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LIGHT ABSORPTION AND EMISSION PHENOMENA IN ANTHRACENE

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For more than 60 years anthracene has been known to chemists as a colorless substance,[1] possessed of a strong violet fluorescence, while the main features of the absorption spectrum are four bands at about 1/λ 2655, 2795, 2935, 3075, the first two being the strongest and narrowest. These bands and other lesser ones may be capable of further resolution. Hyatt[2] has measured as many as 14, but all of the numerous observers with the exception of Taylor and Lewis[3] have agreed that there is no absorption band with a head of greater wave length than 380$\mu\mu$. These authors find bands at 475 and 445$\mu\mu$, respectively. Unfortunately while they base a considerable theoretical discussion on the existence of these two bands they content themselves on the practical side with the bare statement that the bands were found, and with giving their positions. As the locations are almost identical with those of bands described by Morton[4] for the impurity chrysogen[5] occurring in most specimens of anthracene, giving them a yellow color, we have undertaken a careful examination of the absorption spectrum of anthracene in the visible region.

Absorption of Pure Anthracene.—Our raw material (98% pure) was pale lemon yellow. By sublimations, taking first fractions, and subsequent crystallizations a pure white product was obtained, melting to a pale yellow liquid at 216.5°. Before melting, the hot solid acquired a pale

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[1] Anderson, *J. Chem. Soc.*, **15,** 44 (1862).

[2] Hyatt, *Phys. Rev.*, **19,** 391 (1922).

[3] Taylor and Lewis, THIS JOURNAL, **46,** 1606 (1924).

[4] Morton, *Chem. News*, **26,** 199 (1872).

[5] Fritzsche, *Z. Chem.*, **2,** 139 (1866).

yellow color which was lost again on cooling, a phenomenon analogous to that seen on treating similarly certain inorganic substances, for example, zinc oxide.

Some of this material was made into a saturated solution in phenetole, this being the solvent employed by Taylor and Lewis, and examined in a tube 40 cm. long. The column had a distinct yellow tinge, but showed no selective absorption, and the tint was apparently due in large part to the solvent, although the ultraviolet absorption of anthracene does just extend into the visible spectrum for thick layers of solution. Thus 100 cm. of 0.1 M anthracene in chloroform absorbed up to 425$\mu\mu$, and the yellow tint of hot anthracene must be due to the extension of the absorption region at high temperatures. We also examined visually light passed through 140 cm. of 0.1 M anthracene in chloroform solution (=22 mm. of solid), but could not detect any traces of selective absorption. Certainly, there was none at 475 or 445$\mu\mu$.

Absorption of Yellow-tinted Anthracene.—The same raw material was used that was previously employed. It was not sublimed, but was recrystallized thrice from benzene, the first crop of crystals being taken each time. The amount of the coloring matter was insufficient to cause any perceptible difference in the melting point. The absorption of a solution of this anthracene in chloroform consisted in the visible region of bands at 475, 445, 418 and 397$\mu\mu$, respectively. Of these the first was strong, the second a little weaker, but like the two strongest bands of anthracene each had a weak neighbor on the side of shorter wave length; the third was rather broader and not so strong, and the last was almost hidden in the absorption of the anthracene. The chief bands were plainly photographed through a 3cm. layer of 0.1 M solution.

These findings are in excellent agreement with the observations of Morton, and in our minds not the slightest doubt exists that the bands seen in anthracene by Taylor and Lewis were in reality due to the impurity chrysogen. The various workers' results are shown in Table I. The values under "Morton" are our readings of his woodcuts.

Table I

Morton, Chrysogen absorption in benzene, 1/λ	2105	2242	2370	
Taylor and Lewis, Anthracene absorption in phenetole, 1/λ	2105	2247		
Capper and Marsh, Chrysogen absorption in chloroform, 1/λ	2105 (2140)	2247 (2285)	2392	2519

Chrysogen.—The chemical nature of chrysogen, the yellow impurity occurring with anthracene, has not yet been elucidated. It was regarded by Fritzsche as a hydrocarbon.[6] It is easily destroyed by exposure of its xylene solution to actinic light, apparently undergoing polymerization to a colorless substance in the same way as in the case of anthracene, for

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[6] See, however, Nickels, *Chem. News*, **41**, 95 (1880).

