TABLE III

ANAEROBIC FERMENTATION OF CELLULOSE, *p*H 7.4, FIVE DAYS, 37°

Expt.	Cellulose in medium g./150 cc.	Fermented g./150 cc.	% cellulose decomposed
1	1.52	0.95	62.5
2	1.40	.96	68.5
3	1.55	1.01	65.3
4	1.45	1.01	70.0
5	1.43	0.92	64.5
Av.	1.47	.97	66.1

TABLE IV

ANAEROBIC FERMENTATION OF CELLULOSE, *p*H 6, FIVE DAYS, 37°

Expt.	Cellulose in medium g./150 cc.	Fermented g./150 cc.	% cellulose decomposed
6	1.50	0.21	14.1
7	1.48	.28	19.0
8	1.47	.24	16.3
9	1.49	.27	18.1
10	1.46	.22	15.2
Av.	1.48	.24	16.5

Anaerobic Fermentation Experiments on Cellulose Humic Acids, Lignin, Lignin Humic Acids, and Humic Acids from Peat.—The above materials were exposed to the action of the anaerobic cellulose-fermenting bacteria under the same conditions as were used in the control experiments on cellulose. None of these products could be fermented by those cultures which were active on cellulose. Even after four weeks no fermentation could be obtained with *p*H 7.4 and 6.

We thank Professor Harold L. Lang for his kind support of this investigation.

Summary

1. (a) A cellulose fermenting bacillus isolated from horse-dung showed in agreement with Sineszko a decomposition of approximately 70% of the cellulose used. Fermentation products are volatile acids, non-volatile acids, and alcohol in medium of *p*H 7.4. (b) The fermentation in medium of *p*H 6 by the same bacteria showed a decomposition of about 20% of the original cellulose.

2. Fermentation experiments carried out with the same culture on cellulose humic acids, lignin, lignin humic acids, and humic acids from peat showed that none of those products can be fermented, neither in medium of *p*H 7.4 or *p*H 6, even after four weeks of incubation.

3. (a) The anaerobic cellulose fermenting *amylobacter navicula* isolated from human feces as described by Clausen showed a fermentation of 63% of cellulose in salt medium of *p*H 7.4 under anaerobic conditions. (b) The same culture in medium of *p*H 6 fermented cellulose in an amount of approximately 15%.

4. Fermentation experiments carried out with the same culture on cellulose humic acids, lignin, lignin humic acids, and humic acids from peat showed that none of those products can be fermented, neither in medium of *p*H 7.4, nor *p*H 6, even after four weeks of incubation.

These experiments prove that derivatives of carbohydrates, like cellulose humic acids, which are formed from carbohydrates of plants are resistant toward the action of bacteria used in these experiments. These cellulose humic acids probably form bituminous coals and crude oil without further activity of bacteria.

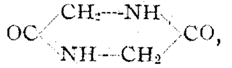
PITTSBURGH, PENNA. RECEIVED MARCH 16, 1938

[CONTRIBUTION FROM GATES AND CRELLIN LABORATORIES OF CHEMISTRY, CALIFORNIA INSTITUTE OF TECHNOLOGY, No. 649]

The Crystal Structure of Diketopiperazine

BY ROBERT B. COREY

Introduction

For many years 2,5-diketopiperazine, "glycine anhydride,"  $OC\begin{smallmatrix}CH_2-NH\\NH-CH_2\end{smallmatrix}CO$, has been of considerable interest to those concerned with the constitution of proteins. Substituted diketopiperazines have been shown to be present among the products of protein hydrolysis[1] and much experimental evidence has suggested that these compounds might play a major role in the elucidation of the structure of protein molecules.[2] Although this importance of diketopiperazine as a basic unit in protein chemistry is not now generally conceded, its relation to the amino acids and dipeptides renders a determination of its structure of fundamental value to further knowledge of these compounds. The present investigation was therefore

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(1) E. Abderhalden and W. Stix, *Z. physiol. Chem.*, **132**, 238 (1924).

(2) E. Klarmann, *Chem. Rev.*, **4**, 51 (1927).

undertaken as a part of a program of research on the structure of proteins now being carried on in this Laboratory.

