

TABLE I
DERIVATIVES OF AMINONAPHTHALENEARSONIC ACIDS

Name, -naphthalenearsonic acid	Yield, %	M. p., °C.	Arsenic analyses, %	
			Calcd.	Found
4-Acetylamino-1	90	271 dec.	24.27	24.15
4-Carbethoxyamino-1	90	250	22.12	22.03
4-β-Hydroxyethyl-1	65	250	24.11	24.03
1-Acetylamino-2	72	240-245 dec.	24.27	24.24
1-Carbethoxyamino-2	95	191 dec.	22.12	21.93

Summary

Better methods have been developed for the separation of the isomeric nitroaminonaphthalenes formed by the nitration of α - and β -naphthylamines, thus permitting their preparation on a large scale.

The nitroaminonaphthalenes have been arsonated and the products, 4-nitro-1-naphthalenearsonic acid, 2-nitro-1-naphthalenearsonic acid, 1-nitro-2-naphthalenearsonic acid, and 8-nitro-2-naphthalenearsonic acid have been isolated, the last three for the first time.

The isomeric nitronaphthalenearsonic acids have been reduced to the corresponding aminonaphthalenearsonic acids and several derivatives of these have been prepared.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, YALE UNIVERSITY]

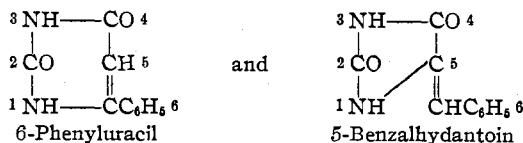
ULTRAVIOLET ABSORPTION SPECTRA OF SOLUTIONS OF SOME SUBSTITUTED PHENYLURACILS¹

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Uracil and hydantoin are quite similar in many ways. Both are urea derivatives, both form sodium salts and both can be alkylated. A comparison of the alkylation products obtained from 6-phenyluracil² and the isomeric 5-benzalhydantoin³ shows analogous changes in physical properties such as melting point and solubility.



In the benzal- and anisalhydantoin series, considerable differences in the

¹ Constructed from a dissertation presented by Janet Evans to the Faculty of the Graduate School of Yale University, in June, 1929, in partial fulfilment of the requirements for the degree of Doctor of Philosophy.

² Evans and Johnson, *THIS JOURNAL*, 52, 4993 (1930).

³ Hahn and Evans, *ibid.*, 50, 806 (1928).

ultraviolet absorption spectra of alkylated compounds occur, so that hydantoin having a substituent in the N-1 position can be readily distinguished from hydantoin of the same series which are unsubstituted or substituted only in the N-3 position.^{3,4,5} The absorption curves for alcohol solutions of 5-benzalhydantoin and methyl-5-benzalhydantoin-N-3-acetate are almost identical and show a single broad absorption band with a maximum about $1/\lambda = 32,000 \text{ cm.}^{-1}$ but these curves differ from those of the two isomeric N-1-methyl-5-benzalhydantoin-N-3-acetic acids. An earlier study of the derivatives of anisalhydantoin⁶ showed an exactly parallel relationship between the ultraviolet absorption spectra of the N-3-substituted N-5-anisalhydantoin and the disubstituted compounds and it was further shown that the type of substituent made little if any difference.

Reasoning by analogy, since hydantoin and uracil have so much in common, it should also be possible to differentiate between N-1 and N-3 substitution products of uracil having an aryl group in the 6-position, if the structure of one compound is definitely known or if there are isomeric N-1 and N-3 substituted compounds.

In order to determine whether absorption spectra can be used to distinguish N-1 and N-3 substituted uracils, measurements of the ultraviolet absorption spectra of some phenyluracils have been made.

Experimental

The preparation, properties and proof of structure of these uracils have been described in a previous paper.² The samples which were used had been recrystallized four times from alcohol or until the melting point remained constant and finally from alcohol which was specially prepared for spectrographic work.⁷ Hundredth molar solutions were made by dissolving the calculated amount in 50 cc. of alcohol. These solutions were then diluted to 0.0002, 0.0001 and 0.00002 *M*.

