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THE CRYSTAL STRUCTURE OF AMMONIUM
1,1,2,6,7,7-HEXACYANOHEPTATRIENIDE.**

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THE CRYSTAL STRUCTURE OF AMMONIUM
1,1,2,6,7,7-HEXACYANOHEPTATRIENIDE

by

James William Edmonds

A THESIS SUBMITTED
IN PARTIAL FULFILLMENT OF THE
REQUIREMENTS FOR THE DEGREE OF

DOCTOR OF PHILOSOPHY

Thesis Director's Signature:

A handwritten signature in cursive script, appearing to read "Ronald E. Linn", is written over a horizontal line.

Houston, Texas

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INTRODUCTION

A priori ideas about the structure of carbanions unstabilized by substituents depend upon analogies with the structure of ammonia. Ammonia and methyl anion are isoelectronic, and the fact that ammonia possesses a rapidly inverting pyramidal structure suggests that the methyl anion also possesses these characteristics. Such a structure puts the unshared pair of electrons of carbon in an sp^3 -orbital, which has 25% s -character.

Two alternative structures are also available. The first places the unshared pair of electrons and the negative charge of the carbanion in a carbon p -orbital. The carbon and three hydrogens are thus planar, the bonding consisting of sp^2 - s -overlap. The second structure is to have the hydrogens bonded through the p -orbitals of an unhybridized carbon, and the unshared pair of electrons in the $2s$ -orbital.

Of the three structural alternatives for carbanions unstabilized by substituents, sp^3 -bonding is most probable, and the carbanions are predicted to obtain a pyramidal configuration similar to ammonia.¹

However, most carbanions are stabilized either by substituents or by having the unshared pair of electrons occupy orbitals very high in $2s$ -character. A direct correlation is observed between the pK_a of the conjugate acid, a measure of the tendency to form the carbanion, and percent s -character in the carbon-hydrogen bond.² This is indicated in Figure I. Electrons in $2s$ -orbitals are closer to the nucleus than those in $2p$ -orbitals, and the carbanion should be more stable the higher the $2s$ -character for the occupied orbital.

Carbanions stabilized by substituents capable of delocalizing the electron pair onto more electronegative elements are expected to approach sp^2 - p or trigonal hybridization. This configuration maximizes the overlap between the p -orbital of the carbon and the non-bonding orbitals of the substituent, permitting the negative charge to reside largely on the heteroatom, i.e.,

The stabilization effect can be readily observed if one compares the pK_a values for the above compounds in Figure I with the pK_a for acetophenone,

$pK_a \approx 19.$

FIGURE I

pK_a versus % $2s$ -character in Carbon-Hydrogen Bonds

As the pK_a decreases, the easier the carbon-hydrogen bond is to break, and the more stable, relatively, is the carbanion.

Nitro and cyano groups, as the carbonyl group in acetophenone above, are expected to have a pronounced stabilizing effect on carbanions. Acyclic carbanions with these functional groups are predicted by Cram to be planar or near planar.³ Slight deviations from planarity are not expected to decrease the conjugative effect, and are thought to be caused by steric, solvation, or ring constituent effects. Hine predicts that the degree of planarity is a function of the extent of resonance stabilization; the longer a conjugated π system, the more planar the carbanion will be.⁴ The discussions by Cram and Hine deal primarily with solution studies of carbanions, the results of which are often inconclusive concerning the best carbanion model to employ in a particular case.

Direct determination of molecular dimensions was performed by C. Bugg, R. Desiderato, and R. L. Sass on ammonium tricyanomethide⁵, pyridinium dicyanomethide⁵, and potassium *p*-nitrophenyldicyanomethide⁶. Their results substantiated to a certain degree the predicted conformation of the carbanions studied. The 3° observed non-planarity in ammonium tricyanomethide decreases as the extent of the carbanion conjugation increases, as in potassium *p*-nitrophenyldicyanomethide. An investigation of ammonium 1,1,2,6,7,7-hexacyanoheptatrienide was initiated as an extension of these studies into the effects of conjugation on the structure of stable linear carbanions.

EXPERIMENTAL

Samples of the potassium and ammonium salts of 1,1,2,6,7,7-hexacyanoheptatrienide, $\text{KC}_{13}\text{H}_3\text{N}_6$ and $\text{NH}_4\text{C}_{13}\text{H}_3\text{N}_6$, were kindly supplied by Dr. R. E. Benson of E. I. du Pont de Nemours and Company. The compounds were prepared by reacting methyl vinyl ether with tricyanovinyl chloride in acetonitrile at room temperature, followed by reflux in methanol and treatment with potassium or ammonium acetate.⁷ The ammonium salt as received consisted of lustrous dark green prismatic crystals suitable for study without further recrystallization. Study crystals used in preliminary film investigations were usually 0.2mm x 0.1mm in cross-section, and 2mm to 3mm in length. A single crystal 0.2mm x 0.1mm x 2mm was chosen for study with the diffractometer. All crystals were mounted on glass fibers with the needle axis parallel to the fiber axis.

Rotation and equi-inclination photographs collected with CuK_α radiation ($\lambda = 1.54051 \text{ \AA}$) indicated the following conditions for reflection:

$$0k0 \quad k = 2n$$

$$h0l \quad l = 2n$$

$$hkl \quad \text{no conditions}$$

These uniquely determine the space group to be $\text{P2}_1/\text{c}$ (C_{2h}^5). The features of the b axis projection of this space group are indicated in Figure II.

The initial cell parameter values were determined from rotation and Weissenberg photographs taken about the a and b axes. The angle β was determined by the method of angular lag.⁸ Second measurements of b

FIGURE II
Space Group $P2_1/c$

and c were made manually, using the PAILRED, by determining the omega angular displacements about the rotation axis of the crystal.⁹ Only the diffraction maxima for 0h0 and 00l were measured, using both molybdenum α_1 ($\lambda = 0.70926 \text{ \AA}$) and α_2 ($\lambda = 0.71354 \text{ \AA}$) monochromatized radiations.

The cell constants so obtained are

$$a = 7.110 (10) \text{ \AA}$$

$$b = 13.405 (1) \text{ \AA}$$

$$c = 14.199 (3) \text{ \AA}$$

$$\beta = 101.683^\circ (500)$$

The density was determined by flotation in a mixture of chlorobenzene and bromobenzene. The observed density of 1.28 gm/cm^3 agrees well with the calculated value of 1.31 gm/cm^3 based upon four $\text{NH}_4\text{C}_{13}\text{H}_3\text{N}_6$ molecules per unit cell.

Two sets of data were collected by two different techniques, both performed at room temperature. The first set was collected visually using a standard Weissenberg camera and nickel foil filtered copper K_α radiation. Using crystals mounted along the a and b axes, multiple film equi-inclination Weissenberg photographs of the $h = 0, 1, 2, 3, 4,$ and 5 layers, and $k = 0, 1, 2,$ and 3 layers were taken. Intensities were estimated with a standard intensity strip and corrected for Lorentz and polarization factors.¹⁰ The different layers were correlated by the method of Dickerson.¹¹ This set of data, containing 1168 visually estimated intensities, was employed in the determination and initial refinement of the trial structure.

The second set of data was collected with a Norelco Philips-Automatic-Indexing-Linear-Reciprocal-Space-Exploring-Diffractometer (PAILRED) employing equi-inclination geometry. All data were collected using quartz monochromatized MoK_α radiation ($\lambda = 0.71069 \text{ \AA}$) and a scintillation counter. The fixed counter-moving crystal method was employed. A 2° scan range and 0.5° per minute scan rate were used for layers $h = 0, 1$, and 2 , and a 3° scan range and 1° per minute scan rate for the layers $h = 3, 4, 5$, and 6 . For all reflections background was measured for a fixed time of 0.4 minutes at the beginning and end of each scan. The counting statistical error, $\Delta I/I$, was calculated for each reflection by the method of Ladell.¹²

$$\frac{\Delta I}{I} = \frac{(T + t^2 B)^{\frac{1}{2}}}{T - tB},$$

where

T = total counts for omega scan,

t = ratio of scan time to background time, and

B = background count.

