Fig. 6. Idealized triclinic subcell $(T\|)$ of isostearic acid.

A packing detail of the methyl end group region is shown in Fig. 5. The H$\cdots$H contacts agree very well with those in the oxo acid. The chains pack laterally in the common triclinic packing $(T\|)$ Abrahamsson, 1959a). The subcell dimensions are

$$a_s = 4\cdot28, \quad b_s = 5\cdot37, \quad c_s = 2\cdot53 \text{ Å},$$
$$\alpha_s = 72\cdot3, \quad \beta_s = 108\cdot8, \quad \gamma_s = 117\cdot2°.$$

The corresponding dimensions for 13-oxoisostearic acid are

$$a_s = 4\cdot27, \quad b_s = 5\cdot39, \quad c_s = 2\cdot55 \text{ Å},$$
$$\alpha_s = 73\cdot9, \quad \beta_s = 108\cdot6, \quad \gamma_s = 119\cdot6°.$$

The closest subcell contacts to $H_A$ are 2·89 Å to $H_B$ and 2·72 Å to $H_B$ translated one $c_s$ distance, 2·94 Å to $H_C$ and 2·70 Å to $H_C$ translated one $c_s$ and finally 2·72 Å to $H_D$ (Fig. 6).

The carbon chain in isostearic acid is more regular than that of 13-oxoisostearic acid. Therefore, there are

large regions in reciprocal space with very weak reflexions. Thus, only 45% of the measured reflexions of isostearic acid are more than two standard deviations above background whereas in 13-oxoisostearic acid, which has a bent chain and contains one more oxygen atom, the corresponding figure is 83%.

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# The Crystal and Molecular Structure of Anhydrobromonitrocamphane

BY G. L. DWIVEDI AND R. C. SRIVASTAVA

Department of Physics, Indian Institute of Technology, Kanpur-16, India

Anhydrobromonitrocamphane crystals are orthorhombic, space group $P2_12_12_1$. The cell dimensions are $a = 10\cdot364$, $b = 9\cdot408$, $c = 10\cdot499$ Å, $Z = 4$. The crystals decompose quite rapidly when exposed to the atmosphere and X-rays. This results in a falling off of intensity with time. A method for correcting the intensity data for the above mentioned effects has been developed and used in the present study. The crystal structure has been solved using the heavy-atom method. The structure is highly disordered so that each type of site is statistically occupied by two optically isomeric forms of the molecule in two orientations. The disorder gives rise to an approximate (100) mirror. The bromine atom and one carbon atom lie on this pseudomirror, while the nitrogen atom and all other carbon atoms are distributed over two positions and the other oxygen atom over four positions. Some atomic positions were very close to their disordered counterparts and could not be refined by routine least-squares analysis. The final refinement was therefore done by the difference Fourier method. The final $R$ value was 0·097. Bond lengths and angles in both orientations of the molecule are normal.

## Introduction

The sulphuric acid transformation of bromonitrocamphane to anhydrobromonitrocamphane has been con-

sidered very unusual and fascinating (Goto, Hirata & Stout, 1968; Ranganathan, 1967). The proposed reaction mechanism is also very uncommon as it involves the initial loss of the nitro group and its subsequent

recombination (van Tamelen & Brenner, 1957; Ranganathan & Raman, 1969). Besides the above interesting features an isoxazoline ring (Fig. 1) is attached to the bicyclic system of this compound and it is of interest to observe the distortions induced in the bicyclic system by the attachment of the isoxazoline ring. Because of these reasons it was considered worthwhile to undertake the crystal structure analysis of anhydrobromonitrocamphane.

In the early stages it was noticed that the crystals are not stable. They started to decay on exposure to air and the process became faster with exposure to X-rays. The intensity of each reflexion therefore decreased with time. The procedure developed and followed for collecting and correcting the intensity data is described in the next section.

## Experimental

### (i) Preliminary measurements

Crystals of anhydrobromonitrocamphane were grown by evaporation of a solution in ethyl alcohol at room temperature (25 to 30°C). Crystals grow as rectangular needles elongated along the $c$ axis with the $\{110\}$ faces well developed. A crystal approximately $0.3 \times 0.3 \times 0.5$ mm in size was chosen for preliminary studies. Oscillation, rotation and equi-inclination Weissenberg photographs about the $c$ axis and the [110] diagonal were taken. The systematic absences observed on the photographs corresponded to the space groups $Cmc2_1$ and $Cmcm$. Accurate cell dimensions were determined from axial reflexions observed on a G. E. diffractometer. The cell dimensions thus obtained are $a = 10.364$, $b = 9.408$ and $c = 10.499$ Å. Density was measured by flotation in an aqueous solution of $ZnCl_2$. The average of several measurements was $1.51$ g.cm$^{-3}$ and, thus, it was deduced that there are four molecules in the unit cell. It was found that reflexions $hkl$ with $h + k = 2n + 1$ and $h0l$ with $l = 2n + 1$ (when $h \neq 0$) were observed using the diffractometer but were very weak and were therefore missed in the photographs. All other systematic absences found in photographs were confirmed. Thus the space group was uniquely assigned as $P2_12_12_1$. The calculated density of crystals was $1.58$ g.cm$^{-3}$.

### (ii) Intensity measurements

Microscopic examination showed that long exposure to the atmosphere causes decomposition in the crystals, they begin to loose their lustre and a whitish powder appears on the surface. In order to protect the crystals from the atmosphere it was necessary to enclose them in thin polythene films.

A well-formed crystal of approximate dimension $0.2 \times 0.2 \times 0.4$ mm was mounted parallel to the $c$ axis on the top of a glass fibre and dipped for a very short time into a solution of polythene in trichloroethylene. The solvent evaporates leaving a thin coating of polythene on the crystal. Uniform coating of an appropriate thickness is achieved by repeated dipping of the crystal in dilute solution.

All the intensity measurements were made at room temperature using a G. E. diffractometer equipped with a single-crystal orienter. Filtered Cu $K\alpha$ radiation was used and a xenon-filled proportional counter was employed for measurement.

The intensity measurements were made for all reflexions in the positive octant within the range of the Eulerian cradle ($2\theta \leq 120°$). The stationary-crystal stationary-counter technique was employed for data collection. All reflexions which differed from the background intensity by less than one standard deviation of the background were classified as unobserved. There were 404 unobserved reflexions out of a total of 900 reflexions recorded. A very large number of unobserved reflexions satisfied the condition $h + k = 2n + 1$. Filters of varying thicknesses had to be used for very intense reflexions to avoid counter-coincidence errors. The filter scaling constants were experimentally determined.

The intensity of the $00l$ reflexions ($\chi = 90°$) was checked with $\varphi$ varying from 0 to 360°. No appreciable variation of intensity was observed, which indicated that any absorption correction would be very small. Such a correction was therefore not applied.

It was also noticed that the intensities kept on falling with time, such that at the end of the measurements, the intensity of the reflexions had reached about 40% of their value at the beginning. The following procedure was adopted for correcting the data for this effect.

### (iii) Method of correcting intensity data for fall of intensity with time.

The intensities of five reflexions 200, 550, 350, 040 and 802 which covered a wide range of $\chi$, $\varphi$, $2\theta$ and intensity were measured at suitable intervals during the course of the intensity measurements. It was observed that the rate of fall of intensity was not constant during the period of intensity measurement but varied principally as a function of the time of exposure of the crystal to X-rays. The period of data collection was divided into nine regions in each of which the rate of fall was
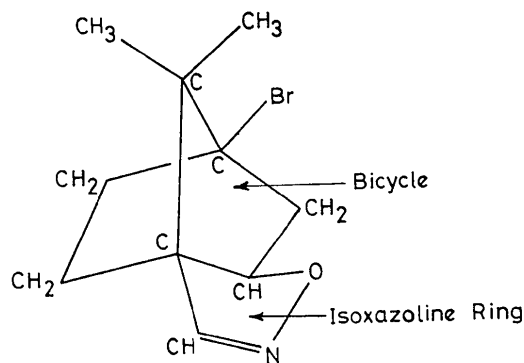


Fig. 1. The structural formula of anhydrobromonitrocamphane.

roughly constant. The relation used for correcting intensity data within a region is

$$I_n = I_{on}(1 - \lambda_n t_n) \qquad (1)$$

and the corrected intensity, $I_o$, for a reflexion measured in the $n$th region is given by the expression

$$I_o = I_n/[(1 - \lambda_1 T_1)(1 - \lambda_2 T_2) \cdots (1 - \lambda_n t_n)], \qquad (2)$$

where $t_n$ is the time passed in $n$th region, $I_n$ is the measured intensity and $T_n$ is total duration of $n$th region.

The decay constants, $\lambda_n$'s, for different regions were calculated from all monitored reflexions. They agreed fairly well within a region and their average values were used for correcting the intensity data. The validity of relation (2) was checked experimentally by observing some reflexions (other than the monitored reflexions) in two different regions of time and comparing the measured intensity with the intensity as calculated from relation (2).

## Structure analysis

Three-dimensional intensity data were obtained and corrected for the fall of intensities with time as explained above. The unobserved reflexions were given $\frac{2}{3}$ the intensity of the weakest observed reflexion and Lorentz and polarization corrections applied to all the data. A three-dimensional Patterson synthesis was calculated for the space group $P2_12_12_1$. Br–Br vectors were easily identified from Harker sections and the Br atom position was assigned $(0.25, 0.10, 0.25)$. A structure-factor calculation with the above coordinates for the Br atom and an assumed isotropic temperature factor of $3.5$ Å$^2$, gave an $R$ index of $0.38$ (defined as $\sum|F_o| - |F_c||/\sum|F_o|$). The isotropic temperature factor of the Br atom was corrected following the procedure described by Buerger (1967). This gave $B = 8.5$ Å$^2$ for the Br atom which appeared to be quite a high value for temperature factor. However, it reduced the $R$ value to $0.34$. High temperature factors for the atoms in the structure were also indicated by quick fall in intensity at higher angles and the tendency of the crystals to disintegrate with time.

A three-dimensional Fourier synthesis with phases corresponding to the Br atom only was effected. This Fourier map showed two mirrors, one parallel to the $YZ$ plane at $x = 0.25$ and the other parallel to the $XY$ plane at $z = 0.25$. These planes do not exist in the space group $P2_12_12_1$ but perhaps resulted from the Fourier synthesis being phased with the heavy atom only. A set of peaks which were of proper heights and were stereochemically reasonable were assigned to all atoms except C(8) and C(9). The centroid of the peak (Ladell & Katz, 1954) was determined in each of the above cases and taken as the position of the atom. The $R$ index with atomic positions and an overall recalculated $B$ of $8.0$ Å$^2$ was $0.28$. It was noticed that the peaks corresponding to C(2) and C(3) were broad and had merged into each other with a hump suggesting a third peak in between. Exactly similar was the appearance of the peaks C'(2) and C'(3) (primed peaks are related to the unprimed by

an approximate mirror parallel to $YZ$) and the hump between them was assigned to C(9). A similar hump between C'(5) and C'(6) was assigned to C(8). This assignment of C(8) and C(9) is in agreement with the stereochemistry of the molecule. Thus, all 13 atoms in the structure were located. A structure-factor calculation with all 13 atoms gave an $R$ index of $0.26$. Several cycles of least-squares refinement were performed for positional and thermal parameters using the program written by Busing, Martin & Levy (1962) but the results were not satisfactory for atoms for which a peak related by mirror planes existed in the electron density maps. The temperature factors of these atoms were oscillating within wide limits and their positions had a tendency to make large shifts along the $y$ direction. The lowest $R$ value reached was $0.24$.

