Some of the physical properties of acetylphenylhydrazine, phthalic anhydride, and s-diphenylcarbazide have been investigated by the methods of x-ray diffraction and chemical microscopy.

The dimensions of the unit cell of acetylphenylhydrazine have been calculated from single crystal x-ray diffraction data. The determination of the density of the compound by the flotation method has permitted the calculation of the number of formula weights per unit cell.

The powder x-ray diffraction patterns of acetylphenylhydrazine and s-diphenylcarbazide have been obtained and the interplanar spacings tabulated with the relative intensities of the corresponding lines.

The form and habit on crystallizing from various solvents and from the melt have been described for each of the compounds. A polymorphic form of acetylphenylhydrazine has been detected by phase change on heating the solid on the hot stage microscope and has been confirmed by powder x-ray analysis.

The refractive indices (except gamma for acetylphenylhydrazine and s-diphenylcarbazide) have been determined for all three compounds by the immersion method. The optic directions have been oriented in relation to the crystal faces commonly observed. The dispersion has been qualitatively described and the sign of double refraction determined for each of the compounds.
CRYSTALLOGRAPHIC AND X-RAY DIFFRACTION INVESTIGATION OF SEVERAL ORGANIC COMPOUNDS

by

WAYNE PAUL VAN METER

A THESIS submitted to OREGON STATE COLLEGE

in partial fulfillment of the requirements for the degree of

MASTER OF SCIENCE

June 1952
APPROVED:

Associate Professor of Chemistry
In Charge of Major

Head of Department of Chemistry

Chairman of School Graduate Committee

Dean of Graduate School

Date thesis is presented July 31, 1957
Typed by Evelyn Kanzelmeyer
ACKNOWLEDGMENT

The author wishes to acknowledge gratefully the sincere and understanding counsel and assistance given throughout the course of this research by Dr. Max E. Williams.
# TABLE OF CONTENTS

<table>
<thead>
<tr>
<th>Section</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>INTRODUCTION</td>
<td>1</td>
</tr>
<tr>
<td>X-RAY DIFFRACTION</td>
<td>3</td>
</tr>
<tr>
<td>CRYSTAL MORPHOLOGY</td>
<td>17</td>
</tr>
<tr>
<td>OPTICAL PROPERTIES</td>
<td>27</td>
</tr>
<tr>
<td>FUSION DATA</td>
<td>38</td>
</tr>
<tr>
<td>PHOTOMICROGRAPHY</td>
<td>43</td>
</tr>
<tr>
<td>SUMMARY</td>
<td>44</td>
</tr>
<tr>
<td>BIBLIOGRAPHY</td>
<td>45</td>
</tr>
</tbody>
</table>

# LIST OF FIGURES

<table>
<thead>
<tr>
<th>Figure</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>Figure 1</td>
<td>5</td>
</tr>
<tr>
<td>Figure 2</td>
<td>12</td>
</tr>
<tr>
<td>Figure 3</td>
<td>19</td>
</tr>
<tr>
<td>Figure 4</td>
<td>24</td>
</tr>
<tr>
<td>Figure 5</td>
<td>31</td>
</tr>
<tr>
<td>Figure 6</td>
<td>40</td>
</tr>
<tr>
<td>Figure 7</td>
<td>41</td>
</tr>
</tbody>
</table>
CRYSTALLOGRAPHIC AND X-RAY DIFFRACTION INVESTIGATION OF SEVERAL ORGANIC COMPOUNDS

INTRODUCTION

The several physical constants of crystalline materials which have been the primary subject of this project are quite characteristic for any compound, but it is probable that a particular value of a quantity for one compound might be duplicated in many others. However, when several different constants have been determined on an unknown sample it is unlikely that all of these values will be duplicated by any one other compound. This, then, offers a method of qualitative analysis or identification which is practically specific, can be used on small samples, and is often more rapid and convenient than other methods of qualitative identification.

The increasing precision and variation during the last few years of the instruments commonly available to the analyst have accentuated the need for a correlated indexing of the most convenient forms of the data obtained by such instruments as the x-ray diffraction apparatus, the chemical microscope, and the refractometer.

One answer to this need appeared in the March, 1946, issue of Analytical Chemistry (1, p.274); it was the first in a series of articles contributed by the Armour Research Foundation of the Illinois Institute of Technology entitled
"Crystallographic Data". It is the purpose of this series, edited by Dr. W. C. McCrone, to build up a backlog of carefully obtained data which will eventually be indexed. That this is only a partial answer is evident when one considers that since its beginning only 45 compounds (as of June, 1951) have appeared in this series, while many new compounds are becoming important to industry and research each year.

We have endeavored in this research project to obtain data, acceptable for publication in the Armour Institute series in Analytical Chemistry, on three organic compounds. This thesis will be devoted to discussions, under each of the measured quantities in turn, of the results of our work with acetylphenylhydrazine, phthalic anhydride, and s-diphenylcarbazide.
X-RAY DIFFRACTION

X-ray diffraction analysis has contributed more to advance the study of crystallography than perhaps any other single experimental tool. Within the actual experience of crystallographers now active in the field the forward steps of the electronics industry have brought about tremendous improvements in the accuracy, versatility, power, and convenience of x-ray instruments.

POWDER METHOD. Of the many methods of handling the sample, x-ray source and beam, and photographic film to obtain diffraction patterns, the powder method (7,6) is probably the most widely used because of its simplicity and rapidity, coupled with specific identification where a compound has been previously indexed.

