Tetrahedron. Vol. 27, pp. 5239 to 5245. Pergamon Press 1971 Printed in Great Britain

BENZOLOGUES OF TERRYLENE

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(*Received in the UK* 2 *June* 1971; *Accepted for publication* 24 *June* 1971)

Abstract—The syntheses of 2,3:12,13-dibenzoterrylene (III), 1,16:2,3:12,13:14,15-tetrabenzoterrylene (VI),2,3:12,13:15,16-tribenzoterrylene (VIII) and 2,3:6,7:8,9:12,13:15,16-pentabenzoterrylene (XI) are described. The comparison of the spectra of these benzologues of terrylene with terrylene itself show the expected shifts derived from the formulae with aromatic sextets. This justifies fully the presentation of the formulae with Robinson's aromatic sextets which provide a clear prediction about colour and reactivity only if applied in the strictest sense.

THE PERI-CONDENSED series: naphthalene, perylene, terrylene and quaterrylene is formally built up by connecting naphthalene complexes with single bonds. This is confirmed by X-ray analysis which determines the bonds length of these bonds between 1·50 and 1·53 Å. The bonds within the naphthalene complexes show a marked resemblance to the lengths in naphthalene.[1]

There are strong spectral shifts towards the red in this series. We have now synthesized benzologues of terrylene in order to see whether the annellation effects are similar to the ones observed in the perylene series.[2] This is found to be the case.

2.3:12.13-dibenzoterrylene (III) was synthesized from 2.3-dichloro-1.4-naphthoquinone which gave the diol (I) with phenanthryl magnesium bromide. Reduction with hydroiodic acid in acetic acid yielded diphenanthryl-dichloro-naphthalene (II). This was condensed to dibenzoterrylene (III) in a short sodium chloride-aluminium chloride melt. the two chlorine atoms being simultaneously removed with the H atoms. This is not the case if 1.4-di(1′-naphthyl) 2.3-dichloronaphthalene is submitted to the melt. In that case 15.16-dichloroterrylene is obtained.[1] The absorption spectrum of the deep violet red 2.3:12.13-dibenzoterrylene (III) is presented in Fig 1 besides the spectrum of terrylene. By comparison with the latter the p-bands of the dibenzo derivate shift slightly towards the violet (−50 Å) whilst the β-bands show a strong shift towards the red (+310 Å. solvent benzene). This annellation effect is the same as in the perylene series.[2]

Like 2.3:10.11-dibenzoperylene.[3] 2.3:12.13-dibenzoterrylene (III) is capable of a diene synthesis with maleic anhydride. Mild dehydrogenating agents like iodine gave the tetraanhydride (IV). whilst strong ones like chloranil yielded mainly the dianhydride (V). The latter can also be obtained by thermal decomposition of IV. Analogous condensation product can be observed with 2.3:10.11-dibenzoperylene[3]. The decarboxylation of the anhydrides yielded 1.16:2.3:12.13:14.15-tetrabenzoterrylene (VI). This yellow hydrocarbon belongs to the class of fully benzenoid hydrocarbons which can be formulated with aromatic sextets only.[3, 4] The increase from 5 sextets in dibenzoterrylene (III) to 7 sextets in tetrabenzoterrylene (VI) produces a drastic shift of the p-bands towards shorter wavelength from 5600 Å to 4350 Å. whilst the

