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(Ph. D. Thesis)

Quintin C. Johnson

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ABSTRACT

Crystal Energy Calculations

Calculations of minimum-energy-structures have been made in an effort to ascertain the effectiveness of the Born expression for the energy of a crystal. This expression assumes an r^{-1} attractive potential due to charge separation and an r^{-n} repulsive force due to the Pauli effect. Application of this model to a number of problems of crystal chemistry indicates that ionic substances may be suitably described by the above potential. This is shown by a comparison of the minimum-energy-structures of LaOCl, YOCl, $SrBr_2$, brookite, and YF_3 to the acutal structures. Consideration of the $CdCl_2$ structure shows that van der Waals forces can not always be neglected.

The Crystal Structure of Semicarbazide Hydrochloride

The structure of semicarbazide hydrochloride, $H_2NHNCONH_2 \cdot HCl$, has been determined by single-crystal x-ray diffraction methods. The space group is $P2_12_12_1$ and the cell dimensions are a = 7.54 ± .02, b = 13.22 ± .03, and c = 4.67 ± .02 Å. The interesting nitrogen-nitrogen single-bond distance is 1.457 ± .007 Å.

A Redetermination of the Crystal Structure of Tetramethylammonium Bromide

In order to determine a fairly reliable carbon-nitrogen bond distance in a quaternary amine, a redetermination of the structure of tetramethylammonium bromide, $(CH_3)_4NBr$, was carried out by single crystal x-ray diffraction methods. The results are in close agreement with work done by previous researchers. The carbon-nitrogen bond distance is equal to 1.50 ± .02 Å. Attempts to localize the hydrogen atoms were unsuccessful.

PART 1. CRYSTAL ENERGY CALCULATIONS

INTRODUCTION

In the past, efforts of Born and others[1] have established a simple model, in classical terms, for the energy of an ionic crystal. This model represents a crystal as the equilibruim configuration resulting from a single attractive and a single repulsive potential. The attractive potential is the well-known Coulomb potential which is due to charge separation in the ionic solid. The repulsive potential, with its true origin in the quantum mechanical Pauli effect, may be considered as a consequence of the fact that ions take up space.

Several functional forms are apparently adequate to describe the repulsive potential, but one in particular is easy to use, i.e.,

$$U_r = e^2 b r^{-n}, \tag{1}$$

where r is the interatomic distance, e is the charge of the electron, n is a constant that describes the elasticity of the ion, and b called the repulsive constant defines an effective radius of the ion. Using this form, the energy of a crystal may then be written as follows:

$$U = \sum \frac{B_{ij} e^2}{r_{ij}^n} + \sum \frac{z_i z_j}{r_{ij}} \quad . \tag{2}$$

B_{ij} is the repulsive constant for ions i and j, z_i represents the charge on ion i. These sums are carried out over the interaction of all pairs of atoms.

The first sum converges rapidly and need be computed only for nearest neighbors; the second, however, converges very slowly. It is because of the slow convergence that little application of this potential model has been made except to very simple structures.

This work is an attempt to answer some structural problems by the application of the above potential. Since the calculations were carried out on an IBM 704, the slow convergence of the Coulomb sum was not a source of difficulty.

COULOMB POTENTIAL

The Coulomb, or Madelung sum

$$U_c = \sum \frac{z_i z_j}{r_{ij}} \quad , \tag{3}$$

may be rewritten as follows:

$$U_c = - \frac{e^2 A}{L} \quad , \tag{4}$$

where L is a unit of measure (in these calculations taken to be the shortest interatomic distance) and A is the Madelung constant corresponding to L as unit distance.

Several methods for the calculation of the Madelung constant are available.[2] The calculations described make use of the method of Bertaut with attention to series termination error.[3] According to this method, the Madelung constant is given by the following expression:

$$A = \frac{(g-Q)L}{RZ} \sum_j (z_j)^2 - \frac{\pi R^2 L}{ZV} \sum_h \left| F \right|^2 \phi \ . \tag{5}$$

The notation is that of Templeton.[4]

REPULSIVE POTENTIAL

To facilitate discussion of the repulsive potential, it is necessary to introduce extra notation. Each atom in the crystal is given two subscripts. The first subscript (i, j) will designate the element, while the second (k, ℓ) will differentiate between atoms of the same element. Four subscripts will then be associated with a distance between atoms. This notation will enable one to identify not only which atoms are involved but also which elements. The repulsive potential then assumes the following form:

$$U_r = e^2 \sum_{i=1}^{m} \sum_{j=1}^{m} B_{ij} \sum_{k=1}^{m_i} \sum_{\ell=1}^{m_{j*}} \left(\frac{1}{2r_{ikj\ell}^n} \right) , \qquad (6)$$

where m is the number of elements and m_i represents the number of atoms of element i. The asterisk on the fourth summation indicates that this summation does not include $\ell = k$ if $i = j$.

Again, taking as a unit of measure the shortest interatomic distance L, and making the following substitution:

$$P_{ij} = \sum_{k=1}^{m_j} \sum_{\ell=1}^{m_{j*}} \frac{1}{2} \left(\frac{L}{r_{ikj\ell}} \right)^n , \qquad (7)$$

one obtains

$$U_r = e^2 \sum_{i=1}^{m} \sum_{j=1}^{m} \frac{B_{ij} P_{ij}}{L^n} . \qquad (8)$$

It should be noted that $B_{ij} = B_{ji}$ as does $P_{ij} = P_{ji}$.

A crystal energy program which computes the two sums of equations (4) and (8) was written for the IBM 704.[4] This program calculates the Madelung sum, the series termination correction, the repulsive potential, and the crystal energy.

REPULSIVE POTENTIAL PARAMETERS

Before equation (8) may be used, it is necessary to evaluate the constants involved. The value of n is quite often evaluated from compressibility measurements.[5] For many crystals compressibility data are compatible with an approximate value of $n = 9$. It is not necessary to adhere rigidly to this value; the functional form of $1/r^9$ is only slightly different from that of $1/r^{10}$ or $1/r^8$. For these calculations a value of $n = 8.25$ was chosen from considerations which will be described later.

Attention may now be focused on the repulsive constants. From equation (8) it may be deduced that there are $n(n+1)/2$ repulsive constants for a structure with n kinds of atoms. Fortunately, not all of these constants are necessary. Consider rutile (TiO_2). It would appear necessary to know B_{11} (cation-cation repulsive constant), B_{12} (cation-anion constant), and B_{22} (anion-anion constant). If the model is to have any significance, however, the repulsive effects should be thought of as arising from Pauli exclusion, i.e., from the fact that one "sphere of charge" can penetrate another "sphere of charge" only with difficulty. Attributing reasonable ionic radii to both titanium and oxygen ions, it is found that although there are titanium-oxygen and oxygen-oxygen contacts in this crystal, the titanium-titanium contact is not possible. Consequently, it is necessary to know only B_{12}, B_{22}, and n in order to calculate the crystal energy of rutile.

POTENTIAL MODEL NEGLECTING ANION-ANION INTERACTIONS

A first approximation to the crystal energy of rutile can be made by assuming that there are no anion-anion contacts. This is equivalent to setting $B_{22} = 0$. Since the sum of equations (4) and (8) is equal to the crystal energy, this function will have a minimum with respect to L at the equilibrium configuration. This allows the determination of the titanium-oxygen repulsive constant as follows:

$$\frac{\partial U}{\partial L} = -\frac{nB_{12}P_{12}e^2}{L^{n+1}} + \frac{Ae^2}{L^2} = 0 \quad , \tag{9}$$

$$B_{12} = \frac{AL^{n-1}}{nP_{12}} \quad . \tag{10}$$

The above approximation has proved useful as a tool in the determination of the correct structure when more than one structure is compatible with x-ray data. In this laboratory the first application of this method was the criticism of the proposed structure of YOF[6] by Templeton.[7]

The alternate structure (rejected by Zacharaisen because of a short yttrium-oxygen bond length) was calculated to be more stable by approximately 100 kcal/mol.

Similar calculations have been carried out on the structures of LaOCl,[8,9] YOCl,[8,10] and $SrBr_2$.[11] These structures are described in Table X.

LaOCl and YOCl

The LaOCl and YOCl calculations were carried out in a manner similar to that of the earlier calculations by Templeton. The metal-oxygen and metal-chlorine repulsive constants were determined by the use of equation (10) applied to data of their respective oxides and chlorides. For both compounds alternate structures were proposed that differed from the x-ray structures by a transposition of the chlorine and oxygen positions. The crystal energies of the two structures for each compound were then computed. Table I gives the results of these calculations. The units of measurements given in this Table are the ones which are used, although not again given, throughout the rest of the Tables and discussion. It is quite obvious from these results that the alternate structure is incorrect in both cases.

$SrBr_2$

The $SrBr_2$ structure comes under consideration because of the nearly identical scattering power of the strontium and bromine atoms. There are three atoms in the asymmetric unit. Strontium and the two bromine atoms are in Wycoff symmetry, c, of space group Pnma. It is conceivable that an error could occur by attributing one of the bromine positions to the strontium.

In addition to a calculation of the crystal energy of the x-ray structure, two additional calculations were carried out in which the strontium and one bromine atom were interchanged. Although it was quite apparent that the x-ray structure was the stable one, repulsive effects had to be considered in order to be certain.

Table I

Comparison of the two possible structures of LaOCl and YOCl

Structure	(a)	(b)	(c)
Reported LaOCl	162.6	338.1	-1310.6
Alternate LaOCl	162.6	338.1	- 957.5
Reported YOCl	112.1	191.2	-1385.3
Alternate YOCl	112.1	191.2	-1083.5

(a) Metal-oxygen repulsive constant in units of $(\mathring{A})^{7.25}$

(b) Metal-chlorine repulsive constant in units of $(\mathring{A})^{7.25}$

(c) Crystal energy in kcal/mol

Table II

Crystal energies of the three possible $SrBr_2$

Structure	(a)	(b)	(c)	(d)	(e)	(f)
X-ray	0.1432	-485.6	411	-426.7	-410.9	-414.3
Alternate 1	0.0857	-368.8	522	-333.6	-324.1	-326.2
Alternate 2	0.0981	-402.8	498	-362.5	-351.6	-354.0

(a) (Repulsive energy due to Sr-Br) $/B_{Sr-Br}$

(b) Coulomb energy

(c) Sr-Br repulsive constant calculated for each strucutre

(d) Crystal energy calculated with $B_{Sr-Br} = 411$

(e) Crystal energy calculated with $B_{Sr-Br} = 522$

(f) Crystal energy calculated with $B_{Sr-Br} = 498$

Assuming in turn that each of the three structures is correct, it is possible to solve for three different values of the strontium-bromine repulsive constant. Using these three repulsive constants, three different crystal energies for each structure may then be calculated. From the results shown in Table II, it is possible to see that the x-ray structure is the stable form, since the crystal energies of this structure are the lowest of any of the energies. It may be observed, incidentally, that since this structure is the only correct structure, the value of B_{12} equal to 411 is the only strontium-bromine repulsive constant with significance.

POTENTIAL MODEL ASSUMING ANION-ANION INTERACTIONS

Oxygen-Oxygen Repulsive Constant

It is now of interest to calculate the importance of the anion-anion interaction. In the preceding discussion where only cation-anion effects were considered, the repulsive constants were easily obtained by means of equation (10). For the anion-anion constants, different tactics must be employed.

If, for a particular ionic substance, the force law represents an adequate explanation of the structure, and if the structure is accurately known, the determination of additional parameters in the force law is a simple matter. For every experimental parameter in the structure, an equation may be written. One says that, since the crystal energy is a function of these parameters, it must necessarily be at its minimum when these same parameters assume their equilibrium values. For any experimental parameter, q_i, it is then possible to write

$$\frac{\partial U}{\partial q_i} = 0 \quad . \tag{11}$$

If the structure were accurate and the model acceptable, these equations would be self-consistent and could therefore be solved for the unknown repulsive constants. In actual practice such is not the case. One of the difficulties lies in the scarcity of ionic substances whose

parameters are accurately known. Other difficulties are due to departure from ionicity, quantum mechanical effects, and an inadequate model.

