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The Crystal Structure of DL-Allantoin

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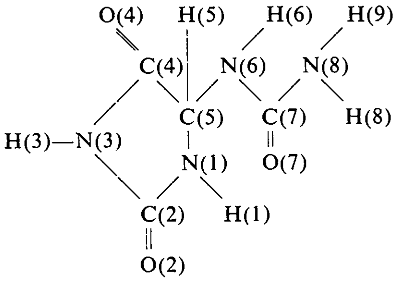
The crystal structure of DL-allantoin, $C_4H_6O_3N_4$, has been determined with the use of three-dimensional photographic data. The space group is $P2_1/c$ with cell dimensions $a=8{\cdot}024$, $b=5{\cdot}153$, $c=14{\cdot}797$ Å, $\beta=93{\cdot}01°$ and four molecules in the unit cell. The phase problem was solved with the Sayre equation, and the structure was refined by anisotropic least-squares analysis. The final unweighted R index for 1124 observed reflexions was 0·087. The most interesting feature of the structure is the hydrogen bonding, which involves the three carbonyl oxygens, three imido and two amido hydrogen atoms and links the molecules into an intricate three-dimensional network.

Introduction

Allantoin (I), $C_4H_6O_3N_4$, is formed by the room temperature oxidation of uric acid. It is a product of purine metabolism and is present both in animals and in plants.



(I)

This three-dimensional single-crystal structure analysis of the DL form was undertaken to determine the details of the molecular geometry and hydrogen bonding in the crystalline state.

Crystal data

DL-Allantoin crystallizes from aqueous solutions in plates, which are usually elongated along [010] and tabular parallel to (100) or (001). The observed forms are {001}, {100}, {110} and sometimes {10$\bar{2}$}. The morphological symmetry is $2/m$. There is a slight cleavage parallel to (100).

The unit-cell dimensions measured on a diffractometer with copper radiation ($K\alpha_1$: 1·5405 Å, $K\alpha_2$: 1·5443 Å) are

$$a=8{\cdot}024\pm0{\cdot}008,\quad b=5{\cdot}153\pm0{\cdot}004,$$
$$c=14{\cdot}797\pm0{\cdot}008\ \text{Å},\quad \beta=93{\cdot}01\pm0{\cdot}04°,$$
$$V=611{\cdot}0\ \text{Å}^3\,.$$

The axial ratio is $a:b:c=1{\cdot}5572:1:(2\times1{\cdot}4358)$, compared with 1·5587:1:1·4348 as listed by Groth (1910), who gives $\beta=93{\cdot}28°$. With a measured density of $D_m=1{\cdot}722\pm0{\cdot}005$ g.cm^{-3} there are four (4·008) formula units $C_4H_6O_3N_4$ ($M=158{\cdot}12$) in the unit cell, and $F(000)$ is 328. The systematic extinctions $h0l$ for l odd and $0k0$ for k odd establish the space group $P2_1/c$.

Experimental

Two small crystals with nearly square cross section were selected for collecting data about the a and b axes. The dimensions were $0{\cdot}25\times0{\cdot}29\times0{\cdot}21$ mm^3 and $0{\cdot}17\times0{\cdot}15\times0{\cdot}42$ mm^3, respectively. They were dipped repeatedly into liquid air to reduce extinction effects. Integrated equi-inclination multiple film intensities of layers $0kl$ to $5kl$ and $h0l$ to $h4l$ were recorded on a STOE Weissenberg camera with Cu $K\alpha$ radiation. The intensities were eye-estimated against a calibration chart and processed to structure amplitudes in the usual way. No correction for absorption or extinction was applied. The interlayer correlation was carried out by the method of Rollett & Sparks (1960). Of 1396 independent reflexions in the copper sphere 1292 were recorded. Of these, 162 were too weak to be estimated and were assigned half the minimum observed intensity.

Structure determination and refinement

Preliminary values for the scale and temperature factor were derived from a Wilson plot and used to calculate the normalized structure amplitudes. The phase problem was solved with the Sayre equation following the computer-programmed method developed in this laboratory by Beurskens (1964).* In this way 398 signs were accumulated in a straightforward procedure,

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* The data used in this stage of the structure analysis were eye-estimated from a set of *un*integrated Weissenberg photographs made by Dr G. E. Gurr, Materials Physics Research, Central Research Laboratories, Minnesota Mining and Manufacturing Company, St. Paul 19, Minnesota. I thank Dr Gurr for putting these photographs and the results of his preliminary work at my disposal.

which was then discontinued because of the occurrence of an increasing number of inconsistencies in the sign relationship. These signs, which included those of all the stronger reflexions, were used with the normalized structure amplitudes in a three-dimensional Fourier synthesis. All the C, N and O atoms of the structure were directly revealed [Fig. 1(*a*)] and the initial *R* value was 0·17.

The structure was refined by several cycles of isotropic and then anisotropic least-squares calculation on an IBM 7090 computer using the full-matrix program of Busing, Martin & Levy (1962). The expression minimized was $\Sigma w(F_o - kF_c)^2$. The Hughes (1941) weighting scheme was applied with $|F_{\min}| = 2{\cdot}0$. Unobserved and six strong low order reflexions were assigned zero weight. The final unweighted *R* value with all atoms, for the 1124 observed reflexions used in the refinement, was 0·087. The scattering factors for the heavier atoms were taken from Berghuis, Haanappel, Potters, Loopstra, MacGillavry & Veenendaal (1955) and for hydrogen from McWeeny (1951).

At the conclusion of the isotropic calculations all six hydrogen atoms of the asymmetric unit were resolved in a difference Fourier synthesis [Fig. 1(*b*)]. Their contributions to the structure factors were included in the subsequent anisotropic refinement of the heavier atoms. Finally, two cycles of least squares were computed to refine the hydrogen positional parameters using reflexions with $\sin\theta < 0{\cdot}7$ only. With and without the final hydrogen atom contributions the *R* index for these reflexions was 0·092 and 0·112, respectively. Throughout the calculations the thermal parameters of the hydrogen atoms were set equal to those of the heavier atoms to which they are bonded. A final difference-Fourier synthesis was computed with the hydrogen contributions removed from the calculated structure factors [Fig. 1(*c*)]. It was clear that the interpretation of the hydrogen atom positions from the first difference map [Fig. 1(*b*)] was correct, because the result of the refinement was a considerable enhancement of the same hydrogen peaks.

Table 1 shows the atomic parameters. The observed and calculated structure factors are listed in Table 2.

The structure of the molecules

The bond lengths and bond angles with their estimated standard deviations are given in Fig. 2 and Table 3. Of the five peptide C(O)–NH type bonds, C(2)–N(3) is the longest at 1·397 Å, C(7)–N(6) and C(4)–N(3) are intermediate at 1·368 and 1·362 Å, and C(2)–N(1) and C(7)–N(8) are the shortest at 1·341 and 1·335 Å. The LCAO–MO calculations of Pullman & Pullman (1963) correctly predict the sequence C(2)–N(3) > C(7)–N(6) ≃ C(4)–N(3) but do not account for the significant shortening of the remaining bonds C(2)–N(1) and C(7)–N(8). The two C–N bonds involving the tetrahedral carbon atom C(5) are 1·461 Å for C(5)–N(1) in the ring and 1·424 Å for the C(5)–N(6) linkage between the hydantoin and the urea residues. The adjacent C(4)–C(5) bond of 1·535 Å is longer than the value sometimes proposed for an sp^2–sp^3 carbon–carbon single bond (*e.g.* Lide, 1962). The two C=O bonds on the ring are not significantly different and have a mean value of 1·216 Å, which is a common mean value for carbonyl

Table 1. *Atomic parameters*

Estimated standard deviations in parentheses refer to the last decimal position reported.

Positional parameters in fractional coordinates:

	x	*y*	*z*
C(2)	0·0007(4)	0·2996(6)	0·0876(2)
C(4)	0·2834(4)	0·3529(6)	0·0932(2)
C(5)	0·2116(4)	0·5506(6)	0·1583(2)
C(7)	0·3149(4)	0·3118(5)	0·2902(2)
N(1)	0·0343(3)	0·4843(6)	0·1497(2)
N(3)	0·1514(3)	0·2267(5)	0·0517(2)
N(6)	0·2881(3)	0·5444(5)	0·2474(2)
N(8)	0·3923(4)	0·3192(5)	0·3723(2)
O(2)	−0·1354(3)	0·2125(5)	0·0629(2)
O(4)	0·4296(3)	0·3210(4)	0·0792(2)
O(7)	0·2640(3)	0·1062(4)	0·2538(1)
H(1)	−0·045(8)	0·561(15)	0·181(5)
H(3)	0·156(8)	0·076(14)	0·014(5)
H(5)	0·239(8)	0·736(13)	0·131(5)
H(6)	0·303(9)	0·722(13)	0·275(5)
H(8)	0·429(9)	0·189(13)	0·387(5)
H(9)	0·431(8)	0·474(14)	0·392(4)

Table 1 (*cont.*)

Thermal parameters after conversion from β_{ij} to B_{ij} (Å^2). The expression for the temperature factor consistent with the B_{ij} values is:

$$\exp\{-\tfrac{1}{4}(B_{11}h^2a^{*2} + B_{22}k^2b^{*2} + B_{33}l^2c^{*2} + B_{23}2klb^*c^* + B_{31}2lhc^*a^* + B_{12}2hka^*b^*)\}.$$

	B_{11}	B_{22}	B_{33}	B_{23}	B_{31}	B_{12}
C(2)	1·69(12)	1·43(12)	1·56(11)	0·08(9)	−0·03(9)	0·06(9)
C(4)	1·84(12)	0·92(10)	1·12(10)	0·19(8)	0·21(8)	−0·10(9)
C(5)	1·92(12)	0·71(10)	1·53(11)	0·06(8)	0·05(9)	−0·00(9)
C(7)	1·53(11)	0·82(11)	1·35(11)	−0·04(8)	0·30(8)	−0·07(8)
N(1)	1·69(11)	1·81(11)	2·04(11)	−0·68(9)	0·00(8)	0·22(9)
N(3)	1·77(11)	1·20(10)	1·45(10)	−0·48(8)	0·08(8)	−0·11(8)
N(6)	2·58(12)	0·58(9)	1·49(10)	−0·19(7)	−0·22(8)	−0·16(8)
N(8)	2·67(12)	1·55(11)	1·48(10)	−0·07(8)	−0·38(9)	0·31(9)
O(2)	1·67(10)	2·46(11)	2·63(10)	−0·87(8)	−0·02(8)	−0·41(8)
O(4)	1·81(9)	1·60(9)	1·98(9)	−0·45(7)	0·23(7)	−0·18(7)
O(7)	2·57(8)	0·73(8)	1·84(9)	−0·10(6)	0·05(7)	−0·25(7)

Table 2. *The observed and calculated structure factors*

Each five columns between vertical lines are h, k, l, $|F_o|$, F_c. 162 unobserved and six strong low order reflexions, both excluded from the final refinement, are marked with an asterisk.

