furnace, strong evidence would be obtained in favor of the temperature hypothesis. In other words, a point has been reached in the study of SiC growth where experimentation is necessary before further theoretical work seems likely to be beneficial.

Note added in proof, 27 *February* 1952. For each of the five types of SiC described above cell dimensions are given in kX. units to agree with earlier published data which, although reported as Ångström units, were really in kX. units.

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The Crystal Structure of the Urea–Hydrocarbon Complexes*

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The structure of the urea–normal hydrocarbon complex has been determined. The unit cell is hexagonal, $a_0 = 8{\cdot}230$, $c_0 = 11{\cdot}005$ Å, space group $C6_12\text{–}D_6^2$, six urea molecules per unit cell. The general features of the structure and the nitrogen positions of the urea were obtained directly from an implication diagram or Patterson–Harker section $P(x, y, \frac{1}{6})$ which, for this space group, is essentially equivalent to an electron-density projection along the c axis. The urea molecules form a hollow channel structure in which the n-hydrocarbon molecules are enclosed. The hydrocarbons are in an extended planar zigzag configuration with their long axis parallel to the c axis. The electron-density projection and the implication diagram indicate that the time average of the positions of the plane of the hydrocarbon molecule are randomly disposed over positions perpendicular to the a axis and at multiples of 60° to this position. Diffuse bands observed in most of the complexes are attributed to the hydrocarbon molecules which behave as a system of linear gratings regularly arrayed in the $x\,y$ plane but with random z coordinates.

Introduction

The formation of crystalline complexes of urea with normal hydrocarbons, fatty acids and other straight-chain molecules was first reported by Bengen. In view of the weak interactions normally expected between hydrocarbons and urea, the formation of stable crystalline complexes of urea and n-hydrocarbons at first appeared somewhat surprising. A general investigation of the field of urea complexes was carried out at these and associated laboratories (Fetterly; Redlich, Gable, Dunlop & Millar, 1950) with the object of securing basic data required for various applications. In the early stages of this work an investigation of the structure of these complexes was therefore undertaken to determine the molecular configuration and its relation to the stability of the complexes. A brief resumé of these results has already appeared (Smith, 1950). Since the completion of most of this work several additional papers (Zimmerschied, Dinerstein, Weitkamp & Marschner, 1949*a*, *b*, 1950; Schlenk, 1949) on these complexes, including a brief account of the structure determination by C. Hermann (Schlenk, 1949), have appeared. Although the preliminary results of Hermann are in general agreement with those reported in this investigation there are differences in several of the bond distances and parameters. The more detailed structure investigation leads to some additional conclusions, including an explanation of the stability of the complex somewhat different from that presented by Schlenk (1949).

Preliminary crystallographic data

Preliminary X-ray examination of a number of urea complexes of n-hydrocarbons of various chain length C_8–C_{50} by the powder method indicated that they all had a similar structure which was different from that of urea. Similar powder patterns were also obtained with urea complexes of various straight-chain alcohols, acids, esters, etc. The n-hexadecane ($C_{16}H_{34}$)–urea complex was selected for detailed structure investigation because of the relative stability of this complex and the availability of reasonably pure n-hexadecane. Single-crystal work was also carried out with the 1,10-dibromodecane–urea complex.

Long needle-like crystals of the hexadecane–urea complex, hexagonal in cross section, form when n-hexadecane is added to a solution of urea in water, methyl or isopropyl alcohol, etc. The single crystals used for the X-ray work were all grown slowly from

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* A preliminary account of this paper was presented at the A.S.X.R.E.D. meeting in Philadelphia, December 1949.

solutions of urea in isopropyl alcohol to eliminate the possibility of the occlusion of solvent molecules such as methanol. The crystals used for the *c*-axis data were 0·24 mm. in cross section and 0·30 mm. in length. Those used for the *a*-axis (hexagonal) and the orthohexagonal *a*-axis data were 0·26×0·36 and 0·24×0·32 mm. respectively. The crystals were aligned from oscillation photographs and complete *c*- and *a*-axis equi-inclination Weissenberg patterns were taken with nickel-filtered Cu $K\alpha$ radiation. Zero-level Weissenberg data around the *a* axis of the orthohexagonal unit cell were also taken.

The unit cell for the complexes is hexagonal

$$a_0 = 8{\cdot}230 \pm 0{\cdot}004 \text{ and } c_0 = 11{\cdot}005 \pm 0{\cdot}005 \text{ Å}.$$

The dimensions of the unit cell were determined from powder data taken with a 57·3 mm. radius camera using quartz as an internal standard. The Weissenberg data showed no systematic extinctions other than $(00.L)$ when L is unequal to a multiple of six. The extinctions and symmetry of the Weissenberg patterns established the space group as $C6_12\text{–}D_6^2$ or its enantiomorph $C6_52\text{–}D_6^3$. There are six urea molecules per unit cell ($c_0 = 11{\cdot}01$ Å). For those hydrocarbons whose chain length is equal to, or very slightly greater than, an integral multiple of the urea spiral repeat (11·01 Å) the *c* axis is a multiple of 11·01 Å; the *c* repeat for the *n*-hexadecane complex is 22·02 Å, for example.

The intensities were mainly estimated visually, using the multiple-film technique (de Lange, Robertson & Woodward, 1939). Some intensities were also measured using a modified Applied Research Co. densitometer. The intensities of the stronger inner reflections were determined from microphotometer traces of powder patterns to eliminate extinction effects. The intensities were corrected (Buerger & Klein, 1945) for appropriate Lorentz and polarization factors and, in the powder and rotation patterns, for the multiplicity factors. Because of the small size of the *n*-hexadecane–urea crystals the absorption corrections were negligible.

Determination of the crystal structure

It was immediately apparent that a channel structure consistent with many of the observed properties of the complexes could be formed by placing the urea molecules at the equivalent positions of space group $C6_12$. The calculated structure factors for the trial structure with the urea molecules in positions consistent with those of space group $C6_12$ with the orientation as shown in *Internationale Tabellen zur Bestimmung von Kristallstrukturen* were not, however, in agreement with observed values. It became apparent from calculations carried out with Bragg–Lipson charts (Bragg & Lipson, 1936) that any arrangement of the ureas consistent with this orientation of the space group would not lead to correct values for the structure factor. More direct methods were therefore tried. Calculations based on a rough provisional channel structure indicated that urea complexes of 1,6-$C_6H_{12}Br_2$ and 1,10-$C_{10}H_{20}Br_2$ would have sufficient electron density at the center of symmetry in projection to make positive all the significant $F(HK.0)$ reflections observable with Cu $K\alpha$ radiation. The dibromo compounds were not immediately available; however, another direct method having some additional advantages is applicable to structures with space group $C6_12$.

Buerger (1946, 1948) has shown that for certain axial symmetries the interpretation of Patterson–Harker diagrams (Patterson, 1935; Harker, 1936) can be simplified by transforming it to an implication diagram. For only four of the space groups, $C6_1$, $C6_5$, $C6_12$ and $C6_52$, the implication diagram is free of ambiguities and satellitic peaks, and is therefore a map of the crystal structure. A Patterson–Harker section $P(x, y, \frac{1}{6})$, which for space group $C6_12$ is equal to the implication diagram, should therefore give a map of the crystal structure projected onto the plane normal to the sixfold axis. As Buerger pointed out, it is thus possible to get what is equivalent to a Fourier projection of the electron density without any knowledge of the phases of the Fourier coefficients.

Since the coefficients of the implication function involve terms in $F^2_{HK.L}$ rather than $F_{HK.0}$ the more intense reflections make a larger relative contribution in the Fourier representation of the implication diagram than in the Fourier representation of the electron density. The relative error caused by neglecting the weaker outer reflections, therefore, will be less in general for the implication diagram than for the

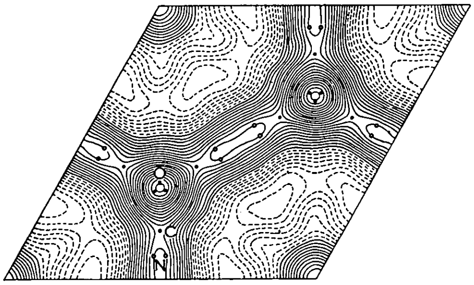

Fig. 1. Patterson–Harker section $P(x, y, \frac{1}{6})$, *n*-hexadecane–urea complex. Positions of the oxygen, nitrogen and carbon atoms in the urea molecules indicated. (Zero–5th level *c*-axis data.)

