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On Nitroguanidines. I. Two Crystalline Modifications of *N*-Methyl-*N*-nitroso-*N'*-nitroguanidine,* a Potent Carcinogen in the Nitrimino–Amino Form

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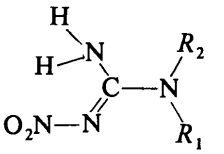
Abstract

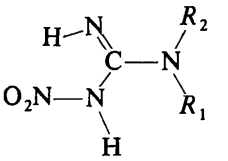
The structures of two crystal modifications of $C_2H_5N_5O_3$ ($M_r = 147{\cdot}094$) have been determined by X-ray diffraction at 115 K. The space groups of the two forms were $P2_1/a$, with $a = 9{\cdot}757$ (1), $b = 11{\cdot}092$ (1), $c = 11{\cdot}589$ (2) Å and $\beta = 114{\cdot}62°$ ($V = 1140{\cdot}2$ Å^3), and $Pbca$, with $a = 6{\cdot}6305$ (10), $b = 10{\cdot}6992$ (6) and $c = 16{\cdot}8385$ (7) Å ($V = 1194{\cdot}5$ Å^3). The former has two molecules in the asymmetric unit. Full-matrix least-squares refinements terminated at $R = 0{\cdot}040$ and $R_w = 0{\cdot}040$ for the monoclinic form and at $R = 0{\cdot}039$ and $R_w = 0{\cdot}036$ for the orthorhombic form. The estimated standard deviations in bond lengths and angles are 0·001 Å and 0·1° for the non-hydrogen atoms. The molecules comprise unsymmetrically conjugated guanidine moieties in the nitrimino–amino form, with the conjugation restricted to these groups. Significant differences in the N—N bond lengths may, in part, be a consequence of rather strong interactions between the nitro and nitroso groups in the monoclinic crystals. These interactions are not observed in the orthorhombic crystals. Variations in the N—O distances are interpreted as resulting from differences in hydrogen bonding. All hydrogen bonds may be interpreted as bifurcated interactions. Two of these are intramolecular, caused by the planar geometry of the molecules.

Introduction

Nitroguanidines are commonly described by the structures (I) or (II) and, although Bryden, Burkardt, Hughes & Donohue (1956) showed nitroguanidine to be in the nitrimino–amino form (I), the nitramino–imino form (II) seems to be most frequently accepted for various derivatives, including the title compound, *N*-methyl-*N*-nitroso-*N'*-nitroguanidine (MNNG), where $R_1 = CH_3$ and $R_2 = NO$.



(I)



(II)

The nitroguanidines form a conjugated bonding system where the nature of individual bonds in the guanidine moieties depends largely on the substituents on the N atoms. In order to obtain more information about this structural dependency, X-ray diffraction studies are now being undertaken for a series of different nitroguanidines at this laboratory. As the guanidine group is fairly common in biological systems, such as kreatine, guanine and arginine, its structural properties may be of biochemical interest.

MNNG is known to be a very potent mutagen and carcinogen (Yamamoto, Kondo & Sugimura, 1978) and although the mechanism of its activity is not known (Haerlin, Sussmuth & Lingens, 1970) it is clear that the result is methylation of DNA. Free radicals of MNNG may be of importance (Ioki, Imamura, Nagata & Nakadata, 1975), and since little is known about these, a single-crystal ESR analysis was undertaken, but so far we have not been able to interpret the spectra because of their complexity.

As the title compound was found in two crystalline modifications, one of which had two independent molecules, this investigation afforded an opportunity to compare three independent molecules.

Experimental

The two crystal modifications were both grown from methanol solutions under only slightly different conditions. A monoclinic form (*M*) was obtained by evaporation at 293 K, whereas an orthorhombic form (*O*) resulted when the evaporation was performed at 278 K. The latter is not stable for more than a few

* Name slightly altered from the usual *N*-methyl-*N'*-nitro-*N*-nitrosoguanidine to stress that the compound is a nitroguanidine.

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weeks at temperatures above 273 K. The molecules are not affected by this process, since the same crystalline form is obtained when recrystallizing under the same conditions. The precise conditions needed to distinguish between the two crystal modifications were not determined.

