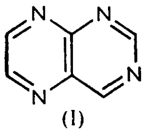
692. *The Crystal and Molecular Structure of Pteridine.*

By T. A. Hamor and J. Monteath Robertson.

Pteridine (I) crystallises in the non-centrosymmetric space group $Pna2_1$ with four molecules per unit cell. *X*-Ray analysis shows that the molecule is planar to within 0·06 Å, with standard deviations in co-ordinates of about 0·03 Å. The carbon–nitrogen bond lengths vary between 1·28 and 1·41 Å, and the carbon–carbon lengths between 1·35 and 1·42 Å. These measurements have been compared with molecular-orbital calculations of the bond lengths.

Pteridine (I), which is the parent substance of a large number of naturally occurring compounds of biological importance, is highly unstable, being rapidly decomposed by dilute acid and alkali at room temperature. In solution it is decomposed on exposure to daylight, but the solid, although volatile, can be preserved without much difficulty. In the course of an extensive study of the simpler natural and synthetic pteridines, Albert [1] has found that they are, in general, unstable to acid and alkali unless powerfully electron-donating groups (hydroxyl, amino, etc.) are present, and he has further pointed out that this instability appears to be due to the fact that in pteridine the four ring-nitrogen atoms are competing for the π-electrons contributed by the six carbon atoms. The aromatic stabilisation is therefore much diminished and the pteridine molecule may in consequence be non-planar. Our present *X*-ray investigation of the crystal and molecular structure of pteridine has been undertaken at the suggestion of Professor Albert in order to examine this point and attempt a full determination of the structure and geometry of the molecule.



(I)

No *X*-ray structural investigation of a pteridine or any other azanaphthalene has so far been reported. The related pyrimidine, pyrazine, and purine ring systems have, however, been examined by *X*-ray and electron-diffraction methods. The work on the pyrimidines includes a very accurate three-dimensional determination of the structure of 4-amino-2 : 6-dichloropyrimidine [2] and less accurate studies of certain other trisubstituted derivatives such as 2-amino-4 : 6-dichloropyrimidine [3] and 2-hydroxy-4 : 6-dimethylpyrimidine dihydrate.[4] The pyrimidine ring was found to be planar, within the limits of the experimental errors (standard deviations are about 0·02 Å in the three-dimensional work). For the carbon–carbon and carbon–nitrogen bonds in pyrimidine Clews and Cochran [2] have suggested lengths of 1·38 and 1·33 Å, and angles of 130°, 114°, 124°, and

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[1] Albert, Brown, and Cheeseman, *J.*, 1951, 474; 1952, 1620; 1952, 4219; Albert and Brown, *J.*, 1953, 74; Albert, Brown, and Wood, *J.*, 1954, 3832; Mason, *J.*, 1955, 2336; Albert, *J.*, 1955, 2690; Albert, *Quart. Rev.*, 1952, **6**, 197.

[2] Clews and Cochran, *Acta Cryst.*, 1949, **2**, 46.

[3] Clews and Cochran, *ibid.*, 1948, **1**, 4.

[4] Pitt, *ibid.*, 1948, **1**, 168.

114° for NCN, CNC, NCC, and CCC. These values are, however, based on studies of substituted pyrimidines only.

Pyrazine has been examined in the gas phase by electron-diffraction [5] and is reported to have a planar ring. From an *X*-ray crystal investigation using three-dimensional data [6] tetramethylpyrazine is found to be planar with carbon–carbon and carbon–nitrogen bonds of 1·44 and 1·31 Å (mean), and all ring angles within 2° of 120°. In the related structures of melamine [7] and *s*-triazine [8] the rings are apparently planar.

Of substances containing the purine ring system, salts of adenine [9–10] and guanine [11] have been studied, and in both substances the purine ring has been found apparently planar, although not all the atomic co-ordinates could be accurately determined. Carbon–nitrogen bond lengths in adenine vary from 1·30 to 1·38 Å and carbon–carbon from 1·37 to 1·40 Å.

The general conclusion from these results is that the ring systems are planar, although the bonds vary in length. In most cases examined electron-donating substituents have been present, and small deviations from a planar structure would have been difficult to detect. The possibility that the pteridine ring system is non-planar is certainly not excluded.

