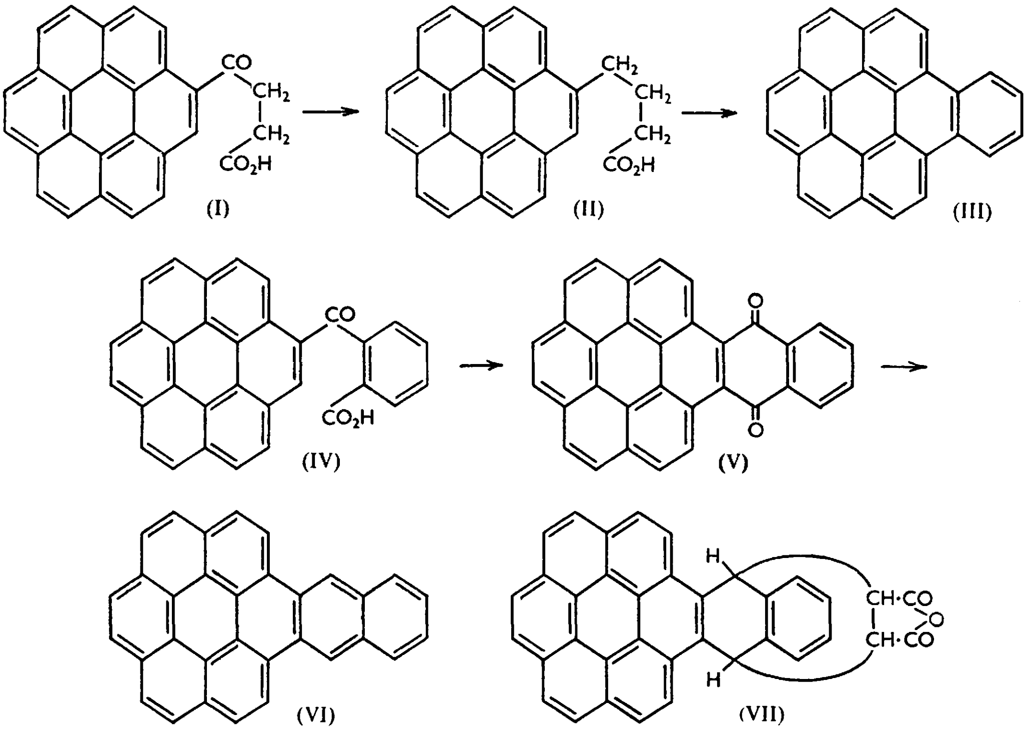
314. 1 : 2-*Benzocoronene and Naphtho*(2′ : 3′-1 : 2)*coronene.*

By E. Clar and M. Zander.

Coronene, condensed with succinic anhydride, gives the keto-acid (I) which on reduction and cyclisation in sodium chloride–zinc chloride affords 1 : 2-benzocoronene (III). Coronene was also condensed with phthalic anhydride to the keto-acid (IV); cyclisation then afforded the quinone (V) which was reduced to the naphthocoronene (VI); this adds maleic anhydride to give compound (VII).

Coronene is now easily accessible from commercial perylene.[1] We have therefore started to synthesise systematically the benzologues of coronene. Coronene with succinic anhydride and aluminium chloride gives the keto-acid (I), reduced by the Huang-Minlon method to the butyric acid (II), which cyclised in a melt of sodium chloride and zinc chloride, with simultaneous aromatisation of the newly formed ring, to 1 : 2-benzocoronene (III). This is pale yellow, as is coronene.



(I) (II) (III)

(IV) (V)

(VI) (VII)

In attempts to condense coronene with phthalic anhydride and aluminium chloride,

---

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

benzene and nitrobenzene proved unsuitable solvents. We therefore used *o*-dichlorobenzene which is described in patents [2] as a solvent for three-fold condensation of phthalic anhydride with coronene. A monocarboxylic acid (IV) was obtained which was easily cyclised to the monoquinone (V) by boiling benzoyl chloride. Its melting point and its vat are the same as those reported for the alleged triquinone.[2] Naphthocoronene (VI) was obtained by reduction of the quinone (V) with pyridine, zinc dust, and acetic acid. The yellow naphthocoronene showed acene character and added maleic anhydride, giving the adduct (VII).

The ultraviolet absorption spectra of the butyric acid (II) and of the adduct (VII) (Fig. 1) are of typical coronene form, the α-bands of the adduct being more intense, as is characteristic for cyclic alkyl derivatives. In passing from benzocoronene (III) to naphthocoronene (VI) (Fig. 2), the red shift of the *p*-bands (470 Å) is considerably greater than in passing from coronene to benzocoronene (345 Å). This accords with the asymmetric annellation effect in the pyrene and perylene series; [3] it shows that the spectral properties of condensed systems become increasingly acene-like when benzene rings are annellated linearly and asymmetrically.