1	0	0	16.0	16.5	-5	0	12	3.8	-3.4	-7	1	4	19.9	-20.6	1	1	11	1.7*	0.8	7	2	1	2.3	2.4
2	0	0	34.5	-41.9	6	0	12	2.5	2.1	8	1	4	4.4	3.8	-1	1	11	13.3	12.2	-7	2	1	2.7	2.9
3	0	0	21.1	24.8	-6	0	12	19.0	-20.3	-8	1	4	6.1	-6.0	2	1	11	6.6	-5.1	8	2	1	1.4*	-0.7
4	0	0	13.5	13.2	7	0	12	14.7	15.7	9	1	4	7.2	-6.2	-2	1	11	7.8	7.0	-8	2	1	9.8	-10.1
5	0	0	5.8	4.4	-7	0	12	2.8	1.9	-9	1	4	1.3*	-0.7	3	1	11	4.1	-3.2	9	2	1	2.5	2.3
6	0	0	1.8*	-0.7	0	0	14	7.4	6.1	0	1	5	9.9	9.4	-3	1	11	3.1	3.1	-9	2	1	2.5	2.4
7	0	0	31.7	38.2	1	0	14	11.2	-12.1	1	1	5	17.2	-16.5	4	1	11	4.9	4.7	0	2	2	46.4	-57.5
8	0	0	4.5	2.7	-1	0	14	16.0	16.8	-1	1	5	9.4	9.1	-4	1	11	1.5*	0.8	1	2	2	32.6	-35.4
9	0	0	3.8	-3.1	2	0	14	21.5	24.4	2	1	5	15.1	-13.8	5	1	11	5.4	-5.0	-1	2	2	5.7	-4.1
0	0	2	17.2	-17.7	-2	0	14	5.4	4.8	-2	1	5	16.5	15.5	-5	1	11	4.3	4.0	2	2	2	2.5	-1.7
1	0	2	2.8	1.6	3	0	14	6.0	-4.8	3	1	5	11.4	10.7	6	1	11	3.6	-3.0	-2	2	2	15.8	14.8
-1	0	2	36.5	48.8	-3	0	14	1.6*	2.3	-3	1	5	6.3	5.6	-6	1	11	5.0	5.2	3	2	2	7.4	6.5
2	0	2	31.3	38.6	4	0	14	9.0	-9.3	4	1	5	10.6	9.2	7	1	11	10.2	-8.9	-3	2	2	14.7	15.5
-2	0	2	52.3*	75.6	-4	0	14	8.3	-8.1	-4	1	5	3.5	1.8	-7	1	11	1.4*	0.5	4	2	2	11.3	-10.0
3	0	2	33.2	-35.4	5	0	14	1.4*	1.4	5	1	5	14.6	-14.3	-8	1	11	1.0*	0.6	-4	2	2	9.7	8.9
-3	0	2	52.0*	-67.6	-5	0	14	13.3	14.3	-5	1	5	8.7	7.3	0	1	12	6.3	5.0	5	2	2	1.3*	0.1
4	0	2	30.7	-36.1	-6	0	14	7.0	6.8	6	1	5	16.2	-16.7	1	1	12	10.6	10.2	-5	2	2	3.5	-2.5
-4	0	2	42.1	-48.1	0	0	16	1.7*	1.5	-6	1	5	19.9	20.3	-1	1	12	1.7*	1.3	6	2	2	13.0	-13.4
5	0	2	11.0	-10.3	1	0	16	1.7*	-1.5	7	1	5	6.8	5.7	2	1	12	6.2	4.8	-6	2	2	11.4	11.3
-5	0	2	39.3	46.6	-1	0	16	9.8	-10.2	-7	1	5	8.6	7.6	-2	1	12	2.7	1.6	7	2	2	14.6	-16.2
6	0	2	4.7	5.0	2	0	16	2.3	-2.4	8	1	5	3.1	-3.0	3	1	12	9.9	-9.3	-7	2	2	13.2	-12.8
-6	0	2	15.1	14.0	-2	0	16	9.3	-8.4	-8	1	5	3.5	-3.1	-3	1	12	15.0	-16.0	8	2	2	5.1	-5.1
7	0	2	2.0*	-2.2	3	0	16	10.0	-10.6	9	1	5	5.5	-4.6	4	1	12	11.0	-10.7	-8	2	2	4.4	-4.9
-7	0	2	20.7	22.1	-3	0	16	3.4	-3.1	-9	1	5	8.0	6.7	-4	1	12	15.0	-14.7	9	2	2	1.0*	-0.2
8	0	2	1.9*	1.5	4	0	16	9.8	-9.5	0	1	6	28.1	-29.4	5	1	12	12.4	-14.0	-9	2	2	6.8	6.1
-8	0	2	12.0	11.1	-4	0	16	13.5	-14.1	1	1	6	15.9	15.1	-5	1	12	13.4	14.4	0	2	3	44.0	51.7
9	0	2	5.0	4.7	5	0	16	11.3	-13.8	-1	1	6	25.9	-25.9	6	1	12	6.7	6.9	1	2	3	11.0	-9.2
-9	0	2	1.6*	2.2	-5	0	16	6.1	6.6	2	1	6	24.2	-24.7	-6	1	12	1.5*	0.1	-1	2	3	34.3	-36.6
10	0	2	8.1	-7.6	0	0	18	9.4	-9.2	-2	1	6	15.1	14.9	7	1	12	6.4	5.9	2	2	3	20.3	-19.8
0	0	4	22.7	-25.8	1	0	18	12.4	13.1	3	1	6	19.0	19.1	-7	1	12	1.2*	0.2	-2	2	3	1.9	0.4
1	0	4	22.1	-25.7	-1	0	18	4.0	-3.6	-3	1	6	31.8	34.3	0	1	13	18.0	-18.7	3	2	3	25.3	24.8
-1	0	4	15.0	17.3	2	0	18	4.0	3.3	4	1	6	17.1	16.8	1	1	13	1.8*	-0.3	-3	2	3	20.8	21.4
2	0	4	18.7	-18.7	-2	0	18	7.3	-7.2	-4	1	6	31.0	33.9	-1	1	13	4.5	-3.5	4	2	3	19.3	19.2
-2	0	4	59.6*	-104.8	-3	0	18	11.3	-12.7	5	1	6	6.2	5.0	2	1	13	1.4*	-0.4	-4	2	3	27.3	29.7
3	0	4	5.5	-5.2	1	1	0	39.2*	-56.8	-5	1	6	23.9	-29.6	-2	1	13	1.4*	0.1	5	2	3	1.4*	1.0
-3	0	4	2.9	-2.6	2	1	0	43.2	56.2	6	1	6	1.7*	-1.7	3	1	13	9.3	-9.4	-5	2	3	7.7	6.4
4	0	4	10.0	9.7	3	1	0	12.7	-12.4	-6	1	6	7.6	5.1	-3	1	13	1.5*	1.2	6	2	3	13.8	-13.5
-4	0	4	5.4	5.8	4	1	0	5.6	4.9	7	1	6	6.1	-5.6	4	1	13	6.2	-6.3	-6	2	3	18.6	-19.8
5	0	4	34.5	-39.6	5	1	0	13.3	-13.4	-7	1	6	4.4	-4.6	-4	1	13	7.7	-7.4	7	2	3	11.2	11.7
-5	0	4	29.5	-33.0	6	1	0	6.4	5.0	8	1	6	5.3	-5.1	5	1	13	6.6	-6.1	-7	2	3	14.6	15.3
6	0	4	16.3	15.3	7	1	0	1.7*	-2.1	-8	1	6	11.4	-12.0	-5	1	13	7.2	-6.7	8	2	3	1.3*	-0.6
-6	0	4	14.3	-13.6	8	1	0	13.0	-12.1	9	1	6	1.0*	0.5	6	1	13	2.8	-2.2	-8	2	3	5.7	5.1
7	0	4	2.0*	0.4	9	1	0	6.1	5.8	-9	1	6	9.3	8.8	-6	1	13	5.6	5.5	9	2	3	9.1	-8.8
-7	0	4	11.2	9.0	0	1	1	26.8	-30.4	0	1	7	9.0	-7.8	-7	1	13	3.1	-2.0	-9	2	3	1.0*	-1.2
8	0	4	8.9	-7.5	1	1	1	25.9	29.1	1	1	7	24.6	-25.1	0	1	14	8.0	-7.8	0	2	4	14.7	13.7
-8	0	4	6.8	6.2	-1	1	1	36.4	-50.0	-1	1	7	20.2	-21.3	1	1	14	10.8	10.4	1	2	4	2.3	-0.9
·9·	0	4	4.4	4.5	2	1	1	16.9	-16.4	2	1	7	14.0	12.2	-1	1	14	8.6	8.2	-1	2	4	39.8	-44.1
-9	0	4	12.4	-12.5	-2	1	1	2.9	2.7	-2	1	7	12.7	-12.3	2	1	14	2.8	2.7	2	2	4	19.1	-17.9
-10	0	4	6.5	-6.5	3	1	1	7.4	-6.2	3	1	7	4.1	-4.1	-2	1	14	17.5	-18.9	-2	2	4	3.5	3.3
0	0	6	54.3*	-76.8	-3	1	1	20.4	-20.5	-3	1	7	7.2	7.0	3	1	14	18.6	-21.1	3	2	4	11.4	10.1
1	0	6	26.8	29.4	4	1	1	15.1	-14.3	4	1	7	9.6	-8.2	-3	1	14	12.4	-12.7	-3	2	4	9.8	9.0
-1	0	6	9.7	8.1	-4	1	1	27.0	-28.9	-4	1	7	1.2*	1.0	4	1	14	7.5	-7.1	4	2	4	2.5	-1.9
2	0	6	31.5	34.2	5	1	1	2.6	-2.1	5	1	7	3.3	2.8	-4	1	14	6.7	-6.5	-4	2	4	4.7	3.9
-2	0	6	12.5	11.4	-5	1	1	13.7	-11.9	-5	1	7	5.8	-5.7	5	1	14	7.1	-6.7	5	2	4	6.7	5.6
3	0	6	26.5	-26.6	6	1	1	7.7	6.5	6	1	7	1.7*	1.4	-5	1	14	3.0	-3.2	-5	2	4	11.3	-10.9
-3	0	6	11.2	10.2	-6	1	1	1.6*	-1.0	-6	1	7	15.9	-16.3	6	1	14	3.1	2.3	6	2	4	3.7	-3.6
4	0	6	17.6	16.5	7	1	1	8.3	7.8	7	1	7	6.2	5.6	-6	1	14	3.6	4.1	-6	2	4	11.4	-11.3