The results of our present analysis of the pteridine structure are given below. The work has been hampered by the fact that only extremely thin crystals could be prepared. However, nearly half of the possible reflections have been observed with copper radiation in the three principal zones, and by successive two-dimensional refinements the errors have been reduced as far as possible. After allowance for the fact that the structure is non-centrosymmetrical and most of the phase constants are unrestricted, standard deviations in the final bond lengths are about 0·035 Å. The maximum displacement of the ring atoms from a planar structure is found to be 0·06 Å, and the mean displacement 0·025 Å. In view of the comparatively small number of structure factors used, these results cannot be regarded as indicating any significant departure from a strictly planar molecule. The observed carbon–nitrogen bond lengths vary between 1·28 and 1·41 Å, and the carbon–carbon bonds between 1·35 and 1·42 Å. These results have been compared with molecular-orbital calculations of the lengths, and the agreements are found in general to be within the limits of possible error.

Crystal Data.—Pteridine, $C_6H_4N_4$; *M*, 132·1; m. p. 139°; *d*, calc. 1·483, found 1·487. Orthorhombic, $a = 24{\cdot}70 \pm 0{\cdot}05$, $b = 3{\cdot}79 \pm 0{\cdot}01$, $c = 6{\cdot}32 \pm 0{\cdot}01$ Å. Volume of the unit cell, 592 Å^3. Absent spectra, $(0kl)$ when $k + l$ is odd, $(h0l)$ when h is odd. Space group, $\text{Pna}2_1$ (C_{2v}^9) or Pnam (D_{2h}^{16}). $\text{Pna}2_1$ is obtained as a result of this investigation. Four asymmetric molecules per unit cell. Absorption coefficient for *X*-rays ($\lambda = 1{\cdot}54$ Å) $\mu = 9{\cdot}74$ cm.$^{-1}$. Total number of electrons per unit cell = F(000) = 272.

Good crystals could only be obtained by vacuum-sublimation and these were in the form of extremely thin yellow plates with (100) prominently developed, and a tendency to elongate in the *b* axial direction. They are volatile at room temperature and very soluble in most common solvents.

Analysis of the Structure.—It was not found possible to distinguish between the two possible space groups on the basis of polarity tests or from a statistical examination of the intensities.[12] From the chemical structure, the molecule may have a plane of symmetry, and it may also simulate centrosymmetry rather closely. As there are only four molecules in the unit cell, the higher symmetry space group (Pnam) would demand either a molecular plane or a centre of symmetry. Although these cannot be excluded, it is found that the special positions in this space group, together with the cell dimensions and molecular-packing requirements, make any such arrangement of the molecules virtually impossible.

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[5] Schomaker and Pauling, *J. Amer. Chem. Soc.*, 1939, **61**, 1769.
[6] Cromer, Ihde, and Ritter, *ibid.*, 1951, **73**, 5587.
[7] Hughes, *ibid.*, 1941, **63**, 1737.
[8] Wheatley, *Acta Cryst.*, 1955, **8**, 224.
[9] Broomhead, *ibid.*, 1948, **1**, 324.
[10] Cochran, *ibid.*, 1951, **4**, 81.
[11] Broomhead, *ibid.*, 1951, **4**, 92.
[12] Wilson, *ibid.*, 1949, **2**, 318; Howells, Phillip, and Rogers, *ibid.*, 1950, **3**, 210.

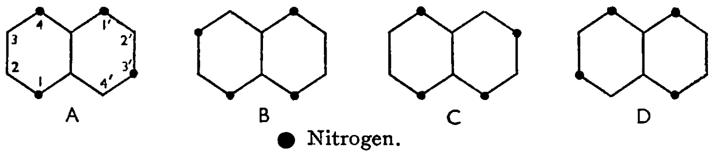
The lower-symmetry space group, $Pna2_1$, was therefore assumed, with the four molecules in general positions.

As the b axis is only 3·79 Å in length, it is safe to assume that the molecules must lie approximately in the (010) plane, the maximum permitted deviation being about 26° if a van der Waals contact distance of 3·4 Å is to be maintained between the molecular planes. A clue regarding the relative positions of the molecules in the unit cell is provided by the fact that the ($h00$) reflections are only present when $h = 4n$, up to the 24th order. This complete quartering means that the x co-ordinate of the centre of the reference molecule must be rather accurately $a/8$. Similarly, a consideration of the ($hk0$) reflections leads to a position of approximately $b/4$ for the molecular centre. With an origin chosen on the two-fold screw axis parallel to c the co-ordinates of the four molecular centres in the unit cell then become $a/8, b/4, 0$; $-a/8, -b/4, c/2$; $3a/8, 3b/4, c/2$; $5a/8, b/4, 0$. These positions are also found to lead to a reasonable system of molecular packing.

