Acta Cryst. (1969). B**25**, 2355

The Crystal and Molecular Structure of 2-Acetyl-3-indazolinone, $C_9H_8N_2O_2$

By Douglas L. Smith and Eileen K. Barrett

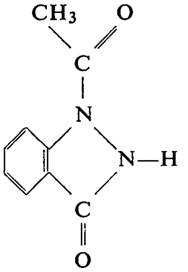
Research Laboratories, Eastman Kodak Company, Rochester, New York 14650, *USA*

(*Received* 31 *December* 1968)

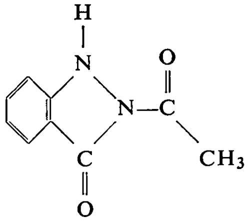
The molecular structure of the unstable, low-melting (175–177°C) isomer of acetyl indazolinone, $C_9H_8N_2O_2$, has been determined from single-crystal, X-ray intensity data collected with an automated diffractometer. The crystals are monoclinic, space group $P2_1/n$, with four molecules in a unit cell of dimensions $a=11{\cdot}354$, $b=5{\cdot}683$, $c=13{\cdot}088$ Å; $\beta=107{\cdot}44°$. The structure was solved by direct phasing of the structure amplitudes by the symbolic addition procedure and refined by full-matrix least-squares. Hydrogen atoms were located and refined. The final value of the discrepancy index is $R=0{\cdot}039$ for 1283 reflections. The results show that the unstable isomer is 2-acetyl-3-indazolinone.

Introduction

The use of 3-indazolinone and certain substituted 3-indazolinones as coupling agents for the production of color photographic images has been the subject of several patents (Barr, Henn & Salminen, 1962; Jennen & Eerdekens, 1954, 1960; Jennen, 1953, 1954). In particular, acetylation of 3-indazolinone under certain conditions leads to either of two isomers, 1-acetyl-3-indazolinone (*A*) or 2-acetyl-3-indazolinone (*B*) (Jennen, 1957; Jennen & Eerdekens, 1954). The lower melting isomer (hereafter called AIU) is unstable and is converted to the higher melting isomer (hereafter called AIS) in alkaline solution at room temperature or by heat (Young, 1965; Jennen, 1957). Reports in the literature (Janssen, 1962; Jennen, 1957) have supported the view that 2-acetyl-3-indazolinone (*B*) is the unstable isomer, AIU. However, some work in our laboratories (Young, 1965), involving direct synthesis of the couplers and the nature of the dyes formed on development, would be more easily explained if 2-acetyl-3-indazolinone (*B*) were the stable isomer, AIS.



(*A*)



(*B*)

To resolve this ambiguity in structure assignment, we have determined the crystal and molecular structure of AIU by single-crystal, X-ray diffraction techniques. The structure ultimately found for this isomer is 2-acetyl-3-indazolinone.

Experimental

Samples of both isomers were supplied by D. V. Young, of these laboratories. The sample of AIU already contained suitable single crystals; recrystallization of AIS

Table 1. *Crystal data for* AIU

$C_9H_8N_2O_2$, M.W. 176·18, m.p. 175–177°
2-Acetyl-3-indazolinone.
Colorless, irregular plates.
Monoclinic (Cu $K\alpha_1=1{\cdot}54051$ Å), $a=11{\cdot}354\pm0{\cdot}001$ Å
$b=5{\cdot}683\pm0{\cdot}001$
$c=13{\cdot}088\pm0{\cdot}001$
$\beta=107{\cdot}44\pm0{\cdot}01°$
Volume of unit cell, $805{\cdot}7\pm0{\cdot}3$ Å^3.
Density, calculated ($Z=4$) 1·452 g.cm^{-3}
measured (flotation) 1·44 g.cm^{-3}
Linear absorption coefficient, $\mu=8{\cdot}9$ cm^{-1} (Cu $K\alpha$)
Total number of electrons per unit cell $F(000)=368$
Absent spectra: $h0l$ for $h+l$ odd, $0k0$ for k odd
Space group $P2_1/n$ (C^5_{2h})
General positions: $\pm(x, y, z; \frac{1}{2}+x, \frac{1}{2}-y, \frac{1}{2}+z)$.

from acetone yielded satisfactory crystals. Small crystals of both materials were attached to thin glass rods with Canada balsam. Space group extinctions and preliminary lattice dimensions were obtained from precession photographs.

(A), AIS

The colorless acicular (*b*) crystals (m.p. 213–216 °C) are monoclinic with cell parameters:

$a=17{\cdot}02\pm0{\cdot}03$, $b=5{\cdot}29\pm0{\cdot}01$, $c=9{\cdot}02\pm0{\cdot}02$ Å, $\beta=100{\cdot}4\pm0{\cdot}1$ °.

Systematic absences are $h0l$ for $h+l$ odd and $0k0$ for k odd. These absences are consistent with space group $P2_1/n$ (C^5_{2h}). Four molecules per unit cell give a calculated density of 1·46 g.cm^{-3} in agreement with the observed density of 1·47 g.cm^{-3} obtained by flotation. No further work has been done with this isomer since the crystals are small and of generally poor quality.

(B), AIU

Some difficulty was experienced in finding untwinned crystals of AIU, but eventually an untwinned, irregular, platy crystal approximately 0·57 × 0·34 × 0·05 mm was chosen for intensity data collection on an automatic Picker four-circle goniostat. Narrow source, open-counter ω scans (Furnas, 1957) through several reflections showed the mosaicity to range from 0·15° to 0·25° for various directions in the crystal. Twenty-five reflections at moderately high Bragg angles (Cu $K\alpha$ radiation) were accurately centered through very narrow vertical and horizontal slits at a take-off angle of 0·5°. These observations were used as input to the computer program *PICK*2 (Ibers, 1966) which refined the cell and orientation parameters by the method of least-squares and generated the cards to control the automated goniostat. The refined cell parameters as well as other crystal data are given in Table 1.

Intensity data were collected with Ni-filtered Cu radiation at a take-off angle of 2·0°. A scintillation detector was used and the pulse-height analyzer was set for an approximately 90% window. All 1377 unique reflections for $2\theta<130°$ were measured by the θ–2θ scan technique (Furnas, 1957) at a 2θ scan rate of 1·0° min^{-1}. The scan range varied from 1·6° at low 2θ to 3·7° at high 2θ. Stationary crystal-stationary counter background counts were taken for 40 sec at each end of the scan. For count rates above 13,000 c.p.s. brass attenuators (~68% attenuation) were automatically inserted in the diffracted beam by the Picker system.

To check electronic and crystal stability during the period of data collection, the intensity of the $21\bar{6}$ reflection was measured every 50th reflection. The small (~2%) systematic decrease observed in this standard intensity over the period of data collection was not considered to be significant. The standard deviation of $21\bar{6}$, calculated from 31 observations, was 2·7 times what one would expect on the basis of counting statistics alone.

The reduction of the intensity data to structure amplitudes was accomplished with the computer program *DACOR* written by one of us (DLS). The background for a reflection was approximated by a straight line between the two measured background points. The intensities, corrected for background, were next corrected for Lorentz and polarization effects but not for absorption. Standard deviations $\sigma(I)$ were based on counting statistics and were corrected to $\sigma(F)$. Of the 1377 measured reflections, 110 were less than $2\sigma(I)$ and were considered as unobserved. The intensities of these unobserved reflections were then set equal to $2\sigma(I)$ and corrected to structure amplitudes, F_{lim}.

Determination and refinement of the structure

The structure was solved by the direct phasing of the structure amplitudes by the symbolic addition procedure of Karle & Karle (1966). The magnitudes of the normalized structure factors, $|E_{\mathbf{H}}|$, were computed from

$$E^2_{\mathbf{H}}=F^2_{\mathbf{H}}/\varepsilon\sum_{j=1}^{N}f^2_{j\mathbf{H}}$$

where $\varepsilon=2$ when $\mathbf{H}$ is $h0l$ or $0k0$, $\varepsilon=1$ otherwise, N is the number of atoms in the unit cell, $f_{j\mathbf{H}}$ is the atomic scattering factor for the jth atom, and the $F^2_{\mathbf{H}}$ have been placed on an absolute scale and corrected for thermal motion by means of a least-squares fit of a Wilson (1942) plot.