-4	0	6	28.5	-32.4	-7	1	1	11.7	-11.4	-7	1	7	8.5	7.8	0	1	15	11.4	11.9	7	2	4	17.3	18.7
5	0	6	22.9	23.0	8	1	1	8.8	8.2	8	1	7	4.0	-3.4	1	1	15	7.6	7.1	-7	2	4	1.5*	-0.3
-5	0	6	10.6	10.9	-8	1	1	1.6*	-0.7	-8	1	7	7.7	7.1	-1	1	15	6.6	-6.7	8	2	4	6.9	7.5
6	0	6	2.0*	0.3	9	1	1	6.7	-6.0	-9	1	7	5.9	-5.7	2	1	15	4.4	-4.6	-8	2	4	1.3*	0.8
-6	0	6	13.9	12.5	-9	1	1	2.3	2.9	0	1	8	13.9	13.4	-2	1	15	10.6	-10.7	9	2	4	7.6	-7.0
7	0	6	22.6	-24.3	0	1	2	35.1	-43.6	1	1	8	10.1	-9.7	3	1	15	1.3*	1.2	-9	2	4	1.8	1.3
-7	0	6	35.7	-42.9	1	1	2	25.5	-28.6	-1	1	8	4.0	2.7	-3	1	15	2.7	2.3	0	2	5	24.0	-23.6
8	0	6	8.6	-8.8	-1	1	2	31.9	-41.8	2	1	8	9.7	9.2	4	1	15	1.1*	1.8	1	2	5	21.3	-23.2
-8	0	6	3.0	-2.9	2	1	2	12.7	-12.4	-2	1	8	14.6	14.4	-4	1	15	3.6	3.0	-1	2	5	15.1	15.1
9	0	6	3.4	2.8	-2	1	2	18.4	-17.6	3	1	8	4.6	3.4	5	1	15	6.0	5.4	2	2	5	22.4	23.1
-9	0	6	3.4	3.2	3	1	2	4.9	4.1	-3	1	8	6.8	6.5	-5	1	15	7.2	-7.4	-2	2	5	11.1	11.0
0	0	8	4.4	2.8	-3	1	2	26.5	26.9	4	1	8	10.3	9.6	-6	1	15	3.5	-3.5	3	2	5	1.7	-0.4
1	0	8	30.3	-33.1	4	1	2	16.5	14.9	-4	1	8	13.3	12.5	0	1	16	1.5*	-0.3	-3	2	5	8.4	-7.6
-1	0	8	7.0	-6.6	-4	1	2	19.5	-20.3	5	1	8	12.8	12.4	1	1	16	4.0	3.6	4	2	5	3.0	-2.4
2	0	8	34.7	-38.7	5	1	2	1.2*	0.1	-5	1	8	9.8	9.1	-1	1	16	1.5*	-0.0	-4	2	5	4.1	3.7
-2	0	8	4.0	2.0	-5	1	2	6.7	6.0	6	1	8	9.2	-9.2	2	1	16	5.2	-4.3	5	2	5	6.2	5.2
3	0	8	32.2	34.3	6	1	2	10.7	-9.5	-6	1	8	4.5	-3.9	-2	1	16	7.4	-7.5	-5	2	5	12.8	13.0
-3	0	8	22.6	23.9	-6	1	2	4.7	-4.1	7	1	8	15.0	16.3	3	1	16	5.5	-4.4	6	2	5	14.4	15.0
4	0	8	17.1	16.0	7	1	2	23.1	-25.0	-7	1	8	5.9	-5.0	-3	1	16	1.2*	0.4	-6	2	5	10.4	-8.9
-4	0	8	27.0	29.4	-7	1	2	19.5	-20.1	8	1	8	1.2*	1.7	4	1	16	0.9*	0.6	7	2	5	10.9	-10.9
5	0	8	3.7	3.4	8	1	2	7.0	-6.6	-8	1	8	3.2	2.9	-4	1	16	12.4	-13.1	-7	2	5	2.7	-1.7
-5	0	8	8.8	-7.9	-8	1	2	1.6*	-0.4	-9	1	8	8.6	7.9	-5	1	16	4.7	-4.3	8	2	5	10.6	-10.9
6	0	8	23.1	-25.7	9	1	2	1.3*	-0.5	0	1	9	10.8	9.8	0	1	17	6.9	6.9	-8	2	5	6.0	-5.9
-6	0	8	3.6	-3.0	-9	1	2	5.5	-5.2	1	1	9	1.5*	-1.3	1	1	17	2.5	2.0	9	2	5	11.7	12.3
7	0	8	15.4	-15.8	0	1	3	32.2	36.7	-1	1	9	3.7	3.9	-1	1	17	6.6	7.0	-9	2	5	4.0	3.6
-7	0	8	1.9*	2.4	1	1	3	41.7	54.8	2	1	9	10.1	8.3	2	1	17	1.0*	0.5	0	2	6	32.8	36.1
8	0	8	5.7	5.1	-1	1	3	17.2	16.7	-2	1	9	1.2*	0.5	-2	1	17	8.7	8.2	1	2	6	23.5	23.2
-8	0	8	1.7*	-0.8	2	1	3	0.8*	-1.5	3	1	9	6.7	5.9	3	1	17	6.4	6.6	-1	2	6	19.4	19.6
9	0	8	10.6	-13.0	-2	1	3	4.5	3.7	-3	1	9	3.5	-2.8	-3	1	17	5.1	-5.4	2	2	6	22.0	22.9
-9	0	8	6.1	-5.7	3	1	3	8.8	7.0	.4	1	9	7.0	6.7	0	1	18	3.0	3.4	-2	2	6	17.2	17.5
0	0	10	28.3	-31.7	-3	1	3	10.2	-9.7	-4	1	9	3.5	-2.3	1	1	18	3.2	3.5	3	2	6	2.8	2.2
1	0	10	1.7*	-0.4	4	1	3	7.9	6.3	5	1	9	10.0	9.4	-1	1	18	2.2	-2.5	-3	2	6	17.6	-18.0
-1	0	10	31.2	-35.6	-4	1	3	23.5	25.2	-5	1	9	9.8	9.9	2	1	18	3.4	-3.6	4	2	6	10.8	-9.8
2	0	10	9.7	-9.6	5	1	3	20.2	21.2	6	1	9	9.7	9.3	-2	1	18	5.4	4.9	-4	2	6	8.4	8.0
-2	0	10	36.4	43.1	-5	1	3	7.0	-6.0	-6	1	9	10.5	-10.4	0	2	0	30.2	-37.6	5	2	6	19.5	19.5
3	0	10	19.4	19.5	6	1	3	5.6	4.3	7	1	9	1.4*	-1.2	1	2	0	9.5	9.3	-5	2	6	12.6	12.8
-3	0	10	11.3	10.1	-6	1	3	1.6*	0.1	-7	1	9	11.7	-11.4	2	2	0	11.9	-11.1	6	2	6	15.2	17.3
4	0	10	6.7	-6.6	7	1	3	9.4	-9.3	8	1	9	3.0	-2.3	3	2	0	19.1	17.7	-6	2	6	5.9	-5.0
-4	0	10	8.0	7.2	-7	1	3	4.4	3.6	-8	1	9	5.2	-4.3	4	2	0	33.0	35.5	7	2	6	3.7	4.8
5	0	10	9.4	7.8	8	1	3	3.8	3.2	0	1	10	34.1	38.3	5	2	0	3.5	-2.6	-7	2	6	6.2	6.1
-5	0	10	11.5	-11.6	-8.	1	3	5.1	-5.0	1	1	10	14.4	-13.9	6	2	0	10.2	-9.9	8	2	6	6.3	6.6
6	0	10	5.8	5.7	9	1	3	5.9	4.5	-1	1	10	1.6*	-0.8	7	2	0	16.8	-18.9	-8	2	6	3.7	-3.9
-6	0	10	2.0*	0.5	-9	1	3	3.4	-2.9	2	1	10	13.1	12.7	8	2	0	5.6	-6.[illegible]	9	2	6	9.7	9.7
7	0	10	3.0	-2.7	0	1	4	59.4*	-99.2	-2	1	10	4.5	-2.9	9	2	0	3.6	-3.7	-9	2	6	3.2	2.8
-7	0	10	1.8*	-0.6	1	1	4	14.8	-13.6	3	1	10	7.8	6.2	0	2	1	6.3	-4.6	0	2	7	4.2	-4.1
-8	0	10	7.9	-8.4	-1	1	4	12.7	-12.7	-3	1	10	5.1	4.2	1	2	1	8.4	-7.4	1	2	7	16.9	-15.8
-9	0	10	10.5	13.7	2	1	4	21.2	-21.2	4	1	10	12.0	-12.5	-1	2	1	20.8	-20.9	-1	2	7	15.1	14.6
0	0	12	22.0	22.1	-2	1	4	30.3	32.8	-4	1	10	1.4*	1.4	2	2	1	28.8	28.3	2	2	7	7.8	-7.2
1	0	12	1.9*	1.4	3	1	4	35.5	35.6	5	1	10	4.3	4.0	-2	2	1	33.3	35.3	-2	2	7	18.9	-19.1
-1	0	12	6.6	6.2	-3	1	4	12.2	-12.7	-5	1	10	5.9	5.2	3	2	1	19.8	18.9	3	2	7	4.5	-4.2
2	0	12	3.4	-3.0	4	1	4	8.5	6.9	6	1	10	4.4	4.6	-3	2	1	8.7	8.7	-3	2	7	14.0	13.3
-2	0	12	8.8	-7.7	-4	1	4	18.4	19.1	-6	1	10	8.1	-7.6	4	2	1	11.7	-12.3	4	2	7	21.1	22.2
3	0	12	12.7	10.8	5	1	4	4.3	3.1	7	1	10	9.7	9.6	-4	2	1	15.1	-15.4	-4	2	7	5.4	-4.3
-3	0	12	1.6*	1.4	-5	1	4	3.0	-2.3	-7	1	10	14.6	16.3	5	2	1	17.0	16.7	5	2	7	15.6	-16.1
4	0	12	19.8	21.9	6	1	4	6.6	-6.3	8	1	10	3.6	3.8	-5	2	1	2.7	-1.8	-5	2	7	3.9	-3.0
-4	0	12	27.1	30.6	-6	1	4	12.3	-11.2	-8	1	10	1.2*	-0.6	6	2	1	6.1	-5.9	6	2	7	3.3	-2.7
5	0	12	6.4	6.0	7	1	4	24.0	-26.7	0	1	11	6.6	-5.4	-6	2	1	16.8	17.9	-6	2	7	5.7	-4.8