The monoclinic form gave small, prismatic crystals, light yellow and with poorly developed faces, whereas those of the orthorhombic modification are large, brownish-orange in colour and with well developed faces. The space groups were uniquely determined from systematic absences [$0k0$, $k = 2n + 1$ and $h0l$, $h = 2n + 1$ for (M) and $hk0$, $h = 2n + 1$; $h0l$, $l = 2n + 1$ and $0kl$, $k = 2n + 1$ for (O)] to be $P2_1/a$ and $Pbca$; both modifications have $Z = 8$, and the densities were $d_{calc} = 1{\cdot}714$ (at 115 K) and $d_{obs} = 1{\cdot}7$ Mg m^{-3} (at 295 K) for (M), and $d_{calc} = 1{\cdot}636$ (at 115 K) and $d_{obs} = 1{\cdot}6$ Mg m^{-3} (at 295 K) for (O). The cell dimensions were determined from least-squares fits to 30 reflexions for each modification, measured on an automatic Syntex $P\bar{1}$ diffractometer using graphite-monochromated Mo $K\bar{\alpha}$ radiation ($\lambda = 0{\cdot}71069$ Å). The same diffractometer was used for the data collection.

The data were converted to relative structure amplitudes in the usual way by programs locally adapted for a CDC 6600 computer (Groth, 1973). These programs were used throughout this work except where indicated otherwise.

Absorption and extinction corrections were not applied.

Structure determination and refinements

Both crystal structures were solved by direct methods (Germain, Main & Woolfson, 1971). All non-hydrogen atoms were readily located and their parameters, including anisotropic thermal parameters, were refined by full-matrix least-squares techniques. The H atoms were located by Fourier methods and were subsequently included in the least-squares refinements with isotropic temperature factors.* The atomic form factors used were those of Doyle & Turner (1968) for C, N and O, and those of Stewart, Davidson & Simpson (1965) for H. Final atomic coordinates from a refinement with all reflexions having $\sin\theta/\lambda > 0{\cdot}3$ Å^{-1} and modified weights for $\sin\theta/\lambda < 0{\cdot}6$ Å^{-1} are given in Tables 1 and 2.* The final residual electron densities were never above $0{\cdot}25$ e Å^{-3}, except for regions between bonded atoms.

* Lists of structure factors, anisotropic thermal parameters, atomic parameters from high-angle refinements, data concerning rigid-body motion and details of the refinements have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 35673 (29 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. *Atomic coordinates for the monoclinic form*

Coordinates are from the refinement with $\sin\theta/\lambda > 0{\cdot}3$ Å^{-1} and the weights modified by a sinusoidal function varying from 0 to 1 as $\sin\theta/\lambda$ varies from 0·0 to 0·6 Å^{-1}.

