V. B. Bala for taking and measuring powder photographs and H. J. Seubert for the drawing of the figures.

References

BOND, W. L. (1958). *Rev. Sci. Instrum.* **29**, 654.
BOOTH, D. P. (1957). Conf. on use of IBM 650 for Crystal Structure Analysis Computations, *Acta Cryst.* **10**, 384.
DAUBEN, C. H. & TEMPLETON, D. H. (1955). *Acta Cryst.* **8**, 841.
EULER, R., ROSCH, H., WERTZ, G. & HELLNER, E. (1957). Fourth International Congress, International Union of Cryst. Montreal, July 10–19. Abstr. No. 3.16. (*Acta Cryst.* (1957), **10**, 763.)
GELLER, S. & BALA, V. B. (1956). *Acta Cryst.* **9**, 1019.
GRAHAM, A. R. (1951). *Amer. Min.* **36**, 436.
HENDERSHOT, O. P. (1937). *Rev. Sci. Instrum.* **8**, 436.
International Tables for X-ray Crystallography, vol. I. Birmingham: Kynoch Press.
Internationale Tabellen zur Bestimmung von Kristallstrukturen (1935), vol. II. Berlin: Borntraeger.
MOOSER, E. & PEARSON, W. B. (1956). *J. Electronics*, **2**, 629.
RAMDOHR, P. (1938). *Sitzungsber. Preuss. Akad. Wiss. Phys.-Math. Kl.* VI, 71.
THOMAS, L. H. & UMEDA, K. (1957). *J. Chem. Phys.* **26**, 293.
VIERVOLL, H. & ÖGRIM, O. (1949). *Acta Cryst.* **2**, 277.
WERNICK, J. H. & BENSON, K. E. (1957). *J. Phys. Chem. Solids*, **3**, 157.
WERNICK, J. H., GELLER, S. & BENSON, K. E. (1958*a*). *J. Phys. Chem. Solids*, **4**, 154.
WERNICK, J. H., GELLER, S. & BENSON, K. E. (1958*b*). *J. Phys. Chem. Solids.* (In the press.)
WINKLER, U. (1955). *Helv. Phys. Acta*, **28**, 633.
WOOD, E. A. (1956). *Rev. Sci. Instr.* **27**, 60.

Acta Cryst. (1959). **12**, 54

The Crystal Structures of Some Anthracene Derivatives.
III. 9:10-Dichloroanthracene

By JAMES TROTTER*

Division of Pure Physics, National Research Council, Ottawa, Canada

(*Received* 10 *July* 1958)

Crystals of 9:10-dichloroanthracene are monoclinic with four molecules in the unit cell, and the structure has been determined by Patterson and Fourier projections along the *a* and *c* crystal axes. Values of the bond lengths and valency angles in the molecule and intermolecular distances have been obtained.

Introduction

Continuing the investigation of the crystal structures of anthracene derivatives with substituents in the 9 and 10 positions (Trotter, 1958*a*, *b*), the structure of 9:10-dichloroanthracene has been determined. Since the crystals are not isomorphous with those of the dibromo analogue, the structure analysis has of course been carried out completely independently.

Experimental

Crystals of 9:10-dichloroanthracene, which were obtained by crystallization from petroleum ether, are greenish-yellow in colour, and consist of plates elongated along the *a*-axis with (010) developed, and smaller (001) faces. The density was determined by flotation in aqueous potassium iodide solution. The unit-cell dimensions and space group were determined from rotation and oscillation photographs of a crystal rotating about the *a*-axis, *hkl* Weissenberg films with $h = 0, 1, 2, 3,$ and *h*0*l*, *h*1*l*, *hk*0 and *hk*1 precession films.

Crystal data

9:10-Dichloroanthracene, $C_{14}H_8Cl_2$; $M = 247{\cdot}1$; m.p. 209–210 °C.

Monoclinic,

$a = 7{\cdot}04 \pm 0{\cdot}02$, $b = 17{\cdot}93 \pm 0{\cdot}04$, $c = 8{\cdot}63 \pm 0{\cdot}02$ Å, $\beta = 102° 56' \pm 10'$.

Volume of the unit cell = 1062·3 Å³. Density, calculated (with four molecules per unit cell) = 1·535 g.cm.⁻³, measured = 1·525 g.cm.⁻³. Absorption coefficient for X-rays, $\lambda = 1{\cdot}542$ Å, $\mu = 51{\cdot}3$ cm.$^{-1}$; $\lambda = 0{\cdot}7107$ Å, $\mu = 5{\cdot}85$ cm.$^{-1}$.