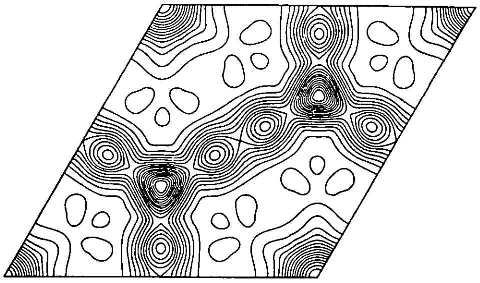

Fig. 2. Fourier projection onto (001) plane of hexagonal unit cell.

corresponding series for the electron density. $P(x, y, \frac{1}{6})$ was computed, therefore, initially using only the 0–5th levels c-axis Weissenberg data. The general features of the structure were readily apparent from the implication diagram $P(x, y, \frac{1}{6})$ (Fig. 1). The final $(HK.0)$ electron-density projection is shown in Fig. 2. for comparison. Although the individual oxygen, nitrogen and carbon atoms of the urea molecules are not resolved, the projection of the interpenetrating urea spirals and of the straight-chain hydrocarbon are apparent. The implication diagram indicates that the hydrocarbons are not freely rotating around their long axis but that the time average of the positions of the plane of the molecule are randomly disposed over positions perpendicular to the a-axis and at multiples of 60° to this position.

By transforming the configuration of equivalent points for the orientation of space group $C6_12$ shown in *Internationale Tabellen* a new configuration was obtained which was consistent with that expected from the implication diagram.

Although the individual nitrogen, oxygen and carbon atoms are not resolved in the implication diagram because of overlapping, one maximum lying alone the twofold axis in the $(\bar{1}2.0)$ plane is resolved (Figs. 1 and 4). Since the C–O axis of the urea molecule must lie along a twofold axis, it was apparent from the implication diagram that this maximum must represent either the oxygen atom or the unresolved nitrogen atoms in projection. The configuration initially tried was that in which the density maximum represented the oxygen position. The intensities for a number of the most important $(HK.0)$ reflections were calculated for various different positions of the nitrogen atoms, consistent with the known bond distances in urea and for small variations of the oxygen positions along the twofold axis. Although fair agreement between calculated and observed intensities could be obtained for most of the reflections calculated for some of the configurations, there were serious discrepancies that could not be removed. None of the configurations of the nitrogen tried gave reasonable van der Waals packing radii for some of the N · · · N distances in adjacent urea molecules and in addition none of the arrangements gave N–H · · · O bonds that were planar with the urea molecules.

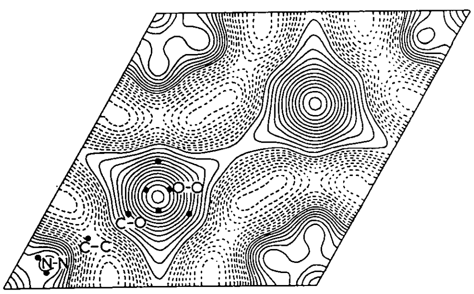

Fig. 3. Patterson–Harker section $P(x, y, \frac{1}{2})$, n-hexadecane–urea complex. Various vector interactions are indicated.

The other configuration in which the resolved maximum was interpreted as unresolved nitrogen atoms was in better agreement with the Patterson–Harker section $P(x, y, \frac{1}{2})$ shown in Fig. 3, in which the various vector interactions for this configuration in relation to the maxima are indicated. Excellent agreement between calculated and observed intensities with no serious discrepancies was also obtained with this configuration. In addition, it gave reasonable N–H · · · O bond distances and angles and normal van der Waals distances.

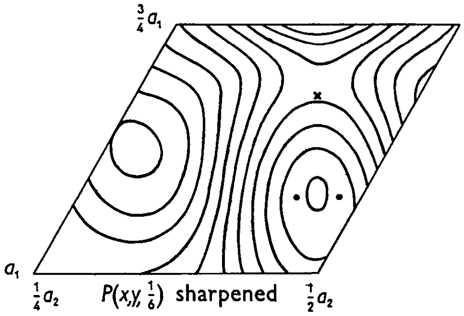

Fig. 4. Patterson–Harker section $P(x, y, \frac{1}{6})$ sharpened. Positions of the nitrogen and carbon atoms of the urea molecule indicated.

The density maxima for the unresolved nitrogen atoms in a Patterson–Harker section $P(x, y, \frac{1}{6})$, calculated with series sharpened in the manner described by Patterson, were much better resolved (Fig. 4). It is interesting to note that the sharpened section using only 0–5th level c-axis Weissenberg data gave better resolution than an unsharpened $P(x, y, \frac{1}{6})$ using the entire data observable with Cu $K\alpha$ radiation. Values for the x, y parameters for the nitrogen atoms quite close to the final ones were obtained directly from the sharpened $P(x, y, \frac{1}{6})$. The parameters were then refined by comparing calculated and observed intensities for the $(HK.0)$ reflections as a function of the parameter values using Bragg & Lipson charts.

The hydrocarbon molecules, as indicated by the implication diagram, were assumed to be at the special positions $(0,0,z)$ in a planar zigzag configuration with the time average direction of the plane of the molecules randomly disposed among the directions perpendicular to the a axis and at multiples of 60° to this direction.

The calculated structure factors for the $(HK.0)$ and $(H0.L)$ reflections were in good agreement with the observed F's.

Disposition of the *n*-hydrocarbons

Samples of 1,10-$C_{10}H_{20}Br_2$ were obtained while the work on the n-hexadecane structure was in progress, and single crystals of its urea-complex were prepared. Rotation and zero-, 1st- and 2nd-level Weissenberg patterns around the a and c axes confirmed the unit cell and space group obtained with the n-hexadecane complex. The lattice constants agreed within the limit of experimental error with those obtained with n-hexadecane–urea complex. There are several features of the diffraction patterns that are of interest. In addition to the normal spot pattern, a series of diffuse bands parallel to the layer lines are present in the rotation pattern around the c axis, and in the a-axis Weissenberg patterns (Figs. 5 and 6). In the decamethylene dibromide–urea complex and most of the other n-hydrocarbon–urea complexes the chain length is not an integral multiple of the urea spiral repeat. This results effectively in a one-dimensional disorder along the c axis and the decamethylene-dibromide (or n-hydrocarbon) molecules behave as a system of linear gratings regularly arrayed in the $x\,y$ plane with random z coordinates. From measurements of the repeat distance of the diffuse bands, the length of the decamethylene dibromide molecule in the complex was computed. The value obtained, 17·6 Å, is in agreement within the limit of experimental error with that calculated for a straight-chain planar zigzag configuration. Somewhat similar diffraction effects have been reported by Powell (1948a).

By comparison of the a-axis zero-level Weissenberg patterns of n-hexadecane and 1,10-dibromodecane–urea complex (Figs. 5(a) and 6) it will be noticed that additional spots with fractional L indices, i.e. (10. $\frac{1}{2}$), (20. $\frac{1}{2}$) etc., are present in the n-hexadecane pattern. These additional spots arise entirely from contributions of the hydrocarbon molecules. The doubling of the c repeat distance in the n-hexadecane complex indicates that the latter hydrocarbon must be slightly shorter in the complex than in the extended planar zigzag configuration. In the latter configuration, assuming the C–C bond to be 1·54 Å, the C–C–C angle to be tetrahedral and the van der Waals radius of the CH_3 group to be 2·0 Å, the chain length is 22·84 Å, which is quite close to twice the c repeat (22·02 Å). A slight deviation from the extended zigzag configuration or a rotation of the end methyl groups could readily account for the observed shortening of the n-hexadecane molecule in the complex.

The occurrence of discrete spots instead of diffuse bands for those reflections arising entirely from the hydrocarbon molecules indicates that the latter are not randomly disposed in respect to their z coordinate. If the hexadecane molecule were randomly arrayed along the z axis, the intersection of the reciprocal lattice with the sphere of reflection would give rise to a series of diffuse bands similar to those observed with the 1,10-dibromodecane–urea complex. Crystals of the n-hexadecane–urea complex used for the structure investigation were grown very slowly. Faint diffuse bands rather than spots were actually observed with one of the less carefully prepared n-hexadecane–urea crystals used in the preliminary work. As an additional confirmation, single crystals of the urea complex of n-dodecane ($C_{12}H_{26}$), whose chain length is unequal to an integral multiple of the urea c repeat, were prepared. The occurrence of diffuse bands rather than spots is readily apparent in the a axis zero-level Weissenberg pattern (Fig. 5(c)). The length of the n-dodecane molecule in the complex was calculated from the diffuse-band repeat. The value obtained (17·6 Å) is in agreement with that calculated (17·83 Å) for the extended zigzag configuration.

