Ketten bilden über gemeinsame Kanten aus Sauerstoffatomen auch in der *y*-Richtung unbegrenzte Verbände. Benachbarte zweidimensionale Netzwerke dieser Art werden durch die Anionen und F–H···O-Wasserstoffbrücken miteinander verbunden.

Die Autoren danken Herrn Privatdozent Dr H. Falius, Braunschweig, für die Anregung zu dieser Arbeit und Überlassung von Kristallmaterial, dem Rechenzentrum der Technischen Universität Braunschweig und dem Deutschen Rechenzentrum in Darmstadt für Rechenzeit sowie der Deutschen Forschungsgemeinschaft und dem Fonds der Chemischen Industrie für Leihgaben und Sachmittel.

Literatur

Albrand, K.-R., Altenburg, H. & Mootz, D. (1970). 11. Diskussionstagung der Sektion für Kristallkunde der Deutschen Mineralogischen Gesellschaft in Saarbrücken, Vortragsreferate *Z. Kristallogr.* **142**, 415.

Falius, H., Mootz, D. & Altenburg, H. (1970). *Angew. Chem.* **82**, 443.

Hanson, H. P., Herman, F., Lea, I. D. & Skillman, S. (1964). *Acta Cryst.* **17**, 1040.

Philippot, E. & Lindqvist, O. (1970). *C. R. Acad. Sci. Paris*, **270** C, 1395.

Stewart, R. F., Davidson, E. R. & Simpson, W. T. (1965). *J. Chem. Phys.* **42**, 3175.

Acta Cryst. (1971). **B27**, 1986

The Crystal Structure of 4-Cyanopyridine

By Michael Laing,* Neil Sparrow and Polly Sommerville

Department of Chemistry, University of Natal, Durban, South Africa

(*Received* 30 *October* 1970)

The crystal structure of 4-cyanopyridine, $C_6N_2H_4$, has been determined from three-dimensional single-crystal X-ray data collected by standard film techniques. The crystals are orthorhombic, space group *Pccn*, with $a=3{\cdot}82\pm0{\cdot}01$, $b=6{\cdot}12\pm0{\cdot}01$, $c=23{\cdot}22\pm0{\cdot}02$ Å; $Z=4$; $D_{\rm obs}=1{\cdot}27$, $D_{\rm calc}=1{\cdot}27$ g.cm^{-3}. The structure was refined by the least-squares method to a conventional $R=0{\cdot}105$ for 550 observed and unobserved data. The molecule retains the twofold axis through the cyano group and pyridine nitrogen atom as a required symmetry element in the unit cell. The bond lengths and angles are quite normal. The mode of packing is unusual, and results in a relatively large 'hole' running through the crystal parallel to **a**.

Introduction

4-Cyanopyridine is unique among the simpler 4-substituted derivatives of pyridine, as at room temperature it is a white crystalline solid with little odour, while for example, the 4-methyl, ethyl, vinyl, and chloro compounds are liquids, foul smelling and easily oxidized (Heilbron, 1965). The mode of packing of the molecules was therefore of interest and the structure determination was undertaken.

Experimental

Material was purchased from Aldrich Chemical Company and suitable crystals were obtained by sublimation. A well-formed rectangular parallelepiped $0{\cdot}5\times0{\cdot}2\times0{\cdot}2$ mm was sealed in a capillary and used for all subsequent X-ray work. Oscillation, Weissenberg and precession photographs showed the unit cell to be orthorhombic, and the systematic extinctions, $0kl$ for l odd, $h0l$ for l odd and $hk0$ for $h+k$ odd, were consistent with space group *Pccn*. Unit-cell dimensions were $a=3{\cdot}82\pm0{\cdot}01$, $b=6{\cdot}12\pm0{\cdot}01$, $c=23{\cdot}22\pm0{\cdot}02$ Å, measured from calibrated $0kl$ Weissenberg and $h0l$ precession photographs. The density was measured by flotation in a chlorobenzene–bromobenzene mixture to be $1{\cdot}27\pm0{\cdot}01$ g.cm^{-3}, showing 4 molecules per unit cell.

Because there are 8 equivalent positions in the space group, and only 4 molecules per unit cell, the asymmetric unit consists of only half of the molecule. The twofold axis passing through the cyano group and the nitrogen and γ carbon atoms of the pyridine ring must therefore be coincident with a twofold axis parallel to **c** in the unit cell. The x, y coordinates of these four atoms are thus required to be 0·25, 0·25.

