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The Crystal Structure of 1-Phenyl-2-(2-pyridyl)ethanedione-1,2

By T. Ashida
Institute of Protein Research, Osaka University, Osaka, Japan

S. Hirokawa
Chemistry Department, Defense University, Yokosuka, Japan

and Y. Okaya
IBM Research Center, Yorktown Heights, N.Y., U.S.A.

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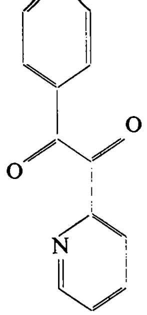
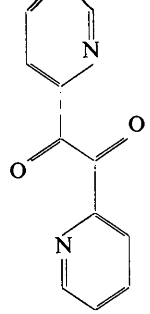
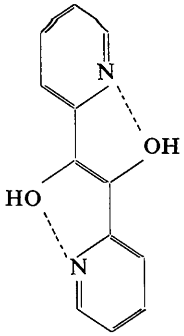
The crystal structure of 1-phenyl-2-(2-pyridyl)ethanedione-1,2 has been determined from three-dimensional intensity data and refined by the least-squares method with anisotropic thermal parameters. The positions of all the hydrogen atoms were found by a three-dimensional difference Fourier synthesis and included in the refinements. The crystal is monoclinic, space group $P2_1/c$, $a = 11{\cdot}45$, $b = 6{\cdot}55$, $c = 14{\cdot}60$ Å and $\beta = 90{\cdot}4°$. The molecular configuration is quite close to that of 2,2′-pyridil, 1,2-di-(2-pyridyl)ethanedione-1,2. The molecule consists of two planar parts, one of which contains a pyridine ring, a carbonyl group and its adjacent carbon atom, and the other contains a phenyl group, a carbonyl group and its nearest carbon atom; the angle between the two planes is 88·1°. The carbonyl oxygen of the phenyl part of the molecule is shifted from the plane by 0·1 Å. The characteristic feature of the crystal structure is plane-to-plane parallel stackings formed by pairs of pyridine rings and phenyl planes. The difference between the melting points of the present crystal and 2,2′-pyridil is discussed in terms of the difference in their crystal structures.

Introduction

The crystal structure of 1,2-di-(2-pyridyl)ethanedione-1,2 (pyridil) (II) has been reported by two of the present authors (Hirokawa & Ashida, 1961). The mode of packing of the molecules in the crystal is unique; in short, it shows a plane-to-plane stacking made by four almost parallel pyridine rings, with interplanar distances corresponding to the normal van der Waals contact. The molecular conformation of 1-phenyl-2-(2-pyridyl)ethanedione-1,2 (hereafter called PPED) (I) is supposed to be similar to that of pyridil; however,


(I) PPED


(II) Pyridil


(III) Pyridoin

the melting point of PPED is 72–73 °C, which is much lower than that of pyridil, 154–155 °C. Such a difference in their melting points may be due to some differences in the mode of contact between the aromatic rings in these two crystals. The present study on PPED was, therefore, initiated in order to obtain further crystallographic information on the packings of molecules in the crystals.

The crystal structure of 1,2-di-(2-pyridyl)ethenediol-1,2 (α-pyridoin) (III) has also been reported by the present authors (Ashida, Hirokawa & Okaya, 1965). It may also be worthwhile to make comparison of the shapes of the three molecules shown above.

The present paper deals with the crystal structure of PPED determined and refined by using three-dimensional intensity data.

Experimental

Well-developed crystals of PPED, $C_{13}H_9NO_2$, recrystallized from a methanol solution were kindly supplied by Prof. D. Oda of the Defense University, who synthesized the substance by oxidation of phenyl 2-picolyl ketone (Oda, 1961). The monoclinic crystals thus obtained are slightly yellowish plates with predominant (001) faces. The unit-cell dimensions are shown in Table 1 together with those of pyridil.

Table 1. *The crystallographic data of* PPED *and pyridil*

	PPED	Pyridil
a	11·45 ± 0·02 Å	6·41 ± 0·02 Å
b	6·55 ± 0·01	13·03 ± 0·02
c	14·60 ± 0·02	12·79 ± 0·03
β	90·4 ± 0·3°	99·5 ± 0·5°
V	1094·9 Å^3	1053·6 Å^3
ϱ_o	1·28 g.cm^{-3}	1·36 g.cm^{-3}
ϱ_c	1·28	1·36
Z	4	4
Space group	$P2_1/c$	$P2_1/n$

Three-dimensional intensity data were obtained from equi-inclination Weissenberg photographs with Cu $K\alpha$ radiation. The crystals were rotated around the b axis ($k=0$ to 4) and the a axis ($h=0$ to 7). More than 90% of the total reflections within the limiting sphere for Cu $K\alpha$ radiation were recorded. Intensities were estimated visually by comparison with a standard scale. They were corrected for the Lorentz and polarization factors, and the effect of elongation of reflections in higher layer photographs was also taken into account by the method of Phillips (1956). The correction for absorption was neglected because of the small size of the crystals used in the experiment. Out of the 2350 reflections recorded, about 700 were too weak to be observed.

Structure determination

Inspection of the unit-cell dimensions of PPED and pyridil shows that these two crystals are not isomorphous with each other; however, each crystal has one short unit-cell axis and it can be expected that the shape of the PPED molecule viewed along the b axis is similar to that of pyridil viewed along its a axis. For pyridil this projection of the structure was solved by application of the direct sign determination method.

At first, the direct method was applied to the projection along the b axis. The formula was $S_{\rm H}=S_{\rm H'}\,.\,S_{\rm H+H'}$, which was first used by Cochran (1952). Although only few reflections are strong enough for sign relationship (only two, $F(004)$ and $F(300)$, have $|U|$ larger than 0·4), signs of about 30 out of 218 $F(h0l)$'s were tentatively given with two unknown parameters. A set of signs out of four possible choices was selected after some more inspections, and it was used to synthesize $\varrho(xz)$, which is shown in Fig. 1. In this synthesis, $F(004)$, of which $|U|=0{\cdot}48$, was not included, because it could not be assigned with reliable sign. By comparing this map with the projection of the crystal structure of pyridil on the (100) plane, and then adding the contribution of $F(004)$ with plausible sign, the rough layout of the molecule was determined. This map could not have been interpreted if the crystal structure of pyridil had not been determined.

The severe overlapping of atoms in the b-axis projection thus obtained makes it difficult to find the y parameters of the atoms by the trial and error method. Therefore a sharpened, origin-removed three-dimensional Patterson function was synthesized. By comparing this with that of pyridil, the molecular configuration of PPED was established to be quite similar to that of pyridil, and the relative y coordinates of the atoms in a molecule were determined approximately. This was done as illustrated in Fig. 2 by selecting a section of the Patterson function for each crystal; the section is so chosen as to show the correspondence of intramolecular vectors for the two crystals. The molecule was then translated from $y=0$ to 0·5 by steps of 0·05, and the R indices for some selected $F(hk0)$ and $F(0kl)$ reflections were computed for each step. By choosing the position of the minimum R, a possible set of coordinates was obtained. The structure factors were then calculated for some of the three-dimensional reflections, and bounded projections, $\int_0^{1/3}\varrho(xyz)dz$ and $\int_0^{1/3}\varrho(xyz)dx$, were synthesized; the layout of the molecule was clearly shown in the projections. The location of the nitrogen atom in the pyridyl ring was determined by inspecting the peak height of the four possible positions in the molecule. This choice was later substantiated by calculating the electron-density function associated with the hydrogen atoms with the usual F_o-F_c method. No density was found near this nitrogen atom in the function; this also rules out the possibility of disorder between the pyridyl and phenyl rings.

The atomic coordinates of the non-hydrogen atoms thus obtained were then refined by the block-diagonal matrix least-squares method with anisotropic temperature factors assigned to each atom. After several cycles, the error index, R, decreased to 11%; then a three-dimensional (F_o-F_c) synthesis was made, and all the hydrogen atoms were found. These hydrogen atoms were then included in the subsequent refinements; only isotropic temperature factors were assigned to account for their thermal vibrations. Finally the error index, R, decreased to 0·079 excluding non-observed reflections. The atomic scattering factors used in the calculations were obtained from *International Tables for X-ray Crystallography* (1962). Comparison between the observed and the calculated structure factors is shown in Table 3. The final atomic coordinates and the vibration factors are listed in Table 2.

