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The Crystal Structure of N-Benzyl-1,4-Dihydronicotinamide

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The structure of N-benzyl-1,4-dihydronicotinamide has been determined from three dimensional X-ray single crystal data. The space group is $P2_1/c$ and $Z=4$. The unit-cell dimensions are

$$a = 12 \cdot 07, \quad b = 5 \cdot 86, \quad c = 20 \cdot 82, \quad \beta = 129° \, 30'.$$

The structure was determined directly from the intensities by the application of probability methods to obtain the phases. The dihydronicotine ring is planar with C=C = 1·32 Å, C–C = 1·51 and 1·53 Å, and C–N = 1·43 and 1·38 Å. The amide group is nearly in the same plane as the dihydronicotine ring. The plane of the benzene ring makes an angle of 83° with the plane of the dihydronicotine ring. Hydrogen bonds connect pairs of molecules into centrosymmetrical dimers.

1. Introduction

Nicotinamide derivatives are essential dietary constituents for many animals. The nicotinamide residue performs an oxidation-reduction function:
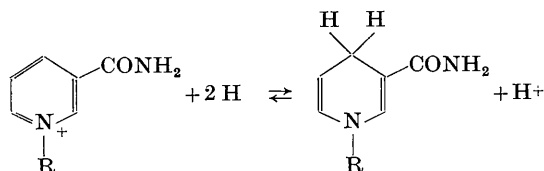
When R is ribose pyrophosphate adenosine, we have the coenzymes DPN and DPNH, respectively. N-benzyl dihydronicotinamide, an analog of DPNH, serves as a good model for the DPN–DPNH transhydrogenase system (Mauzerall & Westheimer, 1955). The crystal structure of nicotinamide has been determined by Wright & King (1954). The particular interest in the dihydronicotinamide derivative is whether the dihydronicotine ring is planar.

2. Experimental measurements

The crystals were yellow, transparent laths, with the b axis as the needle axis. They were very thin. Unit cell dimensions were obtained from rotation and precession photographs. The crystallographic data are:

$$a = 12 \cdot 07, \quad b = 5 \cdot 86, \quad c = 20 \cdot 82, \quad (\text{all } \pm 0 \cdot 3 \%),$$

$$\beta = 129° \, 30' \pm 10', \quad \text{space group } P2_1/c, \quad Z = 4,$$

$$\varrho (\text{X-ray}) = 1 \cdot 252 \text{ g.cm.}^{-3}, \quad \varrho (\text{physical}) = 1 \cdot 257 \text{ g.cm.}^{-3}.$$

Equi-inclination Weissenberg photographs were taken about the b axis, zero through the fourth layer. The shape of the crystals precluded obtaining good intensity data along the other axes. The zero layer about the a axis was used for those $0kl$ reflections

which were not obtainable from the b axis photographs. The intensities were estimated visually, using a calibrated comparison strip, and corrections were made for Lorentz and polarization factors, obliquity, $\alpha_1\alpha_2$ resolution, and spot length. 2014 independent reflections were measured of which 535 intensities were observed to be zero. The data were corrected for vibrational motion and placed on an absolute scale by means of a K curve (Wilson, 1949; Karle & Hauptman, 1953), thus giving F_h^2. From these, the magnitudes of the normalized structure factors were computed by means of

$$E_h^2 = F_h^2 \Big/ \varepsilon \sum_{j=1}^{N} f_{jh}^2 , \qquad (2\cdot1)$$

where, for space group $P2_1/c$, $\varepsilon = 2$ when h is $h0l$ or $0k0$ and $\varepsilon = 1$ otherwise, N is the number of atoms in the unit cell, and f_j is the atomic scattering factor of the jth atom. The theoretical probability distributions of the structure factors for a centrosymmetric crystal and various averages are listed in Table 1 together with actual values for this crystal.

Table 1. *Distributions and averages for structure factors*

	Theoretical	Actual
$\|E\| > 1$	32·0%	25·0%
$\|E\| > 2$	5·0%	4·5%
$\|E\| > 3$	0·3%	0·8%
$\langle\|E\|\rangle$	0·798	0·807
$\langle E^2 \rangle$	1·000	1·017
$\langle\|E^2 - 1\|\rangle$	0·968	1·033

3. Determination of the phases

Sign determination by probability formulas (Hauptman & Karle, 1953; Karle & Hauptman, 1959) requires only the knowledge of the space group, and the magnitudes of the normalized structure factors. To facilitate the determination of the phases, the E_{hkl} were arranged in order of descending E magnitudes in groups where the indices were ggg, ggu, guu, gug, ugu, ugg, uug and uuu (g=even, u=uneven). The $E^2 - 1$ values were also listed.

