The Crystal and Molecular Structure of Phthalyl-Urea*

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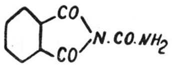
Using the methods of X-ray analysis we have shown that phthalyl-urea has the structure given by the formula (I). Thus we have confirmed the result previously obtained by V. Hahn[1], who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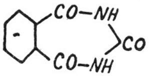
II

used purely chemical methods for the investigation of this structure. The formula (II) quoted usually in chemical literature is therefore inconsistent with the real molecular structure of this compound.

The crystals are monoclinic prismatic. The cell containing four molecules has the dimensions:

$a = 13{\cdot}00$ Å $b = 5{\cdot}21$ Å $c = 12{\cdot}60$ Å $\beta = 98^0$

The space group is $C_{2h}^5 - P2_1/n$.

CRYSTALLOGRAPHIC AND X-RAY DATA

The crystals were grown by slow evaporation from a solution in acetone** and were obtained in the form of monoclinic colourless needles elongated in the direction of the *b* axis, with well developed $\{101\}$ $\{10\bar{1}\}$ and occasionally $\{001\}$ faces. A perfect creavage parallel to the 101) and $10\bar{1}$ was observed. The monoclinic angle as determined optically amounted to $\beta = 98^0$.

The dimensions of the unit cell were obtained by measuring the layer lines of oscillation photographs:

$$a = 13{\cdot}00 \text{ Å} \qquad b = 5{\cdot}21 \text{ Å} \qquad c = 12{\cdot}60 \text{ Å}$$

The density was measured by flotation in a methyl-iodide-benzene mixture and was found to be $1{\cdot}49$ g . cm^{-3}. The density calculated for 4 molecules per unit cell was $1{\cdot}50$ g . cm^{-3}.

The systematic absence of reflexions $0k0$ was for k odd and of reflexions $h0l$ for $h + l$ odd, so that the space group was determined to be $C_{2h}^5 - P2_1/n$.

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** We are indebted to Prof. V. Hahn for supplying the pure material prepared in his laboratory (Organic Chemical Institute, Technical Faculty, University of Zagreb).

All atoms are therefore in general positions and no molecular symmetry is required.

INTENSITY MEASUREMENTS

The h0*l* reflexions (97 in totality) were recorded on oscillation photographs using nickel-filtered copper K-radiation. The photographs were developed in equal standard conditions. The photographic density was determined at the centre of seach spot using a microphotometer and converted into the relative intensity by means of the characteristic curve of the film[2]. The corrections for polarization and Lorentz factors were made in the usual way. No absorption correction was considered necessary. The secondary extinction was not taken into account.

DETERMINATION OF THE APPROXIMATE POSITION OF THE MOLECULES

We started our investigation with the assumption that the real molecular structure was given by formula (I). If that is so the five membered ring together with the carbonyl oxygen atoms would lie in the same plane with the benzene ring. The ureid group would lie out of this plane and could freely rotate about the N-C bond as a rotation axis.

From the value for the period in the *b* axis direction (5·21 Å) and from the value for the diameter of the aromatic carbon atom (3·44 Å) it followed that the molecules had to be inclined to the *B* plane at an angle of about 50°. The Fourier projection along the *b* axis would give therefore the answer to the question which of the two possible structures really occurs. In fact our only aim was to prove this.

It was assumed that the molecules were packed in such a manner that their long axes were nearly parallel to the plane of the projection and that they were rotated about this axis by 50 degrees to the (010) plane. This assumption seemed to us fully justified from the purely geometrical consideration of the packing possibilities. We started with a model based on the known normal bond lengths and intermolecular distances.

The approximate position of the molecules in the projection was obtained by means of Bragg-Lipson charts[3]. It was sufficient to take into account only a few reflexions. From the *F* (103) it followed that the molecules were situated with their long axes in the direction $[10\bar{3}]$, which is also in accordance with the observed cleavage. With the help of the reflexions 103, 200, 10 0 4 and 400, and taking into account the allowed intermolecular approach, our choice of the position was unambigously restricted to only one possibility.

This position was well confirmed by the Patterson synthesis on the (010). A part of this synthesis and the projected molecular model is shown in Fig. 1. It is just the part in the neighbourhood of the origin peak which came out characteristically elongated. This deformation of the origin peak was obviously caused by the maxima belonging to the short interatomic vectors inside the molecule. Unfortunately, these maxima were not resolved and for this reason we received from Patterson projection no more information than from Bragg-Lipson charts.