Absorption max. (Å) *and* log ε (*in parentheses*).

FIG. 1.

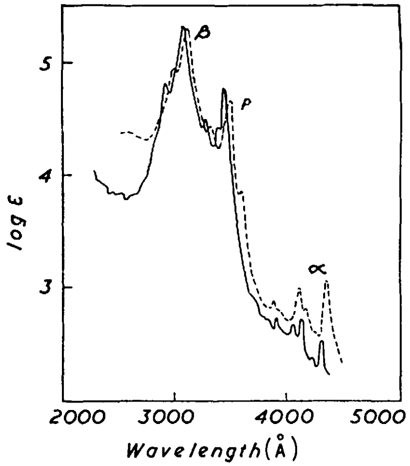


FIG. 2.

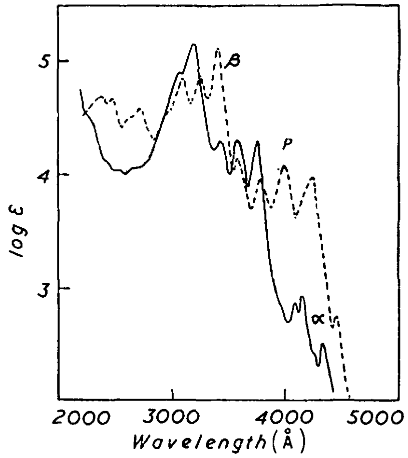


FIG. 1. (——) *γ-Coronenylbutyric acid* (II) *in* C_6H_6, α, 4300 (2·53), 4225 (2·40), 4120 (2·74), 4060 (2·69), 3900 (2·73); *p*, 3440 (4·78), 3390 (4·42), 3280 (4·48); β, 3080 (5·33); *in* EtOH, 2930 (4·80).
(– – –) *Maleic anhydride adduct* (VII), *dipotassium salt in* 50% EtOH, α, 4350 (3·06), 4160 (2·82), 4100 (2·99), 3880 (2·89), 3600 (3·86); *p*, 3480 (4·65), 3320 (4·41); β, 3100 (5·28), 2980 (4·92).

FIG. 2. (——) 1 : 2-*Benzocoronene* (III) *in* C_6H_6, α, 4320 (2·50), 4140 (2·91), 4080 (2·85); *p*, 3760 (4·30), 3580 (4·30), 3430 (4·29); β, 3200 (5·15), 3080 (4·90). (*From* 3000 Å *in* EtOH.)
(– – –) *Naphtho*(2′ : 3′-1 : 2)*coronene* (VI) *in* C_6H_6, α, 4440 (2·74); *p*, 4230 (3·99), 4000 (4·09), 3790 (3·98), 3580 (4·16); β, 3410 (5·12); 3260 (4·88), 3100 (4·86); *in* EtOH, 2720 (4·60), 2480 (4·68), 2390 (4·70).

Although the naphthocoronene contains a system of 5 linearly condensed rings it has not the deep colour and reactivity of a benzologue of pentacene. This is obviously connected with the fact that this naphthocoronene cannot assume a Kekulé structure in which the pentacene system is not quinonoid, so that none of the Kekulé structures characteristic of a pentacene is possible.

EXPERIMENTAL

M. p.s were taken in evacuated capillaries. Microanalyses are by Mr. J. M. L. Cameron and Miss M. W. Christie.

γ-Coronenyl-γ-oxobutyric Acid (I).—Coronene (3 g.) was ground with succinic anhydride

---

[2] I.G. Farbenind. A.-G., F.P. 857,395/1939; General Aniline and Film Corp., U.S.P. 2,210,041/1939; *Chem. Zentr.*, 1941, I, 1096.

[3] Boggiano and Clar, *J.*, 1957, 2681; Clar and Willicks, *Annalen*, 1956, **601**, 193.

(1·1 g.) and suspended in a solution of aluminium chloride (6 g.) in nitrobenzene (30 ml.). After 4 hours' stirring the mixture was decomposed with ice and dilute hydrochloric acid and then boiled. The greenish-yellow precipitate (3·25 g.) was filtered off and washed with benzene, methanol, and dilute hydrochloric acid. The *keto-acid* formed flat yellow needles, m. p. 244—252° (decomp.), from chlorobenzene or xylene, gave a blue solution with sulphuric acid which soon changed to violet, and in xylene had an absorption band at 4440 Å (Found: C, 83·3; H, 4·2. $C_{28}H_{16}O_3$ requires C, 84·0; H, 4·0%).