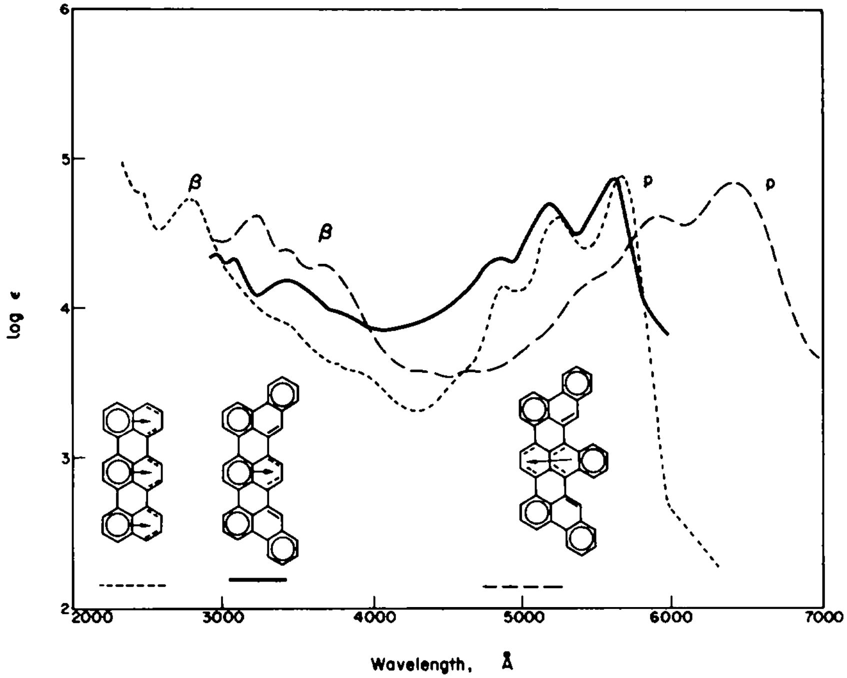


FIG 1. Absorption spectra with max (Å) and log ε in parentheses. ······· Terrylene in benzene: p, 5600(4·90), 5190(4·60), 4830(4·14); β, 2770(4·74); in dioxane; β′, 2440(4·74), —— 2,3; 12,13-Dibenzoterrylene in xylene: p. 5600(4·87). 5170(4·69). 4850(4·32); β. 3450(4·17); in benzene: 3080(4·33). ----- 2.3:12.13:15.16-Tribenzoterrylene in xylene: p. 6420(4·86). 5900(4·63); β. 3680(4·31). 3460(4·40). 3220(4·62).

β-bands shift from 3080 Å to 3310 Å (Fig 2). This annellation effect is quite analogous to the one observed in the perylene series. Tetrabenzoterrylene (VI) like other fully benzenoid hydrocarbons is insoluble in conc sulphuric acid and shows an orange yellow phosphorescence of very long life in solid solution. It is extremely stable and can be sublimed above 500° without decomposition.

Fig 2 shows the absorption spectrum of tetrabenzoterrylene in addition to the one of 6.7:8.9-dibenzoterrylene (3.4:5.6:7.8-tribenzoperopyrene).[5] The latter hydrocarbon has two fixed double bonds if written with 5 aromatic sextets as in XII. The comparison with tetrabenzoterrylene (VI) confirms the rule that no red shift is recorded if rings are annellated to fixed double bonds. Instead small shifts towards shorter wavelengths ($p = 110$ and $\beta = 0$ Å) are often found.[6] This is explained by the fact that only two branches can be in aromatic conjugation in any linear benzologue of triphenylene.[7] Passing from dibenzoterrylene (III) to 2,3:12,13:15,16-tribenzoterrylene (VIII) a strong red shift of both the p- and β-bands is recorded. (Fig 2). Since no new sextet is produced by the annellation of the ring in 15.16-position full aromatic conjugation must take place as in going from naphthalene to anthracene.

Tribenzoterrylene (VIII) was synthesized from anthraquinone and 9-phenanthryl magnesium bromide which gave the diol (VII). This cyclised smoothly in a sodium chloride-aluminium chloride melt to yield the deep blue tribenzoterrylene (VIII). Its