Total number of electrons per unit cell $= F(000) = 504$.

---

* National Research Council Postdoctorate Fellow.

Absent spectra: $h0l$ when h is odd, $0k0$ when k is odd. Space group is uniquely determined as $P2_1/a$–C_{2h}^5.

The intensities of the $0kl$ reflexions were recorded on moving film exposures for a crystal rotating about the a-axis, using Cu $K\alpha$ radiation, the multiple-film technique being used to correlate strong and weak reflexions. The $h0l$ and $hk0$ reflexions were recorded on precession films, using Mo $K\alpha$ radiation, and multiple exposures to correlate strong and weak intensities. All the intensities were estimated visually, the range being about 4000 to 1. The same crystal was used for all the photographs; the cross-section normal to the a-axis was 0·17 mm. × 0·12 mm., and no absorption corrections were applied. The usual Lorentz and polarization factors were applied and the structure amplitudes derived; the absolute scale was established later by correlation with the calculated structure factors. 143 $0kl$, 57 $h0l$ and 72 $hk0$ independent reflexions were observed, representing 71%, 86% and 57% respectively of the possible observable with the radiations and experimental conditions used.

Structure analysis

As there are four molecules of dichloroanthracene in the unit cell, the asymmetric unit is one molecule, and the molecules are in general positions. The three axial Patterson projections were computed, and the $h0l$ and $hk0$ maps indicated that the molecular planes are almost exactly perpendicular to a, so that the best approach to solving the structure was examination of the $0kl$ Patterson map.

[100] *projection*

The single and double Cl–Cl peaks could not be unambiguously picked out on the $0kl$ Patterson map, as in the case of the Br–Br peaks in the dibromo derivative (Trotter, 1958*b*), since their heights were of the same order of magnitude as many of the multiple C–C peaks. There was, however, a row of peaks radiating from the origin, which could be assigned to C–C, C–Cl and Cl–Cl vectors within a single molecule and parallel to the Cl–Cl direction, and utilizing this information and other intramolecular peaks close to the origin, the orientation of the molecule in this projection was established.

The position of the molecular centre was found by moving it along the b-axis until reasonable agreement between F_o and F_c for the $0k0$ reflexions was obtained, and then along the c-axis until the $00l$ reflexions gave good agreement. More than one position was possible on this basis, but all except one were eliminated on considering some general $0kl$ reflexions. Structure factors were calculated for all the $0kl$ reflexions, and

