# 84. *The Crystal Structure of an Overcrowded Aromatic Compound:* 3-*Bromo*-1,8-*dimethylnaphthalene.*

By M. B. JAMESON and B. R. PENFOLD.

The crystal structure of 3-bromo-1,8-dimethylnaphthalene has been determined and parameters have been refined using 1338 $X$-ray reflexions in a three-dimensional least-squares treatment. The results indicate that the molecular overcrowding has been relieved mainly by displacement of the methyl groups within the mean plane of the naphthalene skeleton but that, in addition, there are small but definite departures from planarity within the aromatic rings.

THE observed dissociation constants of a number of methylnaphthoic acids as reported by Fischer *et al.*[1] and in particular, the value for 4,5-dimethyl-1-naphthoic acid, cannot be explained satisfactorily on the assumption that the electronic effects of *peri*-substituted methyl groups are additive. These observations concerning substituents which must be under severe steric compression or molecular overcrowding, led to the question of just what type of modification of the unstrained molecular structure could be associated with such small but measurable electronic effects. 3-Bromo-1,8-dimethylnaphthalene was chosen as a model for examining the effect on the overall molecular configuration of two methyl groups substituted in *peri* positions of a naphthalene ring system.

## EXPERIMENTAL

*Preparation and Crystal Data.*—The compound was prepared by the method described by Mitchell, Topsom, and Vaughan [2] in four steps from naphthalic anhydride. It was recrystallised from ethanol and finally appeared as colourless, flattened needles whose direction of greatest elongation corresponded to the shortest crystallographic axis of the chosen triclinic unit cell.

3-Bromo-1,8-dimethylnaphthalene, $C_{12}H_{11}Br$; $M = 235{\cdot}0$; triclinic, $a = 8{\cdot}56 \pm 0{\cdot}02$, $b = 8{\cdot}59 \pm 0{\cdot}02$, $c = 7{\cdot}71 \pm 0{\cdot}02$ Å, $\alpha = 118{\cdot}8 \pm 0{\cdot}1°$, $\beta = 97{\cdot}9 \pm 0{\cdot}1°$, $\gamma = 91{\cdot}2 \pm 0{\cdot}1°$ (uncertainties are three times the standard errors) assuming $\lambda = 1{\cdot}5418$ Å for Cu-$K_\alpha$ radiation. $U = 489{\cdot}3$ Å$^3$, $D_m = 1{\cdot}57$ (by flotation), $Z = 2$, $D_c = 1{\cdot}59$, $F(000) = 236$, linear absorption coefficient for Cu-$K_\alpha = 55{\cdot}4$ cm.$^{-1}$. A crystallographic centre of symmetry was indicated by Sim's test [3] using a statistical analysis of the intensity distribution of the $hk0$ $X$-ray reflexions, and the space group $P\bar{1}$ ($C_i^1$, No. 2) was confirmed by the structure analysis.

The equi-inclination Weissenberg method was used to record reflexions within the levels $hk0 \cdots 3$ and $0 \cdots 2kl$. 1338 independent reflexions in all, representing 60% of the total Cu-$K_\alpha$ limiting sphere, were accessible in these levels and their intensities were estimated by eye, 54 of them being too weak to observe. Owing to crystal deterioration, three different specimens had to be used. None were large enough to make absorption effects serious and no corrections were made.

Except for the least-squares refinement which is discussed below, all computations were performed on the IBM 1620 computer at the Mobil Computer Laboratory of the University of Canterbury using, in part, programmes [4] supplied by the Institute for Cancer Research (Dr. A. L. Patterson), Philadelphia, U.S.A. Least-squares planes through groups of atoms were evaluated by the method of Schomaker *et al.*[5]

*Structure Determination.*—Bromine co-ordinates were located unambiguously from projections of the Patterson function on (001) and (100). A three-dimensional Fourier synthesis based on the bromine signs then revealed all twelve carbon atoms. Preliminary refinement was by six difference Fourier cycles, in the course of which anisotropic thermal parameters for the

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[1] Fischer, Mitchell, Packer, Topsom, and Vaughan, *J.*, 1963, 2892.

[2] Mitchell, Topsom, and Vaughan, *J.*, 1962, 2526.

[3] Sim, *Acta Cryst.*, 1958, **11**, 420.

[4] Van der Helm, " I.C.R.1, A 3- and 2-dimensional Fourier Summation Program," " I.C.R.4, Structure Factor Program and Least-squares Sum Maker " (1961), and " I.C.R.6, Fourier Data Tape Maker " (1962); Johnson, " I.C.R.13, Neighbour-Finding Distance Program " and " I.C.R.14, Selected Angles and Distances Program " (1962), Institute for Cancer Research, Philadelphia, U.S.A.

[5] Schomaker, Waser, Marsh, and Bergman, *Acta Cryst.*, 1959, **12**, 600.

bromine atom were assigned, using the expression $f = f_0 \exp -(h^2\beta_{11} + k^2\beta_{22} + l^2\beta_{33} + 2hk\beta_{12} + 2kl\beta_{23} + 2hl\beta_{13})$. Finally, two three-dimensional least-squares cycles were performed using the programme ORFLS of Busing, Martin, and Levy.[6] All atoms were refined anisotropically but, because of programme limitations, the thermal parameters of only Br, C(11), C(12), and half the remaining carbon atoms could be varied in each cycle. In the first least-squares cycle, seven scale factors were adjusted and $R$ fell from 0·15 to 0·114. In the second cycle the scale factors were held constant and $R$ fell to its final value of 0·106 for all 1338 observable reflexions, unobserved orders being assigned a value half the minimum observable. The least-squares weighting scheme was based on that of Hughes [7] except for 34 intense inner reflexions which appeared to be suffering from extinction and for which empirical corrections were made from a plot of $F_o/F_c$ against $F_c$. A 50% error was assigned to each of these reflexions to ensure that they were not unduly weighted in the refinement. The correlation matrix put out by the ORFLS computation showed that there were a number of appreciable interactions between $y$ and $z$ co-ordinates of the same atom (a consequence of the use of non-orthogonal reference axes), the largest correlation coefficient being 0·53 for atom C(5). Atomic scattering factors used were, for carbon, those of Berghuis *et al.*,[8] and for bromine, the Thomas–Fermi–Dirac statistical model values,[9] corrected for anomalous dispersion. A final three-dimensional difference map suggested the positions of most of the hydrogen atoms but these were not included in any structure factor calculations. Final positional parameters for all atoms, referred to a centre of symmetry as origin, are given in Table 1 together with standard deviations derived directly from the least-squares inverse matrix. On account of the interactions already mentioned, values for $\sigma Y$ and $\sigma Z$ are likely to be underestimates. Anisotropic thermal parameters are shown in Table 2. Structure amplitudes for all observed reflexions are listed with the calculated values in Table 3.

TABLE 1.

Atomic co-ordinates and standard errors.

| Atom | $x/a$ | $\sigma X$ (Å) | $y/b$ | $\sigma Y$ (Å) | $z/c$ | $\sigma Z$ (Å) |
|---|---|---|---|---|---|---|
| Br | 0·9106 | 0·001 | 0·9005 | 0·001 | 0·7312 | 0·002 |
| C(1) | 0·6226 | 0·010 | 0·4623 | 0·009 | 0·2615 | 0·012 |
| C(2) | 0·7509 | 0·009 | 0·5750 | 0·009 | 0·4005 | 0·011 |
| C(3) | 0·7279 | 0·009 | 0·7479 | 0·009 | 0·5456 | 0·011 |
| C(4) | 0·5868 | 0·011 | 0·8103 | 0·011 | 0·5539 | 0·013 |
| C(5) | 0·3012 | 0·011 | 0·7635 | 0·011 | 0·4315 | 0·014 |
| C(6) | 0·1710 | 0·009 | 0·6589 | 0·009 | 0·2988 | 0·012 |
| C(7) | 0·1811 | 0·009 | 0·4845 | 0·009 | 0·1529 | 0·012 |
| C(8) | 0·3253 | 0·012 | 0·4149 | 0·009 | 0·1263 | 0·012 |
| C(9) | 0·4639 | 0·009 | 0·5175 | 0·009 | 0·2607 | 0·012 |
| C(10) | 0·4533 | 0·009 | 0·6946 | 0·009 | 0·4148 | 0·010 |
| C(11) | 0·6611 | 0·012 | 0·2807 | 0·011 | 0·1112 | 0·014 |
| C(12) | 0·3222 | 0·011 | 0·2272 | 0·011 | −0·0495 | 0·014 |

TABLE 2.

Atomic thermal parameters.

| Atom | $10^5\beta_{11}$ | $10^5\beta_{22}$ | $10^5\beta_{33}$ | $10^5\beta_{12}$ | $10^5\beta_{13}$ | $10^5\beta_{23}$ |
|---|---|---|---|---|---|---|
| Br | 1103 | 1824 | 2311 | −305 | −217 | 646 |
| $C_1$ | 1490 | 928 | 2047 | 402 | 773 | 573 |
| $C_2$ | 939 | 1438 | 1678 | −23 | 218 | 822 |
| $C_3$ | 1253 | 1295 | 1761 | 11 | 281 | 759 |
| $C_4$ | 1356 | 1274 | 2081 | 16 | 580 | 793 |
| $C_5$ | 1269 | 1729 | 2088 | 475 | 198 | 1088 |
| $C_6$ | 798 | 1901 | 2161 | 169 | −248 | 950 |
| $C_7$ | 1283 | 1883 | 2183 | 42 | 348 | 1252 |
| $C_8$ | 1545 | 1255 | 1754 | 183 | 876 | 719 |
| $C_9$ | 1351 | 1136 | 1255 | 163 | 127 | 536 |
| $C_{10}$ | 884 | 1088 | 1243 | 292 | −107 | 525 |
| $C_{11}$ | 1788 | 1383 | 1831 | 488 | 784 | 263 |
| $C_{12}$ | 1427 | 1614 | 1450 | −142 | −40 | 548 |

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[6] Busing, Martin, and Levy, "O.R.F.L.S., A Fortran Crystallographic Least-squares Program," Oak Ridge National Laboratory, Tennessee, 1962.

