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# The Crystal Structure of Fumaric Acid

BY C.J. BROWN

*The Sir William Ramsay and Ralph Forster Laboratories, University College, Gower Street, London W.C.*1, *England*

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The crystal structure of the ordinary form of fumaric acid at room temperature has been determined from three-dimensional X-ray diffraction data on an untwinned crystal. There are six molecules in the monoclinic cell, two lying on centres of symmetry and four in general positions. Both kinds of molecule form parallel hydrogen-bonded chains along **a**, and these chains form sheets parallel to (001). The mean bond lengths are C–C 1·465, C=C 1·348, C–O 1·293 and C=O 1·224 Å, and the mean hydrogen-bond length is 2·684 Å.

## Introduction

The earliest crystallographic measurements on fumaric acid, HOOC–CH=CH–COOH, (Yardley, 1925) were hampered by the complex twinning which generally occurs when aqueous solutions are concentrated, and implied a triclinic unit cell with $\alpha,\beta,\gamma \simeq 90°$. Subsequent work by Reis & Schneider (1928) led to a monoclinic cell in approximate agreement with the present work. Reis & Schneider also assigned coordinates for the centres of the molecules on the evidence of certain strong reflexions, which, although not entirely correct, are closely related to the values now obtained. Shahat (1951) made further investigations of the structure of fumaric acid as well as maleic acid (1952), but no results were reported. Cook, Rowlands & Whiffen (1963) made suggestions regarding the molecular arrangement on the basis of electron spin resonance spectra, but the value of their work as an aid to structure determination was reduced on account of crystal twinning, incorrect assignment of axial directions, and lack of realization of the presence of two kinds of molecule in the crystal. The crystal structure of a polymorph, β-fumaric acid, has been reported by Bednowitz & Post (1965).

## Experimental

Slow evaporation of aqueous alcoholic solutions of fumaric acid yielded an abundant crop of crystals, by far the majority of which were multiply twinned with a profusion of re-entrant angles. Examination between crossed Nicols revealed occasional specimens showing regular extinction, and these were used for this work. Rotation and oscillation photographs about each of the axes were taken for confirming the unit-cell dimensions and space group:

$$a=7{\cdot}619;\ b=15{\cdot}014;\ c=6{\cdot}686\ \text{Å}.\quad \beta=112{\cdot}0°.$$

The absences were $0k0$ for $k \neq 6n$, and $h0l$ for $l \neq 2n$, and from the range of possible space groups $P2_1/c$ was chosen as the most probable compromise; this choice was subsequently confirmed by the result of the structure determination.

The required density for six molecules per unit cell is 1·629, while that published (Tanatar & Chelebiev, 1890) is 1·625 g.cm$^{-3}$. Weissenberg photographs were taken about *b* (zero and ten layers) and *a* (zero layer only) using multiple films and different exposures to cover the entire intensity range. The reflexions were compared visually with a calibrated scale, and by these means 853 independent *hkl* structure amplitudes were obtained in the usual way.

## Determination of the structure

Reis & Schneider's (1928) assignment of the molecular centres was assumed in the first instance, but the uncertainty regarding the space group made it seem worth while to try out a number of variations of this theme. Some trial-and-error calculations were made for the *hk*0 zone, and when there was evidence of agreement between the calculated and observed structure amplitudes, the work was transferred to our Ferranti Pegasus computer, using Cruickshank's (1961) structure-factor and least-squares refinement program, in which there is a facility for selecting terms in restricted ranges of $\theta$. Low order terms having $d > 2$ Å were used initially, and successive cycles of refinement computed with a gradual reduction in the value of *d* until all the structure amplitudes were included. Hydrogen atoms were then inserted at their calculated positions (C–H and O–H=1·08 Å.) but these were not refined; anisotropic temperature factors were calculated for the carbon and oxygen atoms, which were refined by the least-squares program, as were also isotropic temperature factors for the hydrogen atoms. The refinement process was continued until the shifts obtained in both the positional and thermal parameters were considerably less (approximately one-fifth) than the corresponding standard deviations. The final *R* index over the 853 structure amplitudes was 5·9%.

The final values of the atomic parameters are given in Table 1, and the observed and calculated structure amplitudes are listed in Table 2.

### Description of the structure

Molecules of fumaric acid are linked together to form chains by a double hydrogen-bonding system between adjacent carboxylic groups in the manner already found in numerous other organic acids. The distance from a point in one molecule to the next linked in this way is $a = 7{\cdot}619$ Å. It is interesting to note that this corresponds exactly to $b = 7{\cdot}618$ Å in $\beta$-fumaric acid (Bednowitz & Post, 1965), and approximately to $c = 7{\cdot}61$ Å in the related succinic acid (Morrison & Robertson, 1949).

The six fumaric acid molecules in the unit cell are crystallographically of two kinds; two molecules are centrosymmetric with their centres at (0,0,0) and $(0,\frac{1}{2},\frac{1}{2})$, and the other four lie in general positions with their centres approximately at $(\frac{2}{3},\frac{1}{3},0)$, $(\frac{2}{3},\frac{1}{6},\frac{1}{2})$, $(\frac{1}{3},\frac{2}{3},0)$, $(\frac{1}{3},\frac{5}{6},\frac{1}{2})$. The two kinds of molecule lie almost parallel to each other, and form hydrogen-bonded chains in the same direction in the crystal lattice. The result is a staggered arrangement which is shown in the bounded electron density projection (Fig. 1). The explanation of the absence of the $0k0$ reflexions for $k \neq 6n$ is evident from the coordinates. There are no other bonds between molecules; there are, however, several close approaches between atoms O(2)–O(3) 3·14 Å, O(4)–O(5) 3·30 Å, and O(1)–O(4′) 3·26 Å.

The bond lengths and inter-bond angles within the two kinds of molecule are shown in Fig. 2, whence the mean values are C–C 1·465, C=C 1·348, C–O 1·293 and C=O 1·224 Å. These agree well with other determined values excepting perhaps the C=C across the centre of symmetry, which may be longer than expected owing to some undetected systematic error displacing the C(1) peak away from the centre of symmetry. The mean values of the angles, C=C–C 124·1°, C–C=O

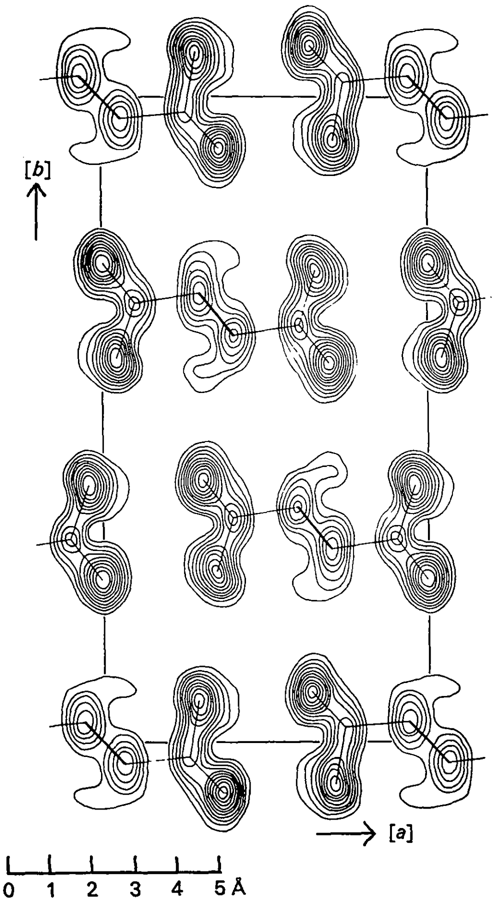

Fig. 1. Bounded electron density projection between limits $z/c = -0{\cdot}15 \rightarrow +0{\cdot}15$. Contours are at arbitrary intervals. The hydrogen atoms are evident.