Integrated multiple-film data were collected by the equi-inclination Weissenberg method using Ni-filtered Cu $K\alpha$ radiation for layers $0kl$ to $3kl$. Of the 550 recordable data, 450 were observed above background. The intensities were estimated by visual comparison with a time-calibrated intensity strip. Lorentz and polarization corrections were calculated and applied to the data by hand. Precession photographs were taken of layers $h0l$ to $h2l$ and these data were used to scale the Weissenberg data and to supply intensities for certain reflections that had been obscured by the beam catcher. Unobserved data were given the value local $I_{\rm min}/2$.

A three-dimensional temperature-sharpened Patterson map was calculated using the 450 observed data. (The values of $F^2_{\rm obs}$ were multiplied by the value

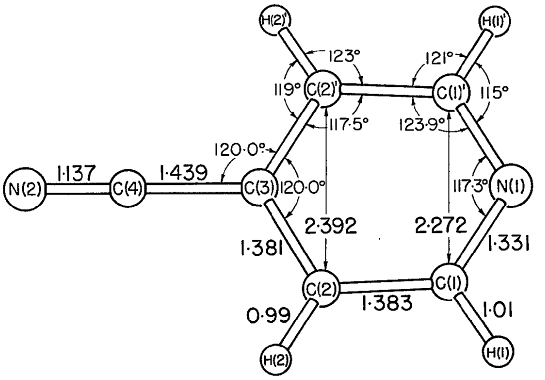


Fig. 1. Bond lengths and angles. The estimated standard deviations in bond lengths are 0·006 Å for N(1)–C(1), C(1)–C(2) and C(2)–C(3), and 0·008 Å for C(3)–C(4) and C(4)–N(2), and in bond angles are 0·3° for C(2)–C(3)–C(4) and 0·5° for all others involving carbon and nitrogen atoms. The bond lengths have not been corrected for thermal motion.

exp (8·0/S) where S was the appropriate value of $\sin^2\theta/\lambda^2$). The pyridine ring–pyridine ring vector of sixfold weight corresponded to the largest peak on the line $u=0·5$, $v=0·5$. From the w coordinate of this peak was deduced the z coordinate of the approximate mid-point of the pyridine ring. The relative coordinates of the atoms within the molecule were easily obtained from the well-defined peaks near the origin, while the orientation of the cyano group was deduced from the relative heights and positions of the peaks in the Harker section at $u=0·5$. The approximate x, y, z coordinates for all the atoms were thus directly determined (Sparrow, 1970).

The structure was refined isotropically to $R=0·2$ by a series of observed and difference Fourier summations, the coordinates being adjusted by the method of Booth (1948). The contributions of the two unique hydrogen atoms were clearly visible in both observed and difference Fourier maps. The two carbon atoms C(1) and C(2) in the general positions (see Fig. 1) were somewhat elongated parallel to the x direction, showing anisotropic thermal motion. All calculations to this stage were carried out on an 8k core IBM 1130 computer at the University of Natal, with the local set of programs (Laing & Sale, 1969).

The structure was then refined anisotropically by the method of least squares using the *CRYM* system at the California Institute of Technology. A Hughes (1941) weighting scheme was used. Weights were proportional to $1/F^2_{\rm obs}$ for $F_{\rm obs}$ greater than $4F_{\rm min}$ and to $1/(F_{\rm obs}\times 4F_{\rm min})$ for $F_{\rm obs}$ less than $4F_{\rm min}$, which was set at 2·5. The function minimized was $\sum w(k^2|F_{\rm obs}|^2-|F_{\rm calc}|^2)^2$ where w = weight, k = scale factor.

Neutral atom scattering factors for N, C, and H were taken from *International Tables for X-ray Crystallography* (1962). An extinction correction of 20×10^{-6} was applied (Larson, 1967), but this parameter was not included in the refinement; absorption corrections were not applied. The hydrogen atoms were included in the structure factor calculations (with positional coordinates deduced from the observed and difference Fourier maps), but their parameters were not refined. The final value of the conventional R was 0·105 for the 550 observed and unobserved data. The final positional and thermal parameters are given in Table 1. The observed and calculated structure factors are listed in Table 2.

