Table 2. *Bond lengths Å with their estimated standard deviations*

		e.s.d($\times 10^3$)			e.s.d($\times 10^3$)
C(1)–C(2)	1·535	15	C(1′)–C(2′)	1·510	12
C(1)–O(1)	1·399	24	C(2′)–C(3′)	1·550	15
C(2)–C(3)	1·545	8	C(2′)–O(2′)	1·409	16
C(2)–O(2)	1·460	15	C(3′)–C(4′)	1·488	15
C(3)–C(4)	1·531	22	C(3′)–O(3′)	1·423	10
C(3)–O(3)	1·393	17	C(4′)–C(5′)	1·489	9
C(4)–C(5)	1·511	14	C(4′)–O(4′)	1·450	18
C(4)–O(4)	1·448	4	C(5′)–C(6′)	1·543	19
C(5)–C(6)	1·510	23	C(6′)–O(6′)	1·417	10
C(6)–O(6)	1·467	18	C(1′)–O(5′)	1·416	12
C(1)–O(5)	1·406	15	C(5′)–O(5′)	1·417	12
C(5)–O(5)	1·472	7	C(1′)–O(4)	1·415	11

these bonds, but there are a few alternative arrangements possible, and our intensity data are unfortunately not good enough to show the H positions on the Fourier maps. A curious feature of the structure is the distance 2·82 Å from O(3) to O(5′) within the same molecule. Since Fig. 2 is a projection down the short *c* axis the levels of the successive screw axes are lower by 1·13 Å ($\frac{1}{2}a \cos \beta$) as we go to the right. Each molecule is held at $c = 4{\cdot}84$ Å from its neighbour by the bonds O(2′)–O(6′), O(3′)–*W*, O(6′)–O(2′), O(3)–O(6), O(6)–O(2). The bonds connecting the molecules in the *a* direction are: O(2′)–O(6′), O(6)–O(2), O(6)–O(3) and O(1)–*W* and O(2)–*W*. In the direction of the *b* axis the bonds holding the molecules together are the bonds to the water molecule (*W*), and also the bonds O(2)–O(4′) and O(1)–O(4′). There are in fact no less than sixteen hydrogen bonds fixing one molecule in place, and these are no doubt sufficient to account for the considerable hardness of the lactose crystal. The water molecule also plays a considerable part in this since it links together oxygens from four different lactose molecules. The bond angles at the water molecule are however rather variable, being from 82 to 126°.

References

Beevers, C. A. & Ehrlich, H. (1959). *Z. Kristallogr.* **112**, 414.

Bhuiya, A. K. & Stanley, E. (1963). *Acta Cryst.* **16**, 981.

Groth, P. (1910). *Chemische Krystallographie*, Vol. 3, p. 450.

Hassel, O. & Ottar, B. (1947). *Acta Chem. Scand.* **1**, 929.

Acta Cryst. (1971). B**27**, 1325

The Crystal and Molecular Structure of 2,3,4,4a,9,9a-Hexahydro-2-methyl-9-phenyl-1*H*-indeno[2,1-*c*]pyridine hydrobromide, $C_{19}H_{22}NBr$

By F. H. Allen, D. Rogers and P. G. H. Troughton

Chemical Crystallography Laboratory, Imperial College, London S.W.7, *England*

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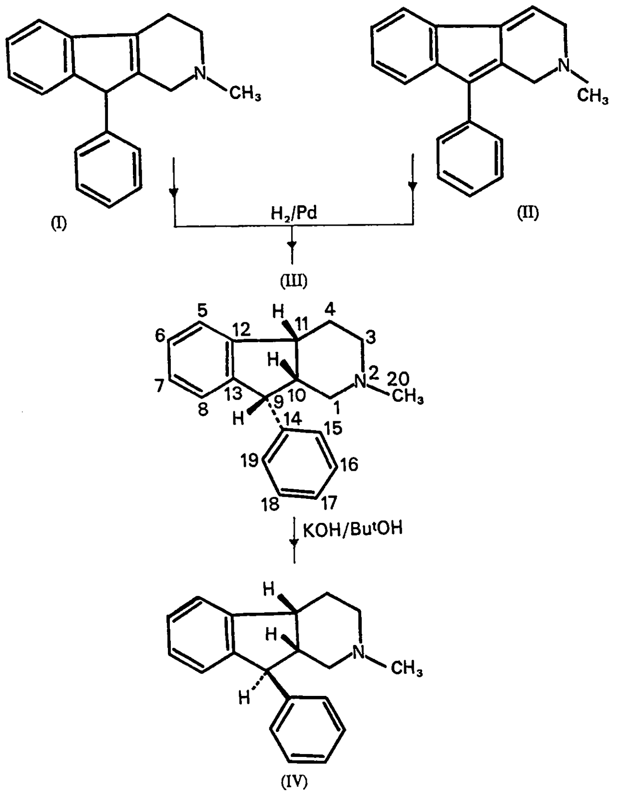
A full three-dimensional X-ray study of 2,3,4,4a,9,9a-hexahydro-2-methyl-9-phenyl-1*H*-indeno[2,1-*c*]pyridine has been carried out using the hydrobromide, $C_{19}H_{22}NBr$. The crystals are monoclinic, space-group $P2_1/c$, with $a = 9{\cdot}853$, $b = 15{\cdot}099$, $c = 11{\cdot}682$ Å, $\beta = 105{\cdot}81°$, and four formula units per cell. The intensities of the 2873 independent reflexions with $\theta \leq 65°$ were measured using a Siemens automatic four-circle single-crystal diffractometer, a coupled ω:2θ scan, and a five-value measuring technique. Bromine was used as a phase-determining heavy atom, and structure solution, using the 2396 reflexions with intensities significantly greater than background, was straightforward. An absorption correction was applied, and block-diagonal least-squares refinement reduced *R* to 0·035. The accuracy of the diffractometer experiment is discussed in some detail. The suggested all-*cis* stereochemistry for the compound has been confirmed, and the geometry of the fused ring system is discussed. A notable feature is the shortness of the N—H---Br bond at 3·124 Å.

Introduction

Catalytic hydrogenation of the antihistamine phenindamine (tetrahydroindenopyridine, I) (Plati & Wenner, 1950), and of the dihydro-1*H*-indeno[2,1-*c*]pyridine (II) (Plati & Wenner, 1955), gave (III) which can be readily isomerized to (IV) using mild alkali (Leeming & Ham, 1968). Correlation of nuclear magnetic resonance evidence with deuteration studies indicated that, although both (III) and (IV) contain three asymmetric centres, they are epimeric at C(9) only, the stereochemistry at C(10), C(11) remaining unchanged. The all-*cis* stereochemistry was proposed for (III), and this leaves the proton at C(9) in an exposed position; this would explain the ready epimerization since this proton is highly hindered in the thermodynamically more stable form (IV).



The n.m.r. spectra were, however, somewhat ambiguous, and in parallel with further chemical work (Ham & Leeming, 1969), we have studied the hydrobromides of (III) and (IV) using X-ray techniques. The relevant crystal data, obtained by visual estimation from oscillation and Weissenberg photographs (Cu $K\alpha$ radiation), are shown in Table 1. Both samples were stable to X-irradiation over the period of this initial investigation. Although no measurements of optical rotation had been made, the symmetry of the (uniquely identifiable) space groups shows the racemic nature of the samples. Since (III) and (IV) were related chemically (by the well-established epimerization), the structure of either hydrobromide would suffice to establish the stereochemistry of both compounds. The hydrobromide of (III) (briefly referred to as PIPH in this paper) was chosen so that the geometry of this rather overcrowded molecule could be studied (if the all-*cis* stereochemistry was confirmed).

Table 1. *Crystal data for the hydrobromides*

Compound	III.HBr	IV.HBr
Formula	$C_{19}H_{22}NBr$	$C_{19}H_{22}NBr$
Habit	Laths	Prisms
System	Monoclinic	Monoclinic
M	344·3	344·3
a (Å)	9·85	11·05
b (Å)	15·05	7·45
c (Å)	11·60	19·30
β°	105·50	94·00
V (Å^3)	1648	1583
D_m (g.cm^{-3})	1·38	1·41
D_c (g.cm^{-3})	1·39	1·44
Z	4	4
μ(cm^{-1})	36·8	38·2
Space group	$P2_1/c$	$P2_1/c$
Crystallinity	Good	Excellent

Experimental

Crystals of PIPH are colourless laths with (100) prominent. A suitable specimen of dimensions 0·61 × 0·20 × 0·04 mm was mounted with Araldite on a short quartz fibre set in dental sticky wax on a Stoë goniometer head. An off-line Siemens four-circle single-

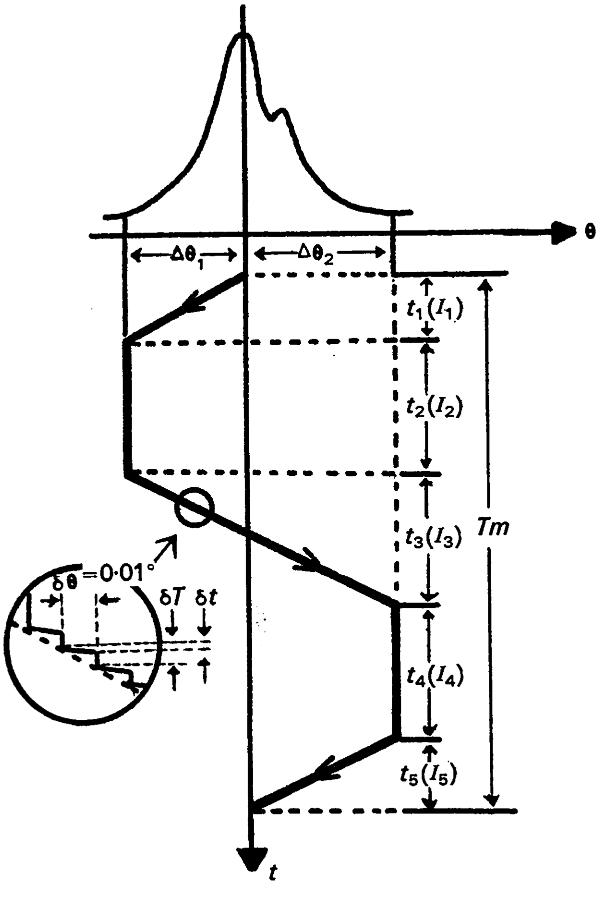


Fig. 1. The scanning sequence employed in the 'five-value' measurement technique. $(t_1+t_5)=t_3=t_2=t_4$. $I_{\text{net}}=\frac{1}{2}[(I_1+I_3+I_5)-(I_2+I_4)]$.

crystal diffractometer (AED) was used throughout for data collection. The crystal was set using the rough cell data of Table 1, and accurate cell parameters were obtained by a least-squares technique applied to the optimum θ-values of some thirty Cu $K\alpha_1$ peaks.

Crystal data

2,3,4,4a,9,9a-hexahydro-2-methyl-9-phenyl-1*H*-indeno-[2,1-*c*]pyridine hydrobromide, $C_{19}H_{22}NBr$.

$M=344\cdot3$.
Monoclinic, $P2_1/c$, C_{2h}^5.
$a=9\cdot853\pm0\cdot002$ Å,
$b=15\cdot099\pm0\cdot002$ Å,
$c=11\cdot682\pm0\cdot004$ Å,
$\beta=105\cdot81\pm0\cdot03°$,
$V=1672$ Å^3,
$D_m=1\cdot38\pm0\cdot03$ g.cm^{-3},
$D_c=1\cdot367$ g.cm^{-3}, for
$Z=4$ molecules per cell.
$\mu=36\cdot22$ cm^{-1} for Cu $K\alpha$ radiation.
$F(000)=712$.

The intensities of the 2873 independent reflexions in the Cu sphere with $\theta\leq65°$ were obtained using the 'five-value' measuring technique illustrated in Fig. 1. The mosaic spreads of some representative reflexions, within θ-limits of $8\rightarrow70°$, were experimentally determined and the data used to allot appropriate scan-ranges $\Delta\theta_1$, $\Delta\theta_2$, to each reflexion.

The machine approximates as closely as possible a constant-count-per-reflexion device (as recommended by Killean, 1967), except for the weakest intensities. This is effected by the automatic selection of the measuring time, per step of 0·01°, below a maximum set by the user, and the automatic introduction of attenuators into the incident beam for very strong reflexions. The majority of reflexions are thus recorded with a nearly uniform and optimum accuracy. A coupled $\omega:2\theta$ $(\omega=\theta)$ scan was used thoughout.