Refinement of the structure

The calculated structure factors for the ($HK.0$) and the ($H0.L$) reflections were in such good agreement with the observed F's that it was possible to proceed directly to the refinement of the structure by Fourier synthesis. The projections were computed with International Business Machines (Shaffer, Schoemaker & Pauling, 1946) using the shorter set of punched cards (Schomaker) corresponding to the Beevers–Lipson strips.

In the ($h0l$) orthohexagonal projection (Fig. 7) the C–O axes of the urea molecules No. 2 and No. 5 lie

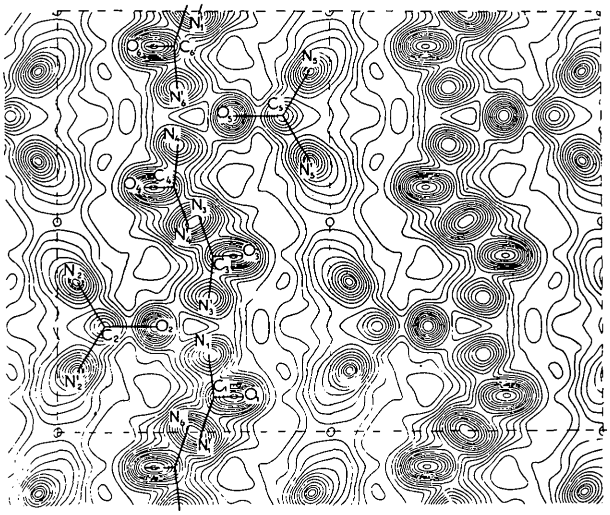

Fig. 7. Fourier projection onto (010) plane of orthohexagonal unit cell (contours at arbitrary intervals).

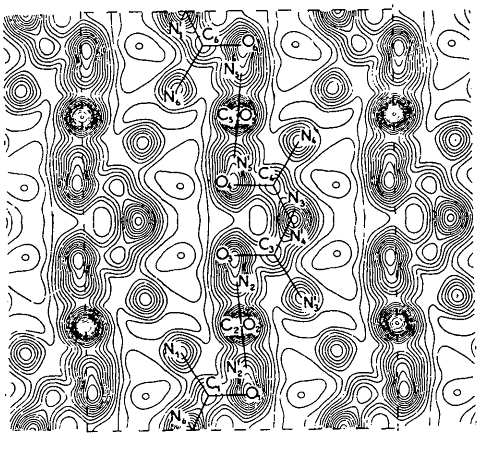

Fig. 8. Fourier projection onto (100) plane of orthohexagonal unit cell (contours at arbitrary intervals).

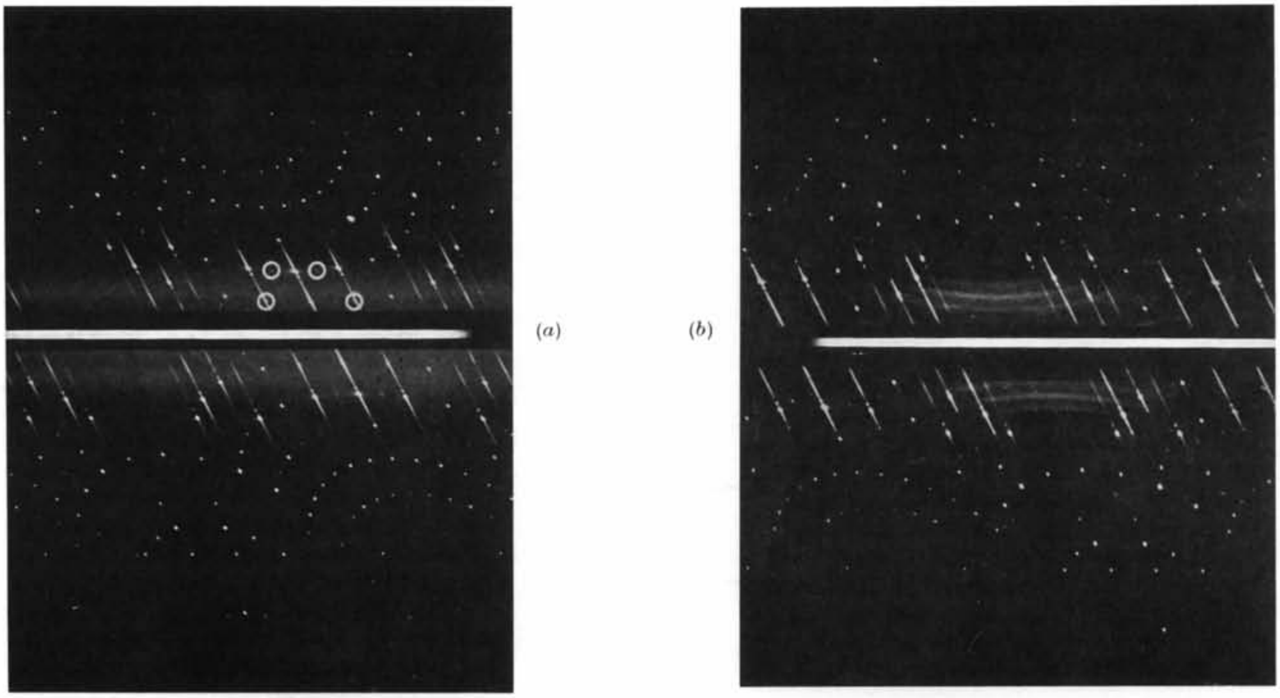

Fig. 5. (*a*) Zero-level *a*-axis Weissenberg pattern *n*-hexadecane–urea complex. Extra spots with fractional *l* indices ($c = 11{\cdot}01$ Å) encircled. (*b*) Zero-level *a*-axis Weissenberg pattern 1,10-dibromodecane–urea complex showing the diffuse bands. (*c*) Zero-level *a*-axis Weissenberg pattern *n*-dodecane–urea complex showing the diffuse bands.

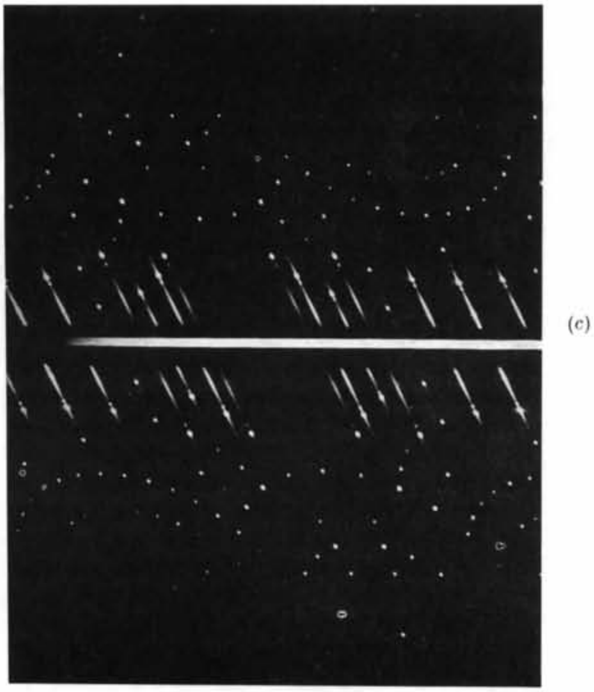

Fig. 5 (*c*).