The phenomenon of x-ray diffraction may be thought of as a "reflection" of the x-rays from the planes of atoms in the crystal at definite, discrete angles, $\Theta$, which depend on the interplanar spacing, $d$, in Angstrom units, and the wave length of the x-rays, $\lambda$, in Angstrom units, according to the Bragg equation (3):

$$n \lambda = 2d \sin \Theta$$  \hspace{1cm} (1)

where $n$ is a small integer, usually 1, denoting the order of the diffraction. Powdering the sample ensures that many particles will be oriented to cause diffraction from each set of planes.
The photographic recording of the angles at which diffraction has occurred during the irradiation of a sample produces a pattern which is, for practical purposes, specific to the compound. The pattern is due to the spatial arrangement of the atoms in the crystal and not to their identity. It is conceivable that identical structure could be found in two compounds, but the differences in the identity of the atoms would probably lead to differences in the intensities of the rays diffracted from planes containing them.

X-ray equipment. The instrument used for the x-ray diffraction work was a General Electric XRD unit equipped with a single-crystal rotation camera with mount, and a recent model powder camera (cat. No. A4926E). The powder camera is depicted in Figure 1, where the primary beam, "a", from the target of the tube is collimated by slits before it strikes the sample at the center of the cylindrical camera. The diffracted rays, "b", pass between the cast aluminum frame pieces and strike the film in its position around the outside of the camera where it is held in place by a split-ring apron. The large fraction of the primary beam which is not diffracted is absorbed in the beam trap, "c". The geometrical dimensions of the camera are such that one centimeter distance on the film subtends a central angle of 4 degrees, permitting rapid calculation of
FIGURE I. X-RAY DIFFRACTION CAMERAS
the interplanar spacings related to particular observed lines.

From the Bragg equation it is plain that larger values of the angle theta will result from increasing the wave length of the x-rays. Because of the large unit cell dimensions of the organic compounds studied, it was found advantageous to use the chromium anode tube \( \lambda_{\text{K}\alpha} = 2.285\text{A} \) rather than one of the tubes with a heavier anode material.

**Preparation and mounting of samples.** The sample, ground in a mullite mortar to pass through a 100 mesh screen, is formed into a cylinder about 0.3 to 0.4 mm in diameter. This was done by dipping a Pyrex fiber in a suitable cement so as to form a thin, uniform layer of the adhesive, then rolling the fiber in the powdered sample and smoothing the coating on the heel of the hand. The fibers were prepared by heating a narrow segment of a piece of Pyrex rod in an oxygen-gas flame and drawing it rapidly to a diameter of about 0.15 mm.

An alternate method of mounting the sample is to fill a very thin-walled capillary (inside diameter about 0.4 mm) with the powdered sample. This was attempted, but the glass cylinder, even as thin as it was, absorbed most of the soft chromium x-rays.

The diameter of the fiber-mounted samples has a very definite effect on the nature of the pattern; if the fiber
itself is too thick it absorbs an appreciable amount of the beam and produces a "hollow" image resembling two lines, rather than a single line. When the sample is much smaller than 0.3 mm in diameter the intensity of the pattern falls off very rapidly for comparable exposure times.

Although the powdering of the sample might produce sufficiently random particle orientation, it is common practice to rotate the specimen during the exposure.

**Aligning the sample fiber.** The sample is supported in the center of the camera by embedding the end of the fiber in a lump of beeswax on a disk of iron about one centimeter in diameter. At the end of the shaft of the electric motor which rotates the specimen is fixed a small magnet; this permits the disk and sample to be moved laterally until the fiber coincides with the axis of rotation. This is a very critical and delicate adjustment, for upon it depends the precision of the location of the lines on the film. The slightest wobbling of the sample will blur the lines. The best method found for centering the sample is to employ a small telescope of short focal length which contains cross hairs. By this means the fiber can be quickly adjusted to be coincident with the rotation axis and perpendicular to the mounting disk.

**X-ray film.** The film used was Kodak Medical X-ray film of the no-screen type. The exposure time varied from
one hour to six hours, depending on the anode material and whether or not a filter was used. The developing procedure was standardized at 4 minutes in Kodak X-ray Developer. A dilute acetic acid short stop was used before fixing.

**Indexing of powder x-ray patterns.** Hanawalt, Rinn, and Frevel (6), by their introduction in 1938 of a system of indexing powder x-ray diffraction patterns, have greatly increased the ease with which this method may be put to use. It is based on the three strongest lines of the pattern, both as to their interplanar spacings and their relative intensities. The values of d are divided into 77 parts to separate the patterns according to the d value of the most intense line. The spacing of the second most intense line serves to place the pattern in one of 77 subgroups in a similar manner. The spacing of the third line places the pattern within its subgroup among the few others whose first two lines possess identical d values. The chances for duplication are remote when the relative intensities of the first three lines are considered, and, in the very few cases which are still ambiguous, the d value and relative intensity of the fourth most intense line may be invoked.

The Hanawalt system has been accepted by the American Society for Testing Materials, which has published a file of cards containing all the known data. New cards are
added as fresh data appear, and the existing cards are occasionally revised.

Interpreting powder patterns. In measuring and interpreting the patterns obtained in the course of this work it was necessary to anticipate the possibility that some of the lines were due to the presence in the beam of the CrKβ wave length (\( \lambda = 2.081 \, \text{Å} \)). This arose from our use of unfiltered radiation for the sake of greater beam intensity. A vanadium foil filter cuts out well over half of the alpha wave length as well as essentially all of the beta wave length. By a simple calculation using the Bragg equation one can determine where the beta line for a given observed line (assumed to be an alpha line) would appear, and then check for the presence of a line at that point. If by chance another alpha falls at that point, or within the range of experimental error (±0.02 cm) of that point, the intensities may aid a decision, because the beta lines are always proportionately weaker than their corresponding alpha lines.