Table 1. *Atomic parameters*

| | $x/a$ | $y/b$ | $z/c$ | $B_{11}$ | $B_{22}$ | $B_{33}$ | $B_{12}$ | $B_{23}$ | $B_{13}$ |
|---|---|---|---|---|---|---|---|---|---|
| C(1) | 0·0672 | −0·0323 | 0·0209 | 2·13 | 5·61 | 3·73 | −0·46 | −0·30 | 1·63 |
| C(2) | 0·2524 | −0·0166 | 0·0095 | 1·70 | 4·37 | 3·39 | −0·48 | 0·12 | 1·20 |
| C(3) | 0·3992 | 0·3507 | −0·0506 | 1·89 | 3·99 | 3·43 | −0·04 | 0·16 | 0·98 |
| C(4) | 0·5898 | 0·3645 | −0·0487 | 1·28 | 6·16 | 3·62 | −0·40 | 0·00 | 0·98 |
| C(5) | 0·7054 | 0·3005 | −0·0642 | 1·71 | 4·71 | 3·84 | −0·47 | −0·23 | 1·33 |
| C(6) | 0·8980 | 0·3167 | −0·0581 | 1·72 | 3·95 | 3·48 | 0·03 | 0·07 | 1·06 |
| O(1) | 0·3669 | −0·0786 | 0·0499 | 2·13 | 4·75 | 5·69 | 0·00 | 0·64 | 1·88 |
| O(2) | 0·2849 | 0·0626 | −0·0416 | 2·28 | 4·12 | 6·10 | −0·09 | 0·86 | 2·05 |
| O(3) | 0·3441 | 0·2682 | −0·0754 | 2·51 | 4·48 | 6·47 | −0·39 | −0·10 | 2·13 |
| O(4) | 0·3040 | 0·4124 | −0·0308 | 2·51 | 4·11 | 6·00 | 0·21 | 0·02 | 1·92 |
| O(5) | 0·9925 | 0·2536 | −0·0766 | 2·05 | 4·69 | 6·66 | −0·14 | −0·70 | 2·16 |
| O(6) | 0·9526 | 0·3989 | −0·0321 | 2·35 | 4·49 | 5·91 | −0·50 | −0·52 | 1·70 |
| H(1) | 0·0354 | −0·0980 | 0·0642 | $B$(isotropic) = 7·13 | | | | | |
| H(2) | 0·4250 | 0·0690 | −0·0449 | | | | | | |
| H(3) | 0·2026 | 0·2623 | −0·0759 | | | | | | |
| H(4) | 0·6412 | 0·4322 | −0·0335 | | | | | | |
| H(5) | 0·6548 | 0·2326 | −0·0824 | | | | | | |
| H(6) | 1·0941 | 0·4043 | −0·0316 | | | | | | |

The values of $B$ are defined by the expression $\exp[-\frac{1}{4}(h^2a^{*2}B_{11} + 2hka^*b^*B_{12} + \ldots)]$ used in the structure amplitude calculations.

Mean e.s.d.'s for carbon atoms: $\sigma(x)$ 0·0027; $\sigma(y)$ 0·0040; $\sigma(z)$ 0·0033 Å

Mean e.s.d.'s for oxygen atoms: $\sigma(x)$ 0·0022; $\sigma(y)$ 0·0029; $\sigma(z)$ 0·0029

Mean e.s.d. for $B_{ij}$ averaged over carbon and oxygen: 0·14 Å$^2$.

