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The Crystal Structure of Methylguanidinium Nitrate*

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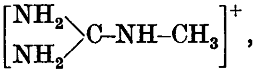
The crystal structure of methylguanidinium nitrate has been determined. The crystal is orthorhombic with probable space group *Pnma*; the unit cell dimensions are $a = 13{\cdot}24$, $b = 6{\cdot}42$, $c = 7{\cdot}29$ Å; $n = 4$.

In this layer structure both the nitrate ion and the CN_3 grouping of the methylguanidinium ion exhibit almost perfect trigonal planar symmetry. In the nitrate ion the average N–O bond length is $1{\cdot}24_4$ Å; in the CN_3 group the C–N bond length averages $1{\cdot}32_6$ Å.

Introduction

Predictions of the configurations of polypeptide chains in proteins have been based on accurate knowledge of the dimensions and configurations of the constituent amino acids and simple peptides. The structures of almost all amino acids, individually or as part of simple peptides, which commonly occur in proteins have been established or are currently being investigated. An exception is arginine, α-amino-δ-guanidino-*n*-valeric acid, for which no structure determination has been reported.

Crystals of arginine suitable for X-ray analysis are not readily prepared; methyl guanidinium salts, however, crystallize easily and their analysis would provide structural data regarding the methylguanidinium ion,



$$\left[\begin{matrix}NH_2\\NH_2\end{matrix}\!>\!C\text{–}NH\text{–}CH_3\right]^+,$$

the non-trivial part of the arginine molecule. The nitrate was chosen in preference to the sulfate‡ for analysis; it is of additional interest because of the differences in the lengths of the N–O bond previously reported for the nitrate ion (Elliott, 1937; Tahvonen, 1948; Grison, Eriks & de Vries, 1950). The results of two determinations of the structure of creatine monohydrate (Jensen, 1954; Mendel & Hodgkin, 1954), which contains the guanidinium grouping, were announced while this investigation was in progress.

Experimental part

Space group and unit-cell dimensions

Methylguanidinium nitrate (m.p. 150° C.) was prepared from the sulfate by the addition of a stoichiometric amount of $Ba(NO_3)_2$, followed by filtration to remove $BaSO_4$ and evaporation of the filtered solution. It crystallized from water in orthorhombic plates or, rarely, in needles. Perfect cleavage was observed normal to the needle axis, *b*, and moderately good cleavage parallel to the needle axis, identified as normal to *a*.

The unit cell dimensions determined with a Straumanis-type camera are, with their standard deviations:

$$a=13{\cdot}243\pm0{\cdot}005,\quad b=6{\cdot}427\pm0{\cdot}002,\quad c=7{\cdot}289\pm0{\cdot}005\ \text{Å}.$$

The observed density is $1{\cdot}459\pm0{\cdot}003$ g.cm.$^{-3}$ compared with 1·457 g.cm.$^{-3}$ calculated for four molecules per unit cell. Systematic absences observed on Weissenberg and precession photographs, namely $hk0$ with h odd and $0kl$ with $k+l$ odd, are characteristic for the two space groups *Pnma* (centrosymmetric, 8 general positions) and $Pn2_1a$ (non-centrosymmetric, 4 general positions). The presence of four molecules in the unit cell is compatible with the centrosymmetric space group if the molecules lie in special positions; of these special positions only the mirror planes at $y = \frac{1}{4}$ and $\frac{3}{4}$ are consistent with the symmetry possible for the molecule. This arrangement would result in a layer structure; it was indicated by the perfect cleavage of the crystal normal to *b*. Furthermore, the relative intensities of corresponding reflections on layers with k even and k odd, respectively, were nearly identical, a distribution of intensities characteristic of a layer structure. The centrosymmetric space group was therefore assumed. A piezoelectric test gave negative results.

Intensity data

For the collection of intensity data a needle crystal of cross-sectional diameter less than 0·2 mm. was

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‡ The commercially available methylguanidinium sulfate crystallizes from water in orthorhombic plates, space group $P2_12_12_1$, and unit-cell dimensions $a = 7{\cdot}16$, $b = 12{\cdot}18$, $c = 13{\cdot}16$ Å. The density calculated for four molecules per unit cell is 1·41 g.cm.$^{-3}$, that observed is 1·42 g.cm.$^{-3}$.

mounted for rotation around the *b* axis, the needle axis. Equi-inclination Weissenberg photographs were taken about this axis, the zero through the fifth layers with Cu $K\alpha$ radiation and, in addition, the zero and first layers with Mo $K\alpha$ radiation, in order to obtain data beyond the Cu sphere of reflection. Furthermore, the sixth layer was photographed with Mo $K\alpha$ radiation; although the seventh and eight layers intersect the Cu sphere of reflection also, the intensities were too low to be significant, because of the high temperature factor normal to the layers. Supplementary photographs of the $hk0$ and $hk1$ nets were taken with another crystal mounted along *c*.

Intensities were visually estimated from multiple films and were corrected for Lorentz and polarization factors. Because of the dimensions of the crystals, corrections for absorption were not considered necessary.

Trial structure

For a crystal of this basic simplicity a variety of approaches for deriving a trial structure might be successful. Examination of the Patterson function, however, appeared to be the most satisfactory method. The three-dimensional Patterson function of this layer structure can be anticipated to consist of one set of maxima at $v = 0$ arising from vectors within one layer and a second set of maxima at $v = \frac{1}{2}$ arising from vectors between adjacent layers of the structure. Therefore, the calculation of the sections $v = 0$ and $v = \frac{1}{2}$ would give all information contained in the Patterson function. Essentially the same information can be obtained from a modified projection suggested by Hughes & Wilson (1949) and also used by Zachariasen (1954) in the refinement of the structure of orthoboric acid.

The modified Patterson function has the form

$$P'(u, w) = \int_0^1 P(u, v, w)(1\pm\cos 2\pi v)dv = \sum_{hl}\{F^2(h0l)\pm F^2(h1l)\}\cos 2\pi(hu+lw)\,.$$

The physical significance of this expression is as follows: the Patterson density P in any plane normal to v is weighted by the function $(1+\cos 2\pi v)$ or $(1-\cos 2\pi v)$, and is projected on to the uw plane. In the first case, peaks in the plane $v = 0$ enter with the weight 2, those in the plane $v = \frac{1}{2}$ with the weight 0; in the second case, the weights are reversed. In the present layer structure one thus obtains projections similar to the sections $v = 0$ and $v = \frac{1}{2}$ by using $h0l$ and $h1l$ data only.

This modification of the Patterson function is one example of what may appropriately be termed *weighted* density projections. In principle, a completely arbitrary choice of weighting is possible, but in practice only simple weighting functions effecting a selection of the experimental data are of value; specific examples are the bounded projection (Booth, 1945) and the generalized projections (Lipson & Cochran, 1953; see also Patterson, 1952).

