planes are also given in the Table 4. These are least-squares planes obtained by the method suggested by Schomaker, Waser, Marsh & Bergman (1959). The atoms are co-planar within experimental error.

The $\beta_{ij}$ were used to calculate the displacements along the principal axes. At the same time the principal axes of the atomic ellipsoids and their direction cosines were determined. These data seem compatible with a libration of the carboxyl groups about the carbon–carbon bonds. This is given in Table 5.

I am much indebted to Dr Sankar K. Dutta for suggesting the problem. Thanks are due to my husband, Dr Ranjit Paul, for many suggestions, help in calculations and constant encouragement. Finally I wish to express my gratitude to Dr C. H. Stam and Prof. C. H. MacGillavry for going through the manuscript very carefully and suggesting valuable improvements.

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# The Identification and Crystal Structure of L-5-Methoxycarbonyl-7-formyl-1,2,5,6-tetrahydro-3*H*-pyrrolo[1,2-a]azepin-3-one, $C_{12}H_{13}NO_4$, a Photolysis Product

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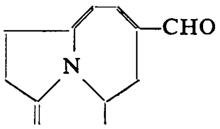
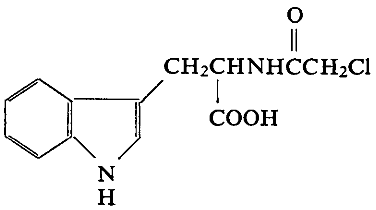
The irradiation of *N*-chloroacetyl-*p*-*O*-methyl-L-tyrosine resulted in the production of an unusual rearrangement product, m.p. 225°. The methyl ester of this product, m.p. 145°, has been identified by an X-ray analysis of its crystal structure to be



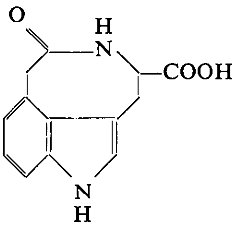
It crystallizes in the orthorhombic system, space group $P2_12_12_1$ with four molecules per unit cell. The cell parameters are $a = 7{\cdot}17$, $b = 10{\cdot}08$, $c = 15{\cdot}99$ Å. A partial structure was obtained by determining phases directly from the structure factor magnitudes by the use of the symbolic addition procedure as applied to noncentrosymmetric crystals. The complete structure evolved by the use of the tangent formula in a recycling procedure.

## Introduction

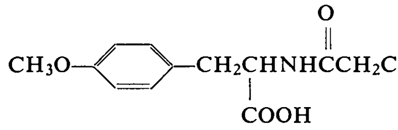
In the study of the effects of irradiation on *N*-chloroacetyl derivatives of amino acids Yonemitsu, Cerutti & Witkop (1966) found that *N*-chloroacetyl-L-tryptophan



undergoes photocyclization to form the tricyclic indole

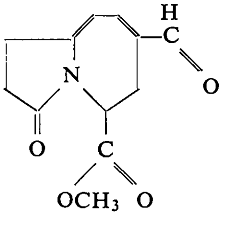


This general preparative method has been applied to other aromatic amino acids. However, when *N*-chloroacetyl-*p*-*O*-methyl-L-tyrosine,



$CH_3O{-}C_6H_4{-}CH_2\underset{COOH}{CH}NH\overset{O}{\overset{\|}{C}}CH_2Cl$,

was subjected to the same process, an unexpected product resulted (Yonemitsu, Witkop & Karle, 1967). It was an acid in the form of a yellow powder, $C_{11}H_{11}NO_4$, m.p. 225°. Reaction with diazomethane formed the methyl ester, $C_{12}H_{13}NO_4$, m.p. 145°, which crystallized in the form of tiny yellow prisms. The purpose of this investigation was to identify the photolysis product. The result of the X-ray analysis shows the unusual product to be



Since the material crystallizes in space group $P2_12_12_1$, the symbolic addition procedure as applied to noncentrosymmetric space groups (Karle & Karle, 1964, 1966*a*) was used for direct phase determination. Initially only a partial structure was obtained. This paper will describe how the remainder of the atoms were located with the use of the tangent formula (Karle & Hauptman, 1956) in a recycling procedure (Karle, 1967).

## Experimental

The crystalline material was supplied by Dr B. Witkop of the National Institutes of Health. The crystal used for the X-ray analysis was a slender prism of size 0·1 × 1·0 × 0·1 mm. It was mounted only parallel to the *b* axis since it was too small to mount along the other axes. Unit-cell parameters were obtained from precession photographs taken with Cu *Kα* radiation. They are:

$$a = 7{\cdot}17 \pm 0{\cdot}02\ \text{Å}$$
$$b = 10{\cdot}08 \pm 0{\cdot}02$$
$$c = 15{\cdot}99 \pm 0{\cdot}03$$
$$\alpha = \beta = \gamma = 90°\ .$$

For four molecules in the unit cell, the computed density is 1·351 g.cm$^{-3}$. Since so little material was available, the density was not measured by flotation. The only systematic absences were for the *h*00, 0*k*0, and 00*l* reflections where *h*, *k*, or *l* are odd. Accordingly the space group is $P2_12_12_1$.

Multiple-film equi-inclination Weissenberg photographs were taken along the *b* axis for the zero through the sixth layer. The exposure time, 40 hours per layer, and the conditions for photographic development, were carefully controlled. The intensities were estimated visually by comparison with a calibrated film strip. Corrections were made for Lorentz and polarization factors. The data were placed on an absolute scale by means of a *K* curve and structure factors $|F|$ and normalized structure factors $|E|$ were computed. The total number of independent data was 990.

## Phase determination

The determination of phases directly from the observed intensities was started in a manner very similar to that used for L-arginine dihydrate and panamine (Karle & Karle, 1964, 1966*b*). The procedure is described in detail in another publication (Karle & Karle, 1966*a*). To initiate the phase determination, the origin was specified by assigning phases to three independent reflections shown in Table 1. Unknown symbols were assigned to several other reflections, as needed, to implement the relationship

$$\varphi_{\mathbf{h}} \approx \langle \varphi_{\mathbf{k}} + \varphi_{\mathbf{h}-\mathbf{k}} \rangle_{\mathbf{k}_r}\ , \qquad (1)$$

which is valid for reflections with large $|E|$ magnitudes. The symbols *a*, *b*, and *c* (Table 1) which were assigned to one- and two-dimensional reflections, are restricted to the values of 0 or $\pi$ according to the requirements of space group $P2_12_12_1$. Symbols *m* and *p* can have any value between 0 and $2\pi$.

Table 1. *Phase assignments for specifying the origin and implementing equation* (1)

| h | $\varphi_{\mathbf{h}}$ | $\lvert E\rvert$ |
|---|---|---|
| 850 | 0 | 3·23 |
| 407 | $+\pi/2$ | 2·32 |
| 540 | $+\pi/2$ | 2·23 |
| 420 | *a* | 2·59 |
| 0012 | *b* | 2·37 |
| 048 | *c* | 2·24 |
| 646 | *m* | 2·32 |
| 557 | *p* | 2·57 |

Equation (1) is used to obtain phases for new reflections from those whose phases are already known. As the procedure progresses, more and more terms can be included in the average for equation (1). Each contributor to a particular phase can be a function of different unknown symbols. In this determination, there were many indications that $a = \pi$ and $b = 2m$ and a few indications that $m = \pm\pi/2$. The indications for *c* were contradictory and those for *p* were complicated combinations of all the other symbols.

The enantiomorph was determined by specifying the sign of a seminvariant, in this case a single phase, $\varphi_{646}$, whose magnitude was close to $\pi/2$. Thus, $m$ was assigned the value $+\pi/2$. The most probable values for the symbols then were: $a=\pi$, $b=\pi$, $m=+\pi/2$, $p=-3\pi/4$ and $c=0$ or $\pi$, giving rise to two possibilities.

The *hkl* reflections with $h$ even had considerably larger $|E|$ magnitudes than those with $h$ odd. Hence it was much easier to obtain phases for those reflections with $h$ even. Forty-seven phases were obtained for reflections with $h$ even and $|E|>1{\cdot}6$ while only 16 phases were determined for reflections with $h$ odd. The tangent formula

$$\tan\varphi_{\mathbf{h}} \simeq \frac{\sum_{\mathbf{k}} |E_{\mathbf{k}}E_{\mathbf{h}-\mathbf{k}}| \sin(\varphi_{\mathbf{k}}+\varphi_{\mathbf{h}-\mathbf{k}})}{\sum_{\mathbf{k}} |E_{\mathbf{k}}E_{\mathbf{h}-\mathbf{k}}| \cos(\varphi_{\mathbf{k}}+\varphi_{\mathbf{h}-\mathbf{k}})} \qquad (2)$$

was then used to refine the initial set of phases and to obtain a total of 238 phases for reflections with $|E|>1{\cdot}2$. Three-dimensional $E$ maps were computed, using these phases for the two most probable choices for the unknown symbols. Neither of these maps appeared to show the molecular structure. Other assignments for the symbols representing phases proved to be even less satisfactory.

A re-examination of the map computed with $a=b=\pi$, $c=0$, $m=+\pi/2$ and $p=-3\pi/4$ showed a partial structure. Five of the six largest peaks appeared to be separated by interatomic distances (Fig. 1, part I). Structure factors were computed on the basis of these five atoms. Phases were accepted if both $|F_c|>\frac{1}{4}|F_o|$ and the corresponding $|E|>1{\cdot}6$. The fifty-eight phases accepted with these criteria were used as initial phases in the tangent formula, equation (2), with which a total of 238 phases were obtained for reflections with $|E|>1{\cdot}2$. An $E$ map computed with these phases reproduced the five original atoms and had five additional strong peaks, all of which were connected by distances and angles of the order usually found in organic molecules (Fig. 1, part II). In retrospect, it was determined that other somewhat weaker peaks also corresponded to atomic positions. However, since the molecular formula of the compound was unknown, it was considered best to use only those peaks which were obviously bonded to each other.

The process was repeated for three more cycles in which initial phases for the reflections with the larger $|E|$ values were obtained from structure factors based on the known atoms. The initial phases were used in conjunction with the tangent formula to obtain about 230 phases for reflections with $|E|>1{\cdot}2$ and $E$ maps were computed based on these phases. The progress in each cycle is shown in Fig. 1. During the whole process the atoms were treated with equal weight. There was no intermediate refinement of atomic positions. As more atoms were added in each cycle, the $R$ index decreased steadily from 64% for five atoms to 28% for seventeen (with $B=3{\cdot}5$). A further description of the procedure for determining a structure from partial structural information by use of the tangent formula will be presented (Karle, 1967). It is interesting to note that there is some correlation between the order of appearance of the atoms and their thermal motions. The three atoms which appeared last have by far the largest thermal motion (Table 2) and also the largest standard deviations.