In the tabulations that follow, the interplanar spacings and accompanying relative intensities are given for acetylpenthalhydrazine and s-diphenylcarbazide. Similar data for phthalic anhydride have been determined (2) and appear in the ASTM card file. In Figure 2 are reproduced powder patterns of the first two of these compounds.
# PRINCIPAL X-RAY DIFFRACTION LINES
## BY THE POWDER METHOD

| Acetyldiphenylhydrazine |   | s-Diphenylcarbazide |   |
|-------------------------|--|--|---------------------|--|
| $d$, Å                    | $I/I_0$ | $d$, Å                    | $I/I_0$ |  |
| 10.65                   | 1.00   | 12.81                   | 0.81   |  |
| 5.17                    | 0.61   | 9.54                    | 0.08   |  |
| 4.72                    | 0.39   | 8.17                    | 0.02   |  |
| 4.63                    | 0.30   | 6.38                    | 1.00   |  |
| 4.34                    | 0.09   | 5.55                    | 0.58   |  |
| 4.00                    | 0.30   | 5.17                    | 0.10   |  |
| 3.95                    | 0.14   | 4.72                    | 0.25   |  |
| 3.72                    | 0.28   | 4.58                    | 0.12   |  |
| 3.47                    | 0.30   | 4.24                    | 0.06   |  |
| 3.33                    | 0.20   | 4.12                    | 0.65   |  |
| 3.06                    | 0.08   | 3.75                    | 0.08   |  |
| 2.92                    | 0.58   | 3.49                    | 0.07   |  |
| 2.88                    | 0.18   | 3.36                    | 0.32   |  |
| 2.66                    | 0.14   | 2.97                    | 0.15   |  |
| 2.56                    | 0.10   | 2.88                    | 0.08   |  |
| 2.50                    | 0.08   | 2.80                    | 0.17   |  |
| 2.43                    | 0.05   | 2.63                    | 0.07   |  |
| 1.86                    | 0.11   | 2.55                    | 0.18   |  |
|                         |        | 2.18                    | 0.05   |  |

### SINGLE-CRYSTAL METHOD.
The Laue method of single-crystal x-ray diffraction analysis consists of placing a stationary crystal in a beam of continuous x-rays. In contrast, we have employed the method whereby a single crystal is rotated in a beam of monochromatic x-rays. In the former, diffraction from many sets of planes is assured by having many wave lengths in the beam; in the present case this is done by rotating the crystal through those positions where the wave length-angle relationship is satisfied for many sets of planes by the one wave length.
Crystal orientation. In the rotating crystal method it is essential that a rational line or direction in the crystal lattice be coincident with the axis of rotation, and that that axis be perpendicular to the x-ray beam. In addition, the film, which is placed cylindrically around the crystal (see Figure 1), must be coaxial with the crystal rotation. When these conditions are fulfilled all the sets of planes whose Miller indices have a common value along the crystallographic axis which is the rotation axis will cause diffraction at one particular angle with the rotation axis; these diffracted rays, in other words, will have as a locus a cone concentric with the rotation axis. Their points of impact on the film surface will describe a circle which, when the film is flattened out, will be a horizontal straight line. There will be a separate line, parallel to all the others, for each different common value of the Miller index along the rotation axis. These are called "layer lines". For example, in Figure 2c is shown the pattern obtained when the "c" crystallographic axis of acetylphenylhydrazine is the rotation axis. The central line is formed by planes having the general index hk0 and is called the zero layer line. The lines immediately above and below this line are the first layer lines and are characterized by the general index hkl. The next lines are the second layer lines having the general index hk2, and so on.
a. Powder method, *s*-diphenylcarbazide

b. Powder method, acetylphenylhydrazine

c. Single crystal rotation method, acetylphenylhydrazine, "c" axis vertical

Figure 2. X-ray diffraction patterns
The crystal selected for use in this type of analysis should be as free from defects as possible and from one to three millimeters long in at least one direction. The crystal used for Figure 2c was a needle crystal grown in ethanol solution which was 3.12 by 0.23 by 0.055 mm in size. The alignment of the crystal in the beam is begun by checking with the polarizing microscope to determine whether some recognizable crystal face is parallel to the internal structure direction which is to be the rotation axis. The crystal is then mounted on a short section of half-millimeter glass rod with a bit of cement and aligned by means of the goniometer head mount at the base of the camera. The camera cylinder is directly removable, and the crystal is brought to coincidence with the cross hairs of a small telescope which is built to fit on the camera track so that its axis lies in the position of the x-ray beam.

Interpretation of single-crystal patterns. The vertical distance between the layer lines is a function of the distance along the rotation axis between identical lattice points and of the geometry of the camera. This "distance between identical lattice points" is the smallest increment of cyclic repetition of crystal structure and is termed the "identity period." The solid formed by adjacent lattice points in the three axial directions is called the
unit cell.

The angle, \( \nu \), which a diffracted ray makes with the primary beam is given by the relation

\[
\sin \nu = \frac{\lambda}{t}
\]

where \( t \) is the identity period. It is also given by the relation

\[
\tan \nu = \frac{y}{r}
\]

where \( y \) is the distance on the film from the center line to the layer line in question and \( r \) is the radius of the camera. Eliminating \( \nu \) from (2) and (3) gives

\[
t = \frac{\lambda}{\sin \tan^{-1} (y/r)}
\]

for a particular layer line. The general form of the equation may be stated as

\[
t = \frac{n \lambda}{\sin \tan^{-1} (y_n/r)}
\]

where \( n \) is the number of the layer line.

