the same physical properties and with the same physical constants except as to polarization.

4. It was found that polarized light beyond any doubt produced a very definite change in the pharmacological properties of the drugs studied as compared both with the normal specimens and with specimens irradiated by non-polarized light.

5. The practical significance of the above observations is discussed.

BALTIMORE, MARYLAND

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE U. G. I. CONTRACTING COMPANY]

THE SHIFT IN A NEAR INFRA-RED ABSORPTION BAND OF SOME BENZENE DERIVATIVES

BY JAMES BARNES AND W. H. FULWEILER

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In connection with a search for possible spectroscopic methods of identifying hydrocarbons some work was done on the absorption spectra of the aromatic series. Aside from the practical aspects of the results obtained it was thought that a preliminary report of some of the data might be of theoretical interest to those who are working in this field.

The extensive investigations of Coblentz[1] and Puccianti[2] on infra-red absorption spectra of organic liquids gave many important results. In recent years, certain special fields have been studied in a more detailed manner. We refer to the works of Márton,[3] Ellis[4] and others who showed that there appeared in the absorption spectra of the carbon-hydrogen compounds which they investigated a series of bands all at approximately the same wave length and that the values of these wave lengths almost formed an harmonic series, the fundamental being near 6.5μ.

Apparatus and Methods

All the above-mentioned observers used a prism spectroscope with a radiometer or a thermopile as the detecting instrument. In our work on the absorption spectra of some hydrocarbons and petroleum oils we have been using a grating spectroscope and photographing the bands on plates sensitized with neocyanine.

The source of radiation was a 65-watt lamp with a short, straight filament. It was surrounded by a hood with a hole in its side. The light passing through this hole fell on a lens which rendered it approximately parallel. It then passed through the absorption cell to another lens which

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[1] Coblentz, *Carnegie Inst. Pub.*, **1905–8.**

[2] Puccianti, *Nuovo Cim.*, **11**, 241 (1900).

[3] Màrton, *Z. physik. Chem.*, **117**, 97 (1925).

[4] Ellis, *Phys. Rev.*, **27**, 298 (1926).

focused the light on the slit of the spectroscope. By means of screens with circular openings placed before and after the cell, only the light passing through the cell fell on the slit. The absorption cells were made from glass tubing 2 cm. in diameter with plane glass windows glued to ground ends and with side tubes for filling. Two lengths of cells were used, 18 and 30 cm., respectively.

A Rowland plane reflection grating was placed on the table of the spectrometer and carefully adjusted. The collimator and camera objectives had apertures of 3.5 cm. and their focal length was approximately 40 cm. Photographs were only taken in the first order spectrum and all lines of the second order which would affect the plates in the region under investigation were absorbed by a thin sheet of red glass placed in front of the slit. The photographs were taken by exposing one-half of the slit to the light after passing through the absorption cell, and the other half to the light from copper and nickel arcs.

Meggers'[5] values for the wave length of the copper lines and Meggers and Kiess'[6] values of the nickel lines in the near infra-red region were taken as standards for measurement. The dispersion of the spectroscope as used was approximately 39.8 Å. per millimeter. Measurements of the plates were made in the usual manner on a comparator reading to 0.001 mm.

Discussion of Results

The results given in Table I are the means of many measurements made upon the center of the absorption bands photographed on two plates for each substance, one with the longer and the other with the shorter cell. The results are believed to be accurate to within ±5 Å.

Table I gives the wave lengths in Å. units and the wave numbers ($1/\lambda$) in cm.$^{-1}$ reduced to vacuum as obtained from Kayser's "Tabelle der Schwingungszahlen."

TABLE I

WAVE LENGTHS AND WAVE NUMBERS OF ABSORPTION BANDS OF BENZENE DERIVATIVES

	λ (Å)	$1/\lambda$ (cm.$^{-1}$)		λ (Å)	$1/\lambda$ (cm.$^{-1}$)
Benzene	8741	11437	*m*-Xylene	8793	11370
Toluene	8758	11415	*p*-Xylene	8808	11350
Ethylbenzene	8772	11397	Diethylbenzene[a]	8799	11362
o-Xylene	8781	11385	Mesitylene	8844	11304

[a] Mixture of *m*- and *p*-diethylbenzene.

Table I shows that there is a progressive shift of the absorption bands toward the longer wave lengths and hence a decrease in the frequencies with the addition of methyl and ethyl groups to the benzene ring.

Table II shows the frequencies ($\nu \times 10^{-11}$) and the difference produced by quantum addition of ethyl and methyl groups, respectively.

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[5] Meggers, *Bur. of Standards, Bull.*, **14**, 385 (1918–19).

[6] Meggers and Kiess, *ibid.*, **14**, 649 (1918–19).