After all the atoms were located, the original phases obtained from equation (1) were examined in order to determine why the entire structure was not revealed in the first map. Of the 63 initial phases obtained from equation (1), fifteen had errors greater than 1 radian. The following two examples show how errors can arise owing to the need to use single contributors to the average in (1) in the initial stages of the phase determination.

| | | $\lvert E\rvert$ | Symbolic addition | Actual $\varphi$ (radians) | |
|---|---|---|---|---|---|
| (1) | $6\bar{4}\bar{6}$ | 2·32 | $+\pi/2$ | $+1{\cdot}50$ | |
| | $\bar{4}57$ | 2·12 | $-\pi/2$ | $-1{\cdot}51$ | |
| | 211 | 2·11 | 0 | $-0{\cdot}01$ | should have been $-0{\cdot}99$ |
| (2) | $\bar{4}20$ | 2·59 | $\pi$ | 3·14 | |
| | 827 | 2·01 | $-\pi/2$ | $-1{\cdot}24$ | |
| | 447 | 1·93 | $+\pi/2$ | $+1{\cdot}90$ | should have been $+2{\cdot}56$ . |

These errors propagated others which were only partially corrected by use of the tangent formula with the 63 initial phases. Nevertheless, for this nearly equal atom structure, equation (1) applied with the original 63 phases sufficed to yield a correct partial structure.

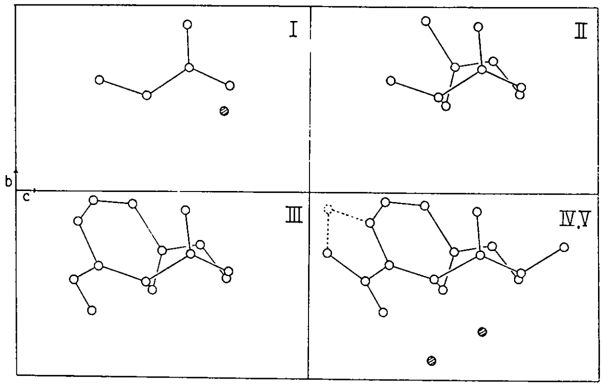


Fig. 1. Part I represents the six largest peaks in the $E$ map computed from the phases obtained from the symbolic addition procedure. The five atoms represented by the open circles were used to obtain initial phases for the tangent formula. A second $E$ map based on the phases resulting from recycling the tangent formula contained ten large peaks shown in part II. A repetition of the procedure yielded fourteen atoms in part III, sixteen atoms in part IV, and seventeen atoms (dotted lines represent last atom obtained) in part V. The dashed circles represent extraneous peaks whose heights were of the same order of magnitude as some of the correct peaks.

## Refinement

One cycle of refinement was performed on the coordinates and isotropic temperature factors with all atoms weighted as carbon atoms. The $B$ values became very small for those five atoms which were the N and four O atoms. These atoms also corresponded to the peaks with the heavier weights in the $E$ maps. With all the atoms labelled properly, several more cycles of refinement with isotropic temperature factors and individual scale factors for each layer resulted in an $R$ value of 12·6%. Several cycles of refinement with anisotropic temperature factors and with the individual scale factors kept constant reduced $R$ to 9·6%. The function minimized was $\Sigma\,(F_o-F_c)^2$ and the atomic scattering factors were taken from *International Tables for Crystallography*. A difference map computed at this stage is shown on the right side of Fig.2. The peaks corresponded to acceptable coordinates for twelve of the thirteen hydrogen atoms. In the vicinity of the position at which the missing hydrogen atom attached to C(2) would be expected to occur, there was an irregular smear of intensity. In addition, there was a spurious peak with intensity comparable to that of the hydrogen atoms. Inclusion of the twelve hydrogen atoms as constant parameters in the least-squares refinement, reduced $R$ to 7·8%.

The observed and calculated $|F|$ values and the phase angles expressed in radians are shown in Table 3. Coordinates and thermal parameters are listed in Table 2. An electron density map based on the phase angles listed in Table 3 is illustrated in Fig.2.

Table 2. *Fractional coordinates* and thermal parameters*

The thermal parameters are defined by $T=\exp\{-(\beta_{11}h^2+\beta_{22}k^2+\beta_{33}l^2+2\beta_{12}hk+2\beta_{13}hl+2\beta_{23}kl)\}$ and each $\beta_{ij}$ is multiplied by $10^4$. The value in parentheses following each parameter is the standard deviation multiplied by $10^4$.

| | $x$ | $y$ | $z$ | $\beta_{11}$ | $\beta_{22}$ | $\beta_{33}$ | $\beta_{12}$ | $\beta_{13}$ | $\beta_{23}$ |
|---|---|---|---|---|---|---|---|---|---|
| O(1) | 1·2799 (11) | 0·1682 (8) | 0·1313 (4) | 285 (18) | 167 (15) | 58 (3) | 59 (14) | 60 (7) | 20 (5) |
| O(2) | 1·1097 (9) | 0·4310 (7) | 0·2903 (4) | 216 (14) | 69 (12) | 47 (3) | −55 (10) | −26 (5) | 4 (4) |
| O(3) | 0·9698 (9) | 0·2795 (6) | 0·3698 (3) | 231 (13) | 80 (9) | 29 (2) | −19 (9) | 0 (5) | −2 (3) |
| O(4) | 0·4857 (10) | 0·2548 (8) | 0·3623 (4) | 248 (15) | 154 (13) | 50 (3) | −13 (12) | 36 (6) | 13 (5) |
| C(1) | 1·0703 (16) | 0·4500 (13) | 0·0362 (5) | 347 (29) | 154 (19) | 34 (3) | −12 (20) | 20 (8) | 17 (6) |
| C(2) | 1·2194 (17) | 0·3451 (13) | 0·0320 (6) | 364 (32) | 173 (21) | 63 (5) | 74 (22) | 84 (11) | 38 (8) |
| C(3) | 1·1870 (14) | 0·2593 (14) | 0·1078 (6) | 224 (22) | 160 (23) | 46 (4) | 19 (17) | 39 (8) | 10 (8) |
| N(4) | 1·0234 (10) | 0·3019 (7) | 0·1455 (3) | 205 (15) | 62 (12) | 27 (2) | 5 (10) | 16 (5) | 0 (4) |
| C(5) | 0·9649 (10) | 0·2404 (8) | 0·2250 (4) | 160 (14) | 38 (13) | 33 (3) | −19 (11) | 12 (6) | 4 (4) |
| C(6) | 0·7520 (12) | 0·2187 (9) | 0·2286 (5) | 185 (16) | 62 (14) | 35 (3) | −41 (12) | −9 (6) | 7 (5) |
| C(7) | 0·6469 (10) | 0·3428 (10) | 0·2439 (5) | 128 (13) | 46 (15) | 41 (3) | 4 (11) | −6 (5) | −11 (5) |
| C(8) | 0·6656 (10) | 0·4547 (10) | 0·1999 (5) | 144 (14) | 57 (15) | 51 (4) | 12 (11) | −13 (6) | 6 (6) |
| C(9) | 0·7909 (12) | 0·4804 (10) | 0·1308 (5) | 209 (19) | 138 (17) | 34 (3) | 7 (14) | −13 (7) | 20 (5) |
| C(10) | 0·9440 (12) | 0·4106 (9) | 0·1086 (5) | 237 (20) | 47 (15) | 32 (3) | −17 (12) | 9 (7) | 9 (5) |
| C(11) | 1·0286 (11) | 0·3315 (11) | 0·2968 (4) | 136 (14) | 69 (17) | 33 (3) | 19 (12) | −10 (6) | 4 (5) |
| C(12) | 1·0111 (20) | 0·3577 (11) | 0·4440 (5) | 479 (37) | 133 (17) | 34 (3) | −46 (23) | −10 (11) | −24 (5) |
| C(13) | 0·5156 (11) | 0·3506 (11) | 0·3188 (6) | 161 (16) | 112 (17) | 48 (4) | −6 (14) | 7 (7) | −5 (6) |

* Coordinates may be substituted directly into equations (3) and (4) representing least-squares planes through parts of the molecule.

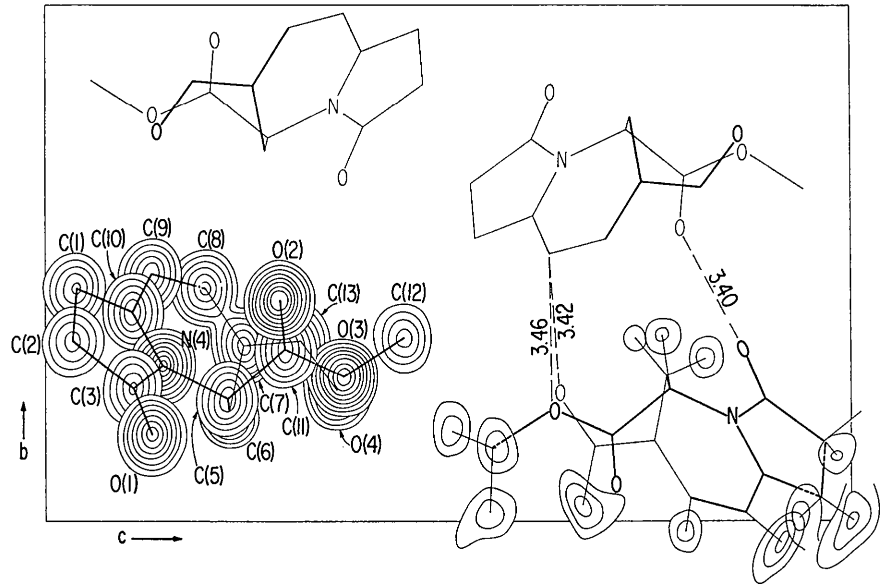


Fig.2. Contents of the unit cell projected down the $a$ axis. On the left-hand side, sections from the final electron density map are plotted. The contours are spaced by 1 e.Å$^{-3}$ beginning with the 1 e.Å$^{-3}$ level. In the difference map on the right-hand side the contours are spaced by 0·1 e.Å$^{-3}$ beginning with the 0·2 e.Å$^{-3}$ level.

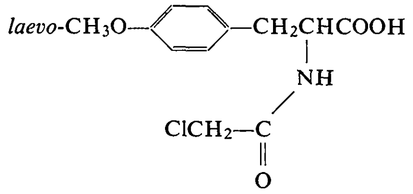
Table 3. *Observed and calculated structure factors*

The columns represent the index $l$, $|F_o|$, $|F_c|$, and $\varphi_{calc}$ (radians).

