The Crystal Structure of Monoclinic Phenylhydrazine Hydrochloride, $C_6H_5NHNH_3Cl$

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Crystal structures of hydrazonium salts containing the $N_2H_6^{2+}$ ion, such as hydrazonium fluoride, $N_2H_6F_2$,[1] chloride, $N_2H_6Cl_2$,[2] and sulfate, $N_2H_6SO_4$,[3] and also hydrazinium salts containing the $N_2H_5^+$ ion, such as hydrazinium bromide, N_2H_5Br,[4] and chloride, N_2H_5Cl,[5] have hitherto been determined by X-ray methods. However, few of the structures of the substituted hydrazine salts have yet been examined. In order to obtain further information about the relationship among these structures of crystals, the substituent effects, and the nature of the chemical bonds in hydrazine salts, the present author has attempted to investigate the crystal structure of phenylhydrazine hydrochloride by means of X-ray analysis. During the preparation of the sample, it was found that this substance was dimorphous, one modification being monoclinic and the other orthorhombic. The crystal structure of the monoclinic modification was first determined; it will be reported on in the present paper and its structure discussed. The structure of the orthorhombic modification will be reported on shortly.

Experimental

Single crystals for this work were obtained from saturated aqueons solution by slow evaporation at room temperature. The crystals were thin plates elongated along direction of the monoclinic c axis and showed an excellent cleavage parallel to the crystal plane (010).

Ni-filtered Cu$K\alpha$ radiation was employed in all X-ray experiments. The specimens used had the following cross-sections at right angles to the axes of rotation: 0.1×0.15 mm. for the c axis rotation, and 0.15×0.2 mm. for the a axis. Crystallographic data were obtained from oscillation and from Schiebold-Sauter and Weissenberg photographs of the equatorial and layer lines about two crystallographic axes (c and a). Photographs of the $(hk0)$, $(0kl)$ and (hkl) reflections were taken by means of an integrating Weissenberg camera for each zone, using the multiple-film technique. Intensities were estimated visually with the aid of standard intensity scales prepared by the exposure time method. The intensity ratios among the multiple-films were determined by the Geiger-Müller counter method. The corrections for polarization and Lorentz factors were made in the usual way. Relative values of the observed structure factors were then deduced by the ordinary procedure. No correction for the absorption was made because samll crystals were employed.

Determination of the Structure

Unit Cell and Space Group.—X-Ray examinations show that the crystal belongs to the monoclinic system and has the following cell dimensions:

$$b = 7.82 \pm 0.03 \text{ Å}$$
$$a = 30.80 \pm 0.06 \text{ Å}$$
$$c = 3.87 \pm 0.02 \text{ Å}$$
$$\beta = 130.3^\circ \pm 0.5^\circ$$

The space group was uniquely determined to be $C_{2h}^5-P2_1/a$ by the observed rules of absent reflections. Though accurate density measurement was difficult and the value thus obtained was rather poor, it was sufficient for the determination of the number of formula units in a cell-four formula units per unit cell. The calculated density is 1.344 g. cm^{-3}.

Approximate Structure. — Direct sign determination of the structure factors, using Harker-Kasper inequalities and Sakurai's chart,[6] gave only the signs of a few structure factors. Since the crystal has a heavy atom (chlorine), the position of this atom was easily determined by the interpretation of the two-dimensional peak-sharpened Patterson projections along the a and c axes. Further, since the lengths of the a and c axes are short, the positions of the phenylhydrazine group could be determined by a carerful interpretation of these Patterson maps. The approximate position of the chlorine atom was found to be (1/4, 0.05, 0). Ignoring the end nitrogen atom (in the present investigation, $N_{(2)}$), we can consider a symmetry axis of the phenylhydrazine group.

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[1] M. L. Kronberg and D. Harker, *J. Chem. Phys.*, **10**, 309 (1942).