A third three-dimensional Fourier synthesis was made with these 13 atomic positions. It showed improvement in the peaks corresponding to the given atoms but the height of their mirror-related peaks, which were ignored, had not diminished by more than 30%. It was therefore realized that the extra peaks corresponded to real structural features and could not be ignored. A disordered structure was therefore postulated which explains all the peaks in the Fourier map. Peaks related by the (001) mirror for the oxygen and nitrogen atoms suggested that the isoxazoline ring can attach itself to either wing of the bicyclic system, i.e. to C(3) or C(5). Thus atoms O and N have two sites available; O(1), O(2) and N(1), N(2) respectively. The two sites of C(10) are very close to each other and cannot be resolved. Besides this, the molecule occurs in two configurations related to each other by an approximate (100) mirror at $x = 0.25$. The situation is clearly illustrated in Figs. 2 and 3. As Br, C(10), N(1) and N(2) are very close to this mirror, they were assigned only one position each. Thus in the asymmetric unit (Fig. 3), Br and C(10) each have one site, all other carbon atoms and the nitrogen atom have two sites each and the oxygen atom has four sites available. The disorder which results from the (100) mirror was not totally unexpected as such a mirror plane characterizes the space groups $Cmc2_1$ and $Cmcm$ which were initially considered as well as $P2_12_12_1$.

All the above atomic positions were given appropriate occupancy factors and were considered to be independent in the structure. A structure-factor calculation with these positions and an overall isotropic $B$ of 8 Å$^2$ gave an $R$ value of $0.24$. One cycle of least-squares refinement of positions and individual isotropic temperature factors was carried out by varying sets of parameters which were not related. This reduced the $R$ value to $0.216$.

Further refinement by least-squares analysis was not proving successful for the light atoms. Their positional and isotropic thermal parameters were oscillating within wide limits. Conversion to anisotropic temperature factors did not help as many of these became negative. These anomalies may be attributed to the overlapping

of electron densities as a result of disorder. The groups of atoms having marked overlap are

(i) C(2), C'(9), C(3)        (v) C'(7), C(1)
(ii) C(5), C'(8), C(6)       (vi) C(7), C'(1)
(iii) C'(2), C(9), C'(3)     (vii) C(4), C'(4)
(iv) C'(5), C(8), C'(6)      (viii) N(1), C(10), N(2) .

An attempt has been made to refine these overlapped positions by some other means and this is described in the next section.

The positional and anisotropic thermal parameters of Br could be refined by the least-squares method resulting in an $R$ value of 0·153. An examination of the observed and calculated structure factors showed that few strong low angle reflexions had a consistently high value for the calculated structure factor. This discrepancy was attributed to secondary extinction. An empirical correction for this (Darwin, 1922) was applied for these reflexions. This correction brought the $R$ value to 0·139.

*Refinement of overlapping positions*

If the contributions of one of the atoms from each of the above eight groups were subtracted from the observed $|F_o|$ we would get a new set of $|F'_o|$ which would correspond to a structure in which these atoms were absent. Using these new $|F'_o|$ one could use the least-squares method to refine the positions of the rest of the atoms. If a structure contains $N$ atoms from which $M$ atoms are to be removed (or their contribution is to be subtracted), then the new set of $F$-values for the remaining $K$ ($=N-M$) atoms is

$$F'_o \ (hkl) = F^N_o \ (hkl) - F^M_c \ (hkl) \qquad (3)$$

where the superscripts represent the number of atoms in the set. $F^N_o$ are the observed structure factors, $F^M_c$ the calculated ones and $F'_o$ are the new data from which the parameters of the $K$ atoms will be refined.

Relation (3) can be written in terms of the real and imaginary parts of the structure factors, as follows:

$$|F'_o(hkl)| = [\{A^N_o(hkl) - A^M_c(hkl)\}^2 \\ + \{B^N_o(hkl) - B^M_c(hkl)\}^2]^{1/2}, \qquad (4)$$

where

$$[\{A^N_o(hkl)\}^2 + \{B^N_o(hkl)\}^2]^{1/2} = |F^N_o|$$

and

$$[\{A^M_c(hkl)\}^2 + \{B^M_c(hkl)\}^2]^{1/2} = |F^M_c| \ .$$

These expressions assume that the atoms substracted from whole structure have been given their correct positional and thermal parameters, which implies that the
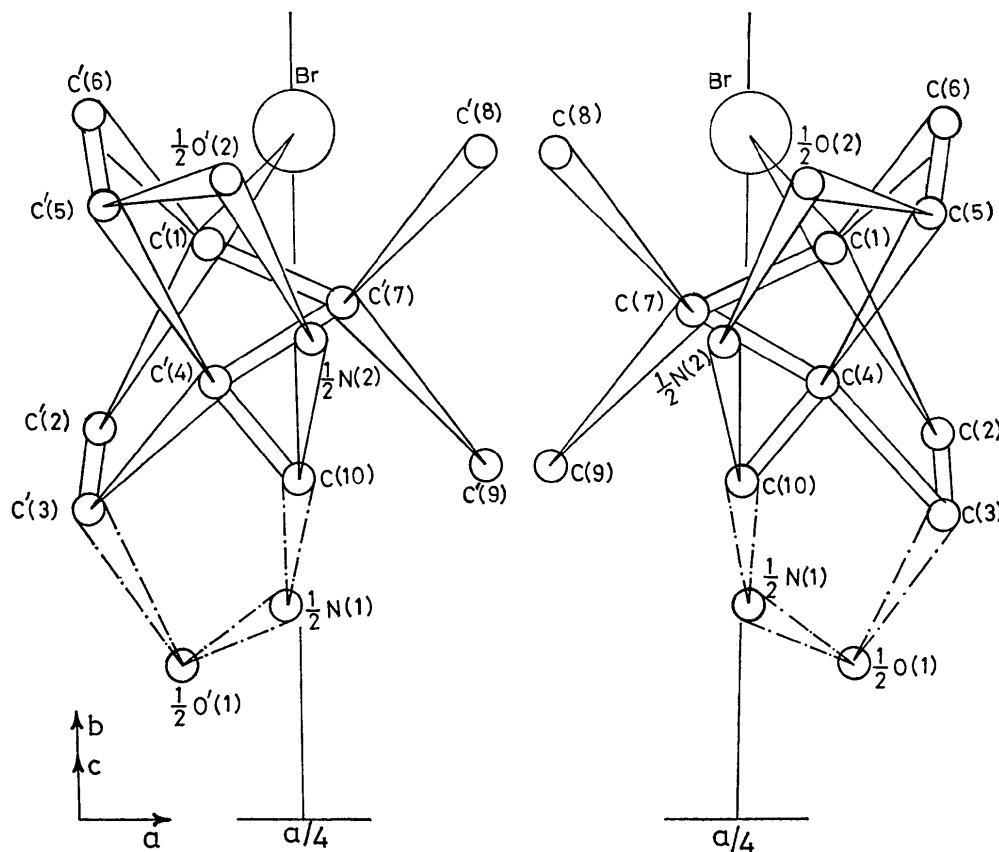


Fig. 2. A perspective drawing of each orientation of the molecule when seen in a plane parallel to (100). These orientations are related by an approximate (100) mirror. One of the two probable isoxazoline rings of each orientation is shown by the broken lines.

Table 1. *Observed and calculated structure factors with phase angles*

The columns are *h*, *k*, *l*, $|F_o|$, $|F_c|$ and $\varphi$ (degrees). Reflexions marked with $ were unobserved. Those marked with * were corrected for extinction and for those marked with +, filters were employed.

