UNCLASSIFIED

AD NUMBER
AD022319
LIMITATION CHANGES
TO: **Approved for public release; distribution is unlimited.**
FROM: **Distribution authorized to U.S. Gov't. agencies and their contractors; Administrative/Operational Use; SEP 1953. Other requests shall be referred to Office of Naval Research, Washington, DC.**
AUTHORITY
ONR ltr dtd 13 Sep 1977

THIS PAGE IS UNCLASSIFIED

AD No. 22 319
ASTIA FILE COPY

4

OFFICE OF NAVAL RESEARCH

Contract Nonr-562(04)

NR-017-607

Annual Report No. 2

Summary for Period

1 September, 1952 - 1 September, 1953

X-RAY STUDIES OF SIMPLE CRYSTALS WITH FREEZING POINTS BELOW ROOM TEMPERATURE

I. THE CRYSTAL STRUCTURE OF ISOCYANIC ACID

II. THE CRYSTAL STRUCTURE OF CYANOGEN CHLORIDE

By

Werner C. von Dohlen

Robert B. Heiart

Gene B. Carpenter, Director

Metcalf Research Laboratory

Brown University

Providence, Rhode Island

1 November, 1953

AD No. 22319a
ASTIA FILE COPY

I. THE CRYSTAL STRUCTURE OF ISOCYANIC ACID

Werner C. von Dohlen and Gene B. Carpenter

ABSTRACT

Isocyanic acid is orthorhombic, space group Pnma. Unit cell dimensions are a = 10.82, b = 5.23, c = 3.57 Å. and the cell contains 4 molecules. Hydrogen bonds are either very weak or absent.

1. INTRODUCTION

The structure of the HNCO molecule in the vapor is well known. Our chief interest lay in finding the pattern of hydrogen bonds expected in this relatively simple situation. Furthermore it was remotely possible that the solid might be composed of cyanic acid molecules, HOCN, rather than isocyanic acid molecules, HCNO.

References to earlier work on the vapor and a description of our preliminary experiments and results are contained in Annual Report No. 1. These results included the two possibilities for the space group, the approximate unit cell dimensions, and the number of molecules per unit cell.

2. EXPERIMENTS

The density of solid isocyanic acid was measured at about -195°C. A liquid sample was frozen slowly up to a mark in a pycnometer, the excess liquid was pumped off, and the pycnometer was sealed and weighed at room temperature.

(The sample of course polymerized inside.) The resulting value was 1.41 g./cc. This verifies that the number of molecules per unit cell is 4.

When a crystal of isocyanic acid is grown in a capillary, it is always oriented with the c axis nearly parallel to the axis of the capillary. In order to obtain x-ray diffraction photographs with a different orientation, a crystal was grown slowly around a bend in a bent capillary. In this way the [102] direction was brought parallel to the axis of rotation. A series of photographs was then prepared; the crystal, however, broke up gradually into several smaller, almost parallel crystals during the course of the experiment, so that the quality of the photographs was not as high as that of earlier sets. It was still possible to extract valuable information from them.

On several occasions powder patterns with fiber-like partial orientation were obtained. These appeared to be of two different kinds.

3. DETERMINATION OF THE STRUCTURE

More detailed and exhausitive measurements on the x-ray records yielded the following more accurate values of the unit cell dimensions:

$\underline{a}$ = 10.82. $\underline{b}$ = 5.23. $\underline{c}$ = 3.57Å all + 0.02Å.

The density calculated from these dimensions with the assumption of four molecules per unit cell is 1.414 g./cc., in agreement with the measured value 1.41 g./cc.

The oscillation photographs were indexed by graphical methods. Intensities were then estimated by the multiple-film technique. Our measurements indicated that the film factor -- the ratio of the intensity on one film to the intensity on the film behind it -- had the value 4.4 for Kodak No - Screen film and CuK_α radiation at normal incidence. These intensities were reduced to structure factor values by the usual methods. Values have been measured for 153 of the 255 structure factors accessible with CuK_α radiation; a further 72 were too weak to observe on the photographs, and 30 could not be examined in these experiments.

The first step in determining the atomic arrangement was the calculation of the Patterson projection P(uv). This vector map revealed a high concentration of peaks along the lines v = 0 and v = $\frac{1}{2}$, and no appreciable peaks between. This indicates that all atoms lie in equidistant parallel layers separated by $\frac{1}{2}\underline{b}$, at least to a good approximation. This pattern results automatically from the possible space group Pnma but could occur only as a somewhat sur-

prising coincidence if the other possible space group, $Pn2_1a$, were correct.

