

Refinement of the structure of anthraquinone*

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With 8 figures

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Auszug

Die Kristallstruktur von Anthrachinon wurde neu untersucht. Die Atomparameter sind zu einer Genauigkeit von $\pm 0,01 \text{ \AA}$ verfeinert worden. Es wurden zweidimensionale (F_o-F_c)-Synthesen und dreidimensionale F_o - und Differential-Synthesen ausgeführt. Die Lagen der Wasserstoffatome konnten angegeben und an Hand der Intensitäten bestätigt werden. Das Molekül, einschließlich aller H-Atome, ist eben. Die Genauigkeit der Analyse und der Atomabstände wird diskutiert.

Abstract

The crystal structure of anthraquinone has been reinvestigated and the atomic parameters have been refined to an accuracy of 0.01 \AA . Two-dimensional (F_o-F_c) synthesis, three-dimensional F_o synthesis and three-dimensional differential synthesis have been used. Hydrogen atoms are detected and their positions are verified. The molecule is planar with all the hydrogen atoms also lying in the same plane. Some data concerning the different atoms are given. The accuracy of the analysis and the bond lengths are discussed.

1. Introduction

The structure of anthraquinone, $C_{14}H_{10}O_2$, was determined by SEN¹ by two-dimensional Fourier synthesis. He² assigned the space group $P2_1/a$ but in his latter work¹ mentioned the observation of a few weak forbidden reflections ($h0l$ with h odd) which led him to ascribe $P2_1$

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¹ S. N. SEN, Crystal structure of anthraquinone, Thesis, Calcutta University (1948).

² S. N. SEN, Crystal structure of anthraquinone. Science and Culture **5** (1940) 717—719.

as the space group. The structure was worked out on the basis of $P2_1/a$ neglecting the contribution of these few, in fact only four, very weak forbidden reflections. F_c values were calculated by using the atomic form factor curves of benzoquinone carbon³ and magnesium oxide oxygen⁴. Although general agreement between F_o and F_c appeared to be somewhat satisfactory, sharp differences between a few intense reflections were quite frequently observed, F_c being less in all these cases. The total electron count that was made for each atom gave a figure 9.5 for oxygen while for each of the other atoms it was about 6.0 including also the carbon atom that forms a double bond with oxygen. A partial ionic character of the oxygen atom was mentioned but the immediate question was wherefrom this extra value of 1.5 for oxygen could have been derived. Probable inaccuracies of the intensity measurements and the termination of Fourier series were thought to be responsible for this. It was thought worthwhile to settle these points of interest by a refinement of the structure by the application of three-dimensional Fourier methods.

The author has in his earlier publications^{5,6} established that the space group of anthraquinone is $P2_1/a$ and the scattering factors appropriate to the different atoms of the substance at room temperature (at which this present analysis was done) were determined by an empirical method developed by him. The refinement of the structure is dealt with in this article.

2. Crystal data

Anthraquinone, $C_{14}H_8O_2$; melting point 273°C ; density measured 1.438, calculated 1.445; monoclinic; revised unit-cell dimensions, $a = 15.810 \pm 0.015 \text{ \AA}$, $b = 3.942 \pm 0.005 \text{ \AA}$, $c = 7.865 \pm 0.010 \text{ \AA}$ and $\beta = 102^\circ 43' \pm 2'$. Space Group $P2_1/a-C_{2h}^5$. Two centrosymmetric molecules per unit cell. Volume of the unit cell = 477.8 \AA^3 . Linear absorption coefficient for x-rays ($\text{CuK}\alpha$), $\mu = 9.1$ per cm; total number of electrons per unit cell, 216.

³ J. M. ROBERTSON, The structure of benzoquinone. Proc. Roy. Soc. [London] A **150** (1935) 106–128.

⁴ E. O. WOLLAN, The electron distribution of magnesium oxide. Physic. Rev. **35** (1930) 1019–1027.

⁵ B. V. R. MURTY, The space group of anthraquinone. Acta Crystallogr. **8** (1955) 113–114.

⁶ B. V. R. MURTY, Atomic form factor curves for carbon and oxygen of $>C=O$ bond of anthraquinone (25° – 35°C). Acta Crystallogr. **10** (1957) 146–147.

