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# The Crystal Structure of bis(*m*-Bromobenzoyl)Methane*

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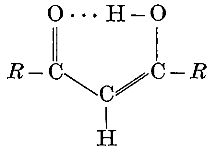
The crystal structure of bis(*m*-bromobenzoyl)methane has been determined, and the three dimensional scintillation counter data refined by anisotropic least squares. The molecule is nearly planar, with a maximum deviation of 0·12 Å from the least squares plane, and is tilted in the unit cell ±29·9° from the (010) plane. The molecule has a short intramolecular hydrogen bonded distance of 2·464 ± 0·015 Å, but the thermal parameters suggest an anomaly. Symmetry requires complete equivalence of the two C–O groups and the intervening C–C bonds of the enol ring, and the thermal parameters support the interpretation that this equivalence is real rather than statistical.

## Introduction

The dibenzoylmethanes have been the subject of considerable study because of their strong hydrogen bonding and their ability to chelate with a variety of metal ions. Infrared spectroscopy has been one of the principal tools used to study both the parent compounds and their chelates, along with studies of substituent effects on the ionization constants. In addition, several X-ray studies of the chelates have been made. It has been established that these $\beta$-diketones exist primarily in the enol form, but whether the enol is a resonance hybrid of



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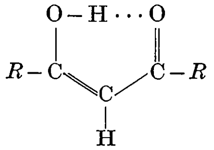

or is better represented by a single structure has remained a matter of conjecture.

Dibenzoylmethane, bis(*m*-chlorobenzoyl)methane, and bis(*m*-bromobenzoyl)methane crystallize in three different space groups, with the halogen substituted compounds having unit cells of about half the volume of the unit cell of dibenzoylmethane itself. Preliminary evidence indicated that the chloro derivative lacked a center of symmetry. Crystals of the bromo derivative were found to possess a center of symmetry, and the molecule also has twofold symmetry in the crystal, reducing the number of parameters. The bromo derivative has a sufficiently heavy atom to make the initial phases of the structure determination simple, but heavy enough to be less than ideal for obtaining precise distances between the lighter atoms.

## Experimental

Bis(*m*-Bromobenzoyl)methane was prepared by reaction of *m*-bromoacetophenone with ethyl *m*-bromobenzoate in the presence of sodium amide (Borduin, 1954). Crystals suitable for X-ray analysis, in the form of thin needles, were obtained by recrystallization from chloroform. Weissenberg and precession photographs indicated the unique space group *Pnca*, with lattice constants

$$a = 26{\cdot}48,\ b = 4{\cdot}054,\ c = 12{\cdot}79\ \text{Å}\,.$$

The observed flotation density was 1·8 g.cm.$^{-3}$; for four molecules in the unit cell the calculated density is 1·85 g.cm.$^{-3}$.

Complete visually judged Weissenberg intensity data were taken using copper radiation, with rotation about the *b* (needle) axis. In addition to the usual Lorentz and polarization corrections, a beam divergence correction (Dumke, 1956) was made, but no absorption correction was made. These data were used for the structure determination; however, because of the relatively high diffracting power of bromine, they were not of sufficient quality to obtain accurate bond distances between the light atoms in this structure.

For the refinement of the atomic positions a new set of data was obtained by counter methods, using a different crystal. The crystal selected for counter measurements was a needle 0·24 mm. in length and of equilateral trapezoidal cross section. The thickness perpendicular to the parallel faces was 0·055 mm.; the long parallel face measured 0·075 mm., and the short parallel face measured 0·048 mm. A General Electric XRD-5 X-ray unit equipped with a single crystal orienter and scintillation counter was used with the moving crystal-moving counter technique ($\theta, 2\theta$

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coupling), 3·0° take off angle and a 2·2° diffracted beam aperture. To eliminate errors involved in planimetering rate meter charts, the total count was recorded directly from the scaler. The copper radiation was filtered through nickel foil placed in the diffracted beam path. A 200 second scan, covering 3·33° in $2\theta$, was used for each reflection; average rate was ten reflections per hour. A standard reflection (24, 0, 0) was taken periodically and all data scaled to it. A slow variation of about 25% was observed in the standard reflection; this variation was probably caused by a faulty X-ray tube, which also showed about 25% iron radiation. Single crystal orienter settings were precalculated on the IBM 650 computer (Tulinsky, 1960). The background for each reflection was estimated from a plot of average background versus $2\theta$. All reciprocal lattice points up to $\theta = 77{\cdot}5°$ were scanned, resulting in 839 observed and 615 unobserved reflections.

The estimated error of each intensity was calculated with the formula

$$\sigma^2(I_0) = C_T + C_B + [0{\cdot}04(C_T - C_B)]^2 + [0{\cdot}1C_B]^2,$$

where $\sigma(I_0)$ is the standard deviation of the observed intensity, $C_T$ are the total counts, and $C_B$ are the background counts. The first two terms in this formula represent the statistical counting error. The third term represents errors proportional to the net count, e.g., fluctuations in the beam intensity, errors in the absorption correction, etc. This term sets a lover limit of 4% in the estimated relative error of $I_0$ when statistical counting errors and background errors become negligible. The last term adds an error contribution caused by uncertainty in the graphically estimated background count. Unobserved reflections were assigned their probable intensity value and probable error depending on the minimum intensity observable at the reciprocal lattice point in question (Hamilton, 1955). Graphical corrections were made for those reflections most seriously affected by noncharacteristic radiation (streaking) or by the iron radiation component. The streaking correction subtracts from the observed intensity, in addition to the normal background, the amount contributed by the streak from reflections radially inward in the reciprocal lattice. This correction can be relatively quite important in those cases where a weak reflection is immediately outward radially from a strong reflection. The streak may extend outward through several reflections, so that the correction is cumulative. On the other hand, the inward-extending shorter wave length streak (including the $\lambda/2$ component) is less important and its correction was neglected. The Lorentz and polarization corrections were made in the usual way. No extinction correction was used.

*Absorption correction.* With the more accurate counter data the absorption correction could not be neglected. Attempts to grind spherical or ellipsoidal crystals failed. It was decided, therefore, to carry out the necessary integration for each reflection on the Cyclone computer. An absorption correction program, designated ABCOR-I, was written for this purpose. The mathematical method used was similar to that used previously (Busing, 1957), but generalized to three dimensional data, and with the number of integration grid points, $m$, variable from $m = 4$ to $m = 7$. Because of memory restrictions, (only 1,024 words of memory were available on the Cyclone), it was necessary to restrict the planes bounding the crystal to be either parallel or perpendicular to the goniometer head axis, a condition frequently met in practice, as it is indeed in this case. The crystal coordinate system was defined by taking the $y$ axis toward the X-ray source, the $z$ axis vertical, and the $x$ axis toward the front of the orienter, when $\varphi = \chi = \theta = 0$. The planes bounding the crystal were expressed on this basis. For a general single crystal orienter setting $(\varphi, \chi, \theta)$, the direction cosines of the incident beam vector, transformed to crystal coordinates, are:

$$\begin{aligned} p_x &= \cos\varphi \cos\chi \sin\theta - \sin\varphi \cos\theta\ , \\ p_y &= \sin\varphi \cos\chi \sin\theta + \cos\varphi \cos\theta\ , \\ p_z &= \sin\chi \sin\theta\ . \end{aligned}$$

The direction cosines of the diffracted beam vector are:

$$\begin{aligned} p_x &= \cos\varphi \cos\chi \sin\theta + \sin\varphi \cos\theta\ , \\ p_y &= \sin\varphi \cos\chi \sin\theta - \cos\varphi \cos\theta\ , \\ p_z &= \sin\chi \sin\theta\ . \end{aligned}$$

The incident and diffracted beam path lengths to each grid point may then be found with the formulas given in Busing's paper, and the integral evaluated. The calculated absorption coefficient of 68·1 cm.$^{-1}$ was used (*Internationale Tabellen zur Bestimmung von Kristallstrukturen*, 1935). To check the accuracy of the integration, the absorption correction for a selected group of 11 reflections was calculated with $m = 4$, 5, and 6. The maximum difference between the $m = 4$ case and the $m = 6$ case was 0·96%, with an average of 0·22%. The maximum difference between the $m = 5$ case and the $m = 6$ case was 0·23%, with an average of 0·15%. It was decided that $m = 4$ would provide sufficient accuracy. The value of the transmission factor varied from 0·45 to 0·72, with an average near 0·65. Each integration with $m = 4$ required approximately 6 seconds on the Cyclone computer. Absorption corrections for the unobserved reflections were obtained graphically.

For carbon and oxygen the scattering factors of Berghuis (1955) were used; for bromine the scattering factor of Thomas & Umeda (1957), corrected for anomalous dispersion (Dauben & Templeton, 1955), was used.

## Structure determination

The projection onto the (010) plane, which has no overlapping atoms, was solved first. The approximate bromine parameters were obtained from the two-dimensional Patterson function. After improving the bromine parameters by calculation of an electron density projection, the oxygen and all carbon atoms were placed in approximate positions based on a planar molecular model with assumed distances and angles. After several cycles of structure factor calculation and electron density projection all atoms were well defined. The projection was then refined by the least-squares method.

The Patterson projection onto the (001) plane indicated a bromine $y$ parameter of $\frac{1}{4}$; however, a planar model based on this bromine $y$ parameter diverged during attempted refinement by the least squares method. The situation was complicated by an ambiguity which remained from the (010) projection, which made possible the substitution of new $z$ parameters $z'=\frac{1}{4}-z$ without affecting the fit to the $(h0l)$ reflections. A bounded Fourier electron density projection between $x=0$ and $x=\frac{1}{4}$ onto the (100) plane suggested that the bromine was shifted away slightly from $y=0{\cdot}25$ but did not indicate which way. The problem was solved by attempting to refine a large number of models having a bromine $y$ parameter shifted by varying amounts both ways from $y=0{\cdot}250$, using a limited number of reflections with the $l$ index odd, and with the $z$ transformation referred to above. Finally a model was found which would converge. The complete three dimensional film data were then refined by the least squares method (43 parameters); the final unweighted discrepancy factor was 0·155 for 587 observed reflections. The standard deviations of distances between light atoms were rather large, about 0·05 Å, with the film data. It was decided to obtain more accurate intensity data using a scintillation counter.

Fourier calculations were made on the IBM 650 using the program of Fitzwater & Williams (1959); least-squares calculations, primarily using only diagonal matrix elements, with individual isotropic temperature factors and layer scale factors, were also made on the IBM 650 using the program of Senko & Templeton (1956).

### *Refinement of the scintillation counter data*

The complete matrix program of Busing & Levy (1960), for the IBM 704, was used for refinement of the scintillation counter data, using individual anisotropic temperature factors and a single scale factor (87 parameters). Convergence was obtained after four anisotropic cycles with a weighted discrepancy factor, including unobserved reflections, of 0·113. However, a study of the individual structure factors revealed unusually poor agreement, greater than six times the expected error, for 26 reflections. These reflections were given zero weight for the following three least-squares cycles, which resulted in a drop of the weighted discrepancy factor, including unobserved reflections, to 0·068.

