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HIGHER ANNELLATED PYRENES—II*

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Abstract—1,2-Benzo-naphtho-[2′,3′:4,5]-pyrene (II), 1,2-benzo-naphtho-[2′,3′:6,7]-pyrene (III) and 1,2-benzo-dinaphtho-[2′,3′:4,5]; [2″,3″:8,9] pyrene (VI) were obtained by pyrolysis of the ketone (I). The hydrocarbon (II) was also prepared by a synthesis with phthalic anhydride. Pyrolysis of the ketone (VII) yields 3,4-benzo-naphtho-[2′,3′:9,10]-pyrene (VIII).

HIGHER annellated pyrenes are important for the investigation of the electronic fine structure of pyrene and for the classification of absorption bands in the pyrene series.

1,2-Benzopyrene reacted with *o*-toluyl chloride and aluminium chloride to form the ketone (I). Its pyrolysis gave mainly 1,2-benzo-naphtho-[2′,3′:4,5]-pyrene (II) but also small quantities of 1,2-benzo-naphtho-[2′,3′:6,7]-pyrene (III) and 1,2-benzo-dinaphtho-[2′,3′:4,5]; [2″,3″:8,9]-pyrene (VI). The first hydrocarbon (II) is identical with the benzonaphthopyrene prepared by Zander[1] by a different synthesis. The structure of the isomeric hydrocarbon (III) can be established by its close relationship to naphtho-[2′,3′:1,2]-pyrene as shown by a comparison of the absorption spectra of the two hydrocarbons in Fig. 2. The benzo-ring in the 1,2-position produces the same small violet shift as in the comparison of the spectra of naphtho-[2′,3′:3,4]-pyrene and 1,2-benzo-naphtho-[2′,3′:4,5]-pyrene (II) in Fig. 1.

This small violet shift can always be observed if a benzene ring is fused to a formally fixed double bond.[2] Fig. 3 also shows this in the comparison of dinaphthopyrene with benzodinaphthopyrene (VI). The latter hydrocarbon therefore, must have been produced by a migration of two *o*-toluyl-radicals to the 5,8-positions of 1,2-benzopyrene.

3,4-Benzopyrene, *o*-toluyl chloride and aluminium chloride gave the ketone (VII) which on pyrolysis cyclized to 3,4-benzo-naphtho-[2′,3′:9,10]-pyrene (VIII). The absorption spectrum of the crude pyrolysate showed also a trace of the isomeric 3,4-benzo-naphtho-[2′,3′:8,9]-pyrene.[3] However, this could not be found again in the chromatographic purified hydrocarbon. Benzonaphthopyrene (VIII) added maleic anhydride to form the adduct (IX), the absorption spectrum of which (Fig. 4) shows that it is a derivative of 3,4-benzopyrene.

A condensation of 1,2-benzopyrene with phthalic anhydride and aluminium chloride gave the ketone acid (IV) which was cyclized to the quinone (V). This has been already obtained by another route[1] and can be reduced to benzonaphthopyrene (II) with zinc dust, pyridine and acetic acid as decribed by Zander.[1]

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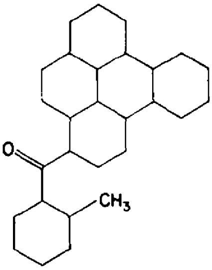
* Part I. B. Boggiano and E. Clar, *J. Chem. Soc.* 2681 (1957).

[1] M. Zander, *Chem. Ber.* **94**, 2894 (1961).

[2] E. Clar, *Tetrahedron* **9**, 202 (1960); E. Clar, A. McCallum and R. A. Robertson, *Tetrahedron.* **18**, 1471 (1962).

[3] J. F. Grove, *J. Chem. Soc.* 483 (1953).



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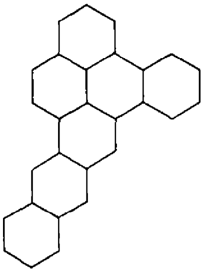

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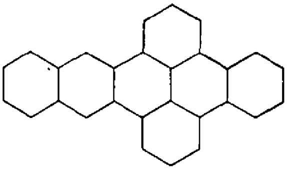

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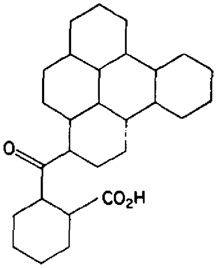