Bernal, in an extensive survey,[3] tabulated the results of a preliminary study of fifteen amino acids and related compounds, including diketopiperazine, by means of X-rays. Diketopiperazine is there described as having a monoclinic unit with $a_0 = 5.19$ Å., $b_0 = 11.5$ Å., $c_0 = 3.96$ Å., $\beta = 83°$, containing two molecules. The space group is $C_{2h}^5 - P2_1/a$. Cleavage is along (010) and (101). The crystals possess negative birefringence with α nearly perpendicular to (101), indicating approximately flat molecules lying in or near this plane. From these data he inferred that "diketopiperazine is built from centro-symmetrical, almost flat, hexagonal molecules linked together in ribbons by their residual electrical forces." No attempt was made, however, to determine from X-ray intensity data the positions of the atoms in this compound or in any other of the compounds studied.

Experimental

The crystals used in this study were prepared by G. A. Albrecht. They consisted of monoclinic prisms, varying in shape from thin needles, elongated in the direction of the *c*-axis, to tiny tabular specimens, less than a half-millimeter in greatest dimension.

Goniometric measurements of the crystals, oscillation and rotation photographs and Weissenberg photographs taken about the *b*- and *c*-axes, using Cu–K radiation, showed diketopiperazine to be built upon a monoclinic unit cell having the dimensions $a_0 = 5.19_2$ Å., $b_0 = 11.50_5$ Å., and $c_0 = 3.96_4$ Å. The angle β is 83 ± 1°. The general absence of all $(h0l)$ reflections having h odd and of odd orders of $(0k0)$ established the space group as $C_{2h}^5 - P2_1/a$. These observations thus confirmed the unit cell and space group previously assigned by Bernal.

Data from $(hk0)$ Reflections.—The relative intensities of $(hk0)$ reflections were obtained from a series of equatorial Weissenberg photographs made with exposure times varying from one hour to thirty-six hours. The specimen used was a needle-shaped crystal about 1 mm. long and less than 0.1 mm. in diameter. It gave sharp, well-defined spots, the intensities of which readily could be estimated by superposition of the films. The data thus obtained are listed in Table I.

The presence of two molecules in the unit cell requires the placing of four atoms each of O, C, methylene C, and N in the four general positions $xyz, \bar{x}\bar{y}\bar{z};\ {}^1/_2 - x, y + {}^1/_2, \bar{z};$ and $x + {}^1/_2, {}^1/_2 - y, z$. This results in a grouping of the atoms in pairs about two centers of symmetry which are connected by the operation of the glide-plane at $y = {}^1/_4$ with glide parallel to the *a*-axis. For convenience, the atoms were arranged about the center of symmetry at $({}^1/_2\ {}^1/_2\ {}^1/_2)$ and its equivalent $(00{}^1/_2)$, each of which thus became the center of symmetry of a molecule.

As a first tentative model, the bonds between C, CH_2, and NH were assumed to form tetrahedral angles with each other to give a "puckered" ring similar to that found for such saturated, six-membered ring structures as benzene hexabromide and hexachloride,[4] dioxane,[5] cyclohexane,[6] and paraldehyde.[7] The C–O bond was oriented so as to be coplanar with the adjacent C–C and C–N bonds and to form equal angles with them. The interatomic distances within the molecule were assumed to be C–O, 1.25 Å., C–N, 1.47 Å., and C–C, 1.54 Å. Packing radii for determining contacts between atoms, or groups, in different molecules were taken as O, 1.35 Å., C, 0.77 Å., CH_2, 1.86–2.00 Å., and NH, 1.5–1.8 Å. Space-filling considerations alone soon made it apparent that CH_2 and NH groups could not lie far from the (101) plane, and investigations were thus limited to rotations near this plane about the center of symmetry.

In all calculations the scattering power of oxygen was assumed to be that determined in single crystals of urea.[8] For carbon and nitrogen the values used were those found in urea and hexamethylenetetramine.[9]

Although some regions were found in which approximate packing was attained, no agreement could be reached between observed and calculated intensities for even the simplest planes. Planes (200), (110), (020), (040), (210), and (120) were most useful since, if the contribution of oxygen were disregarded, the values for their scattering powers were practically unaffected by the angular position of the C–N–C ring. By their use it could be shown that no parameters whatsoever

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(3) J. D. Bernal, *Z. Krist.*, **78**, 363 (1931).