The trial model used in these preliminary tests consisted of two fused regular planar hexagons containing identical atoms (carbon) with bond lengths of 1·40 Å. Structure factors were calculated for various orientations of this model, and the best agreements were obtained when the long axis (L) of the molecule was inclined at about 45° to a in (010), and the plane normal inclined at about 26° to b. At this stage the average discrepancy was about 22% for 50 observed ($h0l$) structure factors. Fourier synthesis now gave excellent resolution of all the atoms in the (010) projection (Fig. 3 is the final result), but owing to the assumed centrosymmetry in the model the phase constants were restricted, and detailed refinement could not proceed on this basis. For the next step it is necessary to establish an asymmetric model.

A difficulty is encountered when we try to insert the nitrogen atoms in our model. The four ways consistent with the chemical structure in which this can be done are shown in Fig. 1, and, although chemically identical, each of these arrangements will lead to a different crystal structure when it is adopted as the asymmetric unit, for which only approximate positions of the hexagons have so far been established. In the case of the (010) projection, structures A and B are identical, and so are C and D, for the special position ($a/8$, 0) found for the model; but in the (001) projection all these structures can be distinguished.

FIG. 1.



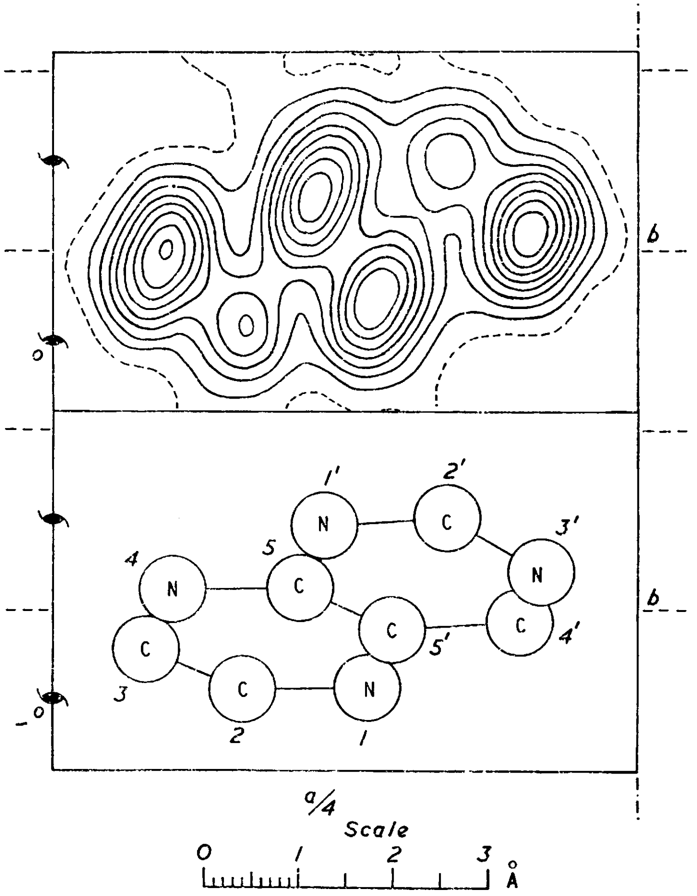
● Nitrogen.

In the (010) Fourier synthesis based on the symmetrical trial model it was found that the atoms 1 and 1′ (Fig. 1) had the highest electron-density peak values (6·2 e.Å^{-2}) and atoms 2 and 2′ the lowest (4·8 e.Å^{-2}); all the other symmetrical pairs had almost identical peak densities of about 5·4 e.Å^{-2}. This is fairly strong direct evidence that atoms 1 and 1′ are nitrogen, and 2 and 2′ are carbon, corresponding to structure A or B.

This result was now confirmed by evaluating the (001) projection from the same symmetrical trial model. (Fig. 2 gives the final result.) The screw axes are here equivalent to centres of symmetry and so the phase constants are restricted to 0 or π. In this case, however, the resolution is poor, and only the atoms 2 and 2′ can be clearly resolved. But the result of this Fourier synthesis showed that these two atoms had the same peak density, and this again excludes structures C and D. This result was followed up by evaluating successive Fourier difference syntheses for the projection, based on the four possible structures and taking into account the resulting hydrogen positions. This calculation proved to be conclusively in favour of structure A, the discrepancy figure for the 33 largest structure factors in this zone being reduced to 9·4%. The observations were later extended, by means of very long exposures, to 49 structure factors, and the final discrepancy figure was 12·2%.