| | | | | | | |
|---|---|---|---|---|---|---|
| 2 | 0 | 0 | 213.0 | +* | 213.5 | 180. |
| 4 | 0 | 0 | 46.4 | + | 43.8 | 0. |
| 6 | 0 | 0 | 55.5 | + | 58.1 | 180. |
| 8 | 0 | 0 | 36.8 | | 37.8 | 0. |
| 10 | 0 | 0 | 1.7 | $ | 3.3 | 180. |
| 1 | 1 | 0 | 64.8 | + | 65.7 | 90. |
| 2 | 1 | 0 | 7.6 | | 1.3 | 180. |
| 3 | 1 | 0 | 31.1 | | 38.9 | 270. |
| 4 | 1 | 0 | 5.6 | | 4.5 | 0. |
| 5 | 1 | 0 | 36.9 | | 37.1 | 90. |
| 6 | 1 | 0 | 1.3 | $ | 1.4 | 0. |
| 7 | 1 | 0 | 26.8 | | 28.2 | 270. |
| 8 | 1 | 0 | 1.6 | $ | 3.3 | 180. |
| 9 | 1 | 0 | 10.9 | | 10.9 | 90. |
| 10 | 1 | 0 | 1.7 | $ | 0.6 | 0. |
| 11 | 1 | 0 | 1.5 | $ | 1.9 | 270. |
| 0 | 2 | 0 | 5.9 | | 4.7 | 0. |
| 1 | 2 | 0 | 1.7 | | 1.5 | 270. |
| 2 | 2 | 0 | 72.3 | + | 71.3 | 180. |
| 3 | 2 | 0 | 0.9 | $ | 1.6 | 90. |
| 4 | 2 | 0 | 76.8 | + | 78.6 | 0. |
| 5 | 2 | 0 | 1.2 | $ | 2.4 | 270. |
| 6 | 2 | 0 | 19.4 | | 18.7 | 180. |
| 7 | 2 | 0 | 1.5 | $ | 3.3 | 90. |
| 9 | 2 | 0 | 1.7 | $ | 1.6 | 270. |
| 10 | 2 | 0 | 9.6 | | 10.4 | 180. |
| 11 | 2 | 0 | 1.5 | $ | 0.1 | 90. |
| 1 | 3 | 0 | 58.7 | + | 59.8 | 270. |
| 2 | 3 | 0 | 10.7 | | 4.0 | 0. |
| 3 | 3 | 0 | 25.9 | | 24.5 | 90. |
| 4 | 3 | 0 | 7.5 | | 4.0 | 180. |
| 5 | 3 | 0 | 19.2 | | 18.2 | 270. |
| 6 | 3 | 0 | 4.3 | | 1.5 | 0. |
| 7 | 3 | 0 | 17.1 | | 15.4 | 90. |
| 8 | 3 | 0 | 1.7 | $ | 1.1 | 180. |
| 9 | 3 | 0 | 4.1 | | 5.5 | 270. |
| 10 | 3 | 0 | 1.6 | $ | 1.0 | 0. |
| 11 | 3 | 0 | 1.4 | $ | 1.1 | 90. |
| 0 | 4 | 0 | 67.3 | + | 60.6 | 180. |
| 1 | 4 | 0 | 6.8 | | 2.3 | 270. |
| 2 | 4 | 0 | 45.9 | | 51.4 | 0. |
| 3 | 4 | 0 | 7.1 | | 5.6 | 90. |
| 4 | 4 | 0 | 29.6 | | 28.7 | 180. |
| 5 | 4 | 0 | 3.6 | | 5.2 | 270. |
| 6 | 4 | 0 | 15.0 | | 14.2 | 0. |
| 7 | 4 | 0 | 4.0 | | 3.5 | 90. |
| 8 | 4 | 0 | 11.1 | | 10.1 | 180. |
| 9 | 4 | 0 | 1.7 | $ | 2.3 | 270. |
| 10 | 4 | 0 | 5.9 | | 4.5 | 0. |
| 1 | 5 | 0 | 80.1 | + | 77.8 | 270. |
| 2 | 5 | 0 | 2.6 | | 2.0 | 0. |
| 3 | 5 | 0 | 59.1 | + | 60.7 | 90. |
| 4 | 5 | 0 | 1.4 | $ | 3.4 | 180. |
| 5 | 5 | 0 | 44.0 | | 42.6 | 270. |
| 6 | 5 | 0 | 1.6 | $ | 3.2 | 0. |
| 7 | 5 | 0 | 26.4 | | 29.4 | 90. |
| 8 | 5 | 0 | 1.7 | $ | 2.0 | 180. |
| 9 | 5 | 0 | 13.1 | | 14.5 | 270. |
| 10 | 5 | 0 | 1.5 | $ | 1.6 | 0. |
| 0 | 6 | 0 | 25.3 | | 39.0 | 180. |
| 1 | 6 | 0 | 4.0 | | 0.1 | 270. |
| 2 | 6 | 0 | 38.4 | | 38.6 | 0. |
| 3 | 6 | 0 | 2.9 | | 1.4 | 90. |
| 4 | 6 | 0 | 31.5 | | 30.5 | 180. |
| 5 | 6 | 0 | 1.6 | $ | 2.7 | 270. |
| 6 | 6 | 0 | 17.3 | | 15.3 | 0. |
| 7 | 6 | 0 | 1.7 | $ | 2.1 | 90. |
| 8 | 6 | 0 | 5.9 | | 6.3 | 180. |
| 9 | 6 | 0 | 1.5 | $ | 1.4 | 270. |
| 1 | 7 | 0 | 25.6 | | 22.6 | 270. |
| 2 | 7 | 0 | 1.6 | $ | 0.3 | 180. |
| 3 | 7 | 0 | 27.9 | | 26.6 | 90. |
| 4 | 7 | 0 | 1.7 | $ | 0.2 | 180. |
| 5 | 7 | 0 | 16.4 | | 18.9 | 270. |
| 6 | 7 | 0 | 1.7 | $ | 0.3 | 0. |
| 7 | 7 | 0 | 1.6 | $ | 4.5 | 90. |
| 8 | 7 | 0 | 1.5 | $ | 0.0 | 180. |
| 0 | 8 | 0 | 1.7 | $ | 3.8 | 0. |
| 1 | 8 | 0 | 1.7 | $ | 0.1 | 90. |
| 2 | 8 | 0 | 4.7 | | 4.4 | 180. |
| 3 | 8 | 0 | 1.7 | $ | 0.3 | 270. |
| 4 | 8 | 0 | 4.2 | | 3.9 | 0. |
| 5 | 8 | 0 | 1.7 | $ | 0.7 | 90. |
| 6 | 8 | 0 | 3.2 | | 2.5 | 180. |
| 7 | 8 | 0 | 1.9 | | 0.8 | 270. |
| 1 | 9 | 0 | 16.0 | | 15.7 | 90. |
| 2 | 9 | 0 | 1.7 | $ | 0.8 | 180. |
| 3 | 9 | 0 | 11.5 | | 10.2 | 270. |
| 4 | 9 | 0 | 1.6 | $ | 1.5 | 0. |
| 5 | 9 | 0 | 7.3 | | 6.8 | 90. |
| 6 | 9 | 0 | 1.4 | $ | 1.6 | 180. |
| 1 | 10 | 0 | 1.5 | $ | 0.6 | 90. |
| 2 | 10 | 0 | 13.9 | | 14.9 | 180. |
| 3 | 10 | 0 | 1.5 | $ | 1.9 | 270. |
| 1 | 0 | 1 | 3.4 | | 0.1 | 90. |
| 2 | 0 | 1 | 1.7 | | 0.8 | 90. |
| 3 | 0 | 1 | 5.7 | | 5.1 | 90. |
| 4 | 0 | 1 | 1.0 | $ | 2.5 | 270. |
| 5 | 0 | 1 | 3.1 | | 4.0 | 270. |
| 6 | 0 | 1 | 1.3 | $ | 2.5 | 90. |
| 7 | 0 | 1 | 3.9 | | 0.8 | 270. |
| 8 | 0 | 1 | 6.0 | | 1.3 | 270. |
| 9 | 0 | 1 | 1.7 | $ | 0.5 | 90. |
| 10 | 0 | 1 | 1.7 | $ | 0.6 | 90. |
| 11 | 0 | 1 | 1.5 | $ | 0.7 | 90. |
| 0 | 1 | 1 | 0.6 | $ | 0.4 | 90. |
| 1 | 1 | 1 | 45.3 | + | 34.0 | 89. |
| 2 | 1 | 1 | 4.1 | | 4.0 | 355. |
| 3 | 1 | 1 | 86.8 | + | 78.1 | 90. |
| 4 | 1 | 1 | 5.5 | | 6.2 | 179. |
| 5 | 1 | 1 | 50.9 | + | 51.7 | 271. |
| 6 | 1 | 1 | 4.4 | | 4.6 | 358. |
| 7 | 1 | 1 | 14.9 | | 11.3 | 97. |
| 8 | 1 | 1 | 1.6 | $ | 2.7 | 174. |
| 9 | 1 | 1 | 14.4 | | 12.2 | 275. |
| 10 | 1 | 1 | 1.7 | $ | 1.8 | 355. |
| 11 | 1 | 1 | 11.1 | | 11.3 | 91. |
| 0 | 2 | 1 | 69.8 | + | 82.0 | 180. |
| 1 | 2 | 1 | 2.2 | | 0.3 | 143. |
| 2 | 2 | 1 | 92.9 | +* | 92.5 | 1. |
| 3 | 2 | 1 | 1.8 | | 1.7 | 266. |
| 4 | 2 | 1 | 75.5 | + | 76.2 | 180. |
| 5 | 2 | 1 | 1.2 | $ | 0.8 | 226. |
| 6 | 2 | 1 | 37.5 | | 39.2 | 1. |
| 7 | 2 | 1 | 1.5 | $ | 3.2 | 79. |
| 8 | 2 | 1 | 21.1 | | 19.8 | 182. |
| 9 | 2 | 1 | 1.7 | $ | 2.0 | 270. |
| 10 | 2 | 1 | 12.4 | | 12.2 | 1. |
| 11 | 2 | 1 | 1.5 | $ | 0.7 | 94. |
| 0 | 3 | 1 | 0.9 | $ | 0.6 | 90. |
| 1 | 3 | 1 | 87.5 | + | 94.7 | 270. |
| 2 | 3 | 1 | 3.8 | | 2.3 | 338. |
| 3 | 3 | 1 | 64.4 | + | 60.1 | 90. |
| 4 | 3 | 1 | 1.5 | | 2.9 | 146. |
| 5 | 3 | 1 | 47.9 | | 47.7 | 270. |
| 6 | 3 | 1 | 1.4 | $ | 3.4 | 333. |
| 7 | 3 | 1 | 33.2 | | 33.0 | 88. |
| 8 | 3 | 1 | 1.7 | $ | 2.6 | 167. |
| 9 | 3 | 1 | 12.8 | | 14.3 | 268. |
| 10 | 3 | 1 | 1.6 | $ | 1.1 | 355. |
| 11 | 3 | 1 | 1.4 | $ | 5.9 | 91. |
| 0 | 4 | 1 | 46.8 | | 55.0 | 180. |
| 1 | 4 | 1 | 4.4 | | 1.1 | 199. |
| 2 | 4 | 1 | 47.2 | | 45.3 | 359. |
| 3 | 4 | 1 | 3.7 | | 1.6 | 9. |
| 4 | 4 | 1 | 32.7 | | 32.2 | 178. |
| 5 | 4 | 1 | 1.4 | $ | 0.9 | 140. |
| 6 | 4 | 1 | 22.7 | | 21.7 | 357. |
| 7 | 4 | 1 | 1.6 | $ | 0.6 | 263. |
| 8 | 4 | 1 | 10.7 | | 11.4 | 176. |
| 9 | 4 | 1 | 1.7 | $ | 0.3 | 126. |
| 10 | 4 | 1 | 4.7 | | 6.0 | 358. |
| 0 | 5 | 1 | 1.2 | $ | 1.8 | 90. |
| 1 | 5 | 1 | 23.8 | | 17.4 | 269. |
| 2 | 5 | 1 | 5.7 | | 1.5 | 290. |
| 3 | 5 | 1 | 8.8 | | 7.4 | 82. |
| 4 | 5 | 1 | 1.4 | $ | 0.7 | 66. |
| 5 | 5 | 1 | 3.5 | | 3.2 | 256. |
| 6 | 5 | 1 | 1.6 | $ | 1.0 | 201. |