A strong reflexion, 080, was chosen as a 'reference' and measured once in every twenty reflexions. This enabled a scale-factor for each batch to be computed during data processing, nullifying fluctuations in the X-ray output or counter efficiency. A plot of the number of counts (N) given by the 'reference' against time (Fig. 2) shows that most measurements lie within a band of width 3σ, but indicates a gradual decline of *ca.* 5% during the two-week period. The latter is thought to be partly due to decreasing output from the Cu tube (over 3000 hours old), and partly to some radiation damage to the crystal.

A check on the crystal setting was provided by the data from axial 'control' reflexions, obtained after each batch of 100 five-value measurements. They were scanned with (*a*) full aperture (count N_t), (*b*) the insertion of a horizontal half-shutter (N_h), and (*c*) the insertion of a vertical half-shutter (N_v). An effective check was obtained by noting the values of N_h and N_v which should stay constant for any *hkl*, and also the ratios

Table 2. *Comparison of* $F^2(hk0)$ *and* $F^2(\bar{h}k0)$

L = 0

|H|	K	F²(HK0)	F²(H̄K0)	ΔF²
10	0	429.03	425.82	3.21
10	1	19.63	15.33	4.60
10	2	27.33	35.85	-8.52
10	3	55.02	58.20	-3.18
10	4	93.42	95.01	-1.59
10	5	49.30	41.06	8.24
10	6	65.11	55.88	9.23
9	0	61.11	69.08	-7.97
9	1	229.84	227.53	2.31
9	2	49.17	47.21	1.96
9	3	394.97	389.35	5.62
9	4	155.29	169.48	-14.19
9	5	154.79	154.85	-0.06
9	6	94.50	95.31	-0.81
9	7	95.96	107.48	-11.52
9	8	8.26	8.04	0.22
9	9	111.46	108.06	3.40
8	0	289.80	288.36	1.44
8	1	433.77	427.13	6.64
8	2	9.53	9.25	0.28
8	3	124.15	124.24	-0.09
8	4	10.04	9.70	0.34
8	5	47.20	49.48	-2.28
8	6	33.90	35.26	-1.36
8	7	469.91	472.61	-2.70
8	8	46.18	55.09	-8.81
8	9	16.50	24.81	-8.31
8	10	8.48	8.20	0.28
8	11	99.51	103.73	-4.22
8	12	39.47	40.14	-0.67
7	0	1283.98	1284.47	-0.49
7	1	8.33	7.97	0.35
7	2	8.50	8.18	0.32
7	3	293.81	300.07	-6.26
7	4	1215.77	1219.76	-3.99
7	5	448.61	449.38	-0.77
7	6	22.85	30.32	-7.47
7	7	778.60	773.63	4.97
7	8	204.47	211.70	-7.27
7	9	10.21	17.20	-6.99
7	10	21.25	20.25	1.00
7	11	8.61	8.66	0.05
7	12	194.42	207.59	-13.17
7	13	7.18	6.84	0.34
6	0	243.33	235.00	8.33
6	1	25.39	21.45	3.94
6	2	47.43	44.22	3.21
6	3	339.22	338.14	1.08
6	4	1319.44	1318.12	1.32
6	5	199.60	197.69	1.91
6	6	485.18	477.28	7.90
6	7	8.51	8.29	0.22
6	8	763.92	794.09	-30.17
6	9	162.64	172.09	-9.45
6	10	184.17	187.23	-3.06
6	11	36.84	38.74	-1.90
6	12	9.07	14.68	-5.61
6	13	12.86	14.68	-1.82
6	14	11.30	9.27	2.03
5	0	228.81	210.30	18.51
5	1	751.12	737.42	13.70
5	2	274.13	266.23	7.90
5	3	1163.53	1165.99	-2.46
5	4	213.84	217.15	-4.31
5	5	985.43	993.47	-8.04
5	6	326.61	330.10	-3.49
5	7	1385.47	1392.61	-7.14
5	8	231.33	226.47	4.86
5	9	163.88	174.63	-10.75
5	10	226.38	225.08	1.30
5	11	229.66	229.22	0.44
5	12	255.84	258.74	-2.90
5	13	11.15	20.83	-9.68
5	14	8.37	8.26	0.11
5	15	30.60	28.01	2.59
4	0	392.33	373.81	18.52
4	1	248.59	241.13	7.46
4	2	195.86	198.94	3.08
4	3	1999.11	2014.13	-15.02
4	4	4953.81	4965.52	-11.71
4	5	663.06	660.19	2.87
4	6	452.29	443.67	8.62
4	7	1831.64	1845.33	-13.69
4	8	753.31	770.06	-16.75
4	9	8.02	7.99	0.03
4	10	322.93	330.18	-7.25
4	11	477.91	481.39	-3.48
4	12	10.12	9.65	0.47
4	13	241.97	228.34	13.63
4	14	228.34	214.56	13.78
4	15	37.90	36.00	1.90
4	16	21.29	31.43	-10.14
3	0	2756.75	2710.12	46.63
3	1	1477.96	1470.36	7.60
3	2	223.91	211.14	12.77
3	3	1382.12	1341.08	41.04
3	4	1814.98	1794.73	20.25
3	5	2444.96	2371.77	73.19
3	6	5.63	5.38	0.25
3	7	1598.98	1607.62	-8.64
3	8	925.47	909.66	15.81
3	9	82.57	86.53	-3.96
3	10	1217.32	1233.32	-16.00
3	11	123.66	111.54	12.12
3	12	177.23	190.38	-13.15
3	13	32.22	30.09	2.13
3	14	143.22	147.35	-4.13
3	15	137.95	137.83	0.12
3	16	7.66	7.48	0.18
3	17	6.44	6.15	0.29
2	0	1781.08	1790.06	-8.98
2	1	7068.67	7042.25	26.42
2	2	4399.66	4397.88	1.78
2	3	100.78	101.13	-0.35
2	4	626.23	605.88	20.35
2	5	1023.48	1039.64	-16.16
2	6	187.83	192.60	-4.77
2	7	353.52	344.86	8.66
2	8	162.26	163.06	-0.80
2	9	234.70	248.18	13.48
2	10	38.13	32.08	6.05
2	11	1325.37	1314.33	11.04
2	12	12.00	9.93	2.07
2	13	9.40	9.71	-0.31
2	14	162.24	161.10	1.14
2	15	51.12	57.76	-6.64
2	16	8.21	8.19	0.02
2	17	6.84	6.66	0.18
1	0	52.42	51.26	1.16
1	1	6589.51	6653.58	-64.07
1	2	748.97	739.96	9.01
1	3	17311.76	17279.77	31.99
1	4	77.66	80.02	-2.36
1	5	522.40	520.06	2.34
1	6	511.82	508.60	3.22
1	7	681.28	675.57	5.71
1	8	159.28	164.16	-4.88
1	9	75.89	74.24	1.65
1	10	40.62	32.80	7.82
1	11	2123.40	2125.14	-1.74
1	12	10.01	9.20	0.81
1	13	215.53	225.84	-10.31
1	14	332.46	335.81	-3.35
1	15	359.90	364.78	-4.88
1	16	22.58	17.77	4.81
1	17	46.79	51.56	-4.77

N_h/N_t, N_v/N_t, which should be equal for reflexions hkl, $\bar{h}\bar{k}\bar{l}$. The values were checked periodically and minor adjustments made to the goniometer arcs when necessary.

The raw intensities were evaluated using the formula quoted in Fig. 1; reflexions whose net count was less than 2·58 σ_I, *i.e.* below the 99 % confidence level, were treated as 'unobserveds' and given intensities equal to

Table 3. *Final observed and calculated structure factors for those reflexions with intensities significantly greater than the background level*

Column headings are L, $10|F_o|$, $10F_c$.

The reflexions omitted for suspected extinction were:

$h\ k\ l$	$10\lvert F_o\rvert$	$10F_c$	$\sin\theta/\lambda$
1 3 0	1525	−1625	0·11248
2 2 1	1585	−1747	0·14159

