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The Crystal and Molecular Structure of 2-Amino-3-Methylbenzoic Acid*

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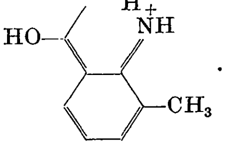
The structure of crystals of 2-amino-3-methylbenzoic acid has been determined and refined extensively by three-dimensional least-squares techniques. The crystals are monoclinic, space group $P2_1/c$, with $a = 11\cdot480$, $b = 4\cdot044$, $c = 15\cdot792$ Å and $\beta = 91°\ 18'$. There are four molecules in the unit cell, and the calculated density is $1\cdot361$ g.cm.$^{-3}$.

Positional and temperature-factor parameters for the eleven heavy atoms and positional coordinates for the nine hydrogen atoms in the molecule were included in the refinement. In addition, separate visual intensity estimates made by the two authors were treated independently, yielding two sets of final parameters. There are no significant differences in the two sets of parameters.

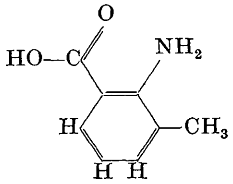
Except for two of the hydrogen atoms of the methyl group, the 2-amino-3-methylbenzoic molecule is approximately planar. The bond distances suggest an appreciable contribution of the form



Two hydrogen bonds are formed: an intermolecular O–H · · · O bond linking pairs of molecules together across symmetry centers and an intramolecular N–H · · · O bond.

Introduction

A preliminary determination by one of us had shown that crystals of 2-amino-3-methylbenzoic acid (I) are



(I)

monoclinic and characterized by symmetry and unit-cell parameters likely to allow facile solution for the crystal structure. It seemed, moreover, that there were a number of questions on which some information could be obtained by structure analysis of crystals of the compound (hereinafter often referred to as AMBA). Very little is known about variations in bond lengths and valence angles within a benzene ring so asymmetrically substituted as the one in this molecule or about the mutual distortional effects produced by the three substitutent groups –COOH, –NH_2, and –CH_3 in vicinal orientation. Also, of course, there was the question of what sort of hydrogen bonding might be displayed in the crystal structure. On the basis of these considerations, it was decided to undertake a complete analysis by three-dimensional methods.

Although it was not so planned from the beginning, the analysis gradually took on, at least in part, the character of a test bearing on the limitations of refinement on data obtained by visual estimation of intensities recorded on film. Early in the work it became clear that a rather precise determination could eventually be attained; and subsequently considerable effort was put forth to insure this outcome, to the extent that a new set of photographic intensities were recorded and estimated by the two authors independently. The two sets of intensity data so derived from the new films by the two authors were processed separately throughout, and refinement was carried out separately on each set of data. Eventually the rather pleasing result was reached that the structures obtained in the two separate refinements are but trivially different.

Experimental data and preliminary solution

Crystal specimens

A sample of AMBA was furnished by Prof. James English of Yale University as part of the Treat B. Johnson collection of organic chemicals. Our crystal specimens were selected from the original samples

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wihthut further treatment. A melting point 174·4–174·9 °C. was determined with a calibrated Anschütz thermometer in a Herschberger type of apparatus. This agrees fairly well with the melting point of 176 °C. reported by Bergmann & Pelchowicz (1953) and is somewhat higher than other reported values (see Beilstein, 1931, 1933, 1951).

The crystals were in the form of needles elongated along *b*, almost rectangular in cross section, showing characteristically the pinacoid forms {100} and {001}. Three different specimens were used in all. Specimen I was about 1 mm. long and 0·18 × 0·25 mm. in cross section. Specimen II, more carefully chosen later, was about the same length but more nearly square in cross section, approximately 0·23 mm. on a side. Specimen III was cut with a razor blade from a larger crystal for mounting along the *a* axis. It was approximately cubic, 0·2 mm. on a side.

Unit cell, space group and intensity measurements

The space group was indicated by the systematic absences (*h*0*l*, *l* odd and 0*k*0, *k* odd) to be $P2_1/c$. Approximate values for the unit-cell parameters were computed from measurements on Weissenberg films. More precise values were obtained by least-squares refinement on data from measurements on two Straumanis-type rotation photographs. An *h*0*l* film was recorded using crystal specimen I and unfiltered Cu *K* radiation, and an *hk*0 film was recorded using specimen III and unfiltered Cr *K* radiation. These two films were indexed with the aid of the corresponding zero-layer Weissenberg photographs. The four cell parameters were adjusted to give the best fit between observed and calculated Bragg angles for nineteen resolved reflections.* For each observation a weight was assigned equal to the reciprocal of the estimated variance of the determination of θ for the center of gravity of the reflection. Since the reflections on the *hk*0 Straumanis photographs, generally rather diffuse, were not numerous in the high angle region, it was necessary to use a number of unresolved α_1–α_2 doublets to secure data for determination of the translation *b*. For most of the doublets the weights were reduced arbitrarily by a factor of two; for others, by a factor of four. After convergence of the least-squares refinement, the value of the standard deviation of an observation of unit weight $(\Sigma\omega(\Delta\theta)^2/[n-p])^{\frac{1}{2}}$, where n is the number of observations and p the number of parameters, was 0·77. That this value is less than unity might suggest that errors of observation have been slightly overestimated in the weighting.

The cell parameters are given in Table 1, with limits of error. The latter are about four times the standard deviations estimated from least squares and correspond to the 99·9% confidence limits, assuming that the deviation of the estimated value of each parameter from its true value has Student's *t* distribution (*International Tables for X-ray Crystallography*, 1959).

Table 1. *Unit-cell parameters of* 2-*amino*-3-*methylbenzoic acid*

(λ(Cu $K\alpha_1$) = 1·5405 Å)

Parameter	Value	Error (see text)
a	11·4803 Å	17 (Å × 10^{-4})
b	4·0445	14
c	15·7923	36
β	91° 18·5′	2′

The density calculated on the basis of four molecules of acid per cell is 1·361 g.cm.$^{-3}$. Since this was considered a reasonable value and the formula and purity of the acid were never in question, the density was not determined experimentally.

The first set of equi-inclination Weissenberg films *hkl* where $k=0, 1, 2, 3$ and 4 was taken using the crystal specimen I and Cu *K* radiation. Intensities were read from the films by one observer with use of the usual scale prepared by recording on one film various appropriate numbers of 'flashes' of the same reflection. From the *h*0*l* data, after correction by the appropriate factors for the Lorentz and polarization effects, a Wilson (1949) plot was made to fix the scale approximately and to estimate an over-all isotropic thermal parameter B of 2·1 Å^2. Coefficients for a Patterson projection on (010) were prepared by sharpening (Patterson, 1935) the values $|F|^2_{h0l}$ by multiplication by the factor $(1/\hat{f}_0^2)\exp(2B\sin^2\theta/\lambda^2)$ and by modifying them further by multiplication by the factor $(2\sin\theta/\lambda)^4\exp[-(4{\cdot}4\sin\theta/\lambda)^2]$ (see Waser & Schomaker, 1953; Shoemaker, 1947; Donohue & Trueblood, 1952). The coefficients were further adjusted so as to remove a spherical peak at the origin, and the Patterson synthesis was computed. From the Patterson map a promising orientation of the molecule was rather easily found. By use of structure-factor graphs the position of the molecule was indicated to be the reasonable one in which the carboxylic acid group lies near a center of symmetry in projection, in close proximity to and presumably hydrogen-bonded to a similar group in a neighboring molecule. After a preliminary structure-factor calculation seemed to confirm the essential correctness of the proposed structure, it was decided to initiate least-squares refinement on the $F(h0l)$'s at once.

In the least-squares refinement weights ω were set equal to $1/F_o^2$ for those reflections with $F_o \geqq 4F_{\text{min.}}$, where $F_{\text{min.}}$ is the minimum observable F_o, and to $\frac{1}{4}F_oF_{\text{min.}}$ for those observed reflections with $F_o \leqq 4F_{\text{min.}}$. The value of $4F_{\text{min.}}$ was taken to be 3·0. Reflections too weak to be observed above background were given zero weight, as was also the (100)

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* We are indebted to Mr Raymond Ellison and Dr H. A. Levy of the Oak Ridge National Laboratory for assistance in the use of the ORACLE least-squares program for cell parameters.

reflection, which had too low a Bragg angle to be recorded.

In the two-dimensional refinement ten least-squares cycles were carried out in which the x and z parameters of the carbon, oxygen, and nitrogen atoms were optimized. Intermixed with the least-squares calculations were three difference syntheses on (010), from which individual anisotropic thermal parameters of the heavy atoms were estimated, as well as approximate x and z coordinates for the nine hydrogen atoms. The usual discrepancy factor R (omitting non-observed reflections) fell from 0·47* to 0·073 at the end of the refinement, when the calculated structure factors included anisotropic thermal parameters and hydrogen parameters.

So pleasing was the promise of a rather precise structure determination as indicated by the level of agreement for the $h0l$ data that it was decided to take a new set of Weissenberg photographs. Crystal specimen II was selected at this point as the best available. With some care, multiple-film exposures of 30–35 hours duration were made for the layers $k=0$ to 4. The resulting films were somewhat more satisfactory than those of the original set as regards variation in spot shape and also as regards the ratio of strongest to weakest intensity—about 50,000:1.

A few Weissenberg films were taken using crystal specimen III, mounted along the c axis. It was soon clear, however, that specimen III was not an acceptable one for recording intensities. The appearance of rings, streaks, and generally somewhat diffuse spots on the films suggested that the crystal had been shattered when it was cut. No other crystal could be cut that was more satisfactory, and the attempt to collect data from a crystal mounted about an axis other than b was abandoned. Even so, only about twenty reflections ($h5l$'s) within the limiting sphere for copper radiation were unrecorded. A total of seven low-order reflections were not observed because they fell within the solid angle subtended by the beam stop. The total number of reflections in the range of reciprocal space explored was 1579, of which 185 were too weak to be observed above background.

The data of the layers $k=0$ to 3 were scaled together through use of data from precisely timed equi-inclination and anti-inclination Weissenberg photographs, one pair for each value of k. The two photographs, each taken with exactly the same oscillation range (approximately 90°), were recorded on different portions of the same film. The procedure, which is essentially that of Stadler (1950), was found to be quite satisfactory. Data of the fourth layer were later correlated to the main body of data empirically at an advanced stage of the structure analysis.

The entire process of reading of intensities, determination of film factors, averaging, and correlation was carried out by the two authors working independently of each other. Two different calibration strips were employed, prepared by identical procedures using the same reflection. Each author used his own approach to the problems presented by variation in spot size and by $\alpha_1-\alpha_2$ splitting. The resulting two sets of data, A and B, were not combined, but instead they were used in separate refinements of the structural parameters.

In general, the agreement between the two sets of observations was good. There were, however, large systematic discrepancies for a number of low-order reflections on the non-equatorial photographs where the spots are contracted. These differences were clearly due to differing estimates of the effect of the contraction on the intensity of the spot. Upon comparison with the final set of calculated structure factors, it appears that one of us (R. M., set B) underestimated the effect. There were also small differences in the two sets of film factors, causing further systematic discrepancies among the strong reflections.