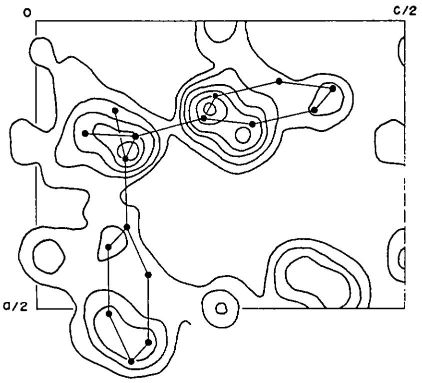


Fig. 1. An approximate electron-density projection along the b axis. The Fourier series contains only 30 terms. The final atomic positions are indicated by dots.

The shifts of parameters at the last stage were quite negligible compared with their standard deviations. The weighting scheme used in the least-squares refinement is; $\omega=1\cdot0$ for $|F_{\rm obs}|\le 25\cdot0$ and $\omega=25\cdot0/|F_{\rm obs}|$ for larger $F_{\rm obs}$'s. Reflections too weak to be observed were given weights of zero. An analysis of the anisotropic thermal vibration factors indicates that the aromatic rings oscillate around the central C–C bond; the phenyl group has a larger amplitude than the pyridyl group. The computations at later stages were done on an IBM 7094 machine at the IBM Research Center with programs written by one of the authors (Okaya, 1963). Some computations at the initial stage were done on a NEAC 2101 at the Institute for Protein Research.

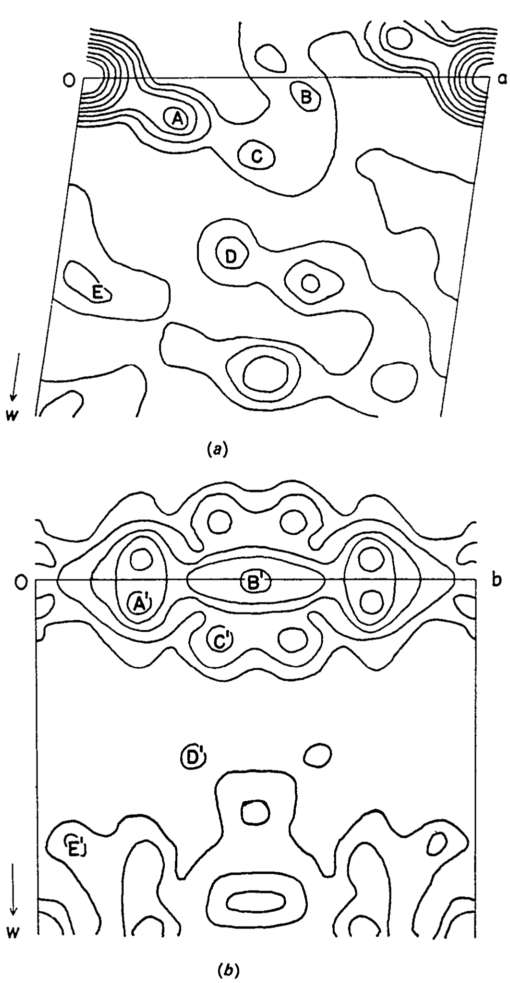


Fig. 2. Comparison of two 3-D sharpened Patterson sections. (*a*) $P(u0w)$ of pyridil. (*b*) A section of PPED with the origin peak removed. The section goes through the origin of the coordinates and is perpendicular to the [101] axis. The peaks A, B, C, D and E in (*a*) correspond to those primed in (*b*).

Discussion

Bond distances, angles and other interatomic distances shorter than 4·0 Å were evaluated on the IBM 7094; they are shown in Figs. 3 and 5.

The molecule consists of two planar parts, each containing an aromatic ring (phenyl or 2-pyridyl) and a carbonyl group attached to the ring; in each plane is also found the carbon atom of the carbonyl group belonging to the other part. The equations of these planes were evaluated by the method of least-squares. The equations are:

$$0\cdot9457X+0\cdot2852Y+0\cdot1556Z-3\cdot7919=0$$

for the plane of the pyridine ring, and

$$-0\cdot0962X-0\cdot3131Y+0\cdot9448Z-4\cdot4509=0$$

for the plane of the phenyl group, where $X=ax\sin\beta$, $Y=by$ and $Z=cz+ax\cos\beta$, respectively. Displacements of the atoms from each evaluated plane are shown in Fig. 4. The C–C bond in the central diketone group is the intersection of the two planes which make an angle of 88·1° with each other. This angle is quite similar to that of 82·7° found in the structure of pyridil. The nitrogen atom in the 2-pyridyl group and O(p) are in a *trans*-configuration around the C(p, 6)–C(p, 7) bond. The two ketonic oxygen atoms are, as in the case of pyridil, in a *gauche* form with respect to the central C(p, 7)–C(φ, 7) bond. Thus, the molecular

Table 2(*a*). *Atomic coordinates in fractions of cell edges and their standard deviations in* 10^{-4} Å

	x	$\sigma(x)$	y	$\sigma(y)$	z	$\sigma(z)$
Pyridyl part						
N	0·18123	33	0·35021	34	0·54276	31
C(p, 2)	0·15339	47	0·40758	48	0·62871	40
C(p, 3)	0·11620	44	0·60321	53	0·65034	43
C(p, 4)	0·10469	42	0·74394	46	0·58125	49
C(p, 5)	0·13250	39	0·69044	40	0·49279	41
C(p, 6)	0·16863	35	0·49216	38	0·47659	35
C(p, 7)	0·20025	36	0·42433	39	0·38338	36
O(p)	0·19539	31	0·53005	29	0·31639	27
H(p, 2)	0·1414		0·2969		0·6680	
H(p, 3)	0·0752		0·6480		0·7168	
H(p, 4)	0·0744		0·8714		0·5963	
H(p, 5)	0·1296		0·7840		0·4438	
Phenyl part						
C(φ, 1)	0·44282	40	0·28278	43	0·39991	41
C(φ, 2)	0·55844	48	0·23040	58	0·40088	51
C(φ, 3)	0·59171	49	0·03429	64	0·37578	55
C(φ, 4)	0·50969	54	−0·10482	51	0·34698	52
C(φ, 5)	0·39244	44	−0·05402	42	0·34587	41
C(φ, 6)	0·35927	37	0·14286	37	0·37174	33
C(φ, 7)	0·23401	38	0·19704	37	0·37074	30
O(φ)	0·15580	27	0·07937	26	0·35408	26
H(φ, 1)	0·4173		0·4075		0·4167	
H(φ, 2)	0·6189		0·3347		0·4238	
H(φ, 3)	0·6828		0·0269		0·3670	
H(φ, 4)	0·5360		−0·2583		0·3338	
H(φ, 5)	0·3209		−0·1614		0·3258	

Table 2 (*b*), *Anisotropic temperature factors for non-hydrogen atoms*

The β's are used in the expression: $\exp\{-(\beta_{11}h^2+\beta_{22}k^2+\beta_{33}l^2+\beta_{12}hk+\beta_{13}hl+\beta_{23}kl)\}$.

	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Pyridyl part						
N	0·0133	0·0353	0·0054	0·0040	−0·0008	−0·0000
C(p, 2)	0·0161	0·0417	0·0054	0·0034	−0·0007	−0·0014
C(p, 3)	0·0125	0·0473	0·0068	0·0029	−0·0007	−0·0065
C(p, 4)	0·0114	0·0349	0·0092	0·0044	0·0009	−0·0084
C(p, 5)	0·0107	0·0301	0·0074	0·0007	−0·0004	−0·0001
C(p, 6)	0·0093	0·0289	0·0054	−0·0010	−0·0007	0·0003
C(p, 7)	0·0100	0·0305	0·0058	−0·0011	−0·0000	0·0009
O(p)	0·0179	0·0360	0·0065	0·0009	0·0000	0·0094
Phenyl part						
C(φ, 1)	0·0099	0·0373	0·0078	−0·0002	−0·0002	−0·0040
C(φ, 2)	0·0117	0·0535	0·0100	−0·0012	−0·0025	−0·0070
C(φ, 3)	0·0117	0·0581	0·0108	0·0078	0·0015	−0·0013
C(φ, 4)	0·0146	0·0409	0·0105	0·0077	0·0037	−0·0027
C(φ, 5)	0·0123	0·0341	0·0078	0·0033	0·0025	−0·0017
C(φ, 6)	0·0108	0·0319	0·0050	−0·0003	0·0011	0·0012
C(φ, 7)	0·0113	0·0317	0·0039	−0·0019	0·0005	0·0006
O(φ)	0·0118	0·0317	0·0075	−0·0070	0·0000	−0·0027

Table 2 (*c*). *Isotropic temperature factors for hydrogen atoms in* 10^{-16} cm²

H(p, 2)	H(p, 3)	H(p, 4)	H(p, 5)	
5·3	4·5	6·2	5·1	
H(φ, 1)	H(φ, 2)	H(φ, 3)	H(φ, 4)	H(φ, 5)
4·0	8·9	9·5	7·1	8·5

configuration of PPED is very close to that of pyridil; this is again illustrated in Fig. 6, which shows a molecule of PPED viewed down the [101] axis. Similarity of this figure to the projection of the structure of pyridil along its *b* axis (see Fig. 1 of Hirokawa & Ashida, 1961) is striking. Then, as will be discussed later, a difference in the mode of packing of the molecules explains the difference in the melting points of these two compounds.

