378. 1 : 12-2 : 3-10 : 11-*Tribenzoperylene.*

By E. Clar and M. Zander.

An improved synthesis of 2 : 3-10 : 11-dibenzoperylene (II) is described. This reacted easily with maleic anhydride to give the adduct (III) which was dehydrogenated to the anhydride (IV). Decarboxylation yielded the tribenzoperylene (V). The unusually low reactivity of this hydrocarbon is related to formula (Va), which consists exclusively of benzenoid rings interlinked by quasi-single bonds.

2 : 3-10 : 11-Dibenzoperylene (II) was obtained from 9 : 9′-diphenanthryl (I) in a sodium chloride–aluminium chloride melt.[1] However the method gives very low yields and sometimes fails completely.[2] We obtained yields of not less than 50% when the cyclisation was carried out in boiling benzene with aluminium chloride and stannic chloride as dehydrogenating agent.

Recently we assumed the existence of a dissociable adduct between perylene and maleic anhydride preceding the formation of 1 : 12-benzoperylenedicarboxylic anhydride.[3] The two " external " benzene rings in dibenzoperylene (II) stabilise the analogous adduct

[1] Joffe, *Zhur. obshchei Khim.*, 1933, **3**, 524; Zinke and Ziegler, *Ber.*, 1941, **74**, 115; Schauenstein and Bürgermeister, *Ber.*, 1943, **76**, 205; Zinke, *Monatsh.*, 1949, **80**, 202.

[2] Badger, Christie, Pryke, and Sasse, *J.*, 1957, 4417.

[3] Clar and Zander, *J.*, 1957, 4616.

(III), so that it could be easily isolated in very good yield though it dissociates smoothly into its components in high-boiling solvents. Its absorption spectrum (Fig. 1) which is related to that of 1 : 9-2 : 3-dibenzanthrene [4] supports the assumption of addition in the 1 : 12-positions of the dibenzoperylene (II), as does the fact that dibenzoperylene (II) is readily oxidised in the same positions.[1] Dehydrogenation of the adduct (III) with chloranil gave the anhydride (IV) which was also obtained directly (and quantitatively) from the dibenzoperylene (II) in boiling maleic anhydride containing chloranil. Hydrolysis

FIG. 1.

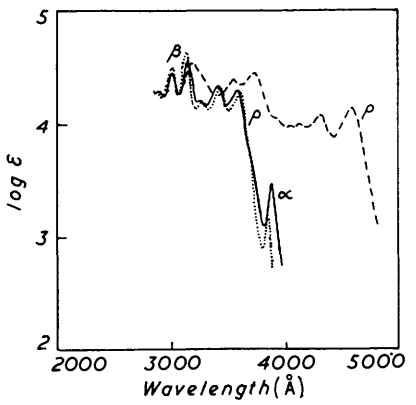


FIG. 2.

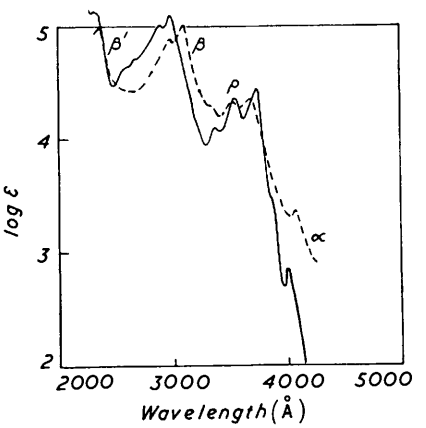


FIG. 1. *Absorption max.* (Å) *and* log ε (*in parentheses*) *of*: (——) *the tetrahydro-anhydride* (III) *in acetic anhydride*: α, 3885 (3·47); *p*, 3590 (4·30), 3410 (4·34), 3245 (4·21); β, 3145 (4·54), 3010 (4046).
(– – –) *The dihydro-anhydride* (VII) *after being boiled in* $C_6H_3Cl_3$ *for* 30 *min. Absorption bands originating from* (VII): *p*, 4580 (4·15), 4310 (4·08), 4140 (4·02). *Absorption bands originating from* (VI): *p*, 3740 (4·46), 3580 (4·41); β, 3200 (4·54).
(. . .) *Maleic anhydride adduct of* (VII) *in acetic anhydride*: α, 3860 (3·16); *p*, 3610 (4·29), 3430 (4·33), 3275 (4·18); β, 3140 (4·64), 3000 (4·49).