Intermolecular non-bonded separations are given in Table 3. Fig. 1 shows the numbering system and the bond lengths and angles. Fig. 2 shows the electron density map, calculated in the plane of the molecule. The thermal vibration ellipsoids are illustrated in Fig. 3, and their parameters are given in Table 4. The mode of packing of the molecules and certain intermolecular separations are shown in Fig. 4.

Discussion

The molecule is planar, with normal bond lengths and angles. The C–N bond length of 1·331 Å in the pyridine ring may be compared with the values of 1·335 Å in isoniazide (Kupfer & Tsoucaris, 1963), 1·340 Å in pyridine (Bak, Hansen-Nygaard & Rastrup-Andersen, 1958), 1·338 Å in *sym*-triazine (Lancaster & Stoicheff, 1956) and 1·33 Å in pyridine-*N*-oxide hydrochloride (Tsoucaris, 1961). The C–C bond lengths of 1·381 and 1·383 Å in the ring are close to those observed in isonia-

Table 1. *Positional parameters, anisotropic temperature factors, and isotropic temperature factors**

The general form of the anisotropic temperature factor is $\exp[-(\beta_{11}h^2+\beta_{22}k^2+\beta_{33}l^2+\beta_{12}hk+\beta_{13}hl+\beta_{23}kl)]$.

	x	y	z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
C(1)	0·3602 (9)	0·4224 (4)	0·1811 (1)	0·108 (3)	0·0315 (7)	0·00170 (5)	0·004 (2)	−0·0020 (5)	−0·0019 (3)
C(2)	0·3640 (8)	0·4320 (4)	0·1216 (1)	0·084 (3)	0·0279 (6)	0·00166 (4)	−0·003 (2)	−0·0007 (4)	0·0001 (2)
C(3)	0·25 reqd	0·25 reqd	0·0919 (1)	0·063 (3)	0·0295 (9)	0·00149 (5)	0·001 (2)	0·0 reqd	0·0 reqd
C(4)	0·25 reqd	0·25 reqd	0·0299 (2)	0·102 (4)	0·0354 (11)	0·00152 (6)	−0·022 (3)	0·0 reqd	0·0 reqd
N(1)	0·25 reqd	0·25 reqd	0·2110 (1)	0·121 (4)	0·0340 (10)	0·00159 (5)	0·011 (3)	0·0 reqd	0·0 reqd
N(2)	0·25 reqd	0·25 reqd	−0·0191 (2)	0·188 (6)	0·0455 (13)	0·00162 (6)	−0·066 (6)	0·0 reqd	0·0 reqd
				B					
H(1)	0·44	0·55	0·205	5·5					
H(2)	0·45	0·56	0·100	5·5					

* The estimated standard deviations, obtained from the *CRYM* structure-factor least-squares program, are shown in parentheses. A full-matrix least-squares refinement by one of the referees indicates that these values are too small, and that e.s.d's of *twice* these values are more realistic. The approximate errors in the hydrogen atom parameters are $x\pm0·02$, $y\pm0·01$, $z\pm0·005$, $B\pm1·0$.

Table 2. *Observed and calculated structure factors* (×10).

The three columns are l index, F_{obs}, F_{calc}. Unobserved data are marked with asterisks.