The phase determination can be begun with Σ_1:

$$sE_{2h,0,2l} \sim s \sum_k (-1)^{k+l}(E_{hkl}^2 - 1) \qquad (3\cdot1)$$

and

$$sE_{2h} \sim s(E_h^2 - 1) . \qquad (3\cdot2)$$

The sign of the 800 reflection with a probability of 0·92 of being + was the only one that could be determined with certainty using (3·1). The next largest probability was $P_+(E_{0,0,10})$ equal to 0·75 which left the sign of 0,0,10 somewhat in doubt. In formula (3·2), a phase is determined only from one other reflection. In order to have a high probability that the phase indication is correct, it is necessary that both E_{2h} and $(E_h^2 - 1)$ have large magnitudes. Signs for three reflections were accepted with this formula. They are listed in Table 2.

Table 2. *Application of Σ_1*

				$P_+(E_{2h})$	
2h	E_{2h}	h	$E_h^2 - 1$	(a)	(b)
420	3·86	210	+9·82	0·99	1·00
$\overline{4}28$	2·07	$\overline{2}14$	+6·88	0·86	0·94
422	2·22	211	+4·86	0·79	0·84

The probability that a certain sign is positive was computed (a) from the hyperbolic tangent formula,

$$P_+(E_{2h}) = \tfrac{1}{2} + \tfrac{1}{2} \tanh \frac{1}{2N^{1/2}} |E_{2h}|(E_h^2 - 1) , \qquad (3\cdot3)$$

analogous to the one derived by Woolfson (1954) for Σ_2 (see (3·4)) and (b) from (3·29) in Monograph I.

Three reflections needed to fix the origin were chosen with large E values and were arbitrarily assigned positive. They were $E_{\overline{12},1,25} = +3\cdot97$, $E_{\overline{10},1,18} = +3\cdot41$ and $E_{\overline{11},1,16} = +3\cdot57$. They fall into the groups guu, gug, and uug, respectively, which are linearly independent (Monograph I). At this point Σ_2,

$$sE_h \sim s \sum_k E_k E_{h-k} \qquad (3\cdot4)$$

was used to obtain more signs. In this formula, the signs of E_k and E_{h-k} need to be known in order to obtain the sign of E_h. Again, only the terms with the largest $|E|$ values to insure greatest probability were used to establish a basic set of signs.

The reflections 102 and 200 were quite intense and it was obvious that the molecules must lie near these planes. From packing considerations, the sign of the 200 could be assumed to be negative, the 102 could be positive or negative depending upon choice of origin. This is immediately confirmed by applying Σ_2 to two of the origin determining phases:

$$
\begin{array}{lll}
\overline{10},1,18 & E_k & = +3\cdot41 \\
11,\overline{1},\overline{16} & E_{h-k} = +3\cdot57 \\
\hline
102 & E_k & = 2\cdot45
\end{array}
$$

$$sE_{102} \sim (+3\cdot41)(+3\cdot57) .$$

If the origin determining phases had other signs assigned to them, E_{102} could just as well have been negative. Knowledge of the sign of E_{200} was not particularly useful, although it was used for corroboration.

Starting with the three origin determining phases and the four phases determined by Σ_1, it was not possible to apply Σ_2 for very long before another phase had to be known in order to continue. Such a phase could have been the 0,0,10 for which one indication from Σ_2 was available. Using two of the initial phases, $\overline{4}28$ and 422, in the Σ_2 formula, the 0,0,10 was determined to be positive with a probability of 0·98, in agreement with the indication from Σ_1 which had a probability of 0·75. Using $+E_{0,0,10}$, over 200 phases with $|E_{hkl}| > 1\cdot5$ were determined by means of Σ_2 to which there were very few exceptions. A Fourier

map was computed from which the structure of the molecule could be deduced. A projection on (010) is illustrated in Fig. 1. This structure, however, is incorrect. The configuration of the molecule is correct, but its placement in the unit cell is not. In the three dimensional analysis, an obvious difficulty is the O–O distance, across a symmetry center, which is only 2·5 Å.