The intensities of the group of reflections showing poor agreement were remeasured, using a different crystal (the original crystal was accidentally lost). A marked improvement in the agreement between observed and calculated values of the intensities was noted in nearly every case. These remeasured intensities, plus the rest of the original data, were used to calculate three dimensional electron density and difference Fourier maps, using the IBM 650. These maps verified the correctness of the model by revealing no spurious holes or peaks in the electron density distribution. Both the electron density and difference maps

Table 1. *Final values of the parameters and their standard deviations*

The form of the temperature factor is $\exp(-\beta_{11}h^2-\beta_{22}k^2-\beta_{33}l^2-2\beta_{12}hk-2\beta_{13}hl-2\beta_{23}kl)$

| Atom | $x$ | $y$ | $z$ | $\beta_{11}$ | $\beta_{22}$ | $\beta_{33}$ | $\beta_{12}$ | $\beta_{13}$ | $\beta_{23}$ |
|---|---|---|---|---|---|---|---|---|---|
| Br | 0·03607 | 0·2306 | 0·15544 | 0·00107 | 0·0695 | 0·00737 | −0·00052 | 0·00083 | 0·0007 |
| $\delta$ | 0·00003 | 0·0003 | 0·00007 | 0·00001 | 0·0006 | 0·00006 | 0·00009 | 0·00002 | 0·0002 |
| O | 0·2097 | 0·848 | 0·2068 | 0·00193 | 0·175 | 0·0023 | −0·0083 | 0·0000 | −0·001 |
| $\delta$ | 0·0002 | 0·002 | 0·0004 | 0·00009 | 0·009 | 0·0003 | 0·0008 | 0·0001 | 0·001 |
| $C_1$ | 0·0883 | 0·399 | 0·0684 | 0·00080 | 0·054 | 0·0057 | 0·0007 | 0·0001 | 0·002 |
| $\delta$ | 0·0002 | 0·002 | 0·0006 | 0·00008 | 0·005 | 0·0005 | 0·0006 | 0·0002 | 0·001 |
| $C_2$ | 0·1291 | 0·553 | 0·1166 | 0·00106 | 0·042 | 0·0039 | 0·0005 | 0·0002 | −0·002 |
| $\delta$ | 0·0002 | 0·002 | 0·0005 | 0·00009 | 0·005 | 0·0004 | 0·0005 | 0·0001 | 0·001 |
| $C_3$ | 0·1678 | 0·683 | 0·0546 | 0·00099 | 0·045 | 0·0033 | 0·0012 | 0.0001 | −0·002 |
| $\delta$ | 0·0002 | 0·002 | 0·0005 | 0·00008 | 0·005 | 0·0003 | 0·0005 | 0·0001 | 0·001 |
| $C_4$ | 0·1648 | 0·651 | 0·9450 | 0·00110 | 0·071 | 0·0040 | 0·0006 | 0·0000 | 0·000 |
| $\delta$ | 0·0002 | 0·002 | 0·0005 | 0·00009 | 0·007 | 0·0004 | 0·0006 | 0·0001 | 0·001 |
| $C_5$ | 0·1234 | 0·494 | 0·9005 | 0·0015 | 0·075 | 0·0044 | −0·0008 | −0·0005 | 0·000 |
| $\delta$ | 0·0003 | 0·002 | 0·0005 | 0·0001 | 0·006 | 0·0004 | 0·0007 | 0·0002 | 0·002 |
| $C_6$ | 0·0843 | 0·366 | 0·9618 | 0·0013 | 0·072 | 0·0050 | −0·0009 | −0·0006 | 0·000 |
| $\delta$ | 0·0003 | 0·002 | 0·0005 | 0·0001 | 0·007 | 0·0005 | 0·0007 | 0·0002 | 0·001 |
| $C_7$ | 0·2101 | 0·850 | 0·1047 | 0·0013 | 0·078 | 0·0036 | 0·0004 | −0·0002 | −0·002 |
| $\delta$ | 0·0003 | 0·002 | 0·0005 | 0·0001 | 0·007 | 0·0004 | 0·0007 | 0·0002 | 0·001 |
| $C_8$ | 0·2500 | 0·000 | 0·0520 | 0·0011 | 0·067 | 0·0028 | −0·0005 | 0·0000 | 0·000 |
| $\delta$ |  |  | 0·0007 | 0·0001 | 0·008 | 0·0005 | 0·0009 |  |  |
| $H_2$ | 0·1308 | 0·574 | 0·2007 | 0·0018 | 0·076 | 0·0076 |  |  |  |
| $H_4$ | 0·1945 | 0·749 | 0·8962 | 0·0018 | 0·076 | 0·0076 |  |  |  |
| $H_5$ | 0·1212 | 0·471 | 0·8163 | 0·0018 | 0·076 | 0·0076 |  |  |  |
| $H_6$ | 0·0524 | 0·245 | 0·9262 | 0·0018 | 0·076 | 0·0076 |  |  |  |
| $H_8$ | 0·2500 | 0·000 | 0·9676 | 0·0018 | 0·076 | 0·0076 |  |  |  |

Table 2. *Comparison of the observed structure factors and the calculated structure factors based on the parameters shown in Table* 1

The first column shows the *h* index, the second is the observed value, and the third the calculated value. The special symbol following the observed value indicates an unobserved reflection entered as its probable value.