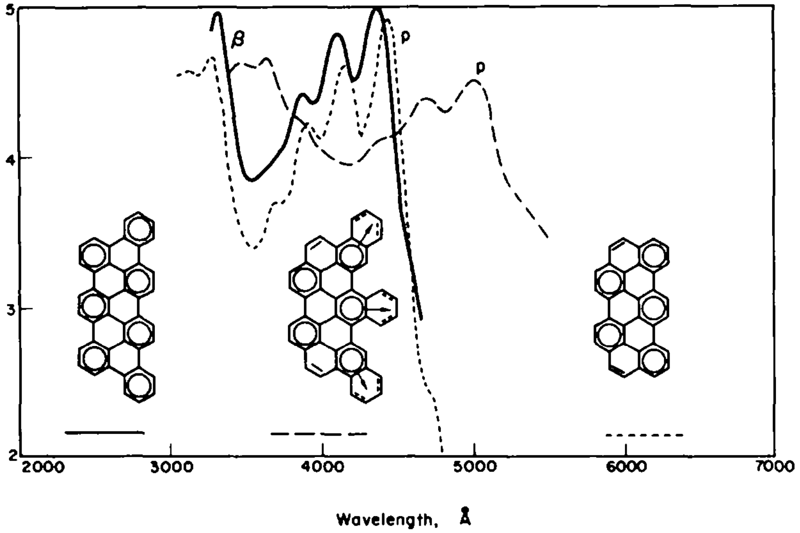


FIG 2. Absorption spectra with max (Å) and log ε in parentheses. ——— 1.16:2.3:12.13:14.15-Tetrabenzoterrylene in 1.2.4-trichlorobenzene: p. 4350(4·99). 4090(4·82). 3870(4·41); β. 3310 (4·95). ······· 6.7:8.9-Dibenzoterrylene in 1.2.4-trichlorobenzene: p. 4460(4·89). 4200(4·60). 3950(4·23). 3750(3·70): β. 3310(4·65). ----- 2.3:6.7:8.9:12.13:15.16-Pentabenzoterrylene in xylene: p. 5010(4·51). 4695(4·41). β. 3645(4·67). 3470(4·64).

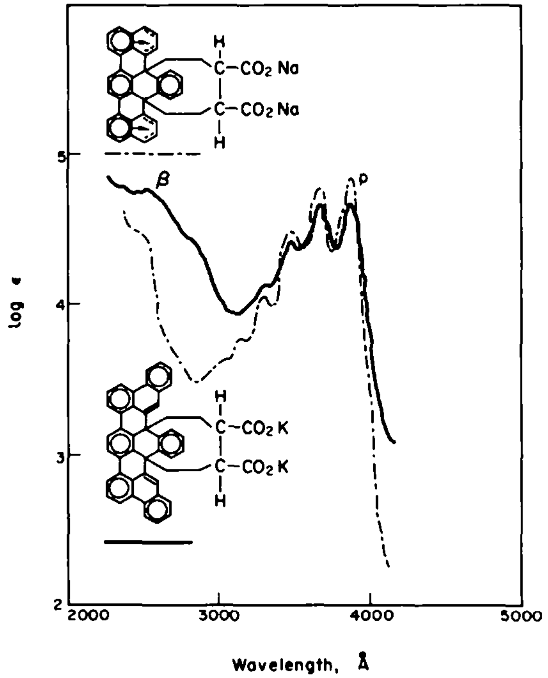
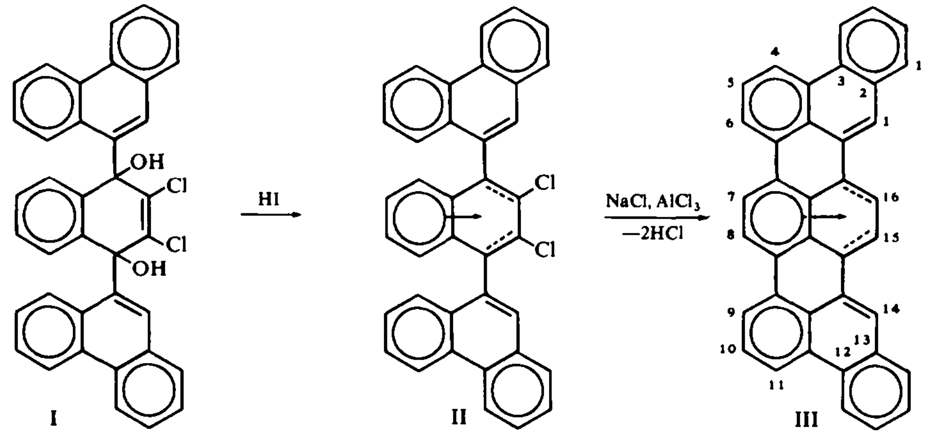


