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Crystal and Molecular Structure of Morpholine Biguanide Hydrobromide

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Morpholine biguanide hydrobromide ($C_8H_{13}N_5O.HBr$) crystallizes in the triclinic space group $P\bar{1}$ with lattice parameters $a=6{\cdot}52$, $b=8{\cdot}29$, $c=10{\cdot}77$ Å; $\alpha=108°42'$, $\beta=109°28'$, $\gamma=97°43'$ and $Z=2$. The structure has been solved by three-dimensional heavy-atom Fourier syntheses. Hydrogen positions have been located by difference Fourier methods. The structure has been refined by full-matrix least-squares methods, the final R value being 0·088. The morpholine ring has been found to assume a chair conformation. A number of valence-bond structures contribute to the normal state of morpholine biguanide hydrobromide molecule; the contribution of each form has been calculated on the basis of the observed bond lengths. Out of the six available hydrogen atoms in the molecule four take part in the formation of hydrogen bonds of the type $N^+{-}H\cdots Br^-$, with values ranging from 3·346 ± 0·015 to 3·423 ± 0·015 Å. The molecules are held together by a three-dimensional network of such hydrogen bonds.

Introduction

In view of the fact that most of the biguanide compounds are known to have medicinal properties (Shapiro, Parrino & Freedman, 1959), determination of the crystal and molecular structure of morpholine biguanide in the form of its different hydrohalides was undertaken by us as a part of our program of research on the structure and functions of biomolecules. In this series, the structure of morpholine biguanide hydrochloride (MBHCl) with space group *Pbca* and $Z=8$, has already been solved by us (Handa & Saha, 1971). The present paper deals with the structural solution of morpholine biguanide hydrobromide (MBHBr).

Preparation of compound and crystals

An aqueous solution of MBHCl was treated with a dilute aqueous solution of potassium hydroxide until the mixture was alkaline. Hydrobromic acid was added to this solution a little in excess. Acetone was then added until the solution became turbid. This solution when kept overnight at about 10°C gives a white precipitate. After filtration the precipitate was washed with acetone.

Single crystals of morpholine biguanide hydrobromide were grown by slow evaporation of an aqueous solution of this compound at room temperature (30°C). The thick, transparent, plate-shaped crystals thus obtained belong to the triclinic system.

Crystallographic data

The unit-cell dimensions as obtained from oscillation, rotation and Weissenberg photographs are:

$$\begin{aligned} a &= 6{\cdot}52 \pm 0{\cdot}015 \text{ Å} & \alpha &= 108°42' \\ b &= 8{\cdot}29 \pm 0{\cdot}016 & \beta &= 109\;\;28 \\ c &= 10{\cdot}77 \pm 0{\cdot}036 & \gamma &= 97\;\;43 \end{aligned}$$

$D_m = 1{\cdot}670$ g cm^{-3}, $D_{cal} = 1{\cdot}672$ g cm^{-3}, $Z=2$.

The statistical test applied to the $hk0$ data revealed the presence of a centre of symmetry in the unit cell indicating that the space group is $P\bar{1}$.

Three-dimensional intensity data were collected from multiple-film equi-inclination Weissenberg photographs using Cu $K\alpha$ radiation. Eight layers by rotation about the c axis and only zero layers about the a and b axes were recorded. The plate-shaped crystals were cut to square cross-sections of 0·019, 0·021 and 0·017 cm, for taking photographs about the a, b and c axes respectively. The intensities of 1780 out of 2032 reflexions accessible to the limiting sphere of Cu $K\alpha$ radiation were estimated visually using intensity strips. Reflexions with vanishingly small intensities were also included by assigning one half the minimum measured intensity. These reflexions were marked as unobserved. The intensity data were corrected for spot shape, Lorentz and polarization factors. As the crystals used were of square cross-sections, absorption corrections were computed using F. R. Ahmed's program for cylindrical crystals, the linear absorption coefficient of MBHBr being 59·8 cm^{-1}.