In the present structure determination the two weighted and sharpened Patterson projections were calculated from $h0l$ and $h1l$ intensities which had been brought to the same relative scale by correlation with photographs taken around the *c* axis. The projection containing the intraplane vectors is shown in Fig. 1.

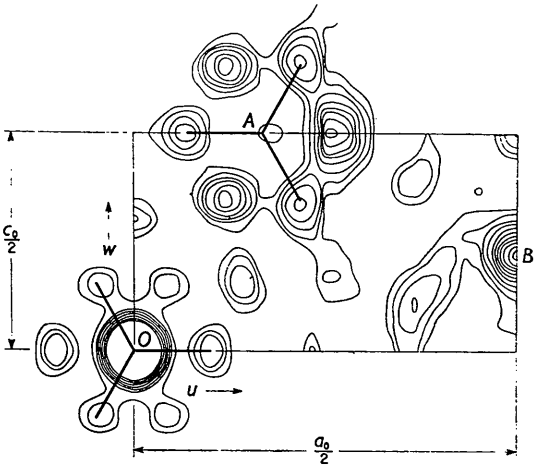


Fig. 1. Patterson function weighted by $(1+\cos 2\pi v)$ and projected along v. Contours at arbitrary intervals.

The hexagonal arrays of peaks around the origin O and around the weak peak A at $u = \frac{1}{6}$, $w = \frac{1}{2}$ are striking. In a first approximation, the structure can be regarded as composed of two identical trigonal 'Y'-shaped units—the NO_3 and the CN_3 groups—and it is easily seen that they will generate these hexagonal arrangements of peaks if they have a separation and orientation as shown in the drawing. A reversal of both the groups in respect to the u direction would also explain the peaks, but is excluded from packing consideration. The second outstanding feature of this Patterson section consists of the high peak B at $u = \frac{1}{2}$, $w = \frac{7}{30}$. It originates from the interaction of equivalent 'Y' units which are related by a screw axis parallel to x, and thus it defines the displacement of the centers of the units from the screw axis.

The projection equivalent to the section $v = \frac{1}{2}$ showed two outstandingly high peaks at $u = \frac{1}{2}$, $w = 0$ and at $u = 0$, $w = \frac{7}{30}$. By interpreting them as being generated by the interactions of non-equivalent 'Y' units in adjacent layers the position of the screw axis parallel to y was obtained.

Finally, on consideration of the packing of the units within a layer, it was recognized that there was only one position where the methyl group could be fitted.

Each peak in the Patterson diagram could be accounted for by interactions arising from the assumed atomic arrangement. The complete trial structure was thus derived.

Refinement of the structure

For the initial refinement of the parameters, Fourier and difference Fourier projections modified by the weighting function $(1+\sin 2\pi y)$ were used. By this mode of weighting only the $(h0l)$ and $(h1l)$ reflections enter into the calculation and the one layer of atoms at $y = \frac{1}{4}$ is projected.

Four Fourier refinements and one difference Fourier refinement were carried out, interspersed by adjustments of scale and temperature factors by least-square methods. A final in-plane temperature-factor coefficient of $\alpha' = 1{\cdot}8\times10^{-16}$ cm.^{2} was found, the temperature factor being defined as $\exp -\alpha'(h^2/4a^2+l^2/4c^2)$. Following the difference Fourier, the contributions of the hydrogen atoms to the structure factors were taken into account. The positions of the hydrogen atoms were chosen near the maxima of the hydrogen peaks in the difference Fourier, and in such a way as to maintain approximately tetrahedral bond angles around the carbon atom and trigonal bond angles around the nitrogen atoms. Average C–H and N–H distances of 0·9 and 0·8 Å, respectively, were indicated and assumed. Although these distances are appreciably shorter than the accepted values for these bond lengths, they are in agreement with the positions of electron-

Table 1. *Atomic parameters*

y = 0·25 if not stated differently

	x	z		x	z
C_0	0·4254	0·3582	H_1	0·053	0·026
C_1	0·2810	0·1482	H_2	0·062	0·209
N_0	0·0919	0·6390	H_3	0·390	0·633
N_1	0·0248	0·1231	H_4	0·306	0·498
N_2	0·3660	0·5047	H_5	0·424	0·102
N_3	0·3885	0·1886	$H_{6,7}$	0·253	0·203*
O_1	0·4983	0·8484	H_8	0·272	0·026
O_2	0·1451	0·7782			
O_3	0·1329	0·4840			

* $y = 0{\cdot}25\pm0{\cdot}11$.

Table 2. *Observed and calculated structure factors*

(The calculations are based on McWeeny (1951) scattering curves)

