

REPORT ON THE THESIS ENTITLED "CRYSTAL STRUCTURE OF
DL-ASPARTIC ACID" SUBMITTED BY MR V. AMRITALINGAM FOR
THE DEGREE OF MASTER OF SCIENCE

Some of the early determinations of the unit cells and the space groups of the simpler amino acids were made nearly twentyfive years ago, and since then the structures, not only of the amino acids but also of the polypeptide chains, have claimed considerable attention from X-Ray crystallographers. Apart from their great importance in biology, and the effective help which a knowledge of their structures could give in determining ultimately the structures of the proteins, the detailed structural analysis of the amino acids themselves are of great interest. Though the technique of structural analysis has made great advances, and many methods are now known for refining the results of analysis, there is no single beaten path by which one can arrive at the structures, and hence the analysis of each amino acid is in a sense an individual problem. Some special or unexpected features observed in the course of the analysis may make a great difference to the facility of analysis, and decide the most effective method of approach, rather than ^{the} a priori merits of the method. In other words, in spite of the techniques of X-Ray analysis being well-known, it requires considerable resourcefulness on the part of the investigator to be able to choose the right combination of the techniques.

This is amply illustrated in the present thesis, which concerns itself with the analysis of the structure of one of the important amino acids occurring in proteins, namely DL-aspartic acid. The basic experimental data on which the structure determination is made by the candidate are the rotation, oscillation, and Weissenberg photographs about the

a and the b axes of the crystal, which is monoclinic, and the intensities of the spots appearing in these diffraction photographs. The candidate has taken the necessary precautions to ensure precision in the measurements: (a) He takes in the same pictures, and under the same conditions, the X-Ray diffraction patterns for NaCl crystal, and uses the latter as comparison standard for the determination of the lattice spacings, and thus eliminates the errors that might creep in otherwise due to the possible shrinkage of the photographic films. (b) In the measurement of the intensities of the spots, he uses the multi-film method originally suggested by Robertson, which is very convenient and fairly dependable. (c) He takes care to choose for the diffracting crystal the optimum size consistent with its known absorption coefficient. (d) He corrects ofcourse for the Lorentz and the polarization effects. Though the intensity values vary over a wide range namely, 1 to 1500, the error in the determination of intensity is estimated at about 5%.

As a first step towards the analysis of the structure, the candidate made the Patterson synthesis for two simple projections, namely okl and hol. This was more in the nature of a preliminary trial. The a axis Patterson pattern contained an number of well resolved peaks, and they were arranged along the a axis. The ^{na} pattern by itself was not of much help. On the other hand in the b axis Patterson pattern, though the peaks were not so well defined, they were arranged in a narrow band inclined at about 30° to the a axis. This feature makes the pattern much more informative than the a axis pattern, since the main chain lengths of the asporatic acid molecules may be presumed to lie in the direction of this narrow band in which the peaks are located, which is a very helpful building ground for constructing trial structu-

res. Utilizing for this purpose some of the well known bond lengths and bond angles, a rough determination of the coordinates of the atoms could be readily made.

The trial structure proposed above enables the candidate to determine the magnitudes and the signs of ^{the} structure factors for different reflections. Though the magnitudes did not fit well with the observed magnitudes, the signs for most of the stronger reflections were found to be correct, as judged by certain well-known criteria due to Grison. Having determined the correct signs for a number of strong reflections, it was possible by the trial and error method to adjust the structure and refine it in stages, so as to yield the correct magnitudes ^{also} of the structure factors.

The final structure arrived at by this method is found to be very similar to those of the other amino acids, which is gratifying. There is, however, a difference, to which pointed attention is drawn by the candidate. "One of the hydrogens of the amino group is internally hydrogen bonded to an oxygen of a carboxyl group forming a closed system of six atoms". This ^{finding also} is not unexpected.

The work embodied in the thesis is of high standard, and the candidate shows not only a commendable acquaintance with the technique of the various methods of X-ray analysis, but also competence in interpreting the data, and resourcefulness in suitably modifying the structures to meet the changing requirements at different stages of the analysis.

I would therefore adjudge the thesis on its merits as "highly commendable".

U. S. Krishna
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