Table 2. *Observed and calculated structure amplitudes*

| H | K | L | F(OBS) | F(CAL) |
|---|---|---|---|---|
| 0 | 0 | 2 | 186.0 | +186.0 |
| 0 | 0 | 4 | 31.6 | +30.1 |
| 0 | 0 | 6 | 4.7 | -3.9 |
| 0 | 0 | 8 | 3.5 | -4.5 |
| 1 | 0 | -8 | 2.0 | +3.0 |
| 1 | 0 | -6 | 6.4 | +5.7 |
| 1 | 0 | -4 | 4.5 | +3.8 |
| 2 | 0 | -6 | 4.0 | +3.5 |
| 2 | 0 | -4 | 9.8 | +10.0 |
| 2 | 0 | -2 | 13.3 | +13.1 |
| 2 | 0 | 0 | 11.7 | -10.3 |
| 2 | 0 | 2 | 24.1 | -24.2 |
| 2 | 0 | 4 | 14.7 | -13.8 |
| 2 | 0 | 6 | 5.4 | -5.0 |
| 3 | 0 | -6 | 5.7 | +5.5 |
| 3 | 0 | -4 | 36.3 | +37.3 |
| 3 | 0 | -2 | 110.5 | +110.5 |
| 3 | 0 | 0 | 110.5 | +112.3 |
| 3 | 0 | 2 | 32.3 | +31.4 |
| 3 | 0 | 4 | 5.7 | -5.3 |
| 3 | 0 | 6 | 6.2 | -6.3 |
| 4 | 0 | -8 | 6.6 | +6.2 |
| 4 | 0 | -6 | 11.0 | +9.8 |
| 4 | 0 | -4 | 8.4 | +8.5 |
| 4 | 0 | -2 | 2.8 | +2.4 |
| 4 | 0 | 0 | 3.0 | -2.9 |
| 4 | 0 | 2 | 3.7 | -3.4 |
| 5 | 0 | -8 | 1.7 | +1.7 |
| 5 | 0 | 0 | 8.7 | -8.1 |
| 5 | 0 | 2 | 12.6 | -11.5 |
| 5 | 0 | 4 | 6.7 | -6.3 |
| 6 | 0 | -8 | 3.5 | +3.7 |
| 6 | 0 | -4 | 3.8 | -4.7 |
| 6 | 0 | -2 | 3.8 | -3.6 |
| 6 | 0 | 0 | 7.9 | -7.4 |
| 6 | 0 | 2 | 12.4 | -11.2 |
| 6 | 0 | 4 | 7.2 | -6.6 |
| 7 | 0 | -6 | 7.9 | -7.1 |
| 7 | 0 | -4 | 5.6 | -5.9 |
| 7 | 0 | 0 | 6.8 | +6.3 |
| 7 | 0 | 2 | 4.9 | +4.8 |
| 8 | 0 | -6 | 6.5 | -6.4 |
| 8 | 0 | -4 | 4.5 | -3.8 |
| 8 | 0 | -2 | 2.7 | +1.7 |
| 9 | 0 | -6 | 3.7 | -3.7 |
| 9 | 0 | -4 | 8.8 | -8.8 |
| 9 | 0 | -2 | 8.9 | -8.8 |
| 9 | 0 | 0 | 6.9 | -6.4 |
| 0 | 1 | 2 | 93.1 | +92.2 |
| 0 | 1 | 3 | 4.6 | +4.9 |
| 0 | 1 | 4 | 52.6 | +50.9 |
| 0 | 1 | 5 | 6.1 | +5.7 |
| 0 | 1 | 6 | 14.1 | +14.9 |
| 0 | 1 | 7 | 4.0 | +4.6 |
| 1 | 1 | -7 | 2.5 | +2.3 |
| 1 | 1 | -5 | 3.7 | +3.9 |
| 1 | 1 | -4 | 3.2 | +2.6 |
| 1 | 1 | -3 | 3.1 | +3.2 |
| 1 | 1 | 1 | 2.9 | -3.1 |
| 1 | 1 | 6 | 2.7 | -2.9 |
| 2 | 1 | -6 | 2.9 | -2.4 |
| 2 | 1 | -5 | 10.2 | -10.5 |
| 2 | 1 | -3 | 29.4 | -29.8 |
| 2 | 1 | -2 | 18.7 | +19.7 |
| 2 | 1 | -1 | 37.6 | -39.7 |
| 2 | 1 | 0 | 38.9 | +39.9 |
| 2 | 1 | 1 | 17.9 | -18.1 |
| 2 | 1 | 2 | 19.6 | +21.4 |
| 2 | 1 | 4 | 3.8 | +3.3 |
| 3 | 1 | -6 | 8.0 | -7.5 |
| 3 | 1 | -4 | 25.7 | -25.6 |
| 3 | 1 | -3 | 3.5 | +3.5 |
| 3 | 1 | -2 | 24.6 | -24.6 |
| 3 | 1 | 0 | 27.6 | +28.8 |
| 3 | 1 | 1 | 3.4 | -3.5 |
| 3 | 1 | 2 | 39.6 | +41.9 |
| 3 | 1 | 3 | 2.7 | -2.7 |
| 3 | 1 | 4 | 17.8 | +18.0 |
| 3 | 1 | 6 | 3.4 | +3.5 |
| 4 | 1 | -7 | 2.5 | +2.4 |
| 4 | 1 | -6 | 4.0 | +3.3 |
| 4 | 1 | -5 | 4.6 | +3.5 |
| 4 | 1 | -4 | 7.6 | +8.4 |
| 4 | 1 | -3 | 6.2 | +5.8 |
| 4 | 1 | -2 | 9.1 | +10.0 |
| 4 | 1 | -1 | 7.9 | +9.2 |
| 4 | 1 | 0 | 4.7 | +5.3 |
| 4 | 1 | 1 | 8.2 | +8.8 |
| 4 | 1 | 3 | 6.2 | +5.6 |
| 4 | 1 | 4 | 4.7 | -3.9 |
| 4 | 1 | 5 | 2.2 | +1.9 |
| 4 | 1 | 6 | 2.9 | -3.4 |
| 5 | 1 | -7 | 2.5 | -2.1 |
| 5 | 1 | -5 | 8.8 | -10.4 |
| 5 | 1 | -3 | 15.5 | -16.8 |
| 5 | 1 | -2 | 9.3 | +10.4 |
| 5 | 1 | -1 | 9.6 | -9.2 |
| 5 | 1 | 0 | 16.1 | +16.8 |
| 5 | 1 | 2 | 6.9 | +7.6 |
| 5 | 1 | 3 | 2.9 | +2.6 |
| 6 | 1 | -8 | 6.8 | +6.1 |
| 6 | 1 | -7 | 3.2 | -3.6 |
| 6 | 1 | -6 | 10.2 | +9.9 |
| 6 | 1 | -4 | 4.7 | +4.7 |
| 6 | 1 | -3 | 2.7 | +2.6 |
| 6 | 1 | 0 | 4.7 | +3.5 |
| 6 | 1 | 1 | 6.4 | -5.9 |
| 6 | 1 | 2 | 3.8 | +2.9 |
| 6 | 1 | 3 | 6.6 | -6.5 |
| 7 | 1 | -6 | 2.5 | -2.2 |
| 7 | 1 | -5 | 3.8 | -3.5 |
| 7 | 1 | -4 | 6.2 | -7.0 |
| 7 | 1 | -3 | 6.4 | -7.2 |
| 7 | 1 | -2 | 8.0 | -8.2 |
| 7 | 1 | -1 | 8.0 | -8.2 |
| 7 | 1 | 0 | 2.9 | -3.1 |
| 7 | 1 | 1 | 5.8 | -5.6 |
| 7 | 1 | 3 | 2.0 | -2.1 |
| 8 | 1 | -7 | 2.7 | -2.6 |
| 8 | 1 | -6 | 2.9 | -2.7 |
| 8 | 1 | -5 | 3.2 | -3.2 |
| 8 | 1 | -4 | 5.7 | -5.5 |
| 8 | 1 | -1 | 8.0 | +7.1 |
| 8 | 1 | 0 | 4.0 | +3.7 |
| 8 | 1 | 1 | 7.4 | +7.8 |
| 9 | 1 | -6 | 5.7 | +6.1 |
| 9 | 1 | -5 | 2.3 | +1.9 |
| 9 | 1 | -2 | 2.9 | -2.1 |
| 0 | 2 | 1 | 20.5 | -20.9 |
| 0 | 2 | 2 | 20.8 | +20.0 |
| 0 | 2 | 3 | 27.2 | -25.9 |
| 0 | 2 | 4 | 23.5 | +23.2 |
| 0 | 2 | 5 | 12.4 | -13.0 |
| 0 | 2 | 6 | 10.6 | +11.9 |
| 0 | 2 | 7 | 4.0 | -4.0 |
| 1 | 2 | -5 | 2.7 | +2.6 |
| 1 | 2 | -4 | 3.9 | +3.6 |
| 1 | 2 | -3 | 6.4 | +6.4 |
| 1 | 2 | -1 | 7.2 | +7.9 |
| 1 | 2 | 0 | 8.0 | -7.1 |
| 1 | 2 | 1 | 5.8 | +6.1 |
| 1 | 2 | 3 | 3.6 | +3.1 |
| 1 | 2 | 4 | 5.7 | +5.9 |
| 1 | 2 | 5 | 4.0 | +3.4 |
| 1 | 2 | 6 | 3.8 | +3.4 |
| 1 | 2 | 7 | 2.7 | +2.7 |
| 2 | 2 | -7 | 4.5 | +4.3 |
| 2 | 2 | -5 | 5.8 | +5.2 |
| 2 | 2 | -4 | 12.4 | -13.7 |
| 2 | 2 | -3 | 6.5 | -6.7 |
| 2 | 2 | -2 | 37.4 | -37.5 |
| 2 | 2 | -1 | 32.6 | -34.3 |
| 2 | 2 | 0 | 30.4 | -30.9 |
| 2 | 2 | 1 | 36.4 | -36.4 |
| 2 | 2 | 2 | 4.4 | -4.6 |
| 2 | 2 | 3 | 16.5 | -15.6 |
| 2 | 2 | 5 | 4.0 | -3.5 |
| 3 | 2 | -8 | 3.4 | +3.0 |
| 3 | 2 | -6 | 14.2 | +13.3 |
| 3 | 2 | -4 | 28.2 | +28.0 |
| 3 | 2 | -3 | 2.0 | +1.6 |
| 3 | 2 | -2 | 17.7 | +16.5 |
| 3 | 2 | -1 | 1.7 | -1.5 |
| 3 | 2 | 0 | 11.3 | -10.9 |
| 3 | 2 | 1 | 7.6 | -7.3 |
| 3 | 2 | 2 | 7.3 | -6.6 |
| 3 | 2 | 3 | 7.4 | -6.4 |
| 3 | 2 | 5 | 3.7 | -2.8 |
| 4 | 2 | -6 | 2.9 | +2.3 |
| 4 | 2 | -5 | 2.7 | -2.4 |
| 4 | 2 | -4 | 4.2 | +4.5 |
| 4 | 2 | -3 | 7.1 | -6.9 |
| 4 | 2 | -2 | 8.0 | +7.1 |
| 4 | 2 | -1 | 7.9 | -7.4 |
| 4 | 2 | 0 | 8.3 | +9.3 |
| 4 | 2 | 2 | 10.2 | +9.8 |
| 4 | 2 | 3 | 4.0 | +3.4 |
| 4 | 2 | 4 | 6.1 | +6.6 |