DETERMINATION OF PHASES AND FOURIER SYNTHESIS

In order to obtain as many reliable values of the atomic coordinates as possible we applied the method of the molecular structure factor devised by Booth[4] for the translatory motion of the whole molecule in the trial and error work. For the computation of the structure amplitudes we used the atomic amplitudes given by Goldschmidt and Llewellyn[5] in their paper on the crystal structure of isatin. After a good agreement had been reached between calculated and observed $|F(h0l)|$ and thus all signs evaluated, we computed the Fourier synthesis on (010) with the use of Beevers-Lipson strips at 6^0 intervals.

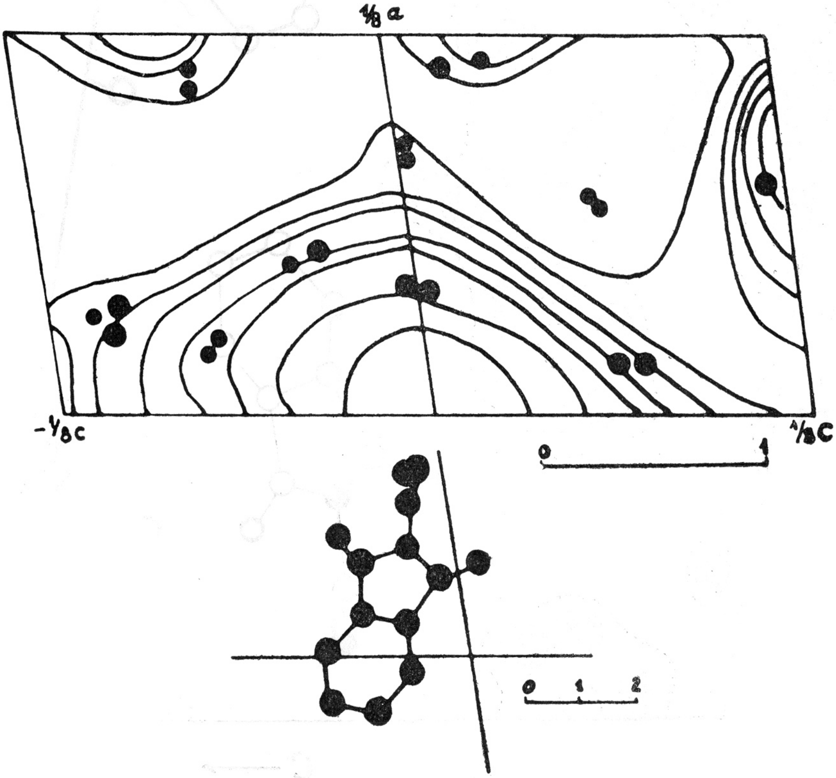


Fig. 1. Patterson projection on (010) plane. Only the part in the neighbourhood of the origin peak is shown. The position and weight of the maxima belonging to the interatomic vectors inside the molecule are indicated by dots. The proper orientation of the molecule is also shown.

Although in this first Fourier synthesis the atomic maxima were badly resolved, our assumption concerning the structure and approximate position of the molecule was confirmed. A large peak which appeared on the side of the five-membered ring showed that there occured an overlapping of the carbonyl oxygen and NH_2 group of the ureid rest. Besides, it followed from the position of this peak that the N-C bond and the long molecular axis did not fall in the same direction. Previously this possibility was not taken into account and for this reason several signs of the structure amplitudes taken into Fourier synthesis were wrong and therefore a bad resolution resulted.

The second synthesis was much better, and in the third one no appreciable change of the coordinate values occured. This third synthesis is shown in Fig. 2. From this synthesis the x, z coordinates were obtained with the help of Booth's table[6] with exception of those for the atoms of the ureide rest. The latter were obtained from the known bond lengths and from the stereochemical relations. We took for C-O and C-N the values 1·38 Å and 1·21 Å respectively and for the angle $\widehat{\mathrm{OCN}}$ 120⁰. It followed that the long axis of the molecule could not be parallel to the (010) plane as it was at first assumed but had to be inclined at an angle of about 3 degrees.

