the positions of the atoms around the points $y=1, z=0$ and $y=0, z=\frac{1}{2}$ in Fig. 3 shows greater overcrowding in the former case (Table 5). The distance between the methyl at C(13) of the primary molecule $(x,y,z)$ and O(4) of the molecule at $(\bar{x}, \frac{1}{2}+y, \bar{z})$ is 3·94 Å and the distance between the same methyl and O(1) of the molecule at $(1-x, \frac{1}{2}+y, \bar{z})$ is 3·79 Å. This methyl is held closely between these oxygen atoms. The ring atom C(6) moves into a position to preserve the tetrahedral arrangement at each carbon atom and becomes *trans* to the methyl C(14).

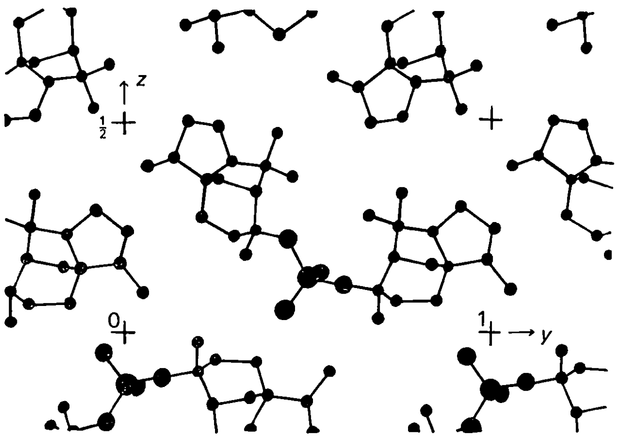


Fig. 3. Molecular packing viewed along the *a* axis.

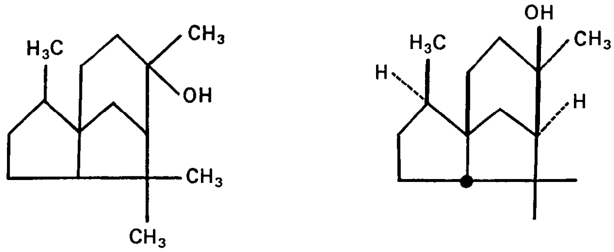


Fig. 4. (+)-cedrol.

### The absolute configuration

Provided precautions are taken in the indexing of the Weissenberg photographs (Peerdeman & Bijvoet, 1956; Raman, 1958; Ramaseshan, 1964) the structure as determined by the anomalous dispersion method will be in the absolute configuration. Fig. 1 then shows the absolute configuration of the molecule of cedryl chromate-and that of (+)-cedrol, deduced from it, is shown in Fig. 4. This is the same as that deduced by Stork & Clarke (1961) from chemical studies.

### References

Amirthalingam, V. & Grant, D. F. (1963). *Acta Cryst.* **16**, 851.
Dauben, C. H. & Templeton, D. H. (1955). *Acta Cryst.* **8**, 841.
Fieser, L. F. & Ourisson, G. (1953). *Bull. Soc. Chim. Fr.* p. 1152.
Gabe, E. J. (1962). *Acta Cryst.* **15**, 759.
Gatehouse, B. M. & Leverett, P. (1969). *J. Chem. Soc.* (*A*), p. 1857.
Grant, D. F., Killean, R. C. G. & Lawrence, J. L. (1969). *Acta Cryst.* **B25**, 374.
Peerdeman, A. F. & Bijvoet, J. M. (1956). *Acta Cryst.* **9**, 1012.
Ramachandran, C. N. & Raman, S. (1956). *Curr. Sci. India*, **25**, 348.
Raman, S. (1958). *Proc. Indian Acad. Sci.* **47**, 1.
Ramaseshan, S. (1964). *Advanced Methods of Crystallography*, Edited by G. N. Ramachandran, p. 67, London: Academic Press.
Scoulaudi, H. (1953). *Acta Cryst.* **6**, 651.
Stork, G. & Clarke, F. H. (1961). *J. Amer. Chem. Soc.* **83**, 3114.
Wilson, A. J. C. (1942). *Nature, Lond.* **150**, 152.

---

*Acta Cryst.* (1972). B**28**, 1345

# The Crystal and Molecular Structure of Difluoromalonic Acid

By J. A. Kanters and J. Kroon

*Laboratorium voor Kristalchemie, Catharijnesingel* 51, *Utrecht, The Netherlands*

(*Received* 31 *August* 1971)

Difluoromalonic acid crystallizes in the monoclinic space group $P2_1/c$ with cell dimensions $a=9{\cdot}59$, $b=5{\cdot}61$, $c=9{\cdot}80$ Å, $\beta=115{\cdot}1°$ and $Z=4$. The crystal is a racemate of two conformational antipodes. The acid molecules in the infinite chains are connected by hydrogen bonds between carboxyl groups across centres of symmetry.

## Introduction

In the crystal structure of α-substituted monocarboxylic acids, such as propionic acid (Strieter & Templeton, 1962), fluoroacetic acid (Kanters, 1972), glycollic acid (Pijper, 1971) and several amino-acids (*e.g.* Kanters, Kroon, Beurskens & Vliegenthart, 1966), it is found that the carboxylic acid group is nearly coplanar with the α-substituent. It appears that such a planar arrangement is favoured. These findings are in accordance with theoretical calculations (van Eijck, 1966). The influence of a second carboxyl group in the α-position upon the conformation can be seen in Table 1.

Two essential cases can be discerned:

(i) the α-substituent is nearly coplanar with one carboxyl group, the other carboxyl group being almost perpendicular to the first;

(ii) both carboxyl groups strive for coplanarity with the plane through C(1)C(2)R or C(3)C(2)R, complete simultaneous coplanarity being impeded by intramolecular contacts O(2)–O(4) (Table 1).

As far as we know the only disubstituted malonic acid derivative whose structure has been determined is dimethylmalonic acid (Haas & Brenner, 1966). The molecule has a twofold rotation axis. Here no coplanarity of the substituent with the carboxyl group is present, this group is rotated 30° out of the C(1)C(2)R plane.

The coplanarity is most pronounced in monofluoromalonic acid (Roelofsen, Kanters, Kroon & Vliegenthart, 1971). Therefore one would predict a marked preference for a coplanar arrangement of both halves of the molecule of difluoromalonic acid. In order to check the validity of this assumption we undertook the structure analysis of difluoromalonic acid.

## Experimental

Difluoromalonic acid was synthesized from the dimethyl ester. Very highly hygroscopic crystals (with dimensions 0·2 × 0·3 × 0·8 mm) were obtained by sublimation *in vacuo*. They were sealed in a Lindemann glass capillary tube. Cell dimensions measured on a General Electric diffractometer were $a=9{\cdot}59\pm0{\cdot}01$, $b=5{\cdot}61\pm0{\cdot}01$, $c=9{\cdot}80\pm0{\cdot}01$ Å and $\beta=115{\cdot}1\pm0{\cdot}1°$ [$\lambda(\text{Mo } K\alpha_1\alpha_2)=0{\cdot}71069$ Å]. From the systematic extinctions the space group $P2_1/c$ was deduced. One independent molecule in the asymmetric unit corresponds to the calculated density of 1·96 g.cm$^{-3}$. The intensities were measured on an automatic Nonius three-circle diffractometer equipped with a monochromator, a scintillation counter and a discriminator. The radiation employed was Mo $K\alpha$, and the $\omega$-scan technique was applied. The 1493 non-zero independent structure amplitudes were corrected for the Lorentz–polarization factors; no absorption correction was applied.

## Determination of the structure

With Wilson's (1942) method an overall temperature factor ($B=2{\cdot}8$ Å$^2$) and the scaling factor were determined. Triple products ($E_{\mathbf{H}1}E_{\mathbf{H}2}E_{\mathbf{H}1+\mathbf{H}2}$) were established such that two of the participating structure factors had $E$ values of at least 1·30, the third $E$ value had to be higher than 1·0. Values of the structure invariants were calculated, applying the $B_{3,0}$ formula (Karle & Hauptman, 1958). The expression used was:

$$E_{\mathbf{H}1}\,.\,E_{\mathbf{H}2}\,.\,E_{\mathbf{H}1+\mathbf{H}2}=AB+C\,.$$

$A$ is a positive constant, $C$ is a small correction term and $B$ is given by:

$$B=\langle(E^2_{\mathbf{K}}-1)\,(E^2_{\mathbf{K}+\mathbf{H}1}-1)\,(E^2_{\mathbf{K}+\mathbf{H}1+\mathbf{H}2}-1)\rangle_{\mathbf{K}}\,,$$

in which the mean value is taken over all 1493 reflexions $\mathbf{K}(hkl)$. Triple products with the highest calculated positive values of $AB+C$ used were in the evaluation of the structure factor signs by a symbolic procedure executed by hand. One single solution was obtained, and the corresponding Fourier synthesis with 384 terms could easily be interpreted.

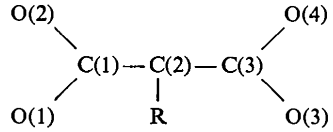
Full-matrix least-squares refinement alternated with

Table 2. *Fractional coordinates and thermal parameters of difluoromalonic acid*

The $\beta_{ij}$ values are defined by the expression for the temperature factor: $\exp\,(-10^{-4}\sum\sum h_ih_j\beta_{ij})$

| | $x$ | $y$ | $z$ | $\beta_{11}$ | $\beta_{22}$ | $\beta_{33}$ | $2\beta_{12}$ | $2\beta_{23}$ | $2\beta_{31}$ |
|---|---|---|---|---|---|---|---|---|---|
| F(1) | 0·6471 | 0·3560 | 0·1716 | 101 | 350 | 76 | 17 | −56 | 82 |
| F(2) | 0·8027 | 0·6289 | 0·3075 | 112 | 182 | 151 | −13 | 60 | 169 |
| O(1) | 0·6819 | 0·6118 | 0·5048 | 92 | 234 | 101 | −57 | −99 | 113 |
| O(2) | 0·5030 | 0·3599 | 0·3505 | 82 | 223 | 104 | −55 | −66 | 108 |
| O(3) | 0·9590 | 0·2248 | 0·3507 | 165 | 552 | 242 | 399 | 424 | 307 |
| O(4) | 0·8402 | 0·1175 | 0·4932 | 169 | 298 | 184 | 227 | 238 | 253 |
| C(1) | 0·6242 | 0·4664 | 0·3929 | 66 | 147 | 71 | 21 | 8 | 70 |
| C(2) | 0·7307 | 0·4263 | 0·3140 | 73 | 158 | 81 | −6 | 12 | 87 |
| C(3) | 0·8536 | 0·2360 | 0·3966 | 77 | 186 | 92 | 29 | 9 | 96 |
| H(1) | 0·6196 | 0·6176 | 0·5459 | $B=3$ Å$^2$ | | | | | |
| H(2) | 1·0164 | 0·1633 | 0·4068 | $B=3$ Å$^2$ | | | | | |

Table 1. *Conformation of some substituted malonic acids*



| Compound | α-Substituent $R$ | Dihedral angle between<br>C(2)C(1)O(2)O(1) and C(1)C(2)$R$ | C(2)C(3)O(4)O(3) and C(3)C(2)$R$ | Distance O(2)–O(4) | Reference |
|---|---|---|---|---|---|
| Methylmalonic acid | $-CH_3$ | 0° | 71° | 3·03 Å | Derissen (1970) |
| Aminomalonic acid | $-NH_2$ | 9 | 18 | 3·06 | Kanters *et al.* (1966) |
| Tartronic acid | –OH | 15 | 18 | 2·92 | van Eijck *et al.* (1965) |
| Fluoromalonic acid | –F | 6 | equivalent | 2·92 | Roelofsen *et al.* (1971) |

a difference Fourier synthesis in order to locate the hydrogen atoms, resulted in the parameters given in Table 2. Scattering factors used were calculated by means of the analytical expression of Moore (1964). Six reflexions, being suspected of extinction, were omitted from the refinement. The isotropic temperature factors of the hydrogen atoms were kept fixed at a $B$ value of 3 Å$^2$. Final shifts in the parameters did not exceed 0·2 $\sigma$. The e.s.d.'s of the coordinates for F, O and C were 0·003 Å and 0·05 Å for H.