FIG. 2. *Absorption max.* (Å) *and* log ε (*in parentheses*) *of*: (——) 1 : 12-2 : 3-10 : 11-*tribenzoperylene* (V) *in* $C_6H_3Cl_3$: α, 4010 (2·86); *p*, 3740 (4·45), 3540 (4·37), 3380 (4·11); *in* EtOH β, 3000 (5·09), 2880 (5·00); β', 2340 (5·14).
(– – –) *Dipotassium* 1 : 12-2 : 3-10 : 11-*tribenzoperylene*-1' : 2'-*dicarboxylate* (*cf.* IV) *in* 50% EtOH: α, 4085 (3·36); *p*, 3680 (4·35), 3520 (4·32); β, 3100 (5·00), 2980 (4·87); β', 2380 (4·99).

and decarboxylation of the anhydride (IV) afforded 1 : 12-2 : 3-10 : 11-tribenzoperylene (V). The absorption spectra of this and of the dicarboxylic acid derived from (IV) are shown in Fig. 2.

An alkaline solution of the dicarboxylic acid derived from the adduct (III) was dehydrogenated by atmospheric oxygen to a yellow acid, derived from (VII). The absorption spectrum of this acid (of VII) shows that it contains the aromatic complex of the dibenzoperylene (II) (Fig. 3). When its solution in trichlorobenzene was boiled the spectrum changed to a type closely related to that of the adduct (III), indicating isomerisation to form (VI) (Fig. 1). The high reactivity of the dibenzoperylene is retained in its derivative (VII) which added another molecule of maleic anhydride to form the adduct (VIII), the spectrum of this further adduct belonged again to type (III)–(VI) (Fig. 1), all these substances being derivatives of 1 : 12-dihydro-2 : 3-10 : 11-dibenzoperylene.

Unlike 1 : 12-2 : 3-8 : 9-tribenzoperylene (IX) which condensed quantitatively [3] with maleic anhydride and chloranil to give the anhydride (X), 1 : 12-2 : 3-10 : 11-tribenzoperylene (V) did not react. The difference between the two hydrocarbons is that the tribenzoperylene (V) can be considered to be a condensed quinquephenyl, as indicated in formula (Va), whilst no analogous arrangement in the isomer (IX) is possible. In the

[4] Clar, *Ber.*, 1943, **76**, 611.

latter at least three double bonds remain outside the benzenoid rings, thus making the molecule sufficiently reactive for the above condensation.

According to formula (Va), 1 : 12-2 : 3-10 : 11-tribenzoperylene contains five benzenoid