-11,0,L		
6	43	47
8	186	198
-11,1,L		
3	85	93
4	43	-50
5	77	83
7	50	60
-11,2,L		
1	127	-137
3	213	-224
4	69	73
5	31	-49
6	32	43
-11,3,L		
2	54	-66
3	63	-68
4	60	64
5	74	-73
7	101	-107
-11,4,L		
1	33	-35
3	51	-51
6	91	-104
-11,5,L		
2	77	82
3	126	-143
4	69	78
5	149	-163
-10,0,L		
2	84	92
4	159	172
6	152	172
8	188	204
-10,1,L		
1	75	-70
2	178	-191
3	276	-278
4	85	-89
5	36	42
6	93	-93
7	58	64
9	61	63
-10,2,L		
1	46	44
2	56	49
3	159	-177
4	111	111
5	88	-97
6	35	-30
7	99	-104
8	97	102
-10,3,L		
2	111	-126
3	70	68
4	109	-112
6	157	-162
7	73	-78
8	32	29
9	95	-100
-10,4,L		
1	75	-81
2	66	65
5	50	-58
6	96	-104
8	99	-104
-10,5,L		
1	82	94
3	43	46
5	39	-35
6	60	58
7	94	-100
8	49	53
-10,6,L		
1	57	62
3	128	132
4	78	-84
5	154	164
6	36	-43
7	90	98
8	73	-86
-10,7,L		
1	48	-52
2	95	101
3	73	-76
4	110	120
5	43	-44
6	61	71
-10,8,L		
1	41	41
3	81	82
4	32	31
-9,0,L		
2	317	-333
4	309	-320
6	179	-187
8	80	84
10	160	169
-9,1,L		
1	103	-101
2	77	-78
3	133	-142
6	171	-176
8	181	-193
9	54	57
10	53	-59
11	145	155
-9,2,L		
2	113	-120
3	49	44
5	173	-180
7	172	-182
8	53	58
9	63	-74
11	50	-63
-9,3,L		
1	94	105
2	47	-74
3	146	153
4	225	-238
6	144	-152
7	59	62
8	212	-226
9	43	-35
-9,4,L		
1	75	77
2	330	338
3	134	126
4	243	269
5	90	-101
8	44	-38
9	34	30
10	167	-171
-9,5,L		
1	79	95
2	90	-87
3	48	54
5	144	153
6	85	82
7	39	-42
9	101	-114
-9,6,L		
1	174	-179
2	63	63
3	42	45
4	130	101
5	88	91
7	181	187
8	57	-65
9	71	82
-9,7,L		
2	87	-84
3	40	-43
4	96	105
5	100	-96
6	137	149
8	129	134
-9,8,L		
2	146	-151
3	159	170
4	199	-206
5	114	129
6	108	-109
7	105	115
8	44	45
-9,9,L		
1	167	-181
2	83	92
3	129	-136
4	53	-54
-9,10,L		
1	31	45
2	54	-66
3	63	68
4	79	-92
5	76	-74
-9,11,L		
2	43	-51
4	40	-47
-8,0,L		
2	350	-359
4	280	-299
6	226	-231
8	243	-258
12	147	156
-8,1,L		
2	214	220
3	65	-79
4	117	117
5	258	-271
6	72	-78
7	110	-117
8	80	-85
9	63	65
10	131	-133
11	45	59
12	69	-77
-8,2,L		
1	156	165
2	132	-125
3	142	150
4	126	-135
6	64	-76
7	261	-279
8	86	-97
9	195	-211
11	151	-163
12	52	51
-8,3,L		
1	81	-80
2	248	261
3	263	269
4	161	166
5	180	189
6	81	-81
7	208	209
8	153	-161
9	52	51
10	230	-242
-8,4,L		
1	111	117
2	81	-63
3	199	-197
4	138	154
5	89	-91
6	163	173
7	92	-91
8	201	211
9	62	-69
10	87	-89
-8,5,L		
1	197	208
3	377	392
4	176	-179
5	297	316
6	45	51
7	145	152
10	81	84
-8,6,L		
1	341	-355
2	66	71
3	117	123
4	120	131
7	164	169
9	181	191
10	84	-88
11	142	158
-8,7,L		
2	180	-190
3	73	-70
4	72	-79
6	141	147
7	72	-72
8	70	69
10	146	159
-8,8,L		
1	100	-105
2	38	40
3	56	-54
4	196	-196
5	49	-36
6	90	-92
7	105	110
8	127	-133
9	137	156
10	39	-42
-8,9,L		
3	186	-195
5	212	-222
6	122	126
7	167	-174
-8,10,L		
1	104	111
2	131	-135
3	142	138
4	87	-93
6	71	-77
7	87	-81
-8,11,L		
1	51	-65
2	163	164
3	98	-110
4	52	54
-8,12,L		
1	69	69
3	48	49
4	50	49
5	76	-81
6	48	51
-7,0,L		
2	282	272
4	88	-100
6	330	-334
8	291	-311
10	205	-213
-7,1,L		
1	193	195
2	217	228
4	255	266
5	128	-130
6	131	129
7	333	-349
9	191	-199
10	147	-150
11	59	-53
12	159	-164
-7,2,L		
1	347	364
3	511	528
4	77	-80
5	350	356
7	93	89
9	83	-86
10	71	-77
11	200	-209
12	71	78
-7,3,L		
1	169	-170
2	328	336
3	59	67
4	326	336
5	42	-45
6	97	102
7	194	200
9	171	171
10	127	-124
11	59	48
12	159	-168
-7,4,L		
1	125	129
2	197	-199
4	123	116
5	173	187
6	310	311
8	158	161
9	135	-142
10	162	174
12	92	80
-7,5,L		
1	447	-461
4	192	-188
7	369	391
8	40	-43
9	235	252
10	60	53
12	65	46
-7,6,L		
1	172	-180
2	186	-184
3	503	-513
4	93	98
5	470	-477
6	162	177
7	245	-261
8	80	81
9	65	57
10	106	120
11	88	93
-7,7,L		
1	392	394
2	66	46
3	263	265
4	215	-231
5	54	64
6	102	-115
7	127	-120
8	62	69
9	113	-108
10	225	238
11	99	-94
-7,8,L		
1	222	-228
2	124	133
3	241	-252
6	155	-158
7	47	47
8	107	-106
9	51	-43
10	95	-101
-7,9,L		
1	226	232
3	49	-44
4	159	156
5	46	-56
6	75	79
7	174	-182
8	115	117
9	206	-216
10	72	89
-7,10,L		
1	115	119
2	61	-63
3	93	94
4	88	-95
5	137	143
6	179	-189
7	95	102
8	108	-113
9	83	-85
-7,11,L		
2	149	149
3	45	-52
4	178	187
5	64	-54
-7,12,L		
1	119	140
2	164	-171
3	136	152
5	78	90
7	38	45
-7,13,L		
1	43	-30
3	73	-74
5	48	48
6	69	-73
-7,14,L		
3	57	-64
-6,0,L		
2	542	578
4	346	363
6	39	41
8	268	-266
10	158	-173
12	264	-276
-6,1,L		
1	343	348
2	191	175
3	239	253
4	340	342
6	285	282
7	147	-146
8	249	260
9	298	-308
10	45	55
11	256	-263
13	111	-100
-6,2,L		
1	82	-78
2	190	187
3	234	231
4	178	173
5	319	333
6	51	28
7	440	466
8	50	-56
9	203	212
11	150	-140
13	96	-102
-6,3,L		
1	181	-186
3	379	-388
4	490	500
5	250	-255
6	427	447
7	60	71
8	180	195
10	135	141
11	164	164
12	137	-145
13	97	70
-6,4,L		
1	106	103
2	158	-171
3	120	135
4	312	-322
5	107	121
6	52	47
7	59	71
8	424	437
9	80	-79
10	336	358
12	175	193
-6,5,L		
1	620	-628
3	279	-286
4	141	-134
6	209	-210
8	134	-141
9	132	134
10	54	53
11	177	188
-6,6,L		
1	199	199
2	145	-152
3	208	-212
4	81	72
5	93	-93
6	47	35
7	164	-178
8	155	164
9	189	-192
10	136	145
11	59	25
-6,7,L		
1	79	80
2	86	-92
3	142	-139
4	471	-483
5	98	-93
6	433	-456
7	105	98
8	133	-136
10	44	-48
-6,8,L		
1	87	90
2	230	239
3	157	-171
4	235	234
5	222	-236
6	57	-57
7	193	-204
8	185	-182
9	61	-69
10	168	-178
11	109	102
-6,9,L		
1	385	392
2	64	-69
3	308	324
5	155	160
6	58	50
7	80	-76
8	51	-44
9	168	-181
11	153	-165
-6,10,L		
1	116	-124
2	115	121
4	89	100
5	220	233
7	165	167
8	161	-168
9	128	134
10	106	-118
-6,11,L		
2	181	195
3	49	61
4	215	225
5	64	-66
6	221	232
7	50	-51
8	173	183
9	58	58
-6,12,L		
1	46	-39
2	143	-144
3	47	42
4	134	-134
5	112	119
7	85	92
8	44	47
-6,13,L		
1	225	-237
2	167	175
3	101	-118
4	62	64
5	41	-40
6	65	74
-6,14,L		
1	62	-68
2	93	-88
4	118	-126
5	39	-42
6	59	68
-6,15,L		
1	100	-117
2	44	43
3	46	-46
-5,0,L		
2	668	693
4	888	890
6	483	487
8	264	268
10	108	-58
12	304	-320
-5,1,L		
1	190	203
2	626	-623
3	368	393
4	308	-288
5	485	498
6	146	158
7	182	185
8	436	446
9	107	-104
10	54	66
11	174	-186
12	98	101
13	120	-124
-5,2,L		
1	688	-702
2	172	173
3	209	-230
5	280	276
6	53	60
7	324	337
9	380	407
10	120	115
11	257	265
12	96	-96
-5,3,L		
1	97	-105
2	275	-297
3	374	-372
4	159	-162
5	316	-306
6	73	85
8	362	380
9	147	-151
10	183	202
11	166	165
12	112	131
13	78	76
-5,4,L		
1	99	-101
2	333	-346
3	84	-91
4	583	-602
5	316	307
6	513	-523
7	88	100
8	180	-187
9	315	318
12	162	166
-5,5,L		
1	281	-291
2	111	123
3	457	-482
5	557	-564
6	60	55
7	223	-245
8	267	-269
9	93	94
10	205	-183
11	232	248
12	64	-88
-5,6,L		
1	512	527
2	76	-80
3	363	375
4	158	-173
5	202	-198
6	161	-177
7	269	-270
9	227	-239
11	145	-150
12	61	72
-5,7,L		
1	114	-125
2	344	355
3	135	145
5	251	248
6	89	-104
7	106	101
8	435	-452
10	249	-265
-5,8,L		
1	139	153
2	325	332
4	212	248
5	74	-80
6	483	501
7	95	-90
8	146	163
11	129	-140
-5,9,L		
1	84	-63
2	122	-131
3	140	139
4	247	-238
5	247	263
7	42	-16
8	57	-53
9	40	27
10	76	74
11	128	-124
-5,10,L		
1	351	-354
2	379	389
4	332	339
5	68	47
6	101	116
7	50	-49
9	178	181
10	104	-106
-5,11,L		
1	98	-105
2	299	-319
4	102	-101
5	71	-78
6	128	132
7	62	-67
8	213	224
9	58	-67
10	61	67
-5,12,L		
1	108	-107
4	68	-66
5	83	92
6	103	-112
7	172	181
9	137	148
-5,13,L		
1	70	-71
2	83	94
3	178	-181
5	225	-243
6	119	120
7	59	-71
-5,14,L		
1	144	147
2	178	-195
3	105	109
4	75	-85
6	83	-86
7	47	-57
-5,15,L		
2	52	49
3	42	-37
4	57	57
-5,16,L		
1	103	104
2	36	-38
-4,0,L		
2	49	48
4	39	58
6	341	375
8	453	474
-4,1,L		
1	143	-160
2	463	-488
3	337	321
4	145	-174
5	698	690
6	34	8
7	485	490
8	46	-25
9	509	540
10	178	181
11	107	111
12	237	262
13	108	-104
-4,2,L		
1	594	-628
2	163	-153
3	683	-708
4	124	-104
5	661	-667
6	296	296
7	169	172
8	177	-169
9	396	399
10	92	-98
11	339	358
13	203	226
-4,3,L		
1	76	55
2	764	-788
4	343	-357
5	264	-261
6	193	-193
7	349	-359
8	174	186
9	87	-99
10	231	243
12	233	239
13	77	88
-4,4,L		
1	381	-371
2	237	233
3	333	-324
4	480	-482
5	47	-55
6	421	-420
7	190	-175
8	454	-476
9	201	197
10	119	-122
-4,5,L		
1	104	124
2	308	307
3	170	152
4	95	105
5	668	-670
6	223	217
7	328	-345
8	71	-78
9	327	-341
10	131	-129
11	75	-81
12	73	-68
13	106	111
-4,6,L		
1	373	392
3	582	607
4	127	-146
5	376	371
6	236	-248
7	98	-83
8	166	-175
9	134	-135
10	48	-42
11	258	-273
-4,7,L		
1	199	-189
2	796	791
3	184	-165
4	205	231
6	249	257
8	133	-130
9	97	107
10	248	-260
12	156	-174
-4,8,L		
1	336	346
2	240	-242
3	147	159
4	225	213
5	222	233
6	308	317
7	163	-161
8	199	208
9	133	-140
10	79	84
11	134	-149
-4 9,L		
1	33	-41
2	238	-224
3	90	87
4	142	138
5	479	499
6	44	-46
7	386	404
8	47	50
9	217	218
10	63	-65
11	81	89
-4,10,L		
1	70	-85
2	64	-63
3	271	-267
4	180	183
5	251	-264
6	92	104
7	40	38
8	280	290
9	227	235
11	125	148
-4,11,L		
1	166	173
2	399	-420
3	124	131
4	180	-187
6	169	-181
10	143	156
-4,12,L		
1	57	-64
2	86	90
3	212	-221
4	68	-62
5	76	-77
6	114	-117
7	72	70
8	115	-113
9	44	34
-4,13,L		
1	52	46
2	193	-198
3	90	-92
4	151	-161
5	88	-94
6	35	-42
7	183	-190
9	169	-184
-4,14,L		
1	132	139
2	59	66
3	149	161
4	65	-65
5	155	168
6	195	-204
8	54	-63
-4,15,L		
2	143	154
3	106	-115
4	52	60
5	64	-66
6	44	51
-4,16,L		
1	100	109
3	193	203
4	63	55
-3,0,L		
2	1107	-1176
4	652	-683
6	455	435
8	407	437
10	423	447
12	158	145
-3,1,L		
1	652	-676
2	334	-341
3	556	-572
4	871	-876
5	300	-292
6	431	-439
7	185	200
8	184	-180
9	432	437
10	100	93
11	168	177
12	136	139
13	152	154
-3,2,L		
1	261	-251
2	161	-162
3	619	-636
4	196	186
5	778	-794
6	60	56
7	715	-703
8	84	-84
9	361	-374
10	119	122
12	69	100
13	246	253
-3,3,L		
1	767	758
2	421	-432
3	446	454
4	279	-321
5	407	392
6	705	-725
7	232	-225
8	58	-61
9	50	-73
10	75	88
11	191	-190
12	148	162
13	119	-111
-3,4,L		
1	135	-135
2	807	817
3	213	-213
4	146	-103
5	242	-255
6	85	-74
7	67	-78
8	378	-408
9	112	-118
10	493	-506
12	177	-184
-3,5,L		
1	577	607
2	111	-88
3	624	624
4	615	573
5	44	47
6	148	152
7	182	-205
8	249	249
9	315	-317
10	60	64
11	191	-202
12	67	-63
13	107	-112
-3,6,L		
1	868	797
2	172	183
3	95	-37
4	66	-55
5	572	595
6	167	-166
7	378	387
8	215	-210
9	52	61
10	218	-230
11	79	-81
-3,7,L		
1	521	487
2	255	258
3	43	-77
4	516	543
5	117	100
6	387	402
7	95	95
8	223	242
9	130	133
11	61	53
12	117	-130
-3,8,L		
1	290	280
2	709	-704
3	139	146
4	100	-109
5	394	410
6	121	-107
7	212	228
8	202	208
10	257	249
12	85	109
-3,9,L		
1	507	-520
3	310	-320
4	58	65
6	235	-230
7	191	190
9	186	200
11	180	196
-3,10,L		
1	102	-101
2	334	-336
3	107	-108
4	133	-134
5	191	-207
6	47	54
7	259	-277
8	122	124
9	119	-127
10	168	178
11	76	-78
-3,11,L		
1	55	61
2	68	-67
3	96	100
4	400	-421
6	262	-274
7	234	242
8	58	-64
10	63	59
-3,12,L		
1	81	-79
2	177	195
3	290	-294
4	66	65
5	167	-178
6	82	-90
7	158	-162
8	77	-88
9	35	-24
10	55	-72
-3,13,L		
1	199	213
3	270	285
4	80	85
5	91	99
7	107	-118
9	127	-132
-3,14,L		
2	43	40
4	39	26
6	56	-51
7	107	118
8	138	-147
-3,15,L		
1	107	107
3	81	71
4	157	167
5	104	-104
6	80	90
-3,16,L		
1	84	89
2	82	-89
3	77	86
5	98	97
-3,17,L		
1	49	-66
-2,0,L		
2	835	-901
4	1109	-1211
6	471	-473
8	123	138
-2,1,L		
1	36	-27
2	74	-59