[7] Hughes, *J. Amer. Chem. Soc.*, 1941, **63**, 1737.

[8] Berghuis, Haanappel, Potters, Loopstra, MacGillavry, and Veenendaal, *Acta Cryst.*, 1955, **8**, 478.

[9] "International Tables for X-ray Crystallography," Kynoch Press, Birmingham, 1962, Vol. III, p. 211.

TABLE 3.

Observed structure amplitudes and calculated structure factors (×10). Reflexions corrected for secondary extinction are marked with an asterisk.

| *h* | *k* | *F*o | *F*c |
|---|---|---|---|
| | l=0 | | |
| 1 | 0 | 43 | 53 |
| 2 | 0 | 78 | -58 |
| 3 | 0 | 63 | 40 |
| 4 | 0 | 243 | -262 |
| 5 | 0 | 327 | -349 |
| 6 | 0 | 204 | -212 |
| 7 | 0 | 139 | -114 |
| 8 | 0 | 91 | -87 |
| 9 | 0 | 36 | 39 |
| 10 | 0 | 45 | 57 |
| 0 | 1 | 44 | -49 |
| -1 | 1 | 757* | 801 |
| 1 | 1 | 278 | 332 |
| -2 | 1 | 517* | 542 |
| 2 | 1 | 69 | 63 |
| 3 | 1 | 192 | -176 |
| -3 | 1 | 256 | 223 |
| 4 | 1 | 399* | -466 |
| -4 | 1 | 40 | 32 |
| -5 | 1 | 166 | -167 |
| 5 | 1 | 368 | -391 |
| 6 | 1 | 227 | -233 |
| -6 | 1 | 257 | -271 |
| 7 | 1 | 63 | 46 |
| -7 | 1 | 236 | -256 |
| -8 | 1 | 99 | -93 |
| 8 | 1 | 50 | 53 |
| 9 | 1 | 116 | 120 |
| -9 | 1 | 36 | -33 |
| -10 | 1 | 61 | 66 |
| 10 | 1 | 96 | 101 |
| 0 | 2 | 65 | 13 |
| 1 | 2 | 72 | -64 |
| -1 | 2 | 544* | 533 |
| -2 | 2 | 514* | 534 |
| 2 | 2 | 208 | -219 |
| 3 | 2 | 768* | -718 |
| -3 | 2 | 340 | 380 |
| 4 | 2 | 255 | -253 |
| -4 | 2 | 76 | 72 |
| -5 | 2 | 82 | 73 |
| 5 | 2 | 127 | -99 |
| -6 | 2 | 111 | -127 |
| 6 | 2 | 30 | -25 |
| -7 | 2 | 191 | -192 |
| 7 | 2 | 22 | 14 |
| 8 | 2 | 145 | 166 |
| -8 | 2 | 95 | -88 |
| -9 | 2 | 102 | -99 |
| 9 | 2 | 124 | 130 |
| 10 | 2 | 76 | 89 |
| -10 | 2 | 48 | -48 |
| 0 | 3 | 314 | -259 |
| 1 | 3 | 294 | -318 |
| -1 | 3 | 309 | 278 |
| 2 | 3 | 391 | -417 |
| -2 | 3 | 275 | 269 |
| 3 | 3 | 292 | -313 |
| -3 | 3 | 285 | 255 |
| 4 | 3 | 189 | -199 |
| -4 | 3 | 332 | 340 |
| 5 | 3 | 36 | -31 |
| -5 | 3 | 129 | 116 |
| 6 | 3 | 147 | 149 |
| -6 | 3 | 21 | 19 |
| 7 | 3 | 149 | 155 |
| -7 | 3 | 39 | -30 |
| -8 | 3 | 141 | -145 |
| 8 | 3 | 166 | 168 |
| 9 | 3 | 116 | 94 |
| -9 | 3 | 84 | -81 |
| -10 | 3 | 55 | -60 |
| 0 | 4 | 84 | -72 |
| 1 | 4 | 285 | -304 |
| -1 | 4 | 407 | -391 |
| -2 | 4 | 48 | 60 |
| 2 | 4 | 360 | -376 |
| 3 | 4 | 129 | -116 |
| -3 | 4 | 234 | 253 |
| -4 | 4 | 252 | 278 |
| 4 | 4 | 21 | -3 |
| 5 | 4 | 116 | 108 |
| -5 | 4 | 138 | 137 |
| 6 | 4 | 183 | 183 |
| -6 | 4 | 132 | 145 |
| 7 | 4 | 188 | 200 |
| -7 | 4 | 32 | -13 |
| 8 | 4 | 93 | 88 |
| -8 | 4 | 42 | -47 |
| -9 | 4 | 44 | -58 |
| 9 | 4 | 13 | 26 |
| -10 | 4 | 17 | -59 |
| 0 | 5 | 277 | -293 |
| 1 | 5 | 252 | -269 |
| -1 | 5 | 170 | -145 |
| 2 | 5 | 244 | -236 |
| -2 | 5 | 106 | -91 |
| 3 | 5 | 184 | 176 |
| -3 | 5 | 50 | 34 |
| 4 | 5 | 136 | 132 |
| -4 | 5 | 108 | 104 |
| -5 | 5 | 141 | 140 |
| 5 | 5 | 160 | 160 |
| 6 | 5 | 158 | 149 |
| -6 | 5 | 71 | 78 |
| -7 | 5 | 83 | 92 |
| 7 | 5 | 106 | 99 |
| 8 | 5 | 14 | 24 |
| -8 | 5 | 34 | 39 |
| -9 | 5 | 22 | -22 |
| 0 | 6 | 206 | -187 |
| 1 | 6 | 131 | -117 |
| -1 | 6 | 146 | -149 |
| 2 | 6 | 226 | 214 |
| -2 | 6 | 159 | -155 |
| 3 | 6 | 55 | -41 |
| -3 | 6 | 126 | -113 |
| 4 | 6 | 143 | 141 |
| -4 | 6 | 45 | -33 |
| 5 | 6 | 184 | 199 |
| -5 | 6 | 131 | 136 |
| -6 | 6 | 89 | 87 |
| 6 | 6 | 103 | 106 |
| -7 | 6 | 78 | 81 |
| 7 | 6 | 14 | 9 |
| 0 | 7 | 55 | -46 |
| 1 | 7 | 59 | 60 |
| -1 | 7 | 144 | -155 |
| 2 | 7 | 73 | 62 |
| -2 | 7 | 110 | -105 |
| -3 | 7 | 77 | -74 |
| 3 | 7 | 170 | 161 |
| 4 | 7 | 131 | 135 |
| -4 | 7 | 38 | -37 |
| 5 | 7 | 71 | 70 |
| -5 | 7 | 21 | -23 |
| 6 | 7 | 27 | -22 |
| -6 | 7 | 43 | 33 |
| -7 | 7 | 32 | 24 |
| -8 | 7 | 47 | 69 |
| 0 | 8 | 20 | 19 |
| 1 | -8 | 20 | 17 |
| 1 | 8 | 90 | 75 |
| 2 | 8 | 86 | 86 |
| -2 | 8 | 96 | -98 |
| 3 | 8 | 88 | 92 |
| -3 | 8 | 66 | -69 |
| 4 | 8 | 69 | 69 |
| -4 | 8 | 37 | -50 |
| -5 | 8 | 54 | -54 |
| 5 | 8 | 20 | -22 |
| -6 | 8 | 24 | 16 |
| -7 | 8 | 12 | 12 |
| 0 | 9 | 49 | 57 |
| 1 | 9 | 92 | 91 |
| 2 | 9 | 12 | 24 |
| 3 | 9 | 25 | 54 |
| -3 | 9 | 45 | -40 |
| -4 | 9 | 40 | -51 |
| -5 | 9 | 16 | -19 |
| | l=1 | | |
| 0 | 0 | 249 | -281 |
| 1 | 0 | 342 | -402 |
| -1 | 0 | 484* | 515 |
| 2 | 0 | 581* | -639 |
| -2 | 0 | 528* | 557 |
| 3 | 0 | 361 | -390 |
| -3 | 0 | 566* | 602 |
| 4 | 0 | 369 | -265 |