k = 0

	h	F$_o$	F$_c$
ℓ = 0	2	41.9	44.4
	4	46.9	-47.4
	6	7.0	8.3
	8	50.2	48.9
	10	9.6	5.4
	12	5.0	-3.2
	14	15.0	15.7
	16	< 1.0	-.2
	18	3.5	-4.3
	20	3.1	-2.3
	22	< 3.4	3.5
ℓ = 1	1	8.9	-6.7
	2	79.0	73.9
	3	13.5	11.6
	4	3.3	-2.2
	5	1.7	2.8
	6	27.7	-25.0
	7	< 1.2	-1.2
	8	26.3	-21.6
	9	21.1	-20.5
	10	3.5	-2.5
	11	6.7	-5.6
	12	8.6	-8.7
	13	2.7	-2.4
	14	2.1	2.5
	15	< 1.3	. 0
	16	< 1.0	.7
	17	4.0	-3.8
	18	2.0	-3.9
	19	5.8	-5.4
	20	< 3.0	.3
	21	< 3.1	-2.8
	22	< 3.2	.3
ℓ = 2	0	11.2	-12.1
	1	29.4	-30.6
	2	9.3	-7.6
	3	7.2	-8.5
	4	16.6	-15.5
	5	21.5	-20.5
	6	7.0	4.6
	7	9.1	9.2
	8	4.8	4.0
	9	1.3	.3
	10	8.6	-7.6
	11	18.0	-17.9
	12	11.1	-10.2
	13	9.1	-8.5
	14	2.1	1.4
	15	1.7	-1.8
	16	4.2	5.3
	17	6.5	7.4
	18	5.2	-5.3
	19	< 3.1	-.4
	20	< 3.2	4.0
	21	< 3.3	.5
	22	< 3.4	2.7
ℓ = 3	1	17.6	16.2
	2	21.1	-20.4
	3	3.1	3.7
	4	8.7	8.5
	5	6.7	5.4
	6	15.9	13.6
	7	2.5	-3.5
	8	21.7	-21.3
	9	25.1	25.2
	10	14.7	-13.9
	11	10.4	10.5
	12	2.2	-.2
	13	< 1.9	.7
	14	< 1.7	1.4
	15	< 1.8	-2.2
	16	< 2.8	-2.4
	17	5.4	5.4
	18	< 3.1	-.3
	19	7.7	7.8
	20	< 3.3	.4
	21	< 3.4	2.8
ℓ = 4	0	10.4	-11.6
	1	11.3	10.1
	2	34.2	-33.3
	3	3.5	3.4
	4	43.3	-44.2
	5	2.1	2.3
	6	14.7	13.1
	7	13.9	-13.2
	8	13.1	12.4
	9	3.3	-3.2
	10	21.1	-22.1
	11	8.9	9.4
	12	13.1	-14.0
	13	1.7	1.4
	14	< 1.8	2.0
	15	4.6	-4.0
	16	6.0	6.5
	17	5.2	-4.1
	18	< 3.1	-4.2
	19	< 3.2	2.3
	20	< 3.3	1.5
	21	< 3.4	-.1
ℓ = 5	1	8.3	-6.7
	2	16.8	-15.9
	3	10.0	-9.4
	4	9.3	-6.7
	5	< 2.8	.5
	6	2.5	2.1
	7	< 2.0	1.0
	8	20.0	19.9
	9	8.3	-7.2
	10	3.1	3.3
	11	2.9	-2.6
	12	3.3	3.2
	13	5.8	6.3
	14	< 2.8	-.1
	15	< 2.9	2.5
	16	< 3.0	.2
	17	< 3.1	-3.2
	18	< 3.2	-.2
	19	< 3.3	.4
	20	< 3.4	.3
ℓ = 6	0	32.5	32.2
	1	10.4	9.9
	2	6.0	5.7
	3	3.3	2.7
	4	9.1	-6.8
	5	4.4	-3.9
	6	2.9	-2.0
	7	3.5	4.0
	8	12.4	11.6
	9	7.2	8.5
	10	5.6	6.7
	11	3.7	3.2
	12	2.7	-2.0
	13	< 2.8	-.2
	14	5.8	6.0
	15	5.6	7.0
	16	< 3.1	3.5
	17	< 3.2	-.4
	18	< 3.3	1.1
	19	< 3.4	-3.5
ℓ = 7	1	5.8	-5.1
	2	< 2.0	-1.8
	3	4.6	4.7
	4	4.0	3.5
	5	5.4	-5.7
	6	4.0	5.1
	7	5.6	-4.3
	8	1.7	-2.4
	9	7.0	-6.8
	10	4.0	2.6
	11	< 2.8	-.4
	12	5.0	6.0
	13	4.8	-6.3
	14	< 3.1	1.8
	15	< 3.2	-.8
	16	< 3.3	-3.1
	17	< 3.3	1.1
	18	< 3.4	-.1
ℓ = 8	0	16.2	16.1
	1	4.8	-5.0
	2	4.6	4.8
	3	3.1	3.0
	4	2.0	-1.4
	5	2.7	2.2
	6	3.1	2.1
	7	1.3	1.1
	8	< 2.8	2.9
	9	< 2.9	-.6
	10	< 2.9	-2.1
	11	< 3.0	-.2
	12	< 3.1	-.2
	13	< 3.2	.9
	14	4.5	5.5
	15	< 3.3	-3.0
	16	< 3.4	-1.1
	17	< 3.5	3.5
ℓ = 9	1	8.1	8.5
	2	2.5	-1.3
	3	< 1.1	-.9
	4	2.0	1.7
	5	2.7	3.6
	6	7.2	6.0
	7	6.2	6.1
	8	6.2	-7.6
	9	< 3.7	3.5
	10	8.9	-7.0
	11	< 3.2	-2.2
	12	< 3.2	-2.9
	13	< 3.3	1.9
	14	< 3.4	3.6
	15	< 3.4	.9
ℓ = 10	0	< 3.0	-2.6
	1	< 3.0	3.7
	2	< 3.0	-2.7
	3	< 3.0	2.2
	4	7.2	-8.3
	5	4.8	-5.9
	6	3.1	2.7
	7	3.1	-2.9
	8	5.4	3.8
	9	< 3.2	1.6
	10	3.3	-4.8
	11	< 3.3	-2.3
	12	5.8	-5.6
	13	< 3.5	-4.0
ℓ = 11	1	< 3.2	-1.9
	2	< 3.2	-2.9
	3	< 3.2	.6
	4	< 3.3	-.4
	5	< 3.3	2.1
	6	< 3.3	-1.4
	7	< 3.3	-1.6
	8	< 3.4	-.2
	9	< 3.4	2.4
	10	< 3.5	-2.5
ℓ = 12	0	< 3.4	-.8
	1	< 3.4	.1
	2	< 3.4	-1.7
	3	< 3.4	-2.7
	4	< 3.4	-.9
	5	< 3.5	1.0

