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MEMORANDUM No. 12/M/49

Interim report on the determination of the crystal structure of oxamide

J. R. C. Duke

Waltham Abbey, Essex.

UNCLASSIFIED

June, 1949

A.R.E.
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Technical Representative for Artillery
OFFICERS GROUP NO. 1
U.S. Navy 100,F.P.O.
New York,N.Y.

Ref: ORD-TRART-110 4 October 1949

SUBJECT: Interim Report on the Determination of the Crystal Structure of Oxamide.

TO : The Chief of Ordnance
Department of the Army
Washington 25, D.C.

Att: ORDTM

1. References:

None.

2. Purpose of this Report:

Forwarded herewith as Enclosure 1 is E.R.D.E. (Explosives Research and Development Establishment) Memorandum No. 12/M/49 - "Interim Report on the Determination of the Crystal Structure of Oxamide" by J.R.C. Duke, dated June 1949.

3. Comments:

The Summary of the Memorandum is repeated herewith for convenience as follows:

"The crystal structure of oxamide has been examined by X-ray methods, employing 2-dimensional Patterson & Fourier projections. An interim report is presented, covering the results so far obtained, and giving details of atomic coordinates, bond lengths and angles, and intermolecular separations; the estimated error of bond lengths is less than ± 0.05A. Further work is in progress, employing 3-dimensional methods, to refine the coordinates as far as possible."

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E.R.D.E. MEMORANDUM No.12/M/49

Interim report on the determination of the crystal structure of oxamide

By

J.R.C.Duke

This memorandum does not contain information of overseas origin

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SUMMARY

The crystal structure of oxamide has been examined by X-ray methods, employing 2-dimensional Patterson & Fourier projections. An interim report is presented, covering the results so far obtained, and giving details of atomic coordinates, bond lengths and angles, and intermolecular separations; the estimated error of bond lengths is less than ± 0.05Å. Further work is in progress, employing 3-dimensional methods, to refine the coordinates as far as possible.

INTRODUCTION

The thermal properties of oxamide are of particular interest, and it was decided to investigate its crystal structure with the object of furthering the understanding of these properties.

Oxamide was described as monoclinic by Schabus in 1855 (Groth); a recent investigation by Misch and van der Wyk (1938) showed it to be triclinic and X-ray investigation indicated that the molecule is planar and parallel to (010) with a C-C bond length of 1.65Å. This unusual result was thought to require confirmation, and it was desired to obtain full information concerning the crystal structure. It will be seen later that the results reported in this Memorandum are in general agreement with those of Misch and van der Wyk, but the C-C bond is found to be of normal single type within the limits of experimental error; a different naming of axes and choice of cell angles has been adopted here, Misch and van der Wyk giving a = 5.18 Å, b = 3.63 Å, c = 5.65 Å, $\alpha = 66^{\circ}5'$, $\beta = 84^{\circ}$, $\gamma = 64^{\circ}$

Crystallographic examination and measurement of intensities

Crystals of oxamide were prepared by growth at a steady temperature of about 75°C, from a filtered, boiling, saturated solution in water. Clusters of lath-shaped crystals were obtained, from which it was possible to cleave length suitable for examination.

X-ray examination of the crystals by the oscillation and rotation methods, using copper radiation, showed that they were triclinic, and the following values were obtained for the unit cell parameters

a = 3.63 Å	(λCuK α= 1.542)	(lath axis)
b = 5.19		
c = 5.64		
$\alpha = 83^{\circ}\ 24'$		
$\beta = 113^{\circ}\ 55'$		
$\gamma = 114^{\circ}\ 51'$		

The density of oxamide is reported to be 1.667 (Schroder (1879), see P.Groth) and it follows that the unit cell contains one molecule; the calculated density is 1.662.

No systematic absences of X-ray reflexions were noted. Only pinacoid forms were observed to be developed on the crystals, (010) and (001) often being marked with close striations which appeared to be the traces of (100) planes. (The crystals showed perfect cleavage parallel to (100)). A test for pyro-electric properties by the rather-inconclusive liquid-air method gave a negative result. On the basis of these observations, the crystals were tentatively assigned to space-group $P\bar{1}$; no evidence was found during the later stages of the analysis which indicated that this was incorrect.