| | | | |
|---|---|---|---|
| | 0 | 0 | L |
| 2 | 75.5 | 92.9 | -3.14 |
| 4 | 41.7 | 39.3 | -3.14 |
| 6 | 4.3 | 4.2 | 0.00 |
| 8 | 48.0 | 45.0 | 0.00 |
| 10 | 14.6 | 12.2 | -3.14 |
| 12 | 49.6 | 46.0 | -3.14 |
| 14 | 8.7 | 8.8 | 0.00 |
| 16 | 5.6 | 4.1 | 0.00 |
| 18 | 3.3 | 3.9 | -3.14 |
| | 0 | 1 | L |
| 2 | 19.2 | 17.6 | -1.57 |
| 3 | 16.1 | 12.0 | 1.57 |
| 4 | 41.1 | 41.3 | -1.57 |
| 5 | 8.6 | 9.3 | -1.57 |
| 6 | 24.5 | 22.0 | 1.57 |
| 7 | 0.0 | 1.0 | -1.57 |
| 8 | 18.7 | 17.0 | -1.57 |
| 9 | 27.2 | 27.6 | 1.57 |
| 10 | 14.4 | 13.1 | -1.57 |
| 11 | 10.9 | 9.5 | -1.57 |
| 12 | 8.6 | 6.4 | -1.57 |
| 13 | 13.6 | 11.4 | 1.57 |
| 14 | 0.0 | 3.2 | -1.57 |
| 15 | 22.7 | 22.9 | -1.57 |
| 16 | 3.4 | 3.0 | 1.57 |
| 17 | 0.0 | 1.3 | 1.57 |
| 18 | 2.4 | 1.7 | 1.57 |
| | 0 | 2 | L |
| 2 | 47.1 | 48.1 | 0.00 |
| 3 | 14.8 | 16.6 | 0.00 |
| 4 | 40.8 | 45.3 | 0.00 |
| 5 | 31.1 | 28.9 | 0.00 |
| 6 | 0.0 | 0.5 | 0.00 |
| 7 | 30.6 | 30.6 | 0.00 |
| 8 | 52.2 | 51.9 | -3.14 |
| 9 | 2.8 | 1.4 | 3.14 |
| 10 | 24.8 | 24.4 | 0.00 |
| 11 | 14.5 | 14.7 | 0.00 |
| 12 | 1.9 | 1.7 | -0.00 |
| 13 | 5.7 | 4.6 | 3.14 |
| 14 | 9.9 | 9.9 | -3.14 |
| 15 | 7.6 | 6.5 | -3.14 |
| 16 | 2.0 | 0.7 | 3.14 |
| 17 | 0.0 | 1.2 | 0.00 |
| 18 | 0.0 | 0.1 | 3.14 |
| | 0 | 3 | L |
| 1 | 33.4 | 33.9 | 1.57 |
| 3 | 9.7 | 7.9 | 1.57 |
| 4 | 29.1 | 29.0 | 1.57 |
| 5 | 45.5 | 49.1 | -1.57 |
| 6 | 9.7 | 7.2 | -1.57 |
| 7 | 58.2 | 50.2 | 1.57 |
| 8 | 9.6 | 9.1 | 1.57 |
| 9 | 9.0 | 6.4 | -1.57 |
| 10 | 13.3 | 11.2 | -1.57 |
| 11 | 3.2 | 3.7 | -1.57 |
| 12 | 3.4 | 2.6 | 1.57 |
| 13 | 20.6 | 22.5 | -1.57 |
| 14 | 18.8 | 23.1 | 1.57 |
| 15 | 8.3 | 7.5 | 1.57 |
| 16 | 2.7 | 1.9 | -1.57 |
| 17 | 2.5 | 2.0 | -1.57 |
| 18 | 5.3 | 4.8 | -1.57 |
| | 0 | 4 | L |
| 1 | 21.0 | 21.0 | 0.00 |
| 2 | 26.7 | 25.0 | -3.14 |
| 3 | 18.2 | 19.0 | -3.14 |
| 4 | 46.1 | 48.6 | -3.14 |
| 5 | 18.6 | 18.8 | -0.00 |
| 6 | 9.7 | 6.1 | 0.00 |
| 7 | 7.9 | 6.8 | 3.14 |
| 8 | 43.3 | 41.7 | 0.00 |
| 9 | 18.3 | 18.7 | -3.14 |
| 10 | 8.8 | 8.2 | -3.14 |
| 11 | 23.5 | 23.4 | 0.00 |
| 12 | 16.3 | 15.0 | -3.14 |
| 13 | 4.5 | 3.6 | -3.14 |
| 14 | 16.3 | 17.4 | 0.00 |
| 15 | 0.0 | 1.4 | 0.00 |
| 16 | 4.4 | 4.4 | 3.14 |
| 17 | 10.3 | 9.6 | -3.14 |
| 18 | 1.7 | 2.3 | -3.14 |
| 19 | 5.5 | 6.0 | 0.00 |
| | 0 | 5 | L |
| 1 | 6.5 | 7.0 | 1.57 |
| 2 | 13.6 | 13.6 | 1.57 |
| 3 | 6.5 | 7.2 | 1.57 |
| 4 | 4.6 | 2.7 | 1.57 |
| 5 | 25.9 | 25.9 | 1.57 |
| 6 | 10.6 | 8.1 | -1.57 |
| 7 | 44.6 | 45.0 | -1.57 |
| 8 | 15.3 | 15.4 | -1.57 |
| 9 | 5.6 | 1.3 | -1.57 |
| 10 | 16.0 | 15.3 | 1.57 |
| 11 | 10.1 | 10.6 | 1.57 |
| 12 | 7.3 | 6.4 | 1.57 |
| 13 | 9.4 | 9.0 | -1.57 |
| 14 | 0.0 | 0.7 | -1.57 |
| 15 | 5.4 | 7.7 | -1.57 |
| 16 | 7.4 | 8.8 | -1.57 |
| 17 | 6.7 | 5.8 | 1.57 |
| 18 | 4.6 | 3.9 | 1.57 |
| | 0 | 6 | L |
| 1 | 21.1 | 20.8 | 0.00 |
| 2 | 5.4 | 9.1 | 0.00 |
| 3 | 19.2 | 17.5 | 0.00 |
| 4 | 11.8 | 11.5 | 0.00 |
| 5 | 32.4 | 33.3 | -3.14 |
| 6 | 16.4 | 14.9 | 0.00 |
| 7 | 0.0 | 0.9 | -0.00 |
| 8 | 13.0 | 11.2 | -3.14 |
| 9 | 11.3 | 11.9 | 0.00 |
| 10 | 14.5 | 15.5 | -3.14 |
| 11 | 13.0 | 14.2 | 0.00 |
| 12 | 6.6 | 6.2 | 0.00 |
| 13 | 11.1 | 11.8 | -3.14 |
| 14 | 0.0 | 1.3 | 3.14 |
| 15 | 0.0 | 1.8 | -0.00 |
| 16 | 8.7 | 7.4 | 0.00 |
| 17 | 6.4 | 6.6 | 0.00 |
| 18 | 6.7 | 7.5 | -3.14 |
| | 1 | 0 | L |
| 1 | 67.1 | 72.1 | 1.57 |
| 2 | 7.1 | 3.3 | -3.14 |
| 3 | 51.2 | 40.9 | 1.57 |
| 4 | 66.6 | 63.1 | -3.14 |
| 5 | 33.5 | 31.9 | 1.57 |
| 6 | 42.1 | 38.8 | 0.00 |
| 7 | 8.9 | 7.9 | -1.57 |
| 8 | 42.8 | 38.9 | -3.14 |
| 9 | 12.5 | 8.8 | 1.57 |
| 10 | 2.4 | 0.3 | 0.00 |
| 11 | 21.4 | 21.5 | 1.57 |
| 12 | 11.1 | 10.5 | -3.14 |
| 13 | 20.4 | 19.8 | -1.57 |
| 14 | 2.0 | 2.0 | 0.00 |
| 15 | 5.3 | 3.8 | 1.57 |
| 16 | 0.0 | 1.5 | 0.00 |
| 17 | 7.6 | 6.7 | -1.57 |
| 18 | 2.0 | 1.9 | 0.00 |
| 19 | 0.0 | 0.1 | 1.57 |
| | 1 | 1 | L |
| 0 | 24.3 | 21.4 | 1.57 |
| 1 | 27.4 | 24.5 | 2.82 |
| 2 | 42.9 | 41.5 | -2.50 |
| 3 | 67.5 | 75.6 | -1.71 |
| 4 | 53.0 | 51.6 | -1.22 |
| 5 | 40.8 | 42.4 | 0.69 |
| 6 | 28.6 | 26.3 | -0.02 |
| 7 | 42.2 | 42.4 | -2.81 |
| 8 | 25.7 | 24.6 | 2.09 |
| 9 | 7.8 | 8.6 | -0.53 |
| 10 | 5.1 | 3.4 | 2.92 |
| 11 | 12.8 | 13.0 | -1.88 |
| 12 | 1.9 | 1.9 | -0.34 |
| 13 | 6.3 | 5.9 | 0.73 |
| 14 | 15.3 | 15.6 | 3.12 |
| 15 | 9.7 | 10.3 | -0.12 |
| 16 | 8.4 | 9.4 | 1.14 |
| 17 | 1.8 | 1.0 | 2.53 |
| 18 | 4.0 | 3.3 | -0.99 |
| 19 | 2.9 | 3.6 | 0.70 |
| | 1 | 2 | L |
| 0 | 74.1 | 77.6 | -1.57 |
| 1 | 24.0 | 22.3 | -1.68 |
| 2 | 68.9 | 69.9 | -0.45 |
| 3 | 53.6 | 52.0 | 0.33 |
| 4 | 25.9 | 25.6 | 1.92 |
| 5 | 9.9 | 10.8 | 0.79 |
| 6 | 34.3 | 32.5 | 3.14 |
| 7 | 11.7 | 10.1 | 1.01 |
| 8 | 3.7 | 1.7 | -1.75 |
| 9 | 17.1 | 15.3 | 3.08 |
| 10 | 9.8 | 9.9 | -0.01 |
| 11 | 3.7 | 3.6 | -0.56 |
| 12 | 21.5 | 23.1 | 1.15 |
| 13 | 8.6 | 7.5 | 1.39 |
| 14 | 14.1 | 14.3 | -2.52 |
| 15 | 9.1 | 8.9 | -2.51 |
| 16 | 6.1 | 7.2 | 0.41 |
| 17 | 0.0 | 1.3 | -2.74 |
| 18 | 0.0 | 0.8 | -1.96 |
| | 1 | 3 | L |
| 0 | 22.2 | 21.1 | 1.57 |
| 1 | 20.8 | 20.0 | -2.77 |
| 2 | 22.4 | 17.9 | 0.40 |
| 3 | 47.5 | 47.1 | 2.39 |
| 4 | 39.3 | 40.2 | 2.82 |
| 5 | 34.6 | 32.6 | -1.51 |
| 6 | 31.5 | 27.2 | 0.30 |
| 7 | 23.1 | 22.0 | -0.54 |
| 8 | 19.4 | 18.7 | -2.37 |
| 9 | 7.7 | 7.3 | -2.63 |
| 10 | 7.7 | 7.7 | 1.30 |
| 11 | 13.3 | 13.2 | 0.15 |
| 12 | 20.3 | 22.5 | -2.84 |
| 13 | 7.5 | 8.1 | 0.83 |
| 14 | 5.7 | 6.4 | 0.66 |
| 15 | 5.9 | 6.4 | -2.03 |
| 16 | 5.9 | 7.7 | -0.52 |
| 17 | 4.5 | 4.6 | 2.48 |
| 18 | 2.6 | 3.1 | 2.97 |
| | 1 | 4 | L |
| 1 | 26.1 | 22.5 | 2.24 |
| 2 | 16.3 | 15.3 | 0.34 |
| 3 | 31.7 | 30.1 | -0.72 |