The determination of the unit cell dimensions is accomplished by mounting the crystals so that patterns are obtained when each of the rational directions in turn is aligned with the axis of rotation.

The locations of planes of symmetry in the patterns is the most positive means of ascertaining the crystal system of the compound. The symmetry about planes both horizontal and vertical in each of the patterns, as may be
seen in Figure 2c, is evidence of the normal class of the orthorhombic system when the three unit cell dimensions are all different. Identical dimensions in two directions would be exhibited by a member of the tetragonal system.

By a more complete analysis of the single-crystal x-ray diffraction patterns the space group data may be obtained.

UNIT CELL DIMENSIONS OF ACETYLPHENYLHYDRAZINE

\[
a = 9.55 \text{ Å} \quad b = 21.54 \text{ Å} \quad c = 7.64 \text{ Å}
\]

Formula weights per unit cell. Where the cell dimensions and the density of a substance are known, the calculation of the number of formula weights per unit cell is a simple step. Since the density of acetylphenyl-hydrazine is not given in the literature, it was determined to three place accuracy by adjusting the composition of a mixture of benzene and carbon tetrachloride to the point where crystals placed in the liquid neither sank nor floated. The density of this liquid mixture was then determined by means of a Westphal type balance.

The quantities involved in the calculation are related in the following manner:

\[
Z = \frac{d V N}{M}
\]

(6)
where \( Z \) is the number of formula weights per unit cell, \( d \) is the density of the crystals, \( V \) is the volume in cm\(^3\) of the unit cell, \( N \) is Avogadro's number, and \( M \) is the molecular weight. Substituting the data for acetylphenylhydrazine,

\[
Z = \frac{1.280 \times 1.57 \times 10^{-21} \times 6.02 \times 10^{23}}{150.2} = 8.06.
\]

From this we may conclude that there are 8 formula weights per unit cell in acetylphenylhydrazine.
CRYSTAL MORPHOLOGY

The external shape and appearance of crystals in any particular preparation are often greatly affected by the conditions under which the crystals grow. The more common variations appear in the types of and angular positions of the faces which appear and the crystallographic direction in which growth is most rapid.

The objective in preparing crystals for examination by chemical microscopy is to produce discrete individual crystals which have clean edges and recognizable forms while keeping the thickness in the order of 50 to 100 microns. The lateral dimensions can be as much as a millimeter or two as long as operations with the cover glass and mounting liquids are conveniently possible.

The exterior form is of no importance in the preparation of samples for powder x-ray analysis; any recrystallization is done in the interest of purity. Single crystal x-ray specimens can usually be chosen from the preparations described above for microscope work.

CRYSTAL PREPARATIONS; FORM AND HABIT. Since the physical history of any particular sample is intimately associated with many of the details of form and habit it is logical to include at this point a discussion of the techniques used to obtain the crystalline specimens. The common step of recrystallizing compounds from liquids in
which they are appreciably soluble has been supplemented by
growing crystals from molten samples and by collecting
sublimates.

The describing of crystals demands that the crystal-
lographic axes be defined or chosen in some way. The most
positive means available is the single crystal x-ray analy-
sis, in which by convention the experimentally determined
cell dimensions are fitted into the arbitrary relationship
\( c < a < b \) (1). From this the axes of acetylphenylhydrazine
and phthalic anhydride have been defined as they are
labeled in Figure 3. In the absence of x-ray data the
assignment of axes is somewhat arbitrary; the axes of the
other substance have been labeled so that the long direc-
tion of crystal elongation in the most stable form is the
"c" axis, and the shortest dimension is the "b" axis.

**Acetylphenylhydrazine.** From acetone solution this
compound forms platy, pinacoidal crystals lying commonly on
the (100) face. Crystals grown from 95% ethanol solution
form plates and needles, the plates usually lying on the
(100) face. From ether the crystals, after drying, hang
together in clumps because of the interlacing of the
needles, which are very small, almost powdery, in size.
Crystals from benzene are blunt-ended needles of about the
same size as those from ether. The compound is not very
soluble in either benzene or ether.
FIGURE 3. ORTHOGRAPHIC PROJECTIONS OF TYPICAL CRYSTALS
All of the preparations above were made by permitting evaporation of the solvent from an open crystallizing dish.

**Phthalic anhydride.** Phthalic anhydride is somewhat soluble in ethanol, but esterification occurs before recrystallization when evaporation in an open dish is permitted. From acetone two general types of crystals can be obtained. When the solution is saturated at 50°C. and allowed to cool slowly, granular crystals appear showing the forms (110), (011), and (111) (see Figure 3b). If the solvent is allowed to evaporate at room temperature, prismatic needles, showing some twinning and intergrowth, are obtained.

Since phthalic anhydride is essentially insoluble in water, it can be caused to crystallize from an acetone solution by the dropwise addition of water while stirring. The resultant crystals are quite small, most of them being granular while a few are needle-like. It was found convenient to use a stirring motor at moderate speed while adding about 15 drops of water per minute from a dropping funnel.