[2] J. Donohue and W. N. Lipscomb, ibid., **15**, 115 (1947).

[3] I. Nitta, K. Sakurai and Y. Tomiie, *Acta Cryst.*, **4**, 289 (1951).

[4] K. Sakurai and Y. Tomiie, ibid., **5**, 289 (1952).

[5] K. Sakurai and Y. Tomiie, ibid., **5**, 293 (1952).

[6] K. Sakurai, ibid., **5**, 546 (1952).

This axis was found to be approximately on (3/4, y, 0). The contribution of each atom except the end nitrogen atom $N_{(2)}$ to $F(hk0)$ and $F(0kl)$ of $k=2n+1$ was essentially zero for these approximate atomic parameters. However, by putting the $N_{(2)}$ atom in an appropriate position, the signs of a sufficient number of structure factors with $k=2n$ and a few signs of structure factors with $k=2n+1$ could be determined, so that the calculation of preliminary Fourier projections $\rho(xy)$ and $\rho(yz)$ could be carried out. After each three successive syntheses of Fourier projections along the c and a axes, it was found that the agreement between F_o and F_c in $F(hk0)$ and in $F(0kl)$ with $k=2n$ was much improved, whereas there still remain large discrepancies with $k=2n+1$, suggesting that either the chlorine atom or the symmetry axis of phenylhydrazine, or both, may not lie precisely on the special lines mentioned above.

Refinement of the Structure.—*xy-Projection.*—The refinement of the coordinates was carried out by the trial and error method at the first stage to find out the direction of the chlorine atom and the symmetry axis of the phnylhydrazine group from the two-fold screw axes, (1/4, y) and (3/4, y) respectively. The further refinement of this projection was carried out by successive (F_o-F_c) syntheses. No attempt was made to introduce individual temperature factors. The temperature factor finally employed for all atoms in this projection was $\exp(-3.8\sin^2\theta/\lambda^2)$. The atomic scattering factors used in the calculation of the structure factors were those given by Berghuis et al.⁷⁾ The final value of the discrepancy index, $\sum||F_o|-|F_c||/\sum|F_o|$, was 0.15 for all $(hk0)$'s, and 0.10 if the unobserved F_o was omitted. The final electron density map is shown in Fig. 1.

yz-Projection.—The refinement of the coordinates was carried out by the trial-and-error method and Fourier syntheses, but no (F_o-F_c) synthesis was tried since all of the atoms in this projection were unresolved. After laborious work, the best z coordinates were finally determined. The values of the discrepancy factor for this zone were 0.16 and 0.12 (if the unobserved F_o was omitted). The temperature factor finally employed for this zone was $\exp(-3.6\sin^2\theta/\lambda^2)$. The final electron density map is shown in Fig. 2.

Two possible structures can be considered from the combinations of atomic coordinates which are determined independently from $\rho(xy)$ and $\rho(yz)$. The best agreement between

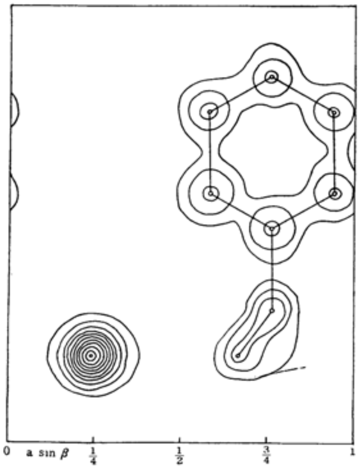

Fig. 1. Electron density distribution projected along the c axis. Contours are at every 2 e. Å^{-2}.