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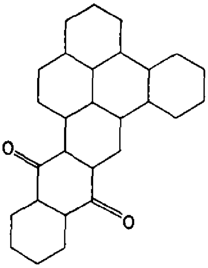

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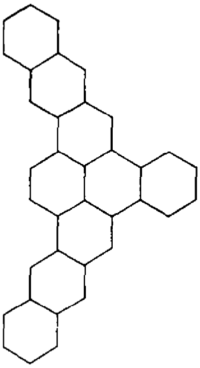

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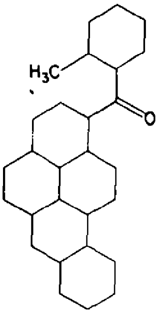

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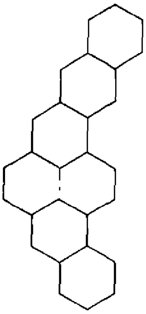
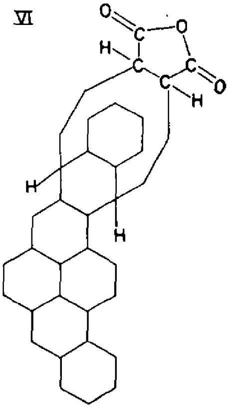
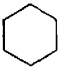


VIII



IX

The double bonds are omitted,  representing aromatic nucleus

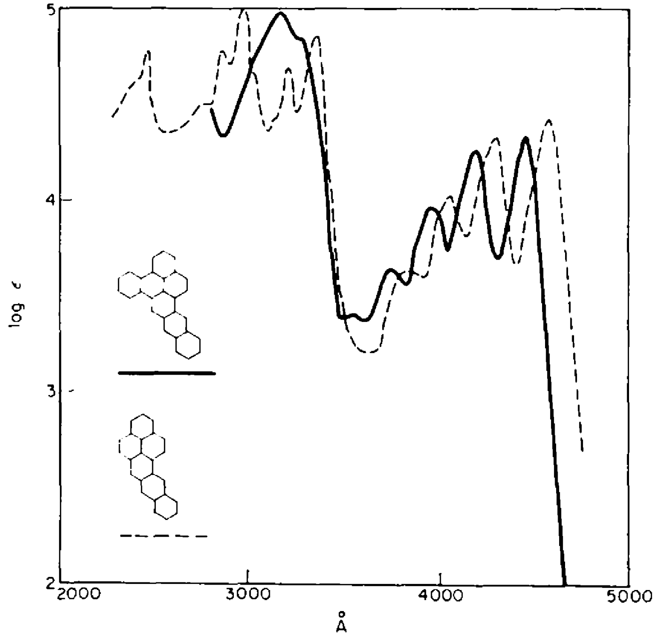


FIG. 1. Absorption max. (Å) and log ε (in parentheses). 1,2-Benzo-naphtho-[2′,3′:4,5]-pyrene (II) in C_6H_6, p: 4460 (4·34), 4200 (4·26), 3965 (3·96), 3750 (3·64); β: 3270 (4·85), 3170 (4·98). Naphtho-[2′,3′:3,4]-pyrene in C_6H_6, from 2800 Å in alcohol, p: 4580 (4·43), 4310 (4·33), 4060 (4·04), 3850 (3·64); β: 3350 (4·85), 3200 (4·70); β′: 2970 (5·00), 2860 (4·77); β″: 2465 (4·78).

EXPERIMENTAL*

5-(o-*Toluyl*)-1,2-*benzopyrene* (I). Aluminium chloride (10 g) was added to a solution of 1,2-benzopyrene (12·5 g) and *o*-toluyl chloride (7 g) in methylene chloride (100 ml). Immediately after the vigorous reaction the orange mixture was decomposed with ice and dil. hydrochloric acid, and the solvent distilled off. The crystallized crude ketone was washed with water and ammonia and recrystallized from xylene. The ketone forms pale yellow plates (10·5 g), m.p. 214–215°, which dissolved in conc. sulphuric acid to give a red solution. (Found: C, 90·8; H, 4·9. $C_{28}H_{18}O$ requires: C, 90·8; H, 4·9%).

In another preparation the methylene chloride was replaced by benzene. 1,2-Benzopyrene (50·5 g), *o*-toluyl chloride (32 g), benzene (200 ml) and aluminium chloride (35 g) gave 74 g crude, crystallized ketone. The identity of the ketones from both methods was proved by m.p. and I.R. spectrum.