3. Experimental

Determination of integrated intensity was carried out by the photographic method using unfiltered Cu radiation and equi-inclination Weissenberg technique. Relative integrated-intensity measurements were made with Moll recording microphotometer and were put on the absolute scale by comparing with (111) and (200) reflections of aluminium from a powder photograph of a mixture of anthraquinone and aluminium in the ratio 4 to 1 by weight. The intensities of all reflections were corrected for the usual Lorentz and polarization factors and geometrical factor⁷. The ($h0l$) reflections were corrected for absorption⁸ also. Out of a possible number of 1091 different reflections with $\text{CuK}\alpha$ radiation, 520 were measured with a high order of accuracy. The weakest and strongest structure factors observed were 1 and 81.6. The observed structure factors are given, along with the corresponding calculated values, in the Table 3.

4. Refinement of the structure

The refinement of the coordinates was made in three steps. All computations were made with Olivetti table-printing calculating machine.

1. Refinement of the X , Z coordinates as far as possible by the application of two successive ($F_o - F_c$) syntheses for the ($h0l$) projection since it was very well resolved.

2. Refinement of the Y coordinates by the application of three-dimensional Fourier synthesis for electron density at different points along lines parallel to the Y direction passing through the refined X , Z points of each atom.

3. Final refinement of the X , Y , Z coordinates by the application of three-dimensional differential synthesis.

(a) Difference synthesis

The two-dimensional Fourier projection ($h0l$) made by SEN⁹ was repeated with 134 reflections out of a possible 161 for this projection with the help of BEEVERS and LIPSON strips prepared in this laboratory. To start with, the phases that were given by SEN¹ were adopted. The projection was given in the earlier publication⁶. The R value obtained

⁷ G. TUNNEL, The rotation factor for equi-inclination Weissenberg photographs. *Amer. Min.* **24** (1939) 448–451.

⁸ G. ALBRECHT, The absorption factor in crystal spectroscopy. *Rev. Sci. Instrum.* **10** (1939) 221–222.

⁹ S. N. SEN, Electron density map of anthraquinone crystal. *Ind. Jour. Physics* **19** (1945) 243–246.

was 19⁰/₀ with coordinates derived from this projection and *f*-curves derived by the author⁶ for the different atoms of this substance at laboratory temperature (25°–35°C) at which the experiment was conducted. The above projection was very well resolved and so it was intended to refine the *X*, *Z* coordinates of all the atoms by successive two-dimensional ($F_o - F_c$) syntheses as a first step in the process of refinement. Two successive ($F_o - F_c$) syntheses were carried out during which the value of *R* fell to 14.7⁰/₀. Anisotropic *f*-values were used for oxygen atom in the D_2 synthesis. The D_2 synthesis for (*h*0*l*) projection is given in Fig. 1.

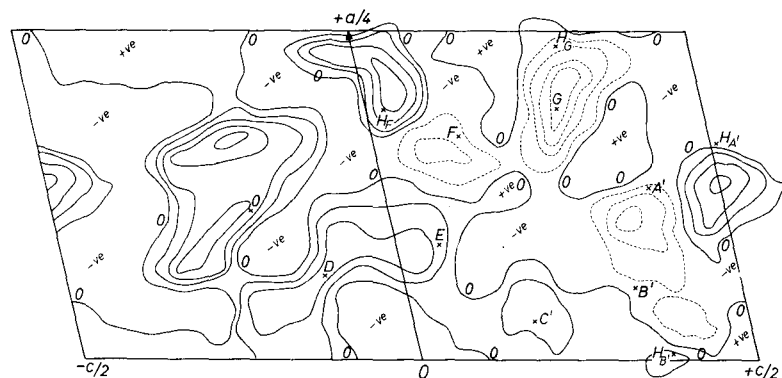


Fig. 1. D_2 synthesis of (*h*0*l*) projection. *D*-values summed up at intervals of $a/60$, $c/30$. Contours are drawn at an interval of $0.2 e/\text{\AA}^2$. The zero contour is indicated by 0 and negative contours are dotted. Atomic positions after the D_1 synthesis are marked (\times). Contours are drawn surrounding the projected atomic positions. The remaining area of projection is indicated + *ve* or - *ve*.

It can be observed from the D_2 contour diagram that the slope of the *D* function at *B'*, *C'* and *D* was almost nil. The temperature factor chosen for the atom *G* must have been incorrect as there remains a persistent sharp depression at the position *G*. The corrected coordinates resulting after the D_2 synthesis were believed to be very close to their real peaks and the further corrections that were to be made to arrive at their final values to be very small. It was considered difficult to arrive at the exact peaks by a further application of *D* synthesis without a full knowledge of the true anisotropic *f* curves for all the atoms involved. Instead, at this stage of refinement, an application of differential synthesis¹⁰ was thought worthwhile.