| | | |
|---|---|---|
| H, 0, 0 | | |
| 2 | 121 | 113 |
| 4 | 55 | 48 |
| 6 | 33 | 28 |
| 8 | 64 | 58- |
| 10 | 89 | 85- |
| 12 | 166 | 160- |
| 14 | 139 | 128- |
| 16 | 150 | 141- |
| 18 | 79 | 75- |
| 20 | 38 | 37- |
| 22 | 24 | 15 |
| 24 | 109 | 110 |
| 26 | 39 | 37 |
| 28 | 35 | 39 |
| 30 | 43 | 40 |
| 32 | 28 | 26 |
| H, 1, 0 | | |
| 2 | 44 | 41- |
| 4 | 289 | 314- |
| 6 | 147 | 147- |
| 8 | 155 | 152- |
| 10 | 109 | 107- |
| 12 | 76 | 74- |
| 14 | 6# | 6- |
| 16 | 45 | 44 |
| 18 | 75 | 75 |
| 20 | 132 | 131 |
| 22 | 62 | 60 |
| 24 | 52 | 52 |
| 26 | 28 | 26 |
| 28 | 17 | 19- |
| 30 | 12 | 13- |
| 32 | 17 | 21- |
| H, 2, 0 | | |
| 0 | 127 | 129- |
| 2 | 117 | 116- |
| 4 | 112 | 112- |
| 6 | 54 | 54- |
| 8 | 78 | 78 |
| 10 | 70 | 69 |
| 12 | 73 | 79 |
| 14 | 92 | 92 |
| 16 | 99 | 106 |
| 18 | 27 | 26 |
| 20 | 8 | 11 |
| 22 | 10 | 12- |
| 24 | 29 | 30- |
| 26 | 22 | 39- |
| 28 | 42 | 43- |
| 30 | 29 | 30- |
| H, 3, 0 | | |
| 2 | 31 | 32 |
| 4 | 46 | 46 |
| 6 | 62 | 70 |
| 8 | 83 | 81 |
| 10 | 70 | 70 |
| 12 | 23 | 21 |
| 14 | 21 | 20- |
| 16 | 24 | 22- |
| 18 | 33 | 34- |
| 20 | 34 | 33- |
| 22 | 19 | 34- |
| 24 | 27 | 28- |
| 26 | 12 | 13- |
| H, 4, 0 | | |
| 0 | 30 | 30 |
| 2 | 36 | 33 |
| 4 | 28 | 26 |
| 6 | 13 | 10 |
| 8 | 7# | 6 |
| 10 | 29 | 28- |
| 12 | 38 | 38- |
| 14 | 36 | 35- |
| 16 | 12 | 9- |
| 18 | 13 | 13- |
| 20 | 5# | 6- |
| H, 5, 0 | | |
| 2 | 10# | 6- |
| 4 | 11# | 6- |
| 6 | 12# | 20- |
| H, 1, 1 | | |
| 0 | 80 | 80- |
| 1 | 44 | 43- |
| 2 | 31 | 31- |
| 3 | 23 | 20 |
| 4 | 127 | 129 |
| 5 | 33 | 32- |
| 6 | 5# | 3- |
| 7 | 25 | 26- |
| 8 | 14 | 14- |
| 9 | 5# | 1 |
| 10 | 15 | 14- |
| 11 | 27 | 29- |
| 12 | 27 | 27- |
| 13 | 10 | 12 |
| 14 | 6# | 10- |
| 15 | 5# | 3 |
| 16 | 6# | 3- |
| 17 | 13 | 13 |
| 18 | 6# | 3- |
| 19 | 10 | 9 |
| 20 | 24 | 24 |
| 21 | 7# | 4- |
| 22 | 11 | 12- |
| 23 | 16 | 17 |
| 24 | 12 | 13- |
| 25 | 6# | 1 |
| 26 | 6# | 2 |
| 27 | 6# | 1 |
| 28 | 22 | 23 |
| 29 | 6# | 7- |
| 30 | 5# | 1- |
| 31 | 5# | 3- |
| 32 | 4# | 1- |
| H, 2, 1 | | |
| 1 | 23 | 26- |
| 2 | 5# | 5- |
| 3 | 31 | 33- |
| 4 | 21 | 22 |
| 5 | 16 | 17 |
| 6 | 5# | 3 |
| 7 | 28 | 30- |
| 8 | 77 | 79- |
| 9 | 25 | 25 |
| 10 | 5# | 11- |
| 11 | 22 | 23 |
| 12 | 6# | 2 |
| 13 | 20 | 21 |
| 14 | 6# | 5 |
| 15 | 18 | 20 |
| 16 | 36 | 36 |
| 17 | 7# | 4- |
| 18 | 7# | 5- |
| 19 | 18 | 18 |
| 20 | 7# | 7- |
| 21 | 7# | 7- |
| 22 | 7# | 8 |
| 23 | 8 | 7- |
| 24 | 11 | 10 |
| 25 | 6# | 8- |
| 26 | 6# | 2 |
| 27 | 12 | 10- |
| 28 | 5# | 7 |
| 29 | 5# | 4- |
| 30 | 4# | 2- |
| H, 3, 1 | | |
| 0 | 6# | 4- |
| 1 | 12 | 12 |
| 2 | 15 | 17- |
| 3 | 6# | 9 |
| 4 | 9 | 13- |
| 5 | 25 | 25 |
| 6 | 6# | 1 |
| 7 | 26 | 26 |
| 8 | 7# | 10- |
| 9 | 8 | 12 |
| 10 | 7# | 1- |
| 11 | 15 | 18 |
| 12 | 50 | 52 |
| 13 | 7# | 8- |
| 14 | 7# | |
| 15 | 6# | 2 |
| 16 | 6# | 2- |
| 17 | 17 | 15- |
| 18 | 7# | 7 |
| 19 | 16 | 15- |
| 20 | 6# | 1 |
| 21 | 11 | 11- |
| 22 | 6# | 4- |
| 23 | 9 | 10- |
| 24 | 5# | 1 |
| 25 | 5# | 1- |
| 26 | 5# | 7- |
| 27 | 4# | 2- |
| H, 4, 1 | | |
| 1 | 3# | 14 |
| 2 | 7# | 9 |
| 3 | 16 | 16 |
| 4 | 7# | 5 |
| 5 | 6# | 6 |
| 6 | 6 | 13 |
| 7 | 7# | 4- |
| 8 | 18 | 16 |
| 9 | 14 | 12- |
| 10 | 6# | 6- |
| 11 | 7# | 5- |
| 12 | 6# | 6 |
| 13 | 12 | 11- |
| 14 | 5# | 10 |
| 15 | 16 | 17- |
| 16 | 11 | 11- |
| 17 | 7 | 8- |
| 18 | 9 | 8- |
| 19 | 5# | 1- |
| 20 | 5# | 3- |
| H, 5, 1 | | |
| 0 | 6# | 7 |
| 1 | 6# | 3- |
| 2 | 6# | 8 |
| 3 | 7# | 8- |
| 4 | 7# | 5 |
| 5 | 8# | 9- |
| 6 | 7# | 7- |
| 7 | 7# | 6- |
| H, 0, 2 | | |
| 0 | 30 | 32 |
| 1 | 140 | 134- |
| 2 | 66 | 67- |
| 3 | 88 | 86- |
| 4 | 129 | 123- |
| 5 | 215 | 214- |
| 6 | 30 | 29- |
| 7 | 189 | 191- |
| 8 | 15 | 14 |
| 9 | 142 | 138- |
| 10 | 21 | 21 |
| 11 | 129 | 124- |
| 12 | 150 | 146 |
| 13 | 6# | 7- |
| 14 | 24 | 25 |
| 15 | 6# | 5 |
| 16 | 31 | 31 |
| 17 | 73 | 72 |
| 18 | 17 | 16 |
| 19 | 101 | 102 |
| 20 | 19 | 11- |
| 21 | 87 | 86 |
| 22 | 19 | 11- |
| 23 | 75 | 71 |
| 24 | 7# | 1 |
| 25 | 17 | 17 |
| 26 | 28 | 27- |
| 27 | 26 | 23 |
| 28 | 32 | 32- |
| 29 | 14 | 11- |
| 30 | 15 | 13- |
| 31 | 23 | 24- |
| 32 | 5# | 4- |
| 33 | 27 | 29- |
| H, 1, 2 | | |
| 1 | 161 | 167- |
| 2 | 30 | 30 |
| 3 | 174 | 182- |
| 4 | 13 | 14 |
| 5 | 45 | 47- |
| 6 | 48 | 51 |
| 7 | 24 | 22- |
| 8 | 129 | 129 |
| 9 | 93 | 91 |
| 10 | 23 | 25 |
| 11 | 91 | 91 |
| 12 | 18 | 19 |
| 13 | 122 | 120 |
| 14 | 6# | 2- |
| 15 | 126 | 126 |
| 16 | 53 | 55- |
| 17 | 72 | 72 |
| 18 | 24 | 24- |
| 19 | 46 | 45 |
| 20 | 21 | 18- |
| 21 | 17 | 13- |
| 22 | 27 | 28- |
| 23 | 21 | 22- |
| 24 | 22 | 20- |
| 25 | 46 | 47- |
| 26 | 7# | 3- |
| 27 | 52 | 51- |
| 28 | 6# | 3- |
| 29 | 32 | 33- |
| 30 | 13 | 12 |
| 31 | 17 | 30- |
| 32 | 20 | 21 |
| H, 2, 2 | | |
| 0 | 52 | 54 |
| 1 | 27 | 31 |
| 2 | 39 | 41 |
| 3 | 71 | 73 |
| 4 | 39 | 40 |
| 5 | 100 | 102 |
| 6 | 15 | 16- |
| 7 | 116 | 120 |
| 8 | 6# | 6 |
| 9 | 89 | 92 |
| 10 | 25 | 28- |
| 11 | 71 | 71 |
| 12 | 43 | 45- |
| 13 | 11 | 15 |
| 14 | 31 | 31- |
| 15 | 16 | 18- |
| 16 | 20 | 21- |
| 17 | 56 | 55- |
| 18 | 21 | 21- |
| 19 | 47 | 47- |
| 20 | 7# | 2 |
| 21 | 56 | 55- |
| 22 | 11 | 10 |
| 23 | 48 | 48- |
| 24 | 18 | 15 |
| 25 | 29 | 29- |
| 26 | 15 | 15 |
| 27 | 10 | 8- |
| 28 | 17 | 16 |
| 29 | 10 | 10 |
| 30 | 5# | 3 |
| H, 3, 2 | | |
| 1 | 71 | 71 |
| 2 | 22 | 22- |
| 3 | 47 | 48 |
| 4 | 27 | 29- |
| 5 | 29 | 30 |
| 6 | 25 | 27- |
| 7 | 6# | 7 |
| 8 | 14 | 16- |
| 9 | 20 | 19- |
| 10 | 7# | 8- |
| 11 | 57 | 58- |
| 12 | 13 | 12- |
| 13 | 59 | 59- |
| 14 | 7# | 3- |
| 15 | 17 | 34- |
| 16 | 7# | 6 |
| 17 | 34 | 32- |
| 18 | 17 | 16 |
| 19 | 20 | 21- |
| 20 | 21 | 21 |
| 21 | 6# | 3- |
| 22 | 16 | 14 |
| 23 | 14 | 14 |
| 24 | 6# | 6 |
| 25 | 12 | 21 |
| 26 | 5# | 2- |
| H, 4, 2 | | |
| 0 | 20 | 21- |
| 1 | 7# | 4- |
| 2 | 16 | 16- |
| 3 | 10 | 19- |
| 4 | 7# | 2- |
| 5 | 30 | 30- |
| 6 | 7# | |
| 7 | 35 | 34- |
| 8 | 7# | 9 |
| 9 | 16 | 31- |
| 10 | 6# | 5 |
| 11 | 12 | 12- |
| 12 | 6# | 3 |
| 13 | 9 | 11- |
| 14 | 6# | 7 |
| 15 | 6# | 8 |
| 16 | 15 | 16 |
| 17 | 13 | 13 |
| 18 | 5# | 5 |
| 19 | 19 | 17 |
| 20 | 5# | 2 |
| H, 5, 2 | | |
| 1 | 13 | 12- |
| 2 | 5# | 2 |
| 3 | 13 | 13- |
| 4 | 6# | 9 |
| 5 | 11 | 10- |
| 6 | 5# | 5 |
| H, 1, 3 | | |
| 0 | 33 | 41- |
| 1 | 15 | 13- |
| 2 | 14 | 14- |
| 3 | 13 | 12 |
| 4 | 27 | 25- |
| 5 | 11 | 10- |
| 6 | 8 | 5- |
| 7 | 5# | 3 |
| 8 | 56 | 57 |
| 9 | 20 | 22- |
| 10 | 13 | 13- |
| 11 | 6# | 3 |
| 12 | 6# | 2- |
| 13 | 6# | 4- |
| 14 | 6# | 4 |
| 15 | 11 | 11 |
| 16 | 39 | 38 |
| 17 | 6# | 2 |
| 18 | 6# | 2 |
| 19 | 7# | 5- |
| 20 | 7# | 5- |
| 21 | 7# | 6- |
| 22 | 7# | |
| 23 | 7# | 12 |
| 24 | 15 | 11- |
| 25 | 7# | 5 |
| 26 | 7# | 8- |
| 27 | 6# | 2 |
| 28 | 6# | 4- |
| 29 | 6# | 7- |
| 30 | 5# | 2- |
| 31 | 5# | 1 |
| 32 | 5# | 4 |
| H, 2, 3 | | |
| 1 | 6# | 8- |
| 2 | 11 | 14 |
| 3 | 6# | 3- |
| 4 | 64 | 63 |
| 5 | 6# | 1- |
| 6 | 6# | 7 |
| 7 | 9 | 11- |
| 8 | 16 | 17 |
| 9 | 6# | 2 |
| 10 | 13 | 15 |
| 11 | 11 | 12 |
| 12 | 6# | 8 |
| 13 | 12 | 12 |
| 14 | 6# | 1- |
| 15 | 7# | 4- |
| 16 | 7# | 4- |
| 17 | 7# | 4- |
| 18 | 7# | 7- |
| 19 | 7# | 10 |
| 20 | 35 | 34- |
| 21 | 7# | 3 |
| 22 | 12 | 11- |
| 23 | 7# | 1- |
| 24 | 6# | 4- |
| 25 | 6# | 2- |
| 26 | 6# | 2- |
| 27 | 5# | 2- |
| 28 | 11 | 9 |
| 29 | 5# | 5- |
| H, 3, 3 | | |
| 0 | 58 | 58 |
| 1 | 7# | 1- |
| 2 | 15 | 14 |
| 3 | 7# | 5 |
| 4 | 7# | 8 |
| 5 | 7# | 6 |
| 6 | 7# | 4 |
| 7 | 9 | 10 |
| 8 | 7# | 8- |
| 9 | 7# | |
| 10 | 17 | 16- |
| 11 | 7# | 7 |
| 12 | 18 | 16- |
| 13 | 7# | 4- |
| 14 | 18 | 18- |
| 15 | 7# | 8 |
| 16 | 19 | 18- |
| 17 | 7# | 4- |
| 18 | 7# | 7- |
| 19 | 7# | 6- |
| 20 | 6# | 4- |
| 21 | 6# | 4- |
| 22 | 6# | 3 |
| 23 | 5# | 1- |
| 24 | 23 | 21 |
| 25 | 5# | 3- |
| 26 | 5# | 5 |
| H, 4, 3 | | |
| 1 | 7# | 5 |
| 2 | 7# | |
| 3 | 7# | 5 |
| 4 | 23 | 20- |
| 5 | 7# | 3 |
| 6 | 21 | 19- |
| 7 | 7# | 4- |
| 8 | 15 | 13- |
| 9 | 7# | 7- |
| 10 | 13 | 11- |
| 11 | 7# | 7 |
| 12 | 6# | 6- |
| 13 | 6# | 1 |
| 14 | 6# | 3 |
| 15 | 11 | 12- |
| 16 | 6# | 6 |
| 17 | 5# | 4- |
| 18 | 14 | 11 |
| 19 | 5# | 1 |
| 20 | 13 | 13 |
| H, 5, 3 | | |
| 0 | 6# | 9- |
| 1 | 5# | 2- |
| 2 | 6# | 8- |
| 3 | 5# | 4- |
| 4 | 5# | 6- |
| H, 0, 4 | | |
| 0 | 180 | 181- |
| 1 | 49 | 53 |
| 2 | 134 | 128- |
| 3 | 89 | 90 |
| 4 | 46 | 47- |
| 5 | 112 | 110 |