The structures of TiO_2 (rutile, anatase, and brookite) were taken as a starting point for the determination of the oxygen-oxygen repulsive constant. These structures are described in Table X. The structures of rutile and anatase are known with considerable accuracy[12] while the brookite structure has been redetermined recently to fair accuracy.[13] Since both Ti^{+4} and $O^{=}$ ions have rare gas configurations, it is expected that the structures should be quite ionic. Finally, the small radius of Ti^{+4} compared with $O^{=}$ enables oxygen ions to interact appreciably with neighboring oxygen ions. It is expected, therefore, that a considerable amount of repulsion arises out of the oxygen-oxygen contacts.

Before going any further, it is necessary to decide what value of n is acceptable for this model. Instead of the usual solution for n based on compressibility data, equation (11) will be utilized.

The structure of rutile, a three parameter structure, permit three equations to be written from equation (11). Since there are only three parameters in the force law (n, B_{12}, B_{22}) the solution would be trivial if the functions were linear. Because these are exponential functions for which the solution is complicated, a graphical solution was sought. For each equation at constant n a straight line results if B_{12} is plotted against B_{22}. These three lines would intersect at the solution provided n is properly chosen. This intersection was found for $n = 8.25$. Similar calculations for the structure of anatase resulted in approximately the same value. Because of the argument stated earlier, it was felt that very little could be gained to compensate for the complexity introduced by redetermining n for each structure considered. For this reason the value of 8.25 was used throughout all the calculations to be described.

The three equations for rutile should also serve to determine the repulsive constants from their intersection at $n = 8.25$. This is true if attention is confined to rutile. It is necessary, however, to be able to extend the parameters determined from rutile to calculations of the crystal energies of anatase and brookite.

A curious result was obtained from the calculation of the following three equations for anatase:

$$\frac{\partial U}{\partial a} = 0, \tag{12-a}$$

$$\frac{\partial U}{\partial c} = 0, \tag{12-b}$$

$$\frac{\partial U}{\partial z} = 0. \tag{12-c}$$

It was noted that equations (12-a) and (12-b) were nearly linearly dependent. Consideration of the structure of anatase shows why this should be so. In the anatase structure, each TiO_6 octahedra has four shared edges. The location of these edges and the dimensions of the unit cell are such that orientation of shared edges with respect to the 3 axes are approximately equal.

The derivative calculations of equations (12-a) and (12-b) amount to a slight compression or expansion of the structure. Since the shared edges are affected most by such a treatment, it is not surprising that equations (12-a) and (12-b) give approximately identical results.

The important thing to notice is that these two equations were nearly linearly dependent. A plot of B_{12} versus B_{22} showed that the two lines resulting from (12-a) and (12-b) were approximately parallel but did not coincide. This noncoincidence is taken to be a warning that the model is encountering difficulty explaining the anatase structure. This difficulty may stem from nonperfect ionic behavior of TiO_2, or, as is more likely the case, it may be caused by the crudeness of the model. In either case, disagreement serves notice that this model should not be trusted to any higher degree of accuracy than can be obtained in the extension of the calculations from rutile to anatase.

In order to determine this accuracy, it is necessary to calculate $\partial U/\partial z(z = z_o + \sigma_z)$ and $\partial U/\partial z(z = z_o - \sigma_z)$ where σ_z is the standard deviation of the parameter z. A plot of these equations together with equations (12-a) and (12-b) is shown in Figure 1. The dotted lines indicate the interval of B_{22} which must be acceptable because of the uncertainty

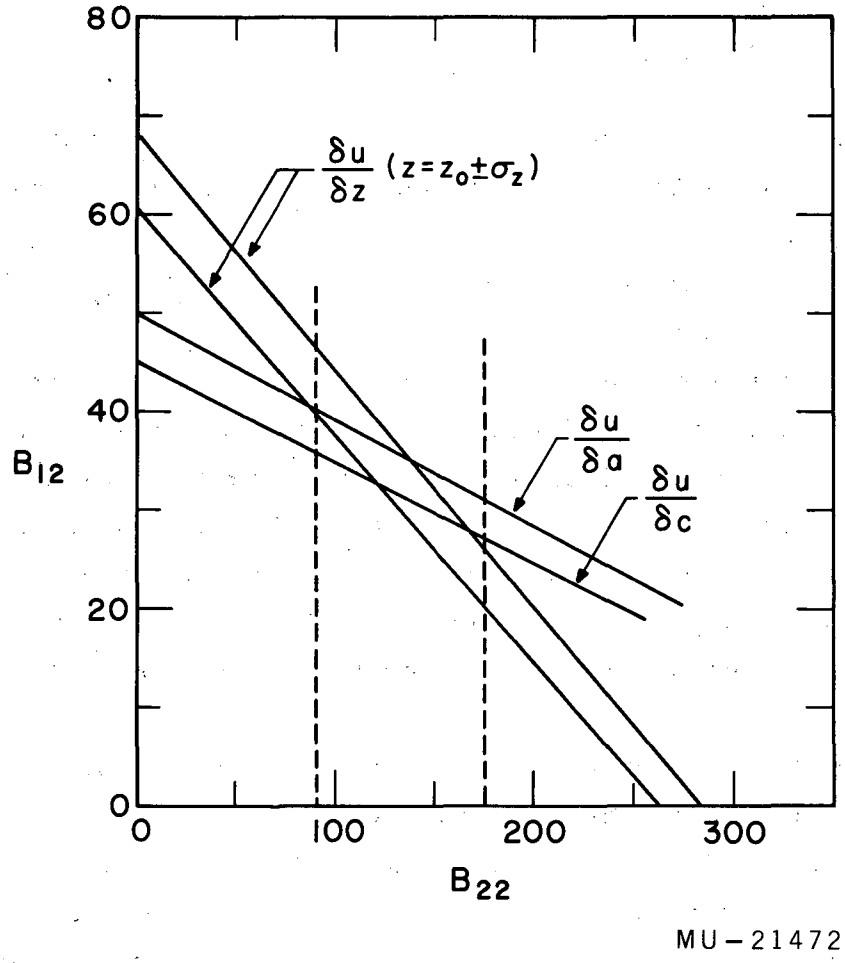

Fig. 1. Plot of B_{12} versus B_{22} for the anatase structure.

in z and the parallel behavior of equations (12-a) and (12-b). If a value of B_{22} is chosen, the value of B_{12} which corresponds to it can then be calculated by means of the following equation:

$$U_c = nU_r \,, \tag{13}$$

where U_c is the Coulomb potential and U_r is the repulsive potential. Equation (13) can be derived from differentiation of the crystal energy with respect to L.

From the graph of Figure 1, a value of $90 \leq B_{22} \leq 175$ is chosen along with the corresponding value of $27 \leq B_{12} \leq 40$.

In order to be more confident of the model, it is expedient to calculate the value of B_{22} by means of another structure, in particular, one in which the coordination is different from that of the TiO_2 structures. Such a structure is corundum, αAl_2O_3. The cell constants of this structure are very accurately known[14] although the two parameters describing the structure are not so well known.[15] The structure is described in Table X. A plot of the curves generated by equation (11) is shown in Figure 2.

Attributing a reasonable uncertainty to the parameters of oxygen and aluminum, it can be seen that the lower boundry of B_{22} may be fixed at $B_{22} \geq 60$. (The intersection of the oxygen and aluminum paramater curves is not taken seriously as these values are not known with enough accuracy). The upper limit, on the other hand, is fairly uncertain; it appears to be greater than 175.

In order to make B_{22} compatible with every structure so far discussed, making it more universally applicable, it can be said that B_{22} is not known any better than $B_{22} = 120 \pm 60$. From equation (13) the titanium-oxygen repulsive constant may be calculated. Given $B_{22} = 120$, it is possible to calculate $B_{Ti-O} = 36.4$.

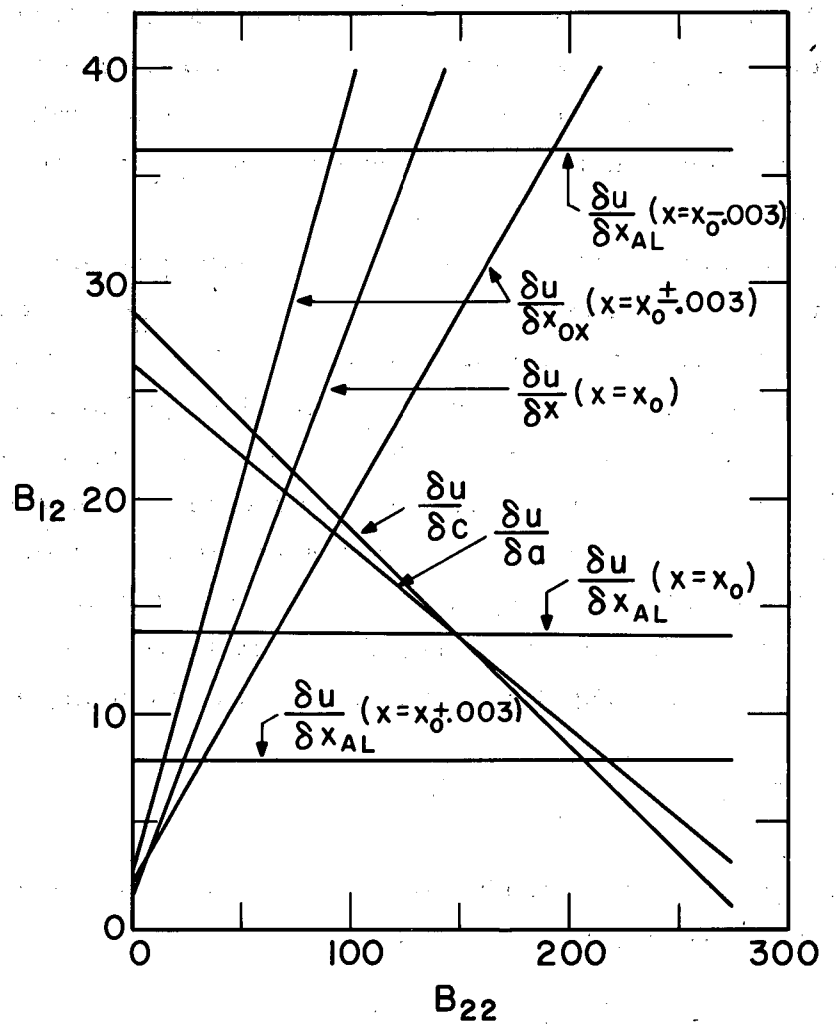

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Fig. 2. Plot of B_{12} versus B_{22} for the corundum structure.

Brookite Minimum-Energy-Structure

Attention was then focussed on the brookite structure in order to determine the usefulness of the model. It is of interest to ascertain whether the polarized octahedra in brookite can be explained by this model, or if not, whether the "minimum-energy-structure" is very close to the actual equilibrium structure.

A plot of the curves obtained by the use of equation (11) is shown in Figure 3. The dotted area is the region of B_{22}, which is acceptable in view of the previous arguments. Clearly, from the intersections outside of this region, it is apparent that the equilibrium structure does not correspond too closely with the "minimum-energy-structure".

In order to calculate the "minimum-energy-structure" (assuming n, B_{12}, and B_{22} are known) it is necessary to make use of the method of steepest descents which will now be discussed briefly.

For a particular structure, the crystal energy may be represented as a function of the repulsive constants and structural parameters,

$$U = f(B_{11}, B_{12}, \cdots, q_1, q_2 \cdots). \tag{14}$$

If this function is expanded by means of Taylor's expansion, neglecting higher order terms, the result is

$$U_o = U + \epsilon_{q_1} \frac{\partial U}{\partial q_1} + \epsilon_{q_2} \frac{\partial U}{\partial q_2} + \cdots \tag{15}$$

(The repulsive constants have been taken as constant.) At equilibrium the derivative of U with respect to q_i is equal to zero, so

$$\frac{\partial U_o}{\partial q_i} = 0 = \frac{\partial U}{\partial q_i} + \epsilon_{q_i} \frac{\partial^2 U}{\partial q_1 \, \partial q_i} + \epsilon_{q_i} \frac{\partial^2 U}{\partial q_2 \, \partial q_i} + \cdots \tag{16}$$

This set of equations permits the solution of the values of ϵ_{q_i} which are the shifts in the parameters necessary to locate the minimum energy, U_o.