A possible explanation for the difficulty in the phase determination was that the 0,0,10 might, in fact, be negative and that the single indication from Σ_2 might have been a rare exception. If the 0,0,10 is chosen to be negative, then an equally consistent set of phases can be obtained using Σ_2. One hundred and four phases with $|E| > 1·9$ were obtained by hand computation. These 104 phases were then put into a Σ_2 computation programmed for the IBM 704 and a search was made among all reflections with $|E| > 1·5$. On the first pass, taking a few minutes, 43 new signs were obtained, accepting only those with at least five contributors and an average $|E_\mathbf{h}E_\mathbf{k}E_{\mathbf{h-k}}| > 10$. Using 147 signs, the next pass yielded 35 additional signs for a total of 182 known phases. All the signs were subsequently shown to be correct. The correct structure was readily found from the new set of phases.

An examination of the initial 104 phases (all correct) showed that there were 360 contributors to Σ_2, 10 of which were exceptions; that is, they disagreed with other contributors to a particular phase. Table 3 lists the number of contributors to Σ_2 and the exceptions as a function of the magnitude of $E_1E_2E_3/N^{\frac{1}{2}}$, a quantity related to the probability that $E_1E_2E_3$ be positive. In the first five categories, corresponding to a probability of more than 0·99 of being correct, there are no exceptions. The last category, $E_1E_2E_3/N^{\frac{1}{2}} = 1·0–1·9$, corresponds to a probability of 0·88–0·98. In this category, 6% were exceptions, a number which is consistent with the probability prediction. (Among them was the combination $\overline{4}2\overline{8} + 422 \rightarrow 0,0,10$.)

The ambiguity in this structure determination arising from the rare coincidence of Σ_1 and the single available contributor to Σ_2 both predicting an incorrect phase for the important 0,0,10 reflection, motivated

Table 3. *Contributors to* Σ_2

$E_1E_2E_3/N^{\frac{1}{2}}$	No. correct	Exceptions
$> 7·0$	1	0
6·0–6·9	1	0
5·0–5·9	5	0
4·0–4·9	18	0
3·0–3·9	60	0
2·0–2·9	134	2
1·0–1·9	131	8

an examination of the predictions from a newer phase determining formula. Formula (3·1·2) in Karle & Hauptman (1959) was used where p, q, and r are given values of 2 and all the atoms are assumed to be equal in weight. The formula reduces to

$$\mathscr{E}_{\mathbf{h}_1}\mathscr{E}_{\mathbf{h}_2}\mathscr{E}_{\mathbf{h}_1+\mathbf{h}_2}$$
$$= \tfrac{1}{8}N^{3/2}\langle(\mathscr{E}_\mathbf{k}^2 - 1)(\mathscr{E}_{\mathbf{h}_1+\mathbf{k}}^2 - 1)(\mathscr{E}_{\mathbf{h}_1+\mathbf{h}_2+\mathbf{k}}^2 - 1)\rangle_\mathbf{k}$$
$$+ N^{-\frac{1}{2}}(\mathscr{E}_{\mathbf{h}_1}^2 + \mathscr{E}_{\mathbf{h}_2}^2 + \mathscr{E}_{\mathbf{h}_1+\mathbf{h}_2}^2 - 2) + \ldots , \quad (3·5)$$

where $\mathscr{E} = |\sqrt{(2)}E$ for the $h0l$ and $0k0$ and $\mathscr{E} = E$ otherwise for space group $P2_1/c$. Some of the results of this formula are listed in Table 4.

