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The Crystal Structure of Nitroguanidine

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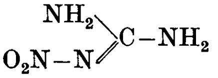
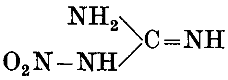
The structure of nitroguanidine has been determined and refined by least-squares and Fourier methods. The molecule has the formula $C(NH_2)_2NNO_2$(I); the structure of the molecule is a resonance hybrid. The bond distances are discussed in terms of the various resonance forms for the molecule. The crystals are held together by a satisfactory system of hydrogen bonds.

Introduction

Two possible structures have been ascribed to nitroguanidine, a symmetric one (I) and an unsymmetric one (II):


(I)


(II)

Each of these structures has a number of resonance forms, and there has been considerable discussion concerning not only which structure is correct, but also which resonance forms predominate. On the basis of certain chemical evidence Thiele (1892) decided in favor of the unsymmetric structure, and since then this structure has been used almost exclusively. Recent chemical and spectroscopic evidence, however, indicates that the symmetric structure may be correct (McKay, Picard & Brunet, 1951). Potentiometric titrations and methylation studies on certain nitroguanidine derivatives led Barton, Hall & Wright (1951) and Kirkwood & Wright (1953) to prefer the symmetric structure for nitroguanidine itself. Dipole moment, ultra-violet absorption spectra, and acid strength determinations (Kumler, 1953; Kumler & Sah, 1953) indicated that the molecule was best represented by (I). The above workers do not agree on the relative importance of the resonance forms of (I), and, moreover, McKay *et al.* (1954) recently showed that potentiometric titration and methylation studies were unreliable as a guide to the structures of these compounds.

Few nitramines have been subjected to X-ray structure analysis. Llewellyn & Whitmore (1948) made a complete analysis of the structure of ethylenedinitramine, and the structure of the disodium salt of this compound was reported by Allentorf & Wright (1953). Costain & Cox (1947) have briefly described the partial analysis of dimethylnitramine. Nitroguanidine has no obvious properties in common with these substances since it is weakly basic to about the same extent as urea, while ethylenedinitramine is acidic. Dimethylnitramine is a volatile, low melting, secondary nitramine, while nitroguanidine melts with decomposition at 246–247° C. (McCrone, 1951). The work described below was undertaken to determine the structure of the nitroguanidine molecule in the solid state.

Experimental

Satisfactory crystals were grown by slow evaporation of an aqueous solution. Examination with an optical goniometer showed the crystals were orthorhombic, and that the forms {110}, {010}, and {301} were present. The unit-cell dimensions, as determined from Weissenberg and rotation photographs, are (λ of Cu $K\alpha$ = 1·542 Å):

$$a_0 = 17{\cdot}58\pm0{\cdot}09,\ b_0 = 24{\cdot}82\pm0{\cdot}12,\ c_0 = 3{\cdot}58\pm0{\cdot}02\ \text{Å}.$$

These data, combined with the observed density of 1·76 g.cm.$^{-3}$ (McCrone, 1951), give 16 molecules per unit cell (the calculated density is 1·771 g.cm.$^{-3}$). The lattice constants agree fairly well with those given by Doll & Grison (1948) and by McCrone (1951).

The following absences were observed on zero-, first-, and second-layer Weissenberg photographs taken about the c axis: (hkl) present only for $h+k = 2n$, $k+l = 2n$; $(h0l)$ present only for $h = 2n$, $l = 2n$, and $h+l = 4n$; $(0kl)$ present only for $k = 2n$, $l = 2n$, and $k+l = 4n$; $(hk0)$ present only for $h = 2n$ and $k = 2n$. The space group is thus uniquely determined as C_{2v}^{19}–$Fdd2$. Since the general position of this space group is sixteenfold, no molecular symmetry is required.

Intensities of the $(hk0)$, $(hk2)$, and some of the $(hk1)$ reflections were estimated visually by means of the multiple-film technique and intensity strips. Of the 144 possible $(hk0)$ reflections, 113 were observed, and of the 118 possible $(hk2)$ reflections, 93 were observed.

