# Hydrogen bond studies.* 85. A very short, asymmetrical, intramolecular hydrogen bond: A neutron diffraction study of pyridine-2,3-dicarboxylic acid (C₇H₅NO₄)†

Åke Kvick‡

*Institute of Chemistry, Uppsala University, Box 531, S-751 21 Uppsala, Sweden*

Thomas F. Koetzle and Robert Thomas

*Chemistry Department, Brookhaven National Laboratory, Upton, New York 11973*

Fusao Takusagawa

*Department of Chemistry, Faculty of Science, Osaka City University; Sugimoto-cho, Sumiyoshi-ku, Osaka, Japan*
(Received 20 December 1973)

A neutron diffraction study of pyridine-2,3-dicarboxylic acid (quinolinic acid) has been carried out. The intensities for 3780 reflexions were measured at the Brookhaven High Flux Beam Reactor. The structure was refined to an $R(F^2)$ of 0.054 using starting parameters from a previous x-ray study. The short intramolecular hydrogen bond [O $\cdots$ O: 2.398(3) Å] has no symmetry restriction operating on the hydrogen atom position and is asymmetric. The two O $\cdots$ H distances are 1.163(5) and 1.238(5) Å, respectively, and the O–H–O angle is 174.4(4)°. The asymmetry of the bond can be explained by the intramolecular environment. The strain in the molecule caused by the short hydrogen bond results in long carbon–carbon bonds to the carboxyl groups [1.516(2) and 1.541(2) Å]. The C–O bond lengths [1.219(3), 1.263(2), 1.222(3), and 1.270(2) Å] vary depending on the hydrogen-bond involvement of the oxygen atoms. The mean C–H distance is 1.087 Å and the N–H distance is 1.036(4) Å. The nitrogen atom is involved in an intermolecular N–H $\cdots$ O hydrogen bond [N $\cdots$ O: 2.725(2), H $\cdots$ O: 1.845(4) Å and angle N–H $\cdots$ O: 140.5(2)°]. There are a number of short intermolecular O $\cdots$ H–C contacts. The refined neutron scattering length for the nitrogen atom is $b_N = 0.925(4) \times 10^{-12}$ cm.

## INTRODUCTION

It has been of interest for some time to study short O $\cdots$ O hydrogen bonds, since the trend in the variation of O–H distance with O $\cdots$ O distance seems to indicate a centered location of the hydrogen atom in these bonds. However, very few compounds involving no symmetry restriction on short O $\cdots$ O hydrogen bonds have been studied by neutron diffraction (see Table X). We have therefore undertaken a neutron study of pyridine-2,3-di-carboxylic acid, in which the oxygen atoms in the short O $\cdots$ O bond of length 2.398(3) Å are chemically and crystallographically nonequivalent. The results indicate that truly centered hydrogen bonds are the exception rather than the rule. The potential functions for these bonds are easily distorted by intra- or intermolecular asymmetries.

The study of this compound is also a part of a systematic study of model compounds for biologically important molecules presently being undertaken at the Institute of Chemistry, University of Uppsala.

## EXPERIMENTAL

### Crystal growth

Crystals of pyridine-2,3-dicarboxylic acid suitable for neutron diffraction were grown from aqueous solution. A prismatic crystal, bounded by eight faces of the type {111} and {110}, and having a volume of 8.4 mm³, was used for data collection. The crystal was mounted, using Metalset A4 epoxy resin, with its (021) reciprocal lattice vector parallel to the axis of the goniometer head.

### Crystal data

Crystal data are given in Table I. The cell dimensions were determined from powder photographs taken with a Guinier–Hägg powder camera at +24 °C with monochromatized CrKα₁ radiation (λ = 2.28962 Å). CoP₃ (a = 7.7073 Å) was used as an internal standard. Twenty-seven reflexions were used in a least-squares procedure to obtain the cell constants.

### Data collection and reduction

The neutron diffraction data were collected at room temperature on an automatic four-circle diffractometer at the Brookhaven National Laboratory High Flux Beam Reactor, using the Multiple Spectrometer Control System.[1]

The intensity data were collected using the θ–2θ scan technique. The scan length was varied according to the formula Δ2θ = 1.0°(1 + 8 tanθ) with the step size chosen to give approximately 40 points in each scan. Data were collected over a complete hemisphere of reciprocal space out to sinθ/λ = 0.668 Å⁻¹ (λ = 1.0147 Å). Two standard reflexions were measured at regular intervals to provide a check on crystal and electronic stability. The variations observed in the intensities did not call for any corrective measures.

Background corrections were made using a method[2] that separates the peak and the background in such a way that σ(I)/I is minimized. I is the integrated intensity and σ(I) its esd based on counting statistics. Squared structure amplitudes were obtained as $F_0^2 = I \sin 2\theta$, and were

TABLE I. Crystal data. Pyridine-2, 3-dicarboxylic acid (quinolinic acid), $C_7H_5NO_4$ f.w. 167.12. Space group $P2_1/c$; monoclinic.

| | |
|---|---|
| $a = 7.4218(8)$ Å | $T = +24\,°C$ |
| $b = 12.705(2)$ | |
| $c = 7.8342(8)$ | |
| $\beta = 116.950(8)°$ | |
| $V = 658.51$ Å$^3$ | |
| $D_x = 1.686$ g/cm$^3$ | |
| $Z = 4$ | |
| $\mu = 1.227$ cm$^{-1}$ for $\lambda = 1.08$ Å. | |

corrected for absorption by the Gaussian integration method, using a grid of 216 points. The crystal shape was represented by eight rational crystal boundary planes. The linear absorption coefficient was calculated assuming the incoherent scattering cross section for hydrogen to be 40 b and using the values of $(\mu/\rho)$ for C, N, and O tabulated in the *International Tables for X-Ray Crystallography*.[3] The transmission factors fell in the range 0.77–0.87 ($\mu = 1.227$ cm$^{-1}$).

The resulting $F_0^2$ values for reflexions of the type $(hkl)$ and $(h\bar{k}l)$ were averaged together and their statistically assigned standard deviations reduced accordingly. After removal of systematically absent reflexions, 1640 independent reflexions remained for use in the refinements. The nonreduced set of collected reflexions contained 3780 observed integrated intensities.

## Structure refinement

The starting parameters for the refinement of the structure of pyridine-2, 3-dicarboxylic acid were the final coordinates from the x-ray analysis.[4] The structure was refined using the full-matrix least-squares program CLINUS. The function minimized was $\sum w(F_0^2 - |F_c|^2)^2$. Each reflexion was assigned a weight $w$, inversely proportional to the estimated variance of the observation

$$w^{-1} = \sigma_c^2(F_0^2) + (kF_0^2)^2 = \sigma^2(F_0^2),$$

where $\sigma_c(F_0^2)$ is based on counting statistics and $k = 0.02$ in the final cycles of refinement. The standard deviation of an observation of unit weight was

$$S = \left[\sum w(F_0^2 - |F_c|^2)^2/(m-n)\right]^{1/2} = 1.80,$$

TABLE II. Neutron scattering length for nitrogen atoms obtained from refinement with diffraction data.[a]

| | $\bar{b}_N \times 10^{-12}$ cm |
|---|---|
| Pyridine-2, 3-dicarboxylic acid | 0.925(4) |
| Urea nitrate[10] | 0.921(4) |
| Urea phosphoric acid[11] | 0.926(6) |
| 9-Methyladenine: 1-methylthymine[8] | 0.910(6), 0.913(6), 0.904(6), 0.904(6), 0.909(6), 0.919(7) |
| 1-Methylthymine[12] | 0.908(4) |
| 2-Amino-5-chloropyridine[13] | 0.931(3), 0.930(3) |
| | $\langle \bar{b}_N \rangle = 0.917(9) \times 10^{-12}$ cm |

[a]The scattering lengths for disordered nitrogen atoms are excluded from the table.

TABLE III. Atomic coordinates with standard deviations in parentheses ($\times 10^4$).

| | $x$ | $y$ | $z$ |
|---|---|---|---|
| N1 | 9371(1) | 1224(1) | 1060(1) |
| C2 | 7349(2) | 1246(1) | −33(1) |
| C3 | 6114(2) | 1263(1) | 886(1) |
| C4 | 7059(2) | 1226(1) | 2889(2) |
| C5 | 9143(2) | 1216(1) | 3946(2) |
| C6 | 10294(2) | 1221(1) | 2964(2) |
| C7 | 6823(2) | 1213(1) | −2174(2) |
| C8 | 3825(2) | 1329(1) | −69(2) |
| O1 | 8247(3) | 1079(2) | −2527(2) |
| O2 | 5005(3) | 1347(2) | −3393(2) |
| O3 | 2873(2) | 1525(2) | −1849(2) |
| O4 | 2983(2) | 1196(2) | 941(2) |
| H1 | 6121(4) | 1214(3) | 3625(4) |
| H2 | 9851(4) | 1212(3) | 5492(3) |
| H3 | 11948(4) | 1215(3) | 3656(4) |
| H4 | 10286(4) | 1208(3) | 381(4) |
| H5 | 3902(5) | 1484(3) | −2609(4) |

where $m$ is the total number of observations and $n$ is the number of parameters varied.

In the final cycles of refinement, 51 positional and 102 anisotropic thermal parameters, one scale factor, and the neutron scattering length for the nitrogen atom were varied. The data were not affected by secondary extinction. In order not to bias the refinement, all reflexions, even those with $F_0^2 < 0$, were included in the refinement. This procedure has been suggested by several authors[5-7] and resulted in smaller standard deviations (10%–20%) in the refined parameters compared to those obtained from a conventional refinement in which reflexions with $F_0^2 < 3\sigma(F_0^2)$ were excluded. The parameters shifted by less than one standard deviation between the two refinements, however.

The final agreement factors were

$$R = \sum |F_0^2 - |F_c|^2| / \sum |F_0|^2 = 0.054,$$

TABLE IV. Thermal parameters with estimated standard deviations ($\times 10^4$).[a]

| | $\beta_{11}$ | $\beta_{22}$ | $\beta_{33}$ | $\beta_{12}$ | $\beta_{13}$ | $\beta_{23}$ |
|---|---|---|---|---|---|---|
| N1 | 96(2) | 56(1) | 92(2) | 1(1) | 57(1) | 1(1) |
| C2 | 99(2) | 42(1) | 79(2) | −1(1) | 52(2) | 0(1) |
| C3 | 89(2) | 42(1) | 82(2) | 2(1) | 49(2) | −1(1) |
| C4 | 110(3) | 54(1) | 86(2) | −1(1) | 61(2) | 2(1) |
| C5 | 120(3) | 63(1) | 82(2) | 4(1) | 52(2) | 2(1) |
| C6 | 93(3) | 65(1) | 91(2) | 2(1) | 43(2) | 1(1) |
| C7 | 135(3) | 60(1) | 87(2) | −4(1) | 67(2) | −2(1) |
| C8 | 91(3) | 57(1) | 124(2) | −1(1) | 59(2) | −3(1) |
| O1 | 188(4) | 114(2) | 121(3) | 6(2) | 111(3) | −3(2) |
| O2 | 161(4) | 99(2) | 79(3) | 4(2) | 42(3) | 6(2) |
| O3 | 100(3) | 113(2) | 124(3) | 8(2) | 30(3) | 14(2) |
| O4 | 118(3) | 96(2) | 162(3) | −4(2) | 92(3) | 2(2) |
| H1 | 192(6) | 105(3) | 155(5) | −1(4) | 123(5) | −2(3) |
| H2 | 205(7) | 116(3) | 99(5) | 13(4) | 55(5) | 6(3) |
| H3 | 123(6) | 122(3) | 166(6) | 13(4) | 55(5) | 6(4) |
| H4 | 193(7) | 96(3) | 165(5) | 11(3) | 132(5) | 6(4) |
| H5 | 187(7) | 113(3) | 161(6) | −9(4) | 52(6) | 15(4) |

[a]The anisotropic thermal parameters are of the form $\exp(-\beta_{11}h^2\cdots - 2\beta_{12}hk\cdots)$.

TABLE V. Observed and calculated neutron squared structure factors. The columns are $k, l, 10F_0^2, 10|F_c^2|, 10^3\sigma$; where $\sigma$ is the value used for weighting in the final least-squares refinement. All reflexions included in the table were used in the refinements. The structure factors are given on an absolute scale (×10).