Only three dimensional data were used in the averages, consisting of $\mathscr{E}^2 - 1$ terms, for the triple products (3·5). Two dimensional data often cause serious errors in the computation of the averages, although two dimensional data are used for the $\mathscr{E}_{\mathbf{h}_1}$, $\mathscr{E}_{\mathbf{h}_2}$, and/or $\mathscr{E}_{\mathbf{h}_1+\mathbf{h}_2}$ factors. The results of computing 25 invariants with the three dimensional data gave either the correct sign for $\mathscr{E}_{\mathbf{h}_1}\mathscr{E}_{\mathbf{h}_2}\mathscr{E}_{\mathbf{h}_1+\mathbf{h}_2}$ or were indefinite (5 such cases), that is, the product was close to zero. The discrepancies between the expected and computed magnitudes of $\mathscr{E}_{\mathbf{h}_1}\mathscr{E}_{\mathbf{h}_2}\mathscr{E}_{\mathbf{h}_1+\mathbf{h}_2}$ are in some cases excessive, and arise from rational dependence among the atoms. It is to be anticipated that this may often be the case because of the regular geometric arrangements of atoms in the unit cells of crystals. The required corrections to bring the expected and computed magnitudes of $\mathscr{E}_{\mathbf{h}_1}\mathscr{E}_{\mathbf{h}_2}\mathscr{E}_{\mathbf{h}_1+\mathbf{h}_2}$ into better agreement are currently being developed in our laboratory. An ideal standard deviation in the computation of this product for this crystal is $\sim 4·5$. In thirty similar calculations chosen at random for

Table 4. *Application of formula* (3·5) *illustrating how this formula may be used to initiate a phase determination from a knowledge of only the measured intensities*

	$\mathbf{h}_1$	$\mathbf{h}_2$	$\mathbf{h}_1 + \mathbf{h}_2$	$\mathscr{E}_{\mathbf{h}_1}\mathscr{E}_{\mathbf{h}_2}\mathscr{E}_{\mathbf{h}_1+\mathbf{h}_2}$		Sign of
				|exp.|	computed	$\mathscr{E}_{\mathbf{h}_1+\mathbf{h}_2}$
①	$\overline{2}14$	$\overline{2}14$	$\overline{4}28$	16·3	$+17·5$	$+$
②	211	211	422	13·0	$+ 8·3$	$+$
③	035	$0\overline{3}5$	0,0,10	9·7	$-20·5$	$-$
④	$\overline{4}04$	$\overline{4}04$	$\overline{8}08$	10·6	$+19·6$	$+$
⑤	$\overline{4}49$	$\overline{4}49$	$\overline{8},0,18$	5·7	$+51·4$	$-$
⑥	110	$1\overline{1}0$	200	7·9	$+23·2$	$-$
⑦	$\overline{8},0,18$	$80\overline{8}$	0,0,10	44·8	$+67·4$	$-$
⑧	$\overline{4}2\overline{8}$	422	0,0,10	16·2	$- 6·0$	$-$
⑨	422	200	622	13·0	$-14·7$	$+$

the mineral spurrite, using (3·5) generalized for unequal atoms, it was found that the agreement between the expected and computed magnitudes of $\mathscr{E}_{h_1}\mathscr{E}_{h_2}\mathscr{E}_{h_1+h_2}$ was much better than that illustrated in Table 4, falling usually within one standard deviation.

Table 4 represents a possible sequence of calculations illustrating how the phase determination may be started. The first six examples show how a phase is obtained without any previous knowledge of phases. The last three examples show how previously determined phases may be used to obtain new ones or to verify ones which had been determined earlier. In the first four cases $\mathscr{E}_{h_1}$ and $\mathscr{E}_{h_2}$ have the same sign, hence their product is always positive. The sign of the unknown $\mathscr{E}_{h_1+h_2}$ will be the sign of the triple product $\mathscr{E}_{h_1}\mathscr{E}_{h_2}\mathscr{E}_{h_1+h_2}$. In the fifth and sixth instances, the signs of $\mathscr{E}_{h_1}$ and $\mathscr{E}_{h_2}$ are opposite to each other for this space group; hence their product is always negative and the sign of the unknown $\mathscr{E}_{h_1+h_2}$ is opposite to that of the triple product. After several phases of the ggg type are obtained in this manner, they can be combined with themselves or with origin determining phases to obtain others. Examples seven and eight illustrate two other ways, in addition to example three, for obtaining the sign of 0,0,10. In seven, $\mathscr{E}_{\bar{8},0,18}$ is negative and $\mathscr{E}_{\bar{8},0,8}$ is positive. Since the triple product is positive, 0,0,10 must be negative. In eight, both $\mathscr{E}_{\bar{4}\bar{2}8}$ and $\mathscr{E}_{422}$ are positive; but the triple product is negative, hence 0,0,10 is again negative (in contradiction to Σ_2). The use of the triple product formula confirms the negative sign for 0,0,10. Examples eight and nine are illustrations of how exceptions of certain contributors to Σ_2 can be revealed by the triple product formula. In the last example, $\mathscr{E}_{422}$ is positive, $\mathscr{E}_{200}$ is negative; but the triple product is negative, hence $\mathscr{E}_{622}$ must be positive, again in contradiction to the contribution of this combination to Σ_2. All the signs determined in Table 4 are correct. Clearly, calculations of the type illustrated in this table would form a sound basis for proceeding with Σ_2 in an unambiguous fashion.

