methylphenanthrol reported by Fieser and Young[2] and did not lower the melting point of this compound in the mixed melting point test. Since these authors conclude their 1-methylphenanthrol to be the 9-derivative, it is assumed that 1-methylphenanthrene on direct nitration produces the 1-methyl-9-nitrophenanthrene.

It is of interest to note that phenanthrene when nitrated under similar conditions yields the 9-derivative.[3] All these facts represent a further support to the suggestion recently made by Campbell and Todd[4] in their work on the constitution of acetylretene of Bogert and Hasselstrom[5] that the phenanthrene nucleus apparently has some inherent orienting influence which overcomes any directing influence of alkyl groups.

Acknowledgment.—Thanks are due to Dr. Louis F. Fieser, Department of Chemistry, Harvard University, Cambridge, Massachusetts, for an authentic sample of 1-methyl-9-phenanthrol.

Experimental

1-Methyl-9-nitrophenanthrene[6].—Fifteen grams of 1-methylphenanthrene[7] was dissolved in 200 cc. of glacial acetic acid. The solution was chilled to 18°, whereby some hydrocarbon separated and with good stirring 30 cc. of nitric acid, of sp. gr. 1.42, was added in the course of twenty minutes. After the first drops were added the mixture was cooled to 5° and kept at 5 to 10° until a clear yellow-colored solution was obtained, which usually required thirty to forty-five minutes. The clear solution was then poured into one liter of water and the sticky brownish resin removed by decanting. This was washed with sodium bicarbonate solution, then with water and stirred with a small quantity of acetone until a thick paste of crystalline material was obtained. Filtration removed some brownish tarry material; yield of solid nitro product 6 g. It was recrystallized from acetone; m. p. 146.5–146.8° (cor.), yellowish needles.

Anal.[8] Calcd. for $C_{15}H_{11}NO_2$: N, 5.90. Found: N, 5.72.

1-Methyl-9-aminophenanthrene.—One and one-half grams of 1-methyl-9-nitrophenanthrene was suspended in 50 cc. of methanol and 20 cc. of water to which was added 2 g. of commercial sodium hyposulfite. The solution was refluxed for one-half hour until all color of the nitro derivative had disappeared and when the amino product started to separate, the solution was poured into 500 cc. of water containing ammonia. The fluffy white precipitate was filtered off, yield about quantitative; m. p. 138–138.5° (cor.), pale yellow needles from methanol.

Anal. Calcd. for $C_{15}H_{13}N$: N, 6.76. Found: N, 7.05.

1-Methyl-9-diacetaminophenanthrene.—Acetylation with a boiling mixture of acetic anhydride and fused sodium acetate gave the diacetate, m. p. 193.7–194.3° (cor.) as prismatic white needles from methanol.

Anal. Calcd. for $C_{19}H_{17}NO_2$: C, 78.33; H, 5.88. Found: C, 78.82; H, 5.90.

1-Methyl-9-hydroxyphenanthrene.—A suspension of 2.5 g. of crude 1-methyl-9-aminophenanthrene in 750 cc. of water containing 10 cc. of concentrated hydrochloric acid was cooled to 0–5°. A concentrated aqueous solution of 1 g. of sodium nitrite was added in two portions and the mixture, which turned bright yellow, was allowed to stand for one and one-half hours, when still some yellowish material remained undissolved. After addition of 2.5 g. of urea the mixture was slowly brought to boiling whereby a reddish resin precipitated; yield, 1.7 g. This was suspended in a dilute potassium hydroxide solution and the mixture refluxed for half an hour. The solution was filtered yielding a colorless filtrate and 0.2 g. of a crimson insoluble dye which, recrystallized once from benzene, melted at 283° (cor.), decomp. After cooling, the alkaline filtrate was acidified with dilute hydrochloric acid and the flocculent precipitate of the phenol recrystallized from benzene; yield 1.2 g. of white fluffy crystals, m. p. 199.5–200.5° (cor.). The 1-methyl-9-phenanthrol turned brownish on storage.

Anal. Calcd. for $C_{15}H_{12}O$: C, 86.51; H, 5.81. Found: C, 86.72; H, 6.03.

1-Methyl-9-acetoxyphenanthrene.—Acetylation with acetic anhydride and fused sodium acetate gave the acetoxy derivative, m. p. 99.5–100.3° (cor.), white needles from alcohol.

Anal. Calcd. for $C_{17}H_{14}O_2$: C, 81.58; H, 5.64. Found: C, 81.65; H, 5.92.

In the mixed melting point test with an authentic sample of 1-methyl-9-acetoxyphenanthrene which had darkened somewhat in ten years of standing and melted at 98–99° (cor.) no depression was observed inasmuch as the mixture melted at 98.5–99.5° (cor.).

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RECEIVED JUNE 11, 1941

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(2) Fieser and Young, THIS JOURNAL, **53**, 4120 (1931).

(3) Schmidt and Strobel, *Ber.*, **36**, 2511 (1903).

(4) Campbell and Todd, THIS JOURNAL, **62**, 1288 (1940).