k = 1

	h	F$_o$	F$_c$
ℓ = 0	2	10.6	-9.1
	4	8.4	-7.6
	6	11.0	11.7
	8	34.1	-31.6
	10	2.8	-2.6
	12	4.4	-2.1
	14	6.0	-5.9
	16	4.4	-5.8
	18	3.8	4.5
	20	5.5	6.9
	22	< 3.7	-2.7
ℓ = 1	0	11.4	-11.0
	1	26.3	26.0
	2	12.1	10.6
	3	42.2	41.4
	4	12.5	-12.3
	5	36.6	-35.6
	6	32.5	30.5
	7	22.9	-20.2
	8	11.7	11.4
	9	1.2	1.7
	10	< 1.6	-1.5
	11	8.6	-7.1
	12	12.1	11.8
	13	8.8	-9.1
	14	6.7	7.1
	15	< 1.3	-.6
	16	2.2	1.3
	17	6.7	7.9
	18	< 3.0	-2.3
	19	3.4	-3.6
	20	6.9	8.1
	21	3.6	-4.5
	22	5.3	5.7
ℓ = 2	1	43.7	-48.3
	2	6.1	4.4
	3	56.5	-62.0
	4	15.7	-12.8
	5	14.9	-11.8
	6	1.4	-2.9
	7	3.6	-2.2
	8	13.1	12.6
	9	1.3	.4
	10	4.6	-3.9
	11	20.8	-20.4
	12	7.1	-7.2
	13	9.0	-7.7
	14	1.2	2.3
	15	< 1.9	-1.4
	16	4.4	4.6
	17	3.8	2.4
	18	< 3.3	-2.9
	19	4.0	3.5
	20	3.4	-3.4
	21	< 3.6	-1.3
	22	< 3.7	1.9
ℓ = 3	0	22.5	-22.5
	1	42.0	44.6
	2	2.6	2.9
	3	7.3	6.6
	4	< 1.4	3.0
	5	31.9	-29.7
	6	13.1	-12.0
	7	6.4	-3.4
	8	1.2	-.6
	9	32.8	32.6
	10	10.6	12.7
	11	15.1	15.0
	12	4.0	4.2
	13	10.6	-11.5
	14	5.3	-5.9
	15	< 2.1	.3
	16	3.8	2.7
	17	2.2	2.0
	18	4.0	4.6
	19	< 3.5	2.5
	20	< 2.4	2.6
	21	< 3.6	-1.1
ℓ = 4	1	5.1	4.8
	2	10.1	-10.0
	3	18.2	18.7
	4	11.5	12.2
	5	5.9	5.3
	6	2.1	4.5
	7	1.2	1.0
	8	1.4	1.3
	9	3.4	-1.6
	10	3.6	1.3
	11	7.5	7.3
	12	12.7	14.0
	13	5.1	4.7
	14	3.2	3.4
	15	4.6	4.8
	16	< 3.1	-2.5
	17	< 3.3	.7
	18	< 3.4	-1.4
	19	< 3.5	-2.4
	20	< 3.6	-2.0
	21	< 3.7	1.7
ℓ = 5	0	4.8	4.1
	1	1.2	-.3
	2	12.1	-11.7
	3	2.8	-1.2
	4	2.2	-2.7
	5	3.6	-2.6
	6	3.2	-4.4
	7	8.4	6.4
	8	7.7	-6.9
	9	9.8	10.8
	10	8.8	-8.4
	11	3.6	4.1
	12	5.9	-6.9
	13	4.2	-4.5
	14	< 3.1	1.7
	15	< 3.1	.7
	16	4.0	-4.4
	17	4.9	5.6
	18	< 3.5	-1.4
	19	3.6	.3
	20	4.6	-4.7
ℓ = 6	1	28.4	29.2
	2	9.0	9.3
	3	2.1	-1.7
	4	3.8	-2.7
	5	10.2	-8.9
	6	< 2.0	.2
	7	10.8	11.6
	8	< 1.9	-1.0
	9	5.9	4.2
	10	4.2	4.5
	11	2.1	2.2
	12	3.6	-3.2
	13	< 3.1	2.4
	14	< 3.2	
	15	< 3.3	2.0
	16	< 3.4	1.2
	17	< 3.5	-3.0
	18	< 3.6	.9
	19	< 3.7	-2.6
ℓ = 7	0	6.0	-5.4
	1	14.2	13.5
	2	6.9	6.7
	3	18.8	19.9
	4	11.5	12.4
	5	12.1	-13.1
	6	4.9	4.9
	7	9.4	-9.7
	8	3.6	-2.9
	9	2.1	1.8
	10	1.2	5
	11	6.1	-5.5
	12	< 3.1	3.3
	13	4.6	-4.0
	14	< 3.3	.1
	15	< 3.4	.8
	16	< 3.5	-.4
	17	4.4	4.6
	18	< 3.7	-1.2
ℓ = 8	1	7.7	-7.9
	2	5.1	-5.1
	3	4.0	-4.9
	4	4.0	-4.1
	5	1.9	1.7
	6	3.0	2.9
	7	1.7	-3.2
	8	< 1.0	-.9
	9	< 3.1	1.4
	10	3.2	-4.0
	11	6.7	-7.3
	12	6.2	-6.9
	13	5.5	-5.2
	14	< 3.5	-2.0
	15	< 3.6	-1.4
	16	< 3.6	1.6
	17	< 3.7	.5
ℓ = 9	0	< 1.1	-.6
	1	3.0	2.6
	2	3.2	3.4
	3	< 1.2	-.2
	4	2.2	-2.7
	5	3.8	-2.4
	6	< 3.1	.1
	7	5.1	-4.7
	8	4.0	3.7
	9	< 3.3	-.2
	10	5.3	5.4
	11	< 3.4	2.0
	12	< 3.4	3.2
	13	< 3.4	-3.2
	14	< 3.6	-3.2
	15	< 3.7	-2.1
ℓ = 10	1	< 3.2	-2.1
	2	< 3.2	1.4
	3	5.7	-6.0
	4	< 3.3	1.5
	5	< 3.3	.6
	6	5.3	-5.4
	7	5.9	5.3
	8	< 3.4	-.1
	9	< 3.5	-1.4
	10	< 3.5	.2
	11	4.4	-4.9
	12	< 3.7	3.1
	13	< 3.7	1.9
ℓ = 11	0	< 3.5	-3.3
	1	< 3.5	2.3
	2	< 3.4	-4.6
	3	< 3.5	-3.2
	4	< 3.5	-.7
	5	4.2	-3.7
	6	< 3.6	-2.8
	7	3.6	3.1
	8	< 3.6	-3.6
	9	6.4	7.2
	10	< 3.7	-2.0
ℓ = 12	1	5.3	5.3
	2	< 3.7	2.7
	3	< 3.7	.9
	4	< 3.7	.2
	5	4.6	-4.2

Table 2 (*cont.*)

k = 2

	h	F_o	F_c
l = 0	2	36.9	-37.1
	4	40.9	38.9
	6	6.5	-9.7
	8	34.7	-37.0
	10	9.0	-5.5
	12	3.2	3.2
	14	12.1	-14.0
	16	< 1.1	.3
l = 1	1	5.4	6.6
	2	51.0	-52.5
	3	8.8	-8.1
	4	< 1.1	1.5
	5	1.8	-2.5
	6	19.8	19.2
	7	< 1.6	1.3
	8	20.9	17.2
	9	16.6	16.5
	10	3.2	2.4
	11	5.9	4.7
	12	6.4	7.3
	13	< 1.8	1.9
	14	< 1.6	-2.1
	15	< 1.4	-.1
	16	< 1.0	-.7
l = 2	0	6.8	5.9
	1	19.9	18.3
	2	8.6	8.5
	3	7.3	8.2
	4	10.9	9.6
	5	13.7	14.0
	6	4.1	-1.8
	7	6.6	-6.2
	8	4.4	-4.2
	9	< 1.8	-.6
	10	7.3	7.1
	11	14.9	15.6
	12	7.9	8.4
	13	7.2	7.2
	14	1.6	-1.0
	15	< 1.4	1.7
	16	2.8	-4.8

