Acknowledgments. The author wishes to thank the Humble Oil and Refining Co. for permission to publish this work. The helpful counsel and advice of Professor Philip S. Bailey is especially appreciated. Thanks are due Mr. Harold Kail for assistance in conducting the experimental work and Dr. B. H. Johnson and Miss Marjorie Walker for certain analyses.

BAYTOWN, TEX.

[CONTRIBUTION FROM MELLON INSTITUTE]

Ultraviolet Spectra of Benzo[c]phenanthrenes

A. WILLIAM JOHNSON

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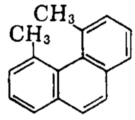
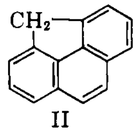
1,8,9-Naphthanthracene (VI) has been prepared by reduction of the ketone (VII). A second hydrocarbon, 2,3-trimethylenepyrene (VIII), was also isolated. Comparison of the ultraviolet spectra of VI with those of other benzo[c]phenanthrenes provided evidence for intramolecular overcrowding between the C_1 and C_{12} hydrogens in benzo[c]phenanthrene.

Jones[1] has attempted to correlate the differences in fine structure observed in the ultraviolet spectra of many polynuclear aromatic hydrocarbons. The "Fine Structure (Fs) Effect," which was an outgrowth of these correlations, referred to an increase of fine structure produced by the fusion of alicyclic rings to an aromatic nucleus.[2] However, Jones and, more recently, Friedel[3] both pointed out a large number of exceptions to the general rule. The latter indicated that the Fs effect, as originally outlined by Jones, was not generally applicable to polynuclear hydrocarbons and in its place offered a tripartite correlation of the spectra of aromatic hydrocarbons containing fused alicyclic rings.

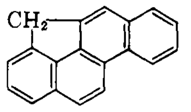
The ultraviolet spectrum of 4,5-dimethylphenanthrene (I) shows a marked decrease in fine structure (band splitting) when compared with the spectrum of 4,5-methylenephenanthrene (II)[2a] (Fig. 1). However, the parent hydrocarbon, phenanthrene, exhibits a spectrum very similar in detail to that of II. Analogous relationships are found in the chrysene[4] and 1,2-benzanthracene[5] series. 4,5-Methylenechrysene (III) and chrysene exhibit more fine structure in their spectra than does 4,5-dimethylchrysene. Similarly, both 1′,9-methylene-1,2-benzanthracene (IV) and 1,2-benzanthracene show more band splitting than 1′,9-dimethyl-