The F_o values of the new set of data A were scaled by comparison of the $F(h0l)$'s with those from the original data from crystal I. Structure analysis was continued with use of data A.

Approximate y coordinates for the eleven heavy atoms were found by systematic trial calculations of $0kl$ structure factors, beginning with the information about the approximate tilt of the molecule that was at hand from the lengths of the bonds in the benzene ring as they appeared in the projection on (010). The y coordinates were refined somewhat (to $R=0·21$, hydrogens excluded) by least-squares and difference-map calculations on the $0kl$ data.

Three-dimensional refinement

Three-dimensional refinement was carried out mainly by the method of least-squares. Two difference maps were calculated at appropriate stages, the first to obtain hydrogen coordinates and the second to refine them. In the least-squares calculations the same weighting scheme was used as in the two-dimensional refinement discussed above. Refinement was first carried out on data A. Seven unrecorded low-order reflections were given zero weight, as were six other reflections of large $|F_o|$ which were feared to be subject to extinction. The least-squares calculations were diagonal with respect to the atomic coordinates. In those cycles in which anisotropic thermal parameters of the Debye factor exp $(-\Sigma\Sigma\beta_{ij}h_ih_j)$ were adjusted, cross terms between the various β_{ij}'s of each atom were retained.

Refinement proceeded very smoothly. In the first few stages a number of indexing errors and arithmetic errors in the data processing, indicated by outstanding discrepancies between F_o and F_c values, were corrected. A synopsis of the entire refinement procedure is presented in Table 2, beyond which little further

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* In part the relatively large initial value of R was the result of an error made when the scale factor was determined from the Wilson plot.

Table 2. *Synopsis of three-dimensional refinement of 2-amino-3-methylbenzoic acid*

In this table X, Y, Z and x, y, z denote coordinates of heavy atoms and hydrogen atoms, respectively

Data	Calculation	Refining or determining	Discrepancy factor R (%)	$\Sigma\omega(\Delta F)^2$	Remarks*
A	L.S. cycles 1–3	Y	21·2 to 16·1	2428 to 1173	Starting parameter from 2-D refinement
	L.S. 4–5	X, Y, Z	15·6 to 15·3	1132 to 1158	
	L.S. 6–8	X, Y, Z, β_{ij}	15·5 to 11·0	1055 to 527	Anisotropic thermal refinement begun
	3-D diff. map 1	x, y, z			Hydrogen peaks of 0·31 to 0·55 e.Å^{-3}
	L.S. 9–15	X, Y, Z, β_{ij}	8·1 to 6·3	300 to 171	Hydrogens included in F_c's. $F(h4l)$'s first included in L.S. 11
	Structure factors		9·2	152	Hydrogens omitted
	3-D diff. map 2	x, y, z			Hydrogen peaks of 0·48 to 0·67 e.Å^{-3}
	L.S. 16–17	X, Y, Z, β_{ij}	5·9 to 5·8	152 to 143	Hydrogens included in F_c's
	L.S. 19–20	x, y, z	5·1 to 5·1	44 to 48	Used only reflections with sin $\theta \leqq 0·7$
	Structure factors		5·6	126	Final F_c's for parameters refined on data A
B	L.S. 18	X, Y, Z, β_{ij}	7·4	159	Heavy-atom parameters from L.S. 17, hydrogen parameters from 3-D difference map 2
	L.S. 21	X, Y, Z, β_{ij}	7·4	145	Hydrogen parameters from L.S. 20. Final F_c's for parameters refined on data B

* Overall scale factor adjusted in each L.S. cycle. Individual scale factors for each layer l adjusted between each cycle after L.S. 10.

explanation is needed. In the first three stages only the shifts of the y parameters were applied, since the starting y parameters were much less reliable than the x and z parameters. Refinement of thermal parameters began in cycle 6. The $F_0(h4l)$ data, scaled to the $F_c(h4l)$ of cycle 10, were first included in the least-squares in cycle 11.

The first 3-D difference map, following L.S. 8, indicated very clearly the approximate coordinates of the nine hydrogen atoms at the centers of peaks of 0·31 to 0·55 e.Å^{-3}. Hydrogen contributions were included in the subsequent least-squares calculations, though the hydrogen parameters were usually held fixed. A few of the hydrogen coordinates determined from difference map 1 were modified slightly to make —as was supposed—more chemical sense. Following cycle 15, structure factors without hydrogen contributions were computed for use in a subsequent difference map 2, from which new hydrogen coordinates were derived. The hydrogen peaks in difference map 2, of height 0·48 to 0·67 e.Å^{-3}, were somewhat more satisfactory in appearance than those in difference map 1. There were no regions in which there was appreciable density other than those in which the hydrogens were located, as indeed was true also in the case of map 1. The appearance of the hydrogen peaks in map 2 is shown in Fig. 1.

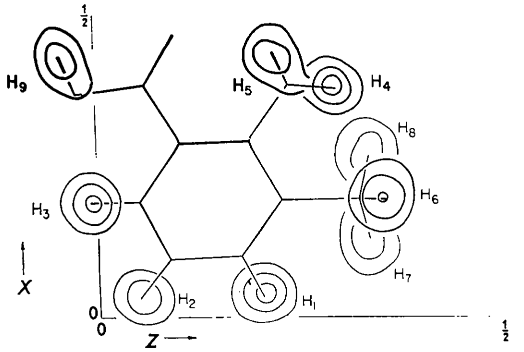

Fig. 1. Composite map on (010) of electron density through centers of hydrogen atoms, from second three-dimensional difference map. The contours are at 0·2, 0·4, and 0·6 e.Å^{-3}.

In least-squares cycles 19 and 20, by which the refinement on data A was concluded, only the coordinates of the hydrogen atoms were adjusted, all other parameters being held fixed. Each hydrogen atom was arbitrarily assigned anisotropic thermal parameters equal to those of the heavy atom to which it is attached, except that increments equivalent to 0·50 cm.$^{-16}$ in the isotropic B were added. These last refinement cycles were apparently meaningful, for the resulting new coordinates appeared to be generally more sensible chemically (see discussion of molecular structure below). In addition, there was a slight decrease in $\Sigma\omega(\Delta F)^2$ and in the R factor (see Table 2) when the new hydrogen coordinates were used in the calculation of structure factors.

After the completion of the refinement on data A, the electron density projected on (010) was computed. The projection is shown in Fig. 2.

Refinement on data B was initiated in L.S. 18 using the structural parameters reached in the refinement on data A through cycle 17. The last cycle, no. 21, used the final hydrogen parameters from refinement

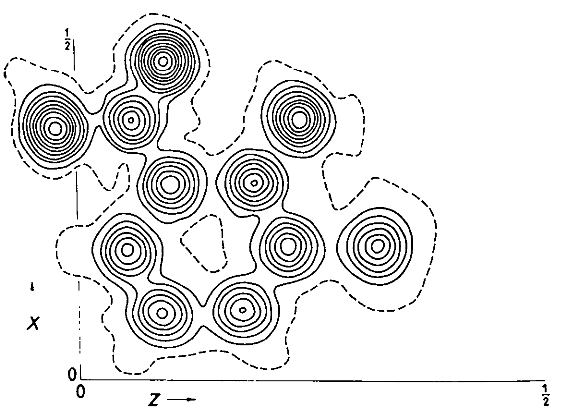

Fig. 2. Final Fourier projection on (010). Contours are at intervals of 1 e.Å^{-2}, beginning with the 1 e.Å^{-2} contour, which is dashed.

cycle 20 on data *A*.* Structure factors corresponding to the revised heavy-atom parameters from L.S. 21 were not computed. As a consequence the values of $\Sigma\omega(\Delta F)^2$ and of the standard deviations of coordinates for structure *B* appear at a very slight disadvantage relative to those for structure *A*.

All calculations required for solution and refinement of the structure were carried out on a Datatron 205 computer. Each least-squares cycle in which heavy-atom coordinates and β_{ij}'s were adjusted and hydrogen-atom contributions to structure factors included required about fourteen hours of machine time. We are grateful to Dr Albert Hybl for much assistance in use of the least-squares program.

Table 3. *Final coordinates* ($\times 10^4$) *of carbon, oxygen, and nitrogen atoms from refinements A and B*

Standard errors ($\times 10^5$) appear in parentheses

Atom		*x*	*y*	*z*
C_1	*A*	2859(12)	5817(33)	1014(8)
	B	2860(12)	5806(36)	1013(9)
C_2	*A*	2901(11)	5197(29)	1896(8)
	B	2900(11)	5197(33)	1896(9)
C_3	*A*	1955(12)	3511(32)	2267(9)
	B	1954(13)	3508(35)	2268(10)
C_4	*A*	1029(14)	2507(37)	1758(11)
	B	1028(15)	2501(41)	1759(12)
C_5	*A*	980(14)	3118(40)	889(10)
	B	978(15)	3111(45)	890(11)
C_6	*A*	1889(13)	4749(37)	526(9)
	B	1889(14)	4752(41)	526(9)
C_7	*A*	3799(12)	7579(35)	594(8)
	B	3799(13)	7570(39)	594(9)
C_8	*A*	1976(15)	2833(41)	3203(10)
	B	1974(17)	2824(47)	3202(11)
N	*A*	3825(11)	6125(35)	2402(8)
	B	3826(12)	6132(40)	2401(8)
O_1	*A*	3658(11)	7879(38)	−234(7)
	B	3656(12)	7879(41)	−235(7)
O_2	*A*	4665(10)	8745(32)	963(7)
	B	4665(11)	8739(34)	963(8)

Final parameters and precision

The final coordinates of the eleven heavy atoms are given in Table 3 for each of the two separate sets of data, *A* and *B*. Standard deviations, calculated from the diagonal terms of the least-squares inverse matrices, are indicated in parentheses after each coordinate. The hydrogen coordinates from the least-squares calculations on data *A* are given in Table 4. Results of the least-squares adjustment of hydrogen coordinates suggest a standard error of about 0·03 Å for each coordinate Final thermal parameters β_{ij}, defined by the Debye factor

Table 4. *Final hydrogen coordinates* ($\times 10^3$), *from least squares on data A*

Atom	*x*	*y*	*z*
H_1	32	129	203
H_2	32	239	51
H_3	189	515	−9
H_4	374	582	297
H_5	438	735	219
H_6	198	480	355
H_7	131	149	337
H_8	268	143	337
H_9	430	899	−44

Table 5. *Final thermal parameters* β_{ij} ($\times 10^5$) *from refinements A and B*

Atom		β_{11}	β_{22}	β_{33}	β_{12}	β_{23}	β_{13}
C_1	*A*	594	4115	265	283	−78	−35
	B	619	3961	276	263	−83	−26
C_2	*A*	548	3710	278	249	−39	−18
	B	578	3528	286	247	−44	−27
C_3	*A*	660	3406	328	176	62	−1
	B	686	3339	333	181	62	2
C_4	*A*	698	4230	410	−117	−26	−4
	B	712	4145	412	−61	−1	−4
C_5	*A*	734	5327	412	−151	−195	−132
	B	747	5327	407	−164	−214	−120
C_6	*A*	715	5219	293	170	−173	−97
	B	728	5343	288	161	−166	−78
C_7	*A*	635	5309	228	275	−8	−3
	B	662	5197	252	278	−14	−5
C_8	*A*	846	5999	342	−91	313	40
	B	861	6060	343	−119	308	50
N	*A*	647	7354	255	−206	−148	60
	B	668	7164	263	−233	133	−64
O_1	*A*	904	10172	242	−617	170	−34
	B	922	10002	234	−683	134	−37
O_2	*A*	677	9100	277	−461	145	−24
	B	713	8814	301	−466	145	−16

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* It is apparent that use of hydrogen parameters based on data *A* in refinement of heavy-atom parameters on data *B* makes the two refinements on data *A* and *B* no longer completely independent. We do not think, however, that this is important.