| 6 | 45 | 42- |
| 7 | 139 | 138 |
| 8 | 22 | 19- |
| 9 | 86 | 86 |
| 10 | 63 | 63 |
| 11 | 82 | 81 |
| 12 | 147 | 141 |
| 13 | 26 | 22- |
| 14 | 85 | 85 |
| 15 | 17 | 19- |
| 16 | 56 | 55 |
| 17 | 60 | 60- |
| 18 | 51 | 51 |
| 19 | 32 | 54- |
| 20 | 30 | 30 |
| 21 | 54 | 53- |
| 22 | 16 | 11- |
| 23 | 44 | 45- |
| 24 | 34 | 32- |
| 25 | 27 | 26- |
| 26 | 31 | 30- |
| 27 | 7# | 7 |
| 28 | 32 | 30- |
| 29 | 16 | 15 |
| 30 | 30 | 31- |
| 31 | 22 | 23 |
| 32 | 22 | 23- |
| H, 1, 4 | | |
| 1 | 115 | 117 |
| 2 | 44 | 43 |
| 3 | 94 | 101 |
| 4 | 87 | 86 |
| 5 | 31 | 32 |
| 6 | 112 | 112 |
| 7 | 5# | 4 |
| 8 | 122 | 120 |
| 9 | 67 | 66- |
| 10 | 74 | 76 |
| 11 | 70 | 71- |
| 12 | 43 | 44 |
| 13 | 83 | 85- |
| 14 | 12 | 11 |
| 15 | 75 | 73- |
| 16 | 41 | 39- |
| 17 | 36 | 36- |
| 18 | 49 | 49- |
| 19 | 25 | 23- |
| 20 | 52 | 50- |
| 21 | 9 | 9 |
| 22 | 48 | 47- |
| 23 | 28 | 29 |
| 24 | 38 | 37- |
| 25 | 36 | 35 |
| 26 | 21 | 22- |
| 27 | 33 | 33 |
| 28 | 6# | 4- |
| 29 | 28 | 28 |
| 30 | 11 | 8 |
| 31 | 7 | 13 |
| H, 2, 4 | | |
| 0 | 64 | 60 |
| 1 | 23 | 24- |
| 2 | 72 | 74 |
| 3 | 44 | 46- |
| 4 | 79 | 81 |
| 5 | 89 | 91- |
| 6 | 14 | 17 |
| 7 | 61 | 62- |
| 8 | 33 | 33- |
| 9 | 60 | 62- |
| 10 | 40 | 39- |
| 11 | 30 | 31- |
| 12 | 45 | 44- |
| 13 | 7# | 9- |
| 14 | 62 | 61- |
| 15 | 14 | 13 |
| 16 | 58 | 58- |
| 17 | 35 | 34 |
| 18 | 35 | 34- |
| 19 | 50 | 51 |
| 20 | 7# | |
| 21 | 38 | 36 |
| 22 | 7# | |
| 23 | 27 | 25 |
| 24 | 6# | 10 |
| 25 | 13 | 11 |
| 26 | 25 | 26 |
| 27 | 5# | 2 |
| 28 | 29 | 30 |
| 29 | 14 | 12- |
| H, 3, 4 | | |
| 1 | 52 | 51- |
| 2 | 28 | 30- |
| 3 | 31 | 31- |
| 4 | 37 | 36- |
| 5 | 19 | 17- |
| 6 | 41 | 39- |
| 7 | 7# | 4 |
| 8 | 42 | 43- |
| 9 | 26 | 25 |
| 10 | 38 | 39- |
| 11 | 22 | 23 |
| 12 | 17 | 15- |
| 13 | 35 | 33 |
| 14 | 7# | 1 |
| 15 | 37 | 37 |
| 16 | 7# | 9 |
| 17 | 23 | 23 |
| 18 | 19 | 16 |
| 19 | 6# | 6 |
| 20 | 26 | 26 |
| 21 | 6# | 6- |
| 22 | 28 | 28 |
| 23 | 15 | 14- |
| 24 | 17 | 15 |
| 25 | 18 | 18- |
| H, 4, 4 | | |
| 0 | 29 | 28- |
| 1 | 7# | 4 |
| 2 | 26 | 25- |
| 3 | 20 | 19 |
| 4 | 7# | 7- |
| 5 | 22 | 20 |
| 6 | 7# | 5- |
| 7 | 21 | 19 |
| 8 | 6# | |
| 9 | 17 | 16 |
| 10 | 14 | 12 |
| 11 | 17 | 16 |
| 12 | 19 | 17 |
| 13 | 6# | 1- |
| 14 | 20 | 18 |
| 15 | 5# | 4- |
| 16 | 13 | 12 |
| 17 | 12 | 11- |
| 18 | 14 | 12 |
| 19 | 13 | 13- |
| H, 1, 5 | | |
| 0 | 53 | 52 |
| 1 | 16 | 17- |
| 2 | 5 | 3- |
| 3 | 19 | 17 |
| 4 | 35 | 37- |
| 5 | 15 | 16 |
| 6 | 6# | 2 |
| 7 | 27 | 26 |
| 8 | 22 | 21 |
| 9 | 6# | 1- |
| 10 | 6# | 4 |
| 11 | 14 | 15 |
| 12 | 22 | 23- |
| 13 | 6# | 3 |
| 14 | 6# | 1- |
| 15 | 6# | 2 |
| 16 | 13 | 14 |
| 17 | 18 | 18- |
| 18 | 7# | 3- |
| 19 | 11 | 9- |
| 20 | 7# | 8- |
| 21 | 12 | 11- |
| 22 | 7# | 4 |
| 23 | 7# | 2 |
| 24 | 14 | 12 |
| 25 | 6# | 6- |
| 26 | 6# | 2- |
| 27 | 6# | 1 |
| 28 | 11 | 10- |
| 29 | 5# | 1 |
| 30 | 5# | 3 |
| 31 | 5# | 3 |
| H, 2, 5 | | |
| 1 | 28 | 29 |
| 2 | 6# | 7 |
| 3 | 13 | 14 |
| 4 | 10 | 9- |
| 5 | 8 | 8 |
| 6 | 6# | 7- |
| 7 | 6# | 4 |
| 8 | 6# | 4 |
| 9 | 8 | 9- |
| 10 | 6# | 2 |
| 12 | 6# | 1- |
| 13 | 20 | 21- |
| 14 | 7# | 3- |
| 15 | 17 | 16- |
| 16 | 7# | 4 |
| 17 | 13 | 13- |
| 18 | 7# | 8 |
| 19 | 7# | 2- |
| 20 | 7# | 3 |
| 21 | 1# | 4 |
| 22 | 6# | 3- |
| 23 | 12 | 8 |
| 24 | 6# | 3- |
| 25 | 12 | 9 |
| 26 | 5# | |
| 27 | 8 | 5 |
| 28 | 5# | 4- |
| 29 | 4# | 5 |
| H, 3, 5 | | |
| 0 | 7# | 9 |
| 1 | 13 | 12- |
| 2 | 7# | 2- |
| 3 | 19 | 10- |
| 4 | 11 | 10- |
| 5 | 12 | 19- |
| 6 | 7# | 2- |
| 7 | 21 | 20- |
| 8 | 7# | 11 |
| 9 | 24 | 25- |
| 10 | 7# | 6 |
| 11 | 7# | 9- |
| 12 | 7# | 9- |
| 13 | 7# | 4- |
| 14 | 7# | 5 |
| 15 | 14 | 13 |
| 16 | 7# | 7 |
| 17 | 13 | 8 |
| 18 | 6# | 4- |
| 19 | 15 | 12 |
| 20 | 6# | 7- |
| 21 | 12 | 11 |
| 22 | 6# | 3- |
| 23 | 11 | 11 |
| 24 | 5# | 2 |
| 25 | 4# | |
| H, 4, 5 | | |
| 1 | 13 | 9- |
| 2 | 7# | 4 |
| 3 | 19 | 19- |
| 4 | 7# | |
| 5 | 7# | 8- |
| 6 | 6# | 1- |
| 7 | 6# | 3 |
| 8 | 6# | 2 |
| 9 | 6# | 6 |
| 10 | 6# | 7 |
| 11 | 16 | 14 |
| 12 | 6# | 2- |
| 13 | 15 | 14 |
| 14 | 6# | 8- |
| 15 | 11 | 9 |
| 16 | 5# | |
| 17 | 5# | 7 |
| 18 | 4# | 1 |
| H, 0, 6 | | |
| 0 | 61 | 60 |
| 1 | 11 | 8- |
| 2 | 139 | 143 |
| 3 | 79 | 76 |
| 4 | 108 | 109 |
| 5 | 37 | 36 |
| 6 | 25 | 23 |
| 7 | 55 | 53 |
| 8 | 38 | 37- |
| 9 | 58 | 56 |
| 10 | 82 | 83- |
| 11 | 32 | 29 |
| 12 | 98 | 99- |
| 13 | 18 | 18 |
| 14 | 91 | 91- |
| 15 | 14 | 9 |
| 16 | 68 | 67- |
| 17 | 15 | 8- |
| 18 | 45 | 43- |
| 19 | 24 | 22- |
| 20 | 7# | |
| 21 | 40 | 39- |
| 22 | 26 | 23 |
| 23 | 24 | 25- |
| 24 | 23 | 18 |
| 25 | 25 | 23- |
| 26 | 50 | 51 |
| 27 | 6# | 7- |
| 28 | 42 | 45 |
| 29 | 9 | 8- |
| 30 | 25 | 25 |
| 31 | 4# | 4 |
| H, 1, 6 | | |
| 1 | 63 | 62 |
| 2 | 64 | 67- |
| 3 | 38 | 37 |
| 4 | 65 | 67- |
| 5 | 37 | 38 |
| 6 | 116 | 120- |
| 7 | 16 | 13- |
| 8 | 110 | 113- |
| 9 | 14 | 10- |
| 10 | 71 | 73- |
| 11 | 23 | 22- |
| 12 | 32 | 31- |
| 13 | 34 | 32- |
| 14 | 7# | 7 |
| 15 | 42 | 40- |
| 16 | 44 | 44 |
| 17 | 35 | 36- |
| 18 | 59 | 58 |
| 19 | 22 | 21- |
| 20 | 51 | 48 |
| 21 | 17 | 14- |
| 22 | 57 | 56 |
| 23 | 7# | 4 |
| 24 | 34 | 33 |
| 25 | 15 | 9 |
| 26 | 12 | 9 |
| 27 | 16 | 16 |
| 28 | 5# | 2- |
| 29 | 16 | 17 |
| 30 | 20 | 21- |
| H, 2, 6 | | |
| 0 | 92 | 94- |
| 1 | 9 | 5- |
| 2 | 80 | 81- |
| 3 | 22 | 19- |
| 4 | 40 | 41- |
| 5 | 42 | 43- |
| 6 | 7# | 4- |
| 7 | 28 | 28- |
| 8 | 6# | 5 |
| 9 | 32 | 31- |
| 10 | 47 | 47 |
| 11 | 23 | 23- |
| 12 | 68 | 69 |
| 13 | 20 | 21- |
| 14 | 63 | 62 |
| 15 | 7# | 2 |
| 16 | 44 | 40 |
| 17 | 7# | 4 |
| 18 | 33 | 32 |
| 19 | 26 | 25 |
| 20 | 7# | 7 |
| 21 | 16 | 12 |
| 22 | 19 | 15- |
| 23 | 23 | 21 |
| 24 | 28 | 28- |
| 25 | 17 | 16 |
| 26 | 29 | 30- |
| 27 | 5# | 8 |
| 28 | 20 | 22- |
| H, 3, 6 | | |
| 1 | 29 | 29- |
| 2 | 27 | 24 |
| 3 | 7# | 8- |
| 4 | 44 | 44 |
| 5 | 7# | 9- |
| 6 | 47 | 47 |
| 7 | 8# | 11- |
| 8 | 40 | 39 |
| 9 | 7# | 4 |
| 10 | 28 | 26 |
| 11 | 17 | 16 |
| 12 | 20 | 19 |
| 13 | 16 | 15 |
| 14 | 7# | 3 |
| 15 | 18 | 17 |
| 16 | 18 | 17- |
| 17 | 13 | 11 |
| 18 | 30 | 28- |
| 19 | 13 | 13 |
| 20 | 32 | 32- |
| 21 | 6# | 7 |
| 22 | 24 | 23- |
| 23 | 5# | 6- |
| 24 | 12 | 13- |
| H, 4, 6 | | |
| 0 | 29 | 28 |
| 1 | 7# | 3- |
| 2 | 23 | 22 |
| 3 | 7# | 8 |
| 4 | 18 | 15 |
| 5 | 6# | 8 |
| 6 | 6# | 5 |
| 8 | 13 | 11- |
| 9 | 6# | 9 |
| 10 | 12 | 12- |
| 11 | 6# | 10 |
| 12 | 17 | 15- |
| 13 | 5# | 2 |
| 14 | 18 | 17- |
| 15 | 5# | 1 |
| 16 | 21 | 21- |
| H, 1, 7 | | |
| 0 | 19 | 17 |
| 1 | 6 | 9- |
| 2 | 28 | 29 |
| 3 | 11 | 10- |
| 4 | 18 | 17- |
| 5 | 9 | 11- |
| 6 | 6# | 4 |
| 7 | 6# | |
| 8 | 9 | 8- |
| 9 | 6# | 6- |
| 10 | 7# | 7- |
| 11 | 12 | 12 |
| 12 | 13 | 14 |
| 13 | 7# | 7- |
| 14 | 18 | 18- |
| 15 | 7# | 1 |
| 16 | 21 | 19- |
| 17 | 7# | 5- |
| 18 | 7# | 3 |
| 19 | 14 | 11 |
| 20 | 7# | 7- |
| 21 | 7# | 6 |
| 22 | 7# | 8 |
| 23 | 6# | 2 |
| 24 | 7# | 6 |
| 25 | 6# | 4- |
| 26 | 6# | 7 |
| 27 | 5# | 2- |
| 28 | 5# | 4- |
| 29 | 4# | 1- |
| H, 2, 7 | | |
| 2 | 14 | 13- |
| 3 | 7# | 9- |
| 4 | 25 | 24- |
| 5 | 7# | 5- |
| 6 | 24 | 24- |
| 7 | 20 | 20 |
| 8 | 13 | 13 |
| 9 | 7# | 4 |
| 10 | 22 | 22- |
| 12 | 7# | 9- |
| 13 | 7# | 1 |
| 14 | 7# | 7 |
| 15 | 7# | 8 |
| 16 | 7# | 11- |
| 17 | 16 | 10 |
| 18 | 19 | 17 |
| 19 | 7# | 4- |
| 20 | 22 | 19 |
| 21 | 6# | 2- |
| 22 | 6# | 8 |
| 23 | 6# | 6- |
| 24 | 6# | |
| 25 | 5# | 6- |
| 26 | 5# | 1 |
| 27 | 5# | 5- |
| H, 3, 7 | | |
| 0 | 28 | 28- |
| 1 | 7# | 3- |
| 2 | 15 | 12- |
| 3 | 18 | 17 |
| 4 | 7# | 3- |
| 5 | 7# | 7 |
| 6 | 7# | 10- |
| 7 | 7# | 5 |
| 8 | 7# | 5 |
| 9 | 7# | 3 |
| 10 | 20 | 18 |
| 11 | 7# | 2 |
| 12 | 7# | 3- |
| 13 | 6# | 1 |
| 14 | 21 | 19 |
| 15 | 6# | 3- |
| 16 | 13 | 11 |
| 17 | 6# | 5- |
| 18 | 6# | 5 |
| 19 | 6# | 5- |
| 20 | 5# | 3 |
| 21 | 10 | 8- |
| 22 | 5# | 3- |
| 23 | 4# | |
| H, 4, 7 | | |
| 1 | 13 | 12 |
| 2 | 6# | 4- |
| 3 | 6# | 3- |
| 4 | 14 | 12 |
| 5 | 6# | 1 |
| 6 | 15 | 14 |
| 7 | 6# | 2 |
| 8 | 6# | 7 |
| 9 | 6# | 2- |
| 10 | 12 | 12 |
| 11 | 5# | 8- |
| 12 | 5# | 3 |
| 13 | 5# | 6- |
| 14 | 5# | 4- |
| 15 | 4# | 1- |
| H, 0, 8 | | |
| 0 | 44 | 41- |
| 1 | 12 | 9 |
| 2 | 24 | 23 |
| 3 | 76 | 78- |
| 4 | 14 | 5 |
| 5 | 74 | 77- |
| 6 | 7# | 9 |
| 7 | 91 | 95- |
| 8 | 34 | 35 |
| 9 | 112 | 120- |
| 10 | 15 | 7 |
| 11 | 38 | 38- |
| 12 | 42 | 43- |