	x	y	z	B* (Å^2)
Molecule *A*				
C(1)	0·12056 (11)	0·61682 (9)	0·51275 (9)	0·84
C(2)	0·22681 (13)	0·49217 (11)	0·38543 (10)	1·17
N(1)	0·22354 (10)	0·53182 (9)	0·50482 (9)	0·89
N(2)	0·00676 (10)	0·63618 (9)	0·39989 (8)	0·97
N(3)	0·14872 (12)	0·66293 (10)	0·62473 (9)	1·18
N(4)	0·32499 (11)	0·49137 (9)	0·61702 (9)	1·08
N(5)	−0·10280 (10)	0·71605 (9)	0·39522 (9)	0·99
O(1)	0·41574 (10)	0·41902 (9)	0·60884 (9)	1·37
O(2)	−0·19198 (10)	0·74523 (9)	0·28729 (8)	1·36
O(3)	−0·11506 (10)	0·75270 (9)	0·49171 (8)	1·41
H(N3)1	0·229 (2)	0·649 (2)	0·686 (2)	1·1
H(N3)2	0·081 (3)	0·707 (2)	0·631 (2)	1·8
H(C2)1	0·326 (3)	0·496 (2)	0·397 (2)	2·1
H(C2)2	0·172 (3)	0·540 (2)	0·326 (3)	2·1
H(C2)3	0·194 (3)	0·418 (3)	0·372 (3)	2·5
Molecule *B*				
C(1)	0·89447 (11)	0·88593 (10)	0·01319 (9)	0·85
C(2)	0·66906 (14)	1·01606 (13)	−0·11248 (11)	1·42
N(1)	0·78502 (11)	0·97036 (9)	0·00665 (9)	0·99
N(2)	0·89074 (11)	0·86204 (9)	−0·10134 (8)	1·00
N(3)	0·98409 (12)	0·84351 (10)	0·12517 (9)	1·21
N(4)	0·78601 (13)	1·00089 (11)	0·12061 (10)	1·48
N(5)	0·99810 (11)	0·78694 (9)	−0·10813 (9)	1·07
O(1)	0·68639 (13)	1·07090 (11)	0·11312 (10)	2·07
O(2)	0·98253 (11)	0·76480 (10)	−0·21714 (9)	1·60
O(3)	1·10449 (10)	0·74613 (10)	−0·01331 (9)	1·60
H(N3)1	0·974 (2)	0·864 (2)	0·190 (2)	1·5
H(N3)2	1·053 (3)	0·799 (2)	0·127 (2)	1·7
H(C2)1	0·605 (5)	0·960 (5)	−0·155 (5)	5·3
H(C2)2	0·650 (4)	1·096 (4)	−0·104 (3)	3·9
H(C2)3	0·709 (4)	1·025 (4)	−0·164 (4)	4·2

* For the non-hydrogen atoms $B = \frac{1}{3}$ trace $\tilde{\mathbf{B}}$.

Table 2. *Atomic coordinates for the orthorhombic form*

Refinement conditions are as given in Table 1.

	x	y	z	B* (Å^2)
C(1)	0·17352 (11)	0·86440 (6)	0·88838 (4)	1·12
C(2)	−0·04003 (13)	0·70767 (7)	0·81299 (5)	1·62
N(1)	−0·00173 (10)	0·83180 (5)	0·84665 (4)	1·29
N(2)	0·30304 (10)	0·76907 (5)	0·89337 (4)	1·21
N(3)	0·18772 (11)	0·97933 (5)	0·91561 (4)	1·47
N(4)	−0·13155 (12)	0·92737 (7)	0·83443 (5)	1·80
N(5)	0·47451 (10)	0·78599 (5)	0·93596 (4)	1·30
O(1)	−0·28110 (11)	0·89894 (7)	0·79631 (5)	2·36
O(2)	0·58449 (9)	0·69266 (5)	0·94015 (4)	1·66
O(3)	0·52122 (11)	0·88602 (6)	0·96819 (5)	2·22
H(N3)1	0·093 (2)	1·030 (1)	0·909 (1)	1·8
H(N3)2	0·290 (2)	0·999 (1)	0·944 (1)	1·7
H(C2)1	−0·153 (4)	0·676 (2)	0·835 (1)	4·6
H(C2)2	0·062 (3)	0·659 (2)	0·824 (1)	3·2
H(C2)3	−0·065 (3)	0·716 (2)	0·759 (1)	3·8

* For the non-hydrogen atoms $B = \frac{1}{3}$ trace $\tilde{\mathbf{B}}$.

Molecular structure

The molecules are in the nitrimino–amino form (I), as shown in Fig. 1. This form is also found in nitroguanidine (Bryden *et al.*, 1956) and in the derivatives

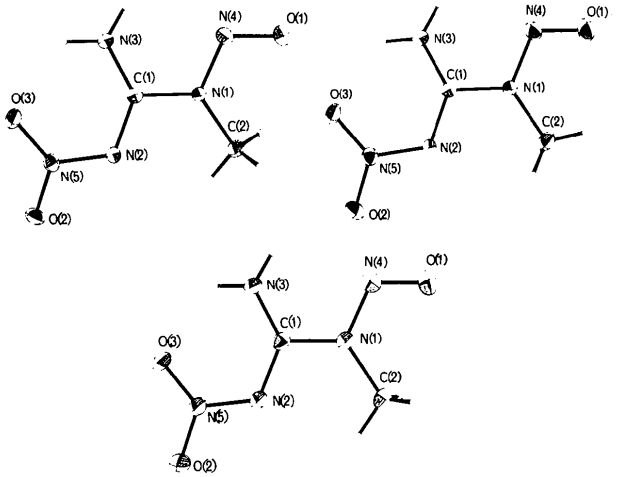


Fig. 1. The molecules with their atomic notation and thermal ellipsoids scaled to 50% probability (Johnson, 1976). Molecules *A* (upper left) and *B* (upper right) are from the monoclinic crystals. The lower drawing represents the title compound in the orthorhombic crystals.