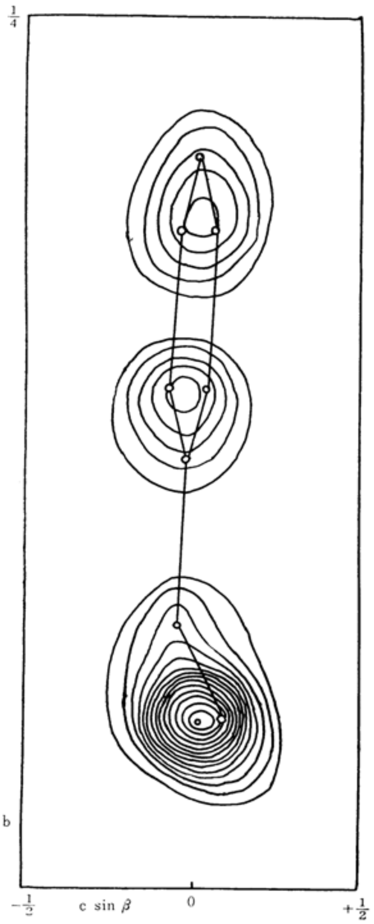

Fig. 2. Electron density distribution projected along the a axis. Contours are at every 2 e. Å^{-2}, the contour at the 2 e. Å^{-2} level being omitted.

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7) J. Berghuis, IJ. M. Haanappel, M. Potters, B. O. Loopstra, C. H. MacGillavry and A. L. Veenendaal, ibid.. **8**, 478 (1955).

F_o and F_c for $F(hkl)$ in these cases was sought so as to find out one reasonable final combination of parameters. Thus, the three dimensional atomic parameters were determined to be as given in Table I.

TABLE I. ATOMIC PARAMETERS

Atom	x	y	z
$C_{(1)}$	0.7608	0.1225	−0.0233
$C_{(2)}$	0.9400	0.1429	0.0433
$C_{(3)}$	0.9367	0.1888	0.0650
$C_{(4)}$	0.7575	0.2092	0.0083
$C_{(5)}$	0.5800	0.1883	−0.0483
$C_{(6)}$	0.5833	0.1425	−0.0700
$N_{(1)}$	0.7633	0.0754	−0.0500
$N_{(2)}$	0.6667	0.0492	0.0900
Cl	0.2433	0.0480	0.0167

The interatomic distances and bond angles calculated from the atomic parameters given in Table I are listed in Table II.

The Accuracy of the Numerical Results.—The standard deviations of the atomic coordinates estimated from the observed $\rho(xy)$ values are $\sigma(x_C)=0.006$, $\sigma(x_N)=0.005$ and $\sigma(x_{Cl})=0.002$ Å while those from the observed $\rho(yz)$ values are $\sigma(z_C)=0.013$, $\sigma(z_N)=0.012$ and $\sigma(z_{Cl})=0.005$ Å. The standard deviations of the C–N and N–N distances derived from these values are $\sigma(\text{C–N})=0.008$ and $\sigma(\text{N–N})=0.012$ Å.

Discussion

Figure 3 shows the atomic arrangement in the crystal projected along the c axis. The figure shows the values of the interatomic distances. The N–N distance is 1.432 Å, with the standard deviation of 0.012 Å. This is significantly shorter than the N–N single bond found in the hydrazine molecule (1.47 Å in the gaseous state[8] and 1.46 Å in a crystal[9]). The value seems to be slightly larger than that in $N_2H_6^{2+}$ (1.40—1.42 Å) and smaller than that in $N_2H_5^+$ (1.45 Å), but such differences may not be significant in view of probable uncertainty of these values. Therefore, it is difficult to say that the N–N distance found in the phenylhydrazine ion is really affected by the substituted phenyl group.