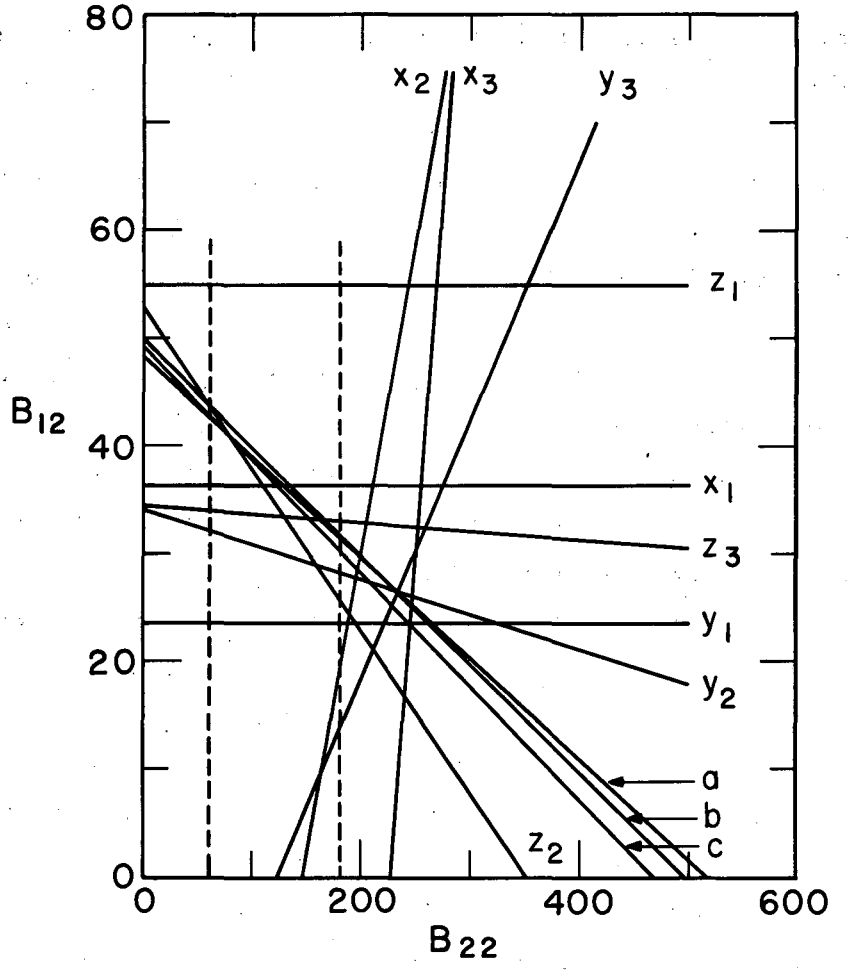

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Fig. 3. Plot of B_{12} versus B_{22} for the brookite structure.

In some cases it becomes necessary to assume that the derivatives of the form $\frac{\partial^2 U}{\partial q_i \partial q_i}$, $i \neq j$, are equal to zero. This diagonal approximation, as it is called, is a crude approximation but does lead to a considerable reduction in the number of calculations without drastically affecting the rate of convergence.

Because the complete, or full matrix, calculation for brookite would take approximately $5\frac{1}{2}$ hours on the IBM 704, the diagonal approximation was utilized. This amounted to a saving of five hours per cycle. A further simplification was made by not permitting the cell constants to vary. It is reasoned that these parameters are known with more certainty than the coordinates of either titanium or oxygen.

The results of several cycles are shown in Table III. The calculation was ended after the third cycle, since it was evident that no appreciable improvement could be made.

Because of an error, the value of B_{12} that was used was somewhat larger than the correct value of 36.4. A calculation made at the end of the third diagonal approximation showed that the calculated shifts would not vary appreciably if, instead of the incorrect value of B_{12}, the correct value were used; consequently it is assumed that the minimum-energy-structure given in Table III is essentially correct.

The standard deviation of the x-ray coordinates is approximately 1 to 3% of the cell constant. The difference of the minimum-energy-structure coordinates from the x-ray structure coordinates is only 0.001 to 0.006. The effect of allowing B_{12} and B_{22} to assume their extreme values is to lessen slightly the agreement of the two structures.

Although the minimum-energy-structure of brookite tended to make the distortion of the TiO_6 octahedra slightly less, this distortion still exists. Whereas the x-ray structure has a variety to titanium-oxygen distances in this octahedron, ranging from 1.84 to 2.03 Å, the minimum-energy-structure range is only 1.92 to 1.99 Å. The polarization parameters, i.e., the distance in Å from the center of gravity of the octahedron to the titanium atom[16] are, 0.17 Å for the x-ray structure

Table III

Minimum-energy-structure calculation of brookite

Atom	Ti			O_1			O_2		
(a)	x	y	z	x	y	z	x	y	z
(b)	0.128	0.098	0.863	0.008	0.147	0.182	0.229	0.110	0.530
(c)	+0.003	+0.014	-0.003	+0.007	+0.015	+0.005	-0.0002	+0.008	-0.0009
(d)	+0.002	+0.008	-0.001	+0.004	+0.009	+0.003	0.000	+0.005	-0.001
(e)	0.130	0.106	0.862	0.012	0.156	0.185	0.229	0.115	0.529
(f)	-0.00005	-0.006	+0.0007	-0.0022	-0.008	-0.007	+0.005	-0.005	-0.002
(g)	0.0000	-0.0025	+0.0003	-0.0012	-0.0038	-0.0020	+0.0020	-0.0025	-0.0008
(h)	0.1300	0.1035	0.8623	0.0108	0.1522	0.1830	0.2310	0.1125	0.5282
(i)	+0.00004	+0.00013	-0.0025	+0.0018	+0.0004	-0.0015	+0.0005	+0.0025	+0.0007
(j)	0.1300	0.1036	0.8610	0.0117	0.1524	0.1822	0.2313	0.1138	0.5286
(k)	0.002	0.006	0.002	0.004	0.005	0.000	0.002	0.004	0.001
(l)	± .002	± .002	± .005	± .002	± .005	± .005	± .001	± .003	± .003

(a) Coordinate
(b) Original value of parameter
(c) Shift calculated by first diagonal approximation
(d) Shift actually used
(e) New value of parameter
(f) Shift calculated by second diagonal approximation
(g) Shift actually used
(h) New value of parameter
(i) Shift calculated by third diagonal approximation
(j) Final value of parameters if 1/2 of the last shifts are applied
(k) Difference of the coordinates of the minimum energy and x-ray structures
(l) Estimate of the uncertainty of the minimum-energy-structure coordinates

and 0.15 Å for the minimum-energy-structure. Considering that the repulsive constants were prejudiced by the use of the fairly symmetric structures of rutile and anatase in their determination, this distortion would appear to be significant.

The results of the brookite calculations are quite encouraging. Reasonable agreement should have been expected, however, because of the close similarity of the three TiO_2 structures. Possibly a better check of the appropriateness of the potential model would be the fluoride structures since these are certainly more ionic than oxide structures.

Fluorine-Fluorine Repulsive Constant

A different approach was tried in the calculation of the fluorine-fluorine repulsive constant. This approach consisted of an attempt to obtain information concerning the constant from a comparison of the MgF_2 and CaF_2 structures.

MgF_2 crystallizes in the rutile structure. This results in the magnesium ions being coordinated by six fluorine ions. The CaF_2 (fluorite) structure is well known. In this structure each ion is in eightfold coordination. These structures are completely described in Table X.

The fact that MgF_2 crystallizes in the rutile rather than the fluorite structure is important. This enables the following equation to be written

$$\left|U(MgF_2)_1\right| > \left|U(MgF_2)_2\right| . \qquad (17)$$

The subscript 1 refers to the true rutile-type structure of MgF_2. The subscript 2 refers to a hypothetical fluorite structure in which the magnesium ions have coordination number eight. This equation together with equation (13) can then be solved for a lower limit of B_{22}. These calculations were made giving the result $B_{22} \geq 10.7$

An equation similar to equation (17) may also be written for CaF_2

$$\left|U(CaF_2)_1\right| > \left|U(CaF_2)_2\right| , \qquad (18)$$

where the subscript 2 again refers to a hypothetical structure, in this case a hypothetical rutile structure. Using the information obtained from this equation and equation (13), it is possible to calculate an upper limit to B_{22}. It was found that $B_{22} \leq 31.0$.

YF_3 Minimum-Energy-Structure

With the determination of reasonable limits for the fluorine-fluorine repulsive constant, it is possible to investigate the minimum-energy-structure of a fluoride. Yttrium trifluoride was chosen as the subject for such an investigation. An obvious reason for this choice is that this structure is expected to be ionic and therefore reasonably well-behaved. Another reason for this choice is that the chosen value of n = 8 1/4 is very close to the value of 8 1/2 suggested by Pauling.[17] on the basis of compressibility data. Finally, the structure of YF_3 was determined in this laboratory[18] so that the data are available for processing and maximum treatment of these data by present machine methods is possible. This structure is summarized in Table X where the parameters are the results of the work to be described.

The standard deviation of the coordinates of yttrium is said to be 0.001 Å. and that of fluorine to be 0.03 Å. In order to determine the fluorine positions with better accuracy, the original data were used for a complete matrix, least-squares calculation with individual isotropic temperature factors by the IBM 704 least-squares program of Busing and Levy.[19]

The temperature factors immediately became negative. A plot of $\sum F_o / \sum |F_c|$ versus $(\sin^2\phi)/\lambda$ was made. It was obvious from this plot that the reason for the poorly-behaved temperature factors could be attributed to the need of an absorption correction. This was indeed recognized by the original investigators, however no correction had been made as the data were taken with an irregularly shaped crystal.

In order to continue refinements by the Busing and Levy program, it was necessary to introduce an artificial absorption correction so that the temperature factors could become positive. This was accomplished by multiplying all the data by $\exp\left[(4\sin^2\theta)/\lambda\right]$.

A number of least-squares refinement cycles were then carried out until the shifts were mathematically negligible. The results of these calculations are given in Table IV.

Table IV.

Final least-squares parameters of YF_3

Atom	Y		F_1		F_2		
Coordinate	x	z	x	z	x	y	z
Least-squares parameter	0.3686	0.0595	0.5266	0.5774	0.1796	0.0740	0.3644

Coordinates which were approximately equal to those of Table IV were used as initial parameters for a minimum-energy-structure calculation of YF_3, n was chosen as 8 1/4, B_{22} was chosen as 25 to satisfy the limit requirements mentioned earlier, and B_{12} was calculated from B_{22} and equation (13).

Taking the cell dimensions as constant, the x and z coordinates of all atoms and the y coordinate of F_2 were allowed to vary. A complete matrix calculation was then made. From this, shifts in the parameters were calculated.

Due to the approximation in the method of steepest descents, the calculated shifts are, quite naturally, expected to be only approximations. Since it is possible that overcorrection could lead to divergence, only a fraction (50-80%) of the calculated shift was used in each case. These modified shifts generated new parameters which served as the basis for five successive diagonal approximation calculations. In each case the shifts which were applied were approximately 50 to 100% of the calculated shifts. The results are shown in Table V.

Since B_{22} was not determined to any greater degree of accuracy than $10.7 \leq B_{22} \leq 31.0$, a calculation was made, after the fifth diagonal approximation, to determine what shifts would be required if B_{22}

Table V.