The absorption spectrum measurements were made with a Hilger quartz spectrograph (E2) using an iron spark as a source of light. The sparking apparatus consisted of a 0.25 kilowatt transformer and condenser of approximately 0.03 m. f. capacity as recommended by Hilger. The spark gap between the rectangular iron electrodes (2 mm. by 3 mm.) was kept at 2 mm. The absorbing medium was contained in small Baly absorption tubes of clear fused quartz with ground quartz connections. Lumière and Jougla photographic plates were used throughout.

The extinction coefficients were determined by the photographic method

⁴ Carr and Dobbrow, *THIS JOURNAL*, **47**, 2961 (1925).

⁵ Maclean, Thesis, Mount Holyoke College, 1926.

⁶ Carr, Report at Richmond meeting of the American Chemical Society, April, 1927.

⁷ Castille and Henri, *Bull. soc. chim. biol.*, **6**, 301 (1924).

of comparison spectra developed by Henri.⁸ The readings were plotted using the logarithm of the extinction coefficient as ordinate and the reciprocal of the wave length or the wave number in cm.^{-1} as abscissa. The extinction coefficient was calculated from the experimental data using the usual formula

$$\epsilon = \frac{0.9}{d \times M} \log \frac{T}{T_0}$$

in which ϵ is the extinction coefficient; 0.9 is a constant depending on the properties of the photographic plate; d is the thickness in centimeters of the solution through which the light passes; M is the concentration in moles per liter of solution; T is the time of the exposure through the solution; and T_0 the time of the exposure through the same thickness of pure alcohol for comparison. T_0 was ten seconds throughout; T was forty or sixty seconds. The thickness d was varied from 0.6 to 6 cm.

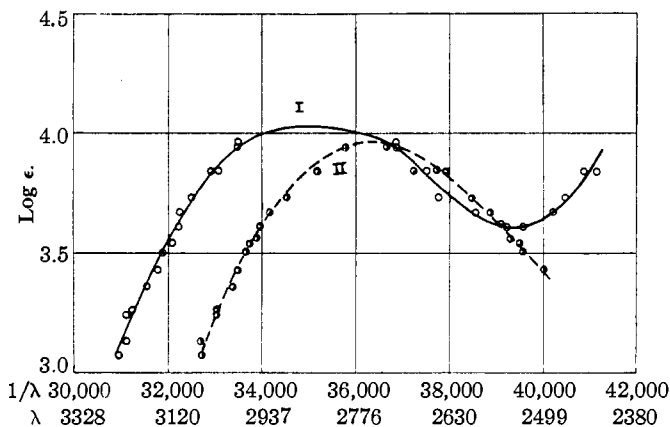


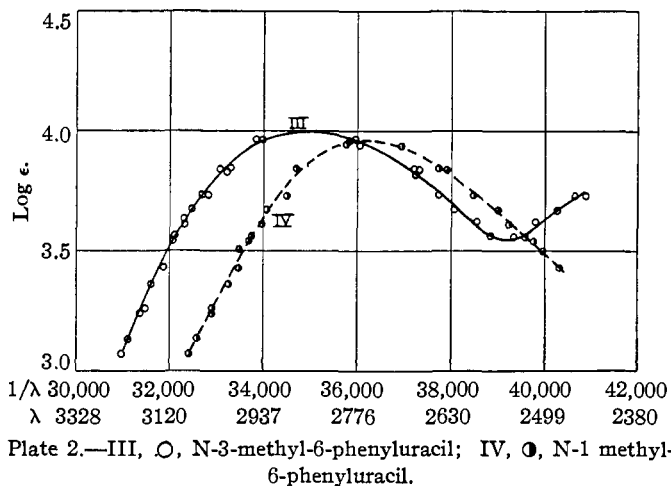
Plate 1.—I, ○, 6-phenyluracil; II, ●, N-1,3-dimethyl-6-phenyluracil.