The phenyl group has ordinary dimensions in this crystal. The C–N bond distance in the phenylhydrazine ion is 1.455 Å, the standard deviation being 0.008 Å. This is slightly shorter than the C–N single bond distance, 1.475 Å, given by Cox and Jeffrey[10] from a survey of many experimental values. Since this shortening is probably significant, there may exist a slight conjugation effect between the lone orbital on the nitrogen atom $N_{(1)}$ and the π-bond orbital on the carbon atom of the phenyl group. From the results of conjugation, the nitrogen atom $N_{(1)}$ has a positive net charge and, therefore, the proton affinity will become weak. Thus, when phenylhydrazine acts as a monoacidic base, the end nitrogen, $N_{(2)}$, will attract the acid proton, forming an $-NH_3^+$ group, and $N_{(1)}$ will remain as an imino –NH– group. This is in accord with the results of the present experiment; i. e., the distances of N···Cl show that $N_{(1)}$ should be the imino –NH– group and $N_{(2)}$, the amino $-NH_3^+$ group.

The direction of the N–N bond deviates far from the plane formed by the phenyl group and the N–C bond, the azimuthal angle being 67.2°. This shows that the conjugation between the phenyl π-orbital and the lone pair orbital on $N_{(1)}$ occurs to a certain extent. As a matter of fact, if the conjugation between the phenyl group and the lone pair on $N_{(1)}$ were sufficiently strong, three bond directions of the imino nitrogen atom (and hence the N–N

TABLE II. INTERATOMIC DISTANCES AND BOND ANGLES (in Å unit)

$C_{(1)}-N_{(1)}$	1.455	$N_{(2)}\cdots N_{(1)}$	3.007
$N_{(1)}-N_{(2)}$	1.432	$N_{(2)}\cdots Cl$	3.134, 3.162, 3.224, 3.498
$C_{(1)}-C_{(2)}$	1.399	$N_{(1)}\cdots Cl$	3.356, 3.430, 3.690, 3.805
$C_{(2)}-C_{(3)}$	1.415	$Cl\cdots Cl$	3.870, 4.755, 4.404
$C_{(3)}-C_{(4)}$	1.417	$C_{(5)}\cdots C_{(3)}$	4.052
$C_{(4)}-C_{(5)}$	1.411	$C_{(5)}\cdots C_{(4)}$	4.134
$C_{(5)}-C_{(6)}$	1.415	$C_{(4)}\cdots C_{(4)}$	4.649
$C_{(6)}-C_{(1)}$	1.419	$C_{(4)}\cdots C_{(3)}$	4.116

$C_{(6)}-C_{(1)}-C_{(2)}$	127.5°	$C_{(5)}-C_{(6)}-C_{(1)}$	118.7°
$C_{(1)}-C_{(2)}-C_{(3)}$	113.9°	$C_{(6)}-C_{(1)}-N_{(1)}$	118.7°
$C_{(2)}-C_{(3)}-C_{(4)}$	119.2°	$C_{(2)}-C_{(1)}-N_{(1)}$	113.8°
$C_{(3)}-C_{(4)}-C_{(5)}$	126.6°	$C_{(1)}-N_{(1)}-N_{(2)}$	120.1°
$C_{(4)}-C_{(5)}-C_{(6)}$	114.1°		

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[8] P. A. Giguère and V. Schomaker, *J. Am. Chem. Soc.*, **65**, 2025 (1943).

[9] R. L. Collin and W. N. Lipscomb, *Acta Cryst.*, **4**, 10 (1951).

[10] E. G. Cox and G. A. Jeffrey, *Proc. Roy. Soc.*, **A207**, 110 (1951).

bond) would be coplanar with the phenyl group. Although the N–N bond deviates from the plane formed by the phenyl group, as has been observed, and the N–H bond lies on this plane, the conjugation is still possible should the –NH– group have a tetrahedral arrangement.

The phenyl group is significantly distorted. The C–C–C angles at $C_{(1)}$ and $C_{(4)}$ are 127.5° and 126.6° respectively; they are significantly larger than 120°. The C–C–C angles at $C_{(2)}$ and $C_{(5)}$ are significantly smaller than those at $C_{(1)}$ and $C_{(4)}$.