Pyrolysis of the ketone (I). The above ketone (74 g) was dissolved in warm xylene washed with hot water and ammonia and the solution filtered. The xylene was distilled off and the ketone heated to 420–440° under CO_2 for 20 min. The solution of the pyrolysate in chlorobenzene was chromatographed on active alumina. 1,2-Benzopyrene was isolated from the first fraction. This was followed by 1,2-benzo-naphtho-[2′,3′:4,5]-pyrene (II; 12·8 g). Heating with maleic anhydride (100 g) at 70–80° for 2 hr gave the adduct which was isolated by the removal of the excess maleic anhydride with water, extraction with sodium hydroxide and acidification with hydrochloric acid. The adduct decomposed on sublimation at 290° and 0·1 Torr, to yield maleic anhydride and the hydrocarbon (II). The former was removed with acetone and the hydrocarbon recrystallized from xylene. It formed yellow needles, m.p. 258–259° (lit[1] 262–263°), which dissolved in conc. sulphuric acid to give a violet solution which changed to green on standing. The absorption spectrum, see Fig. 1.

1,2-*Benzo-naphtho-*[2′,3′:6,7]-*pyrene* (III) was obtained from the above chlorobenzene mother liquors. These were shaken 3 times with conc. sulphuric acid and then with water and ammonia.

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* All m.p. are uncorrected and were taken in evacuated capillaries.

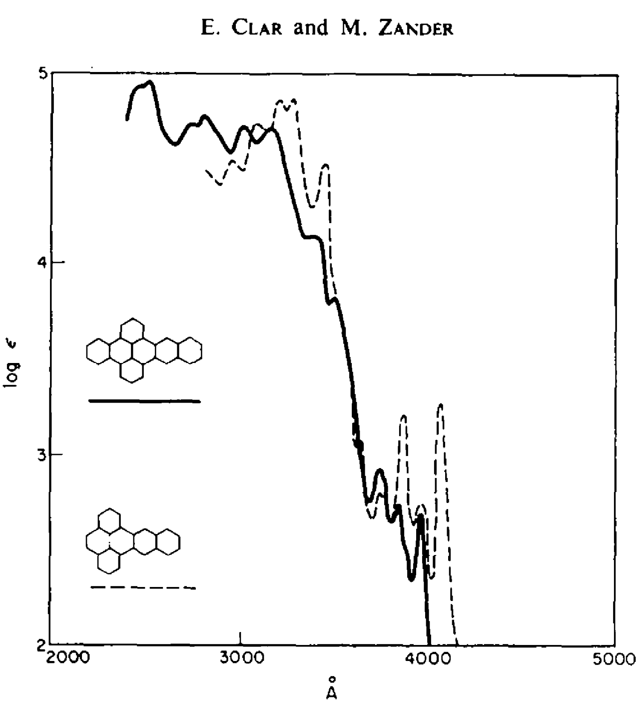

FIG. 2. Absorption max. (Å) and log ε (in parentheses). 1,2-Benzo-naphtho-[2′,3′:6,7]-pyrene (III) in dioxane, α: 3960 (2·70), 3845 (2·74), 3750 (2·92); p: 3500 (3·81), 3400 (4·14); β: 3160 (4·71), 3020 (4·72); β′: 2820 (4·77), 2740 (4·72); β″: 2520 (4·96), 2460 (4·93). Naphtho-[2′,3′:1,2]-pyrene in C_6H_6; α: 4075 (3·26), 3960 (2·74), 3860 (3·20), 3750 (2·80), 3670 (3·08); p: 3450 (4·52); β: 3280 (4·85), 3210 (4·85), 3090 (4·74), 2970 (4·53).

When the chlorobenzene solution was concentrated the spectrum of the crystallized hydrocarbon still showed the presence of 4·5 % of the isomeric hydrocarbon (II). A further purification of the hydrocarbon (0·57 g) by a treatment with maleic anhydride (0·6 g) in boiling xylene (70 ml) for 4 min followed by 3 recrystallizations from xylene gave pure benzonaphthopyrene (III). This crystallized in colourless long needles, m.p. 313°, which did not dissolve in conc. sulphuric acid. It showed I.R. bands (γ-CH) at, 881, 797, 756, 747 cm.$^{-1}$ (Found: C, 95·4; H, 4·8. $C_{28}H_{16}$ requires C, 95·4; H, 4·6 %).