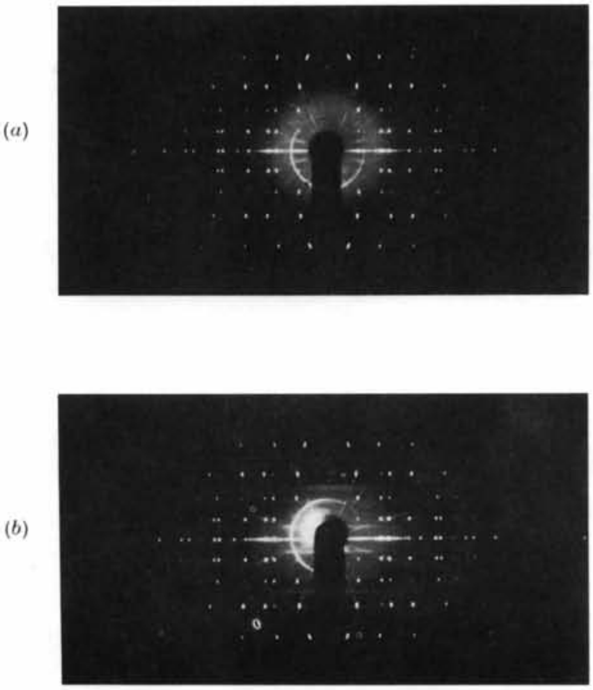

Fig. 6. (*a*) Rotation pattern, *c* axis, *n*-hexadecane–urea complex. (*b*) Rotation pattern, *c* axis, 1,10-dibromodecane–urea complex showing diffuse bands.

in the plane of projection and both atoms are well resolved. The nitrogen atoms of these molecules appear fairly well resolved; however, there is some overlapping with the projection of the hydrocarbons. The projection of the six statistical positions of the hydrocarbon chains is apparent only as a general background which somewhat distorts the N_2 and N_5 atoms. In the calculation of the projection, those terms (L = fraction for c = 11·01 Å) resulting entirely from the contribution of the hydrocarbons were neglected. The nitrogen atoms labeled N_1', N_3' etc. are, however, well resolved. Adjusted parameters for the carbon, oxygen and nitrogen atoms from this projection were then used to compute the signs for the $0kl$) orthohexagonal projection (Fig. 8). The latter projection was used to check the z parameters of the nitrogen atoms and to determine the inclination of the plane of the urea molecules to the c axis more accurately. Final parameters obtained from the Fourier projections are listed in Table 1.

Table 1. *n-Hexadecane–urea complex*

Hexagonal	$a_0 = 8{\cdot}230 \pm 0{\cdot}004$ Å, $c_0 = 11{\cdot}005 \pm 0{\cdot}005$ Å Z = 6 urea
Space Group	$C\,6_1\,2\text{–}D_6^2$
N in (C)	$x, y, \frac{1}{12}+z;\ \bar{y}, \bar{x}, \frac{1}{12}-z;\ x-y, x, \frac{3}{12}+z;$ $x-y, \bar{y}, \frac{3}{12}-z;\ \bar{y}, x-y, \frac{5}{12}+z;$ $x, x-y, \frac{5}{12}-z;\ \bar{x}, \bar{y}, \frac{7}{12}+z;\ y, x, \frac{7}{12}-z;$ $y-x, \bar{x}, \frac{9}{12}+z;\ y-x, y, \frac{9}{12}-z;$ $y, y-x, \frac{11}{12}+z;\ \bar{x}, y-x, \frac{11}{12}-z$
(C) and (O)	$x, \bar{x}, \frac{1}{12};\ 2x, x, \frac{3}{12};\ x, 2x, \frac{5}{12};$ $\bar{x}, x, \frac{7}{12};\ 2\bar{x}, \bar{x}, \frac{9}{12};\ \bar{x}, 2\bar{x}, \frac{11}{12}$ $x=0{\cdot}4415$, $y=0{\cdot}5225$, $z=0{\cdot}1035$ for nitrogen, $x=0{\cdot}3193$ for oxygen, $x=0{\cdot}4094$ for carbon.

The final parameters were then used to calculate the contributions of the urea molecules to the structure factor for comparison with the observed F's. The scattering factors used were taken from the *Internationale Tabellen.*

The contribution of the hydrogen atoms to the structure factor for the hexadecane molecule were included for the ($HK.0$) reflections since they were appreciable for these reflections out to $\sin\theta/\lambda \simeq 0{\cdot}3$. The hydrogen atoms in the urea molecule were also included in the calculation of the final structure factor. The hydrogen atoms were placed midway between the nitrogen and oxygen atoms. A temperature factor of $\exp(-B(\sin\theta/\lambda)^2)$, with $B \simeq 4$ Å^2 for urea and $B \simeq 6$ Å^2 for n-hexadecane, was used for the ($HK.0$) reflections.

The calculated structure factors and observed F's for the ($HK.0$) reflections are shown in Table 2. The percentage discrepancy,

$$100 \sum_{H,K} \big||F_{HK.0,o}| - |F_{HK.0,c}|\big| \div \sum_{H,K} |F_{HK.0,o}|\,, \qquad (1)$$

is 14·6 if the hydrogens are neglected and reduces to 9·7 if they are included.

For the calculation of the contribution of the hydrocarbons to the ($h0l$) orthohexagonal reflections, the six statistically possible positions for the hydrocarbon chain of $2n$ carbon atoms reduce to four in projection. The contribution of the n non-equivalent carbon atoms must be averaged over the $4n$ possible positions. The contributions of the hydrocarbons may be calculated more simply, however, from the Fourier transform (Knott, 1940; Ewald, 1940; Wrinch, 1946) of the n-hexadecane molecule.

Taking the projection of the statistically possible positions of the hydrocarbons shown in Fig. 9(a), and selecting the origin at the center of the molecule, the coordinates for the carbon atoms for the (010) orthohexagonal projection become

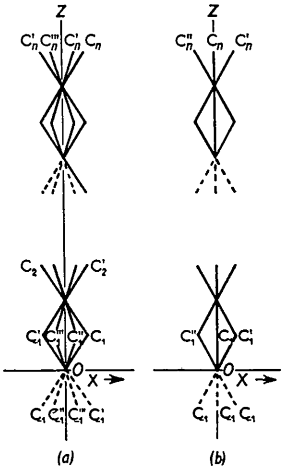

Fig. 9. Projection of statistically possible positions of hydrocarbon chains. (a) Projection along the orthohexagonal b axis. (b) Projection along the orthohexagonal a axis.

$$\begin{aligned} X &= 0{\cdot}444(-1)^{n-1} && \text{for } C_n\,, \\ &= 0{\cdot}444(-1)^{n} && \text{for } C_n'\,, \\ &= 0{\cdot}222(-1)^{n-1} && \text{for } C_n''\,, \\ &= 0{\cdot}222(-1)^{n} && \text{for } C_n'''\,, \\ Z &= 0{\cdot}63(2n-1)\,, \end{aligned}$$

where $2n$ is the number of carbon atoms in the chain.

The Fourier transform for these configurations of the n-hexadecane molecule then becomes

$$T(b_1, b_3) = \frac{f_C \sin 16A}{6 \sin 2A}\,\{\cos(A-B)+\cos(A+B) + 2\cos(A-C) + 2\cos(A+C)\}\,, \qquad (2)$$

where f_C = atomic scattering factor for carbon,

$$A = 2\pi l Z_1 b_3\,, \quad Z_1 = 0{\cdot}69\,,$$
$$B = 2\pi h X_1 b_1\,, \quad X_1 = 0{\cdot}444\,,$$
$$C = 2\pi h X_2 b_1\,, \quad X_2 = 0{\cdot}222\,,$$

and b_1, b_3 are coordinates in reciprocal space.

For the (100) orthohexagonal projection the statistically possible positions of the hydrocarbon chain reduce to three in projection. Taking the origin at the

Table 2. *Structure factors of the* (*HK*.0) *reflections*

HK.0	F_o	F_c	*HK*.0	F_o	F_c	*HK*.0	F_o	F_c
10.0	19·3	−19·8	33.0	21·8	23·4	42.0	3·8	− 2·8
20.0	55·6	57·0	44.0	3·1	3·1	52.0	2·7	2·5
30.0	10·5	9·5	55.0	6·8	4·9	62.0	3·6	− 4·9
40.0	7·4	− 5·1	21.0	15·2	−15·1	72.0	2·3	− 3·7
50.0	2·0	− 2·5	31.0	15·2	16·6	43.0	3·5	− 6·0
60.0	0	− 0·1	41.0	12·2	12·3	53.0	∼ 0	2·9
70.0	1·6	− 2·1	51.0	1·1	3·5	63.0	2·5	2·9
80.0	4·2	− 5·2	61.0	∼ 0	− 0·3	54.0	2·7	− 3·8
11.0	69·3	69·0	71.0	2·4	3·9	64.0	4·2	− 2·9
22.0	34·0	33·5	32.0	11·3	−12·7			

center of the chain, the coordinates of the carbon atoms for the projections of the different configurations indicated by C, C′ and C″ (Fig. 9(*b*)) become

$$\begin{aligned} z &= 0{\cdot}63(2n-1) \quad \text{for} \quad \mathrm{C},\ \mathrm{C}' \text{ and } \mathrm{C}'' , \\ y &= 0{\cdot}000 \quad \text{for} \quad \mathrm{C} , \\ &= 0{\cdot}222(-1)^{n-1} \quad \text{for} \quad \mathrm{C}' , \\ &= 0{\cdot}222(-1)^{n} \quad \text{for} \quad \mathrm{C}'' . \end{aligned}$$

The following expression is then obtained for the Fourier transform:

$$T(b_2, b_3) = \frac{f_{\mathrm{C}} \sin 16A}{3 \sin 2A} \{\cos A + \cos (A-B) + \cos (A+B)\} , \qquad (3)$$

where $A = 2\pi l z b_3, \quad z = 0{\cdot}63$,

and $B = 2\pi k y b_2, \quad y = 0{\cdot}222$,

and b_2, b_3 are coordinates in reciprocal space.