4. Refinement

The approximate coordinates for the molecule were refined by the three dimensional least squares-program prepared for the IBM 704 by Dr W. Busing of Oak Ridge, Tennessee. Each atom was assigned a different isotropic temperature factor. The refinement was terminated when the change in the positional coordinates was insignificant, even though the R factor was still decreasing. No refinement was attempted with anisotropic temperature factors, nor was any attempt made to include the hydrogen atoms. Probably a better R factor would have been obtained if each layer had been scaled individually in the refinement. The final figures for the R factor were: $R(hkl) = 16·7\%$ with non-observed reflections omitted and $R(hkl) = 21·6\%$ for all data.

Table 5. *Fractional coordinates referred to the monoclinic axes and isotropic temperature factors*

Atom	x	y	z	B
C_1	0·2681	0·1101	0·2711	3·40
C_2	0·2299	0·9588	0·2101	4·04
C_3	0·3312	0·8130	0·2199	5·05
C_4	0·4723	0·8116	0·2954	5·34
C_5	0·5067	0·9560	0·3560	5·11
C_6	0·4086	0·1053	0·3455	4·49
C_7	0·1550	0·2724	0·2549	3·96
C_8	0·2566	0·5718	0·3641	4·65
C_9	0·2866	0·6530	0·4326	5·11
C_{10}	0·2494	0·5324	0·4817	4·67
C_{11}	0·1632	0·3199	0·4348	3·48
C_{12}	0·1390	0·2475	0·3666	3·64
C_{13}	0·0994	0·1842	0·4634	3·71
N_1	0·1815	0·3621	0·3278	3·92
N_2	0·1177	0·2551	0·5298	4·89
O	0·0327	0·0033	0·4274	4·58

Final coordinates for the atoms listed as fractions of the unit cell edges and the isotropic temperature factor B for each atom are listed in Table 5. The isotropic temperature factors range from 3·40 to 5·34 and average 4·36 for the carbon atoms, 4·40 for the nitrogen atoms, and 4·58 for the oxygen atom.

A copy of the observed and calculated structure factors has been deposited at the Library of Congress, Washington, D.C. (Call No. 6551).

5. Structure

Electron density projections on (010) and (100) are illustrated in Figs. 2(a) and (b), respectively. A comparison of Fig. 2(a) with Fig. 1, an incorrect representation of the structure, shows that the only essential difference between the two is a shift of ~ 1 Å along the z direction, corresponding to a change from $+(0,0,10)$ to $-(0,0,10)$ along with many other sign changes. Fig. 3 illustrates the contents of a unit cell, projected on (010), and shows the existence of dimers by the formation of N–H $\cdots$ O type hydrogen bonds across centers of symmetry. The molecules lie along the (102) directions. The lack of any type of bonding across the (102) directions, no doubt, accounts for the lath like shape of the crystals. Bond lengths and angles of the N-benzyl dihydronicotinamide molecule are shown in Figs. 4(a) and (b). The standard deviations in coordinates are listed in Table 6. Standard deviations in bond lengths are approximately 0·012 Å and in bond angles 1·0°.
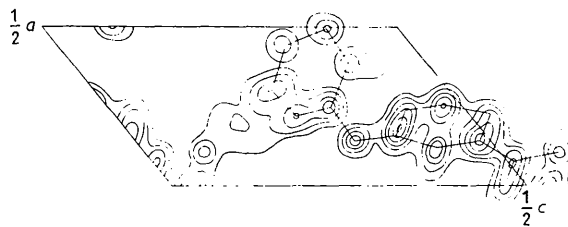