Table 3 (*cont.*)

-2,1,L		
3	1144	-1246
4	90	90
5	159	-196
6	339	-342
7	270	-264
8	439	-449
9	48	65
10	396	-440
11	158	169
13	189	207
-2,2,L		
1	1356	1440
2	499	-469
4	153	146
5	191	-200
6	437	-442
7	529	-537
8	172	157
9	299	-340
10	140	144
11	88	-96
-2,3,L		
1	951	959
2	590	600
3	111	137
4	108	-117
5	286	291
6	895	-866
7	60	59
8	463	-490
9	216	-248
10	407	-445
11	163	-160
13	154	-162
-2,4,L		
1	356	367
2	917	960
3	336	345
4	883	940
5	117	-133
6	437	438
7	94	-107
8	57	50
9	197	-190
10	194	-192
11	64	-80
12	245	-263
-2,5,L		
1	1039	1043
2	424	-442
3	799	825
4	125	-141
5	700	749
6	59	69
7	330	343
8	249	253
9	199	-199
10	127	147
11	281	-302
13	181	-187
-2,6,L		
1	736	-747
2	486	472
3	314	-303
4	244	258
5	533	541
6	184	193
7	442	453
8	49	-34
9	264	279
10	55	-49
11	131	140
-2,7,L		
1	342	-343
2	522	-516
3	314	-306
4	132	145
5	206	-201
6	372	383
7	67	-60
8	463	479
9	81	74
10	374	387
-2,8,L		
1	330	-351
2	542	-539
4	539	-536
5	61	70
6	286	-293
7	252	259
9	39	40
10	137	154
12	143	173
-2,9,L		
1	544	-549
2	157	157
3	268	-293
4	214	210
5	290	-307
6	55	-57
7	211	-225
8	37	24
9	232	240
11	138	146
-2,10,L		
2	189	-206
3	131	134
4	371	-382
5	253	-254
6	43	-58
7	178	-186
8	90	-90
9	124	-128
10	46	59
-2,11,L		
2	135	148
3	61	-61
4	118	116
5	135	-141
6	265	-276
7	63	60
8	210	-224
9	47	-56
10	243	-254
-2,12,L		
1	227	230
2	55	54
3	108	-108
4	232	245
5	72	-74
6	103	114
7	186	-190
9	171	-180
10	94	-103
-2,13,L		
1	174	178
2	60	-57
3	362	371
4	93	-98
5	122	131
6	58	-56
7	127	136
8	42	-39
9	45	-43
-2,14,L		
1	194	-205
2	180	187
3	37	33
4	225	232
6	89	89
-2,15,L		
1	42	25
3	102	98
5	81	83
6	151	160
7	61	58
-2,16,L		
1	186	-195
2	45	-48
3	127	-135
4	120	-133
5	79	79
-2,17,L		
1	106	-103
2	82	91
3	38	-46
-1,0,L		
2	537	-514
4	558	-584
-1,1,L		
1	871	887
2	649	-569
3	947	-954
4	815	827
5	384	-402
6	41	46
7	595	-611
8	222	-241
9	243	-243
10	200	-205
12	172	-176
13	138	143
-1,2,L		
1	60	41
2	42	-33
3	1251	1346
4	121	106
5	193	193
6	206	-201
7	169	-164
9	531	-562
11	351	-361
13	168	-179
-1,3,L		
1	699	-673
2	1189	1271
3	550	542
4	387	401
5	440	438
6	67	68
7	444	437
8	144	-159
9	147	159
10	282	-294
11	89	-72
12	237	-254
-1,4,L		
1	339	-293
2	358	357
3	392	391
4	455	471
5	187	-169
6	701	707
7	59	49
8	492	509
10	196	207
11	110	-116
-1,5,L		
1	336	-336
2	387	-386
3	47	74
4	141	-150
5	409	448
6	208	189
7	347	370
8	78	-60
9	54	66
12	142	134
-1,6,L		
1	633	-657
2	135	119
3	295	-331
4	415	419
5	337	-351
6	356	370
7	56	68
8	232	238
9	433	452
10	95	94
11	270	285
-1,7,L		
1	33	24
2	740	-775
3	126	-127
4	390	-390
5	211	-214
7	93	-97
8	80	87
9	98	-108
10	152	166
12	161	187
-1,8,L		
1	652	-651
2	136	-137
3	342	-330
4	34	-64
5	66	-66
6	359	-383
7	84	79
8	145	-155
9	273	282
10	66	-62
11	204	216
-1,9,L		
1	163	172
3	477	-479
4	156	-136
5	514	-533
7	473	-509
9	170	-181
10	94	-115
-1,10,L		
1	275	288
2	64	65
3	463	479
4	177	-185
5	44	-41
6	236	-252
8	131	-129
9	205	-220
10	67	-67
11	104	-118
-1,11,L		
2	221	229
4	348	357
5	42	36
6	54	-53
8	51	-52
9	49	-44
10	156	-168
-1,12,L		
1	99	106
2	232	219
3	202	213
5	169	172
6	300	317
7	78	-80
8	71	78
9	184	-191
10	70	70
-1,13,L		
1	367	-374
2	221	220
3	203	213
4	104	96
5	112	125
6	92	91
7	110	115
9	85	91
-1,14,L		
2	64	68
3	100	-116
4	82	87
5	83	-96
6	225	233
8	141	151
-1,15,L		
2	170	-184
4	161	-176
6	33	30
7	43	-46
-1,16,L		
1	143	-147
2	44	34
3	100	-98
5	37	-31
-1,17,L		
1	54	55
2	122	-117
0,0,L		
2	742	818
4	550	547
6	101	-137
8	447	-459
10	359	-375
12	127	-134
0,1,L		
1	101	136
2	829	873
3	871	890
4	1094	1166
5	282	-263
6	499	501
7	405	-410
9	347	-363
10	63	-57
11	206	-214
12	164	-176
0,2,L		
0	24	46
1	176	-124
2	59	73
3	1266	1372
4	448	416
5	579	617
6	70	41
7	493	493
8	144	-142
9	153	138
10	125	-131
11	155	-154
13	242	-260
0,3,L		
1	1136	-1180
2	443	460
3	535	-518
4	815	838
5	393	-321
6	683	670
7	131	130
8	258	262
9	338	365
10	214	-226
11	111	103
12	142	-154
0,4,L		
0	1001	-1049
1	346	328
2	858	-881
3	85	102
4	378	-371
5	142	157
6	408	411
7	179	180
8	453	469
9	80	-76
10	177	178
12	168	159
0,5,L		
1	819	-862
2	246	-261
3	461	-470
4	287	-285
5	177	162
6	225	-211
7	424	430
9	466	485
10	127	75
11	355	367
12	96	101
0,6,L		
0	449	-467
1	378	-376
2	352	-352
3	669	-674
4	74	-71
5	687	-701
6	97	97
7	362	-366
8	135	138
9	58	-56
10	108	108
11	210	209
12	104	104
0,7,L		
1	281	271
2	430	-438
3	34	38
4	577	-594
6	498	-515
7	180	-185
8	135	-131
9	96	-105
10	131	147
11	93	-86
12	112	128
0,8,L		
0	784	805
1	208	-201
2	546	602
3	212	-228
4	110	114
5	250	-264
6	201	-217
7	234	-246
8	138	-149
9	73	-83
10	185	-201
0,9,L		
1	353	379
2	71	73
3	452	466
5	45	37
6	135	135
7	283	-292
8	37	-25
9	337	-348
10	120	-125
11	167	-171
0,10,L		
0	617	614
1	39	-34
2	245	254
3	413	427
4	128	127
5	129	133
6	75	-72
7	264	281
8	93	-92
9	102	105
10	74	-74
0,11,L		
1	76	70
2	301	317
3	272	-276
4	330	343
5	130	-118
6	338	353
7	68	-69
9	124	-117
10	72	-79
0,12,L		
0	647	-674
2	145	-153
3	437	439
4	54	-54
5	236	244
6	138	146
7	105	106
8	79	89
9	83	90
0,13,L		
1	238	-254
2	169	-168
3	119	-122
5	45	51
[illegible]	145	152
9	148	159
0,14,L		
0	227	-233
1	116	112
2	44	-44
3	137	-145
7	45	35
8	121	122
0,15,L		
1	43	39
2	115	-121
3	42	-38
4	155	-165
5	43	51
6	184	-198
7	146	147
0,16,L		
3	113	-119
5	95	-96
0,17,L		
1	52	58
2	80	-82
1,0,L		
0	100	-45
2	634	-544
4	733	804
6	465	451
8	250	-264
10	483	-515
12	244	-263
1,1,L		
0	954	-1032
1	675	715
2	215	-190
3	511	563
4	104	-77
5	234	265
6	263	290
7	45	-47
8	449	456
9	77	-82
10	174	183
11	178	-182
1,2,L		
0	310	305
1	225	-223
2	814	801
3	500	479
4	420	391
5	775	781
6	183	-184
7	535	548
8	117	117
9	321	335
10	114	-122
1,3,L		
1	313	-321
2	243	221
3	140	-174
4	334	345
5	124	-134
6	336	362
7	146	151
8	516	531
9	97	106
10	159	177
11	167	180
1,4,L		
0	99	48
1	47	-96
2	927	-970
3	160	-161
4	699	-745
5	318	309
6	81	-67
7	320	344
8	164	170
10	269	266
11	131	145
12	189	208
1,5,L		
0	256	-242
1	1166	-1208
2	94	-95
3	553	-578
4	378	-368
5	533	-544
6	234	-209
7	104	-102
8	219	-243
9	66	64
11	253	255
1,6,L		
0	254	168
1	517	544
2	462	-463
3	35	-50
4	249	-241
5	426	-443
6	141	-142
7	443	-403
8	76	-65
9	217	-230
10	164	165
11	157	-152
1,7,L		
0	293	306
1	144	134
2	428	246
3	73	91
4	224	-235
5	54	59
6	473	-492
7	43	46
8	348	-366
9	45	40
10	75	-73
11	72	-76
1,8,L		
0	142	160
1	227	252
2	442	441
3	50	-49
4	249	302
5	226	-247
6	64	58
7	131	-151
8	176	-165
9	247	-253
10	290	-341
1,9,L		
0	48	-58
1	536	557
2	29	12
3	645	640
4	166	171
5	181	161
7	43	43
11	174	-165
1,10,L		
0	71	77
1	74	69
2	91	103
3	113	149
4	207	242
5	236	252
6	110	140
7	306	340
8	160	-162
9	40	-31
10	89	-95
1,11,L		
0	521	-549
1	123	142
2	75	-78
3	82	70
4	87	92
5	322	329
6	130	144
7	230	235
8	232	246
9	40	56
1,12,L		
0	35	16
1	233	-240
2	65	-73
3	76	-78
4	130	-143
5	138	147
6	144	-157
7	225	237
8	61	60
9	133	142
1,13,L		
0	167	-172
1	124	-135
3	229	-240
4	76	79
5	136	-152
1,14,L		
0	259	-213
2	247	-253
4	221	-224
5	99	-115
6	73	-78
1,15,L		
0	219	236
1	113	-111
3	192	-186
4	137	-149
5	126	-121
6	42	-46
1,16,L		
0	55	67
1	44	94
2	75	91
4	66	86
5	79	-75
1,17,L		
0	81	81
1	122	129
2	69	64
3	57	71
2,0,L		
0	558	-566
2	499	522
4	922	966
6	374	394
8	443	453
10	130	141
12	71	-56
2,1,L		
0	1055	-1139
1	158	-133
2	1064	-1156
3	552	592
4	128	87
5	913	947
7	481	496
8	205	213
9	55	46
10	149	162
12	124	124
2,2,L		
0	743	-754
2	485	-443
3	843	-838
4	134	-164
5	668	-652
6	143	-137
7	341	354
8	159	173
9	315	329
11	243	251
2,3,L		
0	115	-155
1	636	592
2	781	-803
3	330	-332
4	681	-683
5	574	-588
7	48	-85
8	168	145
9	136	-145
10	349	355
11	93	-91
12	71	95
2,4,L		
0	265	-260
1	553	-558
2	128	-148
3	59	49
4	555	-584
5	57	-62
6	546	-553
7	63	88
8	493	-503
10	54	-29
11	122	121
12	68	106
2,5,L		
0	465	351
1	103	158
2	335	342
3	258	-285
4	254	251
5	404	-421
6	47	90
7	245	-312
8	240	-254
11	79	68
2,6,L		
0	155	-125
1	1233	1259
2	374	-340
3	443	449
4	78	-87
5	231	227
6	327	-330
7	65	-93
8	165	-193
9	143	-144
11	241	-223
2,7,L		
0	222	277
1	230	225
2	816	825
3	124	125
4	176	176
5	105	112
6	147	-142
7	160	161
8	140	-193
9	104	-117
10	222	-236
2,8,L		
0	144	121
1	183	218
2	130	136
3	354	376
4	327	319
5	261	255
6	202	215
8	271	279
9	175	-171
2,9,L		
0	176	-179
1	[illegible]	-67
2	34	-36
3	247	256
4	152	-155
5	534	527
7	347	351
8	46	-56
9	125	130
2,10,L		
0	7	-76
1	324	-344
2	175	171
3	359	-372
4	262	266
5	163	-161
6	240	243
7	129	145
8	93	93
9	101	105
10	62	54
2,11,L		
0	414	-437
1	134	-139
2	319	-341
3	42	-45
4	61	-87
5	61	-68
6	71	77
7	46	-105
8	222	229
9	74	75
2,12,L		
0	39	28
1	356	-367
2	190	-203
3	150	-146
4	235	-247
5	63	-66
8	142	-153
2,13,L		
2	39	58
3	93	-94
4	73	-71
5	299	-316
6	60	55
7	105	-115
8	80	94
2,14,L		
0	147	148
1	172	198
2	37	46
3	45	37
4	194	-202
6	48	-50
7	116	-128
2,15,L		
0	83	95
2	181	189
3	45	51
4	103	113
5	66	66
6	43	47
2,16,L		
1	116	112
2	73	-71
2,17,L		
2	63	53
3,0,L		
0	667	-703
2	1166	-1191
4	404	379
6	259	270
8	349	412
10	209	217
3,1,L		
0	497	-484
1	526	-534
2	270	-242
3	234	198
4	376	-340
5	54	-32
6	333	-333
7	438	444
9	232	248
10	101	108
11	142	139
3,2,L		
0	186	-193
1	549	-556
2	127	134
3	505	-556
4	62	50
5	532	-547
6	112	66
8	63	-52
9	131	137
10	113	118
11	142	206
3,3,L		
0	446	-424
1	185	171
2	350	-411
3	67	-75
4	670	-691
5	49	-49
6	63	-72
8	61	-56
9	261	-290
10	54	71
3,4,L		
0	494	516
1	65	-62
2	324	332
3	426	-412
4	573	-554
5	202	-196
6	424	-426
7	239	-261
8	295	-301
9	115	111
10	141	-153