0	0	L
2	20	11
4	124	-130
6	239	260
8	30	27
10	325	421
12	181	-191
14	185	-184
16	4	-7*
18	66	-62
20	134	-153
22	11	-9
24	14	17
26	58	-51
28	9	-8
0	1	L
2	520	-528
4	195	178
6	119	-103
8	258	246
10	7	-3*
12	85	-68
14	87	79
16	46	41
18	76	69
20	52	55
22	89	91
24	11	-11
26	9	9
28	16	14
0	2	L
0	236	-214
2	282	-302
4	400	-431
6	81	46
8	3	0*
10	110	-83
12	3	5*
14	100	-83
16	233	248
18	91	94
20	38	-34
22	44	44
24	10	12
26	68	56
28	8	7
0	3	L
2	161	-133
4	146	130
6	174	157
8	193	-189
10	4	7*
12	117	-103
14	119	106
16	79	76
18	220	-223
20	13	-12
22	3	-2*
24	4	-6*
26	4	0*
0	4	L
0	199	183
2	110	90
4	130	102
6	30	-24
8	21	22
10	71	60
12	28	-26
14	26	22
16	137	-115
18	39	-38
20	4	-1*
22	26	-26
24	13	10
0	5	L
2	147	-148
4	35	33
6	10	8
8	41	43
10	21	-22
12	43	-44
14	32	32
16	23	24
18	4	-5*
20	16	14
22	49	49
0	6	L
0	171	-169
2	5	4*
4	25	24
6	25	-23
8	5	0*
10	53	-53
12	24	26
14	38	38
16	4	-5*
18	15	12
0	7	L
2	20	23
4	4	-3*
6	22	22
8	20	-20
10	3	-4*
12	11	11
14	4	5*
1	0	L
2	616	-651
4	155	224
6	38	-49
8	171	233
10	26	-25
12	148	-134
14	128	111
16	64	60
18	28	16
20	53	53
22	105	100
24	15	-15
26	7	7
28	5	5
1	1	L
0	799	-747
1	213	230
2	151	-135
3	260	-313
4	135	-136
5	17	-12
6	89	-86
7	39	23
8	14	-10
9	59	49
10	239	-200
11	56	48
12	84	82
13	125	-115
14	61	51
15	17	14
16	116	100
17	91	85
18	74	69
19	47	-42
20	60	61
21	22	-22
22	19	18
23	22	24
24	7	-5
25	2	2*
26	33	47
27	8	8
28	7	7
1	2	L
1	134	-153
2	15	-15
3	55	-44
4	67	65
5	99	113
6	135	146
7	32	-32
8	165	-171
9	10	-6
10	5	-3*
11	49	-47
12	59	-56
13	21	-20
14	64	60
15	83	81
16	46	42
17	40	-40
18	191	-167
19	50	-48
20	28	-29
21	33	32
22	24	-24
23	3	0*
24	3	0*
25	3	-2*
26	3	-5*
27	5	-5
28	30	-35
1	3	L
0	98	106
1	52	53
2	141	154
3	25	-18
4	206	227
5	3	1*
6	71	-66
7	18	18
8	3	2*
9	22	18
10	62	57
11	3	1*
12	3	0*
13	21	-18
14	72	68
15	3	-2*
16	190	-194
17	11	10
18	62	-62
19	7	-9
20	42	40
21	14	-13
22	33	-35
23	3	1*
24	3	-2*
25	3	0*
26	38	-43
1	4	L
1	75	-79
2	50	-48
3	39	-31
4	33	-25
5	80	73
6	50	-38
7	3	-1*
8	80	80
9	3	-2*
10	23	-19
11	19	-22
12	16	10
13	9	-5
14	29	-23
15	70	70
16	13	-13
17	22	-20
18	79	78
19	35	-33
20	9	10
21	32	31
22	32	29
23	6	7
24	3	-1*
25	3	0*
1	5	L
0	187	-191
1	43	-41
2	23	-17
3	36	32
4	8	10
5	9	-10
6	19	-15
7	19	-15
8	13	-14
9	3	-3*
10	54	-56
11	11	-13
12	32	31
13	28	30
14	31	30
15	3	0*
16	17	17
17	20	-22
18	15	16
19	21	21
20	36	35
21	3	6*
22	3	3*
1	6	L
1	14	-15
2	78	83
3	9	-10
4	18	-20
5	13	12
6	3	6*
7	3	4*
8	23	-26
9	6	-7
10	5	5
11	9	-9
12	28	33
13	3	-1*
14	11	-15
15	7	8
16	8	-10
17	4	-5*
18	3	1*
1	7	L
0	44	44
1	11	-16