Table 2 (*cont.*)

7	2	7	6.4	7.0
-7	2	7	9.6	-9.1
8	2	7	3.4	-2.6
-8	2	7	3.2	3.9
-9	2	7	2.8	-2.5
0	2	8	32.0	34.0
1	2	8	9.4	8.9
-1	2	8	16.0	16.4
2	2	8	10.1	-8.4
-2	2	8	8.8	-7.6
3	2	8	10.8	-10.1
-3	2	8	3.2	-0.4
4	2	8	5.2	4.0
-4	2	8	6.6	-6.4
5	2	8	22.0	-23.2
-5	2	8	5.8	5.6
6	2	8	3.2	-2.4
-6	2	8	15.1	16.2
7	2	8	12.6	14.4
-7	2	8	15.0	16.0
8	2	8	0.9*	-0.9
-8	2	8	1.1*	1.1
0	2	9	27.5	-29.9
1	2	9	6.7	6.3
-1	2	9	5.8	4.9
2	2	9	20.4	21.3
-2	2	9	11.9	10.3
3	2	9	20.7	-21.3
-3	2	9	2.4	1.8
4	2	9	19.2	-20.7
-4	2	9	16.0	-17.0
5	2	9	10.6	9.8
-5	2	9	3.0	2.9
6	2	9	3.6	4.8
-6	2	9	4.3	3.8
7	2	9	10.3	-11.1
-7	2	9	10.1	-10.8
8	2	9	2.0	1.6
-8	2	9	4.4	3.9
0	2	10	16.6	-17.5
1	2	10	3.2	-2.4
-1	2	10	6.4	4.9
2	2	10	17.6	17.7
-2	2	10	14.0	-14.5
3	2	10	25.7	-29.2
-3	2	10	17.0	-17.1
4	2	10	20.1	-22.4
-4	2	10	19.4	-21.5
5	2	10	4.6	-4.1
-5	2	10	3.4	2.2
6	2	10	1.8	2.1
-6	2	10	1.4*	1.1
7	2	10	1.0*	-0.3
-7	2	10	1.2*	1.7
-8	2	10	8.9	8.8
0	2	11	19.2	20.8
1	2	11	11.5	11.7
-1	2	11	11.4	-11.0
2	2	11	26.5	-30.3
-2	2	11	12.5	-12.7
3	2	11	6.3	6.0
-3	2	11	1.4*	-0.3
4	2	11	3.0	2.5
-4	2	11	4.6	4.0
5	2	11	5.9	-5.7
-5	2	11	9.9	-9.8
6	2	11	3.9	-3.9
-6	2	11	3.8	4.0
7	2	11	2.2	1.8
-7	2	11	1.8	1.8
-8	2	11	3.2	-3.1
0	2	12	15.3	15.7
1	2	12	5.8	5.3
-1	2	12	7.8	-7.1
2	2	12	12.7	-12.9
-2	2	12	18.9	-20.5
3	2	12	3.0	1.8
-3	2	12	2.9	-1.6
4	2	12	1.3*	0.8
-4	2	12	8.7	-8.2
5	2	12	2.4	-1.7
-5	2	12	8.8	-8.7
6	2	12	3.6	4.0
-6	2	12	1.2*	-0.5
-7	2	12	3.8	-3.5
0	2	13	6.7	-6.1
1	2	13	13.0	13.2
-1	2	13	3.5	2.8
2	2	13	2.8	2.8
-2	2	13	14.1	13.7
3	2	13	2.4	2.2
-3	2	13	11.4	-12.0
4	2	13	2.5	-2.4
-4	2	13	1.3*	-0.3
5	2	13	3.2	2.6
-5	2	13	1.4*	-1.4
6	2	13	0.8*	1.3
-6	2	13	8.3	7.7
-7	2	13	4.8	4.9
0	2	14	10.9	-10.0
1	2	14	6.5	6.1
-1	2	14	7.6	8.0
2	2	14	3.7	-3.0
-2	2	14	15.8	17.4
3	2	14	2.1	2.7
-3	2	14	6.9	-7.3
4	2	14	2.6	2.9
-4	2	14	1.2*	0.1
5	2	14	6.8	5.9
-5	2	14	5.8	6.0
-6	2	14	5.9	5.4
0	2	15	14.3	16.6
1	2	15	5.8	-5.7
-1	2	15	4.1	4.1
2	2	15	1.1*	1.5
-2	2	15	10.3	-10.8
3	2	15	9.6	9.2
-3	2	15	5.2	4.5
4	2	15	2.3	2.3
-4	2	15	12.5	13.7
5	2	15	6.0	-6.1
-5	2	15	5.1	-4.6
0	2	16	3.0	-2.8
1	2	16	7.7	-7.8
-1	2	16	1.3*	-0.8
2	2	16	7.2	-6.6
-2	2	16	1.0*	1.5
3	2	16	9.4	8.7
-3	2	16	10.0	10.2
4	2	16	4.6	4.9
-4	2	16	10.7	11.0
0	2	17	2.7	-2.8
1	2	17	4.4	-4.5
-1	2	17	1.9	-1.9
2	2	17	9.2	9.6
-2	2	17	5.7	5.6
-3	2	17	2.8	-3.1
1	3	0	3.6	3.6
2	3	0	6.8	-6.2
3	3	0	4.2	3.2
4	3	0	9.1	-9.0
5	3	0	7.6	-6.9
6	3	0	4.0	3.9
7	3	0	5.9	6.7
8	3	0	3.6	-3.4
9	3	0	6.5	-7.0
0	3	1	5.0	-4.8
1	3	1	16.2	-16.5
-1	3	1	14.8	-14.5
2	3	1	24.0	23.9
-2	3	1	12.3	-11.5
3	3	1	7.3	-6.2
-3	3	1	22.8	22.1
4	3	1	18.7	18.8
-4	3	1	11.5	10.4
5	3	1	11.3	10.3
-5	3	1	9.7	-9.4
6	3	1	1.3*	1.3
-6	3	1	13.0	-13.0
7	3	1	8.8	9.5
-7	3	1	5.6	5.6
8	3	1	2.7	-3.3
-8	3	1	4.2	-4.1
9	3	1	8.4	8.9
-9	3	1	1.9	-2.4
0	3	2	17.6	17.9
1	3	2	12.8	12.5
-1	3	2	12.6	12.4
2	3	2	1.4	0.7
-2	3	2	3.8	-3.4
3	3	2	16.4	-16.1
-3	3	2	15.0	-14.4
4	3	2	7.4	-6.7
-4	3	2	1.2*	1.6
5	3	2	11.5	11.4
-5	3	2	1.4*	0.7
6	3	2	6.6	6.6
-6	3	2	3.1	2.8
7	3	2	1.3*	1.2
-7	3	2	6.1	6.7
8	3	2	4.5	5.1
-8	3	2	1.1*	-0.4
9	3	2	8.0	8.9
-9	3	2	0.7*	-0.3
0	3	3	22.1	22.0
1	3	3	27.1	-27.0
-1	3	3	24.7	24.6
2	3	3	19.5	19.1
-2	3	3	11.9	-11.7
3	3	3	12.0	9.5
-3	3	3	16.4	16.3
4	3	3	8.8	8.4
-4	3	3	2.2	-2.3
5	3	3	3.5	-2.4
-5	3	3	17.9	18.2
6	3	3	10.3	10.8
-6	3	3	11.3	-11.7
7	3	3	6.3	6.5
-7	3	3	13.3	-14.4
8	3	3	12.7	-12.3
-8	3	3	4.1	4.4
-9	3	3	0.6*	-0.9
0	3	4	20.3	19.4
1	3	4	8.1	6.6
-1	3	4	18.6	17.7
2	3	4	10.0	9.3
-2	3	4	9.1	8.1
3	3	4	3.5	-2.7
-3	3	4	9.6	-9.5
4	3	4	5.2	-3.6
-4	3	4	18.9	-20.4
5	3	4	5.9	-5.7
-5	3	4	4.6	4.5
6	3	4	4.4	4.7
-6	3	4	13.8	15.4
7	3	4	15.3	17.7
-7	3	4	5.5	5.7
8	3	4	7.0	7.4
-8	3	4	1.0*	-0.0
0	3	5	23.1	-22.0
1	3	5	9.0	7.5
-1	3	5	4.0	4.2
2	3	5	10.2	-8.5
-2	3	5	12.9	11.1
3	3	5	22.8	-23.2
-3	3	5	3.8	-1.6
4	3	5	11.2	-11.1
-4	3	5	15.0	-15.2
5	3	5	3.0	-2.1
-5	3	5	8.3	8.6
6	3	5	6.1	-5.5
-6	3	5	1.3*	1.4
7	3	5	15.1	-16.9
-7	3	5	3.0	-2.3
8	3	5	8.6	8.8
-8	3	5	5.7	5.3
0	3	6	16.1	15.8
1	3	6	18.9	18.3
-1	3	6	4.8	-4.4
2	3	6	1.6	2.1
-2	3	6	8.0	-7.7
3	3	6	18.6	-19.4
-3	3	6	2.9	2.3
4	3	6	10.9	-11.2
-4	3	6	5.5	-5.3
5	3	6	1.5*	1.2
-5	3	6	3.1	-3.6
6	3	6	2.8	3.0
-6	3	6	1.3*	1.1
7	3	6	1.1*	1.3
-7	3	6	11.6	13.2
8	3	6	2.6	2.2
-8	3	6	7.4	7.7
0	3	7	18.6	-18.6
1	3	7	6.8	6.6
-1	3	7	4.6	2.8
2	3	7	17.0	-17.5
-2	3	7	15.4	-14.8
3	3	7	2.8	-1.1
-3	3	7	16.9	-17.6
4	3	7	16.5	-17.6
-4	3	7	4.6	-4.4
5	3	7	16.8	-17.8
-5	3	7	17.6	-18.8
6	3	7	12.8	14.4
-6	3	7	4.9	4.8
7	3	7	1.5	-1.7
-7	3	7	2.8	-2.7
8	3	7	2.0	2.1
-8	3	7	2.4	-2.4
0	3	8	3.4	3.4
1	3	8	7.0	-5.1
-1	3	8	5.1	4.0
2	3	8	13.8	-14.0
-2	3	8	11.9	-12.0
3	3	8	2.9	-2.3
-3	3	8	14.9	-15.2
4	3	8	2.0	-1.7
-4	3	8	8.1	-7.1
5	3	8	6.7	-6.0
-5	3	8	1.5*	1.1
6	3	8	1.2*	0.4
-6	3	8	1.7	1.5
7	3	8	2.5	-3.7