this 'confidence' threshold. The data were corrected for Lorentz and polarization factors, and placed on a common arbitrary scale. The absolute scale was obtained at a later stage by comparing $\sum|F_o|$ and $\sum|F_c|$.

The equivalent reflexions in the $hk0$ zone (*i.e.* $\bar{h}k0$) were also scanned during the same run and treated in a similar manner. This provided a check on the stability and statistical accuracy of the machine during the whole experiment, since the data were spread evenly over the whole collection period. A comparison of $F^2(hk0)$ and $F^2(\bar{h}k0)$ is shown in Table 2; these values have not been corrected for absorption. An 'agreement factor' of the form:

$$R'=\frac{2\sum|F^2(hk0)-F^2(\bar{h}k0)|}{\sum F^2(hk0)+\sum F^2(\bar{h}k0)}$$

had the low value of 0·012. This was a reflexion not only of the reproducibility of the machine, but also of the very regular crystal cross-section which caused symmetrical absorption errors.

Structure solution and refinement

The position of the bromine ion was obtained from the Harker sections ($x\ \frac{1}{2}\ z$; $0\ y\ \frac{1}{2}$) of a three-dimensional Patterson map based on the 2396 'observed' data. Structure factors were calculated using the phase-angles (0 or π) indicated by this position, together with an estimated B-factor of 3·0 Å^2; after rescaling R was 0·437. The first electron-density map revealed the positions of all 21 non-hydrogen atoms. The coordinates were optimized using the parabola method (Booth, 1948), and a bead model showed chemically sensible geometry.

Refinement began with six cycles of unweighted block-diagonal least-squares approximations using estimated B-factors of 3·5 Å^2 for all atoms except Br, and scattering factors (*International Tables for X-ray Crystallography,* 1962) appropriate to Br^- and N^+; R fell to 0·151. A difference map, using (F_o-F_c) as Fourier coefficients, showed no spurious features but revealed some anisotropy in the structure. The temperature factors were converted to their anisotropic equivalent β_{ij} values in the equation:

$$f=f_0 \exp[-(\beta_{11}h^2+\beta_{22}k^2+\beta_{33}l^2 +2\beta_{12}hk+2\beta_{13}hl+2\beta_{23}kl)]\,.$$

R fell to 0·086 after four cycles. Parameter shifts for N^+ and Br^- were high and these alone were varied for two cycles of full-matrix refinement which reduced R to 0·080.

The hydrogen atoms were now included in calculated positions, which were refined, with fixed B-factors 0·5 Å^2 greater than the final value for the atom to which they were bonded. Unweighted block-diagonal refinement continued to R=0·057. An interesting feature was the movement of H(20) [attached to N(2)] towards N^+; this recurred later and is discussed below.

The data were corrected for absorption using a program kindly supplied by Dr B. J. Brandt of the University of Stockholm. It employs the vector method outlined, and initially programmed, by Coppens, Leiserowitz & Rabinovich (1965), to calculate the directions of the incident and diffracted rays, and also the Gaussian integration technique described by Busing & Levy (1957). A variety of grid sizes were tried using a sample batch of data, and one of 6 × 6 × 6 chosen as the smallest possible without significant loss of accuracy: the correction factors varied by *ca.* 1·5% when the size was increased to 10 × 10 × 10.

The unweighted refinement, from which two reflexions (130, 221) were omitted for suspected extinction, continued smoothly to R=0·038; the great improvement in R was a reflexion of the very anisotropic shape of the crystal, and shows the danger of ignoring absorption effects even when μ is relatively small.

H(20) was now only 0·476 Å from N^+, and nitrogen, and to a lesser extent bromine, showed oscillatory shifts which prevented successful convergence. A further difference map, from which only the non-hydrogen atoms were subtracted, showed a rather diffuse peak of height 0·4 e.Å^{-3} at *ca.* 0·6 Å from N^+. This was attributed (see *Discussion* below) to the centre of gravity of the hydrogen electron density and that due to the nitrogen lone pair. In the absence of facilities for the application of aspherical scattering factors (Dawson, 1964) it was decided to attempt to attain convergence by removing H(20), and by redefining the valence state of nitrogen as N^0. The scheme was successful, and, following the application of a correction for dispersion at Br^- using the values $\Delta f'=-0·9$, $\Delta f''=1·5$ (Dauben & Templeton, 1955), the refinement was concluded at R=0·035. The shifts in non-hydrogen atom parameters were all less than 0·15 of the corresponding estimated standard deviation on the final cycle.

The parameters were refined to convergence twice

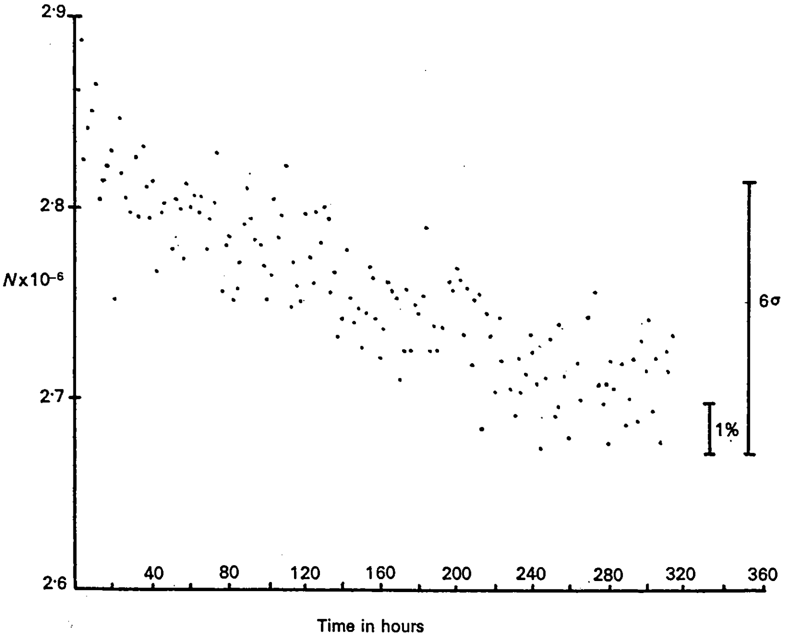


Fig. 2. Plot of the equivalent number of counts (N) given by the reference reflexion, 080, against time in hours, for the whole data-collection period. (Equivalent counts are derived from observed counts by allowing for attenuators and changes in scan rate.)

during this work, the first time being before the application of absorption and dispersion corrections when $R=0{\cdot}057$. Comparison of the two final sets of values shows that the effects of these two corrections can be summarized as follows:

All heavy atoms (*except* H)

$\langle|\Delta x|\rangle = 0{\cdot}00050 \quad |\Delta x|_{\max} = 0{\cdot}00134\ (3{\cdot}1\sigma)$
$\langle|\Delta y|\rangle = 0{\cdot}00015 \quad |\Delta y|_{\max} = 0{\cdot}00044\ (1{\cdot}6\sigma)$
$\langle|\Delta z|\rangle = 0{\cdot}00045 \quad |\Delta z|_{\max} = 0{\cdot}00133\ (3{\cdot}0\sigma)$
$\langle|\Delta\beta_{11}|\rangle = 0{\cdot}00032 \quad |\Delta\beta_{11}|_{\max} = 0{\cdot}00092$
$\langle|\Delta\beta_{22}|\rangle = 0{\cdot}00028 \quad |\Delta\beta_{22}|_{\max} = 0{\cdot}00054$
$\langle|\Delta\beta_{33}|\rangle = 0{\cdot}00037 \quad |\Delta\beta_{33}|_{\max} = 0{\cdot}00118$
$\langle|\Delta\beta_{12}|\rangle = 0{\cdot}00013 \quad |\Delta\beta_{12}|_{\max} = 0{\cdot}00038$
$\langle|\Delta\beta_{13}|\rangle = 0{\cdot}00024 \quad |\Delta\beta_{13}|_{\max} = 0{\cdot}00081$
$\langle|\Delta\beta_{23}|\rangle = 0{\cdot}00018 \quad |\Delta\beta_{23}|_{\max} = 0{\cdot}00153$

Hydrogen atoms (*excluding* H_2O)

$\langle|\Delta x|\rangle = 0{\cdot}0097 \quad |\Delta x|_{\max} = 0{\cdot}0422\ (8{\cdot}0\sigma)$
$\langle|\Delta y|\rangle = 0{\cdot}0039 \quad |\Delta y|_{\max} = 0{\cdot}0122\ (3{\cdot}6\sigma)$
$\langle|\Delta z|\rangle = 0{\cdot}0089 \quad |\Delta z|_{\max} = 0{\cdot}0386\ (8{\cdot}8\sigma)$

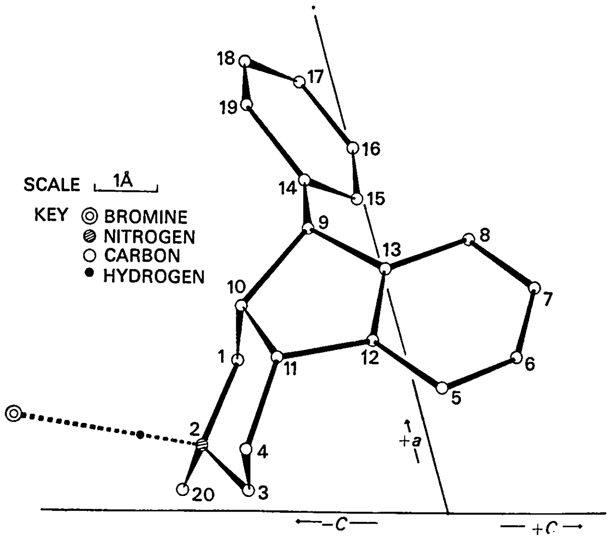


Fig. 3. A molecule of PIPH in *b*-axis projection.

On the whole these were larger than we had expected.

