

maintained below 35° by circulating water through a copper trough holding the apparatus.

To carry out the recovery of the protein, 1 g. of protein picrate (CS-5-7)<sup>5</sup> dissolved in 100 ml. of 50% dioxane, was placed in the third cell from the cathode and 100 ml. of 50% dioxane was placed in each of the other cells. Direct current at 1500–2500 volts was applied at the platinum electrodes in terminal cells for four hours, and the voltage was then increased to 4000 volts for sixty-eight hours. The initial current of 1.1 milliamperes gradually increased to 6.0 and then dropped to 2.9 where it remained constant. At the end of this operation the cathode cell contained a gummy precipitate and nearly colorless solution. The other cells contained picric acid as indicated by the yellow color which was progressively more intense toward

(5) Spies, Bernton and Stevens, *THIS JOURNAL*, **62**, 2793 (1940).

the anode cell. The supernatant liquid in the cathode cell was decanted and the precipitate was dissolved in 30 ml. of water. This solution, decolorized by boiling with activated charcoal, was centrifuged and filtered through a Seitz sterilizing pad. The clear colorless filtrate was poured into 100 ml. of cold ethanol and precipitated by adjusting the pH to 6.3 with dilute acetic acid. A yield of 180 mg. of a white powder was recovered by centrifuging followed by drying in a vacuum over phosphorus pentoxide. The recovered solid contained 19.8% (ash-water free basis) nitrogen and gave protein color tests like CS-13A. The solid diluted to 1:10<sup>6</sup> induced strongly positive cutaneous reactions on cottonseed sensitive patients.

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## COMMUNICATIONS TO THE EDITOR

### ULTRAVIOLET ABSORPTION OF THE DIPHENIC ACIDS

Sir:

Recent studies have emphasized the fact that absorption in the ultraviolet is a measure of resonance or conjugation and that structure is indicated only incidentally as it contributes to this phenomenon. Recently in this Laboratory the absorption curves have been obtained for ortho-ortho', meta-meta' and para-para'-diphenic acids. It is interesting to report the radically different behavior of these three compounds in respect to their ultraviolet absorption.

The *o-o'*-diphenic acid shows an absorption which differs but little from that of benzoic acid. Evidently the carboxyl groups in the *o*-position interfere to such an extent that the coplanar position is impossible and resonance between the rings completely disappears.

On the other hand, the *p-p'*-diphenic acid (in this case the methyl ester) shows a very great absorption with the maximum near 2800 Å. Here we have exact coplanarity with complete resonance throughout.

By far the most interesting of these compounds, however, is the *m-m'*-diphenic acid. While the absorption is much greater than that of the *o-o'*-compound, it is much less than that of the *p-p'*-acid and the maximum is shifted toward shorter wave lengths so that it lies beyond the range of

the medium quartz spectrograph. It is clear that it is not possible for a structure to exist which involves double bonds between the rings and between the ring and the carbon of the carboxyl group at the same time and this is the important structure for total resonance. Hence competition between these structures results in a decreased amount of conjugation.

It is interesting to note that a similar situation arises in the case of diphenylmethane. *p*-Cresol shows a marked increase in absorption and a shift of the maximum toward longer wave lengths. On the other hand, *p*-hydroxydiphenylmethane shows little difference from the diphenylmethane. This is not difficult to understand when we recognize that the principal resonance structure which contributes to the absorption in diphenylmethane is one in which the *p*-carbon acquires a negative charge. This structure does not involve conjugation with the hydroxyl group.

The details of this research will be published later but meanwhile we wish to acknowledge our indebtedness to Dr. N. Kornblum and Messrs. L. Brooks and J. C. Robinson for the preparation of the several acids.

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