k = 2

	h	F_o	F_c
l = 3	1	13.1	-12.3
	2	15.2	15.6
	3	.9	-3.3
	4	7.5	-6.4
	5	4.6	-4.6
	6	11.6	-10.9
	7	< 1.8	2.5
	8	16.3	17.6
	9	19.5	-21.0
	10	12.0	11.5
	11	7.8	-8.9
	12	2.1	.3
	13	< 1.6	-.4
	14	< 1.4	-1.3
	15	< 1.3	1.9
l = 4	0	9.6	9.7
	1	7.7	-6.3
	2	27.5	25.0
	3	4.0	-3.6
	4	33.2	35.8
	5	< 1.8	-.8
	6	12.4	-11.5
	7	10.7	10.3
	8	10.0	-10.4
	9	2.7	3.2
	10	16.7	18.7
	11	7.6	-8.5
	12	10.3	12.2
	13	1.9	-1.1
	14	< 1.2	-1.8
	15	< .4	3.4
l = 5	1	6.0	5.5
	2	14.4	13.2
	3	7.9	8.0
	4	8.2	5.5
	5	< 2.0	-.4
	6	2.3	-1.8
	7	< 2.0	-.8
	8	15.5	-17.2
	9	6.2	5.8
	10	2.8	-2.8

k = 2

	h	F_o	F_c
	11	2.2	2.2
	12	2.6	-2.8
	13	4.7	-5.5
l = 6	0	25.0	-26.9
	1	8.6	-8.9
	2	5.4	-4.7
	3	1.3	-1.5
	4	7.8	5.9
	5	2.9	2.8
	6	2.6	1.8
	7	2.6	-3.0
	8	9.9	-9.9
	9	6.2	-7.6
	10	4.2	-5.9
	11	2.9	-2.7
	12	1.8	1.7
l = 7	1	4.4	4.1
	2	1.8	1.5
	3	3.8	-4.1
	4	3.3	-2.9
	5	4.5	5.0
	6	3.3	-4.4
	7	3.7	3.8
	8	< 1.4	2.1
	9	5.7	6.1
	10	3.2	-2.2
l = 8	0	12.9	-14.2
	1	4.2	4.6
	2	4.1	-3.9
	3	2.8	-2.8
	4	1.3	1.0
	5	2.1	-1.8
	6	2.1	-1.7
	7	< 1.2	-1.0
l = 9	1	5.9	-7.4

k = 3

	h	F_o	F_c
l = 0	2	3.7	8.5
	4	3.2	3.0
	6	4.9	-7.8
	8	17.2	20.2
	10	< 2.0	1.5
	12	3.6	2.0
	14	5.3	4.3
l = 1	0	.9	.7
	1	14.5	-14.8
	2	1.6	-5.3
	3	22.5	-22.5
	4	4.2	5.7
	5	17.2	19.7
	6	16.8	-17.9
	7	14.3	12.4
	8	8.9	-7.4
	9	< 1.9	-.8
	10	< 2.0	1.4
	11	6.8	5.4
	12	8.4	-8.6
	13	5.7	6.6
	14	4.3	-5.3
	15	< 1.3	5
l = 2	1	27.4	26.6
	2	4.2	-2.3
	3	33.2	35.0
	4	9.1	7.2
	5	5.3	6.8
	6	2.9	1.9
	7	< 1.8	1.3
	8	9.0	-8.5
	9	1.4	-.6
	10	2.5	2.6
	11	14.8	14.9
	12	5.4	5.3
	13	6.9	5.8
	14	< 1.5	-1.7
	15	< 1.1	1.1

k = 3

	h	F_o	F_c
l = 3	0	13.5	13.3
	1	22.4	-25.6
	2	2.6	-2.2
	3	3.6	-4.1
	4	1.2	-2.0
	5	21.3	18.7
	6	7.8	7.4
	7	2.0	2.2
	8	< 2.0	.4
	9	21.4	-22.6
	10	7.7	-8.9
	11	12.1	-11.1
	12	2.1	-3.1
	13	7.8	8.6
	14	3.9	4.6
l = 4	1	2.7	-3.0
	2	5.8	6.4
	3	12.7	-11.8
	4	8.0	-8.1
	5	3.2	-3.3
	6	< 2.0	-2.4
	7	1.4	-.6
	8	2.0	-1.3
	9	3.1	1.4
	10	3.4	-1.1
	11	6.1	-5.4
	12	9.3	-10.5
	13	4.2	-3.7
	14	1.4	-2.5
l = 5	0	5.8	-3.6
	1	< 1.9	
	2	8.2	7.5
	3	3.1	1.1
	4	< 2.0	1.4
	5	< 2.0	1.5
	6	2.5	3.3
	7	6.8	-4.6
	8	5.9	5.0

k = 3

	h	F_o	F_c
	9	7.7	-8.0
	10	6.6	6.3
	11	1.8	-3.0
	12	4.6	5.3
l = 6	1	20.4	-20.9
	2	8.0	-6.8
	3	1.5	1.1
	4	2.0	1.9
	5	9.1	6.6
	6	< 1.9	-.3
	7	7.0	-8.4
	8	< 1.7	.9
	9	3.7	-3.1
	10	3.5	-3.5
	11	1.6	-1.3
l = 7	0	4.2	3.3
	1	11.0	-9.5
	2	5.3	-5.0
	3	15.9	-14.8
	4	8.7	-9.0
	5	8.9	9.5
	6	3.9	-3.6
	7	7.2	7.3
	8	2.0	2.2
	9	< 1.0	-1.3
l = 8	1	6.4	6.1
	2	.8	3.8
	3	2	3.8
	4	2.6	3.1
	5	2.0	-1.3
	6	2.0	-2.2

k = 4

	h	F_o	F_c
l = 0	2	14.6	16.6
	4	19.2	-18.2
	6	< 1.4	5.2
	8	15.9	19.5
	10	5.1	3.8
	12	1.1	-2.2
	14	7.7	9.3
l = 1	1	1.1	-3.9
	2	22.7	23.2
	3	3.1	3.6
	4	2.6	-.5
	5	< 1.3	.9
	6	9.7	-9.2
	7	1.1	-.3
	8	12.2	-10.2
	9	8.7	-9.5
	10	2.4	-1.5
	11	3.6	-2.8
	12	4.0	-4.7
	13	< 1.3	-.8
	14	< 1.1	1.4
l = 2	0	3.7	-2.6
	1	8.5	-7.2
	2	4.3	-4.1
	3	4.0	-3.1
	4	3.0	-4.3
	5	5.0	-6.4
	6	2.4	1.0
	7	3.9	3.2
	8	2.6	2.7
	9	< 1.7	.1

k = 4

	h	F_o	F_c
	10	4.7	-4.4
	11	10.1	-10.0
	12	4.3	-5.0
	13	4.6	-4.5
	14	< 1.0	.6
l = 3	1	7.2	5.6
	2	6.4	-7.5
	3	2.8	1.3
	4	4.5	3.1
	5	< 1.6	2.0
	6	5.8	5.7
	7	< 1.7	-1.2
	8	9.5	-10.3
	9	12.8	12.9
	10	7.8	-7.1
	11	3.7	5.0
	12	< 1.3	-.2
	13	< 1.1	.3
	14	< .5	.8
l = 4	0	7.6	-6.2
	1	3.6	3.2
	2	13.5	-12.9
	3	1.9	2.2
	4	16.8	-19.3
	5	< 1.7	.2
	6	9.8	6.9
	7	6.0	-6.0
	8	7.2	6.4
	9	1.6	-2.0
	10	10.8	-11.4
	11	5.5	5.6
	12	7.2	-8.0