Structure determination and refinement

The position of the heavy atom (bromine) was located from Patterson projections along the b and c axes computed on an IBM 1620 using F. R. Ahmed's program. Two-dimensional Fourier maps projected along **b** and **c** were of little help in solving the structure, owing to considerable superposition of peaks. The three-dimensional Fourier synthesis was computed using the heavy-atom phases and the observed structure amplitudes, duly weighted (Woolfson, 1956). A spoke and bead model of the molecule was constructed using the coordinates of the atoms as obtained from a 3D Fourier synthesis. The value of the discrepancy factor, defined by $R=\sum||F_o|-|F_c||/\sum|F_o|$, for this trial structure was 0·24.

The atomic parameters were refined by the full-matrix least-squares method using the modified program (Srikanta, 1964) of Martin, Busing and Levy. The function minimized was $\sum w(|F_o|-|F_c|)^2$ where w is the weighting factor. Unit weight was given to each reflexion. The scattering factors for C, N, O and Br were taken from *International Tables for X-ray Crystallography* (1960). After three cycles of refinement with isotropic temperature factors, the R value was found to be 0·19. Two cycles of further refinement using anisotropic temperature factors for the non-hydrogen atoms reduced the R value to 0·11. Refinement at this stage was stopped as the shifts in atomic coordinates were less than the standard deviations. Positions of hydrogen atoms were then determined from the 3D difference Fourier synthesis. The structure was then refined with anisotropic temperature factors for non-hydrogen atoms and isotropic for hydrogen atoms. The temperature factors assigned to the hydrogen atoms are those of the heavier atoms to which they are attached. The R value at this stage was 0·088 for observed reflexions and 0·095 including unobserved reflexions.

The positional and thermal parameters of the atoms with their estimated standard deviations, based on the final cycle of refinement, are given in Table 1. The observed (F_o) and calculated (F_c) structure factors are given in Table 2. The composite drawings of the electron density and the difference Fourier maps are given in Figs. 1 and 2.

Discussion

The intramolecular bond lengths and angles are given in Table 3(*a*) and (*b*), and shown diagramatically in Fig. 3. The intramolecular bond lengths involving hydrogen atoms are given in Table 3(*c*). The average N–H and C–H bond lengths have been found to be 1·00 and 0·955 Å respectively.

Table 1. *Positional and thermal parameters*

(*a*) Positional parameters of the heavy atoms, with their e.s.d.'s in parentheses. Values are × 10^4.

	x/a	y/b	z/c
Br	1574 (9) Å	2388 (10) Å	4368 (13) Å
C(1)	5511 (88)	2083 (75)	2037 (115)
C(2)	4462 (76	− 396 (75)	2441 (110)
C(3)	558 (83)	−2011 (90)	1016 (127)
C(4)	−1188 (105)	−2612 (109)	1521 (137)
C(5)	3068 (81)	−3299 (80)	2477 (117)
C(6)	1193 (94)	−3863 (100)	2922 (130)
N(1)	5644 (74)	3362 (68)	3264 (90)
N(2)	6303 (79)	2485 (74)	1137 (104)
N(3)	4268 (65)	471 (66)	1601 (89)
N(4)	6371 (67)	−38 (65)	3628 (90)
N(5)	2796 (67)	−1783 (62)	2073 (85)
O(1)	− 897 (67)	−4179 (63)	1756 (82)

Table 1 (*cont.*)

(*b*) Thermal parameters (× 10^5, Å^2) and their estimated standard deviation (× 10^5, Å^2). The temperature factor is of the form

$$T=\exp\left[-(h^2\beta_{11}+k^2\beta_{22}+l^2\beta_{33}+hk\beta_{12}+hl\beta_{13}+kl\beta_{23})\right].$$