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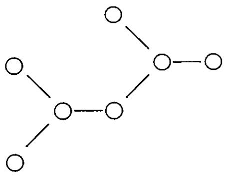
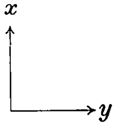
Determination of the atomic positions

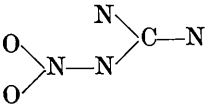
The projection on (001)

The (*hk*0) reflections were used to prepare a Patterson projection down the *c* axis. The details of the solution of this projection are described in full elsewhere* (Donohue & Bryden, 1955). The approximate structure so obtained indicated that the molecule in the asymmetric unit was oriented as follows:

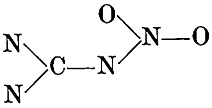




Since the scattering powers of carbon, nitrogen, and oxygen are nearly the same, there are then two possible arrangements (neglecting the hydrogen atoms):



(III)



(IV)

The trial parameters were then used to calculate the structure factors for the 15 (*hk*0) reflections with $\sin\theta < 0{\cdot}325$, in arrangements both (III) and (IV). Bragg–Lipson charts were then used to improve the agreement between observed and calculated structure factors. After three such calculations, the reliability factor R dropped from 0·46 to 0·36 for arrangement (III), and from 0·51 to 0·43 for arrangement (IV). At this point arrangement (IV) was dropped, and the refinement of arrangement (III) was continued by increasing the number of structure factors calculated, and using Fourier projections. The structure refined rapidly, and in preparing the final Fourier projection (Fig. 1) only the term (10,4,0) had to be omitted because its sign was in doubt. Fourier projections were also made with the calculated values of the structure amplitudes in order to determine the back-shift corrections to the parameters.

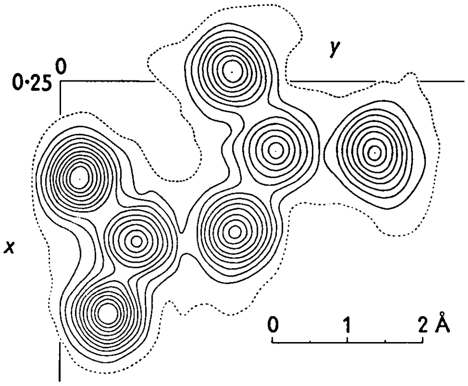


Fig. 1. Fourier projection on (001) of the nitroguanidine molecule.

Determination of the z parameters

Since the (001) projection is completely resolved, approximate z parameters were estimated by assuming that: (1) all C–N bonds were equal; (2) the C–N_2 and N_3–N_4 distances were parallel to the plane of projection (the projected values of these distances are 1·36 Å and 1·35 Å respectively—see Fig. 2 for the numbering of the atoms); and (3) the N–O distances were 1·23 Å, a value close to that reported for various other nitro compounds. These assumptions lead to a nearly planar molecule, the plane of which is tilted about 30° from (001). A comparison of the observed and calculated values of the structure factors for the

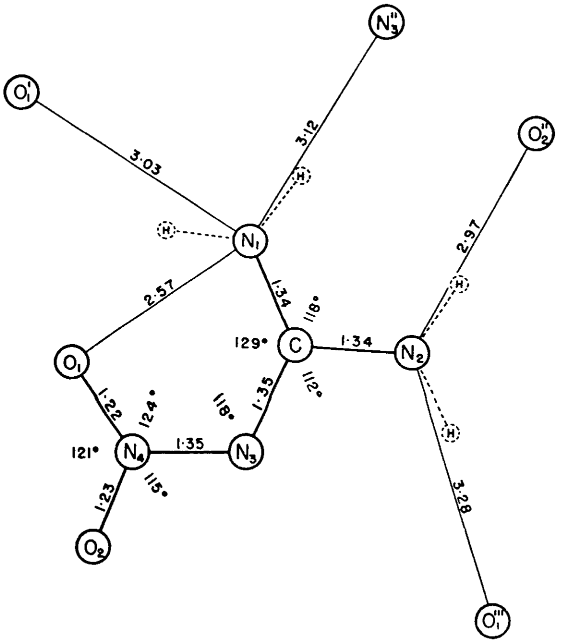


Fig. 2. The nitroguanidine molecule, showing interatomic distances and bond angles.

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* It seems appropriate to restate here that our failure to solve this projection by use of inequalities was probably due to an error of 30% in the estimation of the scale factor. We did not wish to imply in the previous paper anything concerning the relative merit of the superposition method as opposed to inequalities. Our work with the inequalities was carried on during the summer of 1951, and since that time the scale-factor determination has been mislaid, so we are unable to track down the error. We were of course aware that Grison (1951*a* and private communication) had successfully applied the Harker–Kasper method to this zone, but the detailed results of this work (Grison, 1951*b*) did not become available to us until after the publication of our work on the interpretation of the Patterson projection. Grison's x and y parameters, after dividing them by 2 and shifting the origin, differ from ours by an average of 0·011 Å, the maximum difference being 0·033 Å.