The optical characteristics of the crystals were determined, using the polarizing microscope; they are biaxial negative and very highly birefringent. It was found that a cleavage plate lying flat upon a microscope slide exhibited a nearly-symmetrical acute-bisectrix figure when examined in convergent polarized light and could be used for the determination of the β and γ refractive indexes, and a similar cleavage plate was supported with its plane parallel to the microscope axis for the determination of α, the refractive indexes being determined by the immersion method using the Becke line effect. The refractive indexes were found to be

α = 1.43, approximately perpendicular to (100)
β = 1.63, approximately parallel to the c-axis
γ = about 1.76, approximately perpendicular to the c-axis.

/A

A set of overlapping a-axis 15°-oscillation photographs, covering a range of 180°, was taken using copper K α x-radiation (0.0007" Ni filter), and used for the visual estimation of a set of relative intensities of diffracted X-ray beams by the use of a calibrated scale. The estimation was carried out on an illuminated screen in a darkened room under standardised conditions. These intensities were used for the early part of the work, but the results obtained indicated that it would be necessary to use a shorter wave-length radiation; therefore moving-film photographs covering a range of 185° about the a- and c-axes were taken, using molybdenum K α x-radiation (0.004" zirconium filter), and the intensities measured on these films were used for the later stages of the analysis. The multiple-film technique (Robertson, 1943) was employed, the films being interleaved with aluminium foil for the photographs with copper radiation, and with copper foil for those with molybdenum radiation; the observed intensities covered a range of 1400 to 1.

The measured relative intensities were corrected for Lorentz-polarization factor, and converted to relative structure amplitudes by the relation $F = k(I_r/L)^{\frac{1}{2}}$. A correction for absorption was not applied. The crystal used for the a-axis photographs with molybdenum radiation had dimensions 0.25 x 0.25 mm. in cross section, that used for the c-axis films had similar dimensions, so that any absorption correction for molybdenum radiation could be ignored.

Film processing was carried out under standardised conditions at 18°C.

The determination of the structure

The space-group $P\bar{1}$ accommodated 2 assymetric units in general positions, or one centro-symmetrical unit in a special position; the molecule of oxamide must therefore possess a centre of symmetry, which coincides with one of the centres of symmetry of the unit cell, and this was chosen to be the centre at $(0\frac{1}{2}\frac{1}{2})$. Consideration of the unit cell dimensions, refractive indexes and cleavage properties suggested that the structure might consist of planar molecules arranged parallel to (100), and therefore the projection of the structure on this face was investigated first. A 2-dimensional Patterson F^2 synthesis projected upon (100) could be satisfactorily interpreted in terms of such a structure and gave the orientation of the molecule in this projection. A set of approximate y and z coordinates for the atoms of the molecule was derived and used to calculate a set of structure factors; using the calculated signs and the observed amplitudes a 2-dimensional Fourier synthesis was carried out, projected upon (100), and successive refinement led to promising agreement between observed and calculated structure amplitudes. The summations were carried out using Beevers-Lipson strips of 2-figure accuracy, the cell edges being divided into 30 equal parts.

When refinement had been carried as far as possible, it was found that the projected C-C bond had a length of 1.59Å. Since X-ray reflexions had been observed up to the limit of recording ($\xi = 1.99$) of the experimental arrangement with copper radiation, it was thought probable that not all reflexions had been observed with this arrangement, and that the resulting lack of convergence of the Fourier series might lead to incorrect positions of the maxima. It was at this stage that the intensities were re-determined, using molybdenum radiation; fifteen new reflexions were observed, representing an addition of scattering power of about 20% (calculated on intensities). The process of refining the Fourier projections was now continued, incorporating the new terms; no sign changes occurred, but there were some small movements in the positions of maxima. All atoms were clearly resolved, and the values of the y and z coordinates were determined from the summations.

/This

This process of using 2-dimensional Patterson F^2 and Fourier F syntheses was then followed for the projection onto (001); in this projection, resolution of the molecule is less favourable, each peak representing a pair of atoms; the z-coordinates were determined from the positions of the unresolved peaks, assuming the y-coordinates determined from the (100) projection.

Further work is proceeding on recording all the hkl reflexions obtainable with molybdenum radiation, and the refinement will then be continued using 3-dimensional methods.

Results

The values of the coordinates expressed as fractions of the unit cell edges, are summarised as follows:-

	C	O	N
x	-0.003	-0.002	-0.006
y	0.494	0.280	0.273
z	0.362	0.287	0.760

The coordinates of the other half of the molecule are obtained from these by the operation of the centre of symmetry at $(0\frac{11}{22})$.