Sublimation crystals of phthalic anhydride are needles, some 3/8 inch long, which are highly twinned; striations run parallel to the elongation. They were prepared with a cold finger apparatus made from the lower
ends of an eight inch and a six inch test tube, a rubber stopper bored to hold them concentrically, and another rubber stopper provided with two holes for the circulation of cold water. A small amount of the compound was placed in the larger tube and heated in an oil bath; the vapors condensed on the cooled surface of the inside tube. The temperature was held 10 degrees below the melting point for about two hours.

s-Diphenylcarbazide. The evaporation of the solvent from a 95% ethanol solution of s-diphenylcarbazide yielded thin needle crystals whose direction of elongation was coincident with the optical direction alpha. On the other hand, the most prominent elongation of crystals formed in a similar manner from solutions of glacial acetic acid was elongation in the beta direction.

When this compound is dissolved in acetone the crystals which result from evaporation of solvent contain one mole of crystallization of acetone (10, p.1133). When they are heated, as on a melting point block, the acetone is driven off at about 70°C., after which the residue melts at the normal 172-175°C.

CRYSTAL SYSTEM. The polarizing microscope will usually give a definite indication of the crystal system to which a crystalline substance belongs. The best criteria in this determination are the characteristics of
the extinction and of the interference figures which are observed. The details of these quantities are discussed below in the section on optical properties. Gibb (5, p.302) gives a tabulation of the extinction and interference figures common to each of the seven crystal systems.

Each of the three compounds which have been investigated here exhibited the parallel and symmetrical extinction and the biaxial interference figures that are indicative of the orthorhombic system. This result confirms the single crystal x-ray analysis, as noted earlier, of acetylp phenylhydrazine.

INTERFACIAL ANGLES. There are in general two ways to record interfacial angles. The "true" interfacial angle is the actual angle between the two faces as one would see it on looking down their zone axis (a line parallel to both planes). Another notation makes use of the "polar" angle, that which is formed by two lines, one perpendicular to each face, from a point exterior to the faces.

The former type of measurement yielded the data given in Figure 3. This was experimentally convenient in this case because the crystal axes are all rectangular. In the microscopic examination of monoclinic or triclinic crystals it is often just as effective to record the "apparent" angle between two faces. By this is meant the
angle between the edges formed by the intersection of the two faces with a third face (usually a common one which is often parallel to the stage). For example, referring to Figure 3a, the angle given as 104° would be the true angle between domes parallel to the b axis. It is also the angle formed by the projection of 121 and 121 on 010.

The principal interfacial angles measured on acetylphenylhydrazine, phthalic anhydride, and s-diphenylcarbazide have been indicated in Figure 3.

It is very helpful in the interpretation of relationships between observed faces and the crystallographic axes to use a binocular microscope of the Greenough type. This instrument gives a rather deep field and a stereoscopic effect which aids in mentally orienting individual crystals. The crystal dimensions should be in the order of one millimeter for best results.

The definite habits of many compounds as crystallized in various manners causes them to lie nearly always on the same crystal face. The universal stage will sometimes permit measurement of interfacial angles which are otherwise never seen. A rough but effective device was built for the orientation of a needle of acetylphenylhydrazine to permit the measurement of the true angle between the prisms (93° in Figure 3a). Two corks were pierced with two three-inch pieces of common iron wire in
Acetylphenylhydrazine from ethanol solution x30

Phthalic anhydride from acetone by evaporation x30

Phthalic anhydride from acetone by slow evaporation followed by digestion at room temperature x60

s-Diphenylcarbazide from glacial acetic acid x30

s-Diphenylcarbazide from ethanol x30

Figure 4. Photomicrographs of crystals in mounting liquids
such a manner that a crystal mounted at the end of the second wire could be rotated around two horizontal, mutually perpendicular axes. The crystal was mounted on the rounded end of a glass tube similar to an ordinary melting point capillary. The tube was of such a size that it slid to a snug friction fit over the end of the wire. If care is taken to cement the crystal to the tube so that the zone axis in question is nearly perpendicular to the mounting tube, the apparatus can be easily adjusted under the low-power objective until the vertical edge remains stationary with respect to the cross hairs as the microscope is focused up and down. A rotation of the stage then gives the true interfacial angle.

AXIAL RATIO. For the most basic definition of the axial ratio and the best means of determining it we must again refer to the unit cell and its dimensions as determined by single crystal x-ray analysis. The axial ratio is the ratio of the dimensions of the unit cell. Before x-ray analysis became available the axial ratio was determined by noting the most predominant interfacial angles and calculating the ratio of the intercepts of an arbitrarily chosen unit pyramid on the three axes.

The Miller indices given in Figure 3 for acetyl-phenylhydrazine have been deduced by comparing the axial ratio from x-ray data with that from interfacial angle
data. The indices and axial identities given for phthalic anhydride have been deduced from the x-ray data of Becker and Jancke (2), which check closely with calculations from our interfacial angle data. The indices given for s-diphenylcarbazide are somewhat arbitrary and may well be in error by some integer in comparison with those which would be obtained from x-ray data.

In the following table are given the axial ratios as they have been obtained from the two possible sources. The ratio obtained for s-diphenylcarbazide contains no reference to the b axis because no domes or pyramids were observed to cut that axis and the necessary interfacial angle data was not obtainable.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Source</th>
<th>Ratio(a:b:c)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Acetylphenyl-hydrazine</td>
<td>x-ray (4)</td>
<td>0.567:1:0.429</td>
</tr>
<tr>
<td></td>
<td>interfacial angles</td>
<td>0.58:1:0.42</td>
</tr>
<tr>
<td>Phthalic anhydride</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>x-ray (4)</td>
<td>0.567:1:0.429</td>
</tr>
<tr>
<td></td>
<td>interfacial angles</td>
<td>0.58:1:0.42</td>
</tr>
<tr>
<td>s-Diphenyl-carbazide</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>interfacial angles</td>
<td>a:c::1:0.65</td>
</tr>
</tbody>
</table>
OPTICAL PROPERTIES

Light is transmitted by crystals of the cubic or isometric system with the same apparent refractive index regardless of its direction of propagation with reference to the crystallographic axes. Crystals of all other systems possess either two or three different vibration directions which are recognizable through the fact that when viewed from these different directions they exhibit different indices of refraction.