Table 2 (*cont.*)

| | | |
|---|---|---|
| 13 | 32 | 31- |
| 14 | 8# | 10 |
| 15 | 52 | 52 |
| 16 | 22 | 16 |
| 17 | 39 | 38 |
| 18 | 21 | 21- |
| 19 | 48 | 46 |
| 20 | 23 | 20- |
| 21 | 52 | 51 |
| 22 | 7# | 8- |
| 23 | 36 | 35 |
| 24 | 23 | 22- |
| 25 | 34 | 33 |
| 26 | 6# | 1 |
| 27 | 6# | 4 |
| 28 | 5# | 6 |
| 29 | 4# | 7- |
| H, 1, 8 | | |
| 1 | 89 | 93- |
| 2 | 7# | 7- |
| 3 | 59 | 59- |
| 4 | 29 | 29 |
| 5 | 62 | 65- |
| 6 | 7# | 9- |
| 7 | 16 | 12 |
| 8 | 28 | 27- |
| 9 | 25 | 22 |
| 10 | 7# | 1 |
| 11 | 79 | 81 |
| 12 | 16 | 9- |
| 13 | 77 | 79 |
| 14 | 23 | 21- |
| 15 | 54 | 54 |
| 16 | 7# | 5 |
| 17 | 50 | 50 |
| 18 | 7# | 7- |
| 19 | 16 | 9 |
| 20 | 18 | 17- |
| 21 | 7# | 5 |
| 22 | 7# | 11 |
| 23 | 24 | 21- |
| 24 | 16 | 12 |
| 25 | 29 | 28- |
| 26 | 12 | 10 |
| 27 | 29 | 30- |
| 28 | 11 | 15 |
| H, 2, 8 | | |
| 0 | 7# | 10 |
| 1 | 7# | 7 |
| 2 | 7# | 4- |
| 3 | 46 | 46 |
| 4 | 19 | 21- |
| 5 | 57 | 58 |
| 6 | 8# | 9 |
| 7 | 71 | 73 |
| 8 | 7# | 4- |
| 9 | 51 | 51 |
| 10 | 8# | 9- |
| 11 | 21 | 29 |
| 12 | 7# | 7- |
| 13 | 17 | 16 |
| 14 | 7# | 4 |
| 15 | 19 | 12- |
| 16 | 7# | 7 |
| 17 | 31 | 30- |
| 18 | 19 | 17 |
| 19 | 39 | 39- |
| 20 | 6# | 2- |
| 21 | 38 | 37- |
| 22 | 15 | 12 |
| 23 | 25 | 24- |
| 24 | 13 | 11 |
| 25 | 17 | 18- |
| 26 | 4# | |
| H, 3, 8 | | |
| 1 | 42 | 41 |
| 2 | 8# | 10 |
| 3 | 38 | 39 |
| 4 | 7# | 4 |
| 5 | 8# | 12 |
| 6 | 7# | 5- |
| 7 | 7# | 5- |
| 8 | 7# | 3- |
| 9 | 20 | 17- |
| 10 | 7# | 4 |
| 11 | 25 | 23- |
| 12 | 7# | 6 |
| 13 | 28 | 27- |
| 14 | 7# | 8 |
| 15 | 33 | 33- |
| 16 | 6# | 8 |
| 17 | 24 | 24- |
| 18 | 5# | 5 |
| 19 | 13 | 12- |
| 20 | 5# | 5- |
| 21 | 5# | 3 |
| H, 4, 8 | | |
| 0 | 6# | 7 |
| 1 | 16 | 13- |
| 2 | 6# | 3 |
| 3 | 17 | 16- |
| 4 | 6# | 7- |
| 5 | 21 | 19- |
| 6 | 5# | 3 |
| 7 | 18 | 17- |
| 8 | 5# | 1 |
| 9 | 15 | 15- |
| 10 | 5# | 3 |
| 11 | 13 | 12- |
| 12 | 5# | 4 |
| H, 1, 9 | | |
| 0 | 7# | 2 |
| 1 | 15 | 9 |
| 2 | 17 | 12- |
| 3 | 18 | 14- |
| 4 | 7# | 3 |
| 5 | 21 | 15- |
| 6 | 7# | 6 |
| 7 | 7# | 3- |
| 8 | 32 | 32- |
| 9 | 7# | 3 |
| 10 | 23 | 21 |
| 11 | 20 | 14 |
| 12 | 24 | 22 |
| 13 | 20 | 19- |
| 14 | 17 | 12 |
| 15 | 7# | 6- |
| 16 | 26 | 25- |
| 17 | 7# | 3 |
| 18 | 7# | 8 |
| 19 | 13 | 10 |
| 20 | 7# | 5 |
| 21 | 7# | 8 |
| 22 | 6# | 5- |
| 23 | 6# | 1- |
| 24 | 6# | |
| 25 | 5# | 3 |
| 26 | 5# | 4- |
| 27 | 4# | 2- |
| H, 2, 9 | | |
| 1 | 24 | 22- |
| 2 | 16 | 11 |
| 3 | 7# | |
| 4 | 21 | 22- |
| 5 | 7# | 3- |
| 6 | 31 | 28 |
| 7 | 20 | 16 |
| 8 | 22 | 19 |
| 9 | 7# | 4- |
| 10 | 7# | 2 |
| 11 | 8# | 1 |
| 12 | 7# | 1- |
| 13 | 7# | 2 |
| 14 | 7# | |
| 15 | 7# | 4 |
| 17 | 18 | 18 |
| 18 | 18 | 14- |
| 19 | 6# | 3 |
| 20 | 16 | 14 |
| 22 | 12 | 9- |
| 23 | 12 | 8- |
| 24 | 5# | 6- |
| H, 3, 9 | | |
| 0 | 22 | 22- |
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| 2 | 25 | 22 |
| 3 | 20 | 16 |
| 4 | 20 | 14 |
| 5 | 7# | 4 |
| 6 | 7# | 4- |
| 7 | 7# | 4 |
| 8 | 7# | 4- |
| 9 | 7# | 8 |
| 10 | 7# | 6- |
| 11 | 7# | 4 |
| 12 | 15 | 13- |
| 13 | 6# | 4 |
| 14 | 6# | 7- |
| 15 | 6# | 3- |
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| 17 | 5# | 1 |
| 18 | 5# | 5- |
| 19 | 5# | 5- |
| H, 4, 9 | | |
| 1 | 6# | 5 |
| 2 | 15 | 15- |
| 3 | 6# | 5 |
| 4 | 5# | 1 |
| 5 | 5# | 5 |
| 6 | 5# | 5- |
| 7 | 5# | |
| 8 | 10 | 10- |
| 9 | 5# | 2- |
| H, 0,10 | | |
| 0 | 62 | 62- |
| 1 | 7# | 3- |
| 2 | 74 | 76- |
| 3 | 33 | 32 |
| 4 | 37 | 34- |
| 5 | 35 | 35 |
| 6 | 23 | 22- |
| 7 | 22 | 17 |
| 8 | 27 | 23 |
| 9 | 7# | 2 |
| 10 | 63 | 62 |
| 11 | 10 | 13- |
| 12 | 16 | 13- |
| 13 | 19 | 14 |
| 14 | 76 | 78 |
| 15 | 8 | 9- |
| 16 | 52 | 53 |
| 17 | 22 | 20- |
| 18 | 28 | 28 |
| 19 | 25 | 25- |
| 20 | 7# | 10 |
| 21 | 21 | 18- |
| 22 | 13 | 8- |
| 23 | 6# | 1- |
| 24 | 16 | 19- |
| 25 | 4# | 3 |
| 26 | 22 | 24- |
| H, 1,10 | | |
| 1 | 33 | 32 |
| 2 | 30 | 29 |
| 3 | 7# | 8 |
| 4 | 49 | 51 |
| 5 | 7# | 2 |
| 6 | 71 | 73 |
| 7 | 20 | 18- |
| 8 | 24 | 21 |
| 9 | 7# | 9- |
| 10 | 58 | 62 |
| 11 | 22 | 18- |
| 12 | 25 | 22 |
| 13 | 18 | 15- |
| 14 | 7# | 8- |
| 15 | 18 | 9- |
| 16 | 7# | 4 |
| 17 | 18 | 13- |
| 18 | 38 | 38- |
| 19 | 6# | 4 |
| 20 | 36 | 38- |
| 21 | 6# | 10 |
| 22 | 31 | 32- |
| 23 | 20 | 20 |
| 24 | 17 | 19- |
| 25 | 14 | 16 |
| H, 2,10 | | |
| 0 | 53 | 55 |
| 1 | 7# | 6- |
| 2 | 45 | 46 |
| 3 | 18 | 17- |
| 4 | 7# | 8 |
| 5 | 14 | 9- |
| 6 | 23 | 23 |
| 7 | 18 | 14- |
| 8 | 7# | 7- |
| 9 | 19 | 16- |
| 10 | 28 | 25- |
| 11 | 7# | 5- |
| 12 | 36 | 34- |
| 13 | 7# | 8 |
| 14 | 39 | 39- |
| 15 | 7 | 16 |
| 16 | 26 | 26- |
| 17 | 13 | 9 |
| 18 | 15 | 14- |
| 19 | 13 | 10 |
| 20 | 15 | 17- |
| 21 | 12 | 12 |
| 22 | 5# | 4 |
| 23 | 4# | 4 |
| H, 3,10 | | |
| 1 | 7# | 2- |
| 2 | 7# | 4- |
| 3 | 16 | 12- |
| 4 | 22 | 21- |
| 5 | 12 | 9- |
| 6 | 27 | 26- |
| 7 | 7# | 2 |
| 8 | 29 | 29- |
| 9 | 13 | 10 |
| 10 | 22 | 20- |
| 11 | 15 | 12 |
| 12 | 6# | 10- |
| 13 | 14 | 11 |
| 14 | 5# | 2- |
| 15 | 6# | 8 |
| 16 | 12 | 10 |
| 17 | 5# | 1- |
| H, 4,10 | | |
| 0 | 10 | 11- |
| 1 | 5# | 1- |
| 2 | 9 | 9- |
| 3 | 4# | 1- |
| H, 1,11 | | |
| 0 | 7# | 1 |
| 1 | 7# | 9- |
| 2 | 7# | 2- |
| 3 | 7# | 4 |
| 4 | 7# | 5- |
| 5 | 7# | 2- |
| 6 | 7# | 6 |
| 7 | 7# | 4 |
| 8 | 7# | 14- |
| 9 | 26 | 25 |
| 10 | 7# | 3 |
| 11 | 7# | 6- |
| 12 | 7# | 9 |
| 13 | 7# | 2 |
| 14 | 7# | 8 |
| 15 | 17 | 14- |
| 16 | 15 | 10- |
| 17 | 7# | |
| 18 | 6# | 5 |
| 19 | 6# | |
| 20 | 6# | 1- |
| 21 | 5# | 4- |
| 22 | 5# | 3 |
| 23 | 5# | 1 |
| H, 2,11 | | |
| 1 | 7# | 2 |
| 2 | 7# | 7 |
| 3 | 7# | 3 |
| 4 | 7# | 12- |
| 5 | 24 | 24 |
| 6 | 7# | 5 |
| 7 | 7# | 10- |
| 8 | 9 | 13 |
| 9 | 7# | 1- |
| 10 | 7# | 2 |
| 11 | 6# | 12- |
| 12 | 6# | |
| 13 | 16 | 13- |
| 14 | 6# | 4 |
| 15 | 6# | 3- |
| 16 | 6# | 6- |
| 17 | 6# | 5- |
| 18 | 5# | 2- |
| 19 | 6# | 11 |
| 20 | 5# | 7 |
| H, 3,11 | | |
| 0 | 14 | 13- |
| 1 | 6# | 7 |
| 2 | 10 | 9 |
| 3 | 11 | 8- |
| 4 | 6# | 7 |
| 5 | 6# | 5- |
| 6 | 6# | |
| 7 | 13 | 9- |
| 8 | 6# | 1 |
| 9 | 14 | 11- |
| 10 | 6# | 1 |
| 11 | 5# | 2- |
| 12 | 12 | 10- |
| 13 | 5# | 2- |
| 14 | 5# | 1 |
| 15 | 8 | 7 |
| H, 0,12 | | |
| 0 | 8# | 4- |
| 1 | 7# | 7 |
| 2 | 45 | 47 |
| 3 | 31 | 33 |
| 4 | 19 | 17 |
| 5 | 32 | 32 |
| 6 | 7# | 1- |
| 7 | 23 | 24 |
| 8 | 7# | 7- |
| 9 | 31 | 32 |
| 10 | 24 | 23- |
| 11 | 15 | 13 |
| 12 | 29 | 27- |
| 13 | 26 | 26 |
| 14 | 32 | 31- |
| 15 | 7# | 6- |
| 16 | 15 | 12- |
| 17 | 6# | 4- |
| 18 | 6# | 4- |
| 19 | 20 | 19- |
| 20 | 5# | 6 |
| 21 | 23 | 26- |
| 22 | 15 | 16 |
| H, 1,12 | | |
| 1 | 35 | 38 |
| 2 | 25 | 24- |
| 3 | 21 | 21 |
| 4 | 7# | 6- |
| 5 | 18 | 16 |
| 6 | 35 | 35- |
| 7 | 7# | 5- |
| 8 | 27 | 26- |
| 9 | 7# | 1- |
| 10 | 21 | 19- |
| 11 | 22 | 21- |
| 12 | 7# | 2- |
| 13 | 22 | 22- |
| 14 | 6# | 8 |
| 15 | 19 | 20- |
| 16 | 18 | 18 |
| 17 | 27 | 28- |
| 18 | 23 | 23 |
| 19 | 11 | 13- |
| 20 | 6# | 9 |
| 21 | 5# | 7- |
| H, 2,12 | | |
| 0 | 21 | 18- |
| 1 | 7# | 1- |
| 2 | 22 | 20- |
| 3 | 16 | 15- |
| 4 | 16 | 12- |
| 5 | 17 | 16- |
| 6 | 7# | 1 |
| 7 | 27 | 29- |
| 8 | 6# | 1 |
| 9 | 19 | 19- |
| 10 | 19 | 19 |
| 11 | 15 | 13- |
| 12 | 21 | 21 |
| 13 | 6# | 9- |
| 14 | 18 | 17 |
| 15 | 5# | 1- |
| 16 | 5# | 3 |
| 17 | 5# | 9 |
| 18 | 11 | 11 |
| H, 3,12 | | |
| 1 | 6# | 8- |
| 2 | 6# | 4 |
| 3 | 17 | 17- |
| 4 | 14 | 11 |
| 5 | 10 | 10- |
| 6 | 15 | 16 |
| 7 | 5# | 2- |
| 8 | 13 | 11 |
| 9 | 5# | 5 |
| 10 | 5# | 4 |
| 11 | 9 | 9 |
| H, 1,13 | | |
| 0 | 7# | 7 |
| 1 | 7# | |
| 2 | 7# | 9 |
| 3 | 15 | 12- |
| 4 | 7# | 10- |
| 5 | 7# | 6 |
| 6 | 7# | 4 |
| 7 | 7# | 4 |
| 8 | 6# | 5 |
| 9 | 6# | |
| 10 | 13 | 7- |
| 11 | 6# | 4- |
| 12 | 6# | 6- |
| 13 | 6# | 5 |
| 14 | 5# | 2- |
| 15 | 5# | |
| 16 | 5# | 3 |
| 17 | 5# | |
| 18 | 5# | 2- |
| H, 2,13 | | |
| 1 | 6# | 3- |
| 2 | 6# | 2- |
| 3 | 6# | 2 |
| 4 | 6# | 4- |
| 5 | 6# | 3 |
| 6 | 17 | 15- |
| 7 | 6# | 3 |
| 8 | 6# | 1 |
| 9 | 6# | |
| 10 | 6# | 4- |
| 11 | 5# | 1- |
| 12 | 5# | 2- |
| 13 | 5# | 1- |
| 14 | 5# | 1 |
| 15 | 4# | 2- |
| H, 3,13 | | |
| 1 | 5# | 1 |
| 2 | 5# | 7- |
| 3 | 4# | 4- |
| 4 | 4# | 4- |
| H, 0,14 | | |
| 0 | 6# | 7 |
| 1 | 7# | 9 |
| 2 | 7# | 10 |
| 3 | 11 | 19- |
| 4 | 18 | 18 |
| 5 | 25 | 24- |
| 6 | 6# | 8 |
| 7 | 31 | 30- |
| 8 | 6# | 7- |
| 9 | 18 | 15- |
| 10 | 6# | 1- |
| 11 | 6# | 7- |
| 12 | 5# | 2- |
| 13 | 6# | 5- |
| 14 | 14 | 12- |
| 15 | 5# | 3 |
| 16 | 16 | 19- |
| H, 1,14 | | |
| 1 | 25 | 25- |
| 2 | 6# | 3- |
| 3 | 17 | 13- |
| 4 | 6# | 8- |
| 5 | 16 | 12- |
| 6 | 6# | 8- |
| 7 | 6# | 4 |
| 8 | 6# | 13- |
| 9 | 6# | 10 |
| 10 | 15 | 13- |
| 11 | 20 | 18 |
| 12 | 6# | 10- |
| 13 | 20 | 20 |
| 14 | 5# | 3- |
| 15 | 15 | 16 |
| H, 2,14 | | |
| 0 | 13 | 13- |
| 1 | 5# | 8 |
| 2 | 6# | 7- |
| 3 | 15 | 14 |
| 4 | 6# | 3- |
| 5 | 17 | 16 |
| 6 | 6# | 5- |
| 7 | 6# | 9 |
| 8 | 5# | 7- |
| 9 | 18 | 20 |
| 10 | 4# | 4 |
| H, 1,15 | | |
| 0 | 6# | 2 |
| 1 | 5# | 1- |
| 2 | 5# | 1- |
| 3 | 6# | 5- |
| 4 | 5# | 2- |
| 5 | 5# | 4 |
| 6 | 5# | 2- |
| 7 | 5# | 4- |
| 8 | 5# | 5 |
| 9 | 5# | 3- |
| 10 | 4# | 2 |
| H, 0,16 | | |
| 0 | 13 | 14- |
| 1 | 4# | 1- |
| 2 | 14 | 16- |
| 3 | 4# | 3- |
| 4 | 12 | 15- |
| 5 | 4# | 2- |