In a second preparation the pyrolysate was sublimed at 260° and 0·2 Torr. This gave first the hydrocarbon II which was followed at 380° and 0·2 Torr by *1,2-benzo-dinaphtho-[2′,3′:4,5]; [2″,3″:8,9]-pyrene* (VI). It crystallized from 1-methylnaphthalene in brownish-yellow needles, m.p. 393–394°, which dissolved in conc. sulphuric acid to give a blue solution. (Found: C, 95·3; H, 4·5. $C_{36}H_{20}$ requires: C, 95·5; H, 4·5 %).

*5-(*o*-Carboxybenzoyl-1,2-benzopyrene* (IV). Aluminium chloride (4 g) was added to a mixture of 1,2-benzopyrene (3 g) and phthalic anhydride (1·8 g) in benzene (20 ml). A further quantity of aluminium chloride (0·5 g) was added after 7 min and the mixture kept at 40–60° for 30 min. The brown-red double compound was decomposed with dil. hydrochloric acid and the crystallized acid (3 g) separated by filtration and washed with water, methanol and ether. A further portion (0·4 g) was obtained by concentration of the mother liquor. Crystallization from chlorobenzene yielded yellow prisms, m.p. 265–266°, which dissolved in conc. sulphuric acid with a red colour. (Found: C, 83·5; H, 4·2. $C_{28}H_{16}O_3$ requires C, 84·0; H, 4·0 %).

1,2-Benzo-naphtho-[2′,3′:4,5]-pyrene-1′,4′-quinone (V). The acid (2 g) was boiled with benzoyl chloride (12 ml) and 1 drop sulphuric acid added. The mixture was first violet and changed to brown. The quinone (1·6 g) crystallized on cooling in red needles and was washed with nitrobenzene, benzene and ether. Sublimation at 360° and 0·2 Torr yielded red needles which after recrystallization from nitrobenzene and chlorobenzene had m.p. 295–296° (lit[1] 298–299°) and dissolved in conc. sulphuric

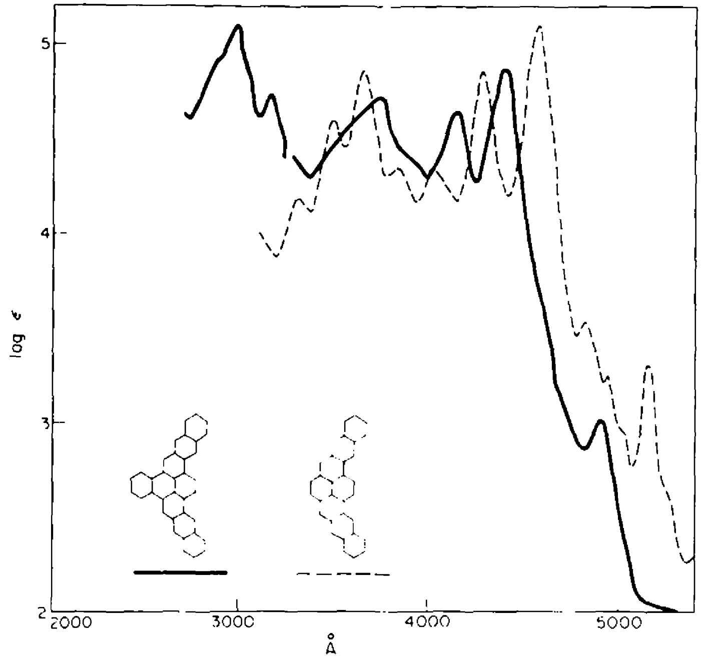

FIG. 3. Absorption max. (Å) and log ε (in parentheses). 1,2-Benzodinaphtho-[2′, 3′:4,5]; [2″,3″:8,9]-pyrene (VI) in $C_6H_3Cl_3$, from 3300 in C_6H_6, α: 4930 (3·01); p: 4430 (4·87), 4150 (4·65), 3900 (4·40); β: 3760 (4·71); β′: 3180 (4·74), 3010 (5·10). Dinaphtho-[2′,3′:3,4]; [2″,3″: 9,10] pyrene in $C_6H_3Cl_3$, α: 5150 (3·30), 4940 (3·25), 4820 (3·55); p: 4560 (5·10) 4270 (4·85), 4030 (4·34), 3820 (4·35); β: 3655 (4·86), 3490 (4·60), 3310 (4·18).

