The crystal structure of phenyl hydrazine, $C_6H_5 \cdot NH : NH_2$

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Auszug

Aus Röntgenaufnahmen in einer für tiefe Temperaturen angepaßten Weissenberg-Kammer ergaben sich für Phenylhydrazin, $C_6H_5 \cdot NH \cdot NH_2$, die Strukturdaten: $a = 9,59$ Å, $b = 5,91$ Å, $c = 12,31$ Å, $\beta = 118°$, $Z = 4$, Raumgruppe $P2_1/c$. Die x- und z-Koordinaten der Atome wurden aus den Interferenzen $h0l$, die y-Koordinaten durch Packungsbetrachtungen bestimmt. Für 385 beobachtete und 300 nichtbeobachtete Interferenzen ist $R = 0,16$. Die Bindung N—N liegt nicht in einer Ebene mit den übrigen Atomen eines Moleküls.

Abstract

X-ray diffraction data from phenyl hydrazine were collected on a Weissenberg Unicam S-35 adapted to low-temperature crystallography by Singh and Ramaseshan. The crystal belongs to the space group $P2_1/c$, with unit-cell dimensions $a = 9.59$ Å, $b = 5.91$ Å, $c = 12.31$ Å and $\beta = 118°$ and four molecular units per cell.

The structure was solved in the (010) projection and the y coordinates were obtained from packing considerations. The R factor for the 385 observed and 300 unobserved reflections in the CuK sphere is 0.16. The N—N bond is off the plane of the remaining atoms of the molecule.

Introduction

Phenyl hydrazine ($C_6H_5 \cdot NH \cdot NH_2$) is liquid at room temperature (m.p. $19°C$). The substance was crystallized in situ on the goniometer head of a Weissenberg Unicam S-35 goniometer adapted for low temperature crystallography by the modifications of Singh and Ramaseshan (1964). Its structure determination was part of a scheme on low temperature crystallography in this laboratory. The preliminary results on the structure were published by the authors earlier (Swaminathan and Srinivasan, 1967).

Crystal data and space group

A needle shaped, pale yellow, transparent single crystal suitable for x-ray study was obtained by the method of SINGH and RAMASESHAN (1964). This was verified by viewing the crystal through crossed polaroids. The crystal grew only along the twofold axis.

The unit-cell dimensions obtained from the x-ray photographs taken down the twofold axis are:

$$a = 9.59 \pm 0.01 \text{ Å}, \quad b = 5.91 \pm 0.02 \text{ Å},$$
$$c = 12.31 \pm 0.01 \text{ Å} \quad \text{and} \quad \beta = 118° \pm 1°.$$

The $h0l$ reflections wits l odd were systematically absent; this is valid for the space groups Pc, $P2/c$ and $P2_1/c$. The non-centrosymmetric space group Pc was rejected by the $N(z)$ vs. z graph. RAMASESHAN (unpublished) had also established from precession and Weissenberg pictures that the space group was the centrosymmetric $P2_1/c$.

It was not possible to measure the density of the crystal. The density of the liquid is 1.0978 g. cm^{-3}. Assuming that the crystal density and the density of the liquid are nearly equal, the number of molecules per unit cell is four. The calculated density of the crystal is 1.170 g. cm^{-3}.

Intensity data for hkl reflections ($k = 0, 1, 2$ and 3) were collected by the multiple-film technique and were measured visually by means of calibrated intensity strips. The Lorentz and polarization corrections were applied and the intensities were put on an absolute scale by WILSON's method. Absorption correction was neglected.

Structure analysis

1. (010) projection

Out of about 100 possible $h0l$ reflections within the sphere of CuK radiation, only about 60 could be recorded. The unitary structure amplitudes of all of them were so low that direct sign determination seemed impossible. A (010) Patterson was made (Fig. 1). The map showed apart from the peak at the origin, a heavy peak at P ($u=0.44$, $w = 0.26$). This was taken to be due to the intermolecular ring-to-ring interaction. The Patterson map near the origin was too diffuse to be of any use in finding the orientation of the molecule, for the intramolecular interaction peaks could not be located.