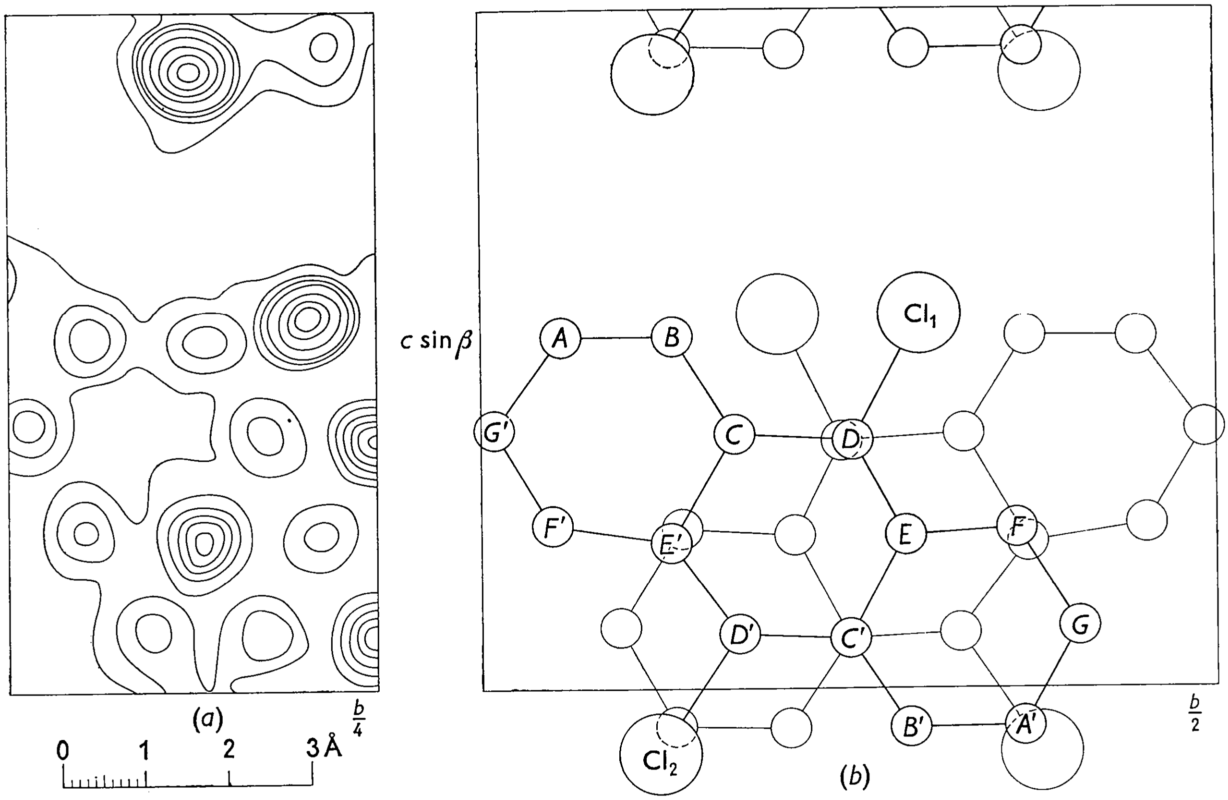

Fig. 1. (*a*) Electron-density projection down [100]. Contours at intervals of 2 e.Å^{-2}, except on the chlorine atoms where contours above 8 e.Å^{-2} are at intervals of 4 e.Å^{-2}. (*b*) Projection of the structure down [100].

the value of the usual discrepancy factor R was 35·8 %. In the structure factor calculation the scattering curve used for chlorine was that given in the *Internationale Tabellen* (1935), McWeeny's curve being used for carbon. The temperature parameter B was taken as 4·8 Å^2 for all the atoms. Hydrogen atoms were of course not included.

Refinement of positional and temperature parameters proceeded by computing successive (F_o-F_c) syntheses, and after three cycles the R value (calculated over the observed planes) had dropped to 13·1 %. Since the calculated structure factors of the high order reflexions had consistently been lower during the refinement process than those observed, an empirical curve for chlorine was used in the final structure factor calculation. This curve fits almost exactly the *Internationale Tabellen* curve with $B =$ 4·8 Å^2 up to $2 \sin \theta$ (Cu $K\alpha$) about 1·2, but thereafter lies slightly above that curve. McWeeny's curve with $B =$ 4·2 Å^2 was used for all the carbon atoms.

Measured and calculated $0kl$ structure factors are listed in Table 3. The final F_o synthesis, computed with measured F_o values and calculated signs, is shown in Fig. 1.

x-coordinates

Since the plane of the molecule is almost perpendicular to a the x-coordinates of all the atoms were readily obtained by varying the x-coordinate of the molecular centre until reasonable agreement between F_o and F_c for the $h0l$ reflexions was obtained. Refinement then proceeded by use of the $hk0$ zone data. Since the overlap of atomic peaks is quite severe even in the c-axis projection, the y-coordinates were fixed at the values obtained from the $0kl$ zone, and only the x-coordinates were refined further. The initial discrepancy factor was 29·4 %, and this was reduced in two cycles of (F_o-F_c) syntheses to 16·0 % (over the observed planes).

No attempt was made to refine the (010) projection independently, since there is a great amount of overlap. Using the x and z coordinates from the $hk0$ and $0kl$ zones, the R value was 15·0 %.

Final F_o and F_c values for the $h0l$ and $hk0$ zones are listed in Table 3. The final $hk0$ zone F_o synthesis is shown in Fig. 2, and a projection of the structure down [001] in Fig. 4.