TABLE II

FREQUENCIES OF ABSORPTION BANDS AND THEIR DIFFERENCES

	Benzene	Ethyl-benzene	Diethyl benzene	Toluene	Xylene[a]	Mesitylene
Frequency × 10^{11}	3431	3419	3409	3424	3410	3391
Difference	...	12	10	7	14	19

[a] Mean of xylenes.

Table III shows that the frequency depends on the position of the methyl groups in the xylenes.

TABLE III

FREQUENCIES OF THE ABSOPTION BANDS OF THE XYLENES AND THEIR DIFFERENCES

Xylene	*o*	*m*	*p*
$\nu \times 10^{11}$	3415	3411	3405
Diff.	...	4	6

While there is probably no justification for extending the Bjerrum-Schwarzschild theory of band spectra to liquids, yet it is of some interest to note that, with the resolving power employed, no doubling of the bands nor any sign of fine structure was observed on any of the photographic plates.

The effect of the addition of methyl or ethyl groups on the molecular forces of the benzene ring is not well understood. However, if the effect is small compared to the effect of the added mass one would expect on a theory such, for example, as that proposed by Debye that the change in the frequency would be inversely proportional to some function of the added mass. The results above are at least in qualitative agreement with such a theory.

In this connection the following data given by Ellis[7] are of interest.

DISPLACEMENT OF A 14μ BAND IN THE SPECTRA OF THE BENZENE DERIVATIVES

Benzene	Toluene	Xylene			Mesitylene
		o-	*m*-	*p*-	
14.1	13.85	13.55	12.95	12.55	11.95

These results taken from Coblentz' curves show that in these bands which Ellis attributes to the carbon-carbon bond, the wave lengths shift progressively toward the shorter wave lengths as methyl groups are added, which is in the opposite direction to the results recorded above.

In conclusion, we wish also to report that plates were taken of the absorption spectrum of benzene produced by a cell of 80 cm. length. No absorption was found at wave lengths 0.835μ and 0.760μ, but a band clearly appeared at 7134 Å. With this length of cell the band at 7134 Å. is easily observed visually.

Summary

By means of a grating and plates sensitized with neocyanine, absorption bands of benzene and of some of its derivatives have been photographed

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[7] Ref. 4, p. 313.

and their wave lengths measured. The results show a progressive shift of the bands toward lower frequencies as methyl and ethyl groups are added. There is also a shift due to the position of the methyl group in the xylenes.

With a cell 80 cm. in length, benzene shows an absorption band at 7134 Å.

PHILADELPHIA, PENNSYLVANIA

[CONTRIBUTION FROM THE COLOR LABORATORY, BUREAU OF CHEMISTRY,
U. S. DEPARTMENT OF AGRICULTURE, NO. 132]

THE CHEMISTRY OF LIGNIN. I. LIGNIN FROM CORN COBS

BY MAX PHILLIPS

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In spite of the extensive literature on lignin the chemistry of this product remains obscure.[1] Nothing definite is known about its constitution, although various formulas have been proposed, among which may be mentioned that of Cross and Bevan[2] for lignin ("lignone") from jute, and those of Green,[3] Klason[4] and Schrauth.[5] Most of these formulas have little definite chemical evidence in their support. That of Schrauth is admittedly speculative, although this investigator has endeavored, with some success, to correlate the conflicting data on lignin found scattered in the literature. The difficulty in deducing a constitutional formula for lignin is primarily due to the fact that as yet no method has been developed for the isolation of lignin in the pure state, nor is there any method known by which its purity may be gaged. The usual criteria of purity cannot, of course, be applied. The problem as to whether lignin is a homogeneous substance or a mixture of closely related chemical substances, therefore, remains unsolved. This has been further complicated by the fact that various investigators have obtained their lignin from different sources and by different methods. It has been obtained from (1) sulfite or soda and sulfate liquors resulting from the preparation of paper pulp from wood, (2) wood treated with 64–72% of sulfuric acid, (3) wood or similar lignin-containing plant material treated with saturated

[1] An extensive review of the literature is found in a recent monograph by Walter Fuchs, "Die Chemie des Lignins," Julius Springer, Berlin, **1926**. Hawley and Wise, in their monograph on "The Chemistry of Wood," The Chemical Catalog Co., New York, **1926**, give a critical review of our present knowledge of the chemistry of lignin, particularly that obtained from wood. An excellent résumé of the literature is given in a paper by Zhereboff [*Paper Trade J.*, **86**, No. 27, 47 (1925)].

[2] Cross and Bevan, "Cellulose," Longmans, Green and Co., London, **2nd ed., 1895**, p. 137; Vol. III, **1912**, p. 104.

[3] Green, *Z. Farben Textilchemie*, **3**, 97 (1904).

[4] Klason, *Ber.*, **56**, 300 (1923).

[5] Schrauth, *Z. angew. Chem.*, **36**, 149 (1923).