Minimum-energy-structure calculation of YF_3

Atom	Y		F_1		F_2		
(a)	x	z	x	z	x	y	z
(b)	0.3682	0.0594	0.526	0.577	0.177	0.074	0.363
(c)	-0.015	-0.011	-0.008	+0.029	-0.023	-0.006	+0.005
(d)	-0.010	-0.008	-0.006	+0.015	-0.012	-0.005	+0.004
(e)	0.358	0.051	0.520	+0.592	0.165	0.069	0.367
(f)	+0.004	-0.009	+0.001	+0.012	-0.009	-0.004	+0.013
(g)	+0.002	-0.006	0.000	+0.008	-0.006	-0.002	+0.008
(h)	0.360	0.045	0.520	0.600	0.159	0.067	0.375
(i)	-0.0029	+0.0029	+0.0055	-0.0043	+0.0004	+0.0009	-0.0046
(j)	-0.0010	+0.0010	+0.0030	-0.0020	0.0000	0.0000	-0.0020
(k)	0.3590	0.0460	0.5230	0.5980	0.1590	0.0670	0.3730
(l)	-0.0002	+0.0007	+0.0023	+0.0018	-0.0003	+0.0005	-0.0010
(m)	-0.0001	+0.0005	+0.0017	+0.0008	-0.0001	+0.0002	-0.0005
(n)	0.3589	0.0465	0.5247	0.5988	0.1589	0.0672	0.3725
(o)	+0.0004	-0.00007	+0.00006	+0.0012	-0.0003	+0.0002	-0.0005
(p)	+0.0001	-0.0001	+0.0001	+0.0008	-0.0002	+0.0002	-0.0003
(q)	0.3590	0.0464	0.5248	0.5996	0.1587	0.0674	0.3722
(r)	+0.0001	+0.00008	+0.0003	+0.0006	-0.0001	+0.0007	-0.0006

(a) Coordinate
(b) Original value of parameter
(c) Shift calculated by complete matrix calculation
(d) Shift actually used
(e) New value of parameter
(f) Shift calculated by first diagonal approximation
(g) Shift actually used
(h) New value of parameter
(i) Shift calculated by second diagonal approximation
(j) Shift actually used
(k) New value of parameter
(l) Shift calculated by third diagonal approximation
(m) Shift actually used
(n) New value of parameter
(o) Shift calculated by fourth diagonal approximation
(p) Shift actually used
(q) New value of parameter
(r) Shift calculated by fifth diagonal approximation

assumed the two extreme values of its range. These calculated shifts were then taken as a measure of the certainty with which the minimum-energy-structure coordinates where known. Table VI gives the standard deviations from the least-squares calculation together with the probable uncertainty of the coordinates of the minimum-energy-structure.

A comparison of the results given in Tables V and VI shows that the agreement of the x and z coordinates of yttrium is not much better than 1%. With respect to the fluorine atoms, the agreement is not quite this good, but in no case is worse than 2%.

It was felt that some of this disagreement could be overcome if the yttrium atoms were tied down to the experimentally determined parameters. A complete matrix calculation and one diagonal approximation calculation starting from the same parameters as the original calculations were made. The coordinates of the yttrium atoms were not allowed to vary but were held to the least-squares values. After the diagonal approximation, it became apparent that considerable disagreement between the least-squares values and this modified minimum-energy-structure would still exist if the calculation were to be carried out to completion. These results are shown in Table VII.

Although considerable disagreement still exists, and interesting observation concerning the usefulness of the model can now be made. It is to be expected that a purely ionic substance would arrange itself so that the ions would be in as highly symmetric, perfect packing as possible. A list of interatomic distances would then be a series of equal or approximately equal distances. The list of interatomic distances for the least-squares structure and for the minimum-energy-structure is given in Table VIII.

From the list of the yttrium-fluorine distances which are less than 2.60 Å, it may be seen that the effect of the minimum-energy-structure calculation was to make the structure more symmetric, i.e., to make the structure more ionic than it apparently is. It is likely that only effects other than those of ionic origin could result in the variety of interatomic distances obtained from the least-squares calculation. Thus it is conceivable that this potential model could serve to determine the extent of the ionic character of a structure.

Table VI

Accuracy of least-squares and minimum-energy-structure calculation of YF_3

Atom	Y		F_1		F_2		
Coordinate	x	z	x	z	x	y	z
Least-squares' σ	0.0003	0.0004	0.0027	0.0028	0.0022	0.0018	0.0031
Uncertainty of minimum-energy-structure	0.0007	0.002	0.0027	0.0074	0.0007	0.0011	0.0031

Table VII

Minimum-energy structure of fluorine positions in YF_3

Atom	Y		F_1		F_2		
(a)	x	z	x	z	x	y	z
(b)	0.3686	0.0595	0.526	0.577	0.177	0.074	0.363
(c)	-----	-----	-0.008	+0.029	-0.023	-0.006	+0.005
(d)	-----	-----	-0.001	+0.020	-0.015	-0.008	+0.012
(e)	-----	-----	0.525	0.597	0.162	0.066	0.375
(f)	-----	-----	+0.005	-0.002	-0.001	+0.0003	-0.002

(a) Coordinates
(b) Original value of parameter
(c) Shift calculated by complete matrix calculation
(d) Shift actually used
(e) New value of parameter
(f) Shift calculated by a diagonal approximation calculation

Table VIII

Y-F distances in YF_3	
Calculation	Distance
Least-squares	2.163
	2.163
	2.252
	2.341
	2.341
	2.346
	2.400
	2.400
	2.486
Minimum-energy-structure	2.217
	2.227
	2.287
	2.287
	2.305
	2.305
	2.309
	2.309
	(2.651)

APPLICATION OF MODEL TO $CdCl_2$

A final application of the potential model was made on the $CdCl_2$ structure in an attempt to determine the nature of the force holding the layers together. The $CdCl_2$ structure[20], described in Table X, consists of layers of Cl-Cd-Cl. . . Cl-Cd-Cl. . . etc, perpendicular to the hexagonal c axis. It is usually thought that van der Waals forces are responsible for holding the layers together, however no calculation had yet been made to determine if it is possible that the Coulomb attraction for one layer could reach across to another layer and thus serve as the cohesive force.

A crystal energy calculation was made in which the layers were maintained rigid but the spacing between layers, i. e., the interlayer chlorine-chlorine distance, was allowed to vary. Since the layers are perpendicular to the c axis, the value given to c suggests the amount of compression or expansion of the distance between layers. c was varied from 60.0 Å down to 15.5 Å with 17.50 Å representing the true cell constant. If c was allowed to vary much below 15.5, the repulsive potential due to the 1-2 interaction began to grow, showing that no possibility of a minimum-energy-structure exists past this point. Above this value the repulsive potential due to the 1-2 interaction is essentially constant so that it may be disregarded when the minimum energy is investigated.

Table IX gives the results of this calculation. U'(Cl-Cl) is equal to the 2-2 repulsive potential divided by B_{22}.

In order to evaluate these data, the question is asked, "Does a plot of the crystal energy of $CdCl_2$ versus the length of the c axis yield a minimum near 17. 5 when B_{22} assumes a reasonable value?" Such a plot for B_{22} = 10, 75, and 100 is shown in Figure 4.

From Figure 4 it may be seen that no minimum exists for B_{22} greater than 100. In such a structure the layers would not attract each other. Contrariwise, if B_{22} were as low as 10, the layers would collapse. Taking B_{22} to be approximately 75, it is noted that the energy curve is approximately straight.

Table IX

Variation of $CdCl_2$ Coulomb and repulsive potentials due to separation of the layers

c cell-constant	U' (Cl-Cl)	-Uc
15.50	.1245	563.379
16.00	.1049	561.893
16.50	.0906	560.834
16.75	.0849	560.404
17.00	.0801	560.031
17.30	.0753	559.622
17.50	.0725	559.428
17.70	.0700	559.228
18.00	.0669	558.963
18.25	.0647	558.786
18.50	.0628	558.634
19.00	.0598	558.418
60.00	.0506	557.677

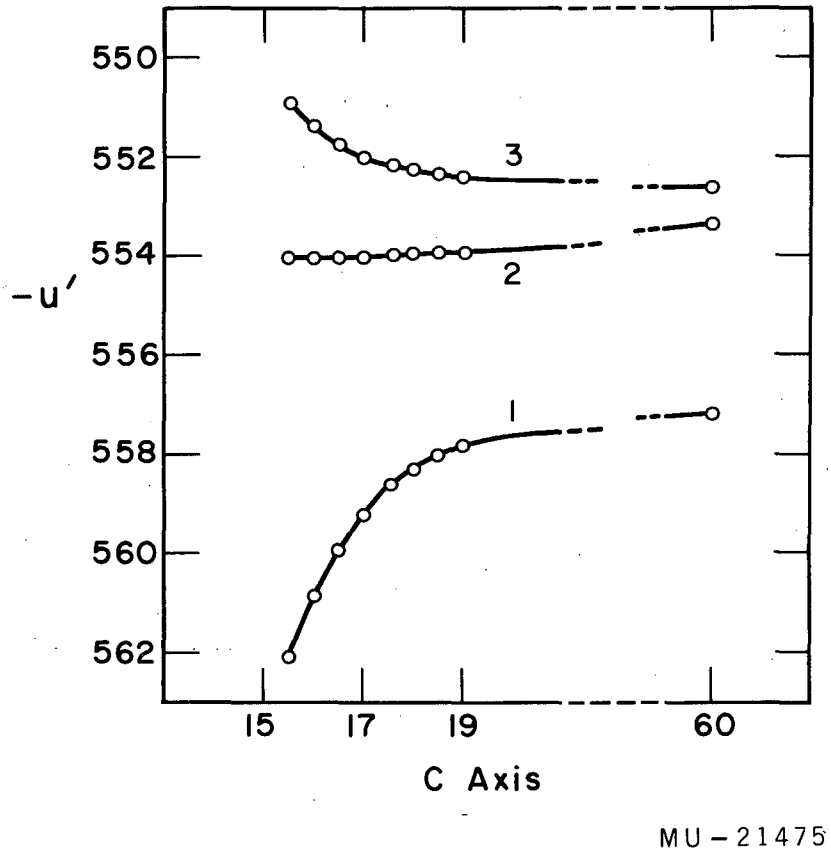

Fig. 4. Plot of the psuedo-crystal energy of $CdCl_2$ versus the length of the e axis.

It is now necessary to determine a crude value for B_{22}, so as to be able to evaluate these results. Using equation (10) the following equation may be written

$$\frac{B_{12}}{B_{13}} = \frac{A_2}{A_3} \left(\frac{R_{12}}{R_{13}}\right)^{n-1} . \tag{22}$$

A_2 refers to the Madelung constant for the structure to which R_{12} refers. A_3 is similarly defined. It is reasonable to assume that a crude approximation to B_{22} may be obtained by a similar equation. If this calculation is made, it is found that $46 \leq B_{Cl-Cl} \leq 125$ or an average value of 86.

These calculations have shown that the Coulomb potential is not the cohesive force in the $CdCl_2$ structure. It is, nevertheless, indirectly responsible for the existence of this particular structure. The effect of the Coulomb potential is to nearly cancel the Pauli repulsion so as to enable a small attractive force between chlorine ions, such as is found in the van der Waals potential, to be responsible for holding these layers together. If it were not for the ability of the Coulomb potential to nearly cancel the Pauli repulsion, the small van der Waals attractive force would not be a sufficient force to hold these layers together at the experimentally observed distance.

DISCUSSION OF RESULTS

The importance of these calculations is that they have served to point out some of the weak points and also some of the strong points in the application of this particular model to the solutions of some crystal chemistry problems. Concern is aroused because the coordinates of the minimum-energy-structure and the x-ray structure do not agree better than approximately 2% in YF_3. As stated before, this disagreement could conceivably be utilized to determine just how ionic a substance actually is.

On the other hand, the success met in the brookite calculations are encouraging. It is possible that much could be learned by calculations of this sort on truly ionic substance. In particular, many structures

exist in which the structure type and cell dimensions are known but the value of the two or three structural parameters have not been determined; they have been accepted as close to the values of a similar structure. In such cases, these parameters could easily be checked to determine if they are reasonably appropriate for the compound.

The usefulness of this model has been conclusively demonstrated in the differentiation of two alternative structures. Alternative structures which, because of similar scattering power of two constituents of the compound, would give practically identical intensity data may be quite readily distinguished by this method. Not to be overlooked, however, is the possible application of this model in the event that a structure anomoly such as is described by A. L. Patterson occurs.[21] In such a case two different structures (homometric structures) give identical intensity data.

Finally, there are quite a number of questions, such as the $CdCl_2$ problem, which could be at least partially answered by the use of this model.

MADELUNG CONSTANTS

These calculations have resulted in an accumulation of reliable Madelung constants. Since there are many applications for these, some effort was made to compile a table of these values. A list of these constants is useless, however, unless the values of the parameters that were used are specified. A description of each structure is given in Table X, where the space group, the Wycoff symmetry, and any parameters involved are listed.

