

# Crystal Structure Analysis for Undergraduates

In the University of London, experimental and theoretical courses in structural crystallography are given at two levels. There are various day and evening graduate courses intended for specialists, two of which are complete two-year intercollegiate courses covering every aspect of modern crystallography. One of these, based on Birkbeck College, has a physical-chemical slant; the other, at the Battersea College of Technology, a metallurgical bias.

The various component Colleges of the University also teach chemical crystallography to their chemistry undergraduates, but usually only in the form of lecture courses. At University College, however, the undergraduates themselves asked for a practical course; and the following article gives an account of such a 25-hour course which has now run annually for over ten years. The aim of the exercise is to make chemistry students appreciate the fundamental theory basic to diffraction analyses of atomic or molecular crystal structures, to realize the potentialities of various techniques and to form a personal judgment of their accuracy; it also gives students the chance of handling crystallographic equipment.

## Preliminary Lecture Course

The practical course is preceded by a few lectures in which the structures of simple atomic and ionic crystals are described systematically and their chemical relevance discussed; the Bragg relation is derived and applied to the various types of diffraction pattern; and the use of diffraction techniques (X-ray, electron, neutron) for identification and chemical analysis is demonstrated by examples. The students are also taught the elements of symmetry, space-group theory, and nomenclature (*4a*), and are shown how the diffraction spectra are dependent upon the distribution of scattering matter. They learn how the simplest types of structure are deduced:

when there are no variable parameters. (All atoms are in special positions.)

when there is only one variable parameter (or a few).

when the attainment of a preliminary structure, suitable for refinement by computer, depends upon the use of modern techniques of phase determination.

## The Experiments

Usually the students work in pairs, 3 or 4 pairs being in the laboratory at any time and each student spending 5 hours a day for five consecutive days on the practical course. The whole class is first shown all the equipment in the laboratory, including some that they will not actually use (such as a crystal-sphere-grinding apparatus, low-temperature and multiple-exposure

photogoniometers, Geiger-counter diffractometers, apparatus for measuring magnetic susceptibilities, etc.) and are told something of the various research problems in progress. They are shown an X-ray tube in pieces and are given special instructions about safety precautions and the importance of avoiding X-ray exposure of any part of the body and especially the fingers. The apparatus is, of course, made as foolproof and accident-proof as possible, but it is nevertheless regarded as very important that students should know what precautions have been taken and the reasons for each of them.

The problems undertaken, in alternate years, are the determination of the structures of urea and hexamethylene tetramine. The students begin with the crystals (dimensions about 0.5 mm each way) and end with a Fourier electron-density map from which the stereochemistry can be seen at a glance and the interatomic distances and angles measured with an accuracy of about 5%. In the case of (tetragonal) urea, half the class determine the projection along the *c* axis [001], the other half that along the *a* axis [100], so that by comparing notes they have the full geometry of the structure (see Figs. 6, 7). In the case of hexamethylene tetramine,  $C_6H_{12}N_4$ , all the class determine a cube-axis projection (see Fig. 9).

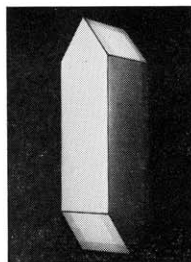


Figure 1. Cardboard model showing idealized shape of urea crystal, symmetry  $42m$ .

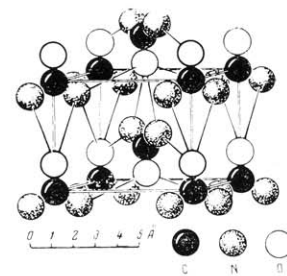


Figure 2. Ball-and-spoke model of urea crystal structure. The long spokes indicate the outline of one unit cell and the general directions of the  $NH \cdots O$  bonds.

Urea,  $CO(NH_2)_2$  is water soluble and crystallizes in space-group  $P4_21m$ . Crystals, a cardboard model of an "ideal crystal" (Fig. 1), and a ball-and-spoke model of the crystal structure (Fig. 2) are provided for examination of the geometrical relationships between them. The students carry out the following experiments, not necessarily in the order given (since they must use certain of the apparatus by turn) but always in a logical order.

Observations using a polarizing microscope.

Measurement of single-crystal density, by flotation.

Measurement of interfacial angles using an optical goniometer.