¹⁰ A. D. BOOTH, A differential Fourier method for refining atomic parameters in crystal structure analysis. *Trans. Faraday Soc.* **42** (1946) 444–448.

(b) Three-dimensional Fourier synthesis

So far we have tried to refine only the X, Z coordinates from the $(h0l)$ projection. No attempt was made to refine the Y coordinates. This could not be done from any two-dimensional projection, because the molecular plane is tilted from (010) by 27° , the other tilts being almost negligible. This is how the molecule is quite well resolved in the $(h0l)$ projection and gives rise to too much overlapping in the other projections. So, for the determination of the Y coordinates of the atoms, it was necessary to carry out a three-dimensional Fourier

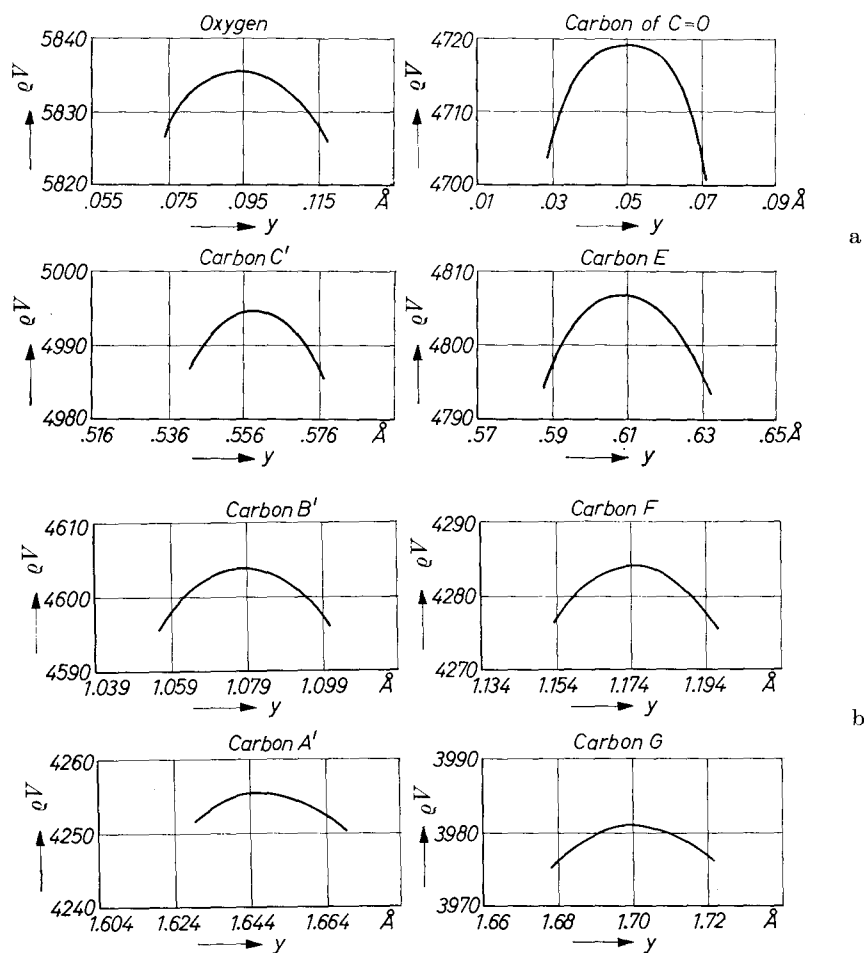


Fig. 2. The variation of (ρV) with Y for different atoms. Three-dimensional Fourier synthesis.

synthesis at different points along the Y direction through the projected centres of the different atoms in the $(h0l)$ projection obtained after D_2 synthesis. The 520 structure factors mentioned earlier were used in the summation for the electron density. The starting phases for $(hk0)$, $(0kl)$ and (hkl) were calculated with the approximate Y coordinates given by SEN¹. Electron densities at a few points at intervals of .02 Å on both sides of the expected maximum value along the direction of each atom were computed and the different maxima were located by the method described by BOOTH¹¹. It is interesting to note that the curves of electron density (Fig. 2) plotted against Y for the different atoms of the molecule are more and more diffuse for atoms more and more away from the centre of the molecule, their peak ρ values being gradually less. This is quite expected because of the possibility of larger amplitudes of thermal vibrations of the end atoms than those of atoms nearer to the centre of the molecule.