All reflections for which $\Delta I/I$ exceeded 0.40 were rejected. A total of 831 reflections were collected above background. Because of noticeable discrepancies in the crystal alignment, 29 additional reflections having a $\sin \theta/\lambda$ value greater than 0.647 were rejected.

Although the effect was minimized, for high values of $\sin \theta/\lambda$, the diffraction maxima appeared broadened and significantly displaced from the center of the scan. The alignment difficulty is attributable mainly

to the fact that the a cell axis was slightly displaced from the omega axis.

If the omega and reciprocal axes are parallel, the detector can be set at the proper $\sin 2\theta$ for a chosen axial reflection, which can then be observed continuously as the crystal is rotated through 360° about the omega axis. In this case the detector is at that point in reciprocal space for which the conditions for reflection by that plane are continuously met, i.e., the detector is located on the reflection cone.

However, if the reciprocal axis is not parallel to the omega axis, as is the case for $P2_1/c$ when the crystallographic a axis is the crystal rotation axis, then the diffraction maxima can be observed for only one small angular orientation of the crystal. Consequently, small deviations from alignment cannot be easily observed or corrected. Therefore, it was felt data with $\sin \theta/\lambda \geq 0.65$ were less reliable, and so rejected.

A total of 802 acceptable intensities corrected for Lorentz, polarization, and Tunell factors were used for the final refinement. The maximum value of μR was 0.02, and therefore no correction for absorption was made.

TRIAL STRUCTURE

General

One of the first procedures in crystal structure determinations after collection and reduction of the data, is to synthesize the Patterson function, either in three-dimensions or in projection. The Patterson function is a collection of all interatomic vectors of an electron density translated to a common origin. The peak size in Patterson space is proportional to the product of the electron densities of the two atoms forming the origin and terminus of the vector. Consequently, for a set of atoms of varying atomic numbers, the greatest contribution to the Patterson function will be from interatomic vectors between atoms with the larger atomic numbers. If a molecule contains one or more heavy atoms, one attempts to correlate the larger peaks in Patterson space with the atomic positions in real space.

If, however, a heavy atom is not present in a molecule, the interpretation of the Patterson function becomes increasingly more difficult as the number of atoms with similar atomic numbers increases. Since the number of peaks in Patterson space is N^2 , where N of these are zero length vectors between an atom and itself, the $N(N - 1)$ peaks containing useful information become extremely large in number and the problem of solution becomes impractical if not nearly impossible.

Because of the availability of the symbolic addition technique, whereby some phases of the larger reflections can be determined to a

calculated degree of probability by using known relationships between the reflections, it was decided to try and apply this means in an attempt to solve the crystal structure. The method can be explained briefly.

Using the symmetry of the space group, equations for the electron density and structure factors in that space group, and Schwartz's inequality, Harker and Kasper derived important inequalities for phase determination.¹³ Karle and Hauptman showed that the inequalities arose from the positivity criterion, namely that the electron density distribution is a non-negative function, and derived a complete set of inequalities expressed as a sequence of relations of successively increasing complexity.¹⁴ The first three of these, all valid for centro and noncentro-symmetric space groups, are

$$F_{000} \geq 0, \quad 9.1$$

$$|F_{hkl}| \leq F_{000}, \quad 9.2$$

and

$$\left| F_{h_1+h_2, k_1+k_2, l_1+l_2} - \frac{F_{h_1 k_1 l_1} F_{h_2 k_2 l_2}}{F_{000}} \right|$$

$$\leq \frac{\left| \begin{array}{cc} F_{000} & F_{\bar{h}_1 \bar{k}_1 \bar{l}_1} \\ F_{h_1 k_1 l_1} & F_{000} \end{array} \right|^{\frac{1}{2}} \left| \begin{array}{cc} F_{000} & F_{\bar{h}_2 \bar{k}_2 \bar{l}_2} \\ F_{h_2 k_2 l_2} & F_{000} \end{array} \right|^{\frac{1}{2}}}{F_{000}} \quad 9.3$$

The first two inequalities are self-explanatory, but the third needs

clarification. Expressed in the following form:

$$|\underline{F}_{\underline{h}} - \delta| \leq r \quad 10.4$$

where

$$\delta = \delta(\underline{h}, \underline{k}) = \underline{F}_{\underline{h}-\underline{k}} \underline{F}_{\underline{k}} / F_{000}, \quad 10.5$$

$$r = \frac{\left| \begin{array}{cc} F_{000} & \underline{F}_{\underline{h}-\underline{k}} \\ \underline{F}_{\underline{h}-\underline{k}} & F_{000} \end{array} \right|^{\frac{1}{2}} \left| \begin{array}{cc} F_{000} & \underline{F}_{\underline{k}} \\ \underline{F}_{\underline{k}} & F_{000} \end{array} \right|^{\frac{1}{2}}}{F_{000}}, \quad 10.6$$

$$\underline{h} = \underline{h}_1 + \underline{h}_2, \text{ and}$$

$$\underline{k} = \underline{h}_2.$$

The first expression implies that the complex structure factor $\underline{F}_{\underline{h}}$ is bounded by a circle in the complex plane whose center is δ and whose radius is r . (Figure III). The larger the values for $|\underline{F}_{\underline{k}}|$ and $|\underline{F}_{\underline{h}-\underline{k}}|$, then the smaller r will be, and the closer $\underline{F}_{\underline{h}}$ will be to the complex number δ . Since the vector $\underline{k}$ can be varied, one gets a number of similar expressions. $\underline{F}_{\underline{h}}$ is then proportional to an average over the various $\delta(\underline{h}, \underline{k})$,

$$\underline{F}_{\underline{h}} \propto \langle \underline{F}_{\underline{k}} \underline{F}_{\underline{h}-\underline{k}} \rangle_{\underline{k}}, \quad 10.7$$

as $\underline{k}$ is varied. When one considers only the larger structure factor magnitudes, one obtains

$$\underline{F}_{\underline{h}} = |\underline{F}_{\underline{h}}| \exp(i\phi_{\underline{h}}), \quad 10.8$$

FIGURE III

$$|\tilde{F}_h - \delta| \leq r$$

and approximately,

$$\varphi_{\underline{h}} \approx \langle \varphi_{\underline{k}} + \varphi_{\underline{h}-\underline{k}} \rangle_{\underline{k}}. \quad 11.9$$

This result closely parallels that of Sayre.¹⁵

To employ these inequalities it is necessary to have a basic set of symbolic phases, which are used to obtain additional phases. This basic set is usually composed of those phases necessary to fix the origin in the crystal,¹⁶ and a few additional phases corresponding to those structure factors having the largest magnitudes.

As the complexity of the crystal increases, the quantity r in 10.4 becomes disproportionately large, until, in general, the inequality by itself imposes no restriction upon the phase of $F_{\underline{h}}$. The inequalities must then be augmented by a more detailed analysis involving algebraic considerations and probability theory. The algebraic considerations are summarized in the Appendix, and lend credence to the interpretation of inequality 10.4, leading to relation 11.9.