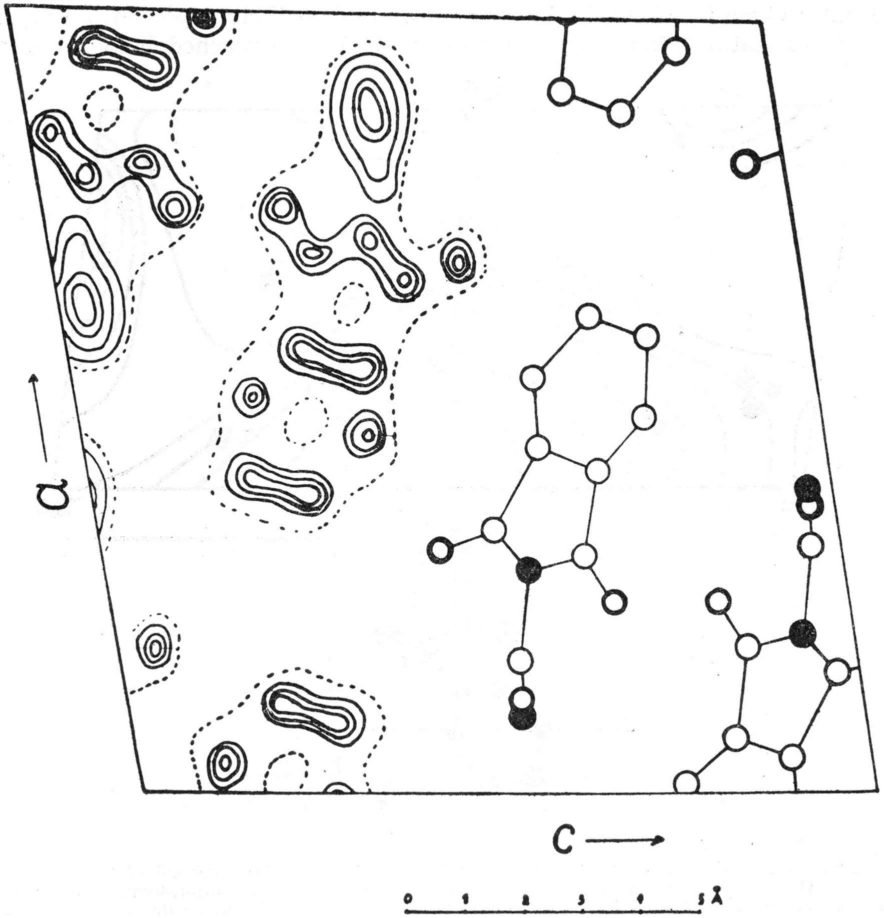


Fig. 2. Fourier projection on (010) plane. Contours are drawn at arbitrary intervals.

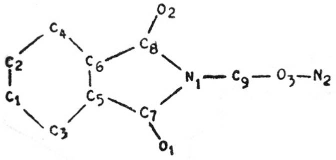
The signs of the structure amplitudes recalculated from this set of parameters remained unchanged. No further refinement of the atomic positions could therefore be obtained with our experimental data.

FINAL PARAMETERS AND DISCUSSION OF THE STRUCTURE

The final x, z parameters are listed in Table 1. With the help of these parameters we calculated the structure amplitudes $F_c(h0l)$. The observed structure amplitudes $F_0(h0l)$ were put on the absolute scale by multiplication with an appropriate factor. This factor amounted to 1·16 and was obtained as the mean value of all ratios between each of the calculated and observed structure amplitudes. The comparison of the observed and calculated structure amplitudes is given in Table 2. The agreement is satisfactory except for a few reflexions, which indicate that our method of the intensity measurement was not fully reliable.

TABLE 1.

Final x, z coordinates



	x	z		x	z
C_1	—0.110	—0·200	C_9	0·340	—0·044
C_2	—0·088	—0·280			
C_3	—0·038	—0·124	O_1	0·188	0·044
C_4	0·005	—0·270	O_2	0·254	—0·188
C_5	0·054	—0·120	O_3	0·400	—0·030
C_6	0·074	—0·200			
C_7	0·154	—0·032	N_1	0·220	—0·080
C_8	0·192	—0·156	N_2	0·405	—0·030

The reliability of the parameter values is usually estimated by means of the »reliability index« R. In the present case we obtained a relativelly high value, i. e. $R = 0{\cdot}30$.