The computer program *ESORT*, written by one of us (DLS), was used to calculate the statistical averages shown in Table 2 for the normalized structure factors. Comparison of these values with theoretical values (Hauptman & Karle, 1953) confirmed the centric space group. Unobserved reflections were included in the Wilson plot and in the statistical averages as $E^2_{\text{lim}}/3$ (Hamilton, 1955). The same program listed all triplet interactions $E_{\mathbf{H}}$, $E_{\mathbf{K}}$, and $E_{\mathbf{H-K}}$ for all $|E|>2{\cdot}0$ and also those interactions of $|E_{\mathbf{H}}|>1{\cdot}6$ with $|E_{\mathbf{K}}|$ and $|E_{\mathbf{H-K}}|>1{\cdot}4$ to facilitate the application of the Σ_2 relationship,

$$sE_{\mathbf{H}}\sim s\,\Sigma\,E_{\mathbf{K}}\,E_{\mathbf{H-K}}\,,$$

of Hauptman & Karle (1953) used in the symbolic addition procedure.

Table 2. *Statistical averages of* $|E|$

		Theoretical	
	Experimental	Centric	Acentric
$\langle\lvert E\rvert\rangle$	0·811	0·798	0·886
$\langle\lvert E^2-1\rvert\rangle$	0·995	0·968	0·736
$\langle\lvert E^2\rvert\rangle$	1·034	1·000	1·000

Three linearly independent reflections with large E magnitudes and many interactions were assigned positive signs to specify the origin. Later phases a, b and c were assigned in sequence to three additional reflections in order to proceed with the phase determination. With these six assignments (Table 3) the phases of 218 of the 237 reflections with $|E|>1{\cdot}4$ were expressed in terms of +, −, or functions of a,b, and c. No phase indication was accepted unless the probability that it was correct was greater than 0·97, as calculated from Woolfson's (1954) formula,

$$P+(E_{\mathbf{H}})=\tfrac{1}{2}+\tfrac{1}{2}\tanh\,(\sigma_3/\sigma_2^{3/2})\,|E_{\mathbf{H}}|\,\sum_{\mathbf{K}}E_{\mathbf{K}}\,E_{\mathbf{H-K}}\,,$$

where $\sigma_n=\sum_{j=1}^{N}Z_j^n$. From interactions among the signs it soon became evident that a was probably −. Later evidence indicated that both b and c were probably +. The three-dimensional E map (Karle, Hauptman, Karle & Wing, 1958), calculated with this most consistent set of phases, yielded all 13 heavy atoms for which the discrepancy index $R_1=\sum\,||F_o|-|F_c^*||/\sum|F_o|$ was 0·27.

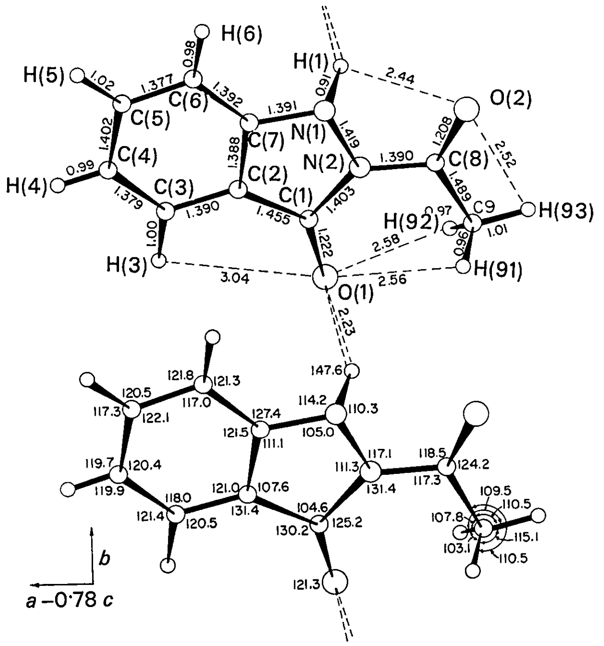


Fig. 1. Configuration, labeling, and interatomic distances and angles for AIU.

Table 3. *Starting set of phases*

h	k	l	$\lvert E\rvert$	Phase
2	1	2	3·82	+
5	2	$\overline{11}$	2·98	+
8	1	$\overline{9}$	2·54	+
2	0	2	2·90	a
4	3	$\overline{12}$	3·09	b
2	1	$\overline{8}$	2·29	c

A full-matrix least-squares refinement was then made with the use of all observed reflections plus those unobserved reflections for which $|F_c^*|>F_{\text{lim}}$. The quantity minimized was $\sum w(|F_o|-|F_c^*|)^2$ where

$$F_c^*|=KF_c\left[1+g\left(\frac{1+\cos^4 2\theta}{(1+\cos^2 2\theta)\sin 2\theta}\right)F_c^2\right]^{-1/2}=KF_c/G\,,$$

in which K is the scale factor, g is the extinction parameter (Zachariasen, 1963; Larson, 1967), and F_c is the

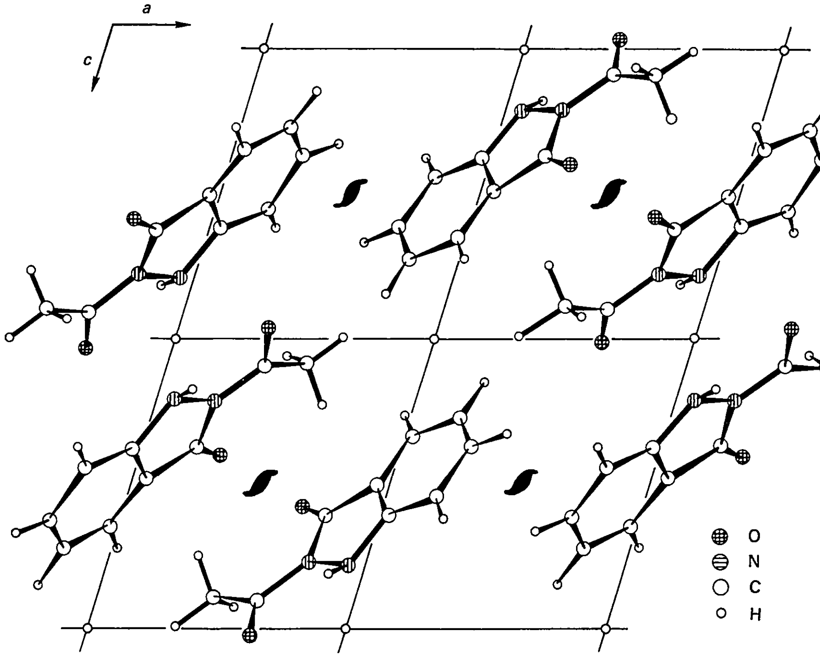


Fig. 2. [010] projection of the structure.

usual calculated structure factor. The weights were defined as

$$w=[\sigma^2(F_o)+(0\cdot03\,F_o)^2]^{-1}\,.$$

Two cycles of least-squares refinement with isotropic temperature factors followed by two cycles with anisotropic temperature factors reduced R_1 to 0·080. A difference Fourier synthesis clearly showed the 8 hydrogen atoms. The hydrogen atoms were assigned isotropic temperature factors and refinement was resumed with all parameters except g allowed to vary. Four cycles resulted in $R_1=0\cdot044$ with only small ($<0\cdot8\sigma$) parameter shifts on the last cycle. Up to this point, g had been held equal to zero. Two refinement cycles in which only K and g were varied reduced R_1 to 0·039 and two more cycles in which all parameters were varied concluded the refinement. For the last cycle of refinement only three of the 151 parameters shifted more than 0·1 σ and the maximum shift was 0·29σ. The final discrepancy indices for the 1267 observed reflections plus the 16 unobserved reflections with $|F_c^*|>F_{\text{lim}}$ were $R_1=0\cdot039$ and $R_2=[\Sigma w(F_o-|F_c^*|)^2/\Sigma wF_o^2]^{1/2}=0\cdot059$. The standard deviation of an observation of unit weight was 1·79. Of the 16 unobserved reflections with $|F_c^*|>F_{\text{lim}}$, none had $|F_c^*|>1\cdot5F_{\text{lim}}$. It is interesting to note that all 218 phases originally derived from the Σ_2 relation were correct.