Structure factors were calculated from these coordinates and an experimental scattering curve was drawn; this was used to calculate structure amplitudes and the expression

$$\frac{\Sigma \left| |F(\text{calc.})| - F(\text{obs.}) \right|}{\Sigma |F(\text{obs.})|}$$

was evaluated. It had the value 0.15 for the okl reflexions and 0.24 for the hko's, and was taken to indicate a satisfactory degree of agreement for this stage of the analysis.

By comparison of the experimental and theoretical scattering curves, the structure amplitudes were placed upon an approximately absolute scale, and contour maps of electron density were drawn. Fig.1 shows the projection of the structure on (100); all atoms are clearly resolved and may be unambiguously identified by the relative heights of the peaks. Fig. 2 shows the projection of the structure on (001), the central peak representing two overlapping carbon atoms and either of the outer peaks representing one oxygen and one nitrogen atom which overlap.

The molecule is both planar and parallel to (100) within the limits of experimental error, and as stated above, it possesses a centre of symmetry; the distances of the atoms from the (100) plane through the origin are:-

C, 0.01Å; C, 0.01Å; N, 0.02Å.

The following bond lengths and angles have been calculated:-

/Intramolecular

Intramolecular distances and angles

C-C	= 1.56Å	C-C-N	= 124°
C-O	= 1.23	C-C-O	= 118½°
C-N	= 1.31	N-C-O	= 117½°

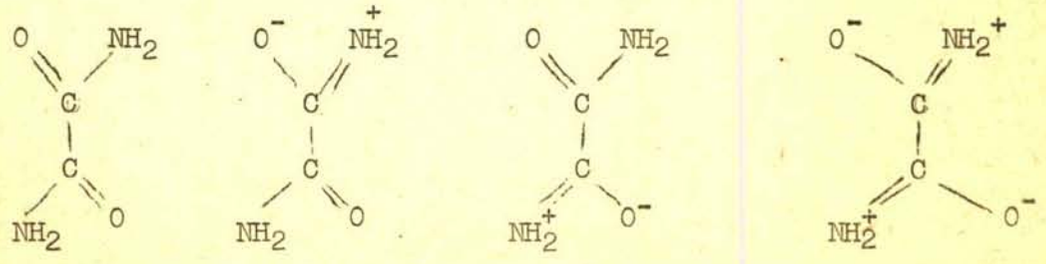
Intermolecular distances

N-O	2.92	Å
	2.96	
	3.46	
	3.52	
	3.66	
N-N	3.54	
	3.63	
	3.77	
O-O	3.30	
	3.63	
	3.98	
N-C	3.67	
	3.68	
C-C	3.31	
	3.63	
C-O	3.11	
	3.18	

The perpendicular distance between the planes of neighbouring molecules is 3.02Å. It is difficult to assign limits of accuracy, but the bond lengths are probably accurate to within less than ± 0.05Å.

Discussion

The discussion of these results must be tentative until the final results of the 3-dimensional analysis are available. The C-C bond appears to be a normal single bond within the limits of error. Adopting the treatment of Pauling (1940), the C-O bond has the length expected for a double bond (1.22Å); the C-N bond length also approaches the value expected for a double bond (1.27Å). It seems possible that within the limits of experimental error, these bond lengths may correspond to single-double bond resonance, in which case the bond lengths expected would be C-O = 1.27Å and C-N = 1.32Å. In this case the molecule could be represented by a resonance structure involving the following states:-



The close approaches of nitrogen and oxygen atoms of neighbouring molecules in the same plane is taken to indicate the presence of hydrogen bonds linking each $-NH_2$ group to two oxygen atoms and each oxygen atom to two $-NH_2$ groups, these bonds linking all the molecules in one plane into an infinite sheet.

There are a number of rather close intermolecular approaches, e.g. the O...O distance of 3.30Å, the C...C distance of 3.31Å and the C...O

/distances

distances of 3.11 and 3.18Å; the compactness resulting from these, and from the hydrogen bond formation is reflected in the high density of oxamide. The close approach of carbon and oxygen may be compared with those recently observed in p-nitroaniline (Abrahams and Robertson, 1948) in which C...O separations of 2.7 - 3.0A were reported between oxygen atoms of a nitro group and carbon atoms of the benzene ring. A parallel may be drawn, although of very doubtful significance, between the situation of a carbon atom in the resonance structure outlined above and that of a carbon atom in a benzene ring on the one hand, and between the situation of an oxygen atom also in the above resonance structure and an oxygen atom in an $-NO_2$ group on the other; in the one case the carbon atoms both form three bonds, two of which involve single-double bond resonance, and in the other the oxygen atoms both form one bond involving single-double bond resonance, and the parallel might be extended to the close C...O approaches in oxamide and p-nitroaniline. This is, of course, entirely speculative.

