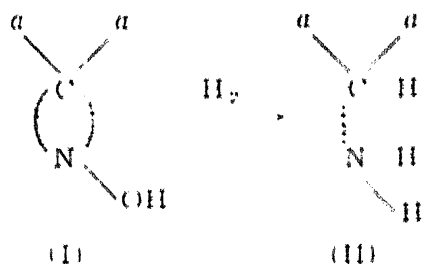


The Space Configuration of Nitrogen in the 3-Covalent State

The configuration of nitrogen compounds of the ammonia (NH_3) or amine (Nabc) type has been an outstanding problem in stereochemistry. There are two alternatives: (a) the nitrogen atom lies in one plane with the three attached groups, so that the molecule has a plane of symmetry; (b) it does not lie in that plane, in which case the molecule has a spatial configuration.

On the latter hypothesis, compounds of the type Nabc should exist in enantiomorphous forms. This has never been observed. Evidence from physical properties of ammonia or amines, however, clearly supports the view that in these compounds, the nitrogen atom does not lie in one plane with the three attached groups. The object of this note is to furnish an unequivocal answer to this question from stereochemical evidence. The work of Mills¹ on centro-asymmetric oximes and hydrazones, has conclusively proved that the doubly linked valencies of nitrogen in the oxime grouping are not coplanar with the singly linked one (I), thus:



On reduction, an oxime (I) gives the corresponding amine (II). If in the molecule of the oxime, under consideration, the plane containing the doubly linked valencies of nitrogen does not *originally* contain the singly linked valency, carrying the hydroxyl group, the position of the latter linkage will remain unaltered relatively to this plane which now contains two single valencies in the resulting amine (II) in place of the original doubly linked valencies (I). In other words, the three valencies of the nitrogen atom in an amine are not coplanar. Figs. 1 and 2 are photographs of the models of an oxime and the corresponding amine: one of the two large connected spheres

(Fig. 1 and 2) represents the carbon atom and the other, the nitrogen atom, plus the effect

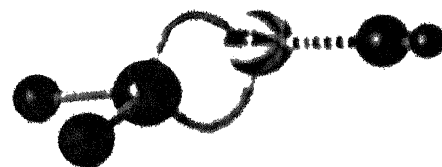


FIG. 1

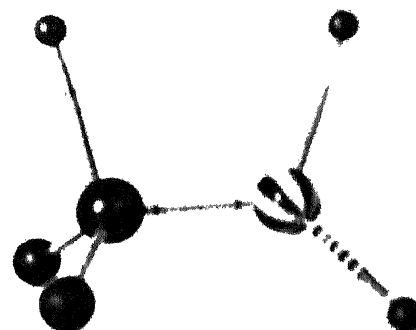


FIG. 2

a smaller sphere representing the oxygen atom is attached, the latter carries a still smaller sphere, representing the hydrogen atom. The striped link, carrying the spheres representing the hydroxyl group, is shown lying outside the plane containing the two links representing the double bond (Fig. 1). It is clearly seen that the link still lies outside the plane containing the two single links, resulting from the double link, in the corresponding model of the amine (Fig. 2). A fuller account of this work will appear elsewhere.

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¹ Mills and Bass, *J. Am. Chem. Soc.*, 67, 2163 (1945); *J. Am. Chem. Soc.*, 67, 1901 (1945).

The Endo Enzyme in Tea Fermentation

The study of the enzyme system responsible for the "fermentation" of tea has been so far conducted on the enzyme extract using aqueous solvents. Both oxidase and peroxidase

actions have been observed in these extracts,^{1,2,3,4} and it is still unknown whether what partakes in the reaction is either one or both of these enzymes.

In addition to these soluble enzymes, however, it has now been found that tea leaf contains an endo-enzyme which is insoluble in the usual aqueous solvents for enzymes. Thus, extraction of the suitably prepared leaf with water, buffer and glycerine solutions still leaves behind an active enzyme, which would also appear to react during fermentation on the polyphenolic substrate.

The presence of this endo-enzyme can be demonstrated as follows:—

The leaf is well ground with sand under acetone and filtered, repeating the operation several times until all the colouring constituents are extracted. The residue, which is almost colourless, is dried in vacuum, thoroughly extracted with solvent buffer solution and washed well. The insoluble leaf tissue thus obtained gives all the reactions familiar to tea fermentation with a tea extract or theotannin isolated according to the method of Shaw.⁵

To indicate the activity of the insoluble enzyme the supernatant liquid is drained off, the residue washed free of colour, and a fresh tea tannin solution added when again the orange red colour is produced.

Sufficient evidence is at hand to show that this enzyme, which is an oxidase in its nature, is different in characteristics from the soluble tea enzyme. Apart from the obvious solubility differences, it would appear to have an optimum pH between 5.0 and 5.5 and withstands concentrations of KCN up to M/50, the usual oxidase or peroxidase being inactivated far below this concentration. Further, the endo-enzyme acts on high concentrations of tea tannin which, it is shown, would inhibit the action of soluble enzymes. The reaction mixture itself with tea tannin has a bright orange red colour identical with the 'tint' of the liquor obtaining when the fermented leaf is infused.

The further nature of this endo-enzyme, the exact mechanism of its action, and the actual

role it plays in 'fermentation', are being investigated.

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December 17, 1938.

¹ Mann, H. H., "The Ferment of the Tea Leaf, Part I, II and III," *Indian Tea Association, Scientific Department*, 1901, 1903, 1904.

² Oparin, *et. al.*, *Biochemical Aspects of Tea Industry, Georgia, U.S.S.R.*, 1935, 107.

³ Kursanov, *ibid.*, 1935, 125.

⁴ Roberts, E. A. H., and Sarma, S. N., *Biochemical Journal*, 1938, **32**, 1819.

⁵ Shaw, W. S., *U.P.I.S.I., Bull. No. 1 (a)*, 1935.

A Note on the Modification of Shellac with Organic Acids

It has been recognised that shellac is mostly composed of hydroxy acids in the form of condensed esters, lactides or lactones. From the constitution of shellac so far understood, it can be said to contain five hydroxyl groups and at least one carboxyl group. The predominance of a large number of hydroxyl groups, free and combined, led to the idea of modifying shellac by esterification with several organic acids and subsequent reduction of residual acidity by combining the esters with mono or polyhydric alcohols. Such combinations might have specially water and heat resistant properties, an expectation fully confirmed by the results of actual experiment.

Shellac was condensed with several organic acids like maleic, phthalic, succinic, adipic, butyric, malic, etc. Later, phosphoric and boric acids were also included in the list, and useful products were obtained. The condensations could be brought about directly or in the presence of solvents and non-solvents of shellac. The alcohols investigated for reducing the final acidity of the condensation products include glycols, glycerine, butyl alcohol, etc. The modifications possess various degrees of hardness, elasticity and adhesion. A typical preparation with maleic acid which (without the final condensation with alcohols) has given promise of an extended use of shellac for special varnishes, is described below.