DOUBLE REFRACTION. When a ray of light enters a randomly oriented anisotropic crystal its transverse vibrations are resolved into two other mutually perpendicular directions which lie in planes also containing two of the optic directions. When the optical system of the microscope contains a polarizing prism (polarizer) below the stage and another similar prism (analyzer) between the stage and the eyepoint, the field will be black when their planes of polarization are crossed. If a doubly refractive crystal is brought into focus at the level of the stage it will also appear black if one of its optic directions is horizontal and parallel to the plane of polarization of either of the prisms. If the stage is rotated to a position where the polarized ray is no longer vibrating along one of the vibration directions of the crystal, the polarized ray will be resolved into two
polarized rays as described above. When these rays reach the analyzer they will be again resolved into its vibration plane and the crystal will appear light against the dark field.

INTERFERENCE FIGURES. The extinction of anisotropic crystals, as just described, is best observed when the rays illuminating the crystal are essentially parallel. The varied coloration of the crystals is caused by destructive interference of that wave length which is retarded an odd number of half wave lengths in one vibration direction compared with the same wave length in the other vibration direction. As the wide-angle substage condenser is raised as far as possible, the rays of polarized light converge sharply on the crystal. Since the amount of retardation varies with the thickness, light of different wave lengths will undergo destructive interference for different thicknesses of material. Thus, the inclined rays, passing through a greater thickness of crystal than do the central rays, will suffer interference at a different wave length. The sum result of this process for all the rays within the angular field of the objective lens is a colored pattern which is visible at the back of the objective on removing the eyepiece or inserting a Bertrand lens to focus the eyepiece on the back of the objective instead of its focal plane.
The shape and position of the interference figure is employed in all measurements of optical properties because it is much more positive proof of the orientation of the crystal than is its external appearance, and can, in fact, be used where there is no evidence of crystal faces or familiar symmetry.

REFRACTIVE INDICES. The measurement of the refractive index of small crystals is accomplished by observing their effect on transmitted light while they are immersed in a liquid of known refractive index. Crystals mounted in a liquid of a different index stand out in strong relief; their edges and contours are easily seen because of the refraction of light rays as they pass from the solid into the liquid, or vice versa. As the index of the liquid is changed, or, as in actual practice, as the crystals are immersed in other liquids of index nearer to their own, the relief or contrast diminishes. When a perfect match is found the crystal will be invisible because there will be no optical discontinuity at the solid-liquid interface. Quite often only inclusions or other internal imperfections of the crystal will be visible.

Influence of temperature. The temperature coefficient of change of the refractive index is nearly always much greater for the immersion liquid than it is for the crystal itself. In fact, change in the refractive index
of the solid is usually smaller than the limit of accuracy in detecting by eye the exact point where the index of the solid and liquid are equal.

It is necessary, however, to know the temperature effect on the liquid and make corrections for it. In determining some of the refractive indices of acetylphenylhydrazine, phthalic anhydride, and s-diphenylcarbazide, the liquids were made of mixtures of n-butyl phthalate and \( \alpha \)-monobromonaphthalene. The temperature coefficient curves for a typical series of liquids are shown in Figure 5. It was found that the temperature coefficient is about \(-0.0004\) refractive index units per degree. Since the inherent accuracy of the immersion method is about \(\pm 0.001\) index units, a difference of two degrees or less between the temperature of the refractometer and that of the microscope stage was negligible.

**High index liquids.** The liquids mentioned in the previous paragraph are suitable for measurements up to a refractive index value of 1.658 (that of \( \alpha \)-monobromonaphthalene). Between this value and 1.74 it was necessary to use a mixture of methylene iodide \((N = 1.74)\) and one of the liquids of lower index.

The Abbe type refractometer is usable up to an index value of 1.700. For liquids above this limit a Zeiss Pulfrich refractometer was employed. In both cases the
FIGURE 5. TEMPERATURE COEFFICIENT CURVES FOR TYPICAL IMMERSION LIQUIDS
crystals were first examined by means of a set of Eastman Kodak standard immersion liquids. When the refractive index was known roughly, a set of 4 to 6 liquids was made up, if the index was in the range of the Abbe refractometer, with a refractive index interval between liquids of 0.002 unit. The index of the solid was then found in relation to those of the known liquids.

Where the index was above 1.700, the limit of the range of the Abbe, the Zeiss Pulfrich refractometer was used by mixing pure methylene iodide and methylene iodide saturated with sulfur in the refractometer cell until the index of the crystals had been closely bracketed by small samples withdrawn from the cell. A reading of the graduated circle was taken just before the withdrawal of each sample.