Determination of the size and shape of the unit cell and the

number of molecules of  $\text{CO}(\text{NH}_2)_2$  in it (Laue and rotation X-ray photographs).

Comparison of a powder photograph with the spot positions and intensities on a rotation photograph and indexing of the powder lines.

Indexing of zero-layer-line spots on the rotation photograph and estimation of their intensities. Reduction of data to give "structure factors" ( $\{hko\}$  or  $\{hOl\}$ ).

Optical synthesis of the observed structure factors, using phase data provided (scale  $1 \text{ cm} = 1 \text{ \AA}$ ).

Measurement of interatomic and intermolecular distances and observation of the general shape of the molecules in relation to their packing.

Urea is uniaxial, with straight extinction when mounted with the prism length (the  $c$  axis) parallel to the microscope stage. It is seen that if one of the pyramid faces is taken as  $(111)$  then the prism faces are  $\{110\}$ , and a rough measurement of either of the angles  $(111):(\bar{1}\bar{1}1)$  or  $(111):(110)$  can be used to give an approximate value of the axial ratio  $c/a$ , to be compared later with the more accurate determination by optical or X-ray goniometer measurements. Students realize that quite simple polarizing-microscope measurements may sometimes be used for nondestructive determinative chemical identification.

*Density by Flotation.* The students select small single crystals, if possible without inclusions or bubbles, and use liquids respectively less and more dense than the specimen, and in which they are not soluble, as components of the flotation mixture. The advisability of accepting the maximum density as correct (since bubbles tend to decrease the density) and the necessity of measuring and recording the ambient temperature are pointed out. For more exact methods, students are referred to the appropriate section of Volume III of "International Tables for X-ray Crystallography" (4c).

The use of density as a check on identification of a very small quantity of material and for purposes of molecular weight determination is indicated.

*Optical Goniometer.* This instrument provides a means of measuring interfacial angles, the accuracy of which is dependent upon the perfection of the faces; in many cases, it can permit easy nondestructive identification of well-crystallized materials. It also familiarizes students with the use of goniometric crystal holders by means of which centering and orientation can be controlled, and a modified form of which they will meet subsequently on the X-ray photogoniometer. It does help them to see visually, by means of microscope and telescope attachments, what will later be happening to the X-ray incident and diffracted beams as the crystal is adjusted on its sliders and arcs.

*Laue Photograph.* The mounting of a film or of a pack of films in a cylindrical camera will be new to students and should be practiced first with old films in the light.

Two Laue photographs have to be taken with either the  $(001)$  axis vertical and  $[110]$ ,  $[\bar{1}\bar{1}0]$  in turn along the incident beam or a  $[100]$  vertical and  $[010]$ ,  $[001]$  in turn along the beam. The crystal setting is made using a small microscope fitted on to the photogoniometer and will not usually be more than approximate. The final adjustment to bring  $[001]$  or  $[100]$  exactly vertical is made from the X-ray photographs since the crystal photograph should be symmetrical about a horizontal line. The original setting of a face  $(110)$  parallel to an arc of the goniometer head and then

normal to the incident beam, which has to be done by eye, is not critical. The final adjustment of the crystal on the arcs, which must be done after measurements of the photographs and calculations from them, must be exact if good rotation photographs, suitable for intensity measurement, are to be obtained. The calculation for adjustment is simple and a good student should not need to be told the necessary formula but may have to be warned to choose a pair of spots above and below the equator which are as near as possible to the vertical plane through the incident beam and the arc parallel to it.

The similarity of the two Laue photographs both taken with  $(001)$  vertical and at right angles to each other, proves the existence of the fourfold symmetry axis. The presence of diffuse streaks and spots, as well as sharp Laue spots, even on a 15-min photograph (Fig. 3) is evidence of thermal vibrations of large amplitude.

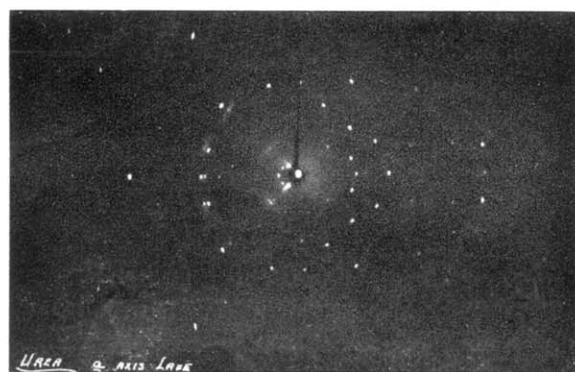


Figure 3. Laue photograph of urea single crystal, taken with white radiation containing a  $\text{CuK}$  characteristic component, which is responsible for the diffuse streaks, these being due to molecular vibrations. The  $[001]$  is vertical; the  $[100]$  is nearly along the incident beam. Exposure time, 15 min.