| 7 | 5 | 1 | 2.0 | | 4.5 | 84. |
| 8 | 5 | 1 | 1.7 | $ | 0.9 | 35. |
| 9 | 5 | 1 | 2.0 | | 2.4 | 255. |
| 10 | 5 | 1 | 1.5 | $ | 0.8 | 202. |
| 0 | 6 | 1 | 13.2 | | 16.5 | 0. |
| 1 | 6 | 1 | 1.4 | $ | 1.1 | 112. |
| 2 | 6 | 1 | 20.1 | | 20.3 | 182. |
| 3 | 6 | 1 | 1.5 | $ | 2.6 | 271. |
| 4 | 6 | 1 | 19.9 | | 19.9 | 2. |
| 5 | 6 | 1 | 2.1 | | 3.1 | 87. |
| 6 | 6 | 1 | 10.2 | | 8.6 | 183. |
| 7 | 6 | 1 | 1.7 | $ | 2.7 | 274. |
| 8 | 6 | 1 | 1.9 | | 1.2 | 24. |
| 9 | 6 | 1 | 1.5 | $ | 1.6 | 100. |
| 0 | 7 | 1 | 1.6 | $ | 0.1 | 270. |
| 1 | 7 | 1 | 33.0 | | 31.5 | 90. |
| 2 | 7 | 1 | 3.7 | | 2.4 | 182. |
| 3 | 7 | 1 | 26.8 | | 24.9 | 271. |
| 4 | 7 | 1 | 1.7 | $ | 3.2 | 2. |
| 5 | 7 | 1 | 19.5 | | 18.4 | 91. |
| 6 | 7 | 1 | 1.7 | $ | 2.8 | 179. |
| 7 | 7 | 1 | 13.2 | | 12.6 | 272. |
| 8 | 7 | 1 | 1.5 | $ | 2.0 | 359. |
| 0 | 8 | 1 | 23.2 | | 22.7 | 0. |
| 1 | 8 | 1 | 1.7 | $ | 1.2 | 67. |
| 2 | 8 | 1 | 21.2 | | 20.5 | 180. |
| 3 | 8 | 1 | 1.7 | $ | 2.5 | 258. |
| 4 | 8 | 1 | 16.6 | | 16.0 | 1. |
| 5 | 8 | 1 | 1.7 | $ | 2.6 | 87. |
| 6 | 8 | 1 | 13.2 | | 13.2 | 180. |
| 7 | 8 | 1 | 1.5 | $ | 2.2 | 270. |
| 0 | 9 | 1 | 1.7 | $ | 0.1 | 270. |
| 1 | 9 | 1 | 14.3 | | 13.6 | 89. |
| 2 | 9 | 1 | 1.7 | $ | 0.5 | 137. |
| 3 | 9 | 1 | 13.3 | | 12.8 | 269. |
| 4 | 9 | 1 | 1.6 | $ | 0.5 | 315. |
| 5 | 9 | 1 | 9.2 | | 9.8 | 90. |
| 6 | 9 | 1 | 1.4 | $ | 0.8 | 166. |
| 1 | 10 | 1 | 1.5 | | 0.6 | 350. |
| 2 | 10 | 1 | 5.6 | | 4.9 | 176. |
| 3 | 10 | 1 | 1.2 | | 0.4 | 123. |
| 0 | 0 | 2 | 171.8 | +* | 180.5 | 180. |
| 1 | 0 | 2 | 9.3 | | 4.3 | 180. |
| 2 | 0 | 2 | 141.0 | +* | 144.4 | 0. |
| 3 | 0 | 2 | 0.9 | $ | 3.2 | 0. |
| 4 | 0 | 2 | 92.7 | + | 89.2 | 180. |
| 5 | 0 | 2 | 1.2 | $ | 2.0 | 180. |
| 6 | 0 | 2 | 54.4 | + | 49.3 | 0. |
| 7 | 0 | 2 | 1.5 | $ | 0.9 | 0. |
| 8 | 0 | 2 | 22.0 | | 20.6 | 180. |
| 9 | 0 | 2 | 1.7 | $ | 0.4 | 180. |
| 10 | 0 | 2 | 4.9 | | 5.7 | 0. |
| 11 | 0 | 2 | 1.5 | $ | 0.1 | 0. |
| 0 | 1 | 2 | 0.7 | $ | 3.2 | 90. |
| 1 | 1 | 2 | 88.5 | +* | 96.6 | 269. |
| 2 | 1 | 2 | 2.3 | | 3.3 | 278. |
| 3 | 1 | 2 | 61.4 | + | 62.3 | 88. |
| 4 | 1 | 2 | 2.8 | | 2.2 | 95. |
| 5 | 1 | 2 | 35.0 | | 33.0 | 267. |
| 6 | 1 | 2 | 1.4 | $ | 1.5 | 219. |
| 7 | 1 | 2 | 18.2 | | 17.4 | 85. |
| 8 | 1 | 2 | 1.6 | $ | 1.8 | 23. |
| 9 | 1 | 2 | 8.3 | | 8.7 | 263. |
| 10 | 1 | 2 | 1.7 | $ | 1.2 | 209. |
| 11 | 1 | 2 | 1.9 | | 3.8 | 84. |
| 0 | 2 | 2 | 28.7 | | 23.5 | 180. |
| 1 | 2 | 2 | 2.7 | | 2.6 | 152. |
| 2 | 2 | 2 | 40.1 | | 31.7 | 356. |
| 3 | 2 | 2 | 4.2 | | 2.1 | 305. |
| 4 | 2 | 2 | 34.6 | | 34.1 | 173. |
| 5 | 2 | 2 | 3.6 | | 1.1 | 96. |
| 6 | 2 | 2 | 21.0 | | 22.8 | 354. |
| 7 | 2 | 2 | 1.5 | $ | 1.2 | 282. |
| 8 | 2 | 2 | 12.9 | | 12.3 | 175. |
| 9 | 2 | 2 | 1.7 | $ | 1.2 | 115. |
| 10 | 2 | 2 | 6.8 | | 6.0 | 349. |
| 11 | 2 | 2 | 1.5 | $ | 0.7 | 296. |
| 0 | 3 | 2 | 1.1 | | 0.9 | 90. |
| 1 | 3 | 2 | 32.7 | | 32.5 | 91. |
| 2 | 3 | 2 | 4.4 | | 3.1 | 178. |
| 3 | 3 | 2 | 23.8 | | 22.0 | 277. |
| 4 | 3 | 2 | 4.7 | | 4.5 | 360. |
| 5 | 3 | 2 | 15.6 | | 12.6 | 106. |
| 6 | 3 | 2 | 4.6 | | 3.6 | 199. |
| 7 | 3 | 2 | 9.7 | | 6.8 | 290. |
| 8 | 3 | 2 | 2.2 | | 1.7 | 26. |
| 9 | 3 | 2 | 2.1 | | 3.6 | 113. |
| 10 | 3 | 2 | 1.6 | $ | 0.5 | 171. |
| 0 | 4 | 2 | 45.1 | | 45.2 | 0. |
| 2 | 4 | 2 | 41.8 | | 43.1 | 181. |
| 3 | 4 | 2 | 6.4 | | 3.8 | 262. |
| 4 | 4 | 2 | 35.2 | | 34.7 | 2. |
| 5 | 4 | 2 | 5.8 | | 4.1 | 99. |
| 6 | 4 | 2 | 22.6 | | 21.9 | 184. |
| 7 | 4 | 2 | 3.9 | | 2.9 | 276. |
| 8 | 4 | 2 | 11.7 | | 10.6 | 10. |
| 9 | 4 | 2 | 1.7 | $ | 1.7 | 82. |
| 10 | 4 | 2 | 2.7 | | 3.7 | 187. |
| 0 | 5 | 2 | 1.3 | $ | 1.3 | 270. |
| 1 | 5 | 2 | 71.6 | + | 71.1 | 90. |
| 2 | 5 | 2 | 2.3 | | 1.9 | 160. |
| 3 | 5 | 2 | 54.5 | + | 53.5 | 270. |
| 4 | 5 | 2 | 1.5 | $ | 3.1 | 360. |
| 5 | 5 | 2 | 34.3 | | 33.9 | 91. |
| 6 | 5 | 2 | 1.6 | $ | 3.3 | 172. |
| 7 | 5 | 2 | 19.6 | | 19.7 | 272. |
| 8 | 5 | 2 | 1.7 | $ | 2.7 | 345. |
| 9 | 5 | 2 | 9.4 | | 9.7 | 91. |
| 10 | 5 | 2 | 1.4 | $ | 1.6 | 176. |
| 0 | 6 | 2 | 35.1 | | 32.3 | 0. |
| 1 | 6 | 2 | 1.4 | $ | 1.4 | 19. |
| 2 | 6 | 2 | 32.9 | | 31.8 | 179. |
| 3 | 6 | 2 | 1.5 | $ | 2.0 | 217. |
| 4 | 6 | 2 | 28.6 | | 27.4 | 358. |
| 5 | 6 | 2 | 1.6 | $ | 2.3 | 50. |
| 6 | 6 | 2 | 18.4 | | 18.2 | 176. |
| 7 | 6 | 2 | 1.7 | $ | 2.0 | 246. |
| 8 | 6 | 2 | 8.1 | | 9.3 | 354. |
| 9 | 6 | 2 | 1.5 | $ | 1.6 | 74. |
| 0 | 7 | 2 | 1.6 | $ | 1.3 | 270. |
| 1 | 7 | 2 | 27.0 | | 26.1 | 90. |
| 2 | 7 | 2 | 1.6 | $ | 1.2 | 90. |
| 3 | 7 | 2 | 19.6 | | 19.6 | 267. |
| 4 | 7 | 2 | 1.7 | $ | 1.3 | 270. |
| 5 | 7 | 2 | 9.5 | | 10.8 | 81. |
| 6 | 7 | 2 | 1.7 | $ | 1.2 | 92. |
| 7 | 7 | 2 | 3.2 | | 4.3 | 254. |
| 8 | 7 | 2 | 1.5 | $ | 0.5 | 279. |
| 0 | 8 | 2 | 1.7 | $ | 3.0 | 180. |
| 1 | 8 | 2 | 1.7 | $ | 1.4 | 360. |
| 2 | 8 | 2 | 1.7 | $ | 3.1 | 12. |
| 3 | 8 | 2 | 2.1 | | 1.0 | 176. |
| 4 | 8 | 2 | 1.7 | $ | 3.1 | 206. |
| 5 | 8 | 2 | 1.6 | $ | 1.0 | 334. |
| 6 | 8 | 2 | 1.6 | $ | 2.4 | 31. |
| 7 | 8 | 2 | 1.5 | $ | 1.1 | 126. |
| 0 | 9 | 2 | 1.7 | $ | 0.1 | 90. |
| 1 | 9 | 2 | 17.6 | | 14.7 | 270. |
| 2 | 9 | 2 | 1.7 | $ | 0.8 | 21. |
| 3 | 9 | 2 | 11.4 | | 10.8 | 91. |
| 4 | 9 | 2 | 1.6 | $ | 1.4 | 198. |
| 5 | 9 | 2 | 6.0 | | 6.0 | 272. |
| 0 | 10 | 2 | 11.8 | | 14.1 | 180. |
| 1 | 10 | 2 | 1.5 | $ | 0.7 | 248. |
| 2 | 10 | 2 | 10.6 | | 12.6 | 0. |
| 3 | 10 | 2 | 1.4 | $ | 1.7 | 90. |
| 1 | 0 | 3 | 4.8 | | 3.0 | 90. |
| 2 | 0 | 3 | 4.6 | | 3.6 | 270. |
| 3 | 0 | 3 | 6.6 | | 3.7 | 270. |
| 4 | 0 | 3 | 1.1 | $ | 4.1 | 90. |
| 5 | 0 | 3 | 1.3 | $ | 3.4 | 90. |
| 6 | 0 | 3 | 1.4 | $ | 3.9 | 270. |
| 7 | 0 | 3 | 1.5 | $ | 3.8 | 270. |
| 8 | 0 | 3 | 1.6 | $ | 3.3 | 90. |
| 9 | 0 | 3 | 1.7 | $ | 1.5 | 90. |
| 10 | 0 | 3 | 1.6 | $ | 2.1 | 270. |
| 11 | 0 | 3 | 1.5 | $ | 0.2 | 90. |
| 0 | 1 | 3 | 2. | | 0.6 | 270. |
| 1 | 1 | 3 | 59.1 | + | 53.1 | 92. |
| 2 | 1 | 3 | 2.3 | | 0.8 | 135. |