We used also the method described lately by Luzzati[7] but without succes. The values of R' plotted against $\sin\Theta$ were distributed irregularly between the curves for $|\Delta r| = 0{\cdot}07$ Å and $|\Delta r| = 0{\cdot}15$ Å respectively. This behaviour of R' may be explained by assuming that the errors in the determination of the structure amplitudes did not follow the normal distribution law. Besides, it seems that the total number of reflexions is actually too small for such a stastistical treatment.

We calculated also the factor ${}_2R_2$ proposed by Booth[8] and given by the expression

$$ {}_2R_2 = \Sigma(|F_o| - |F_c|)^2/\Sigma|F_o|^2 $$

and obtained the result ${}_2R_2 = 0.069$, which gave for the root mean square error the value $\overline{\delta}_2 = 0{\cdot}06$ Å.

Certain information on the accuracy of the parameters can also be obtained from the fact that the interatomic distances in the projection are those which ought to be expected from the normal bond lengths especially from those in the benzene ring.

As pointed out in the beginning of this paper we undertook this work with the aim of establishing whether the molecule contained a five-or a seven-membered ring. After this problem was succesfully solved we did not continue to determine also the y-coordinates and so complete the structure.

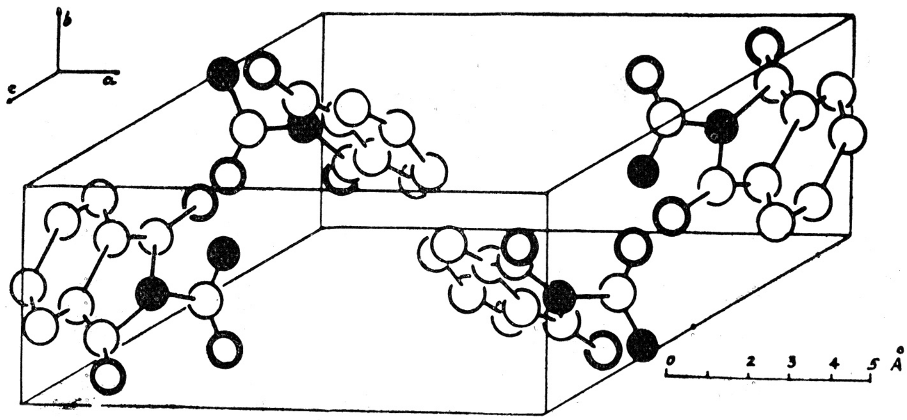


Fig. 3. Perspective representation of the crystal structure of phthalyl-urea.

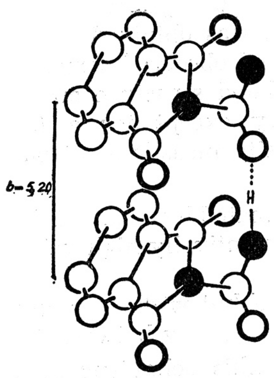


Fig. 4. Arrangement of the molecules along the b-axis direction Hydrogen bond between ureide parts of the molecules is shown.

From the consideratins about the packing of molecules it followed that the molecules related by screw axis symmetry operation are joined by a hydrogen bond in the *b*-axis direction through CO and NH_2 groups of their ureid parts (Fig. 3. and Fig. 4.). The length of the hydrogen bond amounted approximately to 2·82 Å. The growth as well as the other physical properties of the crystals coud be explained by this hydrogen bond.

The authors wish to express their thanks to Prof. V. Hahn for suggesting the problem and to Prof. M. Paić at whose laboratory (Physical Institute, Faculty of Science) the main part of the experimental work was performed.

TABLE 2.