(4) R. G. Dickinson and C. Bilicke, THIS JOURNAL, **50**, 764 (1928).

(5) L. E. Sutton and L. O. Brockway, *ibid.*, **57**, 473 (1935).

(6) L. Pauling and L. O. Brockway, *ibid.*, **59**, 1223 (1937).

(7) D. C. Carpenter and L. O. Brockway, *ibid.*, **58**, 1270 (1936).

(8) R. W. G. Wyckoff, *Z. Krist.*, **81**, 102 (1932).

(9) (a) R. W. G. Wyckoff, *ibid.*, **75**, 529 (1930); (b) R. W. G. Wyckoff and R. B. Corey, *ibid.*, **89**, 462 (1934).

could be assigned to the oxygen atom which would bring agreement between observed and calculated intensities. This model therefore had to be abandoned.

A completely coplanar molecule was next assumed, with interatomic distances the same as in the preceding one except that the distance between the keto carbon and the nitrogen atom was shortened to 1.32 Å. The bond angles were taken to be C–N–C, 110°; N–C–CH_2, 125°; C–CH_2–N, 125° and N–C–O, 117°. This molecule was rotated about the center of symmetry with all atoms in the (101) plane. Excellent agreement for all sixty (*hk*0) reflections was obtained when a line joining the oxygen atoms made an angle of 35° with the XZ-plane, corresponding to the parameters.

O : $x = 0.15$, $y = 0.37$
C : $x = 0.32$, $y = 0.43$
CH_2 : $x = 0.545$, $y = 0.37$
NH : $x = 0.29$, $y = 0.545$

Inspection of the structure factors showed that no change was to be expected in the signs (except in the case of "absent" reflections) without major alterations in atomic positions. A two-dimensional Fourier analysis of the distribution of scattering power in the crystal unit projected on the (001) plane was made according to the equation

$$\rho(x,y) = \text{constant } \Sigma_h \Sigma_k F_{(hk0)} \cos 2\pi(hx + ky)$$

using the observed F's for all planes with signs obtained from the structure factors as listed in Table I. The plot of $\rho(x,y)$ over half of the unit cell is shown in Fig. 1. The positions of the peaks as shown by contour lines indicate small but definite changes in the positions of all atoms except carbon. The corresponding parameters then become

O : $x = 0.160$, $y = 0.368$
C : $x = 0.320$, $y = 0.430$
CH_2 : $x = 0.545$, $y = 0.380$
NH : $x = 0.280$, $y = 0.544$.

In Table I structure factors calculated from these parameters are compared with those obtained from the estimated intensities.

TABLE I

INTENSITIES AND STRUCTURE FACTORS FOR (*hk*0) REFLECTIONS

Indices	Intensities Obsd.	Intensities Corr.	Obsd. *F*	Calcd. *F*
020	4200	7250	31.5	33.8
110	700	753	11.2	15.9
120	665	713	11.9	19.9
130	0	0	0	5.4
040	2800	3890	33.9	–34.4
200	1120	1260	20.7	–25.7
210	560	593	14.4	–18.1
140	182	185	8.0	– 9.0
220	560	593	15.0	–18.6
230	175	178	8.8	–12.0
150	26	26	3.4	– 4.9
240	63	63	5.6	– 5.4
060	70	70	5.9	– 6.5
160	525	554	17.5	–21.0
250	280	288	13.0	13.0
310	0	0	0	0.7
320	30	30	4.3	.8
330	280	288	14.2	–13.5
170	26	26	4.2	– 6.5
260	7	7	2.2	1.8
340	28	28	4.5	5.4
080	28	28	4.6	5.9
270	21	21	4.1	4.2
180	56	56	6.7	– 4.9
350	54	54	6.6	– 6.7
400	0	0	0	0.3
360	91	92	9.1	7.9
410	0	0	0	2.6
280	70	70	8.0	8.9
420	23	23	4.6	4.7
190	0	0	0	– 0.7
430	0	0	0	1.1
370	210	214	14.2	14.0
440	26	26	5.0	5.7
0, 10, 0	91	92	9.5	– 9.0
290	161	164	12.7	–10.6
450	0	0	0	– 1.6
1, 10, 0	0	0	0	– 0.6
380	28	28	5.3	5.1
2, 10, 0	53	53	7.3	7.5
460	0	0	0	– 1.2
1, 11, 0	0	0	0	1.2
390	77	78	8.7	8.0
510	35	37	5.8	5.0
520	98	99	9.7	–11.3
470	26	26	5.0	2.9
530	26	26	5.0	4.2
540	14	14	3.5	1.4
2, 11, 0	53	53	6.8	4.9
480	0	0	0	– 3.4
0, 12, 0	98	99	9.3	–10.1
3, 10, 0	0	0	0	0.8
550	0	0	0	.2
1, 12, 0	28	28	5.0	3.8
490	56	56	6.5	5.9
560	7	7	2.3	4.3
2, 12, 0	0	0	0	2.9
3, 11, 0	19	19	3.6	– 3.9
570	56	56	6.0	– 3.6
600	21	21	3.5	4.7