Structure A being well established in this way, it was now used as an asymmetric model for intensive refinement of the more important (010) projection. This was carried out by conducting two Fourier syntheses at each stage, one containing the observed structure factors (F_0) as coefficients, and the other the previously calculated structure factors (F_c), the phase angles being the same for both syntheses. This procedure allows for simultaneous refinement of the structure and correction for termination of series errors by means of Booth's "back shift" rule.[13] The projection being non-centrosymmetrical, the parameter shifts at each Fourier stage (after the application of termination of series corrections) may be increased beyond the indicated value in order to obtain more rapid convergence to the true structure. For purely asymmetric syntheses a double-shift rule has been suggested,[14] in which the indicated parameter shifts should be doubled at each step to obtain the best possible values. In practice, however, axial reflections with restricted phase constants are generally present, and Shoemaker *et al.*[15] have shown that a 1·7 or 1·6 shift rule may sometimes be best. In this analysis we have used a 1·5 shift rule, which is perhaps slightly on the safe side. After a few cycles, however, the discrepancy in the ($h0l$) structure factors was finally reduced to 9·1%.

FIG. 2. *Electron-density projection on* (001), *showing one molecule. Contour interval,* 1 e.Å^{-2}, *the one-electron line being broken. The molecule is steeply inclined* (*about* 63°) *to this projection plane.*



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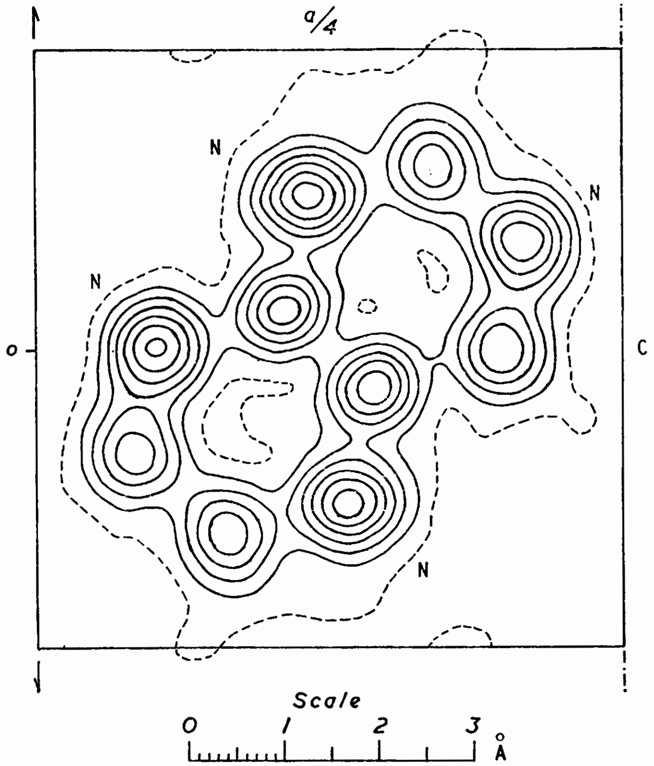
[13] Booth, *Proc. Roy. Soc.*, 1946, *A*, **188**, 77.

[14] Donohue, *J. Amer. Chem. Soc.*, 1950, **72**, 949; Cruickshank, *Acta Cryst.*, 1950, **3**, 10.

[15] Shoemaker, Donohue, Schomaker, and Corey, *J. Amer. Chem. Soc.*, 1950, **72**, 2328.

The final electron-density projection, incorporating the 50 observed structure factors, shows good resolution of all the ring atoms (Fig. 3). Three of the four hydrogen atoms appear as bulges on the one-electron contour line. The peak heights also confirm that the nitrogen atoms occupy positions 1, 4, 1′, and 3′.

FIG. 3. *Electron-density projection on* (010). *Contour scale as in Fig.* 2. *The molecule is inclined at about* 27° *to this projection plane.*



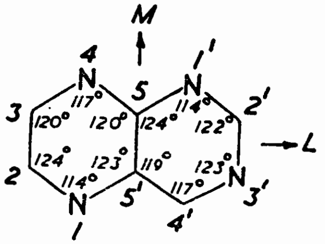


FIG. 4. *Bond angles.*

Co-ordinates and Molecular Dimensions.—The co-ordinates of the ring atoms were determined independently from the projections shown in Figs. 2 and 3, and the mean value is given in Table 1. The hydrogen co-ordinates were calculated on the assumption that they are situated radially at a distance of 1·09 Å from the carbon atoms. The atoms are numbered as indicated in Fig. 4 and the origin is taken on the two-fold screw axis.

The mean plane of the molecule was found by a least-squares method to have the equation :

$$X + 11{\cdot}92Y - 6{\cdot}08Z - 14{\cdot}70 = 0$$

The displacements of the ring atoms from this mean plane are given in the last column of Table 1.

