

C—N bond lengths reported for the protonated biguanide derivatives paludrin* ($1.307 \text{ \AA} \leq \text{C—N} \leq 1.345 \text{ \AA}$ (Brown, 1967) and morpholine biguanide† ($1.311 \text{ \AA} \leq \text{C—N} \leq 1.376 \text{ \AA}$) (Handa & Saha, 1973).

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* Paludrin: *N*-(4-chlorophenyl)-*N'*-(1-methylethyl)-imidodicarbonimidic diamide monohydrochloride, CAS [637-32-1].

† Morpholine biguanide hydrobromide: *N*-(aminoiminomethyl)-4-morpholinecarboximidamide monohydrobromide, CAS [41305-70-8].

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Biguanide Hydrochloride

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Abstract. $\text{C}_2\text{H}_8\text{N}_7\text{Cl}$, monoclinic, $P2_1/n$, $a = 4.384$ (1), $b = 17.549$ (2), $c = 8.363$ (1) \AA , $\beta = 101.76$ (1) $^\circ$ (23 ± 3 $^\circ\text{C}$), $D_m = 1.46$, $D_x = 1.45$ g cm^{-3} , $Z = 4$. The final residual calculated for 1020 observed reflections was 0.045. The molecule exists in a tautomeric form with all C—N bond lengths approximately equal.

Introduction. The compound (BgHCl) was prepared by adding a stoichiometric amount of BaCl_2 to an aqueous solution of biguanide sulfate and removing the BaSO_4 by filtration. Needle-like crystals elongated along [100] were grown from a slowly evaporating aqueous solution and generally showed the forms {100}, {010}, and {011}. The space group was assigned uniquely from the extinct reflections: $h0l$, $h + l = 2n + 1$; and $0k0$, $k = 2n + 1$, observed on Weissenberg and precession photographs. A small crystal, $0.22 \times 0.22 \times 0.15$ mm, was cleaved from a longer crystal and mounted on a quartz fiber with [100] aligned with the ϕ axis for data collection on a Nonius CAD-4 autodiffractometer

equipped with a Cu X-ray tube and graphite monochromator ($\lambda_{\text{CuK}\alpha} = 1.5418 \text{ \AA}$). Lattice parameters were obtained by a least-squares procedure using 18 reflections centred at + and -2θ .

Intensities were measured using the θ – 2θ scan technique with the variable scan rate adjusted to obtain 2500 counts. The scan range was calculated as $\Delta\theta = 0.5 + 0.4 \tan \theta$ and this range was extended 25% on either side to measure background intensities. The intensities and corresponding standard deviations were calculated according to the formulae: $I = [\text{Scan} - (\text{Bkg1} + \text{Bkg2}) \times 2] \times (\text{Scan Rate})$; $\sigma(I) = [\text{Scan} + (\text{Bkg1} + \text{Bkg2}) \times 4]^{1/2} \times (\text{Scan Rate})$, where Scan is the count obtained during the θ – 2θ scan, Bkg1 and Bkg2 are the counts obtained from the background scans and Scan Rate is the scan rate in deg min^{-1} . 15 standard reflections were measured after each 100 data points as a check for crystal deterioration and to monitor instrumental variations. The scaling ratios derived from the standard reflections varied by about $\pm 5\%$ and the data were adjusted accordingly. Within the sphere $2\theta < 150^\circ$, 1308 unique reflections were measured. The 288 reflections with intensities $< 3\sigma(I)$ were defined

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as 'less than' and were included in the refinement of the structure only if $F_c > F_o$. Absorption corrections were not applied.

Scattering factors for H, C, N, and Cl^- were taken from *International Tables for X-ray Crystallography* (1962), Table 3.3.1A, and the anomalous dispersion for Cl^- was taken from Table 3.3.2B. Computations were performed on the University of Pittsburgh PDP/10 computer using the X-RAY system of programs (Stewart, Kruger, Ammon, Dickinson & Hall, 1972; Ernst & Poppleton, 1974). The illustrations were prepared with the aid of ORTEP (Johnson, 1965).