	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Br	1695 (26)	1223 (17)	659 (26)	− 41 (14)	291 (14)	462 (12)
C(1)	1984 (220)	485 (104)	286 (121)	−126 (120)	177 (140)	381 (91)
C(2)	1061 (180)	567 (102)	352 (101)	3 (110)	319 (115)	74 (93)
C(3)	933 (188)	963 (134)	889 (164)	−350 (126)	−400 (130)	475 (108)
C(4)	2581 (282)	1969 (195)	674 (181)	1758 (200)	1335 (162)	1085 (136)
C(5)	1359 (195)	583 (113)	678 (141)	−467 (115)	76 (128)	596 (94)
C(6)	1603 (228)	1314 (159)	733 (191)	−556 (151)	−122 (148)	677 (120)
N(1)	2159 (198)	772 (102)	191 (149)	258 (111)	332 (111)	440 (78)
N(2)	227 (221)	882 (113)	439 (151)	−862 (124)	651 (132)	109 (94)
N(3)	1131 (160)	736 (100)	206 (146)	−511 (101)	−325 (98)	287 (81)
N(4)	1170 (162)	586 (95)	475 (131)	−230 (100)	−225 (103)	178 (78)
N(5)	1440 (166)	541 (90)	114 (120)	−332 (97)	− 60 (97)	370 (71)
O(1)	2197 (177)	1041 (100)	446 (142)	−578 (104)	132 (101)	499 (75)

(*c*) Positional parameters (× 10^4) and isotropic temperature factors of hydrogen atoms.

	x/a	y/b	z/c	T
H(1)	6785 (1677)	4432 (2771)	3885 (1891)	0·984 (4) Å^2
H(2)	4913 (1740)	2619 (2836)	3809 (2014)	1·321 (4)
H(3)	6986 (1256)	1833 (1227)	602 (1426)	1·751 (4)
H(4)	5925 (1243)	3628 (1236)	903 (1399)	1·484 (4)
H(5)	8051 (1162)	535 (1164)	3975 (1365)	1·497 (5)
H(6)	5793 (1142)	− 872 (1161)	3813 (1342)	1·240 (3)
H(7)	− 491 (1184)	−1261 (1208)	651 (1307)	1·185 (5)
H(8)	5 (1192)	−3178 (1180)	300 (1282)	1·053 (5)
H(9)	−2616 (1534)	−2986 (1494)	1001 (1710)	2·166 (6)
H(10)	− 826 (1465)	−1553 (1469)	2320 (1673)	2·313 (5)
H(11)	4676 (1204)	−2783 (1235)	3143 (1491)	0·488 (3)
H(12)	3076 (1201)	−4331 (1213)	1806 (1412)	1·350 (4)
H(13)	1299 (1401)	−2766 (1419)	3623 (1651)	1·862 (4)
H(14)	1455 (1433)	−4735 (1434)	3176 (1613)	1·783 (4)

Table 2. *The observed and calculated structure factors*

Within each group the columns, reading from left to right, contain the values h, $|10F_o|$ and $10F_c$. The unobserved reflexions are not included.