An analysis of the final structure-factor list (Table 3) showed that $\langle(|F_o|-|F_c|)^2\rangle$ was almost constant over the most populated ranges of $|F_o|$; weighted refinement was therefore not attempted. The final positional and anisotropic thermal parameters, shown in Tables 4, 5 and 6, were used to check those reflexions whose intensities were indistinguishable from the background level, and which were not included in the refinement. In general $|F_c|$ was less than $|F_o|$ except for six reflexions which showed surprising disagreement. This was eventually traced to an error in the generation of the diffractometer steering tape: the Eulerian angle χ for these reflexions (and only these reflexions) became greater than 90°, a value not attainable on the AED, and the equivalent reflexions should have been studied; the program switch was incorrectly set and the machine was therefore set up to explore a blank area of reciprocal space. The loss of the crystal prevented the correct measurement of these six reflexions at this late stage.

Table 4. *Final fractional coordinates for the non-hydrogen atoms*

Estimated standard deviations are given in parentheses

	$x(\sigma_x)$	$y(\sigma_y)$	$z(\sigma_z)$
Br	0·15327 (5)	0·38727 (3)	−0·55468 (3)
C(1)	0·25447 (36)	0·29738 (23)	−0·22910 (30)
N(2)	0·11316 (29)	0·31338 (19)	−0·31627 (25)
C(3)	0·03116 (36)	0·37890 (28)	−0·26531 (33)
C(4)	0·10613 (39)	0·46663 (26)	−0·25155 (33)
C(5)	0·20427 (38)	0·48839 (25)	0·02985 (34)
C(6)	0·24945 (42)	0·47413 (27)	0·15154 (35)
C(7)	0·36722 (44)	0·42385 (27)	0·20009 (33)
C(8)	0·44327 (38)	0·38590 (24)	0·12823 (31)
C(9)	0·46669 (33)	0·37161 (21)	−0·09029 (29)
C(10)	0·34228 (33)	0·38194 (22)	−0·20521 (28)
C(11)	0·25779 (34)	0·46072 (22)	−0·17475 (30)
C(12)	0·27930 (33)	0·45007 (21)	−0·04239 (29)
C(13)	0·39820 (33)	0·39916 (21)	0·00620 (28)
C(14)	0·54683 (34)	0·28535 (23)	−0·07511 (31)
C(15)	0·51382 (43)	0·21452 (25)	−0·01130 (38)
C(16)	0·59401 (52)	0·13598 (27)	0·00262 (41)
C(17)	0·70561 (49)	0·12926 (32)	−0·04910 (44)
C(18)	0·73644 (44)	0·19828 (32)	−0·11364 (45)
C(19)	0·65845 (39)	0·27651 (28)	−0·12677 (37)
C(20)	0·03511 (46)	0·22815 (29)	−0·34909 (38)

Table 5. *Final anisotropic thermal parameters* (β_{ij}) *for the non-hydrogen atoms*

	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Br	0·01527	0·00569	0·00609	0·00283	0·00285	0·00052
C(1)	0·00848	0·00330	0·00573	0·00053	−0·00034	0·00017
N(2)	0·00834	0·00332	0·00563	0·00026	−0·00096	0·00009
C(3)	0·00704	0·00561	0·00751	0·00079	−0·00023	−0·00015
C(4)	0·00946	0·00429	0·00706	0·00218	−0·00020	0·00025
C(5)	0·00874	0·00370	0·00872	−0·00049	0·00295	−0·00072
C(6)	0·01279	0·00495	0·00790	−0·00218	0·00506	−0·00312
C(7)	0·01444	0·00455	0·00600	−0·00237	0·00241	0·00001
C(8)	0·01026	0·00306	0·00683	−0·00112	0·00005	0·00074
C(9)	0·00631	0·00290	0·00666	−0·00002	0·00088	0·00004
C(10)	0·00761	0·00304	0·00545	0·00053	0·00157	0·00051
C(11)	0·00783	0·00269	0·00641	0·00073	0·00109	0·00070
C(12)	0·00704	0·00262	0·00631	−0·00039	0·00113	−0·00018
C(13)	0·00726	0·00226	0·00604	−0·00057	0·00062	−0·00001

Table 5 (*cont.*)

	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
C(14)	0·00644	0·00318	0·00737	0·00064	−0·00073	−0·00073
C(15)	0·01167	0·00332	0·00986	0·00081	−0·00049	−0·00016
C(16)	0·01929	0·00323	0·01085	0·00169	−0·00300	−0·00020
C(17)	0·01425	0·00576	0·01362	0·00470	−0·00567	−0·00375
C(18)	0·00968	0·00662	0·01413	0·00266	−0·00008	−0·00389
C(19)	0·00839	0·00515	0·01012	0·00064	0·00066	−0·00218
C(20)	0·01386	0·00474	0·00888	−0·00172	−0·00297	0·00011

Table 6. *Refined fractional coordinates for the hydrogen atoms (estimated standard deviations in parentheses)*

The numerical designation of hydrogen atoms is made up of the number of the C or N atom to which they are bonded, together with a serial number starting from zero.

	$x(\sigma_x)$	$y(\sigma_y)$	$z(\sigma_z)$
H(10)	0·2336 (43)	0·2702 (28)	−0·1660 (37)
H(11)	0·2983 (43)	0·2533 (28)	−0·2673 (36)
H(20)	Position not accurately defined, see *D*iscussion		
H(30)	0·0201 (47)	0·3525 (30)	−0·1899 (39)
H(31)	−0·0634 (46)	0·3842 (30)	−0·3221 (38)
H(40)	0·0580 (46)	0·5054 (31)	−0·2191 (39)
H(41)	0·1079 (47)	0·4879 (31)	−0·3260 (39)
H(50)	0·1258 (44)	0·5249 (29)	0·0005 (38)
H(60)	0·1967 (46)	0·4933 (31)	0·2058 (39)
H(70)	0·3976 (46)	0·4143 (30)	0·2788 (39)
H(80)	0·5264 (44)	0·3497 (29)	0·1629 (37)
H(90)	0·5289 (43)	0·4116 (27)	−0·0986 (36)
H(100)	0·3771 (42)	0·3954 (28)	−0·2739 (36)
H(110)	0·3011 (43)	0·5145 (28)	−0·1886 (36)
H(150)	0·4309 (47)	0·2174 (31)	0·0172 (40)
H(160)	0·5703 (51)	0·0879 (33)	0·0444 (43)
H(170)	0·7650 (53)	0·0745 (34)	−0·0415 (44)
H(180)	0·8148 (52)	0·1954 (34)	−0·1552 (44)
H(190)	0·6762 (48)	0·3211 (31)	−0·1706 (40)
H(200)	0·0908 (50)	0·1969 (32)	−0·3890 (42)
H(201)	−0·0608 (50)	0·2442 (33)	−0·4033 (42)
H(202)	0·0352 (50)	0·1971 (32)	−0·2741 (43)

Discussion of the structure

The [010] projection of the molecule (Fig. 3) shows that the three protons at C(9), C(10), C(11), are all *cis*; the proposed stereochemistry was therefore confirmed and structural formulae (III) and (IV) are correct.

The bond lengths and valence angles (Tables 7 and 8) are subdivided into two groups: those involving C and N, and those involving hydrogen atoms. (Libration corrections were not applied for lack of a relevant program.) The average $C(sp^3)$–$C(sp^3)$ and C–C(aromatic) distances are 1·531 ± 0·005 and 1·513 ± 0·005 Å respectively, not significantly different from the accepted averages of 1·537 and 1·505 Å (Sutton, 1965). The average C–N(quaternary) distance of 1·499 ± 0·005 Å is a little higher than the cited average of 1·479 Å (Sutton, 1965), but comparable values are quoted for DL-β-prodine hydrobromide (Ahmed, Barnes & Masironi, 1963) and hydrochloride (Ahmed & Barnes, 1963) (1·495 Å in each case), piperazine hydrochloride (1·50 Å, Rérat, 1960), and in the piperidine rings of certain alkaloids (Van den Hende & Nelson, 1967; Peerdeman, 1956).

Table 7. *Intramolecular bonded distances, r, together with their estimated standard deviations* (σ_r)

(*a*) Bonds not involving hydrogen atoms

	$r(\sigma_r)$		$r(\sigma_r)$
C(1)—N(2)	1·504 (4) Å	C(9)—C(13)	1·521 (5) Å
C(1)—C(10)	1·525 (5)	C(9)—C(14)	1·508 (5)
N(2)—C(3)	1·499 (5)	C(10)–C(11)	1·548 (5)
N(2)—C(20)	1·495 (5)	C(11)–C(12)	1·511 (5)
C(3)—C(4)	1·504 (6)	C(12)–C(13)	1·387 (4)
C(4)—C(11)	1·522 (5)	C(14)–C(15)	1·392 (6)
C(5)—C(6)	1·386 (5)	C(14)–C(19)	1·398 (6)
C(5)—C(12)	1·390 (6)	C(15)–C(16)	1·410 (6)
C(6)—C(7)	1·373 (6)	C(16)–C(17)	1·395 (8)
C(7)—C(8)	1·392 (6)	C(17)–C(18)	1·368 (7)
C(8)—C(13)	1·387 (5)	C(18)–C(19)	1·395 (6)
C(9)—C(10)	1·560 (4)		

(*b*) Bonds involving hydrogen atoms

The C–H bond lengths are given in groups classified according to the degree of substitution of the carbon atom; the average *r* in each group is compared with the spectroscopic average (Sutton, 1965).

C(aromatic)–H	
C(5)—H(50)	0·93 (4) Å
C(6)—H(60)	0·97 (5)
C(7)—H(70)	0·90 (4)
C(8)—H(80)	0·98 (4)
C(15)–H(150)	0·96 (5)
C(16)–H(160)	0·94 (5)
C(17)–H(170)	1·00 (5)
C(18)–H(180)	1·02 (6)
C(19)–H(190)	0·89 (5)

r = 0·99 Å
Spect. ave. = 1·084 Å

C(methyl)–H	
C(20)–H(200)	0·94 (5) Å
C(20)–H(201)	1·01 (4)
C(20)–H(202)	0·99 (5)

r = 0·98 Å
Spect. ave. = 1·096 Å

C(disubstituted)–H	
C(1)—H(10)	0·91 (5) Å
C(1)—H(11)	0·97 (5)
C(3)—H(30)	1·00 (5)
C(3)—H(31)	0·99 (4)
C(4)—H(40)	0·90 (5)
C(4)—H(41)	0·93 (5)

r = 0·95 Å
Spect. ave. = 1·073 Å

C(trisubstituted)–H	
C(9)—H(90)	0·88 (4) Å
C(10)–H(100)	0·98 (5)
C(11)–H(110)	0·95 (4)

r = 0·94 Å
Spect. ave. = 1·070 Å

The carbon atoms of both benzene rings are closely coplanar, average deviations ($\langle|d|\rangle$) from the mean planes being 0·0022 Å for the fused ring and 0·0043 Å for the phenyl side-group. The discrepancy may be attributed to the higher thermal motion possible in the latter ring, which also accounts for the increased values of the positional standard deviations for C(15)–C(19). The hydrogen atoms do not deviate significantly from the planes described above. In both rings the average C–C distances (1·386 Å in the fused ring, 1·393 in the side group), and the average C–C–C angles (120·0° in each case), agree well with expected values.