The structure was determined by the heavy-atom method. Block-diagonal least-squares refinement of positional and isotropic thermal parameters gave a residual index ($R = \sum ||F_o| - |F_c|| / \sum |F_o|$) of 0.148. A difference Fourier map revealed all eight H atoms, which were assigned isotropic temperature factors equal to those of the heavy atom to which they were bonded. The final cycles of refinement were calculated using the full-matrix method varying all nonhydrogen atom coordinates and anisotropic thermal parameters. The maximum shift in any parameter during the last cycle was 0.3 e.s.d. The coordinates of the H atoms were redetermined from a difference Fourier map after the final cycle of refinement. The final residual index calculated for all reflections was 0.054 and for observed reflections 0.045.

Discussion. The final parameters are given in Table 1.* No e.s.d.'s are shown for the H atoms because they were not allowed to vary during refinement. Bond

* A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 31987 (9 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

lengths and angles are shown in Fig. 1. The e.s.d.'s of bond lengths and angles involving nonhydrogen atoms are approximately 0.005–0.006 Å and 0.4° respectively. The arrangement of biguanide ions around a single Cl^- ion is shown in Fig. 2, together with the distances from the Cl^- ion to the nearest N atoms. The deviations of the terminal N atoms from the plane of $\text{C}(1)-\text{N}(00)-\text{C}(2)$ are indicated in Fig. 3.

The average C–N bond length in the biguanide ion is 1.335 (6) Å, and all the C–N bond lengths fall within two e.s.d.'s of this value. In addition, the bond angles in the two halves of the molecule compare rather closely. A reasonable model for the bonding in this ion (Fanshawe, Bauer, Ullman & Safir, 1964) is that the formal positive charge is delocalized uniformly over the four NH_2 groups and the formal third bond to $\text{N}(00)$ is distributed between $\text{C}(1)-\text{N}(00)$ and $\text{C}(2)-\text{N}(00)$ according to the equivalent mesomeric forms I and II.

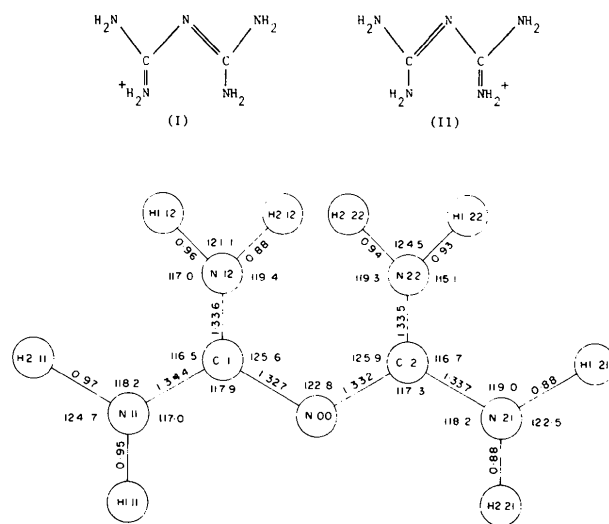


Fig. 1. Bond lengths (Å) and bond angles (°) in biguanide hydrochloride.

Table 1. *Final atomic parameters with their e.s.d.'s*

Final atomic coordinates ($\times 10^4$), anisotropic thermal parameters ($\times 10^4$) and hydrogen isotropic temperature factors ($\times 10^3$). The temperature factors are defined by $\exp[-2\pi^2(h^2 a^{*2} U_{11} + k^2 b^{*2} U_{22} + l^2 c^{*2} U_{33} + 2hka^* b^* U_{12} + 2hla^* c^* U_{13} + 2klb^* c^* U_{23})]$ and $\exp(-8\pi^2 U \sin^2 \theta / \lambda^2)$.

	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> ₁₁	<i>U</i> ₂₂	<i>U</i> ₃₃	<i>U</i> ₁₂	<i>U</i> ₁₃	<i>U</i> ₂₃
Cl	1695 (3)	6470 (1)	633 (1)	528 (7)	271 (5)	300 (6)	69 (5)	121 (5)	29 (4)
C(1)	3791 (11)	6478 (3)	6014 (5)	392 (25)	283 (22)	269 (21)	-21 (20)	68 (18)	29 (18)
C(2)	3842 (10)	5249 (2)	7093 (5)	346 (23)	259 (21)	280 (21)	23 (18)	143 (18)	5 (17)
N(00)	2847 (10)	5757 (2)	5919 (5)	491 (24)	241 (19)	333 (20)	-69 (17)	56 (18)	41 (16)
N(11)	3867 (12)	6845 (2)	4613 (5)	852 (35)	268 (20)	301 (21)	-114 (21)	167 (21)	21 (16)
N(12)	4549 (12)	6886 (2)	7386 (5)	755 (33)	295 (21)	301 (21)	-95 (21)	138 (20)	-7 (17)
N(21)	2357 (10)	4580 (2)	6989 (5)	469 (24)	270 (20)	420 (23)	-54 (17)	106 (19)	45 (17)
N(22)	6280 (10)	5333 (2)	8329 (5)	464 (24)	271 (19)	398 (22)	32 (18)	68 (18)	-14 (17)
	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> _{iso}	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> _{iso}	
H(111)	3480	6550	3640	45	H(121)	710	4510	6200	38
H(112)	4920	7420	7270	44	H(221)	2920	4260	7740	38
H(211)	4430	7380	4670	45	H(122)	6920	4890	8920	38
H(212)	4160	6700	8300	44	H(222)	7440	5790	8420	38