Discussion of Results

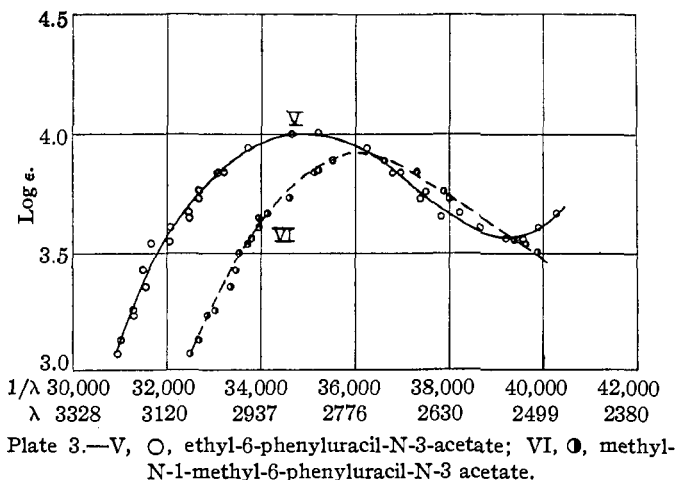
The absorption curves (Plates 1, 2, 3) of non-substituted 6-phenyluracil (Curve I) and the two N-3 substituted derivatives, N-3-methyl-6-phenyluracil (Curve III) and ethyl-6-phenyluracil-N-3-acetate (Curve V), are almost identical. In each case the maximum of the band is at $1/\lambda = 35,000 \text{ cm.}^{-1}$. The N-1-methyl-6-phenyluracil (Curve IV) and the two disubstituted compounds, methyl-N-1-methyl-6-phenyluracil-N-3-acetate (Curve VI) and N-1,3-dimethyl-6-phenyluracil (Curve II), also give almost identical curves but these show a decided difference from the curves of the preceding group. The band is shifted toward the ultraviolet, the maximum being about $36,250 \text{ cm.}^{-1}$. Also the bands of Curves II, IV and VI are somewhat narrower and slightly more persistent than those of

⁸ Henri, "Études de Photochimie," Paris, 1919, p. 5.

Curves I, III and V, although the intensity is less. Evidently substitution for the hydrogen in the N-1 position, whether the hydrogen in the N-3 position has been replaced by a substituent group or not, has considerable



influence on the absorptive power of the molecule. Here, as in the hy-dantoin series, the type of substituent has little effect on the absorption. Therefore, it should be possible to determine the position of the substituent



group in a derivative of 6-phenyluracil by comparison of its absorption spectrum with those already studied. It may also be predicted that N-1 and N-3 derivatives of a uracil having any aryl group in position 6 can be differentiated by means of absorption spectra and that the com-

pounds whose absorption band lies farthest in the ultraviolet may be considered N-1 substituted compounds.

It has been stated that the properties of 6-phenyluracil are to some extent like those of 5-benzalhydantoin. However, 6-phenyluracil does not react so readily as the 5-benzalhydantoin nor is the yield of alkylated product so great. The double bond cannot be reduced at all by the means by which 5-benzalhydantoin is reduced easily. Comparison of their absorption curves shows that both have the same type of selective absorption but the band of 6-phenyluracil (Curve I) occurs much farther out in the ultraviolet ($1/\lambda = 35,000 \text{ cm.}^{-1}$) and is less intense ($\log \epsilon = 4.0$) than that of 5-benzalhydantoin³ ($1/\lambda = 31,750 \text{ cm.}^{-1}$) and ($\log \epsilon = 4.35$). The same relation is maintained between the absorption bands of the other pairs of isomers. This result is in accordance with Henri's conclusion⁹ that the most reactive substances possess the strongest absorption and the absorption bands of a compound are shifted toward the visible as chemically reactive groups are introduced.