clearly showed the presence of five of the six hydrogen atoms in the asymmetric unit, the exception being the enolic hydrogen.

For the final refinement of the revised data these hydrogens were included isotropically at calculated positions along a line parallel to the intersection of the least-squares benzene ring plane and the bisector plane between the neighboring ring atoms at a distance of 1·08 Å from the attached carbon atoms. The $C_8$ hydrogen was placed on the twofold axis 1·08 Å from $C_8$. At the end of the final two least-squares refinement cycles the weighted discrepancy factor, including unobserved reflections, was 0·071; the unweighted discrepancy factor for 839 observed reflections was 0·057. Table 1 gives the final values of the parameters and their standard deviations. The quantity

$$[\Sigma w(F_o-F_c)^2/(m-n)]^{\frac{1}{2}}$$

was 1·48, indicating a reasonable assignment of weighting factors. All standard deviations quoted in this paper are based on the complete inverse matrix including covariances; analysis of the data was greatly facilitated by use of the IBM 704 Function and Error program of Busing (1959). Table 2 gives a comparison of the observed structure factors and the calculated structure factors based on the parameters shown in Table 1.

## Discussion

The structure consists of nearly planar molecules, with their long axis along *a* and short axis along *c*, tilted ±29·9° from the (010) plane (Fig. 1). Least-squares planes were fitted through the benzene ring (*A*), the enol ring (*B*), and the entire molecule (*C*); Table 3 shows the distances of the atoms from each plane and the equations of the planes in Å units. Both the benzene ring and the enol ring are planar within experimental error; the maximum deviation of the entire molecule from its least-squares plane is

Table 3. *Distances from the least-squares planes and equations of the planes in Å units*

| Atom | *A* | *B* | *C* |
|---|---|---|---|
| Br | 0·014 | 0·124 | 0·120 |
| O | −0·041 | −0·001 | −0·001 |
| $C_1$ | 0·001 | 0·026 | 0·022 |
| $C_2$ | −0·005 | 0·026 | 0·023 |
| $C_3$ | 0·005 | −0·026 | −0·028 |
| $C_4$ | −0·002 | −0·100 | −0·102 |
| $C_5$ | −0·002 | −0·104 | −0·108 |
| $C_6$ | 0·003 | −0·038 | −0·042 |
| $C_7$ | 0·025 | 0·001 | 0·000 |
| $C_8$ | 0·082 | 0·000 | 0·000 |