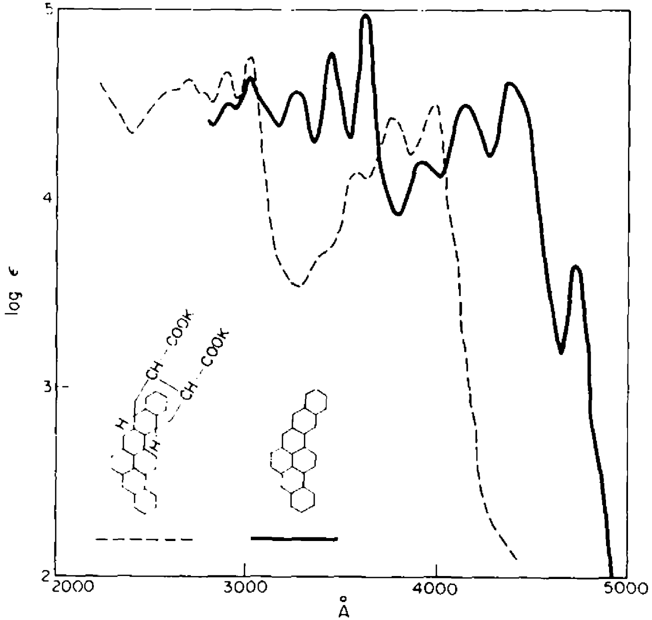

FIG. 4. Absorption max. (Å) and log ε (in parentheses). 3,4-Benzo-naphtho-[2′, 3′:9,10]-pyrene (VIII) in C_6H_6, α: 4720 (3·66); p: 4380 (4·62), 4150 (4·50), 3930 (4·20); β: 3620 (5·00), 3450 (4·78), 3280 (4·57); β′: 3030 (4·64), 2900 (4·50). Maleic anhydride Adduct (IX) in 50% alcohol p: 3970 (4·49), 3745 (4·43), 3570 (4·14), 3400 (3·72); β: 3000 (4·74), 2880 (4·66), 2770 (4·55); β′: 2690 (4·62), 2600 (4·56).

acid first olive-green turning to blue-green on standing. Alkaline sodium dithionite solution produced a red-brown vat. (Found: C, 88·1; H, 3·8. $C_{28}H_{14}O_2$ requires: C, 87·9; H, 3·7%).

Reduction of the above quinone with pyridine, zinc dust and acetic acid as described by Zander[1] gave the hydrocarbon (II) m.p. 259·5–260° (lit[1] m.p. 262–263°). Found: C, 95·3; H, 4·5. $C_{28}H_{16}$ requires: C, 95·4; H, 4·6%).

10-(o-*Toluyl*)-3,4-*benzopyrene* (VII). To a suspension of 3,4-benzopyrene (25 g) and *o*-toluyl chloride (16 g) in methylene chloride (100 ml) aluminium chloride (25 g) was added. The vigorous reaction ceased after 3 min. The mixture was decomposed with dil. hydrochloric acid and the methylene chloride distilled off. The ketone (35 g) was dissolved in hot xylene and washed with water and ammonia and filtered. Repeated crystallization from alcohol–benzene with the addition of active charcoal gave yellow needles, m.p. 163–164°, which dissolved in conc. sulphuric acid to form a blue solution which turned to violet on standing. (Found: C, 90·4; H, 4·9. $C_{28}H_{18}O$ requires: C, 90·8; H, 4·9%).

3,4-*Benzo-naphtho*-[2′,3′:9,10]-*pyrene* (VIII). The washed xylene solution of the crude ketone was concentrated and pyrolysed at 420–430° under CO_2 for 30 min. The pyrolysate (23 g) was extracted with boiling xylene and twice chromatographed on alumina. The hydrocarbon (VIII; 140 mg) had m.p. 292–292·5° and dissolved in conc. sulphuric acid to form a green solution which changed to blue on standing. The absorption spectrum (see Fig. 4). (Found: C, 95·4; H, 4·7. $C_{28}H_{16}$ requires: C, 95·4; H, 4·6%).

Maleic anhydride adduct (IX). The hydrocarbon was boiled for a few min with excess maleic anhydride and hot xylene added. The precipitate crystallized from acetic anhydride in colourless prisms which had m.p. 307° dec. (Found: C, 85·2: H, 4·1. $C_{32}H_{18}O_3$ requires: C, 85·3; H, 4·0%).