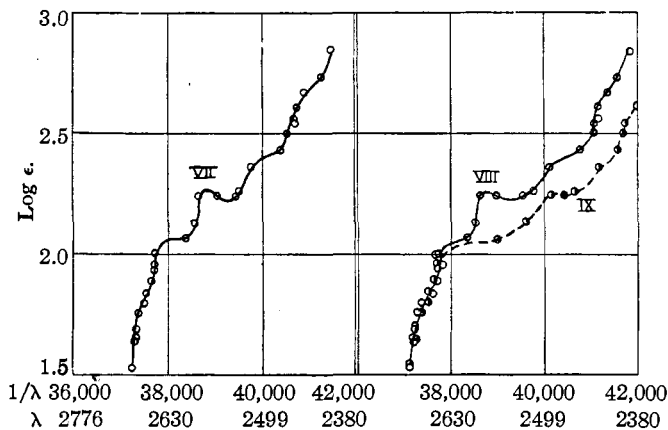


Plate 4.—VII, ○, ethyl-N-1-methyl-6-phenylhydrouracil-N-3-acetate; VIII, ○, N-1-methyl-6-phenylhydrouracil; IX, ●, N-3-methyl-6-phenylhydrouracil.

The groups which absorb light, *i. e.*, chromophoric groups in phenyluracil and in benzalhydantoin are the benzene ring, the double bond between the two carbon atoms 5 and 6, and the two carbonyl groups. In phenyluracil the double bond is in the ring, whereas in benzalhydantoin it is outside. Experimental results, in general, show that a double bond in the ring is less reactive than one in a chain, and these results appear to show that it confers less absorptive powers on the molecule.

The absorption curve of ethyl-N-1-methyl-6-phenylhydrouracil-N-3-acetate (Plate 4, Curve VII) is very similar to that of methyl-N-1-methyl-5-

⁹ Henri, Ref. 8, pp. 174, 187.

benzylhydantoin-N-3-acetate.³ Both show only a tendency to band formation rather than a discrete band and this "step-out" begins at approximately $1/\lambda = 38,000 \text{ cm.}^{-1}$ and $\log \epsilon = 2.0$ for each. As noted above, the corresponding unsaturated compounds, methyl N-1-methyl-6-phenyluracil-N-3-acetate and N-1-methyl-5-benzalhydantoin-N-3-acetic acid, do not show this similarity. Reduction of the double bonds of two unsaturated compounds having the same chromophoric groups but markedly different absorptive powers has produced two compounds of very similar absorptive power although one contains a six- and one a five-membered ring. This also indicates the great difference between the influence on the absorption of a double bond outside a ring and one in the ring.

The curves of N-1-methyl-6-phenylhydrouracil (Curve VIII) and ethyl-N-1-methyl-6-phenylhydrouracil-N-3-acetate (Curve VII) are alike and have "step-outs" which are slightly narrower than that of N-3-methyl-6-phenylhydrouracil (Curve IX) but this difference is not sufficiently characteristic to be used for purposes of identification.

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Summary

1. The ultraviolet absorption spectra of 6-phenyluracil, N-3-methyl-6-phenyluracil, ethyl-6-phenyluracil-N-3-acetate, N-1-methyl-6-phenyluracil, N-1-3-dimethyl-6-phenyluracil, methyl-N-1-methyl-6-phenyluracil-N-3-acetate, N-1-methyl-6-phenylhydrouracil, N-3-methyl-6-phenylhydrouracil, and ethyl-N-1-methyl-6-phenylhydrouracil-N-3-acetate have been measured.

2. The absorption spectra of those uracils having a substituent in the N-1 position have been found to differ from those of uracils which are non-substituted or have substituents in the N-3 position.

3. This difference can be used to distinguish N-1 substituted from N-3 substituted uracils of the type of 6-phenyluracil.

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