The contributions of the *n*-hexadecane molecule were computed for the (*h*0*l*) and (0*kl*) orthohexagonal reflections using a temperature factor with $B \simeq 6$ Å^2. An anisotropic temperature factor would ordinarily be preferable since the long-chain molecules would be expected to oscillate mainly perpendicular to the long-chain axis. Actually the observed decline in intensity with increasing *l* indices was greater than woulf be expected, presumably because of some disorder along the *Z* axis. This may be due partially to the presence of small amounts of other long-chain hydrocarbon impurities in the *n*-hexadecane. Since the principal peaks in the transform should occur at distances $b_3 = \frac{1}{2}m/z = 0{\cdot}794m$ (where *m* is an integer), it is necessary that $1/c \simeq 0{\cdot}794$ for (00*l*) reflections to be strong. If $m = 1$, $l = 17{\cdot}4$ for $c = 22{\cdot}0$ Å. Therefore the contributions to the (0,0,17) and (0,0,18) reflections should be strong. The (0,0,17) reflection, which arises entirely from the diffraction effects of the *n*-hexadecane molecule, was barely observable, much fainter than the value $F = -3{\cdot}5$ calculated with a temperature factor $B \simeq 6{\cdot}0$ Å. The only other region within the sphere of reflection in which the transform can attain appreciable values is in the neighborhood of $l = 0$; therefore it was only necessary to calculate the contribution for the *n*-hexadecane molecule for those reflections with low *l* indices. In this region of $\sin \theta/\lambda$ the exact value of the temperature factor is relatively unimportant.

The contributions of the hydrogens of the hydrocarbons were included in the calculation of the structure factor for the (*HK*.0) reflections. This was obviously impractical for the (*h*0*l*) and (0*kl*) reflections. Failure to include them for these reflections would not introduce serious errors since their contributions

Table 3. *Structure factors for the h*0*l orthohexagonal reflections*

*h*0*l*	*F* urea	*F* n-$C_{16}H_{34}$	F_c	F_o
100			−19·8	19·3
$10\frac{1}{2}$	0	2·18	2·2	2·3
101	− 3·27	−2·11	− 5·4	3·9
$10\frac{3}{2}$	0	1·7	1·7	1·6
102	−21·3	−1·48	−22·8	19·4
$10\frac{5}{2}$	0	−0·3	− 0·3	0·2
103	36.5	−0·01	36·5	36·1
$10\frac{7}{2}$	0	0·22	0·2	0
104			−19·0	19·1
105			3·1	1·8
106			6·2	5·9
107			1·4	1·0
108			6·8	6.2
109			−15·1	15·3
1,0,10			7·7	7·8
1,0,11			1·5	0·9
1,0,12			− 3·1	3·4
1,0,13			0·3	∼ 0
1,0,14			1·6	1·7
200			55·9	56·9
$20\frac{1}{2}$	0	1·24	1·2	1·9
201	−32·4	−1·24	−33·6	34·7
$20\frac{3}{2}$	0	1·03	1·0	0·4
202	7·69	−0·91	6·8	6·4
$20\frac{5}{2}$	0	−0·20	− 0·2	0
203	−24·7	−0·008	−24·7	27·0
204			3·5	2·9
205			7·9	6·3
206			19·1	20·0
207			− 0·2	0
208			− 0·6	∼ 0·9
209			8·5	8·2
2,0,10			1·6	1·3
2,0,11			3·1	2·8
2,0,12			− 1·2	0·5
2,0,13			− 0·3	∼ 0
2,0,14			0·0	0
300			9·5	10·6
$30\frac{1}{2}$	0	0·60	0·6	0·3
301	− 0·88	−0·60	− 1·5	0·6
$30\frac{3}{2}$	0	0·50	0·5	0·3
302	− 1·56	−0·46	− 2·0	2·0
$30\frac{5}{2}$	0	0·10	0·1	0

Table 3 (*cont.*).

*h*0*l*	F_c	F_o
303	−2·3	2·1
304	−12·3	9·2
305	2·8	2·9
306	−16·4	14·9
307	1·8	0·6
308	−2·3	1·3
309	−9·9	9·1
3,0,10	−0·3	∼ 0
3,0,11	0·9	> 0
3,0,12	2·0	1·7
3,0,13	1·0	1·3
400	−5·1	6·7
40$\frac{1}{2}$	0·3	0·4
401	9·7	8·0
40$\frac{3}{2}$	0·2	0
402	10·2	9·8
40$\frac{5}{2}$	0·1	0
403	5·9	5·3
404	5·4	5·0
405	12·5	9·5
406	8·9	8·0
407	−4·9	3·9
408	−0·4	> 0
409	1·1	> 0
4,0,10	2·3	1·6
4,0,11	0·5	> 0
4,0,12	2·0	2·3
500	−2·5	2·1
501	5·9	5·4
502	−8·3	5·9
503	−11·1	10·4
504	4·2	3·5
505	1·7	0·9
506	−5·1	4·7
507	−1·0	0·8
508	−1·2	1·0
509	−1·7	0·6
600	−0·1	∼ 0
601	−7·2	4·3
602	3·2	1·4
603	3·3	2·9
604	7·0	6·5
605	−0·2	1·0
606	−4·0	3·4
607	2·6	3·4
608	2·3	1·1
609	1·6	0·5
700	−2·1	1·6
701	1·8	1·0
702	0·3	1·1
703	1·2	1·4
704	−1·2	0·7
705	−2·2	1·9
706	−1·2	0·8
707	−1·0	0·7
708	−3·7	2·7
709	−2·3	0·7
800	−5·2	4·2
801	2·7	1·8
802	1·3	> 0
803	2·7	0·9
804	2·5	1·1
805	0·4	0·6
806	0·4	0·4
807	0	0
006	−7·6	6·6
0,0,12	7·0	8·4

Table 4. *Structure factors for the* (0*kl*) *orthohexagonal reflections*

0*kl*	F urea	F n-$C_{16}H_{34}$	F_c complex	F_o
020			75·5	76·0
040			38·4	35·6
060			29·9	26·1
080			3·2	3·2
0,10,0			5·6	5·6
02$\frac{1}{2}$	0	1·5	1·5	1·9
021	25·5	−1·6	24·0	21·5
02$\frac{3}{2}$	0	1·3	1·3	> 0
022	11·9	−1·1	10·8	11·4
02$\frac{5}{2}$	0	−0·3	−0·3	∼ 0
023	−4·1	−0·0	−4·1	6·2
024	−13·8	−0·3	−14·0	15·7
025	9·3	−0·4	8·9	7·0
026			22·7	24·5
027			2·2	1·9
028			6·7	5·7
029			0·7	∼ 0
0,2,10			6·7	7·1
0,2,11			3·6	4·0
0,2,12			4·6	5·6
04$\frac{1}{2}$	0	0·6	0·6	> 0
041	−22·6	−0·6	−23·2	23·6
04$\frac{3}{2}$	0	0·5	0·5	> 0
042	16·8	−0·5	16·3	14·8
043		−0·0	−3·7	3·5
044		−0·1	−1·0	1·4
045	8·8		8·8	7·9
046	3·9		3·9	3·8
047	1·7		1·7	1·5
048	3·9		3·9	2·5
049	1·0		1·0	∼ 0
0,4,10	4·5		4·5	3·9
0,4,11	2·1		2·1	2·0
0,4,12	2·1		2·1	2·7
061	−5·7	−0·2	−5·9	7·4
062	2·1	−0·1	2·0	1·7
063	0·6	−0·0	0·6	∼ 0
064	4·1	−0·0	4·1	3·5
065	11·5	−0·0	11·5	9·8
066	0·3		0·3	∼ 0
067	−2·4		−2·4	2·4
068	3·3		3·3	2·5
069	0·2		0·2	∼ 0
0,6,10	1·9		1·9	0·7
0,6,11	0·1		0·1	∼ 0
081	−4·0		−4·0	2·7
082	2·4		2·4	∼ 0
083	−4·5		−4·5	2·3
084	−2·5		−2·5	1·2
085	2·7		2·7	2·9
086	6·4		6·4	5·8
087	−1·6		−1·6	2·4
088	1·5		1·5	1·0
089	0·9		0·9	0·5
0,10,1			2·9	1·2
0,10,2			1·6	0·9
0,10,3			0·4	∼ 0
0,10,4			0·6	∼ 0
006			8·3	7·7
0,0,12			7·0	10·2

would tend partially to cancel out. A modified structure factor (Hughes & Moore, 1949) was used, however, to correct for the effects of the hydrogens. The scattering power of carbon plus the difference between scattering power of O and O^{--} was taken for the scattering power of the CH_2 group. The use of the modified structure factor improved the agreement between the calculated and observed reflections. The F values calculated from the final parameters in Table 1, including the contribution from the n-hexadecane molecule, are given along with the observed F's in Tables 3 and 4. The percentage discrepencies for the $(h0l)$ and $(0kl)$ reflections are 12·8 and 14·8 respectively.