| -4 | 0 | 71 | 67 |
| 5 | 0 | 144 | -105 |
| -5 | 0 | 193 | 155 |
| 6 | 0 | 284 | 267 |
| -6 | 0 | 40 | 26 |
| -7 | 0 | 124 | -102 |
| 7 | 0 | 22 | 15 |
| 8 | 0 | 166 | 138 |
| -8 | 0 | 172 | -163 |
| 9 | 0 | 167 | 153 |
| -9 | 0 | 116 | -119 |
| -10 | 0 | 72 | -74 |
| 0 | -1 | 284 | 225 |
| 0 | 1 | 370 | -370 |
| -1 | -1 | 325 | 412 |
| 1 | -1 | 48 | 7 |
| -1 | 1 | 103 | -97 |
| 1 | 1 | 410* | -446 |
| 2 | 1 | 354 | -395 |
| -2 | 1 | 124 | 94 |
| 2 | -1 | 223 | -211 |
| -2 | -1 | 410* | 467 |
| 3 | 1 | 369 | -413 |
| -3 | 1 | 221 | 213 |
| 3 | -1 | 312 | -327 |
| -3 | -1 | 416* | 456 |
| 4 | 1 | 85 | -64 |
| 4 | -1 | 381 | -415 |
| -4 | -1 | 211 | 217 |
| -4 | 1 | 540* | 583 |
| 5 | 1 | 175 | 145 |
| -5 | -1 | 25 | -13 |
| -5 | 1 | 203 | 224 |
| 5 | -1 | 305 | -287 |
| 6 | 1 | 211 | 201 |
| -6 | 1 | 111 | 97 |
| 6 | -1 | 199 | -214 |
| -6 | -1 | 137 | -143 |
| 7 | 1 | 251 | 231 |
| 7 | -1 | 227 | 206 |
| -7 | -1 | 392 | -399 |
| 8 | 1 | 172 | 160 |
| -8 | 1 | 79 | -89 |
| 8 | -1 | 136 | 127 |
| -8 | -1 | 79 | -77 |
| 9 | 1 | 65 | 60 |
| -9 | 1 | 116 | -109 |
| -9 | -1 | 58 | -49 |
| -10 | 1 | 95 | -94 |
| -10 | -1 | 23 | -20 |
| 0 | -2 | 667* | 747 |
| 0 | 2 | 400 | -368 |
| 1 | 2 | 471* | -487 |
| -1 | 2 | 368 | -433 |
| 1 | -2 | 258 | 286 |
| -1 | -2 | 485* | 522 |
| 2 | 2 | 338 | -335 |
| -2 | -2 | 364 | 400 |
| 2 | -2 | 64 | 22 |
| -2 | 2 | 105 | -66 |
| 3 | 2 | 149 | 92 |
| -3 | 2 | 72 | 93 |
| -3 | -2 | 69 | 44 |
| 3 | -2 | 600* | -541 |
| 4 | -2 | 136 | -165 |
| -4 | -2 | 89 | -74 |
| -4 | 2 | 301 | 302 |
| 4 | 2 | 140 | 99 |
| -5 | 2 | 213 | 224 |
| 5 | -2 | 258 | -237 |
| -5 | -2 | 209 | -224 |
| 5 | 2 | 260 | 250 |
| 6 | 2 | 247 | 235 |
| -6 | 2 | 184 | 182 |
| 6 | -2 | 231 | -204 |
| -6 | -2 | 323 | -327 |
| 7 | 2 | 177 | 170 |
| -7 | 2 | 155 | 156 |
| 7 | -2 | 79 | -66 |
| -7 | -2 | 55 | -38 |
| 8 | 2 | 87 | 78 |
| -8 | 2 | 79 | -61 |
| -8 | -2 | 153 | -153 |
| -9 | -2 | 71 | -66 |
| 9 | 2 | 43 | -33 |
| -10 | 2 | 36 | -31 |
| 0 | -3 | 453* | 490 |
| 0 | 3 | 400 | -394 |
| 1 | 3 | 247 | -231 |
| -1 | 3 | 316 | -358 |
| -1 | -3 | 295 | 279 |
| 1 | -3 | 303 | 333 |
| 2 | -3 | 241 | 232 |
| -2 | -3 | 155 | 140 |
| 2 | 3 | 38 | -4 |
| -2 | 3 | 306 | -277 |
| 3 | 3 | 164 | 165 |
| 3 | -3 | 192 | 190 |
| -3 | -3 | 35 | -21 |
| -3 | 3 | 66 | -45 |
| 4 | 3 | 257 | 285 |
| -4 | 3 | 129 | 95 |
| 4 | -3 | 217 | -228 |
| -4 | -3 | 317 | -318 |
| 5 | 3 | 284 | 307 |
| 5 | -3 | 244 | -227 |
| -5 | -3 | 278 | -286 |
| -5 | 3 | 100 | 106 |
| 6 | 3 | 113 | 90 |
| -6 | 3 | 171 | 164 |
| 6 | -3 | 226 | -202 |
| -6 | -3 | 194 | -220 |
| -7 | 3 | 113 | 110 |
| -7 | -3 | 125 | -117 |
| 7 | 3 | 101 | 82 |
| 8 | 3 | 27 | -21 |
| -8 | -3 | 22 | -8 |
| -8 | 3 | 110 | 122 |
| 9 | 3 | 89 | -85 |
| -9 | -3 | 76 | 73 |
| -10 | 3 | 34 | -43 |
| -10 | -3 | 95 | 103 |
| 0 | 4 | 143 | -105 |
| 0 | -4 | 209 | 166 |
| 1 | 4 | 52 | 29 |
| 1 | -4 | 369 | 402 |
| -1 | -4 | 135 | 129 |
| -1 | 4 | 280 | -283 |
| 2 | 4 | 166 | 148 |
| 2 | -4 | 283 | 299 |
| -2 | -4 | 144 | -107 |
| -2 | 4 | 230 | -209 |
| 3 | 4 | 213 | 201 |
| -3 | 4 | 214 | -207 |
| 3 | -4 | 241 | 250 |
| -3 | -4 | 345 | -335 |
| 4 | 4 | 264 | 272 |
| -4 | 4 | 278 | -302 |
| -4 | -4 | 193 | -214 |
| 4 | -4 | 66 | -18 |
| 5 | 4 | 113 | 109 |
| -5 | 4 | 254 | 251 |
| 5 | -4 | 63 | -78 |
| -5 | -4 | 229 | -244 |
| 6 | 4 | 122 | 123 |
| -6 | 4 | 94 | 94 |
| -6 | -4 | 112 | -121 |
| 6 | -4 | 103 | -103 |
| 7 | 4 | 46 | -36 |
| -7 | 4 | 63 | 62 |
| -7 | -4 | 22 | 14 |
| 8 | 4 | 135 | -116 |
| -8 | 4 | 73 | 77 |
| -8 | -4 | 71 | 73 |
| -9 | 4 | 49 | 52 |
| -9 | -4 | 118 | 112 |
| -10 | 4 | 15 | -10 |
| 0 | -5 | 109 | 79 |
| 0 | 5 | 30 | -32 |
| 1 | 5 | 146 | 134 |
| -1 | 5 | 145 | -116 |
| 1 | -5 | 191 | 172 |
| -1 | -5 | 136 | -133 |
| 2 | -5 | 258 | 279 |
| -2 | -5 | 278 | -259 |
| -2 | 5 | 306 | -310 |
| 3 | 5 | 172 | 181 |
| -3 | 5 | 188 | -171 |
| 3 | -5 | 243 | 249 |
| -3 | -5 | 277 | -278 |
| 4 | 5 | 112 | 119 |
| 4 | -5 | 52 | 33 |
| -4 | -5 | 189 | -198 |
| 5 | 5 | 49 | 47 |
| -5 | 5 | 176 | -190 |
| 5 | -5 | 67 | 60 |
| -5 | -5 | 111 | -102 |
| 6 | 5 | 57 | -63 |
| -6 | 5 | 32 | 25 |
| 6 | -5 | 56 | -29 |
| -6 | -5 | 90 | 88 |
| 7 | -5 | 55 | -44 |
| -7 | -5 | 58 | 34 |