-7	3	8	2.7	-2.9
-8	3	8	2.6	-2.5
0	3	9	9.0	8.2
1	3	9	32.5	36.1
-1	3	9	7.7	-6.4
2	3	9	4.1	-3.5
-2	3	9	2.9	1.3
3	3	9	13.2	-12.8
-3	3	9	2.8	-2.4
4	3	9	11.8	12.0
-4	3	9	5.2	-3.3
5	3	9	10.9	11.4
-5	3	9	9.3	-9.7
6	3	9	7.4	-7.1
-6	3	9	10.8	12.0
7	3	9	7.9	8.3
-7	3	9	3.7	-3.7
0	3	10	9.4	-8.9
1	3	10	6.5	-5.6
-1	3	10	1.6*	1.1
2	3	10	6.3	-5.6
-2	3	10	2.3	1.0
3	3	10	5.9	5.4
-3	3	10	1.3*	-0.1
4	3	10	8.2	7.2
-4	3	10	2.0	-1.2
5	3	10	1.4*	-1.3
-5	3	10	8.5	-8.6
6	3	10	4.2	-3.5
-6	3	10	1.9	-2.1
7	3	10	3.0	-3.2
-7	3	10	0.9*	1.0
0	3	11	22.8	26.1
1	3	11	15.7	-14.9
-1	3	11	12.8	13.3
2	3	11	8.0	7.8
-2	3	11	1.2*	-0.3
3	3	11	16.6	19.1
-3	3	11	2.2	-1.9
4	3	11	8.5	-8.5
-4	3	11	12.6	13.4
5	3	11	1.2*	1.6
-5	3	11	5.9	6.2
6	3	11	2.3	-2.7
-6	3	11	4.2	4.1
-7	3	11	13.3	14.6
0	3	12	11.0	-11.3
1	3	12	8.0	-7.0
-1	3	12	1.6*	2.0
2	3	12	8.6	8.5
-2	3	12	9.4	10.0
3	3	12	7.2	6.8
-3	3	12	7.6	7.3
4	3	12	1.1*	-0.3
-4	3	12	7.1	6.5
5	3	12	4.9	4.9
-5	3	12	1.2*	0.6
6	3	12	0.6*	1.0
-6	3	12	3.6	-3.4
0	3	13	4.1	3.6
1	3	13	1.5*	-1.5
-1	3	13	16.3	-17.6
2	3	13	3.6	-3.[illegible]
-2	3	13	8.9	9.3
3	3	13	2.7	2.0
-3	3	13	3.5	3.3
4	3	13	1.0*	-0.2
-4	3	13	4.2	-4.2
5	3	13	0.9*	-0.1
-5	3	13	5.2	4.9
-6	3	13	2.3	-2.2
0	3	14	2.6	2.2
1	3	14	2.6	-2.6
-1	3	14	6.3	-6.4
2	3	14	4.3	-4.3
-2	3	14	2.3	2.9
3	3	14	2.9	2.5
-3	3	14	8.9	9.5
4	3	14	7.4	7.7
-4	3	14	7.2	6.7
-5	3	14	0.8*	1.[illegible]
0	3	15	8.9	-10.4
1	3	15	8.6	-9.5
-1	3	15	8.9	8.9
2	3	15	8.4	8.2
-2	3	15	4.7	-4.2
3	3	15	0.8*	0.3
-3	3	15	9.9	-10.0
-4	3	15	4.6	4.2
0	3	16	6.5	-6.3
1	3	16	3.8	-3.7
-1	3	16	2.4	1.8
2	3	16	3.7	3.1
-2	3	16	9.0	9.0
0	4	0	9.7	9.0
1	4	0	17.0	19.6
2	4	0	12.1	12.0
3	4	0	7.5	-6.5
4	4	0	8.9	-8.4
5	4	0	6.3	5.8
6	4	0	12.9	14.0
7	4	0	1.1*	0.7
0	4	1	28.7	-34.1
1	4	1	7.1	6.8
-1	4	1	16.9	19.9
2	4	1	13.9	14.3
-2	4	1	17.0	18.2
3	4	1	15.4	-15.2
-3	4	1	13.6	-13.7
4	4	1	4.5	-3.4
-4	4	1	16.0	-16.5
5	4	1	5.5	-5.0
-5	4	1	7.8	7.0
6	4	1	10.3	9.7
-6	4	1	3.1	-2.9
7	4	1	5.3	-4.4
-7	4	1	8.0	-6.6
0	4	2	8.2	9.0
1	4	2	6.8	6.7
-1	4	2	6.2	5.2
2	4	2	13.0	-12.5
-2	4	2	1.0*	0.2
3	4	2	13.2	-13.1
-3	4	2	4.6	-4.2
4	4	2	2.5	-1.3
-4	4	2	4.0	-3.3
5	4	2	2.2	-1.7
-5	4	2	1.8	1.4
6	4	2	8.2	-8.0
-6	4	2	10.0	9.9
7	4	2	1.1*	-0.1
-7	4	2	8.8	8.0
0	4	3	4.3	3.9
1	4	3	6.8	6.9
-1	4	3	10.7	10.1
2	4	3	13.7	-13.2
-2	4	3	27.9	-32.0
3	4	3	14.7	-13.6
-3	4	3	6.1	5.8
4	4	3	11.0	-10.5
-4	4	3	5.8	5.2
5	4	3	16.7	-17.6
-5	4	3	20.2	-21.9
6	4	3	7.3	7.8
-6	4	3	3.4	3.3
7	4	3	1.0*	1.3
-7	4	3	2.4	1.6
0	4	4	6.9	-5.5
1	4	4	1.7	-1.0
-1	4	4	15.0	-13.6
2	4	4	5.6	-4.7
-2	4	4	1.1*	-0.3
3	4	4	3.9	-3.1
-3	4	4	2.6	-2.2
4	4	4	5.7	-5.4
-4	4	4	12.3	-12.9
5	4	4	1.5*	1.4
-5	4	4	12.0	-12.2
6	4	4	1.2*	1.9
-6	4	4	2.7	2.2
7	4	4	3.2	3.2
-7	4	4	4.2	3.8
0	4	5	3.6	-3.4
1	4	5	13.7	14.6
-1	4	5	3.7	-2.4
2	4	5	6.8	-5.7
-2	4	5	5.2	4.0
3	4	5	16.1	-16.7
-3	4	5	18.5	-19.3
4	4	5	11.9	-11.2
-4	4	5	19.6	-20.2
5	4	5	11.4	11.2
-5	4	5	6.4	5.8
6	4	5	6.5	-7.2
-6	4	5	13.5	13.2
-7	4	5	13.4	-13.7
0	4	6	11.2	10.7
1	4	6	4.2	-3.6
-1	4	6	1.5*	0.6
2	4	6	6.9	-6.9
-2	4	6	6.8	-5.9
3	4	6	11.2	10.7
-3	4	6	1.3*	0.8
4	4	6	11.8	11.9
-4	4	6	10.7	10.2
5	4	6	3.2	2.7
-5	4	6	4.1	-4.0
6	4	6	2.7	-3.3
-6	4	6	12.5	-12.6
-7	4	6	0.9*	-0.9
0	4	7	19.5	21.4
1	4	7	1.5*	-1.0
-1	4	7	2.4	-1.0
2	4	7	8.0	-7.0
-2	4	7	5.6	3.8
3	4	7	20.8	24.1
-3	4	7	6.9	-6.6
4	4	7	1.8	-1.9
-4	4	7	8.7	8.4
5	4	7	1.4*	1.7
-5	4	7	8.2	-7.4
6	4	7	3.4	-3.5
-6	4	7	1.1*	1.0
-7	4	7	16.0	18.9
0	4	8	10.4	-9.5
1	4	8	12.4	-12.5
-1	4	8	4.2	4.4
2	4	8	5.2	5.1
-2	4	8	9.8	9.3
3	4	8	7.4	6.8
-3	4	8	8.4	7.1
4	4	8	1.2*	0.1
-4	4	8	5.3	5.1
5	4	8	3.1	-2.6
-5	4	8	4.0	4.3
6	4	8	0.9*	-1.5
-6	4	8	1.0*	-0.1
0	4	9	1.5*	0.1
1	4	9	10.3	9.9
-1	4	9	7.1	-7.4
2	4	9	10.1	9.4
-2	4	9	14.9	17.1
3	4	9	5.8	5.3
-3	4	9	5.7	5.7
4	4	9	1.2*	1.1
-4	4	9	7.4	6.2
5	4	9	1.2*	1.9
-5	4	9	5.7	4.5
-6	4	9	4.4	3.5
0	4	10	11.7	-11.9
1	4	10	11.5	-11.8
-1	4	10	3.1	-2.9
2	4	10	3.2	2.4
-2	4	10	2.1	-0.5
3	4	10	1.2*	1.4
-3	4	10	2.7	2.6
4	4	10	3.9	3.2
-4	4	10	4.6	3.7
5	4	10	1.0*	0.6
-5	4	10	4.5	3.6
-6	4	10	7.9	-8.0
0	4	11	2.4	2.3
1	4	11	11.1	-13.0
-1	4	11	5.2	5.0
2	4	11	2.3	1.2
-2	4	11	11.4	-11.6
3	4	11	5.6	-5.6
-3	4	11	2.2	2.2
4	4	11	14.1	14.0
-4	4	11	9.4	9.0
5	4	11	2.8	2.2
-5	4	11	5.6	5.1
0	4	12	5.8	-6.5
1	4	12	6.2	6.0
-1	4	12	5.4	-5.3
2	4	12	7.8	7.8
-2	4	12	6.6	6.0
3	4	12	1.0*	0.8
-3	4	12	6.5	6.1
4	4	12	4.2	4.2
-4	4	12	4.6	-3.9
0	4	13	10.0	-10.6
1	4	13	16.5	-17.3
-1	4	13	2.4	2.1
2	4	13	8.4	7.3
-2	4	13	2.5	1.8
3	4	13	0.8*	1.1
-3	4	13	6.4	5.7
-4	4	13	11.7	-13.4
0	4	14	4.8	5.1
1	4	14	6.0	6.0
-1	4	14	2.2	1.7
2	4	14	2.9	-2.7
-2	4	14	0.8*	-0.3
1	5	0	19.7	22.4
2	5	0	11.3	-13.0
3	5	0	10.2	-10.6
4	5	0	1.2*	1.3
5	5	0	8.5	8.2
0	5	1	1.7*	1.8
1	5	1	16.7	17.1
-1	5	1	17.8	-18.4
2	5	1	17.6	-19.8
-2	5	1	3.9	-3.4
3	5	1	9.5	-9.5
-3	5	1	7.0	-7.1