An origin-removed and $\hat{f}$ sharpened (010) Patterson map showed better details near the origin. Around the ring-to-ring peak is to be

expected a hexagon of peaks corresponding to the phenyl ring in projection. This, however, did not show up.

Assuming that the peak at P consisted of only six overlapping carbon-to-carbon interactions, this peak was also removed. The Patterson synthesis was made with the coefficients

$$|F|^2 = \frac{|F_o|^2 - (6 f_C{}^2 + 2 f_N{}^2) - 6 f_C{}^2 \cos 2\pi (hu + lw)}{\hat{f}}$$

where $|F_o|^2$ is the temperature-corrected observed intensity placed on absolute scale and f_C, f_N are the atomic scattering factors of the
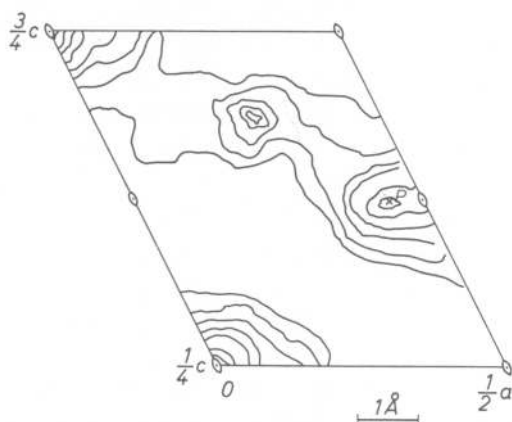

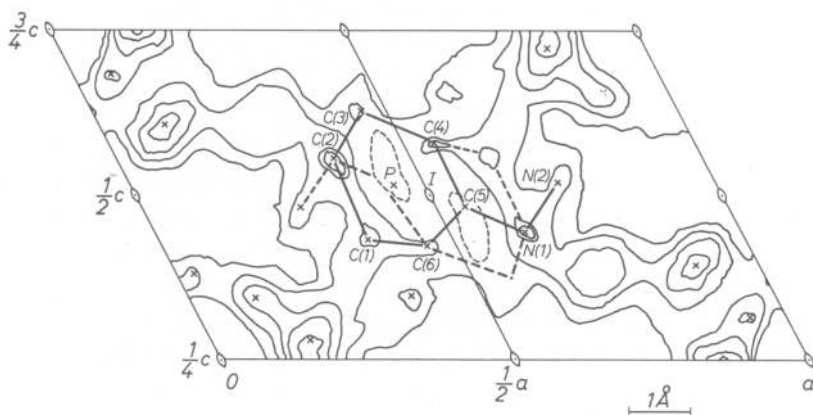Fig. 1. Patterson projection down the b axis

Fig. 2. Patterson projection down the b axis with the peak at the origin and the ring-ring vector peak removed and $\hat{f}$ sharpened. The molecule around the point P is represented by full lines and its inversion due to the centre of symmetry in projection at the point I ($\frac{1}{2}$ $\frac{1}{4}$) by dotted lines

carbon and nitrogen atoms respectively. The temperature factor was assumed to be that obtained from WILSON's plot, 4.78 Å². The atomic scattering factors were taken from the paper of HANSON *et al.* (1964). This map (Fig. 2) revealed the expected disposition of peaks around P, and it corresponded very well with the intramolecular peaks near the origin. The identification of the molecule in projection was easy.