(5) Bogert and Hasselstrom, *ibid.*, **53**, 3462 (1931).

(6) When crude retene, m. p. 96–97° (cor.), is subjected to nitration carried out in a similar manner, about 1% of a crystalline nitro product is obtained melting in a crude state at 259–260° (cor.). Investigation of this product will be the subject matter for a separate publication.

(7) Prepared from retene in accordance with procedure described by Hasselstrom, THIS JOURNAL, **63**, 1164 (1941).

(8) All analyses by Mr. S. Gottlieb, Columbia University, New York City, New York.

The Absorption Spectra of Thiocyano Derivatives of 1,2-Benzanthracene

BY R. NORMAN JONES

The investigation of the influence of substituents on the ultraviolet absorption spectrum of 1,2-benzanthracene[1,2] has been extended to thiocyano derivatives, several of which have been prepared recently in this Laboratory by Wood and Fieser.[3]

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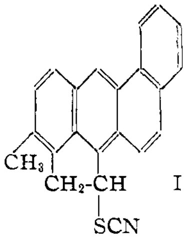
(1) Jones, THIS JOURNAL, **62**, 148 (1940).

(2) Jones, *ibid.*, **63**, 151 (1941).

(3) Wood and Fieser, *ibid.*, **63**, 2323 (1941).

The compounds examined included 9-thiocyano-1,2-benzanthracene, 10-thiocyano-1,2-benzanthracene, 9-thiocyano-10-methyl-1,2-benzanthracene, 10-thiocyanomethyl-1,2-benzanthracene, and a thiocyano derivative of 20-methylcholanthrene which, from chemical evidence,[3] very probably has the structure I rather than the alternate possible structure II.



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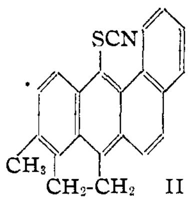

II

TABLE I

WAVE LENGTHS (Å.) OF THE MAXIMA AND CORRESPONDING INTENSITIES (LOG E_{molar}) OF THE SPECTRA OF SOME THIOCYANO DERIVATIVES OF 1,2-BENZANTHRACENE (SOLVENT DIOXANE)

	Max.	Intensity
9-Thiocyano-1,2-benzanthracene	2620	4.45
	2785	4.60
	2895	4.81
	3020	4.89
	3410	3.74
	3600	4.03
	3795	4.23
	(3975)[a]	4.12
	4050	4.25
10-Thiocyano-1,2-benzanthracene	2480	4.44
	2745	4.55
	2840	4.82
	2965	4.93
	(3290)	3.54
	3460	3.79
	3625	3.90
	3730	3.83
	3795	3.75
	3940	3.61
9-Thiocyano-10-methyl-1,2-benzanthracene	2750	4.70
	2850	4.61
	2970	4.68
	3110	4.69
	(3740)	3.96
	3920	4.13
	4155	4.15
10-Thiocyanomethyl-1,2-benzanthracene	2580	4.48
	2745	4.60
	2840	4.86
	2950	4.93
	3440	3.86
	3590	3.98
	3750	3.87
	3790	3.82
	3925	3.46
15-Thiocyano-20-methylcholanthrene	2625	4.49
	2750	4.54
	2865	4.77
	2980	4.87
	3255	3.72
	3410	3.79
	3585	3.93
	3775	3.82
	3925	3.10

[a] Wave lengths in parentheses refer to points of inflection.

The wave lengths and intensities of the maxima in the spectra of these compounds are summarized in Table I and the curves are given in Figs. 1–3. The experimental technique employed has been described previously[1]; the dioxane used as solvent was purified by the method of Hess and Frahm.[4]

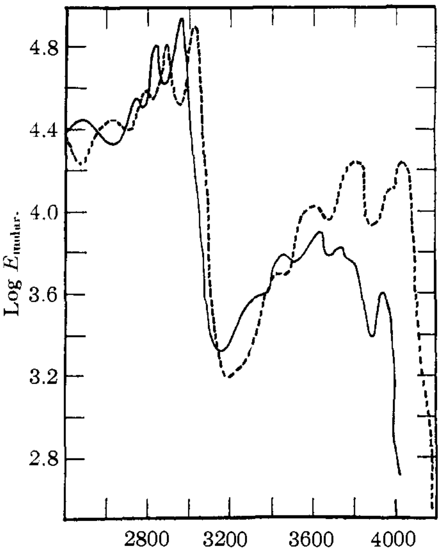

Fig. 1.——, 10-Thiocyano-1,2-benzanthracene; ---, 9-thiocyano-1,2-benzanthracene.

Examination of the curves showed that the spectra may be divided into two groups. The derivatives in which the thiocyano substituent is not attached at the 9 position possess spectra which are very similar to those of the unsubstituted hydrocarbon. In the spectrum of 9-thiocyano-1,2-benzanthracene, however, the intensities of the maxima at wave lengths greater than 3200 Å. are very considerably increased; in the spectrum of 9-thiocyano-10-methyl-1,2-benzanthracene a change in the relative intensities of the short wave length maxima is also noted in addition to this effect. The similarity of the spectra of 10-thiocyano-1,2-benzanthracene, 10-thiocyanomethyl-

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(4) Hess and Frahm, *Ber.*, **71**, 2627 (1938).