This model yields a C—NH₂ bond order of 1.25 and a C—N(00) bond order of 1.5 whereas no significant differences appear in the experimentally observed bond lengths. Consideration of resonance structures I and II leads to the prediction of a planar molecule. In fact, the C(1) and C(2) portions of the molecule are separately planar with the H—N—C—N' torsion angles [N' ≠ N(00)] all being within 8° of 0 or 180°. However, steric interactions appear to prevent the two individually planar portions from attaining coplanarity with each other, the distances H(212)—H(222) (2.4 Å) and N(12)—N(22) (2.89 Å) both representing intramolecular van der Waals contact distances. The molecule is thus unable to assume the coplanarity required for optimum π bonding. This could account for the fact that the C—N(00) bonds are not significantly shorter than the other C—N bonds. The interactions of these two opposing effects (delocalization and steric repulsion) may in turn account for the large bond angles (125°) and C(1) and C(2).

The hydrogen-bonding scheme consists entirely of N—H...Cl⁻ interactions as shown in Fig. 2. All H atoms except H(121) are involved in close contacts

(<2.8 Å) with Cl⁻. Even with the availability of this H atom not otherwise involved in coordination, N(00) does not enter into the hydrogen-bonding scheme. This is somewhat unexpected since the crystal structure of unprotonated biguanide (Ernst & Cagle, 1977) contains two close contacts between N(00) and H atoms which

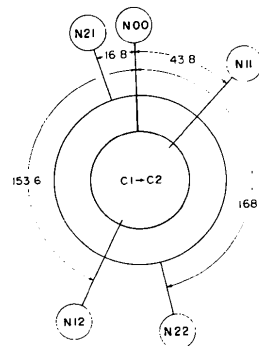


Fig. 3. Dihedral angles projected on a plane perpendicular to the C(1)—C(2) vector. The bridging bonds to N(00) are shown accentuated.

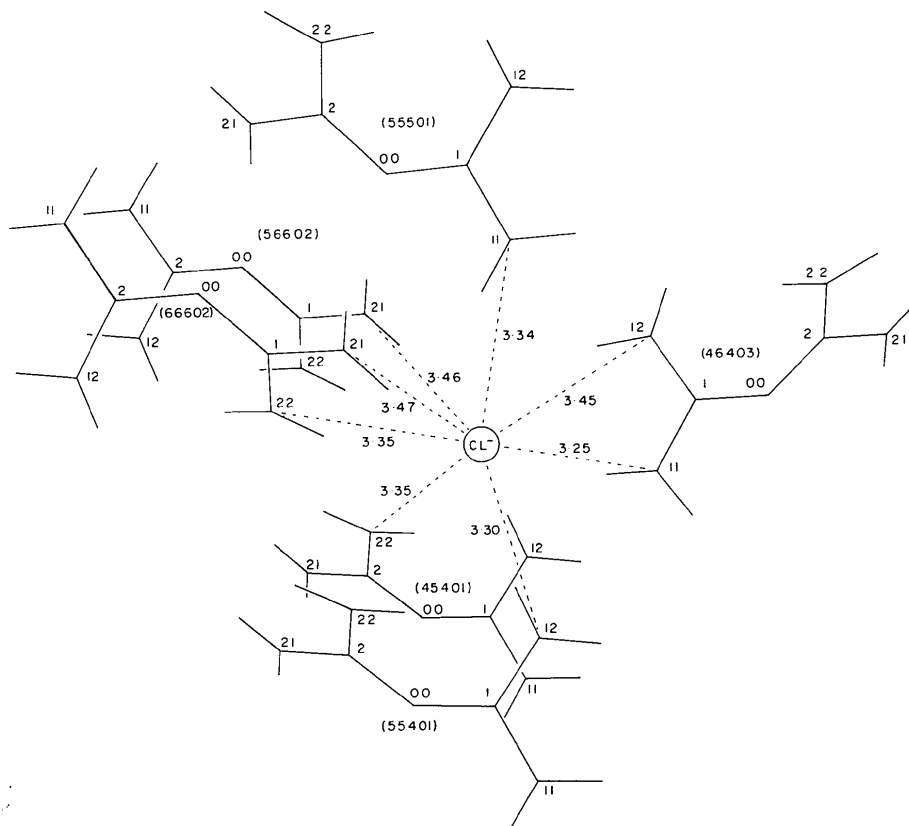
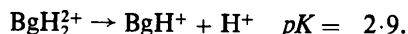
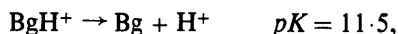