2	6	7
3	35	31
4	10	13
5	4	5*
6	3	0*
7	7	-5
8	9	-9
9	5	-4*
10	18	20
11	3	-4*
12	3	-1*
2	0	L
0	337	-333
2	89	-82
4	75	-84
6	20	-19
8	4	-1*
10	99	-94
12	38	36
14	21	19
16	91	82
18	51	54
20	24	27
22	10	7
24	6	-4
26	35	31
2	1	L
1	161	-220
2	100	147
3	49	-70
4	3	-3*
5	112	132
6	54	68
7	5	-5*
8	92	-114
9	14	13
10	11	13
11	77	-82
12	31	28
13	20	-18
14	8	10
15	109	108
16	12	9
17	46	-45
18	73	-73
19	55	-61
20	29	-29
21	41	42
22	33	-36
23	5	6
24	8	6
25	5	-5
26	4	-3
27	7	-9
2	2	L
0	252	236
1	72	-81
2	61	70
3	129	155
4	76	83
5	8	7
6	27	-18
7	37	-30
8	6	-3*
9	4	-5*
10	81	83
11	26	-24
12	24	-20
13	80	78
14	4	0*
15	19	-17
16	92	-102
17	71	-77
18	49	-42
19	43	40
20	4	-3*
21	13	14
22	14	-13
23	21	-22
24	4	4*
25	4	-3*
26	35	-31
2	3	L
1	29	-27
2	47	-42
3	20	-18
4	30	-24
5	28	25
6	55	-41
7	13	15
8	72	61
9	5	-3*
10	10	-9
11	6	-7
12	4	0*
13	6	5
14	30	-27
15	26	24
16	14	-11
17	4	0*
18	71	66
19	8	-9
20	12	15
21	11	11
22	25	24
23	10	9
24	4	-3*
2	4	L
0	108	-116
1	80	-84
2	44	-40
3	69	76
4	39	-33
5	5	-1*
6	12	11
7	48	-45
8	6	-5
9	12	-14
10	43	-41
11	12	-13
12	12	12
13	65	63
14	4	2*
15	7	-4
16	59	57
17	55	-55
18	22	25
19	43	41
20	8	6
21	23	23
22	7	7
2	5	L
1	45	43
2	49	49
3	14	11
4	6	4
5	35	-33
6	15	15
7	7	5
8	35	-34
9	8	-9
10	9	7
11	12	13
12	15	14
13	4	4*
14	6	4
15	39	-39
16	4	3*
17	10	12
18	21	-25
19	17	11
2	6	L
0	57	58
1	7	-7
2	12	12
3	27	26
4	8	8
5	14	14
6	4	-1*
7	5	-5*
8	5	-2*
9	6	-6
10	22	22
11	4	3*
12	4	-5*
13	10	9
14	4	-5*
15	4	-4*
2	7	L
1	28	31
2	10	-14
3	10	11
4	4	-3*
5	21	-21
6	7	-9
7	4	-1*
3	0	L
2	7	-7
4	44	44
6	60	54
8	51	-45
10	3	0*
12	9	-7
14	48	48
16	33	30
18	71	-72
20	17	-19
22	3	-3*
3	1	L
0	100	95
1	58	-49
2	46	41
3	89	79
4	50	41
5	7	7
6	27	-25
7	25	-23
8	11	-7
9	12	-9
10	46	40
11	10	-9
12	3	-1*
13	54	48
14	4	4*
15	14	-12
16	75	-70
17	45	-47
18	33	-31
19	25	26
20	4	7*
21	9	12
22	3	-2*
23	10	-13
3	2	L
1	66	65
2	88	-90
3	21	18
4	5	-4*
5	48	-40
6	14	-12
7	4	3*
8	48	42
9	8	-5
10	15	-13
11	33	29
12	32	-32
13	7	6
14	4	-5*
15	37	-39
16	4	2*
17	23	21
18	18	21
19	21	22
20	12	13
21	12	-15
22	20	24
3	3	L
0	141	-127
1	18	-19
2	16	-15
3	4	0*
4	15	13
5	3	2*
6	4	0*
7	17	-15
8	4	-6*
9	4	-6*
10	41	-39
11	4	3*
12	16	15
13	9	10
14	25	24
15	4	1*
16	19	17
17	3	-6*
18	14	13
19	7	8
20	20	21
3	4	L
1	44	45
2	41	39
3	16	19
4	6	8
5	36	-34
6	13	12
7	4	-3*
8	25	-24
9	4	0*
10	4	3*
11	15	19
12	14	15
13	4	0*
14	8	8
15	37	-38
16	3	2*
17	13	12
18	18	-19
3	5	L
0	22	25
1	23	22
2	16	17
3	12	-13
4	20	21
5	8	7
6	12	-12
7	8	9
8	8	-6
9	4	1*
10	15	15
11	7	6
12	3	3*
13	18	-17
3	6	L
1	12	10
2	3	0*
3	5	6
4	8	-11
5	5	-7