Table 3. *Bond distances* (Å) *involving non-hydrogen atoms* (*refinement* IV)

	(*M*), molecule *A*	(*M*), molecule *B*	(*O*)
C(1)–N(1)	1·4085 (14)	1·3984 (15)	1·4016 (9)
C(1)–N(2)	1·3341 (14)	1·3391 (14)	1·3358 (9)
C(1)–N(3)	1·3130 (14)	1·3133 (14)	1·3159 (8)
N(1)–C(2)	1·4649 (14)	1·4635 (15)	1·4661 (9)
N(1)–N(4)	1·3415 (13)	1·3596 (14)	1·3521 (10)
N(2)–N(5)	1·3720 (14)	1·3660 (14)	1·3560 (9)
N(4)–O(1)	1·2276 (14)	1·2187 (16)	1·2195 (10)
N(5)–O(2)	1·2327 (13)	1·2326 (14)	1·2383 (8)
N(5)–O(3)	1·2416 (13)	1·2408 (13)	1·2393 (8)

Table 4. *Bond distances* (Å) *involving hydrogen atoms* (*refinement* IV)

	(*M*), molecule *A*	(*M*), molecule *B*	(*O*)
N(3)–H(N3)1	0·82 (2)	0·83 (2)	0·83 (2)
N(3)–H(N3)2	0·85 (3)	0·82 (3)	0·86 (1)
C(2)–H(C2)1	0·92 (3)	0·88 (5)	0·90 (3)
C(2)–H(C2)2	0·86 (3)	0·92 (4)	0·87 (2)
C(2)–H(C2)3	0·87 (3)	0·84 (4)	0·93 (2)

Table 5. *Valence angles* (°) *involving non-hydrogen atoms*

	(*M*), molecule *A*	(*M*), molecule *B*	(*O*)
N(1)–C(1)–N(2)	111·64 (9)	111·97 (9)	111·97 (6)
N(1)–C(1)–N(3)	117·64 (9)	118·20 (10)	117·81 (6)
N(2)–C(1)–N(3)	130·72 (10)	129·83 (11)	130·21 (7)
C(1)–N(1)–C(2)	124·02 (9)	123·77 (10)	124·24 (6)
C(1)–N(1)–N(4)	114·77 (9)	114·70 (9)	114·55 (6)
C(2)–N(1)–N(4)	121·17 (9)	121·33 (10)	121·07 (6)
N(1)–N(4)–O(1)	114·11 (9)	114·01 (10)	114·12 (7)
C(1)–N(2)–N(5)	117·34 (9)	118·23 (9)	118·03 (5)
N(2)–N(5)–O(2)	114·75 (9)	114·24 (9)	114·57 (6)
N(2)–N(5)–O(3)	122·80 (9)	123·37 (9)	123·80 (6)
O(2)–N(5)–O(3)	122·40 (9)	122·37 (10)	121·63 (7)

Table 6. *Valence angles* (°) *involving hydrogen atoms*

	(*M*), molecule *A*	(*M*), molecule *B*	(*O*)
C(1)–N(3)–H(N3)1	121 (1)	121 (2)	121 (1)
C(1)–N(3)–H(N3)2	118 (2)	116 (2)	119 (1)
H(N3)1–N(3)–H(N3)2	122 (2)	123 (2)	121 (1)
⟨N(1)–C(2)–H(C2)⟩*	107	110	109
⟨H(C2)–C(2)–H(C2)⟩*	111	107	110

* Average values.