Data from (*h*0*l*) **Reflections**.—Considerable difficulty was experienced in obtaining a crystal which would yield good photographs when rotated about the *b*-axis. Although most of the thin, needle-like crystals were comparatively perfect and gave excellent reflections, their elongation in the *c*-direction made them of little value for the collection of data about [010]. Attempts were made to mount such specimens rigidly on the *b*-axis and then reduce them to cylindrical form by dissolving away the end portions, but the excessive softness and fragility of the crystals rendered such efforts fruitless. It was therefore necessary to select tiny tabular specimens having dimensions as nearly equal in all directions as possible. Such crystals were generally very imperfect as the result of twinning and internal strains and distortion. Two specimens were finally selected which gave good equatorial reflections with the Weissenberg camera, the first about 0.7 mm. and the second less than 0.3 mm. in greatest dimension. Even with these samples, the slight differences in shape of reflections from planes of widely different position made the estimation of relative intensities less exact than in the case of (*hk*0) reflections. Added to this was the fact that the scattering powers of most planes were structurally weak, so that long exposures, in one case seventy-two hours, were necessary. The estimated intensities and scattering powers calculated from them for all (*h*0*l*) planes capable of reflection are listed in Table II.

As a start in determining the *z*-parameters, the molecule was still assumed to be completely coplanar with all atoms lying in the (101) plane and having the *x*-parameters already accurately determined from (*hk*0) reflection data. Structure factors calculated from these parameters

O : $x = 0.160, y = 0.84$
C : $x = 0.320, y = 0.68$
CH_2 : $x = 0.545, y = 0.455$
NH : $x = 0.280, y = 0.72$

showed general agreement with observed values although some planes, notably (00$\bar{2}$), (40$\bar{1}$), (20$\bar{3}$), and (204), indicated the necessity for further refinement. Since simultaneous displacement of all atoms was probable, recourse was had to a second Fourier analysis, using only those planes whose signs were considered certain. Values of the function

$$\rho(x,z) = \text{constant } \Sigma_h \Sigma_l \, F_{(h0l)} \cos 2\pi(hx + lz)$$

were plotted along lines of constant *x* corresponding to this parameter for each atom. Definite changes in all *z*-parameters were indicated from which structure factors were calculated, to determine the signs of planes previously in doubt. All planes were then introduced into the Fourier summation and the positions of the resulting peaks used to complete the determination