Converting the F_{hkl} 's to unitary structure factors,¹⁷

$$U_{\underline{h}} = F_{\underline{h}} / \sum_{j=1}^N f_j(\underline{h}), \quad 11.10$$

or to normalized structure factors,¹⁸

$$|E_{\underline{h}}|^2 = \frac{|F_{\underline{h}}|^2}{\sum_{j=1}^N f_j^2(\underline{h})},$$

where ϵ is a correction for space group extinctions, greatly strengthens the phase relations and implications drawn from them. The Harker-Kasper inequalities were originally derived in terms of the unitary structure factors, which effectively concentrate the scattering material about the centers of the atoms.

Probability formulas for evaluating the reliability of a sign determination for centro-symmetric crystals were derived by Hauptman and Karle¹⁹ in the form of a series, and later by Woolfson²⁰ in a hyperbolic tangent form. The latter is preferred for applications.

In the 1953 monograph by Hauptman and Karle, four formulas were derived for the simplest centro-symmetric space group, $P\bar{1}$. Of the four,

$$\Sigma_1 = \epsilon_{3/4}^{5/2} (U_{\underline{h}}^2 - \epsilon), \quad 12.12$$

$$\Sigma_2 = \epsilon_{3/2}^{5/2} \sum_{\underline{h}'} U_{\underline{h}'} U_{\underline{h}+\underline{h}'}, \quad 12.13$$

$$\Sigma_3 = \epsilon_{4/4}^{7/2} \sum_{\underline{h}'} U_{\underline{h}'} (U_{\underline{h}+\underline{h}'}^2 - \epsilon), \text{ and } \quad 12.14$$

$$\Sigma_4 = \epsilon_{5/8}^{9/2} \sum_{\underline{h}'} (U_{\underline{h}+\underline{h}'}^2 - \epsilon) (U_{\underline{h}'}^2 - \epsilon), \quad 12.15$$

where $\epsilon_r = \sum_{j=1}^N n_j^r$, $\epsilon = \epsilon_2$, and $n_j = f_j / \sum_{j=1}^N f_j$, only Σ_2 has

general applicability to all $\underline{h}$.²¹ This is the probability equivalent of 9.3, most conveniently applied in Woolfson's form,

$$P_x(\underline{h}) \approx \frac{1}{2} + \frac{1}{2} \tanh \frac{\epsilon_3}{\epsilon_2^{3/2}} \frac{|E_{\underline{h}}|}{\sum_{\underline{k}} E_{\underline{k}} E_{\underline{h}-\underline{k}}}, \quad 12.16$$

where now one chooses to use E 's.

Procedure, According to Computer Method

The programmed symbolic addition procedure used consists of four main programs, FAME, MAGIC, LINK, and SYMPL.²² Each will be described in turn.

The complete set of data, including unobserveds, for the entire experimental sphere of reflection is put on an absolute scale in the FAME routine by Wilson's method.²³ The scaled F_{obs} are then used to calculate the normalized structure factors by the relation 11.11. The E's are then sorted by magnitude, and symbolic signs assigned to the group of largest E's having the most "interactions" relevant to relation 12.16. Certain of these E's are necessary to define the origin, the number required depending upon the space group. The actual assignment of origin is, however, deferred until later. The value of "sigma", $\sigma = \Sigma_3 / \Sigma_2^{3/2}$, is calculated for use with MAGIC.

MAGIC performs the actual iterative generation of phases. From the set of assigned symbols and the value of sigma, the list of E's is searched, all values of $\underline{k}$ satisfying the relation

$$(\underline{h-k}) + \underline{k} = \underline{h},$$

where all three vectors are in the set of measured E's, are used to evaluate

$$P_x(\underline{h}) = \frac{1}{2} + \frac{1}{2} \tanh[(\sigma E_{\underline{h}}) (\sum_{\underline{k}} E_{\underline{h-k}} E_{\underline{k}})].$$

If $P_x(\underline{h}) \geq P$, where P is a pre-set value, then $E_{\underline{h}}$ is given a phase which is the product of the phase symbols for the reflections $\underline{h-k}$ and $\underline{k}$. In

the case of a number of highly probable phase products, only that with the highest probability is accepted. The reflection is then added to the list of known phases, and the process continued. All combinations of $\underline{h-k}$ and $\underline{k}$ are also listed in an array with their subsequent probabilities and phases in symbolic terms, whether or not $P_x(\underline{h}) \geq P$. This is for later use in determining the "best" set of phases. The process continues through the entire set of remaining unknown E's again, if necessary, until a predetermined number of phases is computed.

LINK performs the actual assignment of origin phases. The set of original symbols are divided into eight subgroups based on the parities of the h , k , and l indices. The actual assignment is discussed in great detail by Karle and Hauptman,²⁴ but suffice it to say here that for primitive symmetry, as with $P2_1/c$, the origin is assigned with three E's defined as positive. The three origins must be independent and not come from parity group GGG (even, even, even).

LINK next calculates, for every combination of + and - for each symbolic sign, the relative number of "inconsistencies", according to the formula

$$\text{weighted index} = \sum_1^S \frac{1}{(1 + \text{PARAM} - P)(\text{iteration \#})},$$

where P is the probability of that sign determination. PARAM is an input parameter, usually equal to 0.000001, and S is the number of signs determined. The sets of values for all the symbols are listed in order of increasing value of the weighted index. Hopefully, the correct assignment is one with a relatively low index, although not necessarily the lowest one.

The information is transmitted to the SYMPL routine, which will punch any number of decks of signed E's. SYMPL also deletes, in each deck of E's, any E's which are inconsistent with the assigned values of the symbols. These decks are then used to generate the so called E-maps, using

$$\rho_E(xyz) = \sum_h \sum_k \sum_l E_{hkl} e^{2\pi i(hx+ky+lz)}. \quad 15.17$$

From these E-maps one should be able to observe the atoms in the molecule and discern which set yields atom positions most consistent with both chemical and crystallographic knowledge.²⁵

Solution of Ammonium 1,1,2,6,7,7-hexacyanoheptatrienide

The complete visual data for the ammonium salt was reduced to a set of E's using the FAME routine. Seven intervals were requested for the Wilson plot, the first and last being deleted from the least-square analysis.²⁶ The 30 largest E's and their number of interactions were listed, and from this group the entire array of nine symbols was assigned. It was not known at the time the minimum number of symbols required. The symbols assigned are listed in Table I. The value of sigma ($\sigma = \sum 3 / \sum 2^{3/2}$) was calculated to be 0.1115.

MAGIC was requested to determine 200 phases from the 1168 E's of the visual data record. Four iterations were required to accomplish this, and various parameters were altered automatically during the process to assure the total number of phases would be determined. The results

TABLE I

SYMBOLIC ASSIGNMENTS, FAME

<u>h</u>	<u>k</u>	<u>l</u>	<u> E </u>	<u>Symbol</u>
1	0	12	3.010	A
-2	1	0	6.230	B
-2	2	1	5.658	C
-4	3	1	4.736	D
1	10	5	2.784	E
-1	3	4	3.295	F
-1	1	11	3.077	G
-2	2	0	4.221	H
1	12	4	2.799	J

are summarized in Table II.

The probability level for the listing of the calculated symbol equivalences and probabilities, needed for the calculation of the weighted index, was 0.90. LINK assigned the following origin phases:

h	k	l	Symbol	Value
-4	3	1	D	+
-2	2	1	C	+
-1	1	11	G	+

The weighted index was calculated for each of the remaining 64 (2^6) groups of symbol equivalences. The index varied from a low value of 1716.4 to a maximum of 3,656,844.6. There were two groups of symbol equivalences with a low index of 1716.4. These are summarized below.

Symbol	Sign Value	
	Combination I	Combination II
A	+	-
B	+	+
C*	0	0
D*	0	0
E	-	+
F	-	-
G*	0	0
H	+	-
J	+	+

*Indicates an origin phase. 0 $\equiv$ sign fixed as positive (+).