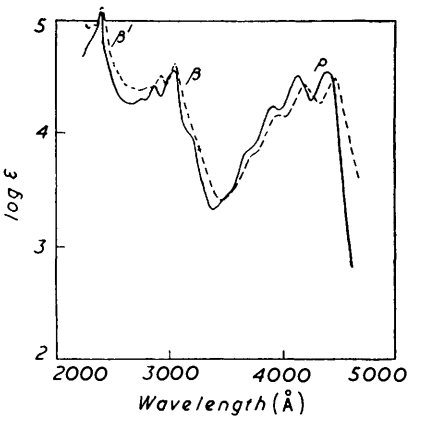
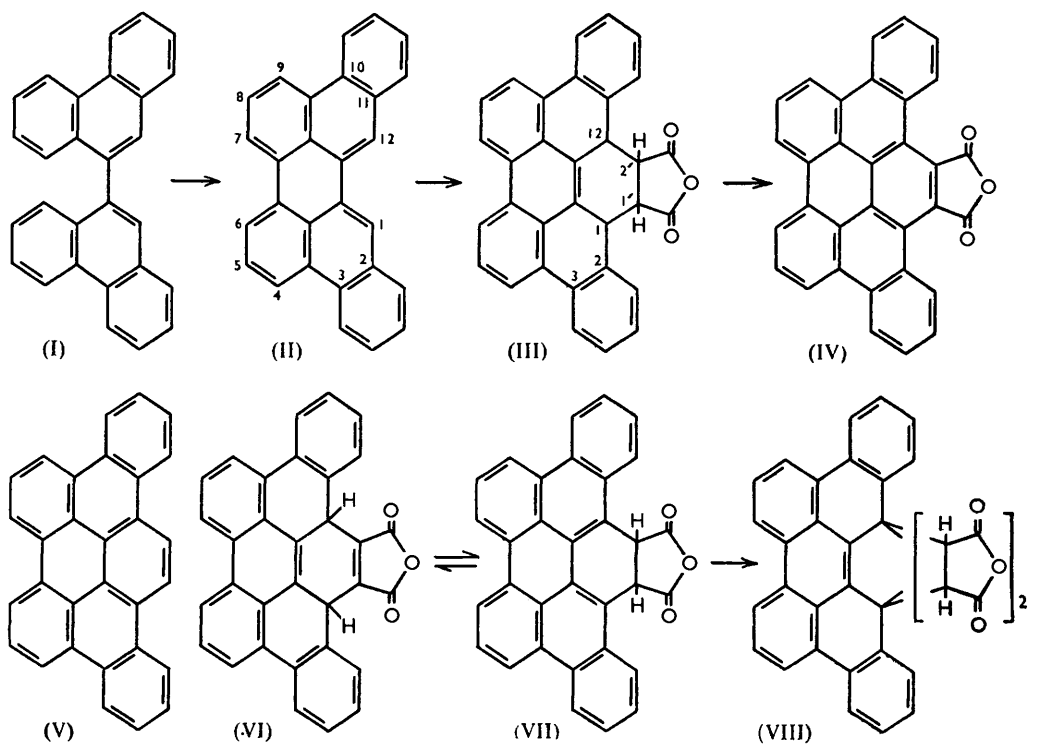


FIG. 3. *Absorption max.* (Å) *and* log ε (*in parentheses*) *of*: (——) 2 : 3-10 : 11-*dibenzoperylene* (II) *in* C_6H_6: *p*, 4400 (4·54), 4140 (4·51), 3920 (4·22); *in* EtOH *β*, 3020 (4·54), 2881 (4·41); *β'*, 2380 (5·05). (– – –) *Dipotassium* 1' : 2'-*dihydro*-1 : 12-2 : 3-10 : 11-*tribenzoperylene*-1' : 2'-*dicarboxylate* (*cf.* VII) *in* 50% EtOH: *p*, 4470 (4·48), 4190 (4·42), 3980 (4·16); *β*, 3050 (4·60), 2930 (4·51); *β'*, 2410 (5·10).

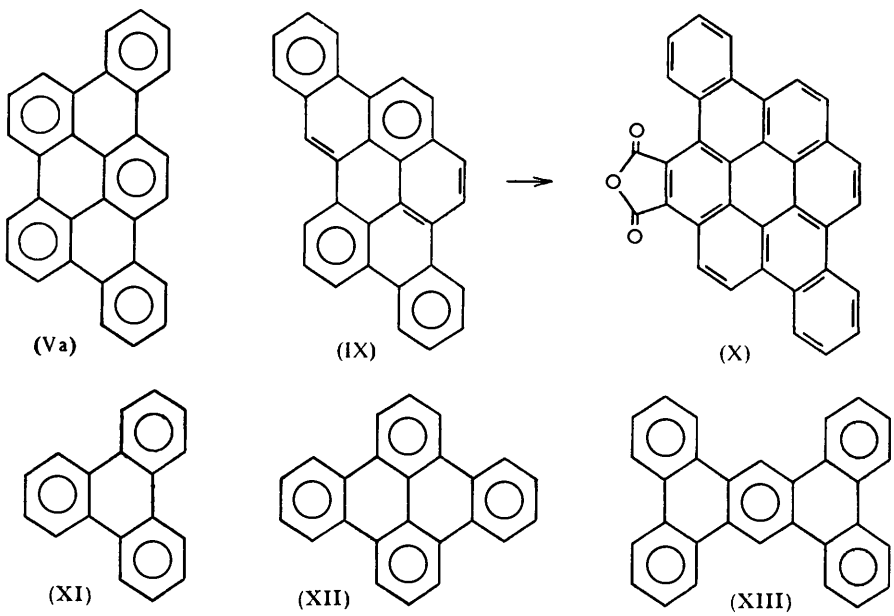
rings (each containing three double bonds) which are interlinked by quasi-single bonds, there being three quasi-empty rings. Such an arrangement accounts for the very low reactivity of the almost colourless hydrocarbon, which does not dissolve even in cold