Table 6. *Observed and calculated structure factors* (×10)

Each group of four columns contains, from left to right, indices l, observed structure factors A, observed structure factors B, and calculated structure factors A. Observed values marked with asterisks were given weights of zero, as were also the unobserved values marked with the < signs

$00l$			
0	-	-	3200
2	47	44	-52
4	141	133	142
6	288	273	-282
8	236	228	-219
10	122	117	104
12	125	130	123
14	171	165	-187
16	16	18	-10
18	<9	<9	7
20	14	14	15
$10l$			
0	-	-	-341
2	643*	590*	-839
4	364	332	-372
6	131	122	120
8	237	226	212
10	42	41	38
12	105	105	102
14	75	77	75
16	123	119	125
18	50	50	45
20	8	8	-9
$\bar{1}0l$			
2	346	332	358
4	<5	<4	3
6	422	398	424
8	593	545	-567
10	106	105	-95
12	116	120	-109
14	16	14	17
16	74	71	-86
18	12	12	14
20	48	50	-48
$20l$			
0	428	390	-433
2	241	219	239
4	311	294	-295
6	401	375	-380
8	98	92	-91
10	77	75	-63
12	14	13	-7
14	34	35	-37
16	113	109	-108
18	15	13	-12
$\bar{2}0l$			
2	258	230	238
4	27	26	-28
6	37	36	-40
8	305	283	300
10	141	134	135
12	136	133	130
14	93	87	101
16	<11	<7	5
18	38	38	-34
20	18	18	22
$30l$			
0	121	112	-106
2	182	168	-169
4	263	241	252
6	158	147	152
8	233	223	217
10	153	146	149
12	26	27	26
14	66	63	-62
16	75	72	76
18	89	83	-80
$\bar{3}0l$			
2	420	378	401
4	255	234	247
6	<7	<7	9
8	<8	<6	-6
10	214	207	-210
12	106	102	-96
14	27	27	26
16	10	8	-7
18	36	35	-29
$40l$			
0	380	350	-362
2	253	249	-254
4	62	58	-52
6	61	63	59
8	89	88	-76
10	337	332	356
12	207	196	-203
14	32	31	31
16	56	56	-56
18	<10	<10	1
$\bar{4}0l$			
2	53	51	44
4	657*	608	-652
6	109	106	-97
8	51	52	53
10	18	20	13
12	127	121	122
14	43	39	-40
16	20	20	-22
18	39	38	37
$50l$			
0	154	143	146
2	234	227	-218
4	443	412	409
6	10	11	12
8	91	85	87
10	312	308	-323
12	260	261	-273
14	26	26	-28
16	18	15	20
18	92	84	83
$\bar{5}0l$			
2	187	179	171
4	588*	521	544
6	72	67	-79
8	<9	<7	1
10	225	212	-223
12	113	109	114
14	131	124	126
16	86	86	89
18	<8	<7	9
$60l$			
0	<9	<10	6
2	397	400	381
4	37	35	30
6	92	87	-76
8	15	12	-14
10	113	109	-110
12	280	257	274
14	86	82	85
16	49	48	47
18	20	20	-20
$\bar{6}0l$			
2	245	223	-234
4	156	143	143
6	139	130	125
8	27	27	28
10	67	72	71
12	352	335	-365
14	57	56	-56
16	48	46	-48
18	40	43	37
$70l$			
0	208	188	-194
2	75	75	-66
4	280	280	-273
6	18	18	18
8	17	18	21
10	<10	<8	10
12	43	39	-42
14	<13	<12	-7
16	<10	<7	-5
$\bar{7}0l$			
2	69	67	-69
4	71	72	-58
6	<9	<9	-2
8	60	61	-61
10	189	182	188
12	15	12	17
14	<10	<12	5
16	24	23	23
18	50	54	-59
$80l$			
0	27	27	22
2	115	114	109
4	130	125	130
6	87	86	-85
8	<10	<7	-2
10	89	89	-91
12	19	20	20
14	50	48	46
16	8	10	6
$\bar{8}0l$			
2	35	35	29
4	<9	<7	12
6	51	52	48
8	116	114	117
10	19	17	-20
12	53	56	52
14	47	51	-45
16	11	10	11
$90l$			
0	117	105	-102
2	37	35	36
4	83	83	-77
6	142	135	155
8	18	17	17
10	94	86	92
12	37	38	35
14	32	29	28
$\bar{9}0l$			
2	19	15	-22
4	70	67	-69
6	34	34	-33
8	40	38	-37
10	29	28	-25
12	21	22	18
14	<9	<10	2
16	37	39	-40
$10,0,l$			
0	205	189	205
2	23	22	23
4	61	56	62
6	17	14	-13
8	172	159	-178
10	27	26	-28
12	<9	<8	4
14	45	44	-40
$\bar{10},0,l$			
2	218	203	-214
4	63	62	-56
6	21	21	-21
8	18	19	17
10	32	31	29
12	44	45	44
14	24	26	-22
$11,0,l$			
0	223	206	222
2	95	88	-95
4	36	35	-35
6	85	82	-92
8	43	42	48
10	37	36	37
12	25	27	26
$\bar{11},0,l$			
2	161	153	155
4	34	30	28
6	<11	<7	10
8	96	92	-102
10	19	18	17
12	15	12	12
$12,0,l$			
0	169	159	-167
2	<10	<10	-13
4	18	15	-16
6	23	24	24
8	27	27	32
10	<7	<7	1
$\bar{12},0,l$			
2	45	42	45
4	29	26	-25
6	46	44	47
8	<9	<8	1
10	28	29	-29
12	20	22	-22
$13,0,l$			
0	<9	<10	0
2	9	8	6
4	27	26	-24
6	42	42	-45
8	<7	<6	1
$\bar{13},0,l$			
2	23	21	22
4	14	12	15
6	39	39	-40
8	41	42	47
$14,0,l$			
0	26	26	-24
2	25	25	26
4	14	13	16
$\bar{14},0,l$			
2	23	22	21
4	11	10	-11
6	29	31	32
$01l$			
1	-	-	-211
2	118	140	115
3	128	155	131
4	17	19	21
5	125	143	-126
6	168	195	-168
7	193	229	193
8	153	174	-154
9	<8	<9	-3
10	144	154	-143
11	66	63	66
12	51	45	-43
13	<10	<10	3
14	70	66	-76
15	11	11	11
16	66	62	-61
17	60	58	-61
18	11	9	-11
19	8	7	7
$11l$			
0	-	-	-16
1	260	356*	283
2	33	40	-25
3	83	100	-88
4	43	45	43
5	355	402	363
6	118	136	-117
7	72	71	72
8	397	440	388
9	47	46	-40
10	100	97	91
11	28	27	-25
12	17	15	7
13	29	28	35
14	35	33	-34
15	36	36	-40
16	47	45	55
17	21	20	25
18	16	15	-13
19	36	35	-35
$\bar{1}1l$			
1	672*	772*	-795
2	715*	811*	836
3	122	136	-117
4	254	288	-260
5	47	50	-48
6	137	153	141
7	32	31	27
8	117	125	120
9	13	11	12
10	153	151	152
11	62	58	-60
12	98	91	93
13	23	21	-29
14	19	19	-17
15	68	63	72
16	61	58	60
17	37	35	35
18	37	36	37
19	13	11	-14
$21l$			
0	912*	947*	-1172
1	267	333	272
2	121	142	-132
3	108	131	117
4	12	12	-9
5	60	68	-61
6	89	96	83
7	168	185	-156
8	14	14	-14
9	<9	<9	-4
10	104	102	105
11	26	26	26
12	144	141	-140
13	117	107	-115
14	114	102	114
15	17	15	-19
16	13	11	11
17	38	36	-38
18	8	8	-11
19	39	38	37
$\bar{2}1l$			
1	448	554*	480
2	41	46	-47
3	352	401	-367
4	296	324	291
5	63	65	-61
6	71	74	-72
7	186	207	-186
8	192	213	-198
9	124	126	124
10	104	97	97
11	96	91	87
12	22	21	21
13	<11	<10	8
14	39	37	-41
15	51	47	-51
16	<11	<11	6
17	48	45	50
18	18	18	-17
19	12	13	14
$31l$			
0	219	257	230
1	144	183	-148
2	12	14	-5
3	78	80	70
4	252	283	252
5	201	219	190
6	55	56	-47
7	25	25	-23
8	66	64	-59
9	55	56	45
10	109	110	-109
11	200	195	-198
12	198	195	-194
13	24	23	23
14	29	28	-32
15	64	63	65
16	27	24	-27
17	50	49	48
18	17	19	16
19	25	26	26
$\bar{3}1l$			
1	133	151	132
2	67	77	-66
3	391	456	402
4	292	312	-281
5	54	56	46
6	80	84	88
7	31	30	30
8	160	167	-158
9	195	197	-197
10	70	72	72
11	64	64	-67
12	124	119	-124
13	38	36	35
14	46	41	-43
15	11	11	10
16	59	57	-63
17	17	15	-21
18	<8	<9	5
19	<7	<8	2
$41l$			
0	22	23	22
1	19	20	20
2	129	135	116
3	146	159	136
4	151	164	138
5	242	251	-216
6	60	63	65
7	133	135	-124
8	40	38	33
9	113	110	-108
10	33	31	-30
11	74	74	75
12	172	164	162
13	168	165	165
14	92	85	92
15	11	10	-11
16	47	43	47
17	28	28	25
18	8	<9	-7
$\bar{4}1l$			
1	68	74	-67
2	339	406	344
3	147	172	-140
4	114	115	-108
5	44	46	38
6	124	125	-123
7	53	57	50
8	43	37	33
9	157	159	159
10	10	9	9
11	112	109	-112
12	243	233	235
13	45	42	-41
14	100	95	100
15	42	39	-38
16	20	15	17
17	14	9	7
18	41	39	-34
19	28	29	27
$51l$			
0	85	96	-82
1	62	64	-57
2	13	13	16
3	184	198	-173
4	289	320	-272
5	109	108	-99
6	35	35	-30
7	96	95	92
8	26	26	29
9	44	41	-38
10	83	78	-81
11	164	156	157
12	<11	<10	1
13	94	83	-88
14	35	32	-34
15	14	12	14
16	52	49	-51
17	36	34	-31
18	58	60	57
$\bar{5}1l$			
1	103	110	100
2	190	211	199
3	110	111	-100
4	106	104	91
5	86	87	87
6	104	104	104
7	<9	<9	4
8	61	62	63
9	<10	<9	10
10	249	236	-241
11	128	119	126
12	44	40	-40
13	48	43	-41
14	37	32	-33
15	31	28	31
16	10	11	-6
17	41	40	-34
18	32	31	29
$61l$			
0	70	70	62
1	95	94	96
2	225	246	223
3	81	78	-69
4	115	118	111
5	121	124	110
6	<9	<9	-10
7	46	45	-45
8	25	24	-25
9	157	150	148
10	215	199	-208
11	<11	<12	-3
12	67	64	63
13	<11	9	5
14	22	21	20
15	15	14	-17
16	33	30	31
17	45	45	-43
$\bar{6}1l$			
1	63	64	-65
2	33	33	-29
3	21	22	-25
4	173	176	-172
5	184	190	-169
6	107	111	-97
7	77	75	74
8	25	25	-19
9	56	52	-52
10	18	15	18
11	113	114	108
12	59	54	52
13	<10	9	1
14	<11	<11	-4
15	33	30	-33
16	40	38	-40
17	<8	8	6
18	13	12	12
$71l$			