SYMPL punched decks for combinations I and II, deleting, because of inconsistencies, 105 E's from both decks. The E-maps were synthesized,

TABLE II

CONTROL PARAMETERS, MAGIC

ITERATION	TOTAL SIGNS	Parameter Values at end of Iteration			
		PROBABILITY 'P'	CONTRIBUTORS *	INCONSISTENCIES *	RATIO C/I *
Initial	9	0.999	0	0	0.0
1	24	0.999	0	0	0.0
2	81	0.999	0	2	5.0
3	139	0.999	0	2	5.0
4	224	0.989	0	2	5.0

*For any one sign determination during an iteration:

Contributors: Minimum number of contributors with $P_{\text{sign}} \geq 'P'$ necessary for sign acceptance.

Inconsistencies: Contributors with opposite sign and $P_{\text{sign}} \geq 'P'$. Minimum number that can be tolerated.

Ratio C/I: Ratio of Contributors to Inconsistencies.

and three-dimensional models were used to facilitate interpretation.

A reasonable trial structure was indicated from the model using the Combination II E's, while no physically meaningful model could be fitted to the peaks in the Combination I model. (See Figure IV and V, respectively.) X, Y, and Z parameters were obtained for the anion atom coordinates, and peak 17 was chosen to be the ammonium ion on the basis of packing considerations.

LEGEND

FIGURES IV AND V

Peak Numeration Indicated Adjacent to Peak Center

**Peak A-axis Parameters (x100), Perpendicular to Page,
Indicated in Parentheses**

$$C' = C \cos(\beta - 90)$$

FIGURE IV

E-map from Combination II Phases

REFINEMENT

The refinement of the trial structure was accomplished by least squares adjustment of the parameters q_i to minimize the function

$$\sum_j [\sqrt{w_j} (F_j^{\text{obs}} - F_j^{\text{calc}}) - \sqrt{w_j} \sum_i \left(\frac{\partial F^{\text{calc}}}{\partial q_i} \right) \Delta q_i]^2 \quad 18.18$$

The conventional reliability index, R

$$R = \frac{\sum_j |F_j^{\text{obs}} - F_j^{\text{calc}}|}{\sum_j |F_j^{\text{obs}}|} \quad 18.19$$

was used to measure the agreement between the calculated and observed structure factors.

The calculations were done using an IBM 7094 computer and the least squares analysis program ORFLS written by Busing, Martin, and Levy.²⁷ Scattering factor tables for carbon and nitrogen were obtained from Cromer and Waber.²⁸ Scattering factor tables for bonded hydrogens were obtained from R. F. Stewart, *et. al.*²⁹ The R index was reduced to 0.21 on the visual data set varying only the positional parameters. Isotropic refinement reduced the R to 0.16 and anisotropic refinement, accomplished by refinement in "blocks" to overcome limited storage capacity, further reduced this index to 0.14 using the visual data set.

Using the diffractometer data, and employing the weighting scheme of Evans³⁰, the value of R was reduced to 0.083, and the weighted R to 0.081.

At this time a difference map was run, Figure VI, which clearly indicated the positional parameters for the hydrocarbon hydrogens and two of the ammonium hydrogens, H(1) at $0.6e/\text{\AA}^3$ and H(2) at $0.5e/\text{\AA}^3$. Expecting the ammonium configuration to be tetrahedral, positional parameters were chosen for H(3), at $0.4e/\text{\AA}^3$, and H(4), at $0.2e/\text{\AA}^3$. Using these additional parameters, the R values were reduced to 0.061 and 0.046, respectively. Because of the low values of the $e/\text{\AA}^3$ for the ammonium hydrogens, it was felt that perhaps the ammonium ion was in actuality randomly oriented in the crystal. Thus a collection of eight "half-hydrogens", located at the apices of a dodecahedron around the ammonium nitrogen, was tried as a model. Two "half-hydrogens" each coalesced on the positions of H(1) and H(2), one on H(3), and the remaining three exhibited only large oscillations of their positional parameters. The R values did not change, so the model was returned to the original tetrahedral ammonium ion.

The final value of R was 0.061, and the weighted R was 0.046. The agreement between the observed and calculated structure factors at this level of refinement can be seen in Table III. The final positional parameters are shown in Table IV, and the final anisotropic thermal parameters are listed in Table V. As a visual aid, a stereo diagram of the anion itself is shown in Figure VII.³¹ This is best viewed with any stereo viewer or lenses available commercially. The electron density calculated at this level of refinement is indicated in Figure VIII.

$C \cdot \cos(\beta - 90)$

FIGURE VI

Difference Map, Composite Projection
(Contours every $0.2 e/\lambda^3$ beginning at $0.2 e/\lambda^3$)

TABLE III

Calculated and Observed Structure Factor Magnitudes (x10)

L	FOI	FC	L	FOI	FC	L	FOI	FC	L	FOI	FC
0,0,L			0,5,L			2 126 -131			8 184 185		
4	781	-783	1	101	100	6	95	-102	10	203	205
6	345	-347	2	566	564	7	307	311	12	104	-96
8	83	-76	3	140	-140	8	334	332			
10	125	125	4	243	243	14	90	85	-1,1,L		
12	118	-127	5	91	90	0,10,L			-12	252	-246
14	180	194	7	227	-232	0	147	-148	-11	305	-305
0,1,L			8	193	203	3	158	-173	-10	250	260
3	100	-103	9	98	93	4	90	-97	-9	107	-115
4	419	-418	10	190	-198	5	159	152	-8	125	128
5	354	339	11	100	111	6	164	163	-5	148	150
6	236	-241	12	85	-92	7	243	260	-4	313	-294
7	214	206	13	153	-166	8	107	102	-3	241	-228
8	266	262	16	114	107	10	97	83	3	83	79
9	265	278	0,6,L			14	171	-148	4	245	247
10	82	55	0	261	254	0,11,L			5	387	-384
12	286	287	1	207	200	1	122	121	9	223	228
15	154	-147	2	466	467	2	74	67	11	335	354
0,2,L			3	98	-94	4	107	111	12	199	-207
2	311	309	4	187	-188	5	211	-222	-1,2,L		
3	544	546	5	240	-237	6	409	426	-11	121	129
4	216	218	6	278	-287	8	142	-150	-8	97	-102
5	162	165	7	115	121	10	83	-81	-7	74	-64
6	63	51	10	86	84	0,12,L			-6	84	-76
8	208	218	11	113	105	2	81	-57	-5	158	-150
10	79	-69	14	81	-52	6	93	-100	-4	798	-780
12	84	-81	0,7,L			9	85	60	-3	160	-157
13	175	179	1	160	149	0,13,L			-2	227	226
0,3,L			2	256	257	2	96	-104	3	189	185
1	250	-250	4	194	210	6	109	76	4	477	483
2	162	-163	6	143	-142	0,14,L			5	348	-351
3	332	328	7	151	154	0	241	-240	6	86	-101
4	273	272	8	76	-40	4	99	94	9	78	74
6	239	230	9	127	128	9	92	93	10	165	-166
10	95	86	11	93	-103	0,15,L			11	90	-98
11	94	-95	0,8,L			7	90	-102	12	291	296
16	148	137	0	127	119	-1,0,L			13	182	-193
0,4,L			1	79	-74	-12	432	-438	-1,3,L		
1	1094	-1092	2	143	135	8	113	116	-16	104	108
2	150	-144	3	72	64	-6	118	107	-15	93	66
3	512	-514	4	133	127	-4	447	-444	-10	73	-39
5	301	289	5	78	-74	4	554	561	-9	251	-256
7	279	284	6	73	51	6	138	138	-5	140	136
13	76	69	9	167	166				-4	69	-44
14	89	-70	0,9,L						-3	120	-113
			1	172	189				-1	185	193
									0	95	-106