The first information in the structure part of Table X is the space group. This is followed by the a, b(if any), c(if any), and β (if any) cell constants. The third piece of information in this table is the symbol of an atom with its Wycoff symmetry. Any x, y, or z parameters for this atom are then listed before another atom is treated in similar fashion.

As an example of this notation, take α-Al_2O_3. The space group is $R\bar{3}c$. Two cell constants are given so they are obviously the hexagonal a and c axis, respectively. Aluminum is in Wycoff symmetry,

Table X

Description of structures for which Madelung constants were calculated

Compound	Structure
$AlCl_3$	C2/m; 5.93, 10.24, 6.17, 108°; Al-g, .167; Cl-i, .226, .219; Cl-j, .250, .175, .781
αAl_2O_3	$R\bar{3}c$; 4.7628, 13.0082; Al-c, .355; O-e, .303
$BeCl_2$	Ibam; 9.86, 5.36, 5.26; Be-a; Cl-j, .109, .203
BeO	$P6_3mc$; 2.698, 4.380; Be-b, (0,0); O-b, .365
BiSCl	Pnma; 7.70, 4.00, 9.87; Bi-c, .140, .138; S-c, .77, .04; Cl-c, .50, .79
$CaCl_2$	Pnnm; 6.25, 6.44, 4.21; Ca-a; Cl-g, .275, .325
$CaTiO_3$	Pm3m; 3.84; Ca-a; Ti-b; O-c
$CdCl_2$	$R\bar{3}m$; 3.86, 17.50; Cd-a; Cl-c, .25
CdI_2 (Bozorth)	$P\bar{3}m1$; 4.240, 6.855; Cd-a; I-d, .25
CdI_2 (Hassel)	$P6_3mc$; 4.240, 13.710; Cd-b, .00 ; I-b, .625; I-a, .375
$LaCl_3$	$P6_3/m$; 7.483, 4.375; La-d; Cl-h, .287, .382
LaF_3	$P6_3/mmc$; 4.148, 7.354; La-c; F-b; F-f, .57
La_2O_3	$P\bar{3}m1$; 3.9373, 6.1299; La-d, .245; O-a; O-d, .645
LaOCl	P4/nmm; 4.119, 6.883; La-c, .178; O-a; Cl-c, .635
βLaOF	$R\bar{3}m$; 4.0507, 20.213; La-c, 242; O-c, .122; F-c, .370
γLaOF	P4/nmm; 4.091, 5.837; La-c, .778; O-a; F-b
$MgAl_2O_4$	Fd3m; 8.0800; Mg-a; Al-d; O-e, .387
MgF_2	$P4_2/mnm$; 4.623, 3.052; Mg-a; F-f, .31
SiF_4	$I\bar{4}3m$; 5.41; Si-a; F-c, .165
βSiO_2	$P6_222$; 5.02, 5.48; Si-c; O-j, .197
$SrBr_2$	Pnma; 11.44, 4.31, 9.22; Sr-c, -.189, .108; Br-c, .103, .119; Br-c .614, -.158
$TiCl_2$	$P\bar{3}m1$; 3.561, 5.875; Ti-a; Cl-d, .25
Rutile	$P4_2/mnm$; 4.5929, 2.9591; Ti-a; O-f, .3056
Anatase	$I4_1/amd$; 3.785, 9.514; Ti-a; O-e, .2064
Brookite	Pbca; 9.184, 5.447, 5.145; Ti-c, .128, .098, .863; O-c, .008, .147, .182; O-c, .229, .110, .530

Table X (continued)

Compound	Structure
UD_3	Pm3n; 6.64; U-a; U-c; D-k, .155, .31
V_2O_5	Pmmn; 11.519, 3.564, 4.373; V-f, .1486, .105; O-f, .149, .458; O-f, .320, .000; O-a, .000
YCl_3	C2/m; 6.92, 11.94, 6.44, 111.0°; Y-g, .166; Cl-i, .211, .247; Cl-j, .229, .179, .760
YF_3	Pnma; 6.353, 6.850, 4.393; Y-c, .3686, .0595; F-c, .527, .577; F-d, .180, .074, .364
Y_2O_3	Ia3; 10.604; Y-b; Y-d, -.030; O-e, .385, .145, .380
YOCl	P4/nmm; 3.903, 6.597; Y-c, .18; O-a; Cl-c, .64
ZnO	$P6_3mc$; 3.2495, 5.2069; Zn-b, (0.0); O-b, .345
ZnS	$P6_3mc$; 3.819, 6.246; Zn-b, (0.0); S-b, .375

c (see Ref. 22). This position has coordinates (0, 0, 0; 1/3, 2/3, 2/3; 2/3, 1/3, 1/3) + 0, 0, z; 0, 0, $\bar{z}$; 0, 0, 1/2 $\pm$z; 0, 0, 1/2-z. The parameter listed after aluminum, 0.355, is the value that should be given to z. Similarily, oxygen is in Wycoff symmetry, e, which also requires one parameter. The value of this parameter is 0.303. No attempt was made to find the latest structures in every case; in most cases these structures correspond to the latest structure listed in the Wycoff tables.

Table XI is the list of Madelung constants for the structures described in Table X. The last digit of the constants may be used but calculations of the cubic structures show that this digit is sometimes in error by as much as 10%

These constants are based on the shortest interatomic distance, L, as the unit of measure. In some cases the average shortest interatomic distance would have had more significance but, since this would have introduced considerable ambiguity concerning what was the average shortest interatomic distance, this convention was not followed.

Alpha[4] is a measure of the extent in reciprocal space for which the series was calculated.

Table XI

Madelung constants

Compound	α/π	L	Correction	Madelung Constant
$AlCl_3$	3	2.29530	0.002	8.303
α Al_2O_3	3	1.84775	0.006	24.242
$BeCl_2$	3	2.01698	0.0011	4.086
BiSCl	3	2.72265	0.003	10.388
$CaCl_2$	3	2.70827	0.0011	4.730
CaF_2	5	2.36035	0.00007	5.03879
$CaTiO_3$	5	1.92000	0.0004	24.7550
$CdCl_2$	3	2.66332	0.0011	4.489
CdI_2 (Bozorth)	5	2.98822	0.00007	4.38190
CdI_2 (Hassel)	5	2.98822	0.00007	4.38409
CsCl	5	3.57062	0.00002	1.76268
Cu_2O	5	1.84117	0.00007	4.44249
$LaCl_3$	3	2.95032	0.002	9.129
LaF_3	3	2.35328	0.002	9.119
La_2O_3	3	2.37110	0.006	24.179
LaOCl	3	2.39637	0.003	10.923
β LaOF	3	2.41943	0.003	11.471
γ LaOF	5	2.42141	0.0002	11.3914
$MgAl_2O_4$	3	1.91731	0.007	31.475
MgF_2	3	1.96768	0.0011	4.762
NaCl	5	2.81384	0.00002	1.74756
SiF_4	3	1.54612	0.004	12.489
β SiO_2	3	1.61913	0.004	17.609
$SrBr_2$	3	3.16054	0.0011	4.624
$TiCl_2$	3	2.52668	0.0011	4.347
Rutile	5	1.94511	0.0003	19.0803
Anatase	5	1.93743	0.0003	19.0691
Brookite	3	1.84244	0.004	18.006
UD_3	3	2.05840	0.002	8.728

Table XI (continued)

Compound	α/π	L	Correction	Madelung Constant
V_2O_5	3	1.54368	0.013	44.32
YCl_3	3	2.58451	0.002	8.313
YF_3	3	2.16297	0.002	8.899
Y_2O_3	3	2.25319	0.006	24.844
YOCl	3	2.28439	0.003	10.916
ZnO	5	1.79638	0.00009	5.99413
ZnS (cubic)	5	2.34087	0.00009	6.55222
ZnS (hexagonal)	5	2.33905	0.00009	6.56292

PART II.

THE CRYSTAL STRUCTURE OF SEMICARBAZIDE HYDROCHLORIDE

INTRODUCTION

In the course of earlier research, interest in a nitrogen-nitrogen single bond led to a search for a suitable structure in which such a bond could be observed with reasonable accuracy, unobstructued by thermal effects or scattering by extremely heavy atoms. For this purpose semicarbazide hydrochloride appeared particularly suitable.

EXPERIMENTAL

Commercially available $CH_5N_3O \cdot HCL$ was recrystallized from water. A slender rod $0.2 \times 0.2 \times 0.6$ mm was obtained. Cell dimensions were derived from quartz-calibrated rotation and zero-layer Weissenberg photographs, with rotation about the c axis. The intensity measurements were made from a set of mulitple-film Weissenberg photographs. A total of 481 independent reflections were recorded of which 110 were too weak to be observed. For this crystal $\mu r = 0.61$.

UNIT CELL AND SPACE GROUP

The Laue symmetry, mmm, and the systematic absences ($h00$, $h = 2n + 1$; $0k0$, $k = 2n + 1$; 00ℓ, $\ell = 2n + 1$) indicated the space group $P2_12_12_1$. Subsequent refinement in this space group confirms this choice.

The cell dimensions are:

$$a = 7.543 \pm 0.015\ \text{Å}$$
$$b = 13.224 \pm 0.026\ \text{Å}$$
$$c = 4.668 \pm 0.015\ \text{Å}$$

The specific gravity as determined by suspension methods was 1.58 gm/cc. Using the above cell-constants and assuming four molecules in the unit cell, the calculated density is 1.59 gm/cc.

DETERMINATION OF THE STRUCTURE

A three-dimensional Patterson map was calculated using an IBM 701 Fourier program.[23] From this map the approximate coordinates of chlorine, carbon, and one atom of nitrogen were obtained. These atoms were the basis for a subsequent Fourier calculation in which only those structure factors that satisfied the following arbitrary standards were used:

$$F_o > F_{min}$$

$$(F_o - F_c) / F_o \lesssim 1/3.$$

From this Fourier calculation eight peaks were located. Two least-squares refinement cycles on the IBM 650[24] were made by using positions obtained from six of these peaks. It was then noticed that a more reasonable structure could be found by a reinterpretation of this Fourier calculation. This structure refined quite well. After the removal of two reflections (040, 200) that were too intense to permit any reasonable accuracy in measurement, and 16 cycles of least-squares, the following agreement factors[24] resulted:

$$R_1 = 0.081$$

$$R_2 = 0.117$$

$$R_3 = 0.123 .$$

The treatment that was used for unobserved reflections was that described by Senko[24] with the exception that for unobserved reflections for which $F_o < F_c$, $(F_o - F_c)$ was used in calculating the shifts.

Possible improvement in the agreement by the introduction of hydrogen atoms was considered. A three-dimensional difference Fourier, $F_o - F_c$ (Cl, O, N, C), was calculated. With the short intermolecular distances and the angles as a guide for the location of

hydrogen bonds, together with this Fourier, an attempt to locate the hydrogen atoms was made. This effort was unsuccessful partly because of the adverse effects of the heavy atoms and partly because not all hydrogen atoms were involved in hydrogen bonding. From this difference-Fourier it was possible to observe, however, that the heavy atoms were correctly located. Table XII gives the final atomic parameters. The observed and calculated structure factors are compared in Table XIV.

DISCUSSION

Although, as stated above, it was not possible to locate the hydrogen positions, the intermolecular distances and the angles indicate which atoms are hydrogen-bonded. These hydrogen bonds are listed in Table XIII. The only other distances that were less than 3.4 Å and were not accounted for were a N_3-Cl distance of 3.27 Å and a N_2-O distance of 3.04 Å. (The numbering of nitrogen atoms is shown in Figure 6). This latter distance can be easily explained, since the N_3 neighbor to this N_2 is involved in a hydrogen bond to that oxygen atom. This N_3-O bond distance is 2.85 Å and the short N_2-O distance in merely a consequence of this fact.

The N_3-Cl distance of 3.27 Å is not an acceptable choice for a hydrogen bond since three other atoms surround this N_3 at more acceptable hydrogen-bond distances. These other three atoms also permit a more regular tetrahedron about the N_3 than would be permitted by this particular chlorine atom.