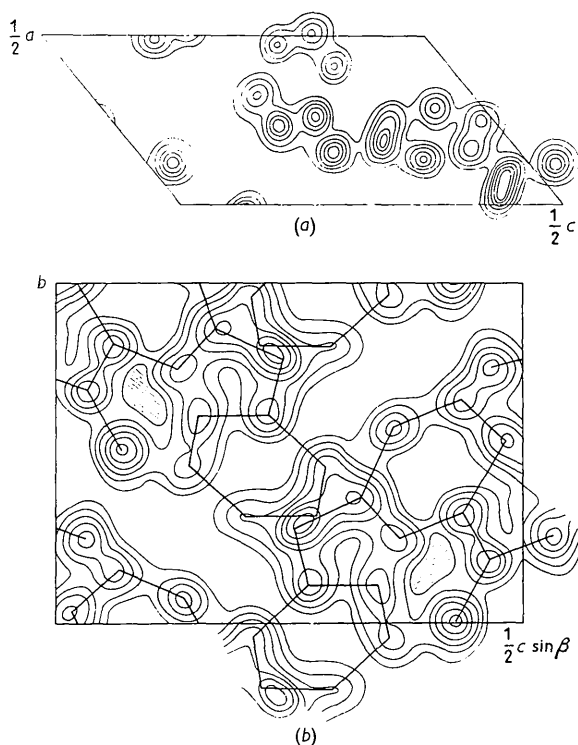Fig. 1. An initial electron-density projection on (010) depicting an incorrect structure.

joins the two rings in the molecule, from this average plane are listed in Table 7. The r.m.s. distance of the benzene ring atoms from the plane is 0·013 Å.
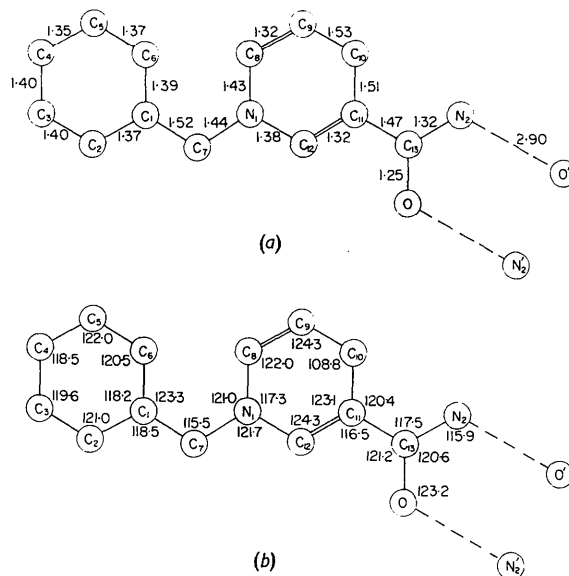

(a)

(b)

Fig. 4. (a) Bond lengths in N-benzyl dihydronicotinamide.
(b) Angles in N-benzyl dihydronicotinamide.

The dihydronicotine ring is also planar and is described by the equation

$$-2 \cdot 6195 X' + 1 \cdot 5388 Y' + 0 \cdot 0227 Z' + 1 = 0 .$$

The distances of the dihydronicotine ring atoms, C_7, and the amide group from this average plane are listed in Table 8. The r.m.s. distance of the dihydronicotine ring atoms from this plane is 0·019 Å. A plane passed through the amide group intersects the plane through the dihydronicotine ring in an angle of less than 4°, hence the amide group can be considered to be nearly coplanar with the dihydronicotine ring. The plane of the benzene ring intersects the plane of the dihydronicotine ring in an angle of 83°.
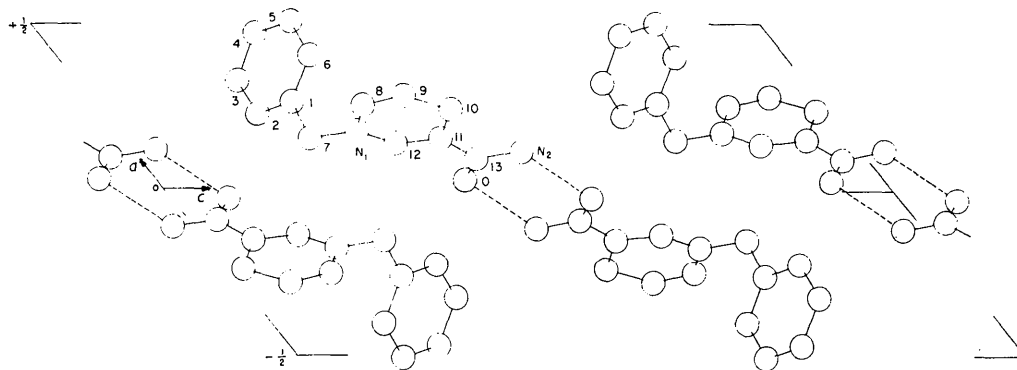

(a)

(b)

Fig. 2. (a) Final electron density projection on (010).
(b) Final electron density projection on (100).