A (010) electron-density projection was made with dependable signs obtained from the above identification and the projection was
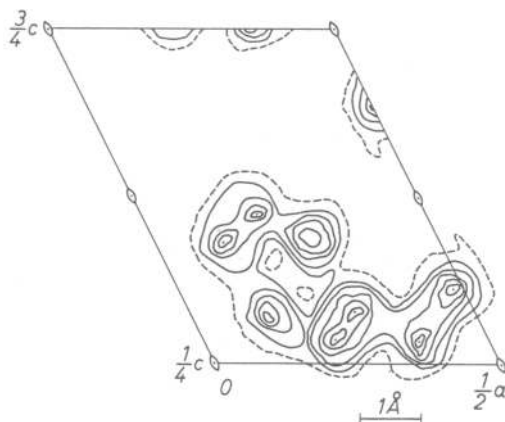
Fig. 3. Electron-density projection $\varrho(xz)$. The contours are at arbitrary intervals

thereafter refined by iterated difference syntheses till the R factor fell to 0.22. The final electron-density projection on the a, c plane is shown in Fig. 3.

2. The y coordinates

Lacking data in another projection, the y coordinates were found purely from packing considerations. The bond distances are all well known. It was assumed (i) that the van der Waals contact distance between carbon atoms was 3.5 Å and (ii) that there was hydrogen bonding between the nitrogen atoms. The hydrogen bond distances were assumed to be 2.9 Å.

From these considerations the third coordinates of the atoms were approximately fixed. When the structure-factor calculations were made for the reflections the agreement was sufficiently good for reflections with even l indices but not for reflections with odd l indices. The origin may have been chosen at a spurious centre of symmetry in the (010) projection. When the z coordinates were all increased by

0.25 c, the agreement became good for both sets of reflections. By trial and error, the coordinates were adjusted till the R factor for the $h1l$ reflections was about 0.25.

3. Refinement

Having got the approximate y coordinates, the structure was taken up for refinement using the hkl reflections. The intramolecular bond distances were calculated and the minimum necessary changes were made in accordance with the known stereochemistry of the molecule. Refinement was done till the overall R factor came down to 0.24 for all observed hkl reflections. The same temperature factor $B = 4.78$ Å² was used throughout.

The coordinates and the temperature factors were then refined using the three-dimensional data by four cycles of least squares on the CDC 3600 computer at the Tata Institute of Fundamental Research, Bombay. The final R factor is 0.16 including the unobserved reflections.

Table 1. *Fractional atomic coordinates and isotropic temperature factors*

	x	y	z	B
C(1)	0.136	0.795	0.321	3.72 Å²
C(2)	0.122	0.719	0.428	4.47
C(3)	0.192	0.517	0.484	3.35
C(4)	0.284	0.374	0.443	2.93
C(5)	0.299	0.451	0.335	2.84
C(6)	0.227	0.657	0.278	2.90
N(1)	0.376	0.314	0.285	3.21
N(2)	0.481	0.127	0.355	3.34

The atomic coordinates and the individual isotropic temperature factors are given in Table 1. Table 2 gives the observed and calculated structure factors. The use of anisotropic thermal parameters brought the R factor to 0.15, but it was found that the anisotropy in thermal movements of the atoms are insignificant.

Discussion

The interatomic distances and the bond angles with their standard deviations calculated by the methods of Cruickshank (1949) and Darlow (1960) are given in Table 3 and shown in Fig. 4. The average carbon-carbon distance in the ring is 1.43 Å and the average bond angle in the ring is 120°.

Table 2. *Observed and calculated structure factors for phenyl hydrazine*

The calculations have been performed with the atomic coordinates given in Table 1 for the asymmetric unit containing one molecule