(*A*) $-1{\cdot}9794x+3{\cdot}5972y-0{\cdot}1270z=1$

(*B*) $-2{\cdot}3866x+4{\cdot}1438y+0{\cdot}0000z=1$

(*C*) $-2{\cdot}2797x+3{\cdot}9642y+0{\cdot}0000z=1$

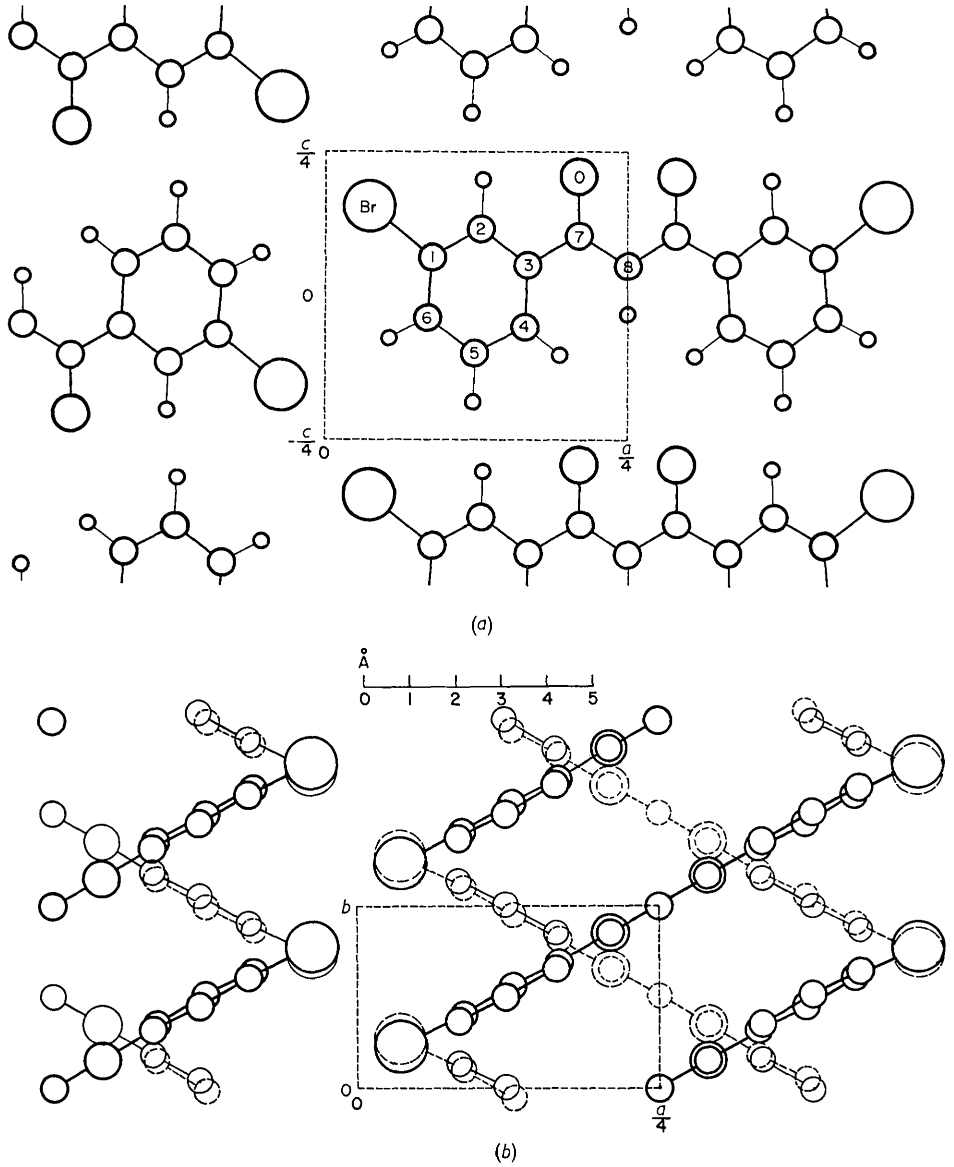


Fig. 1. (*a*) Projection of the structure of the (010) plane, including all hydrogens except the enolic hydrogen in calculated positions; (*b*) Projection of the structure onto the (001) plane, with hydrogens omitted for clarity. The light circles represent atoms behind the asymmetric unit, and the dotted circles represent atoms in front. The asymmetric unit is enclosed in dashed lines.

Table 4. *Intramolecular bond distances and bond angles*

| Atoms | Distance | Atoms | Angle |
|---|---|---|---|
| Br–$C_1$ | 1·901 ± 0·007 Å | Br–$C_1$–$C_2$ | 117·8 ± 0·5° |
| $C_1$–$C_2$ | 1·392 ± 0·009 | $C_6$–$C_1$–$C_2$ | 122·7 ± 0·7 |
| $C_2$–$C_3$ | 1·400 ± 0·009 | $C_6$–$C_1$–Br | 119·5 ± 0·6 |
| $C_3$–$C_4$ | 1·410 ± 0·008 | $C_1$–$C_2$–$C_3$ | 119·1 ± 0·6 |
| $C_4$–$C_5$ | 1·389 ± 0·010 | $C_2$–$C_3$–$C_7$ | 119·3 ± 0·6 |
| $C_5$–$C_6$ | 1·397 ± 0·010 | $C_7$–$C_3$–$C_4$ | 121·6 ± 0·6 |
| $C_6$–$C_1$ | 1·375 ± 0·009 | $C_2$–$C_3$–$C_4$ | 119·2 ± 0·6 |
| $C_3$–$C_7$ | 1·457 ± 0·009 | $C_3$–$C_4$–$C_5$ | 119·6 ± 0·7 |
| $C_7$–$C_8$ | 1·393 ± 0·008 | $C_4$–$C_5$–$C_6$ | 121·6 ± 0·6 |
| $C_7$–O | 1·306 ± 0·008 | $C_5$–$C_6$–$C_1$ | 117·8 ± 0·7 |
| O–O | 2·464 ± 0·015 | $C_3$–$C_7$–O | 115·6 ± 0·6 |
| | | $C_8$–$C_7$–O | 119·4 ± 0·7 |
| | | $C_3$–$C_7$–$C_8$ | 125·0 ± 0·6 |
| | | $C_7$–$C_8$–$C_7$ | 122·2 ± 0·8 |
| | | $C_7$–O–O | 89·5 ± 0·8 |

0·120 Å, with the bromine atom being above the plane, and $C_4$, $C_5$, and $C_6$ being below the plane. The inclination of the benzene ring from the molecular plane is ± 1·7°. The intramolecular distances and angles (Table 4), which are uncorrected for thermal motion, are all very close to the expected values, with an average benzene ring C–C distance of 1·394 Å. The C–O bond (1·306) is intermediate between the normal C=O (1·23) and C–O (1·43) distances, but perhaps slightly longer than expected for 50% double bond character (1·29). The $C_7$–$C_8$ distance (1·393) is the same as the C–C distances in the benzene ring within experimental error, and is considerably shorter than the normal single bond value. The $C_3$–$C_7$ distance

(1·457) is also shorter than the single bond value, but in good agreement with a single bond C–C between carbons with planar trigonal coordination (Dewar & Schmeising, 1960). The short O–O distance of 2·464 Å confirms the presence of a strong hydrogen bond; the standard deviation for this distance is larger than the others because of the larger thermal motion and the twofold symmetry relationship between these atoms. The Br–$C_1$ distance (1·901 ± 0·007) is longer than the corresponding distance observed by electron diffraction methods in bromobenzene (1·86 ± 0·02), Yuzawa & Yamaka, 1953), or in *p*-fluorobromobenzene (1·87 ± 0·02, Oosaka & Akimoto, 1953), or observed crystallographically in 1,3,5-tribromobenzene (1·86 ± 0·04, Milledge & Pant, 1960). The Br–$C_1$ distance is especially sensitive to systematic errors, which cause ripples in the electron density map in the vicinity of the heavy atom; during the process of refining the various sets of data this effect was noticed as erratic changes in this distance until the final cycles. In view of this fact, and of the rather large standard deviations reported in the literature cited above, no significance is attached to the difference between the value found here and those cited above.

Table 5. *Nearest non-bonded neighbor distances less than* 3 Å

| Atoms | Distance (Å) | Atoms | Distance (Å) | Atoms | Distance (Å) |
|---|---|---|---|---|---|
| Br–Br | 3·689 | $C_2$–$C_4$ | 2·42 | $C_5$–$H_4$ | 2·15 |
| –$C_2$ | 2·83 | –$C_5$ | 2·78 | –$H_6$ | 2·16 |
| –$C_6$ | 2·84 | –$C_6$ | 2·43 | $C_6$–$H_5$ | 2·14 |
| –$H_2$ | 2·93 | –$C_7$ | 2·46 | $C_7$–$C_7$ | 2·44 |
| –$H_6$ | 2·96 | $C_3$–$C_5$ | 2·42 | –$H_2$ | 2·68 |
| O–$C_2$ | 2·71 | –$C_6$ | 2·82 | –$H_4$ | 2·73 |
| –$C_3$ | 2·34 | –$C_8$ | 2·53 | –$H_8$ | 2·14 |
| –$C_7$ | 2·78 | –$H_2$ | 2·16 | $C_8$–$H_4$ | 2·68 |
| –$C_8$ | 2·33 | –$H_4$ | 2·16 | $H_2$–$H_5$ | 2·38 |
| –$H_2$ | 2·37 | –$H_8$ | 2·76 | –$H_5$ | 2·67 |
| –$H_4$ | 2·49 | $C_4$–$C_6$ | 2·43 | $H_4$–$H_5$ | 2·47 |
| –$H_5$ | 2·83 | –$C_7$ | 2·50 | –$H_8$ | 2·01 |
| $C_1$–$C_3$ | 2·41 | –$C_8$ | 2·99 | $H_5$–$H_6$ | 2·48 |
| –$C_4$ | 2·76 | –$H_5$ | 2·14 | | |
| –$C_5$ | 2·37 | –$H_8$ | 2·68 | | |
| –$H_2$ | 2·15 | | | | |
| –$H_6$ | 2·15 | | | | |

The nearest non-bonded neighbors distance (Table 5), based on the calculated hydrogen positions, show that the oxygen atom is surrounded by $H_2$, $H_4$, and $H_5$ at 2·37, 2·49, and 2·83 Å respectively, which restrict its lateral motion. The closest intermolecular non-bonded approaches are between $H_2$ and $H_5$, at 2·38 and 2·67 Å. A close intramolecular approach occurs between $H_4$ and $H_8$, at 2·01 Å, assuming that these hydrogens lie in the planes of the benzene and enol rings respectively. The perpendicular distance between least-squares molecular planes is 3·514 Å. Table 6 shows the amplitudes and directions of the principal thermal axes, referred to the least-squares molecular plane. The standard deviations shown are based on the complete inverse matrix of the normal equations and thus include the effect of covariances. The rather large magnitudes of the standard deviations reflect the fact that the thermal parameters are more sensitive to errors in the experimental data than are the positional parameters. In particular it is seen that small differences in the orientation of the thermal ellipsoids are of no statistical significance. The thermal stereograms (Fig. 2) do not show any pronounced oscillation of this rather rigid molecule about its major axes, as would have been expected. Possibly any such motion is masked by systematic errors in the observed light atom vibrations in the presence of the heavy atom, but it seems more likely that they are masked by the peculiarities of the enol ring (see below).

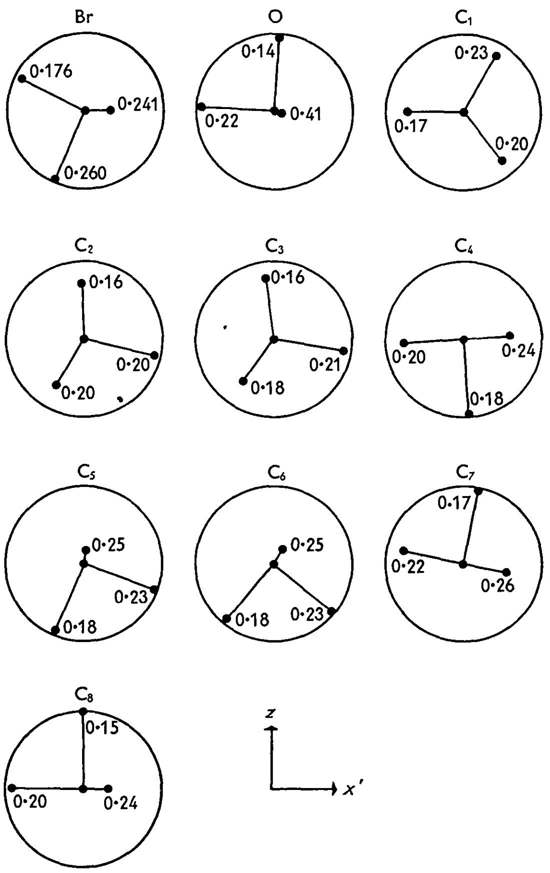


Fig. 2. Thermal stereograms for the atoms, transformed so that the plane of the paper is the least-squares molecular plane. The *X′* axis is in the direction of the longest dimension of the molecule, and the *Y′* axis is perpendicular to the molecular plane. The directions of the r.m.s. thermal axes are shown stereographically, and the length of the axes are indicated in Å.