Table 1. *Coordinates of the atoms*

Atom	x/a	y/b	z/c
Cl_1	0·2620	0·2976	0·5505
Cl_2	0·1137	0·1223	−0·0939
A	0·2540	0·0540	0·5170
B	0·2523	0·1292	0·5177
C	0·2180	0·1708	0·3732
D	0·2180	0·2471	0·3749
E	0·1850	0·2880	0·2268
F	0·1830	0·3644	0·2353
G	0·1460	0·4060	0·0901
A′	0·1093	0·3691	−0·0556
B′	0·1130	0·2924	−0·0580
C′	0·1489	0·2494	0·0761
D′	0·1530	0·1735	0·0822
E′	0·1830	0·1298	0·2213
F′	0·1830	0·0477	0·2403
G′	0·2180	0·0086	0·3803

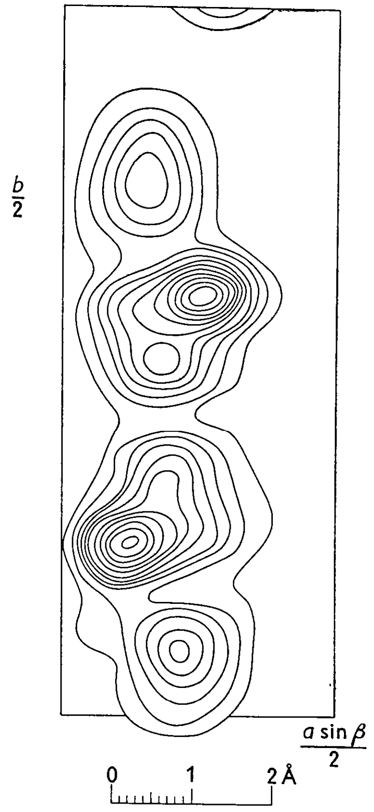

Fig. 2. Electron-density projection down [001]. Contours at intervals of 2 e.Å^{-2}.

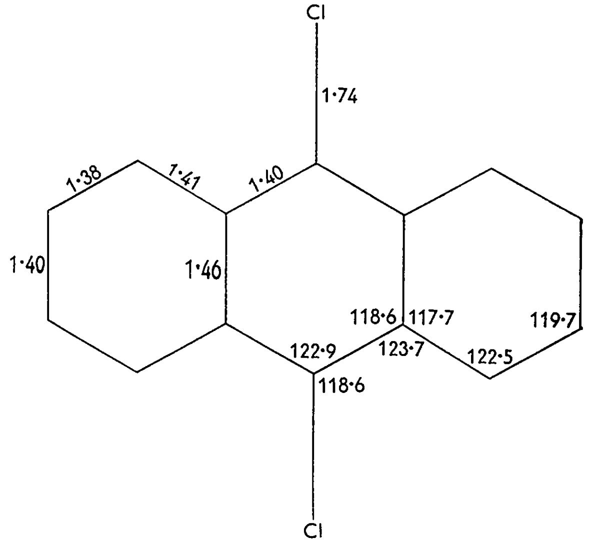

Fig. 3. Bond lengths and valency angles.

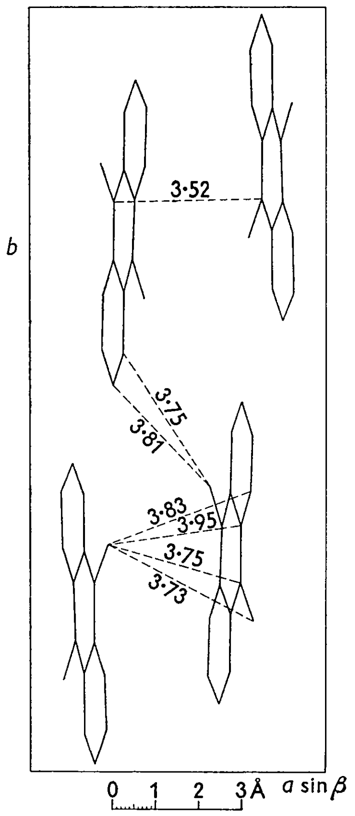

Fig. 4. Projection of the structure down [001], showing the shorter intermolecular contacts.

Coordinates and molecular dimensions

The final coordinates of the atoms, referred to the monoclinic axes and expressed as fractions of the unit-cell edges, are listed in Table 1, the labelling of the atoms being shown in Fig. 1.

The coordinates of the atoms can be fitted to an equation of the form

$$lX'+mY+nZ'+p = 0\,,$$

where X', Y, Z' are coordinates, expressed in Å units and referred to orthogonal axes a, b and c', c' being taken perpendicular to the a and b crystal axes. l, m, n and p were determined by the method of least squares to be 0·9995, 0·0050, 0·0319 and −0·9304 respectively. The root mean square deviation of the atoms from this plane is 0·02 Å.