TABLE 3. (*Continued.*)

| $h$ | $k$ | $F_o$ | $F_c$ |
|---|---|---|---|
| 7 | 5 | 106 | -100 |
| -7 | 5 | 70 | 70 |
| -8 | 5 | 61 | 54 |
| -8 | -5 | 121 | 106 |
| -9 | 5 | 31 | 45 |
| -9 | -5 | 86 | 103 |
| 0 | 6 | 142 | 128 |
| 0 | -6 | 128 | -137 |
| 1 | 6 | 172 | 158 |
| -1 | 6 | 112 | 108 |
| -1 | -6 | 175 | -159 |
| 1 | -6 | 42 | 42 |
| 2 | 6 | 79 | 80 |
| -2 | 6 | 125 | -126 |
| 2 | -6 | 85 | 65 |
| -2 | -6 | 188 | -194 |
| 3 | 6 | 143 | 149 |
| -3 | 6 | 113 | -100 |
| 3 | -6 | 58 | 44 |
| -3 | -6 | 158 | -157 |
| 4 | -6 | 385 | 388 |
| 4 | 6 | 37 | 31 |
| -4 | 6 | 106 | -112 |
| -4 | -6 | 105 | -103 |
| -5 | 6 | 97 | -96 |
| 5 | 6 | 38 | -37 |
| -5 | -6 | 50 | 42 |
| 6 | 6 | 116 | -99 |
| -6 | 6 | 36 | -38 |
| -6 | -6 | 58 | 48 |
| -7 | 6 | 26 | 18 |
| -7 | -6 | 130 | 141 |
| -8 | 6 | 41 | 46 |
| -8 | -6 | 103 | 118 |
| 0 | -7 | 151 | -146 |
| 0 | 7 | 108 | 117 |
| 1 | 7 | 118 | 129 |
| -1 | 7 | 49 | 48 |
| 1 | -7 | 55 | -48 |
| -1 | -7 | 178 | -200 |
| 2 | 7 | 72 | 79 |
| -2 | 7 | 54 | 46 |
| 2 | -7 | 39 | 20 |
| -2 | -7 | 177 | -166 |
| 3 | -7 | 113 | 115 |
| 3 | 7 | 19 | 16 |
| -3 | 7 | 48 | -35 |
| -3 | -7 | 22 | 14 |
| 4 | 7 | 45 | -54 |
| -4 | 7 | 64 | -61 |
| -4 | -7 | 31 | 24 |
| 4 | -7 | 56 | -13 |
| -5 | 7 | 69 | -76 |
| 5 | -7 | 94 | 126 |
| -5 | -7 | 83 | 85 |
| 5 | 7 | 110 | -107 |
| -6 | -7 | 96 | 110 |
| 6 | -7 | 50 | 64 |
| -7 | 7 | 27 | -22 |
| -7 | -7 | 81 | 82 |
| 0 | 8 | 75 | 78 |
| 0 | -8 | 70 | -72 |
| -1 | 8 | 49 | 52 |
| 1 | -8 | 162 | -172 |
| -1 | -8 | 69 | -63 |
| 1 | 8 | 60 | 50 |
| 2 | -8 | 34 | -29 |
| -2 | 8 | 115 | 87 |
| 2 | 8 | 22 | 15 |
| 3 | 8 | 54 | -56 |
| -3 | -8 | 20 | -17 |
| -4 | 8 | 44 | -41 |
| -4 | -8 | 75 | 79 |
| 4 | -8 | 51 | 22 |
| 5 | -8 | 66 | 63 |
| -5 | 8 | 37 | 26 |
| -5 | -8 | 70 | 93 |
| -6 | 8 | 46 | -69 |
| 6 | -8 | 41 | 63 |
| -6 | -8 | 67 | 86 |
| 0 | -9 | 66 | -61 |
| 0 | 9 | 20 | 18 |
| -1 | 9 | 28 | 42 |
| -1 | -9 | 36 | -25 |
| 1 | -9 | 60 | -58 |
| -2 | 9 | 45 | 69 |
| -2 | -9 | 37 | 35 |
| 2 | -9 | 89 | -63 |
| 3 | -9 | 39 | -31 |
| -3 | -9 | 42 | 52 |
| 4 | -9 | 36 | -22 |
| -4 | -9 | 59 | 83 |
| 2 | -10 | 66 | -57 |
| l=2 | | | |
| 0 | 0 | 443* | -438 |
| 1 | 0 | 287 | -338 |
| -1 | 0 | 599* | -618 |
| 2 | 0 | 315 | -344 |
| -2 | 0 | 270 | -255 |
| 3 | 0 | 283 | 363 |
| -3 | 0 | 20 | 10 |
| 4 | 0 | 345 | 340 |
| -4 | 0 | 229 | 206 |
| 5 | 0 | 249 | 236 |
| -5 | 0 | 149 | 155 |
| 6 | 0 | 131 | 115 |
| -6 | 0 | 228 | 245 |
| 7 | 0 | 175 | 176 |
| -7 | 0 | 190 | 170 |
| -8 | 0 | 46 | 43 |
| -9 | 0 | 33 | 19 |
| -10 | 0 | 47 | -44 |
| 0 | 1 | 276 | -280 |
| 0 | -1 | 54 | -63 |
| 1 | 1 | 126 | -99 |
| 1 | -1 | 261* | -351 |
| -1 | 1 | 553* | -509 |
| -1 | -1 | 797 | -858 |
| 2 | 1 | 256 | 244 |
| -2 | 1 | 317 | -328 |
| 2 | -1 | 353 | -400 |
| -2 | -1 | 53 | 21 |
| 3 | 1 | 261 | 250 |
| -3 | 1 | 231 | -238 |
| 3 | -1 | 198 | -237 |
| -3 | -1 | 222 | 268 |
| 4 | 1 | 285 | 315 |
| -4 | 1 | 155 | -146 |
| 4 | -1 | 83 | 66 |
| -4 | -1 | 269 | 276 |
| 5 | 1 | 278 | 290 |
| -5 | 1 | 176 | 169 |
| 5 | -1 | 218 | 206 |
| -5 | -1 | 297 | 328 |
| 6 | 1 | 119 | 106 |
| -6 | 1 | 155 | 138 |
| 6 | -1 | 341 | 336 |
| -6 | -1 | 252 | 254 |
| -7 | 1 | 176 | 158 |
| 7 | -1 | 153 | 157 |
| -7 | -1 | 100 | 79 |
| 7 | 1 | 20 | -20 |
| -8 | 1 | 178 | 159 |
| 8 | -1 | 88 | 83 |
| 8 | 1 | 102 | -102 |
| -8 | -1 | 90 | -87 |
| 9 | 1 | 72 | -128 |
| -9 | 1 | 32 | 16 |
| -9 | -1 | 72 | -65 |
| -10 | 1 | 15 | 5 |
| -10 | -1 | 100 | -96 |
| 0 | -2 | 919* | -1001 |
| 0 | 2 | 104 | -103 |
| 1 | 2 | 91 | 73 |
| -1 | 2 | 163 | 95 |
| 1 | -2 | 563* | -552 |
| -1 | -2 | 770* | 815 |
| 2 | 2 | 389 | 403 |
| 2 | -2 | 296 | -284 |
| -2 | -2 | 272 | 261 |
| -2 | 2 | 540* | -529 |
| 3 | 2 | 281 | 294 |
| 3 | -2 | 292 | -303 |
| -3 | -2 | 211 | 197 |
| -3 | 2 | 370 | -367 |
| 4 | 2 | 217 | 221 |
| 5 | 2 | 119 | 122 |
| -5 | 2 | 25 | -27 |
| 5 | -2 | 148 | 127 |
| -5 | -2 | 242 | 223 |
| 6 | -2 | 184 | 164 |
| -6 | -2 | 59 | 51 |
| -6 | 2 | 27 | 30 |
| 7 | 2 | 155 | -150 |
| -7 | 2 | 143 | 143 |
| -7 | -2 | 35 | -27 |