In Table 3 the observed and calculated structure factors are compared ($R$=0·078). A final difference Fourier synthesis showed two appreciable peaks (0·4 and 0·5 e.Å$^{-3}$) at the centres of the C–C bonds; all other peaks were lower.

## Discussion of the structure

The molecular geometry can be inferred from Table 4, which also contains the relevant data concerning hydrogen bonding. The conformation of the molecule resembles that of the malonic acid molecule (Goedkoop & MacGillavry, 1957). One carboxyl group, C(3)O(3) O(4), lies nearly in the carbon-chain plane (deviation 11°) with the usual *cis* position of the C=O bond with respect to the C–C bond (Kanters, Kroon, Peerdeman & Schoone, 1967), the other group being turned nearly perpendicular to it (84°). This conformation therefore strongly differs from that found in the mono-substituted derivative in which both carboxyl groups strive after planarity with the fluorine atom. The dihedral

Table 3. *Observed and calculated structure factors*

Values are ten times the absolute scale. Reflexions that were omitted from the refinement are marked with a cross.

| | | | | | |
|---|---|---|---|---|---|
| -13 | 0 | 2 | 58 | 50 | |
| | | 4 | 9 | 12 | |
| | | 6 | 78 | -71 | |
| | | 8 | 136 | 131 | |
| | | 10 | 55 | 58 | |
| -12 | 0 | 2 | 14 | -1 | |
| | | 4 | 13 | 3 | |
| | | 6 | 109 | 108 | |
| | | 8 | 24 | 31 | |
| | | 10 | 25 | -23 | |
| | | 12 | 46 | 47 | |
| -11 | 0 | 2 | 15 | -14 | |
| | | 4 | 55 | -54 | |
| | | 6 | 21 | -22 | |
| | | 8 | 108 | -109 | |
| | | 10 | 18 | 21 | |
| | | 12 | 24 | -19 | |
| -10 | 0 | 0 | 25 | -17 | |
| | | 2 | 63 | -67 | |
| | | 4 | 40 | 45 | |
| | | 6 | 27 | -28 | |
| | | 8 | 9 | -2 | |
| | | 10 | 22 | -21 | |
| | | 12 | 104 | -98 | |
| -9 | 0 | 0 | 90 | -102 | |
| | | 2 | 55 | 55 | |
| | | 4 | 225 | 232 | |
| | | 6 | 160 | -172 | |
| | | 8 | 66 | -66 | |
| | | 10 | 68 | 76 | |
| | | 14 | 29 | 24 | |
| -8 | 0 | 0 | 55 | 52 | |
| | | 2 | 96 | 96 | |
| | | 4 | 269 | -286 | |
| | | 6 | 114 | -119 | |
| | | 8 | 57 | 67 | |
| | | 10 | 77 | -77 | |
| | | 12 | 38 | 43 | |
| | | 14 | 15 | -25 | |
| -7 | 0 | 0 | 137 | -138 | |
| | | 2 | 251 | 252 | |
| | | 4 | 99 | 94 | |
| | | 6 | 140 | -135 | |
| | | 8 | 155 | 147 | |
| | | 10 | 94 | 94 | |
| | | 12 | 57 | -51 | |
| | | 14 | 5 | 1 | |
| -6 | 0 | 0 | 394 | 403 | |
| | | 2 | 206 | 205 | |
| | | 4 | 28 | -29 | |
| | | 6 | 255 | 265 | |
| | | 8 | 91 | 93 | |
| | | 10 | 79 | 92 | |
| | | 12 | 64 | 65 | |
| | | 14 | 24 | 8 | |
| -5 | 0 | 2 | 45 | 43 | |
| | | 4 | 405 | -423 | |
| | | 6 | 39 | -39 | |
| | | 8 | 95 | 99 | |
| | | 10 | 50 | -50 | |
| | | 12 | 54 | -57 | |
| | | 14 | 20 | -30 | |
| -4 | 0 | 0 | 98 | -105 | |
| | | 2 | 449 | -476 | |
| | | 4 | 13 | -11 | |
| | | 6 | 72 | -76 | |
| | | 8 | 57 | -63 | |
| | | 10 | 90 | -89 | |
| | | 12 | 70 | -71 | |
| | | 14 | 29 | 28 | |
| -3 | 0 | 2 | 53 | 58 | |
| | | 4 | 237 | 246 | |
| | | 6 | 139 | -150 | |
| | | 8 | 51 | -47 | |
| | | 10 | 73 | 83 | |
| | | 12 | 26 | 28 | |
| | | 14 | 3 | -9 | |
| -2 | 0 | 2 | 361 | 403 | |
| | | 4 | 649 | -774 | × |
| | | 8 | 175 | 185 | |
| | | 10 | 181 | -177 | |
| | | 12 | 10 | 0 | |
| -1 | 0 | 2 | 466 | 557 | × |
| | | 4 | 16 | 6 | |
| | | 6 | 83 | -83 | |
| | | 8 | 109 | -114 | |
| | | 10 | 41 | 44 | |
| | | 12 | 27 | 24 | |
| 0 | 0 | 2 | 28 | -32 | |
| | | 4 | 203 | -201 | |
| | | 6 | 436 | 445 | |
| | | 10 | 85 | 84 | |
| | | 12 | 46 | 45 | |
| 1 | 0 | 0 | 118 | -114 | |
| | | 2 | 306 | -322 | |
| | | 4 | 160 | 160 | |
| | | 6 | 95 | -110 | |
| | | 8 | 88 | 90 | |
| | | 12 | 47 | -53 | |
| 2 | 0 | 0 | 308 | -320 | |
| | | 2 | 402 | -417 | |
| | | 4 | 60 | -70 | |
| | | 6 | 143 | -141 | |
| | | 10 | 36 | -34 | |
| | | 12 | 5 | -15 | |
| 3 | 0 | 2 | 28 | 27 | |
| | | 4 | 145 | -150 | |
| | | 6 | 153 | 160 | |
| | | 8 | 13 | 18 | |
| | | 10 | 22 | -19 | |
| 4 | 0 | 2 | 50 | -49 | |
| | | 4 | 65 | -54 | |
| | | 6 | 75 | 76 | |
| | | 8 | 22 | -24 | |
| | | 10 | 32 | -35 | |
| 5 | 0 | 2 | 165 | -169 | |
| | | 4 | 137 | 142 | |
| | | 6 | 115 | -113 | |
| | | 8 | 72 | -72 | |
| | | 10 | 43 | 44 | |
| 6 | 0 | 2 | 29 | 37 | |
| | | 4 | 41 | -39 | |
| | | 6 | 70 | 71 | |
| | | 8 | 46 | 43 | |
| 7 | 0 | 2 | 93 | 97 | |
| | | 4 | 59 | 67 | |
| | | 6 | 34 | -43 | |
| | | 8 | 11 | -1 | |
| 8 | 0 | 2 | 120 | -123 | |
| | | 4 | 62 | -63 | |
| | | 6 | 10 | -11 | |
| 9 | 0 | 2 | 11 | -6 | |
| | | 4 | 5 | 7 | |
| | | 6 | 24 | 26 | |
| 10 | 0 | 2 | 24 | 35 | |
| 11 | 0 | 2 | 67 | -60 | |
| -13 | 1 | 1 | 4 | -6 | |
| | | 2 | 26 | 19 | |
| | | 3 | 17 | 22 | |
| | | 4 | 20 | 11 | |
| | | 5 | 44 | -41 | |
| | | 6 | 20 | 19 | |
| | | 7 | 13 | 12 | |
| | | 8 | 32 | -31 | |
| | | 9 | 30 | 35 | |
| | | 10 | 15 | 14 | |
| -12 | 1 | 0 | 11 | 2 | |
| | | 1 | 33 | 28 | |
| | | 2 | 18 | 16 | |
| | | 3 | 9 | -13 | |
| | | 4 | 39 | -44 | |
| | | 5 | 13 | -13 | |
| | | 6 | 27 | -24 | |
| | | 7 | 89 | 85 | |
| | | 8 | 9 | 19 | |
| | | 9 | 77 | -76 | |
| | | 10 | 22 | 18 | |
| | | 11 | 8 | -14 | |
| | | 12 | 13 | -11 | |
| -11 | 1 | 0 | 34 | 36 | |
| | | 2 | 79 | -80 | |
| | | 3 | 23 | -22 | |
| | | 4 | 54 | 49 | |
| | | 5 | 25 | -25 | |
| | | 6 | 70 | 69 | |
| | | 7 | 97 | -89 | |
| | | 8 | 80 | -73 | |
| | | 9 | 5 | -3 | |
| | | 10 | 63 | 56 | |
| | | 11 | 59 | 57 | |
| | | 12 | 30 | 28 | |
| | | 13 | 55 | -53 | |
| -10 | 1 | 0 | 25 | 34 | |
| | | 1 | 14 | 6 | |
| | | 2 | 15 | 3 | |
| | | 3 | 70 | -73 | |
| | | 4 | 30 | 31 | |
| | | 5 | 97 | 101 | |
| | | 6 | 30 | 34 | |
| | | 7 | 62 | 55 | |
| | | 8 | 75 | 72 | |
| | | 9 | 28 | 27 | |
| | | 10 | 26 | 23 | |
| | | 12 | 12 | -16 | |
| | | 13 | 7 | -5 | |
| -9 | 1 | 0 | 165 | -159 | |
| | | 1 | 23 | 19 | |
| | | 2 | 96 | -97 | |
| | | 3 | 180 | 178 | |
| | | 4 | 127 | 124 | |
| | | 5 | 26 | 22 | |
| | | 6 | 87 | -84 | |
| | | 7 | 19 | 21 | |
| | | 8 | 51 | -53 | |
| | | 9 | 65 | 71 | |
| | | 10 | 36 | -39 | |
| | | 11 | 11 | 0 | |
| | | 12 | 44 | -38 | |
| | | 13 | 61 | 60 | |
| -8 | 1 | 0 | 89 | -87 | |