The bond lengths and valency angles in the dichloroanthracene molecule were calculated from the coordinates of Table 1, and the values after averaging over chemically-equivalent bonds and angles are shown in Fig. 3.

Discussion

Due to overlap in all three projections Cruickshank's (1949) formulae for the standard deviations of the atomic positions cannot strictly be applied here, but they give the order of magnitude of the accuracy. For the mean bond lengths, obtained by averaging over chemically-equivalent bonds, the estimated standard deviations are about 0·015 Å for a Cl–C bond, and about 0·02 Å for a C–C bond.

The molecule is completely planar within the limits of experimental error, the root mean square deviation from the mean molecular plane being 0·02 Å. The Cl–C distance (1·74 Å) corresponds to a single bond. The C–C bond lengths are compared in Table 2 with the lengths of the corresponding bonds in anthracene (Sinclair, Robertson & Mathieson, 1950; Cruickshank, 1956). There are no significant differences. It can be concluded then that the replacement of the hydrogen atoms in the 9 and 10 positions of anthracene by chlorine atoms does not disturb the planarity of the molecule, nor does it cause any changes in the C–C distances; the Cl atoms are joined to the 9 and 10 carbon atoms by single bonds.

Table 2. *Bond lengths in anthracene and 9:10-dichloroanthracene*

Bond	Anthracene	9 : 10-Dichloroanthracene
A–B	1·37 Å	1·38 Å
B–C	1·43	1·41
C–D	1·40	1·40
A–G′	1·42	1·40
C–E′	1·44	1·46
Cl–*D*	—	1·74

All the intermolecular distances correspond to normal van der Waals interactions. The shortest Cl–Cl, Cl–C and C–C contacts are 3·73, 3·70 and 3·52 Å respectively. The C–C distances of 3·52 Å are between carbon atoms *D* and *C′* of the standard molecule and the corresponding atoms of the molecule related by the glide plane (Fig. 4). These pairs of atoms overlap very closely in the *a*-axis projection, and the planes of the two molecules are nearly parallel. In the *c*-direction the shortest contacts are Cl–C = 3·70, 3·76 Å and C–C = 3·80, 4·02, 4·08 Å. The shorter intermolecular distances are illustrated in Fig. 4.

The author wishes to thank Dr W. H. Barnes for his interest in this problem and for much helpful discussion, Mrs M. E. Pippy for assistance with many of the calculations, and Dr F. R. Ahmed for computing some of the Fourier series.

References

Cruickshank, D. W. J. (1949). *Acta Cryst.* **2**, 65.
Cruickshank, D. W. J. (1956). *Acta Cryst.* **9**, 915.
Internationale Tabellen zur Bestimmung von Kristallstrukturen (1935), vol. 2, p. 571. Berlin: Borntraeger.
Sinclair, V.C., Robertson, J.M. & Mathieson, A.McL. (1950). *Acta Cryst.* **3**, 251.
Trotter, J. (1958*a*). *Acta Cryst.* **11**, 564.
Trotter, J. (1958*b*). *Acta Cryst.* **11**, 803.