The bond distances and angles in the pyridine ring are, as a whole, very close to those of pyridil or of α-pyridoin, and also to those of the free pyridine molecule and other compounds with pyridine rings; also normal is the configuration of the phenyl group. The dimensions of the central part of the molecule, the diketone group, are also very close to those of pyridil; the central C–C bond is a pure single bond, C(p, 6)−C(p, 7) and C(φ, 6)−C(φ, 7) are slightly shorter than the single

Table 3. *Comparison between the observed and calculated structure factors*

The values have been multiplied by 10.

	FO	FC
H,K= 0, 0		
L=4	1310	1412
6	453	432
8	376	348
10	80	82
14	0	3
14	33	28
18	23	20
H,K= 1, 0		
L=2	754	739
4	61	51
6	9	17
8	56	66
10	33	30
12	61	55
14	0	6
16	33	33
18	28	32
H,K= 2, 0		
L=0	330	337
2	247	247
4	202	191
6	152	153
8	25	29
10	64	73
12	225	213
14	47	44
16	40	40
18	30	29
H,K= 3, 0		
L=0	1363	1492
2	856	812
4	281	273
6	87	103
8	14	6
10	18	16
12	14	15
14	61	57
16	12	1
18	8	11
H,K= 4, 0		
L=0	735	744
2	529	488
4	337	324
6	114	111
8	130	120
10	93	83
12	68	67
14	86	80
16	0	7
18	0	6
H,K= 5, 0		
L=0	416	394
2	83	78
4	81	66
6	25	24
8	33	34
10	0	5
12	111	110
14	111	97
16	0	1
H,K= 6, 0		
L=0	171	178
2	409	384
4	35	45
6	36	35
8	0	21
10	50	50
12	46	46
14	46	39
16	0	6
H,K= 7, 0		
L=0	105	101
0	105	101
2	204	204
4	0	12
6	0	4
8	17	19
10	0	4
12	73	68
14	50	41
16	0	13
H,K= 8, 0		
L=0	23	28
2	55	52
4	29	29
6	174	159
8	114	105
10	104	96
12	0	6
14	120	111
H,K= 9, 0		
L=0	0	0
2	42	37
4	0	9
6	114	101
8	30	26
10	94	86
12	0	0
14	0	4
H,K= 10, 0		
L=0	0	7
2	50	54
4	32	29
6	0	20
8	71	60
10	0	12
12	0	5
H,K= 11, 0		
L=0	0	14
2	0	0
4	0	3
6	41	40
8	61	48
10	0	5
12	0	3
H,K= 12, 0		
L=0	0	1
2	0	3
4	0	1
6	0	3
8	16	18
10	0	7
H,K= 13, 0		
L=0	0	7
2	40	30
4	13	7
6	25	23
8	15	15
H,K= 14, 0		
L=0	0	2
2	13	10
4	16	13
6	0	7
H,K= 0, 1		
L=1	244	260
2	717	761
3	477	467
4	200	217
5	308	308
6	441	488
7	160	184
8	247	249
9	39	30
10	60	59
11	79	87
12	0	4
13	93	87
14	14	15
15	16	27
16	22	23
17	13	12
18	10	13
H,K= 1, 1		
L=0	219	281
1	467	492
2	78	67
3	524	520
4	37	37
5	289	272
6	21	22
7	253	259
8	34	38
9	180	175
10	34	22
11	66	65
12	69	75
13	74	83
14	32	35
15	16	17
16	14	12
17	7	7
18	0	3
H,K= 2, 1		
L=0	112	117
1	500	516
2	164	164
3	43	61
4	370	356
5	37	36
6	138	138
7	97	98
8	65	78
9	64	65
10	23	25
11	34	35
12	108	116
13	109	115
14	46	58
15	16	9
16	8	13
17	0	5
18	18	20
H,K= 3, 1		
L=0	411	474
1	732	734
2	155	153
3	70	73
4	81	72
5	93	103
6	124	115
7	135	141
8	169	165
9	65	70
10	29	35
11	30	32
12	0	8
13	70	79
14	14	5
15	0	1
16	0	2
17	13	12
18	0	3
H,K= 4, 1		
L=0	355	354
1	187	191
2	42	48
3	204	197
4	60	70
5	74	70
6	0	4
7	0	9
8	0	6
9	47	57
10	0	14
11	74	80
12	0	8
13	54	64
14	29	29
15	15	11
16	0	7
17	6	6
18	0	10
H,K= 5, 1		
L=0	15	7
1	355	332
2	13	11
3	214	225
4	109	121
5	126	126
6	158	148
7	150	149
8	41	39
9	55	52
10	0	9
11	0	5
12	14	16
13	97	107
14	22	25
15	17	20
16	0	0
17	0	7
H,K= 6, 1		
L=0	190	192
1	226	242
2	344	344
3	77	85
4	92	94
5	39	53
6	0	12
7	0	4
8	31	40
9	17	17
10	17	21
11	0	6
12	0	10
13	41	38
14	0	3
15	0	14
16	0	11
H,K= 7, 1		
L=0	194	195
1	104	102
2	48	54
3	64	69
4	0	19
H,K= 7, 1		
5	32	44
6	0	5
7	61	70
8	10	5
9	14	23
10	31	31
11	0	3
12	0	1
13	34	33
14	32	30
15	17	18
16	0	4
H,K= 8, 1		
L=0	0	4
1	160	156
2	0	15
3	34	43
4	22	29
5	55	62
6	32	41
7	0	9
8	88	101
9	0	4
10	21	21
11	31	36
12	46	50
13	46	44
14	21	22
15	10	12
H,K= 9, 1		
L=0	23	31
1	85	82
2	184	187
3	146	166
4	124	134
5	46	54
6	33	45
7	101	73
8	32	35
9	30	35
10	20	23
11	22	20
12	14	15
13	31	32
14	0	10
H,K= 10, 1		
L=0	53	51
1	17	19
2	0	11
3	0	19
4	23	24
5	17	18
6	32	45
7	14	20
8	0	0
9	0	7
10	0	13
11	0	9
12	0	1
13	12	17
H,K= 11, 1		
L=0	47	51
1	54	61
2	23	33
3	0	5
4	0	10
5	22	27
6	0	4
7	0	15
8	0	14
9	0	5
10	0	13
11	0	0
12	0	12
H,K= 12, 1		
L=0	0	2
1	0	5
2	23	28
3	41	43
4	27	26
5	0	3
6	0	5
7	0	15
8	0	3
9	0	3
10	0	5
H,K= 13, 1		
L=1	8	12
2	0	12
3	21	22
4	24	23
5	0	5
6	0	8
7	0	3
8	0	5
H,K= 14, 1		
L=0	12	14
1	24	23
2	0	3
3	0	12
4	0	4
5	0	13
H,K= 0, 2		
L=0	130	144
1	146	140
2	361	358
3	214	206
4	78	80
5	12	6
6	389	369
7	35	35
8	15	8
9	124	125
10	78	78
11	50	55
12	0	18
13	62	60
14	13	18
15	32	35
16	0	7
17	32	31