h	k	l	F_o	F_c
1	0	0	4.3	−3.4
2			10.3	−10.4
3			5.7	−5.8
4			<0.5	−0.1
5			2.4	−2.8
6			0.8	1.5
7			0.6	0.3
8			1.6	1.6
0	0	2	4.8	−5.1
1			18.9	19.5
3			0.9	−1.1
4			1.4	−1.5
5			1.1	−1.1
6			2.7	−2.5
7			1.0	1.3
8			1.0	−1.2
9			0.6	0.2
0	0	4	2.5	1.6
2			1.7	−1.8
4			0.7	−0.2
5			3.6	3.8
6			1.2	−1.4
7			1.6	−1.0
0	0	6	1.9	2.2
1			4.1	4.1
3			1.8	−1.8
5			2.3	−1.0
6			1.4	1.8
0	0	8	1.9	−1.7
1			1.0	−0.6
2			1.4	1.3
3			1.2	−1.2
4			1.1	1.0
5			1.2	1.1
0	0	10	0.8	−0.7
1			0.8	0.7
2			0.7	−0.4
3			0.7	−0.4
4			1.6	−0.4
1	0	−2	11.2	−11.1
2			2.2	−2.3
3			4.4	−4.1
4			0.5	1.0
5			0.8	−1.0
6			4.6	5.2
7			1.2	1.6
8			2.1	−2.5
9			0.9	−1.2
1	0	−4	6.0	5.5
2			11.0	−10.8
3			4.3	3.2
4			4.4	−3.4
5			6.2	6.7
7			1.6	−2.2
8			1.1	−1.2
9			1.4	1.7
1	0	−6	9.0	−7.6
3			1.0	−1.1
4			1.4	1.7
5			0.5	0.4
6			0.5	1.2
7			1.9	2.9
8			2.1	−2.5
1	0	−8	1.5	−1.2
2			1.4	1.1
3			1.4	−0.5
4			1.5	1.7
5			1.7	2.0
6			3.9	4.3
7			6.7	−6.7
8			1.9	−2.1
9			1.4	1.6
1	0	−10	0.9	0.8
5			2.5	1.9
6			5.1	−4.1
8			1.2	2.0
1	1	0	2.5	2.0
2			14.1	15.4
4			2.5	−2.6
5			1.2	−1.5
6			0.6	−0.6
7			1.0	−1.2
10			2.0	2.1
0	1	1	7.5	8.5
1			10.1	9.6
2			11.5	−10.7
3			2.6	−2.0
4			1.9	2.3
0	1	2	1.4	1.1
1			10.3	−9.7
2			1.6	−1.6
3			8.1	7.0
4			3.5	3.3
5			1.9	2.0
6			1.0	1.2
8			0.9	−0.4

h	k	l	F_o	F_c
9	1	2	0.8	−0.9
0	1	3	3.4	2.7
1			0.9	1.2
2			2.9	2.9
3			5.5	−5.2
4			1.5	1.6
8			0.7	0.8
0	1	4	1.3	−0.9
1			1.6	2.4
2			1.9	−2.0
3			2.3	−2.2
4			0.8	0.7
5			1.8	1.3
7			1.2	1.2
8			0.6	−0.8
0	1	5	3.5	3.6
1			0.9	1.2
2			1.0	−0.9
4			0.7	−0.8
5			1.4	1.3
0	1	6	0.8	−0.7
1			1.7	−1.2
3			2.4	2.4
6			<0.6	−0.1
0	1	7	1.7	−1.5
1			2.7	2.6
2			1.0	−1.1
3			0.7	−0.7
0	1	8	1.3	0.8
2			1.9	−1.6
3			2.2	−1.7
4			1.8	1.6
1	1	9	0.6	0.5
2			1.0	0.9
3			1.5	−1.3
0	1	10	0.8	0.5
1			0.9	0.5
2			0.8	0.8
4			0.8	−0.1
1	1	−1	5.7	−5.4
2			6.5	−6.0
3			4.5	5.4
4			1.2	−2.0
5			0.5	0.8
6			0.5	−0.9
7			1.3	1.5
8			1.6	−1.9
1	1	−2	9.2	8.5
2			6.0	−6.4
3			5.2	2.5
4			4.3	−4.5
5			1.2	−1.8
8			0.9	0.4
9			1.4	1.8
2	1	−3	0.5	0.9
3			6.0	−6.2
4			1.0	−0.4
5			1.2	1.2
6			3.0	3.6
7			1.0	−1.4
8			1.0	−1.2
9			0.6	0.5
1	1	−4	2.6	−2.7
2			5.5	5.2
3			2.2	−2.1
4			4.3	−4.8
5			3.5	3.4
1	1	−5	3.5	−3.4
2			2.8	−3.6
3			1.1	−0.8
4			4.0	3.9
5			1.0	1.1
7			1.1	−1.5
9			1.2	−1.2
1	1	−6	1.9	1.5
2			0.5	0.3
3			5.7	−4.7
4			2.3	2.3
5			2.2	−2.3
6			1.6	1.1
8			1.3	1.7
9			1.3	1.7
3	1	−7	2.2	2.0
6			1.6	−1.9
7			1.1	1.5
8			2.7	−2.9
9			1.3	1.6
2	1	−8	1.8	−1.6
4			2.0	−2.0
5			2.9	3.0
6			1.3	1.5
8			0.9	0.9
9			2.0	−2.1
3	1	−9	1.2	−1.2
5			3.2	3.0
7			2.6	−2.4