| | | | | |
|---|---|---|---|---|
| 0,K,L | | | | |
| 0 | 2 | 128 | 125 | 280 |
| 0 | 4 | 15 | 15 | 90 |
| 0 | 6 | 27 | 22 | 186 |
| 0 | 8 | 35 | 33 | 287 |
| 1 | 1 | 606 | 575 | 1225 |
| 1 | 2 | 41 | 36 | 100 |
| 1 | 3 | 75 | 68 | 185 |
| 1 | 4 | 212 | 205 | 475 |
| 1 | 5 | 44 | 46 | 175 |
| 1 | 6 | 805 | 784 | 1718 |
| 1 | 7 | 23 | 24 | 175 |
| 1 | 8 | 14 | 12 | 163 |
| 1 | 9 | 71 | 59 | 317 |
| 2 | 0 | 5 | 0 | 41 |
| 2 | 1 | 49 | 45 | 116 |
| 2 | 2 | 6 | 5 | 38 |
| 2 | 3 | 672 | 602 | 1380 |
| 2 | 4 | 5 | 4 | 58 |
| 2 | 5 | 94 | 87 | 265 |
| 2 | 6 | 22 | 23 | 178 |
| 2 | 7 | 435 | 428 | 1012 |
| 2 | 8 | 5 | 4 | 169 |
| 2 | 9 | 319 | 344 | 876 |
| 3 | 1 | 563 | 560 | 1148 |
| 3 | 2 | 59 | 58 | 149 |
| 3 | 3 | 70 | 63 | 181 |
| 3 | 4 | 163 | 148 | 381 |
| 3 | 5 | 12 | 12 | 102 |
| 3 | 6 | 713 | 671 | 1537 |
| 3 | 7 | 15 | 16 | 148 |
| 3 | 8 | 8 | 11 | 175 |
| 3 | 9 | 64 | 64 | 404 |
| 4 | 0 | 4570 | 4566 | 9191 |
| 4 | 1 | 2 | 1 | 38 |
| 4 | 2 | 74 | 66 | 185 |
| 4 | 3 | 20 | 21 | 89 |
| 4 | 4 | 13 | 14 | 81 |
| 4 | 5 | 30 | 27 | 149 |
| 4 | 6 | 29 | 28 | 183 |
| 4 | 7 | 25 | 22 | 207 |
| 4 | 8 | 37 | 38 | 248 |
| 4 | 9 | 11 | 8 | 290 |
| 5 | 1 | 367 | 354 | 767 |
| 5 | 2 | 23 | 22 | 86 |
| 5 | 3 | 77 | 80 | 208 |
| 5 | 4 | 159 | 153 | 395 |
| 5 | 5 | 81 | 84 | 254 |
| 5 | 6 | 541 | 514 | 1199 |
| 5 | 7 | 31 | 27 | 237 |
| 5 | 8 | 17 | 9 | 226 |
| 6 | 0 | 4 | 0 | 110 |
| 6 | 1 | 95 | 97 | 230 |
| 6 | 2 | 27 | 29 | 105 |
| 6 | 3 | 403 | 377 | 865 |
| 6 | 4 | 13 | 12 | 105 |
| 6 | 5 | 25 | 27 | 153 |
| 6 | 6 | 95 | 92 | 323 |
| 6 | 7 | 261 | 239 | 703 |
| 6 | 8 | 13 | 14 | 194 |
| 7 | 1 | 334 | 327 | 719 |
| 7 | 2 | 44 | 45 | 149 |
| 7 | 3 | 78 | 78 | 231 |
| 7 | 4 | 83 | 85 | 259 |
| 7 | 5 | 2 | 3 | 131 |
| 7 | 6 | 363 | 349 | 876 |
| 7 | 7 | 7 | 11 | 131 |
| 7 | 8 | 9 | 6 | 145 |
| 8 | 0 | 2508 | 2388 | 5067 |
| 8 | 1 | 4 | 2 | 75 |
| 8 | 2 | 6 | 6 | 73 |
| 8 | 3 | 27 | 27 | 133 |
| 8 | 4 | 10 | 10 | 147 |
| 8 | 5 | 26 | 27 | 172 |
| 8 | 6 | 35 | 29 | 258 |
| 8 | 7 | 25 | 19 | 234 |
| 8 | 8 | 33 | 36 | 291 |
| 9 | 1 | 159 | 148 | 406 |
| 9 | 2 | 16 | 17 | 110 |
| 9 | 3 | 52 | 52 | 200 |
| 9 | 4 | 62 | 61 | 243 |
| 9 | 5 | 60 | 61 | 274 |
| 9 | 6 | 204 | 191 | 612 |
| 9 | 7 | 15 | 19 | 185 |
| 10 | 0 | 2 | 1 | 180 |
| 10 | 1 | 119 | 110 | 357 |
| 10 | 2 | 31 | 29 | 180 |
| 10 | 3 | 156 | 159 | 441 |
| 10 | 4 | 2 | 2 | 152 |
| 10 | 5 | 1 | 2 | 177 |
| 10 | 6 | 52 | 55 | 312 |
| 10 | 7 | 88 | 90 | 419 |
| 11 | 1 | 137 | 134 | 418 |
| 11 | 2 | 13 | 13 | 167 |
| 11 | 3 | 59 | 63 | 278 |
| 11 | 4 | 52 | 52 | 294 |
| 11 | 5 | 2 | 2 | 215 |
| 11 | 6 | 121 | 125 | 517 |
| 11 | 7 | 10 | 7 | 270 |
| 12 | 0 | 976 | 906 | 2241 |
| 12 | 1 | 1 | 2 | 163 |
| 12 | 2 | 3 | 1 | 159 |
| 12 | 3 | 12 | 10 | 194 |
| 12 | 4 | 7 | 4 | 191 |
| 12 | 5 | 6 | 6 | 185 |
| 12 | 6 | 16 | 15 | 247 |
| 13 | 1 | 55 | 49 | 283 |
| 13 | 2 | 7 | 9 | 157 |
| 13 | 3 | 16 | 17 | 222 |
| 13 | 4 | 15 | 18 | 219 |
| 13 | 5 | 21 | 21 | 269 |
| 13 | 6 | 40 | 45 | 465 |
| 14 | 0 | 2 | 2 | 280 |
| 14 | 1 | 60 | 57 | 340 |
| 14 | 2 | 13 | 13 | 209 |
| 14 | 3 | 49 | 50 | 339 |
| 14 | 4 | 1 | 0 | 229 |
| 14 | 5 | 2 | 0 | 258 |
| 15 | 1 | 45 | 46 | 222 |
| 15 | 2 | 4 | 2 | 106 |
| 15 | 3 | 29 | 26 | 241 |
| 15 | 4 | 24 | 26 | 234 |
| 16 | 0 | 274 | 260 | 820 |
| 16 | 1 | 1 | 1 | 158 |
| 16 | 2 | 3 | 3 | 163 |
| 16 | 3 | 2 | 2 | 127 |
| 1,K,L | | | | |
| 0 | -8 | 2 | 2 | 177 |
| 0 | -6 | 100 | 101 | 289 |
| 0 | -4 | 207 | 211 | 450 |
| 0 | -2 | 220 | 244 | 460 |
| 0 | 0 | 18 | 19 | 51 |
| 0 | 2 | 347 | 372 | 726 |
| 0 | 4 | 46 | 49 | 158 |
| 0 | 6 | 289 | 289 | 701 |
| 0 | 8 | 176 | 184 | 578 |
| 1 | -9 | 3 | 3 | 150 |
| 1 | -8 | 17 | 21 | 147 |
| 1 | -7 | 10 | 7 | 136 |
| 1 | -6 | 143 | 153 | 378 |
| 1 | -5 | 1 | 1 | 78 |
| 1 | -4 | 31 | 31 | 115 |
| 1 | -3 | 192 | 196 | 405 |
| 1 | -2 | 389 | 379 | 792 |
| 1 | -1 | 80 | 76 | 170 |
| 1 | 0 | 322 | 337 | 658 |
| 1 | 1 | 54 | 61 | 131 |
| 1 | 2 | 21 | 16 | 66 |
| 1 | 3 | 70 | 72 | 180 |
| 1 | 4 | 88 | 93 | 239 |
| 1 | 5 | 155 | 158 | 403 |
| 1 | 6 | 55 | 56 | 227 |
| 1 | 7 | 51 | 49 | 290 |
| 1 | 8 | 98 | 90 | 357 |
| 2 | -9 | 1 | 0 | 207 |
| 2 | -8 | 1 | 0 | 172 |
| 2 | -7 | 33 | 28 | 194 |
| 2 | -6 | 11 | 6 | 134 |
| 2 | -5 | 214 | 216 | 489 |
| 2 | -4 | 8 | 8 | 65 |
| 2 | -3 | 441 | 431 | 916 |
| 2 | -2 | 7 | 6 | 47 |
| 2 | -1 | 325 | 300 | 667 |
| 2 | 0 | 4 | 4 | 29 |
| 2 | 1 | 329 | 330 | 684 |
| 2 | 2 | 8 | 7 | 51 |
| 2 | 3 | 5 | 2 | 64 |
| 2 | 4 | 2 | 1 | 62 |
| 2 | 5 | 111 | 107 | 316 |
| 2 | 6 | 0 | 0 | 137 |
| 2 | 7 | 5 | 0 | 170 |
| 2 | 8 | 3 | 0 | 229 |
| 3 | -9 | -1 | 3 | 226 |
| 3 | -8 | 13 | 15 | 192 |
| 3 | -7 | 5 | 5 | 126 |
| 3 | -6 | 108 | 110 | 310 |
| 3 | -5 | 2 | 0 | 89 |
| 3 | -4 | 40 | 36 | 136 |
| 3 | -3 | 160 | 174 | 357 |
| 3 | -2 | 432 | 438 | 893 |
| 3 | -1 | 162 | 153 | 348 |
| 3 | 0 | 537 | 519 | 1097 |
| 3 | 1 | 16 | 18 | 62 |
| 3 | 2 | 6 | 2 | 49 |
| 3 | 3 | 32 | 27 | 119 |
| 3 | 4 | 112 | 102 | 302 |
| 3 | 5 | 156 | 138 | 407 |
| 3 | 6 | 16 | 15 | 160 |
| 3 | 7 | 56 | 54 | 279 |
| 3 | 8 | 55 | 58 | 341 |
| 4 | -9 | 1 | 1 | 195 |
| 4 | -8 | 1 | 0 | 182 |
| 4 | -7 | 3 | 5 | 163 |
| 4 | -6 | 46 | 43 | 201 |
| 4 | -5 | 30 | 33 | 139 |
| 4 | -4 | 256 | 262 | 565 |
| 4 | -3 | 4 | 4 | 49 |
| 4 | -2 | 137 | 148 | 309 |
| 4 | -1 | 4 | 3 | 37 |
| 4 | 0 | 14 | 14 | 59 |
| 4 | 1 | 5 | 4 | 47 |
| 4 | 2 | 280 | 292 | 601 |
| 4 | 3 | 5 | 5 | 61 |
| 4 | 4 | 33 | 29 | 140 |
| 4 | 5 | 5 | 6 | 115 |
| 4 | 6 | 249 | 229 | 645 |
| 4 | 7 | 6 | 5 | 147 |
| 4 | 8 | 137 | 124 | 502 |
| 5 | -9 | 6 | 2 | 202 |
| 5 | -8 | 7 | 9 | 172 |
| 5 | -7 | 25 | 24 | 205 |
| 5 | -6 | 76 | 83 | 269 |
| 5 | -5 | 2 | 0 | 70 |
| 5 | -4 | 7 | 8 | 70 |
| 5 | -3 | 116 | 125 | 285 |
| 5 | -2 | 187 | 177 | 415 |
| 5 | -1 | 24 | 22 | 82 |
| 5 | 0 | 180 | 167 | 393 |
| 5 | 1 | 73 | 79 | 186 |
| 5 | 2 | 33 | 31 | 120 |
| 5 | 3 | 78 | 76 | 220 |
| 5 | 4 | 30 | 28 | 149 |
| 5 | 5 | 79 | 72 | 277 |
| 5 | 6 | 51 | 46 | 264 |
| 5 | 7 | 13 | 9 | 194 |
| 5 | 8 | 43 | 48 | 319 |
| 6 | -9 | 0 | 1 | 244 |
| 6 | -8 | 0 | 0 | 188 |
| 6 | -7 | 6 | 5 | 124 |
| 6 | -6 | 21 | 25 | 183 |
| 6 | -5 | 71 | 72 | 237 |
| 6 | -4 | 27 | 29 | 137 |
| 6 | -3 | 167 | 162 | 391 |
| 6 | -2 | 23 | 23 | 99 |
| 6 | -1 | 324 | 288 | 688 |
| 6 | 0 | 21 | 21 | 83 |
| 6 | 1 | 154 | 153 | 357 |
| 6 | 2 | 24 | 24 | 108 |
| 6 | 3 | 3 | 0 | 81 |
| 6 | 4 | 3 | 2 | 114 |
| 6 | 5 | 68 | 64 | 258 |
| 6 | 6 | 1 | 0 | 167 |
| 6 | 7 | 5 | 2 | 196 |
| 6 | 8 | 2 | 0 | 238 |
| 7 | -8 | 1 | 6 | 205 |
| 7 | -7 | 13 | 13 | 181 |
| 7 | -6 | 29 | 37 | 186 |
| 7 | -5 | 8 | 7 | 111 |
| 7 | -4 | 18 | 18 | 134 |
| 7 | -3 | 106 | 104 | 280 |
| 7 | -2 | 248 | 235 | 552 |
| 7 | -1 | 149 | 139 | 352 |
| 7 | 0 | 459 | 459 | 918 |
| 7 | 1 | 4 | 4 | 59 |
| 7 | 2 | 2 | 0 | 77 |
| 7 | 3 | 1 | 2 | 107 |
| 7 | 4 | 47 | 55 | 209 |
| 7 | 5 | 42 | 42 | 210 |
| 7 | 6 | 1 | 0 | 176 |
| 7 | 7 | 16 | 14 | 214 |
| 8 | -8 | 2 | 0 | 204 |
| 8 | -7 | 5 | 6 | 195 |
| 8 | -6 | 0 | 0 | 161 |
| 8 | -5 | 38 | 39 | 196 |
| 8 | -4 | 284 | 285 | 665 |
| 8 | -3 | 0 | 1 | 93 |
| 8 | -2 | 36 | 37 | 136 |
| 8 | -1 | 5 | 5 | 60 |
| 8 | 0 | 5 | 5 | 61 |
| 8 | 1 | 2 | 3 | 44 |
| 8 | 2 | 129 | 133 | 341 |
| 8 | 3 | 6 | 4 | 107 |
| 8 | 4 | 6 | 6 | 111 |
| 8 | 5 | 13 | 9 | 167 |
| 8 | 6 | 114 | 117 | 416 |
| 8 | 7 | 9 | 8 | 190 |
| 9 | -8 | 0 | 1 | 213 |
| 9 | -7 | 26 | 33 | 237 |
| 9 | -6 | 12 | 19 | 179 |
| 9 | -5 | 5 | 3 | 148 |
| 9 | -4 | 2 | 0 | 128 |
| 9 | -3 | 43 | 42 | 174 |
| 9 | -2 | 54 | 51 | 206 |
| 9 | -1 | 10 | 12 | 87 |
| 9 | 0 | 93 | 85 | 272 |
| 9 | 1 | 34 | 34 | 159 |
| 9 | 2 | 19 | 22 | 134 |
| 9 | 3 | 48 | 44 | 217 |
| 9 | 4 | 2 | 1 | 147 |
| 9 | 5 | 22 | 18 | 186 |
| 9 | 6 | 11 | 13 | 176 |