Fig. 2. Close-contact distances (Å) between the chloride and biguanide ions. The numbers in parentheses represent the symmetry operation generating a particular biguanide ion in the convention used in *ORTEP*. The first three digits represent unit-cell translations and the final digit represents one of the following operations: (1) x, y, z ; (2) $-x, -y, -z$; (3) $\frac{1}{2} + x, \frac{1}{2} - y, \frac{1}{2} + z$; (4) $\frac{1}{2} - x, \frac{1}{2} + y, \frac{1}{2} - z$. The coordinates presented in Table 1 are represented by the symmetry operation (55501).

may be weak hydrogen bonds. Assuming that the positive charge in the monoprotonated biguanide is completely delocalized over the four $-\text{NH}_2$ groups, it might be expected that the N(00) lone pair of electrons would still be able to function as an acceptor in a hydrogen bond. The apparently low affinity of N(00) in BgH^+ for coordination with H observed here may reflect the large difference between the first and second dissociation constants (Kurzer & Pitchfork, 1968):



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N-Nitropyrazole*

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Abstract. $\text{C}_3\text{H}_3\text{N}_3\text{O}_2$, $P2_1/c$, monoclinic, $a = 7.337$ (1), $b = 10.032$ (1), $c = 7.199$ (1) Å, $\beta = 116.6$ (2)°, $M_r = 113.1$, $Z = 4$, $D_x = 1.585$ g cm $^{-3}$. The molecule is planar and the O–N–O angle, 128.5 (2)°, is slightly larger than in other N–NO $_2$ fragments. ^{14}N nuclear quadrupole resonance data for several pyrazoles and 1,2,4-triazoles are listed.

Introduction. Five-membered N heterocycles have been studied as models of simple aromatic systems, some of which are of biological and pharmaceutical interest. Pyrazole has received repeated attention. The structure first reported by Ehrlich (1960) was later refined using neutron data by Larsen, Lehmann, Søtofte & Rasmussen (1970) and has recently been restudied with X-ray data at 295 and 108 K by La Cour & Rasmussen (1973). However, few *N*-substituted azole derivatives have been studied and we report here the structure of

the only *N*-nitroazole so far prepared. This work was done in conjunction with nitrogen nuclear quadrupole resonance studies of pyrrole, pyrazole, imidazole, triazoles, and their *N*-acetyl derivatives.

$\text{C}_3\text{H}_3\text{N}_3\text{O}_2$ was prepared as described by Hüttel & Büchele (1955) by treating pyrazole nitrate with acetic anhydride. The compound is stable and melts at 93 °C without decomposition. Although it can be crystallized from high-boiling petroleum spirit, suitable crystals for X-ray studies were obtained by sublimation at 85° *in vacuo*. A crystal in the shape of a rhombic prism approximately 0.3 × 0.15 × 0.15 mm was sealed in a thin-walled capillary tube for data collection.

Oscillation and Weissenberg films showed systematic absences $h0l$, l odd, and $0k0$, k odd, consistent with the monoclinic space group $P2_1/c$. Data were collected at room temperature on a Picker four-circle computer-controlled diffractometer. The unit-cell parameters were refined with a routine program available for the diffractometer. Intensity data for 674 independent reflections ($\sin \theta_{\max}/\lambda = 0.556$) were collected by the $\theta/2\theta$ scan method using graphite-monochromated Cu $K\alpha$ radiation ($\lambda = 1.5418$ Å). A correction factor of

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