A final difference Fourier synthesis contained values between $-0\cdot20$ and $+0\cdot30$ e.Å^{-3} and thus verified the structure. However, the difference electron density was generally >0 in the vicinity of the mean molecular planes, particularly between atoms, and <0 in the regions between the molecules. This systematic distribution of residual density is undoubtedly caused by the neglect of bonding effects on the atomic scattering factors; it has been observed by Cady (1967), Fritchie (1966) and Hanson (1966), among others, and is discussed in detail by Hirshfeld & Rabinovich (1967), O'Connell, Rae & Maslen (1966), Rae & Maslen (1965), Dawson (1965) and Stewart, Davidson & Simpson (1965).

The final positional and thermal parameters, with standard deviations estimated from the full-matrix least-squares process, are given in Table 4. The average standard deviations of the positional parameters expressed in Å are 0·0013 for O and N, 0·0015 for C, and 0·022 for H. Two other parameters refined in the least-squares process were the scale factor, $K=8\cdot013\pm0.038$, and the extinction coefficient,* $g=(0\cdot269\pm0\cdot031)+10^{-4}$. The final values of the observed and calculated structure amplitudes are compared in Table 5.

The Fourier computer program used in this analysis was obtained from Professor J. Trotter (1965). The full-matrix least-squares refinement utilized a modification of the Busing, Martin & Levy (1962) program *ORFLS*. The atomic scattering factors used for all atoms were obtained from *International Tables for X-ray Crystallography* (1962). All computations were performed on an IBM System 360 computer.

Description and discussion of the structure

The structure determination has shown that AIU is 2-acetyl-3-indazolinone. Thus AIS, the stable isomer,

---

* A referee has noted that there has been an overcorrection for the extinction effect (see 202 and 212). This is undoubtedly a result of our method for determining g. We used a least-squares procedure in which all reflections were included and which was biased against the stronger reflections by the weighting scheme. Thus g was probably determined mainly by the reflections which were least affected by extinction.

Table 4. *Final atomic parameters with their estimated standard deviations in parentheses*

Thermal parameters are defined by the expression:

$$T_i=\exp\,[-\tfrac{1}{4}(B_{11}h^2a^{*2}+B_{22}k^2b^{*2}+B_{33}l^2c^{*2}+2B_{12}hka^*b^*+2B_{13}hla^*c^*+2B_{23}klb^*c^*)]\,.$$

	x	y	z	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
O(1)	0·34275 (11)	−0·28796 (19)	0·79572 (9)	4·44 (5)	2·69 (5)	4·32 (5)	−0·72 (4)	1·45 (4)	−0·63 (4)
O(2)	0·31809 (13)	0·24484 (21)	1·01240 (10)	6·51 (8)	4·59 (6)	4·77 (6)	−1·23 (5)	3·25 (6)	−1·74 (5)
N(1)	0·46770 (11)	0·25925 (20)	0·89409 (10)	3·53 (6)	2·46 (5)	3·02 (5)	−0·51 (4)	1·00 (4)	−0·25 (4)
N(2)	0·38670 (10)	0·06660 (18)	0·88906 (9)	2·94 (5)	2·42 (5)	2·74 (5)	−0·26 (3)	0·76 (4)	−0·11 (3)
C(1)	0·39437 (12)	−0·09686 (23)	0·81098 (10)	2·90 (6)	2·44 (6)	2·72 (6)	0·21 (4)	0·45 (4)	−0·11 (4)
C(2)	0·47678 (12)	0·01186 (24)	0·75836 (10)	2·80 (5)	2·63 (6)	2·69 (5)	0·38 (4)	0·46 (4)	0·06 (4)
C(3)	0·51562 (14)	−0·06125 (28)	0·67234 (12)	3·69 (7)	3·38 (7)	3·31 (6)	0·60 (5)	1·03 (5)	−0·27 (5)
C(4)	0·59377 (14)	0·08456 (29)	0·63865 (13)	3·65 (7)	4·66 (8)	3·27 (6)	0·68 (5)	1·42 (5)	0·10 (5)
C(5)	0·63411 (14)	0·29745 (33)	0·69181 (12)	3·46 (6)	4·42 (8)	3·62 (7)	−0·01 (6)	1·19 (5)	0·64 (6)
C(6)	0·59648 (14)	0·37145 (27)	0·77726 (12)	3·52 (6)	3·31 (7)	3·30 (6)	−0·35 (5)	0·91 (5)	0·19 (5)
C(7)	0·51577 (12)	0·22491 (23)	0·80915 (11)	2·89 (6)	2·57 (6)	2·53 (5)	0·27 (4)	0·45 (4)	0·14 (4)
C(8)	0·31131 (13)	0·07519 (26)	0·95528 (11)	3·46 (6)	3·48 (7)	2·63 (6)	−0·01 (5)	0·83 (5)	−0·01 (5)
C(9)	0·22537 (16)	−0·12557 (33)	0·94959 (14)	3·70 (7)	4·42 (8)	3·72 (7)	−0·79 (6)	1·43 (6)	−0·34 (6)
H(1)	0·4267 (17)	0·3971 (32)	0·8914 (14)	1·88 (36)					
H(3)	0·4906 (17)	−0·2194 (33)	0·6386 (14)	1·64 (33)					
H(4)	0·6237 (19)	0·0365 (37)	0·5784 (16)	2·82 (40)					
H(5)	0·6956 (19)	0·3944 (34)	0·6666 (17)	2·83 (41)					
H(6)	0·6232 (18)	0·5227 (36)	0·8129 (16)	2·66 (38)					
H(91)	0·2701 (22)	−0·2715 (40)	0·9629 (17)	3·42 (48)					
H(92)	0·1748 (22)	−0·1411 (41)	0·8761 (19)	3·80 (49)					
H(93)	0·1708 (21)	−0·0951 (40)	0·9968 (19)	4·54 (55)					

must be 1-acetyl-3-indazolinone. Fig. 1 shows the labeling, configuration, and interatomic distances (uncorrected for thermal motion) and angles for the AIU molecule. Estimated standard deviations for the distances and angles were calculated from the coordinate standard deviations obtained in the least-squares process. The e.s.d.'s are less than 0·003 Å for heavy-atom separations and 0·03 Å for distances involving hydrogen atoms. The e.s.d.'s for the angles (Darlow, 1960) are less than 0·2° for heavy-heavy-heavy, 1·5° for heavy-heavy-hydrogen, and 2·0° for hydrogen-heavy-hydrogen.

Table 5. *Observed and calculated structure factors for* AIU

The column headings are h, l, $10G\lvert F_o\rvert/k$ and $10F_c$. An asterisk designates 'less than'.