Table 3. *Intermolecular non-bonded separations*

Atom in asymmetric unit	to atom	
N(1)···	C(1′)	3·54 Å
C(1)···	C(1′)	3·84
C(1)···	H(1′)	3·09
H(1)···	N(1′)	2·58
C(2)···	N(2″)	3·41
H(2)···	N(2″)	2·49
C(3)···	N(2″)	3·98
C(4)···	N(2″)	3·62
C(4)···	C(4″)	3·87
N(2)···	N(2″)	3·71
C(1)···	N(1‴)	3·63
C(1)···	C(1‴)	3·65
C(2)···	C(3‴)	3·63
C(2)···	C(2‴)	3·70

Equivalent positions

′ $x+\frac{1}{2},\ -y-1,\ -z+\frac{1}{2}$

″ $x+\frac{1}{2},\ y+\frac{1}{2},\ -z$

‴ $-x+\frac{3}{2},\ -y+\frac{1}{2},\ z$

The least-squares plane is defined by atoms C(1) C(2) C(3) C(4) N(1) N(2). Direction cosines of the normal to the plane referred to *a*, *b* and *c* are 0·930, −0·367 and 0·000 respectively. Origin-to-plane distance = 0·33 Å

Deviation from plane (Å):

C(1)	C(2)	C(3)	C(4)	N(1)	N(2)	H(1)	H(2)
0·004	−0·004	0·000	0·000	0·000	0·000	0·00	0·01

Table 4. *The observed thermal ellipsoids*

	$\sqrt{\bar{u}^2}$	Direction cosines referred to		
	(Å)	*a*	*b*	*c*
C(1)	0·21	−0·092	−0·369	−0·925
	0·25	0·198	−0·917	0·346
	0·28	−0·976	−0·151	0·158
C(2)	0·21	0·096	−0·014	0·995
	0·23	0·200	0·980	−0·006
	0·25	0·975	−0·200	−0·097
C(3)	0·20	0·0	0·0	−1·0
	0·22	−0·996	0·091	0·0
	0·24	0·091	0·996	0·0
C(4)	0·20	0·0	0·0	−1·0
	0·24	−0·589	−0·808	0·0
	0·29	−0·808	0·589	0·0
N(1)	0·21	0·0	0·0	1·0
	0·25	−0·239	0·971	0·0
	0·30	0·971	0·239	0·0
N(2)	0·21	0·0	0·0	1·0
	0·26	0·470	0·883	0·0
	0·40	0·883	−0·470	0·0

zide which range from 1·381 to 1·389 Å (Kupfer & Tscoucaris, 1963) and to those of 1·394 Å found in pyridine (Bak *et al.*, 1958).

The values of 1·439 Å for C(ring)–C(nitrile) and 1·137 Å for C≡N are similar to the expected values of 1·43 and 1·15 Å respectively. (Sutton, 1965). The

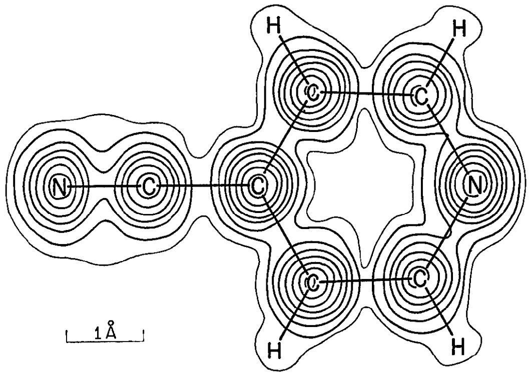


Fig. 2. Electron density map calculated in the plane of the molecule. Contours are drawn at 0·5, 1, 2, 3 *etc.* e.Å^{-3}.

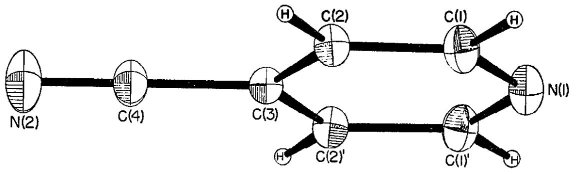


Fig. 3. Thermal vibration ellipsoids, viewed in projection down **b**.

C–N–C and N–C–C angles of 117·3 and 123·9° are close to the values of 116·9° and 123·8° respectively observed in pyridine.

There are few short intermolecular non-bonded contacts and it appears that the forces holding the structure together are of three types: (i) between the π clouds of the pyridine rings stacked by translation along **a**, (ii) between pairs of C≡N groups related by centres of symmetry, and (iii) for a molecule of type 1 (Fig. 4), between C(1)–H(1) and the pyridine nitrogen N(1) of a molecule of type 2 (related by a 2_1 screw axis), and between C(2)–H(2) and the cyano nitrogen N(2) of a molecule of type 3 (related by a centre of inversion).