h	k	l	F_o	F_c
9	1	−9	1.9	1.6
2	1	−10	1.0	−0.9
3			0.6	0.2
4			2.7	2.5
5			1.5	1.3
6			2.5	−2.0
8			1.1	−1.3
1	2	0	1.1	−1.5
2			2.4	−2.6
3			1.2	1.4
4			4.1	4.4
1	2	1	2.2	−1.8
3			5.1	6.4
4			5.2	−6.2
7			1.4	1.9
8			1.0	−1.4
0	2	2	5.2	4.6
1			1.3	−1.4
2			5.4	−4.2
3			4.0	−3.9
5			3.8	3.5
6			0.6	0.4
1	2	3	2.9	2.2
2			3.7	−3.3
3			1.4	1.7
4			3.2	2.9
5			2.3	−2.0
1	2	4	3.4	2.4
3			2.1	−1.5
4			2.0	−1.5
6			1.1	1.5
0	2	5	1.5	1.3
1			3.2	−3.0
2			2.7	−2.3
3			1.3	−1.5
0	2	6	2.3	2.4
1			0.9	−1.1
0	2	7	1.3	1.6
2			2.6	−2.2
3			0.6	0.9
0	2	8	1.3	1.2
1			2.6	2.3
3			1.5	−1.1
0	2	9	0.6	−1.0
1			2.1	1.8
0	2	10	1.6	−0.3
5			<0.5	0
1	2	−1	4.1	−3.1
2			4.9	4.8
3			3.8	−3.1
4			1.9	1.7
7			1.1	−1.4
8			0.7	−1.4
1	2	−2	1.5	1.1
2			1.1	1.2
3			1.0	1.6
4			1.8	−2.4
5			1.3	2.0
7			2.2	−3.0
9			0.7	1.0
1	2	−3	<0.5	−0.2
2			6.3	5.3
4			2.4	0.9
5			2.9	−3.2
6			1.6	2.1
7			1.0	−1.4
8			1.5	2.0
1	2	−4	2.0	1.2
2			0.8	−0.1
3			5.8	−4.0
4			2.3	2.5
5			1.1	1.6
1	2	−5	3.2	3.1
2			1.9	−1.3
3			3.3	−3.1
4			2.7	−2.6
5			3.6	3.8
7			0.7	0.6
8			0.7	−1.2
1	2	−6	1.4	1.3
2			3.0	−2.5
3			1.5	1.5
4			0.7	0.8
5			0.9	0.3
7			0.8	−1.7
2	2	−7	0.6	−0.5
5			0.7	0.8
9			1.0	1.1
1	2	−8	1.0	−1.0
3			1.1	−1.2
4			0.9	−1.4
5			0.6	0.6
9			0.6	0.8
1	2	−9	0.5	0.7