h	l	$10G\lvert F_o\rvert/k$	$10F_c$
***** K= 0 *****			
0	2	496	491
0	4	124	117
0	6	170	169
0	8	91	84
0	10	156	152
0	12	95	97
0	14	98	99
1	1	221	229
1	-1	584	671
1	3	398	424
1	-3	193	202
1	5	75	86
1	-5	360	354
1	7	260	255
1	-7	278	258
1	9	293	287
1	-9	230	219
1	11	8	6
1	-11	66	68
1	13	44	45
1	-13	115	116
2	0	341	359
2	2	1932	1512
2	-2	7	12
2	4	58	65
2	-4	703	725
2	6	43	40
2	-6	147	140
2	8	132	134
2	-8	18	18
2	10	81	82
2	-10	46	45
2	12	13	19
2	-12	172	178
2	-14	167	170
3	1	152	160
3	-1	336	354
3	3	173	175
3	-3	95	108
3	5	124	122
3	-5	416	461
3	7	125	127
3	-7	339	327
3	9	70	67
3	-9	76	85
3	11	40	41
3	-11	96	92
3	13	75	75
3	-13	101	105
3	-15	26	27
4	0	193	203
4	2	11	4
4	-2	404	432
4	4	66	74
4	-4	278	271
4	6	148	144
4	-6	375	387
4	8	36	34
4	-8	62	68
4	10	111	108
4	-10	114	120
4	12	42	39
4	-12	155	158
4	-14	13	19
5	1	156	152
5	-1	72	68
5	3	39	37
5	-3	351	374
5	5	49	48
5	-5	254	254
5	7	109	110
5	-7	21	18
5	9	46	47
5	-9	119	128
5	11	7*	3
5	-11	44	42
5	-13	69	64
5	-15	29	31
6	0	233	235
6	2	66	68
6	-2	197	192
6	4	21	26
6	-4	338	342
6	6	104	104
6	-6	61	60
6	8	51	48
6	-8	83	87
6	10	8*	8
6	-10	129	125
6	-12	37	35
6	-14	43	38
7	1	53	51
7	-1	146	148
7	3	23	23
7	-3	122	121
7	5	108	111
7	-5	81	73
7	7	71	71
7	-7	219	219
7	9	42	47
7	-9	103	101
7	-11	92	92
7	-13	99	104
8	0	150	147
8	2	201	202
8	-2	184	185
8	4	55	58
8	-4	129	131
8	6	55	55
8	-6	144	149
8	8	18	16
8	-8	232	223
8	-10	80	81
8	-12	41	40
8	-14	21	26
9	1	85	84
9	-1	11	13
9	3	52	53
9	-3	65	66
9	5	38	36
9	-5	11	7
9	7	104	108
9	-7	231	232
9	-9	186	188
9	-11	55	59
9	-13	24	21
10	0	133	139
10	2	61	65
10	-2	40	43
10	4	19	21
10	-4	52	54
10	6	62	64
10	-6	23	25
10	-8	35	38
10	-10	11	9
10	-12	73	73
11	1	41	39
11	-1	56	57
11	3	30	31
11	-3	113	114
11	-5	169	170
11	-7	198	196
11	-9	43	39
11	-11	10	10
12	0	8*	4
12	2	86	86
12	-2	44	45
12	-4	104	99
12	-6	8*	0
12	-8	42	38
12	-10	20	21
13	-3	19	18
13	-5	64	63
13	-7	43	43
***** K= 1 *****			
0	1	303	321
0	2	31	33
0	3	251	258
0	4	168	166
0	5	48	49
0	6	293	302
0	7	128	117
0	8	130	130
0	9	18	4
0	10	8*	6
0	11	14	12
0	12	13	11
0	13	95	97
0	14	26	26
1	0	648	650
1	1	608	595
1	-1	155	176
1	2	571	568
1	-2	239	259
1	3	377	385
1	-3	25	20
1	4	284	282
1	-4	6*	2
1	5	114	116
1	-5	46	43
1	6	29	24
1	-6	99	101
1	7	74	69
1	-7	397	401
1	8	13	13
1	-8	78	77
1	9	8*	5
1	-9	81	79
1	10	88	86
1	-10	8*	4
1	11	93	93
1	-11	11	8
1	12	45	45
1	-12	15	13
1	13	8*	1
1	-13	8*	3
1	14	32	32
1	-14	101	104
2	0	248	246
2	1	589	589
2	-1	38	39
2	2	1372	1185
2	-2	265	289
2	3	77	78
2	-3	94	94
2	4	156	151
2	-4	34	31
2	5	107	107
2	-5	109	108
2	6	40	41
2	-6	226	227
2	7	7*	3
2	-7	67	61
2	8	110	110
2	-8	308	299
2	9	159	149
2	-9	78	72
2	10	41	39
2	-10	75	78
2	11	26	25
2	-11	104	104
2	12	107	105
2	-12	37	37
2	13	8*	2
2	-13	50	51
2	-14	33	30
2	-15	40	41
3	0	208	195
3	1	349	355
3	-1	36	36
3	2	589	598
3	-2	56	51
3	3	94	92
3	-3	70	72
3	4	333	335
3	-4	94	104
3	5	211	211
3	-5	354	369
3	6	113	108
3	-6	61	66
3	7	57	49
3	-7	58	57
3	8	55	53
3	-8	106	106
3	9	62	66
3	-9	74	72
3	10	58	54
3	-10	39	38
3	11	67	65
3	-11	149	154
3	12	49	48
3	-12	93	94
3	13	8*	1
3	-13	70	74
3	-14	19	19
3	-15	31	27
4	0	143	139
4	1	133	133
4	-1	40	36
4	2	85	87
4	-2	585	623
4	3	261	254
4	-3	37	38
4	4	453	456
4	-4	153	153
4	5	48	47
4	-5	167	155
4	6	8	5
4	-6	286	286
4	7	21	19
4	-7	174	164
4	8	26	27
4	-8	7*	4
4	9	37	36
4	-9	32	31
4	10	10	6
4	-10	134	139
4	11	105	102
4	-11	113	121
4	12	86	86
4	-12	133	137
4	-13	96	97
4	-14	21	21
4	-15	16	13
5	0	8	7
5	1	101	98
5	-1	29	26
5	2	124	123
5	-2	120	114
5	3	46	48
5	-3	216	221
5	4	268	262
5	-4	184	184
5	5	61	58
5	-5	182	173
5	6	91	90
5	-6	65	68
5	7	32	33
5	-7	102	105
5	8	34	31
5	-8	31	34
5	9	12	11
5	-9	193	194
5	10	55	52
5	-10	82	83
5	11	9	3
5	-11	8*	11
5	-12	8*	12
5	-13	10	8
5	-14	8*	10
5	-15	55	58
6	0	330	327
6	1	99	101
6	-1	86	89
6	2	65	62
6	-2	52	52
6	3	96	98
6	-3	18	18
6	4	64	61
6	-4	6*	1
6	5	82	79
6	-5	107	95
6	6	25	25
6	-6	123	130
6	7	25	25
6	-7	25	25
6	8	27	28
6	-8	112	113
6	9	38	39
6	-9	153	155
6	10	28	25
6	-10	147	148
6	-11	181	185
6	-12	14	17
6	-13	28	27
6	-14	30	33
6	-15	26	26
7	0	83	84
7	1	86	83
7	-1	141	144
7	2	87	87
7	-2	170	164
7	3	101	98
7	-3	193	196
7	4	20	21
7	-4	87	84
7	5	60	57
7	-5	45	50
7	6	65	68
7	-6	22	21
7	7	8*	3
7	-7	39	38
7	8	36	35
7	-8	74	75
7	9	18	18
7	-9	113	112
7	-10	60	65
7	-11	25	27
7	-12	8*	4
7	-13	28	28
7	-14	8*	0
8	0	8*	6
8	1	43	43
8	-1	46	46
8	2	34	36
8	-2	32	32
8	3	59	59
8	-3	33	32
8	4	58	57
8	-4	55	55
8	5	64	68
8	-5	18	20
8	6	46	48
8	-6	8*	3
8	7	25	29
8	-7	59	59
8	8	47	48
8	-8	131	129
8	-9	194	197
8	-10	53	51
8	-11	44	42
8	-12	18	13
8	-13	48	50
8	-14	51	48
9	0	93	93
9	1	59	58
9	-1	123	120
9	2	25	24
9	-2	111	109
9	3	42	43
9	-3	28	28
9	4	59	58
9	-4	103	101
9	5	18	20
9	-5	141	140
9	6	43	45
9	-6	8*	1
9	7	8*	7
9	-7	78	78
9	-8	22	22
9	-9	47	47
9	-10	24	26
9	-11	42	44
9	-12	28	29
9	-13	21	17
10	0	9*	5
10	1	13	12
10	-1	70	73
10	2	45	44
10	-2	17	20
10	3	44	41
10	-3	26	25
10	4	74	77
10	-4	8*	6
10	5	7*	2
10	-5	28	29
10	6	7*	4
10	-6	203	196
10	-7	138	141
10	-8	82	80
10	-9	17	15
10	-10	37	33
10	-11	50	52
10	-12	20	21
11	0	81	81
11	1	15	17
11	-1	39	37
11	2	51	55
11	-2	110	109
11	3	12	12
11	-3	38	37
11	4	7*	5
11	-4	58	55
11	-5	50	52
11	-6	62	62
11	-7	31	32
11	-8	58	59
11	-9	33	32
11	-10	18	20
11	-11	8*	10
12	0	8*	5
12	1	78	80
12	-1	23	22
12	-2	47	47
12	-3	38	35
12	-4	29	28
12	-5	87	86
12	-6	42	42
12	-7	18	18
12	-8	23	21
12	-9	8*	0
12	-10	76	72
13	-2	36	37
13	-3	75	73
13	-4	53	54
13	-5	83	80
13	-6	34	35
13	-7	18	18
***** K= 2 *****			
0	0	267	268
0	1	146	151
0	2	63	55
0	3	184	180
0	4	141	137
0	5	70	65
0	6	165	159
0	7	143	141
0	8	69	72
0	9	79	76
0	10	219	216
0	11	20	19
0	12	36	38
0	13	23	24
0	14	26	29
1	0	113	113
1	1	209	208
1	-1	223	243
1	2	52	45
1	-2	217	204
1	3	24	21
1	-3	243	243
1	4	76	81
1	-4	53	54
1	5	147	138
1	-5	7	3
1	6	23	21
1	-6	70	72
1	7	81	71
1	-7	29	28
1	8	21	22
1	-8	8	15
1	9	49	49
1	-9	37	34
1	10	8*	5
1	-10	95	95
1	11	83	81
1	-11	49	47
1	12	20	16
1	-12	80	81
1	13	12	10
1	-13	60	59
1	-14	8*	0
2	0	158	144
2	1	178	178
2	-1	297	310
2	2	157	154
2	-2	32	31
2	3	91	96
2	-3	72	71
2	4	50	46
2	-4	458	475
2	5	62	54