| 3 | 1 | 3 | 13.4 | | 3.3 | 22. |
| 4 | 1 | 3 | 1.2 | $ | 1.3 | 354. |
| 5 | 1 | 3 | 10.6 | | 13.6 | 103. |
| 6 | 1 | 3 | 1.4 | $ | 2.1 | 178. |
| 7 | 1 | 3 | 30.0 | | 28.4 | 276. |
| 8 | 1 | 3 | 2.2 | | 1.7 | 349. |
| 9 | 1 | 3 | 17.4 | | 13.9 | 98. |
| 10 | 1 | 3 | 1.6 | $ | 0.7 | 149. |
| 11 | 1 | 3 | 2.6 | | 2.8 | 286. |
| 0 | 2 | 3 | 76.6 | + | 73.0 | 0. |
| 1 | 2 | 3 | 1.2 | | 1.2 | 50. |
| 2 | 2 | 3 | 57.1 | + | 59.6 | 181. |
| 3 | 2 | 3 | 1.7 | | 3.2 | 262. |
| 4 | 2 | 3 | 45.9 | | 47.4 | 2. |
| 5 | 2 | 3 | 1.3 | $ | 3.4 | 67. |
| 6 | 2 | 3 | 39.3 | | 39.6 | 182. |
| 7 | 2 | 3 | 1.6 | $ | 2.7 | 236. |
| 8 | 2 | 3 | 23.2 | | 23.4 | 2. |
| 9 | 2 | 3 | 1.7 | $ | 2.5 | 76. |
| 10 | 2 | 3 | 8.3 | | 8.8 | 183. |
| 11 | 2 | 3 | 1.4 | $ | 1.9 | 264. |
| 0 | 3 | 3 | 3.6 | | 2.2 | 270. |
| 1 | 3 | 3 | 66.6 | + | 66.7 | 89. |
| 2 | 3 | 3 | 1.1 | $ | 2.6 | 99. |
| 3 | 3 | 3 | 57.4 | + | 58.0 | 269. |
| 4 | 3 | 3 | 3.3 | | 3.0 | 281. |
| 5 | 3 | 3 | 35.4 | | 32.0 | 88. |
| 6 | 3 | 3 | 1.5 | $ | 2.3 | 93. |
| 7 | 3 | 3 | 15.8 | | 15.7 | 264. |
| 8 | 3 | 3 | 1.7 | $ | 1.1 | 284. |
| 9 | 3 | 3 | 10.1 | | 11.1 | 85. |
| 10 | 3 | 3 | 1.6 | $ | 0.8 | 146. |
| 0 | 4 | 3 | 33.3 | | 34.1 | 0. |
| 1 | 4 | 3 | 1.4 | | 2.5 | 16. |
| 2 | 4 | 3 | 33.6 | | 35.5 | 177. |
| | 4 | 3 | 1.3 | $ | 3.4 | 212. |
| 4 | 4 | 3 | 32.4 | | 29.9 | 356. |
| 5 | 4 | 3 | 2.4 | | 2.9 | 40. |
| 6 | 4 | 3 | 19.5 | | 18.8 | 174. |
| 7 | 4 | 3 | 1.7 | $ | 1.2 | 209. |
| 8 | 4 | 3 | 9.8 | | 11.2 | 351. |
| 9 | 4 | 3 | 1.6 | $ | 0.8 | 335. |
| 10 | 4 | 3 | 4.1 | | 5.9 | 171. |
| 0 | 5 | 3 | 1.3 | $ | 3.7 | 270. |
| 1 | 5 | 3 | 7.7 | | 5.6 | 79. |
| 2 | 5 | 3 | 1.4 | $ | 3.2 | 70. |
| 3 | 5 | 3 | 8.4 | | 7.8 | 250. |
| 4 | 5 | 3 | 1.5 | $ | 1.9 | 234. |
| 5 | 5 | 3 | 3.2 | | 5.1 | 62. |
| 6 | 5 | 3 | 1.7 | $ | 1.5 | 31. |
| 7 | 5 | 3 | 1.7 | $ | 1.5 | 165. |
| 8 | 5 | 3 | 1.7 | $ | 1.8 | 203. |
| 9 | 5 | 3 | 1.6 | $ | 1.5 | 323. |
| 0 | 6 | 3 | 19.2 | | 18.9 | 189. |
| 1 | 6 | 3 | 1.5 | $ | 1.1 | 316. |
| 2 | 6 | 3 | 13.0 | | 13.3 | 4. |
| 3 | 6 | 3 | 2.4 | | 1.9 | 104. |
| 4 | 6 | 3 | 7.3 | | 5.8 | 192. |
| 5 | 6 | 3 | 1.7 | $ | 1.7 | 275. |
| 6 | 6 | 3 | 7.3 | | 5.4 | 14. |
| 7 | 6 | 3 | 1.7 | $ | 1.3 | 108. |
| 8 | 6 | 3 | 4.7 | | 5.4 | 194. |
| 9 | 6 | 3 | 1.4 | $ | 1.0 | 296. |
| 0 | 7 | 3 | 1.6 | $ | 0.5 | 90. |
| 1 | 7 | 3 | 28.3 | | 26.9 | 270. |
| 2 | 7 | 3 | 1.6 | $ | 2.2 | 353. |
| 3 | 7 | 3 | 24.3 | | 22.6 | 91. |
| 4 | 7 | 3 | 1.7 | $ | 3.5 | 181. |
| 5 | 7 | 3 | 18.1 | | 15.2 | 273. |
| 6 | 7 | 3 | 2.6 | | 2.8 | 2. |
| 7 | 7 | 3 | 9.6 | | 8.9 | 96. |
| 8 | 7 | 3 | 1.9 | | 1.3 | 186. |
| 0 | 8 | 3 | 9.8 | | 11.2 | 180. |
| 1 | 8 | 3 | 1.7 | $ | 0.9 | 222. |
| 2 | 8 | 3 | 12.1 | | 12.7 | 360. |
| 3 | 8 | 3 | 1.7 | $ | 1.9 | 65. |
| 4 | 8 | 3 | 15.4 | | 14.4 | 181. |
| 5 | 8 | 3 | 1.6 | $ | 2.2 | 258. |
| 6 | 8 | 3 | 10.8 | | 11.7 | 1. |
| 7 | 8 | 3 | 1.4 | $ | 1.7 | 82. |
| 0 | 9 | 3 | 1.6 | $ | 0.8 | 90. |
| 1 | 9 | 3 | 14.7 | | 12.3 | 269. |
| 2 | 9 | 3 | 1.6 | $ | 0.9 | 269. |
| 3 | 9 | 3 | 10.3 | | 10.5 | 87. |
| 4 | 9 | 3 | 1.5 | $ | 0.9 | 118. |
| 5 | 9 | 3 | 6.8 | | 8.2 | 267. |
| 0 | 10 | 3 | 2.1 | | 2.3 | 180. |
| 1 | 10 | 3 | 1.5 | $ | 1.0 | 169. |
| 2 | 10 | 3 | 3.0 | | 3.7 | 352. |
| 0 | 0 | 4 | 32.5 | | 43.2 | 0. |
| 1 | 0 | 4 | 5.7 | | 4.7 | 0. |
| 2 | 0 | 4 | 101.2 | + | 91.5 | 180. |
| 3 | 0 | 4 | 4.9 | | 4.2 | 180. |
| 4 | 0 | 4 | 91.4 | + | 86.4 | 0. |
| 5 | 0 | 4 | 1.4 | $ | 3.1 | 0. |
| 6 | 0 | 4 | 17.9 | | 16.8 | 180. |
| 7 | 0 | 4 | 1.6 | $ | 1.7 | 180. |
| 8 | 0 | 4 | 8.4 | | 3.0 | 180. |
| 9 | 0 | 4 | 1.7 | $ | 0.6 | 0. |
| 10 | 0 | 4 | 1.6 | $ | 6.4 | 180. |
| 0 | 1 | 4 | 3.3 | | 4.2 | 270. |
| 1 | 1 | 4 | 48.2 | + | 53.4 | 90. |
| 2 | 1 | 4 | 5.0 | | 3.8 | 96. |
| 3 | 1 | 4 | 56.0 | + | 56.2 | 268. |
| 4 | 1 | 4 | 2.4 | | 3.1 | 236. |
| 5 | 1 | 4 | 31.7 | | 35.7 | 84. |
| 6 | 1 | 4 | 3.6 | | 1.4 | 92. |
| 7 | 1 | 4 | 12.6 | | 14.4 | 261. |
| 8 | 1 | 4 | 1.7 | $ | 0.7 | 295. |
| 9 | 1 | 4 | 5.9 | | 6.6 | 82. |
| 10 | 1 | 4 | 1.6 | $ | 1.5 | 15. |
| 0 | 2 | 4 | 46.3 | | 44.5 | 0. |
| 1 | 2 | 4 | 1.1 | $ | 2.4 | 359. |
| 2 | 2 | 4 | 9.6 | | 9.6 | 170. |
| 3 | 2 | 4 | 3.5 | | 2.1 | 138. |
| 4 | 2 | 4 | 11.2 | | 7.2 | 213. |
| 5 | 2 | 4 | 4.4 | | 1.9 | 303. |
| 6 | 2 | 4 | 17.6 | | 15.7 | 166. |
| 7 | 2 | 4 | 1.6 | $ | 0.9 | 161. |
| 8 | 2 | 4 | 15.3 | | 13.5 | 349. |
| 9 | 2 | 4 | 1.7 | $ | 0.7 | 334. |
| 10 | 2 | 4 | 1.6 | $ | 2.1 | 134. |
| 0 | 3 | 4 | 1.2 | $ | 0.3 | 270. |
| 1 | 3 | 4 | 3.3 | | 4.6 | 287. |
| 2 | 3 | 4 | 3.0 | | 2.3 | 5. |
| 3 | 3 | 4 | 16.3 | | 14.9 | 104. |
| 4 | 3 | 4 | 5.9 | | 3.1 | 185. |
| 5 | 3 | 4 | 10.8 | | 8.3 | 301. |
| 6 | 3 | 4 | 4.8 | | 2.9 | 10. |
| 7 | 3 | 4 | 1.7 | $ | 3.5 | 184. |
| 8 | 3 | 4 | 1.7 | $ | 1.5 | 203. |
| 9 | 3 | 4 | 2.9 | | 2.5 | 333. |
| 10 | 3 | 4 | 1.5 | $ | 0.5 | 61. |
| 0 | 4 | 4 | 42.2 | | 41.1 | 180. |
| 1 | 4 | 4 | 2.9 | | 1.5 | 216. |
| 2 | 4 | 4 | 40.1 | | 36.3 | 3. |
| 3 | 4 | 4 | 4.4 | | 2.3 | 79. |
| 4 | 4 | 4 | 27.8 | | 27.7 | 185. |
| 5 | 4 | 4 | 5.4 | | 3.1 | 273. |
| 6 | 4 | 4 | 16.4 | | 16.6 | 9. |
| 7 | 4 | 4 | 1.7 | $ | 2.5 | 97. |
| 8 | 4 | 4 | 7.0 | | 6.3 | 200. |
| 9 | 4 | 4 | 1.6 | $ | 1.0 | 282. |
| 10 | 4 | 4 | 1.4 | $ | 2.6 | 25. |
| 0 | 5 | 4 | 2.9 | | 1.8 | 90. |
| 1 | 5 | 4 | 35.0 | | 33.9 | 271. |
| 2 | 5 | 4 | 3.1 | | 2.1 | 314. |
| 3 | 5 | 4 | 37.0 | | 35.4 | 91. |
| 4 | 5 | 4 | 1.6 | $ | 2.3 | 158. |
| 5 | 5 | 4 | 26.5 | | 27.5 | 271. |
| 6 | 5 | 4 | 1.7 | $ | 2.7 | 349. |
| 7 | 5 | 4 | 12.6 | | 12.9 | 91. |
| 8 | 5 | 4 | 1.6 | $ | 2.6 | 171. |
| 9 | 5 | 4 | 4.7 | | 5.0 | 271. |
| 0 | 6 | 4 | 35.7 | | 33.1 | 180. |
| 1 | 6 | 4 | 2.9 | | 1.4 | 192. |
| 2 | 6 | 4 | 27.0 | | 26.2 | 359. |
| 3 | 6 | 4 | 1.6 | $ | 1.7 | 10. |
| 4 | 6 | 4 | 16.5 | | 16.2 | 176. |
| 5 | 6 | 4 | 1.7 | $ | 1.8 | 191. |
| 6 | 6 | 4 | 12.2 | | 12.1 | 352. |