Table 6. *Standard deviations*

	$\sigma(x)$	$\sigma(y)$	$\sigma(z)$
Carbon	0·008 Å	0·007	0·007
Nitrogen	0·007	0·006	0·007
Oxygen	0·005	0·005	0·006

The benzene ring is well described by the equation

$$-0 \cdot 0936 X' - 0 \cdot 2596 Y' + 0 \cdot 2555 Z' + 1 = 0 ,$$

where X', Y', and Z' refer to orthogonal axes such that

$$X' = X \sin \beta, \quad Y' = Y, \quad \text{and} \quad Z' = X \cos \beta + Z .$$

Distances of the benzene ring atoms and C_7, which

Fig. 3. The contents of a unit cell projected on (010) illustrating the dimers formed by hydrogen bonds across symmetry centers.

Table 7. *Distances of atoms from an average plane through the benzene ring*

Atom	Δ	Atom	Δ
C_1	-0.014 Å	C_5	$+0.011$ Å
C_2	$+0.022$	C_6	-0.022
C_3	-0.013		
C_4	-0.003	C_7	-0.047

Table 8. *Distances of atoms from an average plane through the dihydronicotine ring*

Atom	Δ	Atom	Δ
N_1	-0.014 Å	C_7	-0.077 Å
C_8	$+0.006$		
C_9	$+0.015$	C_{13}	$+0.144$
C_{10}	-0.034	O	$+0.141$
C_{11}	$+0.026$	N_2	$+0.216$
C_{12}	-0.004		

The closest intermolecular distance (not involving hydrogen) is 3·22 Å between an O and C_7, the carbon linking the two rings. All other intermolecular distances are greater than 3·50 Å.

6. Discussion of structure

The configuration of the dihydronicotine ring is of particular importance since it also occurs in the co-enzyme DPNH. It is of interest to note that it is essentially planar. The two C=C bonds are 1·32 Å, the value for double bonds, and the two C–C bonds are 1·51 and 1·53 Å, essentially the expected value for a single bond. The angle formed by the single C–C bonds is tetrahedral, within the limits of error. The three bonds to the N atoms in the ring are coplanar, but not equal. The two C–N distances in the ring are 1·43 and 1·38 Å. Similar differences in C–N distances in heterocyclic rings have been previously noted, for example, in caffeine (D. June Sutor, 1958).

The amide group is nearly in the plane of the dihydronicotine ring, i.e. within 4°. This differs markedly from the situation in benzamide (Penfold & White, 1959) and nicotinamide (Wright & King, 1954) where the amide group is twisted 26° and 24° respectively, from the plane of the ring. The explanation for non-planarity in the latter two molecules is steric hindrance between a hydrogen in the NH_2 group and a hydrogen on the ortho ring carbon. In the present molecule such steric hindrance apparently does not occur since the two hydrogens on the ring ortho carbon atom, C_{10}, can straddle the hydrogen from the NH_2 group.

The distances in the amide group are similar to those found in benzamide (Penfold & White, 1959). They are listed in Table 9. The length of the N–H · · · O hy-

drogen bond agrees with values found in many other molecules.

Table 9. *Bond lengths and angles in the amide group*

Bond or angle	This molecule	Benzamide
C–C	1·47 Å	1·48
C–N	1·32	1·31
C–O	1·25	1·24
O–C–N	120·6°	122°
C–C–N	117·5	116
C–C–O	121·2	122
N–H · · · O	2·90 Å	2·96

The average bond in the benzene ring is 1·38 Å. The variation among the individual bonds is similar to that usually found in benzene rings. The bond length of C_1–C_7, 1·52 Å, is essentially that of a single bond. The intermolecular distance of 3·22 between C_7 · · · O is not unusual. Short intermolecular C · · · O distances have occurred, for example, in nicotinamide, 3·24 Å, (Wright & King, 1954) and (p-ClC_6H_4)$_2SO_2$, 3·21–3·27 Å, (Sime & Abrahams, 1960).

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