2	-5	152	147
2	6	135	134
2	-6	16	17
2	7	26	29
2	-7	22	17
2	8	8*	11
2	-8	196	194
2	9	100	97
2	-9	49	48
2	10	95	93
2	-10	8*	1
2	11	115	116
2	-11	130	133
2	12	55	57
2	-12	61	63
2	13	7*	1
2	-13	35	36
2	-14	46	43
3	0	108	104
3	1	130	125
3	-1	6*	3
3	2	80	75
3	-2	79	83
3	3	337	330
3	-3	155	160
3	4	31	33
3	-4	262	263
3	5	101	103
3	-5	211	222
3	6	127	126
3	-6	95	88
3	7	25	24
3	-7	37	38
3	8	35	31
3	-8	27	21
3	9	102	95
3	-9	64	62
3	10	21	23
3	-10	56	59
3	11	73	71
3	-11	64	63
3	12	11	9
3	-12	21	17
3	-13	127	129
3	-14	54	51
4	0	34	28
4	1	132	127
4	-1	132	132
4	2	219	208
4	-2	131	129
4	3	277	272
4	-3	181	185
4	4	416	413
4	-4	18	22
4	5	7*	0
4	-5	143	140
4	6	28	25
4	-6	101	101
4	7	87	82
4	-7	27	27
4	8	17	17
4	-8	121	127
4	9	16	16
4	-9	170	175
4	10	39	38
4	-10	115	117
4	11	8*	3
4	-11	38	33
4	-12	10	12
4	-13	61	61
4	-14	11	11
5	0	196	188
5	1	208	204
5	-1	176	175
5	2	143	143
5	-2	233	235
5	3	308	304
5	-3	122	126
5	4	93	91
5	-4	136	129
5	5	136	133
5	-5	66	67
5	6	149	149
5	-6	185	177
5	7	8*	3
5	-7	11	11
5	8	68	66
5	-8	18	17
5	9	24	25
5	-9	106	105
5	10	19	17
5	-10	9	9
5	11	62	67
5	-11	203	205
5	-12	124	124
5	-13	16	21
5	-14	42	40
6	0	211	214
6	1	85	82
6	-1	66	65
6	2	49	50
6	-2	7*	3
6	3	8*	2
6	-3	202	200
6	4	140	141
6	-4	142	142
6	5	173	169
6	-5	92	90
6	6	191	192
6	-6	124	115
6	7	8*	2
6	-7	126	128
6	8	18	19
6	-8	83	83
6	9	100	98
6	-9	49	52
6	10	63	64
6	-10	197	197
6	-11	41	38
6	-12	39	40
6	-13	8*	4
6	-14	31	31
7	0	75	71
7	1	38	38
7	-1	80	78
7	2	100	96
7	-2	66	67
7	3	97	96
7	-3	13	15
7	4	115	115
7	-4	197	197
7	5	122	123
7	-5	77	69
7	6	59	58
7	-6	106	105
7	7	13	8
7	-7	148	143
7	8	91	94
7	-8	41	39
7	9	40	40
7	-9	147	151
7	-10	88	83
7	-11	78	82
7	-12	43	46
7	-13	24	26
7	-14	20	18
8	0	31	29
8	1	98	96
8	-1	45	46
8	2	100	99
8	-2	64	64
8	3	36	38
8	-3	8*	5
8	4	8*	9
8	-4	9	12
8	5	9	4
8	-5	81	80
8	6	50	54
8	-6	49	53
8	7	72	72
8	-7	116	116
8	8	17	21
8	-8	197	193
8	-9	20	21
8	-10	8*	9
8	-11	49	49
8	-12	17	19
8	-13	23	27
9	0	24	25
9	1	8*	10
9	-1	75	74
9	2	25	23
9	-2	69	70
9	3	71	71
9	-3	120	120
9	4	24	21
9	-4	137	141
9	5	12	10
9	-5	8*	6
9	6	8*	5
9	-6	91	91
9	-7	27	27
9	-8	13	15
9	-9	82	84
9	-10	37	40
9	-11	26	24
9	-12	8	2
9	-13	34	34
10	0	95	96
10	1	29	29
10	-1	27	28
10	2	26	25
10	-2	24	25
10	3	106	106
10	-3	42	38
10	4	32	29
10	-4	112	113
10	5	52	53
10	-5	68	65
10	-6	10	13
10	-7	36	36
10	-8	53	51
10	-9	43	43
10	-10	10	12
10	-11	29	23
10	-12	66	59
11	0	10	9
11	1	74	74
11	-1	67	68
11	2	15	14
11	-2	56	56
11	3	67	66
11	-3	34	36
11	-4	48	51
11	-5	24	22
11	-6	9	1
11	-7	19	20
11	-8	22	22
11	-9	10	12
11	-10	8*	9
12	0	8*	6
12	-1	8*	1
12	-2	68	67
12	-3	13	13
12	-4	95	93
12	-5	31	32
12	-6	71	69
12	-7	8*	5
12	-8	17	15
***** K= 3 *****			
0	1	32	37
0	2	6*	2
0	3	22	23
0	4	7*	0
0	5	36	30
0	6	148	148
0	7	38	35
0	8	8	2
0	9	129	132
0	10	70	71
0	11	58	55
0	12	11	7
0	13	44	46
1	0	277	271
1	1	79	79
1	-1	21	20
1	2	248	230
1	-2	84	86
1	3	68	68
1	-3	180	174
1	4	157	148
1	-4	9	15
1	5	8*	5
1	-5	259	252
1	6	110	106
1	-6	51	50
1	7	130	129
1	-7	81	78
1	8	63	65
1	-8	27	26
1	9	147	144
1	-9	154	158
1	10	15	12
1	-10	11	9
1	11	61	65
1	-11	63	65
1	12	29	30
1	-12	55	56
1	-13	45	43
2	0	42	35
2	1	17	14
2	-1	60	60
2	2	165	159
2	-2	110	111
2	3	7*	5
2	-3	137	139
2	4	38	40
2	-4	36	34
2	5	73	75
2	-5	38	36
2	6	90	92
2	-6	62	54
2	7	8*	2
2	-7	34	40
2	8	32	32
2	-8	112	111
2	9	8*	2
2	-9	63	61
2	10	26	28
2	-10	49	51
2	11	63	64
2	-11	46	44
2	12	87	91
2	-12	27	23
2	-13	23	25
3	0	96	100
3	1	204	201
3	-1	344	345
3	2	66	59
3	-2	115	121
3	3	87	87
3	-3	210	207
3	4	7*	10
3	-4	36	37
3	5	124	124
3	-5	73	72
3	6	45	48
3	-6	49	52
3	7	26	26
3	-7	169	175
3	8	79	76
3	-8	107	109
3	9	27	30
3	-9	19	21
3	10	58	54
3	-10	99	101
3	11	90	91
3	-11	50	50
3	-12	83	86
3	-13	30	30
4	0	167	162
4	1	17	13
4	-1	88	85
4	2	61	62
4	-2	206	217
4	3	37	38
4	-3	32	34
4	4	8*	7
4	-4	108	110
4	5	8*	6
4	-5	49	48
4	6	43	42
4	-6	123	125
4	7	82	83
4	-7	50	50
4	8	140	139
4	-8	57	59
4	9	8*	5
4	-9	14	11
4	10	25	23
4	-10	100	106
4	-11	9*	7
4	-12	160	153
4	-13	35	35
5	0	10	13
5	1	162	156
5	-1	22	26
5	2	57	56
5	-2	18	23
5	3	8*	5
5	-3	113	114
5	4	13	14
5	-4	50	50
5	5	194	192
5	-5	81	80
5	6	62	57
5	-6	98	102
5	7	141	140
5	-7	100	97
5	8	9*	8
5	-8	12	12
5	9	17	15
5	-9	48	49
5	10	44	46
5	-10	60	64
5	-11	47	46
5	-12	10	12
5	-13	36	35
6	0	8*	3
6	1	78	78
6	-1	76	78
6	2	20	17
6	-2	125	128
6	3	64	64
6	-3	20	21
6	4	39	39
6	-4	134	132
6	5	62	64
6	-5	91	89
6	6	109	109
6	-6	64	60
6	7	17	11
6	-7	13	14
6	8	24	23
6	-8	241	241
6	9	13	14
6	-9	10	4
6	-10	121	116
6	-11	21	21
6	-12	11	9
6	-13	10	3
7	0	24	24
7	1	133	136
7	-1	8*	2
7	2	119	116
7	-2	31	30
7	3	40	44
7	-3	8*	6
7	4	48	48
7	-4	36	34
7	5	146	149
7	-5	166	166
7	6	59	60
7	-6	95	97
7	7	154	155
7	-7	83	83
7	8	10	11
7	-8	11	15
7	-9	108	107
7	-10	54	54
7	-11	54	50
7	-12	8*	4
7	-13	30	29
8	0	88	87
8	1	100	100
8	-1	61	59
8	2	141	142
8	-2	184	190
8	3	100	101
8	-3	79	79
8	4	32	30
8	-4	86	81
8	5	62	66
8	-5	8*	1
8	6	8*	5
8	-6	205	208
8	-7	12	15
8	-8	32	33
8	-9	32	35
8	-10	21	22
8	-11	12	15
8	-12	8*	4
9	0	23	20
9	1	74	73
9	-1	8*	11
9	2	22	22
9	-2	76	75
9	3	76	75
9	-3	57	62
9	4	75	77
9	-4	67	67
9	5	60	65
9	-5	74	75
9	-6	18	20
9	-7	104	97
9	-8	24	27
9	-9	16	20
9	-10	34	31
9	-11	38	41
10	0	56	61
10	1	18	15
10	-1	28	29
10	2	24	26
10	-2	10	10
10	3	20	22
10	-3	17	14
10	-4	73	74
10	-5	34	35
10	-6	78	76
10	-7	44	44
10	-8	9	8
10	-9	52	52
10	-10	36	31
11	0	30	29
11	1	19	20
11	-1	27	26
11	-2	9	10
11	-3	8*	7
11	-4	9	7
11	-5	52	46
11	-6	29	26
11	-7	49	48
11	-8	37	37
***** K= 4 *****			
0	0	146	137
0	1	16	15
0	2	28	26
0	3	187	188
0	4	48	49
0	5	58	58
0	6	11	5
0	7	115	111
0	8	67	66
0	9	116	118
0	10	74	78
0	11	25	23
1	0	50	48
1	1	68	67
1	-1	122	129
1	2	141	138
1	-2	129	126
1	3	75	75
1	-3	116	113
1	4	80	80
1	-4	165	166
1	5	8*	4
1	-5	56	56
1	6	123	125
1	-6	11	14
1	7	103	101
1	-7	77	81
1	8	66	66
1	-8	36	38
1	9	45	46
1	-9	37	38
1	10	11	12
1	-10	58	60
1	11	17	16
1	-11	11	13
1	-12	8	5
2	0	121	121
2	1	60	59
2	-1	119	120
2	2	35	33
2	-2	24	20
2	3	8*	1
2	-3	15	15
2	4	25	22
2	-4	76	74
2	5	115	112
2	-5	131	128
2	6	108	109
2	-6	55	56
2	7	64	65
2	-7	168	174
2	8	65	66
2	-8	106	108
2	9	44	46
2	-9	8*	1
2	10	49	48