| 4 | 2 | 5 | 3.8 | +4.2 |
| 5 | 2 | -7 | 4.4 | +4.4 |
| 5 | 2 | -6 | 2.9 | -2.4 |
| 5 | 2 | -4 | 14.5 | -14.5 |
| 5 | 2 | -3 | 15.7 | -14.4 |
| 5 | 2 | -2 | 23.8 | -25.1 |
| 5 | 2 | -1 | 24.1 | -24.7 |
| 5 | 2 | 0 | 13.9 | -12.7 |
| 5 | 2 | 1 | 17.0 | -16.2 |
| 5 | 2 | 3 | 4.9 | -5.1 |
| 6 | 2 | -7 | 7.2 | -7.8 |
| 6 | 2 | -6 | 10.3 | +9.8 |
| 6 | 2 | -5 | 11.0 | -11.4 |
| 6 | 2 | -4 | 15.3 | +16.3 |
| 6 | 2 | -3 | 6.6 | -5.7 |
| 6 | 2 | -1 | 4.7 | +4.5 |
| 6 | 2 | 0 | 17.5 | -17.4 |
| 6 | 2 | 1 | 8.9 | +8.0 |
| 6 | 2 | 2 | 17.0 | -15.2 |
| 6 | 2 | 3 | 6.5 | +5.6 |
| 6 | 2 | 4 | 7.6 | -7.9 |
| 7 | 2 | -7 | 2.0 | +2.2 |
| 7 | 2 | -5 | 4.6 | +4.9 |
| 7 | 2 | -3 | 4.7 | +4.9 |
| 7 | 2 | -2 | 4.9 | -5.1 |
| 7 | 2 | 0 | 5.6 | -6.0 |
| 7 | 2 | 1 | 3.6 | -3.0 |
| 7 | 2 | 2 | 3.8 | -3.2 |
| 7 | 2 | 3 | 4.0 | -3.9 |
| 8 | 2 | -7 | 2.2 | -1.8 |
| 8 | 2 | -5 | 7.4 | -6.6 |
| 8 | 2 | -4 | 8.7 | -8.9 |
| 8 | 2 | -3 | 11.7 | -11.2 |
| 8 | 2 | -2 | 11.7 | -11.4 |
| 8 | 2 | -1 | 9.8 | -9.3 |
| 8 | 2 | 0 | 4.6 | -3.7 |
| 8 | 2 | 1 | 3.2 | -3.3 |
| 8 | 2 | 2 | 2.5 | +2.1 |
| 9 | 2 | -6 | 6.5 | +6.4 |
| 9 | 2 | -5 | 3.8 | -3.2 |
| 9 | 2 | -4 | 4.9 | +5.1 |
| 9 | 2 | -2 | 4.9 | -4.7 |
| 9 | 2 | -1 | 3.8 | +4.2 |
| 9 | 2 | 0 | 8.8 | -9.6 |
| 0 | 3 | 1 | 119.2 | +119.3 |
| 0 | 3 | 2 | 6.7 | +6.0 |
| 0 | 3 | 3 | 38.9 | +39.0 |
| 0 | 3 | 4 | 12.0 | +12.9 |
| 0 | 3 | 5 | 3.8 | +3.8 |
| 0 | 3 | 6 | 8.7 | +9.5 |
| 0 | 3 | 7 | 3.1 | -2.9 |
| 1 | 3 | -7 | 4.2 | +4.3 |
| 1 | 3 | -6 | 2.9 | +2.2 |
| 1 | 3 | -5 | 8.4 | +8.2 |
| 1 | 3 | -4 | 5.1 | +5.5 |
| 1 | 3 | -3 | 9.4 | +9.1 |
| 1 | 3 | -2 | 10.3 | +10.5 |
| 1 | 3 | -1 | 2.5 | +2.4 |
| 1 | 3 | 0 | 3.6 | -4.1 |
| 1 | 3 | 1 | 5.8 | -4.7 |
| 1 | 3 | 2 | 20.8 | -18.6 |
| 1 | 3 | 3 | 3.0 | -3.3 |
| 1 | 3 | 4 | 11.3 | -10.3 |
| 2 | 3 | -6 | 6.2 | +6.1 |
| 2 | 3 | -5 | 6.5 | +6.9 |
| 2 | 3 | -4 | 14.1 | +15.6 |
| 2 | 3 | -3 | 10.2 | +11.5 |
| 2 | 3 | -2 | 13.9 | +13.0 |
| 2 | 3 | 0 | 4.4 | -4.2 |
| 2 | 3 | 1 | 12.6 | -13.0 |
| 2 | 3 | 2 | 3.5 | -3.6 |
| 2 | 3 | 3 | 10.5 | -10.5 |
| 2 | 3 | 4 | 3.8 | +3.2 |
| 2 | 3 | 5 | 4.7 | -5.1 |
| 2 | 3 | 6 | 2.3 | +3.0 |
| 2 | 3 | 7 | 2.5 | -2.3 |
| 3 | 3 | -8 | 5.8 | -5.1 |
| 3 | 3 | -6 | 6.8 | -7.0 |
| 3 | 3 | -5 | 4.6 | +4.8 |
| 3 | 3 | -4 | 8.9 | +9.5 |
| 3 | 3 | -3 | 20.0 | +18.6 |
| 3 | 3 | -2 | 48.5 | +48.1 |
| 3 | 3 | -1 | 31.7 | +31.3 |
| 3 | 3 | 0 | 48.4 | +50.9 |
| 3 | 3 | 1 | 17.5 | +17.6 |
| 3 | 3 | 2 | 23.0 | +22.8 |
| 3 | 3 | 4 | 8.8 | +8.1 |
| 3 | 3 | 5 | 2.5 | -2.6 |
| 3 | 3 | 6 | 2.7 | +2.8 |
| 4 | 3 | -7 | 8.8 | +8.1 |
| 4 | 3 | -6 | 3.9 | +3.1 |
| 4 | 3 | -5 | 12.0 | +11.8 |
| 4 | 3 | -4 | 4.2 | +4.8 |
| 4 | 3 | -3 | 7.6 | +8.5 |
| 4 | 3 | -2 | 3.6 | +3.1 |
| 4 | 3 | -1 | 2.0 | -1.9 |
| 4 | 3 | 0 | 5.3 | -5.1 |
| 4 | 3 | 1 | 7.5 | -6.6 |
| 4 | 3 | 2 | 8.3 | -7.1 |
| 4 | 3 | 3 | 4.7 | -4.1 |
| 4 | 3 | 4 | 2.7 | -2.9 |
| 5 | 3 | -8 | 2.0 | +3.3 |
| 5 | 3 | -7 | 4.2 | +4.0 |
| 5 | 3 | -6 | 7.9 | +8.1 |
| 5 | 3 | -5 | 6.2 | +6.0 |
| 5 | 3 | -4 | 11.7 | +12.1 |
| 5 | 3 | -3 | 4.3 | +3.0 |
| 5 | 3 | -2 | 2.3 | +2.6 |
| 5 | 3 | -1 | 3.5 | -3.3 |
| 5 | 3 | 0 | 6.2 | -7.5 |
| 5 | 3 | 1 | 6.6 | -6.8 |
| 5 | 3 | 3 | 3.8 | -4.2 |
| 5 | 3 | 4 | 3.9 | +4.0 |
| 6 | 3 | -8 | 3.0 | -2.2 |
| 6 | 3 | -6 | 4.6 | +3.8 |
| 6 | 3 | -5 | 8.8 | -9.7 |
| 6 | 3 | -4 | 27.8 | +27.0 |
| 6 | 3 | -3 | 19.2 | -19.9 |
| 6 | 3 | -2 | 46.5 | +46.1 |
| 6 | 3 | -1 | 21.1 | -20.9 |
| 6 | 3 | 0 | 31.0 | +30.7 |
| 6 | 3 | 1 | 12.4 | -13.4 |
| 6 | 3 | 2 | 9.4 | +8.1 |
| 6 | 3 | 3 | 4.5 | -5.0 |
| 7 | 3 | -7 | 4.6 | -4.1 |
| 7 | 3 | -5 | 3.8 | -4.5 |
| 7 | 3 | -1 | 2.9 | +2.4 |
| 7 | 3 | 1 | 3.6 | +3.5 |
| 7 | 3 | 2 | 2.2 | -2.1 |
| 8 | 3 | -6 | 6.7 | +6.4 |
| 8 | 3 | -4 | 6.1 | +5.4 |
| 8 | 3 | -2 | 3.6 | -3.5 |
| 8 | 3 | 0 | 7.6 | -8.6 |
| 9 | 3 | -6 | 6.0 | +6.7 |
| 9 | 3 | -5 | 7.2 | -6.5 |
| 9 | 3 | -4 | 16.1 | +17.5 |
| 9 | 3 | -3 | 9.6 | -9.3 |
| 9 | 3 | -2 | 19.0 | +18.7 |
| 9 | 3 | -1 | 8.1 | -7.1 |
| 9 | 3 | 0 | 7.3 | +7.8 |
| 0 | 4 | 1 | 28.9 | +29.4 |
| 0 | 4 | 2 | 8.3 | -7.8 |
| 0 | 4 | 3 | 34.0 | +37.0 |
| 0 | 4 | 4 | 9.3 | -8.1 |
| 0 | 4 | 5 | 17.2 | +16.6 |
| 0 | 4 | 7 | 3.7 | +4.4 |
| 1 | 4 | -5 | 6.5 | +6.6 |
| 1 | 4 | -3 | 22.7 | +22.6 |
| 1 | 4 | -2 | 11.3 | +10.7 |
| 1 | 4 | -1 | 33.6 | +33.0 |
| 1 | 4 | 0 | 31.0 | +31.0 |
| 1 | 4 | 1 | 16.0 | +16.5 |
| 1 | 4 | 2 | 19.2 | +20.7 |
| 1 | 4 | 4 | 3.6 | +3.3 |
| 1 | 4 | 6 | 2.5 | -2.1 |
| 2 | 4 | -5 | 3.7 | +3.3 |
| 2 | 4 | -4 | 2.2 | -1.8 |
| 2 | 4 | -3 | 8.4 | +8.6 |
| 2 | 4 | -1 | 9.6 | +8.6 |
| 2 | 4 | 0 | 12.7 | -12.1 |
| 2 | 4 | 1 | 4.6 | -3.9 |
| 2 | 4 | 2 | 15.5 | -15.3 |
| 2 | 4 | 3 | 7.5 | -7.0 |
| 2 | 4 | 4 | 7.6 | -7.3 |
| 2 | 4 | 5 | 2.7 | -2.9 |
| 3 | 4 | -7 | 2.5 | -2.1 |
| 3 | 4 | -6 | 10.6 | -10.1 |
| 3 | 4 | -5 | 8.3 | -7.5 |
| 3 | 4 | -4 | 20.2 | -21.3 |
| 3 | 4 | -3 | 13.0 | -12.8 |
| 3 | 4 | -2 | 11.5 | -11.1 |
| 3 | 4 | 0 | 9.8 | +9.1 |
| 3 | 4 | 1 | 15.7 | +14.8 |
| 3 | 4 | 2 | 5.8 | +4.8 |
| 3 | 4 | 3 | 11.7 | +10.4 |
| 3 | 4 | 5 | 2.5 | +2.8 |
| 4 | 4 | -5 | 10.5 | +10.0 |
| 4 | 4 | -4 | 5.0 | +5.1 |
| 4 | 4 | -3 | 19.4 | +20.4 |
| 4 | 4 | -2 | 15.0 | +16.7 |
| 4 | 4 | -1 | 18.6 | +17.8 |