## Table 1 (cont.)

```
7 6 4   1.6 S   1.9  43.      3 0 6   5.5   3.4  0.      1 4 7   1.9   2.3  8.      2 3 9   1.7 S  0.7 270.
8 6 4   4.7    8.1 171.       4 0 6  35.2  34.7 180.     2 4 7   9.1   8.0 172.     3 3 9   4.8   4.4  87.
0 7 4   1.7 S  2.4  90.       5 0 6   1.6 S  2.3 180.     3 4 7   1.7 S  1.8 193.    4 3 9   1.7 S  0.8  82.
1 7 4  19.9   19.4 268.       6 0 6  11.4   13.0  0.      4 4 7   3.9   7.1 344.     5 3 9   2.7   3.9 261.
2 7 4   1.7 S  2.3 283.       7 0 6   1.7 S  1.0  0.      5 4 7   1.7 S  1.4  1.      6 3 9   1.5 S  0.7 281.
3 7 4   8.6    9.4  77.       8 0 6   5.2   3.3 180.      6 4 7   3.4   5.6 163.     0 4 9   0.9   0.9 180.
4 7 4   1.7 S  1.9 100.       9 0 6   1.6 S  0.3 180.     7 4 7   1.6 S  1.1 170.    1 4 9   1.7 S  0.8 192.
5 7 4   1.9    4.6 239.      10 0 6   4.5   2.3  0.       8 4 7   3.1   3.1 344.     2 4 9   1.9   3.4 355.
6 7 4   1.6 S  1.4 270.      10 1 6   3.2   2.8  90.      0 5 7   1.7 S  1.5 270.    3 4 9   1.6 S  0.9  13.
7 7 4   1.5 S  5.0  70.       1 1 6  23.0  23.9 268.      1 5 7   1.7 S  4.1  85.    4 4 9   1.6 S  2.4 164.
0 8 4   3.0    1.3  0.        2 1 6   3.9   2.7 292.      2 5 7   1.7 S  1.5 107.    5 4 9   1.5 S  0.8 177.
1 8 4   1.7 S  1.6 183.       3 1 6  21.5  21.5  85.      3 5 7   1.9   1.7 237.     6 4 9   1.4 S  1.7 332.
2 8 4   1.7 S  1.6 221.       4 1 6   2.7   2.0  96.      4 5 7   1.7 S  1.2 273.    0 5 9   1.6 S  1.1  90.
3 8 4   2.1    1.4 357.       5 1 6  13.7  14.8 261.      5 5 7   1.9   1.3  19.     1 5 9   1.6 S  1.8 262.
4 8 4   1.6 S  2.3  43.       6 1 6   1.6 S  1.6 266.     6 5 7   1.6 S  0.7 66.     2 5 9   1.6 S  1.0 292.
5 8 4   1.6 S  1.2 152.       7 1 6   7.7   7.5  78.      7 5 7   1.8   1.5 216.     3 5 9   1.6 S  0.6  3.
6 8 4   1.5 S  2.1 220.       8 1 6   1.7 S  0.8  66.     0 6 7   1.7 S  3.9 180.    4 5 9   1.5 S  0.6 123.
0 9 4   1.6 S  0.5  90.       9 1 6   2.0   3.3 255.      1 6 7   1.7 S  0.7 331.    5 5 9   1.4 S  0.7 167.
1 9 4  11.2   10.0  92.       0 2 6  16.4  15.5 180.      2 6 7   4.6   4.6  6.      0 6 9   0.9   0.8  0.
2 9 4   1.6 S  0.7 223.       1 2 6   1.4 S  1.9 182.     3 6 7   1.7 S  0.9 129.    1 6 9   1.5 S  0.4 157.
3 9 4   8.9    9.0 274.       2 2 6   9.3  10.9 349.      4 6 7   5.0   4.4 191.     2 6 9   3.2   2.1 186.
4 9 4   1.5 S  0.8  25.       3 2 6   1.5 S  1.3 342.     5 6 7   1.6 S  0.8 298.    3 6 9   1.5 S  0.4 287.
1 0 5   2.0    2.4 270.       4 2 6   7.9   7.8 158.      6 6 7   3.5   2.1 28.      0 8 10 12.1  12.3 180.
2 0 5   1.2 S  3.5  90.       5 2 6   1.6 S  1.3 135.     0 7 7   1.6 S  0.4  90.    1 8 10   3.2   1.0 180.
3 0 5   1.5 S  3.1  90.       6 2 6  10.3   9.0 339.      1 7 7   9.3   7.5 271.     2 8 10   7.7   8.0  0.
4 0 5   1.4 S  3.7 270.       9 2 6   1.6 S  0.5 139.     2 7 7   1.0   1.0 340.     3 8 10   1.6 S  0.7  0.
5 0 5   1.5 S  2.9 270.       0 3 6   1.4 S  0.1 270.     3 7 7   6.4   5.7  93.     4 0 10   5.6   2.7 180.
6 0 5   1.6 S  3.5  90.       1 3 6  14.5   9.5  96.      4 7 7   1.5 S  1.1 170.    5 0 10   1.5 S  0.4 180.
7 0 5   1.6 S  3.5  90.       2 3 6   2.4   1.7 190.      5 7 7   4.0   3.9 278.     6 0 10   1.4 S  1.6  0.
8 0 5   1.7 S  3.2 270.       3 3 6   9.3   8.3 286.      0 8 7   4.6   3.3 180.     0 1 10   1.7 S  0.7  90.
9 0 5   1.7 S  1.2 270.       4 3 6   4.0   1.9  14.      1 8 7   1.5 S  0.6 209.    1 1 10   2.8   2.7 263.
10 0 5   1.5 S  2.1  90.      5 3 6   1.6 S  5.3 121.     2 8 7   3.9   3.5  4.      2 1 10   1.7 S  0.8 300.
0 1 5   2.1    0.5  90.       6 3 6   1.7 S  1.4 184.     3 8 7   1.4 S  0.8  70.    3 1 10   2.0   2.4  75.
1 1 5  20.7   24.7 274.       7 3 6   2.1   3.6 326.      0 0 8  37.3  35.2  0.      4 1 10   1.6 S  0.8 143.
2 1 5   3.5    0.8 350.       3 3 6   1.6 S  0.8  25.     1 0 8   5.3   1.8  0.      5 1 10   1.9   2.0 256.
3 1 5  21.0    7.4 241.       9 3 6   1.5 S  2.5 152.     2 0 8  21.1  20.4 180.     6 1 10   1.4 S  0.3 311.
4 1 5   2.2    0.3 204.       0 4 6  17.9  18.7  0.       3 0 8   2.8   1.6 180.     0 2 10   1.7 S  0.6 180.
5 1 5  15.5    9.9 291.       1 4 6   2.2   1.2  54.      4 0 8   8.6   7.1  0.      1 2 10   1.7 S  0.4 168.
6 1 5   1.6 S  0.7 343.       2 4 6  17.0  16.8 186.      5 0 8   1.2   1.2  0.      2 2 10   1.7 S  1.8 342.
7 1 5  27.5   23.3  97.       3 4 6   1.6 S  2.1 257.     6 0 8  11.4  10.1 180.     3 2 10   1.6 S  0.3 351.
8 1 5   1.7 S  1.2 157.       4 4 6  13.6  12.5  13.      7 0 8   1.6 S  0.7 180.    4 2 10   1.6 S  2.5 161.
9 1 5   9.5   10.4 281.       5 4 6   2.0   2.0  87.      8 0 8   7.6   6.8  0.      5 2 10   1.5 S  0.2 183.
10 1 5   1.5 S  0.7 324.      6 4 6   3.0   7.5 197.      0 1 8   3.2   1.9 270.     0 3 10   1.6 S  0.1  90.
0 2 5   57.4 + 59.3 180.      7 4 6   1.7 S  1.6 286.     1 1 8  12.4  11.5  85.     1 3 10   1.6 S  2.0  96.
1 2 5   3.5    1.3 181.       8 4 6   1.9   3.6  23.      2 1 8   1.6 S  1.8 111.    2 3 10   1.6 S  0.5 179.
2 2 5  40.2   42.3  1.        9 4 6   1.4 S  1.0 122.     3 1 8   5.5   4.9 251.     3 3 10   1.6 S  1.3 299.
3 2 5   3.0    2.3  48.       0 5 6   1.6 S  0.8 270.     4 1 8   1.7 S  1.6 310.    4 3 10   1.5 S  0.6  3.
4 2 5  24.6   23.2 184.       1 5 6  21.4  20.8  91.      5 1 8   2.1   2.2  61.     5 3 10   1.4 S  1.1 143.
5 2 5   1.5 S  2.6 244.       2 5 6   2.6   1.2 120.      6 1 8   1.7 S  0.7  84.    0 4 10   4.0   3.1  0.
6 2 5  21.5   19.1  4.        3 5 6  22.0  20.0 272.      7 1 8   1.6 S  2.3 250.    1 4 10   1.6 S  0.5  30.
7 2 5   1.7 S  1.7  59.       4 5 6   1.7 S  1.6 312.     8 1 8   1.5 S  0.8 206.    2 4 10   1.8   2.5 186.
8 2 5  12.8   13.4 182.       5 5 6  16.3  15.2  92.      0 2 8   2.0   0.8 354.     3 4 10   1.5 S  0.7 258.
9 2 5   1.6 S  1.9 240.       6 5 6   1.7 S  1.6 159.     1 2 8   6.9   7.0 168.     4 4 10   1.4 S  1.4  22.
10 2 5   4.1    5.7  2.       7 5 6   6.9   8.3 270.      2 2 8   1.7 S  0.6 191.    0 5 10   1.5 S  0.4 270.
0 3 5   3.2    2.0  90.       8 5 6   1.5 S  1.4 349.     3 2 8  11.5  10.9 352.     1 5 10   3.2   3.0  90.
1 3 5  22.7   24.2 268.       0 6 6  15.5  15.0  0.       4 2 8  11.5  10.9 352.     2 5 10   1.5 S  0.2  96.
2 3 5   2.8    2.2 264.       1 6 6   2.0   1.5 356.      5 2 8   1.7 S  0.5  5.     1 0 11   1.6 S  0.3  90.
3 3 5  33.6   33.3  87.       2 6 6  12.8  12.9 177.      6 2 8   1.7 S  4.4 161.    2 0 11   1.5 S  0.3 270.
4 3 5   2.7    2.2 101.       3 6 6   1.7 S  1.2 182.     7 2 8   1.6 S  0.5 124.    3 0 11   1.5 S  0.6 270.
5 3 5  24.6   24.3 267.       4 6 6   7.5   9.1 352.      8 2 8   1.8   2.0 319.     4 0 11   1.4 S  0.4  90.
6 3 5   1.6 S  1.8 273.       5 6 6   1.7 S  1.2  24.     0 3 8   1.8   2.0 270.     0 1 11   1.6 S  0.1  90.
7 3 5  11.4   12.3  86.       6 6 6   5.2   6.2 168.      1 3 8   8.6   8.8 274.     1 1 11   1.8   0.1 187.
8 3 5   1.7 S  1.4  88.       7 6 6   1.5 S  1.3 217.     2 3 8   1.7 S  1.1  0.     2 1 11   1.5 S  0.1 214.
9 3 5   7.6    7.6 264.       0 7 6   1.7 S  1.8 270.     3 3 8   1.7 S  3.9 114.    3 1 11   1.8   0.4  55.
10 3 5   1.4 S  0.8 296.      1 7 6   8.6  10.5  86.      4 3 8   1.7 S  1.3 190.    4 1 11   1.4 S  0.1 331.
0 4 5  31.6   29.5 180.       2 7 6   1.7 S  1.8  95.     5 3 8   1.7 S  2.8 310.    0 2 11   1.5 S  0.1  9.
1 4 5   1.6    3.4 188.       3 7 6   6.6   7.0 256.      6 3 8   1.6 S  0.7  20.    1 2 11   1.5 S  0.1 309.
2 4 5  25.6   25.5 355.       4 7 6   1.6 S  1.6 271.     7 3 8   1.9   2.8 126.     2 2 11   1.5 S  1.6 185.
3 4 5   1.9    2.8  20.       5 7 6   3.6   4.0  64.      0 4 8   7.3   5.3 180.     3 2 11   1.5 S  0.2 105.
4 4 5  16.6   15.7 170.       6 7 6   1.5 S  1.3  84.     1 4 8   3.8   0.8 226.     3 3 11   1.5 S  0.1 270.
5 4 5   2.1    2.4 201.       0 8 6   2.3   1.3 18C.      2 4 8   4.7   1.4  76.     1 3 11   1.3 S  2.2  87.
6 4 5   8.5    8.4 345.       1 8 6   1.6 S  1.4  5.      3 4 8   1.7 S  1.4  76.    2 3 11   1.4 S  0.2  49.
7 4 5   1.7 S  1.6  6.        2 8 6   1.7   1.7  43.      4 4 8   4.1   3.6 203.
8 4 5   9.9    6.0 167.       3 8 6   1.5 S  1.2 182.     5 4 8   1.6 S  1.2 270.
9 4 5   1.5 S  0.8 158.       4 8 6   2.4   1.9 227.      6 4 8   1.6 S  3.0  28.
0 5 5   1.5 S  2.5  90.       0 9 6   1.4 S  0.6 270.     7 4 8   1.5 S  0.8 107.
1 5 5   3.2    0.8 184.       1 9 7   5.8   6.0 271.      0 5 8   2.3   0.7  90.
2 5 5   3.2    2.3 265.       2 0 7   1.4 S  0.7  90.     1 5 8  12.8  13.1 270.
3 5 5   5.1    5.0  69.       3 0 7   1.5 S  1.1  90.     2 5 8   1.7 S  0.6 284.
4 5 5   1.6 S  1.8  84.       4 0 7   1.5 S  1.6 270.     3 5 8   8.6   8.6  92.
5 5 5   3.3    4.6 242.       5 0 7   1.6 S  2.5  90.     4 5 8   1.6 S  0.7 145.
6 5 5   1.7 S  1.1 243.       6 0 7   1.6 S  1.1  90.     5 5 8   4.5   5.5 274.
7 5 5   2.0    1.8 352.       7 0 7   1.7 S  2.8 270.     6 5 8   1.5 S  0.7 346.
8 5 5   1.6 S  1.2  18.       8 0 7   1.7 S  0.0 270.     0 6 8   5.3   2.8 180.
0 6 5  16.2   15.3  0.        9 0 7   1.6 S  2.0  90.     1 6 8   1.6 S  0.7 168.
1 6 5   1.6 S  1.1 143.       0 1 7   1.5 S  0.1 270.     2 6 8   3.9   4.1 353.
2 6 5   8.1    8.9 183.       1 1 7   1.5 S  0.1 270.     3 6 8   1.6 S  0.8  1.
3 6 5   1.7 S  1.7 300.       2 1 7   7.3   1.8 108.      4 6 8   4.3   4.9 172.
4 6 5   1.9    1.7  49.       3 1 7   1.5 S  1.2 181.     5 6 8   1.5 S  0.9 205.
5 6 5   1.7 S  1.5 115.      10 1 7  10.8  11.8 279.      0 7 8   1.5 S  1.0  90.
6 6 5   2.7    2.8 215.       4 1 7   1.6 S  1.8  1.      1 7 8   3.3   4.4 244.
7 6 5   1.6 S  0.8 290.      11 1 7   9.4  10.6 106.      2 7 8   1.5 S  1.0 260.
8 6 5   3.7    3.9  19.       5 1 7   1.7 S  1.6 172.     3 7 8   3.7   5.1  78.
0 7 5   1.7 S  0.5 270.       6 1 7   3.0   3.9 299.      1 0 9   1.7 S  0.2 270.
1 7 5  16.0   13.6  90.       8 1 7   1.6 S  1.0 341.     2 0 9   1.7 S  0.1  90.
2 7 5   1.7 S  1.7 163.       9 1 7   1.5 S  3.9 108.     3 0 9   1.7 S  1.1  90.
3 7 5  10.4   13.8 272.       0 2 7   9.8  10.3  0.       4 0 9   1.7 S  1.0 270.
4 7 5   1.7 S  2.3 354.       1 2 7   2.3   1.0 335.      5 0 9   1.7 S  1.0 270.
5 7 5  12.5   10.7  95.       2 2 7  13.5  14.3 183.      6 0 9   1.6 S  1.5  90.
6 7 5   1.6 S  1.8 184.       3 2 7   1.6 S  1.3 141.     7 0 9   1.5 S  0.1 270.
7 7 5   5.9    6.3 278.       4 2 7  16.9  16.4  3.       0 1 9   1.7 S  0.0 270.
0 8 5   8.3    7.7  0.        5 2 7   1.7 S  0.7 346.     2 1 9   3.7 S  0.4 352.
1 8 5   1.7 S  0.0  24.       6 2 7  10.5  11.0 173.      4 1 9   7.0   6.3  98.
2 8 5   7.9    8.3 181.       8 2 7   4.0   5.9  2.       5 1 9   1.7 S  0.9 173.
3 8 5   1.6 S  1.2 245.       9 2 7   1.4 S  0.9  44.     6 1 9   2.9   5.4 285.
4 8 5   7.8    8.7  1.        0 3 7   1.5 S  1.2 270.     0 2 9   1.6 S  0.7 356.
5 8 5   1.5 S  1.6  76.       1 3 7  20.4  21.2  90.      7 1 9   1.5 S  1.2 149.
0 9 5   1.5 S  0.9 270.       2 3 7   1.5 S  1.3  86.     0 2 9   2.4   4.0 180.
1 9 5   7.0    6.3  90.       3 3 7  13.1  13.7 267.      1 2 9   2.1   0.3 116.
2 9 5   1.5 S  0.8  83.       4 3 7   2.1   1.4 279.      2 2 9   5.0   5.9  5.
3 9 5   5.4    6.3 267.       5 3 7   8.0   8.9  83.      3 2 9   1.7 S  0.7 290.
0 0 6  50.1   50.4 180.       6 3 7   1.7 S  1.4 116.     4 2 9   5.9   6.4 183.
1 0 6   8.1    3.6 180.       7 3 7   5.8   6.0 264.      5 2 9   1.6 S  0.6 140.
2 0 6  58.0 + 49.2  0.        0 4 7  10.8   8.8  0.       6 2 9   1.9   3.5  3.
                                                          7 2 9   1.4 S  0.6  30.
                                                          0 3 9   1.6 S  0.7 180.
                                                          1 3 9   1.7 S  0.7  90.
                                                          5.7   4.4 270.
```