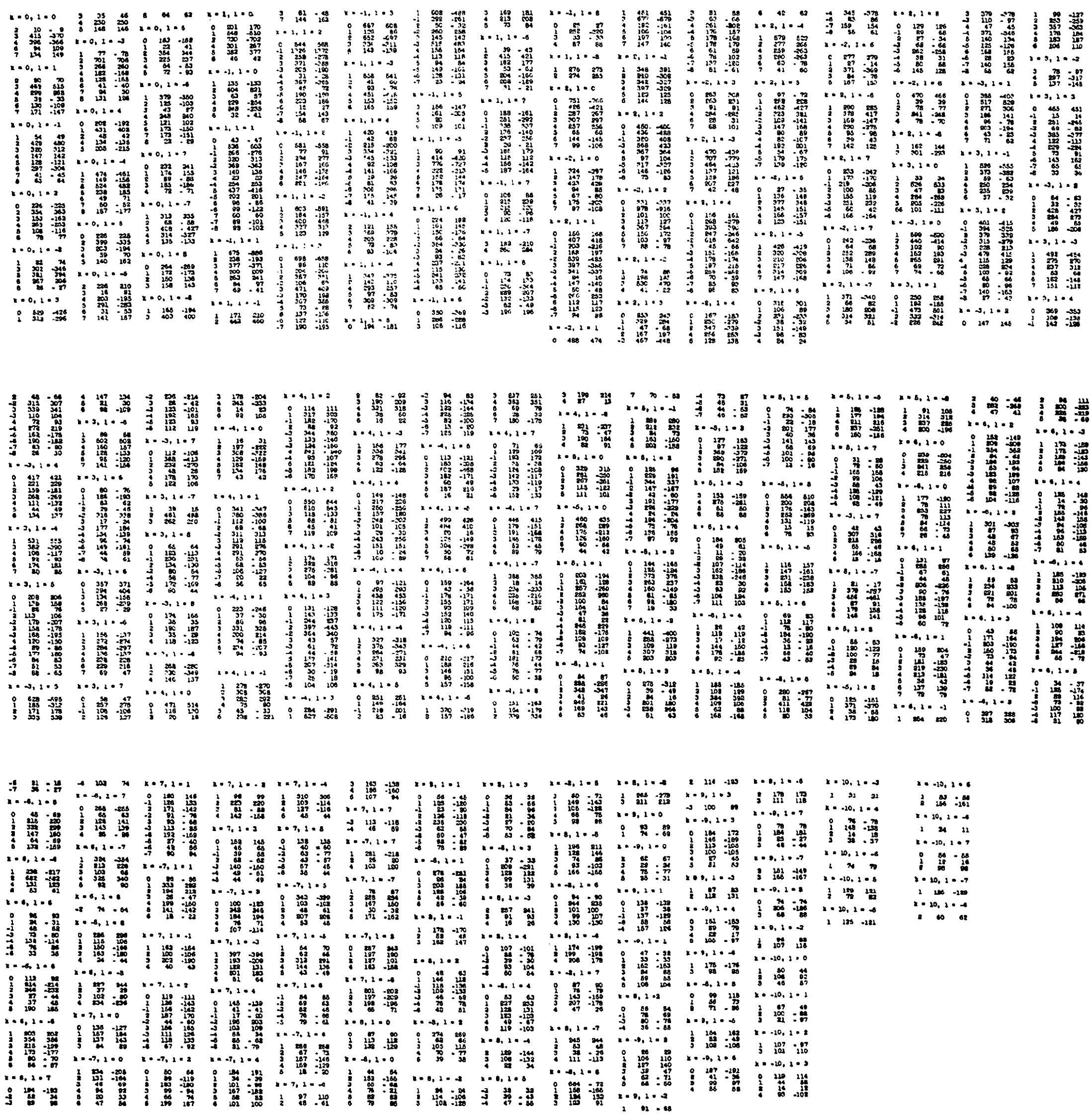

Table 3. *Intramolecular bond lengths and angles*

(*a*) Intramolecular bond lengths (with their e.s.d.'s) and bond orders.

	Bond lengths	Bond order
C(1)–N(1)	1·376 ± 0·037 Å	1·227
C(1)–N(2)	1·349 ± 0·033	1·331
C(1)–N(3)	1·311 ± 0·036	1·541
C(2)–N(3)	1·313 ± 0·028	1·527
C(2)–N(4)	1·373 ± 0·025	1·237
C(2)–N(5)	1·321 ± 0·026	1·476
N(5)–C(3)	1·464 ± 0·028	
C(3)–C(4)	1·522 ± 0·033	
C(4)–O(1)	1·432 ± 0·030	
O(1)–C(6)	1·435 ± 0·028	
C(6)–C(5)	1·523 ± 0·031	
C(5)–N(5)	1·468 ± 0·030	

(*b*) Intramolecular bond angles (with their e.s.d.'s).

N(1)–C(1)–N(2)	121·9 ± 1·0°
N(1)–C(1)–N(3)	119·7 ± 1·0
N(2)–C(1)–N(3)	117·4 ± 0·90
C(1)–N(3)–C(2)	122·3 ± 1·5
N(3)–C(2)–N(4)	123·3 ± 1·1
N(3)–C(2)–N(5)	118·6 ± 1·0
N(4)–C(2)–N(5)	117·7 ± 1·2
C(2)–N(5)–C(5)	124·6 ± 1·2
C(2)–N(5)–C(3)	119·8 ± 1·3
N(5)–C(3)–C(4)	108·5 ± 1·3
C(3)–C(4)–O(1)	108·0 ± 1·2
C(4)–O(1)–C(6)	112·5 ± 1·1
O(1)–C(6)–C(5)	106·1 ± 1·2
C(6)–C(5)–N(5)	110·8 ± 1·3
C(3)–N(5)–C(5)	114·9 ± 1·2

Table 3 (*cont.*)

(*c*) Intramolecular bond distances involving hydrogen atoms and their estimated standard deviations.