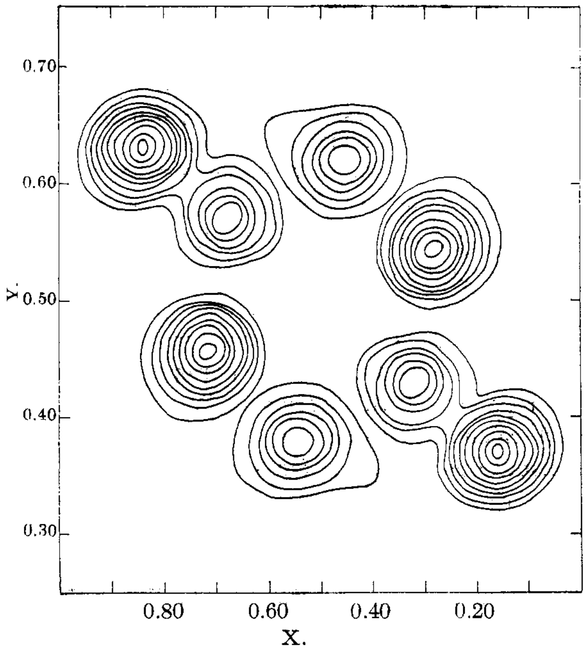


Fig. 1.—Distribution of scattering power, $\rho(x, y)$, for diketopiperazine projected upon the (001) face. Contour lines represent values of $\rho(x, y)$ from 2 to 11.

TABLE II

INTENSITIES AND STRUCTURE FACTORS FOR (*h*0*l*) REFLECTIONS

	Intensities				Obsd. *F*		
	Cryst. 1		Cryst. 2				
Indices	Obsd.	Corr.	Obsd.	Corr.	Cryst. 1	Cryst. 2	Calcd. *F*
001	290	339	425	546	8.4	10.6	−11.3
200	670	1032	500	676	18.7	15.1	−25.7
201	260	299	170	186	10.9	8.6	−12.2
$20\bar{1}$	125	133	160	175	7.8	9.0	− 5.8
002	30	30	54	55	3.8	5.2	− 8.2
202	1000	2075	960	1917	35.6	34.2	36.4
$20\bar{2}$	4	4	5	5	1.7	1.9	− 1.8
003	8	8	8	8	2.6	2.6	− 0.1
400	4	4	5	5	1.8	2.1	.3
401	0	0	0	0	0	0	− 4.3
203	0	0	0	0	0	0	1.1
$40\bar{1}$	125	133	150	163	11.3	12.5	−10.5
402	60	60	80	83	7.6	9.0	−12.1
$20\bar{3}$	250	287	320	384	16.8	19.5	−15.3
$40\bar{2}$	60	60	70	73	7.6	8.4	6.7
004	10	10	10	10	3.0	3.1	− 1.2
403	10	10	20	20	3.0	4.3	− 3.8
204	0	0	0	0	0	0	1.3
$20\bar{4}$	12	12	19	19	2.8	3.5	3.3
$40\bar{3}$	120	129	80	83	8.7	7.0	9.3
601	1	1	5	5	0.7	1.7	− 0.5
600	17	17	25	25	3.2	3.8	4.6
404	6	6	10	10	1.6	2.2	6.0
602	0	0	0	0	0	0	1.1
$60\bar{1}$	125	133	85	89	7.4	6.0	6.7

of the atomic arrangement. The final parameters were found to be

O : $x = 0.160$, $y = 0.368$, $z = 0.885$
C : $x = 0.320$, $y = 0.430$, $z = 0.705$
CH_2 : $x = 0.545$, $y = 0.380$, $z = 0.495$
NH : $x = 0.280$, $y = 0.544$, $z = 0.695$

A comparison of the observed scattering powers of all ($h0l$) planes with those calculated for these positions is shown in Table II. Although careful study of both the Fourier plot and structure factor calculations failed to give justification for any departures from these parameters, certain discrepancies in the agreement between observed and calculated values are to be noted. Most conspicuous is (404), for which the calculated scattering is about equal to that of $(60\bar{1})$ but which gave faint reflections on all films. The reason for this is doubtless to be found in the fact that this plane is practically parallel with the plane of the molecule, a position for which thermal agitation would have greatest effect in reducing the atomic scattering factors with increased sin θ. Thus it is seen that for planes (201), (002), (401), and (402) the intensity observed is less than that calculated, whereas the reverse is true for planes $(20\bar{1})$, $(40\bar{1})$, and $(20\bar{3})$. The positions of these planes relative to the plane of the molecule are shown in Fig. 2. It is seen that those having positive index l are more nearly parallel to the molecular plane than are those of negative index. Discrepancies in these cases are thus doubtless to be attributed in part to the predictable effect of orientation upon atomic scattering factors in crystals of this and similar structure.