c) Differential synthesis

The necessary formulae for the corrections in the X, Y, Z coordinates by the differential synthesis method for monoclinic symmetry were given by BOOTH¹⁰. The electron-density distribution of an atom was assumed to possess spherical symmetry at least in the region of its maximum. $\frac{\partial \rho}{\partial X}$, $\frac{\partial \rho}{\partial Y}$, $\frac{\partial \rho}{\partial Z}$ and $\frac{\partial^2 \rho}{\partial Y^2}$ were obtained by differentiating the Fourier expression for electron density and computed for each atom using all the 520 structure factors. Using these, the corrections in X, Y, Z coordinates of different atoms were calculated. The resulting final coordinates are given in Table 1.

d) Hydrogen atoms

The rough positions of the hydrogen atoms could be located from the D_1 and D_2 syntheses. For better locations of the hydrogen atoms a fresh D_3 synthesis was carried out (excluding the hydrogen atoms) with the final coordinates after differential synthesis of the various carbon and oxygen atoms. Since the final coordinates of the carbon and oxygen atoms are already well refined, if their f curves are correct, hydrogen atoms would be expected to make their appearance in well developed form. The D_3 synthesis is shown in Fig. 3. Hydrogen peak positions from D_3 were located by BOOTH's method¹¹. These gave the tentative X, Z positions of the hydrogen atoms which are verified

¹¹ A. D. BOOTH, Fourier technique in organic structure analysis. Cambridge University Press (1948) 63–65.

as described below. The small D values still persistent at the positions of the other atoms were thought to be due to the slight inaccuracies in the f curves.

Approximate Y coordinates of the different hydrogen atoms were calculated by assuming a bond length of 1.0 Å for C—H bond and that the hydrogen atoms also lie in the same molecular plane as the other atoms. This was not unjustified when similar situations were found in naphthalene¹² and anthracene¹³. To test the reality of these hydrogen

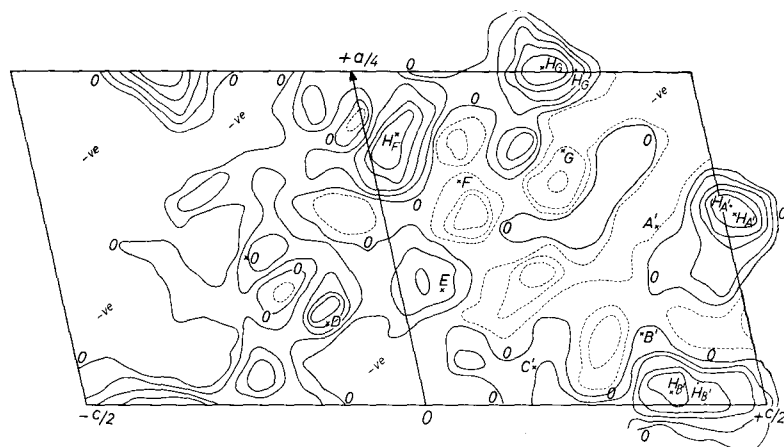


Fig. 3. D_3 synthesis of $(h0l)$ projection. Well developed hydrogen peaks can be observed. Hydrogen peak positions are marked (\times). Trial hydrogen positions for H_G , $H_{A'}$ and $H_{B'}$ indicated by dots. Contours are drawn at an interval of $0.2 e/\text{\AA}^2$. The zero contours are indicated by 0 and the negative contours are dotted. Other atomic positions after differential synthesis are also marked (\times). Contours are drawn surrounding the projected atomic positions. The remaining area of projection is indicated +ve or -ve.

positions, the electron density was calculated by using a three-dimensional Fourier synthesis. The electron density for the position H_F indicated in D_3 came out surprisingly well, viz. $1.17 e/\text{\AA}^3$. A successive application of differential synthesis for Y of this atom indicated an overall correction of $+0.078 \text{\AA}$. Electron density with the corrected Y was $1.20 e/\text{\AA}^3$.

¹² J. M. ROBERTSON, S. C. ABRAHAM and J. G. WHITE, The crystal and molecular structures of naphthalene. II. Structure investigation by the triple Fourier series method. *Acta Crystallogr.* **2** (1949) 238–244.

¹³ J. M. ROBERTSON, A. M. MATHIESON and V. C. SINCLAIR, The crystal and molecular structure of anthracene, II. Structure investigation by the triple Fourier series method. *Acta Crystallogr.* **3** (1950) 251–256.