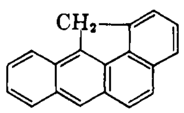
I



II



III



IV

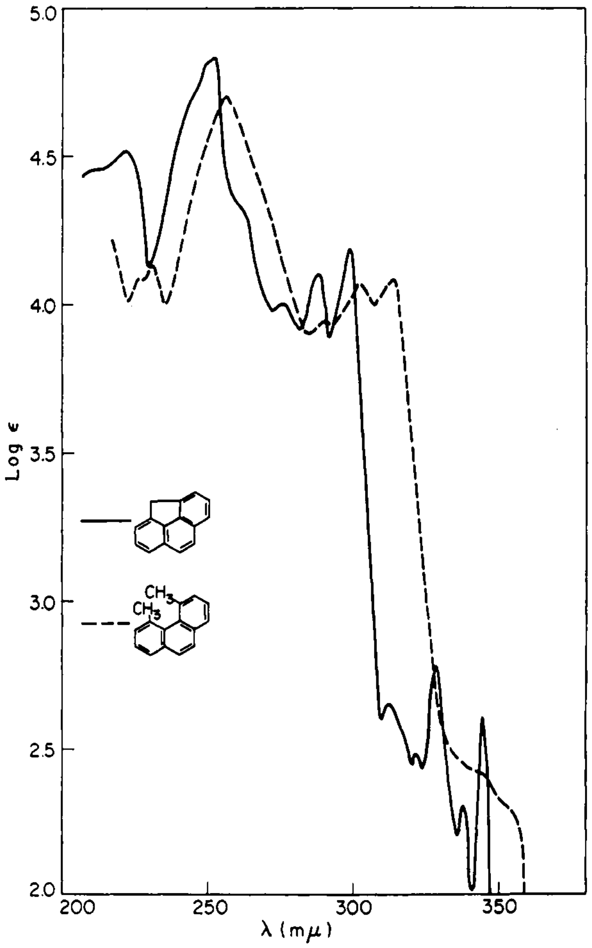


Fig. 1. 4,5-Dimethylphenanthrene (Ref. 2 (b), Spectrum No. 352) (I). 4,5-Methylenephenanthrene (Ref. 2 (b), Spectrum No. 363) (II)

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(1) R. N. Jones, *J. Am. Chem. Soc.*, **67**, 2127 (1945).

(2) (a) R. N. Jones, *Chem. Revs.*, **32**, 1 (1945). (b) For a brief review of the Fs effect see R. A. Friedel and M. Orchin, *Ultraviolet Spectra of Aromatic Hydrocarbons*, John Wiley and Sons, Inc., New York, 1951, p. 23.

(3) R. A. Friedel, *Applied Spectroscopy*, **11**, 13 (1957).

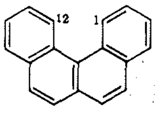
(4) R. N. Jones, *J. Am. Chem. Soc.*, **63**, 313 (1941).

(5) R. N. Jones, *J. Am. Chem. Soc.*, **62**, 148 (1940).

1,2-benzanthracene. These observations have been designated as Fs effects by Jones[2] and Ring-strain effects by Friedel.[3]

It is known that molecules of the 4,5-dimethylphenanthrene type possess streric interferences between the C_4 and C_5 substituents. This was demonstrated by the resolution of 4,5,8-trimethylphenanthryl-1-acetic acid into its optical enantiomorphs.[6] It seems likely that this "intramolecular overcrowding"[7] is responsible for the decrease in fine structure shown by their spectra.[3] In accord with this postulate, the spectrum of 4-methylphenanthrene, which should be intermediate in degree of intramolecular overcrowding between phenanthrene and the 4,5-dimethyl derivative, exhibits fine structure detail intermediate between the latter two compounds. An analogous relationship has been shown to exist in the chrysene series.[2b,3] In all cases, the spectrum of the unsubstituted hydrocarbon, which possesses no steric interferences between the 4 and 5 substituents, exhibits the same amount of fine structure as that of the methylene-bridged compounds.

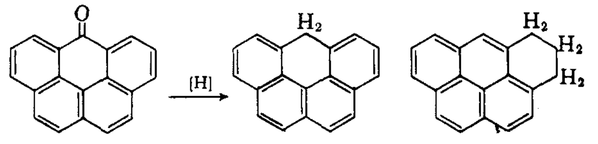
Discussion. It was of interest to ascertain if the above effect, regardless of its name or origin, existed in the benzo[*c*]phenanthrene (V) ring system.



V

It has been noted that the degree of fine structure present in the spectra of derivatives of V increased in the order 1,12-dimethyl< 1-methyl< unsubstituted V.[8] Newman and co-workers have demonstrated that 1-methylbenzo[*c*]phenanthryl-4-acetic acid[9a] and 1,12-dimethylbenzo(c)phenanthryl-5-acetic acid[9b] are nonplanar by resolving them into their optical enantiomorphs. This nonplanarity was attributed to intramolecular overcrowding between the 1 and 12 substituents.

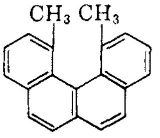
By analogy with the phenanthrene and related systems, it could be predicted that a methylene-bridged hydrocarbon, 1,8,9-naphthanthracene (1,12-methylenebenzo[*c*]phenanthrene) (VI), should afford the spectrum of a 1,12-disubstituted benzo[*c*]phenanthrene devoid of any steric interferences characteristically associated with the 1,12- positions. Its spectrum was expected to exhibit considerable fine structure.