h	k	l	F_o	F_c
2	2	−9	0.9	1.1
3			3.8	−2.9
4			1.1	1.1
5			0.8	0.7
8			1.0	1.1
1	2	−10	1.8	0.2
2			1.3	−1.5
3			1.4	−1.2
4			0.8	1.1
5			0.7	1.1
2	3	0	1.5	−1.1
4			1.0	−1.6
6			3.6	3.5
8			0.7	−0.6
1	3	1	2.3	−2.2
2			2.2	2.2
3			1.9	−1.7
4			1.2	0.9
6			0.8	−1.1
7			0.6	0.8
1	3	2	0.8	−1.0
2			0.7	0.4
3			1.1	−1.0
5			2.7	−2.4
7			0.8	1.5
0	3	3	0.5	−0.8
1			1.8	1.8
2			2.4	−2.5
4			1.5	−1.8
5			2.6	2.8
6			2.2	1.2
7			1.8	−1.3
1	3	4	2.7	1.9
3			0.7	0.7
6			1.0	−0.8
7			1.0	0.2
1	3	5	1.2	−1.0
3			0.8	−0.8
6			0.9	1.2
0	3	6	<0.5	−0.2
5			1.2	−0.4
0	3	7	4.2	3.8
1			<0.5	0.2
2			<0.5	−0.3
0	3	8	1.3	1.2
2			0.7	0.2
0	3	9	1.2	−1.0
1			1.5	0.9
0	3	10	1.8	−1.1
1	3	−1	1.6	1.7
3			2.9	−3.1
4			0.5	0.3
6			3.8	4.1
7			2.1	−2.3
2	3	−2	0.9	1.0
3			0.9	1.0
4			1.2	−1.2
5			2.5	3.0
6			0.7	−1.0
3	3	−3	0.8	0.5
4			3.6	4.1
6			2.8	−3.5
7			1.8	−1.9
8			0.5	0.9
1	3	−4	1.8	1.4
2			<0.5	0.3
3			0.5	−0.5
8			0.9	−0.9
1	3	−5	5.1	5.0
2			1.5	−1.5
3			1.8	−1.6
6			1.0	−0.7
7			1.5	1.2
8			0.9	−1.1
9			0.7	0.7
1	3	−6	1.4	−1.5
2			1.6	1.8
5			0.6	0.8
7			1.6	−2.1
1	3	−7	2.2	−2.3
2			2.3	−2.2
3			0.7	−0.5
7			1.2	1.3
1	3	−8	1.6	−1.3
2			2.7	2.2
3			1.2	0.8
5			1.3	−0.7
6			1.4	−1.5
8			0.8	0.6
2	3	−9	1.2	0.3
1	3	−10	1.6	1.0
2			1.8	−1.2
5			0.8	−0.1
7			0.8	1.0

Table 3. *Interatomic distances and angles*

Lengths		Angles	
C(1)—C(2)	1.45 ± 0.04 Å	C(1)—C(2)—C(3)	120° ± 1°
C(2)—C(3)	1.38 ± 0.03	C(2)—C(3)—C(4)	121 ± 2
C(3)—C(4)	1.45 ± 0.04	C(3)—C(4)—C(5)	119 ± 1
C(4)—C(5)	1.45 ± 0.04	C(4)—C(5)—C(6)	118 ± 2
C(5)—C(6)	1.40 ± 0.03	C(5)—C(6)—C(1)	120 ± 1
		C(6)—C(1)—C(2)	121 ± 1
C(6)—C(1)	1.46 ± 0.04	C(4)—C(5)—N(1)	121 ± 1
C(5)—N(1)	1.42 ± 0.03	C(6)—C(5)—N(1)	120 ± 1
N(1)—N(2)	1.46 ± 0.04	C(5)—N(1)—N(2)	121 ± 2

The shortest intermolecular contacts between different atoms up to 4.00 Å are listed in Table 4 and marked in Fig. 4. The NH···N (hydrogen bond) distance between two neighbouring molecules is 3.23 Å. It is in agreement with the NH···N distance of 3.19 Å obtained by Collin and Lipscomb (1951) in the hydrazine crystal.