The observed bond lengths are given in Table 2, and compared with values calculated by a molecular-orbital method based on the assumption of a strictly planar structure.[16] The observed valency angles are shown in Fig. 4.

TABLE 1. *Co-ordinates.*

Atom	*x*	*y*	*z*	*X* (Å)	*Y* (Å)	*Z* (Å)	Distance from mean plane of molecule (Å)
N(1)	0·1344	0·034	−0·258	3·32	0·13	−1·63	0·01
C(2)	0·0810	0·029	−0·310	2·00	0·11	−1·96	0·04
C(3)	0·0397	0·137	−0·176	0·98	0·52	−1·11	−0·06
N(4)	0·0510	0·306	0·002	1·26	1·16	0·01	0·02
C(5)	0·1057	0·311	0·066	2·61	1·18	0·42	−0·04
N(1′)	0·1158	0·483	0·258	2·86	1·83	1·63	0·00
C(2′)	0·1684	0·507	0·307	4·16	1·92	1·94	0·04
N(3′)	0·2089	0·356	0·182	5·16	1·35	1·15	−0·03
C(4′)	0·1996	0·216	0·002	4·93	0·82	0·01	0·00
C(5′)	0·1449	0·195	−0·065	3·58	0·74	−0·41	0·01
Mol. centre	0·1251	0·259	0·001	3·09	0·98	0·005	—
H(2)	0·0713	−0·079	−0·457	1·76	−0·30	−2·89	—
H(3)	−0·0012	0·116	−0·220	−0·03	0·44	−1·39	—
H(2′)	0·1777	0·628	0·452	4·39	2·38	2·86	—
H(4′)	0·2324	0·113	−0·098	5·74	0·43	−0·62	—

TABLE 2. *Bond lengths* (Å).

	Observed	Calculated	Δ		Observed	Calculated	Δ
N(1)–C(2)	1·36	1·31	0·05	C(2′)–N(3′)	1·40	1·34	0·06
C(2)–C(3)	1·39	1·41	0·02	N(3′)–C(4′)	1·28	1·31	0·03
C(3)–N(4)	1·32	1·31	0·01	C(4′)–C(5′)	1·42	1·425	0·005
N(4)–C(5)	1·41	1·35	0·06	C(5′)–N(1)	1·39	1·35	0·04
C(5)–N(1′)	1·40	1·35	0·05	C(5′)–C(5)	1·35	1·435	0·085
N(1′)–C(2′)	1·34	1·31	0·03				

Root mean square discrepancy, 0·047.

Orientation and Intermolecular Distances.—The orientation of the molecule in the crystal can be expressed by giving the angles *LOa*, *LOb*, etc., which the molecular axes *L*, *M*, and their normal *N* make with the *a*, *b*, and *c* crystal axes. Axes *L* and *M* are taken to lie in the mean plane of the molecule and are directed as shown in Fig. 4.

The arrangement of the molecules in the crystal will be clear from the projections in Figs. 5 and 6 which show the contents of the unit cell in relation to the symmetry elements. Some of the closest intermolecular contacts occur between molecules separated by a *b* translation (Fig. 5). The perpendicular distance between the mean molecular planes is here only 3·36 Å. The atoms in these molecules which overlie each other most closely are N(4) . . . C(3) = 3·36 Å, N(1′) . . . C(5) = 3·37 Å, C(2′) . . . C(4′) = 3·40 Å, C(5′) . . . N(1) = 3·42 Å, and four other pairs at 3·46 Å.

TABLE 3. *Orientation.*

LOa = 46·9°
LOb = 73·3°
LOc = 47·9°
MOa = 135·6°
MOb = 68·6°
MOc = 53·3°
NOa = 85·7°
NOb = 27·3°
NOc = 117·0°

Between the reference molecule (x, y, z) and the one derived from it by the operation of the two-fold screw axis $(\bar{x}, \bar{y}, \frac{1}{2} + z)$ there is one very close approach, N(4) . . . C(3) = 3·46 Å. Between the reference molecule and the one derived by the operation of the *n* glide plane $(\frac{1}{2} - x, \frac{1}{2} + y, \frac{1}{2} + z)$ there occurs another very close approach, N(3′) . . . C(4′) = 3·33 Å. Between molecules separated by a *c* translation (Fig. 6) there are two very

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[16] Goodwin and Porte, following paper.

close contacts, N(1′) . . . C(2) = 3·34 Å, and C(2′) . . . N(1) = 3·39 Å. All other intermolecular distances are greater than about 3·5 Å.