0	31	29	-30
1	105	112	-96
2	72	73	71
3	75	72	67
4	177	183	-157
5	20	19	-15
6	18	17	19
7	110	103	107
8	19	20	-22
9	<11	<10	2
10	190	188	184
11	108	100	-99
12	108	100	104
13	16	14	-17
14	35	32	34
15	28	26	-26
16	32	31	-29
17	8	8	8
$\bar{7}1l$			
1	16	15	-17
2	<9	<9	3
3	96	94	89
4	233	236	214
5	9	10	-4
6	10	10	13
7	142	148	-136
8	<10	<9	7
9	28	27	-23
10	28	26	-26
11	76	79	-78
12	<10	<9	-1
13	121	112	115
14	72	71	72
15	19	19	19
16	56	57	59
17	17	18	19
$81l$			
0	88	88	93
1	151	151	150
2	117	119	-109
3	70	72	62
4	25	25	21
5	15	13	12
6	18	15	14
7	79	76	-86
8	109	99	-113
9	82	82	-89
10	20	19	20
11	16	13	18
12	85	84	-86
13	17	16	16
14	44	40	-40
15	15	14	-10
16	13	13	-14
$\bar{8}1l$			
1	26	25	-27
2	52	50	52
3	15	12	-17
4	70	65	61
5	52	47	46
6	10	9	13
7	19	19	18
8	19	18	-19
9	43	42	43
10	24	23	25
11	54	51	-48
12	142	142	-146
13	65	62	-66
14	<9	<9	-4
15	43	41	38
16	44	46	-44
$91l$			
0	217	212	219
1	39	37	-38
2	73	67	-69
3	115	108	-111
4	19	18	17
5	21	20	-22
6	46	43	-49
7	24	23	-31
8	11	9	12
9	85	82	88
10	51	47	52
11	13	11	11
12	52	46	49
13	24	25	-23
14	35	34	-33
15	<6	<9	-4
$\bar{9}1l$			
1	155	159	162
2	94	90	-90
3	19	20	18
4	49	47	-44
5	20	19	21
6	<11	<10	0
7	31	30	-36
8	43	39	45
9	32	30	-32
10	25	24	27
11	33	30	32
12	15	13	-11
13	14	12	-12
14	27	27	25
15	41	39	-36
$10,1,l$			
0	125	119	-121
1	159	153	-153
2	80	74	-74
3	47	44	47
4	11	<10	-7
5	37	35	-37
6	56	53	55
7	48	46	55
8	40	38	43
9	35	35	-34
10	18	17	19
11	<9	<9	-6
12	<8	<9	-1
13	<7	<8	4
14	<5	<7	-1
$\bar{10},1,l$			
1	23	19	-20
2	26	21	23
3	<11	<10	0
4	20	19	17
5	34	32	31
6	26	25	-29
7	61	57	65
8	48	44	41
9	23	20	-22
10	<10	<11	3
11	12	11	-11
12	33	29	32
13	15	15	15
14	42	42	-39
$11,1,l$			
0	17	15	17
1	49	46	51
2	37	38	38
3	40	38	-27
4	<11	<11	5
5	25	22	25
6	85	82	-89
7	34	30	34
8	<10	<10	5
9	<9	<9	4
10	27	25	-28
11	11	10	11
12	14	14	-15
$\bar{11},1,l$			
1	103	98	-104
2	60	55	-57
3	47	42	43
4	11	<11	10
5	25	25	-27
6	33	33	35
7	31	29	30
8	36	34	-40
9	14	11	14
10	13	12	-9
11	14	13	14
12	<7	<8	-4
13	8	7	-4
$12,1,l$			
0	87	83	-89
1	39	36	38
2	18	18	-20
3	17	17	19
4	10	<9	-8
5	53	51	56
6	33	30	33
7	11	9	-12
8	59	63	65
9	8	7	-7
10	33	30	34
$\bar{12},1,l$			
1	20	19	-20
2	93	87	-94
3	74	69	-74
4	36	33	-33
5	<10	<10	11
6	16	14	-16
7	24	21	-25
8	<8	<9	-4
9	21	24	25
10	43	44	41
11	10	9	-9
$13,1,l$			
0	53	55	-56
1	<9	<9	-7
2	13	10	13
3	9	9	10
4	24	23	22
5	15	15	-18
6	22	24	27
7	18	19	-20
8	14	13	-17
$\bar{13},1,l$			
1	66	65	68
2	52	47	52
3	<9	<9	5
4	20	18	20
5	31	28	-29
6	24	25	22
7	20	21	-18
8	34	31	-34
9	11	11	-15
$14,1,l$			
0	38	38	43
1	8	7	-11
2	<7	<7	1
3	21	22	22
4	15	14	16
$\bar{14},1,l$			
1	19	18	-21
2	21	21	24
3	36	35	38
4	52	51	-52
5	17	18	19
$02l$			
0	-	-	-234
1	-	-	22
2	55	56	-56
3	143	157	144
4	35	41	-37
5	<6	<6	-3
6	69	66	-73
7	44	42	-39
8	53	54	53
9	109	115	-122
10	19	19	17
11	19	20	-22
12	68	63	-65
13	32	31	-32
14	<10	8	5
15	37	35	36
16	16	16	19
17	41	40	-43
18	<6	<7	1
$12l$			
0	38	39	-44
1	151	152	156
2	107	119	107
3	51	58	-51
4	148	166	146
5	154	160	146
6	135	137	-130
7	24	26	-22
8	36	37	-38
9	82	80	83
10	92	90	-95
11	83	82	-85
12	155	151	-165
13	43	38	48
14	62	58	64
15	10	9	8
16	16	14	15
17	8	7	9
18	<7	<7	2
$\bar{1}2l$			
1	47	43	42
2	316	335	312
3	202	221	-214
4	74	78	75
5	61	66	65
6	69	75	67
7	54	56	52
8	82	81	80
9	69	70	68
10	56	58	-59
11	23	25	24
12	50	46	47
13	29	30	-28
14	16	12	15
15	18	17	-20
16	<9	<8	-3
17	37	36	39
18	12	11	13
$22l$			
0	169	193	-171
1	21	25	20
2	25	29	25
3	178	191	165
4	64	68	-62
5	73	74	-64
6	22	25	22
7	213	222	-210
8	61	62	56
9	34	38	-34
10	27	30	30
11	<9	<10	9
12	136	128	142
13	137	128	133
14	111	105	120
15	16	17	-19
16	11	11	9
17	13	14	13
18	8	7	6
$\bar{2}2l$			
1	27	33	25
2	143	162	-143
3	317	335	321
4	154	155	144
5	28	30	-25
6	52	52	47
7	7	7	4
8	67	71	70
9	130	155	-141
10	75	77	-76
11	98	92	103
12	105	99	-107
13	26	25	27
14	87	77	-80
15	37	34	37
16	39	40	-36
17	40	38	-43
18	<6	<7	-5
$32l$			
0	14	17	13
1	113	119	-100
2	31	34	-33
3	57	59	-50
4	140	142	-135
5	279	288	-269
6	129	129	114
7	88	92	88
8	58	58	-53
9	27	28	24
10	35	33	-35
11	109	100	106
12	85	84	90
13	117	107	-117
14	89	85	-87
15	23	23	-23
16	33	33	-36
17	20	21	-22
18	10	12	-13
$\bar{3}2l$			
1	451	494	-451
2	509	564	-537
3	32	34	-32
4	67	66	-55
5	29	31	27
6	25	27	-23
7	96	92	95
8	12	10	3
9	16	16	12
10	243	246	263
11	142	143	-146
12	24	23	26
13	34	34	-36
14	15	12	12
15	10	9	8
16	42	41	41
17	63	57	60
18	24	25	-25
$42l$			
0	299	327	286
1	<6	<7	4
2	162	169	162
3	43	44	-43
4	48	47	41
5	152	164	147
6	56	58	52
7	62	64	54
8	34	34	-29
9	<9	<9	-1
10	45	42	-43
11	<10	<10	-3
12	13	12	-12
13	42	38	40
14	41	39	-42
15	27	27	29
16	24	25	-25
17	7	6	8
$\bar{4}2l$			
1	202	209	186
2	64	67	53
3	139	154	-132
4	50	52	-40
5	24	26	20
6	9	9	9
7	124	132	-130
8	124	132	-130
9	142	149	152
10	75	77	75
11	16	14	-16
12	21	21	22
13	37	36	39
14	22	21	-22
15	33	35	-31
16	41	40	43
17	12	11	15
$52l$			
0	62	65	-59
1	41	40	34
2	7	6	7
3	70	70	-64
4	16	16	-13
5	112	111	-110
6	15	14	-16
7	26	29	27
8	79	79	76
9	<9	<10	2
10	<10	<10	4
11	48	44	46
12	42	40	43
13	20	17	-21
14	41	37	40
15	36	35	-36
16	14	13	-12
$\bar{5}2l$			
1	31	30	23
2	66	71	63
3	25	27	23
4	77	79	-71
5	37	36	33
6	63	70	-68
7	85	86	90
8	22	22	-23
9	39	38	-39
10	91	91	-92
11	<10	<10	0
12	13	11	9
13	45	41	-45
14	16	13	-16
15	9	8	6
16	40	40	-42
17	26	27	-30
$62l$			
0	46	48	50
1	47	48	49
2	35	35	23
3	11	10	-10
4	36	37	-32
5	76	79	73
6	36	35	-39
7	16	17	-23
8	119	118	-130
9	25	23	23
10	38	34	-36
11	46	42	-43
12	17	14	-17
13	28	29	-28
14	45	45	-46
15	<8	5	-2
16	14	15	14
$\bar{6}2l$			
1	50	50	49
2	36	35	32
3	67	70	-65
4	32	33	-29
5	44	41	-41
6	27	30	22
7	31	34	-30
8	31	33	31
9	<10	<12	-8
10	13	12	-11
11	27	27	23
12	40	37	37
13	15	13	16
14	46	42	49
15	25	26	-24
16	7	6	7
$72l$			
0	169	172	179
1	46	44	-43
2	117	120	-124
3	47	44	-50
4	19	20	-20
5	<9	<10	5
6	20	20	-21
7	<10	<10	-11
8	67	64	-65
9	119	110	124
10	145	136	158
11	50	49	-51
12	16	14	16
13	16	15	16
14	<8	<7	1
15	37	35	-36
$\bar{7}2l$			
1	84	87	-95
2	102	109	111
3	32	28	-30
4	9	7	11
5	42	40	36
6	81	83	84
7	68	75	77
8	24	22	-29
9	<10	<10	-4
10	38	35	-39
11	22	22	23
12	16	14	12
13	36	35	-35
14	80	80	-81
15	40	39	40
16	16	18	-18
$82l$			
0	113	113	-120
1	180	175	-192
2	167	181	-191
3	96	90	93
4	35	34	34
5	<10	<10	3
6	16	13	13
7	65	65	74
8	98	93	106
9	121	113	-120
10	68	64	71
11	24	22	-25
12	24	24	-24
13	23	22	-21
14	<7	<7	-4
$\bar{8}2l$			
1	22	22	19
2	33	33	-32
3	42	38	41
4	56	54	-60
5	118	115	-125
6	<10	<10	6
7	24	24	-33
8	12	9	10
9	29	30	30
10	<10	<9	-6
11	57	55	61
12	55	56	56
13	9	9	-8
14	9	11	9
15	40	41	-43
$92l$			
0	69	69	-69
1	114	101	111
2	92	89	95
3	10	10	1
4	37	34	30
5	<11	<10	-7
6	13	12	11
7	36	34	-34
8	32	28	32
9	10	8	-12
10	88	89	-92
11	59	62	60
12	37	35	-37
13	7	7	10
$\bar{9}2l$			
1	32	29	30
2	28	27	28
3	15	12	12
4	34	32	33
5	50	45	55
6	56	50	-58
7	89	87	-94
8	18	16	22
9	10	9	-8
10	<10	<9	5
11	56	56	-61
12	13	13	-14
13	69	72	72
14	71	75	82
$10,2,l$			
0	16	14	-17
1	15	13	-13
2	54	49	52
3	24	22	-25
4	10	10	13
5	37	34	35
6	12	12	16
7	37	35	36
8	22	21	23
9	16	16	17
10	<8	<7	1
11	18	18	-20
12	6	5	6
$\bar{10},2,l$			
1	36	34	33
2	<10	<10	1
3	<10	<10	-4
4	50	45	49
5	15	12	13
6	17	17	-20
7	18	19	24
8	<10	<9	3