| | | 1 | 16 | -10 | |
| | | 2 | 35 | 40 | |
| | | 3 | 81 | -85 | |
| | | 4 | 48 | -44 | |
| | | 5 | 100 | -103 | |
| | | 6 | 28 | -39 | |
| | | 7 | 17 | -13 | |
| | | 8 | 99 | -103 | |
| | | 9 | 27 | -24 | |
| | | 10 | 66 | -65 | |
| | | 11 | 7 | -13 | |
| | | 12 | 19 | 17 | |
| | | 13 | 28 | -29 | |
| | | 14 | 19 | -15 | |
| -7 | 1 | 0 | 12 | 14 | |
| | | 1 | 62 | -61 | |
| | | 2 | 97 | 100 | |
| | | 3 | 82 | -85 | |
| | | 4 | 45 | 42 | |
| | | 5 | 18 | 28 | |
| | | 6 | 78 | 78 | |
| | | 7 | 7 | -7 | |
| | | 8 | 89 | -92 | |
| | | 9 | 91 | -96 | |
| | | 10 | 23 | 20 | |
| | | 11 | 17 | -13 | |
| | | 12 | 73 | 77 | |
| | | 13 | 34 | -33 | |
| | | 14 | 15 | -4 | |
| -6 | 1 | 0 | 15 | -6 | |
| | | 1 | 130 | 127 | |
| | | 2 | 40 | 27 | |
| | | 3 | 28 | 27 | |
| | | 4 | 199 | 195 | |
| | | 5 | 55 | -58 | |
| | | 6 | 207 | -212 | |
| | | 7 | 33 | 29 | |
| | | 8 | 43 | -48 | |
| | | 10 | 136 | 131 | |
| | | 11 | 11 | 4 | |
| | | 12 | 55 | -47 | |
| | | 13 | 50 | 49 | |
| | | 14 | 11 | 5 | |
| -5 | 1 | 0 | 82 | 84 | |
| | | 1 | 183 | -181 | |
| | | 2 | 116 | -114 | |
| | | 3 | 161 | -163 | |
| | | 4 | 212 | 211 | |
| | | 6 | 90 | -91 | |
| | | 7 | 130 | -129 | |
| | | 8 | 37 | -43 | |
| | | 9 | 31 | 35 | |
| | | 10 | 76 | 74 | |
| | | 11 | 18 | 18 | |
| | | 12 | 15 | 18 | |
| | | 13 | 56 | -51 | |
| | | 14 | 27 | -31 | |
| -4 | 1 | 0 | 111 | -113 | |
| | | 1 | 81 | 71 | |
| | | 2 | 628 | 665 | |
| | | 3 | 173 | -176 | |
| | | 4 | 59 | -58 | |
| | | 5 | 256 | 250 | |
| | | 6 | 106 | -108 | |
| | | 7 | 60 | 65 | |
| | | 8 | 319 | 322 | |
| | | 9 | 89 | -89 | |
| | | 10 | 7 | -8 | |
| | | 11 | 3 | 5 | |
| | | 12 | 13 | -19 | |
| | | 13 | 26 | 26 | |
| | | 14 | 27 | 23 | |
| -3 | 1 | 0 | 373 | -365 | |
| | | 1 | 96 | 94 | |
| | | 2 | 107 | -91 | |
| | | 3 | 700 | 767 | × |
| | | 4 | 85 | 88 | |
| | | 5 | 12 | 5 | |
| | | 7 | 50 | -43 | |
| | | 8 | 59 | -63 | |
| | | 9 | 199 | 200 | |
| | | 10 | 7 | 10 | |
| | | 11 | 32 | 33 | |
| | | 12 | 17 | -11 | |
| | | 14 | 10 | -16 | |
| -2 | 1 | 0 | 160 | -152 | |
| | | 1 | 275 | -270 | |
| | | 2 | 62 | -59 | |
| | | 3 | 118 | -118 | |
| | | 4 | 406 | -410 | |
| | | 5 | 74 | -73 | |
| | | 7 | 79 | 89 | |
| | | 8 | 83 | -82 | |
| | | 9 | 11 | -15 | |
| | | 10 | 57 | -52 | |
| | | 11 | 46 | -47 | |
| | | 12 | 26 | -23 | |
| -1 | 1 | 0 | 316 | -295 | |
| | | 1 | 149 | 148 | |
| | | 2 | 184 | 190 | |
| | | 3 | 170 | -170 | |
| | | 4 | 194 | 193 | |
| | | 5 | 159 | -152 | |
| | | 6 | 46 | -45 | |
| | | 7 | 19 | -21 | |
| | | 8 | 10 | 2 | |
| | | 9 | 133 | -136 | |
| | | 10 | 19 | -21 | |
| | | 11 | 9 | 3 | |
| | | 13 | 12 | 17 | |
| 0 | 1 | 1 | 287 | 296 | |
| | | 2 | 360 | 365 | |
| | | 3 | 228 | -220 | |
| | | 4 | 182 | 186 | |
| | | 5 | 33 | 36 | |
| | | 6 | 183 | -181 | |
| | | 7 | 12 | -6 | |
| | | 9 | 51 | 56 | |
| | | 10 | 47 | 49 | |
| | | 11 | 19 | 22 | |
| | | 13 | 9 | -17 | |
| 1 | 1 | 1 | 707 | -836 | × |
| | | 2 | 130 | 136 | |
| | | 3 | 27 | 24 | |
| | | 4 | 183 | -176 | |
| | | 5 | 176 | 167 | |
| | | 6 | 6 | -2 | |
| | | 7 | 121 | -114 | |
| | | 8 | 24 | -24 | |
| | | 9 | 23 | 24 | |
| | | 10 | 18 | -13 | |
| | | 12 | 32 | 25 | |
| 2 | 1 | 1 | 143 | 143 | |
| | | 2 | 625 | 717 | × |
| | | 3 | 130 | 127 | |
| | | 4 | 86 | -87 | |
| | | 5 | 194 | -195 | |
| | | 6 | 66 | -74 | |
| | | 7 | 36 | 34 | |
| | | 8 | 128 | 128 | |
| | | 9 | 24 | -24 | |
| | | 10 | 11 | 19 | |
| | | 11 | 24 | -21 | |
| | | 12 | 20 | -19 | |
| 3 | 1 | 1 | 265 | 263 | |
| | | 2 | 158 | -150 | |
| | | 3 | 243 | 245 | |
| | | 4 | 32 | -35 | |
| | | 5 | 29 | -27 | |
| | | 6 | 89 | 88 | |
| | | 7 | 69 | 67 | |
| | | 8 | 7 | -12 | |
| | | 9 | 45 | 47 | |
| | | 10 | 26 | 20 | |
| | | 11 | 13 | 9 | |
| 4 | 1 | 1 | 134 | 141 | |
| | | 2 | 119 | -120 | |
| | | 3 | 170 | -165 | |
| | | 4 | 218 | -219 | |
| | | 5 | 130 | 129 | |
| | | 6 | 33 | 39 | |
| | | 7 | 14 | 16 | |
| | | 8 | 10 | 6 | |
| | | 9 | 42 | -43 | |
| | | 10 | 34 | -35 | |
| 5 | 1 | 1 | 14 | -13 | |
| | | 2 | 117 | -126 | |
| | | 3 | 26 | -28 | |
| | | 4 | 114 | 116 | |
| | | 5 | 84 | -89 | |
| | | 6 | 7 | -2 | |
| | | 7 | 55 | -54 | |
| | | 8 | 6 | -13 | |
| | | 9 | 17 | 15 | |
| 6 | 1 | 1 | 69 | -72 | |
| | | 2 | 39 | 38 | |
| | | 3 | 21 | -18 | |
| | | 4 | 43 | 48 | |
| | | 5 | 3 | 4 | |
| | | 6 | 18 | -14 | |
| | | 7 | 37 | 37 | |
| | | 9 | 8 | 12 | |
| 7 | 1 | 1 | 28 | -22 | |
| | | 2 | 52 | 50 | |
| | | 3 | 24 | 24 | |
| | | 4 | 63 | -57 | |
| | | 5 | 35 | 38 | |
| | | 7 | 15 | -12 | |
| 8 | 1 | 1 | 37 | 36 | |
| | | 2 | 83 | 79 | |
| | | 3 | 45 | -42 | |
| | | 4 | 14 | -11 | |
| | | 5 | 43 | -45 | |
| | | 6 | 25 | -22 | |
| | | 7 | 9 | -1 | |
| 9 | 1 | 1 | 40 | -41 | |
| | | 2 | 66 | -75 | |
| | | 3 | 44 | 43 | |
| | | 5 | 15 | 21 | |
| | | 6 | 24 | 23 | |
| 10 | 1 | 1 | 81 | 84 | |
| | | 2 | 13 | -11 | |
| | | 3 | 17 | -8 | |
| | | 4 | 23 | -22 | |
| 11 | 1 | 1 | 22 | -19 | |
| | | 2 | 27 | -28 | |
| | | 3 | 23 | -31 | |
| 12 | 1 | 1 | 40 | -39 | |
| -13 | 2 | 3 | 36 | 39 | |
| | | 4 | 12 | -8 | |
| | | 5 | 39 | 36 | |
| | | 6 | 20 | 20 | |
| | | 8 | 18 | 20 | |
| | | 9 | 20 | 24 | |
| | | 10 | 34 | -29 | |
| -12 | 2 | 2 | 16 | 27 | |
| | | 3 | 57 | -52 | |
| | | 4 | 6 | 9 | |
| | | 5 | 56 | -56 | |
| | | 6 | 43 | 37 | |
| | | 8 | 25 | -27 | |
| | | 9 | 45 | -43 | |
| | | 10 | 37 | -37 | |
| | | 11 | 47 | -46 | |
| -11 | 2 | 0 | 53 | 55 | |
| | | 1 | 11 | -17 | |
| | | 3 | 18 | -12 | |
| | | 4 | 10 | -20 | |
| | | 5 | 17 | 12 | |
| | | 6 | 26 | -24 | |
| | | 7 | 59 | -58 | |
| | | 8 | 35 | -29 | |
| | | 9 | 54 | -56 | |
| | | 10 | 38 | 35 | |
| | | 11 | 6 | -10 | |
| | | 12 | 21 | 19 | |
| -10 | 2 | 0 | 37 | 38 | |
| | | 2 | 59 | -53 | |
| | | 3 | 60 | 59 | |
| | | 4 | 27 | -24 | |
| | | 5 | 20 | 12 | |
| | | 6 | 17 | 16 | |
| | | 7 | 46 | -43 | |
| | | 8 | 34 | 34 | |
| | | 9 | 117 | 113 | |
| | | 10 | 17 | 10 | |
| | | 12 | 28 | -35 | |
| | | 13 | 14 | -17 | |
| -9 | 2 | 0 | 17 | -19 | |
| | | 1 | 72 | -73 | |
| | | 2 | 19 | -17 | |