The end nitrogen atom, $N_{(2)}$, has three nearest chlorine neighbors, the N$\cdots$Cl distances being 3.134, 3.162 and 3.224 Å. Besides, $N_{(2)}$ is in contact with the $N_{(1)}$ belonging to the neighboring molecule, the distance being 3.007 Å. Two of the $N_{(2)}\cdots$Cl contacts, with 3.134 and 3.162 Å, and the $N_{(2)}\cdots N_{(1)}$ contact with 3.007 Å may be hydrogen bonds. This arrangement more or less resembles that formed in N_2H_5Cl,[5] although the hydrogen bonds in the latter are slightly stronger than those of the former. From the point of view of atomic arrangement, the $N_{(2)}\cdots$Cl with the distance of 3.224 Å is not a hydrogen bond. It is of interest to see that the $-NH_3^+$ groups in aniline hydrochloride[11] and cyclohexylamine hydrochloride[12] have no neighboring chlorine ion which is linked by a hydrogen bond.

The nitrogen atom, $N_{(1)}$, which is linked to the phenyl group has two nearest chlorine neighbors, the N$\cdots$Cl distances being 3.356 and 3.430 Å. Although these distances are not short enough, the directions connecting $N_{(1)}$ with the two chlorine atoms in question extend in the same proper directions as the NH$\cdots$Cl bonds. Since only one NH$\cdots$Cl hydrogen bond is possible for $N_{(1)}$, we must decide which direction is the proper hydrogen bond. If the former is the direction of NH$\cdots$Cl, the lone pair on the $N_{(1)}$ will lie nearly on the plane formed by the phenyl group, and, hence, the conjugation will not occur. On the other hand, if the latter is the NH$\cdots$Cl hydrogen bond, the lone pair on the $N_{(1)}$ can reserve a tendency to conjugate with the phenyl group. Therefore, it may be reasonable that the N$\cdots$Cl with the distance of 3.430 Å should be the weak hydrogen bond required by $N_{(1)}$ and that the N$\cdots$Cl with the distance of 3.356 Å should be a van der Waals contact. Such very weak hydrogen bonds are also found in the crystal of hydrazinium chloride, where the $-NH_2$ group of $N_2H_5^+$ ion has three chlorine neighbors, and two of the N$\cdots$Cl have proper directions as NH$\cdots$Cl hydrogen bonds, the distances being 3.43 and 3.49 Å.

The slightly positive net charge on the $N_{(1)}$ atom due to some conjugation effect, as has been mentioned before, will decrease the proton affinity of $N_{(1)}$. This can explain the fact that the NH$\cdots$N hydrogen bond (3.007 Å) in this crystal is slightly longer than that found in N_2H_5Cl, where the distace is 2.96 Å.

Phenylhydrazine ions are linked by the NH$\cdots$N hydrogen bonds, which form an infinite zig-zag chain along the c axis. This type of linkage is different from that found in N_2H_5Cl and N_2H_5Br, where the NH$\cdots$N hydrogen bond makes infinite spiral chains.

The projections of the crystal structure along the c and a axes are illustrated in Figs. 3 and 4 respectively. The figures given show the interatomic distances. Each two phenylhydrazine and chlorine ions are linked into a pair by $NH^+\cdots$Cl hydrogen bonds approximately on the (001) plane. Such dimers of