Table 2 (*cont.*)

4	5	1	5.3	-4.9	3	5	4	7.4	7.8	2	5	7	11.4	12.0	-2	5	10	2.1	1.5	-4	6	2	7.7	9.3
-4	5	1	17.5	-19.4	-3	5	4	12.9	14.6	-2	5	7	5.0	4.9	3	5	10	4.9	4.6	0	6	3	3.2	-3.7
5	5	1	1.4*	-0.7	4	5	4	11.3	13.2	3	5	7	4.8	4.0	-3	5	10	3.9	-4.2	1	6	3	6.6	5.3
-5	5	1	12.7	-12.3	-4	5	4	4.8	-5.0	-3	5	7	1.7	-1.4	-4	5	10	3.2	-2.7	-1	6	3	11.3	-9.7
0	5	2	4.5	4.1	5	5	4	1.3*	-2.5	4	5	7	4.2	4.2	0	5	11	11.4	-11.8	2	6	3	9.1	8.4
1	5	2	13.4	-14.9	-5	5	4	5.3	-4.9	-4	5	7	1.0*	-0.2	-1	5	11	4.8	5.0	-2	6	3	13.6	13.8
-1	5	2	6.7	6.2	0	5	5	8.9	8.6	5	5	7	6.3	6.8	2	5	11	4.7	-4.2	3	6	3	4.0	3.5
2	5	2	8.8	-8.9	1	5	5	7.8	7.2	-5	5	7	12.9	13.0	-2	5	11	3.4	2.7	-3	6	3	11.0	12.3
-2	5	2	8.3	-7.6	-1	5	5	8.7	-8.3	0	5	8	6.5	-6.4	-1	5	12	7.5	-7.9	-4	6	3	4.7	4.9
3	5	2	7.4	7.3	2	5	5	1.1*	-0.1	1	5	8	7.4	6.9	0	6	0	9.2	8.6	0	6	4	13.2	-13.5
-3	5	2	9.7	-9.7	-2	5	5	6.4	6.2	-1	5	8	6.7	-6.8	1	6	0	7.4	-6.4	1	6	4	5.4	-4.7
4	5	2	6.0	5.4	3	5	5	1.1*	-0.2	2	5	8	4.4	-4.2	2	6	0	9.1	8.9	-1	6	4	6.3	5.9
-4	5	2	9.7	11.0	-3	5	5	14.7	16.6	-2	5	8	2.4	-1.6	3	6	0	10.4	11.2	2	6	4	7.2	7.6
5	5	2	1.4*	0.8	4	5	5	8.3	8.9	3	5	8	7.7	-7.1	4	6	0	0.7*	-0.7	-2	6	4	8.3	-8.1
-5	5	2	1.4*	-1.9	-4	5	5	5.9	5.8	-3	5	8	1.0*	0.6	0	6	1	1.3*	0.2	-3	6	4	5.7	-5.2
0	5	3	1.7*	-0.1	5	5	5	3.7	3.8	4	5	8	4.3	4.5	1	6	1	8.6	-7.3	0	6	5	3.9	-3.6
1	5	3	3.6	3.0	-5	5	5	3.8	-3.0	-4	5	8	3.2	-2.4	-1	6	1	5.3	5.3	1	6	5	3.4	-4.5
-1	5	3	17.3	18.3	0	5	6	5.3	-6.1	-5	5	8	4.5	4.4	2	6	1	9.3	8.9	-1	6	5	1.2*	-0.1
2	5	3	6.9	6.0	1	5	6	12.3	-13.2	0	5	9	2.2	2.1	-2	6	1	7.0	6.9	2	6	5	1.7	-1.9
-2	5	3	5.2	5.2	-1	5	6	3.4	3.7	1	5	9	2.6	-3.1	3	6	1	12.3	13.3	-2	6	5	2.5	-2.2
3	5	3	11.7	13.1	2	5	6	13.5	15.8	-1	5	9	10.6	-10.2	-3	6	1	0.8*	1.4	0	6	6	1.1*	-2.3
-3	5	3	19.3	-21.7	-2	5	6	2.2	-1.0	2	5	9	0.9*	-1.3	4	6	1	0.6*	1.3	1	6	6	6.9	6.6
4	5	3	6.9	-7.2	3	5	6	7.1	6.6	-2	5	9	0.9*	-1.5	-4	6	1	0.6*	1.0	-1	6	6	1.1*	1.5
-4	5	3	10.1	11.3	-3	5	6	3.0	3.2	3	5	9	5.3	4.7	0	6	2	3.1	2.7	2	6	6	1.8	2.1
5	5	3	1.3*	1.1	4	5	6	9.0	-8.9	-3	5	9	13.9	14.8	1	6	2	1.4*	-2.6	-2	6	6	4.7	-4.7
-5	5	3	1.4*	2.2	-4	5	6	11.0	10.2	4	5	9	7.4	8.3	-1	6	2	5.0	-4.5	0	6	7	4.9	-5.0
0	5	4	1.7*	0.2	5	5	6	2.3	-2.3	-4	5	9	0.8*	-0.4	2	6	2	2.7	-2.0	1	6	7	3.0	-2.8
1	5	4	9.3	-9.3	-5	5	6	10.9	10.5	0	5	10	7.5	-8.3	-2	6	2	0.8*	-2.2	-1	6	7	4.8	-4.2
-1	5	4	6.8	-6.3	0	5	7	6.2	-6.1	1	5	10	1.3*	2.0	3	6	2	0.8*	0.8					
2	5	4	5.4	3.9	1	5	7	15.4	-17.2	-1	5	10	8.9	7.7	-3	6	2	0.8*	1.9					
-2	5	4	5.4	5.0	-1	5	7	1.6*	1.1	2	5	10	2.5	2.3	4	6	2	3.1	3.2					

groups. The C=O distance of 1·248 Å in the urea part of the molecule is significantly longer but shorter than the value 1·268 Å (corrected for thermal motion: 1·276 Å) for urea itself (Caron & Donohue, 1964). The lengths of the C–H and N–H bonds are reasonable in view of the rather big estimated standard deviations.

Various least-squares planes through different parts of the molecule were calculated with the method of Schomaker, Waser, Marsh & Bergman (1959). The five ring atoms are coplanar within 0·034 Å. The five ring atoms and the two carbonyl oxygens on the ring are planar within 0·044 Å. The largest displacement of the chain atoms N(6), C(7), O(7) and N(8) and the ring atom C(5) from a common least-squares plane is 0·024 Å. This plane and the best plane through the hydantoin residue make an intersecting angle of 80° to the side of the atoms N(3), C(4) and O(4). Because of the tetrahedral nature of the carbon atom C(5) this angle is not a dihedral angle about the hydantoin–urea linkage. The conformation of this bond, C(5)–N(6), is shown in Fig. 3. The conformation of the peptide-like bond C(7)–N(6) is *trans* with respect to the adjacent atoms C(5) and N(8), as apparent from Fig. 4 and 5. This and the approximately coplanar environment of this bond reflect the characteristic features of open chain peptide linkages.

Table 3. *Valence bond lengths and bond angles*

Bond lengths. For distances between heavy atoms the estimated standard deviation is $\sigma = 0{\cdot}004$ Å; for distances between a heavy and a hydrogen atom $\sigma = 0{\cdot}07$ Å.

C(O)–NH		X–H	
C(2)–N(1)	1·341 Å	C(5)–H(5)	1·07 Å
C(2)–N(3)	1·397	N(1)–H(1)	0·89
C(4)–N(3)	1·362	N(3)–H(3)	0·96
C(7)–N(6)	1·368	N(6)–H(6)	1·01
C(7)–N(8)	1·335	N(8)–H(8)	0·76
		N(8)–H(9)	0·90
C=O			
C(2)–O(2)	1·219 Å	C(4)–C(5)	1·535 Å
C(4)–O(4)	1·213	C(5)–N(1)	1·461
C(7)–O(7)	1·248	C(5)–N(6)	1·424

Bond angles. For angles involving heavy atoms only, the estimated standard deviation is somewhat smaller than 0·3°, for all other angles it is 4° and greater [7° for the angle H(8)–N(8)–H(9)].

C(2)–N(1)–C(5)	112·7°	C(2)–N(1)–H(1)	123°
N(1)–C(2)–N(3)	107·7	C(5)–N(1)–H(1)	124
N(1)–C(2)–O(2)	127·7	C(2)–N(3)–H(3)	120
N(3)–C(2)–O(2)	124·6	C(4)–N(3)–H(3)	127
C(2)–N(3)–C(4)	111·6	C(4)–C(5)–H(5)	105
C(5)–C(4)–O(4)	126·6	N(1)–C(5)–H(5)	113
N(3)–C(4)–O(4)	126·5	N(6)–C(5)–H(5)	107
C(4)–C(5)–N(1)	100·7	C(5)–N(6)–H(6)	113
C(4)–C(5)–N(6)	114·1	C(7)–N(6)–H(6)	127
N(1)–C(5)–N(6)	116·5	C(7)–N(8)–H(8)	113
C(5)–N(6)–C(7)	119·9	C(7)–N(8)–H(9)	117
N(6)–C(7)–N(8)	116·8	H(8)–N(8)–H(9)	124
N(6)–C(7)–O(7)	120·2		
N(8)–C(7)–O(7)	122·9		

The hydrogen bonding

There are five crystallographically independent hydrogen bonds in the crystal structure corresponding to the five hydrogen atoms in the molecule which are bonded to nitrogen. The imido nitrogen atoms N(1), N(3) and N(6) participate in one hydrogen bond each and amido N(8) in two. Of the three carbonyl oxygens per molecule, O(2) accepts one hydrogen bond and O(4) and O(7) two each. All the hydrogen bonding is between NH and CO groups of different molecules. There are no intramolecular hydrogen bonds involving such atomic arrangements as (II) or (III). An intramolecular hydrogen bond N(1)H---O(7), (II), is not in agreement with the observed distance H(1)---O(7) of more than 3·5 Å. To form the hypothetical structure (III), the atoms C(5) and N(8) must be on the same side of the bond C(7)–N(6), but this is not in agreement with the conformation observed in the crystal.