18	0	6
H,K= 1, 2		
L=0	83	94
1	204	203
2	169	170
3	318	312
4	140	154
5	143	151
6	171	163
7	80	53
8	89	78
9	40	44
10	21	19
11	39	42
12	30	33
13	46	51
14	0	1
15	28	26
H,K= 1, 2		
16	0	12
17	0	1
18	7	12
H,K= 2, 2		
L=0	330	314
1	397	350
2	290	282
3	73	80
4	118	113
5	0	7
6	72	62
7	198	203
8	36	41
9	31	37
10	69	70
11	39	44
12	13	17
13	66	64
14	25	29
15	17	15
16	0	11
17	23	14
18	0	4
H,K= 3, 2		
L=0	133	137
1	96	97
2	164	172
3	84	91
4	103	98
5	144	134
6	192	189
7	178	180
8	18	7
9	32	32
10	0	0
11	36	40
12	13	16
13	0	3
14	18	19
15	0	3
16	0	8
17	0	5
H,K= 4, 2		
L=0	106	88
1	331	318
2	49	55
3	145	156
4	286	267
5	205	200
6	178	165
7	48	61
8	182	174
9	111	109
10	58	57
11	0	10
12	0	1
13	61	62
14	0	11
15	13	18
16	0	8
17	12	12
H,K= 5, 2		
L=0	321	307
1	226	211
2	131	118
3	27	25
4	46	42
5	73	73
6	60	70
7	137	137
8	67	66
9	64	66
10	0	2
11	0	1
12	0	13
13	0	15
14	14	10
15	0	1
16	0	2
17	0	7
H,K= 6, 2		
L=0	201	197
1	175	173
2	94	89
3	72	74
4	127	130
5	27	24
6	26	29
7	98	95
8	65	63
9	20	26
10	18	19
11	13	19
12	12	16
13	0	4
14	0	0
15	13	11
16	8	6
H,K= 7, 2		
L=0	30	36
1	140	137
2	46	48
3	64	63
4	39	42
5	61	61
6	40	36
7	0	4
8	80	82
9	36	39
10	0	3
11	26	26
12	0	3
13	15	18
14	0	8
15	0	9
H,K= 8, 2		
L=0	54	54
1	30	28
2	0	7
3	15	26
4	60	59
5	32	32
6	42	48
7	48	49
8	36	41
9	0	4
10	0	16
11	15	15
12	0	4
13	12	15
14	0	2
15	0	1
H,K= 9, 2		
L=0	177	164
1	125	125
2	104	91
3	0	1
4	60	60
5	36	37
6	0	1
H,K= 9, 2		
7	44	47
8	39	40
9	34	33
10	27	24
11	22	23
12	14	13
13	12	12
14	0	6
H,K= 10, 2		
L=0	62	67
1	96	91
2	48	55
3	67	64
4	45	52
5	34	45
6	0	3
7	0	5
8	15	12
9	26	29
10	0	4
11	0	6
12	0	9
13	0	13
H,K= 11, 2		
L=0	0	10
1	0	7
2	21	28
3	0	14
4	30	36
5	0	3
6	14	15
7	26	24
8	13	12
9	0	6
10	0	7
11	13	16
H,K= 12, 2		
L=0	29	32
1	29	31
2	44	41
3	28	29
4	21	21
5	12	14
6	12	7
7	0	11
8	0	7
9	0	11
H,K= 13, 2		
L=0	0	2
1	26	23
2	0	13
3	17	17
4	17	19
5	0	8
6	16	15
7	0	0
H,K= 14, 2		
L=0	8	9
1	0	5
2	0	3
3	0	9
H,K= 0, 3		
L=1	31	48
2	130	124
3	167	168
4	74	73
5	34	37
6	46	48
7	0	7
8	60	62
9	0	12
10	63	65
11	0	10
12	30	25
13	31	37
14	0	1
15	24	23
16	0	8
17	0	6
H,K= 1, 3		
L=0	228	197
1	270	256
2	55	49
3	94	102
4	9	13
5	35	47
6	16	22
7	51	50
8	26	34
9	61	68
10	0	4
11	86	90
12	24	32
13	25	37
14	26	27
15	45	44
16	7	9
17	14	18
H,K= 2, 3		
L=0	355	337
1	23	22
2	273	256
3	178	187
4	88	84
5	54	57
6	101	93
7	71	79
8	37	41
9	50	50
10	0	5
11	0	11
12	0	7
13	44	50
14	33	35
15	11	13
16	0	0
17	11	17
H,K= 3, 3		
L=0	22	25
1	25	22
2	0	4
3	35	36
4	37	28
5	67	67
6	49	52
7	0	5
8	30	34
9	28	27
10	26	31
11	52	59
12	15	17
13	0	10
14	29	31
15	16	16
16	22	24
17	0	2
H,K= 4, 3		
L=0	97	102
H,K= 4, 3		
1	52	58
2	92	80
3	67	77
4	27	29
5	49	46
6	68	64
7	62	63
8	0	4
9	17	26
10	46	46
11	28	35
12	14	16
13	0	9
14	0	0
15	25	29
16	0	8
H,K= 5, 3		
L=0	186	178
1	50	44
2	61	52
3	88	98
4	17	13
5	23	19
6	27	14
7	0	2
8	17	15
9	30	31
10	0	5
11	0	12
12	14	22
13	0	20
14	0	5
15	20	15
16	10	15
H,K= 6, 3		
L=0	70	76
1	109	108
2	69	74
3	12	15
4	14	17
5	26	33
6	0	10
7	23	20
8	18	25
9	15	17
10	0	3
11	52	60
12	16	20
13	0	1
14	23	20
15	22	22
H,K= 7, 3		
L=0	114	105
1	78	79
2	26	29
3	62	63
4	25	24
5	72	80
6	18	21
7	35	34
8	0	14
9	15	19
10	14	17
11	14	19
12	0	1
13	28	28
14	0	6
15	12	19
H,K= 8, 3		
L=0	14	12
1	25	25
2	21	21
3	18	23
4	10	11
5	10	13
6	21	27
7	0	17
8	10	17
9	0	2
10	0	6
11	26	31
12	14	12
13	0	0
14	0	0
H,K= 9, 3		
L=0	18	25
1	0	6
2	18	16
3	21	26
4	21	34
5	48	54
6	17	24
7	33	38
8	22	27
9	0	3
10	0	9
11	24	22
12	12	18
13	11	16
H,K= 10, 3		
L=0	23	25
1	14	16
2	0	1
3	0	8
4	0	3
5	23	26
6	14	18
7	32	37
8	15	19
9	0	5
10	0	4
11	0	1
12	0	4
H,K= 11, 3		
L=0	14	11
1	16	16
2	16	25
3	0	4
4	25	27
5	0	9
6	17	21
7	0	4
8	12	12
9	0	5
10	0	7
H,K= 12, 3		
L=0	0	12
1	8	15
2	11	10
3	10	16
4	10	10
5	20	19
6	21	20
7	24	25
8	0	3
H,K= 13, 3		
L=0	0	4
1	0	7
2	0	7
H,K= 13, 3		
3	21	20
4	0	3
5	10	16
H,K= 0, 4		
L=0	21	19
1	16	3
2	50	50
3	60	65
4	88	86
5	27	32
6	65	61
7	14	10
8	70	65
9	68	67
10	110	108
11	0	20
12	45	45
13	14	15
14	24	23
15	0	0
16	0	5
H,K= 1, 4		
L=0	37	30
1	169	142
2	31	30
3	7	5
4	60	61
5	181	175
6	147	138
7	97	91
8	34	32
9	130	125
10	15	22
11	56	60
12	30	33
13	26	26
14	0	4
15	37	37
16	0	10
H,K= 2, 4		
L=0	27	21
1	21	31
2	185	170
3	269	241