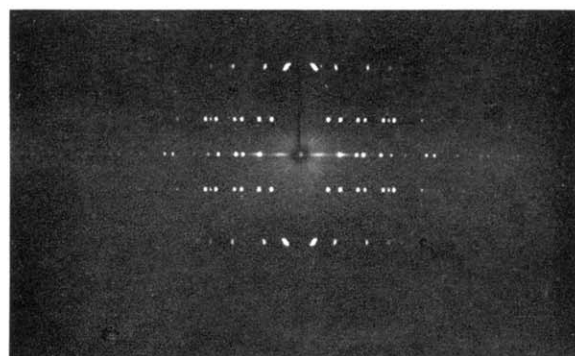


Figure 4. Rotation photograph of urea,  $[001]$  vertical, showing layer lines  $hk2$ ,  $hk1$ ,  $hk0$ ,  $hk\bar{1}$ ,  $hk\bar{2}$ .  $\text{CuK}\alpha$  (filtered Ni).

*Rotation Photograph.* Once the crystal has been accurately set,  $[001]$  or  $[100]$  vertical, the taking of a rotation photograph is simply a matter of inserting a Ni filter to eliminate  $\text{CuK}\beta$  (and some continuous) radiation, releasing the crystal spindle, and of exposing to the  $\text{CuK}\alpha$  incident beam for about 30 min (Fig. 4).

The films are processed at a standard temperature in a thermostatted darkroom, and the critical effect of temperature on the chemical reactions involved in photographic processing is pointed out. So also is the

(differential) effect of humidity on the dimensions of the film after processing and at the time of measurement. This is more critical than temperature and is often overlooked even by experienced research workers. It is one of the main reasons why standard marks on the film are required in precision work.

The following sets of measurement are made on the processed film when it is dry:

Averaged distances  $y_n$  between pairs of layer lines  $n$  and  $\bar{n}$ ; hence a calculation of the repeat (identity) distance  $c$  or  $a$  (Å).

Distances  $x$  between pairs of similar spots along the equatorial layer-line; hence a calculation of the Bragg angles  $\theta$  and the spacings  $d$  (Å).

Intensities  $I$  (averaged for each pair) of the equatorial layer-line spots, by eye estimation using a comparison intensity scale which is provided (2).

The Table of  $d$  and  $I$  entered into the laboratory notebooks should contain a column into which the indices  $hk0$  or  $h0l$  will be subsequently entered.

**Powder Photograph.** A few small crystals are ground very finely using an agate mortar and pestle. Mixed with a little cellulose acetate, the powder can easily be rolled into a cylinder of size about  $1 \times \frac{1}{4} \times \frac{1}{4}$  mm<sup>3</sup>. This specimen is then centered on the camera spindle, with its cylinder axis vertical, and a Ni filter inserted for the exposure. It is educationally helpful to use not a "strip," but a full cylindrical film for the powder photograph (Fig. 5) so that the latter can be superimposed on the well-set (or mis-set) rotation photographs and the positions of lines and spots compared and so that the effects of preferred orientation can be understood even if they are not actually observed.

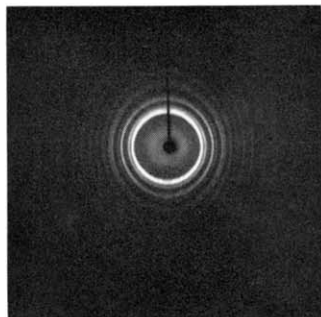


Figure 5. Powder photograph of urea, CuK (filtered Ni) radiation.

The appearance of a strip can of course be shown by masking, and the special features of a normal "strip" powder camera demonstrated. The intensities of powder lines and rotation spots should also be compared and the necessity of a correction for multiplicity on powder photographs will be appreciated by reference to an offset rotation photograph.