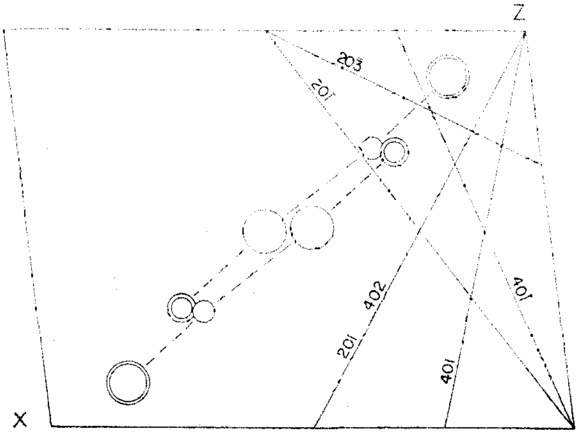


Fig. 2.—The relative positions of some planes (having positive and negative values of l) with respect to the plane of the molecule.

Discussion of the Structure

The positions of the atoms in an elementary unit cell and in three adjacent cells are shown in Fig. 3a. The molecule of diketopiperazine is found to be a nearly plane hexagon inclined at about 5.5° to (101). Interatomic distances within the molecule are C–O, 1.25 Å.; C–N, 1.33 Å.; C–C, 1.47 Å.; and N–CH_2, 1.41 Å., all accurate to about ± 0.03 Å.

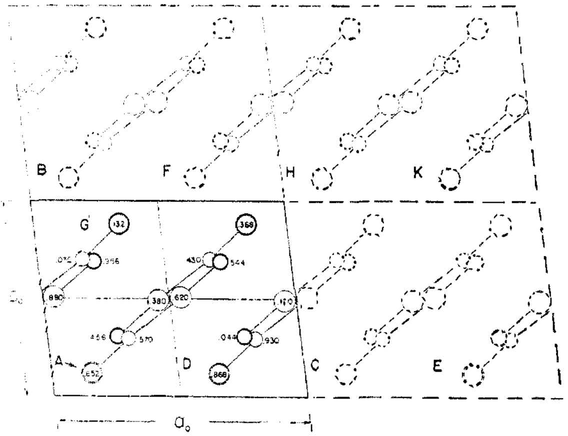


Fig. 3a.—Arrangement of diketopiperazine molecules in the unit cell. Numerals show the y-parameters of the atoms. Letters refer to subsequent packing drawing.

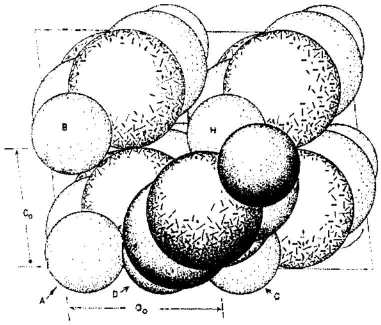
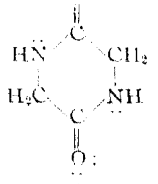
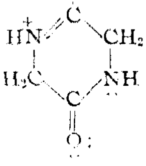
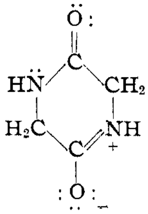


Fig. 3b.—A packing drawing of diketopiperazine viewed along the b-axis showing four molecules in the same layer at the centers of adjacent unit cells and one in the layer immediately above.

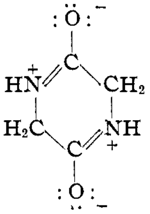
The molecule may be expected to resonate among the structures


I


II



III



IV

The bond distances for C–O and C–N should then have the values characteristic of resonance of this type, which are about 1.25 and 1.33 Å., respectively, as observed. Similar values are also found for other resonating molecules of like type.[6] In urea[9b] the interatomic distances within the molecules were found to be C–O, 1.24 Å. and C–NH_2, 1.37 Å., and in thiourea[10] C–NH_2 is 1.35 Å. The shortening of the CH_2–N and CH_2–C distances below the single bond values 1.47 and 1.54 Å., respectively, is surprising. It is possible that it is to be attributed, in part at least, to the effect of electric charge,[11] and perhaps to a resonance of a new type, involving double bonds with the methylene group. It is of interest that in hexamethylenetetramine[9b] the separation CH_2–N is 1.42 Å., almost exactly that found in the present structure (1.41 Å.).