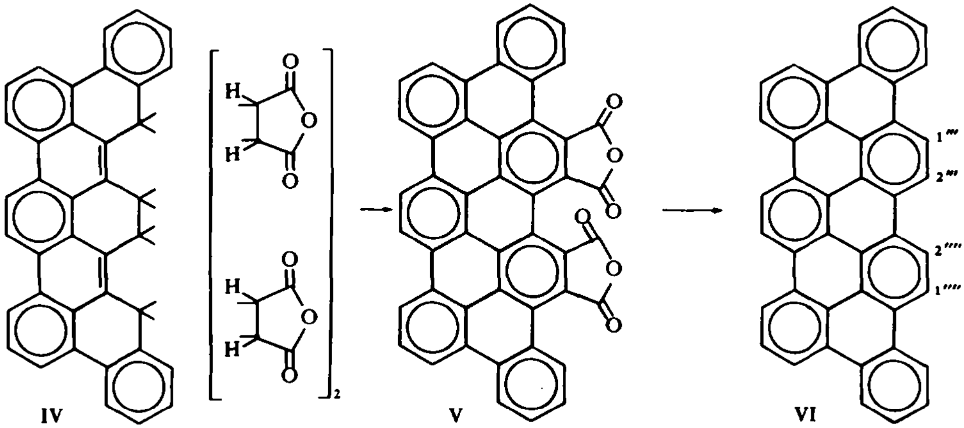
FIG 3. Absorption spectra with max (Å) and log ε in parentheses. ——— Di-K-salt of the maleic anhydride adduct of 2,3:12,13:15,16-tribenzoterrylene in water: p, 3880(4·68), 3670(4·66), 3480(4·42), 3300(4·12): β, 2520(4·77), -·-·- Di-Na-salt of the maleic anhydride adduct of 7,8-benzoterrylene in water: p, 3880(4·84), 3670(4·79), 3470(4·50), 3300(4·06), 3150(3·78): β, 2500(4·50).

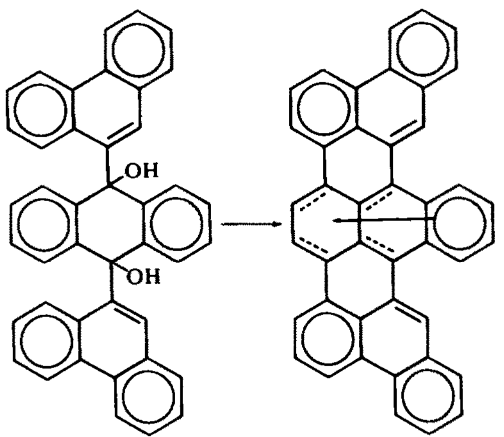
reaction with boiling maleic anhydride resulted in the formation of the colourless adduct (IX). Its absorption spectrum (Fig 3) in alkaline solution is very similar to the maleic anhydride adduct of 7.8-dibenzoterrylene[8] (Fig 3) just as the p-bands of naphthalene and phenanthrene are at similar positions (2850 and 2925 Å resp). There is less certainty about the relation of the rather broad β-bands.

A more energetic benzenogenic diene synthesis with maleic anhydride and a dehydrogenating agent produces the dianhydride (X). Decarboxylation with soda-lime yields the red 2.3:6.7:8.9:12.13:15.16-pentabenzoterrylene (XI). Comparison with 6.7:8.9-dibenzoterrylene (XII)[5] shows that there can be no increase in the number of sextets in passing from XI to XII. The result is a big red shift of the p- and β-bands amounting to 550 and 330 Å resp.