| 9 | 7 | 2 | 0 | 221 |
| 10 | -7 | -1 | 0 | 216 |
| 10 | -6 | 11 | 16 | 205 |
| 10 | -5 | 8 | 9 | 211 |
| 10 | -4 | 15 | 13 | 173 |
| 10 | -3 | 27 | 29 | 178 |
| 10 | -2 | 16 | 16 | 127 |
| 10 | -1 | 213 | 193 | 536 |
| 10 | 0 | 24 | 23 | 143 |
| 10 | 1 | 34 | 30 | 203 |
| 10 | 2 | 10 | 10 | 156 |
| 10 | 3 | 1 | 0 | 114 |
| 10 | 4 | -1 | 0 | 166 |
| 10 | 5 | 21 | 22 | 207 |
| 10 | 6 | -3 | 0 | 212 |
| 10 | 7 | 12 | 7 | 352 |
| 11 | -7 | 12 | 14 | 270 |
| 11 | -6 | 8 | 8 | 151 |
| 11 | -5 | 18 | 10 | 225 |
| 11 | -4 | 2 | 6 | 180 |
| 11 | -3 | 51 | 47 | 261 |
| 11 | -2 | 53 | 52 | 269 |
| 11 | -1 | 68 | 69 | 278 |
| 11 | 0 | 240 | 233 | 626 |
| 11 | 1 | 0 | 2 | 138 |
| 11 | 2 | 1 | 1 | 152 |
| 11 | 3 | 1 | 0 | 157 |
| 11 | 4 | 22 | 22 | 233 |
| 11 | 5 | 2 | 4 | 230 |
| 11 | 6 | 2 | 1 | 242 |
| 12 | -7 | -1 | 2 | 268 |
| 12 | -6 | 8 | 6 | 236 |
| 12 | -5 | 17 | 13 | 239 |
| 12 | -4 | 167 | 161 | 551 |
| 12 | -3 | 1 | 1 | 179 |
| 12 | -2 | 7 | 7 | 120 |
| 12 | -1 | 1 | 4 | 160 |
| 12 | 0 | 1 | 1 | 155 |
| 12 | 1 | 1 | 0 | 152 |
| 12 | 2 | 31 | 31 | 229 |
| 12 | 3 | 0 | 0 | 188 |
| 12 | 4 | 2 | 0 | 195 |
| 12 | 5 | 4 | 5 | 238 |
| 12 | 6 | 48 | 41 | 382 |
| 13 | -6 | 0 | 3 | 250 |
| 13 | -5 | 0 | 2 | 233 |
| 13 | -4 | -2 | 0 | 213 |
| 13 | -3 | 12 | 8 | 207 |
| 13 | -2 | 9 | 9 | 138 |
| 13 | -1 | 13 | 9 | 177 |
| 13 | 0 | 42 | 39 | 269 |
| 13 | 1 | 5 | 4 | 123 |
| 13 | 2 | 4 | 9 | 169 |
| 13 | 3 | 17 | 18 | 206 |
| 13 | 4 | 3 | 0 | 225 |
| 13 | 5 | 12 | 4 | 238 |
| 14 | -5 | 0 | 1 | 228 |
| 14 | -4 | -1 | 2 | 233 |
| 14 | -3 | 3 | 6 | 200 |
| 14 | -2 | 7 | 6 | 192 |
| 14 | -1 | 91 | 79 | 398 |
| 14 | 0 | 15 | 12 | 234 |
| 14 | 1 | 0 | 1 | 200 |
| 14 | 2 | 0 | 1 | 197 |
| 14 | 3 | 0 | 2 | 214 |
| 14 | 4 | 2 | 0 | 229 |
| 15 | -4 | 4 | 2 | 185 |
| 15 | -3 | 22 | 16 | 236 |
| 15 | -2 | 6 | 4 | 138 |
| 15 | -1 | 27 | 24 | 181 |
| 15 | 0 | 85 | 80 | 294 |
| 15 | 1 | 1 | 1 | 140 |
| 15 | 2 | 2 | 1 | 150 |
| 15 | 3 | 2 | 0 | 174 |
| 16 | -3 | 0 | 2 | 177 |
| 16 | -2 | 6 | 2 | 152 |
| 16 | -1 | 1 | 2 | 161 |
| 16 | 0 | -2 | 0 | 165 |
| 16 | 1 | 0 | 0 | 146 |
| 16 | 2 | 4 | 4 | 162 |
| 2,K,L | | | | |
| 0 | -10 | 24 | 25 | 302 |
| 0 | -8 | 63 | 71 | 302 |
| 0 | -6 | 141 | 142 | 365 |
| 0 | -4 | 519 | 551 | 1073 |
| 0 | -2 | 19 | 17 | 64 |
| 0 | 0 | 175 | 199 | 376 |
| 0 | 2 | 85 | 75 | 208 |
| 0 | 4 | 1073 | 1170 | 2230 |
| 0 | 6 | 59 | 55 | 271 |
| 0 | 8 | 15 | 12 | 232 |
| 1 | -10 | -2 | 0 | 191 |
| 1 | -9 | 14 | 13 | 178 |
| 1 | -8 | 94 | 88 | 301 |
| 1 | -7 | 8 | 10 | 86 |
| 1 | -6 | 14 | 15 | 109 |
| 1 | -5 | 21 | 24 | 102 |
| 1 | -4 | 659 | 651 | 1351 |
| 1 | -3 | 58 | 53 | 139 |
| 1 | -2 | 260 | 261 | 537 |
| 1 | -1 | 275 | 293 | 574 |
| 1 | 0 | 113 | 123 | 253 |
| 1 | 1 | 32 | 34 | 100 |
| 1 | 2 | 42 | 43 | 124 |
| 1 | 3 | 231 | 253 | 523 |
| 1 | 4 | 10 | 4 | 133 |
| 1 | 5 | 205 | 217 | 534 |
| 1 | 6 | 10 | 10 | 145 |
| 1 | 7 | 93 | 101 | 373 |
| 1 | 8 | 59 | 53 | 317 |
| 2 | -10 | 0 | 1 | 243 |
| 2 | -9 | 5 | 10 | 196 |
| 2 | -8 | 1 | 0 | 164 |
| 2 | -7 | 56 | 60 | 233 |
| 2 | -6 | 0 | 0 | 109 |
| 2 | -5 | 425 | 413 | 906 |
| 2 | -4 | 1 | 0 | 74 |
| 2 | -3 | 44 | 38 | 124 |
| 2 | -2 | 3 | 3 | 33 |
| 2 | -1 | 351 | 407 | 728 |
| 2 | 0 | 0 | 0 | 37 |
| 2 | 1 | 171 | 176 | 378 |
| 2 | 2 | 3 | 0 | 68 |
| 2 | 3 | 47 | 50 | 154 |
| 2 | 4 | 5 | 3 | 107 |
| 2 | 5 | 58 | 57 | 241 |
| 2 | 6 | 4 | 4 | 102 |
| 2 | 7 | 51 | 44 | 311 |
| 2 | 8 | 3 | 1 | 254 |
| 3 | -9 | 17 | 14 | 238 |
| 3 | -8 | 94 | 92 | 346 |
| 3 | -7 | 23 | 20 | 185 |
| 3 | -6 | 6 | 3 | 114 |
| 3 | -5 | 81 | 84 | 227 |
| 3 | -4 | 420 | 421 | 889 |
| 3 | -3 | 0 | 0 | 50 |
| 3 | -2 | 81 | 88 | 194 |
| 3 | -1 | 294 | 301 | 617 |
| 3 | 0 | 126 | 134 | 285 |
| 3 | 1 | 31 | 32 | 105 |
| 3 | 2 | 61 | 61 | 180 |
| 3 | 3 | 182 | 178 | 427 |
| 3 | 4 | 0 | 1 | 121 |
| 3 | 5 | 195 | 178 | 514 |
| 3 | 6 | -1 | 0 | 167 |
| 3 | 7 | 138 | 122 | 493 |
| 3 | 8 | 82 | 95 | 471 |
| 4 | -9 | 1 | 1 | 211 |
| 4 | -8 | 45 | 44 | 254 |
| 4 | -7 | 9 | 9 | 119 |
| 4 | -6 | 134 | 134 | 359 |
| 4 | -5 | 6 | 4 | 106 |
| 4 | -4 | 365 | 374 | 785 |
| 4 | -3 | 0 | 1 | 64 |
| 4 | -2 | 5 | 3 | 46 |
| 4 | -1 | 4 | 3 | 51 |
| 4 | 0 | 104 | 112 | 246 |
| 4 | 1 | 6 | 4 | 61 |
| 4 | 2 | 76 | 63 | 210 |
| 4 | 3 | 3 | 2 | 87 |
| 4 | 4 | 1022 | 995 | 2134 |
| 4 | 5 | 14 | 11 | 147 |
| 4 | 6 | 49 | 44 | 261 |
| 4 | 7 | 2 | 1 | 208 |
| 5 | -9 | 11 | 14 | 182 |
| 5 | -8 | 50 | 48 | 271 |
| 5 | -7 | 3 | 1 | 173 |
| 5 | -6 | 44 | 48 | 198 |
| 5 | -5 | 0 | 0 | 103 |
| 5 | -4 | 406 | 423 | 872 |
| 5 | -3 | 179 | 183 | 411 |
| 5 | -2 | 314 | 323 | 670 |
| 5 | -1 | 161 | 160 | 362 |
| 5 | 0 | 40 | 42 | 125 |
| 5 | 1 | 13 | 13 | 88 |
| 5 | 2 | 29 | 31 | 117 |
| 5 | 3 | 129 | 130 | 345 |
| 5 | 4 | 9 | 5 | 118 |
| 5 | 5 | 159 | 162 | 449 |
| 5 | 6 | 21 | 20 | 190 |
| 5 | 7 | 52 | 46 | 314 |
| 6 | -9 | 5 | 5 | 226 |
| 6 | -8 | 2 | 0 | 177 |
| 6 | -7 | 31 | 35 | 206 |
| 6 | -6 | 3 | 2 | 94 |
| 6 | -5 | 214 | 228 | 517 |
| 6 | -4 | 3 | 0 | 92 |
| 6 | -3 | 56 | 58 | 173 |
| 6 | -2 | 11 | 11 | 69 |
| 6 | -1 | 146 | 158 | 344 |
| 6 | 0 | 1 | 1 | 37 |
| 6 | 1 | 79 | 82 | 215 |
| 6 | 2 | 1 | 2 | 91 |
| 6 | 3 | 17 | 18 | 129 |
| 6 | 4 | 13 | 11 | 148 |
| 6 | 5 | 40 | 31 | 243 |
| 6 | 6 | 16 | 13 | 224 |
| 6 | 7 | 59 | 45 | 349 |
| 7 | -9 | 13 | 12 | 236 |
| 7 | -8 | 42 | 46 | 242 |
| 7 | -7 | 8 | 9 | 124 |
| 7 | -6 | 23 | 18 | 195 |
| 7 | -5 | 57 | 63 | 219 |
| 7 | -4 | 149 | 158 | 390 |
| 7 | -3 | 0 | 2 | 79 |
| 7 | -2 | 20 | 20 | 100 |
| 7 | -1 | 159 | 149 | 374 |
| 7 | 0 | 54 | 54 | 165 |
| 7 | 1 | 12 | 12 | 91 |
| 7 | 2 | 50 | 52 | 190 |
| 7 | 3 | 34 | 34 | 163 |
| 7 | 4 | 15 | 14 | 176 |
| 7 | 5 | 89 | 95 | 349 |
| 7 | 6 | 0 | 1 | 188 |
| 7 | 7 | 76 | 72 | 391 |
| 8 | -8 | 12 | 10 | 189 |
| 8 | -7 | 13 | 11 | 200 |
| 8 | -6 | 101 | 108 | 354 |
| 8 | -5 | 11 | 10 | 136 |
| 8 | -4 | 117 | 125 | 333 |
| 8 | -3 | 1 | 0 | 94 |
| 8 | -2 | 7 | 3 | 95 |
| 8 | -1 | 3 | 2 | 59 |
| 8 | 0 | 22 | 21 | 137 |
| 8 | 1 | 11 | 11 | 103 |
| 8 | 2 | 38 | 36 | 168 |
| 8 | 3 | 2 | 0 | 133 |
| 8 | 4 | 586 | 596 | 1322 |
| 8 | 5 | 13 | 12 | 207 |
| 8 | 6 | 18 | 18 | 204 |
| 8 | 7 | 7 | 0 | 229 |
| 9 | -8 | 15 | 19 | 198 |
| 9 | -7 | 2 | 0 | 183 |
| 9 | -6 | 33 | 33 | 220 |
| 9 | -5 | 0 | 0 | 138 |
| 9 | -4 | 94 | 99 | 308 |
| 9 | -3 | 164 | 157 | 423 |
| 9 | -2 | 186 | 176 | 458 |
| 9 | -1 | 61 | 62 | 214 |
| 9 | 0 | 4 | 4 | 107 |
| 9 | 1 | 5 | 3 | 89 |
| 9 | 2 | 21 | 19 | 144 |
| 9 | 3 | 25 | 26 | 178 |
| 9 | 4 | 2 | 1 | 178 |
| 9 | 5 | 77 | 78 | 358 |
| 9 | 6 | 14 | 15 | 186 |
| 10 | -8 | 4 | 0 | 226 |
| 10 | -7 | 5 | 10 | 224 |
| 10 | -6 | 6 | 5 | 204 |
| 10 | -5 | 68 | 75 | 305 |
| 10 | -4 | 0 | 1 | 145 |
| 10 | -3 | 53 | 49 | 233 |
| 10 | -2 | 4 | 5 | 105 |
| 10 | -1 | 29 | 28 | 176 |
| 10 | 0 | 5 | 2 | 109 |
| 10 | 1 | 26 | 27 | 180 |
| 10 | 2 | 1 | 2 | 152 |
| 10 | 3 | 0 | 1 | 135 |
| 10 | 4 | 6 | 6 | 200 |
| 10 | 5 | 14 | 14 | 201 |
| 10 | 6 | 9 | 6 | 236 |
| 11 | -7 | 1 | 0 | 224 |
| 11 | -6 | 5 | 7 | 232 |
| 11 | -5 | 20 | 17 | 186 |
| 11 | -4 | 54 | 55 | 296 |
| 11 | -3 | 0 | 0 | 149 |
| 11 | -2 | 9 | 11 | 132 |
| 11 | -1 | 32 | 34 | 185 |
| 11 | 0 | 5 | 6 | 150 |
| 11 | 1 | 0 | 4 | 149 |
| 11 | 2 | 20 | 18 | 190 |
| 11 | 3 | -1 | 0 | 195 |
| 11 | 4 | 21 | 19 | 250 |
| 11 | 5 | 34 | 37 | 314 |
| 12 | -7 | 5 | 5 | 266 |
| 12 | -6 | 67 | 66 | 398 |
| 12 | -5 | 10 | 9 | 197 |
| 12 | -4 | 24 | 26 | 211 |
| 12 | -3 | 1 | 1 | 180 |
| 12 | -2 | 6 | 4 | 168 |
| 12 | -1 | 0 | 0 | 156 |
| 12 | 0 | 0 | 3 | 169 |
| 12 | 1 | 9 | 10 | 162 |
| 12 | 2 | 18 | 14 | 236 |
| 12 | 3 | 1 | 0 | 200 |
| 12 | 4 | 247 | 245 | 761 |
| 12 | 5 | 9 | 4 | 277 |
| 13 | -6 | 12 | 12 | 217 |
| 13 | -5 | 6 | 2 | 219 |