Table XIII shows two distances involving the N_1 atom. Although the angles involved are compatible with an N_1-N_3 bond or an N_1-Cl bond it is unlikely that both distances represent hydrogen bonding, since the angle between these bonds would be 65 degrees. Since both distances are somewhat longer than a typical nitrogen-nitrogen or nitrogen-chlorine hydrogen bond distances, no definite assignment can be made, although the N_1-N_3 bond does appear more likely.

Table XII

Final atomic parameters of semicarbazide hydrochloride

Atom	B	x	y	z	σ_x	σ_y	σ_z
Cl	3.119	0.74598	0.63998	0.96540	0.00022	0.00013	0.00056
O	3.02	0.2434	0.5869	0.8206	0.0006	0.0004	0.0015
N_1	3.50	0.0728	0.6614	0.4780	0.0009	0.0005	0.0021
N_2	2.79	0.3656	0.6329	0.3933	0.0007	0.0004	0.0019
N_3	2.80	0.5113	0.5647	0.4612	0.0007	0.0004	0.0019
C	2.07	0.2219	0.6244	0.5771	0.0007	0.0004	0.0020

Table XIII

Suspected hydrogen bonding in semicarbazide hydrochloride

Bond	Distance (Å)	Comments
$N_1 \cdot\cdot H \cdot\cdot Cl$	3.37	Not necessarily bonded
$N_1 \cdot\cdot H \cdot\cdot N_2$	3.19	Not necessarily bonded
$N_2 \cdot\cdot H \cdot\cdot O$	2.89	Bonding within [010] plane
$N_3 \cdot\cdot H \cdot\cdot Cl$	3.08	Bonding within [010] plane
$N_3 \cdot\cdot H \cdot\cdot Cl$	3.11	Bonding within [010] plane
$N_3 \cdot\cdot H \cdot\cdot O$	2.85	Bonding across [010] planes

h	k	ℓ	F_o	F_c
0	1	2	59	86
0	1	3	7	9
0	2	0	15	14
0	2	1	47	51
0	2	2	23	22
0	2	3	14	13
0	3	1	16	13
0	3	2	46	49
0	3	3	14	12
0	4	1	29	30
0	4	2	87	95
0	4	3	24	20
0	5	1	35	38
0	5	2	40	37
0	5	3	49	53
0	6	0	22	23
0	6	1	17	17
0	6	2	65	57
0	6	3	30	31
0	7	1	21	21
0	7	2	13	13
0	7	3	9*	7
0	8	0	53	54
0	8	1	18	22
0	8	2	38	34
0	8	3	12	12
0	9	1	25	26
0	9	2	12	11
0	9	3	44	47
0	10	0	56	58
0	10	1	13*	3
0	10	2	52	54
0	10	3	23	24
0	11	1	13*	1
0	11	2	12*	11
0	11	3	12	9
0	12	0	14	14
0	12	1	14*	2
0	12	2	17	18
0	12	3	9*	4
0	13	1	13*	9
0	13	2	15	17
0	13	3	21	22
0	14	0	39	42
0	14	1	12*	6
0	14	2	23	26
0	14	3	6	6
0	15	1	18	20
0	15	2	8	9
0	16	0	10	9
0	16	1	8*	5
1	0	1	41	34
1	0	2	4*	1
1	0	3	22	22
1	1	0	35	40
1	1	1	45	35
1	1	2	58	61
1	1	3	30	33
1	2	0	28	27
1	2	1	150	184
1	2	2	20	17
1	2	3	59	73
1	3	0	21	27
1	3	1	64	58
1	3	2	51	50
1	3	3	31	32
1	4	0	68	71
1	4	1	80	79
1	4	2	44	45
1	4	3	10	10
1	5	0	38	43
1	5	1	51	54
1	5	2	34	33
1	5	3	31	32
1	6	0	9*	9
1	6	1	102	110
1	6	2	32	31
1	6	3	37	36
1	7	0	58	60
1	7	1	34	37
1	7	2	27	27
1	7	3	16	20
1	8	0	16	13
1	8	1	66	67
1	8	2	26	26
1	8	3	12	12
1	9	0	21	19
1	9	1	33	35
1	9	2	12*	7
1	9	3	16	19
1	10	0	13*	4
1	10	1	50	51
1	10	2	16	17
1	10	3	10*	6
1	11	0	40	42
1	11	1	13*	8
1	11	2	17	20
1	11	3	11	11
1	12	0	16	13
1	12	1	33	39
1	12	2	16	18
1	12	3	15	16
1	13	0	14	12
1	13	1	15	13
1	13	2	21	19
1	13	3	11	9
1	14	0	12	13
1	14	1	20	18
1	14	2	10*	9
1	14	3	8	6
1	15	0	11	14
1	15	1	13	12
1	15	2	10	12
1	16	1	17	18
2	0	1	10	9
2	0	2	24	21
2	0	3	21	23
2	1	0	19	18
2	1	1	109	117
2	1	2	34	30
2	1	3	39	39
2	2	0	18	16
2	2	1	84	88
2	2	2	45	43
2	2	3	49	56
2	3	0	7*	1
2	3	1	91	89
2	3	2	26	21
2	3	3	18	18
2	4	0	115	144
2	4	1	33	32
2	4	2	50	52
2	4	3	13	15
2	5	0	9*	1
2	5	1	51	48
2	5	2	25	22
2	5	3	44	43
2	6	0	11	13
2	6	1	20	24
2	6	2	53	53
2	6	3	27	29
2	7	0	18	18
2	7	1	16	18
2	7	2	13	13
2	7	3	18	18
2	8	0	73	81
2	8	1	19	20
2	8	2	58	61
2	8	3	17	19
2	9	0	14	9
2	9	1	26	28
2	9	2	12*	4
2	9	3	37	37
2	10	0	15	12
2	10	1	13*	4
2	10	2	27	29
2	10	3	15	16
2	11	0	16	11
2	11	1	36	37
2	11	2	12*	7
2	11	3	14	16
2	12	0	23	22
2	12	1	13*	12
2	12	2	27	28
2	12	3	15	18
2	13	0	13*	8
2	13	1	20	22
2	13	2	11*	11
2	13	3	21	22
2	14	0	17	22
2	14	1	11*	5
2	14	2	16	16
2	14	3	9	10
2	15	1	23	21
2	15	2	7*	1
2	16	1	7*	7
3	0	1	26	21
3	0	2	47	40
3	0	3	8*	7
3	1	0	33	33
3	1	1	41	34
3	1	2	69	64
3	1	3	21	20
3	2	0	8*	2
3	2	1	57	53
3	2	2	23	23
3	2	3	52	54
3	3	0	100	114
3	3	1	46	43
3	3	2	66	73
3	3	3	8*	7
3	4	0	51	48
3	4	1	23	23
3	4	2	46	47
3	4	3	16	18
3	5	0	30	25
3	5	1	12	13
3	5	2	34	35
3	5	3	10	11
3	6	0	32	30
3	6	1	53	51
3	6	2	39	39
3	6	3	32	32
3	7	0	95	101
3	7	1	28	28
3	7	2	45	46
3	7	3	10*	4
3	8	0	19	16
3	8	1	27	29
3	8	2	35	35
3	8	3	14	17
3	9	0	21	23
3	9	1	16	18
3	9	2	19	21
3	9	3	10*	5
3	10	0	15	15
3	10	1	37	38
3	10	2	20	23
3	10	3	11	12
3	11	0	46	48
3	11	1	14*	3
3	11	2	15	20
3	11	3	9	10
3	12	0	13*	1
3	12	1	24	26
3	12	2	22	20
3	12	3	13	16
3	13	0	14	15
3	13	1	12*	7
3	13	2	20	19
3	13	3	6*	4
3	14	0	11*	3
3	14	1	17	18
3	14	2	10	10
3	15	0	11	13
3	15	1	8*	6
4	0	0	111	128
4	0	1	39	34
4	0	2	62	55
4	0	3	13	12
4	1	0	17	10
4	1	1	69	65
4	1	2	23	22
4	1	3	20	19
4	2	0	26	26
4	2	1	66	60
4	2	2	12	14
4	2	3	42	40
4	3	0	10*	6
4	3	1	30	28
4	3	2	10*	3
4	3	3	17	17
4	4	0	65	72
4	4	1	18	14
4	4	2	46	39
4	4	3	22	23
4	5	0	11*	4
4	5	1	80	79
4	5	2	12	9
4	5	3	39	40
4	6	0	16	16
4	6	1	35	34
4	6	2	22	21
4	6	3	39	41
4	7	0	18	20
4	7	1	14	12
4	7	2	17	18
4	7	3	13	10
4	8	0	18	12
4	8	1	14	9
4	8	2	24	23
4	8	3	16	19
4	9	0	14*	3
4	9	1	44	44
4	9	2	12	12
4	9	3	31	30
4	10	0	20	21
4	10	1	17	14
4	10	2	34	30
4	10	3	25	26
4	11	0	13*	13
4	11	1	12	6
4	11	2	11*	11
4	11	3	8*	6
4	12	0	13*	4
4	12	1	12*	10
4	12	2	17	16
4	12	3	9	10
4	13	0	11*	5
4	13	1	13	14
4	13	2	14	13
4	14	0	20	23
4	14	1	9*	4
4	14	2	16	19
5	0	1	12	9
5	0	2	27	27
5	0	3	10	10
5	1	0	21	21
5	1	1	14	13
5	1	2	42	36
5	1	3	14	11
5	2	0	12*	4
5	2	1	54	50
5	2	2	18	18
5	2	3	49	49
5	3	0	44	40
5	3	1	31	28
5	3	2	35	27
5	3	3	10*	1
5	4	0	12	3
5	4	1	36	38
5	4	2	26	28
5	4	3	10*	9
5	5	0	13*	5
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5	5	3	13	11
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5	8	2	22	25
5	8	3	14	12
5	9	0	14*	3
5	9	1	21	22
5	9	2	12*	2
5	9	3	10	9
5	10	0	18	18
5	10	1	20	19
5	10	2	20	20
5	10	3	7*	7
5	11	0	39	41
5	11	1	12*	10
5	11	2	15	17
5	11	3	6*	7
5	12	0	11*	9
5	12	1	20	18
5	12	2	18	19
5	13	0	10*	5
5	13	1	9*	9
5	13	2	9	10
6	0	0	69	67
6	0	1	20	22
6	0	2	32	29
6	0	3	10*	1
6	1	0	36	34
6	1	1	35	32
6	1	2	18	17
6	1	3	13	9
6	2	0	16	14
6	2	1	32	29
6	2	2	27	22
6	2	3	26	25
6	3	0	28	30
6	3	1	38	35
6	3	2	16	16
6	3	3	10*	6
6	4	0	61	58
6	4	1	17	18
6	4	2	36	33
6	4	3	10*	3
6	5	0	20	21
6	5	1	16	15
6	5	2	13	11
6	5	3	13	12
6	6	0	24	23
6	6	1	14	11
6	6	2	35	34
6	6	3	14	16
6	7	0	12	9
6	7	1	13*	8
6	7	2	12*	6
6	7	3	8*	3
6	8	0	28	29
6	8	1	13*	7
6	8	2	27	26
6	8	3	9	11
6	9	0	17	14
6	9	1	19	18
6	9	2	10	8
6	9	3	18	17
6	10	0	12	14
6	10	1	11*	3
6	10	2	21	19
6	10	3	10	10
6	11	0	11*	1
6	11	1	11	9
6	11	2	8*	1
6	12	0	9*	1
6	12	1	8	7
6	13	0	10	11
7	0	1	13*	3
7	0	2	12*	2
7	0	3	12	8
7	1	0	14*	2
7	1	1	26	27
7	1	2	21	18
7	1	3	18	16
7	2	0	31	32
7	2	1	46	39
7	2	2	13	13
7	2	3	29	26
7	3	0	26	26
7	3	1	25	23
7	3	2	24	23
7	3	3	12	11
7	4	0	13*	5
7	4	1	16	11
7	4	2	11*	6
7	4	3	8*	2
7	5	0	13*	5
7	5	1	15	14
7	5	2	12	9
7	5	3	11	10
7	6	0	13*	9
7	6	1	30	26
7	6	2	11	12
7	6	3	13	12
7	7	0	33	33
7	7	1	14	14
7	7	2	22	19
7	7	3	6*	1
7	8	0	12*	2
7	8	1	21	20
7	8	2	12	10
7	9	0	11*	2
7	9	1	16	11
7	9	2	8*	2
7	10	0	9*	1
7	10	1	19	15
7	11	0	18	19
8	0	0	53	47
8	0	1	12*	2
8	0	2	26	19
8	0	3	6*	1
8	1	0	17	16
8	1	1	21	20
8	1	2	18	17
8	1	3	14	13
8	2	0	12*	5
8	2	1	12*	8
8	2	2	10*	1
8	2	3	7	5
8	3	0	11	10
8	3	1	12*	6
8	3	2	11	10
8	3	3	5*	3
8	4	0	37	34
8	4	1	11*	6
8	4	2	19	15
8	5	0	18	18
8	5	1	30	25
8	5	2	17	16
8	6	0	10*	1
8	6	1	10*	5
8	6	2	7*	6
8	7	0	10*	7
8	7	1	9*	1
8	7	2	6*	5
8	8	0	15	14
8	8	1	8*	8
8	9	0	10	10
9	0	1	9*	6
9	0	2	6*	1
9	1	0	12	9
9	1	1	9*	2
9	1	2	20	17
9	2	0	9*	2
9	2	1	21	15
9	3	0	20	15
9	3	1	8*	6
9	4	0	8*	1
9	5	0	7*	1

Table XIV. Observed and calculated structure factors for semicarbazide hydrochloride. *indicates minimum observable structure factor.