| | | 3 | 16 | 13 | |
| | | 4 | 32 | -28 | |
| | | 5 | 16 | -17 | |
| | | 6 | 57 | 50 | |
| | | 7 | 34 | 28 | |
| | | 8 | 22 | 26 | |
| | | 9 | 26 | -30 | |
| | | 10 | 55 | -53 | |
| | | 11 | 20 | -14 | |
| | | 12 | 34 | 27 | |
| | | 13 | 42 | 37 | |
| -8 | 2 | 0 | 13 | 9 | |
| | | 1 | 146 | 150 | |
| | | 2 | 94 | -88 | |
| | | 3 | 133 | 133 | |
| | | 4 | 53 | -57 | |
| | | 5 | 207 | -209 | |
| | | 6 | 54 | 55 | |
| | | 7 | 153 | 145 | |
| | | 9 | 32 | 32 | |
| | | 11 | 52 | -50 | |
| | | 12 | 12 | -1 | |
| | | 13 | 39 | 35 | |
| -7 | 2 | 0 | 26 | -21 | |
| | | 1 | 119 | 122 | |
| | | 2 | 189 | -183 | |
| | | 3 | 85 | -86 | |
| | | 4 | 92 | 93 | |
| | | 5 | 287 | 287 | |
| | | 6 | 174 | 174 | |
| | | 7 | 68 | 72 | |
| | | 8 | 73 | -78 | |
| | | 9 | 34 | -30 | |
| | | 10 | 51 | -52 | |
| | | 11 | 139 | 135 | |
| | | 12 | 11 | -10 | |
| | | 13 | 17 | -19 | |
| | | 14 | 22 | 15 | |
| -6 | 2 | 0 | 94 | -91 | |
| | | 1 | 81 | 82 | |
| | | 2 | 77 | 75 | |
| | | 3 | 249 | -248 | |
| | | 4 | 202 | 201 | |
| | | 5 | 9 | 4 | |
| | | 6 | 32 | -37 | |
| | | 7 | 38 | -43 | |
| | | 8 | 74 | -74 | |
| | | 9 | 53 | -53 | |
| | | 11 | 39 | -37 | |
| | | 12 | 37 | 37 | |
| | | 13 | 10 | -16 | |
| | | 14 | 27 | 26 | |
| -5 | 2 | 0 | 7 | 9 | |
| | | 1 | 462 | -449 | |
| | | 2 | 34 | -26 | |
| | | 3 | 49 | 46 | |
| | | 4 | 20 | 21 | |
| | | 5 | 146 | -145 | |
| | | 6 | 36 | -32 | |
| | | 7 | 237 | -245 | |
| | | 8 | 16 | -19 | |
| | | 11 | 83 | -79 | |
| | | 13 | 23 | -11 | |
| | | 14 | 8 | -8 | |
| -4 | 2 | 0 | 15 | -14 | |
| | | 1 | 35 | 31 | |
| | | 2 | 38 | -35 | |
| | | 3 | 122 | 116 | |
| | | 4 | 69 | 73 | |
| | | 5 | 75 | -81 | |
| | | 6 | 13 | 18 | |
| | | 7 | 104 | 94 | |
| | | 8 | 114 | -122 | |
| | | 9 | 26 | 31 | |
| | | 10 | 10 | -7 | |
| | | 11 | 9 | 3 | |
| | | 12 | 31 | 32 | |
| | | 13 | 7 | 12 | |
| | | 14 | 17 | -16 | |
| -3 | 2 | 0 | 97 | 84 | |
| | | 1 | 258 | 242 | |
| | | 2 | 9 | -6 | |
| | | 3 | 176 | -159 | |
| | | 4 | 7 | 22 | |
| | | 5 | 62 | 55 | |
| | | 6 | 85 | -87 | |
| | | 7 | 150 | 46 | |
| | | 8 | 21 | 20 | |
| | | 9 | 145 | -140 | |
| | | 10 | 74 | 71 | |
| | | 11 | 54 | 56 | |
| | | 12 | 9 | 2 | |
| | | 13 | 36 | 37 | |
| -2 | 2 | 0 | 257 | -247 | |
| | | 1 | 229 | 207 | |
| | | 2 | 295 | -278 | |
| | | 3 | 13 | 13 | |
| | | 4 | 96 | 94 | |
| | | 5 | 73 | -79 | |
| | | 6 | 32 | 29 | |
| | | 7 | 67 | -69 | |
| | | 8 | 62 | 61 | |
| | | 9 | 94 | 87 | |
| | | 10 | 24 | 21 | |
| | | 11 | 19 | -18 | |
| | | 12 | 30 | -36 | |
| | | 13 | 50 | -43 | |
| -1 | 2 | 0 | 303 | -305 | |
| | | 1 | 12 | 11 | |
| | | 3 | 26 | -25 | |
| | | 4 | 89 | 91 | |
| | | 5 | 540 | 537 | |
| | | 6 | 78 | 79 | |
| | | 7 | 8 | -8 | |
| | | 8 | 38 | -37 | |
| | | 9 | 15 | -1 | |
| | | 10 | 50 | -47 | |
| | | 11 | 60 | 56 | |
| | | 12 | 16 | 17 | |
| 0 | 2 | 0 | 167 | -167 | |
| | | 1 | 209 | 200 | |
| | | 2 | 73 | 68 | |
| | | 3 | 137 | 127 | |
| | | 4 | 143 | 147 | |
| | | 5 | 189 | -179 | |
| | | 6 | 28 | -26 | |
| | | 7 | 49 | 53 | |
| | | 8 | 16 | -11 | |
| | | 9 | 30 | 24 | |
| | | 10 | 21 | 22 | |
| | | 11 | 29 | -26 | |
| 1 | 2 | 1 | 828 | -916 | × |
| | | 2 | 69 | -61 | |
| | | 3 | 96 | -78 | |
| | | 4 | 187 | 179 | |
| | | 5 | 96 | -96 | |
| | | 7 | 149 | -153 | |
| | | 8 | 34 | -36 | |
| | | 9 | 17 | -14 | |
| | | 10 | 15 | -14 | |
| | | 11 | 12 | -14 | |
| | | 12 | 7 | -10 | |
| 2 | 2 | 1 | 101 | 95 | |
| | | 2 | 293 | 277 | |
| | | 3 | 39 | 27 | |
| | | 4 | 18 | 16 | |
| | | 5 | 9 | -13 | |
| | | 6 | 123 | -124 | |
| | | 7 | 17 | 24 | |
| | | 8 | 41 | -44 | |
| | | 9 | 17 | -9 | |
| 3 | 2 | 1 | 210 | 197 | |
| | | 2 | 112 | 107 | |
| | | 3 | 29 | 23 | |
| | | 4 | 98 | -96 | |
| | | 5 | 24 | -25 | |
| | | 6 | 30 | -35 | |
| | | 7 | 53 | 54 | |
| | | 8 | 35 | 38 | |
| | | 10 | 16 | 17 | |
| 4 | 2 | 1 | 19 | -29 | |
| | | 2 | 28 | -21 | |
| | | 3 | 37 | -37 | |
| | | 4 | 62 | 55 | |
| | | 5 | 17 | -14 | |
| | | 6 | 23 | 22 | |
| | | 7 | 49 | -47 | |
| | | 8 | 8 | -13 | |
| | | 9 | 17 | 11 | |
| | | 10 | 9 | 15 | |
| 5 | 2 | 1 | 14 | 7 | |
| | | 2 | 64 | 64 | |
| | | 3 | 9 | 8 | |
| | | 5 | 133 | 131 | |
| | | 6 | 38 | -37 | |
| | | 8 | 29 | 29 | |
| | | 9 | 13 | -16 | |
| 6 | 2 | 1 | 56 | 58 | |
| | | 2 | 10 | -12 | |
| | | 4 | 20 | -4 | |
| | | 5 | 91 | -98 | |
| | | 6 | 26 | 26 | |
| | | 7 | 27 | 26 | |
| | | 8 | 24 | 26 | |
| 7 | 2 | 1 | 145 | -145 | |
| | | 2 | 33 | 33 | |
| | | 3 | 39 | -37 | |
| | | 4 | 22 | 24 | |
| | | 6 | 24 | 26 | |
| | | 7 | 15 | -9 | |
| | | 8 | 23 | -25 | |
| 8 | 2 | 1 | 135 | 141 | |
| | | 2 | 14 | 13 | |
| | | 3 | 53 | -52 | |
| | | 6 | 19 | -22 | |
| 9 | 2 | 2 | 15 | 10 | |
| | | 3 | 10 | 1 | |
| | | 4 | 15 | 9 | |
| | | 5 | 21 | 26 | |
| 10 | 2 | 1 | 45 | -44 | |
| | | 2 | 52 | 49 | |
| | | 3 | 20 | 21 | |
| | | 4 | 15 | -9 | |
| 11 | 2 | 1 | 27 | 30 | |
| 12 | 2 | 0 | 19 | -12 | |
| | | 1 | 33 | 31 | |
| -13 | 3 | 3 | 32 | -32 | |
| | | 4 | 13 | 5 | |
| | | 6 | 10 | 12 | |
| | | 7 | 32 | 29 | |
| | | 8 | 27 | 21 | |
| -12 | 3 | 0 | 41 | -38 | |
| | | 1 | 49 | -46 | |
| | | 3 | 17 | 16 | |
| | | 4 | 31 | -28 | |
| | | 5 | 45 | 47 | |
| | | 7 | 62 | -59 | |
| | | 8 | 36 | 32 | |
| | | 9 | 13 | 11 | |
| | | 10 | 38 | -37 | |
| -11 | 3 | 0 | 17 | 15 | |
| | | 1 | 17 | 16 | |
| | | 2 | 16 | 16 | |
| | | 3 | 22 | -11 | |
| | | 4 | 33 | 33 | |
| | | 5 | 8 | 7 | |
| | | 6 | 51 | 47 | |
| | | 7 | 15 | 10 | |
| | | 8 | 51 | -51 | |
| | | 9 | 13 | 6 | |
| | | 10 | 17 | -7 | |
| -10 | 3 | 0 | 82 | 80 | |
| | | 1 | 76 | -75 | |
| | | 2 | 67 | 66 | |
| | | 3 | 59 | 58 | |
| | | 4 | 17 | 20 | |
| | | 5 | 68 | -64 | |
| | | 6 | 16 | -16 | |
| | | 7 | 12 | -22 | |
| | | 8 | 52 | 54 | |
| | | 9 | 39 | 35 | |
| | | 10 | 53 | 54 | |
| | | 11 | 64 | -60 | |
| | | 12 | 15 | 5 | |
| -9 | 3 | 0 | 30 | -33 | |
| | | 1 | 13 | -22 | |
| | | 2 | 38 | -35 | |
| | | 3 | 28 | -24 | |
| | | 4 | 24 | -21 | |
| | | 6 | 93 | -93 | |
| | | 7 | 18 | -20 | |
| | | 8 | 19 | 15 | |
| | | 9 | 92 | -88 | |
| | | 10 | 16 | -20 | |