Figure 3 is a diagrammatic projection of two layers of the structure perpendicular to (100) (not along the a-axis) to illustrate the relationship of the molecules in a plane to one another, and to illustrate the relationship of successive planes of molecules; the black circles represent atoms in the higher plane. The hydrogen bonds link molecules in planes parallel to the paper, and the close intermolecular approaches of undefined type occur between molecules of succeeding planes parallel to the paper.

It will be possible to discuss the structure with more certainty when the results of the 3-dimensional analysis are available.

S.No.90
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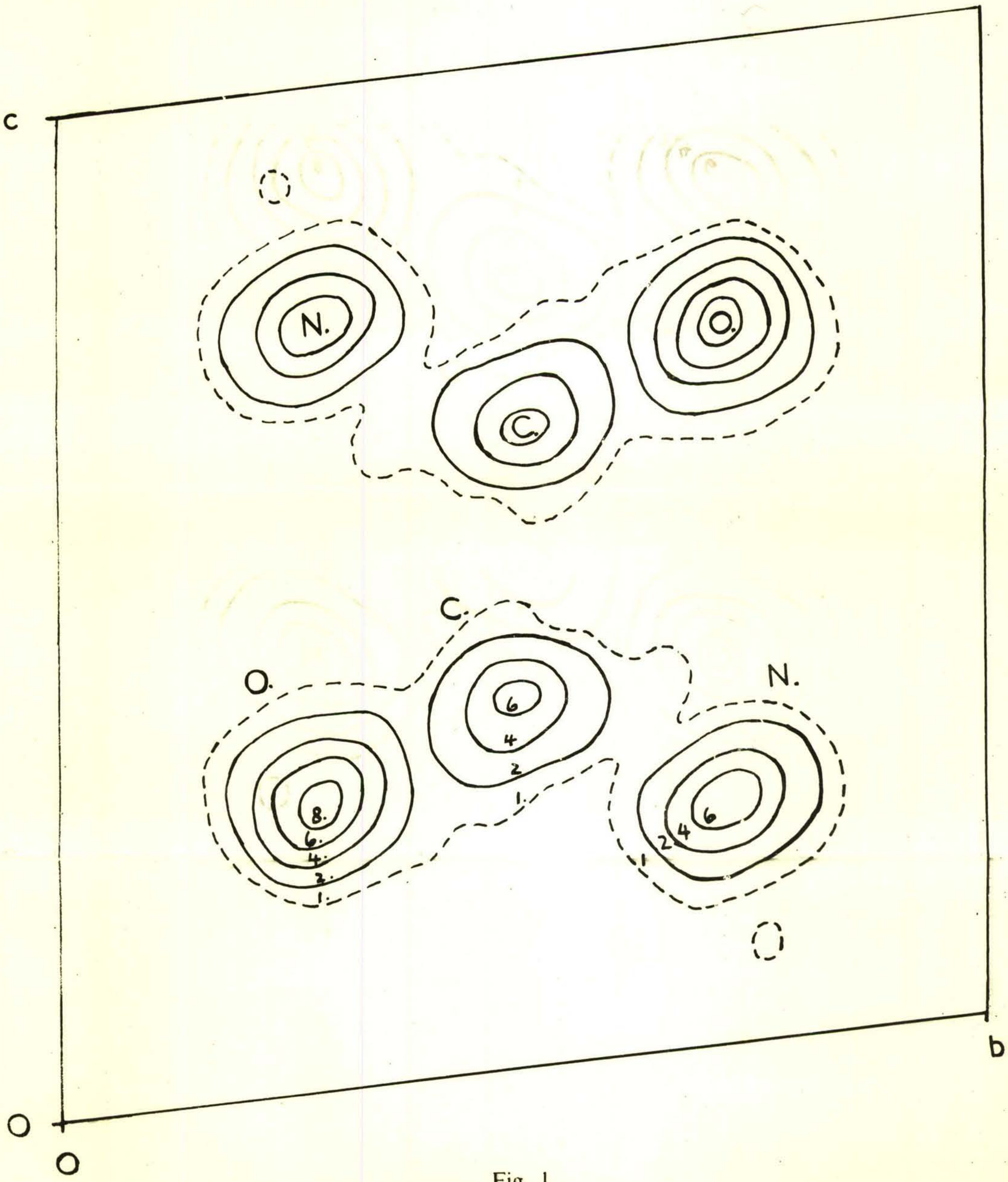

Fig. 1

Projection on (100),
showing electron density
in electrons/$\mathring{A}^2$.