Accuracy.—Standard deviations for the atomic co-ordinates were estimated by Cruickshank's method.[17] The results obtained have been increased by a factor of 2 to allow for the non-centred projection, and allowance has also been made for the comparatively small number of F values available in relation to the number of unknown parameters. The y co-ordinates were obtained from a largely unresolved projection for which Cruickshank's treatment is not strictly applicable, and the standard deviations in this case have been increased by a further 25%.

FIG. 5. *Projection on* (001) *showing minimum intermolecular contacts.*

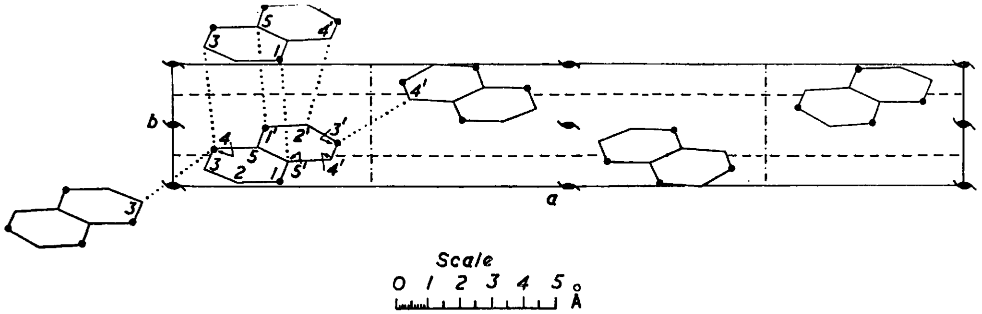
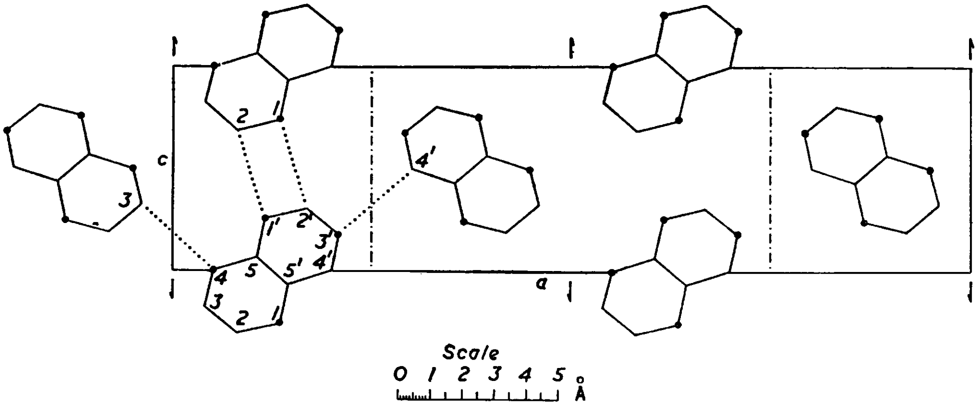


FIG. 6. *Projection on* (010) *showing minimum intermolecular contacts.*



After allowance for all these factors we obtain the following values :

Carbon	$\sigma(x) = 0{\cdot}022$ Å; $\sigma(y) = 0{\cdot}03$ Å; $\sigma(z) = 0{\cdot}023$ Å.
Nitrogen	$\sigma(x) = 0{\cdot}018$ Å; $\sigma(y) = 0{\cdot}025$ Å; $\sigma(z) = 0{\cdot}019$ Å.

The standard deviation of a C–C bond is 0·035 Å and of a C–N bond 0·033 Å. The standard deviation of a bond angle is about 2·3°, and the standard deviation of electron density is 0·27 e.Å^{-2} for the (001) projection and 0·42 e.Å^{-2} for the (010) projection.

Discussion.—One of the most important questions involved in this analysis is whether the pteridine molecule is strictly coplanar. It is certainly nearly so, and the small deviations found are given in Table 1. The mean displacement of 0·03 Å is certainly not significant. The maximum displacement of a carbon atom is 0·06 Å, and this is measured

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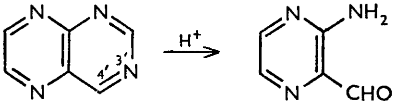
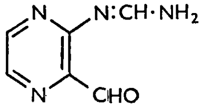
[17] Cruickshank, *Acta Cryst.*, 1949, **2**, 65, 154; 1950, **3**, 72; Cruickshank and A. P. Robertson, *ibid.*, 1953, **6**, 698.

almost entirely by the *y* co-ordinate. In the usual notation we have $t = \delta l/\sigma = 2{\cdot}00$. The *y* co-ordinates were determined from 49 independent structure factors, resulting in 29 degrees of freedom. For $P = 0{\cdot}05$ the value of t for such a distribution is 2·045. The displacement of this atom is therefore not significant, or at most is of possible significance only. The maximum displacement of a nitrogen atom is 0·03 Å, for which $t = 1{\cdot}20$, and this is not significant. It may therefore be said that the pteridine molecule is planar to within the limits of experimental error. Owing to the non-centrosymmetric structure, and especially because of the comparatively small number of observed reflections, these limits are unfortunately rather wide. Deviations of up to 0·06 Å from a planar structure cannot be excluded.