An [001] projection of the structure of semicarbazide hydrochloride may be seen in Figure 5. From this drawing it can be seen that a $CON_3H_6^+$ ion and a Cl^- ion lie approximately in a {010} plane. There are four such planes in the unit cell. Not counting the two uncertain N_1 hydrogen bonds, only one hydrogen bond is involved in bonding across these {010} planes whereas the rest of the hydrogen bonds in this structure are utilized to hold these {010} planes together. This would be expected to give rise to crystals which had a tendency to grow in the direction of the c axis and cleave rather easily in the {010} plane. Observation confirmed this.

The final intramolecular bond distances and angles are shown in Figure 6. The standard deviation of the bond distances is about 0.01 Å for all distances other than the N_2-N_3 distance. The nitrogen-nitrogen bond distance of 1.457 ± 0.007 Å is in close agreement with that reported for N_2H_4 (1.46 Å), $(CH_3)_2N_2H_2$ (1.46 Å)[25] and cyclopropane carbohydrazide (1.43 Å)[26].

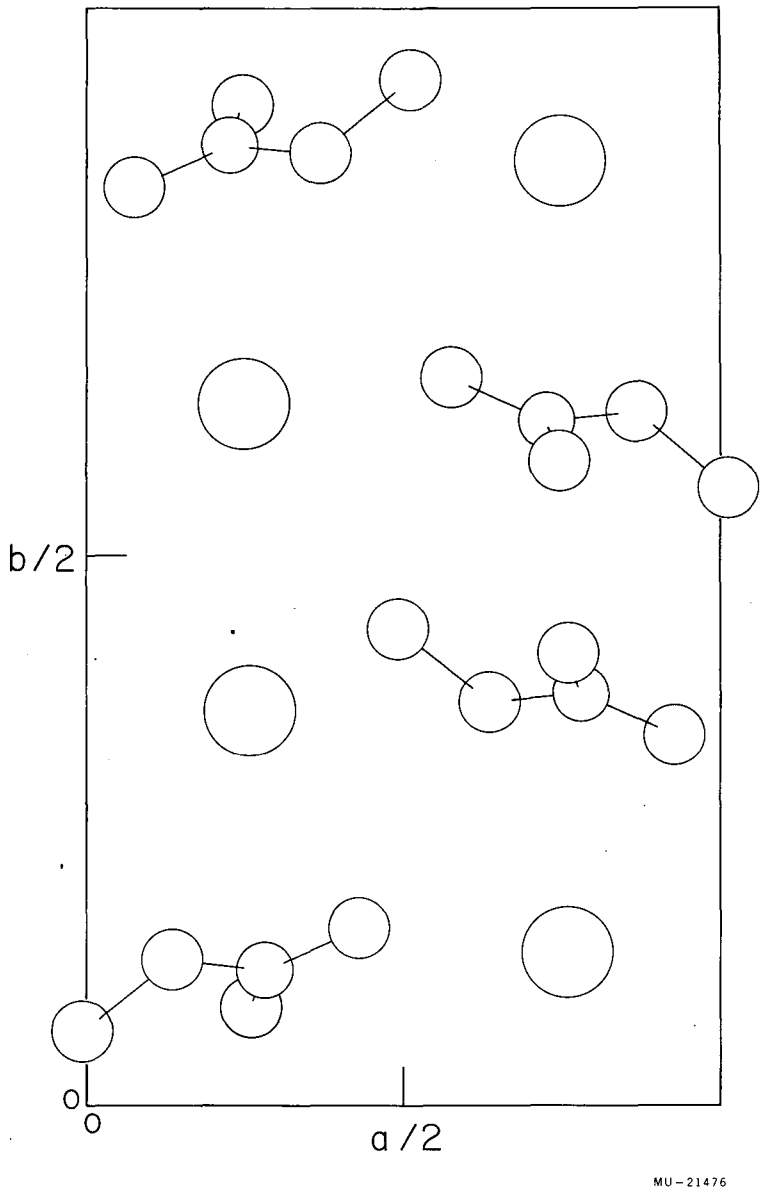

Fig. 5. [001] projection of semicarbazide hydrochloride.

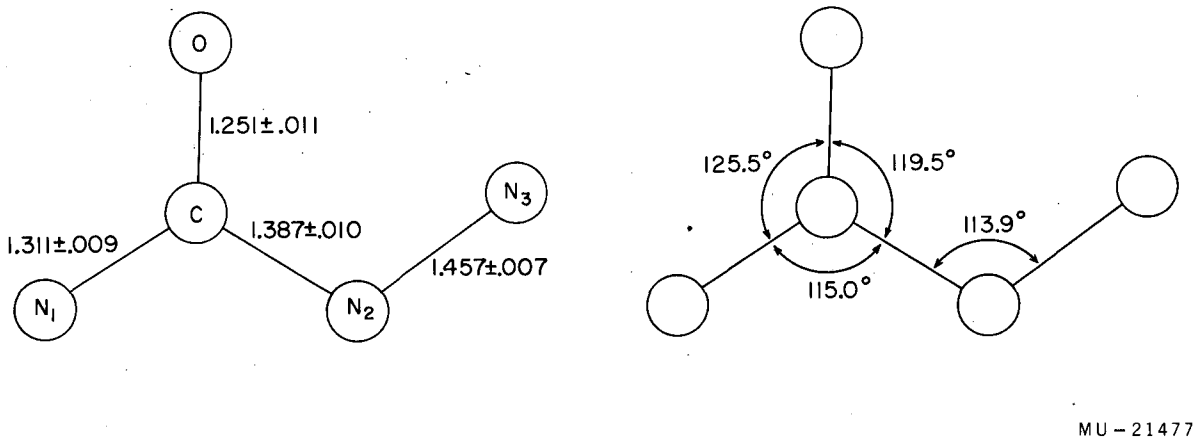

Fig. 6. Bond distances and angles in semicarbazide hydrochloride.

PART III. A REDETERMINATION OF THE CRYSTAL STRUCTURE OF TETRAMETHYLAMMONIUM BROMIDE

INTRODUCTION

A search for an acceptable value of the carbon-nitrogen bond-length in a quaternary amine, revealed that no reliable data were available. The values 1.55 ± 0.04 Å[27]; 1.50, 1.52, 1.53, and 1.60 ± 0.03 Å[28]; and 1.52, 1.54, 1.55, 1.56, and 1.58 ± 0.02 Å[29] were subject to such large variations and standard deviations that they had to be considered only approximate. The values 1.48-1.51 Å obtained from relatively simple compounds[30] were unacceptable, since only powder methods were employed. A redetermination of the simple compound tetramethylammonium bromide, by the use of modern techniques was undertaken in an attempt to improve the reliability of this bond length.

EXPERIMENTAL

Commercially available tetramethylammonium bromide was recrystallized from water. A rod-shaped piece approximately 0.2 × 0.2 × 0.5 mm was sliced from one of the tetragonal crystals which resulted. A complete set of multiple-film Weissenberg photographs with rotation about [100] were taken using this crystal. The intensities from the Weissenberg photographs were measured by visual comparison with a set of standard intensities. A total of 198 independent reflections were read of which 20 were too weak to be observed. For this crystal $\mu r = 0.79$ but no absorption correction of these data was made.

UNIT CELL AND SPACE GROUP

Systematic absences were observed for (hk0) with $h + k = 2n + 1$, corresponding to the space group P4/nmm which is the choice of the earlier workers. The space group is unequivocably confirmed by the final structure.

The cell constants, which were determined by measurement of the powder pattern from a camera with a 114.59 mm diameter, are:

$$a = 7.704 \pm 0.010 \text{ Å},$$

$$c = 5.501 \pm 0.008 \text{ Å}.$$

The values given by Vegard [31] are in slight disagreement after the kX correction is made. These values are:

$$a = 7.723 \text{ Å},$$

$$c = 5.512 \text{ Å}.$$

REFINEMENT OF THE STRUCTURE

The final parameters of Vegard[31] were used for an initial structure. Choosing the center of symmetry as origin, these parameters, as shown in Figure 7, were:

$$u = 0.625,$$

$$x = 0.903,$$

$$z = 0.161.$$

After five least-squares refinement cycles by the IBM 650 program of Senko, [24] which was modified for the space group P4/nmm, the reliability factor R_1 was equal to 12.65%. At this point, reflections (111) and (200), which were too intense to measure with any degree of certainty, were removed; a different treatment of unobserved reflections was employed; and hydrogen atoms were introduced.

The treatment that was used for unobserved reflections was described in the earlier section on the crystal structure of semicarbazide hydrochloride.

The problem of hydrogen atoms offered three possible solutions. The absence of even the slightest intensity for reflection (hk0) with $h + k = 2n + 1$ indicates that the hydrogen atoms are either rotating or are in one of two possible positions consistent with the symmetry of the space group P4/nmm. Since free rotation could only be proved by the absence of the other two possible solutions, the latter were both tried.

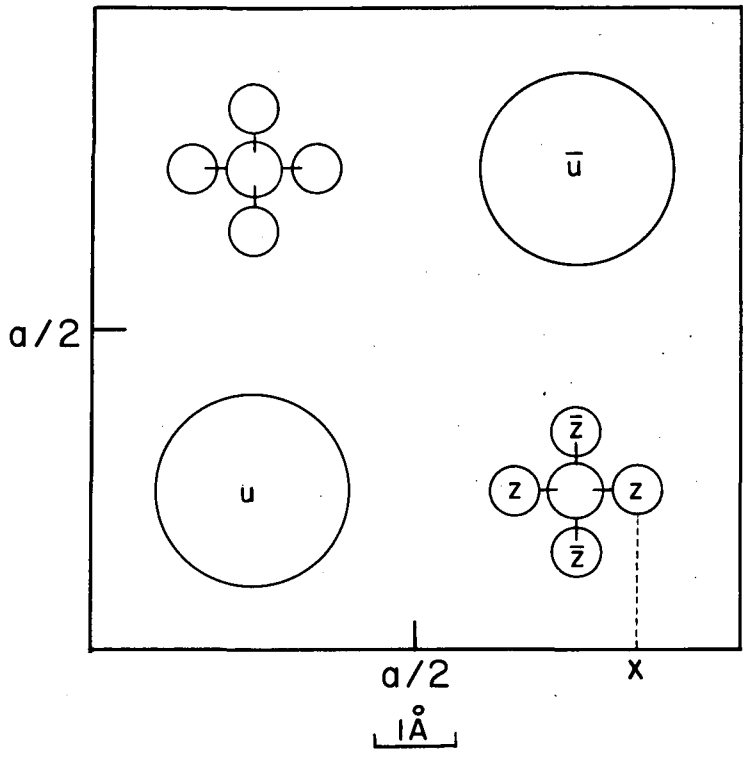

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Fig. 7. [001] projection of the unit cell of tetramethylammonium bromide.