| 13 | -4 | 5 | 6 | 156 |
| 13 | -3 | 66 | 56 | 350 |
| 13 | -2 | 55 | 50 | 301 |
| 13 | -1 | 14 | 19 | 195 |
| 13 | 0 | 0 | 0 | 175 |
| 13 | 1 | 0 | 1 | 192 |
| 13 | 2 | 4 | 6 | 223 |
| 13 | 3 | 3 | 1 | 219 |
| 13 | 4 | 2 | 0 | 255 |
| 14 | -5 | 14 | 18 | 223 |
| 14 | -4 | 4 | 1 | 117 |
| 14 | -3 | 18 | 19 | 210 |
| 14 | -2 | 0 | 1 | 210 |
| 14 | -1 | -1 | 3 | 222 |
| 14 | 0 | 0 | 2 | 210 |
| 14 | 1 | 8 | 10 | 219 |
| 14 | 2 | 1 | 2 | 226 |
| 14 | 3 | 8 | 1 | 240 |
| 15 | -4 | 20 | 19 | 223 |
| 15 | -3 | 3 | 0 | 163 |
| 15 | -2 | 5 | 7 | 157 |
| 15 | -1 | 4 | 3 | 148 |
| 15 | 0 | 1 | 0 | 145 |
| 15 | 1 | 4 | 2 | 146 |
| 15 | 2 | 3 | 2 | 177 |
| 16 | -3 | 3 | 1 | 166 |
| 16 | -2 | 2 | 1 | 156 |
| 16 | -1 | 1 | 0 | 153 |
| 16 | 0 | 2 | 1 | 152 |
| 16 | 1 | 6 | 4 | 172 |
| 3,K,L | | | | |
| 0 | -10 | 361 | 394 | 945 |
| 0 | -8 | 64 | 69 | 287 |
| 0 | -6 | 19 | 19 | 150 |
| 0 | -4 | 27 | 24 | 101 |
| 0 | -2 | 723 | 680 | 1481 |
| 0 | 0 | 531 | 542 | 1101 |
| 0 | 2 | 186 | 201 | 434 |
| 0 | 4 | 19 | 14 | 174 |
| 0 | 6 | 5 | 2 | 199 |
| 1 | -10 | 8 | 7 | 199 |
| 1 | -9 | 20 | 23 | 174 |
| 1 | -8 | 38 | 33 | 192 |
| 1 | -7 | 277 | 255 | 668 |
| 1 | -6 | 1781 | 1749 | 3642 |
| 1 | -5 | 122 | 118 | 302 |
| 1 | -4 | 22 | 17 | 97 |
| 1 | -3 | 722 | 668 | 1470 |
| 1 | -2 | 83 | 80 | 191 |
| 1 | -1 | 178 | 173 | 381 |
| 1 | 0 | 31 | 27 | 105 |
| 1 | 1 | 195 | 202 | 443 |
| 1 | 2 | 56 | 54 | 175 |
| 1 | 3 | 452 | 416 | 991 |
| 1 | 4 | 1031 | 1119 | 2180 |
| 1 | 5 | 4 | 0 | 153 |
| 1 | 6 | 2 | 0 | 183 |
| 1 | 7 | 57 | 51 | 340 |
| 2 | -10 | 2 | 1 | 224 |
| 2 | -9 | 60 | 62 | 285 |
| 2 | -8 | 1 | 0 | 155 |
| 2 | -7 | 804 | 789 | 1721 |
| 2 | -6 | 3 | 0 | 126 |
| 2 | -5 | 179 | 183 | 417 |
| 2 | -4 | 0 | 0 | 71 |
| 2 | -3 | 553 | 499 | 1147 |
| 2 | -2 | 3 | 2 | 54 |
| 2 | -1 | 889 | 898 | 1816 |
| 2 | 0 | 2 | 1 | 57 |
| 2 | 1 | 201 | 199 | 457 |
| 2 | 2 | 2 | 2 | 78 |
| 2 | 3 | 704 | 716 | 1497 |
| 2 | 4 | 12 | 6 | 166 |
| 2 | 5 | 122 | 118 | 407 |
| 2 | 6 | 0 | 0 | 184 |
| 2 | 7 | 52 | 55 | 310 |
| 3 | -10 | 15 | 11 | 253 |
| 3 | -9 | 7 | 11 | 218 |
| 3 | -8 | 14 | 10 | 192 |
| 3 | -7 | 255 | 240 | 636 |
| 3 | -6 | 1639 | 1641 | 3362 |
| 3 | -5 | 52 | 49 | 168 |
| 3 | -4 | 63 | 60 | 181 |
| 3 | -3 | 723 | 726 | 1445 |
| 3 | -2 | 1 | 0 | 55 |
| 3 | -1 | 289 | 289 | 619 |
| 3 | 0 | 4 | 2 | 53 |
| 3 | 1 | 134 | 139 | 327 |
| 3 | 2 | 82 | 79 | 238 |
| 3 | 3 | 368 | 345 | 829 |
| 3 | 4 | 985 | 981 | 2089 |
| 3 | 5 | 9 | 5 | 167 |
| 3 | 6 | 2 | 1 | 179 |
| 3 | 7 | 48 | 37 | 311 |
| 4 | -10 | 296 | 304 | 859 |
| 4 | -9 | 5 | 2 | 201 |
| 4 | -8 | 73 | 75 | 324 |
| 4 | -7 | 0 | 0 | 151 |
| 4 | -6 | 38 | 36 | 184 |
| 4 | -5 | 3 | 1 | 98 |
| 4 | -4 | 7 | 4 | 76 |
| 4 | -3 | 2 | 2 | 45 |
| 4 | -2 | 600 | 608 | 1235 |
| 4 | -1 | 15 | 15 | 72 |
| 4 | 0 | 460 | 478 | 973 |
| 4 | 1 | 3 | 4 | 49 |
| 4 | 2 | 177 | 173 | 444 |
| 4 | 3 | 15 | 12 | 124 |
| 4 | 4 | 21 | 14 | 188 |
| 4 | 5 | 3 | 2 | 162 |
| 4 | 6 | 3 | 1 | 197 |
| 4 | 7 | 2 | 0 | 235 |
| 5 | -9 | 42 | 37 | 297 |
| 5 | -8 | 38 | 37 | 256 |
| 5 | -7 | 189 | 183 | 508 |
| 5 | -6 | 1191 | 1225 | 2493 |
| 5 | -5 | 153 | 151 | 392 |
| 5 | -4 | 12 | 11 | 96 |
| 5 | -3 | 328 | 326 | 712 |
| 5 | -2 | 102 | 106 | 257 |
| 5 | -1 | 26 | 20 | 114 |
| 5 | 0 | 23 | 23 | 104 |
| 5 | 1 | 200 | 216 | 468 |
| 5 | 2 | 17 | 17 | 113 |
| 5 | 3 | 376 | 364 | 870 |
| 5 | 4 | 810 | 809 | 1748 |
| 5 | 5 | 6 | 6 | 159 |
| 5 | 6 | 0 | 2 | 198 |
| 5 | 7 | 48 | 40 | 369 |
| 6 | -9 | 57 | 58 | 329 |
| 6 | -8 | 1 | 1 | 192 |
| 6 | -7 | 451 | 461 | 1055 |
| 6 | -6 | 3 | 1 | 148 |
| 6 | -5 | 200 | 210 | 491 |
| 6 | -4 | 0 | 0 | 88 |
| 6 | -3 | 253 | 246 | 567 |
| 6 | -2 | 13 | 13 | 80 |
| 6 | -1 | 469 | 455 | 995 |
| 6 | 0 | 3 | 2 | 76 |
| 6 | 1 | 134 | 137 | 353 |
| 6 | 2 | 0 | 3 | 113 |
| 6 | 3 | 433 | 449 | 996 |
| 6 | 4 | 28 | 24 | 286 |
| 6 | 5 | 82 | 79 | 356 |
| 6 | 6 | 2 | 0 | 202 |
| 7 | -9 | 8 | 9 | 199 |
| 7 | -8 | 5 | 0 | 183 |
| 7 | -7 | 150 | 144 | 469 |
| 7 | -6 | 987 | 1019 | 2096 |
| 7 | -5 | 13 | 16 | 122 |
| 7 | -4 | 91 | 89 | 281 |
| 7 | -3 | 372 | 365 | 826 |
| 7 | -2 | 32 | 35 | 132 |
| 7 | -1 | 151 | 152 | 368 |
| 7 | 0 | 2 | 1 | 88 |
| 7 | 1 | 89 | 96 | 270 |
| 7 | 2 | 62 | 57 | 241 |
| 7 | 3 | 211 | 221 | 561 |
| 7 | 4 | 593 | 595 | 1356 |
| 7 | 5 | 0 | 2 | 197 |
| 7 | 6 | 0 | 3 | 210 |
| 8 | -9 | 5 | 3 | 229 |
| 8 | -8 | 59 | 69 | 312 |
| 8 | -7 | 1 | 0 | 189 |
| 8 | -6 | 43 | 56 | 233 |
| 8 | -5 | 3 | 6 | 86 |
| 8 | -4 | 6 | 6 | 90 |
| 8 | -3 | 3 | 2 | 95 |
| 8 | -2 | 406 | 398 | 896 |
| 8 | -1 | 20 | 21 | 132 |
| 8 | 0 | 313 | 324 | 719 |
| 8 | 1 | 2 | 1 | 115 |
| 8 | 2 | 108 | 103 | 334 |
| 8 | 3 | 14 | 12 | 158 |
| 8 | 4 | 19 | 13 | 245 |
| 8 | 5 | 1 | 1 | 189 |
| 8 | 6 | 0 | 0 | 240 |
| 9 | -8 | 12 | 17 | 183 |
| 9 | -7 | 97 | 99 | 401 |
| 9 | -6 | 534 | 571 | 1231 |
| 9 | -5 | 92 | 94 | 315 |
| 9 | -4 | 21 | 22 | 154 |
| 9 | -3 | 124 | 125 | 340 |
| 9 | -2 | 33 | 33 | 160 |
| 9 | -1 | 1 | 0 | 108 |
| 9 | 0 | 3 | 2 | 89 |
| 9 | 1 | 127 | 127 | 375 |
| 9 | 2 | 1 | 2 | 138 |
| 9 | 3 | 208 | 212 | 541 |
| 9 | 4 | 367 | 377 | 945 |
| 9 | 5 | 16 | 14 | 243 |
| 10 | -8 | 4 | 1 | 246 |
| 10 | -7 | 183 | 190 | 604 |
| 10 | -6 | 2 | 1 | 215 |
| 10 | -5 | 156 | 155 | 492 |
| 10 | -4 | 2 | 0 | 154 |
| 10 | -3 | 75 | 78 | 279 |
| 10 | -2 | 19 | 15 | 166 |
| 10 | -1 | 125 | 126 | 401 |
| 10 | 0 | 1 | 0 | 146 |
| 10 | 1 | 65 | 59 | 248 |
| 10 | 2 | 1 | 0 | 166 |
| 10 | 3 | 193 | 196 | 530 |
| 10 | 4 | 14 | 15 | 226 |
| 10 | 5 | 40 | 41 | 330 |
| 11 | -7 | 54 | 58 | 366 |
| 11 | -6 | 404 | 429 | 1059 |
| 11 | -5 | 9 | 6 | 238 |
| 11 | -4 | 52 | 52 | 275 |
| 11 | -3 | 92 | 92 | 348 |
| 11 | -2 | 38 | 34 | 234 |
| 11 | -1 | 31 | 33 | 215 |
| 11 | 0 | 0 | 0 | 157 |
| 11 | 1 | 57 | 57 | 308 |
| 11 | 2 | 21 | 22 | 237 |
| 11 | 3 | 107 | 104 | 473 |
| 11 | 4 | 274 | 272 | 858 |
| 11 | 5 | 3 | 0 | 255 |
| 12 | -7 | 2 | 0 | 249 |
| 12 | -6 | 33 | 33 | 328 |
| 12 | -5 | 13 | 7 | 253 |
| 12 | -4 | 13 | 9 | 211 |
| 12 | -3 | 1 | 1 | 182 |
| 12 | -2 | 178 | 167 | 549 |
| 12 | -1 | 12 | 9 | 142 |
| 12 | 0 | 156 | 159 | 508 |
| 12 | 1 | 0 | 0 | 185 |
| 12 | 2 | 47 | 40 | 329 |
| 12 | 3 | 2 | 3 | 239 |
| 12 | 4 | 15 | 8 | 277 |
| 13 | -6 | 170 | 184 | 656 |
| 13 | -5 | 31 | 30 | 275 |
| 13 | -4 | 24 | 22 | 250 |
| 13 | -3 | 47 | 49 | 316 |
| 13 | -2 | 4 | 4 | 211 |
| 13 | -1 | 2 | 1 | 199 |
| 13 | 0 | 1 | 0 | 218 |
| 13 | 1 | 42 | 41 | 329 |
| 13 | 2 | 2 | 0 | 214 |
| 13 | 3 | 75 | 81 | 426 |
| 14 | -5 | 66 | 61 | 427 |
| 14 | -4 | 3 | 0 | 226 |
| 14 | -3 | 24 | 23 | 322 |
| 14 | -2 | 7 | 9 | 153 |
| 14 | -1 | 19 | 23 | 257 |
| 14 | 0 | -2 | 0 | 208 |
| 14 | 1 | 18 | 16 | 239 |
| 14 | 2 | 0 | 2 | 236 |
| 14 | -3 | 62 | 66 | 416 |
| 15 | -4 | 18 | 16 | 213 |
| 15 | -3 | 15 | 16 | 185 |
| 15 | -2 | 7 | 10 | 139 |
| 15 | -1 | 4 | 5 | 157 |
| 15 | 0 | 0 | 0 | 150 |
| 15 | 1 | 22 | 22 | 189 |
| 16 | -2 | 51 | 44 | 276 |
| 16 | -1 | 1 | 2 | 170 |
| 4,K,L | | | | |
| 0 | -10 | 35 | 37 | 285 |
| 0 | -8 | 210 | 224 | 573 |
| 0 | -6 | 673 | 654 | 1432 |
| 0 | -4 | 7 | 6 | 71 |
| 0 | -2 | 495 | 483 | 1040 |
| 0 | 0 | 40 | 39 | 148 |
| 0 | 2 | 373 | 359 | 838 |
| 0 | 4 | 2 | 0 | 86 |
| 0 | 6 | 25 | 37 | 251 |
| 1 | -10 | 99 | 88 | 359 |
| 1 | -9 | 18 | 15 | 159 |
| 1 | -8 | 91 | 94 | 296 |
| 1 | -7 | 117 | 111 | 321 |
| 1 | -6 | 93 | 87 | 280 |
| 1 | -5 | 63 | 67 | 197 |
| 1 | -4 | 1 | 2 | 76 |
| 1 | -3 | 39 | 35 | 134 |
| 1 | -2 | 1 | 1 | 75 |
| 1 | -1 | 142 | 143 | 339 |
| 1 | 0 | 21 | 20 | 108 |
| 1 | 1 | 7 | 4 | 76 |
| 1 | 2 | 92 | 86 | 281 |
| 1 | 3 | 78 | 77 | 286 |
| 1 | 4 | 3 | 0 | 153 |
| 1 | 5 | 7 | 7 | 122 |
| 1 | 6 | 18 | 15 | 238 |
| 2 | -10 | 3 | 0 | 209 |
| 2 | -9 | 81 | 78 | 341 |
| 2 | -8 | 0 | 0 | 168 |