N-methyl-*N'*-nitroguanidine, *N,N*-dimethyl-*N'*-nitroguanidine and 2-nitriminoimidazolidine (Nordenson, 1981), and this may be the general form for the solid phases. Whether this applies to the molecules in solution and in the gas phase is still an open question.*

Various derived quantities based on coordinates from Tables 1 and 2 are given in Tables 3–7. As expected, all three molecules are roughly planar, with the (*O*) molecule closest to exact planarity. The most pronounced corrugation is found in molecule *A* of (*M*), where the torsion angles around C(1)–N(1) and N(2)–N(5) deviate by more than 10° from ideal values. No other deviations from ideal torsion angles exceed 6·7°. A small deviation from planarity around N(1) is found in all molecules, the largest being in molecule *B* of (*M*). The deviations from ideal torsion angles around the N–N bonds are associated with a corresponding lengthening of the bond distances.

Table 3 reveals that the main differences between the three molecules are among the N–N and N–O bonds. These differences may be explained by slight alterations of the conjugation, possibly caused by the different environments. If the O atom in an N–O bond is involved in hydrogen bonding the observed N–O distance is somewhat longer than for those not engaged in hydrogen bonding. The lengthening is about 0·01 Å. Thus, N(4)–O(1) of molecule *A* (*M*), where the O atom is involved in hydrogen bonding, is 0·009 Å longer than those in the other two, and the N(5)–O(2) bonds of both molecules of (*M*), where the O atoms are

* Liquid-chromatographic purification of the title compound in water/methanol (3:7) solution indicates the possible existence of two forms by the presence of two peaks, but NMR spectra do not, so far, support the existence of more than one form.

Table 7. *Torsion angles* (°)

E.s.d.'s are 1–2° for angles involving hydrogen atoms and 0·16–0·18° for those involving other atoms.

	(*M*), molecule *A*	(*M*), molecule *B*	(*O*)
N(2)–C(1)–N(1)–N(4)	−168·3	−178·2	−175·2
N(2)–C(1)–N(1)–C(2)	14·1	6·8	0·5
N(3)–C(1)–N(1)–N(4)	11·5	1·1	4·5
N(3)–C(1)–N(1)–C(2)	−166·2	−173·9	−179·8
N(1)–C(1)–N(2)–N(5)	179·0	175·8	−176·6
N(3)–C(1)–N(2)–N(5)	−0·7	−3·4	3·8
C(1)–N(1)–N(4)–O(1)	−178·7	−177·3	178·2
C(2)–N(1)–N(4)–O(1)	−1·0	−2·2	2·4
C(1)–N(2)–N(5)–O(2)	169·1	176·6	177·8
C(1)–N(2)–N(5)–O(3)	−13·5	−4·9	−2·6
N(1)–C(1)–N(3)–H(N3)1	8	2	2
N(2)–C(1)–N(3)–H(N3)1	−173	−179	−178
N(1)–C(1)–N(3)–H(N3)2	−173	−174	175
N(2)–C(1)–N(3)–H(N3)2	7	5	−5
Conformation of the methyl group compared to the ideal staggered conformation			
Maximum deviation	15	27	8
Minimum deviation	11	6	0
Average deviation	13·5	18·5	1
Minimum value for H–C(2)–N(1)–C(1)	13	−38	1

Table 8. *Bond distances* (Å) *obtained from a refinement using reflexions with* $\sin\theta/\lambda > 0{\cdot}7$ Å^{-1} *and values corrected for rigid-body motion*

The e.s.d.'s for the observed values are 0·002–0·003 Å for (*M*) and 0·001 Å for (*O*).

	Observed values			Corrected values		
	(*M*), *A*	(*M*), *B*	(*O*)	(*M*), *A*	(*M*), *B*	(*O*)
C(1)–N(1)	1·406	1·398	1·400	1·407	1·401	1·403
C(1)–N(2)	1·336	1·340	1·337	1·337	1·343	1·338
C(1)–N(3)	1·315	1·314	1·314	1·317	1·316	1·316
N(1)–C(2)	1·464	1·462	1·465	1·467	1·465	1·467
N(1)–N(4)	1·343	1·358	1·350	1·345	1·360	1·351
N(2)–N(5)	1·370	1·363	1·353	1·371	1·365	1·355
N(4)–O(1)	1·224	1·219	1·216	1·226	1·222	1·218
N(5)–O(2)	1·231	1·236	1·237	1·233	1·239	1·237
N(5)–O(3)	1·240	1·239	1·237	1·243	1·241	1·239