| 7 | -2 | 120 | 98 |
| 8 | 2 | 165 | -127 |
| -8 | 2 | 111 | 96 |
| -8 | -2 | 80 | -70 |
| -9 | 2 | 88 | 74 |
| -9 | -2 | 129 | -123 |
| -10 | 2 | 44 | 31 |
| -10 | -2 | 94 | -90 |
| 0 | -3 | 173 | 183 |
| 0 | 3 | 150 | 132 |
| 1 | 3 | 288 | 275 |
| -1 | 3 | 146 | -130 |
| 1 | -3 | 184 | -183 |
| -1 | -3 | 114 | 99 |
| 2 | 3 | 389* | 446 |
| 2 | -3 | 285 | -329 |
| -2 | -3 | 283 | 309 |
| -2 | 3 | 107 | -80 |
| 3 | 3 | 163 | 172 |
| -3 | 3 | 233 | -216 |
| 3 | -3 | 313 | -333 |
| -3 | -3 | 295 | 339 |
| 4 | 3 | 78 | 67 |
| -4 | 3 | 217 | -213 |
| 4 | -3 | 279 | -279 |
| -4 | -3 | 339 | 393 |
| 5 | 3 | 74 | -64 |
| -5 | 3 | 168 | -139 |
| 5 | -3 | 141 | -118 |
| -5 | -3 | 109 | 80 |
| 6 | 3 | 134 | -127 |
| -6 | 3 | 32 | -22 |
| -6 | -3 | 107 | -101 |
| 7 | 3 | 157 | -141 |
| -7 | 3 | 35 | -28 |
| -7 | -3 | 241 | -198 |
| -8 | 3 | 61 | 70 |
| -8 | -3 | 99 | -99 |
| 8 | 3 | 108 | -116 |
| -9 | -3 | 114 | -118 |
| -9 | 3 | 102 | 83 |
| -10 | -3 | 45 | -41 |
| -10 | 3 | 50 | 49 |
| 0 | 4 | 254 | 230 |
| 0 | -4 | 276 | 320 |
| 1 | 4 | 369 | 392 |
| 1 | -4 | 78 | 53 |
| -1 | -4 | 285 | 279 |
| -1 | 4 | 100 | 103 |
| -2 | 4 | 78 | 47 |
| 2 | -4 | 187 | -163 |
| 2 | 4 | 86 | -70 |
| -2 | -4 | 302 | 339 |
| 3 | 4 | 141 | 133 |
| -3 | 4 | 87 | -75 |
| -3 | -4 | 338 | 372 |
| 3 | -4 | 310 | -321 |
| -4 | 4 | 179 | -163 |
| 4 | -4 | 158 | -162 |
| -4 | -4 | 115 | -100 |
| 4 | 4 | 29 | 22 |
| 5 | 4 | 132 | -137 |
| -5 | 4 | 224 | -222 |
| 5 | -4 | 191 | -214 |
| -5 | -4 | 104 | -89 |
| 6 | 4 | 194 | -183 |
| -6 | 4 | 57 | -58 |
| 6 | -4 | 114 | -93 |
| -6 | -4 | 135 | -111 |
| -7 | -4 | 143 | -145 |
| 7 | 4 | 114 | -120 |
| 8 | 4 | 61 | -74 |
| -8 | -4 | 166 | -149 |
| -8 | 4 | 54 | 35 |
| -9 | -4 | 61 | -56 |
| 0 | 5 | 225* | 216 |
| 0 | -5 | 438 | 453 |
| 1 | 5 | 88 | 70 |
| -1 | 5 | 191 | 200 |
| 1 | -5 | 135 | 126 |
| -1 | -5 | 230 | 213 |
| 2 | 5 | 118 | 116 |
| -2 | 5 | 79 | 40 |
| -2 | -5 | 194 | 170 |
| 2 | -5 | 16 | -12 |
| 3 | 5 | 71 | -67 |
| 3 | -5 | 72 | -40 |
| -3 | -5 | 67 | 49 |
| 4 | 5 | 153 | -157 |
| 4 | -5 | 198 | -162 |
| -4 | -5 | 103 | -98 |
| -4 | 5 | 50 | -35 |
| 5 | 5 | 158 | -168 |
| 5 | -5 | 172 | -168 |
| -5 | -5 | 183 | -168 |
| -5 | 5 | 50 | -48 |
| 6 | 5 | 97 | -85 |
| -6 | 5 | 96 | -110 |
| 6 | -5 | 93 | -92 |
| -6 | -5 | 219 | -190 |
| 7 | 5 | 48 | -46 |
| -7 | 5 | 62 | -51 |
| 7 | -5 | 82 | -96 |
| -7 | -5 | 112 | -99 |
| -8 | 5 | 63 | -59 |
| -8 | -5 | 89 | -76 |
| -9 | 5 | 33 | 27 |
| 0 | -6 | 28 | 34 |
| 0 | 6 | 101 | 83 |
| -1 | 6 | 112 | 97 |
| -1 | -6 | 203 | 178 |
| 1 | -6 | 270 | 274 |
| 2 | 6 | 33 | -32 |
| 2 | -6 | 196 | 202 |
| -2 | -6 | 91 | 73 |
| -2 | 6 | 150 | 167 |
| 3 | 6 | 91 | -96 |
| -3 | 6 | 56 | 55 |
| 3 | -6 | 69 | 75 |
| -3 | -6 | 117 | -109 |
| 4 | 6 | 145 | -150 |
| -4 | -6 | 177 | -162 |
| 4 | -6 | 110 | -114 |
| 5 | 6 | 68 | -66 |
| 5 | -6 | 72 | -57 |
| -5 | -6 | 162 | -166 |
| -5 | 6 | 18 | -21 |
| 6 | 6 | 37 | -53 |
| -6 | 6 | 75 | -68 |
| -6 | -6 | 137 | -129 |
| 6 | -6 | 101 | -140 |
| -7 | 6 | 38 | -41 |
| 7 | -6 | 54 | -74 |
| -7 | -6 | 62 | -60 |
| -8 | 6 | 26 | -32 |
| -8 | -6 | 45 | 32 |
| 0 | -7 | 139 | 118 |
| 0 | 7 | 30 | 19 |
| 1 | 7 | 86 | -72 |
| -1 | 7 | 83 | 72 |
| 1 | -7 | 138 | 139 |
| -1 | -7 | 40 | 32 |
| 2 | 7 | 43 | -59 |
| -2 | 7 | 57 | 56 |
| 2 | -7 | 145 | 147 |
| -2 | -7 | 56 | -61 |
| 3 | -7 | 83 | 79 |
| -3 | -7 | 284 | -291 |
| 3 | 7 | 108 | -108 |
| -3 | 7 | 80 | 87 |
| 4 | 7 | 67 | -70 |
| -4 | 7 | 43 | 41 |
| -4 | -7 | 71 | -59 |
| 4 | -7 | 59 | 25 |
| -5 | -7 | 89 | -76 |
| 5 | -7 | 58 | -28 |
| -6 | -7 | 53 | -49 |
| 6 | -7 | 67 | -28 |
| -7 | -7 | 13 | 14 |
| 0 | 8 | 52 | -60 |
| 0 | -8 | 45 | 18 |
| -1 | -8 | 77 | -76 |
| -1 | 8 | 12 | 3 |
| 1 | -8 | 45 | 40 |
| 2 | -8 | 71 | 63 |
| -2 | -8 | 175 | -178 |
| -2 | 8 | 57 | 39 |
| -3 | 8 | 38 | 42 |
| 3 | -8 | 82 | 92 |
| -3 | -8 | 47 | 24 |
| 4 | -8 | 88 | 125 |
| -4 | 8 | 19 | 28 |
| -4 | -8 | 130 | -132 |
| -5 | -8 | 72 | -72 |
| 5 | -8 | 52 | 2 |
| -6 | -8 | 41 | 37 |
| 0 | -9 | 76 | -74 |
| -1 | -9 | 91 | -87 |