4	67	68
5	0	15
6	67	71
7	108	106
8	86	84
9	149	144
10	72	72
11	84	93
12	0	7
13	32	33
14	32	29
15	0	7
16	0	0
H,K= 3, 4		
L=0	26	26
1	67	65
2	92	85
3	58	52
4	74	78
5	200	191
6	0	6
7	0	11
8	25	26
9	20	23
10	71	66
11	40	45
12	15	19
13	20	22
14	22	23
15	0	6
16	0	8
H,K= 4, 4		
L=0	25	26
1	18	11
2	137	115
3	65	69
4	88	97
5	72	71
6	45	48
7	25	26
8	0	0
9	70	63
10	31	34
11	0	5
12	50	48
13	31	32
14	14	14
15	0	5
H,K= 5, 4		
L=0	54	52
1	17	26
2	51	50
3	103	104
4	46	53
5	14	15
6	20	23
7	39	44
8	0	12
9	66	64
10	0	8
11	51	57
12	0	9
13	0	12
14	0	5
15	0	10
H,K= 6, 4		
L=0	110	93
1	103	99
2	0	4
3	105	105
3	105	105
4	114	109
5	171	166
6	84	84
7	20	25
8	15	20
9	26	30
10	0	7
11	44	46
12	15	22
13	20	21
14	0	0
H,K= 7, 4		
L=0	44	55
1	15	14
2	62	64
3	82	99
4	28	27
5	54	62
6	26	28
7	72	74
8	15	30
9	40	44
10	14	20
11	18	18
12	14	12
H,K= 7, 4		
13	25	26
H,K= 8, 4		
L=0	58	62
1	32	39
2	32	32
3	0	14
4	70	76
5	61	66
6	15	12
7	0	13
8	14	18
9	0	15
10	0	7
11	25	23
12	0	6
H,K= 9, 4		
L=0	26	30
1	0	8
2	0	7
3	0	12
4	27	27
5	48	51
6	46	47
7	0	21
8	20	19
9	0	11
10	0	5
11	0	2
H,K= 10, 4		
L=0	0	2
1	0	3
2	14	22
3	0	6
4	31	29
5	26	28
6	18	17
7	12	21
8	0	10
9	0	5
10	0	10
H,K= 11, 4		
L=0	0	10
1	15	21
2	0	3
3	0	9
4	14	20
5	14	18
6	0	7
7	0	3
8	0	0
H,K= 12, 4		
L=0	0	9
1	0	2
2	0	0
3	0	8
4	0	0
5	0	11
6	0	18
H,K= 0, 5		
L=1	66	64
2	48	46
3	48	41
4	130	127
5	126	109
6	13	12
7	9	7
8	20	25
9	13	12
10	14	18
11	51	46
12	9	9
13	12	14
14	9	7
15	15	14
H,K= 1, 5		
L=0	77	72
1	77	70
2	34	36
3	77	73
4	0	2
5	50	41
6	10	13
7	54	49
8	10	9
9	17	27
10	0	10
11	24	26
12	16	18
13	20	17
14	9	11
15	13	15
H,K= 2, 5		
L=0	55	60
1	66	72
2	33	41
3	65	66
4	58	61
5	100	96
6	55	58
7	109	104
8	117	120
9	71	68
10	11	14
11	32	25
12	29	31
13	12	6
14	12	12
H,K= 3, 5		
L=0	42	46
1	0	3
2	89	88
3	39	44
4	108	117
5	124	139
6	0	10
7	51	58
8	0	3
9	45	50
10	34	43
11	13	15
12	9	6
13	18	21
14	0	9
H,K= 4, 5		
L=0	0	0
1	90	94
2	13	19
3	55	59
4	63	62
5	13	24
6	56	54
7	44	51
8	58	48
9	25	23
10	29	27
11	12	15
12	0	6
13	10	16
H,K= 4, 5		
14	0	5
H,K= 5, 5		
L=0	16	12
1	78	78
2	13	15
3	13	17
4	56	42
5	79	87
6	0	9
7	39	40
8	0	11
9	78	86
10	51	39
11	0	5
12	11	9
13	11	14
H,K= 6, 5		
L=0	51	45
1	18	19
2	0	10
3	63	64
4	0	12
5	54	57
6	59	58
7	55	67
8	37	36
9	29	31
10	0	3
11	12	17
12	14	11
13	0	6
H,K= 7, 5		
L=0	12	43
1	41	47
2	33	42
3	31	40
4	36	39
5	0	14
6	0	12
7	22	23
8	17	16
9	23	20
10	12	3
11	12	15
12	0	3
H,K= 0, 6		
L=0	33	36
1	15	16
2	44	42
3	24	27
4	124	112
5	24	30
6	21	18
7	15	17
8	14	11
9	0	3
10	15	16
11	0	7
12	24	19
13	0	2
H,K= 1, 6		
L=0	0	0
1	0	2
2	22	19
3	0	6
4	49	47
5	46	48
6	29	30
7	0	0
8	16	13
9	9	9
10	15	18
11	0	6
12	17	17
13	5	6
H,K= 2, 6		
L=0	31	38
1	89	91
2	26	18
3	29	32
4	12	4
5	29	34
6	22	20
7	16	20
8	14	12
9	0	4
10	9	9
11	0	6
12	10	11
H,K= 3, 6		
L=0	26	35
1	12	5
2	14	21
3	52	55
4	74	80
5	16	24
6	16	18
7	13	9
8	28	24
9	12	12
10	8	9
11	0	4
12	0	1
H,K= 4, 6		
L=0	13	11
1	31	32
2	0	7
3	0	10
4	22	25
5	0	2
6	25	27
7	0	4
8	0	7
9	0	3
10	20	20
11	11	10
12	0	10
H,K= 5, 6		
L=0	18	22
1	0	6
2	12	16
3	12	10
4	0	0
5	0	0
6	0	8
7	30	20
8	20	16
9	13	11
10	14	17
11	21	18
H,K= 6, 6		
L=0	0	13
1	0	0
2	12	12
3	0	4
4	18	22
5	0	1
6	0	1
H,K= 6, 6		
7	27	20
8	13	16
9	0	1
10	0	7
H,K= 7, 6		
L=0	0	8
1	0	4
2	0	1
3	13	21
4	0	13
5	0	4
6	0	13
7	0	6
8	0	2
9	22	23
H,K= 0, 7		
L=1	14	9
2	22	20
3	11	9
4	0	4
5	35	34
6	22	17
7	0	0
8	0	2
9	29	26
10	24	22
H,K= 1, 7		
L=0	11	15
1	22	23
2	28	30
3	14	10
4	0	2
5	22	17
6	22	20
7	16	12
8	0	7
9	7	7
10	9	11
H,K= 2, 7		
L=0	0	5
1	0	6
2	0	2
3	0	11
4	0	4
5	31	23
6	25	25
7	11	9
8	15	15
9	9	9
10	0	0
H,K= 3, 7		
L=0	10	9
1	28	24
2	13	11
3	10	7
4	9	2
5	9	14
6	24	22
7	0	2
8	16	14
9	13	11
H,K= 4, 7		
L=0	15	21
1	0	1
2	42	37
3	13	14
4	12	9
5	0	7
6	13	13
7	10	11
8	15	18
9	0	1
H,K= 5, 7		
L=0	12	14
1	0	5
2	0	1
3	0	1
4	28	25
5	20	19
6	12	12
7	0	1
8	14	17
H,K= 6, 7		
L=0	0	2
1	0	9
2	0	4
3	0	5
4	0	5
5	16	15
6	0	6
7	0	0
H,K= 7, 7		
L=0	0	4
1	0	0
2	13	13
3	21	19
4	15	12
5	0	4
H,K= 0, 8		
L=0	11	8
1	15	11
2	7	6
3	9	9
4	14	14
5	0	1
H,K= 1, 8		
L=0	0	1
1	0	1
2	28	21
3	7	4
4	0	4
5	13	13
H,K= 2, 8		
L=0	13	12
1	14	15
2	21	18
3	0	8
4	27	24
5	7	10
H,K= 3, 8		
L=0	0	4
1	0	2
2	0	2
3	0	5
4	11	14
H,K= 4, 8		
L=0	0	2
1	0	3
2	13	12
3	0	11