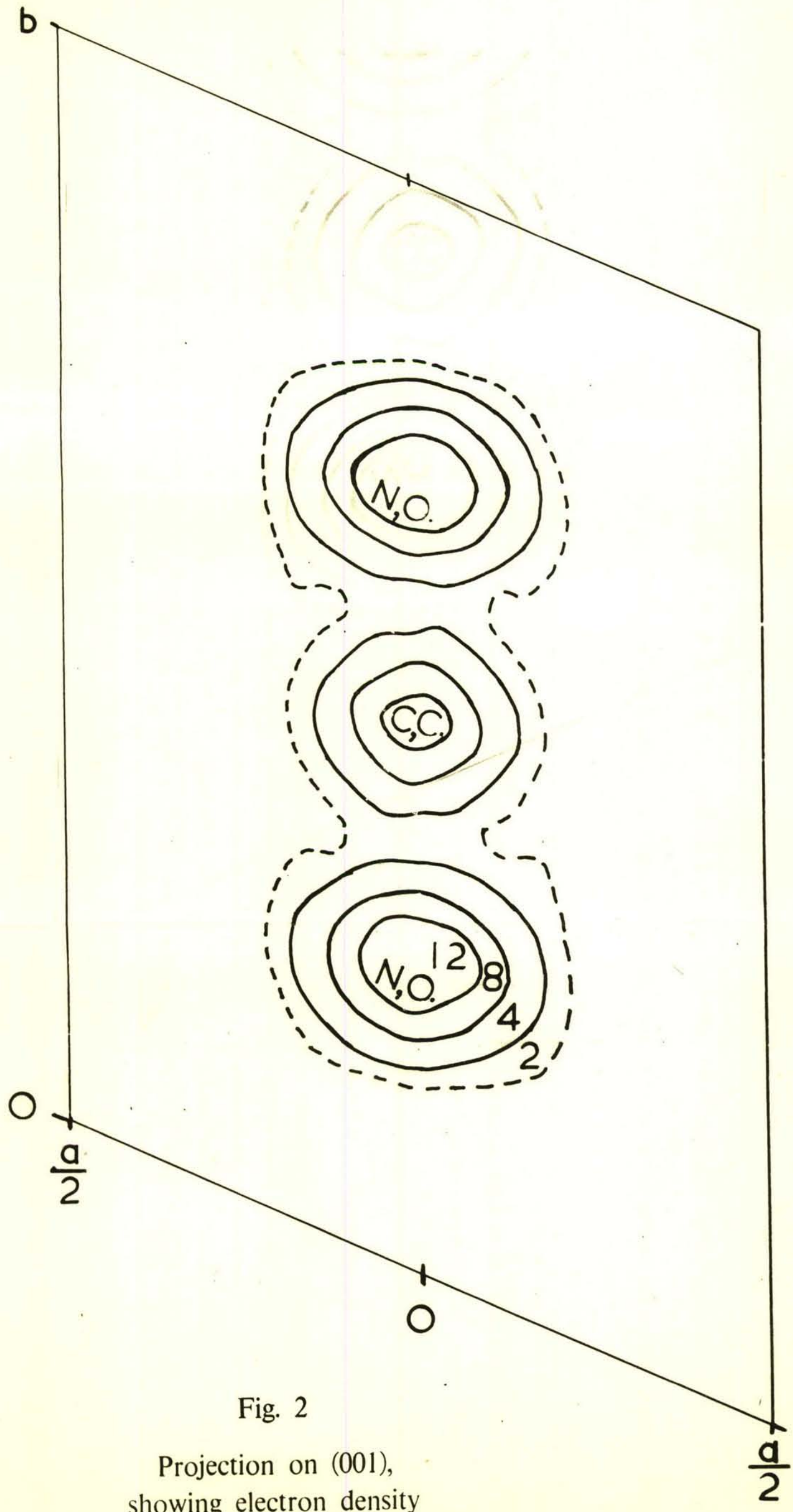

Fig. 2

Projection on (001), showing electron density in electrons/Å^2.