9	<10	10	8
10	17	18	-17
11	<8	<8	-2
12	69	71	-74
$11,2,l$			
0	26	27	-27
1	25	24	25
2	<10	<9	-2
3	24	23	24
4	23	22	21
5	9	9	-8
6	26	26	-28
7	27	28	-26
8	8	7	-4
9	23	25	-25
10	10	9	-10
$\bar{11},2,l$			
1	18	18	20
2	12	9	8
3	<10	<9	2
4	44	42	-47
5	17	17	19
6	<9	8	-7
7	<9	7	7
8	<8	<7	5
9	28	27	-28
10	7	7	8
$12,2,l$			
0	9	8	-5
1	21	19	20
2	21	20	21
3	9	7	6
4	13	11	-13
5	34	32	33
6	18	19	-15
7	26	26	-27
8	14	14	-16
$\bar{12},2,l$			
1	11	10	10
2	38	36	38
3	9	8	-7
4	53	52	53
5	20	20	-19
6	14	12	14
7	<7	<6	6
8	10	11	9
9	-	5	-5
$13,2,l$			
0	<7	<6	-3
1	<7	<6	-1
2	<7	<7	2
3	28	29	32
4	22	24	-26
5	-	28*	-53
$\bar{13},2,l$			
1	50	50	-55
2	82	83	-88
3	59	61	-61
4	20	22	23
5	10	11	10
$03l$			
1	-	-	-102
2	94	102	103
3	16	16	-16
4	13	12	-12
5	48	53	-47
6	73	80	-68
7	19	20	-21
8	52	55	-51
9	82	79	83
10	22	24	25
11	50	48	-52
12	100	99	111
13	80	85	86
14	73	79	83
15	22	22	-24
16	9	11	-14
$13l$			
0	89	90	93
1	41	45	42
2	110	114	-110
3	51	55	47
4	93	110	-96
5	79	90	-78
6	24	27	21
7	40	42	38
8	46	42	41
9	<8	<8	-2
10	28	27	28
11	50	47	49
12	25	26	27
13	29	28	-32
14	96	95	-103
15	59	63	-66
16	<6	<6	-1
$\bar{1}3l$			
1	100	105	113
2	99	101	105
3	71	71	-66
4	66	73	64
5	<6	<8	-1
6	<9	<8	1
7	102	100	-101
8	37	36	36
9	83	80	82
10	139	136	-145
11	29	32	33
12	78	80	-81
13	46	43	52
14	32	32	36
15	32	32	34
16	7	7	5
$23l$			
0	54	54	51
1	22	23	-22
2	88	104	88
3	11	14	-13
4	33	38	-33
5	85	100	86
6	129	143	132
7	36	37	36
8	82	84	-79
9	16	18	17
10	24	24	-25
11	27	28	28
12	14	14	-18
13	55	55	-60
14	<8	<7	4
15	7	8	9
16	<6	<6	1
$\bar{2}3l$			
1	88	103	96
2	48	55	-40
3	7	8	-6
4	5	7	-4
5	13	12	11
6	60	67	-65
7	22	24	-21
8	105	100	101
9	155	150	-159
10	13	10	-7
11	34	34	35
12	16	17	-19
13	38	37	-42
14	8	8	5
15	39	38	37
16	23	24	-23
$33l$			
0	16	16	12
1	20	23	-19
2	57	69	-59
3	9	9	-7
4	19	21	-18
5	98	106	-97
6	33	33	27
7	15	15	-12
8	26	26	26
9	32	30	-32
10	17	17	17
11	<9	<8	0
12	56	55	60
13	23	23	-27
14	<8	7	7
15	<7	7	7
$\bar{3}3l$			
1	52	55	49
2	108	123	106
3	52	56	49
4	44	43	-41
5	57	61	-55
6	58	62	54
7	26	28	25
8	25	27	-25
9	57	61	-60
10	50	47	50
11	14	12	14
12	11	11	-11
13	11	9	9
14	16	18	20
15	18	20	-20
$43l$			
0	63	71	61
1	32	34	32
2	20	24	21
3	92	94	-87
4	77	81	74
5	<8	<8	-4
6	61	61	-57
7	75	73	67
8	54	55	-57
9	19	18	-16
10	20	19	-21
11	31	29	-29
12	18	16	-19
13	<9	<8	5
14	41	42	-48
15	<6	<6	1
$\bar{4}3l$			
1	95	107	-97
2	11	11	11
3	205	213	205
4	103	106	99
5	79	79	79
6	14	14	-12
7	21	22	21
8	25	26	-26
9	9	8	4
10	23	24	-25
11	53	50	-55
12	9	8	-9
13	<8	<8	0
14	36	38	-40
15	17	17	18
$53l$			
0	73	76	77
1	7	7	-1
2	75	79	-74
3	64	68	-67
4	23	24	-21
5	80	79	76
6	55	56	-54
7	26	26	-27
8	14	12	12
9	61	64	66
10	92	87	97
11	11	9	11
12	46	46	-46
13	35	36	37
14	8	8	10
$\bar{5}3l$			
1	103	104	-95
2	240	229	-234
3	64	65	-62
4	41	41	40
5	39	39	42
6	<8	<8	-1
7	<8	8	-11
8	42	40	45
9	67	67	66
10	56	54	61
11	28	28	-31
12	27	30	-30
13	26	27	-28
14	29	31	29
15	10	11	-14
$63l$			
0	145	145	-141
1	153	152	-157
2	118	123	-127
3	57	60	58
4	81	78	75
5	28	28	32
6	24	25	26
7	<9	8	8
8	45	40	45
9	24	24	26
10	16	16	-18
11	50	47	-50
12	<8	<8	-4
13	37	39	-40
$\bar{6}3l$			
1	46	47	44
2	38	39	35
3	85	87	-90
4	32	31	-26
5	21	22	23
6	38	39	-47
7	<9	<8	7
8	31	30	-32
9	<9	<8	7
10	52	51	54
11	<9	<8	0
12	16	16	-14
13	45	46	48
14	23	24	-22
$73l$			
0	10	9	-9
1	24	24	24
2	124	116	121
3	122	114	121
4	16	13	-15
5	12	9	8
6	<9	<8	4
7	20	19	23
8	51	51	-54
9	38	39	-43
10	<9	<8	-6
11	17	16	-17
12	11	9	-9
13	10	9	12
$\bar{7}3l$			
1	<8	<8	0
2	<8	<8	-1
3	10	8	-9
4	22	23	25
5	40	39	-49
6	<9	<8	2
7	51	48	54
8	16	15	-18
9	9	8	-8
10	44	46	-46
11	<8	<7	2
12	31	31	29
13	15	17	-16
$83l$			
0	11	11	-10
1	60	61	63
2	8	8	4
3	15	15	-13
4	16	16	-16
5	<9	<8	2
6	<9	<8	-1
7	23	24	25
8	46	46	51
9	64	69	-72
10	20	21	23
11	20	22	22
12	-	9	-10
$\bar{8}3l$			
1	32	31	-32
2	<9	8	8
3	<9	<8	2
4	56	53	-56
5	<10	<8	-4
6	51	50	54
7	33	31	-35
8	19	20	-22
9	21	22	-24
10	14	15	14
11	<7	6	5
12	20	21	22
$93l$			
0	41	38	-39
1	54	51	56
2	10	9	10
3	16	16	-16
4	23	21	24
5	9	9	-10
6	21	20	-23
7	73	73	-77
8	49	55	53
9	36	35	-36
10	51	53	-59
$\bar{9}3l$			
1	<9	<8	2
2	16	17	17
3	13	12	-13
4	<9	<8	0
5	11	9	12
6	50	46	52
7	23	27	27
8	10	8	-9
9	10	11	13
10	20	21	-22
11	18	19	20
$10,3,l$			
0	<9	<9	-6
1	<9	<9	-1
2	52	49	55
3	21	20	-21
4	<9	<8	-2
5	14	15	-16
6	9	8	11
7	19	21	-22
8	-	41	-45
$\bar{10},3,l$			
1	9	8	8
2	18	17	-20
3	41	40	41
4	39	39	-38
5	24	24	-27
6	33	33	-34
7	<7	<8	4
8	23	25	27
9	17	19	18
$11,3,l$			
0	42	40	44
1	19	20	-20
2	13	12	-11
3	17	18	18
4	20	22	-22
5	19	20	-21
6	14	14	-17
$\bar{11},3,l$			
1	12	11	-13
2	55	59	58
3	36	34	-32
4	20	22	22
5	<6	<6	-1
6	19	20	-23
7	-	24	-33
$12,3,l$			
0	-	11	14
$\bar{12},3,l$			
1	-	31	40
2	-	9	-14
$04l$			
0	-	-	54
1	89	91	-89
2	43	39	36
3	4	4*	-4
4	16	14	-12
5	11	8	7
6	107	110	104
7	45	40	42
8	124	126	-124
9	56	54	56
10	16	14	-15
11	<7	<9	-4
12	20	21	-24
13	25	24	-34
$14l$			
0	45	44	37
1	49	52	-48
2	49	52	-46
3	8	8	7
4	41	40	-32
5	15	16	13
6	35	34	-30
7	39	35	31
8	44	40	-42
9	49	51	-53
10	65	66	67
11	19	19	-21
12	21	21	23
13	-	8	-19
$\bar{1}4l$			
1	37	38	32
2	7	6	-2
3	31	31	-25
4	20	21	-18
5	16	15	-12
6	31	30	27
7	23	23	-21
8	59	55	59
9	59	58	62
10	37	37	-40
11	7	8	6
12	33	30	33
13	-	9	-13
$24l$			
0	39	39	-32
1	78	83	68
2	31	32	-27
3	16	16	-12
4	11	11	8
5	6	<8	6
6	<6	<9	0
7	<7	<9	2
8	31	31	28
9	48	44	-42
10	20	19	-19
11	20	19	20
12	16	18	-19
$\bar{2}4l$			
1	28	28	23
2	6	6	3
3	23	25	-23
4	22	24	17
5	52	51	-48
6	49	46	-42
7	21	21	-20
8	60	58	62
9	<7	<10	3
10	7	8	-9
11	19	20	20
12	26	27	30
$34l$			
0	16	16	15
1	13	13	-12
2	29	29	-27
3	53	52	-46
4	23	24	24
5	7	7*	5
6	19	17	-16
7	13	12	11
8	<7	<9	-5
9	44	42	38
10	36	36	34
11	<6	<8	0
12	<5	<5	2
$\bar{3}4l$			
1	22	24	22
2	22	24	17
3	10	8	-8
4	<6	<8	-1
5	<6	<9	-1
6	11	12	-13
7	<6	<9	1
8	<7	<9	2
9	15	11	-12
10	<7	<10	-5
11	<7	<9	0
12	20	21	-22
$44l$			
0	50	47	-44
1	71	68	-63
2	83	83	-77
3	21	21	18
4	105	110	112
5	35	31	33
6	24	22	-24
7	<7	<9	-4
8	49	47	46
9	13	12	13
10	<6	<9	5
11	55	60	-68
$\bar{4}4l$			
1	54	52	49
2	11	10	-8
3	22	23	-21
4	56	56	-57
5	7	8*	-10
6	31	30	32
7	16	17	-17
8	<7	<8	2
9	19	21	-23
10	9	8	-8
11	20	22	22
12	-	16*	18
$54l$			
0	17	17	-15
1	<7	<9	3
2	130	125	129
3	85	83	84
4	<7	<9	3
5	21	22	23
6	39	37	-36
7	7	8	-8
8	23	24	-24
9	29	31	-28
10	22	23	-27
$\bar{5}4l$			
1	13	11	13
2	83	80	86
3	55	52	56
4	68	66	-71
5	17	16	-17
6	17	16	-19
7	19	21	-23
8	7	<10	-6
9	35	37	-36
10	<6	<8	7
11	23	26	26
$64l$			
0	20	20	-20
1	37	35	35
2	24	22	26
3	10	9	12
4	102	99	-103
5	7	8	-8
6	28	28	26
7	18	19	-19
8	<6	<9	4
9	16	16	-20
$\bar{6}4l$			
1	28	28	-26
2	15	15	17
3	65	66	69
4	113	109	116
5	43	43	44
6	48	49	-48
7	<7	<10	3
8	<6	<9	0
9	8	9	11
10	16	17	-21
$74l$			
0	<8	<10	2
1	26	28	30
2	10	8	-10
3	16	15	-15
4	<7	<10	4
5	24	26	-26
6	<6	<9	1
7	14	14	-14
8	7	9	-8
$\bar{7}4l$			
1	34	34	-34
2	93	94	-93
3	27	27	-28
4	42	40	42
5	19	20	19
6	<7	<9	-2
7	<6	<8	7
8	24	28	27
9	14	14	18
$84l$			
0	16	16	15
1	17	18	17
2	<7	<9	3
3	<6	<9	-7
4	<6	<8	1
5	14	15	-15
6	24	26	-28
$\bar{8}4l$			
1	26	24	24
2	19	20	21
3	43	43	-44
4	11	9	-10
5	14	12	-13
6	<5	<7	6
7	9	8	10
$94l$			
0	<6	<7	-5
1	17	16	18
2	14	13	-13
3	16	17	-19
$\bar{9}4l$			
1	16	15	15
2	27	29	-29
3	18	20	19
4	9	8	-9