L	FOI	FC	L	FOI	FC	L	FOI	FC	L	FOI	FC
-1,3,L			-1,6,L			-1,9,L			12 100 -92		
1	134	139	-10	133	-124	-11	96	-80	-1,13,L		
2	92	-99	-9	142	-142	-6	107	119	-10	144	149
3	409	405	-8	117	119	-5	168	-169	-4	86	-79
4	959	-965	-7	89	-84	-4	181	-175	-2	105	-98
5	414	-413	-6	125	121	-2	76	-81	4	185	164
8	146	158	-5	69	80	-1	154	-147	12	108	-95
9	75	76	-4	81	-82	0	145	-150	-1,14,L		
10	120	128	-3	273	266	2	201	-207	-2	119	106
12	161	-173	-2	308	-310	3	106	108	9	144	135
16	99	49	-1	73	-62	5	76	78	-1,15,L		
-1,4,L			0	137	142	6	167	-177	-3	115	-116
-17	117	92	1	155	145	15	89	-26	-2	83	-83
-11	173	174	2	165	178	-1,10,L			2	88	50
-10	106	104	4	240	-244	-9	123	124	-2,0,L		
-6	63	45	6	255	262	-6	161	162	-12	334	339
-5	618	-597	7	68	-69	-5	304	-314	-10	124	-124
-4	250	263	11	258	264	-4	282	-298	-8	73	-80
-3	304	300	-1,7,L			-3	121	-116	-6	217	-225
-2	411	-401	-11	124	-137	0	109	114	-4	99	-101
-1	61	60	-10	106	-109	2	112	112	6	144	-149
0	281	-284	-8	123	136	3	112	-113	8	409	-412
1	108	-100	-6	167	171	4	84	102	16	83	74
2	262	263	-4	156	-169	5	108	-116	-2,1,L		
3	343	343	-2	90	-107	6	198	-208	-14	108	79
4	262	265	-1	183	-178	7	90	-73	-13	110	99
5	285	-275	0	81	-95	9	102	-110	-11	97	104
6	120	113	1	80	74	-1,11,L			-8	112	-94
9	220	-227	2	75	75	14	94	-45	-5	109	-118
13	79	92	3	280	-283	9	93	-109	4	752	-758
-1,5,L			4	202	-192	7	84	-100	6	189	-191
-11	101	117	5	78	78	5	112	108	9	213	-217
-9	90	-104	6	307	316	4	346	-362	10	198	197
-8	109	133	7	121	109	2	138	-147	13	98	-99
-7	133	-122	8	94	94	-4	115	131	14	84	86
-5	157	149	-1,8,L			-6	137	-134	15	135	118
-4	207	-214	-10	142	-123	-1,12,L			16	129	-109
-2	194	195	-6	179	-184	-12	90	-61	-2,2,L		
-1	243	232	-4	140	152	-8	134	139	-16	97	81
0	248	-246	-3	284	-284	-6	86	69	-14	84	-37
4	79	-67	-2	190	-194	-4	229	217	-13	131	138
6	108	117	2	201	223	0	102	-84	-9	165	180
7	155	-174	3	67	-41	2	94	-91	-7	128	123
8	81	90	6	203	-203	4	80	-59	-6	285	293
12	75	37	7	110	-113	5	213	-206			
13	93	107	10	208	227	8	87	63			
17	107	-100				10	101	72			

L	FO	FC	L	FO	FC	L	FO	FC	L	FO	FC
	-2,2,L		8	111	-113	1	119	-129	7	109	116
-4	464	465	10	174	166	2	90	-89	8	232	247
-3	537	-539	11	106	-138	3	96	93	9	104	-104
3	215	211				4	193	-190			
5	85	-78		-2,5,L		8	273	-274		-2,11,L	
6	157	-171	-11	87	97	9	149	-144	-7	223	-203
7	147	-145	-9	90	-79	10	109	95	-6	214	220
8	85	70	-7	70	-36				-5	102	95
11	71	-30	-5	240	-248		-2,8,L		-3	141	145
12	168	181	-4	86	86	-14	108	95	2	140	145
13	185	-179	-3	68	66	-9	97	108	3	75	35
16	103	-82	-2	88	-92	-3	128	-133	5	83	72
			-1	356	347	-2	215	-224	6	78	-58
	-2,3,L		1	439	-435	2	91	84	14	134	-123
-16	92	87	2	229	-221	3	226	232			
-15	129	128	3	90	-89	4	136	132		-2,12,L	
-9	150	-158	5	252	246	5	95	107	-7	136	136
-8	180	184	7	74	68	6	121	-118	-6	161	-153
-6	117	110	8	154	-153	7	313	-319	0	123	111
-5	132	-150	9	76	-68	8	297	-300	2	103	122
-4	93	104	10	136	-114	10	89	-64	5	187	-191
-3	176	-167	13	96	92	11	120	-100	6	128	129
-2	291	285	16	109	-124	12	96	87	10	92	-78
-1	166	154									
3	222	214		-2,6,L			-2,9,L			-2,13,L	
5	434	-432	-14	93	75	-14	133	139	-7	104	105
7	259	-268	-6	74	-72	-10	103	-100	0	162	165
9	145	-153	-5	143	146	-9	111	-112	4	89	-86
12	131	-114	-3	86	-92	-6	96	103	5	90	101
13	238	264	-1	285	-282	-5	302	322	6	190	-194
15	109	114	0	133	129	-4	274	276	7	129	158
			2	202	-192	-3	95	-74			
	-2,4,L		3	84	-90	-1	71	-73		-2,14,L	
-13	88	79	4	217	-218	0	126	124	4	83	89
-11	102	-92	6	124	119	1	117	-117	9	101	-127
-10	77	-57	7	202	-218	4	105	-102			
-8	72	81	8	166	164	6	207	-215		-2,15,L	
-7	316	325	10	112	-114	7	337	-341	0	84	-76
-6	109	110	11	101	77	9	90	85			
-5	135	136	12	77	-56					-3,0,L	
-3	285	285	13	94	-88		-2,10,L		-12	299	285
-2	96	-90	16	93	93	-9	104	94	-10	231	-243
-1	372	-366				-8	145	-133	-4	407	430
0	102	-106		-2,7,L		-7	205	199	-2	311	310
1	211	-203	-9	102	112	-6	232	243	14	131	114
2	678	-670	-8	173	174	-5	122	122			
3	89	-95	-6	298	-303	0	109	-102		-3,1,L	
4	147	143	-4	64	21	2	122	-116	-12	175	-171
6	358	361	-2	231	221	5	90	92	-8	162	153
7	144	153	-1	460	-462	6	193	-197			