| 2 | -7 | 44 | 40 | 219 |
| 2 | -6 | 5 | 1 | 104 |
| 2 | -5 | 181 | 186 | 441 |
| 2 | -4 | 3 | 2 | 66 |
| 2 | -3 | 43 | 42 | 140 |
| 2 | -2 | 14 | 16 | 86 |
| 2 | -1 | 10 | 9 | 84 |
| 2 | 0 | 5 | 4 | 86 |
| 2 | 1 | 58 | 60 | 207 |
| 2 | 2 | 1 | 1 | 113 |
| 2 | 3 | 126 | 134 | 384 |
| 2 | 4 | 0 | 2 | 161 |
| 2 | 5 | 0 | 0 | 184 |
| 2 | 6 | 1 | 1 | 207 |
| 3 | -10 | 98 | 92 | 420 |
| 3 | -9 | 6 | 3 | 185 |
| 3 | -8 | 45 | 42 | 263 |
| 3 | -7 | 48 | 45 | 222 |
| 3 | -6 | 60 | 51 | 222 |
| 3 | -5 | 23 | 21 | 120 |
| 3 | -4 | 9 | 8 | 82 |
| 3 | -3 | 14 | 12 | 87 |
| 3 | -2 | 2 | 1 | 65 |
| 3 | -1 | 164 | 168 | 389 |
| 3 | 0 | 46 | 48 | 154 |
| 3 | 1 | 2 | 2 | 88 |
| 3 | 2 | 56 | 49 | 212 |
| 3 | 3 | 50 | 52 | 235 |
| 3 | 4 | 3 | 0 | 141 |
| 3 | 5 | 11 | 12 | 208 |
| 3 | 6 | 28 | 25 | 270 |
| 4 | -10 | 29 | 26 | 255 |
| 4 | -9 | 3 | 1 | 196 |
| 4 | -8 | 153 | 158 | 475 |
| 4 | -7 | 0 | 0 | 145 |
| 4 | -6 | 555 | 547 | 1221 |
| 4 | -5 | 6 | 5 | 88 |
| 4 | -4 | 6 | 2 | 76 |
| 4 | -3 | 34 | 34 | 133 |
| 4 | -2 | 294 | 295 | 650 |
| 4 | -1 | 38 | 43 | 137 |
| 4 | 0 | 15 | 16 | 90 |
| 4 | 1 | 15 | 17 | 112 |
| 4 | 2 | 275 | 271 | 649 |
| 4 | 3 | 0 | 0 | 143 |
| 4 | 4 | 7 | 4 | 136 |
| 4 | 5 | 5 | 5 | 152 |
| 4 | 6 | 26 | 24 | 268 |
| 5 | -9 | 18 | 16 | 236 |
| 5 | -8 | 122 | 128 | 398 |
| 5 | -7 | 169 | 176 | 485 |
| 5 | -6 | 73 | 76 | 267 |
| 5 | -5 | 63 | 63 | 219 |
| 5 | -4 | 1 | 0 | 95 |
| 5 | -3 | 24 | 26 | 112 |
| 5 | -2 | 2 | 0 | 76 |
| 5 | -1 | 47 | 45 | 160 |
| 5 | 0 | 28 | 31 | 159 |
| 5 | 1 | 3 | 0 | 105 |
| 5 | 2 | 49 | 49 | 216 |
| 5 | 3 | 110 | 110 | 369 |
| 5 | 4 | 1 | 1 | 149 |
| 5 | 5 | 7 | 3 | 204 |
| 5 | 6 | 9 | 5 | 222 |
| 6 | -9 | 42 | 45 | 262 |
| 6 | -8 | 0 | 0 | 201 |
| 6 | -7 | 36 | 41 | 237 |
| 6 | -6 | 10 | 7 | 130 |
| 6 | -5 | 119 | 122 | 345 |
| 6 | -4 | 7 | 6 | 97 |
| 6 | -3 | 75 | 79 | 239 |
| 6 | -2 | 63 | 61 | 208 |
| 6 | -1 | 25 | 28 | 139 |
| 6 | 0 | 10 | 11 | 96 |
| 6 | 1 | 26 | 26 | 155 |
| 6 | 2 | 5 | 4 | 114 |
| 6 | 3 | 91 | 94 | 345 |
| 6 | 4 | 8 | 7 | 172 |
| 6 | 5 | 4 | 2 | 108 |
| 7 | -9 | 2 | 0 | 212 |
| 7 | -8 | 21 | 21 | 215 |
| 7 | -7 | 19 | 24 | 190 |
| 7 | -6 | 30 | 29 | 189 |
| 7 | -5 | 3 | 2 | 131 |
| 7 | -4 | 5 | 5 | 134 |
| 7 | -3 | 0 | 0 | 106 |
| 7 | -2 | 12 | 12 | 114 |
| 7 | -1 | 81 | 87 | 251 |
| 7 | 0 | 91 | 95 | 275 |
| 7 | 1 | 1 | 2 | 36 |
| 7 | 2 | 12 | 11 | 126 |
| 7 | 3 | 42 | 41 | 256 |
| 7 | 4 | 0 | 0 | 198 |
| 7 | 5 | 6 | 10 | 249 |
| 8 | -9 | 2 | 1 | 230 |
| 8 | -8 | 60 | 58 | 323 |
| 8 | -7 | 3 | 1 | 180 |
| 8 | -6 | 306 | 325 | 764 |
| 8 | -5 | 5 | 4 | 144 |
| 8 | -4 | 2 | 1 | 123 |
| 8 | -3 | 36 | 36 | 176 |
| 8 | -2 | 68 | 71 | 234 |
| 8 | -1 | 44 | 46 | 185 |
| 8 | 0 | 1 | 0 | 128 |
| 8 | 1 | 18 | 21 | 155 |
| 8 | 2 | 124 | 116 | 413 |
| 8 | 3 | 1 | 0 | 175 |
| 8 | 4 | 21 | 19 | 235 |
| 8 | 5 | 6 | 5 | 213 |
| 9 | -8 | 87 | 91 | 386 |
| 9 | -7 | 135 | 147 | 491 |
| 9 | -6 | 30 | 27 | 249 |
| 9 | -5 | 16 | 14 | 161 |
| 9 | -4 | 1 | 0 | 134 |
| 9 | -3 | 2 | 6 | 132 |
| 9 | -2 | 2 | 2 | 118 |
| 9 | -1 | 5 | 5 | 120 |
| 9 | 0 | 48 | 48 | 215 |
| 9 | 1 | 0 | 0 | 146 |
| 9 | 2 | 10 | 11 | 138 |
| 9 | 3 | 87 | 95 | 366 |
| 9 | 4 | 4 | 3 | 196 |
| 9 | 5 | 1 | 1 | 234 |
| 10 | -8 | 4 | 0 | 231 |
| 10 | -7 | 27 | 32 | 239 |
| 10 | -6 | 4 | 7 | 219 |
| 10 | -5 | 45 | 45 | 285 |
| 10 | -4 | 0 | 0 | 156 |
| 10 | -3 | 79 | 77 | 302 |
| 10 | -2 | 35 | 31 | 200 |
| 10 | -1 | 29 | 30 | 190 |
| 10 | 0 | 3 | 1 | 171 |
| 10 | 1 | 4 | 6 | 187 |
| 10 | 2 | 8 | 4 | 194 |
| 10 | 3 | 56 | 52 | 345 |
| 10 | 4 | 10 | 7 | 268 |
| 11 | -7 | 18 | 17 | 272 |
| 11 | -6 | 25 | 21 | 250 |
| 11 | -5 | 0 | 0 | 217 |
| 11 | -4 | 0 | 0 | 183 |
| 11 | -3 | 1 | 0 | 167 |
| 11 | -2 | 16 | 17 | 201 |
| 11 | -1 | 28 | 27 | 204 |
| 11 | 0 | 74 | 77 | 342 |
| 11 | 1 | 16 | 8 | 234 |
| 11 | 2 | 9 | 2 | 215 |
| 11 | 3 | 24 | 22 | 287 |
| 11 | 4 | -1 | 0 | 263 |
| 12 | -7 | 0 | 1 | 280 |
| 12 | -6 | 129 | 142 | 521 |
| 12 | -5 | 0 | 1 | 206 |
| 12 | -4 | 1 | 2 | 200 |
| 12 | -3 | 9 | 10 | 210 |
| 12 | -2 | 13 | 8 | 228 |
| 12 | -1 | 16 | 17 | 188 |
| 12 | 0 | 3 | 1 | 219 |
| 12 | 1 | 6 | 7 | 208 |
| 12 | 2 | 33 | 28 | 318 |
| 12 | 3 | 0 | 0 | 259 |
| 13 | -6 | 3 | 4 | 262 |
| 13 | -5 | -2 | 0 | 237 |
| 13 | -4 | -1 | 0 | 200 |
| 13 | -3 | -2 | 1 | 193 |
| 13 | -2 | 4 | 3 | 204 |
| 13 | -1 | -1 | 0 | 207 |
| 13 | 0 | 29 | 28 | 292 |
| 13 | 1 | 3 | 0 | 216 |
| 13 | 2 | 3 | 2 | 238 |
| 14 | -5 | 7 | 8 | 284 |
| 14 | -4 | -2 | 0 | 218 |
| 14 | -3 | 33 | 34 | 284 |
| 14 | -2 | 4 | 6 | 153 |
| 14 | -1 | 13 | 11 | 219 |
| 14 | 0 | 0 | 1 | 227 |
| 14 | 1 | 5 | 2 | 235 |
| 15 | -4 | 2 | 0 | 185 |
| 15 | -3 | 2 | 0 | 189 |
| 15 | -2 | 13 | 9 | 176 |
| 15 | -1 | 6 | 7 | 122 |
| 15 | 0 | 34 | 31 | 235 |
| 5,K,L | | | | |
| 0 | -10 | 43 | 50 | 293 |
| 0 | -8 | 40 | 46 | 232 |
| 0 | -6 | 33 | 34 | 178 |
| 0 | -4 | 474 | 481 | 1026 |
| 0 | -2 | 9 | 6 | 88 |
| 0 | 0 | 1051 | 1093 | 2189 |
| 0 | 2 | 252 | 257 | 636 |
| 0 | 4 | 5 | 3 | 186 |
| 1 | -10 | 105 | 109 | 373 |
| 1 | -9 | 31 | 27 | 193 |
| 1 | -8 | 2 | 1 | 128 |
| 1 | -7 | 247 | 248 | 580 |
| 1 | -6 | 38 | 37 | 174 |
| 1 | -5 | 87 | 81 | 263 |
| 1 | -4 | 164 | 162 | 412 |
| 1 | -3 | 37 | 32 | 148 |
| 1 | -2 | 573 | 578 | 1209 |
| 1 | -1 | 4 | 4 | 69 |
| 1 | 0 | 21 | 17 | 136 |
| 1 | 1 | 179 | 192 | 459 |
| 1 | 2 | 76 | 78 | 281 |
| 1 | 3 | 8 | 4 | 170 |
| 1 | 4 | 0 | 2 | 196 |
| 1 | 5 | 13 | 12 | 238 |
| 2 | -10 | 6 | 3 | 166 |
| 2 | -9 | 3 | 0 | 188 |
| 2 | -8 | 2 | 0 | 162 |
| 2 | -7 | 625 | 620 | 1373 |
| 2 | -6 | 1 | 0 | 128 |
| 2 | -5 | 69 | 69 | 222 |
| 2 | -4 | 1 | 0 | 98 |
| 2 | -3 | 9 | 5 | 94 |
| 2 | -2 | 15 | 14 | 106 |
| 2 | -1 | 235 | 235 | 558 |
| 2 | 0 | 2 | 3 | 48 |
| 2 | 1 | 140 | 134 | 383 |
| 2 | 2 | 7 | 10 | 100 |
| 2 | 3 | 248 | 265 | 662 |
| 2 | 4 | 3 | 1 | 192 |
| 2 | 5 | 11 | 11 | 205 |
| 3 | -10 | 148 | 150 | 556 |
| 3 | -9 | 8 | 7 | 148 |
| 3 | -8 | 3 | 3 | 170 |
| 3 | -7 | 171 | 172 | 480 |
| 3 | -6 | 34 | 31 | 181 |
| 3 | -5 | 49 | 46 | 191 |
| 3 | -4 | 162 | 162 | 411 |
| 3 | -3 | 13 | 12 | 107 |
| 3 | -2 | 453 | 459 | 992 |
| 3 | -1 | 2 | 0 | 99 |
| 3 | 0 | 22 | 20 | 138 |
| 3 | 1 | 173 | 180 | 476 |
| 3 | 2 | 84 | 79 | 332 |
| 3 | 3 | 9 | 9 | 174 |
| 3 | 4 | 2 | 0 | 176 |
| 3 | 5 | 19 | 18 | 240 |
| 4 | -10 | 44 | 43 | 291 |
| 4 | -9 | 3 | 1 | 190 |
| 4 | -8 | 32 | 27 | 230 |
| 4 | -7 | 5 | 0 | 161 |
| 4 | -6 | 17 | 16 | 161 |
| 4 | -5 | 0 | 0 | 120 |
| 4 | -4 | 310 | 325 | 708 |
| 4 | -3 | 0 | 0 | 103 |
| 4 | -2 | 5 | 3 | 101 |
| 4 | -1 | 34 | 39 | 159 |
| 4 | 0 | 685 | 733 | 1465 |
| 4 | 1 | 43 | 47 | 203 |
| 4 | 2 | 184 | 179 | 516 |
| 4 | 3 | 5 | 6 | 114 |
| 4 | 4 | 2 | 1 | 197 |
| 4 | 5 | 0 | 1 | 206 |
| 5 | -9 | 29 | 32 | 262 |
| 5 | -8 | 1 | 0 | 191 |
| 5 | -7 | 179 | 182 | 515 |
| 5 | -6 | 28 | 28 | 188 |
| 5 | -5 | 59 | 59 | 248 |
| 5 | -4 | 48 | 48 | 190 |
| 5 | -3 | 67 | 67 | 224 |
| 5 | -2 | 379 | 388 | 851 |
| 5 | -1 | 3 | 2 | 112 |
| 5 | 0 | 23 | 24 | 176 |
| 5 | 1 | 111 | 113 | 352 |
| 5 | 2 | 54 | 50 | 272 |
| 5 | 3 | 4 | 1 | 174 |
| 5 | 4 | 5 | 2 | 194 |
| 5 | 5 | 9 | 5 | 172 |
| 6 | -9 | 4 | 1 | 205 |
| 6 | -8 | 0 | 0 | 182 |
| 6 | -7 | 309 | 325 | 782 |
| 6 | -6 | 0 | 1 | 142 |
| 6 | -5 | 80 | 73 | 283 |
| 6 | -4 | 0 | 1 | 129 |
| 6 | -3 | 1 | 1 | 119 |
| 6 | -2 | 57 | 59 | 218 |
| 6 | -1 | 115 | 123 | 346 |
| 6 | 0 | 8 | 4 | 133 |
| 6 | 1 | 132 | 131 | 403 |
| 6 | 2 | 33 | 35 | 242 |
| 6 | 3 | 121 | 128 | 442 |
| 6 | 4 | 4 | 2 | 213 |
| 7 | -9 | -1 | 0 | 209 |
| 7 | -8 | 3 | 2 | 187 |
| 7 | -7 | 69 | 63 | 316 |
| 7 | -6 | 18 | 17 | 160 |
| 7 | -5 | 11 | 7 | 126 |
| 7 | -4 | 74 | 74 | 267 |
| 7 | -3 | 13 | 9 | 127 |
| 7 | -2 | 228 | 233 | 576 |
| 7 | -1 | 8 | 6 | 131 |