| 4 | 40.9 | 39.8 | -1.95 |
| 5 | 31.4 | 30.2 | -3.11 |
| 6 | 29.9 | 28.1 | 1.28 |
| 7 | 23.3 | 21.3 | -0.48 |
| 8 | 10.3 | 10.6 | 0.57 |
| 9 | 21.6 | 20.5 | 2.55 |
| 10 | 19.1 | 17.9 | -0.78 |
| 11 | 1.9 | 2.0 | -1.44 |
| 12 | 11.7 | 9.6 | -2.66 |
| 13 | 4.9 | 4.5 | 1.03 |
| 14 | 15.6 | 17.3 | 1.62 |
| 15 | 0.0 | 0.6 | -1.83 |
| 16 | 4.4 | 4.9 | 0.74 |
| 17 | 0.0 | 1.2 | 1.35 |
| 18 | 6.2 | 6.7 | -1.13 |
| | 1 | 5 | L |
| 0 | 9.0 | 9.4 | 1.57 |
| 1 | 11.9 | 10.7 | 1.48 |
| 2 | 18.5 | 19.2 | -2.98 |
| 3 | 15.4 | 13.7 | 1.61 |
| 4 | 25.7 | 27.9 | -2.65 |
| 5 | 13.8 | 14.4 | -2.16 |
| 6 | 10.4 | 9.2 | 2.02 |
| 7 | 11.9 | 9.9 | 2.45 |
| 8 | 4.1 | 4.4 | 2.03 |
| 9 | 20.4 | 18.2 | 0.33 |
| 10 | 15.6 | 15.0 | -2.85 |
| 11 | 9.9 | 10.1 | 1.18 |
| 12 | 13.3 | 13.4 | -0.50 |
| 13 | 15.8 | 15.5 | -2.41 |
| 14 | 5.7 | 4.9 | 1.92 |
| 15 | 3.1 | 3.2 | 2.76 |
| 16 | 6.9 | 7.8 | 0.71 |
| 17 | 4.6 | 4.8 | 0.66 |
| 18 | 6.0 | 6.0 | -1.11 |
| | 1 | 6 | L |
| 0 | 31.0 | 31.2 | -1.57 |
| 1 | 18.9 | 20.5 | -1.57 |
| 2 | 13.8 | 11.9 | 2.50 |
| 3 | 14.8 | 14.0 | 1.26 |
| 4 | 17.1 | 16.6 | 1.09 |
| 5 | 13.7 | 10.8 | -2.14 |
| 6 | 18.2 | 17.6 | -2.08 |
| 7 | 17.9 | 17.2 | 1.65 |
| 8 | 12.2 | 12.9 | -1.46 |
| 9 | 5.4 | 5.2 | 0.45 |
| 10 | 10.3 | 10.6 | 2.24 |
| 11 | 9.2 | 8.1 | -2.19 |
| 12 | 6.6 | 6.0 | 1.38 |
| 13 | 11.0 | 11.5 | -0.90 |
| 14 | 0.0 | 2.3 | -2.28 |
| 15 | 8.4 | 8.0 | 2.69 |
| 16 | 0.0 | 0.2 | 2.87 |
| 17 | 5.1 | 4.6 | 0.82 |
| | 2 | 0 | L |
| 0 | 69.2 | 73.6 | 0.00 |
| 1 | 18.8 | 14.7 | 1.57 |
| 2 | 16.1 | 12.4 | -3.14 |
| 3 | 25.1 | 21.1 | 1.57 |
| 4 | 26.8 | 22.9 | -3.14 |
| 5 | 4.5 | 4.7 | -1.57 |
| 6 | 30.4 | 26.3 | 0.00 |
| 7 | 19.4 | 16.6 | 1.57 |
| 8 | 11.5 | 10.8 | -3.14 |
| 9 | 13.2 | 11.5 | -1.57 |
| 10 | 5.5 | 6.6 | -3.14 |
| 11 | 0.0 | 1.0 | 1.57 |
| 12 | 10.0 | 8.7 | -3.14 |
| 13 | 0.0 | 1.7 | -1.57 |
| 14 | 9.7 | 8.3 | 0.00 |
| 15 | 4.0 | 4.8 | -1.57 |
| 16 | 0.0 | 0.8 | 0.00 |
| 17 | 0.0 | 1.4 | -1.57 |
| 18 | 0.0 | 1.4 | -3.14 |
| 19 | 0.0 | 2.9 | -1.57 |
| | 2 | 1 | L |
| 0 | 33.8 | 32.8 | -3.14 |
| 1 | 86.4 | 91.8 | -0.99 |
| 2 | 27.3 | 26.7 | 0.96 |
| 3 | 62.4 | 64.3 | 2.19 |
| 4 | 37.2 | 33.9 | -2.59 |
| 5 | 31.1 | 28.9 | 0.09 |
| 6 | 30.1 | 27.8 | 1.18 |
| 7 | 28.1 | 25.1 | -0.55 |
| 8 | 11.1 | 10.2 | -0.17 |
| 9 | 12.6 | 11.3 | -2.15 |
| 10 | 7.2 | 6.0 | -2.38 |
| 11 | 15.9 | 15.6 | 1.18 |
| 12 | 4.4 | 3.2 | -2.93 |
| 13 | 15.2 | 15.1 | 1.93 |
| 14 | 10.7 | 10.2 | -0.97 |
| 15 | 10.9 | 11.4 | -1.26 |
| 16 | 4.3 | 4.0 | 1.37 |
| 17 | 3.5 | 4.8 | -1.65 |
| 18 | 3.3 | 3.1 | 0.98 |
| 19 | 5.8 | 5.7 | 2.29 |
| | 2 | 2 | L |
| 0 | 46.3 | 45.2 | -3.14 |
| 1 | 63.0 | 65.9 | -0.20 |
| 2 | 31.7 | 29.6 | -0.07 |
| 3 | 32.5 | 31.1 | 0.72 |
| 4 | 47.1 | 46.2 | 0.15 |
| 5 | 36.7 | 35.5 | 2.44 |
| 6 | 27.7 | 25.5 | -2.85 |
| 7 | 18.4 | 15.9 | -1.46 |
| 8 | 22.4 | 22.9 | 2.21 |
| 9 | 11.9 | 12.3 | -1.53 |
| 10 | 13.6 | 13.4 | 0.37 |
| 11 | 5.7 | 5.3 | 0.14 |
| 12 | 11.9 | 11.9 | -0.40 |
| 13 | 9.1 | 10.0 | -3.07 |
| 14 | 16.3 | 17.4 | 2.93 |
| 15 | 2.0 | 3.0 | -2.65 |
| 16 | 5.6 | 5.3 | 3.05 |
| 17 | 0.0 | 1.6 | -0.71 |
| 18 | 6.8 | 6.6 | 0.28 |
| | 2 | 3 | L |
| 0 | 41.2 | 41.3 | -3.14 |
| 1 | 37.8 | 35.1 | 2.20 |
| 2 | 40.5 | 37.8 | 0.25 |
| 3 | 15.2 | 15.6 | -1.33 |
| 4 | 38.7 | 36.3 | -2.78 |
| 5 | 37.4 | 37.3 | -1.53 |
| 6 | 47.3 | 48.1 | -1.74 |
| 7 | 32.6 | 29.9 | 1.14 |
| 8 | 13.3 | 13.1 | -0.02 |
| 9 | 25.5 | 24.4 | 2.26 |
| 10 | 5.9 | 7.3 | 1.32 |
| 11 | 12.6 | 12.5 | -0.72 |
| 12 | 15.1 | 17.2 | -0.79 |
| 13 | 8.1 | 7.3 | -2.02 |
| 14 | 10.6 | 10.8 | 2.63 |
| 15 | 0.0 | 2.2 | -1.41 |
| 16 | 4.8 | 5.9 | 1.12 |
| 17 | 4.9 | 4.0 | 2.73 |
| 18 | 3.8 | 3.7 | 0.15 |
| | 2 | 4 | L |
| 0 | 15.3 | 16.0 | 0.00 |
| 1 | 64.7 | 65.9 | 2.74 |
| 2 | 29.8 | 27.8 | -1.43 |
| 3 | 17.1 | 16.8 | -1.59 |
| 4 | 19.3 | 17.9 | 2.25 |
| 5 | 45.3 | 44.6 | -0.16 |
| 6 | 24.3 | 22.7 | 1.03 |
| 7 | 0.0 | 2.0 | -0.48 |
| 8 | 29.3 | 28.9 | 0.34 |
| 9 | 12.4 | 10.7 | 3.10 |
| 10 | 27.1 | 25.8 | -2.43 |
| 11 | 4.4 | 4.8 | 1.31 |
| 12 | 10.4 | 10.1 | 2.40 |
| 13 | 20.8 | 22.6 | -0.32 |
| 14 | 7.8 | 8.9 | -0.26 |
| 15 | 4.1 | 3.6 | 2.31 |
| 16 | 3.8 | 4.2 | -2.85 |
| 17 | 8.9 | 8.3 | -2.87 |
| 18 | 6.8 | 5.3 | -2.79 |
| | 2 | 5 | L |
| 0 | 3.6 | 3.0 | 3.14 |
| 1 | 12.4 | 12.6 | 1.30 |
| 2 | 15.6 | 13.9 | 1.94 |
| 3 | 24.7 | 22.9 | 1.85 |
| 4 | 6.6 | 5.5 | 1.46 |
| 5 | 22.9 | 23.9 | 1.48 |
| 6 | 14.8 | 14.0 | -2.22 |
| 7 | 23.9 | 22.0 | -1.75 |
| 8 | 18.8 | 18.8 | -0.49 |
| 9 | 12.8 | 11.0 | -1.46 |
| 10 | 16.6 | 17.5 | 2.51 |
| 11 | 4.8 | 3.5 | 2.51 |
| 12 | 16.4 | 17.3 | 0.96 |
| 13 | 6.7 | 7.4 | -0.67 |
| 14 | 8.5 | 9.2 | -1.78 |
| 15 | 6.0 | 7.4 | -1.73 |
| 16 | 5.4 | 5.1 | 0.03 |
| 17 | 3.6 | 3.6 | 2.85 |
| 18 | 2.4 | 2.1 | 1.40 |
| | 2 | 6 | L |
| 0 | 22.9 | 21.8 | -3.14 |
| 1 | 16.4 | 14.2 | -0.08 |
| 2 | 16.3 | 14.5 | 1.72 |
| 3 | 3.2 | 2.4 | 0.03 |
| 4 | 19.0 | 18.2 | 0.02 |
| 5 | 12.3 | 12.3 | 2.05 |
| 6 | 1.7 | 3.7 | -0.30 |
| 7 | 13.5 | 12.6 | -1.84 |
| 8 | 25.8 | 27.1 | 2.93 |
| 9 | 18.9 | 21.5 | 0.46 |
| 10 | 9.4 | 7.1 | 0.12 |
| 11 | 0.0 | 2.1 | -2.58 |
| 12 | 5.9 | 7.0 | 0.15 |
| 13 | 5.1 | 5.9 | 2.63 |
| 14 | 3.4 | 2.8 | -2.26 |
| 15 | 8.4 | 7.0 | -0.59 |
| | 3 | 0 | L |
| 1 | 41.5 | 36.6 | 1.57 |
| 2 | 18.7 | 16.4 | 0.00 |
| 3 | 21.3 | 18.5 | -1.57 |
| 4 | 11.0 | 10.4 | -3.14 |
| 5 | 15.6 | 14.3 | 1.57 |
| 6 | 12.2 | 9.2 | 0.00 |
| 7 | 5.1 | 4.1 | -1.57 |
| 8 | 23.3 | 20.7 | -3.14 |
| 9 | 10.9 | 10.3 | 1.57 |
| 10 | 5.3 | 5.7 | 0.00 |
| 11 | 6.1 | 4.8 | -1.57 |
| 12 | 6.3 | 6.5 | 0.00 |
| 13 | 10.0 | 10.6 | -1.57 |