Table 5 (*cont.*)

2	-10	8*	5
2	-11	29	29
2	-12	40	38
3	0	48	44
3	1	67	67
3	-1	45	46
3	2	66	64
3	-2	8*	3
3	3	129	131
3	-3	89	86
3	4	197	191
3	-4	117	119
3	5	118	115
3	-5	31	33
3	6	25	27
3	-6	93	95
3	7	10	12
3	-7	125	131
3	8	20	21
3	-8	85	91
3	9	45	48
3	-9	73	71
3	10	19	17
3	-10	65	68
3	-11	15	15
3	-12	14	13
4	0	141	138
4	1	72	70
4	-1	71	73
4	2	108	107
4	-2	106	116
4	3	116	120
4	-3	13	8
4	4	63	64
4	-4	42	44
4	5	36	40
4	-5	97	102
4	6	8*	1
4	-6	56	55
4	7	10	7
4	-7	17	15
4	8	49	49
4	-8	35	34
4	9	50	53
4	-9	58	60
4	-10	87	85
4	-11	13	12
4	-12	17	19
5	0	110	111
5	1	80	80
5	-1	144	142
5	2	47	46
5	-2	140	144
5	3	71	75
5	-3	22	24
5	4	13	10
5	-4	78	78
5	5	88	88
5	-5	128	128
5	6	92	91
5	-6	23	23
5	7	8*	5
5	-7	144	146
5	8	14	13
5	-8	154	157
5	-9	98	98
5	-10	72	72
5	-11	49	45
5	-12	17	13
6	0	210	212
6	1	74	72
6	-1	67	72
6	2	131	129
6	-2	22	20
6	3	41	40
6	-3	35	38
6	4	21	18
6	-4	110	111
6	5	102	101
6	-5	26	25
6	6	34	33
6	-6	36	35
6	7	26	26
6	-7	44	47
6	-8	14	14
6	-9	50	47
6	-10	48	46
6	-11	10	9
7	0	65	66
7	1	55	57
7	-1	34	36
7	2	40	41
7	-2	30	29
7	3	46	45
7	-3	51	46
7	4	39	39
7	-4	18	13
7	5	21	21
7	-5	40	47
7	6	16	16
7	-6	136	134
7	-7	92	92
7	-8	82	84
7	-9	8*	3
7	-10	45	40
7	-11	8	4
8	0	10	13
8	1	34	36
8	-1	29	32
8	2	60	63
8	-2	16	13
8	3	14	16
8	-3	22	22
8	4	17	17
8	-4	43	42
8	5	9	12
8	-5	22	23
8	-6	79	79
8	-7	52	49
8	-8	55	52
8	-9	7*	2
8	-10	21	20
9	0	14	16
9	1	8	5
9	-1	8*	3
9	2	8	9
9	-2	34	36
9	3	8*	8
9	-3	50	48
9	-4	39	42
9	-5	8	3
9	-6	37	37
9	-7	36	38
9	-8	69	64
9	-9	25	24
10	0	58	59
10	-1	8*	4
10	-2	58	58
10	-3	45	42
10	-4	67	68
10	-5	21	22
10	-6	8*	1
10	-7	22	18
***** K= 5 *****			
0	1	61	59
0	2	125	127
0	3	23	22
0	4	47	46
0	5	21	22
0	6	36	40
0	7	22	22
0	8	8*	3
0	9	8*	7
1	0	63	62
1	1	149	150
1	-1	77	78
1	2	121	119
1	-2	137	136
1	3	136	129
1	-3	42	39
1	4	42	42
1	-4	127	127
1	5	28	26
1	-5	8*	3
1	6	31	32
1	-6	159	156
1	7	50	49
1	-7	89	92
1	8	31	33
1	-8	42	41
1	9	9	9
1	-9	25	25
1	-10	63	61
2	0	99	98
2	1	131	131
2	-1	31	30
2	2	119	117
2	-2	30	33
2	3	37	39
2	-3	13	15
2	4	58	59
2	-4	66	64
2	5	81	83
2	-5	40	40
2	6	43	43
2	-6	8*	4
2	7	12	10
2	-7	75	75
2	8	12	14
2	-8	75	81
2	-9	28	27
2	-10	40	38
3	0	157	151
3	1	59	63
3	-1	32	31
3	2	22	22
3	-2	192	202
3	3	84	86
3	-3	29	28
3	4	52	49
3	-4	143	149
3	5	27	25
3	-5	100	106
3	6	8	7
3	-6	9*	10
3	7	22	24
3	-7	26	27
3	8	60	58
3	-8	8*	2
3	-9	82	85
3	-10	31	31
4	0	22	26
4	1	8*	7
4	-1	23	23
4	2	8	4
4	-2	130	134
4	3	62	60
4	-3	75	79
4	4	87	87
4	-4	17	13
4	5	19	20
4	-5	81	82
4	6	8	9
4	-6	131	133
4	7	32	32
4	-7	30	29
4	-8	8*	2
4	-9	58	59
4	-10	29	28
5	0	88	90
5	1	10	10
5	-1	14	10
5	2	79	79
5	-2	20	23
5	3	43	44
5	-3	45	46
5	4	19	21
5	-4	76	77
5	5	11	13
5	-5	88	90
5	6	29	25
5	-6	73	73
5	-7	17	19
5	-8	29	29
5	-9	44	44
6	0	16	18
6	1	34	32
6	-1	38	41
6	2	59	55
6	-2	19	13
6	3	19	16
6	-3	41	38
6	4	36	35
6	-4	52	51
6	5	9	6
6	-5	46	44
6	-6	13	7
6	-7	32	31
6	-8	15	12
6	-9	26	25
7	0	29	25
7	1	19	19
7	-1	11	9
7	2	7*	6
7	-2	46	48
7	3	58	55
7	-3	72	76
7	-4	39	39
7	-5	44	46
7	-6	29	24
7	-7	43	42
7	-8	21	21
8	0	17	16
8	1	7*	1
8	-1	30	27
8	-2	8	10
8	-3	54	54
8	-4	8*	4
8	-5	53	51
8	-6	8*	9
***** K= 6 *****			
0	0	169	168
0	1	96	97
0	2	42	39
0	3	40	43
0	4	69	68
0	5	48	49
0	6	48	49
1	0	84	86
1	1	26	24
1	-1	89	93
1	2	68	67
1	-2	79	80
1	3	34	33
1	-3	8*	4
1	4	91	93
1	-4	99	101
1	5	28	27
1	-5	8	1
1	6	72	71
1	-6	51	49
2	0	21	21
2	1	27	27
2	-1	8*	10
2	2	98	94
2	-2	58	61
2	3	47	48
2	-3	33	35
2	4	79	77
2	-4	88	91
2	5	8*	2
2	-5	11	11
2	-6	9	4
3	0	8*	4
3	1	51	50
3	-1	16	16
3	2	30	31
3	-2	8*	3
3	3	43	41
3	-3	8*	5
3	4	7*	9
3	-4	42	44
3	-5	59	61
3	-6	29	29
4	0	25	23
4	1	42	41
4	-1	15	16
4	2	23	20
4	-2	44	45
4	3	29	26
4	-3	30	30
4	-4	16	13
4	-5	57	59
4	-6	22	25
5	0	59	58
5	1	61	58
5	-1	9	11
5	-2	54	54
5	-3	74	75
5	-4	21	20
5	-5	18	15