This article is copyrighted as indicated in the article. Reuse of AIP content is subject to the terms at: http://scitation.aip.org/termsconditions. Downloaded to IP: 129.237.46.100 On: Wed, 24 Sep 2014 19:29:19

TABLE V (*Continued*)

| | | | | |
|---|---|---|---|---|
| 7 | 0 | 25 | 24 | 194 |
| 7 | 1 | 94 | 100 | 344 |
| 7 | 2 | 43 | 43 | 245 |
| 7 | 3 | 8 | 5 | 188 |
| 7 | 4 | 6 | 3 | 205 |
| 8 | -9 | 0 | 1 | 233 |
| 8 | -8 | 8 | 5 | 182 |
| 8 | -7 | 3 | 1 | 191 |
| 8 | -6 | 3 | 1 | 167 |
| 8 | -5 | 0 | 0 | 148 |
| 8 | -4 | 48 | 101 | 338 |
| 8 | -3 | 2 | 2 | 132 |
| 8 | -2 | 3 | 1 | 135 |
| 8 | -1 | 43 | 41 | 225 |
| 8 | 0 | 221 | 235 | 599 |
| 8 | 1 | 46 | 49 | 282 |
| 8 | 2 | 68 | 69 | 328 |
| 8 | 3 | 7 | 4 | 216 |
| 8 | 4 | 1 | 0 | 214 |
| 9 | -8 | 0 | 0 | 206 |
| 9 | -7 | 59 | 66 | 312 |
| 9 | -6 | 17 | 16 | 235 |
| 9 | -5 | 24 | 27 | 188 |
| 9 | -4 | 1 | 0 | 153 |
| 9 | -3 | 54 | 56 | 264 |
| 9 | -2 | 149 | 152 | 436 |
| 9 | -1 | 0 | 1 | 157 |
| 9 | 0 | 22 | 26 | 178 |
| 9 | 1 | 39 | 37 | 270 |
| 9 | 2 | 22 | 22 | 223 |
| 9 | 3 | 4 | 0 | 206 |
| 10 | -8 | 3 | 0 | 239 |
| 10 | -7 | 92 | 104 | 417 |
| 10 | -6 | 0 | 0 | 196 |
| 10 | -5 | 57 | 52 | 300 |
| 10 | -4 | -2 | 0 | 180 |
| 10 | -3 | 0 | 1 | 167 |
| 10 | -2 | 40 | 39 | 275 |
| 10 | -1 | 40 | 45 | 258 |
| 10 | 0 | 4 | 0 | 189 |
| 10 | 1 | 78 | 80 | 402 |
| 10 | 2 | 19 | 15 | 240 |
| 10 | 3 | 42 | 33 | 333 |
| 11 | -7 | 18 | 12 | 288 |
| 11 | -6 | 12 | 8 | 208 |
| 11 | -5 | 1 | 0 | 206 |
| 11 | -4 | 29 | 21 | 265 |
| 11 | -3 | 11 | 6 | 232 |
| 11 | -2 | 101 | 98 | 417 |
| 11 | -1 | 12 | 13 | 193 |
| 11 | 0 | 20 | 16 | 233 |
| 11 | 1 | 40 | 36 | 306 |
| 11 | 2 | 14 | 11 | 278 |
| 12 | -7 | 3 | 1 | 130 |
| 12 | -6 | 0 | 0 | 233 |
| 12 | -5 | 1 | 0 | 223 |
| 12 | -4 | 14 | 14 | 195 |
| 12 | -3 | 3 | 4 | 219 |
| 12 | -2 | 1 | 0 | 211 |
| 12 | -1 | 11 | 10 | 196 |
| 12 | 0 | 42 | 44 | 329 |
| 12 | 1 | 11 | 12 | 206 |
| 12 | 2 | 24 | 20 | 343 |
| 13 | -6 | 7 | 8 | 244 |
| 13 | -5 | 10 | 11 | 245 |
| 13 | -4 | 5 | 4 | 226 |
| 13 | -3 | 20 | 22 | 210 |
| 13 | -2 | 48 | 46 | 353 |
| 13 | -1 | -2 | 1 | 240 |
| 13 | 0 | 16 | 14 | 269 |
| 13 | 1 | 1 | 8 | 277 |
| 14 | -4 | -1 | 0 | 266 |
| 14 | -3 | 2 | 4 | 246 |
| 14 | -2 | 17 | 11 | 269 |
| 14 | -1 | 22 | 16 | 291 |
| | | 6,K,L | | |
| 0 | -10 | 644 | 704 | 1539 |
| 0 | -8 | 231 | 244 | 637 |
| 0 | -6 | 65 | 64 | 256 |
| 0 | -4 | 50 | 46 | 201 |
| 0 | -2 | 2467 | 2537 | 5073 |
| 0 | 0 | 59 | 59 | 241 |
| 0 | 2 | 39 | 35 | 278 |
| 0 | 4 | 73 | 80 | 381 |
| 1 | -10 | 50 | 42 | 286 |
| 1 | -9 | 3 | 2 | 160 |
| 1 | -8 | 31 | 33 | 206 |
| 1 | -7 | 2 | 0 | 125 |
| 1 | -6 | 453 | 451 | 1030 |
| 1 | -5 | 83 | 78 | 283 |
| 1 | -4 | 426 | 409 | 944 |
| 1 | -3 | 558 | 560 | 1208 |
| 1 | -2 | 8 | 0 | 137 |
| 1 | -1 | 16 | 19 | 165 |
| 1 | 0 | 5 | 3 | 97 |
| 1 | 1 | 90 | 87 | 336 |
| 1 | 2 | 4 | 2 | 179 |
| 1 | 3 | 182 | 191 | 572 |
| 1 | 4 | 108 | 102 | 460 |
| 2 | -10 | 3 | 0 | 257 |
| 2 | -9 | 3 | 0 | 119 |
| 2 | -8 | 4 | 1 | 171 |
| 2 | -7 | 11 | 8 | 150 |
| 2 | -6 | 5 | 2 | 107 |
| 2 | -5 | 248 | 243 | 613 |
| 2 | -4 | 14 | 11 | 124 |
| 2 | -3 | 747 | 753 | 1589 |
| 2 | -2 | 10 | 7 | 115 |
| 2 | -1 | 26 | 26 | 189 |
| 2 | 0 | 1 | 0 | 127 |
| 2 | 1 | 572 | 576 | 1302 |
| 2 | 2 | 4 | 1 | 173 |
| 2 | 3 | 111 | 100 | 461 |
| 2 | 4 | 4 | 0 | 228 |
| 3 | -10 | 45 | 39 | 329 |
| 3 | -9 | 10 | 6 | 216 |
| 3 | -8 | 53 | 51 | 303 |
| 3 | -7 | 3 | 1 | 164 |
| 3 | -6 | 481 | 481 | 1085 |
| 3 | -5 | 91 | 85 | 311 |
| 3 | -4 | 325 | 327 | 762 |
| 3 | -3 | 442 | 459 | 981 |
| 3 | -2 | 17 | 11 | 160 |
| 3 | -1 | 12 | 11 | 132 |
| 3 | 0 | 0 | 1 | 143 |
| 3 | 1 | 123 | 128 | 402 |
| 3 | 2 | 32 | 31 | 248 |
| 3 | 3 | 190 | 194 | 576 |
| 3 | 4 | 127 | 112 | 502 |
| 4 | -9 | 3 | 1 | 216 |
| 4 | -8 | 167 | 165 | 532 |
| 4 | -7 | 8 | 8 | 161 |
| 4 | -6 | 51 | 49 | 228 |
| 4 | -5 | 11 | 10 | 147 |
| 4 | -4 | 48 | 45 | 213 |
| 4 | -3 | 17 | 15 | 169 |
| 4 | -2 | 1974 | 2085 | 4064 |
| 4 | -1 | 0 | 0 | 142 |
| 4 | 0 | 61 | 63 | 258 |
| 4 | 1 | 5 | 2 | 134 |
| 4 | 2 | 15 | 15 | 193 |
| 4 | 3 | 7 | 7 | 226 |
| 4 | 4 | 57 | 48 | 353 |
| 5 | -9 | 3 | 1 | 207 |
| 5 | -8 | 13 | 16 | 170 |
| 5 | -7 | 2 | 0 | 177 |
| 5 | -6 | 281 | 289 | 713 |
| 5 | -5 | 42 | 39 | 220 |
| 5 | -4 | 358 | 343 | 843 |
| 5 | -3 | 403 | 415 | 929 |
| 5 | -2 | 9 | 1 | 157 |
| 5 | -1 | 41 | 43 | 203 |
| 5 | 0 | 1 | 1 | 156 |
| 5 | 1 | 24 | 22 | 200 |
| 5 | 2 | 3 | 0 | 145 |
| 5 | 3 | 95 | 95 | 420 |
| 5 | 4 | 77 | 73 | 392 |
| 6 | -9 | 8 | 10 | 227 |
| 6 | -8 | 8 | 7 | 198 |
| 6 | -7 | 14 | 11 | 177 |
| 6 | -6 | 7 | 9 | 120 |
| 6 | -5 | 187 | 175 | 530 |
| 6 | -4 | 54 | 47 | 243 |
| 6 | -3 | 492 | 522 | 1115 |
| 6 | -2 | 32 | 30 | 215 |
| 6 | -1 | 19 | 16 | 178 |
| 6 | 0 | 0 | 0 | 164 |
| 6 | 1 | 299 | 305 | 775 |
| 6 | 2 | 1 | 4 | 200 |
| 6 | 3 | 38 | 37 | 276 |
| 7 | -9 | 3 | 7 | 256 |
| 7 | -8 | 46 | 47 | 300 |
| 7 | -7 | -1 | 1 | 191 |
| 7 | -6 | 299 | 306 | 768 |
| 7 | -5 | 48 | 46 | 257 |
| 7 | -4 | 179 | 181 | 514 |
| 7 | -3 | 226 | 235 | 584 |
| 7 | -2 | 28 | 24 | 232 |
| 7 | -1 | 21 | 22 | 180 |
| 7 | 0 | 11 | 15 | 177 |
| 7 | 1 | 70 | 71 | 348 |
| 7 | 2 | 70 | 68 | 354 |
| 7 | 3 | 96 | 96 | 414 |
| 8 | -8 | 56 | 55 | 344 |
| 8 | -7 | 18 | 13 | 256 |
| 8 | -6 | 22 | 23 | 198 |
| 8 | -5 | 10 | 8 | 175 |
| 8 | -4 | 33 | 33 | 236 |
| 8 | -3 | 17 | 14 | 157 |
| 8 | -2 | 1089 | 1148 | 2338 |
| 8 | -1 | 3 | 1 | 169 |
| 8 | 0 | 60 | 60 | 310 |
| 8 | 1 | 5 | 7 | 198 |
| 8 | 2 | 3 | 0 | 208 |
| 8 | 3 | 7 | 7 | 246 |
| 9 | -8 | 13 | 7 | 257 |
| 9 | -7 | 0 | 0 | 200 |
| 9 | -6 | 135 | 140 | 459 |
| 9 | -5 | 14 | 12 | 207 |
| 9 | -4 | 198 | 190 | 580 |
| 9 | -3 | 199 | 205 | 572 |
| 9 | -2 | 3 | 1 | 196 |
| 9 | -1 | 39 | 39 | 278 |
| 9 | 0 | 1 | 2 | 193 |
| 9 | 1 | 2 | 4 | 79 |
| 9 | 2 | 1 | 1 | 220 |
| 10 | -7 | 9 | 10 | 208 |
| 10 | -6 | 8 | 4 | 185 |
| 10 | -5 | 93 | 87 | 415 |
| 10 | -4 | 37 | 33 | 319 |
| 10 | -3 | 254 | 265 | 740 |
| 10 | -2 | 21 | 18 | 264 |
| 10 | -1 | 4 | 6 | 226 |
| 10 | 0 | 2 | 0 | 220 |
| 10 | 1 | 106 | 100 | 518 |
| 10 | 2 | 0 | 2 | 265 |
| 11 | -7 | -1 | 0 | 256 |
| 11 | -6 | 113 | 112 | 510 |
| 11 | -5 | 17 | 14 | 258 |
| 11 | -4 | 78 | 72 | 394 |
| 11 | -3 | 85 | 88 | 404 |
| 11 | -2 | 11 | 14 | 217 |
| 11 | -1 | 27 | 27 | 298 |
| 11 | 0 | 10 | 10 | 204 |
| 11 | 1 | 15 | 20 | 269 |
| 12 | -6 | 7 | 7 | 236 |
| 12 | -5 | 1 | 1 | 240 |
| 12 | -4 | 9 | 13 | 172 |
| 12 | -3 | 6 | 3 | 252 |
| 12 | -2 | 413 | 425 | 1105 |
| 12 | -1 | 1 | 2 | 239 |
| 12 | 0 | 39 | 38 | 357 |
| 13 | -4 | 67 | 72 | 406 |
| 13 | -3 | 72 | 74 | 461 |
| 13 | -2 | 0 | 1 | 297 |
| 13 | -1 | 18 | 16 | 306 |
| | | 7,K,L | | |
| 0 | -8 | 145 | 133 | 477 |
| 0 | -6 | 27 | 25 | 208 |
| 0 | -4 | 217 | 228 | 569 |
| 0 | -2 | 36 | 39 | 215 |
| 0 | 0 | 0 | 2 | 167 |
| 0 | 2 | 159 | 156 | 535 |
| 1 | -9 | 205 | 194 | 584 |
| 1 | -8 | 48 | 49 | 237 |
| 1 | -7 | 18 | 17 | 149 |
| 1 | -6 | 6 | 3 | 146 |
| 1 | -5 | 61 | 51 | 258 |
| 1 | -4 | 237 | 222 | 604 |
| 1 | -3 | 7 | 6 | 108 |
| 1 | -2 | 186 | 183 | 514 |
| 1 | -1 | 68 | 71 | 292 |
| 1 | 0 | 0 | 1 | 169 |
| 1 | 1 | 25 | 25 | 264 |
| 1 | 2 | 43 | 41 | 299 |
| 1 | 3 | 0 | 3 | 250 |
| 2 | -9 | 38 | 32 | 327 |
| 2 | -8 | 3 | 1 | 193 |
| 2 | -7 | 14 | 10 | 170 |
| 2 | -6 | 0 | 0 | 159 |
| 2 | -5 | 200 | 192 | 546 |
| 2 | -4 | 1 | 0 | 150 |
| 2 | -3 | 68 | 58 | 271 |
| 2 | -2 | 2 | 1 | 147 |
| 2 | -1 | 3 | 1 | 159 |
| 2 | 0 | 0 | 1 | 166 |
| 2 | 1 | 4 | 0 | 187 |
| 2 | 2 | 0 | 0 | 214 |
| 2 | 3 | 17 | 14 | 261 |
| 3 | -9 | 240 | 219 | 722 |
| 3 | -8 | 75 | 73 | 347 |
| 3 | -7 | 4 | 2 | 145 |
| 3 | -6 | 14 | 13 | 188 |
| 3 | -5 | 47 | 41 | 254 |
| 3 | -4 | 179 | 169 | 494 |
| 3 | -3 | 8 | 4 | 146 |
| 3 | -2 | 190 | 186 | 537 |
| 3 | -1 | 39 | 42 | 231 |
| 3 | 0 | 2 | 0 | 171 |
| 3 | 1 | 9 | 8 | 161 |
| 3 | 2 | 10 | 5 | 216 |
| 3 | 3 | 0 | 3 | 248 |
| 4 | -9 | 9 | 5 | 234 |
| 4 | -8 | 109 | 102 | 411 |
| 4 | -7 | 0 | 0 | 194 |
| 4 | -6 | 26 | 24 | 205 |
| 4 | -5 | 0 | 0 | 164 |
| 4 | -4 | 198 | 198 | 555 |
| 4 | -3 | 8 | 6 | 139 |
| 4 | -2 | 22 | 24 | 179 |
| 4 | -1 | 3 | 2 | 169 |
| 4 | 0 | 4 | 0 | 123 |
| 4 | 1 | 3 | 4 | 216 |
| 4 | 2 | 109 | 109 | 583 |
| 5 | -9 | 116 | 108 | 489 |
| 5 | -8 | 22 | 21 | 254 |
| 5 | -7 | 17 | 18 | 182 |
| 5 | -6 | 2 | 1 | 168 |
| 5 | -5 | 28 | 27 | 195 |
| 5 | -4 | 138 | 136 | 443 |
| 5 | -3 | 1 | 0 | 53 |
| 5 | -2 | 91 | 96 | 355 |
| 5 | -1 | 62 | 64 | 295 |
| 5 | 0 | 5 | 3 | 190 |
| 5 | 1 | 42 | 48 | 298 |
| 5 | 2 | 50 | 49 | 321 |
| 6 | -9 | 16 | 14 | 214 |
| 6 | -8 | 2 | 2 | 219 |
| 6 | -7 | 21 | 18 | 248 |
| 6 | -6 | 3 | 1 | 192 |
| 6 | -5 | 113 | 112 | 387 |
| 6 | -4 | -1 | 0 | 162 |
| 6 | -3 | 83 | 84 | 346 |
| 6 | -2 | 5 | 2 | 175 |
| 6 | -1 | 6 | 3 | 196 |
| 6 | 0 | 4 | 1 | 183 |
| 6 | 1 | -1 | 1 | 209 |
| 6 | 2 | 6 | 1 | 245 |
| 7 | -8 | 51 | 53 | 331 |
| 7 | -7 | 3 | 2 | 160 |
| 7 | -6 | 10 | 13 | 145 |
| 7 | -5 | 16 | 14 | 209 |
| 7 | -4 | 61 | 65 | 287 |
| 7 | -3 | 4 | 1 | 170 |
| 7 | -2 | 104 | 113 | 389 |
| 7 | -1 | 13 | 14 | 185 |
| 7 | 0 | 1 | 0 | 176 |
| 7 | 1 | 5 | 5 | 216 |
| 7 | 2 | 2 | 1 | 334 |
| 8 | -8 | 51 | 53 | 332 |
| 8 | -7 | 0 | 1 | 200 |
| 8 | -6 | 21 | 21 | 216 |
| 8 | -5 | 0 | 1 | 186 |
| 8 | -4 | 122 | 131 | 437 |
| 8 | -3 | 5 | 1 | 220 |
| 8 | -2 | 4 | 6 | 117 |
| 8 | -1 | 3 | 0 | 179 |
| 8 | 0 | 4 | 2 | 222 |
| 8 | 1 | 7 | 4 | 236 |
| 9 | -7 | 9 | 4 | 203 |
| 9 | -6 | 5 | 5 | 224 |
| 9 | -5 | 7 | 8 | 183 |
| 9 | -4 | 38 | 42 | 286 |
| 9 | -3 | 6 | 5 | 206 |
| 9 | -2 | 30 | 30 | 241 |
| 9 | -1 | 31 | 32 | 296 |
| 9 | 0 | 1 | 2 | 218 |
| 9 | 1 | 32 | 35 | 280 |
| 10 | -6 | 4 | 0 | 215 |
| 10 | -5 | 36 | 41 | 292 |
| 10 | -4 | 2 | 0 | 224 |
| 10 | -3 | 81 | 83 | 415 |
| 10 | -2 | 0 | 0 | 244 |
| 10 | -1 | 7 | 1 | 209 |
| 10 | 0 | -1 | 0 | 264 |
| 11 | -5 | 7 | 4 | 256 |
| 11 | -4 | 23 | 15 | 280 |
| 11 | -3 | 5 | 6 | 250 |
| 11 | -2 | 51 | 51 | 346 |
| 11 | -1 | 0 | 3 | 263 |
| | | 8,K,L | | |
| 0 | -8 | 2 | 2 | 217 |
| 0 | -6 | 461 | 443 | 1102 |
| 0 | -4 | 93 | 86 | 382 |
| 0 | -2 | 15 | 17 | 173 |
| 0 | 0 | 42 | 39 | 305 |
| 1 | -9 | 8 | 10 | 153 |
| 1 | -8 | 5 | 1 | 153 |
| 1 | -7 | 15 | 16 | 158 |
| 1 | -6 | 15 | 12 | 237 |
| 1 | -5 | 33 | 30 | 218 |
| 1 | -4 | 6 | 1 | 173 |
| 1 | -3 | 157 | 153 | 486 |
| 1 | -2 | 7 | 8 | 230 |
| 1 | -1 | 12 | 16 | 167 |
| 1 | 0 | 24 | 23 | 257 |
| 1 | 1 | -2 | 0 | 220 |
| 2 | -9 | 5 | 4 | 250 |
| 2 | -8 | 0 | 1 | 222 |
| 2 | -7 | 32 | 37 | 283 |
| 2 | -6 | 5 | 2 | 195 |
| 2 | -5 | 20 | 13 | 188 |
| 2 | -4 | 7 | 2 | 172 |
| 2 | -3 | 101 | 92 | 404 |
| 2 | -2 | 3 | 0 | 138 |
| 2 | -1 | 43 | 40 | 315 |
| 2 | 0 | 1 | 1 | 212 |
| 2 | 1 | 54 | 48 | 329 |
| 3 | -9 | 27 | 24 | 275 |
| 3 | -8 | -3 | 0 | 215 |
| 3 | -7 | 13 | 14 | 180 |
| 3 | -6 | 42 | 34 | 309 |
| 3 | -5 | 32 | 28 | 249 |
| 3 | -4 | 0 | 0 | 179 |
| 3 | -3 | 174 | 170 | 541 |
| 3 | -2 | 0 | 0 | 186 |
| 3 | -1 | 8 | 10 | 170 |
| 3 | 0 | 8 | 8 | 191 |
| 3 | 1 | 9 | 7 | 192 |
| 4 | -8 | 2 | 4 | 218 |
| 4 | -7 | 4 | 0 | 205 |
| 4 | -6 | 363 | 350 | 920 |
| 4 | -5 | 7 | 7 | 178 |
| 4 | -4 | 61 | 64 | 318 |
| 4 | -3 | 8 | 8 | 157 |
| 4 | -2 | 17 | 15 | 186 |
| 4 | -1 | 0 | 1 | 184 |
| 4 | 0 | 26 | 22 | 261 |
| 4 | 1 | 5 | 2 | 238 |
| 5 | -8 | 3 | 0 | 215 |
| 5 | -7 | 6 | 2 | 162 |
| 5 | -6 | 4 | 5 | 148 |
| 5 | -5 | 16 | 15 | 169 |
| 5 | -4 | 4 | 3 | 135 |
| 5 | -3 | 80 | 80 | 355 |
| 5 | -2 | 15 | 17 | 170 |
| 5 | -1 | 30 | 22 | 273 |
| 5 | 0 | 14 | 15 | 223 |
| 6 | -8 | 7 | 5 | 198 |
| 6 | -7 | 25 | 28 | 226 |
| 6 | -6 | 3 | 6 | 233 |
| 6 | -5 | 13 | 7 | 210 |
| 6 | -4 | 7 | 7 | 166 |
| 6 | -3 | 53 | 54 | 315 |
| 6 | -2 | 7 | 0 | 190 |
| 6 | -1 | 27 | 22 | 272 |
| 6 | 0 | 6 | 7 | 241 |
| 7 | -7 | 5 | 1 | 207 |
| 7 | -6 | 53 | 48 | 322 |
| 7 | -5 | 18 | 14 | 235 |
| 7 | -4 | 0 | 0 | 192 |
| 7 | -3 | 99 | 100 | 414 |
| 7 | -2 | 3 | 1 | 219 |
| 7 | -1 | 14 | 11 | 247 |
| 7 | 0 | 5 | 0 | 170 |
| 8 | -7 | 3 | 1 | 220 |
| 8 | -6 | 177 | 173 | 596 |
| 8 | -5 | 3 | 7 | 79 |
| 8 | -4 | 26 | 28 | 230 |
| 8 | -3 | 10 | 10 | 224 |
| 8 | -2 | 11 | 10 | 216 |
| 8 | -1 | 7 | 3 | 241 |
| 9 | -6 | 10 | 4 | 239 |
| 9 | -5 | 4 | 5 | 240 |
| 9 | -4 | 2 | 2 | 225 |
| 9 | -3 | 32 | 31 | 257 |
| 9 | -2 | 19 | 11 | 325 |
| | | 9,K,L | | |
| 0 | -8 | 37 | 33 | 315 |
| 0 | -6 | 48 | 46 | 300 |
| 0 | -4 | 12 | 13 | 172 |
| 0 | -2 | 329 | 334 | 882 |
| 1 | -8 | 32 | 32 | 257 |
| 1 | -7 | 61 | 56 | 296 |
| 1 | -6 | 177 | 180 | 583 |
| 1 | -5 | 3 | 1 | 215 |
| 1 | -4 | 49 | 45 | 310 |
| 1 | -3 | 23 | 18 | 308 |
| 1 | -2 | 5 | 1 | 218 |
| 1 | -1 | 39 | 30 | 322 |
| 2 | -8 | 3 | 0 | 230 |
| 2 | -7 | 85 | 79 | 377 |
| 2 | -6 | 5 | 3 | 147 |
| 2 | -5 | 4 | 1 | 209 |
| 2 | -4 | 4 | 0 | 204 |
| 2 | -3 | 142 | 146 | 507 |
| 2 | -2 | 2 | 0 | 226 |
| 2 | -1 | 34 | 25 | 305 |
| 3 | -7 | 38 | 45 | 296 |
| 3 | -6 | 151 | 147 | 532 |
| 3 | -5 | 0 | 0 | 201 |
| 3 | -4 | 32 | 30 | 269 |
| 3 | -3 | 26 | 22 | 248 |
| 3 | -2 | 6 | 0 | 226 |
| 3 | -1 | 27 | 24 | 281 |
| 4 | -7 | 6 | 9 | 151 |
| 4 | -6 | 45 | 38 | 324 |
| 4 | -5 | -1 | 2 | 215 |
| 4 | -4 | 15 | 16 | 216 |
| 4 | -3 | 0 | 0 | 209 |
| 4 | -2 | 281 | 294 | 816 |
| 5 | -7 | 57 | 59 | 366 |
| 5 | -6 | 123 | 122 | 498 |
| 5 | -5 | 13 | 13 | 240 |
| 5 | -4 | 31 | 29 | 285 |
| 5 | -3 | 20 | 14 | 225 |
| 5 | -2 | 7 | 2 | 234 |
| 6 | -6 | 13 | 13 | 267 |
| 6 | -5 | 1 | 0 | 224 |
| 6 | -4 | 0 | 0 | 219 |
| 6 | -3 | 74 | 77 | 383 |
| 7 | -4 | 11 | 10 | 179 |