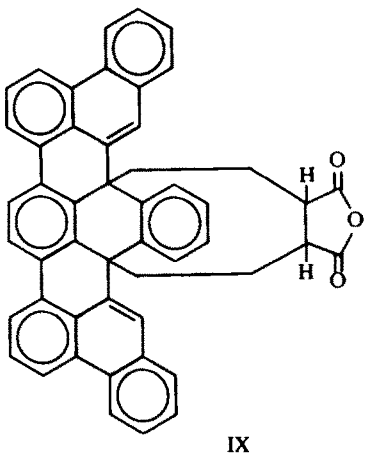
The above comparisons fully justify the presentation of the formulae with Robinson's aromatic sextets which only give a clear insight into the electronic fine structure and the resulting colour. reactivity and stability if applied in the strictest sense i.e. it must symbolize six π-electrons and the double bond two π-electrons. Since there can be only one true double bond in any aromatic ring[7] an alternative position for this double bond could be symbolized by a dashed line. If the double bond is about equally divided between two positions two dashed lines may be used.



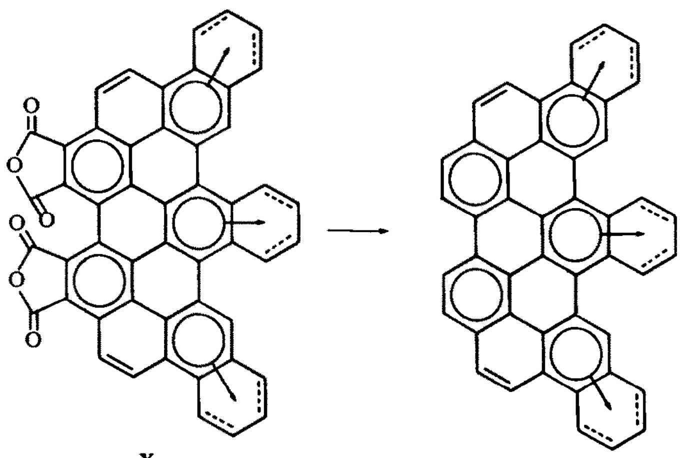




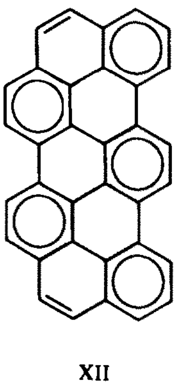
VII VIII



IX



X XI



XII

Note for the presentation of the formulae: Robinson's aromatic sextet, the circle, symbolizes strictly 6 π-electrons. An arrow stands for 2 π-electrons which can migrate from the sextet to the neighbouring ring giving it an inherent sextet. This is different from an induced sextet as in the middle ring of phenanthrene. This is not marked in this paper. Since there can be only one true double bond in any aromatic ring an alternative position for this double bond is symbolized by a dashed line. If a double bond is about equally divided between two positions two dashed lines are used.

EXPERIMENTAL*

1.4-*Di(9'-phenanthryl)* *1.4-dihydroxy-1.4-dihydro-2.3-dichloronaphthalene* (I). To a Grignard soln prepared from Mg (35·5 g), 9-bromophenanthrene (350 g) and ether (500 ml). 2.3-dichloro-1.4-naphthoquinone (54·6 g) suspended in benzene (150 ml) was gradually added. The mixture became green and changed to dark yellow. It was refluxed for 4 hr. On decomposing the mixture with ice and AcOH a ppt was formed in the organic layer. This was filtered off and washed with water. EtOH and ether. yield 52 g. Concentration of the mother liquor gave a further 15 g. The product was recrystallized 3 times from xylene and dried at 120° for 48 hr. (Found: C. 77·9; H. 4·3. $C_{38}H_{24}O_2Cl_2$ requires: C. 78·2; H. 4·1%). The almost colourless needles. m.p. 335–338° dec. dissolved in conc H_2SO_4 to give a dark yellow brown soln.

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* M.ps are uncorrected and were taken in evacuated capillaries.

1.4-*Di(9′-phenanthryl) 2.3-dichloronaphthalene* (II). A suspension of the above diol (25 g) in AcOH (312 ml) was refluxed and stirred. HI (31·25 ml. 55%) was added dropwise during 20 min. The mixture was refluxed for 1 hr. After cooling the light brown ppt (18·4 g) was filtered off and washed with AcOH. benzene and ether. Recrystallization first from nitrobenzene and then twice from xylene gave almost colourless prisms. m.p. 420° dec. which dissolved slowly in conc H_2SO_4 with a yellowish tinge. (Found: C. 82·9; H. 4·2. $C_{38}H_{22}Cl_2$ requires: C. 83·1; H. 4·0%).