The rigid-body approximations (Schomaker & Trueblood, 1968) gave reasonably good fits, with $[\sum (U_{ij,\mathrm{obs}} - U_{ij,\mathrm{calc}})^2/6(N_a - N_p)]^{1/2}$ of 0·0013 (*M*,*A*), 0·0017 (*M*,*B*) and 0·0017 (*O*). Additional data concerning these corrections have been deposited.

involved in only very weak hydrogen bonds, are 0·007 Å shorter than the average value of 1·2400 (15) Å* for the remaining four N–O bonds of the nitro groups. These differences are, however, reduced by the high-angle refinements ($\sin\theta/\lambda > 0{\cdot}7$ Å^{-1}) and when rigid-body-motion corrections are applied (Table 8). Such lengthenings of the N–O bonds may add double-bond character to the adjacent N–N bonds, thereby making them shorter. The next bond in the sequence, the guanidino C–N bond, may also be affected by being lengthened. This alteration in the conjugation corresponds well to the differences observed in the nitrosamino groups, but is somewhat less satisfactory for the nitrimino groups, where the stretching of the N–N bonds in (*M*) seems larger than expected from this simple model. The rather strong interactions between the nitro and nitroso groups in (*M*) may tend to make the N–N bonds longer than in (*O*), as observed for all such bonds except N(1)–N(4) of molecule *A* (*M*).

Except for C(1)–N(1) of molecule *A* (*M*), which is significantly longer than the other two, the corresponding C–N bonds are equal within 2·5σ. As was the case for the N–O bonds, the differences in C(1)–N(1) are reduced in the high-angle refinements, and even more so when the rigid-body-motion corrections are applied. Average values for the C–N bonds are (values in parentheses are sample e.s.d.'s and those in square brackets are for high-angle refinements corrected for rigid-body motion): C(1)–N(1): 1·403 (5) [1·404 (3)]; C(1)–N(2): 1·336(3) [1·339 (3)]; C(1)–N(3): 1·314 (2) [1·316 (1)]; C(2)–N(1): 1·465 (1) Å [1·466 (1) Å].

The small but occasionally significant differences in the valence angles (Table 5) relate to the differences in bond distances such that the smaller angles are associated with the longer bonds.

Analysis of the thermal motion* shows that the r.m.s. vibrational amplitudes are about 10% larger in molecule *B* of (*M*) than in molecule *A*, and another 10% higher in (*O*). The temperature factors of the methyl H atoms in molecule *B* are three times as large as those in *A*, and this might indicate rotation of this group. A careful search through the difference Fourier maps, however, did not support this assumption.

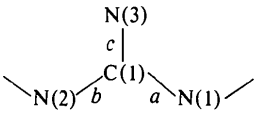
Difference Fourier maps with low-angle data ($\sin\theta/\lambda < 0{\cdot}7$ Å^{-1}) based on atomic parameters from high-angle refinements ($\sin\theta/\lambda > 0{\cdot}7$ Å^{-1}) revealed residuals at the expected positions of bonds and lone pairs. The electron densities range from 0·25 to 0·55 e Å^{-3} for bonds and from 0·20 to 0·45 e Å^{-3} for lone pairs. The peaks corresponding to H atoms have densities ranging from 0·7 to 1·0 e Å^{-3}.

The guanidino moiety has a very high degree of conjugation over the amino and nitrimino groups, whereas the nitrosamino group does not seem to participate much in this conjugation. The same unsymmetrical conjugation is observed in other guani-

* The values in parentheses here and for average values given later are sample e.s.d.'s; $\sigma = [\sum_i (x_i - \bar{x})^2/(n-1)]^{1/2}$.

* See deposition footnote.