| 14 | 4.9 | 3.9 | -3.14 |
| 15 | 0.0 | 0.5 | 1.57 |
| 16 | 0.0 | 0.1 | -0.00 |
| 17 | 4.4 | 2.3 | 1.57 |
| 18 | 3.8 | 3.6 | -3.14 |
| 19 | 3.8 | 3.7 | -1.57 |
| | 3 | 1 | L |
| 0 | 28.6 | 28.1 | -1.57 |
| 1 | 1.3 | 2.8 | 0.65 |
| 2 | 23.0 | 22.0 | 2.93 |
| 3 | 32.2 | 32.4 | 1.10 |
| 4 | 38.1 | 35.6 | 0.05 |
| 5 | 25.8 | 23.8 | -2.71 |
| 6 | 13.3 | 10.2 | -1.13 |
| 7 | 21.7 | 19.4 | -0.97 |
| 8 | 11.1 | 9.3 | 2.72 |
| 9 | 12.2 | 10.6 | 2.03 |
| 10 | 3.3 | 3.0 | 2.83 |
| 11 | 11.2 | 10.5 | 2.29 |
| 12 | 16.3 | 17.9 | 0.64 |
| 13 | 3.5 | 2.5 | 1.39 |
| 14 | 10.5 | 10.7 | -2.41 |
| 15 | 9.5 | 9.4 | -1.09 |
| 16 | 0.0 | 1.2 | 2.71 |
| 17 | 0.0 | 2.3 | 1.10 |
| 18 | 3.3 | 3.5 | 1.76 |
| | 3 | 2 | L |
| 0 | 22.8 | 19.0 | -1.57 |
| 1 | 24.2 | 21.9 | -1.55 |
| 2 | 6.4 | 5.7 | 2.71 |
| 3 | 13.8 | 13.1 | 1.66 |
| 4 | 19.9 | 18.0 | -2.95 |
| 5 | 14.9 | 14.2 | 2.98 |
| 6 | 15.2 | 12.5 | 1.32 |
| 7 | 26.0 | 27.3 | 0.31 |
| 8 | 14.0 | 12.3 | -2.89 |
| 9 | 18.9 | 17.2 | -2.05 |
| 10 | 6.7 | 5.7 | 2.07 |
| 11 | 8.0 | 6.6 | 2.00 |
| 12 | 0.0 | 2.7 | 1.85 |
| 13 | 10.6 | 11.4 | 1.46 |
| 14 | 2.8 | 3.2 | -0.48 |
| 15 | 4.3 | 4.2 | -0.94 |
| 16 | 3.0 | 2.7 | -1.63 |
| 17 | 0.0 | 2.7 | -1.37 |
| | 3 | 3 | L |
| 0 | 24.1 | 23.6 | -1.57 |
| 1 | 18.9 | 16.3 | -2.43 |
| 2 | 10.7 | 9.6 | -2.97 |
| 3 | 11.6 | 9.4 | 2.34 |
| 4 | 20.5 | 18.7 | -1.36 |
| 5 | 13.6 | 14.0 | -2.80 |
| 6 | 10.7 | 9.0 | 2.57 |
| 7 | 15.2 | 13.1 | -0.65 |
| 8 | 17.5 | 17.1 | -0.12 |
| 9 | 6.0 | 6.0 | 2.98 |
| 10 | 4.8 | 4.9 | 1.83 |
| 11 | 0.9 | 11.4 | -1.35 |
| 12 | 16.1 | 18.1 | 3.08 |
| 13 | 9.9 | 11.3 | 0.85 |
| 14 | 8.9 | 8.2 | 0.97 |
| 15 | 4.9 | 5.4 | -3.01 |
| 16 | 0.0 | 2.1 | 0.21 |
| 17 | 5.1 | 4.4 | -0.66 |
| 18 | 0.0 | 1.1 | 0.96 |
| | 3 | 4 | L |
| 0 | 14.6 | 14.0 | 1.57 |
| 1 | 10.7 | 9.7 | -2.58 |
| 2 | 30.0 | 30.8 | -2.60 |
| 3 | 41.3 | 41.1 | -0.62 |
| 4 | 10.0 | 9.3 | 3.13 |
| 5 | 12.0 | 11.4 | 0.14 |
| 6 | 8.3 | 8.2 | -0.96 |
| 7 | 20.6 | 20.0 | 2.09 |
| 8 | 10.8 | 11.0 | 1.52 |
| 9 | 12.1 | 12.4 | -2.44 |
| 10 | 18.3 | 18.1 | -2.35 |
| 11 | 6.9 | 4.8 | 2.31 |
| 12 | 4.0 | 4.5 | -1.05 |
| 13 | 0.0 | 0.7 | 1.99 |
| 14 | 8.4 | 10.2 | 1.00 |
| 15 | 7.3 | 8.9 | 2.44 |
| 16 | 0.0 | 1.4 | 1.08 |
| 17 | 0.0 | 1.3 | -1.18 |
| | 3 | 5 | L |
| 0 | 2.6 | 3.8 | -1.57 |
| 1 | 23.9 | 23.3 | -0.91 |
| 2 | 13.0 | 11.7 | -1.80 |
| 3 | 13.3 | 13.0 | 3.04 |
| 4 | 24.2 | 23.9 | 1.14 |
| 5 | 6.8 | 6.3 | -1.55 |
| 6 | 31.5 | 31.2 | -3.02 |
| 7 | 11.4 | 9.8 | -1.82 |
| 8 | 7.0 | 6.7 | -0.28 |
| 9 | 18.6 | 19.5 | -0.62 |
| 10 | 5.9 | 6.9 | 2.89 |
| 11 | 3.4 | 3.6 | -2.87 |
| 12 | 3.9 | 4.4 | 0.20 |
| 13 | 7.0 | 7.4 | -3.03 |
| 14 | 0.0 | 1.9 | 0.33 |
| 15 | 3.4 | 2.6 | 0.48 |
| 16 | 6.8 | 5.3 | 3.14 |
| 17 | 1.3 | 2.1 | -0.45 |
| | 3 | 6 | L |
| 0 | 11.9 | 12.0 | -1.57 |
| 1 | 18.6 | 17.4 | 0.91 |
| 2 | 11.4 | 11.2 | 2.34 |
| 3 | 4.9 | 4.7 | -0.82 |
| 4 | 11.9 | 11.2 | 0.73 |
| 5 | 11.4 | 10.4 | 3.00 |
| 6 | 14.7 | 14.8 | -1.40 |
| 7 | 13.0 | 12.8 | -0.26 |
| 8 | 7.5 | 8.0 | 0.33 |
| 9 | 8.0 | 7.3 | 2.76 |
| 10 | 0.0 | 0.8 | -0.86 |
| 11 | 5.6 | 4.9 | -2.50 |
| 12 | 2.6 | 3.7 | 1.61 |
| 13 | 4.8 | 6.1 | -2.28 |
| | 4 | 0 | L |
| 0 | 62.0 | 60.7 | 0.00 |
| 1 | 4.8 | 6.0 | 1.57 |
| 2 | 3.4 | 2.1 | 3.14 |
| 3 | 0.0 | 1.5 | 1.57 |
| 4 | 39.2 | 36.6 | -3.14 |
| 5 | 20.5 | 18.8 | -1.57 |
| 6 | 17.0 | 13.9 | 0.00 |
| 7 | 37.9 | 35.4 | 1.57 |
| 8 | 17.0 | 16.6 | 0.00 |
| 9 | 14.6 | 15.7 | -1.57 |
| 10 | 13.5 | 12.6 | -3.14 |
| 11 | 16.2 | 16.1 | -1.57 |
| 12 | 13.7 | 13.3 | -3.14 |
| 13 | 8.3 | 6.6 | 1.57 |
| 14 | 5.7 | 5.7 | 0.00 |
| 15 | 5.3 | 6.3 | 1.57 |
| 16 | 2.8 | 4.2 | 0.00 |
| 17 | 3.4 | 3.0 | -1.57 |
| 18 | 0.0 | 1.2 | -3.14 |
| | 4 | 1 | L |
| 0 | 19.0 | 19.4 | 0.00 |
| 1 | 7.1 | 6.4 | -1.61 |
| 2 | 5.4 | 5.0 | 1.61 |
| 3 | 6.9 | 5.6 | 1.53 |
| 4 | 2.9 | 1.1 | -2.27 |
| 5 | 5.4 | 3.7 | 1.11 |
| 6 | 16.7 | 14.8 | 2.79 |
| 7 | 12.3 | 11.3 | -0.59 |
| 8 | 16.3 | 15.8 | -0.02 |
| 9 | 8.6 | 9.1 | 1.46 |
| 10 | 6.0 | 5.9 | -0.80 |
| 11 | 9.3 | 8.9 | -1.63 |
| 12 | 2.9 | 2.1 | 1.66 |
| 13 | 8.6 | 8.5 | 2.14 |
| 14 | 5.4 | 5.7 | -2.78 |
| 15 | 7.3 | 7.3 | -1.38 |
| 16 | 0.0 | 2.7 | -1.53 |
| 17 | 0.0 | 0.3 | 0.23 |
| 18 | 3.1 | 3.4 | 0.69 |
| | 4 | 2 | L |
| 0 | 56.0 | 56.5 | -3.14 |
| 1 | 7.5 | 7.2 | 2.78 |
| 2 | 32.2 | 29.8 | -0.49 |
| 3 | 28.2 | 27.1 | 0.69 |
| 4 | 13.2 | 12.9 | 0.93 |
| 5 | 13.3 | 13.1 | 3.04 |
| 6 | 11.5 | 9.2 | -2.12 |
| 7 | 21.4 | 20.9 | -0.56 |
| 8 | 12.9 | 13.0 | 2.23 |
| 9 | 7.4 | 6.0 | 1.98 |
| 10 | 3.5 | 3.2 | -0.61 |
| 11 | 0.0 | 0.7 | -2.90 |
| 12 | 14.7 | 15.9 | -0.38 |
| 13 | 4.4 | 3.0 | -2.31 |
| 14 | 8.9 | 8.9 | 2.93 |
| 15 | 6.9 | 7.4 | -1.90 |
| 16 | 1.9 | 1.1 | 0.03 |
| 17 | 2.8 | 3.2 | 1.26 |
| | 4 | 3 | L |
| 0 | 19.4 | 19.1 | -3.14 |
| 1 | 13.7 | 11.0 | 0.96 |
| 2 | 23.6 | 20.5 | -1.52 |
| 3 | 17.6 | 19.1 | -0.58 |
| 4 | 15.6 | 15.7 | 1.53 |
| 5 | 12.1 | 11.9 | -1.59 |
| 6 | 5.2 | 3.4 | -1.59 |
| 7 | 18.5 | 18.3 | 2.34 |
| 8 | 12.2 | 12.9 | 2.08 |
| 9 | 20.6 | 21.6 | 0.21 |
| 10 | 7.6 | 8.1 | -1.18 |
| 11 | 4.1 | 3.1 | -0.47 |
| 12 | 6.0 | 6.3 | 0.13 |
| 13 | 6.7 | 7.3 | -1.62 |
| 14 | 4.8 | 5.2 | 2.01 |
| 15 | 6.2 | 7.9 | 1.88 |
| 16 | 0.0 | 1.4 | 1.27 |
| 17 | 4.3 | 4.7 | -0.82 |
| | 4 | 4 | L |
| 0 | 18.8 | 20.3 | 0.00 |
| 1 | 23.7 | 23.8 | 2.51 |
| 2 | 20.5 | 21.0 | -2.78 |
| 3 | 8.7 | 7.6 | -2.02 |
| 4 | 12.6 | 11.6 | 1.78 |
| 5 | 12.9 | 12.6 | -0.46 |
| 6 | 10.8 | 9.4 | 2.14 |
| 7 | 24.6 | 26.1 | 2.56 |
| 8 | 28.1 | 29.7 | 0.29 |
| 9 | 12.3 | 11.5 | -0.57 |
| 10 | 11.5 | 11.4 | 2.84 |