$$R_w=\left[\sum w\,\left|F_0^2-|F_c|^2\right|^2\Big/\sum wF_0^4\right]^{1/2}=0.082\ .$$

The corresponding conventional $R(F)$ was 0.040 if the 453 reflexions with $F_0^2 < 3\sigma_c(F_0^2)$ were excluded from the calculation.

A concluding difference synthesis was featureless, with the highest residual peak corresponding to less than $\frac{1}{20}$ of an oxygen atom.

The neutron scattering lengths[8] were taken to be $\bar{b}_C = 0.6626$, $\bar{b}_O = 0.575$, and $\bar{b}_H = -0.3723$ (all $\times 10^{-12}$ cm). The value used for the nitrogen atom ($\bar{b}_N = 0.925(4)\times 10^{-12}$ cm) was obtained from the refinement. The scattering length presently accepted for nitrogen ($\bar{b}_N = 0.94$[9]) appears to be somewhat higher than the refined values obtained in a number of recent studies.[8,10–13] These values are presented in Table II.

The refined atomic parameters are listed in Tables III and IV and the observed and calculated squared structure factors are tabulated in Table V.

All calculations were carried out on the CDC 6600 computers at the Brookhaven National Laboratory, except for preparation of the illustrations, which was done on the IBM 370/155 and IBM 1800 computers in Uppsala.

## DESCRIPTION AND DISCUSSION

### Molecular structure

The molecular structure of pyridine-2, 3-dicarboxylic acid in the crystalline state is illustrated in Fig. 1. The molecules occur in the zwitterion form, with the proton from one of the carboxyl groups attached to the nitrogen atom. The carboxyl groups are bonded to each other by a very short, asymmetrical hydrogen bond [O⋯O: 2.398(3) Å].

The tendency for this bond to be as linear as possible while keeping H5 close to the planes of the carboxyl groups seems to strain the molecule. The single C–C bonds are both considerably longer than the expected value of 1.48 Å[14] for an $sp^2$–$sp^2$ carbon–carbon bond. The C3–C8 bond length is 1.516(2) Å with a C2–C3–C8 angle of 126.5(1)°, while the C2–C7 distance is still longer [1.541(2) Å], with an even larger C3–C2–C7 angle [131.2(1)°]. Both angles are much larger than the expected 120° angle around $sp^2$ hybridized atoms. There are also small but significant deviations from planarity in the pyridine skeleton (see Table VI). The dihedral angles between the least-squares plane through the pyridine ring and the planes of the carboxyl groups are 10.7 and 8.0°. The larger rotation is around the C3–C8 bond. The rotations about the C–C single bonds place the oxygens participating in the intramolecular hydrogen bond on the same side of the plane through the pyridine ring. These rotations are very similar to those found in potassium hydrogen chloromaleate,[15] a compound possessing a short O⋯O hydrogen bond comparable to that found in pyridine-2, 3-dicarboxylic acid. The rather large distortions from normally favored geometries indicate that the O⋯O distance of 2.398 Å is at the extreme lower end of the distance range for oxygen–oxygen hydrogen bonds. A detailed discussion of this hydrogen bond is given below.

This article is copyrighted as indicated in the article. Reuse of AIP content is subject to the terms at: http://scitation.aip.org/termsconditions. Downloaded to IP: 129.237.46.100 On: Wed, 24 Sep 2014 19:29:19
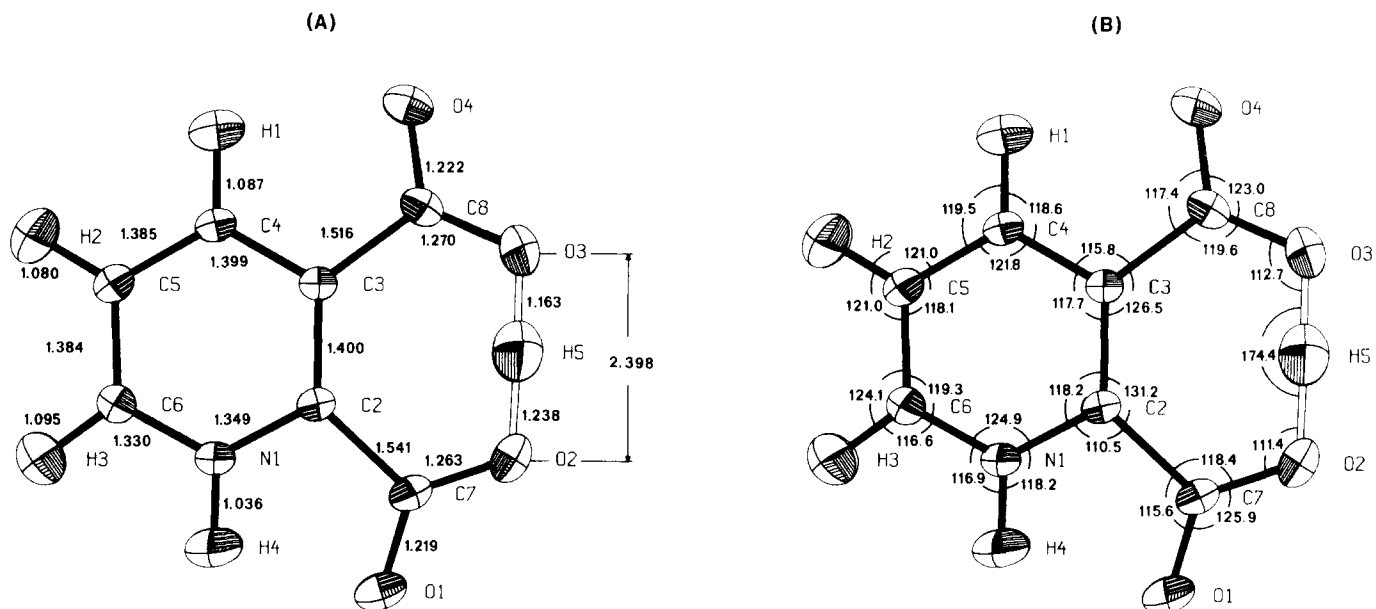
**(A)**

**(B)**

FIG. 1. Bond distances (A) and angles (B). The atomic notation in the figure is used throughout the paper. Standard deviations of distances are given in Table VII. The angles involving heavy atoms all have standard deviations of 0.1° except for the angles C2–C7–O1, O1–C7–O2, and C3–C8–O3, which have standard deviations of 0.2°. The angle O2–H5–O3 has a standard deviation of 0.4°; all other angles involving hydrogen atoms have standard deviations of 0.2°.

The bond lengths and angles are illustrated in Fig. 1, and the distances are also listed in Table VII. The molecular dimensions involving the heavy atoms agree well with dimensions found in the x-ray study.[4] As expected, the extra annular proton on the nitrogen atom opens the carbon–nitrogen–carbon angle [∠C2–N1–C6 = 124.9(1)°]. The different carbon–oxygen distances can be explained by different hydrogen-bond involvement and electronic environment. The mean C–H distance is 1.087 Å.

The thermal motion of the atoms are illustrated in Fig. 2 and the rms displacements along the principal axes are listed in Table VIII.

## Crystal packing

The crystal structure consists of layers of molecules closely parallel to the planes of the pyridine rings. Figures 3 and 4 give stereoscopic illustrations of the packing of the different neighboring layers, all of which are almost perpendicular to the crystallographic *b* axis. The closest interlayer contacts occur between carbon and oxygen atoms and are listed in Table IX. A.

Molecules related by translation along the crystallographic *a* direction are linked to produce infinite chains by means of N–H··· O hydrogen bonds with N··· O dis-

TABLE VI. Deviations of the atoms from the least-squares plane through the six heavy atoms in the pyridine ring.

|     | Deviation (Å)   |
| --- | --------------- |
| N1  | 0.005(1)        |
| C2  | 0.003(2)        |
| C3  | − 0.012(2)      |
| C4  | 0.013(2)        |
| C5  | − 0.001(2)      |
| C6  | − 0.012(2)      |
| C7  | 0.064(2)        |
| C8  | − 0.069(2)      |
| O1  | 0.223(3)        |
| O2  | − 0.081(3)      |
| O3  | − 0.297(3)      |
| O4  | 0.101(3)        |
| H1  | 0.032(5)        |
| H2  | − 0.013(4)      |
| H3  | − 0.024(5)      |
| H4  | 0.021(5)        |
| H5  | − 0.250(5)      |

TABLE VII. Intramolecular bond lengths.[a]

|         | Neutron (Å)        | X-ray[b] (Å) |
| ------- | ------------------ | ------------ |
| C2–N1   | 1.349(1)[1.353]    | 1.345(3)     |
| C6–N1   | 1.330(1)[1.333]    | 1.323(3)     |
| H4–N1   | 1.036(4)[1.039]    | 0.89(5)      |
| C3–C2   | 1.400(2)[1.404]    | 1.400(4)     |
| C7–C2   | 1.541(2)[1.545]    | 1.545(4)     |
| C4–C3   | 1.399(1)[1.403]    | 1.395(3)     |
| C8–C3   | 1.516(2)[1.521]    | 1.518(3)     |
| C5–C4   | 1.385(1)[1.389]    | 1.376(3)     |
| H1–C4   | 1.087(4)[1.090]    | 1.01 (4)     |
| C6–C5   | 1.384(2)[1.388]    | 1.387(4)     |
| H2–C5   | 1.080(3)[1.083]    | 1.00(3)      |
| H3–C6   | 1.095(3)[1.098]    | 0.85(4)      |
| O1–C7   | 1.219(3)[1.222]    | 1.215(4)     |
| O2–C7   | 1.263(2)[1.266]    | 1.257(3)     |
| O3–C8   | 1.270(2)[1.273]    | 1.263(3)     |
| O4–C8   | 1.222(3)[1.226]    | 1.228(4)     |
| O2–H5   | 1.238(5)           | 1.44(5)      |
| O3–H5   | 1.163(5)           | 1.03(5)      |

[a]Values in squared brackets are corrected for rigid-body motion.
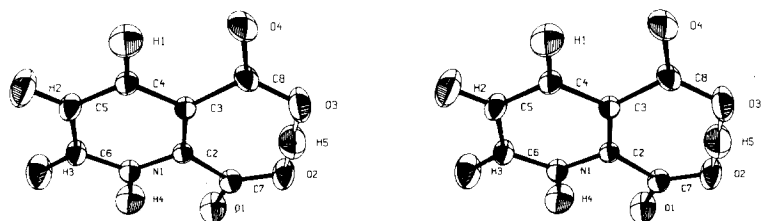[b]Distances recalculated with our cell dimensions.