L	FOI	FC	L	FOI	FC	L	FOI	FC	L	FOI	FC
	-3,1,L		4	251	-252	3	99	-104	16	144	132
-5	77	51	5	122	123	6	206	209			
-3	265	268	6	115	-130	7	208	209		-4,1,L	
4	279	267	10	141	123	8	91	-48	-13	129	-127
5	477	475	12	243	-239				-10	118	-82
6	101	110	13	122	98		-3,9,L		-6	123	-110
7	71	57				-9	105	-66	-3	142	172
9	128	-137		-3,5,L		-5	260	259	-2	95	96
10	124	133	-10	174	162	-4	232	241	4	332	-322
11	145	-150	-9	107	108	-3	107	-120	5	216	217
17	120	-89	-8	101	-115	2	111	111	6	91	98
			-5	267	-272	5	91	116	7	199	196
	-3,2,L		-4	115	145	10	109	78	9	167	172
-14	123	76	-3	123	120	11	106	-111	15	138	-129
-11	243	-238	-2	94	-97						
-6	94	-90	1	123	-116		-3,10,L			-4,2,L	
-5	172	181	4	600	602	-4	107	-128	-12	130	-127
-4	144	151	5	188	-173	3	170	159	-11	163	145
-3	154	-165	6	168	-169	4	145	146	-10	150	119
-2	80	96	7	98	-114	5	113	112	-7	165	-156
5	235	226	8	89	-89				-6	100	-83
8	222	-214					-3,11,L		-5	139	-142
9	132	139		-3,6,L		-8	108	-110	-3	119	-119
11	197	208	-5	245	251	-4	168	-136	-2	113	-119
			-4	183	-193	-1	143	131	-1	154	-172
	-3,3,L		-2	312	317	2	118	121	5	138	152
-10	161	-155	-1	165	157	12	114	118	6	82	63
-9	143	125	0	82	73				7	82	-82
-8	116	-122	1	116	-128		-3,12,L		8	116	123
-5	119	125	2	153	-150	-5	145	158	9	141	-134
-4	82	-69	4	102	70	0	138	-120			
-3	100	-90	6	153	-152	3	103	117		-4,3,L	
-2	224	217	10	111	-120	4	186	-171	-7	128	-145
-1	286	-281	11	99	-85	5	159	148	-5	97	81
1	88	-84				6	128	119	-4	88	103
2	144	130		-3,7,L		7	113	-84	-1	254	256
3	278	-272	-3	179	172				0	659	-666
4	141	146	0	219	229		-3,13,L		1	761	759
5	238	237	2	120	115	5	157	-153	2	264	262
6	170	-170	5	102	-95				5	288	-304
7	83	92	6	130	125		-3,14,L		6	168	-160
11	184	-213	7	177	167	-3	202	192	7	175	-185
12	274	265	8	132	-126				8	141	142
13	205	-208	10	159	-158		-4,0,L		9	114	119
						-6	179	-181	11	136	115
	-3,4,L			-3,8,L		-4	289	-305			
-4	118	126	-5	138	135	-2	266	259		-4,4,L	
-3	120	-136	-4	224	251	6	130	125	-8	158	175
-1	259	264	-3	186	175	8	85	57	-7	115	-103
2	306	-301	-2	227	239	10	145	-137			

L	(FO)	FC	L	(FO)	FC	L	(FO)	FC	L	(FO)	FC
	-4,4,L		9	115	-134	-1	127	-142		-6,1,L	
-4	140	-128				4	184	-186	-7	135	103
-3	92	85		-4,9,L					-2	153	154
-1	116	127	-5	205	-201		-5,4,L		-1	120	-120
0	114	106	-2	112	-101	-10	180	-191	6	99	101
1	184	-185	-1	181	163	-1	156	-165			
2	330	338	1	96	75	0	127	-127		-6,2,L	
5	112	-95				4	140	-143	4	109	-106
12	143	-168		-4,10,L		5	93	91	5	149	157
13	181	186	-6	111	-57	6	117	128	7	99	103
			-4	119	85	7	111	101	8	118	-117
	-4,5,L		2	128	-108	8	111	125			
-8	130	-99				11	203	-95		-6,3,L	
-3	108	114		-4,11,L					-1	140	-146
-2	129	-133	0	182	-154		-5,5,L		0	94	137
0	116	118	2	139	-125	-2	163	-172	2	188	-184
2	81	102	4	133	103	-1	123	124	9	111	-99
4	193	198				0	130	-115			
7	117	103		-4,12,L		2	98	-111		-6,4,L	
9	97	86	-7	205	-182	4	192	-194	0	423	-430
13	114	-80	-3	119	83	6	128	102	1	215	220
			7	120	-127	10	152	142	2	94	-51
	-4,6,L		9	153	132	11	148	109	3	104	-110
-8	127	-122				12	134	-152			
-6	158	163		-4,13,L		13	132	146		-6,5,L	
-1	345	347	-6	143	-166				-1	115	-110
3	142	-152	6	138	125		-5,6,L		0	129	141
6	129	-125				-2	164	-174	1	245	-257
7	147	148		-5,0,L		4	204	207	2	205	194
8	255	248	-8	146	-128	7	178	-193	3	101	104
11	119	103	-4	191	-195				7	157	-168
12	104	-42	6	143	-150		-5,7,L		8	293	-309
			8	169	176	-8	130	67	13	153	128
	-4,7,L					-4	377	-356			
-4	159	-172		-5,1,L		-3	139	-132		-6,6,L	
-1	113	-92	-5	117	-141	-2	117	92	-5	200	189
2	122	-127	5	270	-270	6	190	-215	2	113	-67
3	131	-121	14	119	101				6	192	-150
6	266	277					-5,8,L		7	184	-174
7	243	255		-5,2,L		-5	150	-146	8	221	-183
8	393	383	-12	184	-138				9	118	78
			-11	178	189		-5,9,L		13	138	-112
	-4,8,L		-3	113	121	-4	139	129			
-6	262	-247	-2	125	-149	4	145	-120		-6,7,L	
-5	284	-284	4	162	160				-6	178	159
-2	117	95	6	83	82		-5,10,L		-5	149	157
1	127	129	13	123	94	-2	132	-96	6	119	-123
6	118	95				11	153	-112	8	130	126
7	226	228		-5,3,L							
8	202	-195	-2	112	114		-6,0,L			-6,9,L	
						-6	144	160	2	128	126

TABLE IV

FINAL POSITIONAL PARAMETERS

<u>ATOM</u>	<u>X</u>	<u>Y</u>	<u>Z</u>
AMMN	0.30088 (87)	0.53137 (33)	0.07359 (34)
N1	0.00111 (95)	0.13400 (36)	0.56896 (39)
N2	0.08379 (111)	0.17260 (47)	0.88201 (41)
N3	0.25224 (94)	0.44481 (39)	0.86532 (37)
N4	0.41768 (103)	0.73969 (42)	0.66067 (41)
N5	0.50386 (100)	0.83537 (42)	0.42332 (41)
N6	0.27973 (102)	0.55468 (43)	0.27475 (37)
C1	0.04521 (100)	0.18405 (47)	0.63532 (45)
C2	0.08941 (113)	0.20500 (47)	0.80897 (50)
C3	0.21067 (106)	0.40075 (47)	0.79712 (45)
C4	0.38109 (110)	0.68615 (46)	0.59926 (45)
C5	0.43814 (110)	0.75727 (52)	0.42406 (44)
C6	0.31808 (108)	0.60190 (46)	0.34401 (46)
C7	0.36252 (97)	0.65960 (44)	0.42981 (43)
C8	0.33359 (98)	0.62059 (45)	0.51635 (41)
C9	0.26424 (89)	0.52468 (42)	0.52761 (39)
C10	0.24063 (90)	0.48523 (42)	0.61394 (39)
C11	0.17553 (97)	0.38933 (41)	0.62217 (40)
C12	0.15897 (99)	0.34385 (43)	0.70749 (41)
C13	0.09859 (102)	0.24692 (49)	0.71774 (43)

<u>ATOM</u>	<u>X</u>	<u>Y</u>	<u>Z</u>
H9	0.23111 (556)	0.48319 (244)	0.46943 (222)
H10	0.27476 (607)	0.52577 (255)	0.68044 (237)
H11	0.15447 (551)	0.35311 (249)	0.56523 (227)
H1	0.39420 (920)	0.57715 (408)	0.06337 (387)
H2	0.19715 (1891)	0.55540 (677)	0.02303 (650)
H3	0.33562 (1210)	0.47201 (485)	0.06706 (443)
H4	0.28329 (1263)	0.54359 (488)	0.13129 (492)