Both in making up liquids to known refractive index values on these instruments and in observing crystals mounted in the liquids a sodium lamp was used to eliminate possible confusion or error due to differences in dispersive power of the various liquids and solids.
INDICES OF REFRACTION

<table>
<thead>
<tr>
<th>Compound</th>
<th>Index</th>
<th>Value obtained (±0.002)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Acetylphenyl-hydrazine</td>
<td>alpha</td>
<td>1.585</td>
</tr>
<tr>
<td></td>
<td>beta</td>
<td>1.609</td>
</tr>
<tr>
<td>Phthalic Anhydride</td>
<td>alpha</td>
<td>1.508</td>
</tr>
<tr>
<td></td>
<td>beta</td>
<td>1.690</td>
</tr>
<tr>
<td></td>
<td>gamma</td>
<td>1.784</td>
</tr>
<tr>
<td>s-Diphenyl-carbazide</td>
<td>alpha</td>
<td>1.610</td>
</tr>
<tr>
<td></td>
<td>beta</td>
<td>1.677</td>
</tr>
</tbody>
</table>

OPTIC AXIAL ANGLE. Among anisotropic crystals there are some that have two different refractive indices and others that have three. Those that have only two possess one particular direction from which the crystal appears isotropic. It exhibits no extinction, but it does possess an interference figure which indicates that it is not in truth isotropic. This direction is called the optic axis. Substances that have three indices of refraction possess two such axes, which lie in the plane formed by two of the optic directions. This plane is then termed the optic plane, and the angle between the optic axes is called the optic axial angle.

This angle can be found by orienting a crystal with a universal stage and actually turning the angle between positions of isotropic behavior and reading the angle on
the graduated circle. It is also possible to calibrate a micrometer eyepiece by examining the interference figures of several substances of known optic axial angle.

The angle can also be calculated, when all three indices of refraction are known, from the relation given by Gibb (5, p. 291):

\[
\cos^2 V = \frac{\gamma^2 (\beta^2 - \alpha^2)}{\beta^2 (\gamma^2 - \alpha^2)} \quad (7)
\]

where \( V \) is the optic axial angle inside the crystal, and \( \alpha, \beta, \gamma \) are the indices of refraction.

Substituting the experimentally determined values for phthalic anhydride,

\[
\cos^2 V = \frac{3.183(2.855-2.274)}{2.855(3.183-2.274)}
\]

= 0.714

\( \cos V = 0.846 \)

\( V = 32.3^\circ \)

\( 2V = 64.6 = 64^\circ 36' \)

**SIGN OF DOUBLE REFRACTION.** One of the three biaxial optic directions is always in the position of the bisector of the acute angle between the optic axes. This direction is called the acute bisectrix. In a crystal whose sign of double refraction is positive this direction will be that of the highest index of refraction. Conversely, a negative crystal has its smallest index of refraction in the position of the acute bisectrix.
The determination of the sign is very quickly done by observing the effect of a quartz wedge compensator on the colored rings of the interference figure seen when the acute bisectrix is vertical. The direction of the slow ray (highest index of refraction) is detected by noting in which quadrants compensation of the color-producing retardation occurs.

**SIGN OF DOUBLE REFRACTION**

<table>
<thead>
<tr>
<th>Compound</th>
<th>Sign</th>
</tr>
</thead>
<tbody>
<tr>
<td>Acetylphenyl-hydrazine</td>
<td>+</td>
</tr>
<tr>
<td>Phthalic Anhydride</td>
<td>-</td>
</tr>
<tr>
<td>s-Diphenyl-carbazide</td>
<td>+</td>
</tr>
</tbody>
</table>

**DISPERSION.** The variations in refractive index of a substance with changes in the wave length of the light is called the dispersion. The dispersion is quantitatively measured by determining the difference in the refractive index given by two of the lines of the hydrogen arc spectrum.

One of the effects of dispersion in crystals is to cause differences in the optic angle for different colors. A qualitative measure of the dispersion can be obtained by noting on the acute bisectrix interference figure whether the inside or outside of the dark band through the optic
axis position is tinged with red color. If the red is toward the outside while the inner side is tinged violet or blue, the indication is that the optic axis is less for red than for violet light.

The tabulation below gives the dispersions as they have been observed for the compounds listed. The color effect for acetylphenylhydrazine and s-diphenylcarbazide could be seen only by moving the mirror at the base of the microscope to direct the strongest light upon the optic axis area of the interference figure.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Dispersion</th>
</tr>
</thead>
<tbody>
<tr>
<td>Acetylphenylhydrazine</td>
<td>v&gt;r (slight)</td>
</tr>
<tr>
<td>Phthalic Anhydride</td>
<td>v&gt;r</td>
</tr>
<tr>
<td>s-Diphenylcarbazide</td>
<td>v&gt;r (very slight)</td>
</tr>
</tbody>
</table>

OPTIC DIRECTION LOCATIONS WITH REFERENCE TO CRYSTALLOGRAPHIC AXES. It is often convenient for persons using tabulated crystallographic data to have given the positions of the optic directions of a crystalline material in relation to the crystallographic axes. When the crystallographic axes have been either arbitrarily selected from an examination of the external appearance or
the true set determined by single crystal x-ray analysis, the interference figures of one or two views of the crystal will usually locate the acute bisectrix ($B_{x_a}$) and the optic plane. This is sufficient to correlate fully the optic and crystallographic directions.

**LOCATIONS OF OPTIC DIRECTIONS**

<table>
<thead>
<tr>
<th>Compound</th>
<th>Optic direction</th>
<th>Crystallographic location</th>
</tr>
</thead>
<tbody>
<tr>
<td>Acetylphenylhydrazine</td>
<td>$B_{x_a}$</td>
<td>$\perp (010)$</td>
</tr>
<tr>
<td></td>
<td>Optic plane</td>
<td>(100)</td>
</tr>
<tr>
<td>Phthalic anhydride</td>
<td>$B_{x_a}$</td>
<td>$\perp (100)$</td>
</tr>
<tr>
<td></td>
<td>Optic plane</td>
<td>(001)</td>
</tr>
<tr>
<td>s-Diphenylcarbazide</td>
<td>$B_{x_a}$</td>
<td>$\perp (010)$</td>
</tr>
<tr>
<td></td>
<td>Optic plane</td>
<td>(100)</td>
</tr>
</tbody>
</table>
FUSION DATA

In observing the crystallographic behavior of a substance, the manner in which it fuses or crystallizes from the melt is often peculiar to that substance. Other physical properties are sometimes revealed in response to heat and can be conveniently detected and observed with the hot-stage microscope.