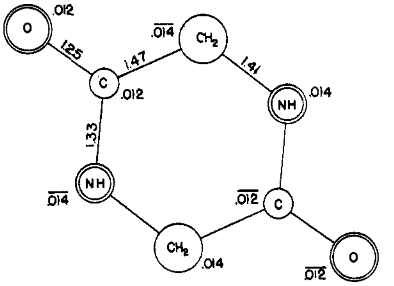


Fig. 4.—The diketopiperazine molecule as viewed perpendicular to a median plane. Dimensions are in Ångström units.

The angles between all bonds are 120 ± 3°. The extent to which the molecule, indicated by the parameter values, departs from true planarity is most readily shown by passing a median plane between the atoms and observing the distance of each atom from this plane. Figure 4 is a view perpendicular to such a plane in which numerals, positive and negative, show the distances in Ångström units of each atomic position above and below it. It is seen that none deviates from the plane by as much as 0.015 Å., which is within the limit of error of the determination of the atomic positions themselves. The completely coplanar configuration is, of course, expected for resonance among the structures I to IV, in consequence of the stereochemical properties of the C–N double bonds in the ring. Thus the observed coplanarity provides strong evidence for resonance, inasmuch as all known six-membered rings, involving only single bonds, are puckered.[4–7]

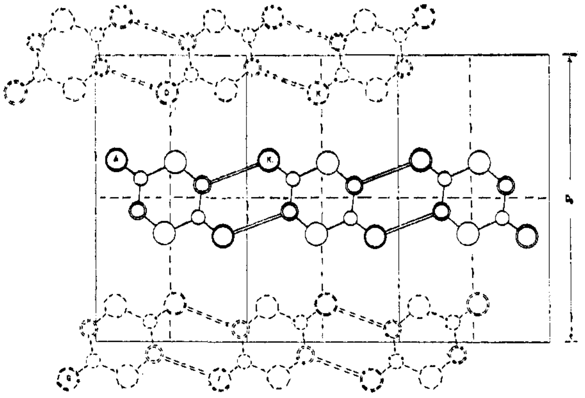


Fig. 5a.—A view perpendicular to (101) showing chains of molecules held together by hydrogen bonds.

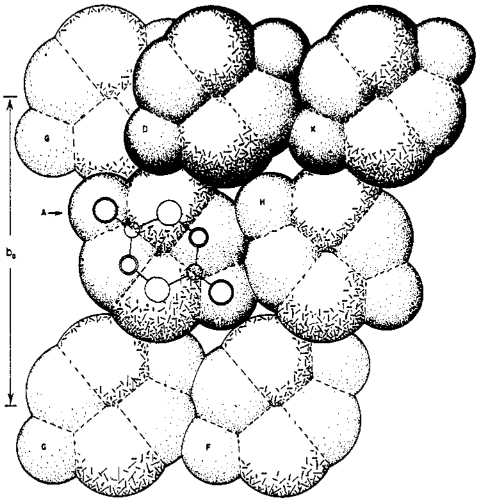


Fig. 5b.—A packing drawing of some of the molecules of Fig. 5a. The radius of the carbon atom is too small to permit its appearance in this and other packing figures.

The packing of the molecule is shown in Figs. 3b, 5b, and 6. In these drawings CH_2 is given a radius of 1.98 Å.; NH, 1.8 Å. and O, 1.35 Å. The radius of carbon (0.77 Å.) is too small to permit its appearance. Each CH_2 group is at a distance of 3.96 Å. from four other CH_2 groups, two in the same layer with it and two others above or below.

(10) R. W. G. Wyckoff and R. B. Corey, *Z. Krist.*, **81**, 386 (1932).

(11) N. Elliott, THIS JOURNAL, **59**, 1380 (1937).

Figure 3b shows the packing of adjacent CH_2 groups in the same layer, contacts between those in different layers being indicated in Figs. 5b and 6. Each oxygen is in contact with two CH_2 groups, one at 3.32 Å. in the same layer (B in Fig. 3b) and one at 3.33 Å. in the layer above or below (C in Figs. 3b and 6). Each nitrogen is distant 3.55 Å. from a CH_2 group (molecules A and B, Fig. 6) and 3.69 Å. from another nitrogen (Fig. 5b). The very pronounced cleavage along (010) and that along (101) are clearly brought out in Fig. 6.