SCALE FACTORS

S _{0hℓ}	0.95412 (337)
S _{1hℓ}	0.95600 (322)
S _{2hℓ}	0.97851 (351)
S _{3hℓ}	0.92926 (726)
S _{4hℓ}	0.68667 (604)
S _{5hℓ}	0.97954 (1346)
S _{6hℓ}	1.05219 (1360)

TABLE V

ANISOTROPIC TEMPERATURE FACTORS
($\times 10^5$)

<u>ATOM</u>	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
AMMN	1964 (185)	377 (35)	408 (32)	45 (68)	187 (61)	-25 (28)
N1	2087 (212)	537 (42)	549 (40)	-295 (79)	97 (77)	-183 (34)
N2	3725 (278)	743 (48)	569 (44)	-135 (95)	473 (91)	297 (39)
N3	2361 (217)	509 (41)	375 (35)	-34 (77)	34 (77)	-54 (31)
N4	2536 (234)	601 (43)	583 (42)	-365 (85)	255 (83)	-226 (36)
N5	2751 (238)	387 (37)	754 (49)	-390 (84)	519 (82)	9 (36)
N6	2461 (226)	801 (48)	321 (35)	-104 (83)	116 (78)	-81 (35)
C1	773 (207)	348 (46)	423 (44)	37 (81)	178 (79)	76 (37)
C2	1320 (234)	399 (45)	488 (45)	-117 (82)	229 (89)	78 (39)
C3	1333 (212)	379 (46)	345 (41)	-150 (84)	11 (83)	-8 (36)
C4	1461 (226)	345 (44)	379 (41)	-72 (85)	278 (82)	-27 (36)
C5	1006 (211)	402 (45)	433 (44)	161 (95)	171 (78)	32 (41)
C6	1064 (209)	398 (47)	374 (41)	94 (85)	231 (80)	181 (37)
C7	1183 (211)	289 (44)	358 (42)	11 (80)	343 (77)	-31 (34)
C8	661 (191)	388 (45)	311 (41)	35 (79)	69 (71)	-6 (35)
C9	612 (188)	322 (41)	263 (36)	-55 (72)	99 (67)	-89 (29)
C10	582 (185)	301 (42)	270 (36)	76 (71)	172 (65)	-90 (30)
C11	980 (207)	229 (39)	303 (38)	39 (74)	94 (71)	-61 (30)
C12	791 (191)	288 (42)	276 (38)	-32 (74)	-53 (66)	42 (30)
C13	1457 (244)	359 (42)	304 (40)	-120 (86)	122 (83)	65 (35)

TABLE V

ISOTROPIC TEMPERATURE FACTORS

<u>ATOM</u>	<u>B</u>	
H9	1.5000*	
H10	2.3113	(1.1036)
H11	1.2838	(1.0899)
H1	6.8302	(2.1180)
H2	18.2228	(4.3388)
H3	10.0314	(2.7032)
H4	11.0307	(2.8746)

*Set at 1.5000 and not varied.

FIGURE VII
1,1,2,6,6,7,7-hexacyanoheptatrienide Anion
(Stereo Pair)

$C \cos(\beta - 90^\circ)$

FIGURE VIII

Final Electron Density Composite A-axis Projection
(Contours every $1 \text{ e}/\text{\AA}^3$ beginning at $1 \text{ e}/\text{\AA}^3$)

DISCUSSION

The dimensions of the 1,1,2,6,7,7-hexacyanoheptatrienide anion are presented in Figure IX.

The observed bond lengths correlate quite well with the trend observed in the calculated bond orders and distances, presented in Figure X. These results are from extended Hückel calculations, assuming a planar molecule and using a wave function of the form $\alpha = 0.48$.³²

The carbon chain bond lengths vary from 1.374 Å to 1.402 Å, and are close to a bond order of 1.5. The slight variations are in agreement with those expected from investigation of the possible resonance forms and their relative contribution.

The shortening of the C-N bonds, which vary from 1.118 Å to 1.154 Å, and the lengthening of the C(chain)-C(cyano) bonds, when compared to similar

FIGURE IX

Observed Anion Dimensions

FIGURE X

Calculated Anion Bond Orders, Distances, and Charge Distribution

bonds in potassium para-nitrophenyldicyanomethide, ammonium tricyanomethide, and pyridinium dicyanomethide, are understood when resonance contributors of the form

are considered. Observed values for C-N bond lengths in the non-resonance stabilized molecules acetonitrile, CH_3CN , and propionitrile, $\text{CH}_3\text{CH}_2\text{CN}$, are 1.155 Å and 1.156 Å, respectively.^{33,34}

The assumption of planarity in the extended Hückel calculations is verified by the calculation of various least-square planes through portions of the anion.³⁵ These results are listed in Table VI. C(13) lies approximately 0°7' (0.007 Å), and C(7) about 0°2' (0.003 Å) above the planes described by C(1), C(2) and C(12), and C(5), C(6) and C(8), respectively. Within experimental error the anion appears to be planar.

The slight distortion exhibited by the four terminal cyano groups has been observed previously in the structures of pyridinium dicyanomethide and potassium para-nitrophenyldicyanomethide.³⁶ It does not, therefore, appear to be anomalous. The structures of other cyano bearing carbanions indicate that the carbon attached to the cyano groups tends to assume a non-planar configuration as the availability of resonance stabilization is reduced. This conclusion, predicted by Hine, is also indicated in the structure of potassium 4,4-dinitro-2-butenamide³⁷, which is not significantly non-planar with respect to the carbon bonded to the two nitro groups. As with the carbanion studied above, 4,4-dinitro-2-butenamide

TABLE VI

LEAST SQUARE PLANES

Plane 1. $6.610x - 4.264y - 6.487z = -0.487$

Atoms Defining Plane	$\Delta, \text{\AA}$
C7	-0.043
C8	-0.013
C9	0.038
C10	0.031
C11	0.053
C12	-0.026
C13	-0.039

Additional Atoms

N1	0.114
N2	-0.248
N3	-0.202
N4	-0.051
N5	-0.229
N6	0.047
C1	0.040
C2	-0.152
C3	-0.119
C4	-0.042
C5	-0.127
C6	-0.001

Plane 2. $6.704x - 4.233y - 1.196z = -1.236$

Atoms Defining Plane	$\Delta, \text{\AA}$
C1	0.0000
C2	0.0000
C12	0.0000

Atoms Not Defining Plane	$\Delta, \text{\AA}$
C13	0.0068

Plane 3. $6.472x - 4.980y - 4.247z = -0.953$

Atoms Defining Plane	$\Delta, \text{\AA}$
C5	0.0000
C6	0.0000
C8	0.0000

Atoms Not Defining Plane	
C7	0.0033

has a large π system with which to delocalize the negative charge. The planarity of 1,1,2,6,7,7-hexacyanoheptatrienide is indicated in Figures VII and XI as stereo pairs.

The crystal packing appears to be quite normal. The closest cation-anion approaches are:

N(7)-N(1)	2.973 Å
N(7)-N(3)	3.124 Å
N(7)-N(4)	3.358 Å
N(7)-N(5)	3.327 Å

The ammonium ions related by a center of symmetry are 4.445 Å apart. The environment about the two ammonium ions is indicated in Figure XII. The distances shorter than 5.0 Å, except the ammonium-ammonium interaction, are indicated by heavy lines. The crystal packing in three dimensions is indicated in Figures XI and XIII.