MELTING POINTS. The melting point of each of the preparations was checked against the value, shown in the table below, as it appears in the literature. Only preparations whose melting points agreed closely with the literature values were used for the determination of physical properties.

MELTING POINTS

<table>
<thead>
<tr>
<th>Compound</th>
<th>m.p., °C.</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Acetylphenylhydrazine</td>
<td>129</td>
<td>(8, p.336)</td>
</tr>
<tr>
<td>Phthalic anhydride</td>
<td>130.8</td>
<td>(8, p.604)</td>
</tr>
<tr>
<td>s-Diphenylcarbazide</td>
<td>175</td>
<td>(10, p.1133)</td>
</tr>
</tbody>
</table>

These values were checked on the melting point block and used, along with naphthalene (m.p. = 80.2°C. (8, p.562)), to calibrate the thermometer of the hot-stage microscope. The hot-stage thermometer, however,
was used only to keep track of the approximate temperature, and not to make any quantitative measurements.

SUBLIMATION. Only phthalic anhydride, of the compounds studied, showed any tendency to sublime readily. It was necessary to change the glass compartment-cover on the hot-stage microscope several times during each fusion study because the sublimate obscured the field. Some of the sublimate crystals which formed in this manner are shown in Figure 6. The production of larger quantities of the sublimate has been described under crystal preparations.

FORMATION OF A GLASS. One of the compounds, s-diphenylcarbazide, undergoes slight decomposition at the melting point (10, p.1132). This probably contributes to its habit of forming a glass unless seeded and held just below the melting point. The crystals in Figure 7 were grown from the melt in about two hours by this procedure.

POLYMORPHISM. When a compound has more than one crystalline phase, each possessing its own physical constants and usually a temperature range over which it is the most stable form, the phases are called polymorphic forms. The presence of this behavior is noticed by changes in the crystalline form or optical properties as the substance undergoes temperature changes. These commonly occur while the solid is being warmed, or while it is
Sublimates on the hot-stage microscope compartment cover

growing rapidly parallel to the rods x40

growing slowly, near the melting point, perpendicular to the edge x40

Crystallizations from the melt

Figure 6. Photomicrographs of phthalic anhydride
Growing slowly at about 140°C
x40

Growing very slowly at about 155°C
x40

s-Diphenylcarbazide

Growing rapidly x40

Growing slowly near the melting point x40

Acetylphenylhydrazine

Figure 7. Photomicrographs of crystallizations from the melt
solidifying from the melt under controlled conditions.

s-Diphenylcarbazide, upon being warmed on the hot stage, underwent a fracturing or crumbling at something less than 100°C. that resembled a change of form. However, the powder x-ray diffraction patterns of both the stable (normal) form and the form that had apparently changed were identical and it is thought that no polymorphism was observed. In the case where crystals were obtained from the melt, they gave the same powder x-ray pattern also, which confirms this conclusion.

There was no evidence in any way for polymorphism in the case of phthalic anhydride.

Acetylyphenylhydrazine behaved in a manner quite similar to s-diphenylcarbazide when warmed to about 85°C. on the hot stage; the powder x-ray pattern in this case, however, was definitely different from that of the low-temperature form. This same high-temperature form pattern was obtained from all crystals formed by crystallization from the melt, and it seems certain that there are at least two polymorphic forms of s-diphenylcarbazide.
PHOTOMICROGRAPHY

Although the photomicrographs found in Figures 4, 6, and 7 are incidental to the experimental determinations of physical constants and required somewhat less time and effort than other phases of the project, the technique employed will be briefly described.

The camera was a "Micca," built by the Leitz company, which fits into the microscope drawtube when the eyepiece has been removed. The film, chosen for fine grain, was DuPont Defender Fine Grain Pan. High contrast was sought in the developing procedure by using the DuPont 6-D formula and standardizing the time at 20 minutes. DuPont 1f fixer was used.

That some of the photomicrographs show fairly low contrast is due to both the very nature of the quite transparent crystals and the inexperience of the operator in handling the lighting. The microscope-lamp distance and the substage position were held constant, but the differences in the optical systems of the hot-stage and the Spencer research model microscopes influence the intensity of the lighting.

The focus was adjusted by correlating by trial and error exposures the focus at the film surface with that observed through the right-angle eyepiece built into the camera.
SUMMARY

The purpose of the work reported in this thesis was to determine for several industrially or analytically important compounds those physical constants which can be determined by crystallographic and x-ray diffraction methods. Those chosen were acetylphenylhydrazine, phthalic anhydride, and s-diphenylcarbazide.

Some of the more basic theoretical concepts have been discussed, along with the experimental results and the methods used and developed during the course of the project.

X-ray diffraction studies yielded values of the cell dimensions of acetylphenylhydrazine and powder method patterns of this compound and s-diphenylcarbazide. Powder patterns of phthalic anhydride agreed with previously published data.

Studies with the chemical microscope and the refractometer have provided crystallographic descriptions of all three compounds including their optical properties, interfacial angles, and behavior on crystallizing from various solvents and from the molten state.