| | | 11 | 12 | -4 | |
| | | 12 | 38 | -37 | |
| -8 | 3 | 1 | 115 | 112 | |
| | | 2 | 52 | 53 | |
| | | 4 | 214 | -195 | |
| | | 5 | 11 | -9 | |
| | | 6 | 40 | -43 | |
| | | 7 | 18 | 20 | |
| | | 8 | 25 | 20 | |
| | | 9 | 29 | 24 | |
| | | 10 | 71 | -69 | |
| | | 11 | 53 | 53 | |
| | | 12 | 16 | 2 | |
| -7 | 3 | 0 | 128 | 124 | |
| | | 1 | 34 | -31 | |
| | | 2 | 58 | -54 | |
| | | 3 | 10 | 16 | |
| | | 4 | 140 | -135 | |
| | | 5 | 67 | 68 | |
| | | 6 | 178 | 171 | |
| | | 7 | 12 | 14 | |
| | | 8 | 38 | 43 | |
| | | 9 | 50 | 43 | |
| | | 10 | 15 | 15 | |
| | | 11 | 42 | -39 | |
| | | 12 | 4 | 12 | |
| | | 13 | 9 | 3 | |
| -6 | 3 | 0 | 7 | 5 | |
| | | 1 | 96 | -89 | |
| | | 2 | 207 | -197 | |
| | | 3 | 138 | 136 | |
| | | 4 | 82 | 80 | |
| | | 5 | 13 | 11 | |
| | | 6 | 68 | 68 | |
| | | 7 | 128 | -127 | |
| | | 8 | 23 | -19 | |
| | | 9 | 51 | 50 | |
| | | 10 | 18 | 21 | |
| | | 11 | 30 | 34 | |
| | | 12 | 45 | -45 | |
| | | 13 | 11 | -16 | |
| -5 | 3 | 0 | 6 | 12 | |
| | | 1 | 151 | 144 | |
| | | 2 | 106 | -97 | |
| | | 3 | 35 | -34 | |
| | | 4 | 142 | 136 | |
| | | 5 | 153 | -146 | |
| | | 7 | 241 | 235 | |
| | | 8 | 15 | -5 | |
| | | 9 | 18 | 18 | |
| | | 10 | 37 | -32 | |
| | | 11 | 50 | -47 | |
| | | 12 | 7 | 1 | |
| | | 13 | 45 | 40 | |
| -4 | 3 | 0 | 26 | 26 | |
| | | 1 | 111 | -104 | |
| | | 2 | 335 | 314 | |
| | | 3 | 150 | 135 | |
| | | 4 | 28 | 26 | |
| | | 5 | 52 | -45 | |
| | | 6 | 68 | 76 | |
| | | 7 | 29 | -29 | |
| | | 8 | 145 | 141 | |
| | | 9 | 18 | -19 | |
| | | 10 | 59 | -62 | |
| | | 12 | 27 | 25 | |
| | | 13 | 9 | -7 | |
| -3 | 3 | 0 | 19 | 16 | |
| | | 1 | 146 | 133 | |
| | | 2 | 29 | -33 | |
| | | 3 | 431 | -417 | |
| | | 4 | 33 | -26 | |
| | | 5 | 9 | 11 | |
| | | 6 | 46 | 53 | |
| | | 7 | 33 | -32 | |
| | | 8 | 146 | -144 | |
| | | 9 | 116 | -111 | |
| | | 10 | 15 | 3 | |
| | | 11 | 20 | 23 | |
| | | 12 | 48 | 49 | |
| | | 13 | 12 | -11 | |
| -2 | 3 | 0 | 149 | 135 | |
| | | 1 | 6 | 19 | |
| | | 2 | 254 | -244 | |
| | | 3 | 18 | 16 | |
| | | 4 | 323 | -303 | |
| | | 5 | 10 | 4 | |
| | | 6 | 82 | -80 | |
| | | 7 | 16 | 13 | |
| | | 8 | 66 | -74 | |
| | | 9 | 30 | 24 | |
| | | 10 | 12 | 7 | |
| | | 11 | 23 | -20 | |
| | | 12 | 29 | -27 | |
| -1 | 3 | 0 | 39 | 44 | |
| | | 1 | 58 | -51 | |
| | | 2 | 207 | -197 | |
| | | 3 | 158 | 150 | |
| | | 4 | 72 | 69 | |
| | | 5 | 82 | 73 | |
| | | 6 | 34 | 33 | |
| | | 7 | 34 | -35 | |
| | | 8 | 55 | 53 | |
| | | 9 | 16 | 16 | |
| | | 10 | 13 | 7 | |
| | | 11 | 15 | -4 | |
| | | 12 | 19 | -14 | |
| 0 | 3 | 1 | 51 | 55 | |
| | | 2 | 74 | -80 | |
| | | 3 | 17 | -17 | |
| | | 4 | 70 | 69 | |
| | | 5 | 36 | -35 | |
| | | 6 | 55 | 52 | |
| | | 8 | 36 | 35 | |
| | | 10 | 17 | 10 | |
| | | 11 | 34 | 33 | |
| | | 12 | 19 | 17 | |
| 1 | 3 | 1 | 239 | 233 | |
| | | 2 | 259 | -239 | |
| | | 3 | 42 | -41 | |
| | | 4 | 6 | 1 | |
| | | 5 | 17 | -13 | |
| | | 6 | 87 | 82 | |
| | | 7 | 153 | 150 | |
| | | 8 | 31 | -25 | |
| | | 10 | 23 | -23 | |
| | | 11 | 36 | -32 | |
| 2 | 3 | 1 | 65 | -62 | |
| | | 2 | 194 | 188 | |
| | | 3 | 76 | 76 | |
| | | 4 | 171 | 167 | |
| | | 5 | 98 | 100 | |
| | | 6 | 22 | 26 | |
| | | 7 | 85 | -84 | |
| | | 8 | 2 | 11 | |
| | | 9 | 14 | 11 | |
| | | 10 | 18 | -13 | |
| | | 11 | 35 | 32 | |
| 3 | 3 | 1 | 13 | -14 | |
| | | 2 | 40 | 37 | |
| | | 3 | 325 | -309 | |
| | | 4 | 63 | 63 | |
| | | 6 | 7 | 6 | |
| | | 7 | 20 | 20 | |
| | | 8 | 30 | -34 | |
| | | 9 | 41 | -36 | |
| | | 10 | 8 | 10 | |
| 4 | 3 | 1 | 240 | -239 | |
| | | 2 | 112 | -108 | |
| | | 3 | 152 | 144 | |
| | | 4 | 124 | -121 | |
| | | 5 | 18 | 14 | |
| | | 6 | 16 | -17 | |
| | | 7 | 46 | -41 | |
| | | 8 | 32 | -29 | |
| | | 10 | 28 | -19 | |
| 5 | 3 | 2 | 78 | -75 | |
| | | 3 | 57 | 51 | |
| | | 4 | 91 | 88 | |
| | | 6 | 37 | -38 | |
| | | 7 | 12 | -19 | |
| | | 8 | 34 | -29 | |
| | | 9 | 19 | 14 | |
| 6 | 3 | 1 | 17 | 8 | |
| | | 2 | 24 | 27 | |
| | | 3 | 20 | -21 | |
| | | 4 | 20 | 18 | |
| | | 5 | 17 | -13 | |
| | | 6 | 13 | -21 | |
| | | 7 | 22 | 18 | |
| | | 8 | 38 | 42 | |
| 7 | 3 | 1 | 68 | 61 | |
| | | 2 | 3 | -4 | |
| | | 3 | 24 | 25 | |
| | | 4 | 31 | -32 | |
| | | 6 | 20 | 21 | |
| 8 | 3 | 1 | 19 | -22 | |
| | | 2 | 30 | 36 | |
| | | 5 | 31 | 24 | |
| | | 6 | 21 | 13 | |
| 9 | 3 | 1 | 31 | -32 | |
| | | 2 | 36 | -38 | |
| | | 3 | 27 | -26 | |
| | | 4 | 47 | 43 | |
| 10 | 3 | 1 | 34 | -35 | |
| | | 2 | 14 | 18 | |
| | | 3 | 55 | 50 | |
| 11 | 3 | 1 | 33 | 27 | |
| | | 2 | 30 | 29 | |
| -12 | 4 | 2 | 29 | -24 | |
| | | 3 | 7 | -2 | |
| | | 4 | 18 | 17 | |
| | | 5 | 17 | -15 | |
| | | 6 | 35 | -39 | |
| | | 8 | 15 | -12 | |
| -11 | 4 | 1 | 24 | 19 | |
| | | 2 | 25 | 21 | |
| | | 3 | 14 | -16 | |
| | | 4 | 45 | 45 | |
| | | 5 | 7 | 5 | |
| | | 6 | 15 | -5 | |
| | | 7 | 9 | 4 | |
| | | 8 | 59 | 57 | |
| | | 9 | 34 | -32 | |
| | | 10 | 15 | 15 | |
| -10 | 4 | 0 | 42 | -44 | |
| | | 1 | 9 | 1 | |
| | | 2 | 36 | 31 | |
| | | 3 | 49 | -49 | |
| | | 4 | 29 | 22 | |
| | | 5 | 19 | 20 | |
| | | 6 | 14 | 15 | |
| | | 8 | 30 | 22 | |
| | | 9 | 13 | 3 | |
| | | 10 | 17 | -12 | |
| | | 11 | 40 | 37 | |
| -9 | 4 | 0 | 13 | -8 | |
| | | 1 | 79 | -83 | |
| | | 2 | 84 | 81 | |
| | | 3 | 9 | -7 | |
| | | 4 | 43 | -41 | |
| | | 5 | 18 | 13 | |
| | | 6 | 28 | 19 | |
| | | 8 | 30 | -27 | |
| | | 9 | 32 | 24 | |
| | | 10 | 51 | -50 | |
| | | 11 | 32 | -36 | |
| | | 12 | 30 | 32 | |
| -8 | 4 | 0 | 56 | 48 | |
| | | 1 | 19 | -19 | |
| | | 2 | 75 | 71 | |
| | | 3 | 44 | 40 | |
| | | 4 | 51 | 51 | |
| | | 5 | 25 | 29 | |
| | | 6 | 48 | -45 | |
| | | 7 | 37 | -35 | |
| | | 8 | 10 | -18 | |
| | | 9 | 39 | -36 | |
| | | 10 | 116 | 114 | |
| | | 11 | 11 | 17 | |
| | | 12 | 11 | -2 | |
| -7 | 4 | 0 | 95 | 90 | |
| | | 1 | 78 | 75 | |
| | | 2 | 90 | -94 | |
| | | 3 | 13 | -10 | |
| | | 4 | 89 | -87 | |
| | | 6 | 16 | 15 | |
| | | 7 | 38 | 38 | |
| | | 8 | 23 | -24 | |
| | | 9 | 17 | 19 | |
| | | 10 | 23 | -22 | |
| | | 12 | 11 | -7 | |
| -6 | 4 | 0 | 127 | -124 | |
| | | 1 | 95 | -100 | |
| | | 3 | 51 | 51 | |