| 11 | 11.1 | 10.8 | -2.80 |
| 12 | 0.0 | 1.3 | -2.97 |
| 13 | 10.1 | 11.3 | -0.31 |
| 14 | 6.8 | 8.7 | 0.28 |
| 15 | 5.3 | 5.4 | 2.38 |
| 16 | 1.6 | 1.9 | -1.98 |
| | 4 | 5 | L |
| 0 | 23.8 | 23.0 | 0.00 |
| 1 | 7.0 | 7.8 | -1.12 |
| 2 | 20.3 | 18.5 | 2.70 |
| 3 | 5.4 | 4.8 | -1.13 |
| 4 | 18.1 | 19.3 | -2.61 |
| 5 | 26.4 | 26.2 | 1.60 |
| 6 | 12.4 | 12.6 | 1.45 |
| 7 | 23.7 | 24.6 | -1.63 |
| 8 | 16.3 | 16.6 | -1.63 |
| 9 | 7.3 | 6.5 | 2.16 |
| 10 | 11.5 | 13.1 | 0.94 |
| 11 | 0.0 | 1.4 | 1.24 |
| 12 | 3.6 | 4.6 | 3.08 |
| 13 | 4.2 | 5.7 | 1.58 |
| 14 | 7.1 | 6.3 | -0.30 |
| 15 | 2.9 | 3.9 | -1.47 |
| 16 | 2.7 | 2.8 | -1.33 |
| | 4 | 6 | L |
| 0 | 10.6 | 7.9 | 0.00 |
| 1 | 7.2 | 8.1 | 2.20 |
| 2 | 9.3 | 8.4 | 1.38 |
| 3 | 14.9 | 15.6 | -0.67 |
| 4 | 6.9 | 6.1 | 1.86 |
| 5 | 18.9 | 20.0 | -2.58 |
| 6 | 13.3 | 14.6 | -0.72 |
| 7 | 7.6 | 7.2 | 3.00 |
| 8 | 16.8 | 18.0 | 2.65 |
| 9 | 15.6 | 15.0 | 0.69 |
| 10 | 9.2 | 10.7 | 0.54 |
| 11 | 3.5 | 3.3 | -2.24 |
| 12 | 7.4 | 8.4 | -2.64 |
| | 5 | 0 | L |
| 1 | 2.5 | 3.1 | -1.57 |
| 2 | 6.7 | 5.8 | -3.14 |
| 3 | 11.1 | 9.6 | 1.57 |
| 4 | 1.8 | 0.9 | -3.14 |
| 5 | 5.0 | 3.7 | 1.57 |
| 6 | 2.7 | 3.1 | 0.00 |
| 7 | 11.2 | 9.9 | -1.57 |
| 8 | 16.1 | 13.9 | -3.14 |
| 9 | 8.7 | 8.7 | 1.57 |
| 10 | 2.0 | 0.9 | -3.14 |
| 11 | 0.0 | 0.9 | 1.57 |
| 12 | 0.0 | 1.1 | -3.14 |
| 13 | 0.0 | 1.1 | -1.57 |
| 14 | 4.8 | 5.8 | 0.00 |
| 15 | 0.0 | 0.2 | 1.57 |
| 16 | 0.0 | 1.8 | -3.14 |
| | 5 | 1 | L |
| 0 | 6.8 | 6.1 | -1.57 |
| 1 | 7.2 | 5.8 | 2.76 |
| 2 | 12.3 | 11.8 | 2.50 |
| 3 | 14.2 | 13.1 | -0.13 |
| 4 | 18.2 | 17.2 | -1.22 |
| 5 | 3.3 | 3.7 | 2.25 |
| 6 | 2.0 | 2.2 | -0.47 |
| 7 | 12.4 | 11.8 | -2.24 |
| 8 | 7.6 | 7.0 | 1.51 |
| 9 | 6.1 | 6.2 | -2.41 |
| 10 | 6.1 | 5.7 | 2.52 |
| 11 | 6.3 | 5.5 | 1.06 |
| 12 | 0.0 | 1.1 | 2.52 |
| 13 | 0.0 | 1.3 | 2.06 |
| 14 | 3.8 | 4.4 | -3.12 |
| 15 | 2.6 | 2.9 | 2.81 |
| 16 | 2.2 | 1.9 | 0.93 |
| 17 | 3.4 | 3.7 | -1.29 |
| | 5 | 2 | L |
| 0 | 6.4 | 4.0 | -1.57 |
| 1 | 13.3 | 11.2 | -1.40 |
| 2 | 9.7 | 9.6 | -1.28 |
| 3 | 7.0 | 6.5 | 1.86 |
| 4 | 12.7 | 11.7 | 0.82 |
| 5 | 14.2 | 15.6 | -0.71 |
| 6 | 23.0 | 23.0 | -3.08 |
| 7 | 3.5 | 3.3 | -2.55 |
| 8 | 14.1 | 15.3 | -0.65 |
| 9 | 6.4 | 7.0 | 2.28 |
| 10 | 8.6 | 8.4 | 1.95 |
| 11 | 7.9 | 8.8 | -2.29 |
| 12 | 3.3 | 3.5 | 0.85 |
| 13 | 4.0 | 4.7 | 0.00 |
| 14 | 5.7 | 6.3 | -2.63 |
| 15 | 3.6 | 3.4 | -2.85 |
| 16 | 0.0 | 2.1 | -0.77 |
| | 5 | 3 | L |
| 0 | 9.9 | 7.9 | 1.57 |
| 1 | 13.7 | 13.4 | -1.12 |
| 2 | 13.7 | 15.3 | -1.10 |
| 3 | 11.7 | 10.4 | 1.78 |
| 4 | 14.6 | 16.1 | 1.03 |
| 5 | 13.9 | 13.0 | -1.55 |
| 6 | 10.2 | 11.5 | -2.24 |
| 7 | 9.9 | 10.1 | 0.16 |
| 8 | 2.0 | 3.6 | 0.63 |
| 9 | 6.1 | 6.6 | -3.04 |
| 10 | 8.8 | 9.5 | -1.41 |
| 11 | 3.4 | 4.4 | -0.95 |
| 12 | 3.7 | 3.6 | 2.16 |
| 13 | 3.0 | 2.0 | 1.82 |
| 14 | 1.9 | 3.6 | 0.97 |
| 15 | 2.3 | 2.7 | -3.04 |
| 16 | 3.2 | 3.7 | -2.32 |
| | 5 | 4 | L |
| 0 | 29.1 | 32.4 | 1.57 |
| 1 | 11.4 | 10.8 | 1.92 |
| 2 | 11.4 | 8.2 | -1.06 |
| 3 | 7.3 | 6.8 | 0.34 |
| 4 | 8.9 | 7.5 | -2.80 |
| 5 | 14.0 | 15.2 | -0.76 |
| 6 | 10.6 | 11.3 | 0.60 |
| 7 | 13.7 | 13.8 | -2.52 |
| 8 | 5.7 | 5.4 | -3.13 |
| 9 | 0.0 | 1.4 | 1.69 |
| 10 | 5.5 | 5.8 | 0.17 |
| 11 | 5.6 | 6.1 | 0.49 |
| 12 | 12.8 | 13.5 | -2.30 |
| 13 | 8.3 | 6.6 | -3.13 |
| 14 | 9.6 | 9.7 | 0.52 |
| 15 | 5.8 | 4.9 | -0.23 |
| | 5 | 5 | L |
| 0 | 16.7 | 18.0 | -1.57 |
| 1 | 19.1 | 20.3 | 1.93 |
| 2 | 16.8 | 17.2 | 2.22 |
| 3 | 7.3 | 6.7 | -1.35 |
| 4 | 8.3 | 8.4 | -1.07 |
| 5 | 16.1 | 16.7 | 0.79 |
| 6 | 6.2 | 7.4 | 0.82 |
| 7 | 22.4 | 24.6 | -2.20 |
| 8 | 6.7 | 7.9 | -0.06 |
| 9 | 7.5 | 9.1 | 1.23 |
| 10 | 7.7 | 8.2 | -2.93 |
| 11 | 3.4 | 2.8 | 0.26 |
| 12 | 8.7 | 6.7 | 0.13 |
| 13 | 3.9 | 3.7 | -2.05 |
| 14 | 3.4 | 3.7 | -0.28 |
| | 5 | 6 | L |
| 0 | 1.9 | 1.2 | -1.57 |
| 1 | 9.5 | 9.8 | 0.65 |
| 2 | 9.5 | 8.0 | -2.96 |
| 3 | 8.5 | 9.5 | -2.91 |
| 4 | 13.0 | 13.3 | 1.72 |
| 5 | 4.8 | 4.4 | 0.80 |
| 6 | 5.9 | 7.4 | -0.75 |
| 7 | 4.5 | 3.9 | 1.84 |
| 8 | 8.1 | 8.0 | -1.24 |
| 9 | 4.9 | 5.5 | 0.15 |
| 10 | 4.4 | 5.5 | 2.54 |
| 11 | 7.5 | 6.6 | 2.53 |
| 12 | 2.4 | 2.4 | -0.40 |
| 13 | 3.9 | 4.1 | -1.25 |
| 14 | 4.8 | 5.2 | -2.97 |
| | 6 | 0 | L |
| 0 | 17.0 | 16.0 | 0.00 |
| 1 | 0.0 | 2.5 | 1.57 |
| 2 | 9.5 | 8.8 | -3.14 |
| 3 | 4.9 | 4.9 | 1.57 |
| 4 | 6.3 | 6.0 | -3.14 |
| 5 | 0.0 | 1.6 | -1.57 |
| 6 | 5.7 | 5.3 | 0.00 |
| 7 | 9.3 | 9.2 | 1.57 |
| 8 | 0.0 | 1.4 | 0.00 |
| 9 | 4.4 | 4.5 | -1.57 |
| 10 | 0.0 | 0.4 | -3.14 |
| 11 | 0.0 | 0.3 | -1.57 |
| 12 | 0.0 | 1.7 | 0.00 |
| 13 | 0.0 | 0.1 | 1.57 |
| 14 | 0.0 | 1.7 | 0.00 |
| 15 | 0.0 | 0.7 | -1.57 |
| | 6 | 1 | L |
| 0 | 8.9 | 8.9 | 0.00 |
| 1 | 9.8 | 8.5 | -2.27 |
| 2 | 8.0 | 7.9 | 3.13 |
| 3 | 5.3 | 5.3 | 1.54 |
| 4 | 9.0 | 8.5 | 1.74 |
| 5 | 0.0 | 0.7 | -2.22 |
| 6 | 4.4 | 6.8 | -2.99 |
| 7 | 10.0 | 9.1 | 0.00 |
| 8 | 11.4 | 12.3 | 0.48 |
| 9 | 0.0 | 1.2 | 3.05 |
| 10 | 4.6 | 5.3 | -2.65 |
| 11 | 4.4 | 4.3 | 1.83 |
| 12 | 0.0 | 1.9 | 2.83 |
| 13 | 4.1 | 4.4 | 1.10 |
| 14 | 3.6 | 3.5 | 0.11 |
| 15 | 2.2 | 2.2 | -0.84 |
| | 6 | 2 | L |
| 0 | 14.0 | 13.6 | -3.14 |
| 1 | 15.0 | 15.1 | -0.53 |
| 2 | 2.9 | 2.9 | 2.13 |
| 3 | 8.1 | 7.5 | 2.42 |
| 4 | 9.9 | 10.0 | 0.06 |
| 5 | 14.5 | 15.0 | 1.65 |
| 6 | 4.1 | 3.1 | -2.30 |
| 7 | 14.7 | 16.4 | -1.65 |
| 8 | 8.0 | 7.7 | 2.31 |
| 9 | 0.0 | 1.8 | 1.53 |
| 10 | 5.9 | 6.2 | 1.13 |
| 11 | 0.0 | 2.1 | 1.90 |
| 12 | 6.3 | 4.5 | -1.17 |
| 13 | 2.5 | 2.1 | 1.76 |
| 14 | 2.2 | 1.7 | 1.70 |
| 15 | 3.0 | 3.3 | -2.12 |
| | 6 | 3 | L |
| 0 | 2.9 | 1.5 | -0.00 |
| 1 | 11.5 | 12.4 | -2.97 |