The intricate three-dimensional network, in which the molecules are hydrogen bonded, is shown in Figs. 4

and 5, which are projections along [010] and [$10\bar{1}$]. Hydrogen bonds of the type N(1)(H) · · · O(7) of 2·920 Å link like molecules (*i.e.* all D or all L) into infinite spirals around the twofold screw axes at $0,y,\frac{1}{4}$ and

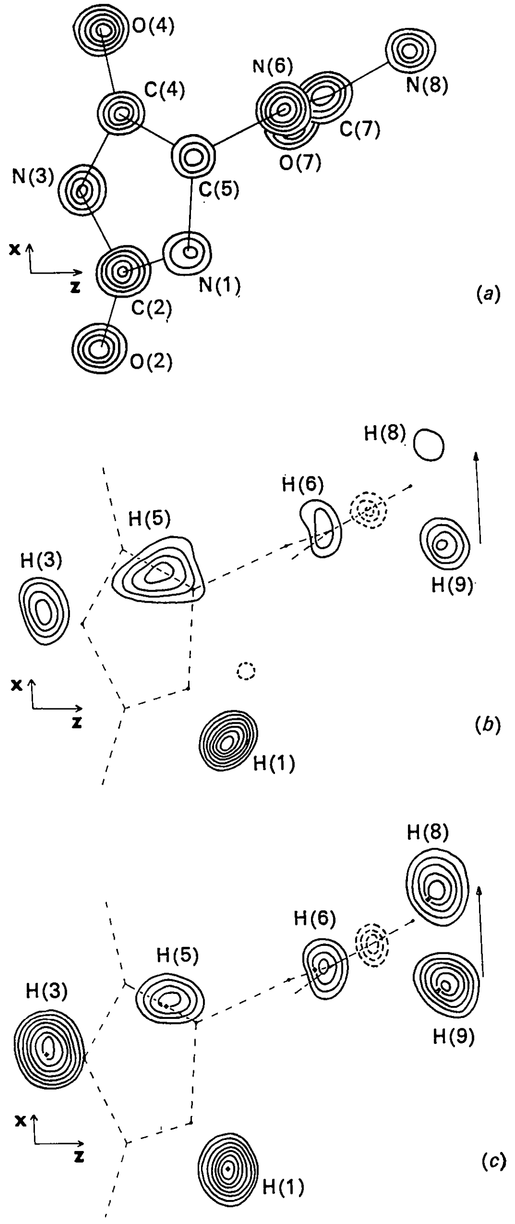
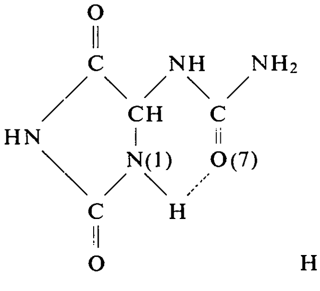
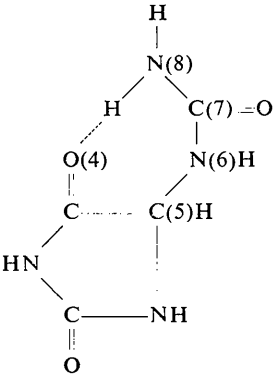


Fig. 1. (*a*) Three-dimensional Fourier synthesis of DL-allantoin computed with 398 normalized structure amplitudes and signs determined by means of the Sayre equation. Equidistant contour lines start at the same arbitrary level for every atom. (*b*) Difference Fourier synthesis showing the hydrogen peaks, computed at the end of the isotropic refinement from reflexions with sin $\theta < 0{\cdot}7$ only. The maximum H(9) actually lies on top of H(8) as indicated by the arrow. Contour lines are drawn every 0·05 e.Å^{-3}, starting with 0·95 e.Å^{-3}. The maxima shown by dashed lines are too far away from any of the heavier atoms to be interpretable as hydrogen. (*c*) The same as (*b*), but based on the final parameters of the heavier atoms. The crosses indicate the hydrogen positions as obtained by the least-squares refinement.



(II)



(III)

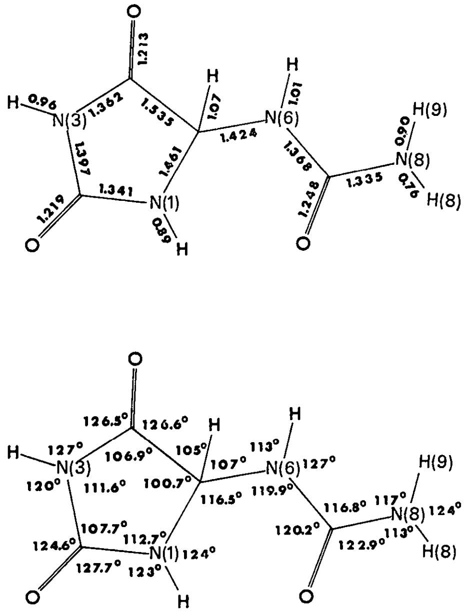


Fig. 2. DL-allantoin, schematic representation of the molecule with valence bond lengths and bond angles.

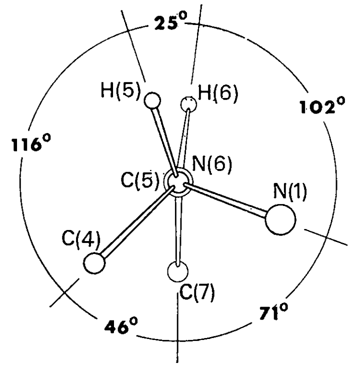


Fig. 3. The conformation of the bond C(5)–N(6). The projection is along the direction of the bond with N(6) behind C(5). The configuration at the asymmetric carbon atom C(5), as shown in this figure, refers to the molecules in x,y,z in Figs. 4 and 5, and is consistent with the atomic parameters of Table 1 in a right-handed coordinate system.

symmetry related positions. Two hydrogen bonds N(3)(H) · · · O(2) of 2·827 Å join unlike molecules together in pairs (*i.e.* D, L) across the centers of symmetry at 0, 0, 0 and related positions. The planes of the two hydantoin residues (hydrogen atoms excluded) in such a pair are displaced from each other by 0·30 Å. Hydrogen bonds N(6)(H) · · · O(7) of 2·903 Å link every molecule to two others related to it by a full lattice translation up and down the *b* axis. The length of the remaining two hydrogen bonds, N(8)(H8) · · · O(4) and N(8)(H9) · · · O(4) is 3·007 and 3·023 Å, respectively. These bonds form double zigzag chains extending infinitely along the *b*-axis direction and linking molecules which lie around the screw axes at $\frac{1}{2},y,\frac{1}{4}$ and related positions.

The assignment of all hydrogen bonds with respect to the donor and acceptor atoms is unique as shown by the corresponding H···O distances and N–H···O angles in Table 4. With an angle N–H · · · O of 144° the hydrogen bond N(6)(H)···O(7) of 2·903 Å (H···O distance 2.03 Å) shows the largest deviation from linearity. This is accompanied by rather unusual values of 89·0°, 150·2° and 147·1° for the angles C(5)–N(6) · · · O(7), C(7)–N(6) · · · O(7) and C(7)=O(7) · · · N(6), respectively. If, as an alternative assignment, the next shortest intermolecular distance from N(6), which is to the O(2) at $\bar{x},\frac{1}{2}+y,\frac{1}{2}-z$, is ascribed to a hydrogen bond, the corresponding angles C(5)–N(6)---O(2), C(7)–N(6)---O(2) and C(2)=O(2)---N(6) of 129·1°, 83·7° and 102·3° would be more reasonable. But the much longer distances N(6)---O(2) at 3·239 Å and H(6)---O(2) at 2·82 Å and the rather small angle N–H---O of 106° are unfavorable for a hydrogen bond and make this alternative assignment unlikely. The various angles which involve the remaining hydrogen bonds (Table 4) lie in the range of commonly accepted values.

The intermolecular distances less than 3·3 Å, other than those of the hydrogen bonds, are given in Fig. 4 and Table 5. It is interesting to note that the shortest non-binding N · · · O separation of 3·079 Å is only 0·056 Å longer than the longest N(H) · · · O hydrogen

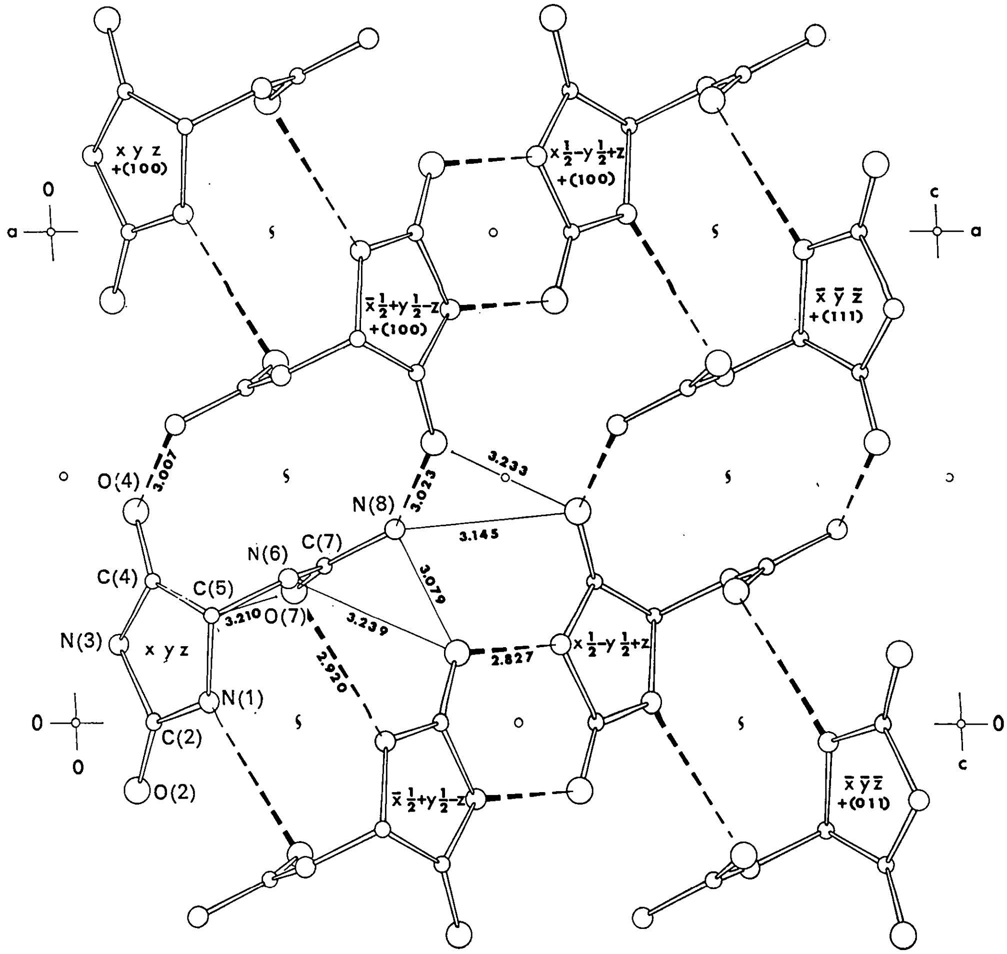


Fig. 4. The crystal structure of DL-allantoin viewed down the *b* axis. Broken lines represent hydrogen bonds; the hydrogen atoms are omitted for clarity. Thin lines are other intermolecular distances less than 3·3 Å. The figure does not show the N(6)H · · · O(7) hydrogen bonds by which molecules are linked into chains along the *b*-axis direction.