| 4 | 4 | 0 | 21.7 | +22.1 |
| 4 | 4 | 1 | 5.4 | +4.4 |
| 4 | 4 | 2 | 13.3 | +12.1 |
| 4 | 4 | 3 | 2.9 | -2.7 |
| 4 | 4 | 4 | 2.7 | +2.4 |
| 4 | 4 | 5 | 3.6 | -3.5 |
| 5 | 4 | -8 | 2.2 | +2.2 |
| 5 | 4 | -7 | 3.4 | +3.0 |
| 5 | 4 | -5 | 4.7 | +4.5 |
| 5 | 4 | -4 | 2.7 | +2.1 |
| 5 | 4 | -2 | 4.2 | +3.6 |
| 5 | 4 | -1 | 4.2 | -4.2 |
| 5 | 4 | 0 | 4.3 | -3.8 |
| 5 | 4 | 1 | 6.5 | -6.5 |
| 5 | 4 | 2 | 8.8 | -8.2 |
| 5 | 4 | 3 | 4.6 | -4.3 |
| 5 | 4 | 4 | 3.8 | -3.8 |
| 6 | 4 | -8 | 6.5 | -6.3 |
| 6 | 4 | -7 | 8.3 | +7.0 |
| 6 | 4 | -6 | 14.1 | -14.0 |
| 6 | 4 | -5 | 8.8 | +8.2 |
| 6 | 4 | -4 | 15.0 | -15.1 |
| 6 | 4 | -3 | 3.8 | +3.3 |
| 6 | 4 | -1 | 2.7 | -2.6 |
| 6 | 4 | 0 | 10.5 | +11.8 |
| 6 | 4 | 1 | 6.2 | -5.0 |
| 6 | 4 | 2 | 6.5 | +5.5 |
| 6 | 4 | 3 | 3.8 | -4.2 |
| 7 | 4 | -6 | 3.2 | -3.1 |
| 7 | 4 | -4 | 4.7 | -4.5 |
| 7 | 4 | -3 | 3.8 | -3.8 |
| 7 | 4 | -2 | 2.9 | -3.2 |
| 7 | 4 | -1 | 4.7 | -5.5 |
| 7 | 4 | 1 | 3.5 | -3.4 |
| 7 | 4 | 2 | 2.0 | -1.6 |
| 8 | 4 | -5 | 6.9 | -6.6 |
| 8 | 4 | -4 | 7.5 | +6.5 |
| 8 | 4 | -3 | 11.0 | -10.1 |
| 8 | 4 | -2 | 11.0 | +10.9 |
| 8 | 4 | -1 | 8.2 | -7.4 |
| 8 | 4 | 0 | 6.1 | +6.3 |
| 8 | 4 | 1 | 3.8 | -2.9 |
| 9 | 4 | -6 | 5.0 | -5.6 |
| 9 | 4 | -5 | 4.6 | +3.8 |
| 9 | 4 | -4 | 2.5 | -2.8 |
| 9 | 4 | -2 | 4.3 | +5.1 |
| 9 | 4 | -1 | 2.2 | -2.4 |
| 0 | 5 | 1 | 4.7 | +5.4 |
| 0 | 5 | 2 | 31.0 | +28.9 |
| 0 | 5 | 3 | 13.9 | +14.7 |
| 0 | 5 | 4 | 12.0 | +12.9 |
| 0 | 5 | 5 | 10.6 | +12.0 |
| 0 | 5 | 7 | 5.1 | +5.9 |
| 1 | 5 | -4 | 4.6 | -4.4 |
| 1 | 5 | -3 | 3.4 | +3.0 |
| 1 | 5 | -2 | 17.9 | -19.2 |
| 1 | 5 | -1 | 16.8 | +18.5 |
| 1 | 5 | 0 | 22.0 | -21.1 |
| 1 | 5 | 1 | 26.6 | +25.6 |
| 1 | 5 | 2 | 1.7 | -1.3 |
| 1 | 5 | 3 | 15.5 | +15.8 |
| 1 | 5 | 4 | 7.2 | +6.8 |
| 1 | 5 | 5 | 5.4 | +6.3 |
| 1 | 5 | 6 | 4.3 | +5.0 |
| 2 | 5 | -8 | 2.0 | +2.6 |
| 2 | 5 | -6 | 5.4 | +5.6 |
| 2 | 5 | -4 | 8.9 | +8.9 |
| 2 | 5 | -3 | 6.1 | +6.8 |
| 2 | 5 | -2 | 13.9 | +14.2 |
| 2 | 5 | -1 | 13.9 | +13.4 |
| 2 | 5 | 0 | 14.1 | +13.6 |
| 2 | 5 | 1 | 9.4 | +10.0 |
| 2 | 5 | 2 | 2.0 | +2.4 |
| 2 | 5 | 4 | 2.7 | -3.1 |
| 2 | 5 | 5 | 3.8 | -3.3 |
| 3 | 5 | -7 | 3.4 | +3.8 |
| 3 | 5 | -6 | 4.7 | -4.7 |
| 3 | 5 | -5 | 9.1 | +9.5 |
| 3 | 5 | -4 | 16.5 | -16.8 |
| 3 | 5 | -3 | 9.3 | +10.3 |
| 3 | 5 | -2 | 16.1 | -15.7 |
| 3 | 5 | 0 | 18.4 | +16.8 |
| 3 | 5 | 1 | 2.9 | -2.6 |
| 3 | 5 | 2 | 26.3 | +25.4 |
| 3 | 5 | 4 | 10.6 | +10.3 |
| 4 | 5 | -6 | 2.7 | -2.7 |
| 4 | 5 | -4 | 9.7 | -10.7 |
| 4 | 5 | -3 | 7.9 | +8.1 |
| 4 | 5 | -2 | 16.5 | -18.0 |
| 4 | 5 | -1 | 21.1 | +19.0 |
| 4 | 5 | 0 | 9.8 | -9.1 |
| 4 | 5 | 1 | 17.0 | +18.1 |
| 4 | 5 | 2 | 3.7 | +3.9 |
| 4 | 5 | 3 | 10.6 | +10.2 |
| 4 | 5 | 4 | 6.2 | +6.7 |
| 4 | 5 | 5 | 3.4 | +4.0 |
| 5 | 5 | -8 | 6.6 | +5.4 |
| 5 | 5 | -6 | 8.3 | +8.4 |
| 5 | 5 | -5 | 3.9 | +4.1 |
| 5 | 5 | -4 | 7.5 | +7.3 |
| 5 | 5 | -3 | 7.2 | +6.7 |
| 5 | 5 | -2 | 5.9 | +6.4 |
| 5 | 5 | -1 | 6.9 | +5.9 |
| 5 | 5 | 0 | 7.2 | +5.9 |
| 5 | 5 | 1 | 2.7 | +1.9 |
| 5 | 5 | 3 | 2.5 | -2.7 |
| 5 | 5 | 4 | 2.0 | -2.6 |
| 5 | 5 | 5 | 4.0 | -4.2 |
| 6 | 5 | -6 | 5.6 | -5.5 |
| 6 | 5 | -5 | 6.6 | +5.3 |
| 6 | 5 | -4 | 9.4 | -9.3 |
| 6 | 5 | -3 | 4.6 | +3.8 |
| 6 | 5 | -1 | 6.1 | -5.3 |
| 6 | 5 | 0 | 15.0 | +15.2 |
| 6 | 5 | 1 | 10.6 | -9.9 |
| 6 | 5 | 2 | 16.1 | +15.5 |
| 6 | 5 | 3 | 6.6 | -7.7 |
| 6 | 5 | 4 | 6.7 | +6.8 |
| 7 | 5 | -3 | 3.8 | +3.6 |
| 7 | 5 | -2 | 3.8 | -3.8 |
| 7 | 5 | -1 | 2.7 | +2.2 |
| 7 | 5 | 0 | 3.7 | -3.7 |
| 7 | 5 | 2 | 2.7 | -2.9 |
| 8 | 5 | -7 | 2.9 | +3.4 |
| 8 | 5 | -6 | 1.7 | -2.1 |
| 8 | 5 | -4 | 6.6 | -6.5 |
| 8 | 5 | -3 | 4.2 | -4.1 |
| 8 | 5 | -2 | 4.2 | -4.4 |
| 8 | 5 | -1 | 7.2 | -6.6 |
| 8 | 5 | 1 | 4.3 | -4.6 |
| 9 | 5 | -5 | 2.2 | +2.0 |
| 9 | 5 | -2 | 2.3 | +2.2 |
| 9 | 5 | -1 | 3.0 | -3.4 |
| 0 | 6 | 0 | 63.6 | -64.2 |
| 0 | 6 | 1 | 0.9 | +1.2 |
| 0 | 6 | 2 | 35.3 | -32.4 |
| 0 | 6 | 3 | 5.8 | +5.3 |
| 0 | 6 | 5 | 5.8 | +6.4 |
| 0 | 6 | 7 | 4.2 | +4.2 |
| 1 | 6 | -7 | 4.7 | +3.6 |
| 1 | 6 | -6 | 5.9 | +4.6 |
| 1 | 6 | -5 | 5.9 | +5.2 |
| 1 | 6 | -4 | 11.7 | +11.9 |
| 1 | 6 | -3 | 4.3 | +4.1 |
| 1 | 6 | -2 | 13.3 | +13.4 |
| 1 | 6 | 0 | 3.9 | -4.0 |
| 1 | 6 | 1 | 5.2 | -5.0 |
| 1 | 6 | 2 | 12.6 | -11.9 |
| 1 | 6 | 3 | 3.8 | -3.3 |
| 1 | 6 | 4 | 5.7 | -6.0 |
| 2 | 6 | -4 | 4.0 | +3.8 |
| 2 | 6 | 1 | 5.6 | +6.1 |
| 2 | 6 | 2 | 3.0 | +2.8 |
| 2 | 6 | 3 | 9.4 | +9.0 |
| 2 | 6 | 5 | 5.8 | +5.8 |
| 3 | 6 | -7 | 3.2 | -3.6 |
| 3 | 6 | -6 | 2.7 | -2.6 |
| 3 | 6 | -4 | 16.8 | -17.3 |
| 3 | 6 | -3 | 10.6 | +11.3 |
| 3 | 6 | -2 | 49.2 | -49.9 |
| 3 | 6 | -1 | 25.0 | +22.7 |
| 3 | 6 | 0 | 52.6 | -51.2 |
| 3 | 6 | 1 | 16.1 | +15.2 |
| 3 | 6 | 2 | 16.8 | -15.0 |
| 3 | 6 | 3 | 5.9 | +5.5 |
| 3 | 6 | 4 | 2.7 | +2.9 |
| 3 | 6 | 6 | 2.9 | +3.0 |
| 4 | 6 | -8 | 3.1 | +3.9 |
| 4 | 6 | -7 | 3.2 | +3.9 |
| 4 | 6 | -6 | 9.1 | +8.3 |
| 4 | 6 | -5 | 4.6 | +4.0 |
| 4 | 6 | -4 | 11.3 | +11.3 |
| 4 | 6 | -2 | 3.7 | +4.0 |
| 4 | 6 | 0 | 7.6 | -8.0 |
| 4 | 6 | 2 | 9.1 | -8.7 |
| 4 | 6 | 4 | 3.5 | -3.3 |
| 5 | 6 | -8 | 2.5 | +2.6 |
| 5 | 6 | -7 | 2.2 | +2.1 |
| 5 | 6 | -6 | 5.7 | +6.5 |
| 5 | 6 | -4 | 5.9 | +6.8 |
| 5 | 6 | 1 | 8.4 | +7.6 |
| 5 | 6 | 2 | 3.8 | +3.6 |