For both cases the hydrogen atoms were placed in tetrahedral arrangement 1.08 Å from the carbon atoms. The space group requires that one hydrogen atom of each methyl group lie in the mirror plane, co-planar with the methyl carbon, the nitrogen, and the opposite methyl carbon. Figure 8 (a)(b) shows the two possible configurations.

After three least-squares cycles with the structure shown in Figure 8 (a) the following reliability factors were obtained:

$$R_1 = 0.101,$$

$$R_2 = 0.106,$$

$$R_3 = 0.109.$$

Further refinements resulted in no gain over these values. In this structure (Fig. 8(a)) as in the other (Fig. 8(b)), the hydrogen atoms were not permitted to refine but were shifted only by an amount necessary for them to remain in tetrahedral configuration about the carbon at a distance of 1.08 Å.

After seven cycles with the structure shown in Figure 8(b) the following reliability factors resulted:

$$R_1 = 0.095,$$

$$R_2 = 0.098,$$

$$R_3 = 0.101.$$

Detailed difference-Fourier (F_o-F_c(Br, N, C)) sections at y = 1/4 were made of both structures by use of the final coordinates given in Table XV for bromine, nitrogen, and carbon. In structure 8(b) the Fourier was positive not only where the H_1 of structure 8(b) would be placed, but also where the H_1 of structure 8(a) would be placed. The heights of both areas were approximately the same. In structure 8(a) both areas were again positive, but there was a noticable difference in in heights. On this Fourier the 8(b) H_1 height was about 7% greater than the corresponding height on the first Fourier, whereas the 8(a) H_1 height was about 40% less.

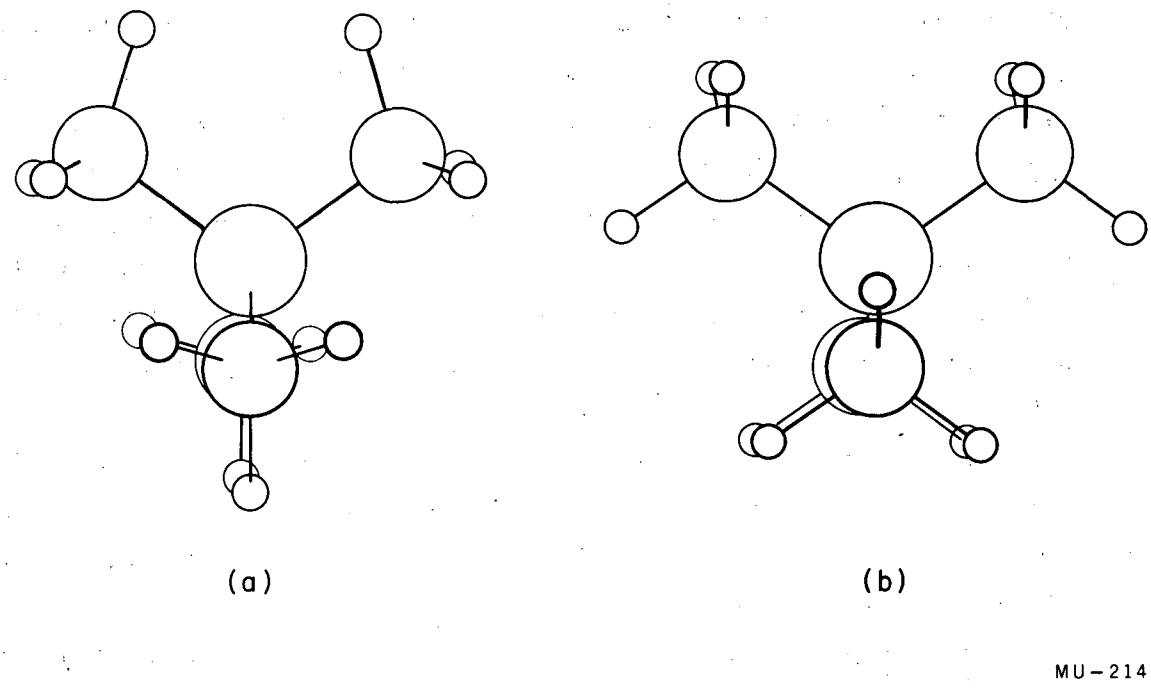

Fig. 8. (a)(b) Configuration of tetramethylammonium ion for the two possible hydrogen positions.

The final atomic parameters, together with temperature factors and standard deviations, are given in Table XV. Table XVI gives the important distances for both structures.

DISCUSSION OF THE STRUCTURE

The results of the structure determination of tetramethylammonium bromide do not permit a definite conclusion concerning the hydrogen atoms. On the one hand, the least-squares calculation gives about 5% better agreement in R_1 for the 8(b) structure, the Fourier maps show slight preference for this structure, and packing efficiency is better in this structure. On the other hand, the Fourier maps were quite ambiguous, since there were considerable positive areas that could not be attributed to the hydrogen atoms. These areas contained heights in excess of the heights of the locations of the suspected hydrogen atoms. The positive areas at the locations of the suspected hydrogen atoms could have been caused as easily by poor data or diffraction effects as by actual hydrogen atoms.

It can not be said from this evidence, however, that there is free rotation. At best, it is concluded that structure 2-a is not likely, whereas free rotation or structure 2-b are conceivable solutions, with considerable evidence favoring the latter.

The important carbon-nitrogen bond as determined from the final refinement of structure 8(b) is 1.50 ± 0.02 Å.

The observed and calculated structure factors from structure 8(b) are compared in Table XVII.

Table XV

Final structure parameters for tetramethylammonium bromide

Structure	Atom	B	x	y	z	σ_x	σ_y	σ_z
Fig. 8(a)	Br	2.536	$\frac{1}{4}$	$\frac{1}{4}$	0.6238	--	-----	0.0008
	N	2.06	$\frac{1}{4}$	3/4	0	--	-----	-----
	C	3.58	$\frac{1}{4}$	0.9089	0.1568	--	0.022	0.004
	H_1	4.75	$\frac{1}{4}$	0.8708	0.3457	--	-----	-----
	H_2	4.75	0.3645	0.9852	0.1190	--	-----	-----
Fig. 8(b)	Br	2.591	$\frac{1}{4}$	$\frac{1}{4}$	0.6240	--	-----	0.0008
	N	2.30	$\frac{1}{4}$	3/4	0	--	-----	-----
	C	3.54	$\frac{1}{4}$	0.9075	0.1603	--	0.0020	0.0037
	H_1	4.75	$\frac{1}{4}$	0.0219	0.0470	--	-----	-----
	H_2	4.75	0.3645	0.9075	0.2737	--	-----	-----

Table XVI

Distances in tetremethylammonium bromide

Structure	Atoms	Distance	σ_d
Fig. 8(a)	C-N	1.50	0.02
	Br-C	3.68	0.02
	Br-N	4.373	0.005
Fig. 8(b)	C-N	1.50	0.02
	Br-C	3.67	0.02
	Br-N	4.361	0.005

h k ℓ	F_o	F_c
0 0 1	7	9-
0 0 2	9	7-
0 0 3	23	24
0 0 4	44	39-
0 0 5	30	25
0 0 6	7	6
0 0 7	3	4-
1 0 1	38	42
1 0 2	59	70-
1 0 3	35	33
1 0 4	3	1
1 0 5	18	16-
1 0 6	22	18
1 0 7	9	9-
1 1 0	33	31-
1 1 2	2*	1-
1 1 3	38	36-
1 1 4	41	36
1 1 5	16	14-
1 1 6	6	5
2 0 1	34	29
2 0 2	8	7-
2 0 3	35	32-
2 0 4	36	32
2 0 5	24	22-
2 0 6	3	3-
2 1 1	59	63-
2 1 2	45	44
2 1 3	36	33-
2 1 4	4	4
2 1 5	25	20
2 1 6	18	16-
2 2 0	54	57
2 2 1	45	42-
2 2 2	11	10
2 2 3	43	40
2 2 4	29	25-
2 2 5	21	19
2 2 6	2*	1-
3 0 1	17	15-
3 0 2	65	70
3 0 3	30	27-
3 0 4	7	7-
3 0 5	9	9
3 0 6	20	17-
3 1 0	54	60
3 1 1	44	47-
3 1 2	14	11-
3 1 3	22	19

h k ℓ	F_o	F_c
3 1 4	40	35-
3 1 5	16	14
3 1 6	2*	1-
3 2 1	32	31
3 2 2	47	50-
3 2 3	29	27
3 2 4	3*	1
3 2 5	11	12-
3 2 6	18	15
3 3 0	56	59-
3 3 1	32	30
3 3 2	12	11
3 3 3	8	7-
3 3 4	36	35
3 3 5	12	14-
3 3 6	1*	1-
4 0 0	56	61
4 0 1	28	23-
4 0 2	11	8
4 0 3	31	27
4 0 4	30	25-
4 0 5	21	17
4 0 6	2*	2
4 1 1	45	44
4 1 2	37	33-
4 1 3	29	25
4 1 4	5	5-
4 1 5	19	17-
4 1 6	15	13
4 2 0	41	44-
4 2 1	29	31
4 2 2	9	8-
4 2 3	34	33-
4 2 4	20	19
4 2 5	14	15-
4 3 1	30	27-
4 3 2	39	38
4 3 3	20	21-
4 3 4	2*	1-
4 3 5	11	11
4 3 6	11	12-
4 4 0	35	34
4 4 1	23	24-
4 4 2	7	7
4 4 3	25	28
4 4 4	13	15-
4 4 5	10	12
5 0 1	27	24
5 0 2	40	41-

h k ℓ	F_o	F_c
5 0 3	21	20
5 0 4	3*	1
5 0 5	11	10-
5 0 6	13	13
5 1 0	31	30-
5 1 1	39	36
5 1 2	4	2
5 1 3	22	20-
5 1 4	24	24
5 1 5	10	9-
5 2 1	29	29-
5 2 2	29	30
5 2 3	21	20-
5 2 4	3*	2
5 2 5	12	13
5 3 0	34	35
5 3 1	29	26-
5 3 2	4	4-
5 3 3	11	11
5 3 4	27	24-
5 3 5	10	9
5 4 1	22	24
5 4 2	21	23-
5 4 3	17	16
5 4 4	2*	2-
5 4 5	9	11-
6 0 0	44	50-
6 0 1	13	13
6 0 2	3*	1
6 0 3	11	12-
6 0 4	23	21
6 0 5	16	14-
6 1 1	19	20-
6 1 2	33	30
6 1 3	18	17-
6 1 4	3*	1-
6 1 5	8	9
6 2 0	35	38
6 2 1	15	16-
6 2 2	3*	2
6 2 3	13	16
6 2 4	16	17-
6 2 5	12	12
6 3 1	11	12
6 3 2	35	32-
6 3 3	13	14
6 3 4	2*	3
6 3 5	3	5-
6 4 0	26	29-

h k ℓ	F_o	F_c
6 4 1	11	14
6 4 2	2*	2-
6 4 3	14	14-
6 4 4	11	13
7 0 1	21	17-
7 0 2	22	24
7 0 3	12	14-
7 0 4	2*	1-
7 1 0	15	17
7 1 1	24	24-
7 1 2	3*	1-
7 1 3	15	15
7 1 4	15	15-
7 2 1	19	21
7 2 2	17	18-
7 2 3	12	14
7 3 0	16	21-
7 3 1	18	18
7 3 2	2*	2
7 3 3	9	9-
7 3 4	13	16
7 4 1	16	17-
7 4 2	11	14
7 4 3	9	11-
8 0 0	25	26
8 0 1	9	10-
8 0 2	2*	1
8 0 3	10	10
8 0 4	9	12-
8 1 1	13	15
8 1 2	14	16-
8 1 3	11	11
8 2 0	16	20-
8 2 1	9	11
8 2 2	2*	2-
8 2 3	9	13-
8 3 1	8	10-
8 3 2	15	17
8 3 3	8	9-
8 4 0	14	16
8 4 1	6	10-
9 0 1	5	7
9 0 2	16	17-
9 1 0	12	14-
9 1 1	8	12
9 2 1	5	9-
9 2 2	11	14
9 3 0	13	15
9 3 1	6	9-

Table XVII. Observed and calculated structure factors for tetramethylammonium bromide. *indicates minimum observable structure factor.

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