dianthracene made from pure white anthracene on decomposition yielded again white anthracene, but yellow-tinted anthracene was re-formed if the original was yellow. It seems certain, therefore, that it contains a system similar to the central ring of anthracene. Its absorption and fluorescence spectra are remarkably similar to those of anthracene except in position, and there seem to be some grounds for thinking that it may be naphthacene or 2,3-benzanthracene.[7]

Fluorescence of Anthracene.—Pure white anthracene fluoresces violet-blue, showing four indistinct maxima similar to the Tesla-luminescence spectrum,[8] but with a trace of chrysogen present the whole character of the fluorescence of the solid is changed to a magnificent green glow, and bands may be observed at $1/\lambda$ 2008, 1869 and 1730. They are broad and the first two are the most brilliant. The measurements of all three agree with those determined by Morton, but we failed to observe a fourth in the red region, and found only a continuous spectrum here. The fluorescence may be excited very conveniently free from all extraneous light by the cathodic bombardment of the solid. The green fluorescence is not stimulated by the direct incidence of light of a wave length similar to that of chrysogen absorption, at least not to a detectable extent. A plate on which some yellow anthracene solution was allowed to dry, when placed in the spectrograph could be seen to fluoresce green only under the impact of waves shorter than about $410\mu\mu$. With white anthracene in the same circumstances the violet fluorescence ceased at almost the same limit. Since light of a wave length capable of causing violet fluorescence in anthracene is required also for the production of the green fluorescence of chrysogen we may conclude that the green fluorescence of chrysogen is dependent for its stimulation on the potential emission of fluorescent light by anthracene. Solutions or vapor of anthracene show only the violet fluorescence even when chrysogen is present. The case of the solid suggests a parallel to the phosphorescence of certain sulfides where the color and brilliance are dependent upon the presence of traces of various impurities.

Polymerization of Anthracene.—Pure white anthracene showing no absorption bands at 445 and $475\mu\mu$ can be polymerized just as readily as yellow-tinted specimens, so that light of these wave lengths is evidently not the causative agent as Taylor and Lewis argue, but the polymerization must be due to the absorption of light in the ordinary ultraviolet region for anthracene. Since the effect may be obtained readily in glass vessels the activating light must lie between the first absorption band of anthracene at $375\mu\mu$ and the transparency limit of glass at about $310\mu\mu$, that is, in the region of the four most characteristic anthracene bands. Absorption in

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[7] Gabriel and Leupold, *Ber.*, **31,** 1272 (1898).

[8] McVicker, Marsh and Stewart, *J. Chem. Soc.*, **127,** 999 (1925).

the same spectral region is involved in the production of both the polymerization and fluorescence.

Absorption of Dianthracene.—Since incorrect data render valueless the calculation by which Taylor and Lewis arrive at the conclusion that dianthracene should absorb at 707$\mu\mu$ it remains to offer an explanation of the decrease in infra-red transmission found in their dianthracene solution after exposure to this radiation, which they take to be a proof of photochemical decomposition. It is possible that the effect may be due to the solvent phenetole and not to the minute quantity of dissolved dianthracene. Apparently a blank on the phenetole alone was not tried. All the benzenoid substances examined by Russell and Lapraik[9] show a well-marked absorption band at just this wave length, indicating some special sensitivity to light at this point.

We have been led by the above observations to seek instances of similar phenomena in related substances, and have examined fluorene and phenanthrene. We find that after special purification of these substances all visible fluorescence is lost, but by ordinary methods traces of anthracene are always retained sufficient to cause the apparent fluorescence commonly ascribed to these compounds. Details of this work, however, cannot be given here.

We desire to express our indebtedness to Mr. T. H. Nunan, M.Sc., for help in the early stages of this work.

Summary

Bands found in anthracene solutions at 445 and 475$\mu\mu$ by Taylor and Lewis were not the photochemically active ones, but were due to the presence of chrysogen. Hence, the deduction that dianthracene should absorb at 707$\mu\mu$ does not follow, and their evidence brought forward to show that light of this wave length is capable of bringing about a photochemical depolymerization of dianthracene is inconclusive. The absorption and fluorescence spectra of chrysogen are similar in form to those of anthracene but occur at greater wave lengths. The fluorescence is remarkable in its intensity and mode of stimulation, and the substance readily polymerizes in a manner similar to that of anthracene.

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[9] Russell and Lapraik, *J. Chem. Soc.*, **39,** 168 (1881).