2.3:12.13-*Dibenzoterrylene* (III). The above dichloro compound (2 g) and NaCl (1 g) were powdered together and added to a melt of NaCl (3 g) $AlCl_3$ (15 g) and Zn dust (0·5 g) at 110°. After stirring for 1 min. the mixture was decomposed in dil HCl. The ppt (1·9 g) was filtered off. and washed with water. The Zn dust was dissolved in conc HCl and the reddish violet ppt (1·9 g) filtered off. washed with dil HCl. water and then ammonia. The product from 7 melts (13·2 g) was dissolved in hot xylene and chromatographed on 600 g highly active alumina. The column was eluted at 60° with hot xylene. The first coloured fraction contained 2.3-benzoperylene which was identified by its absorption spectrum[9]. The column was then heated to 110°. Concentration of the violet red soln gave dark brownish red needles. m.p. 450°. which dissolved in conc H_2SO_4 to form a greenish blue soln which turned to blue on heating. The hydrocarbon can be sublimed in vacuum. (Found: C, 95·8; H, 4·2. $C_{38}H_{20}O$ requires: C, 95·8; H, 4·2%).

Tetra-adduct with maleic anhydride (IV). Dibenzoterrylene (10 mg) was powdered and added to refluxing maleic anhydride (300 mg). Small portions of I_2 were gradually added to the deep violet soln. which turned brown. The mixture was refluxed for 2 hr always ensuring that the vapour contained excess iodine. The iodine and some maleic anhydride were distilled off. After cooling acetone was added. the ppt filtered off and washed with acetone. yield 9 mg. The yellowish brown crystals. m.p. 420° dec. dissolved colourless in conc H_2SO_4. The soln in dil KOH showed absorption bands at: α. 4100(3·82); p. 3380(4·82). 3080(4·85); 2450(4·98). (Found: C. 74·4; H. 2·8. $C_{52}H_{24}O_{12}$ requires: C. 74·3; H. 2·9%).

1.16:2.3:12.13:14.15-*Tetrabenzoterrylene-1‴.2‴.1⁗.2⁗-tetracarboxylic-dianhydride* (V). This compound can be obtained if in the above synthesis the I_2 is replaced by an excess of chloranil. Although the spectrum is closely related to VI it still contains some tetrahydride which make the C. H determination unsatisfactory. It is also obtained by sublimation of the tetraanhydride. Spectrum: p. 4270(4·77), 4070(4·70); β, 3300(5·00), 2450(5·31).

1.16:2.3:12.13:14.15-*Tetrabenzoterrylene* (VI). The tetra-adduct IV (534 mg) was powdered with soda-lime and a drop of alcohol to ensure intimate contact of the particles. The mixture was then heated to 350° under N_2 for 1 hr in order to remove alcohol and moisture. The sublimation was carried out at 450–500°/ 2×10^{-4}. The orange yellow sublimate was resublimed. yield 15·1 mg. (Found: C. 96·2; H. 3·8. $C_{42}H_{20}$ requires: C. 96·2; H. 3·8%). The hydrocarbon does not melt below 540°. is insoluble in conc H_2SO_4 and almost insoluble in organic solvents. However. it can be recrystallized from boiling pyrene under N_2. When cooled slowly large orange yellow plates are obtained which are filtered off after 1-methylnaphthalene was added in order to keep the pyrene in solution. The crystals were washed with hot xylene.