Table 2 (*cont.*)

| H | K | L | F(OBS) | F(CAL) |
|---|---|---|---|---|
| 5 | 6 | 3 | 11.0 | +10.5 |
| 5 | 6 | 4 | 2.7 | +2.4 |
| 6 | 6 | -6 | 7.6 | -7.4 |
| 6 | 6 | -5 | 9.1 | +8.2 |
| 6 | 6 | -4 | 19.0 | -21.2 |
| 6 | 6 | -3 | 18.7 | +21.0 |
| 6 | 6 | -2 | 32.6 | -32.4 |
| 6 | 6 | -1 | 23.3 | +22.1 |
| 6 | 6 | 0 | 20.8 | -22.1 |
| 6 | 6 | 1 | 10.2 | +9.5 |
| 6 | 6 | 2 | 3.4 | -3.7 |
| 7 | 6 | -5 | 3.4 | -2.5 |
| 8 | 6 | -6 | 5.9 | +4.8 |
| 8 | 6 | -5 | 4.4 | +3.7 |
| 8 | 6 | -4 | 3.1 | +2.9 |
| 8 | 6 | -1 | 3.0 | -3.0 |
| 9 | 6 | -5 | 5.7 | +6.1 |
| 9 | 6 | -4 | 4.0 | -4.2 |
| 9 | 6 | -3 | 8.3 | +9.6 |
| 9 | 6 | -2 | 4.0 | -4.4 |
| 9 | 6 | -1 | 5.6 | +6.8 |
| 0 | 7 | 2 | 11.3 | -11.8 |
| 0 | 7 | 3 | 1.9 | -1.8 |
| 0 | 7 | 4 | 3.8 | -3.8 |
| 0 | 7 | 7 | 2.2 | +1.9 |
| 1 | 7 | -5 | 2.3 | +2.2 |
| 1 | 7 | -4 | 4.7 | +4.4 |
| 1 | 7 | -3 | 9.7 | +8.6 |
| 1 | 7 | -2 | 20.0 | +19.2 |
| 1 | 7 | -1 | 20.7 | +21.4 |
| 1 | 7 | 0 | 22.9 | +23.0 |
| 1 | 7 | 1 | 25.3 | +22.9 |
| 1 | 7 | 2 | 8.9 | +9.3 |
| 1 | 7 | 3 | 8.9 | +8.6 |
| 1 | 7 | 4 | 3.2 | +3.0 |
| 1 | 7 | 7 | 2.2 | -2.2 |
| 2 | 7 | -5 | 3.4 | +3.4 |
| 2 | 7 | -4 | 10.6 | +10.4 |
| 2 | 7 | -3 | 5.8 | +5.8 |
| 2 | 7 | -2 | 13.2 | +13.5 |
| 2 | 7 | -1 | 3.7 | -3.5 |
| 2 | 7 | 1 | 16.0 | -15.6 |
| 2 | 7 | 2 | 6.1 | -6.3 |
| 2 | 7 | 3 | 11.0 | -11.6 |
| 2 | 7 | 4 | 3.4 | -2.4 |
| 2 | 7 | 5 | 3.1 | -3.5 |
| 3 | 7 | -5 | 6.7 | -6.8 |
| 3 | 7 | -4 | 8.6 | +7.9 |
| 3 | 7 | -3 | 8.6 | -9.4 |
| 3 | 7 | -2 | 8.6 | +8.5 |
| 3 | 7 | 0 | 9.7 | -9.3 |
| 3 | 7 | 1 | 6.6 | +5.9 |
| 3 | 7 | 2 | 16.9 | -15.8 |
| 3 | 7 | 3 | 3.4 | +3.5 |
| 3 | 7 | 4 | 7.5 | -7.5 |
| 4 | 7 | -5 | 5.4 | +4.8 |
| 4 | 7 | -4 | 7.2 | +7.3 |
| 4 | 7 | -3 | 11.6 | +11.4 |
| 4 | 7 | -2 | 14.1 | +14.6 |
| 4 | 7 | -1 | 17.1 | +16.0 |
| 4 | 7 | 0 | 10.4 | +11.3 |
| 4 | 7 | 1 | 12.1 | +12.1 |
| 4 | 7 | 2 | 4.0 | +3.2 |
| 4 | 7 | 3 | 4.2 | +4.2 |
| 5 | 7 | -7 | 6.9 | +6.3 |
| 5 | 7 | -6 | 8.7 | +9.7 |
| 5 | 7 | -5 | 8.3 | +8.7 |
| 5 | 7 | -4 | 15.0 | +16.7 |
| 5 | 7 | -3 | 3.2 | +3.8 |
| 5 | 7 | -2 | 8.6 | +9.3 |
| 5 | 7 | -1 | 12.4 | -11.0 |
| 5 | 7 | 0 | 5.2 | -6.0 |
| 5 | 7 | 1 | 16.0 | -18.1 |
| 5 | 7 | 2 | 7.5 | -8.2 |
| 5 | 7 | 3 | 9.7 | -10.4 |
| 5 | 7 | 4 | 2.7 | -3.2 |
| 6 | 7 | -7 | 5.4 | -5.2 |
| 6 | 7 | -6 | 5.4 | +6.1 |
| 6 | 7 | -5 | 8.9 | -9.6 |
| 6 | 7 | -4 | 7.6 | +7.9 |
| 6 | 7 | -3 | 7.4 | -6.4 |
| 6 | 7 | -1 | 5.4 | +4.5 |
| 6 | 7 | 0 | 10.6 | -11.4 |
| 6 | 7 | 1 | 7.3 | +8.0 |
| 6 | 7 | 2 | 10.6 | -11.7 |
| 6 | 7 | 3 | 3.4 | +3.8 |
| 7 | 7 | -5 | 2.9 | -2.6 |
| 7 | 7 | -4 | 3.3 | -2.5 |
| 7 | 7 | -3 | 4.0 | -3.5 |
| 7 | 7 | -2 | 4.0 | -3.7 |
| 7 | 7 | -1 | 2.5 | -2.7 |
| 7 | 7 | 0 | 3.7 | -3.8 |
| 7 | 7 | 2 | 2.2 | -2.5 |
| 8 | 7 | -6 | 3.7 | +2.6 |
| 8 | 7 | -5 | 7.3 | +6.3 |
| 8 | 7 | -4 | 1.9 | +1.4 |
| 8 | 7 | -3 | 4.3 | +4.4 |
| 8 | 7 | -2 | 4.6 | -4.6 |
| 8 | 7 | -1 | 1.9 | -2.0 |
| 8 | 7 | 0 | 7.8 | -8.0 |
| 8 | 7 | 1 | 4.0 | -5.1 |
| 9 | 7 | -4 | 1.4 | +1.5 |
| 0 | 8 | 1 | 7.2 | +7.1 |
| 0 | 8 | 2 | 3.2 | -3.1 |
| 0 | 8 | 3 | 8.1 | +8.8 |
| 0 | 8 | 5 | 2.5 | +2.7 |
| 1 | 8 | -5 | 3.6 | -3.3 |
| 1 | 8 | -4 | 3.2 | -3.1 |
| 1 | 8 | -3 | 7.8 | -8.1 |
| 1 | 8 | -1 | 11.7 | -12.7 |
| 1 | 8 | 0 | 10.6 | +11.4 |
| 1 | 8 | 1 | 2.5 | -2.5 |
| 1 | 8 | 2 | 9.4 | +9.9 |
| 1 | 8 | 3 | 8.7 | +8.4 |
| 1 | 8 | 4 | 3.6 | +2.0 |
| 1 | 8 | 5 | 8.0 | +7.7 |
| 2 | 8 | -6 | 4.0 | -4.8 |
| 2 | 8 | -5 | 5.7 | +5.7 |
| 2 | 8 | -3 | 17.5 | +17.0 |
| 2 | 8 | -2 | 19.7 | +20.8 |
| 2 | 8 | -1 | 29.4 | +28.4 |
| 2 | 8 | 0 | 28.6 | +26.8 |
| 2 | 8 | 1 | 20.0 | +18.9 |
| 2 | 8 | 2 | 11.7 | +10.7 |
| 2 | 8 | 3 | 4.2 | +3.7 |
| 3 | 8 | -6 | 5.4 | -5.1 |
| 3 | 8 | -5 | 2.5 | -2.4 |
| 3 | 8 | -4 | 9.7 | -11.0 |
| 3 | 8 | -3 | 6.1 | -5.5 |
| 3 | 8 | -2 | 6.1 | -7.4 |
| 3 | 8 | 0 | 3.2 | +2.8 |
| 3 | 8 | 1 | 11.7 | +10.2 |
| 3 | 8 | 2 | 4.2 | +3.8 |
| 3 | 8 | 3 | 8.9 | +8.2 |
| 3 | 8 | 5 | 2.0 | +2.7 |
| 4 | 8 | -5 | 5.2 | -4.8 |
| 4 | 8 | -4 | 2.5 | -2.1 |
| 4 | 8 | -3 | 7.4 | -7.3 |
| 4 | 8 | -2 | 3.1 | +2.7 |
| 4 | 8 | -1 | 4.9 | -4.2 |
| 4 | 8 | 0 | 8.8 | +8.1 |
| 4 | 8 | 1 | 5.4 | +4.5 |
| 4 | 8 | 2 | 7.2 | +6.8 |
| 4 | 8 | 3 | 8.0 | +8.1 |
| 4 | 8 | 4 | 3.0 | +3.5 |
| 4 | 8 | 5 | 5.2 | +5.3 |
| 5 | 8 | -7 | 5.6 | +6.0 |
| 5 | 8 | -5 | 16.0 | +15.1 |
| 5 | 8 | -4 | 14.1 | +14.2 |
| 5 | 8 | -3 | 25.0 | +26.6 |
| 5 | 8 | -2 | 27.4 | +30.0 |
| 5 | 8 | -1 | 27.6 | +27.6 |
| 5 | 8 | 0 | 25.2 | +24.2 |
| 5 | 8 | 1 | 12.7 | +13.0 |
| 5 | 8 | 2 | 7.1 | +6.8 |