concentrated sulphuric acid. Formula (Va) represents, not all possible arrangements of the double bonds, but the majority of all Kekulé structures, *i.e.*, the rings indicated by circles are benzenoid.

Only three other hydrocarbons of the tribenzoperylene type (Va) are known, namely,

triphenylene (XI), 1 : 2-6 : 7-dibenzopyrene [5] (XII), and 1 : 2-3 : 4-5 : 6-7 : 8-tetrabenzoanthracene [6] (XIII). These hydrocarbons also do not dissolve in concentrated sulphuric acid to form coloured solutions of the protonated molecules. They show very strong phosphorescence of long life in solid solution at low temperature.[7] Their absorption



bands are the most strongly shifted to the violet among the spectra of the isomeric aromatic hydrocarbons, except for the corresponding polyphenyl with the same number of benzenoid rings; their chemical inertness may be related to this fact.

Experimental

M. p.s were taken in evacuated capillaries. Microanalyses by Mr. J. M. Cameron and his staff.

2 : 3-10 : 11-*Dibenzoperylene* (II).—Powdered aluminium chloride (1 g.) was added to a solution of 9 : 9′-diphenanthryl [8] (1 g.) and stannic chloride (1 g.) in benzene (10 ml.). The mixture was refluxed for 1 hr. Hydrogen chloride was evolved. After decomposition with dilute hydrochloric acid the dibenzoperylene (1 g.) was filtered off from the organic layer and washed with benzene, dilute hydrochloric acid, water, and aqueous ammonia. The crude product was sublimed in a vacuum and recrystallised from xylene. The yellow needles (0·5 g.) dissolved in concentrated sulphuric acid to give a violet solution and had m. p. 330—332° (lit.,[1,2] 315—318°, 329—332°, 334—336°, and 343—345°).

1 : 12 : 1′ : 2′-*Tetrahydro*-1 : 12-2 : 3-10 : 11-*tribenzoperylene*-1′ : 2′-*dicarboxylic Anhydride* (III).—(*a*) Dibenzoperylene (0·1 g.) and maleic anhydride (3 g.) in dry xylene (30 ml.) were refluxed for 20 min. The *adduct*, which crystallised from the hot solution, was filtered off and washed with xylene and benzene (52 mg.). It became yellow at 250° and melted at 316—320° (decomp.). It did not dissolve in cold concentrated sulphuric acid and gave a green solution changing to red-brown when heated (Found: C, 86·0; H, 4·0. $C_{32}H_{18}O_3$ requires C, 85·3; H, 4·0%). The adduct dissociated in boiling nitrobenzene solution from which dibenzoperylene,

[5] Sako, *Bull. Chem. Soc. Japan*, 1934, **9**, 55; Clar, *Ber.*, 1943, **76**, 609; Lüttringhaus and Schubert, *Naturwiss.*, 1955, **42**, 17; Wittig and Lehmann, *Chem. Ber.*, 1957, **90**, 875.
[6] Lambert and Martin, *Bull. Soc. chim. belges*, 1952, **61**, 124.
[7] Clar and Zander, *Chem. Ber.*, 1956, **89**, 749.
[8] Bachmann, *J. Amer. Chem. Soc.*, 1934, **56**, 1363.

m. p. 332—335°, crystallised on cooling. This hydrocarbon contained a trace of the anhydride (IV), as found in the absorption spectrum.

(*b*) Dibenzoperylene (0·2 g.) and maleic anhydride (5 g.) were refluxed for 30 min. Hot xylene was added to the solution and the precipitated adduct (0·15 g.) filtered off and washed.