Table 3 (*cont.*)

| | | | | |
|---|---|---|---|---|
| -6 | 4 | 4 | 56 | -50 |
| | | 5 | 63 | 66 |
| | | 6 | 227 | -224 |
| | | 7 | 84 | -81 |
| | | 9 | 9 | 7 |
| | | 10 | 8 | 1 |
| | | 12 | 60 | -54 |
| -5 | 4 | 0 | 56 | 57 |
| | | 1 | 6 | 12 |
| | | 2 | 21 | -17 |
| | | 3 | 32 | 37 |
| | | 4 | 43 | -35 |
| | | 5 | 114 | -106 |
| | | 6 | 57 | 53 |
| | | 7 | 51 | -54 |
| | | 8 | 105 | 108 |
| | | 9 | 42 | 39 |
| | | 12 | 19 | -17 |
| -4 | 4 | 0 | 42 | -42 |
| | | 1 | 11 | -1 |
| | | 2 | 150 | 148 |
| | | 3 | 19 | -19 |
| | | 5 | 40 | -41 |
| | | 6 | 135 | 132 |
| | | 7 | 116 | 116 |
| | | 8 | 35 | 35 |
| | | 9 | 4 | 1 |
| | | 10 | 28 | -29 |
| | | 11 | 20 | -19 |
| | | 12 | 30 | 24 |
| -3 | 4 | 0 | 104 | 97 |
| | | 1 | 16 | -19 |
| | | 2 | 68 | 65 |
| | | 3 | 21 | 21 |
| | | 4 | 104 | -102 |
| | | 5 | 57 | 55 |
| | | 6 | 36 | 38 |
| | | 8 | 12 | -13 |
| | | 9 | 10 | 14 |
| | | 10 | 31 | -29 |
| | | 11 | 27 | 28 |
| | | 12 | 11 | -2 |
| -2 | 4 | 0 | 164 | 155 |
| | | 1 | 45 | -46 |
| | | 2 | 88 | -83 |
| | | 3 | 49 | -46 |
| | | 4 | 217 | 210 |
| | | 5 | 23 | 23 |
| | | 6 | 10 | 15 |
| | | 7 | 36 | -35 |
| | | 8 | 47 | -42 |
| | | 9 | 18 | 14 |
| | | 10 | 65 | 65 |
| | | 11 | 16 | 1 |
| | | 12 | 15 | -9 |
| -1 | 4 | 0 | 149 | 142 |
| | | 1 | 11 | 9 |
| | | 2 | 24 | 17 |
| | | 3 | 138 | 136 |
| | | 4 | 29 | -30 |
| | | 5 | 79 | -78 |
| | | 6 | 30 | -25 |
| | | 7 | 40 | 42 |
| | | 8 | 20 | 16 |
| | | 9 | 10 | 13 |
| | | 10 | 27 | -30 |
| | | 11 | 58 | -58 |
| -1 | 4 | 12 | 24 | 25 |
| 0 | 4 | 0 | 348 | -352 |
| | | 1 | 80 | 76 |
| | | 2 | 33 | 28 |
| | | 3 | 17 | 19 |
| | | 4 | 157 | -158 |
| | | 5 | 32 | -27 |
| | | 6 | 237 | -229 |
| | | 8 | 34 | 34 |
| | | 9 | 38 | -33 |
| | | 10 | 11 | 3 |
| | | 11 | 24 | 21 |
| 1 | 4 | 1 | 98 | 101 |
| | | 2 | 76 | -79 |
| | | 3 | 168 | -169 |
| | | 4 | 168 | -165 |
| | | 5 | 46 | -47 |
| | | 6 | 131 | 129 |
| | | 7 | 17 | 7 |
| | | 8 | 16 | 12 |
| | | 10 | 27 | -26 |
| | | 11 | 17 | 8 |
| 2 | 4 | 1 | 77 | -68 |
| | | 2 | 98 | 81 |
| | | 3 | 37 | 28 |
| | | 4 | 6 | -2 |
| | | 5 | 36 | 32 |
| | | 6 | 81 | 85 |
| | | 8 | 19 | 13 |
| | | 10 | 20 | 19 |
| 3 | 4 | 1 | 85 | 77 |
| | | 2 | 172 | -166 |
| | | 3 | 56 | 52 |
| | | 4 | 14 | 7 |
| | | 5 | 19 | -20 |
| | | 6 | 20 | 18 |
| | | 7 | 16 | 21 |
| | | 8 | 12 | 13 |
| | | 9 | 35 | 34 |
| | | 10 | 17 | -19 |
| 4 | 4 | 1 | 34 | 34 |
| | | 2 | 39 | -35 |
| | | 3 | 110 | -109 |
| | | 4 | 120 | 133 |
| | | 5 | 23 | 20 |
| | | 6 | 19 | 18 |
| | | 7 | 57 | 57 |
| | | 8 | 22 | -27 |
| | | 9 | 33 | -30 |
| 6 | 4 | 1 | 28 | -28 |
| | | 2 | 40 | -43 |
| | | 3 | 12 | -16 |
| | | 4 | 30 | -26 |
| | | 6 | 36 | -38 |
| | | 7 | 6 | -7 |
| 7 | 4 | 1 | 13 | -18 |
| | | 2 | 46 | -51 |
| | | 3 | 13 | -12 |
| | | 4 | 36 | -37 |
| | | 5 | 8 | -15 |
| | | 6 | 14 | 17 |
| 8 | 4 | 1 | 14 | 13 |
| | | 3 | 9 | -13 |
| | | 5 | 5 | 5 |
| 9 | 4 | 1 | 14 | -5 |
| | | 2 | 69 | -67 |
| | | 3 | 10 | -10 |
| 9 | 4 | 4 | 13 | 10 |
| 11 | 4 | 0 | 11 | 3 |
| -11 | 5 | 2 | 41 | 38 |
| | | 3 | 40 | 33 |
| | | 4 | 31 | -31 |
| | | 5 | 19 | -26 |
| | | 6 | 14 | -11 |
| | | 7 | 22 | 26 |
| -10 | 5 | 0 | 16 | 5 |
| | | 1 | 15 | -1 |
| | | 2 | 43 | -45 |
| | | 3 | 36 | -32 |
| | | 4 | 13 | 0 |
| | | 5 | 33 | -39 |
| | | 6 | 19 | 22 |
| | | 7 | 9 | 18 |
| | | 8 | 37 | -35 |
| | | 9 | 23 | -20 |
| -9 | 5 | 1 | 6 | 1 |
| | | 2 | 8 | -14 |
| | | 3 | 69 | -74 |
| | | 4 | 33 | 29 |
| | | 5 | 12 | -11 |
| | | 6 | 55 | 64 |
| | | 7 | 19 | -19 |
| | | 8 | 16 | 10 |
| | | 9 | 59 | -58 |
| | | 10 | 16 | -13 |
| -8 | 5 | 0 | 38 | -44 |
| | | 1 | 4 | 11 |
| | | 2 | 46 | 45 |
| | | 3 | 7 | -10 |
| | | 4 | 94 | 100 |
| | | 5 | 29 | 30 |
| | | 6 | 26 | -23 |
| | | 8 | 29 | -30 |
| | | 9 | 42 | 46 |
| | | 10 | 15 | 4 |
| -7 | 5 | 1 | 26 | -22 |
| | | 2 | 21 | 16 |
| | | 4 | 2 | -6 |
| | | 5 | 56 | 56 |
| | | 6 | 55 | -54 |
| | | 7 | 27 | 29 |
| | | 9 | 7 | 7 |
| | | 10 | 18 | 23 |
| | | 11 | 9 | -3 |
| -6 | 5 | 0 | 37 | -41 |
| | | 1 | 14 | -17 |
| | | 3 | 29 | 23 |
| | | 4 | 24 | 20 |
| | | 5 | 13 | 11 |
| | | 6 | 19 | 17 |
| | | 7 | 40 | -41 |
| | | 8 | 78 | -37 |
| | | 9 | 26 | -29 |
| | | 10 | 10 | -6 |
| | | 11 | 9 | 8 |
| -5 | 5 | 0 | 11 | -16 |
| | | 1 | 41 | 40 |
| | | 2 | 136 | 137 |
| | | 3 | 46 | 43 |
| | | 4 | 85 | -88 |
| | | 5 | 13 | 9 |
| | | 6 | 104 | -112 |
| | | 7 | 19 | 20 |
| | | 8 | 54 | 54 |
| -5 | 5 | 9 | 19 | 15 |
| | | 10 | 23 | 26 |
| | | 11 | 9 | 5 |
| -4 | 5 | 0 | 30 | 35 |
| | | 1 | 28 | -32 |
| | | 2 | 150 | -158 |
| | | 3 | 40 | 35 |
| | | 4 | 52 | -54 |
| | | 5 | 19 | -19 |
| | | 6 | 66 | 61 |
| | | 7 | 22 | -26 |
| | | 8 | 53 | -50 |
| | | 10 | 14 | -8 |
| | | 11 | 3 | 5 |
| -3 | 5 | 2 | 19 | 16 |
| | | 3 | 146 | -148 |
| | | 4 | 11 | 4 |
| | | 5 | 71 | -72 |
| | | 6 | 29 | 31 |
| | | 7 | 40 | -42 |
| | | 9 | 41 | -44 |
| -2 | 5 | 0 | 31 | -36 |
| | | 1 | 27 | -29 |
| | | 2 | 29 | -28 |
| | | 3 | 30 | -26 |
| | | 4 | 146 | 148 |
| | | 5 | 55 | 55 |
| | | 6 | 48 | -49 |
| | | 7 | 11 | -3 |
| | | 8 | 22 | 23 |
| | | 9 | 36 | 41 |
| | | 10 | 38 | 39 |
| | | 11 | 5 | 2 |
| -1 | 5 | 0 | 121 | -117 |
| | | 1 | 62 | -65 |
| | | 2 | 75 | 78 |
| | | 3 | 113 | 117 |
| | | 4 | 31 | 27 |
| | | 5 | 84 | 83 |
| | | 8 | 18 | 24 |
| | | 9 | 31 | 39 |
| | | 10 | 29 | -28 |
| | | 11 | 11 | 12 |
| 0 | 5 | 1 | 48 | -51 |
| | | 2 | 166 | 164 |
| | | 3 | 69 | 74 |
| | | 4 | 40 | -43 |
| | | 5 | 81 | -84 |
| | | 6 | 24 | 25 |
| | | 8 | 24 | -20 |
| | | 9 | 6 | 10 |
| | | 10 | 15 | -10 |
| 1 | 5 | 1 | 88 | 92 |
| | | 2 | 30 | 26 |
| | | 4 | 39 | -44 |
| | | 5 | 8 | -5 |
| | | 6 | 40 | -40 |
| | | 7 | 29 | 32 |
| | | 9 | 30 | -28 |
| | | 10 | 44 | 43 |
| 2 | 5 | 1 | 67 | 73 |
| | | 2 | 167 | -178 |
| | | 3 | 20 | 12 |
| | | 4 | 25 | 24 |