Table 4. *Geometry of hydrogen bonds*

Internal dimensions

	N(1)H ··· O(7)	N(3)H ··· O(2)	N(6)H ··· O(7)	N(8)H(8)···O(4)	N(8)H(9)···O(4)
N in molecule at x,y,z, O in molecule at:	$\bar{x},\frac{1}{2}+y,\frac{1}{2}-z$	$\bar{x},\bar{y},\bar{z}$	x,y,z +(0,1,0)	$\bar{x},\frac{1}{2}+y,\frac{1}{2}-z$ +(1,−1,0)	$\bar{x},\frac{1}{2}+y,\frac{1}{2}-z$ +(1,0,0)
d(N–H)	0·89 Å	0·96 Å	1·01 Å	0·76 Å	0·90 Å
d(H ··· O)	2·07	1·87	2·03	2·25	2·14
d(N ··· O)	2·920	2·827	2·903	3·007	3·023
∠(N–H ··· O)	159°	173°	144°	172°	167°

Additional angles

C–N ··· O	
C(2)–N(1) ··· O(7)	110·3°
C(5)–N(1) ··· O(7)	136·6
C(2)–N(3) ··· O(2)	115·5
C(4)–N(3) ··· O(2)	131·5
C(5)–N(6) ··· O(7)	89·0
C(7)–N(6) ··· O(7)	150·2
C(7)–N(8)(H8) ··· O(4)	112·7
C(7)–N(8)(H9) ··· O(4)	115·6

C=O ··· N	
C(2)–O(2) ··· N(3)	119·1°
C(4)–O(4) ··· (H8)N(8)	107·2
C(4)–O(4) ··· (H9)N(8)	121·6
C(7)–O(7) ··· N(1)	103·2
C(7)–O(7) ··· N(6)	147·1
O(4) ··· N(8) ··· O(4)	117·4 (2)
N(8) ··· O(4) ··· N(8)	
N(1) ··· O(7) ··· N(6)	81·9

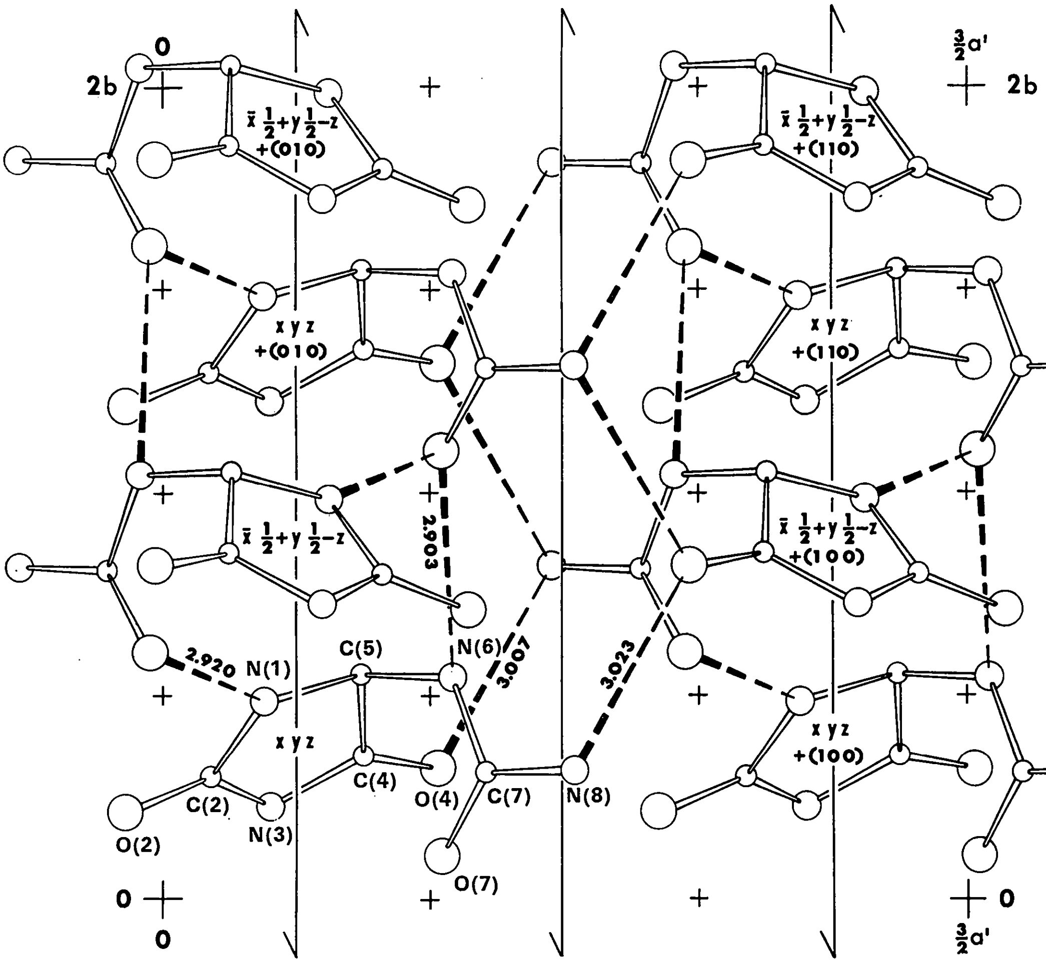


Fig. 5. The crystal structure of DL-allantoin viewed in the [10$\bar{1}$] direction. Broken lines represent hydrogen bonds. The hydrogen atoms are omitted for clarity as are all molecules generated from the original one by centers of symmetry or glide planes. Thus the figure does not show the N(3)H ··· O(2) hydrogen bonds which link enantiomorphous molecules into pairs across centers of symmetry.

bond distance of 3·023 Å. A unique distinction between these would have been impossible without the direct location of the hydrogen atoms.

Table 5. *Non-hydrogen-bonding intermolecular distances less than* 3·3 Å *between the heavier atoms*

Atom *i*	Atom *j*	in molecule at:	Distance d_{ij}
C(5)	O(7)	$x,y,z+(0,1,0)$	3·210 Å
N(6)	O(2)	$\bar{x},\frac{1}{2}+y,\frac{1}{2}-z$	3·239
N(8)	O(2)	$\bar{x},\frac{1}{2}+y,\frac{1}{2}-z$	3·079
N(8)	O(4)	$x,\frac{1}{2}-y,\frac{1}{2}+z$	3·145
O(4)	O(4)	$\bar{x},\bar{y},\bar{z}+(1,1,0)$	3·233

In addition to the least-squares refinement program referred to previously the following computer programs were used in this analysis: IBM 7070 programs for data processing (McMullan, 1964), Fourier syntheses (Chu & McMullan, 1962), structure factors (Shiono, 1962) and IBM 1620 programs for the direct method of sign determination (Beurskens, 1963) and for the calculation of inter and intra-molecular geometry (Chu, 1963).

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References

BERGHUIS, J., HAANAPPEL, IJ. M., POTTERS, M., LOOPSTRA, B. O., MACGILLAVRY, C. H. & VEENENDAAL, A. L. (1955). *Acta Cryst.* **8**, 478.
BEURSKENS, P. T. (1963). Technical Report October 1963, Crystallography Laboratory, University of Pittsburgh.
BEURSKENS, P. T. (1964). *Acta Cryst.* **17**, 462.
BUSING, W. R., MARTIN, K. O. & LEVY, H. A. (1962). *ORFLS – A Fortran Crystallographic Least Squares Program,* ORNL-TM-305. Oak Ridge National Laboratory, Tennessee.
CARON, A. & DONOHUE, J. (1964). *Acta Cryst.* **17**, 544.
CHU, S. C. (1963). Technical Report No. 45, Crystallography Laboratory, University of Pittsburgh.
CHU, S. C. & MCMULLAN, R. K. (1962). Program No. 377, I.U.Cr. *World List of Crystallographic Computing Programs.*
GROTH, P. (1910). *Chemische Krystallographie.* Vol. 3, p. 583. Leipzig: Engelmann.
HUGHES, E. W. (1941). *J. Amer. Chem. Soc.* **63**, 1737.
LIDE, D. R. (1962). *Tetrahedron,* **17**, 125.
MCMULLAN, R. K. (1964). Unpublished work.
MCWEENY, H. (1951). *Acta Cryst.* **4**, 513.
PULLMAN, B. & PULLMAN, A. (1963). *Quantum Biochemistry.* New York: John Wiley.
ROLLETT, J. S. & SPARKS, R. A. (1960). *Acta Cryst.* **13**, 273.
SCHOMAKER, V., WASER, J., MARSH, R. E. & BERGMAN, G. (1959). *Acta Cryst.* **12**, 600.
SHIONO, R. (1962). Programs Nos. 330, 376, I.U.Cr. *World List of Crystallographic Computing Programs* and Technical Report No. 29, Computation and Data Processing Center and Crystallography Laboratory, University of Pittsburgh.

Acta Cryst. (1965). **19**, 734

A Theory of the Joint Probability Distribution of Complex-Valued Structure Factors

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The joint probability distribution of complex-valued structure factors, which may be used for the statistical determination of the phase angles in non-centrosymmetric crystals, is derived as an extension of our previous theory for real-valued structure factors (Naya, Nitta & Oda, 1964). The probability distribution function is given in a form of an orthogonal series based upon the associated Laguerre polynomials. The application of the theory is also illustrated in some special examples.

Introduction

In a previous paper (Naya, Nitta & Oda, 1964), the present authors dealt with a theory of the joint probability distribution of signs of structure factors which is applicable to centrosymmetric space groups. A theory of the joint probability distribution of complex-valued structure factors for non-centrosymmetric crystals may similarly be formulated and will be useful for statistical determination of the relevant phase angles. Although studies along this line have been published by Bertaut (1956) and Karle & Hauptman (1956), it seems that much is still left open regarding the complex structure factors. In this paper, we extend our theory of the statistical method of the sign determination in real structure factors to the phase angle determination in complex structure factors.

In §1 is introduced a concept of the joint probability distribution of phase angles. In §2 is given a formulation of the joint probability distribution of complex structure factors, from which the explicit expression of the joint probability of phase angles can be derived.