A relatively sensitive, although only qualitative, test of the deviation of the molecules from these planes was carried out as follows. If the molecules lie in these parallel planes, then (as it works out) the structure factors for fixed indices h and ℓ should be the same for all even values of the index k (except for the normal decline with increasing scattering angle) and separately the same for all odd values of k. The structure factor values were arranged to enable this prediction to be tested, and it was qualitatively verified. Thus it is concluded that the molecules can deviate only slightly, if at all, from the mirror planes.

The space group Pnma then requires that the y-coordinate of all atoms be either 1/4 or 3/4 (in fractions of the b cell edge), and packing considerations require that all atoms in one molecule have the same y-coordinate. The choice between these values amounts merely to the choice of origin of the unit cell, so that all y-coordinates were chosen to be $\frac{1}{4}$. Six additional coordinates are then needed to define the positions of the three atoms (other than hydro-

gen) in one molecule; the positions of the other molecules are then determined by symmetry.

The next step was to attempt to choose the three x-coordinates so as to give interatomic vectors satisfying the Patterson projection P(uv). The first choice was then refined by the usual Fourier method, in the xy plane. The electron density projection $\rho(xy)$ showed three atoms clearly, and also two smaller peaks which were believed to be spurious. However the magnitudes of the structure factors F_{hk0} calculated for this structure were in only fair agreement with the measured magnitudes; the usual discrepancy factor was about 35%. Consequently it had to be concluded that this structure was erroneous.

A second trial structure was quickly found which appeared to be in slightly better agreement with the Patterson projection. The Fourier refinement procedure was followed again, and this time the discrepancy factor reduced smoothly to a reasonable value.

The next step was the construction of a second Patterson projection, P(uw). Comparison with P(uv) showed that the x-coordinates previously found had to be changed to $\frac{1}{4}$-x in each case; this amounts only to changing the origin

from one symmetry element to another and represents only making a choice between two alternatives that could have been deduced from P(uv).

The approximate structure is then defined by the parameters in Table I.

Table I

Coordinate	Atom N	Atom C	Atom O
x	0.064	0.169	0.269
y	0.250	0.250	0.250
z	0.118	0.216	0.328

In order to test the general correctness of this structure, the complete set of structure factors was calculated for comparison with the observed values. The numerical part of these calculations was kindly performed for us by the Office of Statistical Services of the Massachusetts Institute of Technology. The agreement was qualitatively very good. In order to make a quantitative comparison, it was necessary to determine the best scale factor for the observed magnitudes (since only relative values were measured) and the best temperature factor for the calculated magnitudes. The slightly elliptical shape of the atoms in the Fourier

projections indicated that an anisotropic temperature factor was required, which involves 3 adjustable parameters. These 3 parameters and the scale factor were determined simultaneously by a least-squares treatment of observed and calculated (hk0) and (h0ℓ) structure factor magnitudes. The introduction of these parameters then yielded a discrepancy factor of 17.1% for the complete set of structure factors, omitting those which were not observed. This value is sufficiently good to insure the general correctness of the structure. It will be necessary in the future work to make only small adjustments in the atomic positions to arrive at the structure in best agreement with the total data.

4. DESCRIPTION OF THE STRUCTURE

The approximate structure determined as described presents the following picture. The HNCO molecules are arranged in infinite zig-zag chains running through the crystal parallel to a. These chains lie in the mirror planes of Pnma perpendicular to b. The chains then pack together side by side to form plane sheets in these mirror planes. These sheets finally stack together to form the complete crystal; the orientation of the molecules along

a alternates in adjacent sheets.

Important distances and angles are:

N - C = 1.19 Å	C - N...O = 159°
C - O = 1.15	N...O - C = 164°
N...O = 3.20	

The intramolecular distances are similar to those found in the isolated molecule (in the vapor). The surprising feature is the long (3.21 Å) hydrogen bond and the awkward angle (159°) that it makes with the axis of the molecule. Both features indicate that it is much weaker than was expected, and may not even justifiably be called a hydrogen bond at all. If, on the other hand, the molecule were in the cyanic acid form HOCN the angle (164°) is even more awkward.

The hydrogen atom itself has not yet been located in any Fourier projection; it may be discernable in a section of a 3 dimensional Fourier syntheses.

