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The Crystal Structure of Hydrazine

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The crystal structure of hydrazine is monoclinic C_{2h}^2–$P2_1/m$ with two N_2H_4 molecules in a cell of dimensions $a = 3{\cdot}56$, $b = 5{\cdot}78$, $c = 4{\cdot}53$ A., and $\beta = 109{\cdot}5°$. The N–N bond lies in the mirror plane with nitrogen atoms at $x_1 = 0{\cdot}037$, $z_1 = 0{\cdot}362$, and at $x_2 = 0{\cdot}736$, $z_2 = 0{\cdot}050$. The N–N bond distance is 1·46 A., and nearest non-bonded distances are 3·19, 3·25 and 3·30 A. The structure suggests an eclipsed configuration for the hydrazine molecule in the crystal, and does not appear to permit residual entropy to be retained at low temperatures.

Introduction

As part of a program of low-temperature studies the crystal structure of hydrazine was studied in order to determine the N–N bond distance, the molecular symmetry, and the nature of the hydrogen bonding. No previous X-ray investigation of the solid has been reported, but a value of 1·47 A. for the bond distance has been determined in an electron-diffraction study of the gas molecule (Giguère & Schomaker, 1943). An interpretation of the spectroscopic data and a determination of the heat capacity of hydrazine in the range from 12 to 340° K. have been made (Scott, Oliver, Gross, Hubbard & Huffman, 1949). The spectroscopic data do not appear to determine uniquely whether the hydrogen atoms in the molecules are in one of the opposed or staggered configurations, but the staggered configuration of molecular symmetry C_2 is favored. The calorimetric data yield for gaseous hydrazine at 298·16° K. an entropy which is 0·44 cal./deg./mole less than that calculated from structural parameters and spectroscopic assignments. While this difference is less than the combined uncertainty of the calorimetric and calculated values, these authors suggested the possibility of randomness of orientation in the solid, leaving residual entropy not included in the calorimetric value. Partly because of this possibility we have carried out a detailed determination of the crystal structure of hydrazine with the results described below.

Experimental

The sample of hydrazine was obtained from the late Dr H. M. Huffman, Bureau of Mines, Bartlesville, Oklahoma. He found it to be 99·75 mole % hydrazine, with a melting-point of 1·4° C. Samples of this material were distilled under vacuum into thin Pyrex capillary tubes less than 1 mm. in diameter. These tubes were sealed off on the vacuum line after freezing the material with liquid nitrogen, and were mounted directly on the goniometer heads of the Buerger precession or Weissenberg goniometers. All photographs were taken with Mo *K* or Mo *Kα* radiation. The approximate structure was determined from the precession photographs by trial-and-error methods, and the final parameters were determined from a Weissenberg photograph of the *h0l* zone, which gave a well-resolved projection of the structure. The main advantage of the use of the precession camera in studies of crystals below room temperature is that several zones may be recorded for a crystal with a given orientation inside the capillary, and it is therefore possible to cover a large region of reciprocal space without regrowing the crystal or reorienting the capillary with respect to the goniometer head. Use of the Weissenberg method for the *h0l* zone insured convergence of the Fourier series. In addition, it proved to be somewhat more convenient to obtain this zone on the Weissenberg goniometer because of a slight tendency for the crystals to grow with the *b* axis along the axis of the capillary.

The capillary, mounted on the goniometer head, was cooled by means of a cold air stream from a vacuum-jacketed nozzle mounted coaxially with the capillary. The air was obtained from a compressor, was then thoroughly dried by means of standard drying agents, and was then cooled by passing through coils immersed in a mixture of solid CO_2 and secondary butyl alcohol. The samples generally froze into a polycrystalline mass after undercooling sometimes by as much as 30°. In some of the early experiments the mass of crystals, usually oriented approximately in the same direction, would anneal to a single crystal if maintained for a few hours at a few degrees below the melting point. In later experiments this procedure was not as successful as repeated remelting of the solid, except for a small seed crystal, and regrowing slowly in a temperature gradient. This gradient was established by placing a tiny cardboard disc with a small hole in its center over the tip of the capillary. Thus by careful adjustment of the rate of flow of the air stream all of the solid could be melted except for a tiny fragment in the tip of the capillary, and the crystal could be regrown by increasing the rate of

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flow of the air stream. This procedure was found to yield single crystals consistently if reasonable care was taken. In the few precession photographs where fragments gave extra reflections, these could easily be identified and disregarded.