$$\exp\left(-\sum_{i=1}^{3}\sum_{j=1}^{3}\beta_{ij}h_ih_j\right),$$

are presented in Table 5. No standard deviations for thermal parameters were provided by the least-squares program employed in the refinement. Calculated and observed structure factors are given in Table 6.

That the precision of the refinement on the one set of data is essentially the same as that of the refinement on the other is apparent at once from the two values of $\Sigma\omega(\Delta F)^2$ for A and B in Table 2 and also from the standard deviations in Table 3. The slight variation of magnitude (ranging from 1·2 to 1·9 Å × 10^{-3}) of the standard deviation are very similar in the two sets of coordinates. The corresponding variations in standard deviations of bond length and of angles are of course very similar also (ranging from 1·7 to 2·3 Å × 10^{-3} and from 0·12° to 0·16° respectively).

It is now appropriate, and most interesting, to analyze the two sets of parameters to determine what

Table 7. *Statistical comparison of structures A and B for 2-amino-3-methylbenzoic acid*

Differences in		Maximum	Average	Approx. st. dev. of difference
Heavy-atom positions	x	0·0025 Å	0·0012 Å	0·0025 Å
	y	0·0045	0·0022	0·0025
	z	0·0025	0·0010	0·0025
	r	0·0046	0·0036	0·0025
Bond lengths between heavy atoms		0·005	0·002	0·003
Bond angles involving heavy atoms only		0·16°	0·08°	0·2°
Root-mean-square displacements in principal axis directions		0·009 Å	0·002 Å	

Multi-parameter significance tests on differences in the

11 pairs of heavy-atom x's	$T^2 = 6\cdot0$, $P \gg 5\%$, not significant
11 pairs of heavy-atom y's	$T^2 = 16\cdot1$, $P > 5\%$, not significant
11 pairs of heavy-atom z's	$T^2 = 5\cdot8$, $P \gg 5\%$, not significant
33 pairs of heavy-atom x, y, z's	$T^2 = 27\cdot9$, $P > 5\%$, not significant

Table 8. *Description of thermal ellipsoids*

Axis 1 of the reference Cartesian system is along the vector from C_6 to C_3; axis 2 is in the direction of the product of this vector crossed into the vector from C_5 to C_1; axis 3 completes the right-handed system

		From refinement *A*				From refinement *B*			
		R.m.s.d.	Angle (°) to ref. axis			R.m.s.d.	Angle (°) to ref. axis		
Ellipsoid	Axis	(Å)	1	2	3	(Å)	1	2	3
C_1	1	0·172	79	167	97	0·171	92	176	87
	2	0·178	152	103	65	0·183	156	87	66
	3	0·215	116	88	154	0·215	114	92	156
C_2	1	0·165	79	168	95	0·163	80	170	89
	2	0·184	150	102	62	0·185	148	98	59
	3	0·204	118	90	152	0·208	120	96	149
C_3	1	0·164	109	23	102	0·163	108	23	103
	2	0·204	158	105	75	0·206	161	106	80
	3	0·213	101	106	161	0·216	96	106	163
C_4	1	0·185	96	41	130	0·185	100	35	123
	2	0·217	107	54	42	0·217	109	62	35
	3	0·229	19	74	81	0·229	21	72	79
C_5	1	0·182	60	73	145	0·183	61	70	143
	2	0·219	115	25	86	0·222	116	27	83
	3	0·254	40	72	55	0·252	41	73	54
C_6	1	0·175	36	81	124	0·178	33	77	120
	2	0·202	99	10	87	0·205	101	13	84
	3	0·239	124	93	146	0·236	121	91	149
C_7	1	0·170	10	83	98	0·178	11	85	99
	2	0·192	93	21	69	0·193	93	15	75
	3	0·223	100	70	158	0·224	100	76	163
C_8	1	0·188	28	108	70	0·188	28	106	68
	2	0·238	113	96	24	0·239	118	127	49
	3	0·239	104	161	102	0·242	87	139	131
N	1	0·171	22	95	112	0·174	24	95	113
	2	0·209	68	81	24	0·212	67	86	24
	3	0·252	92	170	80	0·250	93	174	84
O_1	1	0·173	8	87	97	0·170	9	86	98
	2	0·232	83	88	7	0·230	82	91	8
	3	0·303	87	176	88	0·304	86	176	91
O_2	1	0·185	14	89	104	0·193	9	89	99
	2	0·205	77	80	16	0·209	82	83	11
	3	0·282	87	170	81	0·279	88	173	83

differences, if any, have statistical significance. First we consider relative displacements of corresponding atoms between the two structures and differences between corresponding bond lengths and angles, in each case in relation to the appropriate standard deviations of the differences, calculated for two independent determinations (see Table 7). Clearly there are no significant differences between the two structures so far as positions of heavy atoms are concerned. This conclusion is strengthened by results of application of the statistic T^2 (Cruickshank & Robertson, 1953) to the values of Δx, Δy, Δz* (see again Table 7).

No statistical tests can be applied to the differences between the two sets of β_{ij}'s, since standard deviations are not available. It is noteworthy, however, that the computed root-mean-square vibrational displacements in the principal-axis directions differ by no more than 0·009 Å maximum and 0·002 Å average. Moreover, the orientations of the principal axes are markedly similar (see Fig. 8, Table 8). It seems probable that there is little if any more significance in the differences in thermal parameters than in those between atomic coordinates.

The fact that the two least-squares refinements on the two sets of data are of about equal precision and that the resulting two structures are not found significantly different on statistical analysis is not inconsistent with the observation made earlier that there are a number of discrepancies among large, low-order structure factors between the two sets of data. Since the discrepant reflections have relatively low weights, the effect of the discrepancies is more obvious as it affects the R factor (see Table 2) than as it affects precision.

Discussion of structural results

Packing of molecules and hydrogen bonding

A model of the structure of AMBA viewed down the b axis is shown in Fig. 3. There are no unusual features of intermolecular packing. As already indicated, the structure exhibits the frequently observed feature of dimerization of acid molecules through hydrogen bonding between carboxylic acid groups about a symmetry center. The O_1–O_2 distance is 2·645 Å, a rather characteristic value, and the angle O_1–H · · · O_2 is 170°.