The five-membered ring C(9)–C(13) adopts the envelope conformation (Brutcher, Roberts, Barr & Pear-

Table 8. *Valence angles, θ, in the asymmetric unit, together with estimated standard deviations, σ_{σ}*

(*a*) Angles not involving hydrogen atoms

End—apex—end	θ	σ	End—apex—end	θ	σ
C(1)—N(2)—C(3)	109·7°	0·3°	C(1)—N(2)—C(20)	110·6°	0·3°
C(1)—C(10)-C(9)	110·3	0·3	C(1)—C(10)-C(11)	111·8	0·3
N(2)—C(1)—C(10)	111·3	0·3	N(2)—C(3)—C(4)	108·8	0·3
C(3)—N(2)—C(20)	112·0	0·3	C(3)—C(4)—C(11)	112·7	0·3
C(4)—C(11)-C(10)	114·4	0·3	C(4)—C(11)-C(12)	116·8	0·3
C(5)—C(6)—C(7)	120·6	0·4	C(5)—C(12)-C(11)	128·8	0·3
C(5)—C(12)-C(13)	120·8	0·3	C(6)—C(5)—C(12)	118·9	0·3
C(6)—C(7)—C(8)	120·8	0·4	C(7)—C(8)—C(13)	119·1	0·3
C(8)—C(13)-C(9)	129·8	0·3	C(8)—C(13)-C(12)	119·9	0·3
C(9)—C(10)-C(11)	103·0	0·3	C(9)—C(13)-C(12)	110·1	0·3
C(9)—C(14)-C(15)	122·4	0·4	C(9)—C(14)-C(19)	118·7	0·3
C(10)—C(9)—C(13)	102·0	0·3	C(10)—C(9)—C(14)	116·8	0·3
C(10)—C(11)-C(12)	102·7	0·3	C(11)—C(12)-C(13)	110·2	0·3
C(13)—C(9)—C(14)	118·2	0·3	C(14)—C(15)-C(16)	120·2	0·4
C(14)—C(19)-C(18)	120·5	0·4	C(15)—C(14)-C(19)	119·0	0·4
C(15)—C(16)-C(17)	119·6	0·4	C(16)—C(17)-C(18)	120·2	0·4
C(17)—C(18)-C(19)	120·5	0·5			

(*b*) Angles involving hydrogen atoms

End—apex—end	θ	σ	End—apex—end	θ	σ
C(1)—C(10)-H(100)	109·4°	2·4°	N(2)—C(1)—H(10)	104·3°	2·4°
N(2)—C(1)—H(11)	104·2	2·2	N(2)—C(3)—H(30)	106·7	2·7
N(2)—C(3)—H(31)	107·4	2·8	N(2)—C(20)-H(200)	103·4	3·0
N(2)—C(20)-H(201)	106·3	2·8	N(2)—C(20)-H(202)	107·6	2·7
C(3)—C(4)—H(40)	108·5	3·0	C(3)—C(4)—H(41)	109·7	2·7
C(4)—C(3)—H(30)	115·2	2·5	C(4)—C(3)—H(31)	110·3	2·7
C(4)—C(11)-H(110)	105·3	2·2	C(5)—C(6)—H(60)	123·1	2·4
C(6)—C(5)—H(50)	118·1	2·9	C(6)—C(7)—H(70)	121·4	3·1
C(7)—C(6)—H(60)	116·1	2·5	C(7)—C(8)—H(80)	120·6	2·7
C(8)—C(7)—H(70)	117·9	3·1	C(9)—C(10)-H(100)	111·0	2·2
C(10)—C(1)—H(10)	118·0	2·5	C(10)—C(1)—H(11)	111·0	2·6
C(10)—C(9)—H(90)	104·1	2·4	C(10)—C(11)-H(110)	108·8	2·8
C(11)—C(4)—H(40)	109·6	2·5	C(11)—C(4)—H(41)	107·8	2·7
C(11)—C(10)-H(100)	111·1	2·5	C(12)—C(5)—H(50)	123·1	2·9
C(12)—C(11)-H(110)	108·7	2·4	C(13)—C(8)—H(80)	120·4	2·7
C(13)—C(9)—H(90)	110·8	2·9	C(14)—C(9)—H(90)	104·2	2·7
C(14)—C(15)-H(150)	119·7	2·7	C(14)—C(19)-H(190)	118·5	3·2
C(15)—C(16)-H(160)	119·9	3·2	C(16)—C(15)-H(150)	119·9	2·8
C(16)—C(17)-H(170)	122·1	3·3	C(17)—C(16)-H(160)	120·4	3·3
C(17)—C(18)-H(180)	122·8	2·9	C(18)—C(17)-H(170)	117·7	3·3
C(18)—C(19)-H(190)	121·0	3·2	C(19)—C(18)-H(180)	116·8	2·9
H(10)—C(1)—H(11)	106·8	3·8	H(30)—C(3)—H(31)	108·3	3·8
H(40)—C(4)—H(41)	108·4	4·1	H(200)-C(20)-H(201)	112·5	4·0
H(200)-C(20)-H(202)	109·9	4·2	H(201)-C(20)-H(202)	116·1	4·1

son, 1959); atoms C(9,11,12,13) are strictly coplanar ($\langle|d|\rangle = 0{\cdot}00068$ Å) with C(10) 0·55 Å from this plane. This conformation ideally has C_s symmetry. Minimum-energy calculations (Pitzer & Donath, 1959; Hendrickson, 1961, 1963) have only been carried out on cyclopentane and have endorsed this conformation and have given theoretical optimum values for sp^3–sp^3 torsion angles (ω), and valence angles (θ); these values are compared with data from the present study in Table 9. The ring in this structure is neither cyclopentane nor, because of its fusion to a benzene ring, is it cyclopentene (for which no minimum-energy calculations seem to have been published), so one can hardly have expected such close agreement of the figures in Table 9. Nonetheless, the ring deviates surprisingly little from the ideal C_s symmetry: the major distortions are in ω_1, ω_5, and θ_3, θ_4, due to its fusion to two six-membered rings.

Table 9. *Comparison of torsion angles, ω*, and valence angles, θ, for the five-membered ring in* PIPH *with values predicted from minimum-energy calculations for the C_s-(envelope)-form of cyclopentane*

The parameters are shown below:

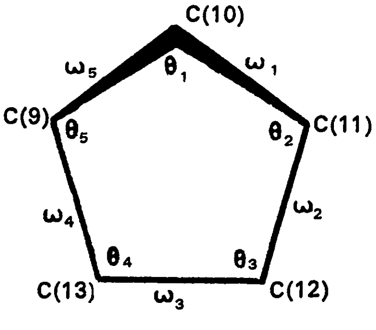


Table 9 (*cont.*)

Parameter	This work	Pitzer & Donath† (1959)	Hendrickson (1961, 1963)
ω_1	32·82°	46·1°	41·7°
ω_2	−21·02	−28·6	−25·9
ω_3	−0·16	0·0	0·0
ω_4	21·04	28·6	25·9
ω_5	−32·71	−46·1	−41·7
θ_1	102·99	100·4	101·7
θ_2	102·66	102·4	103·6
θ_3	110·19	105·6	106·0
θ_4	110·13	105·6	106·0
θ_5	101·96	102·4	103·6

* Calculated using the bonding-array method (Allen & Rogers, 1969).

† Values quoted are those recalculated by Hendrickson (1961, 1963).

The heterocyclic ring adopts the chair conformation but is distorted from the symmetrical minimum-energy form for cyclohexane (Hendrickson, 1967) by ring fusion, and also by the presence of a nitrogen atom at position 2. Hendrickson's calculations give all valence angles as 111·6° and all ω-values as 54·4°; in this work the former vary from 108·75 to 114·38° but average 111·45°, while the latter vary from 41·90 to 65·03° (average 53·66°).

The high accuracy of the intensity data allowed a complete refinement of all hydrogen atom positions [except for H(20)]. The successful refinement of the methyl hydrogen atoms [H(200–202)] was no doubt due to their proximity to hydrogen atoms at C(1), C(3), and to some bonding electron density in the sense N→Br (see below). To minimize non-bonded repulsions the substituents at N(2) and C(20) adopt the staggered conformation, as shown in the Newman projection (Newman, 1955) down this bond (Fig. 4); the relevant H–H and C–H non-bonded distances are also given.

The C–H bond lengths [Table 7(*b*)] have an overall average of 0·95 Å, some 0·13 Å shorter than values obtained spectroscopically or by neutron diffraction. This effect has been noted in previous X-ray studies (*e.g.* Marsh, 1958), and has been ascribed to the 'pulling' of the hydrogen *K*-electron density towards the heavier atom during bond formation. It has been shown (Tomiie, 1958) that the observed shift in the electron-density maximum (*ca.* 0·13 Å) is consistent with valence-bond calculations. The difficulty encountered in the refinement of H(20) is thus explicable since one would expect the H-electron to be more strongly attracted to N^+ than towards a neutral atom, *e.g.* carbon. The assumption of spherical scattering factors gives a very poor approximation to the true distribution in this case.

Thus, while the C–H distances obtained here are in good agreement with other X-ray results, they do not represent true inter-nuclear separations. They have been grouped in Table 7(*b*) according to the degree of substitution, and differing hybridization states, of the carbon atoms. In general the trend in $\langle r_{C-H} \rangle$-values follows that obtained spectroscopically (Sutton, 1965), but further discussion would be profitless in view of the high σ_r-values obtained for these bonds in this study. The bond angles involving hydrogen atoms [Table 8(*b*)] are not significantly different from expected values. This is reasonable since, although the r_{C-H} values are foreshortened, the vector sense of the C–H bond remains unchanged.

Fig. 3 shows that a hydrogen bond is postulated between nitrogen and bromine; the valence angles,

$$C(1)-N(2)-Br = 110{\cdot}03^\circ$$
$$C(3)-N(2)-Br = 109{\cdot}34$$
$$C(20)-N(2)-Br = 105{\cdot}07\ ,$$

tend to support this proposition. Similar results have been reported for other quaternary amine hydrobromides and the N–Br distance in the present study (3·124 Å) is somewhat shorter than other quoted values, *viz.* 3·17 Å in 19-propylthevinol HBr (Van den Hende & Nelson, 1967) and in strychnine HBr.$2H_2O$ (Peerdeman, 1956), 3·209 Å in DL-β-prodine hydrobromide (Ahmed, Barnes & Masironi, 1963), 3·26 Å in (+)-hetisine HBr (Przybylska, 1963), 3·35 Å in D(−)-isoleucine hydrobromide (Trommel & Bijvoet, 1954), and 3·38 Å in 11-aminoundecanoic acid HBr.$6H_2O$ (Sim, 1955). The impossibility of fixing the position of the proton H(20) prevents discussion of the linearity of the bond.

Molecular overcrowding

A Dreiding model of the all-*cis* stereochemistry made prior to structure solution, indicated that the phenyl side-group must twist about the bond C(9)–C(14) in order to minimize H–H and C–H non-bonded inter-

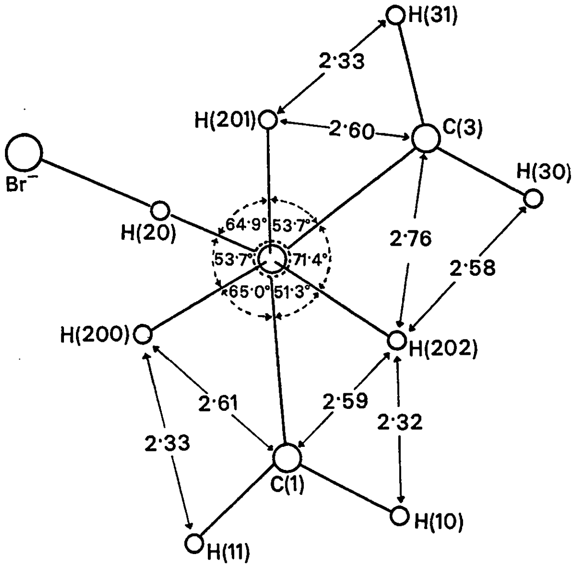


Fig. 4. Newman projection down the bond C(20)–N(2) showing the staggered conformation of the substituents.

actions. This has been confirmed by the X-ray study (see Figs. 3 and 5): the angle between the mean planes through the fused-ring system and the phenyl group is 73°. The closest contacts involve H(150) and H(190), bonded to the nearest 'corners' of the phenyl ring, *viz.*

H(150)–H(10)	2·56 Å	H(190)–H(90)	2·33 Å
H(150)–H(80)	2·63	H(190)–H(100)	3·08
H(150)–C(13)	2·76	H(190)–C(9)	2·62
H(150)–C(9)	2·71		

If we take the van der Waals radii of hydrogen and carbon as 1·2 and 2·0 Å respectively (Pauling, 1965), the distances quoted are close to the appropriate radial sums. The orientation of the phenyl ring is, as expected, explicable in terms of the minimization of non-bonded interactions between the ring systems.