Most of the precession photographs were taken with the crystal at a temperature of about $-15°$ C. Here no appreciable difficulties were encountered with moisture condensation. During the somewhat longer Weissenberg photographs the crystals decomposed to such an extent that the single crystal was destroyed, apparently by a mild explosion inside the capillary. When the temperature was lowered to $-40°$ C., for the Weissenberg photographs, the rate of decomposition was sufficiently slow that exposures of as long as 12 hr. were successful. Moisture condensation was minimized by placing a small cylindrical jacket of cellulose acetate around the nozzle of the vacuum-jacketed tube for cold air. This jacket surrounded the crystal but did not touch the goniometer head. A stream of warm dry air was played on the outside of the jacket during the exposure. Moisture condensation was also decreased in the later experiments by working in a dehumidified room where the vapor pressure of water was maintained at less than 5 mm. The temperature of the crystal was measured by means of a copper–constantan thermocouple with its cold junction placed about 1 mm. from the capillary.

Although no essential modifications of the precession camera were made for low-temperature work, it was clearly necessary to provide changes in the Weissenberg camera that would permit placement of a layer-line screen and camera in position without disturbing the vacuum-jacketed cold-air tube. The most satisfactory method we found was to make use of a camera of radius about 4·3 cm. to replace the usual 2·8 cm. radius camera. A segment of the circular cross section in the back-reflection region was removed so that the camera could be placed over the spindle of the Weissenberg goniometer without disturbing the crystal. The missing region of the camera caused no significant loss of reciprocal-lattice points when molybdenum radiation was employed. The layer-line screen was made in three coaxial sections which could be slid on to the spindle of the goniometer when they were not in use. The crystal was oriented by the use of oscillation photographs on a flat-plate camera which was attached to the base of the Weissenberg goniometer, and was removed when the moving-film exposure was started.* As an aid in the intensity measurements, the multiple-film technique was used in which the films were interleaved with approximately 0·001 in. brass foil.

Determination of the structure

The unit cell and space group were determined from zero- and first-level precession photographs about [100], [001], [101] and [10$\bar{1}$]. The lattice is monoclinic with the systematic extinction only of 0*k*0 when *k* is odd. The lattice parameters are

$$a=3{\cdot}56\pm0{\cdot}01\text{ A},\quad b=5{\cdot}78\pm0{\cdot}01\text{ A},$$
$$c=4{\cdot}53\pm0{\cdot}01\text{ A.},\quad \beta=109°\,30'\pm6'.$$

The two possible space groups are C_{2h}^2–$P2_1/m$ and C_2^2–$P2_1$. Assumption of two N_2H_4 molecules in the unit cell leads to a calculated density of 1·20 g.cm.$^{-3}$. Although the density of the solid was not measured, the density of the liquid is 1·01 g.cm.$^{-3}$ at 15° C. (*International Critical Tables*, 1926, vol. 1, p. 108), and the solid was observed to sink rapidly in the liquid at the freezing-point.

The approximate structure was derived from these photographs* by the following procedure. The integrated intensities were estimated visually with the aid of a standard scale, and were converted to structure factors in the usual way (Buerger, 1944). Because (020) is one of the strongest reflections and (040) shows a normal decline with respect to (020), it was assumed that the nitrogen atoms lie very nearly in planes perpendicular to *b* and separated by $\frac{1}{2}b$. If N_2H_4 molecules are present in the solid, the N–N bond must be in or near these planes, which are too far apart (2·9 A.) to correspond to a bond distance. Three possible arrangements for the nitrogen atoms are possible:

(*a*) The special positions of $P2_1/m$, in which the molecules lie in the mirror plane, with nitrogen atoms at

$$x_1, 0, z_1;\quad \bar{x}_1, \tfrac{1}{2}, \bar{z}_1;\quad x_2, 0, z_2;\quad \bar{x}_2, \tfrac{1}{2}, \bar{z}_2.$$