The only suggestion that can now be offered for the absence of strong hydrogen bond runs as follows. Strong hydrogen bonds must certainly be formed if one infinite chain of isocyanic acid molecules is formed. Then when these chains pack together, the van der Waals attractions between

adjacent chains produce a sufficient distortion of the chain to weaken greatly the hydrogen bond. A drawing of the structure with van der Waals radii for the atoms makes this appear plausible.

A more extensive discussion of the structure will not be justified until the refinement is completed.

Evidence for the existence of another solid modification is accumulating, but nothing is known of its structure.

AD No. 223 319B
ASTIA FILE COPY

II. THE CRYSTAL STRUCTURE OF CYANOGEN CHLORIDE

Robert B. Heiart and Gene B. Carpenter

A. ABSTRACT

Cyanogen chloride is orthorhombic, space group probably Pmmn. Unit cell dimensions are a = 5.68, b = 3.97, and c = 5.74 Å and the cell contains 2 molecules. In the tentative structure, the molecules are parallel to c; then the molecules must be pressed closer together along c than would be expected from van der Waals contacts.

1. INTRODUCTION

Cyanogen chloride, ClCN, seems an attractive material to study by the same low temperature techniques developed for isocyanic acid. Although there can be no hydrogen-bonding, there is reason to expect that exceptionally strong forces act between the Cl atom of one molecule and the N atom of another; such an attraction is in some ways analogous to a hydrogen bond. Evidence for this comes from studies of cyanogen iodide; Townes and Dailey[1] found, from nuclear

---

(1) C.H. Townes and B.P. Dailey, J. Chem. Phys. 20 35 (1952)

---

quadrupole coupling studies that the bond character differs in the solid from that in the vapor; Ketelaar and Zwartsen-

berg[2] found, from a crystal structure determination, that

---

(2) J.A.A. Ketelaar and J.W. Zwartsenberg. Rec. Trav. Chim, 58, 448 (1939)

---

the I of one molecule lies very near the N of another molecule, nearer than would be expected for a normal van der Waals contact. But the I···N distance in ICN cannot be measured very accurately because the I atom dominates the observed x-ray diffraction. Thus ClCN, with its smaller halogen atom, furnishes a good test and extension of these ideas.

2. EXPERIMENTS

A 30 ml. sample of cyanogen chloride* was purified by

---

*The material was given to us by Dr. D.J. Berets of the American Cyanimid Company.

---

distillation over zinc powder, agitation with zinc oxide, and a final distillation through a drying tower containing phosphorous pentoxide. This process was designed to remove Cl_2, HCl, HCN, and H_2O, which were believed to be the most likely impurities.

Small portions were distilled into capillaries, which were then sealed off with the body of the capillary immersed

in liquid nitrogen. The capillaries were less than 0.05 cm. in internal diameter.

Such a ClCN-filled capillary was fastened to the goniometer head of a Unicam rotation-oscillation x-ray camera. The sample was then frozen by a jet of cold nitrogen as was described in Annual Report No. 1. By freezing the sample slowly, and by running through cycles of partial melting and refreezing, the sample could be converted into what appeared to be a single crystal in some region of the capillary.

A series of x-ray photographs was then prepared at -30°C. with the well-crystallized portion of the sample rotating or oscillating in the x-ray beam. An improved film holder held the film in place around the crystal.

The crystals usually grew with the same crystal direction, named c, parallel to the axis of the capillary. Rotation and oscillation photographs were obtained from two crystals.

The density of solid ClCN was measured by a pycnometric method; the value is 1.55 g./cc. at about -30°C.

3. RESULTS

Although both crystals gave rotation photographs like that from a perfectly-oriented single crystal, analysis of

the oscillation photographs showed that, in both cases, the "crystal" was in fact comprised of several smaller crystals, each with its c axis parallel to the axis of rotation, but with various orientations of the a and b axes. Thus when the $\ell = 0$ reciprocal lattice net was constructed, it turned out that at least three main grids were necessary to index all the reflections. Considerable information was, however, obtained from these photographs.

The ClCN crystal is orthorhombic with a = 5.68, b = 3.97, and c = 5.74 Å. The unit cell volume and the measured density correspond to 2 ClCN molecules per unit cell. The systematic absences indicated the probable space groups to be Pmmn and $Pm2_1n$.

Intensities were measured visually by the multiple-film technique. In order to reduce absorption complications, each (hkℓ) intensity value was the sum of the intensities measured for each observed member of the form {hkℓ} for all these crystal fragments. Structure factor magnitudes were computed from the intensities as usual.