TABLE 3. (*Continued.*)

| *h* | *k* | *F*o | *F*c |
|---|---|---|---|
| 1 | -9 | 32 | 23 |
| -2 | -9 | 71 | -67 |
| 2 | -9 | 64 | 35 |
| -3 | -9 | 65 | -73 |
| 3 | -9 | 50 | 48 |
| -4 | -9 | 23 | -18 |
| -5 | -9 | 25 | 32 |
| 0 | -10 | 36 | -30 |
| -1 | -10 | 52 | -55 |
| 1 | -10 | 64 | -68 |
| -2 | -10 | 35 | -39 |
| 2 | -10 | 22 | 9 |
| | l=3 | | |
| 0 | 0 | 94 | 61 |
| 1 | 0 | 304 | 311 |
| -1 | 0 | 49 | -10 |
| 2 | 0 | 464* | 499 |
| -2 | 0 | 306 | -318 |
| 3 | 0 | 194 | 214 |
| -3 | 0 | 293 | -311 |
| 4 | 0 | 153 | 153 |
| -4 | 0 | 261 | -271 |
| 5 | 0 | 33 | -20 |
| -5 | 0 | 140 | -133 |
| 6 | 0 | 126 | -89 |
| -6 | 0 | 41 | -43 |
| 7 | 0 | 157 | -149 |
| -7 | 0 | 39 | 39 |
| 8 | 0 | 157 | -150 |
| -8 | 0 | 150 | 159 |
| 9 | 0 | 56 | -65 |
| -9 | 0 | 59 | 60 |
| -10 | 0 | 47 | 43 |
| 0 | 1 | 303 | 322 |
| 0 | -1 | 96 | -93 |
| 1 | 1 | 326 | 364 |
| -1 | 1 | 119 | 116 |
| 1 | -1 | 145 | 132 |
| -1 | -1 | 250 | -222 |
| 2 | 1 | 247 | 272 |
| -2 | 1 | 72 | -59 |
| -2 | -1 | 272 | -373 |
| 2 | -1 | 160 | 164 |
| 3 | 1 | 179 | 189 |
| -3 | 1 | 214 | -220 |
| 3 | -1 | 329 | 367 |
| -3 | -1 | 281 | -349 |
| -4 | 1 | 191 | -202 |
| 4 | -1 | 319 | 321 |
| -4 | -1 | 313 | -358 |
| 4 | 1 | 26 | -16 |
| 5 | 1 | 198 | -213 |
| -5 | 1 | 177 | -200 |
| 5 | -1 | 124 | 121 |
| -5 | -1 | 118 | 116 |
| 6 | 1 | 143 | -146 |
| -6 | 1 | 136 | -117 |
| 6 | -1 | 83 | 52 |
| -6 | -1 | 101 | 111 |
| 7 | 1 | 171 | -162 |
| -7 | 1 | 28 | -26 |
| 7 | -1 | 100 | -92 |
| -7 | -1 | 120 | 121 |
| 8 | 1 | 111 | -96 |
| 8 | -1 | 161 | -142 |
| -8 | -1 | 126 | 140 |
| -8 | 1 | 19 | -16 |
| 9 | -1 | 126 | -133 |
| -9 | -1 | 87 | 80 |
| 9 | 1 | 19 | -10 |
| -9 | 1 | 110 | 104 |
| -10 | 1 | 84 | 75 |
| -10 | -1 | 20 | 26 |
| 0 | 2 | 313 | 302 |
| 0 | -2 | 245 | -311 |
| 1 | 2 | 215 | 217 |
| 1 | -2 | 193 | -175 |
| -1 | -2 | 651* | -643 |
| -1 | 2 | 290 | 280 |
| 2 | 2 | 121 | 84 |
| -2 | 2 | 137 | 114 |
| 2 | -2 | 158 | 166 |
| -2 | -2 | 228 | -293 |
| -3 | 2 | 57 | 48 |
| 3 | -2 | 245 | 250 |
| -3 | -2 | 135 | -125 |
| 3 | 2 | 12 | 4 |
| -4 | 2 | 69 | -66 |
| 4 | -2 | 288 | 283 |
| -4 | -2 | 135 | 126 |
| 5 | 2 | 145 | -110 |
| -5 | 2 | 339 | -390 |
| 5 | -2 | 327 | 336 |
| -5 | -2 | 64 | 44 |
| 6 | 2 | 214 | -212 |
| -6 | 2 | 44 | -42 |
| 6 | -2 | 94 | -71 |
| -6 | -2 | 149 | 141 |
| 7 | 2 | 132 | -127 |
| -7 | 2 | 56 | -45 |
| 7 | -2 | 79 | 66 |
| -7 | -2 | 173 | 168 |
| -8 | 2 | 51 | -39 |
| -8 | -2 | 143 | 153 |
| 9 | -2 | 25 | -68 |
| -9 | -2 | 25 | 26 |
| -10 | 2 | 47 | 44 |
| -10 | -2 | 14 | -17 |
| 0 | 3 | 208 | 227 |
| 0 | -3 | 253 | -322 |
| -1 | 3 | 226 | 202 |
| 1 | -3 | 289 | -285 |
| -1 | -3 | 293 | -330 |
| 1 | 3 | 170 | 177 |
| 2 | 3 | 138 | -109 |
| -2 | 3 | 201 | 200 |
| 2 | -3 | 106 | -81 |
| -2 | -3 | 186 | -209 |
| 3 | 3 | 184 | -188 |
| -3 | 3 | 77 | 47 |
| -3 | -3 | 72 | -59 |
| 3 | -3 | 40 | -54 |
| 4 | 3 | 163 | -171 |
| -4 | 3 | 73 | -63 |
| 4 | -3 | 145 | 139 |
| -4 | -3 | 169 | 178 |
| 5 | 3 | 174 | -192 |
| 5 | -3 | 196 | 186 |
| -5 | -3 | 225 | 231 |
| -5 | 3 | 120 | 116 |
| 6 | 3 | 111 | -87 |
| 6 | -3 | 282 | 314 |
| -6 | -3 | 215 | 231 |
| -6 | 3 | 180 | -205 |
| -7 | 3 | 119 | -108 |
| 7 | -3 | 63 | 63 |
| -7 | -3 | 228 | 228 |
| -8 | 3 | 17 | -34 |
| -8 | -3 | 111 | -109 |
| -9 | 3 | 28 | -24 |
| -9 | -3 | 17 | -16 |
| -10 | -3 | 28 | -27 |
| 0 | -4 | 289 | -342 |
| 0 | 4 | 27 | 17 |
| 1 | 4 | 144 | -127 |
| -1 | 4 | 139 | 122 |
| 1 | -4 | 287 | -356 |
| -1 | -4 | 74 | -76 |
| 2 | 4 | 56 | -44 |
| -2 | 4 | 253 | 255 |
| 2 | -4 | 336 | -412 |
| -2 | -4 | 64 | 66 |
| 3 | 4 | 179 | -180 |
| -3 | 4 | 121 | 112 |
| 3 | -4 | 116 | 76 |
| -3 | -4 | 216 | 210 |
| 4 | 4 | 148 | -147 |
| -4 | 4 | 87 | 82 |
| -4 | -4 | 192 | 218 |
| 4 | -4 | 17 | 9 |
| -5 | -4 | 199 | 222 |
| 5 | 4 | 120 | -100 |
| 5 | -4 | 90 | 84 |
| -6 | 4 | 61 | -47 |
| 6 | -4 | 161 | 161 |
| -6 | -4 | 142 | 136 |
| 6 | 4 | 20 | -23 |
| 7 | 4 | 73 | 76 |
| -7 | 4 | 77 | -73 |
| -7 | -4 | 72 | -48 |
| -8 | 4 | 54 | -54 |
| -8 | -4 | 61 | 41 |
| -9 | -4 | 72 | -61 |
| -10 | -4 | 81 | -105 |
| 0 | -5 | 185 | -158 |
| 0 | 5 | 40 | -28 |
| 1 | 5 | 124 | -108 |
| -1 | 5 | 63 | 56 |
| 1 | -5 | 178 | -182 |
| -1 | -5 | 118 | 97 |
| 2 | 5 | 172 | -164 |
| -2 | 5 | 44 | 35 |
| 2 | -5 | 175 | -196 |
| -2 | -5 | 143 | 146 |
| -3 | 5 | 142 | 135 |
| 3 | 5 | 130 | -127 |
| -3 | -5 | 190 | 216 |
| 4 | 5 | 93 | -81 |
| -4 | 5 | 94 | 92 |
| -4 | -5 | 291 | 270 |
| -5 | 5 | 37 | 41 |
| -5 | -5 | 103 | 96 |
| 5 | 5 | 48 | 31 |
| 6 | 5 | 41 | 59 |
| -6 | -5 | 24 | 32 |
| -7 | -5 | 65 | -54 |
| -8 | -5 | 96 | -91 |
| -8 | 5 | 22 | -26 |
| -9 | -5 | 91 | -97 |
| 0 | 6 | 88 | -78 |
| 0 | -6 | 116 | 103 |
| 1 | 6 | 108 | -100 |
| -1 | 6 | 36 | -34 |
| 1 | -6 | 95 | -74 |
| -1 | -6 | 118 | 101 |
| 2 | 6 | 113 | -110 |
| 2 | -6 | 115 | -120 |
| -2 | -6 | 217 | 211 |
| -2 | 6 | 29 | -17 |
| 3 | 6 | 39 | -34 |
| -3 | 6 | 86 | 88 |
| 3 | -6 | 148 | -209 |
| -3 | -6 | 213 | 223 |
| -4 | 6 | 71 | 63 |
| -4 | -6 | 59 | 65 |
| 4 | 6 | 39 | 17 |
| -5 | -6 | 50 | 45 |
| -6 | 6 | 86 | 90 |
| -6 | -6 | 64 | -59 |
| -7 | -6 | 113 | -125 |
| -7 | 6 | 15 | -11 |
| -8 | -6 | 82 | -80 |
| -9 | -6 | 45 | -63 |
| 0 | 7 | 82 | -79 |
| 0 | -7 | 117 | 110 |
| 1 | 7 | 43 | -51 |
| -1 | 7 | 62 | -69 |
| 1 | -7 | 61 | 64 |
| -1 | -7 | 173 | 195 |
| 2 | 7 | 25 | -25 |
| -2 | -7 | 159 | 153 |
| -2 | 7 | 27 | -25 |
| 2 | -7 | 255 | -29 |
| -2 | 7 | 27 | -25 |
| -3 | -7 | 92 | 83 |
| -3 | 7 | 18 | 8 |
| -4 | 7 | 20 | 26 |
| -4 | -7 | 20 | -23 |
| -5 | 7 | 43 | 68 |
| -5 | -7 | 63 | -60 |
| -6 | -7 | 123 | -123 |
| -7 | -7 | 40 | -35 |
| -8 | -7 | 71 | -77 |
| 0 | -8 | 127 | 127 |
| 1 | -8 | 64 | 59 |
| -1 | -8 | 86 | 77 |
| -2 | -8 | 70 | 71 |
| -3 | -8 | 14 | 3 |
| -4 | -8 | 52 | -47 |
| -5 | -8 | 95 | -95 |
| -6 | -8 | 65 | -72 |
| -7 | -8 | 63 | -79 |
| 0 | -9 | 104 | 108 |
| 1 | -9 | 102 | 69 |
| -1 | -9 | 53 | 48 |
| 1 | -9 | 70 | 69 |
| 2 | -9 | 67 | 61 |
| -3 | -9 | 93 | -94 |
| -4 | -9 | 33 | -43 |
| -5 | -9 | 60 | -69 |
| 0 | -10 | 60 | -25 |
| 1 | -10 | 88 | 79 |
| -1 | -10 | 64 | -6 |
| 2 | -10 | 52 | 45 |
| -2 | -10 | 59 | -32 |
| | l=4 | | |
| 1 | 0 | 264 | 238 |
| -1 | 0 | 170 | 156 |
| 2 | 0 | 95 | -61 |
| -2 | 0 | 405* | 449 |
| 0 | 1 | 189 | 180 |
| 0 | -1 | 318 | 311 |
| 1 | -1 | 371 | 368 |
| -1 | 1 | 275 | 281 |
| -1 | -1 | 246 | 238 |
| 2 | -1 | 104 | 78 |
| -2 | 1 | 106 | 97 |
| -2 | -1 | 80 | 85 |
| 0 | -2 | 254 | 217 |
| 0 | 2 | 21 | 18 |
| 1 | -2 | 269 | 259 |
| -1 | -2 | 91 | 85 |
| -1 | 2 | 120 | 105 |
| 2 | -2 | 454* | 475 |
| -2 | 2 | 157 | 149 |
| -2 | -2 | 124 | -136 |
| 0 | 3 | 185 | -195 |
| 0 | -3 | 24 | 15 |
| 1 | -3 | 101 | 76 |
| -1 | -3 | 289 | 267 |
| -1 | 3 | 29 | -25 |
| 2 | -3 | 271 | 230 |
| -2 | 3 | 129 | 118 |
| -2 | -3 | 388* | -477 |
| 0 | 4 | 127 | -138 |
| 0 | -4 | 40 | -35 |
| -1 | 4 | 114 | -105 |
| -1 | -4 | 651* | -662 |
| 1 | -4 | 160 | 137 |
| 2 | -4 | 178 | 156 |
| -2 | 4 | 93 | -83 |
| -2 | -4 | 83 | -74 |
| 0 | -5 | 229 | -215 |
| 0 | 5 | 100 | -106 |
| 1 | -5 | 122 | -110 |
| -1 | 5 | 110 | -104 |
| -1 | -5 | 170 | -193 |
| -2 | 5 | 56 | -47 |
| -2 | -5 | 185 | -176 |
| 0 | 6 | 20 | 16 |
| 0 | -6 | 190 | -195 |
| 1 | -6 | 211 | -182 |
| -1 | 6 | 78 | -77 |
| -1 | -6 | 130 | -129 |
| -2 | 6 | 69 | -69 |
| 2 | -6 | 140 | -127 |
| -2 | -6 | 80 | -82 |
| 0 | -7 | 205 | -195 |
| 1 | -7 | 174 | -165 |
| -1 | -7 | 62 | 61 |
| 2 | -7 | 109 | -92 |
| -2 | -7 | 44 | 33 |
| 0 | -8 | 58 | 47 |
| 1 | -8 | 73 | -50 |
| -1 | -8 | 21 | -26 |
| 2 | -8 | 110 | -92 |
| -2 | -8 | 80 | 67 |
| 0 | -9 | 28 | 25 |
| -1 | -9 | 61 | 62 |
| 1 | -9 | 19 | -8 |
| 2 | -9 | 91 | -61 |
| -2 | -9 | 88 | 100 |
| 0 | -10 | 24 | 37 |
| -1 | -10 | 60 | 68 |
| -2 | -10 | 62 | 55 |
| | l=5 | | |
| 0 | 0 | 154 | -140 |
| 1 | 0 | 232 | -206 |
| 2 | 0 | 218 | -175 |
| -2 | 0 | 90 | 93 |
| 0 | 1 | 151 | -137 |
| 0 | -1 | 25 | -7 |
| 1 | -1 | 184 | -140 |
| -1 | 1 | 89 | -79 |
| -1 | -1 | 172 | 166 |
| 2 | -1 | 168 | -149 |
| -2 | 1 | 38 | -24 |
| -2 | -1 | 193 | 204 |
| 0 | 2 | 196 | -186 |
| 0 | -2 | 193 | 187 |
| -1 | 2 | 182 | -184 |