While the two C–H···N arrangements can hardly be called 'hydrogen bonds' (Donohue, 1968), their presence seems to be more than coincidence because they effectively prevent the usual 'bump-in-hollow' packing parallel to **b** (Kitaigorodskii, 1961).

The distance between N(1) in any molecule and N(2) of the molecule related to it by the *c* glide, is 6·27 Å. These molecules do not 'touch'; neither do those related by unit translation parallel to **b**. This results in a 'hole' of diameter about 1 Å that runs through the crystal parallel to **a**. Its presence is the cause of the relatively low density of the material.

The thermal motion parameters show that the molecule is vibrating about a point close to C(3), with the cyano group 'wagging' roughly parallel to the *a* axis. This is physically reasonable, as the N···N separation in this direction is 3·82 Å, while the contacts in other directions are shorter; 3·41, 3·62, and 3·71 Å (Table 3, Fig. 4) [The relatively high thermal motion of the structure as a whole was evident from the areas of diffuse scattering surrounding certain reflexions on the Weissenberg photographs. This effect is well known in crystals of planar aromatic compounds (Hoppe, 1957; Amoros, Canut & de Acha, 1960; Laing, 1964).]

It would appear that this structure is not 'maximum close packed' as a result of the molecule retaining its twofold axis of symmetry in the crystal. While space group *Pccn* is permissible (but improbable for molecules of symmetry $\bar{1}$), space group *Pbcn* would be more suitable for molecules of symmetry 2, while *Pnma* would be more suitable for molecules of symmetry *m* (Kitaigorodskii, 1961, p. 100). Were the molecule to retain no symmetry element (other than 1) in the crystal, it is easy to show, with the aid of suitable ('Leybold') models, that a more dense structure could be achieved by simple 'bump-in-hollow' packing by translation. One is therefore led to conclude that this is a unique structure, and that the C–H···N interactions somehow force the molecules to pack in this manner (Fig. 5).

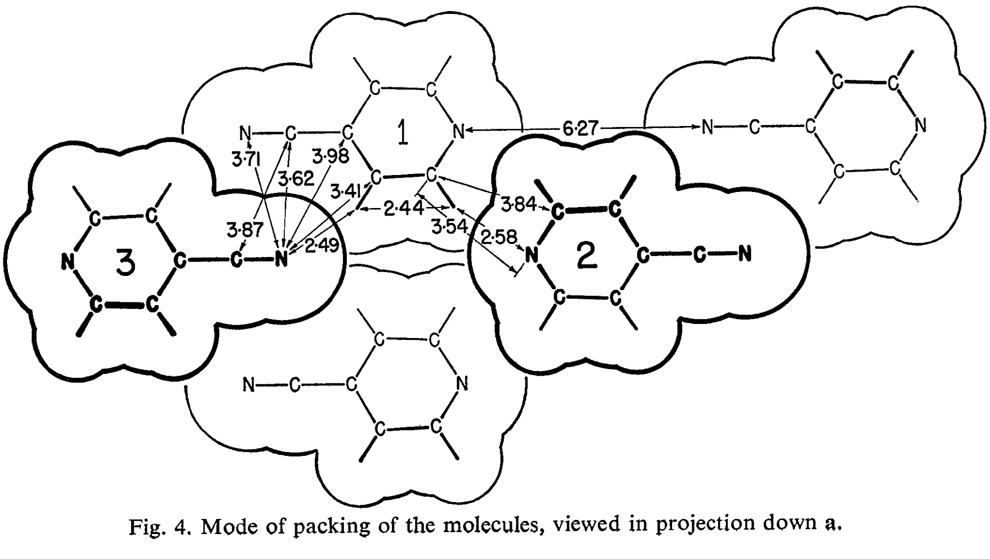


Fig. 4. Mode of packing of the molecules, viewed in projection down **a**.

We are grateful to the South African Council for Scientific and Industrial Research for a grant to cover running expenses and to the Chemistry Department, California Institute of Technology, for a grant to cover the cost of the final refinement. M. Laing wishes to thank the faculty of the Chemistry Department, San Fernando Valley State College and especially Dr R. E. Marsh, of the California Institute of Technology for their generosity and hospitality during his stay in Los Angeles in 1970. The diagrams were prepared by Miss Lillian Casler.

References

AMOROS, J. L., CANUT, M. L. & DE ACHA, A. (1960). *Z Kristallogr.* **114**, 39.