Molecular packing

The molecular packing projected down the *a* axis is shown in Fig. 5, in which the individual asymmetric units are identified by Roman numerals which have the following significance:

I	x	y	z
II	x	$\frac{1}{2}-y$	$\frac{1}{2}+z$
III	x	y	$1+z$
IV	x	$\frac{1}{2}-y$	$\frac{3}{2}+z$
V	$\bar{x}$	$\frac{1}{2}+y$	$-\frac{1}{2}-z$
VI	$\bar{x}$	$1-y$	$\bar{z}$
VII	$\bar{x}$	$\frac{1}{2}+y$	$\frac{1}{2}-z$
VIII	$\bar{x}$	$1-y$	$1-z$

The zigzag formation of Br$^-$ ions at any one level in x (*e.g.* Br$_{\rm II}$, Br$_{\rm III}$, Br$_{\rm IV}$) is important in stabilizing the molecular arrangement. If we take the ionic radius of Br$^-$ as 1·95 Å and the van der Waals radius of hydrogen as 1·2 Å (Pauling, 1965), then their sum (3·15 Å) is comparable with the intermolecular distances shown below:

Br$_{\rm III}$	–H(10)$_{\rm II}$	2·92 Å
	–H(202)$_{\rm II}$	2·81
	–H(150)$_{\rm II}$	3·07
	–H(60)$_{\rm I}$	3·35
	–H(70)$_{\rm I}$	3·50
Br$_{\rm IX}$	–H(170)$_{\rm VII}$	3·07
	–H(40)$_{\rm VI}$	3·31
	–H(41)$_{\rm VI}$	3·19

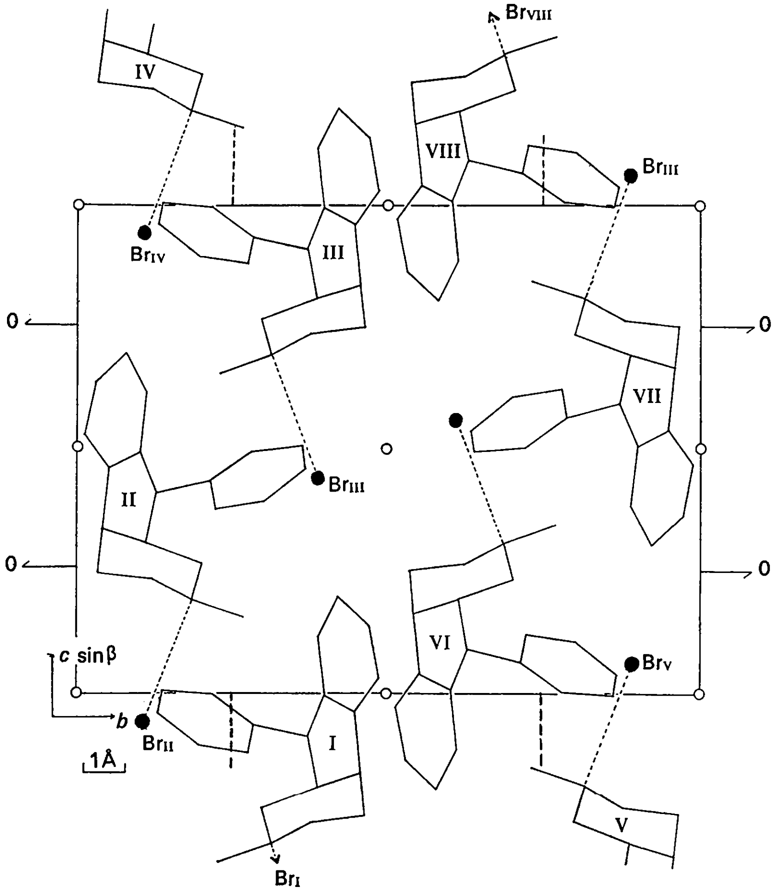


Fig. 5. The molecular packing in a-axis projection. The significance of the Roman numerals is given in the text.

The values above, taken together with the strong hydrogen bond, Br_n–$N(2)_n$, in any molecule (n), show the 'cementing' effect of the Br^- ions.

Additional stability is provided by the close approach of pairs of molecules (*e.g.* I and VI) across centres of symmetry; Fig. 6 shows the appearance of one such pair viewed along the *c* axis. The planes of the indene portions are parallel and the closest C–C contacts are:

$C(9)_{VI}$–$C(5)_{I}$	3·773 Å	$C(9)_{VI}$–$C(8)_{I}$	3·821 Å
$C(9)_{VI}$–$C(6)_{I}$	3·804	$C(9)_{VI}$–$C(12)_{I}$	3·715
$C(9)_{VI}$–$C(7)_{I}$	3·874	$C(9)_{VI}$–$C(13)_{I}$	3·742

The three *cis* protons of molecule (I), *i.e.* $H(90,100,110)_{I}$ protrude into this gap, opposite the fused benzene ring of molecule (VI). The closest contact, $H(110)_{I}$–$H(80)_{VI}$ at 2·62 Å, is only slightly longer than twice the van der Waals radius of hydrogen (2·40 Å). Since all contacts occur twice, *i.e.* $C(5)_{I}$–$C(9)_{VI}$ = $C(5)_{VI}$–$C(9)_{I}$, the stability introduced by this interaction is high.

Conclusion

Following the completion of this study we learned, by private communication, that the n.m.r. spectra had been successfully interpreted by Dr H. Booth of Nottingham University, England, who independently confirmed the all-*cis* stereochemistry. We are grateful to Dr Booth for permission to mention this result.

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References

Ahmed, F. R. & Barnes, W. H. (1963). *Acta Cryst.* **16**, 1249.

Ahmed, F. R., Barnes, W. H. & Masironi, L. Di M. (1963). *Acta Cryst.* **16**, 237.

Allen, F. H. & Rogers, D. (1969). *Acta Cryst.* B**25**, 1326.

Booth, A. D. (1948). *Fourier Techniques in Organic Structure Analysis.* Cambridge Univ. Press.

Brutcher, F. V., Roberts, T., Barr, S. J. & Pearson, N. (1959). *J. Amer. Chem. Soc.* **81**, 4915.

Busing, W. R. & Levy, H. A. (1957). *Acta Cryst.* **10**, 180.

Coppens, P., Leiserowitz, L. & Rabinovich, D. (1965). *Acta Cryst.* **18**, 1035.

Dauben, C. H. & Templeton, D. H. (1955). *Acta Cryst.* **8**, 841.

Dawson, B. (1954). *Acta Cryst.* **17**, 997.

Ham, A. L. & Leeming, P. R. (1969). *J. Chem. Soc.* (*C*), p. 523.

Hendrickson, J. B. (1961). *J. Amer. Chem. Soc.* **83**, 4537.

Hendrickson, J. B. (1963). *J. Amer. Chem. Soc.* **85**, 4059.

Hendrickson, J. B. (1967). *J. Amer. Chem. Soc.* **89**, 7036.

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

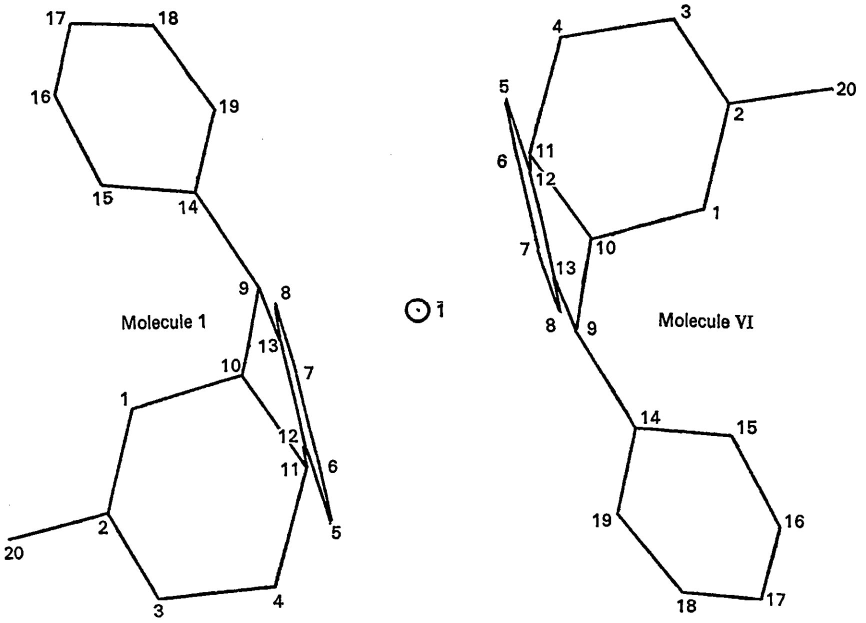

Fig. 6. Two molecules, related by a centre of symmetry, viewed along the *c* axis.

KILLEAN, R. C. G. (1967). *Acta Cryst.* **23**, 54.
LEEMING, P. R. & HAM, A. L. (1968). Paper presented to The Chemical Society Heterocyclic Group, London.
MARSH, R. E. (1958). *Acta Cryst.* **11**, 654.
NEWMAN, M. S. (1955). *J. Chem. Educ.* **32**, 344.
PAULING, L. (1965). *The Nature of the Chemical Bond.* Ithaca: Cornell Univ. Press.
PEERDEMAN, A. F. (1956). *Acta Cryst.* **9**, 824.
PITZER, K. S. & DONATH, W. E. (1959). *J. Amer. Chem. Soc.* **81**, 3213.
PLATI, J. T. & WENNER, W. (1950). *J. Org. Chem.* **15**, 259.
PLATI, J. T. & WENNER, W. (1955). *J. Org. Chem.* **20**, 1412.
PRZYBYLSKA, M. (1963). *Acta Cryst.* **16**, 871.
RÉRAT, C. (1960). *Acta Cryst.* **13**, 459.
SIM, G. A. (1955). *Acta Cryst.* **8**, 833.
SUTTON, L. E. (1965). Ed. *Tables of Interatomic Distances and Configurations in Molecules and Ions* (lst Supplement). Special Publication No. 18. London: The Chemical Society.
TOMIIE, Y. (1958). *J. Phys. Soc. Japan*, **13**, 1030.
TROMMEL, J. & BIJVOET, J. M. (1954). *Acta Cryst.* **7**, 703.
VAN DEN HENDE, J. H. & NELSON, N. R. (1967). *J. Amer. Chem. Soc.* **89**, 2901.

Acta Cryst. (1971). B**27**, 1337

The Crystal Structures of Monoclinic 5-Ethylbarbituric Acid and 5-Hydroxy-5-ethylbarbituric Acid

BY B. M. GATEHOUSE* AND B. M. CRAVEN

Department of Crystallography, University of Pittsburgh, Pittsburgh, Pa. 15213, *U.S.A.*

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The crystal data for the two forms of 5-ethylbarbituric acid (EBA) are (I) monoclinic (m.p. 194–196°), $a=11\cdot151$, $b=6\cdot838$, $c=9\cdot536$ Å, $\beta=92°21'$, space group $P2_1/c$ with four molecules per cell; (II) triclinic (m.p. 142–145°), $a=6\cdot018$, $b=5\cdot344$, $c=12\cdot121$ Å, $\alpha=93°38'$, $\beta=105°42'$, $\gamma=94°19'$, space group $P1$ or $P\bar{1}$ with two molecules per cell. The crystal structure of (I) is reported together with that of the oxidation product 5-hydroxy-5-ethylbarbituric acid (HEBA) which is monoclinic (m.p. 207–209°), $a=10\cdot088$, $b=6\cdot298$, $c=11\cdot914$ Å, $\beta=99°36'$, space group $P2_1/n$ with four molecules per cell. The X-ray diffraction data (Cu $K\alpha$ radiation) were obtained using an automatic four-circle diffractometer. All hydrogen atoms were found in difference Fourier syntheses. Full-matrix least-squares refinement gave R values of 0·06 and 0·05 respectively. The rings in both EBA and HEBA have a 'flap' conformation with C(5) displaced from an otherwise nearly flat ring. In EBA the ethyl group is *equatorial*, while in HEBA it is *axial*. All NH and OH hydrogen bond donor groups form hydrogen bonds. The acidic hydrogen atom H(5) in EBA is not hydrogen bonded. The non-hydrogen-bonded carbonyl oxygen atom O(6) makes close approaches (2·93 and 3·04 Å) to carbonyl carbon atoms C(4) and C(6) of an adjacent molecule.

Introduction

The crystal structure of a monoclinic form of 5-ethylbarbituric acid (Fig. 1, R = H), hereafter EBA, has been determined for the purpose of a comparison of the molecular structure and stereochemistry of the parent acid with that of the carbanion which is found in the crystal structure of the 5/3 hydrate of the corresponding potassium salt (Gartland & Craven, 1970*a*).

At first, crystals of an apparent monohydrate of EBA were studied. However, a crystal structure determination, which is also reported in this paper, showed the material to be the oxidation product, 5-hydroxy-5-ethylbarbituric acid (Fig. 1, R = OH), hereafter HEBA.

Subsequently, both a triclinic and a monoclinic form of EBA were crystallized. Crystal data are given for the triclinic form, but no further work on this crystal structure is intended.

Experimental

The synthesis of EBA was by condensation of the diethyl ester of ethylmalonic acid with urea in the presence of sodium ethoxide. The reaction mixture, after recrystallization from hot water in air contained the product together with what we have shown by crystal structure determination to be HEBA. The latter can also be formed by the oxidation of EBA with peroxide or dichromate ion (Aspelund, 1933).

The triclinic form of EBA (m.p. 142–145 °C) does not appear to have been previously characterized. It was obtained by recrystallization from absolute ethanol. Recrystallization from isoamyl acetate solution converted the triclinic into the monoclinic form. Both forms were at least partially converted to HEBA when dissolved in water and left for several days in air.

The crystal data for the two forms of EBA and for HEBA are listed in Table 1. The melting points werg determined from single crystals of each material using a hot stage microscope. Crystal densities were meas-

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* On leave from the Chemistry Department, Monash University, Australia.