The F's for a number of $(h0l)$ reflections to which only the hydrocarbon molecules contribute were also calculated for a freely rotating hydrocarbon chain. A more general expression than that given by Bijvoet & Ketelaar (1932) for a free rotator can be derived for a rotating chain molecule. The assumption is made that there is no strict phase relationship between the rotating molecules in neighboring cells. For the $(h0l)$ reflections the following expression is obtained:

$$F_{h0l} = \left\{\frac{f_{\mathrm{C}}}{2\pi} J_0\left(2\pi r_{\mathrm{C}} \frac{h}{a} A\right) + \frac{f_{\mathrm{H}}}{\pi} J_0\left(2\pi r_{\mathrm{H}} \frac{h}{a} A\right)\right\} \sum_{n=1}^{n} \cos\left(2\pi \frac{l}{c} z_n A\right),$$

where

$$A = \frac{\left(\frac{4}{3}\frac{h^2}{a^2} + \frac{l^2}{c^2}\right)^{\frac{1}{2}}}{\left(\frac{h^2}{a^2} + \frac{l^2}{c^2}\right)^{\frac{1}{2}}},$$

$z_n = z$ coordinates of C and H atoms,

r_{C} and r_{H} = radius of rotation of C and H atoms respectively.

The calculated results are listed in Table 5.

Table 5. *Comparison of structure factors for freely rotating and randomly disposed hydrocarbon chains; $(h0l)$ orthogonal reflections*

$h0l$	F_r	F_d	F_o
$10\frac{1}{2}$	1·84	2·18	2·3
$10\frac{3}{2}$	0·88	1·7	1·6
$10\frac{5}{2}$	0·28	0·30	0·2
$10\frac{7}{2}$	0·20	0·22	0
$20\frac{1}{2}$	0·94	1·24	1·9
$20\frac{3}{2}$	0·92	1·03	0·4
$20\frac{5}{2}$	0·46	−0·20	0
$30\frac{1}{2}$	0·48	0·60	0·30
$30\frac{3}{2}$	0·28	0·50	0·30
$30\frac{5}{2}$	0·16	0·10	0
$40\frac{1}{2}$	0·31	0·3	0·4
$40\frac{3}{2}$	0·22	0·21	0
$40\frac{5}{2}$	0·00	0·10	0

F_r = Structure factors for rotating model.

F_d = Structure factors for randomly disposed chains at 60° positions.

The agreement between calculated and observed F's appears to be slightly better for the random positions; however, in view of the assumptions made in the calculations, it is probably not possible on the basis of these data alone to decide between the two models. The electron-density projections and implication diagrams, however, favor the statistical configuration.

Description of the structure

The structure of the complex is illustrated in Fig. 10 and the packing arrangement looking along the c axis in Fig. 11, in which the van der Waals packing radii are indicated. In text figures the atoms belonging to a given molecule are indicated by subscripts. The dimensions of the channel formed by the urea are such that it will just accommodate the planar zigzag hydrocarbon molecule. The plane passing through both nitrogen atoms of a given urea molecule is almost parallel to the c axis (see Figs. (8) and 10(b)). The arrangement of the hydrogen bonds, which are indicated by broken lines, is shown in Fig. 10.

In Fig. 10(a), for simplicity only the hydrogen bonds from the nitrogen of the urea molecule indicated with subscript 4 are indicated. Each oxygen is hydrogen bonded to four nitrogen atoms and each nitrogen to two oxygen atoms. The hydrogen bonds, which are essentially coplanar with the urea molecules to which the nitrogens are attached, are of two types. The shorter bonds indicated by $N_4\text{–}H\cdots O_5$ and $N_4'\text{–}H\cdots O_3$ are about 2·93 Å in length. The longer bonds, illustrated by $N_4\text{–}H\cdots O_6$ and $N_4'\text{–}H\cdots O_2$, are about 3·04 Å. The C–N–H $\cdots$ O bond angles are about 136° and 116° respectively for the strong and weak bonds. The agreement between the calculated and observed F's would indicate that the probable error of a bond length is not greater than about 0·02 Å.

The bond distances and intermolecular contacts, including hydrogen bonds, for the urea–hydrocarbon complex and for tetragonal urea (Wyckoff & Corey, 1934) are given in Table 6.

Table 6. *Interatomic distances*

Urea–hydrocarbon complex		Tetragonal urea	
C–O	1·28 Å	C–O	1·25 Å
C–N	1·33	C–N	1·37
$N_1\ldots N_1$	2·30	N...N	2·31
$N_1\ldots N_3$	3·55		
$N_1\text{–}H\ldots O_2$	2·93	N–H...O	2·98
$N_1\text{–}H\ldots O_3$	3·04	N–H...O	3·03

The shorter N–H $\cdots$ O bonds in the complex and in the tetragonal urea, 2·93 and 2·98–2·99 Å respectively, probably differ by somewhat more than the probable error in the two structure determinations. The difference in the C–N distances 1·33 and 1·37 Å and the C–O distances 1·28 and 1·25 Å in the complex and in urea respectively, although probably within

