica gel using toluene–light petroleum (1 : 1) as eluant and gave hexabeno[a,c,g,i,m,o]triphenylene (13) as yellow crystals (5 mg), m.p. >360 °C (Found:  $M^+$ , 528.188.  $C_{42}H_{28}$  requires  $M$ , 528.188);  $\nu_{max}$ , 3 060, 880, 815, and 735  $cm^{-1}$ ;  $\lambda_{max}$  ( $CH_2Cl_2$ ) 240, 251sh, 303sh, 351sh, 365, and 380sh (log  $\epsilon$  4.48, 4.45, 3.99, 4.20, 4.31, and 4.04, respectively);  $\delta$  7.21 and 7.55br (t, 2- and 3-H or *vice versa*), 8.15 and 8.54br (d, 1- and 4-H or *vice versa*) (the other protons are equivalent, by symmetry, to 1-, 2-, 3-, and 4-H).

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