Table 3 (*cont.*)

	FO	FC
H,K= -1, 0		
L=2	236	239
4	903	902
6	378	345
8	190	167
10	131	114
12	92	77
14	31	29
16	0	14
18	56	49
H,K= -2, 0		
L=2	146	150
4	37	43
6	319	298
8	68	67
10	16	12
12	23	22
14	0	1
16	71	57
18	10	5
H,K= -3, 0		
L=2	233	245
4	166	166
6	477	449
8	148	129
10	59	56
12	28	27
14	17	15
16	21	12
18	28	29
H,K= -4, 0		
L=2	85	79
4	0	13
6	175	172
8	120	106
10	26	31
12	37	32
14	17	8
16	29	25
18	15	17
H,K= -5, 0		
L=2	105	102
2	105	102
4	262	249
6	65	54
8	156	130
10	20	15
12	85	80
14	24	13
16	53	38
H,K= -6, 0		
L=2	309	298
4	263	250
6	378	361
8	0	17
10	68	74
12	24	17
14	15	14
16	0	7
H,K= -7, 0		
L=2	25	23
4	46	35
6	0	18
8	86	74
10	32	36
12	0	2
14	0	13
16	33	30
H,K= -8, 0		
L=2	30	28
4	28	29
6	20	17
8	0	3
10	0	0
12	45	33
14	0	6
H,K= -9, 0		
L=2	23	23
4	112	100
6	80	74
8	14	9
10	22	18
12	32	25
14	0	11
H,K=-10, 0		
L=2	0	1
4	21	22
6	0	13
8	42	28
10	15	10
12	16	14
H,K=-11, 0		
L=2	56	51
4	24	21
6	58	43
8	0	5
10	16	15
12	21	14
H,K=-12, 0		
L=2	18	11
4	0	13
6	20	23
8	18	17
10	28	25
H,K=-13, 0		
L=2	28	22
4	0	10
6	0	7
8	0	5
H,K=-14, 0		
L=2	25	23
4	0	5
6	0	7
H,K= -1, 1		
L=1	696	744
2	107	122
3	241	250
4	591	615
5	168	170
6	14	8
7	151	168
8	235	248
9	187	172
10	147	150
11	135	144
12	203	214
13	106	113
14	0	8
15	20	25
16	41	44
17	7	4
18	11	15
H,K= -2, 1		
L=1	233	249
2	103	110
2	103	110
3	338	341
4	163	160
5	235	250
6	209	201
7	161	154
8	104	111
9	121	112
10	165	152
11	74	77
12	10	18
13	14	20
14	0	5
15	24	24
16	23	26
17	25	20
18	16	21
H,K= -3, 1		
L=1	235	262
2	200	201
3	44	49
4	107	103
5	253	278
6	150	156
7	34	37
8	54	54
9	39	39
10	46	49
11	32	35
12	14	6
13	79	84
14	43	53
15	0	5
16	8	17
17	13	16
18	9	12
H,K= -4, 1		
L=1	139	142
2	231	225
3	144	163
4	138	148
5	96	97
6	65	72
7	11	15
8	12	14
9	64	67
10	80	90
11	66	67
12	67	69
13	39	43
14	9	11
15	9	13
16	0	0
17	23	17
18	0	13
H,K= -5, 1		
L=1	158	157
2	73	84
3	86	94
4	16	9
5	296	295
6	101	104
7	26	30
8	0	7
9	72	72
10	105	103
10	105	103
11	70	74
12	46	54
13	0	10
14	0	8
15	0	9
16	0	6
17	20	15
H,K= -6, 1		
L=1	36	38
2	72	70
3	89	93
4	93	101
5	97	107
6	0	3
7	0	1
8	70	77
9	46	55
10	0	1
11	14	18
12	29	33
13	42	51
14	15	19
15	0	7
16	17	21
17	0	2
H,K= -7, 1		
L=1	68	75
2	112	107
3	54	58
4	26	28
5	59	66
6	13	14
7	9	5
8	0	20
9	0	2
10	70	74
11	10	17
12	0	17
13	9	13
14	34	34
15	0	2
16	22	23
H,K= -8, 1		
L=1	29	33
2	0	2
3	53	56
4	0	4
5	75	79
6	0	3
7	0	13
8	0	9
9	0	3
10	0	0
11	9	16
12	9	7
13	16	17
14	22	24
15	0	0
H,K= -9, 1		
L=1	111	109
2	77	76
3	58	59
4	37	41
5	96	101
6	42	47
7	0	3
8	0	1
9	0	0
10	0	7
11	17	22
12	8	14
13	12	11
14	0	4
H,K=-10, 1		
L=1	0	0
2	74	79
3	47	44
4	0	6
5	0	4
6	0	8
7	0	15
8	0	10
9	0	5
10	0	6
11	0	0
12	0	1
13	0	0
H,K=-11, 1		
L=1	0	13
2	14	20
3	17	25
4	32	38
5	28	28
6	16	19
7	30	32
8	23	25
9	0	6
10	0	3
11	10	12
12	0	5
H,K=-12, 1		
L=1	24	24
2	0	5
3	34	38
4	15	11
5	27	30
6	14	11
7	13	13
8	0	9
9	0	2
10	0	5
H,K=-13, 1		
L=1	14	12
2	0	6
3	15	18
4	15	21
5	0	0
6	11	17
7	10	12
8	0	4
H,K=-14, 1		
L=1	0	8
2	0	8
3	0	4
4	0	6
5	16	21
H,K= -1, 2		
L=1	142	147
2	251	255
3	128	126
4	45	41
5	27	27
6	253	227
7	277	256
8	43	46
9	32	31
10	113	120
11	16	18
12	64	63
13	67	65
14	56	65
15	32	37
16	0	0
17	12	9
18	0	5
H,K= -2, 2		
L=1	236	232
2	329	319
3	338	333
4	41	16
5	281	269
6	0	2
7	14	21
8	71	64
9	143	143
10	103	104
11	92	93
12	80	78
13	113	117
14	39	41
15	14	13
16	0	10
17	25	24
18	0	5
H,K= -3, 2		
L=1	18	21
2	110	113
3	39	39
4	23	21
5	0	6
6	128	125
7	98	103
8	0	0
9	17	25
10	27	32
11	0	4
12	65	75
13	0	9
14	0	10
15	0	0
16	24	21
17	0	0
H,K= -4, 2		
L=1	88	83
2	241	243
3	75	56
4	72	62
5	47	41
6	28	20
7	24	18
8	12	20
9	0	13
10	59	61
11	71	82
12	67	72
13	27	26
14	0	1
15	0	5
16	0	0
17	0	5
H,K= -5, 2		
L=1	51	58
2	151	141
3	110	109
4	46	44
5	35	35
6	51	48
7	0	14
8	34	37
9	18	24
10	64	59
11	40	48
12	24	23
13	36	45
14	0	1
15	0	4
16	15	10
17	0	2
H,K= -6, 2		
L=1	0	0
2	0	10
3	59	52
4	13	5
5	62	59
6	52	44
7	29	27
8	22	12
9	58	63
10	36	33
11	0	0
12	31	32
13	36	34
14	10	13
15	0	14
16	14	12
H,K= -7, 2		
L=1	45	39
2	80	77
3	22	30
4	14	3
5	15	12
6	0	9
7	0	4
8	0	17
9	0	11
10	107	108
11	16	12
12	66	54
13	31	29
14	35	32
15	0	6
16	0	2
H,K= -8, 2		
L=1	48	49
2	34	35
3	62	57
4	0	8
5	0	9
6	35	42
7	102	100
8	77	82
9	0	3
10	41	35
11	81	71
12	27	24
13	0	1
14	9	12
15	12	20
H,K= -9, 2		
L=1	70	73
2	0	0
3	64	64
4	62	63
5	20	22
6	0	4
7	66	65
8	31	29
9	0	10
10	0	0
11	36	34
12	12	5
13	0	5
14	0	10
H,K=-10, 2		
L=1	36	43
2	22	29
3	16	18
4	44	47
5	98	90
6	0	9
7	34	31
8	60	51
9	51	43
10	36	36
11	0	5
12	0	1
13	8	15
H,K=-11, 2		
L=1	0	0
2	12	16
3	15	15
4	34	38
5	12	12
6	52	49
7	0	5
8	30	28
9	0	0
10	12	9
11	0	2
H,K=-12, 2		
L=1	0	2
2	0	5
3	0	1
4	0	7
5	0	14
6	0	8
7	0	4
8	23	17
9	0	6
10	0	2
H,K=-13, 2		
L=1	0	6
2	0	2
3	0	1
4	0	5
5	30	29
6	10	11
7	14	15
H,K=-14, 2		
L=1	0	9
2	0	3
3	0	4
H,K= -1, 3		
L=1	313	310
2	379	362
3	198	208
4	165	157
5	20	22
6	169	159
7	105	112
7	105	112
8	142	148
9	69	82
10	0	4
11	33	37
12	52	50
13	14	14
14	46	46
15	13	15
16	0	7
17	20	23
H,K= -2, 3		
L=1	203	196
2	33	40
3	99	112
4	184	186
5	64	72
6	89	88
7	177	160
8	102	111