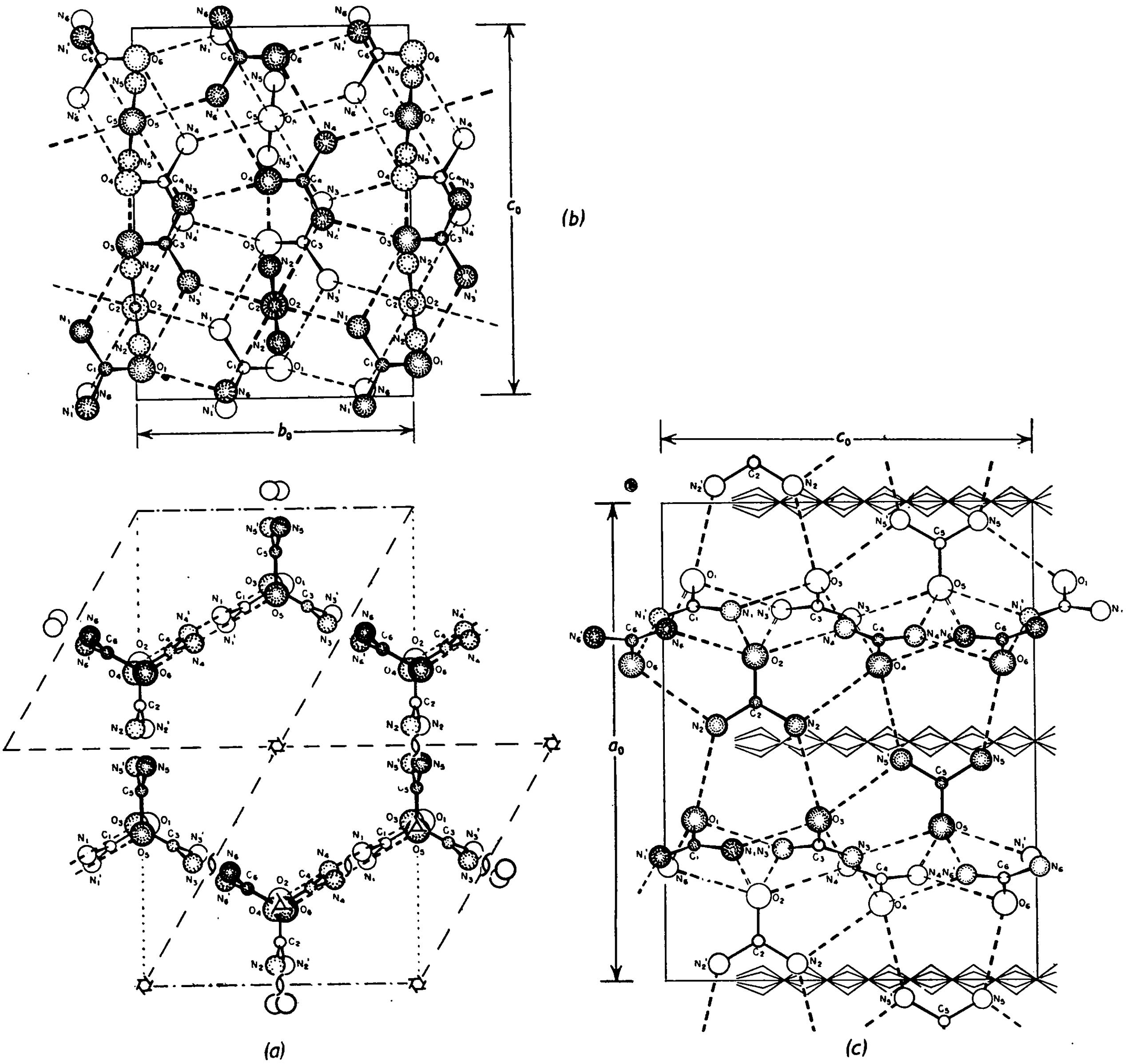

Fig. 10. (*a*) View of the *n*-hexadecane–urea structure along the *c* axis. Hydrogen bonds between nitrogen of urea molecules with subscript 4 are indicated by broken lines. The hexagonal and orthohexagonal unit cells are outlined by broken and dotted lines respectively. (*b*) Projection of structure along the orthohexagonal *a* axis, illustrating hydrogen bonding. (*c*) Projection of structure along the orthohexagonal *b* axis. The hydrogen bonds are indicated by heavy broken lines. The light double lines indicate hydrogen bonds connecting atoms directly below those shown in the figure. The projection of the statistically possible positions of the hydrocarbon chain are also indicated.

the combined error of the two structure determinations, are both in the right direction expected for the increased stabilization of the ionic form as indicated by a shorter N–H · · · O bond. The C–N–H · · · O bond angles, 116° and 136°, are somewhat closer to 120° than those in tetragonal urea, 99° and 128°. This also suggests that the configuration in the complex may be more favorable for the formation of shorter hydrogen bonds than that in the tetragonal structure.

The hydrogen bonds between the hydrogen of the NH_2 group and the oxygen of the adjacent urea molecules account largely for the stability of the complex. The van der Waals forces or polarization interactions between the oxygen of the urea and the carbon and hydrogen of the hydrocarbon, although small for each atom pair, undoubtedly contribute to the stability of the structure because of the large number of interactions involved. The latter forces probably account for the tendency of the hydrocarbon to take the statistically preferred positions indicated by the implication diagram and the ($hk0$) electron-density projection. It is, however, unnecessary to

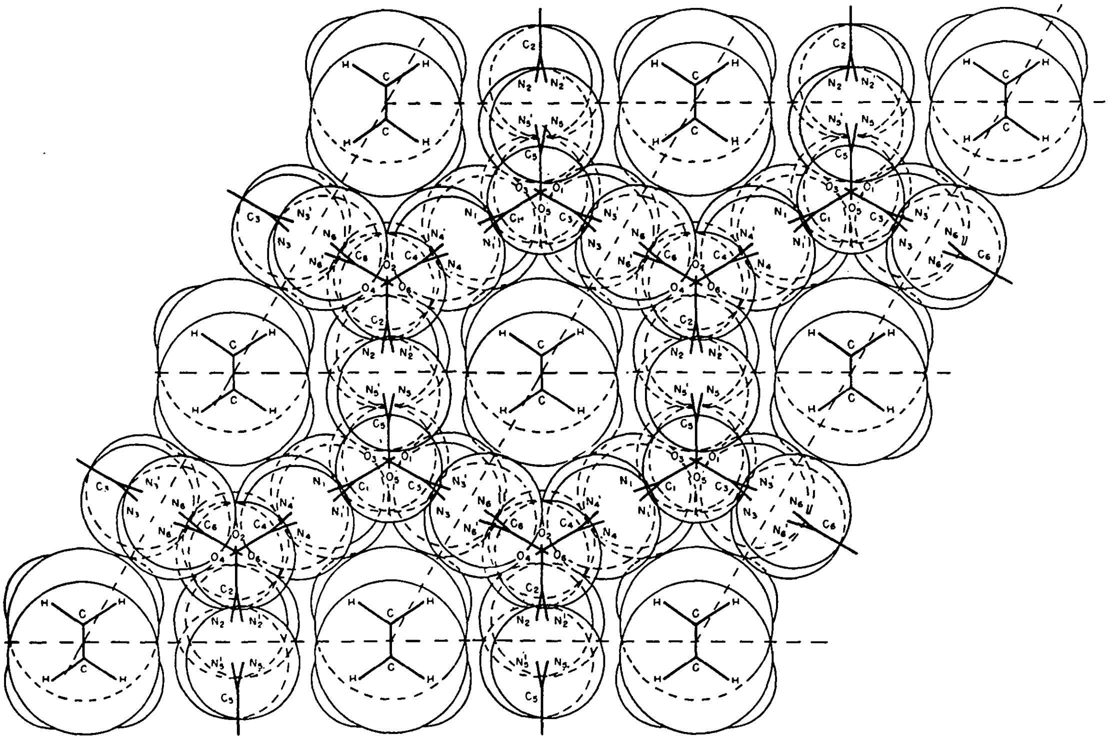

Fig. 11. View of the structure along the *c* axis showing packing arrangement.

assume any unusually strong interaction between the hydrocarbons and the urea such as that indicated by Schlenk (1949) ($\sim$ 2800 cal. per CH_2 group) to explain the stability of the structure.

The stability of the complex involves (1) hydrogen bonding between adjacent urea molecules, and (2) van der Waals forces between urea molecules themselves and between urea and hydrocarbon. The heat of formation of the complex from solid urea and solid hydrocarbon involves (1) differences in hydrogen bond energy between those in urea and those in the complex, and (2) differences in the sum of the van der Waals forces in the tetragonal urea plus those of the solid hydrocarbon and those in the complex. Taking the thermal data of Redlich *et al.* (1950) and of Zimmerschied *et al.* (1949*a*, *b*, 1950), namely, $\Delta H =$ 20·5–22·8 kcal/mol *n*-hexadecane for the process

$$\text{Complex } (s) = \text{urea } (s) + \text{hydrocarbon } (1)\,,$$

and subtracting the heat of fusion of *n*-hexadecane, we obtain $\Delta H = 8{\cdot}28$–$10{\cdot}6$ kcal/mol of hexadecane or 0·69–0·85 kcal/mol of urea for the same process, with all the materials in the solid state. A comparison of the materials in the solid state is preferable because of the similarity in the configuration of the *n*-hexadecane molecule in the complex and in the solid hydrocarbon.

The energy associated with the observed shortening of the hydrogen bonds in the complex compared with those of the tetragonal urea is of the order of magnitude of that required to explain the observed heat of formation. Another factor that may contribute to the stability of the complex is that the van der Waals forces in the tetragonal urea (Wyckoff & Corey, 1934) may be less than normal because of the relatively open structure (Fig. 12), while those in the complex would appear to be about normal (Pauling, private communication). This is also indicated by the volume occupied in the complex by 12 urea and one *n*-hexadecane molecules, 1290·5 Å^3, compared to that occupied by the same number of ureas in tetragonal urea and one molecule in the solid hydrocarbon, $911{\cdot}6 + 410{\cdot}6 = 1322{\cdot}2$ Å^3. (The lattice constants of tetragonal urea were taken as $a_0 = 5{\cdot}67$, $c_0 = 4{\cdot}726$ Å and the hydrocarbons were assumed to be in the orthorhombic form $a_0 = 7{\cdot}48$, $b_0 = 4{\cdot}99$ and $c_0 =$

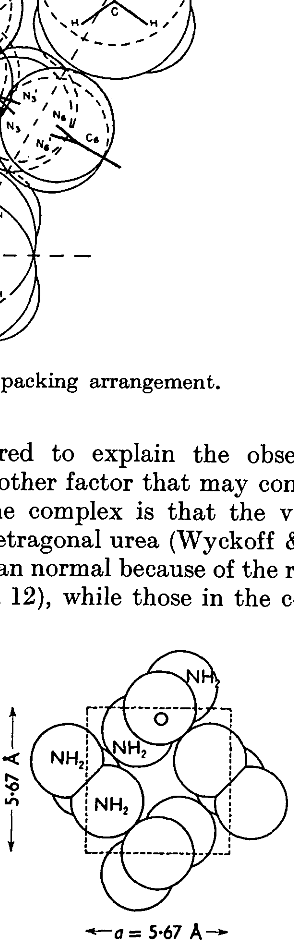

Fig. 12. Tetragonal urea structure.