The bond lengths observed in pteridine are given in Table 2, together with certain molecular-orbital calculations for this structure. Again owing to the rather large uncertainties in our observed lengths, it would not be profitable to discuss these figures in detail at the present stage. The mean discrepancy between observed and calculated lengths is within the limits of experimental error. It is of interest, however, that the largest discrepancy occurs in the case of the central bond, C(5′)–C(5), where the observed value is much too low. In the naphthalene structure [18] where much more accurate data are available, a similar, though smaller, discrepancy is found. In both molecules it appears that the symmetrical Kekulé structure should be given more weight in the calculations, but any theoretical justification for this is hard to find. Much the shortest observed bond length in pteridine is N(3′)–C(4′) = 1·28 Å. Nucleophilic substitution is known to take place at atom 4′. On treatment with acid pteridine is converted into 2-aminopyrazine-3-aldehyde, and ring fission probably takes place at this bond. More recently it has been shown [19] that pteridine can be split to form the derivative (II) by treatment with 2N-aqueous sodium carbonate at 20°.





(II)

With regard to the minimum intermolecular-approach distances observed in the crystal structure, it is of interest that the majority of the contacts of less than 3·5 Å, and all those under 3·4 Å, are between a carbon atom of one molecule and a nitrogen atom of another molecule. However, none of these distances (minimum 3·33 Å) is less than the sum of the van der Waals radii of the atoms concerned, and it is not necessary to invoke any form of hydrogen bond.

EXPERIMENTAL

It was not possible to obtain satisfactory single crystals of pteridine from any of the usual solvents owing to its extreme solubility. By vacuum-sublimation fine plates were obtained, developed on (100), but the maximum thickness of these was only about 0·02 mm. Rotation, oscillation, and moving-film photographs were taken about each of the crystallographic axes with copper *K*α radiation (λ = 1·542 Å). The multiple-film technique [20] was employed on the Weissenberg exposures, and the intensities were estimated visually. For the (*hk*0) and (*h*0*l*) zones the crystals employed had cross sections perpendicular to the rotation axes of 0·50 by 0·02 mm., and approximate absorption corrections were worked out graphically. The correction factor varied from 1·02 to 1·31. For the (0*kl*) zone the crystal cross section was 0·70 by 0·60 mm. and absorption corrections were neglected. In this zone only 9 out of a possible 18 reflections could be recorded.

The mosaic crystal formula was assumed, and the resulting structure factors (F_0) are given in Table 4.

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[18] Abrahams, Robertson, and White, *Acta. Cryst.*, 1949, **2**, 233, 238; Ahmed and Cruickshank, *ibid.*, 1952, **5**, 852.

[19] Albert, Brown, and Wood, *J.*, 1956, 2066.

[20] Robertson, *J. Sci. Instr.*, 1943, **20**, 175.

TABLE 4. *Measured and calculated structure factors and phase angles* (α).