Table 3. *Observed and calculated structure factors*

hkℓ	F_o	F_c
000	-	+504
200	170	-173
400	<5	- 5
600	6	-12
800	4	+14
020	92	-99
040	53	-49
060	<3	+ 7
080	34	+37
0,10,0	9	+13
0,12,0	47	-49
0,14,0	<5	+ 4
0,16,0	22	+27
0,18,0	<5	- 5
0,20,0	3	+ 2
0,22,0	7	- 6
001	9	+11
002	89	+83
003	35	-35
004	12	- 2
005	30	-26
006	49	-51
007	42	-37
008	6	- 2
009	12	+10
0,0,10	<4	- 1
011	55	-59
012	6	+ 4
013	64	+68
014	12	-11
015	31	+28
016	43	-38
017	23	+23
018	8	- 4
019	<5	- 2
0,1,10	4	- 2
021	3	- 3
022	30	-39
023	8	- 2
024	4	+ 4
025	<4	- 3
026	12	+14
027	3	+ 2
028	11	+14
029	7	- 6
0,2,10	8	+ 8
031	<2	+ 4
032	21	+27
033	34	+39
034	35	+35
035	17	-15
036	5	+ 5
037	13	- 9
038	6	- 5
039	7	- 5
0,3,10	9	- 7
041	79	-78
042	4	- 4
043	24	+26
044	4	- 1
045	31	+31
046	14	+14
047	14	+13
048	<6	- 1
049	4	- 6
0,4,10	10	-10
051	19	-22
052	26	-27
053	28	-36
054	29	-26
055	<5	- 4
056	<5	0
057	10	+ 9
058	7	+ 5
059	<5	+ 4
0,5,10	4	+4
061	27	-27
062	<3	- 3
063	<4	+ 5
064	<4	0
065	9	+13
066	<5	+ 1
067	4	+ 3
068	<5	0
069	<5	0
0,6,10	<3	- 3
071	9	-11
072	28	-24
073	10	- 5
074	21	-23
075	8	+ 8
076	3	- 4
077	16	+14
078	<5	+ 3
079	9	+ 4
0,7,10	<3	+ 2
081	50	+50
082	10	- 7
083	11	+11
084	23	-23
085	11	-11
086	12	-12
087	18	-18
088	5	+ 7
089	<4	- 3
0,8,10	11	+11
091	18	-19
092	30	+32
093	<5	+ 5
094	24	+29
095	14	-14
096	<6	- 2
097	11	- 8
098	<5	- 1
099	8	- 7
0,9,10	<2	- 3
0,10,1	6	- 8
0,10,2	21	+20
0,10,3	7	- 8
0,10,4	4	- 7
0,10,5	<5	- 1
0,10,6	8	- 7
0,10,7	8	+10
0,10,8	14	-11
0,10,9	7	+ 9
0,11,1	19	+23
0,11,2	6	+ 7
0,11,3	49	+52
0,11,4	8	+ 8
0,11,5	17	+18
0,11,6	13	-11
0,11,7	<5	+ 1
0,11,8	14	-11
0,11,9	4	- 4
0,12,1	<5	- 2
0,12,2	10	-12
0,12,3	29	+29
0,12,4	25	-25
0,12,5	8	+11
0,12,6	12	+13
0,12,7	<5	+ 2
0,12,8	7	+ 6
0,12,9	14	-13
0,13,1	12	-12
0,13,2	8	- 1
0,13,3	57	-57
0,13,4	11	-14
0,13,5	4	- 9
0,13,6	13	+ 7
0,13,7	<5	- 4
0,13,8	8	+ 8
0,13,9	<2	+ 3
0,14,1	12	-11
0,14,2	<5	- 1
0,14,3	13	- 8
0,14,4	15	+16
0,14,5	8	+ 8
0,14,6	<5	+ 2
0,14,7	8	+ 4
0,14,8	3	- 3
0,15,1	<5	- 2
0,15,2	8	-10
0,15,3	3	- 5
0,15,4	<6	- 3
0,15,5	<5	+ 3
0,15,6	4	+ 5
0,15,7	<4	+ 5
0,15,8	<3	+ 5
0,16,1	<6	+ 3
0,16,2	<6	+ 9
0,16,3	5	- 4
0,16,4	<5	- 5
0,16,5	8	- 9
0,16,6	<4	- 7
0,16,7	8	- 8
0,17,1	<6	+ 2
0,17,2	<6	+ 5
0,17,3	3	+ 8
0,17,4	<5	+ 1
0,17,5	6	+ 7
0,17,6	12	- 7
0,17,7	<3	+ 1
0,18,1	10	+ 4
0,18,2	<5	- 4
0,18,3	3	+ 2
0,18,4	<5	- 4
0,18,5	<4	- 3
0,18,6	<3	+ 1
0,19,1	<5	+ 3
0,19,2	13	+15
0,19,3	<5	+ 1
0,19,4	12	+12
0,19,5	3	- 3
0,19,6	<2	+ 2
0,20,1	12	-15
0,20,2	8	+ 4
0,20,3	<4	- 2
0,20,4	5	+ 6
0,20,5	2	+ 6