TABLE 3. (*Continued.*)

| *h* | *k* | *Fo* | *Fc* |
|---|---|---|---|
| -1 | -2 | 166 | 189 |
| 1 | -2 | 150 | 94 |
| 2 | -2 | 252 | -192 |
| -2 | 2 | 153 | -134 |
| -2 | -2 | 238 | 259 |
| 0 | 3 | 76 | -87 |
| 0 | -3 | 224 | 223 |
| 1 | -3 | 123 | 94 |
| -1 | 3 | 101 | -106 |
| -1 | -3 | 165 | 188 |
| 2 | -3 | 112 | 85 |
| -2 | -3 | 199 | 228 |
| -2 | 3 | 60 | -63 |
| 0 | -4 | 213 | 222 |
| 1 | -4 | 286 | 249 |
| -1 | -4 | 194 | 206 |
| -1 | 4 | 50 | -46 |
| 2 | -4 | 162 | 144 |
| -2 | 4 | 87 | -76 |
| -2 | -4 | 108 | -90 |
| 0 | 5 | 55 | 58 |
| 0 | -5 | 119 | 96 |
| 1 | -5 | 211 | 196 |
| -1 | -5 | 65 | 43 |
| 2 | -5 | 105 | 87 |
| -2 | 5 | 48 | -47 |
| -2 | -5 | 89 | -73 |
| 0 | -6 | 9 | -13 |
| -1 | -6 | 123 | -119 |
| 1 | -6 | 63 | 48 |
| 2 | -6 | 246 | 255 |
| -2 | -6 | 133 | -146 |
| 0 | -7 | 55 | -48 |
| -1 | -7 | 193 | -166 |
| -2 | -7 | 107 | -92 |
| 2 | -7 | 39 | 31 |
| 0 | -8 | 106 | -106 |
| -1 | -8 | 63 | -57 |
| 1 | -8 | 55 | -56 |
| -2 | -8 | 86 | -90 |
| 0 | -9 | 56 | -59 |
| 1 | -9 | 74 | -72 |
| -1 | -9 | 65 | -64 |
| 2 | -9 | 98 | -99 |
| 0 | -10 | 35 | -38 |
| 1 | -10 | 34 | -31 |
| -1 | -10 | 11 | 1 |
| 2 | -10 | 28 | 19 |
| l=6 | | | |
| 0 | 0 | 204 | -214 |
| -1 | 0 | 156 | -153 |
| -2 | 0 | 142 | -125 |
| 0 | 1 | 67 | 61 |
| 0 | -1 | 200 | -201 |
| 1 | -1 | 188 | -159 |
| -1 | 1 | 129 | -136 |
| -1 | -1 | 134 | -128 |
| -2 | -1 | 63 | -51 |
| -2 | 1 | 142 | -137 |
| -2 | -1 | 31 | 17 |
| 0 | 2 | 59 | 51 |
| 0 | -2 | 131 | -115 |
| 1 | -2 | 224 | -215 |
| -1 | -2 | 61 | -55 |
| 2 | -2 | 158 | -131 |
| -2 | 2 | 52 | -53 |
| -2 | -2 | 96 | -95 |
| 0 | 3 | 73 | 70 |
| 0 | -3 | 43 | -39 |
| 1 | -3 | 246 | -219 |
| -1 | 3 | 37 | 35 |
| -1 | -3 | 34 | 32 |
| 2 | -3 | 136 | -118 |
| -2 | 3 | 26 | -24 |
| -2 | -3 | 93 | 88 |
| 0 | -4 | 62 | 55 |
| -1 | 4 | 82 | 86 |
| -1 | -4 | 138 | 125 |
| 1 | -4 | 20 | 18 |
| 2 | -4 | 197 | -195 |
| -2 | 4 | 27 | 26 |
| -2 | -4 | 104 | 131 |
| 0 | -5 | 58 | 45 |
| 1 | -5 | 85 | 64 |
| -1 | -5 | 14 | 23 |
| 2 | -5 | 22 | 4 |
| -2 | -5 | 262 | 356 |
| 0 | -6 | 144 | 163 |
| -1 | -6 | 207 | 237 |
| 1 | -6 | 90 | 83 |
| 2 | -6 | 22 | 21 |
| -2 | -6 | 104 | -102 |
| 0 | -7 | 91 | 90 |
| 1 | -7 | 92 | 92 |
| -1 | -7 | 41 | 45 |
| 2 | -7 | 60 | 63 |
| 0 | -8 | 26 | 29 |
| 1 | -8 | 62 | 52 |
| -1 | -8 | 20 | 0 |
| 2 | -8 | 106 | 102 |
| -2 | -8 | 43 | -51 |
| 0 | -9 | 11 | -5 |
| 1 | -9 | 52 | 45 |
| -1 | -9 | 92 | -110 |
| 2 | -9 | 61 | 60 |
| 0 | -10 | 38 | -36 |
| 1 | -10 | 14 | -18 |
| 2 | -10 | 14 | -22 |
| -2 | -10 | 40 | -46 |
| l=7 | | | |
| 0 | 0 | 148 | 159 |
| -2 | 0 | 43 | -38 |
| 0 | 1 | 48 | 51 |
| 0 | -1 | 31 | -29 |
| -1 | 1 | 59 | 52 |
| -1 | -1 | 41 | -35 |
| -2 | -1 | 71 | -73 |
| -2 | 1 | 34 | 17 |
| 0 | 2 | 43 | 60 |
| 0 | -2 | 51 | -49 |
| -1 | 2 | 67 | 68 |
| -1 | -2 | 98 | -97 |
| 1 | -2 | 35 | 29 |
| 2 | -2 | 77 | 66 |
| -2 | 2 | 23 | 60 |
| -2 | -2 | 86 | -109 |
| 0 | -3 | 115 | -114 |
| -1 | 3 | 29 | 63 |
| -1 | -3 | 130 | -150 |
| 2 | -3 | 38 | -27 |
| -2 | 3 | 34 | 48 |
| -2 | -3 | 72 | -78 |
| 0 | -4 | 92 | -101 |
| 1 | -4 | 194 | -172 |
| -1 | -4 | 64 | -67 |
| 2 | -4 | 44 | -43 |
| -2 | -4 | 63 | -48 |
| 0 | -5 | 88 | -96 |
| 1 | -5 | 74 | -66 |
| 2 | -5 | 105 | -90 |
| -2 | -5 | 45 | -35 |
| 0 | -6 | 20 | -23 |
| 1 | -6 | 72 | -68 |
| -1 | -6 | 36 | 32 |
| 2 | -6 | 103 | -92 |
| -2 | -6 | 125 | 135 |
| 0 | -7 | 41 | 42 |
| 1 | -7 | 63 | -60 |
| -1 | -7 | 35 | 46 |
| -2 | -7 | 86 | 86 |
| 0 | -8 | 51 | 56 |
| 1 | -8 | 79 | 77 |
| -1 | -8 | 53 | 64 |
| -2 | -8 | 45 | 52 |
| 2 | -8 | 70 | -63 |
| 0 | -9 | 39 | 43 |
| 1 | -9 | 28 | 38 |
| -1 | -9 | 62 | 65 |
| 2 | -9 | 33 | 24 |
| 0 | -10 | 29 | 28 |
| 1 | -10 | 32 | 33 |
| 2 | -10 | 11 | 26 |
| l=8 | | | |
| 0 | 0 | 38 | 36 |
| -1 | 0 | 43 | 45 |
| -2 | 0 | 70 | 75 |
| 0 | -1 | 28 | -17 |
| -1 | 1 | 18 | 22 |
| -1 | -1 | 105 | 125 |
| -2 | 1 | 42 | 47 |
| -2 | -1 | 33 | 35 |
| 0 | -2 | 147 | 166 |
| -1 | -2 | 26 | 36 |
| 0 | -3 | 52 | 61 |
| 1 | -3 | 89 | 80 |
| -1 | -3 | 27 | -25 |
| -2 | -3 | 70 | -60 |
| 0 | -4 | 19 | -16 |
| 1 | -4 | 51 | 51 |
| -1 | -4 | 34 | -37 |
| 2 | -4 | 72 | 73 |
| -2 | -4 | 30 | -34 |
| 0 | -5 | 77 | -80 |
| 1 | -5 | 42 | 45 |
| -1 | -5 | 54 | -66 |
| -2 | -5 | 53 | -61 |
| 2 | -5 | 19 | 38 |
| 0 | -6 | 60 | -61 |
| 1 | -6 | 81 | -94 |
| -1 | -6 | 51 | -51 |
| 0 | -7 | 12 | -20 |
| 1 | -7 | 45 | -34 |
| -1 | -7 | 18 | -39 |
| 2 | -7 | 48 | -54 |
| -2 | -7 | 120 | -126 |
| 0 | -8 | 40 | -45 |
| 1 | -8 | 43 | -55 |
| -1 | -8 | 23 | -16 |
| 2 | -8 | 35 | -10 |
| -2 | -8 | 91 | 99 |
| -1 | -9 | 19 | 19 |
| 1 | -9 | 25 | -24 |
| 2 | -9 | 12 | -11 |
| -2 | -9 | 20 | 31 |
| l=9 | | | |
| -1 | -1 | 9 | -14 |
| 0 | -2 | 45 | -47 |
| -1 | -2 | 57 | 72 |
| -2 | -2 | 44 | 54 |
| 0 | -3 | 51 | 55 |
| -1 | -3 | 25 | 32 |
| -2 | -3 | 27 | 42 |
| 0 | -4 | 46 | 52 |
| -1 | -4 | 34 | 43 |
| -2 | -4 | 24 | 33 |
| 0 | -5 | 76 | 72 |
| -1 | -5 | 16 | 32 |
| -2 | -5 | 24 | -23 |
| 0 | -6 | 23 | -14 |
| 1 | -6 | 61 | 61 |
| -1 | -6 | 16 | -9 |
| 2 | -6 | 37 | 56 |
| -2 | -6 | 23 | -19 |
| 0 | -7 | 9 | 9 |
| 2 | -7 | 12 | 21 |
| -2 | -7 | 15 | -15 |
| 0 | -8 | 18 | -19 |

Standard errors in bond lengths, derived from the listed co-ordinate errors are: for C–C bonds, a maximum of 0·015 Å; for C–Br, 0·011 Å. The corresponding mean standard error for bond angles is 0·8°. Because of the parameter interactions, we shall assume the slightly higher values of 0·17Å, 0·13Å, and 1·0°, respectively, in the subsequent discussion.

## DESCRIPTION OF THE STRUCTURE AND DISCUSSION

Views of the molecular packing in the crystal structure are shown in Fig. 1. There are no unusually short intermolecular distances, the closest contacts being 3·48 Å for C(1) · · · C(10) and 3·88 Å for Br · · · C(12). The only markedly anisotropic atom is Br whose direction of maximum vibration is approximately normal to the molecular plane.

All bond lengths and angles within the molecule are shown in Fig. 2. Although there are differences of up to 0·04 Å within pairs of equivalent bonds, none of these differences rates as being definitely significant. Furthermore no bond within the aromatic nucleus differs significantly from the length of the corresponding bond in naphthalene,[10] the greatest observed difference of this kind being 0·03 Å. Both C–$CH_3$ bonds have lengths appropriate to the states of hybridisation of the bonded atoms and the C–Br length is not significantly different from other precise values (1·885 and 1·901 Å) for similar environments.[11]

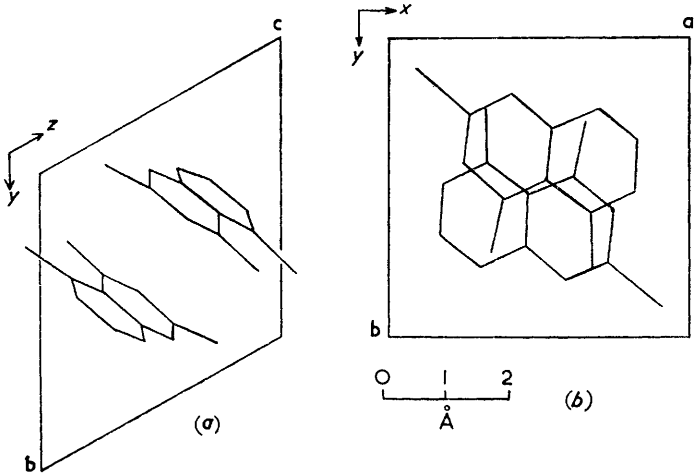

FIG. 1. View of molecules in projection (a) down the *a* axis and (b) down the *c* axis showing the contents of one unit cell.