54 (*hk*2) reflections with $\sin\theta < 0{\cdot}75$ gave an *R* value of 0·163. Since this agreement is quite satisfactory, the *z* parameters were then improved by a least-squares refinement of these 54 reflections. All shifts were small, the largest being 0·02 Å. The *R* value dropped to 0·111 during this refinement.

The use of (*hkl*) reflections with $l = 2n$ does not, however, distinguish between four possible orientations of the molecule, all of which give identical calculated values of $|F(h,k,2n)|$. These orientations may be expressed as whether the origin as chosen above lies on a twofold axis or a twofold screw axis and whether the plane of the molecule has a positive or negative intercept on the *c* axis.

Although it is possible that some of the above lead to improbable intermolecular interatomic distances, the choice of which of the four resulting arrangements was the correct one was made in a straightforward way by calculating values of $|F(hk1)|$ for 12 of the (*hk*1) reflections for each of them. The resulting *R* values were 0·712, 0·141, 0·435, and 0·690. The second of these was obviously obtained from the correct orientation.

Table 1. *Atomic parameters*

	x	σ	*y*	σ	*z*
O_1	0·1770	0·0002	0·0114	0·0002	0·208
O_2	0·0743	0·0012	0·0256	0·0001	0·509
N_1	0·2568	0·0008	0·0929	0·0002	0·000
N_2	0·1953	0·0008	0·1719	0·0001	0·151
N_3	0·1359	0·0004	0·0967	0·0005	0·325
N_4	0·1306	0·0006	0·0425	0·0003	0·343
C	0·1980	0·0001	0·1180	0·0003	0·160

Table 2. *Observed and calculated structure amplitudes*

The left hand column is the value of *h*, the middle column the observed structure amplitude, and the right column the calculated structure amplitude*

	*h*00	
0	—	800
4	91	107
8	44	49
12	< 6	3
16	63	75
20	7	7
	*h*20	
2	15	17
4	143	127
6	24	18
8	11	6
10	42	48
12	13	19
14	7	8
16	49	56
18	12	10
20	8	13
22	6	8
	*h*40	
0	22	6
2	168	166
4	113	100
6	135	121
8	79	87
10	5	5
12	48	54
14	17	12
16	< 7	4
18	14	17
20	27	38
22	15	20
	*h*60	
2	13	14
4	60	63
6	83	75
8	5	6
10	70	79
12	23	24
14	9	11
16	< 7	4
18	13	10
20	< 5	3
22	< 3	1
	*h*80	
0	64	68
2	132	118
4	< 4	1
6	87	70
8	74	65
10	43	53
12	23	31
14	7	7
16	7	1
18	24	31
20	< 5	5
22	< 2	3
	h,10,0	
2	118	95
4	41	34
6	18	14
8	16	14
10	22	25
12	10	17
14	18	23
16	< 7	3
18	9	10
20	5	2
	h,12,0	
0	50	47
2	168	137
4	44	49
6	21	21
8	10	13
10	44	51
12	30	30
14	14	20
16	< 7	6
18	9	12
20	5	6
	h,14,0	
2	29	20
4	< 6	1
6	24	23
8	13	18
10	< 7	4
12	7	4
14	26	29
16	9	9
18	26	30
20	< 3	0·3
	h,16,0	
0	69	76
2	23	21
4	22	21
6	13	12
8	50	53
10	48	50
12	8	12
14	30	37
16	14	14
18	6	7
	h,18,0	
2	45	42
4	43	42
6	54	57
8	23	23
10	26	33
12	31	32
14	11	11
16	18	16
18	< 4	4
	h,20,0	
0	< 7	9
2	< 7	9
4	18	18
6	55	52
8	65	70
10	28	29
12	< 7	6
14	6	4
16	< 5	1
	h,22,0	
2	22	25
4	7	5
6	9	6
8	25	26
10	26	27
12	< 6	4
14	6	8
16	11	14
	h,24,0	
0	10	12
2	22	18
4	< 7	1
6	14	15
8	< 7	6
10	< 6	0·4
12	20	18
14	8	8
	h,26,0	
2	10	11
4	31	30
6	7	8
8	10	11
10	9	10
12	14	14
	h,28,0	
0	14	14
2	< 6	1
4	6	7
6	< 5	1
8	< 5	1
10	4	4
	h,30,0	
2	< 5	4
4	25	22
6	4	5
8	< 2	3
	h,32,0	
0	< 3	1
2	< 2	4
	*h*02	
2	62	68
6	113	122
10	65	65
14	24	25
18	< 9	3
	*h*22	
0	28	31
2	42	39