0,21,1	<4	+ 2
0,21,2	<4	- 5
0,21,3	<3	0
0,21,4	10	-10
0,22,1	4	+ 4
0,22,2	8	- 8
0,22,3	<2	+ 2
2,$\underline{0}$,$\overline{10}$	13	+10
20$\underline{9}$	<5	0
20$\underline{8}$	7	-9
20$\underline{7}$	15	+ 6
20$\underline{6}$	21	+21
20$\underline{5}$	5	- 4
20$\underline{4}$	59	-54
20$\underline{3}$	7	- 7
20$\underline{2}$	55	-60
20$\bar{1}$	146	+154
201	52	+48
202	10	+ 6
203	62	+59
204	12	+10
205	16	-13
206	<5	- 1
207	7	+11
208	<5	- 1
20$\underline{9}$	12	-12
40$\underline{9}$	<5	0
40$\underline{8}$	32	+20
40$\underline{7}$	29	+30
40$\underline{6}$	20	+15
40$\underline{5}$	6	+ 5
40$\underline{4}$	26	+23
40$\underline{3}$	27	+31
40$\underline{2}$	10	+ 1
40$\bar{1}$	162	-157
401	27	-39
402	9	+12
403	7	- 2
404	12	+15
405	38	+32
406	26	+25
40$\underline{7}$	5	+ 4
60$\underline{8}$	13	- 5
60$\underline{7}$	11	-13
60$\underline{6}$	<5	- 1
60$\underline{5}$	18	+17
60$\underline{4}$	<5	+ 2
60$\underline{3}$	13	+22
60$\bar{2}$	20	-29
60$\bar{1}$	42	+44
601	6	- 1
602	13	-22
603	8	- 7
604	6	+ 2
60$\underline{5}$	3	- 2
80$\underline{4}$	<3	+ 7
80$\underline{3}$	6	- 3
80$\underline{2}$	33	+39
80$\bar{1}$	<4	+ 1
110	27	+25
120	30	-40
130	5	- 7
140	71	-69
150	10	-13
160	54	+54
170	18	+25
180	77	-64
190	<5	- 1
1,10,0	<5	- 4
1,11,0	<5	- 4
1,12,0	7	+ 7
1,13,0	14	-12
1,14,0	7	- 1
1,15,0	<6	+ 1
1,16,0	32	+28
1,17,0	14	+14
1,18,0	28	-25
1,19,0	<6	- 4
1,20,0	<5	0
1,21,0	<4	- 5
210	122	-136
220	37	+41
230	45	-40
240	20	-22
250	20	+27
260	12	-13
270	43	+35
280	12	+12
290	39	-31
2,10,0	<5	- 6
2,11,0	13	-16
2,12,0	19	+15
2,13,0	<6	+ 9
2,14,0	<6	- 7
2,15,0	14	+14
2,16,0	9	- 7
2,17,0	<6	- 8
2,18,0	7	+ 5
2,19,0	7	- 7
2,20,0	8	-10
310	16	-24
320	6	- 6
330	<5	+ 6
340	23	+31
350	7	- 6
360	<5	- 2
370	8	-16
380	34	+24
390	9	+ 7
3,10,0	9	-10
3,11,0	<6	+ 1
3,12,0	16	-12
3,13,0	7	+10
3,14,0	19	+15
3,15,0	<6	- 1
3,16,0	6	- 8
3,17,0	10	-13
3,18,0	3	+ 3
3,19,0	<4	+ 2
410	20	+23
420	<5	- 5
430	<5	+ 1
440	37	+36
450	3	+ 6
460	15	+12
470	<6	+ 2
480	30	-29
490	15	+12
4,10,0	<6	+ 5
4,11,0	11	-10
4,12,0	<6	+ 2
4,13,0	7	+ 7
4,14,0	<6	+ 8
4,15,0	<6	- 1
4,16,0	<5	- 4
510	<6	+ 3
520	<6	+ 5
530	<6	+ 4
540	11	-18
550	28	+21
560	7	+ 9
570	8	- 9
580	<6	- 5
590	12	- 8
5,10,0	<6	+ 2
5,11,0	<6	+ 6
5,12,0	<6	+ 7
5,13,0	<6	+ 4
5,14,0	<5	-10
5,15,0	<5	0
5,16,0	<4	+ 4
610	10	+12
620	<6	+ 5
630	<6	+ 6
640	<6	0
650	<6	- 7
660	<6	- 4
670	5	- 9
680	<6	+ 3
690	6	- 3
6,10,0	6	-10
6,11,0	11	+12
6,12,0	11	+12
6,13,0	<4	- 7
710	<5	- 4
720	<5	+ 5
730	<5	+ 1
740	<5	+ 9
750	<5	- 7
760	11	-17
770	<5	+ 5
780	<5	+ 3