Observed and calculated strukture factors

h0l	F_o	F_c	*h0l*	F_o	F_c
200	6	— 6	$10\bar{1}$	46	—55
400	30	—17	301	23	—29
600	12	—20	$30\bar{1}$	23	+21
800	7	— 6	501	58	+60
10 00	6	+ 6	$50\bar{1}$	40	+22
101	70	+60	701	18	—10

$h0l$	F_o	F_c	$h0l$	F_o	F_c
$70\bar{1}$	25	—16	905	0	+ 3
901	23	—14	$90\bar{5}$	13	—18
$90\bar{1}$	14	—15	$11\,05$	0	— 1
$11\,01$	15	—15	$11\,0\bar{5}$	0	— 2
$11\,0\bar{1}$	0	0	006	13	+15
002	23	+22	206	23	—30
202	29	—30	$20\bar{6}$	12	+15
$20\bar{2}$	23	—20	406	5	+ 1
402	30	—36	$40\bar{6}$	17	—20
$40\bar{2}$	19	—24	606	12	— 4
602	28	+32	$60\bar{6}$	6	— 8
$60\bar{2}$	8	+ 4	806	12	+ 7
802	12	—15	$80\bar{6}$	7	— 7
$80\bar{2}$	7	— 5	$10\,06$	0	— 3
$10\,02$	18	— 8	$10\,0\bar{6}$	0	— 1
$10\,0\bar{2}$	0	+ 2	107	12	+24
103	0	— 6	$10\bar{7}$	4	— 7
$10\bar{3}$	70	—69	307	17	+ 9
303	12	+ 4	$30\bar{7}$	0	— 2
$30\bar{3}$	12	—11	507	6	+10
503	5	+ 8	$50\bar{7}$	9	+13
$50\bar{3}$	23	+26	707	2	— 4
703	5	— 4	$70\bar{7}$	9	+12
$70\bar{3}$	35	+26	907	0	— 2
903	0	+ 4	$90\bar{7}$	6	— 9
$90\bar{3}$	12	+ 8	$11\,07$	12	— 6
$11\,03$	9	— 3	$11\,0\bar{7}$	0	0
$11\,0\bar{3}$	9	0	008	14	—15
004	30	+34	208	5	+ 6
204	46	—34	$20\bar{8}$	37	+39
$20\bar{4}$	35	+56	408	0	— 2
404	40	—38	$40\bar{8}$	5	+ 9
$40\bar{4}$	23	—26	608	5	+ 6
604	4	— 4	$60\bar{8}$	0	+ 2
$60\bar{4}$	8	— 4	808	12	+ 9
804	14	+14	$80\bar{8}$	14	—18
$80\bar{4}$	7	+ 5	$10\,08$	8	+ 4
$10\,04$	23	+26	$10\,0\bar{8}$	0	+ 4
$10\,0\bar{4}$	6	— 7	109	5	— 1
105	12	—15	$10\bar{9}$	7	— 2
$10\bar{5}$	30	+32	309	17	+22
305	21	+12	$30\bar{9}$	9	—12
$30\bar{5}$	47	—48	509	23	—26
505	5	— 8	$50\bar{9}$	12	+ 8
$50\bar{5}$	12	+ 4	709	6	— 4
705	12	+ 1	$70\bar{9}$	0	+ 2
$70\bar{5}$	2	+ 5	909	0	— 2

$h0l$	F_o	F_c	$h0l$	F_o	F_c
90$\bar{9}$	0	— 2	80 10	0	+ 2
00 10	3	— 2	80 $\overline{10}$	0	+ 1
20 10	12	— 2	10 11	0	+ 4
20 $\overline{10}$	12	+13	10 $\overline{11}$	0	— 2
40 10	12	+ 6	30 11	0	+ 1
40 $\overline{10}$	0	+ 1	30 $\overline{11}$	12	+ 8
60 10	12	—18	50 11	5	— 6
60 $\overline{10}$	0	+ 2	50 $\overline{11}$	12	— 8

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8. A. D. Booth, loc. cit., p. 102.

IZVOD

Kristalna i molekularna struktura ftalil-uree

D. Grdenić i A. Bezjak

Pomoću metoda rentgenske strukturne analize ustanovili smo, da ftalil-urea ima strukturu prikazanu formulom (I). Tako smo potvrdili rezultat istraživanja, što ga je dobio V. Hahn,[1] koji je upotrebio posve kemijske metode. U literaturi uobičajena formula (II) ne odgovara prema tome stvarnoj strukturi molekule tog spoja.

Kristali pripadaju monoklinskoj holoedriji. Elementarna ćelija sadržava četiri molekule i ima dimenzije:

$a = 13{,}00$ Å $\quad b = 5{,}21$ Å $\quad c = 12{,}60$ Å $\quad \beta = 98^\circ$

Prostorna grupa je $C_{2h}^{5} — P2_1/n$.

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