9	30	43
10	17	20
11	15	17
12	15	18
13	0	4
14	0	7
15	0	18
16	0	1
17	0	5
H,K= -3, 3		
L=1	129	119
2	89	98
3	90	113
4	75	79
5	68	67
6	11	18
7	67	63
8	63	68
9	14	13
10	0	8
11	34	30
12	18	20
13	0	11
14	16	8
15	0	3
16	11	14
17	0	10
H,K= -4, 3		
L=1	168	169
2	173	159
3	50	48
4	142	146
5	81	77
6	59	47
7	196	185
8	140	150
9	29	36
10	0	5
11	24	31
12	54	55
13	22	20
14	0	3
15	0	3
16	0	8
H,K= -5, 3		
L=1	97	74
2	0	6
3	78	73
4	177	163
5	96	87
6	62	67
7	17	33
8	126	135
9	52	60
10	30	29
11	51	52
12	34	39
13	0	2
14	25	21
15	11	11
16	9	12
H,K= -6, 3		
L=1	28	34
2	69	80
3	108	114
4	37	41
5	0	5
6	72	78
7	17	28
8	15	0
9	0	6
10	15	18
11	14	19
12	24	25
13	15	5
14	0	9
15	0	7
H,K= -7, 3		
L=1	84	85
2	17	21
3	88	95
4	159	156
5	41	38
6	84	96
7	149	159
8	128	133
9	33	41
10	72	70
11	0	5
12	54	52
13	14	12
14	24	21
15	14	20
H,K= -8, 3		
L=1	17	30
2	0	8
3	33	35
4	0	12
5	110	113
6	48	53
7	10	19
8	0	7
9	0	1
10	16	20
11	46	46
12	0	3
13	26	28
14	5	9
H,K= -9, 3		
L=1	0	8
2	46	43
3	37	39
4	45	54
5	0	14
6	43	42
7	21	22
8	35	46
9	30	29
10	0	8
11	10	12
12	0	5
13	8	12
H,K=-10, 3		
L=1	18	22
2	14	11
3	21	20
4	44	49
5	60	59
6	32	36
7	0	6
8	46	46
9	0	0
11	32	32
12	20	27
H,K=-11, 3		
L=1	16	14
2	0	12
3	0	7
4	0	7
5	12	16
6	43	42
7	28	28
8	0	8
9	32	30
10	27	29
H,K=-12, 3		
L=1	0	10
2	0	4
3	14	17
4	10	7
5	10	12
6	0	6
7	0	1
8	0	2
H,K=-13, 3		
L=1	0	4
2	0	5
3	0	3
4	0	7
5	11	14
6	0	6
H,K= -1, 4		
L=1	11	5
2	26	13
3	17	27
4	78	75
5	0	4
6	93	90
7	65	61
8	94	90
9	108	107
10	12	10
11	0	6
12	11	19
13	10	5
14	0	6
15	20	24
16	0	8
H,K= -2, 4		
L=1	12	12
2	51	45
3	79	74
4	37	35
5	64	64
6	91	86
7	40	46
8	34	45
9	81	80
10	74	77
11	0	13
12	25	24
13	0	3
14	21	21
15	25	22
16	0	9
H,K= -3, 4		
L=1	62	62
2	37	39
3	14	14
4	25	24
5	22	20
6	31	33
7	0	3
8	0	1
9	28	29
10	78	70
11	0	3
12	0	0
13	0	8
14	0	2
15	0	2
16	0	5
H,K= -4, 4		
L=1	68	72
2	18	22
3	28	23
4	31	33
5	21	25
6	98	95
7	98	96
8	78	73
9	24	26
10	0	6
11	34	35
12	0	7
13	18	21
14	0	3
15	26	25
H,K= -5, 4		
L=1	20	19
2	79	80
3	0	4
4	0	7
5	17	17
6	140	133
7	15	32
8	28	36
9	15	21
10	0	11
11	14	13
12	20	22
13	8	14
14	0	7
15	0	1
H,K= -6, 4		
L=1	0	6
2	0	0
3	97	101
4	98	96
5	11	12
6	34	37
7	28	28
8	20	15
9	11	12
10	52	51
11	0	9
12	0	0
13	11	12
14	8	11
H,K= -7, 4		
L=1	141	133
2	0	0
3	0	6
4	67	70
5	60	67
6	58	58
7	0	15
8	15	23
9	18	26
10	0	2
11	0	8
12	28	23
13	21	17
H,K= -8, 4		
L=1	28	34
2	0	1
3	0	10
4	0	7
5	0	17
6	40	35
7	0	9
8	18	24
9	0	0
10	15	15
11	13	5
12	12	7
13	6	10
H,K= -9, 4		
L=1	26	25
2	0	8
3	37	34
4	41	44
5	0	1
6	0	17
7	14	11
8	0	3
9	17	18
10	0	6
11	10	6
12	0	4
H,K=-10, 4		
L=1	32	34
2	0	6
3	17	18
4	0	2
5	0	9
6	18	22
7	0	11
8	0	6
9	12	12
10	0	0
H,K=-11, 4		
L=1	15	13
2	0	0
3	0	8
4	28	23
5	0	6
6	7	8
7	6	6
8	17	15
H,K=-12, 4		
L=1	24	24
2	20	15
3	0	5
4	0	4
5	0	11
6	0	5
H,K= -1, 5		
L=1	44	45
2	39	38
3	65	63
4	14	21
5	55	60
6	0	9
7	82	71
8	80	80
9	10	10
10	24	28
11	23	20
12	12	15
13	14	11
14	9	8
15	14	18
H,K= -2, 5		
L=1	11	12
2	12	14
3	42	43
4	103	106
5	55	52
6	28	34
7	35	38
8	61	74
9	15	19
10	29	34
11	15	19
12	9	15
13	0	8
14	17	19
H,K= -3, 5		
L=1	113	120
2	88	97
3	80	92
4	12	2
5	23	29
6	45	46
7	22	23
8	35	41
9	24	31
10	29	35
11	32	40
12	0	12
13	0	4
14	0	1
H,K= -4, 5		
L=1	0	11
2	0	3
3	0	6
4	0	14
5	0	3
6	0	10
7	0	14
8	29	32
9	27	36
10	0	5
11	11	17
12	0	4
13	14	20
14	22	20
H,K= -5, 5		
L=1	29	35
2	0	11
3	34	37
4	31	33
5	0	11
6	13	17
7	0	1
8	18	16
9	27	38
10	33	33
11	11	11
12	0	0
13	0	13
H,K= -6, 5		
L=1	90	89
2	13	13
3	18	31
4	0	4
5	0	5
6	29	30
7	0	10
8	33	31
9	0	12
10	24	28
11	0	4
12	0	5
13	0	0
H,K= -7, 5		
L=1	0	14
2	29	25
3	0	4
4	46	56
5	0	4
6	15	12
7	15	22
8	17	20
9	16	17
10	0	0
11	13	16
12	9	8
H,K= -1, 6		
L=1	34	34
2	20	19
3	0	5
4	51	49
5	0	6
6	0	0
7	0	2
8	0	5
9	0	0
10	0	2
11	0	5
12	6	8
13	5	8
H,K= -2, 6		
L=1	41	46
2	12	13
3	27	35
4	27	32
5	15	14
6	36	36
7	31	33
8	23	20
9	13	19
10	9	9
11	0	0
12	10	10
H,K= -3, 6		
L=1	69	80
2	52	60
3	63	65
4	121	122
5	63	68
6	0	3
7	28	30
8	35	32
9	0	0
10	8	13
11	20	25
12	0	3
H,K= -4, 6		
L=1	33	37
2	53	56
3	15	25
4	45	53
5	59	63
6	12	17
7	0	13
8	13	7
9	31	31
10	13	11
11	0	10
12	14	15
H,K= -5, 6		
L=1	0	9
2	0	3
3	29	30
4	26	29
5	0	10
6	0	9
7	0	3
8	31	31
9	25	23
10	0	3
11	10	14
H,K= -6, 6		
L=1	0	6
2	51	56
3	20	23
4	49	48
5	0	15
6	0	13
7	0	7
8	12	12
9	26	26
10	0	7
H,K= -7, 6		
L=1	0	7
2	29	35
3	17	11
4	33	37
5	18	20
6	0	7
7	0	0
8	0	6
9	18	17
H,K= -1, 7		
L=1	0	3
2	0	5
3	13	10
4	0	1
5	14	12
6	27	25
7	13	11
8	0	2
9	0	5
10	0	0
H,K= -2, 7		
L=1	51	42
2	0	5
3	18	23
4	31	28
5	0	10
6	0	6
7	0	10
8	0	3
9	0	4
10	20	21
H,K= -3, 7		
L=1	20	18
2	0	4
3	0	0
4	0	3
5	11	11
6	0	4
7	12	13
8	17	20
9	11	8
H,K= -4, 7		
L=1	0	4
2	13	17
3	15	18
4	17	17
5	18	19
6	0	0
7	15	16
8	0	6
9	25	25
H,K= -5, 7		
L=1	20	25
2	0	2
3	12	10
4	11	12
5	20	13
6	0	7
7	11	7
8	0	5
H,K= -6, 7		
L=1	0	15
2	12	15
3	16	20
4	12	14
5	11	6
6	0	4
7	6	10
H,K= -7, 7		
L=1	15	15
2	0	0
3	0	2
4	15	12
5	16	12
H,K= -1, 8		
L=1	14	10
2	27	23
3	23	17
4	0	2
5	0	1
H,K= -2, 8		
L=1	14	13
2	10	10
3	0	0
4	15	13
5	0	1
H,K= -3, 8		
L=1	0	1
2	0	3
3	10	9
4	8	10
H,K= -4, 8		
L=1	0	5
2	15	13
3	0	7