k = 4

	h	F_o	F_c
l = 5	1	3.4	-3.4
	2	9.7	-8.0
	3	5.2	-4.8
	4	5.7	-3.2
	5	< 1.7	.2
	6	< 1.7	.9
	7	< 1.6	.6
	8	11.5	10.9
	9	3.3	-3.5
	10	2.3	1.8
	11	1.9	-1.5
l = 6	0	16.7	16.4
	1	4.8	5.6
	2	3.1	2.8
	3	< 1.6	.5
	4	5.3	-3.7
	5	< 1.6	-1.4
	6	2.6	-1.2
	7	1.9	1.9
	8	5.8	6.4
	9	3.6	5.2
	10	2.4	3.9
l = 7	1	< 1.4	-2.4
	2	< 1.4	-.9
	3	1.9	2.7
	4	2.3	2.0
	5	3.1	-3.4
	6	1.4	2.9
	7	1.8	-2.4
l = 8	0	7.9	9.4
	1	2.6	-3.1
	2	2.1	2.6
	3	1.4	2.0

k = 5

	h	F_o	F_c
l = 0	2	1.7	-3.2
	4	< 1.5	-.9
	6	< 1.8	3.0
	8	7.2	-9.6
	10	< 1.9	-.8
	12	3.2	-1.4
l = 1	0	2.2	.3
	1	6.5	5.9
	2	< 1.5	1.4
	3	9.3	9.0
	4	< 2.0	-1.7
	5	5.2	-7.9
	6	5.7	7.1
	7	5.5	-6.0
	8	3.1	3.6
	9	< 2.4	.3
	10	< 2.3	-1.1
	11	4.1	-3.3
	12	3.7	4.9
	13	2.3	-3.8
l = 2	1	12.4	-11.0
	2	2.2	.7
	3	13.4	-14.4
	4	3.6	-2.9
	5	1.3	-2.3
	6	1.9	-1.2
	7	2.2	-.4
	8	4.3	4.4
	9	1.4	.6
	10	< 1.8	-1.3
	11	6.4	-8.4
	12	2.4	-2.9

k = 5

	h	F_o	F_c
l = 3	0	5.8	-6.0
	1	9.1	10.6
	2	< 1.8	1.1
	3	1.6	1.7
	4	1.6	
	5	10.5	-9.1
	6	3.5	-3.3
	7	< 2.0	-.9
	8	< 2.0	-.2
	9	12.2	11.9
	10	3.2	4.9
	11	6.1	6.5
l = 4	1	< 1.7	1.3
	2	1.4	-2.5
	3	6.2	5.6
	4	4.0	4.2
	5	< 1.7	1.4
	6	2.2	.7
	7	1.9	.4
	8	1.6	1.1
	9	2.1	-.9
	10	2.5	.5
	11	2.8	3.2
l = 5	0	4.3	2.7
	1	< 1.7	.3
	2	2.7	-3.8
	3	2.4	-.9
	4	< 1.7	-.4
	5	< 1.6	-.6
	6	1.3	-2.1
	7	3.8	2.3
	8	2.3	-2.8
	9	4.2	4.8
l = 6	1	11.1	11.3
	2	5.4	3.8
	3	< 1.5	-.4
	4	< 1.4	-.9
	5	5.6	-3.9
	6	< 1.3	.2
	7	2.7	4.7

k = 5

	h	F_o	F_c
l = 7	0	1.9	-2.3
	1	5.2	5.2
	2	2.2	2.7
	3	7.2	8.7
	4	4.1	5.3

k = 6

	h	F_o	F_c
l = 0	4	6.7	6.5
	8	4.7	-8.5
	14	3.0	-4.8
l = 1	4	1.8	0
	6	3.3	3.6
	8	6.0	4.9
	9	3.6	4.3
	7	1.9	-1.6
	11	5.2	5.1
l = 2	1	2.2	-2.3
	2	1.5	2.8
	3	2.8	.2
	4	1.8	-1.2
	5	1.0	-.9
	6	2.2	-2.5
	8	4.0	4.8
	9	6.1	-6.4
	10	3.1	3.4
l = 3	0	4.6	3.2
	2	5.5	5.5
	4	5.3	8.6
	6	5.4	-3.3
	7	2.9	3.0
	8	3.7	-3.3
	10	4.4	5.8
	11	2.2	-2.9
	12	3.4	4.1
l = 4	2	5.6	4.0
	3	2.4	2.3
	4	3.1	1.4
	8	5.5	-5.7
l = 5	0	7.3	-8.2
	4	3.1	1.8
l = 6	0	3.6	-5.0

density maxima for hydrogen atoms observed previously (Cochran, 1953).

The value of the discrepancy factor R for the $(h0l)$ and $(h1l)$ reflections was now 0·117, and it was decided to use all the 639 observed reflections for the refinement of the x and z parameters by the method of least squares. In a first step, an average temperature-factor coefficient normal to the layers was determined by least-squares treatment of the $(hk0)$ and $(hk1)$ reflections obtained from a crystal rotated around c. The value $\beta = 4{\cdot}7 \times 10^{-16}$ cm.^{2} was found, the temperature factor being defined by $\exp(-\beta k^2/4b^2)$. In the calculation of structure factors, the temperature factors were included, and also the hydrogen-atom contributions to all reflections with $\sin\theta_{\mathrm{Cu}} < 0{\cdot}6$; a scale factor for each k level was determined by comparing observed and calculated structure factors. The data were then submitted to two consecutive least-squares treatments. In the second of the least-squares refinements an average parameter shift of 0·004 Å and a maximum shift of 0·008 Å were obtained, and

Table 3. *Discrepancy factor R as a function of k*

k	No. of observed reflections	R
0	137	0·094
1	150	0·098
2	97	0·101
3	92	0·137
4	77	0·158
5	58	0·240
6	28	0·257
hk	639	0·119