structure has already been refined to a fair degree of accuracy. This condition is satisfied in the present case as the R value has already reached 0·139. It is also desirable that the subtracted part is small compared to the total structure. In the first calculation, atoms C(1),

C(4), C(7), N(2), C(9), C'(9), C(8) and C'(8) were excluded, i.e. nearly 20% of the total number of electrons present in the structure, and the least-squares refinement was carried out on positional parameters only. The R value dropped to 0·106. A second calculation

was done including all the above atoms but excluding C'(6), C'(2), C(6), C(2), C'(1), C'(4), C'(7) and N(1), and the least-squares refinement of the positional parameters with the new $F'_o$ gave $R$ as 0·10. All refined positional parameters were used for the structure-factor calculation which gave an $R$ value of 0·117, when related to the observed structure factors. Observed and calculated structure factors are given in Table 1.

A difference synthesis was made to check the correctness of the final structure. Shifts in atomic positions and changes in thermal parameters were quite clear from the remanent electron-density distribution at the atomic positions. Thermal parameters were corrected by systematically making small changes in their values, and atomic positions corrected by the $n$-shift rule (Buerger, 1967). These corrections were done by taking successive difference syntheses. It was observed in the Fourier and difference-Fourier syntheses that the electron density contours of most of the atoms were ellipsoidal and their principal axes were almost parallel to the crystallographic axes. Therefore, the $b_{ii}$ part of the anisotropic temperature factors was corrected, and $b_{ij}$ $(i \neq j)$ were kept zero. All positional and thermal parameters are listed in Table 2. The final $R$ value is 0·097 for observed reflexions only and 0·13 with unobserved reflexions included. No attempt was made to locate the hydrogen atoms.
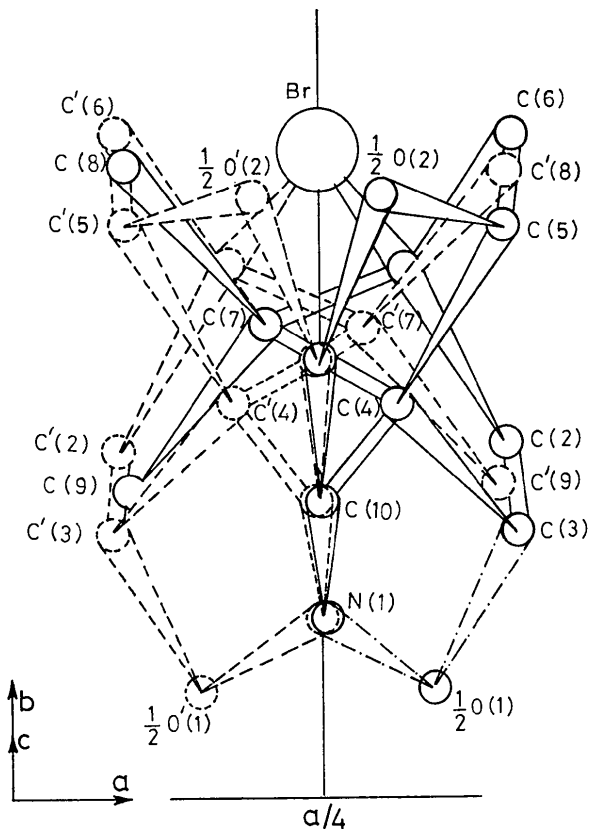
Table 2. *The final atomic parameters in the structure of anhydrobromonitrocamphane*

Anisotropic temperature factors are of the form:

$$\exp - (b_{11}h^2 + b_{22}k^2 + b_{33}l^2 + 2b_{12}hk + 2b_{13}hl + 2b_{23}kl).$$

All values have been multiplied by $10^4$.

| | $x$ | $y$ | $z$ | $b_{11}$ | $b_{22}$ | $b_{33}$ | $b_{12}$ | $b_{13}$ | $b_{23}$ |
|---|---|---|---|---|---|---|---|---|---|
| Br | 2518 | 950 | 2480 | 181 | 155 | 276 | −19 | 33 | 13 |
| C(1) | 2961 | 8956 | 2443 | 100 | 150 | 175 | 0 | 0 | 0 |
| C(2) | 3721 | 8600 | 1291 | 115 | 150 | 185 | 0 | 0 | 0 |
| C(3) | 3810 | 6986 | 1333 | 125 | 170 | 210 | 0 | 0 | 0 |
| C(4) | 2960 | 6647 | 2477 | 140 | 200 | 220 | 0 | 0 | 0 |
| C(5) | 3750 | 7016 | 3650 | 134 | 180 | 220 | 0 | 0 | 0 |
| C(6) | 3775 | 8610 | 3666 | 120 | 160 | 195 | 0 | 0 | 0 |
| C(7) | 1965 | 7886 | 2463 | 155 | 210 | 250 | −46 | −67 | −100 |
| C(8) | 1069 | 7850 | 3690 | 148 | 202 | 243 | 0 | 0 | 0 |
| C(9) | 1040 | 7850 | 1330 | 148 | 202 | 243 | 0 | 0 | 0 |
| C(10) | 2500 | 5114 | 2500 | 180 | 200 | 220 | 0 | 0 | 0 |
| N(1) | 2398 | 4821 | 1269 | 195 | 267 | 176 | 0 | 0 | 0 |
| N(2) | 2420 | 4871 | 3742 | 195 | 267 | 176 | 0 | 0 | 0 |
| O(1) | 3236 | 5907 | 500 | 186 | 226 | 181 | 0 | 0 | 0 |
| O(2) | 3236 | 5932 | 4500 | 186 | 226 | 181 | 0 | 0 | 0 |
| C'(1) | 2028 | 8972 | 2500 | 100 | 150 | 175 | 0 | 0 | 0 |
| C'(2) | 1192 | 8651 | 1333 | 115 | 150 | 185 | 0 | 0 | 0 |
| C'(3) | 1190 | 6986 | 1333 | 125 | 170 | 210 | 0 | 0 | 0 |
| C'(4) | 2084 | 6620 | 2500 | 140 | 200 | 220 | 0 | 0 | 0 |
| C'(5) | 1166 | 7016 | 3666 | 134 | 180 | 220 | 0 | 0 | 0 |
| C'(6) | 1191 | 8610 | 3700 | 115 | 155 | 190 | 0 | 0 | 0 |
| C'(7) | 3131 | 7887 | 2500 | 100 | 110 | 125 | 0 | 0 | 0 |
| C'(8) | 3886 | 7850 | 3697 | 148 | 202 | 243 | 0 | 0 | 0 |
| C'(9) | 3891 | 7850 | 1283 | 148 | 202 | 243 | 0 | 0 | 0 |
| O'(1) | 1726 | 5907 | 500 | 186 | 226 | 181 | 0 | 0 | 0 |
| O'(2) | 1700 | 5907 | 4500 | 224 | 272 | 219 | 0 | 0 | 0 |

Atomic form factors for Br, N, O and C were taken from *International Tables for X-ray Crystallography* (1968).