VII VI VIII

Vollmann and co-workers[10] originally prepared VI *via* zinc dust distillation of 1,8,9-naphthanthrone-10 (VII) or of 3-carboxy-1,8,9-naphthanthrone-2. In our hands zinc–sodium hydroxide reduction of the ketone (VII) afforded the hydrocarbon (VI) in 20% yield, but Clemmensen reduction afforded a mixture of VI and a second hydrocarbon. The latter, through a comparison of ultraviolet spectra, has been tentatively identified as 2,3-trimethylenepyrene (VIII), previously prepared by Scholl and Meyer.[11] Recently, Clar and Stewart[12a] performed a reduction of VII and reported isolating only VIII, no mention being made of VI.[12b] The formation of VIII in these reductions finds analogy in the report that reduction of benzanthrone with phosphorus and hydriodic acid afforded only 1,10-trimethylenephenanthrene.[13]

As expected, the spectrum of VI was similar in over-all shape to that of 1,12-dimethylbenzo[*c*]phenanthrene (IX) but the former possessed a much larger number of well defined absorption maxima (Fig. 2). A comparison with the spectrum of benzo[*c*]phenanthrene (V) indicated that VI exhibits even more fine structure than the former (Figs. 2 and 3). In fact, the spectrum of V resembles that of IX more closely than that of VI. This relationship is in contrast with the phenanthrene-like systems in which there is essentially no difference between the spectra of the unsubstituted and the bridged hydrocarbons. This suggested that even in benzo[*c*]phenanthrene (V) itself there exists significant intramolecular overcrowding between the C_1 and C_{12} hydrogen atoms. This conclusion has been supported by the recently completed x-ray analysis of benzo[*c*]phenanthrene in which the molecule was found to be considerably distorted in order to prevent carbons 1 and 12 from approaching closer than 3.0 Å, the minimal approach distance of sp^2 hybridized carbon atoms



IX

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(6) M. S. Newman and A. B. Hussey, *J. Am. Chem. Soc.*, **69**, 3023 (1947).

(7) M. S. Newman, *J. Am. Chem. Soc.*, **62**, 2295 (1940).

(8) M. S. Newman and M. Wolf, *J. Am. Chem. Soc.*, **74**, 3225 (1952).

(9) (a) M. S. Newman and W. B. Wheatley, *J. Am. Chem. Soc*, **70**, 1913 (1948). (b) M. S. Newman and R. M. Wise, *J. Am. Chem. Soc.*, **78**, 450 (1956)

(10) H. Vollman *et al.*, *Ann.*, **531**, 1 (1937).

(11) R. Scholl and K. Meyer, *Ber.*, **69**, 156 (1936).

(12) (a) E. Clar and D. G. Stewart, *J. Am. Chem. Soc.*, **75**, 2667 (1953). (b) In spite of this report, Clar and Stewart (ref. 16) had described the spectrum of VI earlier. However, their method of preparation of VI was not revealed and remains a mystery.

(13) E. Clar and Fr. Furnari, *Ber.*, **65**, 1420 (1932).