Table 6. *Short intermolecular contacts*

Hydrogen bond		
N(1)···O(1$^{\text{i}}$)	=O(1)···N(1$^{\text{ii}}$)	3·033 Å
H(1)···O(1$^{\text{i}}$)	=O(1)···H(1$^{\text{ii}}$)	2·228
Heavy atom contacts < 3·5 Å		
O(1)···N(2$^{\text{iii}}$)	=N(2)···O(1$^{\text{iv}}$)	3·089
O(1)···C(1$^{\text{iii}}$)	=C(1)···O(1$^{\text{iv}}$)	3·167
N(1)···C(8$^{\text{v}}$)	=C(8)···N(1$^{\text{v}}$)	3·291
O(1)···C(8$^{\text{iii}}$)	=C(8)···O(1$^{\text{iv}}$)	3·318
N(2)···N(2$^{\text{v}}$)		3·339
O(1)···C(7$^{\text{ii}}$)	=C(7)···O(1$^{\text{i}}$)	3·369
N(1)···N(2$^{\text{v}}$)	=N(2)···N(1$^{\text{v}}$)	3·377
O(2)···C(6$^{\text{vi}}$)	=C(6)···O(2$^{\text{vi}}$)	3·417
O(2)···C(1$^{\text{v}}$)	=C(1)···O(2$^{\text{v}}$)	3·491
Heavy atom-hydrogen contacts < 3·0 Å		
O(2)···H(6$^{\text{vi}}$)	=H(6)····O(2$^{\text{vi}}$)	2·55
C(7)···H(92$^{\text{iv}}$)	=H(92)···C(7$^{\text{iii}}$)	2·83
O(2)···H(91$^{\text{i}}$)	=H(91)···O(2$^{\text{ii}}$)	2·84
C(2)···H(92$^{\text{iv}}$)	=H(92)···C(2$^{\text{iii}}$)	2·85
O(2)···H(4$^{\text{vii}}$)	=H(4)····O(2$^{\text{viii}}$)	2·88
O(2)···H(5$^{\text{vii}}$)	=H(5)····O(2$^{\text{viii}}$)	2·88
C(6)···H(3$^{\text{i}}$)	=H(3)····C(6$^{\text{ii}}$)	2·97
O(1)···H(92$^{\text{iii}}$)	=H(92)···O(1$^{\text{iv}}$)	2·98
Hydrogen-hydrogen contacts < 2·9 Å		
H(5)···H(93$^{\text{viii}}$)	=H(93)···H(5$^{\text{vii}}$)	2·44
H(3)···H(6$^{\text{ii}}$)	=H(6)····H(3$^{\text{i}}$)	2·75
H(4)···H(6$^{\text{ix}}$)	=H(6)····H(4$^{\text{x}}$)	2·80
H(4)···H(93$^{\text{xi}}$)	=H(93)···H(4$^{\text{xii}}$)	2·84

i	x	$1+y$	z
ii	x	$-1+y$	z
iii	$\frac{1}{2}-x$	$-\frac{1}{2}+y$	$\frac{3}{2}-z$
iv	$\frac{1}{2}-x$	$\frac{1}{2}+y$	$\frac{3}{2}-z$
v	$1-x$	$-y$	$2-z$
vi	$1-x$	$1-y$	$2-z$
vii	$-\frac{1}{2}+x$	$\frac{1}{2}-y$	$\frac{1}{2}+z$
viii	$\frac{1}{2}+x$	$\frac{1}{2}-y$	$-\frac{1}{2}+z$
ix	$\frac{3}{2}-x$	$-\frac{1}{2}+y$	$\frac{3}{2}-z$
x	$\frac{3}{2}-x$	$\frac{1}{2}+y$	$\frac{3}{2}-z$
xi	$\frac{1}{2}+x$	$-\frac{1}{2}-y$	$-\frac{1}{2}+z$
xii	$-\frac{1}{2}+x$	$-\frac{1}{2}-y$	$\frac{1}{2}+z$

The shorter intermolecular contacts, listed in Table 6, are consistent with van der Waals radii (Pauling, 1960) with the exception of H(1)...O(1$^{\text{i}}$) where a normal hydrogen bond occurs. The oxygen atom O(2) has several short intermolecular contacts but none short enough to be a hydrogen bond. Intramolecular hydrogen bonds which involve O(2) are ruled out since none of the intramolecular O...H distances is less than Bartell's (1960) hard-shell distances. Fig. 2 shows the packing of the molecules in the [010] projection of the structure. The hydrogen bonds join molecules in chains along **b**.