Table 9. *Comparison of bond distances* (Å) *and angles* (°) *of the guanidine moiety with those of some other relevant structures*



a	*b*	*c*	∠*ab*	∠*ac*	∠*bc*	Reference
1·409	1·334	1·313	111·6	117·6	130·7	(*M*), *A*
1·398	1·339	1·313	112·0	118·2	129·8	(*M*), *B*
1·402	1·336	1·316	112·0	117·8	130·2	(*O*)
1·34	1·35	1·34	118	112	129	*a*
1·42	1·28	1·30	107·7	120·9	131·4	*b*
1·401	1·330	1·316	118·1	114·7	127·2	*c*
1·420	1·313	1·342	119·1	113·4	127·5	*d*
1·398	1·317	1·336	114·2	118·6	127·2	*e*
1·344	1·326	1·313	116·4	116·1	127·5	*f*
1·329	1·348	1·334	115·8	118·1	126·0	*g*
1·333	1·341	1·339	117·6	118·7	123·8	*h*

References: (*a*) Nitroguanidine (Bryden *et al.*, 1956); (*b*) $N^2,N^{2\prime}$-dichloroazoformamidine (Bryden, 1958); (*c*), (*d*) and (*e*) 5-methoxy-2-sulphanilamidopyrimidine (Giuseppetti, Tadini, Bettinetti & Giordano, 1977); (*f*) and (*g*) sulphaguanidine monohydrate and *trans*-dichlorobis(sulphaguanidine)palladium(II) (Alléaume, Gulko, Herbstein, Kapon & Marsh, 1976); (*h*) cyanoguanidine (Eisenstein & Hirshfeld, 1979).

dine moieties possessing an electron-attracting substituent (sulphate) on the N atom corresponding to N(1) (Table 9). Those lacking such a substituent generally have guanidino C—N bonds of approximately the same length. The valence angles of all guanidino moieties of Table 9 exhibit a pattern with one angle close to 130° (average value from Table 9: 128·2°), and the other two not far from 115° (averages 114·8 and 116·9°).

Crystal structure

Stereoviews of the crystal structures (Johnson, 1976), shown in Figs. 2 and 3, reveal large differences in the two packing modes. In (*O*) the hydrogen-bonding system (details in Table 10) forms a band of molecules along [010] between which ordinary van der Waals interactions prevail, whereas in (*M*) additional, quite strong interactions are found. These interactions, between the nitro and nitroso groups, are of two kinds. The first is between centrosymmetrically related molecules nearly parallel to each other with one directly above the other. In this way the nitro group of one molecule is directly above the nitroso group of the other with a separation of ~3·2 Å. The second interaction is between molecules nearly perpendicular to each other and related through the screw axis. The N···O separations are 2·9 and 3·0 Å. Through these interactions each of the two molecules of (*M*) forms sheets with a weave-like pattern, parallel to the *ab* plane at $z \sim 0$ (*B*) and $z \sim \frac{1}{2}$ (*A*). These sheets are connected by hydrogen bonds (Table 11) and van der Waals interactions.

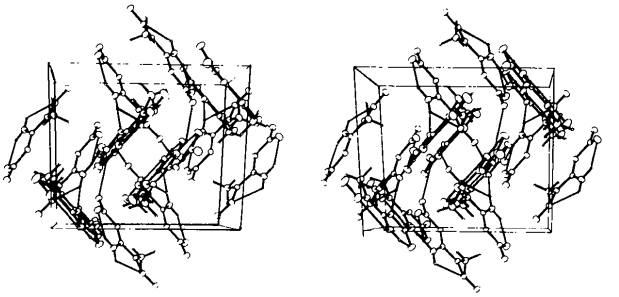


Fig. 2. Stereodrawing (Johnson, 1976) of the monoclinic form (*M*) of *N*-methyl-*N*-nitroso-*N'*-nitroguanidine. The view is along the positive *c* axis with *b* pointing to the right and *a* up.