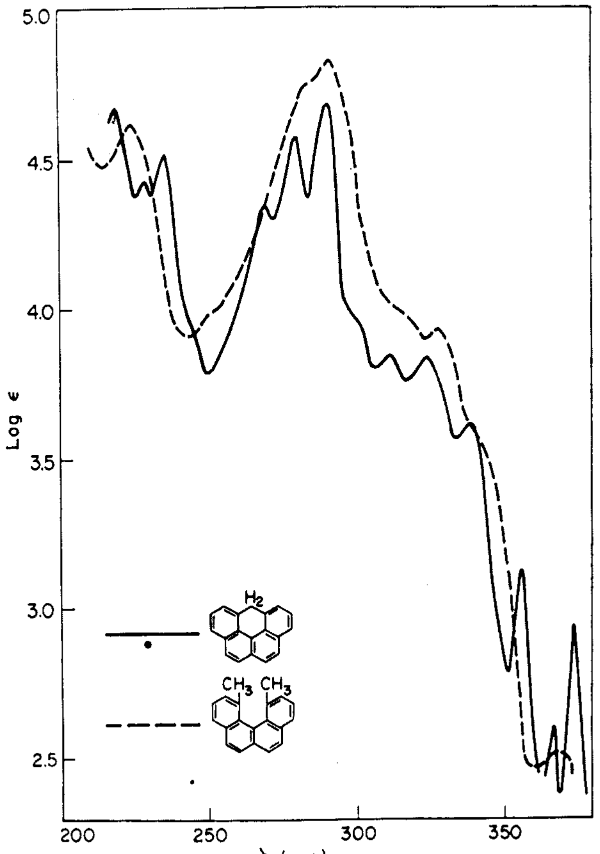
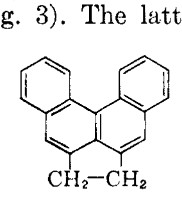


Fig. 2. 1,12-Dimethylbenzo[c]phenanthrene (IX). 1,8,9-Naphthanthracene (VI)

carrying hydrogen.[14] This is the first time in a series of this type that the unsubstituted hydrocarbon has been found to spectrally and, therefore, structurally resemble an overcrowded derivative more closely than a planar, bridged derivative. It is thus apparent that reliable evidence regarding steric interactions in polynuclear systems may be obtained by an examination of the UV spectra of a properly constituted series of derivatives.

Further evidence for steric interferences between the 1 and 12 hydrogens in benzo[c]phenanthrene was obtained by a comparison of its spectrum with that of the elusive and only recently synthesized hydrocarbon, 6,7-dimethylenebenzo[c]phenanthrene (X)[15] (Fig. 3). The latter exhibited more fine structure detail than V in the long wave-length region. This is probably due to the severe limitations imposed on the freedom of the aromatic nucleus by the restraining dimethylene bridge. The spectrum of 6,7-trimethylenebenzo[c]phenanthrene[16] also exhibited fine structure detail similar to that shown by X. Since introduction of a carbon bridge increased the fine structure, the original molecule must have been somewhat flexible due to intramolecular overcrowding.[17]



X

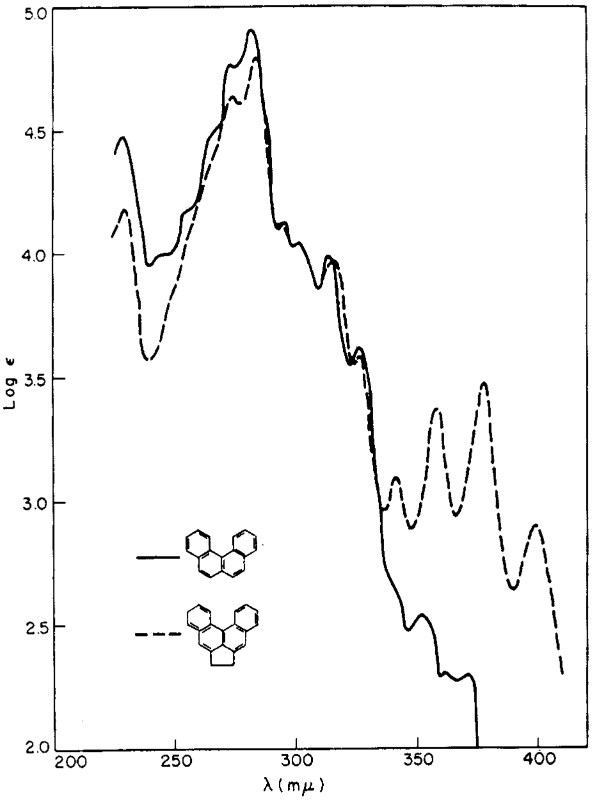


Fig. 3. Benzo[c]phenanthrene (V). 6,7-Dimethylenebenzo-[c]phenanthrene (X)

Friedel[3] observed that the greatest spectral effect of a fused alicyclic ring was the enhancement of the intensity of the longest wave-length bands. This effect has indeed been observed in the spectra of both VI and X.