22·84 Å.) Although the difference in the van der Waals forces would be difficult to estimate, a rough approximation of the energy associated with the shortening of an N–H · · · O hydrogen bond can be made by comparing known hydrogen-bond distances as a function of known bond energies. Data of this type are not available for N–H · · · O bonds, but they are available (Pauling) for O–H · · · O bonds. These data give a value of $\Delta H \simeq 0{\cdot}3$ kcal/mol for a change in bond distance $\Delta\delta$ of 0·01 Å. Taking the observed value of $\Delta\delta = 0{\cdot}05$ Å, one obtains a ΔH (shortening) $\sim$ 3.0 kcal/mol urea. This value would be much too high because of the greater strength of the O–H · · · O bond compared with that of the N–H · · · O bond; however it is an indication of the order of magnitude of the energy available.

Additional evidence that there is no unusually strong interaction between the hydrocarbon and the urea is given by the intermolecular distances. The closest possible approach between a carbon atom of the hydrocarbon and an oxygen atom of the urea, assuming both have the same z coordinate, is $\simeq 4{\cdot}1$ Å, which is as large as or larger than normal van der Waals distances for these atoms.

The urea–hydrocarbon complexes are similar in some respects to the interesting series of molecular complexes investigated by Powell and coworkers (Powell, 1948*b*, 1950*a*, *b*, *c*; Palin & Powell, 1947). In these molecular complexes or clathrate compounds one of the components is trapped in a cavity by cage-forming molecules. The formation of cage structures in general requires strong interactions between neighboring extended groups of atoms or molecules of the same type so that stable configurations can form having an open structure large enough for the inclusion of a molecule of a different type. There is in general no strong interaction between the trapped and the cage-forming molecules, clathrates between quinol and argon, krypton and xenon having been recently formed (Powell, 1950*a*, *b*, *c*). The urea–hydrocarbon complexes resemble the clathrate compounds in that the presence of the long-chain molecule induces the urea to take a configuration different from that of the normal urea structure.

Channel structures somewhat similar in some respects to the urea–hydrocarbon complexes form between amylose and fatty acids (Mikus, Hixon & Rundle, 1946) and between the latter and choleic acid (Go & Kratky, 1934). In the choleic acid complexes the two components are always present in a simple molecular ratio. Unlike the choleic acid complexes or the clathrate compounds of quinol, the urea–hydrocarbon complexes do not approach any simple molecular composition, except possibly in the case of those complexes containing chains of effective length equal to a multiple of the urea c repeat. The composition of the complexes as a function of chain length of the n-hydrocarbons can be calculated directly from the crystal structure. Taking the C–C bond distance = 1·54 Å, the C–C–C bond angle = 109° 28′ and the van der Waals radius of a CH_3 group = 2·0 Å, the length of a hydrocarbon in the extended zigzag configuration is given approximately by

$$l = 1{\cdot}256(n-1)+4{\cdot}0 \text{ Å}\,, \qquad (4)$$

where n is the number of carbon atoms in the straight chain. This expression would hold exactly only for n odd since for n even the maximum length is slightly inclined to the axis passing through alternate carbon atoms. For $n \geq 6$ the difference is quite small, less than the accuracy with which the van der Waals radii are known. From the c repeat distance (11·01 Å), the number of ureas per unit cell and the above expression for the length of a n-hydrocarbon molecule, it follows that the urea/hydrocarbon ratio is given by

$$0{\cdot}6848(n-1)+2{\cdot}181\,. \qquad (5)$$

The calculated curve for the urea/hydrocarbon ratio as a function of the number of carbon atoms is shown in Fig. 13.

Values subsequently measured were in good agreement with the theoretical values. The agreement between the calculated and observed compositions is additional evidence that the hydrocarbons are in the extended state and that the ends of successive hydrocarbon molecules are in normal van der Waals contact. The 2·4 Å holes between the ends of successive hydrocarbon molecules found by Schlenk (1949) arise because of an error in the calculation of the chain lengths, presumably by using an incorrect van der Waals radius for the CH_3 groups. His data for the compositions are in excellent agreement with the values calculated from equation (5) (see Fig. 13). It is of interest that all the observed values (Zimmerschied *et al.*, 1950; Schlenk, 1949; Redlich *et al.*, 1950) for the urea/hydrocarbon ratio for the n-hexadecane complex are lower than that calculated for an extended chain. The values found by Redlich *et al.* (1950) and Schlenk (1949), 11·95 and 12·0 respectively, are in agreement with the value 12·00 expected if the chains were shortened

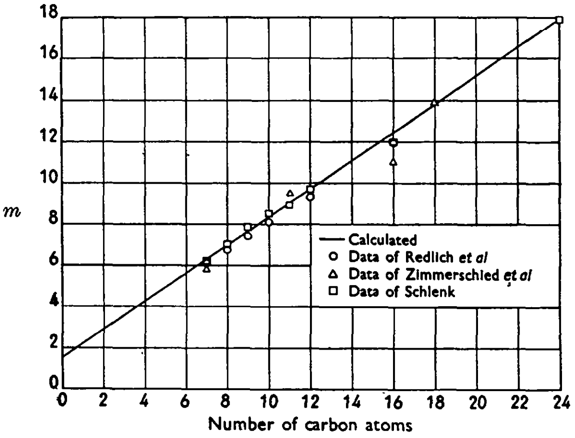

Fig. 13. Molal ratio m(urea/hydrocarbon) of n-paraffins.

in this complex to exactly twice the urea *c* repeat.

The formation of similar urea complexes with *n*-hydrocarbons of different length and with various *n*-alcohols, acids, esters, etc. is readily understandable from the crystal structure. From the dimensions of the channel and from known bond distances, bond angles and van der Waals radii, it was possible to predict in most cases whether or not substituted aliphatic chains would form complexes with urea, and to place the complexes in approximate order of stability.

The cleavage properties of the urea–hydrocarbon complex are satisfactorily accounted for by the structure of the complex. The crystals cleave quite readily along the *a c* plane but fracture if attempts are made to cleave them along the 001 plane or along other directions. It is apparent from Figs. 10(*a*) and 11 that the *a c* plane does not pass through any urea molecule, and cleavage along this direction involves only the breaking of four hydrogen bonds per unit cell.

Although the complexes of urea and various long-chain molecules all have the same hexagonal crystal structure, urea also forms molecular complexes with entirely different structures. The complex of urea and hydrogen peroxide (Tanatar, 1906; Lu, Hughes & Ginguere, 1941), $CO(NH_2)_2 . H_2O_2$, and that of urea–oxalic acid (Sturdivant, Schuch & Merrit, 1950) both have orthorhombic structures. Lutidine (2,6-dimethyl pyridine) (Riethof) and dioxane (Fetterly; Redlich, 1950) form complexes with urea, the latter forming complexes with molal ratios of urea/dioxane of 1:1 and 2:1 (Redlich *et al.*, 1950). Single-crystal rotation patterns of the lutidine and dioxane urea complexes showed, as would be expected, that they have structures entirely different from that of the urea–hydrocarbon complexes. A number of other urea complexes having structures different from that of the urea–hydrocarbon complexes are reported (Schlenk, 1949) to form with ω, ω'-dihalogenated hydrocarbons of short chain length $\sim$ 2–6 carbon atoms.

These crystals differ from the hexagonal complexes in that formation of hydrogen bonds between molecules of both components of the complex is largely responsible for their formation and stability.

The author takes this opportunity of expressing his appreciation to the late Dr O. Beeck for his continued interest and encouragement throughout the course of this work. He also wishes to express his thanks to Drs L. Fetterly, A. Schaerer and particularly to Dr O. Redlich for many helpful discussions. The author is also indebted to Mrs H. P. Stewart and Miss L. Skinner for aid with some of the calculations and to Mr W. Olds and Mr J. Johnson of Shell Oil Company for their assistance in wiring the plug board and for the use of the I.B.M. Tabulator.

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