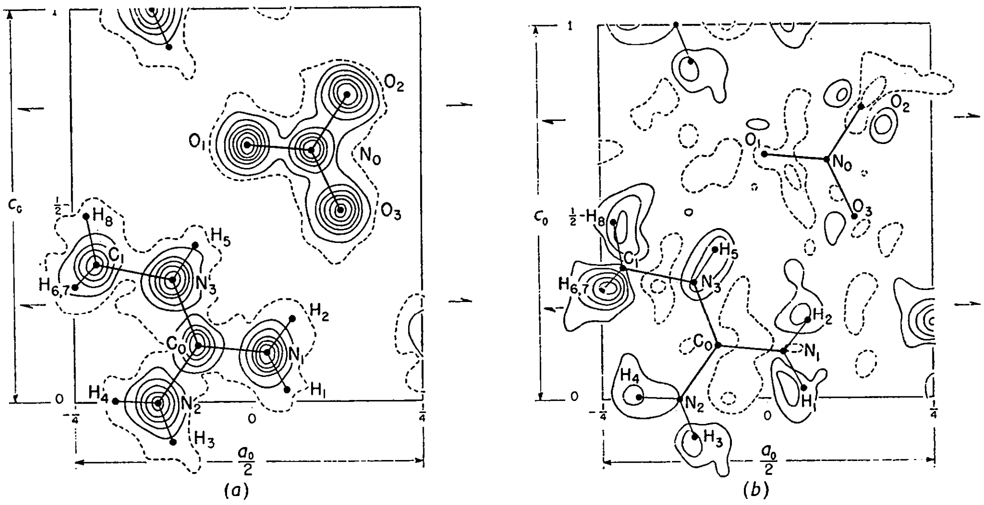


Fig. 2. (a) Electron-density function weighted by $(1+\sin 2\pi y)$ and projected along y. Contours at 2, 4, 8... e.Å^{-2}. Numerically the electron density is doubled compared with an ordinary projection. (b) Difference Fourier projection equivalent to Fourier projection, Fig. 2(a). Contours at 0·5, 1·0... e.Å^{-2}. Negative contours are broken.

since the average standard deviation was found to be 0·005 Å, the parameters had undoubtedly converged. Table 1 contains the final atomic parameters, and Table 2 the observed and calculated structure factors. In Table 3 the discrepancy factors are listed as a function of the level k. The increase of R with k stays within reasonable limits if one takes into account the fact that the experimental data for the weak fifth and sixth levels were relatively poor.

Based on the final structure factors, a weighted Fourier and a weighted difference Fourier projection were calculated. The former, shown in Fig. 2(a), demonstrates the perfect resolution obtained by using zero- and first-level data only. The difference Fourier (Fig. 2(b)) contains very little random background, and, like the final least-squares calculation, does not suggest further shifts in parameters. A strong anisotropic temperature vibration is exhibited by oxygen atom O_2 perpendicular to its bond direction; anisotropic temperature vibrations of the other atoms are either small or obscured by hydrogen peaks. Each of the large peaks near the heavy atoms of the methylguanidinium group can be identified with hydrogen atoms. The peak marked $H_{6,7}$ is undoubtedly caused by the superposition of the two out-of-plane methyl hydrogen atoms; in this type of projection the two atoms combine to an effective weight of about one and one-half times that of a single in-plane hydrogen atom.

In this structure determination the centrosymmetric space group *Pnma* has been assumed; this assumption imposes planar symmetry on the structure. One could have assumed the non-centrosymmetric space group *Pn*2$_1$*a*, in which case the y coordinates of the atoms do not need to correspond to a strictly planar structure. However, if the structure is close to planar the structure factors are insensitive to departures from planarity and effects on the structure factors produced by departures from planarity can be simulated by anisotropic temperature factors. Because of these considerations and the limitations inherent in the data, no attempt was made to detect or evaluate possible deviations from complete planarity of the structure. Even if deviations of 0·2 Å occurred, the bond lengths as calculated for the planar structure are increased by about 1% only. Assuming a planar structure, the average standard deviation is 0·007 Å in a bond length and about 0·5° in a bond angle of 120°.

Discussion of the structure

Configuration and dimensions of the structure

The bond lengths and bond angles in the nitrate and methylguanidinium ions and the lengths of the hydrogen bonds joining them are recorded in Table 4.

Table 4. *Bond lengths and bond angles*

N_0–O_1	1·243 Å	O_1–N_0–O_2	120° 33′
N_0–O_2	1·235	O_2–N_0–O_3	119° 33′
N_0–O_3	1·254	O_3–N_0–O_1	119° 54′
C_0–N_1	1·323	N_1–C_0–N_2	120° 28′
C_0–N_2	1·326	N_2–C_0–N_3	122° 03′
C_0–N_3	1·329	N_3–C_0–N_1	117° 29′
C_1–N_3	1·454	C_1–N_3–C_0	123° 15′

Hydrogen bonds

N_1–O_3	2·995 Å
N_3–O_1	2·875
N_1–O_2'	2·976
N_2–O_1'	3·057
N_2–O_3''	3·091

They are also given in Fig. 3, which shows the orientation of the two ions in the xz plane.

The nitrate ion has planar trigonal symmetry within the accuracy of this investigation. The bond angles deviate by about ½° from 120° and the bond lengths by less than 0·01 Å from the average of 1·244 Å. The dimensions of the nitrate ion have been determined previously. Elliott (1937) and Tahvonen (1948) report N–O bond lengths of 1·21 and 1·22 Å, respectively, for the nitrate ion in $NaNO_3$; Grison *et al.* (1950), in a three-dimensional analysis, finds that the structure of N_2O_5 contains trigonal nitrate ions with a bond length of 1·243 Å.*

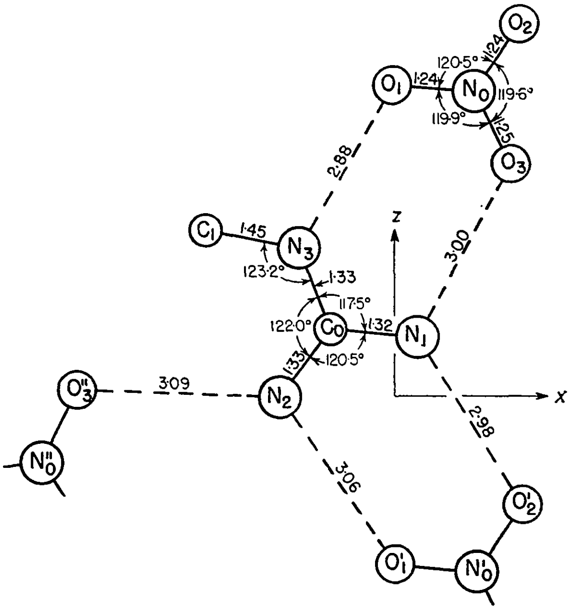
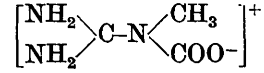


Fig. 3. Schematic drawing of the molecule. Bond lengths are given in Ångström units.