EXPERIMENTAL[18]

Reduction of 1,8,9-naphthanthrone. A. Clemmensen reduction. A solution of 2.5 g. (0.01 mole) of ketone (VII) in 15 ml. of toluene was heated under reflux for 26 hr. with 4.3 g. of zinc amalgam and 10 ml. of concentrated hydrochloric acid. The solution was cooled, the organic layer separated, and the aqueous portion extracted exhaustively with benzene. The combined organic layers were dried and the solvent removed

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[14] G. M. J. Schmidt and F. H. Herbstein, *J. Chem. Soc.*, 3302 (1954).

[15] D. D. Phillips and D. N. Chatterjee, *J. Am. Chem. Soc.*, **80**, 4364 (1958).

[16] E. Clar and D. G. Stewart, *J. Am. Chem. Soc.*, **74**, 6235 (1952).

[17] L. L. Ingraham in "Steric Effects in Organic Chemistry," ed. by M. S. Newman, John Wiley and Sons, Inc., New York, 1956, p. 479.

[18] Ultraviolet spectra were recorded in 95% ethanol solution using Beckmann DK and Cary model 11 spectrophotometers. Analyses are by Schwarzkopf Microanalytical Laboratory, Woodside 77, N. Y. Melting points are uncorrected.

leaving 2.3 g. of a brown solid mass, m.p. 140°. A solution of 0.5 g. of the latter was taken up in 10 ml. of benzene and passed through a column containing 15 g. of neutral alumina (Merck) to afford 0.05 g. of crude hydrocarbon (benzene eluent) and 0.30 g. of unchanged ketone (VII) (chloroform eluent). The former was recrystallized from 95% ethanol as pale yellow needles, m.p. 118–120°, unchanged upon further recrystallization.

This hydrocarbon (50 mg.) was dissolved in 2 ml. of benzene-hexane (50:50) and passed through a column containing 5 g. of acidic alumina (Merck). The first fraction (10 mg.) was recrystallized from 95% ethanol to afford VIII as colorless fine needles, m.p. 108–109°, λ_{EtOH}^{max} (log ϵ) 235 mμ (4.7), 244 (4.9), 256 (4.1), 266 (4.5), 277 (4.7), 313 (4.1), 327 (4.5), 343 (4.6), 357 (3.5), 369 (2.8), and 377 (3.4). (Lit., m.p. 107–108°,[11] 112–113°[12]; the spectra were superimposable in all respects.[12])

The second fraction (20 mg.) was recrystallized from 95% ethanol to afford VI as pale yellow plates, m.p. 123–124°, λ_{EtOH}^{max} (log ϵ) 218 mμ (4.6), 228 (4.4), 235 (4.5), 269 (4.4), 279 (4.6), 290 (4.7), 311 (3.9), 325 (3.9), 340 (3.8), 356 (3.3), 367 (2.9), 374 (3.2). (Lit.,[10] m.p. 134°.)

Anal. Calcd. for $C_{19}H_{12}$: C, 94.97; H, 5.03. Found: C, 94.80; H, 5.09.

B. Zinc-sodium hydroxide reduction. A mixture of 1.0 g. of ketone (VII) and 8 g. of zinc dust in 60 ml. of 10% sodium hydroxide solution was covered with 10 ml. of 1-hexanol and heated under reflux for 6 hr. The solution was evaporated and acidified with 6*N* hydrochloric acid. The resulting black precipitate was filtered, dried, and pyrolyzed for 15 min. at 280° and 0.5 mm. pressure. The yellow sublimate (0.30 g.) was chromatographed on 10 g. of acidic alumina to afford 0.13 g. of hydrocarbon (VI) and 0.08 g. of unchanged ketone (VII). The former was recrystallized from 95% ethanol as pale yellow plates, m.p. 123–124°, undepressed on admixture with that prepared *via* method A.

