

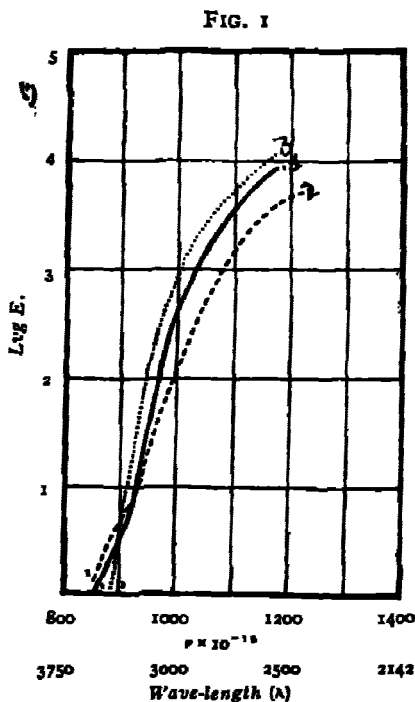
**RELATIONS BETWEEN CHEMICAL ACTIVITY AND ABSORPTION IN  
THE ULTRAVIOLET OF CERTAIN ORGANIC MOLECULES.  
PART VII. ABSORPTION SPECTRA OF THE AMIDES  
OF ACETOACETIC ACID**

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The following substances have been examined for the absorption spectra in the ultraviolet in aqueous solution : (1) acetoacetanilide, (2) acetoacet-*o*-tolylamide, (3) acetoacet-*p*-tolylamide, (4) acetoacet-1:3:4-xylylamide, (5) acetoacet- $\alpha$ -naphthylamide and (6) acetoacet- $\beta$ -naphthylamide.

At the outset the following substituted amides of acetoacetic acid were examined for their absorption spectra in the ultraviolet:—1. Acetoacetanilide 2. Acetoacet-*o*-tolylamide. 3. Acetoacet-*p*-tolylamide 4. Acetoacet-1:3:4-xylylamide 5. Acetoacet- $\alpha$ -naphthylamide 6. Acetoacet- $\beta$ -naphthylamide.

Of these the first three have already been studied by Ramart, Naik and Trivedi (*Bull. Soc. Chim.*, 1934, 1, 525.) by means of Zeiss spectrograph in alcoholic solution. In Fig. 1 are given the curves as obtained by these workers).



The nature of these curves shows that a considerable quantity of the enol form is present in the alcoholic solution. This is especially evident from the fact that the bands due to the ketonic groups are not shown.

Secondly, the curves show that the presence of methyl groups considerably alters the position of the curves. Again the position of the methyl groups in the nucleus with regard to -NH- grouping also brings about a change in the position of these curves.

In the present study, alcohol has been replaced by water as a solvent. The curves obtained are shown in Fig. 1.

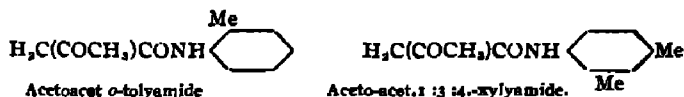
Two points emerge out clearly with reference to these curves:—

1. The characteristic bands due to the presence of simple ketonic form are observed between the wave-lengths 2800-2400 Å. This must be ascribed to the ketonic structure of the amides persisting in aqueous solution.

It is of interest to note that the previous workers. Ramart, Naik and Trivedi (*loc. cit.*) show the presence of enol-form which must be ascribed to the alcoholic solution. It is well-known that such keto-enol transformations depend upon the solvent used.

2. The disposition and the direction of the curves remain the same as in the absorption spectra obtained by Ramart, Naik and Trivedi. It can be said that the total effects of the groups carried by the two carbonyl groups remain the same as in the previous work.

In Fig. 2 is also traced the curve of absorption spectra of acetoacet-2:3:4-xylylamide. It will be seen that there is a close resemblance between these curves and that of the acetoacet-*o*-tolylamide. This must be attributed to the similarity of structures of these two substances as indicated below.



The difference in the degree of absorption is due to the presence of  $\text{CH}_3$  group in *para* position to- NH- group.

FIG. 2

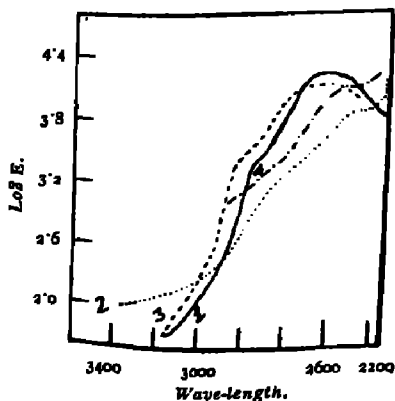


FIG. 3

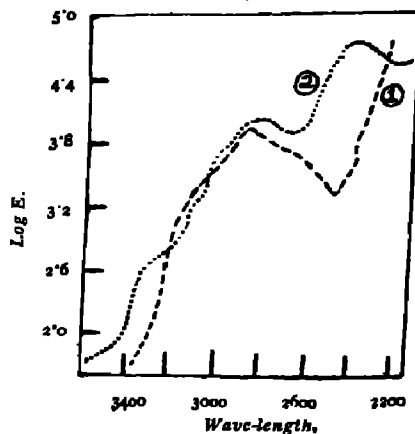


FIG. 4

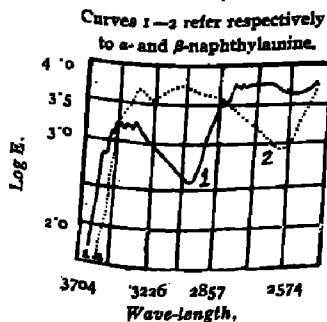
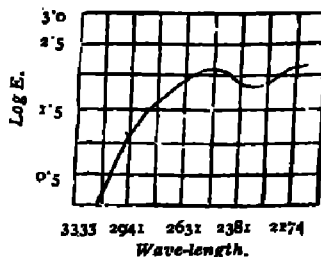


FIG. 5



Thus structural similarities are translated by light absorption as represented by the curves.

In Fig. 3 are shown the curves for (1) Acetoacet- $\alpha$ -naphthylamide. (2) Acetoacet- $\beta$ -naphthylamide.

The bands are characteristics of the naphthyl residue and they also show the peculiarities of the ketonic groups viz. the disposition of the crest between 2800-2400 $\text{\AA}$ . The distinct difference between the curves of  $\alpha$ -naphthylamide and  $\beta$ -naphthylamide must be attributed to the structures of their amino residues. Other workers have also observed such differences. Curves for the absorption of  $\alpha$ -naphthylamine and  $\beta$ -naphthylamine also exhibit similar difference. (Krüss, *Z. physikal. Chem.*, 1884, 81, 251) (*vide* Fig. 4).

This point also brings into relief the relationship between absorption spectra and structures of organic substances. This fact is well brought out in relief by reference to the curve of absorption spectra of ethyl acetoacetate itself (Grossmann, *Z. physikal. Chem.*, 1924, 109, 305) (*vide* Fig. 5). It will be seen that the chief characteristics of curves shown above persist. The difference in disposition of curves is due to the difference in structure, because in all the above cases the ester group,  $-\text{COOC}_2\text{H}_5$ , has been replaced by groups such as  $-\text{CONHR}$ .

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