| 2 | 4.5 | 3.4 | -1.66 |
| 3 | 9.0 | 9.7 | -1.92 |
| 4 | 7.6 | 8.0 | 1.94 |
| 5 | 11.5 | 12.1 | 0.86 |
| 6 | 9.9 | 10.2 | -1.92 |
| 7 | 7.9 | 7.4 | -2.72 |
| 8 | 1.9 | 1.3 | 1.53 |
| 9 | 5.0 | 4.6 | 1.53 |
| 10 | 6.7 | 8.1 | 0.84 |
| 11 | 4.5 | 6.3 | -2.49 |
| 12 | 5.3 | 5.4 | -1.81 |
| 13 | 6.2 | 6.5 | 0.16 |
| 14 | 5.9 | 5.6 | 2.01 |
| | 6 | 4 | L |
| 0 | 3.5 | 3.3 | 0.00 |
| 1 | 17.5 | 17.2 | 2.72 |
| 2 | 13.1 | 13.6 | -1.00 |
| 3 | 8.9 | 9.1 | -1.59 |
| 4 | 15.8 | 16.8 | -2.81 |
| 5 | 5.6 | 5.9 | -1.72 |
| 6 | 18.2 | 20.1 | 1.50 |
| 7 | 7.2 | 7.7 | 0.94 |
| 8 | 9.7 | 10.3 | -0.84 |
| 9 | 5.1 | 6.0 | -2.82 |
| 10 | 6.3 | 8.5 | -1.24 |
| 11 | 4.7 | 3.3 | 2.35 |
| 12 | 7.3 | 6.7 | 2.52 |
| 13 | 4.2 | 3.6 | -1.31 |
| | 6 | 5 | L |
| 0 | 15.7 | 16.0 | 0.00 |
| 1 | 9.6 | 9.9 | 0.35 |
| 2 | 9.6 | 9.0 | -2.76 |
| 3 | 8.9 | 8.3 | -1.99 |
| 4 | 0.0 | 1.4 | -0.87 |
| 5 | 8.0 | 8.9 | 1.39 |
| 6 | 3.7 | 4.7 | 0.28 |
| 7 | 9.5 | 10.4 | -1.42 |
| 8 | 6.0 | 5.1 | 2.76 |
| 9 | 4.0 | 4.6 | -2.80 |
| 10 | 7.0 | 5.7 | -0.55 |
| 11 | 9.3 | 8.9 | 1.10 |
| 12 | 7.8 | 7.7 | 2.89 |
| 13 | 6.3 | 6.9 | -1.74 |
| | 6 | 6 | L |
| 0 | 5.5 | 5.8 | 0.00 |
| 1 | 6.3 | 5.5 | -0.76 |
| 2 | 10.1 | 11.2 | 2.20 |
| 3 | 9.4 | 9.9 | 1.65 |
| 4 | 8.6 | 8.9 | -0.47 |
| 5 | 3.0 | 3.8 | -2.18 |
| 6 | 1.7 | 1.4 | -1.82 |
| 7 | 2.8 | 2.1 | -3.07 |
| 8 | 4.2 | 3.0 | -3.11 |
| 9 | 1.8 | 0.6 | -0.92 |
| 10 | 2.8 | 3.4 | 1.25 |
| 11 | 2.0 | 3.0 | 0.91 |
| 12 | 1.9 | 3.2 | -0.95 |
| | 7 | 0 | L |
| 1 | 6.9 | 8.4 | -1.57 |
| 2 | 2.0 | 1.0 | -3.14 |
| 3 | 0.0 | 0.7 | 1.57 |
| 4 | 0.0 | 0.1 | 3.14 |
| 5 | 3.3 | 2.2 | -1.57 |
| 6 | 5.7 | 5.6 | 0.00 |
| 7 | 2.6 | 1.1 | 1.57 |
| 8 | 4.3 | 3.8 | -3.14 |
| 9 | 2.4 | 2.3 | -1.57 |
| 10 | 0.0 | 0.2 | 0.00 |
| 11 | 4.2 | 3.4 | -1.57 |
| 12 | 0.0 | 0.9 | 0.00 |
| 13 | 3.3 | 3.0 | -1.57 |
| | 7 | 1 | L |
| 0 | 8.0 | 7.8 | 1.57 |
| 1 | 6.3 | 6.5 | 0.00 |
| 2 | 6.0 | 5.7 | -2.01 |
| 3 | 3.4 | 2.1 | -2.79 |
| 4 | 2.8 | 3.0 | 0.37 |
| 5 | 0.0 | 2.0 | 2.23 |
| 6 | 5.4 | 6.1 | -0.07 |
| 7 | 0.0 | 1.1 | -1.39 |
| 8 | 4.3 | 4.5 | -2.64 |
| 9 | 3.3 | 3.7 | -0.12 |
| 10 | 3.8 | 3.1 | 0.81 |
| 11 | 5.1 | 5.0 | 2.68 |
| 12 | 4.2 | 3.3 | -0.78 |
| | 7 | 2 | L |
| 0 | 9.0 | 10.9 | 1.57 |
| 1 | 2.8 | 3.1 | -1.33 |
| 2 | 6.8 | 7.1 | -0.48 |
| 3 | 3.9 | 3.3 | -2.08 |
| 4 | 1.9 | 1.6 | 0.70 |
| 5 | 3.3 | 3.0 | 1.95 |
| 6 | 7.0 | 7.3 | -3.04 |
| 7 | 5.1 | 5.2 | -0.21 |
| 8 | 3.0 | 4.3 | 1.07 |
| 9 | 0.0 | 0.8 | -3.00 |
| 10 | 0.0 | 0.8 | -1.03 |
| 11 | 0.0 | 1.8 | -1.[illegible] |
| 12 | 0.0 | 1.0 | 0.13 |
| | 7 | 3 | L |
| 0 | 4.3 | 5.8 | 1.57 |
| 1 | 9.6 | 9.9 | 1.55 |
| 2 | 5.8 | 6.8 | -0.48 |
| 3 | 0.0 | 3.1 | 3.10 |
| 4 | 0.0 | 1.1 | -0.39 |
| 5 | 1.8 | 1.7 | -1.69 |
| 6 | 0.0 | 1.6 | 2.11 |
| 7 | 0.0 | 1.7 | 0.54 |
| 8 | 2.8 | 2.4 | -1.88 |
| 9 | 2.6 | 3.2 | -2.04 |
| 10 | 5.9 | 6.6 | 0.84 |
| 11 | 2.6 | 2.7 | 1.24 |
| 12 | 3.1 | 4.6 | -1.90 |
| | 7 | 4 | L |
| 0 | 1.9 | 1.4 | 1.57 |
| 1 | 4.2 | 4.6 | 3.10 |
| 2 | 4.9 | 4.7 | 2.67 |
| 3 | 5.2 | 6.1 | -1.03 |
| 4 | 5.7 | 7.2 | -2.51 |
| 5 | 8.7 | 9.4 | 0.64 |
| 6 | 5.1 | 6.1 | 0.49 |
| 7 | 10.2 | 10.0 | -3.10 |
| 8 | 3.2 | 4.2 | -1.05 |
| 9 | 2.4 | 2.4 | -0.33 |
| 10 | 5.3 | 5.4 | 2.19 |
| 11 | 3.8 | 3.6 | -2.11 |
| | 7 | 5 | L |
| 0 | 2.4 | 4.3 | -1.57 |
| 1 | 6.9 | 8.0 | 1.56 |
| 2 | 5.4 | 5.2 | 0.13 |
| 3 | 7.5 | 8.2 | -1.68 |
| 4 | 2.9 | 3.1 | 2.84 |
| 5 | 3.4 | 2.7 | 1.51 |
| 6 | 3.2 | 3.1 | -2.48 |
| 7 | 3.1 | 3.3 | 0.92 |
| 8 | 2.8 | 2.3 | 1.46 |
| 9 | 5.8 | 5.2 | -1.84 |
| 10 | 3.2 | 2.7 | -1.35 |
| | 7 | 6 | L |
| 0 | 1.9 | 0.6 | 1.57 |
| 1 | 2.7 | 3.4 | -0.78 |
| 2 | 2.6 | 2.1 | 0.67 |
| 3 | 6.8 | 6.9 | 1.61 |
| 4 | 0.0 | 0.6 | -2.40 |
| 5 | 6.8 | 6.9 | -2.12 |
| 6 | 2.8 | 2.9 | -0.14 |
| 7 | 3.6 | 3.6 | 0.25 |
| 8 | 3.9 | 4.8 | -2.93 |
| | 8 | 0 | L |
| 0 | 4.5 | 3.6 | 0.00 |
| 1 | 3.0 | 3.4 | 1.57 |
| 2 | 5.8 | 5.9 | -3.14 |
| 3 | 4.7 | 5.7 | -1.57 |
| 4 | 5.2 | 4.0 | 0.00 |
| 5 | 4.3 | 4.0 | -1.57 |
| 6 | 0.0 | 1.1 | -3.14 |
| 7 | 7.6 | 6.1 | 1.57 |
| 8 | 0.0 | 0.1 | 0.00 |
| 9 | 0.0 | 0.7 | 1.57 |
| 10 | 2.3 | 3.3 | -3.14 |
| | 8 | 1 | L |
| 0 | 3.4 | 3.6 | -3.14 |
| 1 | 5.4 | 6.7 | -0.61 |
| 2 | 5.8 | 6.4 | 0.90 |
| 3 | 6.4 | 5.0 | 2.35 |
| 4 | 2.0 | 2.5 | -1.95 |
| 5 | 1.9 | 0.6 | 2.30 |
| 6 | 3.1 | 1.9 | 1.89 |
| 7 | 1.7 | 1.0 | -1.36 |
| 8 | 4.6 | 3.4 | -0.74 |
| | 8 | 2 | L |
| 0 | 5.2 | 5.6 | -3.14 |
| 1 | 3.5 | 2.3 | -0.16 |
| 2 | 4.0 | 3.0 | -0.31 |
| 3 | 4.8 | 3.7 | -2.61 |
| 4 | 3.3 | 0.5 | -1.08 |
| 5 | 7.3 | 7.4 | 1.52 |
| 6 | 1.7 | 1.5 | -1.74 |
| 7 | 7.8 | 7.8 | -1.24 |
| | 8 | 3 | L |
| 0 | 6.1 | 6.1 | -3.14 |
| 1 | 5.4 | 5.4 | -3.01 |
| 2 | 4.6 | 5.0 | -0.00 |
| 3 | 6.9 | 7.7 | 0.18 |
| 4 | 0.0 | 1.2 | 2.04 |
| 5 | 6.4 | 5.6 | -2.36 |
| 6 | 0.0 | 1.6 | -1.31 |
| 7 | 4.4 | 3.9 | 2.02 |
| 8 | 3.8 | 3.3 | 2.51 |
| | 8 | 4 | L |
| 0 | 3.9 | 4.1 | -3.14 |
| 1 | 6.6 | 5.7 | 1.95 |
| 2 | 3.9 | 3.7 | 1.13 |
| 3 | 6.3 | 5.9 | -2.10 |
| 4 | 6.8 | 6.3 | -1.64 |
| 5 | 3.4 | 3.2 | -0.12 |
| 6 | 7.7 | 8.1 | 1.61 |
| 7 | 3.2 | 4.2 | 2.05 |
| | 8 | 5 | L |
| 0 | 12.3 | 12.5 | 0.00 |
| 1 | 5.7 | 5.5 | -0.73 |
| 2 | 9.6 | 10.0 | -3.01 |
| 3 | 2.0 | 3.2 | 2.43 |
| 4 | 3.6 | 3.2 | -0.14 |
| 5 | 2.7 | 2.8 | 1.63 |
| | 8 | 6 | L |
| 0 | 2.3 | 1.6 | 0.00 |
| 1 | 2.8 | 3.4 | -2.91 |
| 2 | 5.4 | 6.5 | 1.49 |
| 3 | 1.7 | 2.4 | 0.47 |
| | 9 | 0 | L |
| 1 | 2.2 | 1.5 | 1.57 |
| 2 | 0.0 | 0.4 | 3.14 |
| 3 | 3.3 | 3.6 | -1.57 |
| 4 | 1.8 | 1.7 | -3.14 |
| | 9 | 1 | L |
| 0 | 0.0 | 0.1 | -1.57 |
| 1 | 4.7 | 4.3 | 1.80 |
| 2 | 0.0 | 0.4 | -2.69 |
| 3 | 3.9 | 3.9 | -0.91 |