**Determination of Unit-cell Size and of the Number of Molecules in the Unit Cell.** Since urea is tetragonal,  $a = b \neq c$ ,  $\alpha = \beta = \gamma = 90^\circ$ . This may be demonstrated by orthogonal Laue photographs and by optical goniometric measurements.

Students working with the prism axis [001] as rotation axis will have determined  $c$  from layer-line separations. They determine  $a$  from the  $d(hk0)$  values measured from the equatorial layer-line spots. It is found that odd orders of  $h00$  are absent. This is evidence of two-fold screw axes ( $2_1$ ) parallel to [100] and [010]. The indices  $hk0$  of all spots on the zero layer line are easily determined. The row lines connecting  $hk0$ ,  $hk1$ ,  $hk\bar{1}$ ,  $hk2$ , etc. on successive layer lines are easily recognized and this facilitates the indexing of all the  $hkl$  reflections.

The value for  $a$  ( $=b$ ) has been determined from layer-

line separations. The value for  $c$  is determined from the  $d(0kl)$  values measured on the equatorial layer line.

The reflections on the 1st, 2nd, etc., layer lines will be  $1kl$ ,  $2kl$ , etc., and can usually be identified by inspection, as above. The difference in certain multiplicities for rotation and powder reflections may be pointed out.

When all the  $hkl$  spots on the rotation photograph have been identified, superposition of the powder photograph will identify the powder lines; and intensities can be visually compared. The powder line intensities are then listed as  $VS$ ,  $S$ ,  $MS$ ,  $M$ ,  $MW$ ,  $W$ ,  $VW$ . The use of charts and other independent means of identifying indices of lines on powder photographs generally can be mentioned, but in this short course there is no time to attempt these in practice. References to suitable books (see Bibliography) are of course given, and the use of powder photography in the "fingerprint method" of chemical identification, using the ASTM index, or a direct comparison method, is again emphasized. This is probably the principal future use of X-ray techniques as far as the majority of chemists are concerned.

Given  $a$ ,  $c$ , and the density  $\rho$ , the number  $n$  of  $\text{CO}(\text{NH}_2)_2$  molecules in the unit cell is derived from

$$a^3 \rho = nM/N$$

where  $M$  is the molecular weight and  $N = 6.024 \times 10^{23}$ .

**Optical Synthesis of Structure.** The "structure factor"  $F$  (on a relative scale) for each reflection can be obtained from the observed intensity  $I$  as follows:

$$I = F^2 \cdot \frac{1 + \cos^2 2\theta}{\sin 2\theta} \cdot P \cdot \text{constant}$$

where the unknown constant is independent of angle apart from an absorption factor which is negligible except for more refined structure analyses. The angle factor, which allows for the polarization of the X-ray beam and the period of reflection time of each plane, is obtained from tables to which the students are referred (3).  $P$  is the multiplicity, with which they should have become thoroughly familiar.

Each  $F$  value represents a scattered wave in a particular direction, of an amplitude dependent upon the distribution of scattering matter relative to the set of ( $hkl$ ) planes giving the spot in question. It can be represented, as a sine function, by a set of optical fringes of suitable contours. An optical reconstruction of the projected crystal structure can be made by superposing, photographically, on a single sheet of film or paper, as many sine waves as there are reflections observed on the equatorial layer line ( $(hk0)$  for an [001] projection (Fig. 6);  $(0kl)$  for a [100] projection (Fig. 7)). These fringes must have the correct relative spacings (wavelength proportional to  $d(hkl)$ ), orientations (corresponding with the relative orientations of the reflecting planes), amplitudes (exposure times proportional to  $F$ ) and phases. The phases are supplied. They cannot be directly observed by the student and are obtained in this case by calculation from a trial structure; the student does not have time in this course to carry out these calculations. He may do so as an exercise on some other occasion.

There are various devices available for making such optical Fourier syntheses, for example, by means of



Huggins' masks, Lipson's X-ray microscope, or the von Eller photosommateur. We use the latter (1) in which the origin of the sine wave is a line source of light passing through a specially-designed diffraction grating. This is movable on an optical bench, to and fro (for adjustment of spacing) or from side to side (for adjustment of phase). The photographic paper is in a cassette capable of rotation normal to the optical bench length and carrying with it a mounting to which can be fastened a "reciprocal net," made by the student on a scale that will give a final reproduction in which  $1\text{ cm} \equiv 1\text{ \AA}$ . This can be found by trial before the course begins, together with a suitable total exposure time, the latter being fairly critical if a good picture is to be obtained.