For the H_G and $H_{A'}$ hydrogen atoms attached to the end carbon atoms G and A' of the molecule, the electron densities were calculated to be respectively $0.25 e/\text{\AA}^3$ and $0.50 e/\text{\AA}^3$ which were not possible at all. A scanning along Y direction in each case did not improve matters. This is apparently due to wrong X, Z coordinates for these atoms. This is an experimental verification of the spuriousness introduced, probably due to f curves of the end atoms influencing the hydrogen positions. A probe into the causes of these low electron densities, obviously wrong X, Z positions, was considered advisable before performing any calculations on the fourth hydrogen atom H_B .

A careful study of the X, Z positions of the different hydrogen atoms on the D_3 contour diagram gave a clue to the problem. While the hydrogen H_F ($\rho = 1.20 e/\text{\AA}^3$) was found to be situated in the D_3 projection almost exactly on the line connecting the opposite carbon atoms of the benzene ring, the positions of the other hydrogen atoms were considerably off for no obvious reason. It was expected that these hydrogen atoms also may be at least close to the symmetrical positions. With this in view and keeping practically the same distances from their respective carbon atoms as in D_3 projection, trials were given by changing the X, Z positions of the hydrogen atoms $H_G, H_{A'}$ and H_B . Their new approximate Y coordinates were calculated again by assuming them to be possibly in the molecular plane with a C—H bond of 1.0 \AA . Three-dimensional Fourier syntheses for the electron density

Table 1. *Final coordinates (rounded off to the decimal) of the asymmetric unit of anthraquinone molecule, molecular centre of symmetry as origin. Coordinates are accurate to within 0.01 \AA*

Atom	X	Y	Z
A'	2.076 \AA	1.646 \AA	3.121 \AA
B'	0.814 \AA	1.080 \AA	2.675 \AA
C'	0.430 \AA	0.560 \AA	1.360 \AA
E	1.316 \AA	0.602 \AA	0.490 \AA
F	2.609 \AA	1.175 \AA	0.945 \AA
G	3.003 \AA	1.702 \AA	2.244 \AA
D	0.941 \AA	0.052 \AA	-0.915 \AA
O	1.736 \AA	0.092 \AA	-1.687 \AA
H_F	3.188 \AA	1.277 \AA	0.374 \AA
H_G	3.955 \AA	2.301 \AA	2.565 \AA
$H_{A'}$	2.365 \AA	2.144 \AA	4.030 \AA
H_B	0.250 \AA	1.097 \AA	3.219 \AA

were carried out at these trial positions. The results immediately appeared as anticipated. The different Y coordinates were then refined by successive application of the differential method again. Electron densities at these positions were calculated to be respectively 0.96, 1.15 and 1.13 $e/\text{\AA}^3$.

5. Atomic coordinates, bond lengths, valency angles and molecular plane

The coordinates of the remaining atoms of the unit cell can be readily obtained from the

space-group symmetry $P2_1/a$. The different bond lengths on the basis of the above coordinates were calculated and directly marked in Fig. 4.

The different atoms of the anthraquinone molecule are found to closely conform to a planar configuration. The equation of the molecular plane is given by $-0.3049 X' + 0.8891 Y - 0.3414 Z' = 0$,

where $X' = X + Z \cos \beta$

and $Z' = Z \sin \beta$,

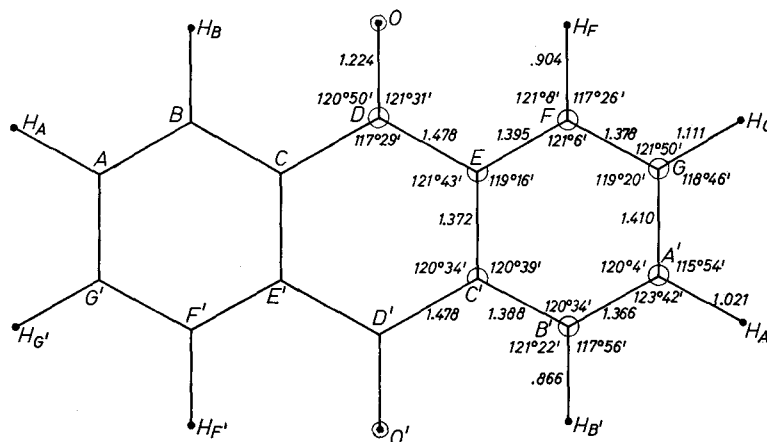


Fig. 4. Bond lengths and bond angles of anthraquinone molecule.