(*b*) The general positions of $P2_1$, which are the same as (*a*) except that the molecule is tipped slightly out of the plane perpendicular to *b*, with nitrogen atoms at

$$x_1, y_1, z_1;\quad \bar{x}_1, \tfrac{1}{2}+y_1, \bar{z}_1;\quad x_2, y_2, z_2;\quad \bar{x}_2, \tfrac{1}{2}+y_2, \bar{z}_2.$$

(*c*) The general positions of $P2_1/m$, with nitrogen atoms at

$$x, y, z;\quad \bar{x}, \bar{y}, \bar{z};\quad \bar{x}, \tfrac{1}{2}+y, \bar{z};\quad x, \tfrac{1}{2}-y, z.$$

Arrangement (*c*) was shown to produce unsatisfactory agreement for (001), (002) and (003) for all possible values of the *z* parameter, by the use of graphs of the trigonometric part of these structure factors. Since decision between arrangements (*a*) and (*b*) involves only determination of the *y* parameter, which must be very nearly zero because of the normal decline of (020) and (040), it was then decided first to obtain approximate values of the *x* and *z* parameters from the precession data. A consideration of several reflections with small indices, including the very intense (10$\bar{1}$) reflection, led quickly to a structure which gave satisfactory agreement between observed and calculated structure

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* In some of the early experiments the 2·8 cm. radius camera was first loaded and then slid over the spindle of the Weissenberg goniometer. In this position it was not in the path of diffractions to the flat-plate camera on which the orientation photographs were taken, but it could be moved into position when the crystal was properly oriented. Here, again, a layer-line screen which could be slid into position was improvised.

* The first-level photograph about [011] was unsatisfactory, apparently because the crystal was not centered, and was not included in the intensity estimates.

factors. The calculations were made with the use of a scattering curve for the NH_2 group* obtained from the scattering curves (*Internationale Tabellen*, 1935, vol. 1) for nitrogen, oxygen and oxide ion:

$$f_{NH_2}=f_N+(f_{O^{-}}-f_O).$$

A least-squares refinement (Hughes, 1941) of the $h0l$ reflections in the range of the precession photographs yielded further improvement of the parameters.

Since it was obvious that the $h0l$ projection would be centrosymmetric and well resolved, Weissenberg photographs of this zone were taken, and the intensities were estimated and reduced to structure factors (Lu, 1943).

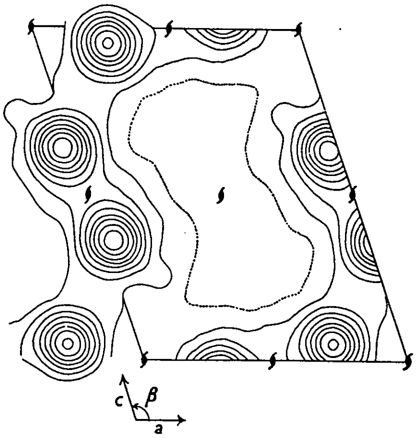

Fig. 1. Fourier projection of hydrazine on (010). Contours are at intervals of 1 e.A.$^{-2}$. The one-electron contour is dotted.

The final Fourier summation shown in Fig. 1 was carried out at 6° intervals with the use of the Patterson–Tunell strips. With the use of final x and z parameters from this projection a set of structure factors of the form hkl was chosen consisting of those most sensitive to variation in the y parameter. Best agreement between the observed and calculated structure factors was obtained for $y_1=y_2=0$, and the agreement began to be poor for $y_1>0{\cdot}010$ and $y_2<-0{\cdot}010$. There appears, moreover, to be no structural reason for expecting y_1 and y_2 to be different from zero. It may be added that assumption of $y_1=0{\cdot}01$ and $y_2=-0{\cdot}01$ would increase the N–N bond distance by only 0·005 A. A least-squares determination of the scale factor and temperature factor of the $h0l$ zone was made after the final position parameters were obtained from the Fourier projection. The temperature factor thus determined was

$$\exp(-2{\cdot}9\sin^2\theta/\lambda^2),$$

and was in excellent agreement with a somewhat less reliable temperature factor determined by a least-squares treatment of the data from the precession photographs.