The average N–O bond length found in the present investigation may be significantly greater than the value reported for $NaNO_3$. One might expect that the presence of the hydrogen bonds in methylguanidinium nitrate would tend to lengthen the N–O bond, in analogy to the effects observed for the C–O bonds in the carboxyl group, but in view of the agreement between our result and that of Grison *et al.* this interpretation of the discrepancy is questionable.

In the methyl guanidinium ion the CN_3 group is also nearly trigonal. The C–N bond lengths are identical within 0·006 Å; the bond angles deviate, however, by a significant amount from 120°. The angle N_2–C_0–N_3 is increased and the angle N_1–C_0–N_3 is decreased by 2°, presumably because of repulsion between the methyl group and the amide group N_2.

The methyl guanidinium configuration occurs also in creatine



$$\left[\begin{matrix}NH_2\\NH_2\end{matrix}\!\!>\!C\!-\!N\!<\!\!\begin{matrix}CH_3\\COO^-\end{matrix}\right]^+,$$

the structure of which has been determined by Mendel & Hodgkin (1954) from three-dimensional data, and independently by Jensen (1954) from two-dimensional data. The three central C–N bonds in creatine are also approximately trigonally arranged and have an average length of 1·33 Å compared with 1·326 Å in the methylguanidinium ion.

The length of the N–CH_3 bond and the angle C–N–CH_3 in creatine are reported as 1·49 Å and 121° by Mendel & Hodgkin; the values of 1·454 Å and 123° were found in this structure. The bond length falls within the range of values reported for the C–N single bond in amino acids and peptides (1·45–1·49 Å), and the angle agrees with the nearly equivalent angle C–N–C′ in the peptide link (122–123°). A small but significant displacement of the methyl group by 0·06 Å from the plane of the guanidinium group is reported for creatine. In the methylguanidinium ion,

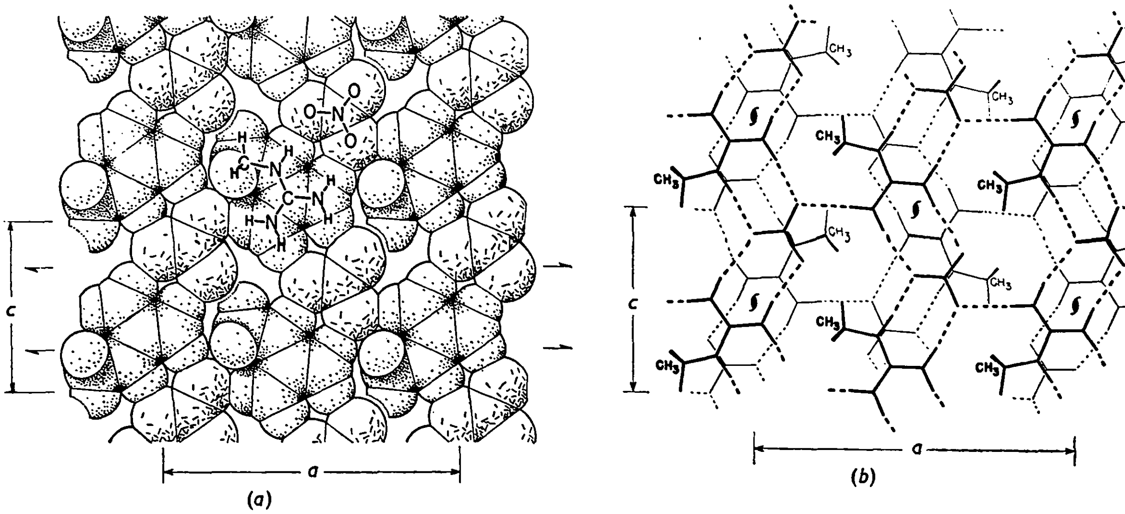


Fig. 4. (*a*) Packing drawing of one layer of molecules. (*b*) Schematic drawing of the structure seen along *b*.

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* *Note added in proof*, 26 *September* 1955.—In the discussion of the nitrate ion the accurate determination of the (ionic) nitric acid trihydrate structure (Luzzati, 1953) was overlooked. The dimensions of the nitrate ion in that structure do not differ significantly from the dimensions found in methylguanidinium nitrate.

it does not seem very likely that the methyl group is displaced from the plane $y = \frac{1}{4}$. However, a moderate displacement would escape detection, as indicated in a previous section.

Packing of the ions

The arrangement of the groups of atoms in this crystal structure is best discussed in reference to Fig. 4. Fig. 4(*a*) is a packing drawing of one layer of the structure seen along the *b* axis. The arrangement is, as expected, ionic; each cation has two equidistant anions as nearest neighbors, and vice versa. The ions are tied into chains along *c* by four of the five available hydrogen bonds. The chains in turn are held together by the fifth hydrogen bond parallel to *a*.

Although the direction of the N · · · O and the N–H vectors almost coincide, and therefore conditions seem favorable for good hydrogen bonding, the observed N–H · · · O distances are, with one exception, rather long (Table 4). This may be understood from packing considerations. The bulky methyl group of one chain is centered between two nitrate groups of a neighboring chain, forcing both the nitrate groups and adjacent chains apart. Despite the separation, the one methyl hydrogen atom which lies in the mirror plane interferes somewhat with an oxygen atom; the distance between the centers of the oxygen and hydrogen atoms is only 2·25 Å, if one assumes a length of 1·1 Å for the C–H bond and tetrahedral angles around the carbon atom. Although this close contact could be real (Morrison & Robertson, 1949), it may be that the methyl group is displaced by a small amount out of the plane and simultaneously rotated around the C–N bond so as to increase the separation of the atomic centers; ample space would be available between layers for such a displacement.

The separation of 3·21 Å found between the layers of atoms might seem to be surprisingly large. It is, however, consistent with separations found in other layer structures; for example, 3·24 Å in *N*-acetylglycine (Carpenter & Donohue, 1950) and 3·38 Å in succinamide (Pasternak, 1953). The two out-of-plane methyl hydrogen atoms, although displaced by about 0·9 Å from the plane, are not responsible for this separation. As Fig. 4(*a*) illustrates, the layers show holes in unique positions in the otherwise dense packing, and it is opposite these holes that the out-of-plane hydrogen atoms of adjacent layers are located.

The superposition of the two layers of atoms in the unit cell is shown in Fig. 4(*b*). The chains consisting of nitrate and guanidinium ions alternating along *c* are stacked neatly on top of each other in the *b* direction and form a layer of relatively high density parallel to the *bc* plane. The methyl groups protrude on both sides of these layers and pack loosely with the methyl groups from adjacent layers. Thus a separation into alternating layers of polar and non-polar groups is effected. A similar separation of polar and non-polar groups seems to occur quite generally in other structures. It occurs, for example, in the structures of glycyltyrosine hydrochloride (Smits & Wiebenga, 1953) and of glycyltryptophan dihydrate (Pasternak, 1954).

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