X' , Y and Z' being referred to a , b and c^* axes of the unit cell, and -0.3049 , $+0.8891$, -0.3414 are the direction cosines of the normal to the plane of the molecule. The different tilts of the normal to the molecular plane with the a , b and c^* axes of the crystal are respectively $107^\circ 45'$, $27^\circ 14'$, $109^\circ 58'$. The tilt of the molecular plane from the plane of $(h0l)$ projection is $27^\circ 14'$, as against 27° found earlier by SEN¹. The $>C=O$ bond is tilted from the $(h0l)$ projection by only 2° , as against $3^\circ 48'$ found by SEN. The deviations of the different atoms from the plane indicated above are given in the following table.

Table 2. Deviation of the atoms from the molecular plane
 $-0.3049 X' + 0.8891 Y - 0.3414 Z' = 0$

Atom	Deviation	Atom	Deviation
A'	0.001 Å	D	0.002 Å
B'	0.001 Å	O	0.001 Å
C'	0.005 Å	H_F	0.064 Å
E	0.004 Å	H_G	0.158 Å
F	0.002 Å	$H_{A'}$	0.113 Å
G	0.001 Å	$H_{B'}$	0.043 Å

Table 3. *Observed and calculated structure factors*

h k l	F _o	F _c	h k l	F _o	F _c	h k l	F _o	F _c	h k l	F _o	F _c
0 2 0	13.0	15.2	$\overline{20}$ 0 3	3.5	3.6	$\overline{10}$ 0 9	4.0	- 2.5	12 3 0	3.6	- 4.4
0 0 1	36.7	29.4	2 0 4	43.1	- 40.3	$\overline{12}$ 0 9	1.5	- 0.2	15 3 0	1.2	- 0.2
0 0 2	41.7	- 37.2	4 0 4	4.0	- 3.4	$\overline{2}$ 0 10	5.3	- 4.4	16 3 0	4.3	- 2.5
0 0 3	13.1	- 10.0	6 0 4	4.0	- 4.0	$\overline{4}$ 0 10	8.8	- 5.4	1 4 0	1.7	0.5
0 0 4	25.5	- 27.7	8 0 4	19.0	18.8	$\overline{8}$ 0 10	4.8	4.5	8 4 0	3.2	- 1.6
0 0 5	1.8	- 2.8	10 0 4	19.4	24.0	0 1 1	51.5	- 57.2	1 1 1	81.6	87.9
0 0 7	6.4	- 3.4	12 0 4	3.4	- 1.7	0 1 2	8.2	- 7.7	2 1 1	29.4	- 29.1
0 0 8	2.1	- 0.5	$\overline{2}$ 0 4	11.3	7.4	0 1 3	32.9	- 27.6	3 1 1	20.6	19.5
2 0 0	38.6	37.4	$\overline{4}$ 0 4	2.5	2.2	0 1 4	11.0	- 16.4	4 1 1	2.2	- 0.9
4 0 0	42.8	- 40.2	$\overline{6}$ 0 4	11.0	- 8.8	0 1 5	8.6	11.9	5 1 1	29.6	- 31.3
6 0 0	4.8	- 6.9	$\overline{8}$ 0 4	10.1	- 13.5	0 1 6	1.2	0.3	6 1 1	19.3	- 14.3
8 0 0	15.0	- 17.5	$\overline{10}$ 0 4	12.0	11.7	0 1 7	3.7	- 1.1	7 1 1	15.6	- 14.6
10 0 0	4.4	- 4.1	$\overline{12}$ 0 4	4.9	5.5	0 2 1	1.6	- 1.8	8 1 1	16.0	14.2
12 0 0	5.7	- 6.5	$\overline{14}$ 0 4	9.1	- 9.6	0 2 2	13.1	- 16.5	9 1 1	7.0	- 7.8