hkl	F_0	F_c	α°	*hkl*	F_0	F_c	α°	*hkl*	F_0	F_c	α°
000	—	272·0	—	20,0,2	13·4	13·3	2	15,1,0	9·6	11·8	0
200	<0·6	0·2	180	22,0,2	3·7	3·5	282	16,1,0	<2·1	1·7	180
400	73·5	63·1	180	24,0,2	7·3	7·9	179	17,1,0	15·3	14·2	180
600	<1·1	0·0	—	203	24·3	25·1	87	18,1,0	16·2	14·8	0
800	11·7	11·2	180	403	15·4	13·8	157	19,1,0	14·3	15·0	180
10,0,0	<1·6	0·3	0	603	6·7	6·9	285	20,1,0	<2·5	0·1	0
12,0,0	41·0	37·7	180	803	4·7	4·7	38	21,1,0	5·7	8·7	0
14,0,0	<2·0	3·1	0	10,0,3	14·4	14·3	273	22,1,0	4·8	4·7	180
16,0,0	<2·3	1·1	180	204	10·2	9·9	82	23,1,0	3·0	3·6	0
18,0,0	<2·5	1·1	0	404	11·8	11·0	183	30,1,0	2·1	2·7	180
20,0,0	9·0	7·9	0	604	<3·3	2·7	84	120	<1·8	1·4	0
22,0,0	<3·8	0·9	180	804	<3·4	1·7	40	220	<1·8	0·6	0
24,0,0	4·9	6·2	0	10,0,4	<3·5	1·9	242	320	6·1	3·9	180
020	<1·8	5·2	0	12,0,4	9·4	10·3	175	420	19·0	21·0	180
040	<2·3	4·2	0	14,0,4	16·6	16·7	272	520	8·4	7·7	0
002	27·2	25·1	180	16,0,4	6·7	6·8	3	620	3·0	0·1	0
004	29·4	26·2	357	18,0,4	7·9	8·0	86	720	7·1	6·9	180
006	<3·8	3·4	14	205	5·8	3·5	262	820	12·7	12·7	0
011	64·2	75·4	87	405	10·9	10·3	181	920	11·3	11·5	180
013	13·0	10·5	93	605	14·3	16·3	92	10,2,0	4·1	0·0	—
015	8·7	7·7	91	805	6·0	5·4	356	11,2,0	7·5	7·4	0
022	36·4	40·8	181	10,0,5	<3·9	4·9	90	12,2,0	9·0	10·2	0
024	4·8	3·1	13	12,0,5	9·9	8·2	181	13,2,0	<2·3	1·8	180
031	5·9	7·1	296	14,0,5	7·6	8·6	271	14,2,0	<2·3	0·3	180
033	9·0	5·9	256	16,0,5	7·8	7·7	5	15,2,0	2·7	2·9	180
201	44·9	53·9	93	18,0,5	3·5	4·6	270	16,2,0	2·8	3·3	0
401	41·5	45·7	2	206	<3·8	0·7	45	17,2,0	6·1	5·4	180
601	32·5	28·9	96	406	11·4	10·5	3	18,2,0	<2·5	0·3	0
801	27·9	27·7	1	606	6·3	5·0	268	19,2,0	4·1	5·2	0
10,0,1	21·5	20·8	92	806	12·9	12·3	183	20,2,0	9·8	12·0	180
12,0,1	24·1	24·1	186	10,0,6	4·4	3·8	93	21,2,0	7·3	6·2	0
14,0,1	19·2	18·3	277	110	<3·0	8·4	0	22,2,0	<2·3	0·0	—
16,0,1	14·5	15·7	355	210	69·9	73·8	180	23,2,0	<2·3	0·0	—
18,0,1	16·6	14·7	276	310	23·3	22·9	0	24,2,0	3·2	4·4	0
20,0,1	18·1	20·3	179	410	1·2	2·0	180	130	<2·3	2·1	0
22,0,1	9·3	8·7	90	510	11·8	12·2	180	230	<2·3	3·4	0
202	4·4	6·4	307	610	28·9	28·3	180	330	<2·3	3·5	0
402	20·9	23·6	356	710	1·4	5·6	0	430	3·0	2·4	180
602	27·7	28·8	263	810	1·8	3·2	0	530	3·5	4·1	180
802	24·0	23·8	188	910	12·7	9·2	180	630	3·0	2·1	0
10,0,2	27·2	27·9	102	10,1,0	20·1	18·3	180	730	6·0	8·9	180
12,0,2	<2·9	1·9	286	11,1,0	10·3	11·0	180	830	3·9	1·0	0
14,0,2	6·6	7·2	104	12,1,0	<1·8	2·8	0	930	3·2	3·4	0
16,0,2	<3·4	0·8	21	13,1,0	15·0	15·1	0	22,3,0	2·5	3·3	0
18,0,2	<3·6	1·1	326	14,1,0	18·1	16·2	0				

The various Fourier syntheses were effected by the usual numerical methods. The structure factors and phase constants were finally recalculated from the latest atomic positions (Table 1) and are given in Table 4 under F_c and α. In these calculations the f curves of McWeeny[21] were used for carbon, nitrogen, and hydrogen, with a temperature factor of $B = 4{\cdot}8 \times 10^{-16}$, which was derived from a comparison of observed and calculated structure factors. The final discrepancies, expressed as $\sum|F_0 - F_c|/\sum F_0$, were 9·1% for the (*h*0*l*) zone, 12·2% for the (*hk*0) zone, and 11·1% overall.

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[21] McWeeny, *Acta Cryst.*, 1951, **4**, 513.