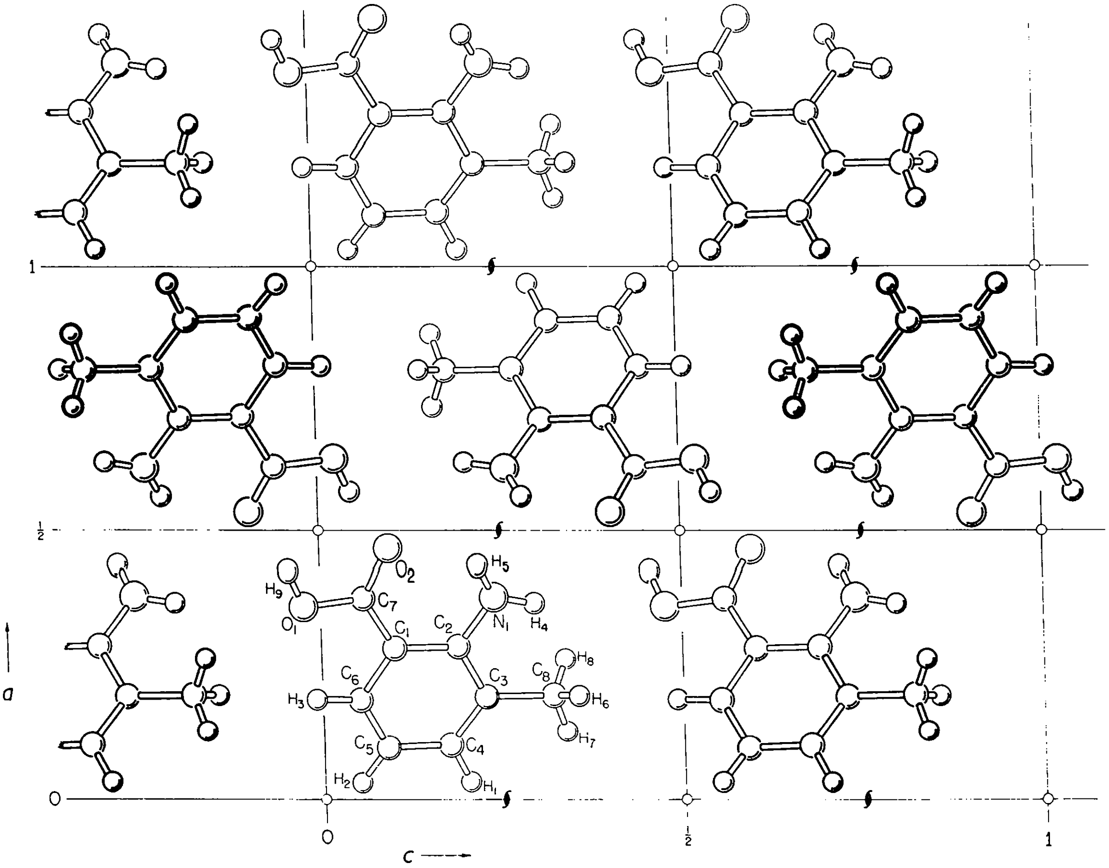

Fig. 3. Model of the structure of 2-amino-3-methylbenzoic acid projected on (010).

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* In applying the multi-parameter significance test T^2, covariances have, of necessity, been neglected in approximating the values of T^2. We do not think this neglect invalidates the conclusion, since the covariances are surely quite small relative to the variances.

There is no other intermolecular hydrogen bonding. One of the two hydrogen atoms on nitrogen does not participate in hydrogen bonding. The other is involved in an intramolecular bond N–H · · · O_2 of which the angle is 131° and the N–O distance is 2·706 Å. Other details of distances and angles involved in hydrogen bonding are shown in Figs. 4 and 5.

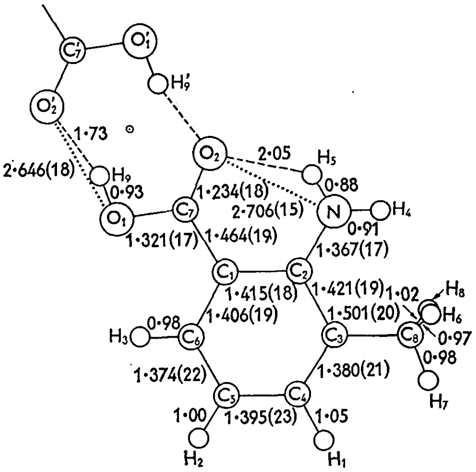

Fig. 4. Average bond lengths (Å) in the molecule of 2-amino-3-methylbenzoic acid from the two refinements *A* and *B*. Standard deviations ($\times 10^4$) from refinement *A* are given in parentheses for bonds between heavy atoms.

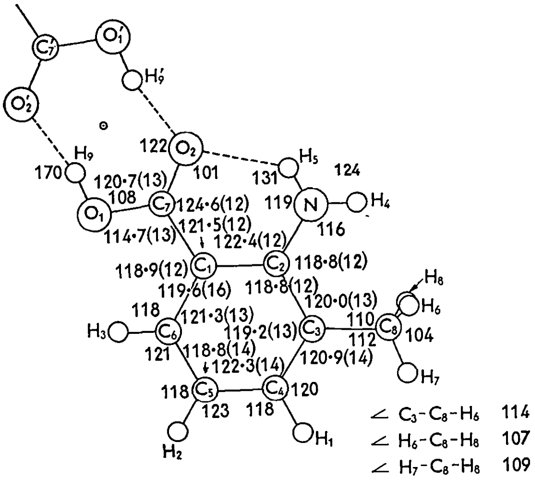

Fig. 5. Average bond angles in the molecule of 2-amino-3-methylbenzoic acid from the two refinements *A* and *B*. Standard deviations (degrees $\times 10^2$) from refinement *A* are given in parentheses for those angles involving heavy atoms only.

Intermolecular distances have been exhaustively calculated to a limit of 5 Å. No unusual van der Waals approaches occur, the shortest H–H distance being 2·6 Å. The perpendicular spacing between adjacent benzene rings in the molecules stacked along the *b* axis is 3·53 Å. Packing drawings corresponding to views along [010] and [101] are shown in Figs. 6 and 7.

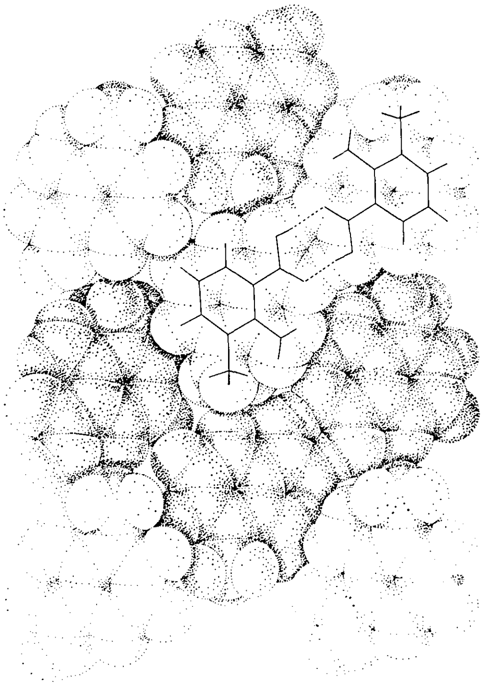

Fig. 6. Packing drawing of the structure of 2-amino-3-methylbenzoic acid, view along [010].

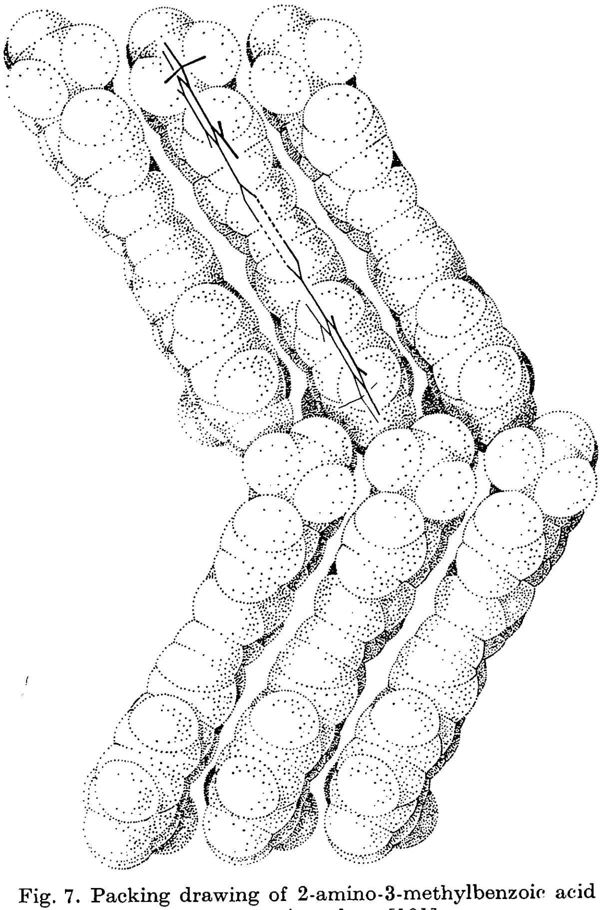

Fig. 7. Packing drawing of 2-amino-3-methylbenzoic acid structure, view along [101].

Thermal ellipsoids

For each of the two sets of β_{ij}'s, principal-axis transformations have been performed on the thermal ellipsoids of the eleven heavy atoms and the orientation of each axis and the root-mean-square vibrational displacement along each axis computed. The numerical results are given in Table 8, and a pictorial representation of them is shown in Fig. 8, in which the mean-square displacement in each of the principal-axis directions is plotted on the axis as it projects on the average plane of the benzene ring. For aid in perception of the axial directions, ellipses have been drawn through the points representing the mean-square displacements.*

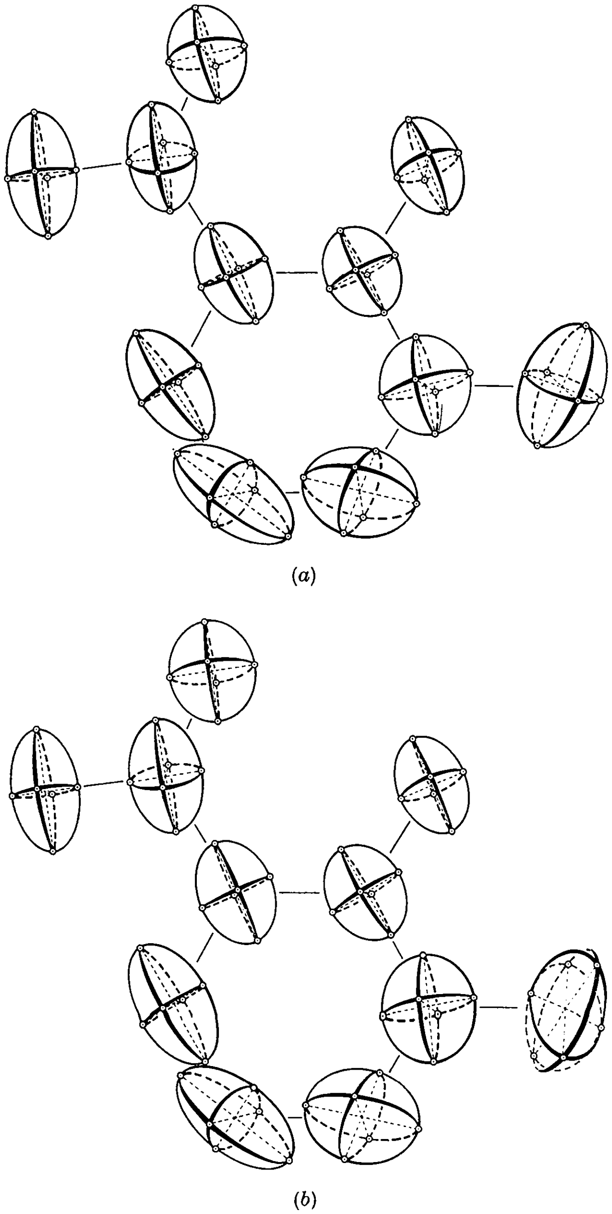

Fig. 8. The mean-square vibrational displacements in principal-axis directions projected onto the average plane of the benzene ring (see text for further explanation). (*a*) Structure *A*. (*b*) Structure *B*.