N(1)–H(1)	0·984 (267) Å
N(1)–H(2)	0·942 (150)
N(2)–H(3)	0·906 (138)
N(2)–H(4)	1·176 (148)
N(4)–H(5)	0·983 (116)
N(4)–H(6)	1·010 (141)
C(3)–H(7)	1·057 (129)
C(3)–H(8)	0·906 (149)
C(4)–H(9)	0·853 (141)
C(4)–H(10)	0·998 (242)
C(5)–H(11)	1·087 (100)
C(5)–H(12)	0·943 (225)
C(6)–H(13)	0·926 (350)
C(6)–H(14)	0·869 (206)

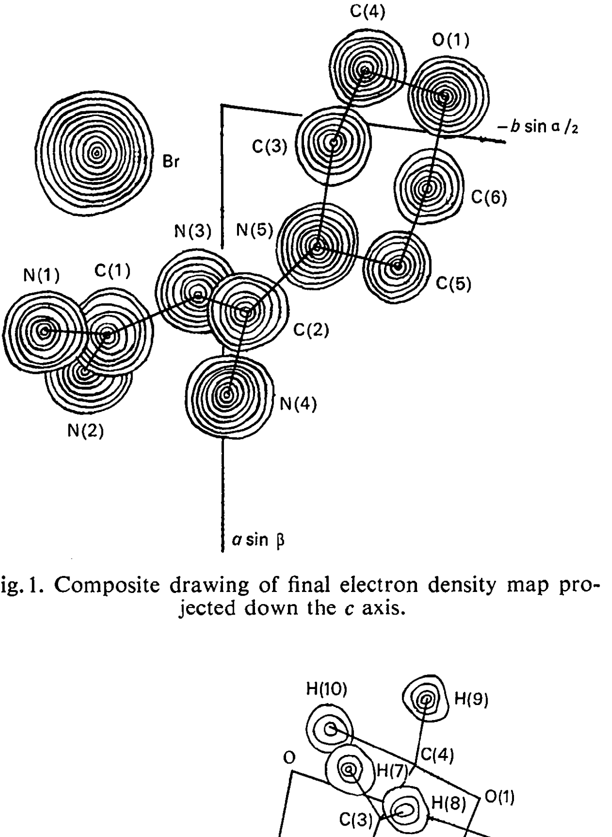

Fig. 1. Composite drawing of final electron density map projected down the *c* axis.

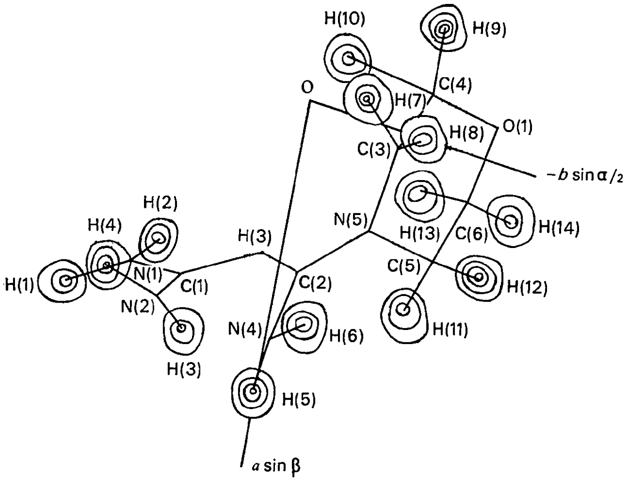

Fig. 2. Composite drawing of difference Fourier map projected down the *c* axis.

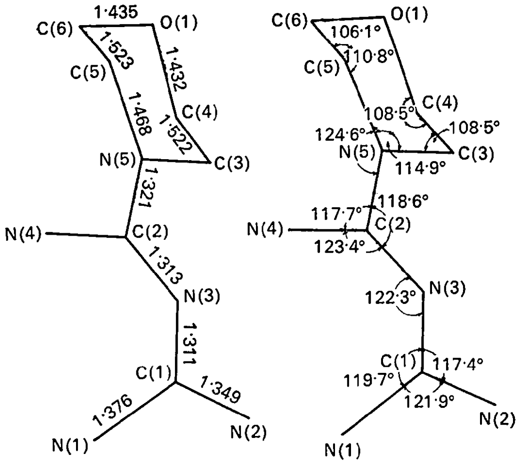

Fig. 3. Intramolecular bond lengths and bond angles.