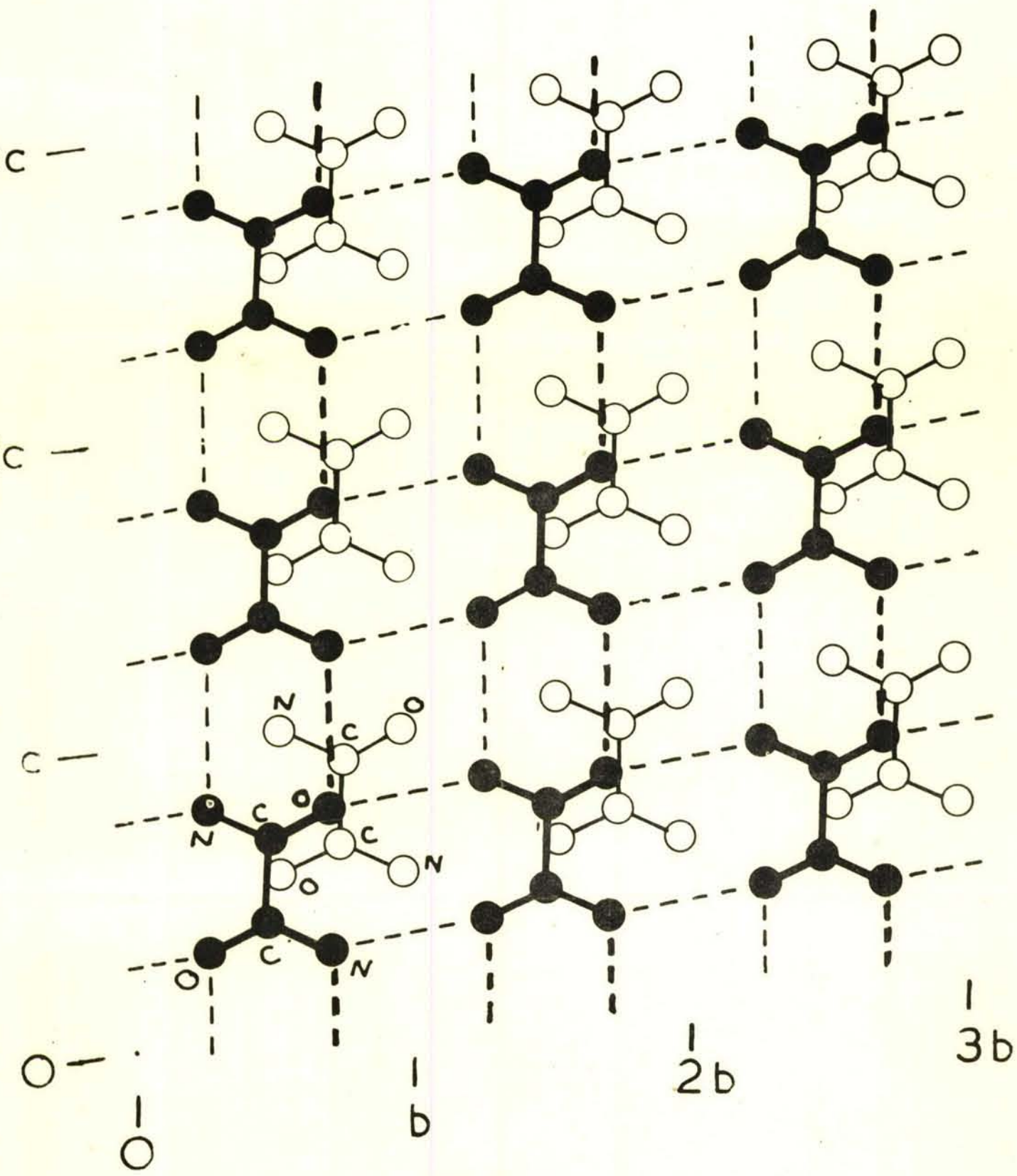

FIG. 3.

Diagrammatic projection, perpendicular to (100), of two adjacent layers of the structure. The black circles represent atoms in the higher layer, and hydrogen bonds are denoted by broken lines. Pairs of molecules which partly overlap in this projection are related by the a-translation of the unit cell, and it is between the carbon and oxygen atoms of these pairs of molecules that the short intermolecular distances have been found.