14 0 0	8.6	- 7.2	$\overline{16}$ 0 4	6.8	- 5.4	0 2 3	9.0	- 12.1	10 1 1	15.8	15.6
16 0 0	4.8	3.3	$\overline{18}$ 0 4	5.3	- 3.0	0 2 4	6.7	11.7	13 1 1	4.1	- 4.4
2 0 1	8.8	- 9.3	2 0 5	10.1	12.3	0 2 5	3.9	6.8	14 1 1	5.5	- 5.9
4 0 1	17.3	17.1	4 0 5	6.7	- 5.5	0 2 6	5.4	- 7.2	15 1 1	4.3	- 5.7
6 0 1	52.8	- 48.6	6 0 5	4.4	- 1.8	0 2 7	2.7	0	$\overline{1}$ 1 1	3.6	- 5.4
8 0 1	47.8	- 45.3	8 0 5	28.0	27.8	0 2 8	1.5	1.0	$\overline{2}$ 1 1	1.8	- 1.7
10 0 1	8.6	7.5	10 0 5	8.5	8.9	0 2 9	1.4	0.4	$\overline{3}$ 1 1	31.7	- 25.5
12 0 1	8.8	10.8	12 0 5	5.9	- 3.9	0 3 1	1.7	- 0.6	$\overline{4}$ 1 1	5.8	- 5.8
14 0 1	5.6	- 2.2	$\overline{2}$ 0 5	1.8	0.6	0 3 2	4.5	6.0	$\overline{6}$ 1 1	15.8	- 12.5
16 0 1	8.3	- 7.6	$\overline{4}$ 0 5	11.0	- 11.3	0 3 4	4.0	1.1	$\overline{7}$ 1 1	4.9	5.1
$\overline{2}$ 0 1	36.9	41.8	$\overline{6}$ 0 5	4.6	- 3.8	0 3 5	4.1	- 4.3	$\overline{8}$ 1 1	9.9	12.6
$\overline{4}$ 0 1	24.7	- 23.9	$\overline{8}$ 0 5	14.1	17.8	0 3 8	4.8	- 5.2	$\overline{9}$ 1 1	6.5	8.4
$\overline{6}$ 0 1	25.8	28.4	$\overline{12}$ 0 5	13.8	- 13.4	1 1 0	37.5	34.1	$\overline{11}$ 1 1	6.2	- 10.8
$\overline{8}$ 0 1	12.8	16.0	$\overline{14}$ 0 5	7.2	- 3.8	2 1 0	65.2	- 66.9	$\overline{12}$ 1 1	4.9	5.1
$\overline{12}$ 0 1	16.0	14.7	$\overline{16}$ 0 5	5.2	3.8	3 1 0	41.0	38.1	$\overline{13}$ 1 1	4.4	1.7
$\overline{14}$ 0 1	5.4	0.2	2 0 6	8.1	10.1	4 1 0	19.7	- 16.4	$\overline{14}$ 1 1	14.8	12.0
$\overline{18}$ 0 1	3.2	1.8	4 0 6	4.1	- 3.2	5 1 0	37.4	- 36.5	$\overline{15}$ 1 1	16.4	14.1
$\overline{20}$ 0 1	10.2	- 5.2	8 0 6	3.4	- 2.0	6 1 0	25.5	- 19.9	1 1 2	22.0	- 19.9
2 0 2	22.4	20.8	10 0 6	5.3	- 3.7	7 1 0	22.3	- 17.4	2 1 2	7.3	8.1
4 0 2	14.1	18.1	12 0 6	4.5	2.8	8 1 0	16.9	- 15.5	3 1 2	6.6	4.9
6 0 2	10.1	- 8.8	$\overline{2}$ 0 6	6.7	3.0	9 1 0	6.7	8.7	5 1 2	22.6	24.5
8 0 2	4.9	- 5.8	$\overline{4}$ 0 6	30.4	35.4	10 1 0	5.3	3.4	6 1 2	2.9	1.3
14 0 2	9.1	- 7.3	$\overline{6}$ 0 6	14.7	11.7	12 1 0	3.7	- 1.9	7 1 2	17.6	- 16.1
16 0 2	5.1	- 3.7	$\overline{10}$ 0 6	10.0	- 6.4	14 1 0	3.8	- 1.0	8 1 2	8.1	8.8
18 0 2	2.4	0.4	$\overline{12}$ 0 6	15.7	- 16.1	15 1 0	3.8	- 6.0	9 1 2	17.4	- 19.4
$\overline{2}$ 0 2	32.6	- 26.1	$\overline{14}$ 0 6	6.0	- 4.3	19 1 0	1.8	3.0	12 1 2	6.3	- 7.3
$\overline{4}$ 0 2	26.3	- 23.6	$\overline{16}$ 0 6	6.0	3.4	1 2 0	9.1	12.0	16 1 2	4.6	2.5