FIG. 2. Stereoscopic illustration of the thermal ellipsoids in the molecule. The ellipsoids are drawn at the 50% probability level.
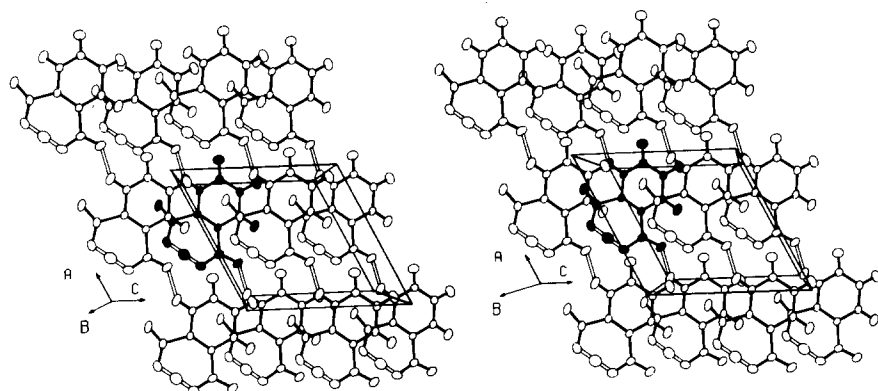


FIG. 3. A stereoscopic view of the crystal packing. In this figure the molecular layers at $y \sim \frac{1}{8}$ and $y \sim \frac{3}{8}$ are illustrated. Covalent bonds are filled and hydrogen bonds are open. The asymmetric unit is indicated by black ellipsoids.
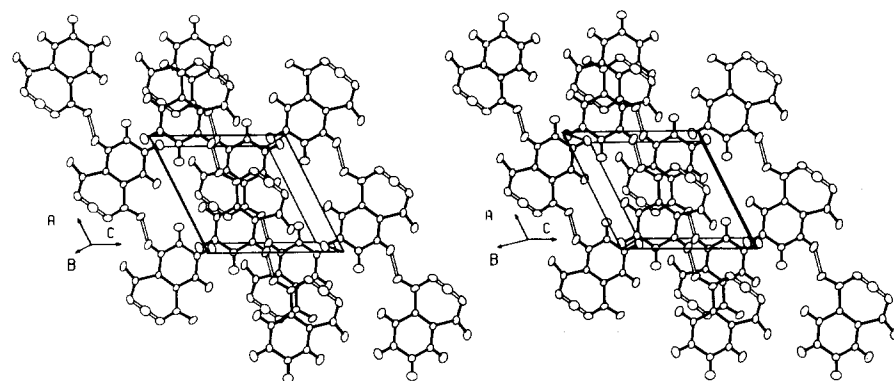


FIG. 4. A stereoscopic view of the crystal packing showing the layers at $y \sim \frac{3}{8}$ and $y \sim \frac{5}{8}$.

TABLE VIII. The root-mean-square components $R_i$(Å) of thermal displacement of the atoms along the principal axes ($\times 10^3$).

|    | $R_1$    | $R_2$    | $R_3$    |
|----|----------|----------|----------|
| N1 | 213(1)   | 156(1)   | 125(3)   |
| C2 | 185(2)   | 151(1)   | 124(4)   |
| C3 | 185(2)   | 147(1)   | 125(4)   |
| C4 | 210(2)   | 160(1)   | 123(4)   |
| C5 | 228(2)   | 162(2)   | 136(3)   |
| C6 | 230(2)   | 150(2)   | 141(3)   |
| C7 | 223(2)   | 174(1)   | 128(4)   |
| C8 | 216(2)   | 175(2)   | 133(3)   |
| O1 | 305(3)   | 210(2)   | 126(6)   |
| O2 | 284(2)   | 197(3)   | 139(2)   |
| O3 | 305(3)   | 192(4)   | 145(2)   |
| O4 | 280(2)   | 202(2)   | 134(5)   |
| H1 | 293(4)   | 219(2)   | 145(9)   |
| H2 | 309(4)   | 220(5)   | 156(4)   |
| H3 | 317(4)   | 209(5)   | 164(4)   |
| H4 | 281(4)   | 222(3)   | 142(10)  |
| H5 | 308(4)   | 223(7)   | 190(3)   |

tances of 2.725(2) Å. The bond is bent with an N1–H4–O4 angle of 140.5(2) Å; the H4$\cdots$O4 distance is 1.845(4) Å and the N1–H4 bond length is 1.036(4) Å. The hydrogen bonds and the short H$\cdots$O contacts within a layer are further illustrated in Fig. 5. It can be disputed whether the contacts marked with thin lines in the figure are hydrogen bonds or van der Waals contacts. The C5–H2$\cdots$O3 contact with an H2$\cdots$O3 distance of 2.300(4) Å and C5–H2$\cdots$O3 angle of 142.5(2)° might possibly be considered as a C–H$\cdots$O hydrogen bond, but interactions of this kind are certainly fairly weak and are probably better considered as van der Waals contacts.[16] The complete geometrical details for short intramolecular contacts are given in Table IX. B.

### The intramolecular hydrogen bond

The short intramolecular hydrogen bond O2$\cdots$O3 [2.398(3) Å] is found to involve a slightly noncentered hydrogen atom 1.163(5) Å from O3 and 1.238(5) Å from

TABLE IX. Distances and angles for hydrogen bonds and short intermolecular contacts.

A. Closest contact between layers (symmetry operation applied is given in parentheses)

| | |
|---|---|
| C2···O4 $(1-x, \bar{y}, \bar{z})$ | 3.168(3) Å |
| C6···O1 $(2-x, \bar{y}, \bar{z})$ | 3.188(3) Å |
| C7···O4 $(1-x, \bar{y}, \bar{z})$ | 3.193(3) Å |
| C8···O2 $(x, \frac{1}{2}-y, \frac{1}{2}+z)$ | 3.189(3) Å |

B. Within a layer

| X–H···Y | X···Y(Å) | X–H(Å) | H···Y(Å) | X–H···Y(°) |
|---|---|---|---|---|
| O3–H5···O2 | 2.398(3) | 1.163(5) | 1.238(5) | 174.4(4) |
| N1–H4···O4 | 2.725(2) | 1.036(4) | 1.845(4) | 140.5(2) |
| C5–H2···O1 | 3.127(3) | 1.080(3) | 2.351(4) | 127.3(2) |
| C5–H2···O3 | 3.225(2) | 1.080(3) | 2.300(4) | 142.5(3) |
| C6–H3···O2 | 3.369(2) | 1.095(3) | 2.401(3) | 146.5(3) |

O2. It is most likely that this asymmetry is imposed on the bond by the asymmetric location of the nitrogen atom with respect to the hydrogen bond. The crystal environment of O2 and O3 are rather similar (Fig. 5). An INDO calculation,[17] where the effect of the crystal field was neglected, gave an equilibrium hydrogen position in agreement with experiment to better than 0.01 Å. The theoretical hydrogen position was deduced from the energy points obtained when the hydrogen atom was displaced by ±0.1 Å from the experimentally found position. The semiempirical calculation supports the belief that intramolecular forces rather than crystal forces distort the symmetry of the short hydrogen bond. Asymmetry in the molecule does not always give asymmetry in comparable bonds, however. This is illustrated in potassium hydrogen chloromaleate,[15] where the hydrogen atom is effectively centered in an intramolecular hydrogen bond [O···O: 2.403(3) Å] between the carboxyl groups. The effect of the asymmetry in this molecule seems to be compensated by environmental dissimilarities. One of the oxygens participating in the bond has a $K^+$···O contact of 2.845(3) Å, whereas the other oxygen atom has no short ionic contact. The fact that small differences in the intermolecular environment may cause deviations from a centered bond is evidenced in bis(2-ami-



FIG. 5. Short intermolecular contacts within a molecular layer. Covalent bonds are filled and hydrogen bonds are open; other short contacts are illustrated by thin lines.

no-2-methyl-3-butanone oximato) nickel (II) chloride monohydrate,[18] in which the O–H distances are 1.242(5) and 1.187(5) Å in a bond with an O···O distance of 2.420(3) Å. This effect has also been noted in *p*-toluidinium bifluoride,[19] in which different hydrogen bonding to the fluorine atoms in the $(HF_2)^-$ ion give H–F distances of 1.025(6) and 1.235(6) Å.

The potentials governing the position of the hydrogen atom in these very short bonds seem to be very sensitive to asymmetry in the molecule and in the molecular environment. Truly centered hydrogen bonds are therefore probably exceptional in structures where this special case is not a demand of symmetry.

A survey of the short O···O hydrogen bonds not subjected to symmetry restrictions that have been studied with neutron diffraction is given in Table X.

TABLE X. Short O···O hydrogen bonds, with no symmetry restrictions, which have been studied by neutron diffraction.

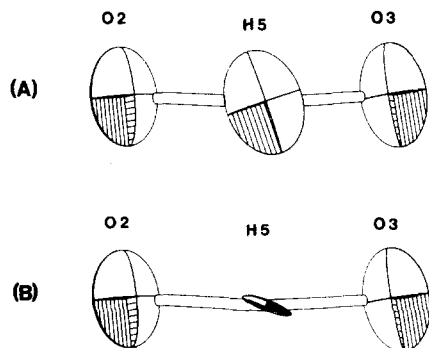| | O···O(Å) | O–H(Å) | O···H(Å) | O–H···O (Å) |
|---|---|---|---|---|
| Pyridine-2, 3-dicarboxylic acid | 2.398(3) | 1.163(5) | 1.238(5) | 174.4(4) |
| $K^+C_4H_2ClO_4^-$ [15] | 2.403(3) | 1.199(5) | 1.206(5) | 175.4(4) |
| $\{Ni(C_5H_{11}N_2O)_2H\}^+Cl^- \cdot H_2O$ [18] | 2.420(3) | 1.187(5) | 1.242(5) | 169.9(3) |
| $K^+HO(CH_2COO)_2^-$ [20] | 2.476(2) | 1.152(3) | 1.328(3) | 174.2(3) |
| $C_6H_2(NO_2)_3SO_3H \cdot 4H_2O$ [21] | 2.436(2) | 1.128(3) | 1.310(3) | 175.0(3) |
| $C_6H_3(COOH)(OH)SO_3H \cdot 3H_2O$ [22] | 2.436(4) | 1.095(6) | ··· | ··· |
| $(NH_2)_2CO : H_3PO_4$ [11] | 2.421(3) | 1.207(6) | 1.223(6) | 169.9(4) |

FIG. 6. Thermal ellipsoids drawn at the 50% probability level for the short intramolecular hydrogen bond. The normal ellipsoids are shown in (A). The mean thermal motion of the oxygen atoms has been subtracted from the hydrogen atom H5 in (B). The rms components of thermal displacement of H5 along the principal ellipsoid axes in (B) are 0.149(11), 0.113(6), and 0.017(85) Å.

## Thermal motion

The thermal motion parameters $\beta_{ij}$ were converted to thermal vibration tensor elements $U_{ij}$, referred to an orthogonal Cartesian axial system parallel to $a$, $b$, and $c*$. The tensor elements $U_{ij}$ of the nitrogen and carbon atoms were fitted to rigid-body motions expressed in terms of T, L, and S tensors.[23] The rms deviation of the experimental $U_{ij}$ from those calculated from the values of T, L, and S is 0.0005 Å$^2$. The rms amplitudes of translation along the principal axes are 0.18, 0.15, and 0.12 Å, with the largest translation perpendicular to the plane of the molecule. The librations have rms amplitudes of 3.8, 3.2, and 2.4°. The smallest libration is about an axis perpendicular to the plane of the molecule. The effective screw translations were 0.003 Å or smaller. Corrections to bond lengths between atoms in the rigid body were obtained from the rigid-body librations and are included in Table VII.

## HYDROGEN-BOND DYNAMICS

It has been shown by several authors (e.g., Hamilton,[24]) that neutron diffraction data can be used to study the potential functions governing hydrogen atoms in hydrogen bonds.

We have attempted to study the dynamics in the short hydrogen bond in pyridine-2, 3-dicarboxylic acid by subtracting the averaged thermal motion of the oxygen atoms O2 and O3 from the motion of H5. The resulting thermal ellipsoid is illustrated in Fig. 6(B). This procedure gives an approximate picture of how the hydrogen atom moves relative to the oxygen atoms. As can be seen from Fig. 6(B), the largest principal axis of the thermal ellipsoid lies approximately along the line between O2 and O3. The difference mean-square amplitude of vibration for H5 along the O2–O3 bond is 0.0193(33) Å$^2$. Assuming a normal vibration in which the hydrogen atom moves along this bond, we get a calculated stretch frequency of about 870 cm$^{-1}$ using the relationship

$$\omega = 16.8/m\langle r^2 \rangle \quad,$$

where $\langle r^2 \rangle$[24] is expressed in Å$^2$, $m$ in amu and $\omega$ in cm$^{-1}$. This formula applies for a harmonic oscillator. We have also studied the ir spectrum of the compound. It suggests two possible frequencies for the stretch; one around 1000 cm$^{-1}$, and one close to 1400 cm$^{-1}$. The higher frequency corresponds to a mean-square amplitude of vibration of 0.012 Å$^2$, while the lower frequency corresponds to a mean-square amplitude of 0.0168 Å$^2$. The discrepancy between the vibrational minimal rms amplitude and the amplitude observed from the diffraction experiment is 0.029 Å. The smallness of this difference indicates that a disordered hydrogen in a double minimum potential cannot be present.

Considering the fact that a C–H stretching vibration is certainly a good approximation of a normal vibration, a check was made on the quality of the thermal parameters by calculating the C–H stretch frequencies. These three frequencies are known from the ir experiment to fall in the range 3075–3105 cm$^{-1}$. The quantities $\langle r^2_{C-H}(H) \rangle - \langle r^2_{C-H}(C) \rangle$ along the C–H bonds were 0.0058, 0.0043, and 0.0068 Å$^2$. The corresponding calculated stretch frequencies were about 2900, 3900, and 2500 cm$^{-1}$. The thermal parameters obtained by neutron diffraction evidently give frequencies of the right order of magnitude, which may subsequently be used for dynamical discussion purposes.

## ACKNOWLEDGMENTS

*Part 84 will appear in Acta Crystallogr.

†Research performed under the auspices of the U. S. Atomic Energy Commission.

‡Research collaborator at the Brookhaven National Laboratory.

[1]D. R. Beaucage, M. A. Kelley, D. Ophir, S. Rankowitz, R. J. Spinrad, and R. Van Norton, Nucl. Instrum. Methods 40, 26 (1966).

[2]M. S. Lehmann, W. C. Hamilton, and F. K. Larsen, American Crystallographic Association Meeting Abstracts 09, Albuquerque, New Mexico, 1972.

[3]*International Tables for X-Ray Crystallography*, edited by C. H. MacGillavry, C. D. Riecks, and K. Lonsdale (Kynoch, Birmingham, England, 1962), Vol. 3, p. 197.

[4]F. Takusagawa, K. Hirotsu, and A. Shimada, Bull. Chem. Soc. Japan 46, 2372 (1973).

[5]V. Schomaker (private communication), 1969.

[6]F. L. Hirshfeld and D. Rabinovich, Acta Crystallogr. A 29, 510 (1973).

[7]F. H. Moore, Ninth Int. Congress of Crystallography Abstracts XXV-15, Kyoto, Japan, 1972.

[8]M. N. Frey, T. F. Koetzle, M. S. Lehmann, and W. C. Hamilton, J. Chem. Phys. 59, 915 (1973).

[9]G. E. Bacon, Acta Crystallogr. A **28**, 357 (1972).

[10]J. E. Worsham, Jr. and W. R. Busing, Acta Crystallogr. B **25**, 572 (1969).

[11]E. C. Kostansek and W. R. Busing, Acta Crystallogr. B **28**, 2454 (1972).

[12]Å. Kvick, T. F. Koetzle, and R. Thomas (unpublished).

[13]Å. Kvick, T. F. Koetzle, and R. Thomas, J. Chem. Phys. (to be published).

[14]M. J. S. Dewar and H. N. Schmeising, Tetrahedron **5**, 166 (1959).

[15]R. D. Ellison and H. A. Levy, Acta Crystallogr. **19**, 260 (1965).

[16]T. F. Koetzle, W. C. Hamilton, and R. Parthasarathy, Acta Crystallogr. B **28**, 2083 (1972).

[17]J. A. Pople, D. L. Beveridge, and P. A. Dobosh, J. Chem. Phys. **49**, 2027 (1967).

[18]E. O. Schlemper, W. C. Hamilton, and S. La Placa, J. Chem. Phys. **54**, 3990 (1971).

[19]J. M. Williams and L. F. Schneemeyer, J. Am. Chem. Soc. **95**, 5780 (1973).

[20]J. Albertsson and I. Grenthe, Acta Crystallogr. B **29**, 2751 (1973).

[21]J. -O. Lundgren and R. Tellgren (unpublished).

[22]J. M. Williams, S. W. Peterson, and H. A. Levy, American Crystallographic Association Meeting Abstracts **17**, Albuquerque, NM, 1972.

[23]V. Schomaker and K. N. Trueblood, Acta Crystallogr. B **24**, 63 (1968).

[24]W. C. Hamilton, Natl. Bur. Stand. (U.S.) Spec. Publ. **301**, 193 (1969).