The mean equation of the plane of the phenyl ring and the nitrogen N(1) attached to it is:

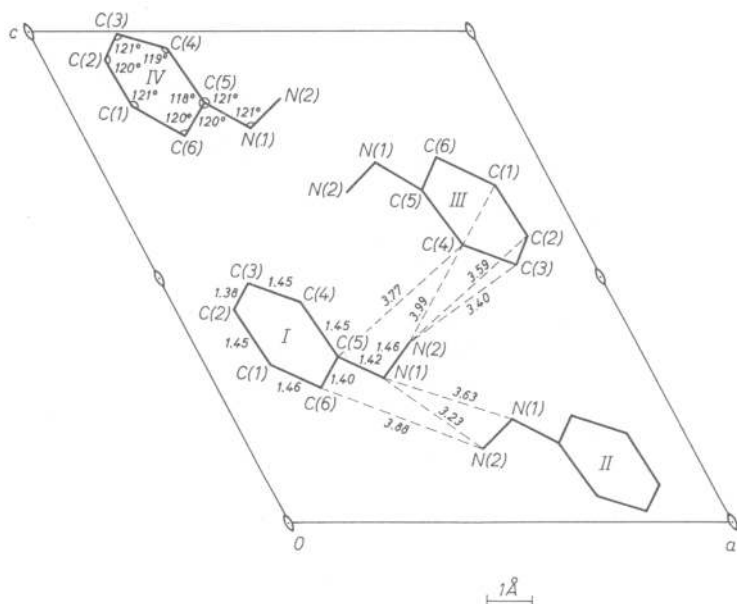$$1.247\,x + y + 1.218\,z - 8.195 = 0.$$

Fig. 4. Projection of the structure onto (010) showing the intramolecular and intermolecular distances and bond angles

Table 4. *Shortest intermolecular contacts*

			x	y	z
I	molecule at		x	y	z
II	molecule at		$1-x$	$\frac{1}{2}+y$	$\frac{1}{2}-z$
III	molecule at		$1-x$	$1-y$	$1-z$
IV	molecule at		x	$\frac{1}{2}-y$	$\frac{1}{2}+z$

N(1,I)—N(2,II)	3.23 Å	C(5,I)—C(4,III)	3.77 Å
N(2,I)—C(3,III)	3.40	N(2,I)—C(4,III)	3.81
N(2,I)—C(2,III)	3.59	C(6,I)—N(2,II)	3.88
N(1,I)—N(1,II)	3.63	N(2,I)—C(1,III)	3.99

Table 5. *Deviation of atoms from the mean plane of the ring*

Atom	C(1)	C(2)	C(3)	C(4)	C(5)	C(6)	N(1)	N(2)
Deviation	+0.04	+0.06	+0.07	+0.06	−0.05	+0.06	−0.03	+0.26 Å

The deviation of the atoms from the mean plane is given in Table 5. All the atoms except the nitrogen N(2) are on the plane within the limits of error. The tilt of the N—N bond with respect to the plane is 10°. The off-plane N—N bond is confirmed also by the dipole-moment studies and Raman spectra of hydrazines (DURRANT and DURRANT, 1962).

Acknowledgements

References

R. L. COLLIN and W. N. LIPSCOMB (1951), The crystal structure of hydrazine. Acta Crystallogr. 4, 10—14.

D. W. J. CRUICKSHANK (1949), The accuracy of atomic coordinates derived by least squares of Fourier method. Acta Crystallogr. 2, 154—157.

S. F. DARLOW (1960), Errors in bond angles. Acta Crystallogr. 13, 683.

P. J. DURRANT and B. D. DURRANT (1962), Introduction to advanced inorganic chemistry. (Longman's Green, London), 703.

H. P. HANSON, F. HERMAN, J. D. LEA and S. SKILLMAN (1964), HFS atomic scattering factors. Acta Crystallogr. 17, 1040—1044.

A. K. SINGH and S. RAMASESHAN (1964), A low temperature attachment to the Weissenberg goniometer. Proc. Ind. Acad. Sci. 60A, 20—24.

S. SWAMINATHAN and S. SRINIVASAN (1967), The crystal and molecular structure of phenyl hydrazine ($C_5H_6NHNH_2$). Curr. Sci. (India) 36, 336—337.