9.10-*Di(9′-phenanthryl) 9.10-dihydroxy-9.10-dihydroanthracene* (VII). A very finely divided suspension of anthraquinone (39·6 g) in benzene (150 ml) was prepared by shaking the mixture with glass balls for 2 days. A Grignards soln obtained from 9-bromophenanthrene (200 g) and Mg (19·6 g) in ether (400 ml) was added to the above suspension. The mixture which changed from dark brown to light yellowish green was shaken as above for 3 days. Decomposition with AcOH and ice yielded a ppt from the organic layer which was filtered off. washed with AcOH. water. EtOH and then ether. The wet product was thoroughly treated with NaOH-NaS_2O_4 soln in order to remove unreacted anthraquinone. After 5 extraction the filtrate was no longer red and the product showed no CO absorption in the IR. yield 37·2 g. The diol VII was three times recrystallized from xylene. It formed prisms. m.p. 420° dec which dissolved in conc H_2SO_4 to give a dark leaf green soln which turned golden brown on heating. (Found: C. 89·6; H. 4·6. $C_{42}H_{28}O_2$ requires: C. 89·3; H. 5·0%).

2.3:12.13:15.16-*Tribenzoterrylene* (VIII). The diol VII (3 g) was powdered with NaCl (3 g) and added to a melt of NaCl (3 g). $AlCl_3$ (24 g) and two drops of pyridine. The temp was kept just below 110°. After stirring the melt for 1 min. it was decomposed with dil HCl boiled. filtered and washed with water. The yield from four batches was 11·8 g.

The crude hydrocarbon was added to boiling xylene. the soln freed from water and chromatographed on alumina (400 g). The first coloured fraction contained 1.2:10.11-dibenzoperylene[10] which was formed as a cleavage product. It was obtained in a crystallized state and identified by its absorption spectrum. The column was then heated to 110° and eluted with hot xylene. The blue soln yielded VIII (2·19 g) on concentration. Recrystallization gave dark blue needles. m.p. 310°. which had a purple metallic lustre and dissolved in conc H_2SO_4 to form a blue soln. (Found: C. 95·9; H. 4·2. $C_{42}H_{22}$ requires: C. 95·8; H. 4·2%).

The hydrocarbon can be sublimed in vacuum.

Endocyclic addition product with maleic anhydride (IX). The hydrocarbon (6 mg) was added to refluxing maleic anhydride (200 mg). The deep blue soln bleached soon and light yellow crystals began to separate. After refluxing for 1 min AcOH (10 ml) was added and the crystals filtered off. washed with AcOH and acetone. yield 2·2 mg. Since the adduct tends to decay into its components the crude product cannot be recrystallized. For further purification it was boiled with AcOH. It formed prisms, m.p. 240° dec., which dissolved without colour in conc H_2SO_4. The soln turned light blue green on standing.

2,3:6,7:8,9:12,13:15,16-*Pentabenzoterrylene-1″,2″,1‴,2‴-tetracarboxylic-dianhydride* (X). Tribenzoterrylene (560 mg) were powdered and added to 12 g maleic anhydride. Small crystals of I_2 were added to the refluxing mixture during 2 hr always ensuring that an excess of I_2 was visible in the vapours. Some maleic anhydride and excess I_2 were distilled off. the mixture cooled and acetone (20 ml). The ppt was filtered off and washed with acetone. yield 536 mg. The dark brown prisms. m.p. 380° dec. dissolved in conc H_2SO_4 to form a green soln which became brown on heating. (Found: C. 83·9; H. 2·8. $C_{50}H_{18}O_6$ requires: C. 84·0; H. 2·5%).

2,3:6,7:8,9:12,13:15,16-*Pentabenzoterrylene* (XI). The dianhydride X (250 mg) was powdered thoroughly with soda-lime (1 3 g) and two drops of EtOH added to aid intimate contact. The mixture was heated under N_2 at 350° for 2 hr. Sublimation in vacuum gave a product which still contained some dianhydride. The sublimate was therefore powdered with KOH. a drop of EtOH added and the mixture transferred to a boat. covered with soda-lime and sublimed at 350°/1 × 10^{-4}. Dark reddish brown needles. m.p. 330°. were obtained which dissolved in conc H_2SO_4 only after standing for days with a slight violet colour. (Found: C. 96·0; H. 3·9. $C_{46}H_{22}$ requires: C. 96·1; H. 3·9%).

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