| 5 | 8 | 4 | 2.2 | -1.9 |
| 6 | 8 | -7 | 2.5 | +1.8 |
| 6 | 8 | -6 | 6.5 | -5.7 |
| 6 | 8 | -4 | 8.0 | -6.6 |
| 6 | 8 | -1 | 2.5 | +2.6 |
| 6 | 8 | 0 | 2.5 | +2.4 |
| 6 | 8 | 1 | 7.6 | +6.5 |
| 6 | 8 | 3 | 4.7 | +5.2 |
| 7 | 8 | -3 | 2.3 | -2.0 |
| 7 | 8 | -1 | 2.3 | -2.3 |
| 7 | 8 | 1 | 1.7 | -1.6 |
| 7 | 8 | 2 | 1.7 | -1.2 |
| 8 | 8 | -5 | 6.0 | +5.7 |
| 8 | 8 | -4 | 8.9 | +9.9 |
| 8 | 8 | -3 | 9.8 | +9.5 |
| 8 | 8 | -2 | 9.8 | +10.4 |
| 8 | 8 | -1 | 8.9 | +8.7 |
| 8 | 8 | 0 | 4.2 | +3.8 |
| 0 | 9 | 1 | 23.4 | -25.1 |
| 0 | 9 | 3 | 8.1 | -6.8 |
| 0 | 9 | 4 | 2.3 | -2.4 |
| 1 | 9 | -6 | 7.2 | +7.2 |
| 1 | 9 | -4 | 7.4 | +7.7 |
| 1 | 9 | -3 | 5.8 | +4.8 |
| 1 | 9 | -2 | 1.5 | +1.5 |
| 1 | 9 | -1 | 3.8 | +3.9 |
| 1 | 9 | 0 | 1.0 | -0.7 |
| 1 | 9 | 1 | 6.6 | -5.6 |
| 1 | 9 | 2 | 5.3 | +4.3 |
| 1 | 9 | 3 | 7.2 | -7.5 |
| 1 | 9 | 4 | 4.3 | +5.0 |
| 1 | 9 | 5 | 3.4 | -3.6 |
| 1 | 9 | 6 | 2.7 | +3.2 |
| 2 | 9 | -6 | 5.2 | -4.8 |
| 2 | 9 | -5 | 2.5 | -2.7 |
| 2 | 9 | -4 | 10.6 | -11.3 |
| 2 | 9 | -3 | 2.9 | -3.0 |
| 2 | 9 | -2 | 8.6 | -9.3 |
| 2 | 9 | 0 | 5.4 | +5.4 |
| 2 | 9 | 1 | 5.2 | +4.3 |
| 2 | 9 | 2 | 11.7 | +10.9 |
| 2 | 9 | 4 | 6.1 | +5.8 |
| 2 | 9 | 5 | 3.1 | -2.7 |
| 3 | 9 | -5 | 3.5 | -4.1 |
| 3 | 9 | -4 | 3.4 | -4.1 |
| 3 | 9 | -3 | 15.3 | -14.5 |
| 3 | 9 | -2 | 13.9 | -14.6 |
| 3 | 9 | -1 | 22.9 | -23.8 |
| 3 | 9 | 0 | 13.9 | -15.2 |
| 3 | 9 | 1 | 13.7 | -13.9 |
| 3 | 9 | 2 | 8.2 | -8.3 |
| 3 | 9 | 4 | 3.2 | -3.7 |
| 3 | 9 | 5 | 2.5 | +3.0 |
| 4 | 9 | -7 | 2.3 | +2.3 |
| 4 | 9 | -6 | 5.6 | +5.5 |
| 4 | 9 | -5 | 4.3 | +3.8 |
| 4 | 9 | -4 | 4.2 | +3.9 |
| 4 | 9 | -3 | 4.0 | +3.6 |
| 4 | 9 | 1 | 5.9 | -6.1 |
| 4 | 9 | 2 | 2.5 | +2.5 |
| 4 | 9 | 3 | 3.4 | -4.2 |
| 4 | 9 | 4 | 2.9 | +2.4 |
| 5 | 9 | -6 | 6.7 | -6.1 |
| 5 | 9 | -4 | 9.8 | -10.9 |
| 5 | 9 | -2 | 3.5 | -3.0 |
| 5 | 9 | -1 | 3.5 | +3.7 |
| 5 | 9 | 0 | 12.4 | +12.3 |
| 5 | 9 | 1 | 5.1 | +6.1 |
| 5 | 9 | 2 | 15.0 | +15.7 |
| 5 | 9 | 3 | 4.5 | +4.0 |
| 5 | 9 | 4 | 8.6 | +9.5 |
| 6 | 9 | -6 | 1.7 | +1.6 |
| 6 | 9 | -5 | 5.1 | -4.5 |
| 6 | 9 | -4 | 4.2 | -3.8 |
| 6 | 9 | -3 | 9.4 | -8.7 |
| 6 | 9 | -2 | 7.9 | -8.3 |
| 6 | 9 | -1 | 9.4 | -8.9 |
| 6 | 9 | 0 | 5.9 | -5.6 |
| 6 | 9 | 1 | 3.2 | -2.8 |
| 6 | 9 | 2 | 2.7 | -2.8 |
| 6 | 9 | 3 | 1.3 | +1.7 |
| 7 | 9 | -6 | 2.0 | -1.9 |
| 7 | 9 | -4 | 2.2 | -2.2 |
| 7 | 9 | 0 | 2.0 | +2.1 |
| 8 | 9 | -4 | 2.2 | -2.0 |
| 8 | 9 | -2 | 1.7 | +1.5 |
| 8 | 9 | -1 | 3.1 | +3.3 |
| 8 | 9 | 0 | 4.2 | +4.8 |
| 0 | 10 | 1 | 5.4 | -5.5 |
| 0 | 10 | 2 | 3.0 | +2.7 |
| 0 | 10 | 3 | 7.3 | -6.6 |
| 0 | 10 | 4 | 4.2 | +4.5 |
| 0 | 10 | 6 | 1.7 | +2.2 |
| 1 | 10 | -6 | 2.9 | +3.0 |
| 1 | 10 | -5 | 5.3 | -5.3 |
| 1 | 10 | -4 | 11.7 | +11.1 |
| 1 | 10 | -3 | 5.8 | -6.1 |
| 1 | 10 | -2 | 16.5 | +15.5 |
| 1 | 10 | -1 | 3.4 | +3.4 |
| 1 | 10 | 0 | 6.0 | +7.0 |
| 1 | 10 | 1 | 13.0 | +12.7 |
| 1 | 10 | 2 | 2.7 | -2.5 |
| 1 | 10 | 3 | 10.2 | +11.1 |
| 1 | 10 | 4 | 4.2 | -4.2 |
| 1 | 10 | 5 | 5.4 | +6.1 |
| 1 | 10 | 6 | 2.2 | -2.8 |
| 2 | 10 | -4 | 3.2 | -3.3 |
| 2 | 10 | -3 | 7.2 | +6.0 |
| 2 | 10 | -2 | 7.9 | -9.1 |
| 2 | 10 | -1 | 9.8 | +10.2 |
| 2 | 10 | 0 | 8.8 | -8.8 |
| 2 | 10 | 1 | 10.2 | +10.7 |
| 2 | 10 | 3 | 7.5 | +6.9 |
| 3 | 10 | -6 | 3.0 | +3.2 |
| 3 | 10 | -5 | 2.3 | +2.3 |
| 3 | 10 | -4 | 5.4 | +5.3 |
| 3 | 10 | -3 | 6.1 | +6.2 |
| 3 | 10 | 0 | 2.9 | -2.4 |
| 3 | 10 | 1 | 8.3 | -7.8 |
| 3 | 10 | 3 | 7.5 | -7.1 |
| 3 | 10 | 5 | 2.7 | -2.8 |
| 4 | 10 | -6 | 3.6 | +3.6 |
| 4 | 10 | -5 | 2.3 | -2.3 |
| 4 | 10 | -4 | 8.2 | +9.0 |
| 4 | 10 | -2 | 8.6 | +8.8 |
| 4 | 10 | -1 | 7.6 | +7.1 |
| 4 | 10 | 0 | 3.8 | +3.2 |
| 4 | 10 | 1 | 9.1 | +8.3 |
| 4 | 10 | 3 | 3.8 | +4.0 |
| 5 | 10 | -7 | 5.2 | +4.9 |
| 5 | 10 | -6 | 4.7 | +5.6 |
| 5 | 10 | -5 | 10.2 | +11.5 |
| 5 | 10 | -3 | 15.0 | +14.8 |
| 5 | 10 | -2 | 8.2 | -9.5 |
| 5 | 10 | -1 | 9.1 | +9.2 |
| 5 | 10 | 0 | 12.0 | -13.1 |
| 5 | 10 | 1 | 2.3 | +2.1 |
| 5 | 10 | 2 | 6.1 | -6.8 |
| 6 | 10 | -5 | 3.6 | +3.0 |
| 6 | 10 | -3 | 2.3 | +2.5 |
| 6 | 10 | -1 | 2.3 | -2.1 |
| 6 | 10 | 1 | 4.6 | -5.0 |
| 7 | 10 | -5 | 2.3 | -2.3 |
| 7 | 10 | -4 | 3.4 | -2.3 |
| 7 | 10 | -3 | 4.6 | -3.7 |
| 7 | 10 | -2 | 4.6 | -4.0 |
| 7 | 10 | -1 | 3.5 | -2.8 |
| 7 | 10 | 0 | 2.5 | -2.9 |
| 7 | 10 | 1 | 2.0 | -2.0 |
| 8 | 10 | -4 | 3.2 | +3.0 |
| 8 | 10 | -3 | 2.0 | +2.1 |
| 8 | 10 | -2 | 2.5 | -2.4 |
| 8 | 10 | -1 | 3.0 | -2.7 |
| 0 | 11 | 2 | 8.4 | -8.4 |
| 0 | 12 | 0 | 15.1 | +15.9 |
| 0 | 12 | 2 | 8.5 | +9.6 |
| 0 | 18 | 0 | 6.2 | -5.2 |