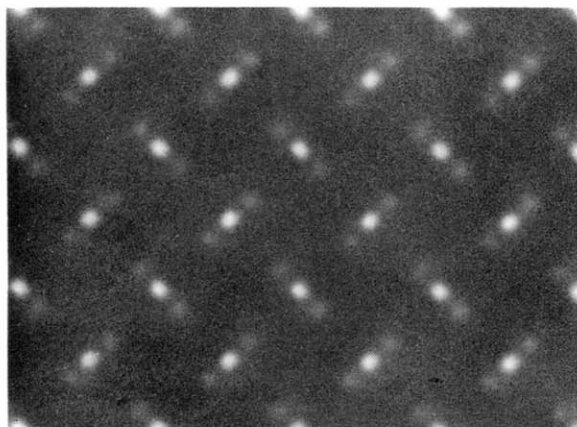


Figure 6. Optical synthesis of urea structure, projected along [001].

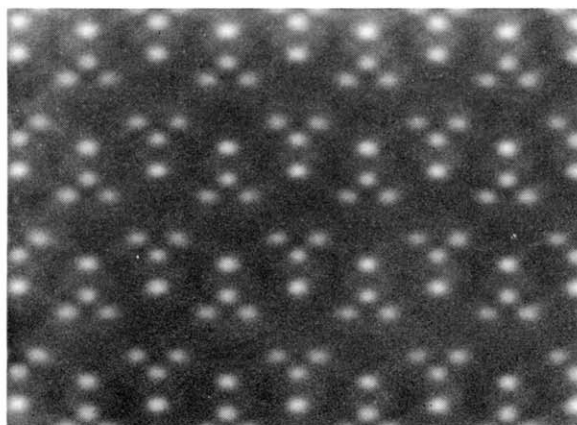


Figure 7. Optical synthesis of urea structure, projected along [100].

The students who have obtained the (001) and the (100) projections (Figs. 6 and 7) should now compare them with each other and with the model (Fig. 2) of the structure as a whole. They can even directly measure, from their photographs, projected C=O and C—N intramolecular distances and  $\text{NH}\cdots\text{O}$  intermolecular distances, and can calculate the actual distances; or they can determine the atomic coordinates from the photographs and hence calculate the bond lengths. These may be compared with similar bond lengths in other compounds by reference to Tables 4.2 (Tables of Bond Lengths between Carbon and other elements) in Vol. III, "International Tables for X-Ray Crystal-

lography." This will give the students some idea of the meaning (and accuracy of measurement) of bond lengths in relation to chemical constitution.

*Hexamethylene tetramine*,  $\text{C}_6\text{H}_{12}\text{N}_4$ , is very soluble in water, slightly soluble in alcohol and is best crystallized from a weakly aqueous alcohol solution. The crystals are cubic, space group  $I43m$ .

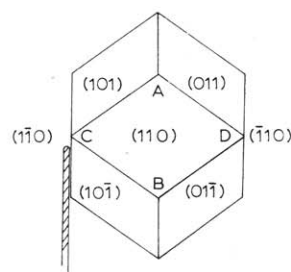


Figure 8. Diagrammatic representation of hexamethylene tetramine crystal, as mounted on glass fiber for Laue or rotation photograph.

The experimental procedure is rather similar to that for urea, except that all the class determine a cube-axis projection (Fig. 9) by setting their crystals with the short diagonal of a (110) face vertical. This is AB in Figure 8, which shows the habit, having twelve similar  $\{110\}$  faces. It would be quite useful if one-half of the class were to set CD

vertical, thus obtaining a (110) projection. This, however, is a little more difficult to visualize in relation to the cubic symmetry.

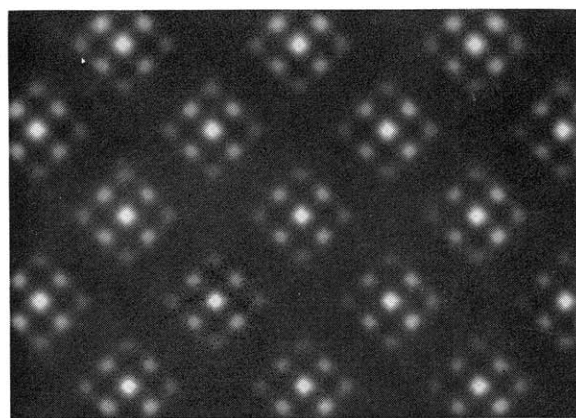


Figure 9. Optical synthesis of hexamethylene tetramine structure, projected along [100].