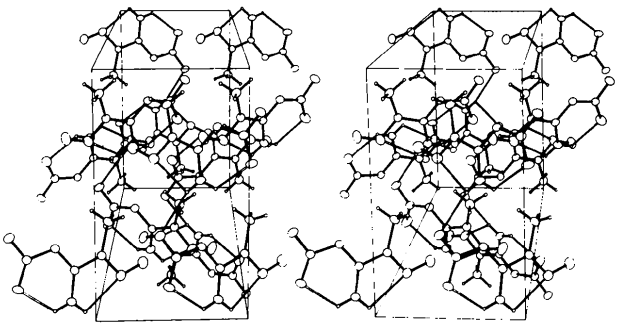


Fig. 3. Stereodrawing (Johnson, 1976) of the orthorhombic (*O*) form of *N*-methyl-*N*-nitroso-*N'*-nitroguanidine. The view is along the negative *c* axis with *a* pointing to the left and *b* down.

The two independent molecules of (*M*) are very roughly related by a pseudo screw axis parallel to $c \sin \beta$.

All the hydrogen bonds may be interpreted as bifurcated, possibly a result of having seven possible acceptor sites and only two donors. The intramolecular interactions are due to the planar geometry of the molecules, and an H(N3)1···N(4) interaction is doubtful as it has an unfavourable H···*A*—*R* angle of 80°. The intermolecular bonds from H(N3)1 have different acceptors for all three molecules, but are all of comparable strength. The hydrogen bonds from H(N3)2 are very much alike, except that O(3) acts as acceptor for the intermolecular bond in (*O*) rather than O(2) as in (*M*).

The energy gain by bifurcating a hydrogen bond has been calculated by *ab initio* methods by Newton, Jeffrey & Takagi (1979) and was found to be 4·2–16·8 kJ mol^{-1}, depending on the precise geometry involved. The geometries used, and cited in their work, do not differ much from those found here.

Table 10. *Details of the hydrogen bonding in the orthorhombic form*

E.s.d.'s are 0·015 Å (*D*–H,H···*A*), 0·001 Å (*D*···*A*) and 1° (*D*–H···*A*). The H···*A*–*R* angles are in the range 96–150°, except for those involving N(4), where they are 80 (H···N–N) and 160° (H···N–O).

D–H···*A*	*D*–H	H···*A*	*D*···*A*	*D*–H···*A*	*A'*···H···*A*	Symmetry code for *A*
N(3)–H(N3)2···O(3)	0·86 Å	1·99 Å	2·582 Å	125°	77°	*x*,*y*,*z*
N(3)–H(N3)2···O(3)	0·86	2·29	3·103	157		$1-x, 2-y, 2-z$
N(3)–H(N3)1···N(4)	0·83	2·24	2·580	105	100	*x*,*y*,*z*
N(3)–H(N3)1···O(2)	0·83	2·17	2·939	154		$\frac{1}{2}-x, \frac{1}{2}+y, z$

Table 11. *Details of the hydrogen bonding in the monoclinic form*

E.s.d.'s of distances involving H are 0·01–0·02 Å, for the others 0·001 Å and for the angles 1–2°. The H···*A*–*R* angles are as in the orthorhombic form.

D–H···*A*	*D*–H	H···*A*	*D*···*A*	*D*–H···*A*	*A'*···H···*A*	Symmetry code for *A*
N(3)*A*–H(N3)2···O(3)*A**	0·85 Å	1·99 Å	2·586 Å	126°	89°	*x*,*y*,*z*
N(3)*A*–H(N3)2···O(2)*B*	0·85	2·42	3·121	141		$x-1, y, z-1$
N(3)*A*–H(N3)1···N(4)*A*	0·82	2·28	2·591	103	98	*x*,*y*,*z*
N(3)*A*–H(N3)1···N(2)*B*	0·82	2·31	3·080	156		$x-\frac{1}{2}, \frac{3}{2}-y, z+1$
N(3)*B*–H(N3)2···O(3)*B*	0·82	1·99	2·587	129	92	*x*,*y*,*z*
N(3)*B*–H(N3)2···O(2)*A*	0·82	2·46	3·089	135		$\frac{3}{2}+x, \frac{3}{2}-y, z$
N(3)*B*–H(N3)1···N(4)*B*	0·83	2·25	2·589	105	99	*x*,*y*,*z*
N(3)*B*–H(N3)1···O(1)*A*	0·83	2·21	2·941	147		$\frac{3}{2}-x, \frac{1}{2}+y, 1-z$

* *A* and *B* following the atom labels signify molecules *A* and *B*.

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