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Table 2 (*cont.*)

4	48	41
6	87	79
8	32	34
10	44	42
12	38	35
14	11	15
16	14	10
18	11	11
20	< 6	5
	*h*42	
2	62	60
4	54	48
6	24	29
8	17	19
10	31	31
12	12	6
14	35	40
16	16	20
18	9	14
20	16	13
	*h*62	
0	92	83
2	30	26
4	66	51
6	20	19
8	10	15
10	24	22
12	18	22
14	24	18
16	11	16
18	< 9	2
20	< 4	5
	*h*82	
2	36	30
4	45	52
6	32	33
8	18	25
10	<11	4
12	25	33
14	14	15
16	<10	12
18	< 8	3
	h,10,2	
0	20	20
2	11	13
4	38	35
6	10	10
8	32	33
10	11	14
12	<11	5
14	11	10
16	< 9	7
18	< 7	5
	h,12,2	
2	18	19
4	57	63
6	24	26
8	19	20
10	<11	11
12	21	21
14	<11	7
16	9	12
18	6	4
	h,14,2	
0	14	14
2	<10	9
4	35	35
6	<11	4
8	40	39
10	15	13
12	24	26
14	<10	5
16	< 8	2
18	< 3	8
	h,16,2	
2	22	22
4	21	22
6	29	33
8	24	22
10	<11	2
12	16	18
14	11	10
16	17	18
	h,18,2	
0	38	48
2	52	49
4	<11	6
6	25	21
8	24	24
10	26	24
12	12	13
14	21	20
16	< 4	10
	h,20,2	
2	26	28
4	29	28
6	12	11
8	<11	4
10	11	8
12	13	15
14	16	17
	h,22,2	
0	28	27
2	16	16
4	32	29
6	11	10
8	14	11
10	9	9
12	14	12
	h,24,2	
2	10	10
4	< 9	5
6	9	7
8	< 8	1
10	9	10
	h,26,2	
0	9	9
2	16	16
4	9	9
6	12	11
8	< 6	3
	h,28,2	
2	< 6	3
4	6	5

* In these calculations scattering factors from the *Internationale Tabellen* (1935, vol. 2, p. 571) were used, modified by an isotropic temperature factor $\exp[-B(\sin\theta/\lambda)^2]$, with $B = 3{\cdot}035$ Å^2.

All 93 of the observed ($hk2$) reflections were then subjected to least-squares refinement. These calculations were made on an IBM-701 computer (Bryden, 1955). Seven least-squares cycles were performed, and the maximum shift in a parameter in the last cycle was 0·002 Å. In order to obtain still more information concerning the x and y parameters, the ($hk0$) reflections were also subjected to least-squares treatment, seven cycles again being made. The maximum shift at the last cycle was in this case 0·001 Å.

We thus have three independent determinations of the x and y parameters: Fourier analysis of the ($hk0$) reflections, least-squares treatment of the ($hk0$) reflections, and least-squares treatment of the ($hk2$) reflections. The unweighted averages of these three values were chosen as the final parameters, which, together with the z parameters, are presented in Table 1. The individual values for the x and y coordinates allow estimation of their standard deviations; these values are also presented in Table 1.

The observed and calculated structure factors of the ($hk0$) and ($hk2$) reflections are presented in Table 2. The values of R are 0·135 and 0·106, respectively, for these two groups. There are a few reflections for which the agreement is not very good, e.g., (040) and (12,4,2). Better over-all agreement and elimination of such discrepancies could undoubtedly have been achieved by taking account of the scattering of the hydrogen atoms and allowing for anisotropic thermal vibration, both of which effects are definitely suggested by the Fourier projection (Fig. 1).