1 : 12-2 : 3-10 : 11-*Tribenzoperylene*-1′ : 2′-*dicarboxylic Anhydride* (IV).—(*a*) Dibenzoperylene (1·5 g.) and chloranil (2·5 g.) in maleic anhydride (40 g.) were refluxed for 30 min. Hot nitrobenzene was added and the precipitated orange-red needles were filtered off and washed with nitrobenzene, benzene, and ether (yield 1·95 g.). Sublimation at 380°/0·05 mm., followed by recrystallisation from nitrobenzene, yielded orange-red needles of *anhydride*, m. p. 430—435°, which did not dissolve in cold concentrated sulphuric acid but in the hot acid gave a pale yellow solution (Found: C, 86·1; H, 3·0. $C_{32}H_{14}O_3$ requires C, 86·1; H, 3·2%).

The residue from the sublimation yielded at 500—550°/0·05 mm. a very small amount of a dark violet sublimate which dissolved in dilute alcoholic-aqueous potassium hydroxide to a solution showing absorption bands at 4450, 4100, 3880, 3680, 3340, and 3200 Å.

(*b*) To a boiling solution of chloranil (100 mg.) in trichlorobenzene (5 ml.) the adduct (III) (50 mg.) was added and the whole refluxed for 20 min. The anhydride (IV), which crystallised, was filtered off and extracted with hot xylene (yield 38 mg.). This anhydride did not contain the above by-product.

1 : 12-2 : 3-10 : 11-*Tribenzoperylene* (V).—The anhydride (IV) (1 g.) and soda-lime (3 g.) were ground together and heated to 350° under nitrogen for 45 min. Sublimation at 400°/0·05 mm. gave the *hydrocarbon* (0·5 g.) as pale yellow needles. Recrystallised from xylene they formed plates on slow cooling and needles on quick cooling, both having m. p. 388—389° (Found: C, 95·9; H, 4·15. $C_{30}H_{16}$ requires C, 95·7; H, 4·3%). This tribenzoperylene did not dissolve in cold concentrated sulphuric acid but in the hot acid gave a violet solution. When an alcoholic solution of the hydrocarbon, cooled in liquid oxygen, was irradiated with a quartz lamp it showed a strong greenish-yellow phosphorescence of long life. The cooled crystalline hydrocarbon had an orange-red phosphorescence.

The tribenzoperylene did not react with boiling maleic anhydride and chloranil.

1′ : 2′-*Dihydro*-1 : 12-2 : 3-10 : 11-*tribenzoperylene*-1′ : 2′-*dicarboxylic Anhydride* (VII).—The anhydride (III) (1 g.) was added to a solution of potassium hydroxide (5 g.) in 90% alcohol (100 ml.). A current of air was bubbled through the solution at 60° for 30 min. Acidification of the filtered solution gave a yellow acid (0·8 g.) which on quick recrystallisation from acetic anhydride yielded the *anhydride* (VII) in yellow prisms, decomp. >300°. Concentrated sulphuric acid gave a greenish-blue solution which changed to brown on heating (Found: C, 86·6; H, 4·0. $C_{32}H_{16}O_3$ requires C, 85·7; H, 3·6%. Owing to a tendency to decompose on heating the percentage of carbon tended to higher values when the substance was dried). The anhydride (VII) was isomerised to the form (VI) at 80—100° or when boiled in trichlorobenzene for a short time. This change is shown in Fig. 1.

Maleic Anhydride Diadduct (VIII).—The anhydride (VII) (50 mg.) and maleic anhydride (2 g.) were refluxed for 10 min. The adduct began to crystallise from the hot solution which was diluted with hot xylene; the solid was collected and washed. The prisms of the *adduct*, m. p. 364° (decomp.), did not dissolve in cold concentrated sulphuric acid and gave a yellow solution on heating (Found: C, 78·8; H, 3·35. $C_{36}H_{18}O_6$ requires C, 79·1; H, 3·3%). The adduct dissociated in boiling trichlorobenzene into the compound (VII) and maleic anhydride, as shown by the absorption spectrum.

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