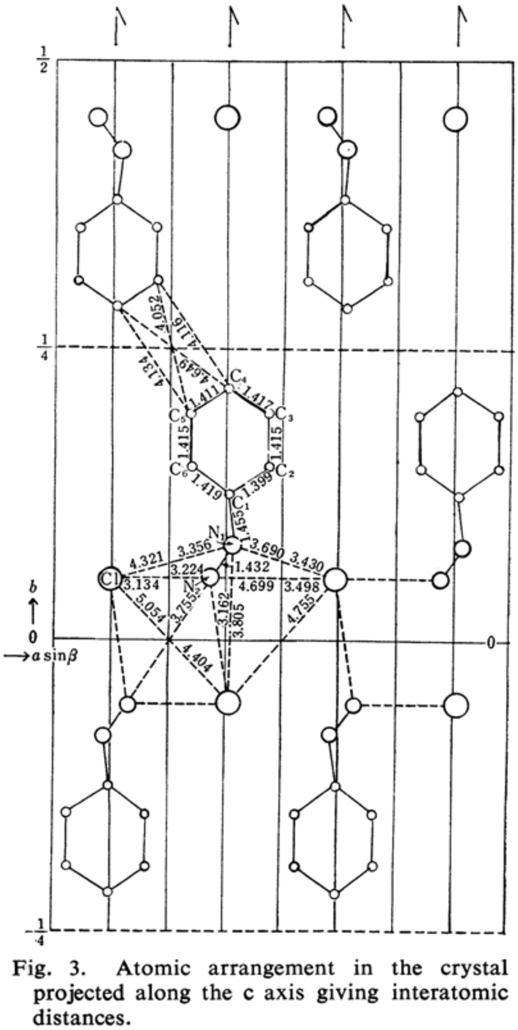

Fig. 3. Atomic arrangement in the crystal projected along the c axis giving interatomic distances.

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[11] C. J. Brown, *Acta Cryst.*, 2, 228 (1949).

[12] A. Shimada, Y. Okaya and M. Nakamura, ibid., 8, 819 (1955).

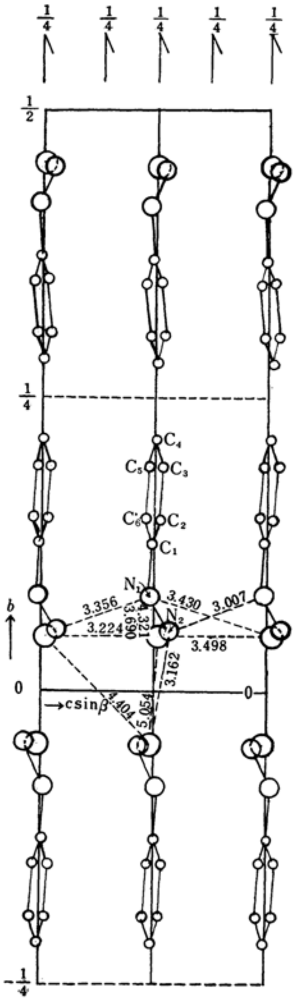

Fig. 4. Atomic arrangement in the crystal projected along the a axis giving interatomic distances.

positive and negative ions linked by hydrogen bonds are found in tropolone hydrochloride.[13] These pairs are linked by weak NH⋯N hydrogen bonds and are piled up into columns in the c axis direction. Such columns are linked by weak NH⋯Cl hydrogen bonds formed by $N_{(1)}$ atoms in the a axis direction.

As for the b axis direction, the phenyl groups are in contact with other phenyl groups by van der Waals force only; therefore, the cohesive force is not strong in this direction. This structural feature is compatible with the observed remarkable cleavage along the (010) plane.

It is of interest to compare the structure of the present crystal with those of aniline hydrochloride[11] and cyclohexylamine hydrochloride[12]. The structure of aniline hydrochloride is of a distorted caesium chloride arrangement, such as is also found in the structures of lower-membered alkylamine hydrochloride. On the other hand, cyclohexylamine hydrochloride crystallizes in a layer structure derivable from the sodium chloride arrangement, which is common in the structures of higher-membered alkylamine hydrochloride. It should be noted that the structure of phenylhydrazine hydrochloride has a remarkable layer structure, like cyclohexylamine hydrochloride, that each phenylhydrazine group is surrounded by six chlorine ions, and that each chlorine ion has six phenylhydrazine rings as its first neighbors. The packing is thus closely related to the sodium chloride type.

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[13] Y. Sasada and I. Nitta, This Bulletin, 30, 62 (1957).