Table 3. *Intramolecular distances and bond angles*

		σ		
$C–N_1$	1·34 Å	0·018 Å	$N_1–C–N_2$	118°
$C–N_2$	1·34	0·010	$N_2–C–N_3$	112
$C–N_3$	1·35	0·016	$N_1–C–N_3$	129
$N_3–N_4$	1·35	0·015	$C–N_3–N_4$	118
$N_4–O_1$	1·22	0·016	$N_3–N_4–O_1$	124
$N_4–O_2$	1·23	0·020	$N_3–N_4–O_2$	115
			$O_1–N_4–O_2$	121

Hydrogen bonds

$N_1 \cdots O_1$	2·57 Å
$N_1 \cdots O_1'$	3·03
$N_1 \cdots N_3''$	3·12
$N_2 \cdots O_2''$	2·97
$N_2 \cdots O_3'''$	3·28

Non-bonded contacts less than 3·3 Å

$O_1 \cdots O_1'$	3·18 Å	(across twofold screw axis)
$O_2'' \cdots O_2'''$	2·90	(across twofold axis)
$N_2 \cdots O_2'''$	2·95	

Discussion

Bond distances and bond angles in the nitroguanidine molecule are given in Table 3 and shown in Fig. 2, together with the shortest intermolecular contacts. The standard errors in the bond distances were calculated by use of the individual standard deviations in the x and y parameters, and on the assumption that the standard deviations in the z parameters are 0·020 Å, or $\sqrt{3}$ times the average standard deviation in an x or y. This procedure gives conservative limits of error of between 0·02 and 0·04 Å for the interatomic distances.

Planarity of the molecule

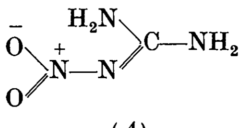
The molecule is planar within the limits of error of the determination. The two largest deviations from a least-squares plane through the seven atoms in the molecule are 0·03 Å for the atoms N_1 and O_1. The close approach of N_1 and O_1 is apparently responsible for the unusually large values of two of the bond angles, 124° for N_3–N_4–O_1 and 129° for N_3–C–N_1. The $N_1 \cdots O_1$ distance in a hypothetical coplanar molecule in which these angles assumed their normal values of 120° would have the impossibly short value of less than 2·2 Å. It is interesting that the strain is relieved largely by an enlargement of these two bond angles, rather than by a great deformation from coplanarity, or of enlargement of the angle C–N_3–N_4, which is about normal. In the isoelectronic nitroacetate ion (Sutor, Llewellyn & Maslen, 1954) the corresponding central bond angle, C_1–C_2–N, is 128°. In this ion, on the other hand, there is no possibility for the formation of an intramolecular hydrogen bond such as exists in nitroguanidine.

Location of the hydrogen atoms

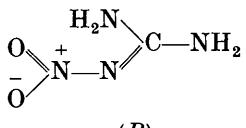
The Fourier projection on (001), Fig. 1, shows faint bulges near atoms N_1 and N_2 in positions expected for the hydrogen atoms. Cochran (1951) has shown that hydrogen atoms can be successfully located by means of (F_o-F_c) synthesis, provided sufficient care is taken in correcting the atomic form factors individually for anisotropic thermal motion. An (F_o-F_c) synthesis for nitroguanidine, prepared from the final F_o and F_c projections, showed, as expected from the asymmetry of the peaks in Fig. 1, small peaks of heights between 0·5 and 1 e.Å^{-2} characteristic of maximum thermal motion approximately in the direction of a. In addition, four peaks, some of which were not resolved from the above, appeared in the positions expected for a molecule with the symmetric structure (I). There was no peak in the position expected for a hydrogen atom covalently bonded to N_3, i.e., the unsymmetric structure (II). Since this evidence was considered as sufficient to establish the existence of the symmetric structure for the nitroguanidine molecule, no additional work was done in refining the (F_o-F_c) synthesis with anisotropic temperature corrections, especially because the intensity data were based upon visual estimates only, and because Dr Cochran has informed us in a private communication that he has commenced the collection of intensity data with a Geiger-counter spectrometer, and will presently refine the (F_o-F_c) synthesis in the usual way with these improved data.