Acknowledgment. The author acknowledges the technical assistance of W. B. White in recording some of the spectra. He wishes to thank Prof. Newman and Dr. Vollmann for their gifts of IX and VII, respectively. He also wishes to thank Drs. Phillips and Chatterjee for information concerning X prior to its publication.

PITTSBURGH 13, PA.

[CONTRIBUTION FROM THE RESEARCH DEPARTMENT OF THE KOPPERS COMPANY, INC.]

Carboxylation of Propargyl Halides

ROBERT W. ROSENTHAL AND LOUIS H. SCHWARTZMAN

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The reactions of propargyl halides with nickel carbonyl have been studied. Carboxylation of propargyl bromide at 70° and atmospheric pressure yielded ethyl 3-bromo-3-butenoate (I). Partial reduction of I with $LiAlH_4$ yielded 3-bromo-3-buten-1-ol which upon ozonolysis yielded formaldehyde. A mechanism is given which postulates the formation of an allenic ester, ethyl 2,3-butadienoate (II), intermediate. In the case of propargyl chloride both II and ethyl 3-chloro-3-butenoate (III) were isolated. Lower yields of product were obtained when the reaction was run under carbon monoxide pressure. This result is consistent with the hypothesis of Wender that the first step of the reaction is the formation of an acetylenic-carbonyl complex and carbon monoxide.

In the course of investigations being carried out in our laboratories, propargyl halides were carboxylated with nickel carbonyl. The recent disclosure by Jones, Whitham, Whiting[1] of similar work made it desirable for us to release our findings.

According to Raphael[2] propargylic bromides in ethanol react with nickel carbonyl and water to yield bromine-free allenic acids. In our laboratories when propargyl bromide in ethanol was caused to react with nickel carbonyl at 70° and atmospheric pressure, an evolution of heat took place and instead of a halogen-free allenic acids being formed, ethyl 3-bromo-3-butenoate, $CH_2{=}CBrCH_2CO_2C_2H_5$ (I), was obtained in 21% yield. The characterization of I presented some interesting problems. Due to the presence of the bromine atom, infrared analysis could not distinguish whether the ester contained a terminal methylene group or a double bond conjugated with the carbonyl group. Semimicro hydrogenation revealed that two moles of hydrogen was absorbed per mole of compound. Although the compound did not give a positive halide test when tested directly with alcoholic silver nitrate, it was found to contain approximately 39% bromine when the solution formed by either hydrogenating the sample or heating it one hour with caustic, was analyzed for halide ion. Saponification equivalents of several samples averaged 190. Vapor phase chromatographic analysis indicated the presence of a single compound of 90+% purity. All these data were consistent with the ethyl ester of a monobromobutenoic acid, which would have a molecular weight of 193 and would, under the conditions used, absorb two moles of hydrogen (hydrogenation of the double bond and hydrogenolysis of the bromine atom). The problem of which isomer was present, however, was as yet undecided. Therefore, the hydrogenated solution was saponified and yielded the potassium salt of an acid which was converted to *n*-butyro-*p*-toluide, and the *p*-bromo- and *p*-phenylphenacyl esters of *n*-butyric acid. Thus the carbon skeleton was that of *n*-butane. The location of the halogen atom was assigned to the third carbon atom by the fact that

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(1) E. R. H. Jones, G. H. Whitham, and M. C. Whiting, *J. Chem. Soc.*, 4628 (1957).

(2) R. A. Raphael, *Acetylene Compounds in Organic Synthesis*, Academic Press, N. Y., 1955, p. 138.