FIGURE XI
Crystal Packing Diagram
(Stereo Pair)

FIGURE XII

Ammonium Environment
(Stereo Pair)

FIGURE XIII
Packing Diagram, [100] Projection

APPENDIX

ALGEBRAIC CONSIDERATIONS³⁸

Defining a quasi-normalized structure factor after Karle and Hauptman,

$$\Xi_{\tilde{k}} = \sigma_2^{-\frac{1}{2}} \sum_{j=1}^N z_j \exp(2\pi i \tilde{k} \cdot \tilde{r}_j), \quad 23.20$$

and the quasi-normalized structure factor for the squared structure,

$$\Xi'_{\tilde{h}} = \sigma_4^{-\frac{1}{2}} \sum_{j=1}^N z_j^2 \exp(2\pi i \tilde{h} \cdot \tilde{r}_j), \quad 23.21$$

where z_j is the atomic number of the j th atom, having coordinates represented by the vector $\tilde{r}_j$ in a unit cell containing N atoms, and

$$\sigma_n = \sum_{j=1}^N z_j^n. \quad 23.22$$

Then,

$$\begin{aligned} \Xi_{\tilde{k}} \Xi_{\tilde{h}-\tilde{k}} &= \sigma_2^{-1} \sum_{j=1}^N z_j^2 \exp(2\pi i \tilde{h} \cdot \tilde{r}_j) \\ &+ \sigma_2^{-1} \sum_{j \neq j'}^N \sum_{j'=1}^N z_j z_{j'} \exp\{2\pi i [\tilde{k} \cdot \tilde{r}_j + (\tilde{h}-\tilde{k}) \cdot \tilde{r}_{j'}]\}. \end{aligned} \quad 23.23$$

Averaged over all values of $\tilde{k}$, the double sum approaches zero. Using 23.21,

$$\begin{aligned} \langle \Xi_{\tilde{k}} \Xi_{\tilde{h}-\tilde{k}} \rangle &= \sigma_2^{-1} \sum_{j=1}^N z_j^2 \exp(2\pi i \tilde{h} \cdot \tilde{r}_j) \\ &= \sigma_4^{\frac{1}{2}} \sigma_2^{-1} \Xi'_{\tilde{h}}. \end{aligned} \quad 23.24$$

Rearranging,

$$\Xi'_h = \sigma_2 \sigma_4^{-1/2} \langle \Xi_k \Xi_{h-k} \rangle_k. \quad 24.25$$

For equal atoms, Ξ'_h coincides with Ξ_h , $\sigma_2 \sigma_4^{-1/2}$ equals $N^{1/2}$, and 24.25 becomes, in this case,

$$\Xi_h = N^{1/2} \langle \Xi_k \Xi_{h-k} \rangle_k. \quad 24.26$$

Equation 24.26 is exact for equal atoms in both centrosymmetric and noncentrosymmetric crystals. Karle and Hauptman derived a relation similar to 24.26, employing probability arguments:

$$\Xi_h \approx \sigma_2^{3/2} \sigma_3^{-1} \langle \Xi_k \Xi_{h-k} \rangle_k. \quad 24.27$$

One works with the approximation 24.27 rather than the exact 24.26, since it defines the phases for Ξ_h rather than for Ξ'_h , which is associated with the squared structure. Actually the Ξ_h and Ξ'_h of large magnitudes do not differ greatly from each other, even when atoms of considerably different atomic number are present in the crystal.

Rewriting 24.27,

$$1 \approx \sigma_2^{3/2} \sigma_3^{-1} \langle |\Xi_h^{-1} \Xi_k \Xi_{h-k}| \exp[i(-\varphi_h + \varphi_k + \varphi_{h-k})] \rangle_k. \quad 24.28$$

Expanding the exponential in terms of cosine and sine,

$$1 \approx \sigma_2^{3/2} \sigma_3^{-1} \langle |\Xi_h^{-1} \Xi_k \Xi_{h-k}| \{ \cos[1(-\varphi_h + \varphi_k + \varphi_{h-k})] + i \sin[1(-\varphi_h + \varphi_k + \varphi_{h-k})] \} \rangle_k. \quad 24.29$$

Considering only the imaginary portion of 24.29,

$$0 \approx \sigma_2^{3/2} \sigma_3^{-1} \langle |\Xi_h^{-1} \Xi_k \Xi_{h-k}| \sin[i(-\varphi_h + \varphi_k + \varphi_{h-k})] \rangle_{k_r}, \quad 25.30$$

where k_r are the restricted values of k for which the values of $|\Xi_k|$ and $|\Xi_{h-k}|$ are large, since probability arguments indicate that for the largest $|\Xi|$ values, $\varphi_h - \varphi_k - \varphi_{h-k}$ is distributed around zero and, generally, assumes small values.

Since $\sigma_2^{3/2} \sigma_3^{-1}$ has a fixed value for a given unit cell and its contents, we have

$$0 \approx \langle |\Xi_h^{-1} \Xi_k \Xi_{h-k}| \sin[i(-\varphi_h + \varphi_k + \varphi_{h-k})] \rangle_{k_r}, \quad 25.31$$

which can be expanded in a Taylor series. Since the argument is small, we take only the first term in the series,

$$0 \approx \langle |\Xi_h^{-1} \Xi_k \Xi_{h-k}| (-\varphi_h + \varphi_k + \varphi_{h-k}) \rangle_{k_r}, \quad 25.32$$

which, since it is an average over k_r , can be expressed as exactly

$$p^{-1} \sum_{k_r} \langle |\Xi_h^{-1} \Xi_k \Xi_{h-k}| (-\varphi_h + \varphi_k + \varphi_{h-k}) \rangle, \quad 25.33$$

where p represents the number of k_r vectors summed over.

Rewriting 25.32,

$$0 \approx -\varphi_h \langle |\Xi_h^{-1} \Xi_k \Xi_{h-k}| \rangle_{k_r} + \langle |\Xi_h^{-1} \Xi_k \Xi_{h-k}| (\varphi_k + \varphi_{h-k}) \rangle_{k_r}, \quad 25.34$$

or, after removing the single-valued Ξ_h ,

$$\varphi_h \langle |\Xi_k \Xi_{h-k}| \rangle_{k_r} \approx \langle |\Xi_k \Xi_{h-k}| (\varphi_k + \varphi_{h-k}) \rangle_{k_r}. \quad 25.35$$

Solving for φ_h ,

$$\varphi_h \approx \frac{\langle | \underline{\underline{M}}_{\underline{\underline{k}} \underline{\underline{h}} - \underline{\underline{k}}} | (\varphi_{\underline{\underline{k}}} + \varphi_{\underline{\underline{h}} - \underline{\underline{k}}}) \rangle_{\underline{\underline{k}}}}{\langle | \underline{\underline{M}}_{\underline{\underline{k}} \underline{\underline{h}} - \underline{\underline{k}}} | \rangle_{\underline{\underline{k}}}} \quad 26.36$$

Expressing this result in such a way to emphasize the fact that the φ_h are defined as weighted linear functions of the other phases associated with the largest $|\underline{\underline{M}}|$ values, we obtain

$$\varphi_h \approx \frac{\sum_{\underline{\underline{k}}} | \underline{\underline{M}}_{\underline{\underline{k}} \underline{\underline{h}} - \underline{\underline{k}}} | (\varphi_{\underline{\underline{k}}} + \varphi_{\underline{\underline{h}} - \underline{\underline{k}}})}{\sum_{\underline{\underline{k}}} | \underline{\underline{M}}_{\underline{\underline{k}} \underline{\underline{h}} - \underline{\underline{k}}} |} \quad 26.37$$

If all the $|\underline{\underline{M}}|$ are approximately of the same magnitude, then

$$\varphi_h \approx \langle \varphi_{\underline{\underline{k}}} + \varphi_{\underline{\underline{h}} - \underline{\underline{k}}} \rangle_{\underline{\underline{k}}}, \quad 26.38$$

in agreement with 11.9.

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