| | | 5 | 16 | 20 |
| | | 6 | 21 | -15 |
| | | 7 | 35 | -36 |
| 2 | 5 | 8 | 47 | -50 |
| | | 9 | 15 | 8 |
| 3 | 5 | 0 | 43 | -46 |
| | | 1 | 68 | -70 |
| | | 2 | 111 | 106 |
| | | 3 | 87 | -84 |
| | | 4 | 68 | -75 |
| | | 5 | 46 | -43 |
| | | 6 | 76 | -76 |
| | | 7 | 24 | -29 |
| | | 8 | 60 | 61 |
| 4 | 5 | 1 | 30 | -37 |
| | | 2 | 31 | -37 |
| | | 3 | 41 | 42 |
| | | 5 | 36 | -38 |
| | | 6 | 49 | 48 |
| | | 8 | 22 | 21 |
| 5 | 5 | 1 | 77 | 83 |
| | | 2 | 41 | 41 |
| | | 3 | 24 | 22 |
| | | 6 | 23 | 21 |
| | | 7 | 37 | 35 |
| 6 | 5 | 2 | 25 | 21 |
| | | 3 | 17 | -24 |
| | | 4 | 13 | 3 |
| 7 | 5 | 0 | 14 | 4 |
| | | 1 | 10 | 8 |
| | | 2 | 27 | 23 |
| | | 4 | 21 | 17 |
| | | 5 | 10 | 5 |
| 8 | 5 | 1 | 38 | 40 |
| | | 2 | 9 | -10 |
| | | 3 | 4 | 8 |
| | | 4 | 18 | -23 |
| -10 | 6 | 4 | 41 | -41 |
| | | 9 | 22 | -23 |
| -9 | 6 | 0 | 11 | 15 |
| | | 2 | 30 | -35 |
| | | 3 | 22 | -6 |
| | | 4 | 28 | 24 |
| | | 5 | 6 | 11 |
| | | 6 | 27 | 8 |
| -8 | 6 | 0 | 14 | 14 |
| | | 1 | 13 | -4 |
| | | 2 | 17 | -16 |
| | | 3 | 10 | -3 |
| | | 4 | 28 | 26 |
| | | 5 | 15 | 10 |
| | | 6 | 9 | 17 |
| | | 7 | 43 | -46 |
| | | 8 | 32 | 31 |
| | | 9 | [illegible] | -3 |
| -7 | 6 | 0 | 33 | -32 |
| | | 2 | 14 | 22 |
| | | 3 | 40 | -38 |
| | | 4 | 16 | 22 |
| | | 5 | 85 | -95 |
| | | 6 | 10 | -6 |
| | | 7 | 19 | 23 |
| | | 8 | 20 | 22 |
| | | 9 | 8 | 21 |
| | | 10 | 41 | -34 |
| -6 | 6 | 0 | 2 | 4 |
| | | 1 | 47 | -39 |
| | | 2 | 17 | -19 |
| | | 3 | 31 | 37 |
| | | 4 | 12 | -19 |
| -6 | 6 | 5 | 53 | 56 |
| | | 6 | 19 | 23 |
| | | 7 | 25 | 29 |
| | | 8 | 42 | -57 |
| | | 9 | 23 | -22 |
| -5 | 6 | 1 | 104 | 120 |
| | | 2 | 11 | 6 |
| | | 3 | 23 | 22 |
| | | 4 | 27 | 26 |
| | | 5 | 12 | 2 |
| | | 7 | 44 | 47 |
| | | 8 | 15 | -21 |
| | | 9 | 17 | 9 |
| | | 10 | 22 | 28 |
| -4 | 6 | 0 | 21 | -24 |
| | | 1 | 7 | -8 |
| | | 2 | 17 | 13 |
| | | 3 | 69 | -72 |
| | | 4 | 31 | 30 |
| | | 5 | 37 | 40 |
| | | 6 | 21 | -21 |
| | | 8 | 33 | 30 |
| | | 9 | 25 | -29 |
| | | 10 | 24 | 16 |
| -3 | 6 | 1 | 10 | -2 |
| | | 2 | 10 | 15 |
| | | 3 | 36 | 34 |
| | | 4 | 33 | -35 |
| | | 5 | 37 | 39 |
| | | 6 | 21 | -23 |
| | | 7 | 59 | -61 |
| | | 8 | 5 | -13 |
| -2 | 6 | 0 | 58 | 62 |
| | | 1 | 22 | -29 |
| | | 2 | 24 | -23 |
| | | 3 | 4 | -3 |
| | | 4 | 49 | -55 |
| | | 5 | 20 | -14 |
| | | 6 | 17 | 38 |
| | | 7 | 16 | -22 |
| | | 9 | 21 | 19 |
| -1 | 6 | 0 | 55 | -53 |
| | | 1 | 65 | -69 |
| | | 2 | 40 | -35 |
| | | 4 | 68 | 73 |
| | | 5 | 93 | -94 |
| | | 6 | 11 | -11 |
| | | 7 | 26 | 18 |
| | | 8 | 2 | -12 |
| | | 9 | 6 | -10 |
| 0 | 6 | 0 | 42 | -35 |
| | | 1 | 21 | 19 |
| | | 2 | 26 | -26 |
| | | 3 | 12 | -15 |
| | | 4 | 25 | -21 |
| | | 5 | 30 | 30 |
| | | 7 | 4 | -14 |
| | | 8 | 9 | -3 |
| | | 9 | 26 | -27 |
| 1 | 6 | 1 | 119 | 111 |
| | | 2 | 36 | 45 |
| | | 3 | 48 | -42 |
| | | 4 | 31 | 24 |
| | | 5 | 50 | 51 |
| | | 6 | 42 | 19 |
| | | 7 | 50 | 50 |
| 1 | 6 | 8 | 20 | -18 |
| 2 | 6 | 1 | 107 | -111 |
| | | 2 | 22 | 26 |
| | | 3 | 38 | 42 |
| | | 4 | 58 | 60 |
| | | 5 | 67 | 70 |
| | | 6 | 16 | 6 |
| | | 7 | 42 | -41 |
| | | 8 | 19 | -12 |
| 3 | 6 | 2 | 8 | -1 |
| | | 3 | 58 | 66 |
| | | 4 | 0 | 16 |
| | | 5 | 41 | -40 |
| | | 6 | 36 | -37 |
| | | 7 | 30 | -31 |
| 4 | 6 | 1 | 16 | -3 |
| | | 2 | 22 | 26 |
| | | 3 | 14 | 5 |
| | | 4 | 43 | -45 |
| | | 5 | 8 | -1 |
| | | 6 | 27 | -26 |
| 5 | 6 | 0 | 11 | 6 |
| | | 2 | 15 | -13 |
| | | 4 | 9 | -4 |
| | | 5 | 34 | -35 |
| 6 | 6 | 1 | 15 | -8 |
| | | 2 | 41 | -43 |
| | | 3 | 41 | -41 |
| 7 | 6 | 2 | 22 | 11 |
| | | 3 | 23 | 17 |
| 8 | 6 | 1 | 19 | -13 |
| | | 2 | 52 | 52 |
| -7 | 7 | 1 | 15 | 6 |
| | | 2 | 29 | -28 |
| | | 3 | 15 | 22 |
| | | 4 | 26 | -34 |
| | | 5 | 38 | -50 |
| | | 6 | 9 | -11 |
| -6 | 7 | 1 | 59 | 60 |
| | | 3 | 49 | -52 |
| | | 4 | 21 | 15 |
| | | 5 | 6 | -15 |
| | | 6 | 29 | 33 |
| | | 7 | 37 | 39 |
| -5 | 7 | 1 | 23 | -26 |
| | | 2 | 23 | 23 |
| | | 3 | 24 | -18 |
| | | 5 | 35 | 40 |
| | | 6 | 14 | 6 |
| | | 7 | 42 | -47 |
| -4 | 7 | 0 | 13 | -19 |
| | | 1 | 23 | -15 |
| | | 2 | 60 | -63 |
| | | 4 | 17 | -19 |
| | | 5 | 13 | 17 |
| | | 7 | 14 | 18 |
| | | 8 | 17 | -22 |
| -3 | 7 | 1 | 7 | -7 |
| | | 2 | 24 | 25 |
| | | 3 | 68 | 78 |
| | | 4 | 40 | 49 |
| | | 5 | 17 | -24 |
| | | 6 | 25 | -20 |
| | | 7 | 16 | 13 |
| | | 8 | 11 | -9 |
| -2 | 7 | 1 | 26 | 31 |
| -2 | 7 | 2 | 43 | 46 |
| | | 3 | 28 | -30 |
| | | 4 | 15 | 5 |
| | | 5 | 5 | 12 |
| | | 7 | 20 | 18 |
| -1 | 7 | 1 | 5 | 17 |
| | | 2 | 26 | -21 |
| | | 3 | 7 | 5 |
| | | 4 | 33 | -36 |
| | | 6 | 19 | 22 |
| | | 7 | 13 | -12 |
| 0 | 7 | 0 | 8 | 0 |
| | | 1 | 17 | 20 |
| | | 2 | 11 | 8 |
| | | 3 | 19 | -20 |
| | | 4 | 22 | -18 |
| | | 5 | 23 | -24 |
| | | 6 | 8 | -10 |
| | | 7 | 17 | 11 |
| 1 | 7 | 0 | 30 | 31 |
| | | 1 | 27 | -32 |
| | | 2 | 28 | -35 |
| | | 3 | 24 | -32 |
| | | 4 | 18 | -19 |
| | | 6 | 36 | 33 |
| 2 | 7 | 0 | 60 | -65 |
| | | 2 | 50 | -52 |
| | | 3 | 28 | -37 |
| | | 4 | 27 | 31 |
| | | 6 | 10 | 8 |
| 3 | 7 | 0 | 16 | 4 |
| | | 1 | 48 | -45 |
| | | 2 | 19 | 22 |
| | | 3 | 56 | 59 |
| 5 | 7 | 0 | 6 | -2 |
| | | 1 | 32 | 32 |
| | | 2 | 27 | 25 |
| | | 3 | 19 | 1 |
| 6 | 7 | 0 | 17 | 29 |
| | | 1 | 21 | -10 |
| | | 2 | 14 | -23 |
| 7 | 7 | 0 | 20 | -4 |
| -4 | 8 | 0 | 12 | -18 |
| | | 1 | 18 | -21 |
| | | 2 | 71 | -33 |
| | | 3 | 25 | -27 |
| -3 | 8 | 0 | 26 | -39 |
| | | 1 | 23 | -15 |
| | | 2 | 12 | 24 |
| | | 3 | 15 | 21 |
| | | 4 | 12 | 14 |
| -2 | 8 | 1 | 29 | 30 |
| | | 2 | 18 | 18 |
| | | 4 | 35 | -32 |
| -1 | 8 | 0 | 17 | 8 |
| | | 1 | 38 | -39 |
| | | 2 | 6 | 8 |
| | | 3 | 29 | -29 |
| | | 4 | 14 | 8 |
| 0 | 8 | 0 | 49 | 56 |
| | | 1 | 19 | 23 |
| | | 3 | 34 | 37 |
| | | 4 | 4 | 5 |
| 2 | 8 | 0 | 7 | -3 |
| | | 1 | 17 | 6 |
| | | 2 | 39 | -40 |