### Discussion

*The disorder*

The treatment of bromonitrocamphane with sulphuric acid is expected to give a racemic mixture of two optically active forms of anhydrobromonitrocamphane. These two optical isomers correspond to the attachment of the isoxazoline ring to C(3) or to C(5). Also the primed and unprimed molecules, *i.e.* the two configurations of the molecule related by the (100 mirror at $x = 0.25$ are orientations of the two optical isomers. Thus both the optical isomers of anhydrobromonitrocamphane exist in the crystal in two orientations.

The peak heights in the Fourier map suggested that the two configurations of the molecule are almost equally probable. This was further checked by making structure factor calculations with varying occupancy factors. The results are shown in Fig. 4. A similar check was made for the probability of isoxazoline ring attached to C(3) or C(5) in a molecule. The results clearly indicate that each type of site in the crystal is statistically occupied by two optically isomeric forms of the molecule in two orientations. This conclusion is further supported by the fact that long-exposure rotation and Weissenberg photographs did not show any trace of weak superlattice lines which would be expected if one



Fig. 3. A perspective drawing of the asymmetric unit in the crystal. The unprimed orientation of the molecule is shown by full lines and the primed by broken lines.

orientation was favoured over the other. Furthermore, these photographs did not show any weak diffuse layers as in 9-bromo-10-methylanthracene (Prout, 1961), Wolffram's red salt (Craven & Hall, 1961) and anthrone (Srivastava, 1964) which indicates that the disorder is present throughout the crystal.

The disorder is rather unusual, indicating the possibility of some special type of twinning. However, no indications of twinning were found by optical means. The X-ray photographs did not show any strange absences either (Donnay, Donnay and Kullerud, 1958), thus indicating the non-existence of any special twinning or composite structure. The proposed disordered structure is therefore the most reasonable explanation consistent with the experimental observations.

*Bond lengths and angles*

Bond lengths and angles in both orientations of the molecule are calculated from the atomic coordinates given in Table 2. The disorder and the consequent overlapping of peaks severely limited the accuracy of the atomic positions, and therefore, bond lengths and angles of both configurations were averaged. The value of bond lengths to 0·01 Å and angles to 1° are shown in Fig. 5. The averaged bond lengths and angles for the bicyclic ring of the present structure are comparable with those of (+)-10-bromo-2-chloro-2-nitrosocamphane (Ferguson, Fritchie, Robertson & Sim, 1961), (+)-3-bromocamphor (Allen & Rogers, 1966) and (−)-2-bromo-2-nitrocamphane (Brueckner, Hamor, Robertson & Sim, 1962).



Fig. 4. The variation of the *R* value with the occupancy factors, $P_1$ and $P_2$ for primed and unprimed orientations respectively.

The C–Br bond length of 1·93 Å is in good agreement with other structures; 1·93 Å in bromoform (Allen & Sutton, 1950), dibromodichloromethane (Capron & Perlinghi, 1936), 1,3-dibromocyclohexane and 1,4-dibromocyclohexane (Allen & Sutton, 1950); 1·94 Å in methyl bromide (Mays & Dailey, 1952) and 1,2,3,4,tetrabromobutane (Allen & Sutton, 1950). The C(10)–N bond length is 1·33 Å. This bond seems to be a partial double bond and is comparable with 1·34 ± 0·05 Å observed in diazomethane (Boersch, 1935),



Fig. 5. (*a*) Average bond lengths in Å. (*b*) Average bond angles in degrees in the molecule. The values for the isoxazoline ring are averaged over all its four orientations.

1·335 and 1·35 Å in urea (Smith, 1952) and thiourea (Wyckoff & Corey, 1932), 1·32 Å in oxamide (Romers, 1953) and in melamine (Hughes, 1941).

The average C–O distance in the isoxazoline ring is 1·46 Å, which is in good agreement with 1·44 Å in formic acid (Erlandsson, 1953) and in methanol (Allen & Sutton, 1950); 1·47 ± 0·04 Å in methyl chloroformate (O'Gorman, Shand & Schomaker, 1950) and 1·47–1·48 Å in chloral hydrate (Kondo & Nitta, 1950).

The average N–O distance of 1·51 Å observed in the present structure is somewhat longer than the single bond distance of 1·44 Å. This discrepancy may be due to inaccuracy in determining the oxygen positions, each of which has an occupancy factor of ¼.

## Geometry of the molecule and packing

The bond lengths and angles of the bicyclic ring closely conform to these in other similar compounds cited above. The isoxazoline ring is not planar and the
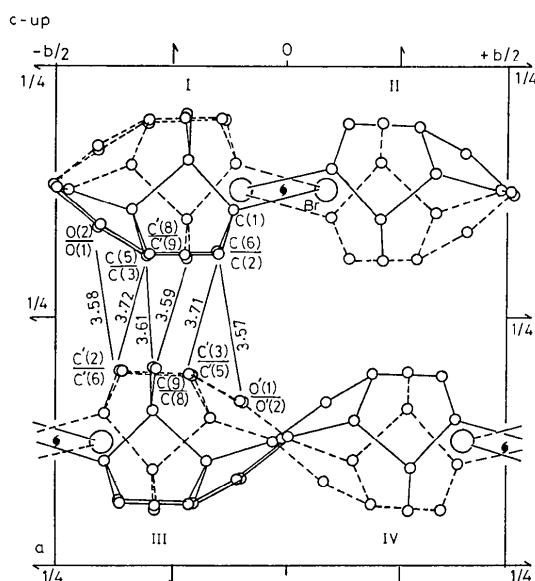
shape can be best understood by looking at the deviations of C(4), C'(4) and all four oxygen positions from the best planes. Equations of these best planes passing through all constituting atoms for all four configurations of isoxazoline ring are given in Table 3. Average deviations of C(4) and C'(4) and oxygens are 0·31 and −0·08 Å.

Figs. 6 and 7 show the packing of both configurations (primed and unprimed) of the molecules in the structure along with the intermolecular contacts. If only one configuration of isoxazoline ring is considered, corresponding to one molecule, then all the intermolecular contacts are greater than 3·5 Å corresponding to normal van der Waals interactions. An unusual approach distance (2·0–2·7 Å) between two neighbouring asymmetric units appears (Fig. 7) when both configurations of the isoxazoline ring for a single molecule are considered.

## Thermal vibrations

The average isotropic temperature factor for the atoms of the molecule is 7·4 Å$^2$ which is certainly a high value and is probably due to the smearing out of electron density as a result of disorder rather than to large thermal movements.

Refined anisotropic temperature factors for all the atoms are listed in Table 2. The anisotropic temperature factors for the Br atom which is not involved in the disorder have been interpreted in terms of the ellipsoids of thermal vibration. The direction cosines of the principal axes of the ellipsoid, relative to the crystal axes, and the root mean square vibrational displacements in Å were calculated for the Br atom using the program written by Dwivedi (1970) and are listed in Table 4.



Fig. 6. A view of the structure along the *c* axis. All the atoms of the asymmetric unit are shown in molecules I and III. The distances of closest approach are shown between the atoms indicated as the denominator for molecule I and the numerator for molecule III.

Table 4. *The direction cosines* ($l_1$, $l_2$, $l_3$) *of the principal axes of the thermal ellipsoids with respect to the crystal axes and the root mean square vibrational displacements in Å for the* Br *atom only*

|     | R.m.s. | $l_1$ | $l_2$ | $l_3$ |
|-----|--------|-------|-------|-------|
| Br  | 0·4114 | +0·3668 | +0·1051 | +0·9243 |
|     | 0·3147 | −0·7998 | +0·5431 | +0·2556 |
|     | 0·2406 | +0·4751 | +0·8331 | −0·2832 |

Table 3. *Equations of the best planes of the four possible orientations of the isoxazoline ring and deviations of the constituting atoms from them*

Equation of plane, $lx + my + nz = p$, where $x$, $y$, $z$ are the coordinates of a point on the plane, $p$ is the perpendicular distance of the plane from the origin and $l$, $m$, $n$ are the direction cosines of the normal.

| Plane through | $l$ | $m$ | $n$ | $p$ | Constituting atoms and their deviations in Å | | |
|---------------|-----|-----|-----|-----|-----|-----|-----|
| C(10), N(1), C(3), C(4), O(1) | −0·8047 | 0·5839 | −0·1069 | 0·6383 Å | C(10) −0·195 | N(1) −0·132<br>C(4) +0·266 | C(3) −0·128<br>O(1) −0·148 |
| C(10), N(2), C(5), C(4), O(2) | −0·8239 | 0·5647 | 0·0472 | 0·7709 | C(10) −0·065 | N(2) −0·065<br>C(4) +0·355 | C(5) −0·065<br>O(2) −0·160 |
| C(10), N(2), C'(5), C'(4), O'(2) | +0·8288 | 0·5347 | 0·1643 | 5·2169 | C(10) −0·065 | N(2) −0·041<br>C'(4) +0·335 | C'(5) −0·053<br>O'(2) −0·008 |
| C(10), N(1), C'(3), C'(4), O'(1) | +0·8335 | 0·5193 | −0·1793 | 4·2868 | C(10) −0·094 | N(1) −0·094<br>C'(4) +0·282 | C'(3) −0·094<br>O'(1) 0·000 |

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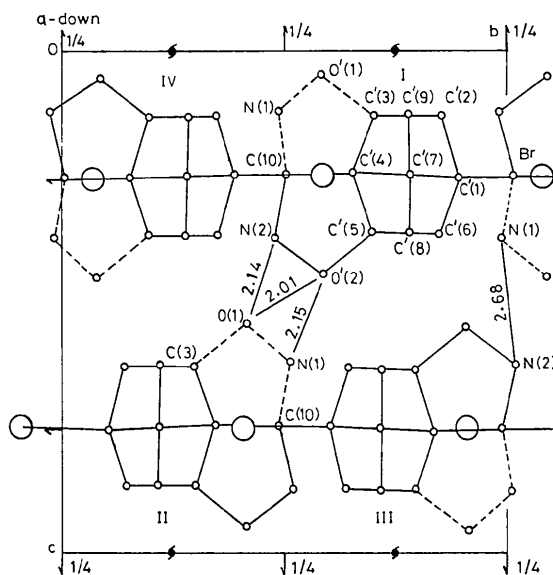WYCKOFF, R. W. G. & COREY, R. B. (1932). *Z. Kristallogr.* **81**, 386.



Fig. 7. A view of the structure along the *a* axis. Only one orientation of the molecule with both its probable isoxazoline rings is shown in figure. The distances of closest approach are shown for an orientation of the isoxazoline ring in which they are shortest.