$\overline{6}$ 0 2	4.4	- 2.3	2 0 7	8.6	- 6.0	2 2 0	5.3	- 5.6	$\overline{1}$ 1 2	9.2	- 8.0
$\overline{8}$ 0 2	4.1	5.8	4 0 7	7.0	- 7.2	3 2 0	16.0	- 17.4	$\overline{2}$ 1 2	7.0	4.5
$\overline{10}$ 0 2	14.1	- 20.7	6 0 7	2.8	- 0.6	4 2 0	13.4	- 18.4	$\overline{3}$ 1 2	7.8	- 5.3
$\overline{12}$ 0 2	21.7	21.2	8 0 7	3.0	- 2.0	5 2 0	23.9	- 25.3	$\overline{5}$ 1 2	20.3	16.3
$\overline{14}$ 0 2	34.1	36.6	$\overline{2}$ 0 7	7.0	- 7.7	6 2 0	10.0	- 10.9	$\overline{6}$ 1 2	23.9	- 23.2
$\overline{16}$ 0 2	3.5	- 0.1	$\overline{4}$ 0 7	21.5	22.4	7 2 0	6.2	8.5	$\overline{7}$ 1 2	18.8	- 15.8
$\overline{18}$ 0 2	6.1	- 4.2	$\overline{6}$ 0 7	25.4	26.3	8 2 0	6.3	9.6	$\overline{8}$ 1 2	8.8	- 8.8
$\overline{20}$ 0 2	3.1	- 3.1	$\overline{8}$ 0 7	4.9	- 6.3	10 2 0	6.2	10.5	$\overline{9}$ 1 2	8.4	- 9.0
2 0 3	51.9	- 50.4	$\overline{10}$ 0 7	7.0	- 4.1	11 2 0	2.6	- 2.4	$\overline{10}$ 1 2	9.0	- 9.9
6 0 3	20.5	22.8	$\overline{14}$ 0 7	2.8	0.7	12 2 0	6.1	- 7.0	$\overline{11}$ 1 2	15.6	14.0
8 0 3	6.7	- 4.7	$\overline{16}$ 0 7	2.8	1.3	13 2 0	7.5	- 5.4	$\overline{12}$ 1 2	20.9	- 17.6
10 0 3	4.4	- 5.4	2 0 8	9.0	- 8.6	14 2 0	1.8	- 1.9	$\overline{13}$ 1 2	10.0	6.6
12 0 3	2.5	- 3.8	6 0 8	4.9	3.7	15 2 0	6.7	- 3.9	$\overline{14}$ 1 2	6.0	5.6
14 0 3	4.7	- 1.0	$\overline{2}$ 0 8	5.4	5.3	16 2 0	7.1	4.2	$\overline{15}$ 1 2	10.4	9.2
16 0 3	4.8	3.4	$\overline{4}$ 0 8	3.7	- 4.0	1 3 0	0.9	6.9	$\overline{16}$ 1 2	10.9	9.2
$\overline{2}$ 0 3	29.0	29.6	$\overline{6}$ 0 8	3.0	- 0.2	2 3 0	9.3	- 11.0	1 1 3	36.2	- 36.4
$\overline{4}$ 0 3	12.5	14.4	$\overline{8}$ 0 8	6.6	- 3.7	3 3 0	5.9	- 8.0	2 1 3	9.7	- 7.9
$\overline{6}$ 0 3	53.3	- 50.8	$\overline{12}$ 0 8	6.6	5.7	4 3 0	1.7	2.6	4 1 3	6.1	6.0
$\overline{8}$ 0 3	23.8	- 23.2	$\overline{14}$ 0 8	1.2	- 0.2	5 3 0	1.6	- 6.9	7 1 3	7.4	11.1
$\overline{10}$ 0 3	7.0	6.9	2 0 9	2.6	1.2	6 3 0	2.2	5.4	8 1 3	5.2	5.3
$\overline{12}$ 0 3	7.2	1.7	$\overline{2}$ 0 9	3.0	1.0	8 3 0	2.5	5.0	9 1 3	8.1	7.9
$\overline{14}$ 0 3	15.4	13.1	$\overline{4}$ 0 9	3.1	- 2.0	9 3 0	5.8	- 1.9	10 1 3	3.8	4.7
$\overline{16}$ 0 3	3.4	4.3	$\overline{6}$ 0 9	4.9	- 3.8	10 3 0	1.7	- 4.5	11 1 3	3.9	- 5.8
$\overline{18}$ 0 3	6.4	- 3.5	$\overline{8}$ 0 9	3.8	- 1.1	11 3 0	2.8	- 2.8	14 1 3	5.3	3.5