angle between the planar carboxyl group 1 and the F(1)–C–C plane is 25°, between carboxyl group 2 and the F(2)–C–C plane 46°. This result strongly suggests that the tendency for coplanarity as found in monofluorocarboxylic acids is seriously hampered in the case of two fluorine substituents.

Table 4. *Interatomic distances and angles in the structure of difluoromalonic acid*

Bond lengths

| | |
|---|---|
| O(1)—C(1) | 1·288 Å |
| O(2)—C(1) | 1·213 |
| O(3)—C(3) | 1·270 |
| O(4)—C(3) | 1·207 |
| F(1)—C(2) | 1·340 |
| F(2)—C(2) | 1·345 |
| C(1)—C(2) | 1·537 |
| C(2)—C(3) | 1·541 |
| O(1)—H(1) | 0·85 |
| O(3)—H(2) | 0·68 |
| O(1)···O(4) | 3·186 |
| O(1)···O(2′) | 2·704(1 – *x*,1 – *y*,1 – *z*) |
| O(3)···O(4′) | 2·690(2 – *x*, – *y*,1 – *z*) |

Bond angles

| | |
|---|---|
| O(1)-C(1)—O(2) | 127·3° |
| O(1)-C(1)—C(2) | 112·6 |
| O(2)-C(1)—C(2) | 120·0 |
| O(3)-C(3)—O(4) | 128·0 |
| O(3)-C(3)—C(2) | 113·2 |
| O(4)-C(3)—C(2) | 118·8 |
| F(1)-C(2)—F(2) | 107·0 |
| C(1)-C(2)—F(1) | 109·6 |
| C(1)-C(2)—F(2) | 111·4 |
| C(3)-C(2)—F(1) | 109·2 |
| C(3)-C(2)—F(2) | 108·4 |
| C(1)-C(2)—C(3) | 111·1 |
| C(1)-O(1)—H(1) | 107 |
| C(3)-O(3)—H(2) | 103 |
| O(1)-H(1)···O(2′) | 175 |
| O(3)-H(2)···O(4′) | 156 |

As in malonic acid (Goedkoop & MacGillavry, 1957) and its derivatives tartronic acid (van Eijck, Kanters & Kroon, 1965), dimethylmalonic acid (Haas & Brenner, 1966), methylmalonic acid (Derissen, 1970) and fluoromalonic acid (Roelofsen *et al.*, 1971), the acid molecules form infinite chains by double carboxyl-group coupling (see Fig. 1). The stacking of the chains is determined by ordinary van der Waals interactions; no particular distances besides those concerning the hydrogen bonds are found in this structure.

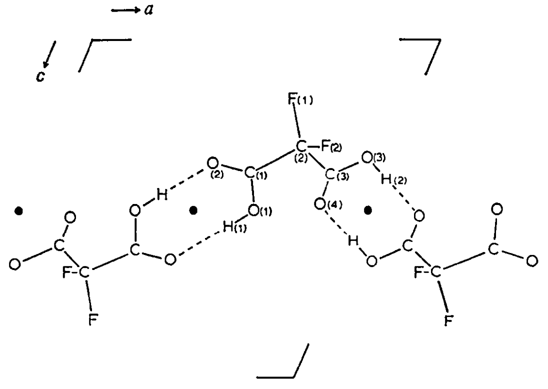


Fig. 1. Projection of the structure along the *b* axis. Hydrogen bonds are shown by dashed lines.

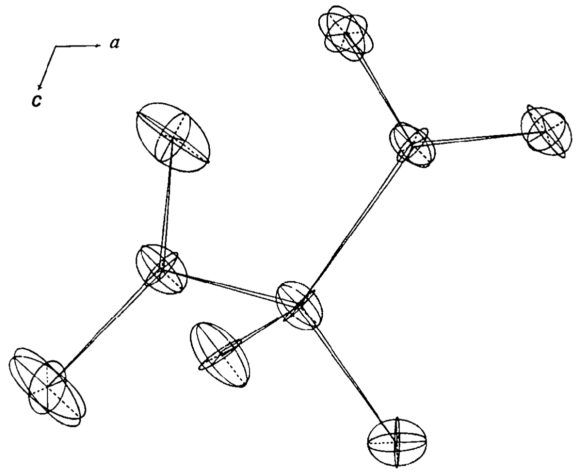


Fig. 2. Shape and orientation of the vibrational ellipsoids in the difluoromalonic acid molecule.

The shape and orientation of the vibrational ellipsoids in the difluoromalonic acid molecule are shown in Fig. 2.

### References

DERISSEN, J. (1970). *Acta Cryst.* B**27**, 910.

EIJCK, B. P. VAN (1966). *Rec. Trav. chim. Pays-Bas*, **85**, 1129.

EIJCK, B. P. VAN, KANTERS, J. A. & KROON, J. (1965). *Acta Cryst.* **19**, 435.

GOEDKOOP, J. A. & MACGILLAVRY, C. H. (1957). *Acta Cryst.* **10**, 125.

HAAS, D. J. & BRENNER, S. A. (1966). *Acta Cryst.* **20**, 709.

KANTERS, J. A. (1972). To be published.

KANTERS, J. A., KROON, J., BEURSKENS, P. T. & VLIEGENTHART, J. A. (1966). *Acta Cryst.* **21**, 990.

KANTERS, J. A., KROON, J., PEERDEMAN, A. F. & SCHOONE, J. C. (1967). *Tetrahedron*, **23**, 4027.

KARLE, J. & HAUPTMAN, H. (1958). *Acta Cryst.* **11**, 264.

MOORE, F. H. (1963). *Acta Cryst.* **16**, 1169.

PIJPER, W. P. (1971). *Acta Cryst.* B**27**, 344.

ROELOFSEN, G., KANTERS, J. A., KROON, J. & VLIEGENHART, J. A. (1971). *Acta Cryst.* B**27**, 702.

STRIETER, F. J. & TEMPLETON, D. H. (1962). *Acta Cryst.* **15**, 1233..

WILSON, A. J. C. (1942). *Nature, Lond.* **150**, 152.

---

*Acta Cryst..* (1972). B**28**, 1349

# Structure Cristalline et Moléculaire du Complexe Oestradiol–Propanol

PAR BERNARD BUSETTA, CHRISTIAN COURSEILLE, SERGE GEOFFRE ET MICHEL HOSPITAL

*Laboratoire de Cristallographie et de Physique Cristalline associé au C.N.R.S., Université de Bordeaux* I,
351 *cours de la Libération*, 33-*Talence*, *France*

(*Reçu le* 1 *décembre* 1971)

The crystallographic structure of the complex oestradiol–propanol ($C_{18}H_{24}O_2.C_3H_8O$) has been determined by X-ray diffraction. Space group: $P2_12_12_1$, $Z=4$, $a=12{\cdot}215$ (4), $b=24{\cdot}251$ (7), $c=6{\cdot}671$ (3) Å. A direct minimization of the residual coefficient $R$ is used to solve the structure. The conformation of the oestradiol molecule previously described is very slightly perturbed by the presence of alcohol in the crystals.

La conformation de la molécule d'oestradiol: $C_{18}H_{24}O_2$ a déjà été décrite dans la publication de la structure hémihydratée (Busetta & Hospital, 1972). Pour voir si l'environnement pouvait affecter la conformation du squelette stéroïdique, nous avons étudié les solvates de l'oestradiol avec le propanol ($C_3H_8O$).

Tableau 1. *Coordonnées relatives* ($\times 10^5$) *et facteurs d'agitation thermique*

| | $x$ | $y$ | $z$ | $B_{11}$ | $B_{22}$ | $B_{33}$ | $B_{23}$ | $B_{13}$ | $B_{12}$ |
|---|---|---|---|---|---|---|---|---|---|
| C(1) | 56106 (31) | 12841 (18) | −27030 (60) | 0·00689 | 0·00266 | 0·01983 | −0·00254 | −0·00135 | −0·00059 |
| C(2) | 67189 (32) | 12069 (17) | −30300 (64) | 0·00745 | 0·00236 | 0·02211 | −0·00248 | 0·00078 | 0·00040 |
| C(3) | 74635 (29) | 13949 (16) | −16217 (66) | 0·00609 | 0·00203 | 0·02634 | −0·00016 | −0·00037 | 0·00023 |
| C(4) | 70847 (32) | 16707 (16) | 504 (51) | 0·00693 | 0·00215 | 0·02340 | −0·00036 | −0·00222 | −0·00101 |
| C(5) | 59786 (30) | 17572 (15) | 3847 (61) | 0·00709 | 0·00176 | 0·02171 | −0·00042 | −0·00036 | −0·00042 |
| C(6) | 56369 (33) | 20667 (18) | 22398 (66) | 0·00807 | 0·00245 | 0·02325 | −0·00344 | 0·00077 | −0·00132 |
| C(7) | 44264 (34) | 22324 (17) | 22608 (73) | 0·00842 | 0·00226 | 0·02877 | −0·00391 | 0·00629 | −0·00061 |
| C(8) | 37189 (30) | 17511 (15) | 15640 (58) | 0·00671 | 0·00200 | 0·01821 | 0·00015 | 0·00082 | −0·00007 |
| C(9) | 39751 (30) | 16233 (16) | −6534 (58) | 0·00716 | 0·00223 | 0·01790 | −0·00015 | 0·00017 | 0·00049 |
| C(10) | 52094 (30) | 15467 (15) | −9965 (60) | 0·00671 | 0·00194 | 0·01977 | 0·00053 | 0·00103 | −0·00003 |
| C(11) | 32794 (33) | 11400 (19) | −14173 (69) | 0·00682 | 0·00309 | 0·02507 | −0·00472 | −0·00233 | −0·00050 |
| C(12) | 20384 (34) | 12187 (21) | −10476 (70) | 0·00642 | 0·00379 | 0·02338 | −0·00342 | −0·00103 | 0·00009 |
| C(13) | 18038 (30) | 13600 (17) | 11524 (63) | 0·00609 | 0·00247 | 0·02108 | 0·00120 | −0·00102 | 0·00083 |
| C(14) | 25069 (31) | 18598 (16) | 17365 (62) | 0·00718 | 0·00212 | 0·02071 | 0·00053 | 0·00246 | 0·00085 |
| C(15) | 20200 (38) | 20504 (20) | 37562 (77) | 0·00938 | 0·00288 | 0·02796 | −0·00292 | 0·00824 | −0·00021 |
| C(16) | 7819 (37) | 19285 (22) | 35426 (82) | 0·00892 | 0·00333 | 0·03141 | −0·00180 | 0·00946 | 0·00054 |
| C(17) | 6616 (32) | 16041 (19) | 15367 (67) | 0·00654 | 0·00308 | 0·02465 | 0·00503 | 0·00183 | 0·00106 |
| C(18) | 19720 (34) | 8584 (19) | 24985 (79) | 0·00694 | 0·00252 | 0·03650 | 0·00295 | −0·00285 | −0·00039 |
| O(83) | 85730 (21) | 13238 (12) | −18576 (48) | 0·00654 | 0·00271 | 0·03087 | −0·00161 | 0·00021 | 0·00012 |
| O(97) | −2168 (23) | 12213 (15) | 16177 (51) | 0·00686 | 0·00422 | 0·02932 | 0·00463 | 0·00112 | −0·00143 |
| C(51) | −2915 (95) | −913 (31) | 82216 (200) | 0·02822 | 0·00317 | 0·09413 | 0·01036 | −0·01434 | −0·00028 |
| C(52) | −10740 (81) | −1525 (25) | 66294 (157) | 0·03250 | 0·00282 | 0·06586 | −0·00104 | 0·01526 | 0·00436 |
| C(53) | −8402 (69) | 1399 (26) | 48036 (111) | 0·02607 | 0·00283 | 0·04682 | −0·00361 | 0·00842 | −0·00318 |
| O(54) | −8668 (30) | 7067 (14) | 50488 (52) | 0·01504 | 0·00280 | 0·03293 | −0·00041 | 0·01174 | 0·00124 |