Results and discussion

The final parameters for the nitrogen atoms are

$$x_1=0{\cdot}037,\quad y_1=0{\cdot}00,\quad z_1=0{\cdot}362,$$
$$x_2=0{\cdot}736,\quad y_2=0{\cdot}00,\quad z_2=0{\cdot}050.$$

On the basis of these nitrogen positions the space group is C_{2h}^2–$P2_1/m$. A diagram of the structure is shown in Fig. 2, and the comparison of observed and calculated structure factors is shown in Table 1. The

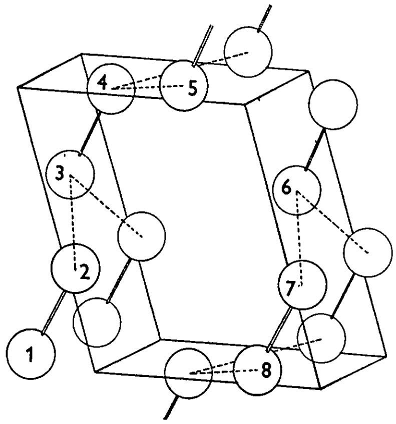

Fig. 2. Isometric drawing of the hydrazine structure. Hydrogen bonds are indicated by broken lines.

Table 1. *Comparison of observed and calculated structure factors*

$h0l$	$F_{obs.}$	$F_{calc.}$	$h0l$	$F_{obs.}$	$F_{calc.}$
001	3·2	3·6	$10\bar{1}$	7·7	−8·5
002	5·0	4·1	$10\bar{2}$	7·0	−7·1
003	5·0	4·6	$10\bar{3}$	<0·3	0·3
004	1·2	−1·4	$10\bar{4}$	3·6	−4·0
005	<0·6	0·3	$10\bar{5}$	1·1	−1·1
006	<0·7	0·04	$10\bar{6}$	<0·5	−0·2
007	<0·8	−0·7	$10\bar{7}$	0·8	−0·7
100	9·9	9·4	$20\bar{1}$	4·5	−5·6
101	5·6	−3·9	$20\bar{2}$	4·6	−5·3
102	2·4	2·5	$20\bar{3}$	1·6	1·7
103	3·3	3·5	$20\bar{4}$	1·5	−1·6
104	<0·4	−0·1	$20\bar{5}$	<0·4	0·2
105	1·3	1·4	$20\bar{6}$	1·1	1·1
106	0·6	0·6	$20\bar{7}$	<0·6	0·04
200	<0·3	0·2	$30\bar{1}$	0·8	1·2
201	6·5	−6·2	$30\bar{2}$	<0·4	0·1
202	1·1	−1·3	$30\bar{3}$	4·1	3·8
203	<0·4	−0·2	$30\bar{4}$	0·5	0·7
204	1·5	−1·3	$30\bar{5}$	0·5	0·7
205	<0·5	0·4	$30\bar{6}$	1·3	1·1
300	2·1	2·1	$30\bar{7}$	<0·6	−0·3
301	1·8	−1·8	$40\bar{1}$	1·2	1·3
302	<0·4	0·1	$40\bar{2}$	<0·6	−0·4
303	<0·5	−0·03	$40\bar{3}$	1·3	1·4
304	1·4	−1·0	$40\bar{4}$	<0·7	−0·4
400	1·6	1·7	$40\bar{5}$	0·4	−0·7
401	<0·5	0·00	$40\bar{6}$	<0·5	0·1
402	1·2	1·0	$50\bar{1}$	<0·5	−0·1
403	<0·6	0·2	$50\bar{2}$	1·3	−1·1
500	<0·8	0·02	$50\bar{3}$	<0·6	−0·1
501	<0·6	−0·4	$50\bar{4}$	<0·5	−0·3
502	<0·6	0·4	$50\bar{5}$	0·6	−0·9

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* The effect of placing hydrogen atoms explicitly at positions inferred from the shortest non-bonded N...N distances was tested after the final parameters were obtained. The slight improvement in the agreement was not regarded as significant, and no signs were changed in the Fourier coefficients of the $h0l$ projection by this refinement.

closest nitrogen–nitrogen distances are the bond distance = 1·46 A.,

$$N_2\ldots N_3=3{\cdot}19\ \text{A.},\quad N_2\ldots N_8=3{\cdot}25\ \text{A.},$$
$$N_5\ldots N_4=3{\cdot}30\ \text{A.},\quad N_7\ldots N_5=3{\cdot}62\ \text{A.},$$
$$\text{and}\quad N_5\ldots N_6=3{\cdot}67\ \text{A.}$$

The bond angles are

$$N_2N_3N_2=125^\circ,\quad N_5N_4N_5=122^\circ,$$
$$N_2N_3N_4=114^\circ,\quad N_3N_4N_5=131{\cdot}5^\circ,$$
$$\text{and}\quad N_1N_2N_8=90^\circ.$$

We believe it unlikely that the actual distances are different from these by as much as 0·02 A.