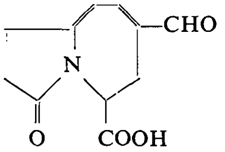
## Discussion

The structure analysis has shown that the irradiation of



$$laevo\text{-}CH_3O\text{—}C_6H_4\text{—}CH_2\underset{\underset{\underset{\underset{O}{\|}}{ClCH_2\text{—}C}}{NH}}{CH}COOH$$

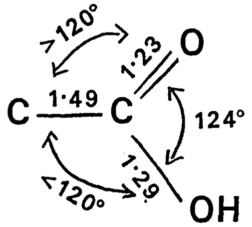
causes ring closure and a drastic rearrangement of the anisole group to yield a material with the formula



A possible mechanism for this rearrangement has been proposed (Yonemitsu, Witkop & Karle, 1967).

The configuration of the methyl ester is seen in Figs. 2 and 3. Except for C(6), the two rings are approximately coplanar and the aldehyde group is roughly parallel to the ester group. Bond distances and angles are illustrated in Fig. 4. Effects of conjugation are apparent in the C(8)–C(9) and C(6)–C(7) bonds which are adjacent to double bonds. Their bond lengths are appreciably shorter than single bond values. Furthermore, the two C–N bonds adjacent to C=C and C=O have values of ~1·38 Å as compared with 1·47 Å for the C–N bond adjacent to a saturated carbon atom. Similar effects on C–N bonds adjacent to unsaturated bonds have been observed in many molecules (*e.g.* Ringertz, 1966). The carbonyl distances C(3)–O(1) and C(13)–O(4) at 1·19 and 1·21 Å are in the range observed for ketones.

In carboxylic acids, the configuration of the acid group tends to be approximately the following (see *e.g.* the compilation by Nardelli, Fava & Giraldi, 1962), where the bond lengths are different from ordinary single and double bond lengths:



However, in the ester group of the present molecule, the C(5)–C(11) bond length is 1·54 Å, the C(11)–O(3) bond length is 1·35 Å, an increase over the value usually found in acids, and the C(11)–O(2) bond is a very short 1·16 Å, a large decrease over the usual value. The values for the angles in the ester group are similar to those found in carboxylic acids.

With the system of alternating single and double bonds in the molecule, it might be expected that the molecule, except for C(6) and the ester group, is nearly planar. The constraints imposed upon the molecule by the five- and seven-membered rings tend to twist the molecule from a planar configuration. After several trials to find groups of atoms which were most nearly coplanar, atoms O(1), C(3), N(4), C(10) and C(1) were chosen to which a least-squares plane was fitted. The equation of this plane is

$$3\cdot7230x+6\cdot0360y+9\cdot7501z=7\cdot0507\,, \qquad (3)$$

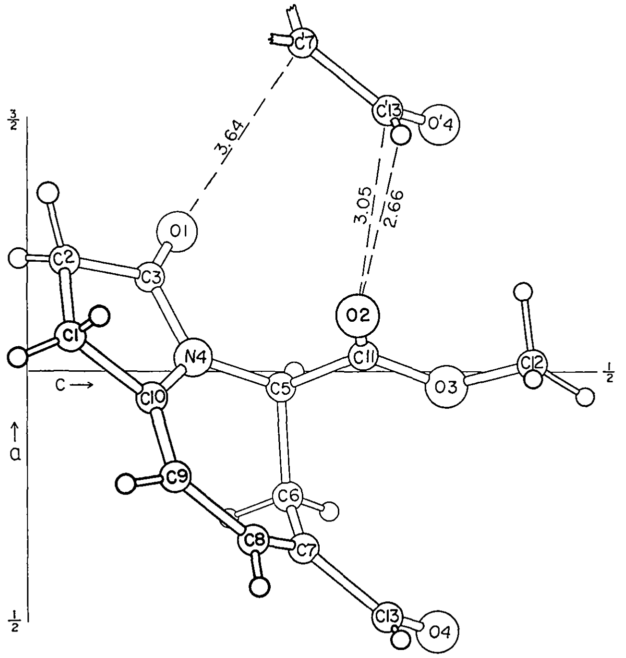


Fig. 3. View of the molecule projected down the *b* axis and closest intermolecular approaches.

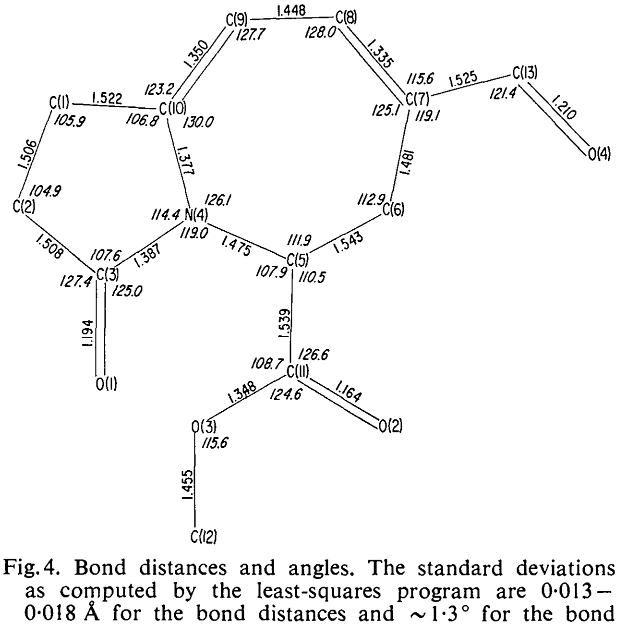


Fig. 4. Bond distances and angles. The standard deviations as computed by the least-squares program are 0·013–0·018 Å for the bond distances and ~1·3° for the bond angles. If all experimental factors were taken into account the values of the standard deviations would increase, perhaps by a factor of 2.

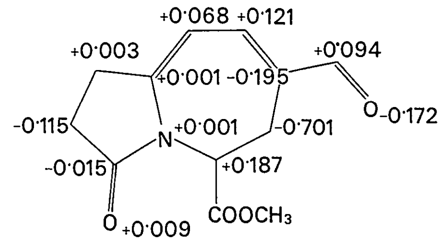


Fig. 5. Deviations (Å) of atoms from the least-squares plane denoted by equation (3).

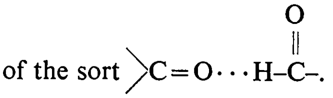
where the value on the right-hand side is the origin-to-plane distance in Å (Schomaker, Waser, Marsh & Bergman, 1959). Deviations from this plane are shown in Fig. 5. It is seen that the deviations are as large as ± 0·2 Å, except, of course, for C(6) at − 0·7 Å, which was not expected to be in the plane. The three bonds to the nitrogen are not completely coplanar since C(5), the saturated carbon atom, is 0·2 Å out of the plane formed by the other atoms. In a diazepinone derivative (Karle & Karle, 1967), one of the bonds to a nitrogen atom situated in a somewhat similar environment deviated from a plane by the same amount.

The five atoms in the ester group form a plane whose equation is

$$6{\cdot}1604x - 5{\cdot}0797y + 1{\cdot}4152z = 5{\cdot}0579\,. \quad (4)$$

The maximum deviation of any of the five atoms is 0·02 Å. The dihedral angle formed by the plane of the ester group with the approximate plane of the molecule is 78·5 °.

The packing of the molecules is shown in Figs. 2 and 3. The closest intermolecular approaches are between O···O and C···O pairs at 3·4 Å and above, except for the carbonyl oxygen, O(2), and the aldehyde carbon, C(13), in the molecule above in the **a** direction (Fig. 3). The distance C(13')–O(2) is only 3·05 Å. The aldehyde hydrogen atom, attached to C(13'), is not oriented directly toward O(2) and the distance between them is 2·66 Å, a van der Waals separation. The orientation of the atoms do not indicate any possible hydrogen bonding of the sort



$$>C=O\cdots H-\overset{\displaystyle O}{\overset{\|}{C}}-.$$

The $y$ and $z$ coordinates for O(3) and O(4) are nearly the same while their $x$ coordinates differ by nearly one-half. This pair of atoms is responsible for the fact that the $hkl$ reflections with $h$ even are considerably stronger than those with $h$ odd.

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## Short Communications

*Contributions intended for publication under this heading should be expressly so marked; they should not exceed about* 1000 *words; they should be forwarded in the usual way to the appropriate Co-editor; they will be published as speedily as possible. Publication will be quicker if the contributions are without illustrations.*

*Acta Cryst.* (1967). **23**, 500

### A note on the structure of pinnoite. By J. Krogh-Moe, *Institute of Chemistry, NLHT, Trondheim, Norway*

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The structure of pinnoite has been studied by Paton & MacDonald, utilizing a pseudo space group. Using the true space group according to Paton and MacDonald and the structure factors observed by these authors, a least-squares refinement based on their structure proposal has been attempted. The overall reliability index came down from 22 % to 15·7 %. The original structure proposal seems to be roughly correct.

The crystal structure of the borate mineral pinnoite, $MgO.B_2O_3\ 3H_2O$, has been studied by Paton & MacDonald (1957). The space group of pinnoite was determined as $P4_2$ in this study. The reported structure, however, was derived on the basis of the space group $P4_2/n$. This was possible because of the presence of a pseudo-symmetry. The computational burden was greatly reduced by working with the pseudo space group, but the overall reliability