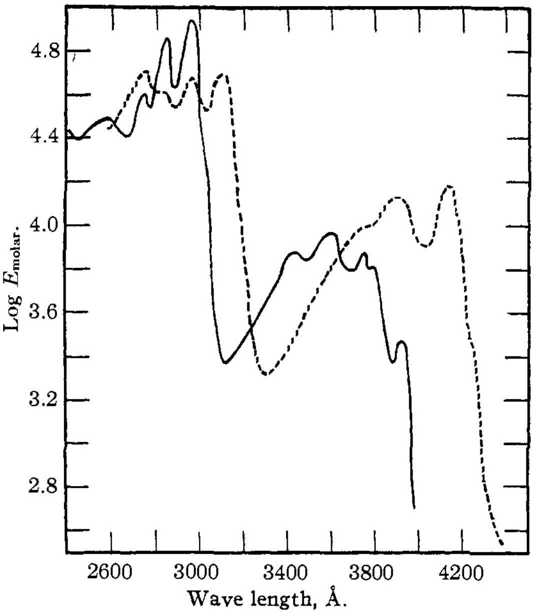

Fig. 2.— ——, 10-Thiocyanomethyl-1,2-benzanthracene; ----, 9-thiocyano-10-methyl-1,2-benzanthracene.

1,2-benzanthracene and 1,2-benzanthracene indicates that in spite of the considerable chemical reactivity and unsaturation of the thiocyano group, its introduction does not significantly alter the excitation levels of the electrons of the aromatic ring system, and in this respect may be compared with the isocyanate group, the introduction of which likewise has little influence on the spectrum of 1,2-benzanthracene.[2] The spectra of ethyl thiocyanate and *n*-butyl thiocyanate[5] show only a low intensity maximum near 2500 Å. (log E = 1.6–1.7) and the additive effect of the thiocyano chromophore is negligible in comparison with that of the aromatic system.

The abnormal behavior of the 9-thiocyano derivatives may be attributed, most probably, to steric effects, the relatively large thiocyano group being under considerable restraint due to interference with the hydrogen atom at the 1′ position. This effect is not observed in 9-methyl-1,2-benzanthracene, probably on account of the smaller size of the methyl group, the spectrum of 4,5-dimethylchrysene, however, in which comparable steric conditions occur, differs from that of chrysene in a very similar manner.[6]

The spectrum of the thiocyano derivative of 20-methylcholanthrene closely resembles that of 1,2-benzanthracene and shows none of the abnormalities associated with a thiocyano substituent at the hindered meso position. The spectrographic evidence therefore favors the structure I in preference to II.

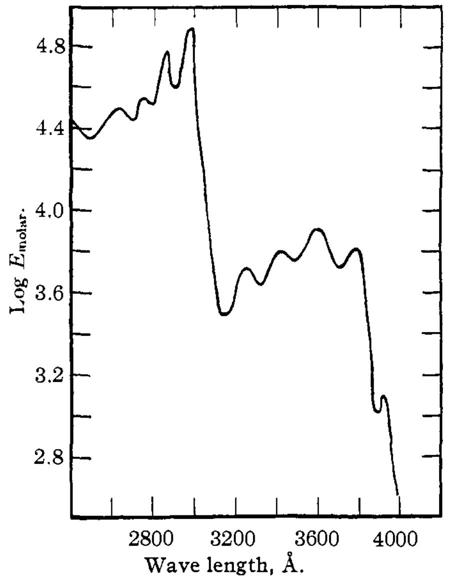

Fig. 3.—15-Thiocyano-20-methylcholanthrene.

On irradiation with ultraviolet light in a dark room these compounds showed no fluorescence with the exception of the 10-thiocyano derivative which fluoresced bright green in the solid state and blue in solution. A sample of 9-methyl-10-thiocyano-1,2-benzanthracene showed similar fluorescence.

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Chlorophyll-Pheophytin: Temperature Coefficient of the Rate of Pheophytin Formation

BY G. MACKINNEY AND M. A. JOSLYN

As reported previously,[1] chlorophyll *a* reacts with acid 8–9 times as rapidly as chlorophyll *b*, in aqueous acetone solution. Measurements have now been made at various temperatures from 0–51° with suitable concentrations of oxalic acid. The pure chlorophyll components were prepared and measurements made as before.[1] At the higher temperatures, the solutions in stoppered test-tubes were rapidly cooled in an ice-bath immediately before measurement. In all cases, acid-free controls were measured under the same conditions. The reaction for each chlorophyll was run at three temperature levels with various concentrations of oxalic acid. Somewhat surprisingly, the plot of ln k/N (k is the first

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(5) Pestemer and Litschauer, *Monatsh.*, **65**, 239 (1935).

(6) Jones, THIS JOURNAL, **63**, 313 (1941).

(1) Mackinney and Joslyn, THIS JOURNAL, **62**, 231 (1940).