The bond distances and angles in AIU appear normal when compared with similar structures (Smith, 1969; Karle & Karle, 1967). The C–O bonds agree well with known ketonic C=O distances (Sutton, 1965). The fact that C(8)–O(2) is shorter than C(1)–O(1) is consistent with the hydrogen bonding. The C–H distances average 0·99 Å and N–H is 0·91 Å, both about 0·1 Å shorter than the true values but both agreeing with typical X-ray results. The C(8)–C(9) separation is normal for this type of single bond and the C(1)–C(2) bond (1·455 Å) is only slightly shorter than is considered normal (Lide, 1962). The N(1)–N(2) bond (1·419 Å) is somewhat shorter than the 1·45 Å for the N–N single bond in hydrazine (Sutton, 1965). The C–N bonds are all shorter than the unconjugated C–N single-bond length of 1·47 Å (Sutton, 1965) but are consistent with the observations of Karle & Karle (1967) for C–N bonds which involve trigonal carbon.

The C–C distances in the benzo ring average 1·388 Å and the C–C–C angles average 120·00°, both values in excellent agreement with the accepted values of 1·394 Å and 120·00°(Sutton, 1965). However, there is some systematic variation in these distances and angles. The bonds C(3)–C(4) and C(5)–C(6) (average 1·378 Å) are shorter than the bonds C(2)–C(3), C(6)–C(7) and C(7)–C(2) (average 1·390 Å), which are in turn shorter than C(4)–C(5) (1·402 Å). Likewise, the C–C–C angles at C(3) and C(6) are smaller than the other four angles of the benzo ring.

Table 7. *Equations of least-squares planes and distances* (Å) *of atoms from these planes*

X, Y and Z are expressed in Å units relative to the Cartesian axial system defined by the a, b and c^* axes. The planes were calculated by the method of Schomaker, Waser, Marsh & Bergman (1959) as modified by Blow (1960).

$$\begin{aligned}
\text{Plane } A:&\quad -0{\cdot}6160X+0{\cdot}4694Y-0{\cdot}6326Z=-7{\cdot}4456\\
B:&\quad -0{\cdot}6235X+0{\cdot}4636Y-0{\cdot}6296Z=-7{\cdot}4476\\
C:&\quad -0{\cdot}5115X+0{\cdot}4640Y-0{\cdot}7233Z=-8{\cdot}3148\\
D:&\quad -0{\cdot}6221X+0{\cdot}4646Y-0{\cdot}6302Z=-7{\cdot}4473\\
E:&\quad -0{\cdot}6038X+0{\cdot}4746Y-0{\cdot}6405Z=-7{\cdot}5062\\
F:&\quad -0{\cdot}5376X+0{\cdot}1410Y-0{\cdot}8313Z=-9{\cdot}6608
\end{aligned}$$

Plane *A*

N(1)	0·036	C(7)	−0·002
N(2)	−0·044	*O(1)	0·083
C(1)	0·018	*C(8)	−0·231
C(2)	0·015	*H(1)	−0·633
C(3)	0·010	*H(3)	0·073
C(4)	−0·017	*H(4)	−0·010
C(5)	−0·011	*H(5)	0·022
C(6)	−0·003	*H(6)	−0·025

Plane *B*

C(2)	0·003	*O(1)	0·047
C(3)	0·005	*C(1)	−0·009
C(4)	−0·009	*C(8)	−0·269
C(5)	0·004	*H(1)	−0·646
C(6)	0·005	*H(3)	0·062
C(7)	−0·007	*H(4)	0·004
*N(1)	0·022	*H(5)	0·047
*N(2)	−0·071	*H(6)	−0·012

Plane *C*

O(2)	−0·001
N(1)	−0·002
N(2)	0·001
C(8)	0·005
C(9)	−0·004
*C(1)	−0·072
*C(7)	−0·229
*H(1)	−0·622

Plane *D*

C(1)	−0·003	*O(1)	0·054
C(2)	0·006	*N(1)	0·026
C(3)	0·006	*N(2)	−0·065
C(4)	−0·010	*H(3)	0·064
C(5)	0·002	*H(4)	0·002
C(6)	0·005	*H(5)	0·043
C(7)	−0·005	*H(6)	−0·013

Plane *E*

N(1)	0·034	*O(1)	0·099
N(2)	−0·030	*C(3)	−0·022
C(1)	0·024	*C(6)	−0·044
C(2)	−0·001	*C(8)	−0·198
C(7)	−0·022	*H(1)	−0·634

Plane *F*

N(2)	0·000
C(7)	0·000
H(1)	0·000
*N(1)	0·382

* Not included in the calculation of the plane.

The overall pattern of bond lengths points to extensive conjugation of the molecule. Thus, it is not surprising to find that the atoms N(1), N(2), C(1)... C(7) which form the fused ring system all lie within 0·05 Å of a plane (*A*, Table 7). Consideration of the surrounding angles shows that C(1) and N(2) are coplanar with their immediate neighbors but that N(1) is tetrahedrally coordinated. In fact, N(1) lies 0·38 Å out of the plane (*F*, Table 7) of its neighbors, a value close to that for an ideal tetrahedron. Consequently, a better description of the molecule is given by two planes. The benzo group plus C(1) form a good plane (*D*, Table 7) and the group N(1), N(2), C(8), C(9), O(2) also form a good plane (*C*, Table 7). The dihedral angle between these planes is 8·3°.

References

Barr, C. R., Henn, R. W. & Salminen, I. F. (1962). U. S. Patent 3,043,694.

Bartell, L. S. (1960). *J. Chem. Phys.* **32**, 827.

Blow, D. M. (1960). *Acta Cryst.* **13**, 168.

Busing, W. R., Martin, K. O. & Levy, H. A. (1962). *ORFLS: A Fortran Crystallographic Least-Squares Program.* Publication ORNL-TM-305, Oak Ridge National Laboratory, Tennessee.

Cady, H. H. (1967). *Acta Cryst.* **23**, 601.

Darlow, S. F. (1960). *Acta Cryst.* **13**, 683.

Dawson, B. (1965). *Aust. J. Chem.* **18**, 595.

Fritchie, C. J., Jr (1966). *Acta Cryst.* **20**, 27.

Furnas, T. C. (1957). *Single Crystal Orienter Instruction Manual.* Milwaukee, Wisconsin: General Electric Co.

Hamilton, W. C. (1955). *Acta Cryst.* **8**, 185.

Hanson, A. W. (1966). *Acta Cryst.* **21**, 97.

Hauptman, H. & Karle, J. (1953). *Solution of the Phase Problem. I. The Centrosymmetric Crystal.* Monograph No. 3, American Crystallographic Association.

Hirshfeld, F. L. & Rabinovich, D. (1967). *Acta Cryst.* **23**, 989.

Ibers, J. A. (1966). Northwestern University, Evanston, Illinois. Private communication.

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

Janssen, R. (1962). *Proc. Intern. Meeting Mol. Spectry.* 4th, Bologna, 1959, **2**, 820.

Jennen, J. J. (1953). Belgian Patent 514,576.

Jennen, J. J. (1954). U. S. Patent 2,673,801.

Jennen, J. J. (1957). *Angew. Chem.* **69**, 732.

Jennen, J. J. & Eerdekens, H. P. (1954). British Patent 720,284.

Jennen, J. J. & Eerdekens, H. P. (1960). U. S. Patent 2,964,402.

Karle, I. L., Hauptman, H., Karle, J. & Wing, A. B. (1958). *Acta Cryst.* **11**, 257.

Karle, J. & Karle, I. L. (1966). *Acta Cryst.* **21**, 849.

Karle, J. & Karle, I. L. (1967). *J. Amer. Chem. Soc.* **89**, 804.

Larson, A. C. (1967). *Acta Cryst.* **23**, 664.

Lide, D. R. (1962). *Tetrahedron,* **17**, 125.

O'Connell, A. M., Rae, A. I. M. & Maslen, E. N. (1966). *Acta Cryst.* **21**, 208.

Pauling, L. (1960). *The Nature of the Chemical Bond.* Ithaca: Cornell Univ. Press. 3rd Ed.

Rae, A. I. M. & Maslen, E. N. (1965). *Acta Cryst.* **19**, 1061.

Schomaker, V., Waser, J., Marsh, R. E. & Bergman, G. (1959). *Acta Cryst.* **12**, 600.

Smith, D. L. (1969). *Acta Cryst.* B **25**, 625.

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

Sutton, L. E. (1965). *Interatomic Distances-Supplement.*