The bond distance of 1·46 A. is in excellent agreement with the electron-diffraction value of 1·47 A. found in hydrazine (Giguère & Schomaker, 1943), and with the unresolved, and therefore less precise, value of 1·45 A. found in dimethylhydrazine (Beamer, 1948) in an electron-diffraction study.

The close non-bonded N...N distances are in good agreement with those observed in other compounds. Values of 3·09 and 3·28 A. are observed in 4-amino-2,6-dichloropyrimidine, 2·96 and 3·07 A. in 5-bromo-4,6-diaminopyrimidine, and 3·21 and 3·37 A. in 2-amino-4,6-dichloropyrimidine (Clews & Cochrane, 1948, 1949). In adenine hydrochloride values of 3·18 and 2·99 A. are reported (Broomhead, 1948). In ammonia the distance is 3·38 A. (Mark & Pohland, 1925), while in NH_4N_3 a distance of 2·98 A. is reported (Frevel, 1936). A very interesting example of non-bonded approach of 3·0 A. has been reported in AgN_3 (Hughes & Pfeiffer, 1949). All of these examples except the last are presumed to involve some hydrogen bonding.

The positions of the hydrogen atoms are of considerable interest, and while we intend to discuss them it must be clear that any suggestion of their presence in the Fourier projection, where they are not resolved, must be doubtful. Any inference of their positions from short non-bonded N...N distances must also be doubtful, because the distances between heavy atoms are appreciably greater than those found when oxygen or fluorine is involved, and may be comparable with close contacts not involving hydrogen bonding.

The calorimetric data already discussed do suggest that hydrogen bonding may be important. The high heat of fusion, 3·0 kcal./mole, appears to be consistent with the large change of density upon melting. Furthermore, the heat of vaporization, 10·7 kcal./mole, is appreciably greater than that expected for dispersion forces alone. A comparison of the boiling points of hydrazine (113·5° C.) and P_2H_4 (51·7° C.) (Royen & Hill, 1936) with those of other liquids (Pauling, 1942, pp. 290, 304) yields an estimate of about 6 kcal./mole for the contribution of the dispersion forces to the heat of vaporization of hydrazine. This estimate assumes an entropy of vaporization of 21 cal./mole degree for an 'unassociated' liquid whose boiling-point is about room temperature. Thus perhaps 7 kcal./mole of N_2H_4 may be attributed to hydrogen bonding in the solid, if we allow about 0·5 kcal./mole for the heat of fusion of an 'unassociated' liquid.

The indications of electron-density contributions from the hydrogen atoms in the Fourier projection may be examined by comparison of the electron density with that expected only from spherically symmetrical nitrogen atoms for which the correction $f_{\mathrm{O}^{-2}}-f_{\mathrm{O}}$ for hydrogens was omitted (Collin & Lipscomb, 1950). The electron density of a Fourier projection obtained with the use of the calculated structure factors is less than that in Fig. 1 by 1·2 e.A.$^{-2}$ at 0, 0, $\frac{1}{2}$ and by 1·3 e.A.$^{-1}$ at $\frac{1}{2}$, 0, 0. That these differences might be significant is suggested by the smaller differences at other points: 0·75 e.A.$^{-2}$ at the origin, and 0·3 e.A.$^{-2}$ at $\frac{1}{2}$, 0, $\frac{1}{2}$. These results are in agreement with the observation that inclusion of hydrogens in the indicated positions produced some slight improvements in the agreement between observed and calculated structure factors, but these improvements were not regarded as outside the limits of error of our visual estimates of the intensities.