BAK, B., HANSEN-NYGAARD, L. & RASTRUP-ANDERSEN, J. (1958). *J. Mol. Spect.* **2**, 361.

BOOTH, A. D. (1948). *Fourier Technique in X-ray Organic Structure Analysis*. Cambridge Univ. Press.

DONOHUE, J. (1968). In *Structural Chemistry and Molecular Biology*, pp. 459–463. San Francisco: Freeman.

HEILBRON, I. M. (1965). *Dictionary of Organic Compounds*, Vol 2, p. 768. Oxford Univ. Press.

HOPPE, W. (1957). *Z. Kristallogr.* **108**, 321, 328, 335.

HUGHES, E. W. (1941). *J. Amer. Chem. Soc.* **63**, 1737.

International Tables for X-ray Crystallography (1962) Vol. III, pp. 202, 204. Birmingham: Kynoch Press.

KITAIGORODSKII, A. I. (1961). *Organic Chemical Crystallography*. New York: Consultants Bureau.

KUPFER, D. & TSOUCARIS, G. (1963). *Rapport d'Activité du Laboratoire de Cristallographie, CNRS*, 1962–1963, p. 5.

LAING, M. & SALE, A. (1969). *Acta Cryst.* B**25**, 1674.

LAING, M. (1964). Ph. D. Thesis, UCLA.

LANCASTER, J. E. & STOICHEFF, B. P. (1956). *Canad. J. Phys.* **34**, 1016.

LARSON, A. C. (1967). *Acta Cryst.* **23**, 664, equation (3).

SPARROW, N. (1970). M. Sc. Thesis, Univ. of Natal.

SUTTON, L. E. (1965). *Table of Interatomic Distances and Configurations in Molecules and Ions*. London: The Chemical Society.

TSOUCARIS, G. (1961). *Acta Cryst.* **14**, 914, 917.

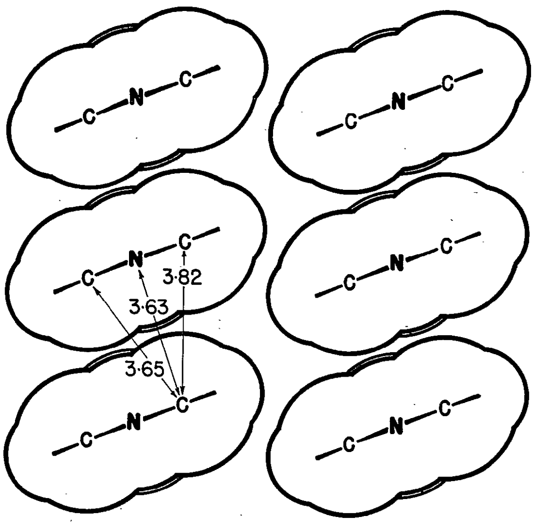


Fig. 5. Mode of packing of the molecules related by simple translations along **a** and **b**, viewed in projection down **c**.

Acta Cryst. (1971). B**27**, 1990

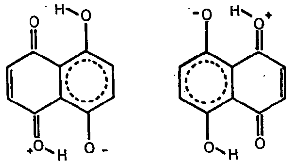
A Further Investigation of the Crystal Structures of Naphthazarin

BY P. D. CRADWICK AND D. HALL

Department of Chemistry, University of Alberta, Edmonton, Alberta, Canada

(*Received* 26 *October* 1969 *and in revised form* 25 *July* 1970)

The crystal structures of two modifications of naphthazarin (formally 5,8-dihydroxy-1,4-naphthaquinone) have been further refined, using three-dimensional X-ray counter data in one case, and previously reported photographic data in the other. The carbon skeleton of the molecule is shown to possess D_{2h} symmetry within the standard deviation in carbon—carbon bond length, which was 0·006 Å in the more accurate study. The phenolic hydrogen atom, which is involved in an intramolecular hydrogen bond between the phenolic and quinonoid oxygen atoms, appears to be non-symmetrically placed between them. This structure can be interpreted in terms of resonance between the zwitterion contributors:



Introduction

Although the compound known as naphthazarin is commonly described as 5,8-dihydroxy-1,4-naphthaquinone, there has been some doubt as to its true structure. There is little difference in nuclear arrangement between the equivalent structures (I) and (III), and it seemed possible that these may have been canonicals of a sym-