bond, showing a little double bond character, and the two C–O bonds are close to the pure double bond.

There is one interesting feature in the configuration of the present substance. The keto oxygen atom closer to the phenyl group, O(φ), is shifted from the phenyl plane by a significant amount of 0·10 Å. The displacement corresponds to an angle of 4·8° between the bond and the phenyl plane. No such deviation from planarity is found in the pyridyl group or the C(p, 7)−O(p) bond. Since O(φ) belongs to a conjugated system formed by the phenyl and carbonyl groups, there must be some reasons, probably imposed by the crystal structure, for such a deviation from planarity. The intramolecular interatomic distance between O(φ) and H(φ, 5) is 2·5 Å, while the corresponding O(p)−H(p, 5) distance in the pyridyl is 2·6 Å. As will be mentioned later, O(φ) has more short intermolecular approaches than the other oxygen does. Such rather crowded surroundings might be one of the reasons.

The arrangement of the molecules in the crystal is shown in Fig. 5, where some important intermolecular distances are shown. When Fig. 5 is compared with the similar drawing of the structure of pyridil (Fig. 3 of Hirokawa & Ashida, 1961) many common features between them are noticed. Almost all of the short intermolecular contacts correspond to the normal van der Waals distances. The oxygen atom O(φ) has two short intermolecular contacts, one of which is to C(φ, 3) of the molecule related to the first by the c glide at $y=\frac{1}{4}$; the separation is 3·23 Å. The features and the magnitudes of the shorter C–O contacts between the molecules are similar to those of pyridil. However, a short distance is found between O(φ) and H(φ, 5) of the molecule in the next cell along the b axis; the separation,

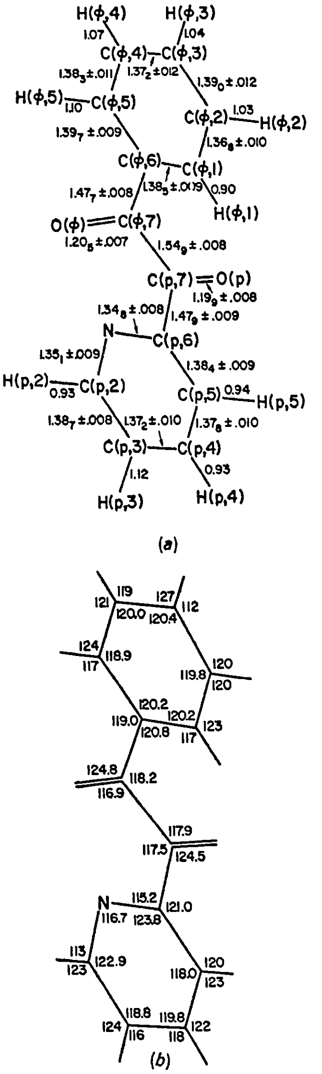


Fig. 3. (a) Bond distances (Å). (b) Bond angles (°).

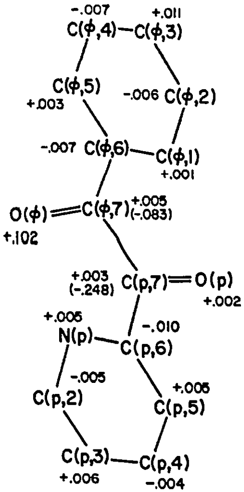


Fig. 4. Displacements of atoms from the least-squares planes. Those in brackets for C(p, 7) and C(φ, 7) are their displacements from the planes of the ring systems to which they do not belong.

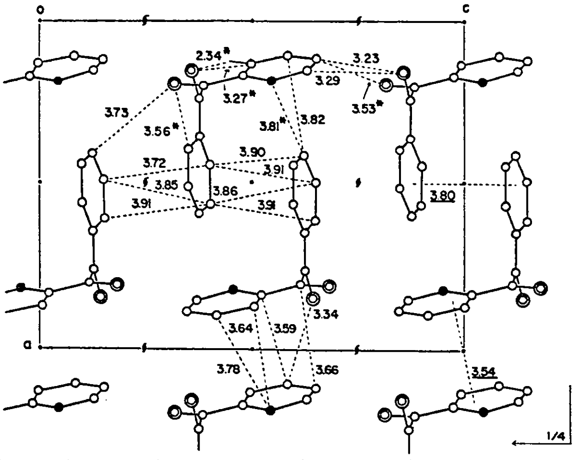


Fig. 5. The crystal structure projected on the [b] plane. Some of the intermolecular distances are shown (Å). Those with asterisks show the distances between the molecules, one of which is in the next cell along the b axis. The two underlined show the interplanar distances between a perpendicular pair.

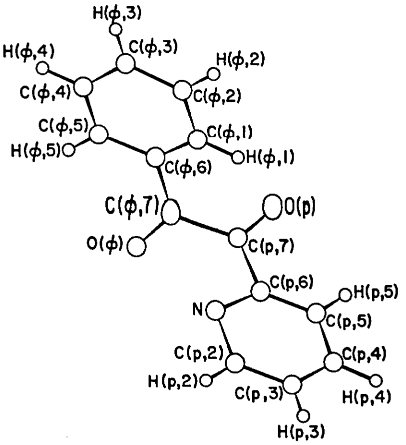


Fig. 6. A PPED molecule viewed down along the [101] axis. This configuration corresponds to that of pyridil viewed down along the b axis of the crystal. (See Fig. 1 of Hirokawa & Ashida, 1961.)

2·3 Å, is slightly shorter than the normal intermolecular contacts.

In the crystal of PPED, there are plane-to-plane parallel stackings. This parallel stacking is one of the most noticeable common features between the present crystal and pyridil. For example, in the structure of α-pyridoin, no such parallel stacking is found. However, in the mode of stacking, one can find distinct differences between these two crystals, because in PPED we can find two different pairs of parallel rings whereas there is a set of four parallel planes in pyridil. One of the pairs consists of two pyridine rings, or more precisely two pyridine parts of molecules, which are related to each other by a center of symmetry; the perpendicular distance between them is 3·54 Å [Fig. 7(*a*)]. This stacking is almost identical with the overlap found in the two asymmetric pairs of the four rings stacked in the structure of pyridil (see Table 4 for numerical values related to the configuration). Almost perpendicular to this pair, there is another stacking made by two phenyl planes. The two planes are also related to each other by a center of symmetry, and the separation is 3·80 Å. The stacking of the phenyl planes is now similar to that of the central two planes in the pyridil structure, though the perpendicular distance in PPED is much longer. Such differences in the modes of packing of the molecules in the crystal may be one of the reasons why the melting point of PPED is considerably lower than that of pyridil. It is interesting that the force between the molecules in the crystal of PPED is, as a whole, weaker than that in pyridil, although the molecular configurations of these two compounds are so close to each other. The difference in the densities of these two compounds can also be explained by the difference in the mode of aromatic ring packing.

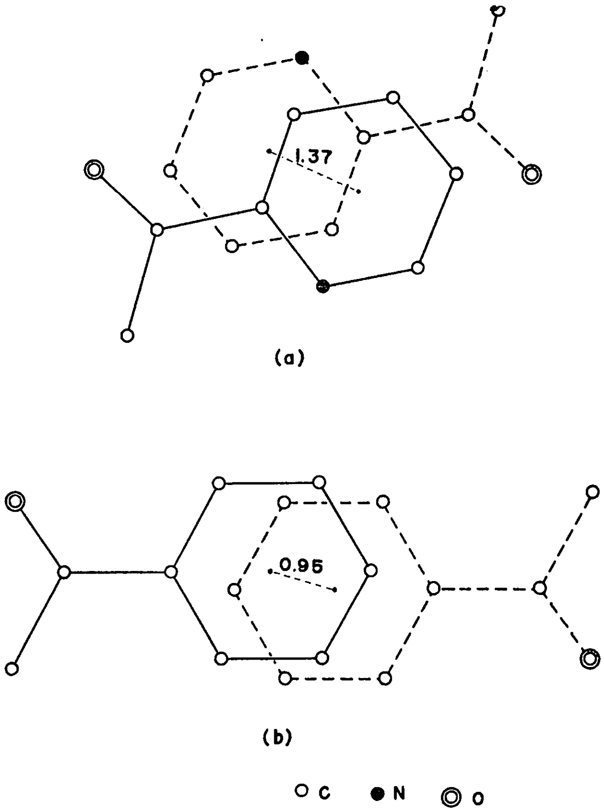


Fig. 7. Two pairs of parallel groups viewed down perpendicular to the planes. (*a*) Two pyridine group. (*b*) Two phenyl planes. The horizontal distances between the planes are also shown to indicate degree of overlapping.

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Table 4. *A comparison of parallel stackings in two crystals*

		Distance 1*	Distance 2†	Angle‡
Pyridil	Py–Py I′	3·56 Å	1·28 Å	70·7°
	Py–Py II″	3·49	1·31	69·9
PPED	Py–Py	3·54	1·37	68·9
	Ph–Ph	3·80	0·95	76·0

* Perpendicular distances between two planes.

† Center-to-center distances of the rings projected on their planes.

‡ Angles between the planes and the lines connecting the centers of two planes.

′ Pair made by one side of four parallel pyridine rings.

″ The central two planes.

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