Table 2. *Comparison of observed and calculated structure factors*

(The origin for Table 2 is at 0, $\frac{1}{4}$, 0 with respect to the origin in the text.)

hkl	$F_{\text{obs.}}$	$F_{\text{calc.}}$
020	13·2	18·3
040	5·8	6·8
011	9·2	−11·3
012	3·1	2·4
013	3·6	−4·1
014	2·3	−2·3
021	2·4	−2·3
022	3·0	−3·0
023	4·3	−3·8
031	4·7	5·3
032	< 1·4	−1·3
033	2·4	3·0
041	< 1·4	0·9
051	2·2	−2·3
110	8·2	7·0
111	3·6	2·6
120	5·5	−6·1
121	3·4	3·0
130	3·2	−3·4
131	1·4	−1·3
140	2·8	2·5
150	2·7	1·5
210	2·6	−2·6
211	1·3	−1·0
212	3·0	3·0
220	< 1·4	0·3
221	3·9	5·0
222	1·6	1·2
230	< 1·3	1·6
231	< 1·1	0·6
240	< 1·1	−0·2
241	2·6	−3·2
310	2·9	−3·2
311	1·7	−1·9
320	3·2	−1·9
321	1·4	1·6
331	1·6	1·5
341	1·5	−1·1
$11\bar{1}$	17·3	15·8
$12\bar{1}$	4·9	5·6
$12\bar{2}$	3·5	4·9
$13\bar{1}$	7·4	−7·9
$14\bar{1}$	2·5	−2·4
$14\bar{2}$	1·8	−2·5
$15\bar{1}$	3·4	3·6
$21\bar{1}$	2·4	2·3
$21\bar{2}$	6·3	−6·0
$22\bar{1}$	4·1	4·2
$22\bar{2}$	4·4	4·0
$23\bar{1}$	1·4	−1·4
$24\bar{1}$	1·7	−2·4
$24\bar{2}$	2·7	−2·5
$25\bar{1}$	< 1·1	0·8
$31\bar{1}$	< 1·1	0·4
$31\bar{2}$	2·9	−2·8
$32\bar{1}$	< 1·1	−1·1
$41\bar{1}$	1·7	1·9
$42\bar{1}$	< 0·8	−1·1
$43\bar{1}$	1·2	−1·6

The most reasonable assumption on the basis of both distances and angles, together with a consideration of the electron density in Fig. 1, is that hydrogen bonds occur in a zigzag chain approximately along *b* ($N_2\ldots N_3$ and $N_4\ldots N_5$). This structure leads to two important conclusions. The first is that the molecule, at least in the crystal, has an eclipsed configuration, instead of a staggered configuration as usually assumed. The second is that because these zigzag chains use up all of the electron pairs (and half the hydrogens) there would be at most only two configurations for each infinite chain, and the residual entropy would accordingly be zero. Although statistically the molecular symmetry in the crystal would be C_s, the symmetry of a single molecule could be either C_2 or C_{2v}. The N–H bonds not involved in these zigzag chains would presumably lie in the mirror planes of the crystal, and there are slight suggestions in the Fourier series of Fig. 1 that this is actually the case. It is interesting that one of the N...N distances in this plane is as short as 3·25 A., and it may well be that one of the hydrogen atoms in this plane is approximately along this distance, although if the above interpretation is correct this hydrogen bond cannot be associated with an electron pair in the neighbouring molecule.

Even if the molecule has the eclipsed form in the crystal there may be some reasonable doubt as to whether in the gas phase hydrazine has one of the eclipsed or staggered configurations. The spectroscopic data, although interpreted on the basis of the staggered configuration of C_2 symmetry, is said not to be seriously in conflict with the *cis*-configuration, which is the eclipsed form of C_{2v} symmetry (Scott *et al.* 1949). Even if the potential barrier of 2·8 kcal./mole, discussed in the calorimetric study, represents the barrier between a more stable staggered configuration and an eclipsed configuration, it is possible that the constraints in the solid state would be sufficient to overcome this barrier at least partly, if not completely, so that the molecule has, either statistically or actually, the eclipsed configuration in the crystal. This behavior seems especially remarkable because the $N_2H_6^{+2}$ ion, which is isoelectronic with ethane, apparently has the staggered configuration in hydrazinium difluoride (Kronberg & Harker, 1942) and in hydrazinium dichloride (Wyckoff, 1923; Donohue & Lipscomb, 1947).

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