119·9°, C–C–O 115·4°, and O=C–O 124·7°, are all within the range usually found in carboxylic acids. The three hydrogen bonds are 2·685, 2·684 and 2·682 Å. These dimensions compare favourably with those found in similar compounds, such as terephthalic acid (Bailey & Brown, 1966), succinic acid (Morrison & Robertson, 1949), benzoic acid (Sim, Robertson & Goodwin, 1955), phthalic acid (Nowacki & Jaggi, 1957) and acrylic acid (Higgs & Sass, 1963). A fuller comparison of the relative dimensions is given in the paper by Higgs & Sass. In general, the C–O bond length lies between 1·21 and 1·30 Å, and the hydrogen bond length between 2·60 and 2·70 Å. It would be an interesting study, now that so many carboxylic acid structure determinations have been carried out, to see if these bond lengths are related in any way to the strength of the acids, or whether they are merely a function of the packing of the molecules or a measure of the degree of disorder in the structure.

Both molecules of fumaric acid are very nearly planar. That situated at the centre of symmetry has an equation, referred to standard orthogonal axes:

$$0{\cdot}0030X+0{\cdot}2593Y+0{\cdot}9658Z=0\,.$$

The normal to this plane makes an angle of 15° with **c*** and 75° with **b**. No atom deviates from this plane by more than 0·002 Å.

The mean plane through the other molecule is not quite such a good fit. Its equation is:

$$-0{\cdot}0044X-0{\cdot}1255Y+0{\cdot}9921Z=-0{\cdot}9856$$

and the mean displacement of the carbon and oxygen atoms from this plane is 0·005 Å. If the two halves of the molecule are taken separately, their normals make an angle of 1·1°. This may be experimental error, but it may represent a slight deformation imposed on the molecule by the packing requirements of its neighbours. The normal to the mean plane of this molecule is inclined by 7·2° to **c*** and by 82·8° to **b**.

The packing of non-bonded sheets of molecules parallel to (001) accounts for the pronounced cleavage in this plane, which is also one of the twin planes in the crystal. It would seem that stacking faults can readily occur across this plane which behaves as a mirror. There is also a weaker cleavage plane parallel to (010). Fig. 3 is a diagrammatic projection of part of the contents of the unit-cell along **b**, showing nearest neighbour contacts across the cleavage plane (001).

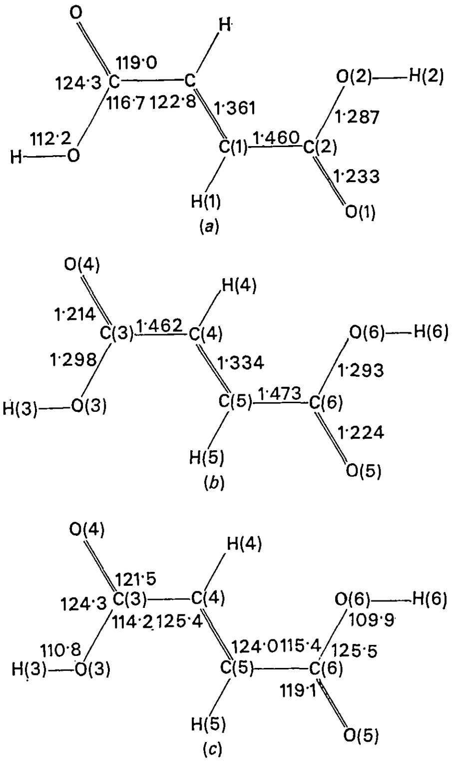

Fig. 2. (*a*) Bond lengths and angles for centrosymmetric molecule. (*b*) Bond lengths, (*c*) angles, for molecule in general position.

The thermal vibrations have not been analysed further. It is evident from the figures in Table 1 that for the carbon atoms the greatest amplitudes of vibration are along **b**, while for the oxygen atoms the greatest amplitudes are along **c**. The low values in the **a** direction are to be expected from the hydrogen bonding, but the values in the other directions would seem to imply an oscillation of the carboxyl group about the carbon to carbon bond.

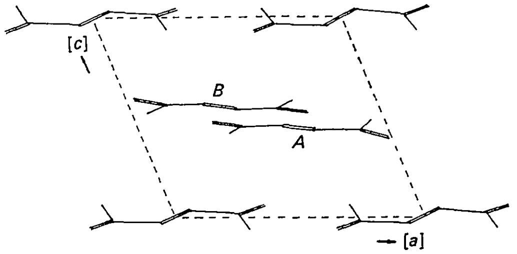

Fig. 3. Diagrammatic representation of nearest-neighbour contacts across the (001) cleavage plane. Molecule *A* has its mid-point near $\frac{2}{3}, \frac{1}{6}, \frac{1}{2}$; molecule *B* has its mid-point near $\frac{1}{3}, -\frac{1}{6}, \frac{1}{2}$.

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# A New Kind of Twinning

By Kathleen Lonsdale
*University College, Gower St., London, W.C.1, England*

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Where a single crystal undergoes chemical decomposition into a twinned crystal of another chemical substance, the twinning may be due to geometrical relationships between the parent crystal and the (secondary) twin individual of the decomposition product and not between the main and secondary twin individuals themselves.

A study has recently been made, by X-ray diffraction techniques, of the decomposition of anthracene photo-oxide, $C_{14}H_{10}O_2$, when single crystals are irradiated by Cu *K* or Mo *K* X-rays, or heated, or both (Lonsdale, Nave & Stephens, 1966). The final product is a severely mosaic twinned mixed crystal of variable proportions