A Patterson projection P(uv) was then constructed. It exhibited perfectly round peaks only, in a centered array. This indicates that the molecules are perpendicular to the

plane of this projection, i.e., parallel to c. This in turn indicates that the proper space group is Pmmn since this arrangement arises automatically in that space group but could arise only by accident in $Pm2_1n$.

Now the expected length of the ClCN molecule computed from Pauling's[3] bond lengths and van der Waals radii, is

---

(3) L. Pauling, "The Nature of the Chemical Bond", Cornell, 1945.

6.21 Å. If the tentative structure described above is indeed correct, then the length of the molecule in the crystal is only 5.74 Å. Thus it appears that the predicted shortening due to strong binding between adjacent molecules is realized in the crystal.

Further work is being directed toward working out the precise positions of the atoms along the c axis.

TECHNICAL REPORTS DISTRIBUTION LIST

BROWN UNIVERSITY

Contract Nonr-562(04), NR 017 607

A. Government Distribution

1. Department of Defense

Research and Development Board
Information Office Library Branch
Pentagon Building
Washington 25, D. C. (2 copies)

Armed Services Technical Information Agency
U. B. Building
Dayton 2, Ohio (2 copies)

2. Department of the Navy

Chief, Bureau of Aeronautics
TD-4
Navy Department
Washington 25, D. C.

Chief, Bureau of Ordnance
Rea
Navy Department
Washington 25, D. C.

Chief, Bureau of Ships
Code 300
Navy Department
Washington 25, D. C.

Chief of Naval Research
Office of Naval Research
Washington 25, D. C.
Attn: Physics Branch (Code 421) (3 copies)

Director,
Naval Research Laboratory
Technical Information Officer (Code 2000 (9 copies)
Code 2021 (2 copies)
Washington 20, D. C.

Director
Office of Naval Research Branch Office
150 Causeway Street
Boston 14, Massachusetts

Director
Office of Naval Research Branch Office
346 Broadway
New York 13, New York

Director
Office of Naval Research Branch Office
86 East Randolph Street
Chicago 1, Illinois

Director
Office of Naval Research Branch Office
100 Geary Street
San Francisco 9, California

Director
Office of Naval Research Branch Office
1031 East Green Street
Pasadena 1, California

Officer in Charge
Office of Naval Research London Branch Office
Navy #100
Fleet Post Office
New York, New York (2 copies)

Physics Department
Post Graduate School
U. S. Naval Academy
Annapolis, Maryland

Librarian
U. S. Naval Post Graduate School
Monterey, California

U. S. Naval Electronics Laboratory Library
San Diego 52, California

Director
Physics Research
Naval Ordnance Laboratory
White Oaks, Maryland

Director
Physics Research
Naval Ordnance Test Station
Inyokern
China Lake, California

3. Department of the Air Force

Commanding General
Air Research and Development Command
Attn: Office of Scientific Research
Post Office Box 1395
Baltimore 3, Maryland (2 copies)

Air Adjutant General
Mail and Receiving Management Division
Headquarters, U.S.A.F.
Washington 25, D. C.

4. Department of the Army

Commanding Officer
Engineering Research and Development Laboratories
Fort Belvoir, Virginia
Attn: Technical Intelligence Branch

Office of Ordnance Research
Box CM, Duke Station
Durham, North Carolina (2 copies)

Signal Corps Engineering Laboratory
Fort Monmouth, New Jersey
Attn: Technical Information Officer

5. Department of Commerce

Office of Technical Services
Technical Reports Section
Department of Commerce
Washington 25, D. C. (2 copies)

Director
National Bureau of Standards
Washington 25, D. C. (2 copies)

Director
National Bureau of Standards
Corona, California

6. Other Agencies

National Research Council
Division of Physical Sciences
National Academy of Sciences
Washington, D. C.

Director
National Science Foundation
Washington 25, D. C.

U. S. Atomic Energy Commission
Technical Information Service
P. O. Box 62
Oak Ridge, Tennessee

B. Non-Government Distribution

Brooklyn Polytechnic Institute
99 Livingston Street
Brooklyn 2, New York
Attn: Professor I. Fankuchen

California Institute of Technology
Norman Bridge Laboratory of Physics
Pasadena, California
Attn: Dr. J. W. M. DuMond

Ohio State University
Department of Physics
Columbus 10, Ohio
Attn: Dr. C. H. Shaw

Washington State University
Department of Physics
Pullman, Washington
Attn: Dr. S. T. Stephenson

University of Wisconsin
Department of Physics
Madison, Wisconsin
Attn: Professor W. W. Beeman