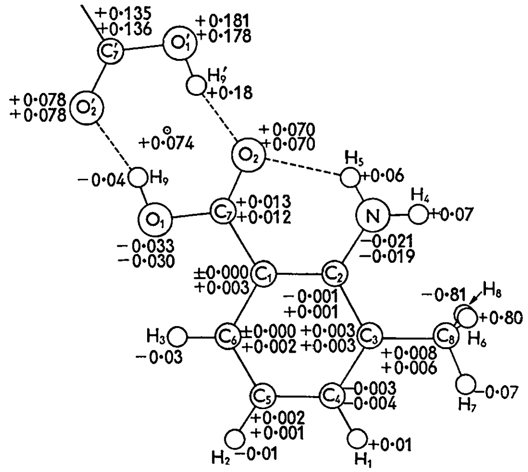

Fig. 9. Deviations (Å) of atoms in structure of 2-amino-3-methylbenzoic acid from best plane of the benzene ring. For each heavy atom, the first value is for structure *A*, the second for structure *B*.

The very close resemblance between the Figs. 8(*a*) and 8(*b*) seems remarkable. The difference in appearance of the two ellipsoids for C_8 is, in fact, misleading. It arises because of the large uncertainty in orientation of axes when an ellipsoid is very nearly an ellipsoid of revolution. As is fairly clear from the figure, for most of the atoms one of the principal axes lies close to the normal to the molecular plane. For each of the atoms N, C_8, O_1, and O_2 the longest principal axis lies near the normal.

No attempt has been made to treat the molecule, or any portion of it, as a rigid body in combined translatory and oscillatory vibrations. The appearance of the ellipsoids in Fig. 8 suggests, however, that the largest translational amplitudes lie along the C_7–C_1–C_4 axis of the molecule and that librational motion of the whole molecule takes place about its center of gravity, located inside of the benzene ring somewhere near the midpoint of the C_1–C_2 bond, accompanied by some intramolecular vibration.

Molecular structure

It would seem reasonable to take as the 'best' values for the bond lengths and angles the average values from the two sets of parameters *A* and *B*. These averages are shown in Figs. 4 and 5. The indicated standard deviation attached to each value of

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* We emphasize that the ellipsoids in Fig. 8 are *not* the thermal ellipsoids whose principal axes have been found, although their axial directions are the same as those of the thermal ellipsoids.

length and angle involving only heavy atoms is the standard deviation from refinement *A*.*

Table 9. *Final bond lengths and angles for structures A and B*

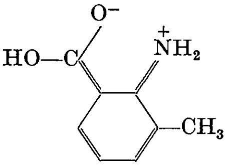
Standard errors of bond lengths ($\times 10^4$) and of angles ($\times 10^2$) are given in parentheses

Bond	*A* (Å)	*B* (Å)	Angle	*A* (°)	*B* (°)
C_1–C_2	1·415(18)	1·415(19)	C_1–C_2–C_3	118·8(12)	118·9(12)
C_2–C_3	1·420(19)	1·422(20)	C_2–C_3–C_4	119·2(13)	119·1(14)
C_3–C_4	1·380(21)	1·380(23)	C_3–C_4–C_5	122·3(14)	122·3(16)
C_4–C_5	1·395(23)	1·395(26)	C_4–C_5–C_6	118·8(14)	118·8(15)
C_5–C_6	1·371(22)	1·376(24)	C_5–C_6–C_1	121·3(13)	121·2(14)
C_1–C_6	1·407(19)	1·405(21)	C_6–C_1–C_2	119·6(12)	119·7(13)
C_1–C_7	1·465(19)	1·463(21)	C_6–C_1–C_7	118·9(12)	118·9(13)
C_2–N	1·367(17)	1·368(19)	C_2–C_1–C_7	121·5(12)	121·5(12)
C_3–C_8	1·502(20)	1·500(23)	C_1–C_2–N	122·4(12)	122·3(12)
C_7–O_1	1·319(17)	1·322(18)	C_3–C_2–N	118·8(12)	118·8(13)
C_7–O_2	1·233(18)	1·235(19)	C_2–C_3–C_8	119·9(13)	120·1(14)
O_1–O_2'*	2·646(18)	2·647(19)	C_4–C_3–C_8	120·9(14)	120·8(15)
			C_1–C_7–O_1	114·7(13)	114·7(13)
			C_1–C_7–O_2	124·5(12)	124·6(13)
			O_1–C_7–O_2	120·8(13)	120·7(15)

* Hydrogen bond. Atom O_2' is related to atom O_2 through center of symmetry.

Since we know of no other instance in which comparable refinements of the same structure have been carried out on two different sets of observations, it seems of interest to report here, in addition to the average values of the bond lengths and angles, the individual values *A* and *B*, for detailed comparison. These are given in Table 9. The largest difference between corresponding bond lengths is 0·005 Å and the average difference is 0·002 Å.

There are obviously quite significant departures from hexagonal symmetry in the benzene ring of the molecule. The rather short C_2–N, C_1–C_7, C_3–C_4, C_5–C_6 bonds and the somewhat long ring bonds C_6–C_1, C_1–C_2, C_2–C_3 indicate some resonance involving a structure as follows:



However, the shortness of the C_2–N bond and the C_1–C_7 bond may be to a considerable extent a hybridization effect. Similarly, the short C_3–C_8 bond probably results from a combination of hyperconjugation and hybridization effects.

The bond lengths and angles involving hydrogen, which are shown in Figs. 4 and 5, have been calculated from the parameters resulting from the least-squares treatment of data *A*. We prefer these lengths and angles over those calculated from the second 3-D difference map, because the bond lengths are systematically somewhat longer, and therefore probably more nearly correct, and because, formally at least, they also correspond to a higher degree of refinement. The average C–H bond is 0·99 Å in length in the methyl group and 1·01 Å in the benzene ring; the average N–H distance in the amino group is 0·90 Å.

Although the over-all symmetry of the molecule, including the hydrogen atoms, is very nearly that of point group *m*, there are significant departures from this symmetry, even among the heavy atoms. Fig. 9 shows, for structures *A* and *B*, the deviation of each atom from the best plane of the six ring atoms as determined by least squares when all the ring atoms were weighted equally (negative deviations are toward the origin from the best plane). For structure *A* the equation of the best plane is:

$$-0{\cdot}45861x+0{\cdot}87366y+0{\cdot}16243z^*=0{\cdot}8272 \text{ (Å)}\,.$$

The deviations of the ring atoms from their best plane are possibly significant ($\chi^2=9{\cdot}8$ on three degrees of freedom, $P\approx 2\%$). The equation for structure *B* is:

$$-0{\cdot}45847x+0{\cdot}87381y+0{\cdot}16202z^*=0{\cdot}8259 \text{ (Å)}\,.$$

In this case the deviations of the ring atoms are generally somewhat larger and apparently slightly more significant ($\chi^2=17{\cdot}4$, $P<0{\cdot}1\%$).

So far as the extra-ring atoms are concerned, the situation is essentially the same for structures *A* and *B*. Atoms C_7, N, and C_8 are staggered slightly above and below the best ring plane, and probably significantly so. Further, the carboxyl group is twisted three degrees around the C_1–C_7 axis. The configuration of the amino group seems clearly to be planar, consistent with a significant contribution from the resonance structure involving a double bond to the nitrogen.

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* We resist the temptation to report smaller standard deviations for the averages, as one might be justified in doing if the two data sets had been entirely independent and subject only to random error. Since the two sets of data were obtained from the same photographs, we fear they may be subject to parallel systematic errors.

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The Structure of Dimolybdenum Carbide by Neutron Diffraction Technique*

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It is generally believed that Mo_2C has either the hexagonal C6 cadmium iodide anti-type structure or the related hexagonal L′3 structure. A neutron diffraction study showed that this is not the case. Mo_2C is only pseudohexagonal and crystallizes with an orthorhombic unit cell with $a = 4{\cdot}72_4$, $b = 6{\cdot}00_4$, and $c = 5{\cdot}19_9$ Å. The atomic arrangement of Mo_2C presents a new structure type. Space group is D_{2h}^{14}–$Pbcn$. Eight molybdenum atoms are in 8(*d*) with $x = 1/4$, $y = 1/8$, $z = 1/12$ and four carbon atoms are in 4(*c*) with $y = 3/8$. The carbon atoms in Mo_2C arrange themselves in such a way that each molybdenum atom has three nearly planar carbon neighbours.

Introduction

In the system molybdenum-carbon two carbide phases exist: The monocarbide, MoC, and the sesquicarbide, Mo_2C. The structure of the monocarbide was solved earlier by one of the authors (Nowotny, Parthé, Kieffer & Benesovsky, 1954). Recent investigations show, however, that it occurs only with a carbon defect and the formula Mo_3C_2 has been suggested for this compound (Rudy, Rudy and Benesovsky, 1962). A structure proposal for Mo_2C dates back as far as 1926. Using the X-ray diffraction technique, Mo_2C was investigated at that time by Westgren & Phragmen. Due to the small scattering factor of carbon, they could determine with certainty only the spatial arrangement of the metal atoms. They found them to be arranged in a hexagonal close packing. For each two molybdenum atoms, one carbon atom can be tentatively placed in one of the octahedral holes. One thus receives a structure proposal for Mo_2C as follows:

C6 *structure type*

Unit cell: Hexagonal: $a = 3{\cdot}002$ Å, $c = 4{\cdot}724$ Å

Space group: D_{3d}^{3}–$P\bar{3}m1$

Point position: 2 Mo in 2(*d*): $1/3, 2/3, z$; $2/3, 1/3, \bar{z}$ with $z = 1/4$

1 C in 1(*a*): 0, 0, 0

This structure is identical to the first CdJ_2(C6) structure type, except the metal and non-metal atoms have been interchanged. This type may be called, therefore, CdJ_2-antitype. However, modern crystal structure compilations (Pearson, 1958) list the Mo_2C structure as belonging to the L′3 structure type with the one carbon atom statistically distributed between two possible places.

L′3 *structure type*

Same hexagonal unit cell dimensions as above.

Space group: D_{6h}^{4}–$P6_3/mmc$

Point positions: 2 Mo in 2(*c*): 1/3, 2/3, 1/4; 2/3, 1/3, 3/4

1 C in 2(*a*): 0, 0, 0; 0, 0, 1/2

To reveal the true carbon atom positions in Mo_2C, a neutron diffraction study was undertaken.

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