Structure of the molecule

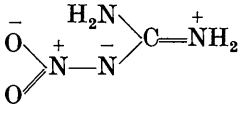
The molecule may be considered as resonating among the following valence bond structures:



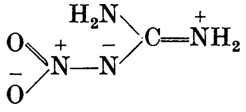
(*A*)



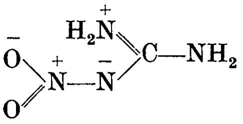
(*B*)



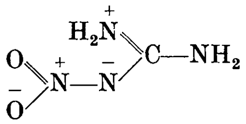
(*C*)



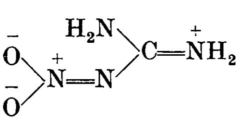
(*D*)



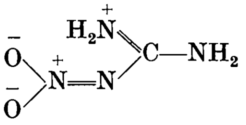
(*E*)



(*F*)



(*G*)



(*H*)

If we set the weights of the above structures at 15% each for (*A*) and (*B*), 10% each for (*G*) and (*H*), and distribute the remaining 50% equally among the other four, application of Pauling's (1940) valence-bond method yields the following results:*

Bond	Double-bond character	Calculated length	Observed length
C–N_1	0·35	1·344 Å	1·34 Å
C–N_2	0·35	1·344	1·34
C–N_3	0·30	1·357	1·35
N_3–N_4	0·20	1·371	1·35
N_4–O_1	0·40	1·243	1·22
N_4–O_2	0·40	1·243	1·23

The total contribution of only 30% of structures (*A*) and (*B*), which do not involve charge separation (other than the resonance in the nitro group) is not

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* Single-bond distances of 1·47 Å for N–N, 1·43 Å for N–O, and double-bond distances of 1·24 Å for N=N, 1·15 Å for N=O, together with bond character–length curve for C–N bonds suggested by Donohue, Lavine & Rollett (1956), were used in these calculations.

in agreement with those previous results (Kirkwood & Wright, 1953; Kumler & Sah, 1953) which were interpreted to indicate that the structure did not consist mainly of what was termed 'zwitterions' or resonance hybrids of 'zwitterions'. Conversely, the total contribution of only 20% of structures (*G*) and (*H*) is at variance with the conclusions of McKay *et al.* (1951, 1954) that the molecule is predominantly in those forms.

Although too much significance cannot be attached to the correlation of bond length with bond character because the distances expected for N=N and N=O double bonds are not accurately known, the virtual equality of the three carbon–nitrogen distances indicates that the structure of the molecule is neither predominantly (*A*) and (*B*) nor (*G*) and (*H*), and, moreover, that structures (*C*), (*D*), (*E*), and (*F*) do contribute significantly.

Hydrogen bonding

A strong intramolecular hydrogen bond is formed between atoms N_1 and O_1. The geometry of this bond is very similar to the intramolecular O–H · · · O bonds in salicylic acid (Cochran, 1953) and maleic acid (Shahat, 1952), and is considerably shorter than the usual N–H · · · O bond, because of the molecular configuration. Two strong intermolecular hydrogen bonds are formed, one by atom N_1 to N_3'', and one by atom N_2 to O_2''. In addition, there are two weaker bonds, N_1 to O_1' and N_2 to O_1'''. The hydrogen bonding scheme is shown in Fig. 3. The strongest hydrogen bonds are in the plane of the molecules, in alternative ribbons along [103] and [$\bar{1}$03] (see Fig. 3). The cleavage is thus not very well defined, and it has been observed that crushing crystals of nitroguanidine produces bundles of fibers elongated along *c* which will give a felt of very low density upon being mixed.

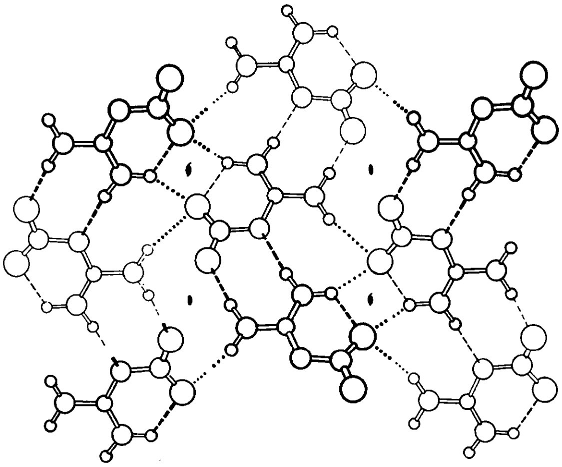

Fig. 3. Arrangement of the nitroguanidine molecules in the crystal, showing the hydrogen bonding scheme. The stronger hydrogen bonds are represented by the broken lines and the weaker ones by the dotted lines.

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