The greatest thermal anisotropy is shown by the bromine and oxygen atoms. The bromine atoms has its minor thermal axis nearly parallel to the Br–$C_1$ bond, as might be anticipated, with the mean and major axes nearly normal to this bond. These axes are

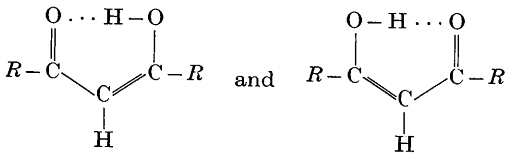
Table 6. *Angle $\theta(I)$ (degrees) between principal thermal axes $R$ and axes $I$ of a Cartesian coordinate system defined by the least-squares molecular plane*

The $X'$ axis is in the direction of the longest dimension of the molecule and the $Y'$ axis is perpendicular to the molecular plane

| Atom | $R$ | R.m.s. amplitude (Å) | $\theta(X')$ | $\theta(Y')$ | $\theta(Z)$ |
|---|---|---|---|---|---|
| Br | 1 | 0·176 ± 0·001 | 32 ± 1 | 109 ± 1 | 115 ± 1 |
| | 2 | 0·241 ± 0·001 | 112 ± 2 | 158 ± 2 | 91 ± 3 |
| | 3 | 0·260 ± 0·001 | 67 ± 2 | 100 ± 3 | 25 ± 1 |
| O | 1 | 0·138 ± 0·008 | 86 ± 4 | 89 ± 1 | 4 ± 4 |
| | 2 | 0·219 ± 0·008 | 174 ± 3 | 86 ± 2 | 86 ± 4 |
| | 3 | 0·408 ± 0·010 | 94 ± 2 | 176 ± 2 | 89 ± 1 |
| $C_1$ | 1 | 0·167 ± 0·009 | 41 ± 11 | 131 ± 11 | 90 ± 9 |
| | 2 | 0·202 ± 0·010 | 60 ± 13 | 55 ± 14 | 130 ± 15 |
| | 3 | 0·229 ± 0·010 | 65 ± 10 | 61 ± 11 | 40 ± 15 |
| $C_2$ | 1 | 0·159 ± 0·010 | 88 ± 11 | 132 ± 10 | 137 ± 10 |
| | 2 | 0·198 ± 0·010 | 158 ± 59 | 107 ± 13 | 77 ± 5 |
| | 3 | 0·200 ± 0·009 | 68 ± 60 | 132 ± 67 | 50 ± 47 |
| $C_3$ | 1 | 0·155 ± 0·009 | 96 ± 9 | 55 ± 15 | 36 ± 16 |
| | 2 | 0·180 ± 0·009 | 114 ± 15 | 44 ± 15 | 125 ± 17 |
| | 3 | 0·208 ± 0·010 | 25 ± 14 | 67 ± 12 | 99 ± 10 |
| $C_4$ | 1 | 0·181 ± 0·009 | 94 ± 21 | 90 ± 17 | 4 ± 20 |
| | 2 | 0·196 ± 0·009 | 142 ± 10 | 52 ± 9 | 93 ± 26 |
| | 3 | 0·244 ± 0·012 | 52 ± 9 | 38 ± 9 | 88 ± 7 |
| $C_5$ | 1 | 0·181 ± 0·010 | 68 ± 9 | 100 ± 7 | 24 ± 8 |
| | 2 | 0·233 ± 0·010 | 158 ± 9 | 92 ± 21 | 68 ± 9 |
| | 3 | 0·254 ± 0·011 | 91 ± 20 | 170 ± 9 | 100 ± 11 |
| $C_6$ | 1 | 0·181 ± 0·010 | 51 ± 9 | 102 ± 7 | 42 ± 9 |
| | 2 | 0·228 ± 0·010 | 140 ± 10 | 92 ± 22 | 50 ± 10 |
| | 3 | 0·248 ± 0·011 | 96 ± 18 | 168 ± 8 | 101 ± 16 |
| $C_7$ | 1 | 0·169 ± 0·010 | 78 ± 8 | 90 ± 7 | 12 ± 8 |
| | 2 | 0·217 ± 0·009 | 142 ± 11 | 54 ± 11 | 80 ± 9 |
| | 3 | 0·257 ± 0·012 | 54 ± 11 | 36 ± 11 | 97 ± 6 |
| $C_8$ | 1 | 0·152 ± 0·013 | 90 | 90 | 0 |
| | 2 | 0·196 ± 0·012 | 161 ± 15 | 71 ± 15 | 90 |
| | 3 | 0·238 ± 0·014 | 109 ± 15 | 161 ± 15 | 90 |

consistent with some motion of the molecule as a whole with relatively large Br–C bending amplitudes.

Of special interest is the thermal stereogram for oxygen. The enol is required by crystal symmetry to have equivalent C–O bonds, but if these were statistically equivalent due to random arrangement of



molecules within the unit cell, then the oxygen and neighboring carbon positions should show abnormally large apparent r.m.s. amplitudes parallel to the C–O bonds. This is clearly not so, and the thermal parameters strongly suggest that the two C–O bonds are equivalent, corresponding to resonance between the two forms shown above. All sensitive distances are also more compatible with this interpretation than any other. Note that C–O is 1·306, $C_3$–$C_7$ is 1·457 (trigonal single bond), and $C_7$–$C_8$ is 1·393 (50% double bond character).

The abnormally low thermal axes in the molecular plane may be the result of the restriction of the oxygen in this plane due to very close hydrogen neighbors (see above). The very high amplitude out of the molecular plane is, however, unexpected and suggestive of an anomaly.

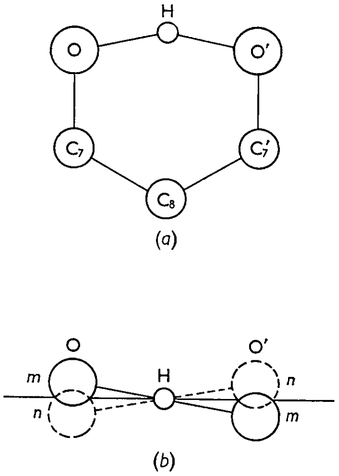


Fig. 3. (*a*) Postulated enol ring structure with non-collinear hydrogen bond; (*b*) side view of oxygen atoms showing effect of O–O repulsion.

It is to be noted that ∠ $C_7$–O–O is only 89·5°, so that ∠ $C_7$–O–H would be abnormally small if H were directly on the line of centers between the oxygen atoms. It seems likely, in the circumstances, that this hydrogen bond is bent, as shown in Fig. 3(*a*). If this is true, then the very close O–O contact of 2·46 Å, among the shortest known for hydrogen bonds, may lead to strong O–O repulsion, and a warping of the oxygen atoms out of the molecular plane as shown in Fig. 3(*b*), so that the oxygen atoms are at random in positions *m* or positions *n* of that figure. This would lead to the apparently very high amplitude normal to the ring. Unfortunately, the X-ray data are not sufficient to confirm this conjecture. This suggestion does, however, have the additional merit that it would lead to some distortion or randomness in the carbon positions near the oxygens, that is, near the center of the molecule, leading to apparently high thermal parameters for the atoms and obscuring the oscillations of this rigid molecule as a whole, which are to be expected. (Possibly the single bond character of $C_3$–$C_7$ reduces the rigidity, also giving some extra torsional freedom to the enol ring which would show most clearly in the thermal parameters of the oxygen atoms.)

In spite of the fact that this structure determination seems to settle the nature of the enols, at least of the aromatic *β*-diketones, the interest in this point and in the short hydrogen bond has caused us to regret the uncertainties introduced by such a heavy atom as bromine. Accordingly, the structure of the corresponding (but not isomorphous) chloro-derivative is in progress.

This problem was suggested to us by Prof. G. S. Hammond in connection with his study of hydrogen bonding, lithium chelation, and other properties of these compounds.

## References

BERGHUIS, J., HAANAPPEL, IJ. M., POTTERS, M., LOOPSTRA, B. O., MACGILLAVRY, C. H. & VEENENDAAL, A. L. (1955). *Acta Cryst.* **8**, 478.
BORDUIN, W. G. (1954). M.S. thesis, Iowa State University.
BUSING, W. R. & LEVY, H. A. (1957). *Acta Cryst.* **10**, 180.
BUSING, W. R. & LEVY, H. A. (1959). *A Crystallographic Function and Error Code for the IBM* 704, ORNL 59-12-3.
BUSING, W. R. & LEVY, H. A. (1960). *A Crystallographic Least-Squares Refinement Program for the IBM* 704, ORNL 59-4-37.
DAUBEN, C. H. & TEMPLETON, D. H. (1955). *Acta Cryst.* **8**, 841.
*Internationale Tabellen zur Bestimmung von Kristallstrukturen*, Vol. 2, p. 577 (1935). Berlin: Borntraeger.
DEWAR, M. J. S. & SCHMEISING, H. N. (1960). *Tetrahedron*, **11**, 96.
DUMKE, W. L. (1956). M.S. thesis, Iowa State University.
FITZWATER, D. R. & WILLIAMS, DONALD E. (1959). *Acta Cryst.* **12**, 350.
HAMILTON, W. C. (1955). *Acta Cryst.* **8**, 185.
MILLEDGE, H. J. & PANT, L. M. (1960). *Acta Cryst.* **13**, 285.
OOSAKA, H. & AKIMOTO, Y. (1953). *Bull. Chem. Soc. Japan*, **26**, 433.
SENKO, M. E. & TEMPLETON, D. R. (1956). Private Communication.
THOMAS, L. H. & UMEDA, K. (1957). *J. Chem. Physics*, **26**, 293.
TULINSKY, A. (1960). Private Communication.
YUZAWA, T. & YAMAKA, M. (1953). *Bull. Chem. Soc. Japan*, **26**, 414.

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*Acta Cryst.* (1962). **15**, 635

# The Crystal Structure and Molecular Configuration of (+)-*S*-Methyl-L-Cysteine Sulphoxide

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(+)-*S*-methyl-L-cysteine sulphoxide crystallizes in the orthorhombic system, space group $P2_12_12_1$, with a unit cell of dimensions

$$a = 5{\cdot}214 \pm 0{\cdot}002,\ b = 7{\cdot}410 \pm 0{\cdot}002,\ c = 16{\cdot}548 \pm 0{\cdot}008\ \text{Å}\ ,$$

and containing four molecules. The crystal structure was determined in projection by a sign-relation method. Final parameters have been determined by three-dimensional least-squares refinement. The structure represents the first determination of the absolute configuration at an asymmetric sulphur atom. The molecular arrangement in the crystalline state consists of pairs of sheets of molecules parallel to (001) held together by hydrogen bonds between the nitrogen of one molecule and surrounding oxygens of different molecules.

## 1. Introduction

(+)-*S*-methyl-L-cysteine sulphoxide [(+)MCS, Fig. 1] is one of a range of biologically active organic sulphoxides which have been extracted in recent years from natural sources (Challenger, 1953; Synge & Wood, 1956). In most of these compounds the sulphur is a centre of asymmetry, though not always the only one, and consequently these substances are optically active and exist in at least two isomeric forms whose configurations are unknown. Following the synthesis and resolution of several of these compounds it has been shown that their biological action depends markedly on the configuration used. It is for this reason important that the configurations of these compounds should be established absolutely. Furthermore, the organic sulphoxides represent a class of compounds little studied so far by X-ray methods, and further information about them is desirable. For both these reasons a study, described here, has been made of (+)MCS.

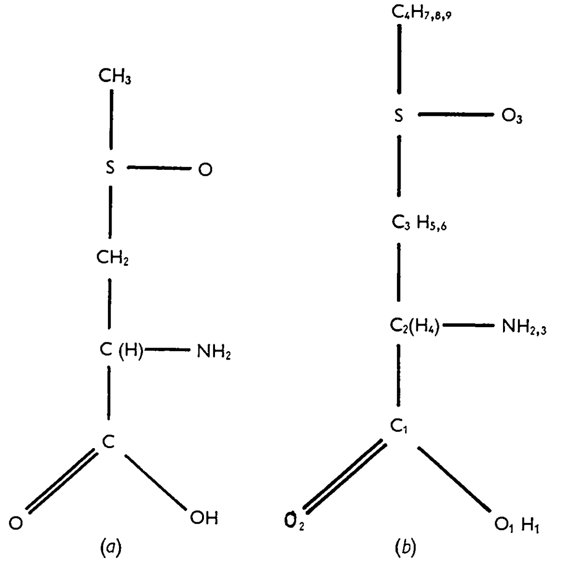

Fig. 1. (*a*) Chemical constitution of (+)-*S*-methyl-L-cysteine sulphoxide. (*b*) Numbering of atoms adopted in text.