Since hexamine is isotropic, it is advisable, when making observations with a polarizing microscope, to give the students a few crystals of urea so that the optical behaviour of the two substances may be compared and contrasted. The  $c/a$  axial ratio for urea may also be measured. For hexamine it is checked that the angles CAD or CBD, which are  $109\frac{1}{2}^\circ$ , can be measured with an accuracy of about 1 in 200 by lining up each face edge in turn with a crosswire (this assumes that a graduated microscope stage is available). Crystals of dimensions about  $\frac{1}{2} \times \frac{1}{2} \times \frac{1}{2}\text{ mm}^3$  should be selected for X-ray work and of about twice this size (linear) for optical goniometry. A few good small crystals without visible inclusions or internal bubbles are also selected for density measurement.

The procedure is then very similar to that for urea, except for the following points:

Since hexamine is frequently rather "perfect," the crystals used for X-ray work need to be first dipped in a little liquid  $\text{N}_2$  (or liquid air) in a watchglass, in order to make their texture more "mosaic." Theory and experiment have shown that the intensity of reflec-

tion from a perfect crystal, which shows strong "extinction" due to multiple internal reflection and other causes which attenuate the primary beam, may be several times less than that from a mosaic crystal. Students may be shown X-ray photographs illustrating the "before" and "after" effects of this sudden thermal shock. Even urea diffraction intensities may sometimes be improved by similar thermal treatment.

Since for any cubic crystal  $1/d^2 = (h^2 + k^2 + l^2)/a^2 = (4\sin^2\theta)/\lambda^2$ , it follows that the values of  $\sin^2\theta$  deduced from a powder photograph of a cubic crystal will be found to be proportional to all or some of the possible values of  $(h^2 + k^2 + l^2)$  where  $h$ ,  $k$ , and  $l$  are integers. This enables the diffracting planes to be indexed ( $hkl$ ), the lattice type to be identified and the value of the lattice constant  $a$  to be determined, given  $\lambda$ .

All three cubic lattices are readily identifiable from the first three reflections of a miset rotation photograph since the multiplicities observed will be

$\{hkl\}$	100	110	111	200	210	211	220	300	310
$P$	(6	12	8)	6	24	24	12	6	24
$I$	...	(12	...	6	...	24)	12	...	24
$F$	...	...	(8	6	...	...	12)	...	...

General multiplicities for the  $\bar{4}3m$  class of the cubic system are

$\{h00\}$	$\{hh0\}$	$\{hhh\}$	$\{hk0\}$	$\{hhl\}$	$\{hkl\}$
6	12	8	24	24	48

The differences between the lattices are due to the following conditions:

- $P$  all  $hkl$  reflections may be observed.
- $I$  only  $hkl$  where  $h+k+l$  is even are present, all others have zero intensity.
- $F$  only  $hkl$  where  $h$ ,  $k$ ,  $l$  are all even or all odd are present; all those with mixed indices are of zero intensity.

The students note that for cubic crystals a second kind of multiplicity may occur where  $h$ ,  $k$ ,  $l$  may be two or more different sets of integers for the same value of  $h^2 + k^2 + l^2$ . Thus  $h^2 + k^2 + l^2 = 18$  will correspond to both  $\{330\}$  and  $\{411\}$ . These would coincide on powder or on  $[110]$  rotation photographs, but would

be differentiated on a Weissenberg (moving film) photograph about  $[110]$  or on a  $[100]$  rotation photograph.

The main result achieved by this exercise, apart from those already mentioned for urea, is the realization of the very high symmetry of the  $C_6N_4H_{12}$  molecule (Fig. 9). The equality of all the carbon atoms cannot be brought out by the formula as printed even in a structural form. It can only be seen in a spatial representation. The C—N distances as measured from the optical projection may be compared with those found for urea, and as recorded for other compounds containing this bond. The significance of the body-centered arrangement of these nearly spherical molecules in relation to intermolecular bonding should be pointed out in contrast with adamantane,  $C_{10}H_{16}$ , which is face-centered cubic.

A copy of the notes issued to students taking this course may be obtained on application to the author.

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