γ-Coronenylbutyric Acid (II).—The acid (I) (2·4 g.), sodium hydroxide (0·72 g.), 90% hydrazine hydrate (0·9 ml.), and diethylene glycol (30 ml.) were refluxed for 1 hr., then water and excess of hydrazine hydrate were distilled off until the temperature rose to 200°. The mixture was then refluxed again for 3 hr. After cooling and dilution with water and hydrochloric acid, the solid was filtered off and washed with dilute hydrochloric acid and water. *γ-Coronenylbutyric acid* formed flat pale yellow needles (1·35 g.), m. p. 277—287° (decomp.) (from xylene), which dissolved in concentrated sulphuric acid to give a yellow-brown solution (Found: C, 87·1; H, 4·9. $C_{28}H_{18}O_2$ requires C, 87·0; H, 4·7%).

1 : 2-*Benzocoronene* (III).—A mixture of the acid (II) (0·8 g.), sodium chloride (6 g.), and zinc chloride (30 g.) was ground and heated at 300° for 45 min. The melt was dissolved in dilute acetic acid, and the residue filtered off and washed with water and aqueous ammonia (yield 0·65 g.). Sublimation below 300°/0·1 mm. yielded a yellow fraction which was discarded and then at 300—320°/0·1 mm. a material which after repeated recrystallisation from xylene gave yellow needles of 1 : 2-*benzocoronene*, m. p. 292—294°, which dissolved in hot concentrated sulphuric acid with a greenish-yellow colour (Found: C, 95·8; H, 4·3. $C_{28}H_{14}$ requires C, 96·0; H, 4·0%). When the melt was held at 270° for 15 min. a different product was obtained which showed absorption bands in xylene at 4420 and 4160 Å and dissolved in cold concentrated sulphuric acid with a red colour.

o-*Carboxybenzoylcoronene* (IV).—Finely powdered coronene (3 g.) and phthalic anhydride (1·65 g.) were suspended in *o*-dichlorobenzene (50 ml.), and powdered aluminium chloride (6 g.) was added at 50° with stirring. The temperature was increased to 65—70° and kept there for 3 hr. After decomposition with ice and hydrochloric acid the yellowish-green solid product was filtered off and washed with benzene, methanol, and hot dilute hydrochloric acid. The crude *acid* (3·4 g.) was dissolved in hot 0·5% potassium hydroxide solution (600 ml.) and after filtration precipitated with dilute hydrochloric acid (yield, 3 g.). Crystallisation from xylene gave yellow needles (2·48 g.), m. p. 297—299° (decomp.), which gave a violet solution with concentrated sulphuric acid soon changing to green and in xylene had an absorption band at 4400 Å (Found: C, 85·6; H, 3·8. $C_{32}H_{16}O_3$ requires C, 85·7; H, 3·6%). Concentration of the *o*-dichlorobenzene mother-liquor yielded less pure acid (0·85 g.).

Naphtho(2′ : 3′-1 : 2)*coronene*-1′ : 4′-*quinone* (V).—The keto-acid (IV) (0·5 g.), benzoyl chloride (0·5 ml.), and 1-chloronaphthalene (2 ml.) were refluxed for 1 hr., the colour changing from green to dark red. The *quinone* (0·44 g.) which crystallised on cooling was filtered off and washed with benzene and ether. It sublimed at 380°/0·3 mm. in dark red needles and, recrystallised from nitrobenzene, had m. p. 347—349° and gave a green solution in concentrated sulphuric acid and a violet vat (Found: C, 89·4; H, 3·4. $C_{32}H_{14}O_2$ requires C, 89·3; H, 3·3%).

Naphtho(2′ : 3′-1 : 2)*coronene* (VI).—The quinone (1 g.) was boiled in pyridine (50 ml.) with zinc dust (10 g.), under an air-trap, and concentrated acetic acid (2 ml.) was added. 80% Acetic acid (8 ml.) was dropped into the mixture during 3 hr. The solution became first deep orange-red and then pale yellow. It was poured into dilute hydrochloric acid and heated until the zinc dissolved. The residue (0·91 g.) was filtered off and washed with water and dilute aqueous ammonia. Crystallisation from xylene yielded yellow needles of the *naphthocoronene* (0·7 g.), m. p. 352—354°, which did not dissolve in cold concentrated sulphuric acid but gave a yellow-green solution on warming (Found: C, 95·9; H, 4·0. $C_{32}H_{16}$ requires C, 96·0; H, 4·0%).

Maleic Anhydride Adduct (VII).—The naphthocoronene (0·1 g.) and maleic anhydride (2 g.) in xylene (20 ml.) were refluxed for 45 min. The *adduct* which crystallised from the hot solution was decanted and washed with hot xylene and then with benzene. The yellow prisms, m. p. 358—360° (decomp.), did not dissolve in cold concentrated sulphuric acid (Found: C, 86·3; H, 3·9. $C_{36}H_{18}O_3$ requires C, 86·7; H, 3·6%).

One of us (M. Z.) is indebted to Rütgerswerke A.-G., Frankfurt/Main, for a scholarship.

UNIVERSITY OF GLASGOW.

[*Received, November* 25*th*, 1957.]