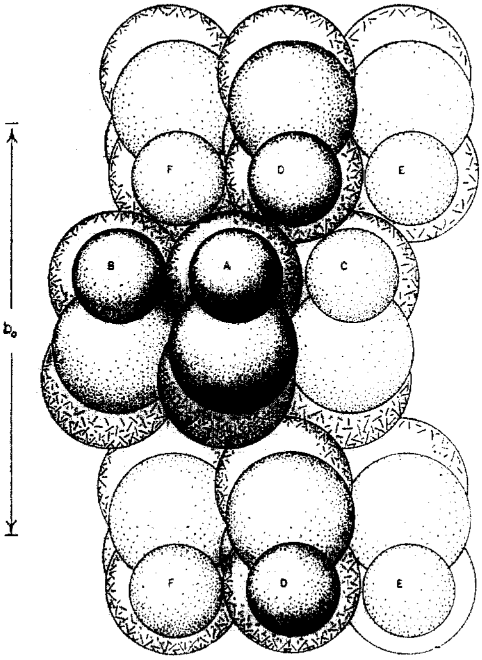


Fig. 6.—A packing drawing of the molecules of diketopiperazine viewed in the direction of the molecular chains.

Assuming tetrahedral bond angles and a C–H distance 1.08 Å., parameters could be assigned to the two methylene hydrogen atoms as follows

H_1: $x = 0.658$, $y = 0.334$, $z = 0.664$
H_2: $x = 0.472$, $y = 0.319$, $z = 0.322$

The distances between hydrogen atoms in adjacent methylene groups then become 2.68 Å. in the same layer, and 2.66 Å. in the next layer. These separations correspond to an atomic domain for hydrogen of radius 1.33–1.34 Å., which is slightly greater than the value 1.29 Å. suggested by Mack[12] from consideration of the packing of organic molecules in which there is no free rotation. Distances between oxygen and hydrogen are 2.57 Å. in the same layer and 2.48 Å. in the next layer, which are slightly less than analogous distances (2.68–2.70 Å.) observed in metaldehyde.[13]

Acknowledgments.—This investigation has been made possible by the financial support of the Rockefeller Institute for Medical Research and the courtesy of the California Institute of Technology in providing the facilities of its laboratories. The author is indebted to Professor Linus Pauling for proposing the subject of this research and for his many suggestions and criticisms throughout the progress of the work, to Dr. J. H. Sturdivant for assistance with experimental details, and to W. R. Newton for the construction of special equipment.

Summary

X-Ray examination of crystals of 2,5-diketopiperazine shows them to be built upon a simple monoclinic unit having $a_0 = 5.19$ Å., $b_0 = 11.50$ Å., $c_0 = 3.96$ Å., and $\beta = 83°$, containing two molecules. All atoms are in the general positions of the space group $C_{2h}^5 - P2_1/a$ with the following parameters: oxygen, $x = 0.160$, $y = 0.368$, $z = 0.885$; carbon, $x = 0.320$, $y = 0.430$, $z = 0.705$; methylene carbon, $x = 0.545$, $y = 0.380$, $z = 0.495$; nitrogen, $x = 0.280$, $y = 0.544$, $z = 0.695$. The molecule is a nearly flat hexagonal ring possessing a center of symmetry, the angles between all bonds being 120 ± 3°. The interatomic distances within the molecule are: carbon–oxygen 1.25 Å., carbon–carbon 1.47 Å.; carbon–nitrogen 1.33 Å. and nitrogen–methylene carbon 1.41 Å., each ± 0.03 Å. All molecules are held together by hydrogen bonds to form long, parallel chains throughout the crystal. Packing of the molecules is discussed.

PASADENA, CALIFORNIA RECEIVED MAY 9, 1938

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[12] E. Mack, THIS JOURNAL, **54**, 2141 (1932).

[13] L. Pauling and D. C. Carpenter, *ibid.*, **58**, 1274 (1936).