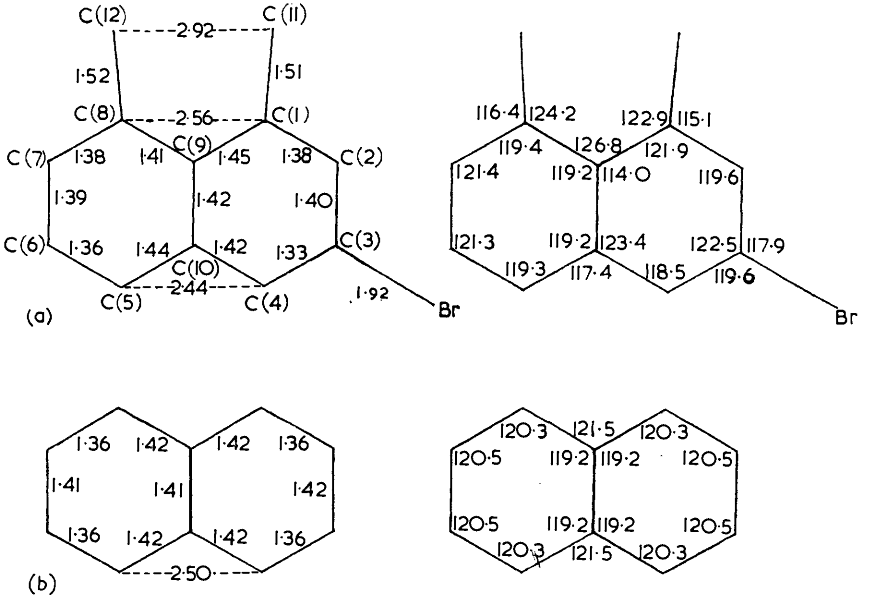

FIG. 2. Interatomic distances (Å) and angles in (*a*) 3-bromo-1,8-dimethylnaphthalene and (*b*) naphthalene.[10]

The molecular distortions relative to an unstrained configuration, both within the aromatic rings and external to them are most interesting. The most obvious result of the overcrowding is that the two methyl groups have been pushed apart by 0·42 Å approximately within the mean aromatic plane. This has been achieved mainly by a sideways

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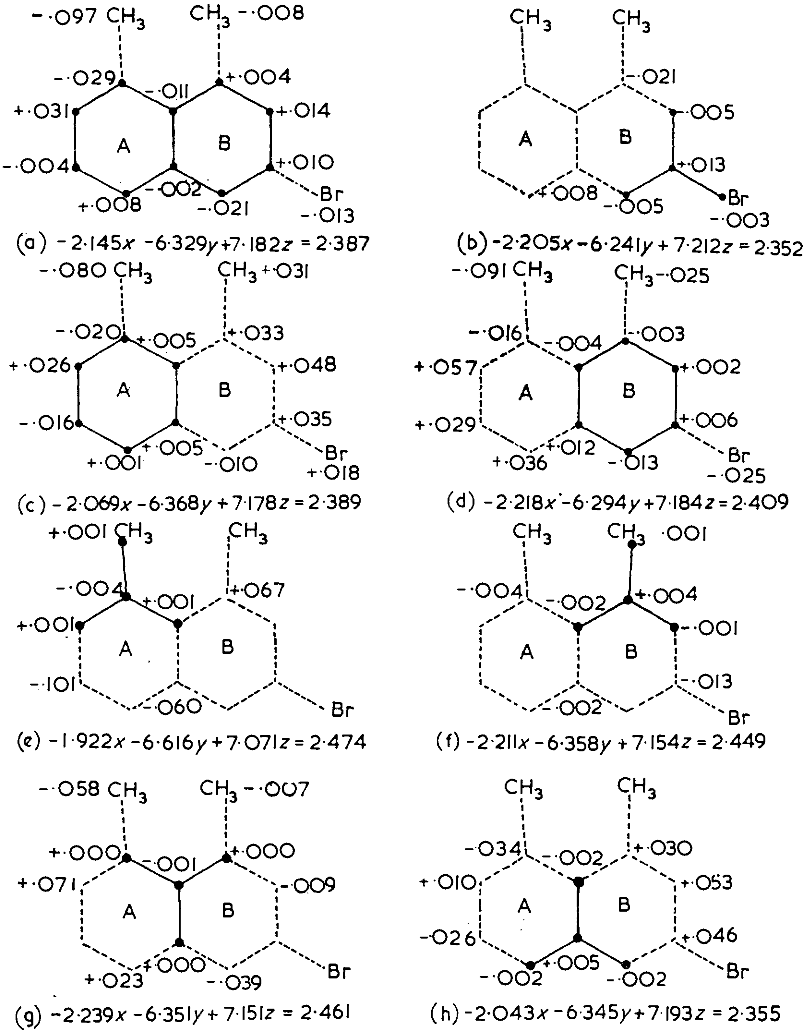
[10] Cruickshank, *Acta Cryst.*, 1957, **10**, 504.

[11] Ferguson and Sim, *Acta Cryst.*, 1962, **15**, 346; Williams, Dumke, and Rundle, *ibid.*, 1962, **15**, 627.

bending of the C–$CH_3$ bonds by 4° each, about C(1) and C(8), respectively. There is also however quite considerable in-plane distortion of the naphthalene nucleus itself as indicated by the inequality of the angles C(8)C(9)C(1) and C(4)C(10)C(5) which in turn leads to the significant difference of 0·12 Å between the non-bonded distances C(4) · · · C(5) and C(1) · · · C(8). While these in-plane effects together make by far the greatest contribution to the relief of the molecular overcrowding, there are also some smaller but systematic out-of-plane distortions which we shall now consider.



(a) $-2{\cdot}145x - 6{\cdot}329y + 7{\cdot}182z = 2{\cdot}387$

(b) $-2{\cdot}205x - 6{\cdot}241y + 7{\cdot}212z = 2{\cdot}352$

(c) $-2{\cdot}069x - 6{\cdot}368y + 7{\cdot}178z = 2{\cdot}389$

(d) $-2{\cdot}218x - 6{\cdot}294y + 7{\cdot}184z = 2{\cdot}409$

(e) $-1{\cdot}922x - 6{\cdot}616y + 7{\cdot}071z = 2{\cdot}474$

(f) $-2{\cdot}211x - 6{\cdot}358y + 7{\cdot}154z = 2{\cdot}449$

(g) $-2{\cdot}239x - 6{\cdot}351y + 7{\cdot}151z = 2{\cdot}461$

(h) $-2{\cdot}043x - 6{\cdot}345y + 7{\cdot}193z = 2{\cdot}355$

FIG. 3. Displacement of atoms from selected molecular planes in A. The atoms contributing to the least-squares planes are joined by full lines and the equations, referred to the original triclinic axes, are given below each Figure.

Only one atom, C(12) shows a significant departure (0·097 Å) from the mean plane of the naphthalene skeleton. However there are definite suggestions that the skeleton itself is non-planar and, as Hirshfeld[12] has recently pointed out, consideration of mean planes through non-planar sets of atoms can be very misleading. A closer examination of ring

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[12] Hirshfeld, *J.*, 1963, 2126.

planarity in the present case shows that the situation is by no means correctly described as a simple out-of-plane bending of C(8)C(12). Results of a planarity analysis of various portions of the molecule are summarised in Fig. 3. The first important feature to note is that the immediate environment of each of the atoms [C(1), C(3), C(8), C(9), C(10)], which is involved in three bonds with other than hydrogen atoms, is closely planar. Each of the three substituents is therefore coplanar with that portion of the naphthalene skeleton to which it is attached. Inspection of Fig. 3 (*c*) shows that there is a considerable torsional strain about the bond C(8)–C(9), the angle of twist being 4°. The consequence of this is that one or both of the aromatic rings will be buckled. In fact the six atoms of ring B show no significant departures from planarity so, to a first approximation, the out-of-plane aromatic distortion appears confined to ring A, a consequence evidently of the effect of the heavy bromine substituent in ring B. Figs. 3(c) and (e) help to indicate the precise nature of the distortion of ring A and in Fig. 4 is shown an end-on view of this ring with the out-of-plane displacements exaggerated. Ring B appears to have remained planar only at the expense of considerable strain in its internal angles C(1)C(9)C(10) and C(4)C(10)C(9), no such strain being apparent in ring A.

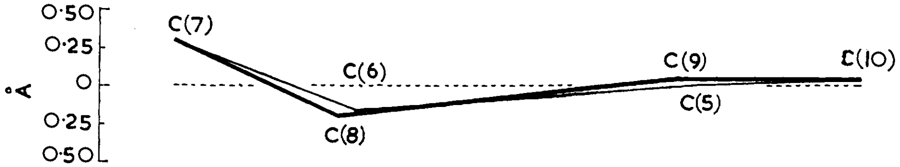

FIG. 4. End-on view of ring A showing the (exaggerated) displacements from the least-squares plane.

Except for the case of octamethylnaphthalene [13] where considerable buttressing effects come into play, we know of no structure analysis involving two methyl groups in adjacent *peri* positions. The results reported by Gafner and Herbstein [14] for 1,4,5,8-tetrachloronaphthalene are, however, relevant. Significant out-of-plane displacements in opposite directions were reported for the *peri* chlorine atoms. An examination of the published displacements shows that here also each chlorine is in fact closely planar with its three nearest carbon atoms and the distortions can be described as twisting about both C(1)C(9) and C(8)C(9) [C(2)C(3) and C(3)C(4) in the original Paper], buckling occurring in both rings.

It is reasonable to assume that the distortions which are observed for 3-bromo-1,8-dimethylnaphthalene are qualitatively those which occur in 4,5-dimethyl-1- and 2-naphthoic acids. Without attempting a detailed analysis of the consequences of these distortions, we are at least in a position to associate the types of in-plane and out-of-plane molecular strain described, with a small but measurable effect on a physical property of the derived acid, the dissociation constant. Extension of this type of structure analysis to other naphthalene compounds is obviously desirable and further work is planned.

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CHEMISTRY DEPARTMENT, UNIVERSITY OF CANTERBURY,
CHRISTCHURCH, NEW ZEALAND.

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[13] Donaldson and Robertson, *J.*, 1953, 17.

[14] Gafner and Herbstein, *Acta Cryst.*, 1962, **15**, 1081.