Morpholine ring

The morpholine ring in MBHBr has been found to assume a chair conformation. As can be seen from Table 3(*a*), the lengths of the two C–C bonds, [C(3)–C(4), C(6)–C(5)], in the morpholine ring are almost equal; so are the two C–N bonds, [C(5)–N(5), C(3)–N(5)], and the two C–O bonds, [C(4)–C(1), O(1)–C(6)], the difference in each case being much less than the e.s.d.'s. The mean C–C (1·523 ± 0·005 Å), C–N (1·466 ± 0·003 Å) and C–O (1·433 ± 0·003 Å) bond lengths are in close agreement with the respective standard bond lengths 1·526 (Lide, 1962), 1·474 and 1·43 Å (Pauling, 1960). The bond angles [Table 3(*b*)] in the morpholine ring, except C(3)–N(5)–C(5), are not significantly different from the tetrahedral angle. The near equality of the bond lengths and angles in the morpholine rings of MBHCl and MBHBr indicates that the replacement of Cl by the heavier atom Br has not produced any extra deformation of the ring system.

The biguanide part of the molecule

A comparison of the carbon–nitrogen bond lengths in the biguanide part of the molecule [Table 3(*a*)] with the standard single, 1·474 Å (Lide, 1962), and double, 1·265 Å, C–N bond lengths indicate that they all have a mixture of single and double bond characters. An earlier study (Ray, 1961) has shown that the biguanide molecule can have a number of tautomeric forms (Fig. 4). Ultraviolet and infrared studies of metal biguanides (Sen, 1966) indicate the presence of a $-\underset{\mathrm{N}}{\underset{|}{\mathrm{C}}}{=}\mathrm{N}{-}\underset{\mathrm{N}}{\underset{\|}{\mathrm{C}}}-$ group in the biguanide molecule. This suggests that the tautomer form *B* is the most probable one for the present molecule. The probable resonance forms for this tautomer are given in Fig. 5. As the biguanide molecule is a resonance hybrid, all or some of these resonance forms are expected to contribute to the final form of the molecule. An examination of these forms indicates that the contributions of the forms *E* and *F* should be

Table 4. *Carbon–nitrogen bonds*

Bonds	Calculated bond character	Observed bond character	Observed length	Calculated length
C(1)–N(3)	1·485 Å	1·541 Å	1·311 ± 0·028 Å	1·319 Å
C(2)–N(3)	1·485	1·527	1·313 ± 0·036	1·319
C(2)–N(5)	1·300	1·476	1·321 ± 0·037	1·356*
C(1)–N(2)	1·300	1·331	1·349 ± 0·025	1·356
C(1)–N(1)	1·215	1·227	1·376 ± 0·026	1·379
C(2)–N(4)	1·215	1·237	1·373 ± 0·033	1·379

minimal, because they involve charge separation. A quantitative estimate of the contributions of each of these resonance forms has been made on the basis of the observed bond lengths in the present compound by using the relation (Donohue, 1956, 1970),

$$r_x = r_1 - (r_1 - r_2)3x/(2x+1)$$

where r_x is the calculated bond length for a particular double-bond character x. r_1 and r_2 are single and double-bond lengths respectively.

The above relation reduces to

$$x = \Delta r/(0{\cdot}627 - 2\Delta r)$$

where $\Delta r = r_1 - r_x$, r_x being the observed bond length.

Our calculation shows that the contributions of the forms *A*, *B*, *C*, *D*, *E* and *F* are 28·5, 19·5, 20·5, 28·5, 1·5 and 1·5% respectively. Within the limits of accuracy of our calculation, the forms *B* and *C* may be regarded as having an equal contribution of 20% each. The contributions thus assigned to the various forms appear to be reasonable both with regard to the attached group and the distribution of single and double bonds in each of these forms. The relevant bond lengths and bond characters calculated on the basis of the assigned contributions are given in Table 4.

Table 5. *Least-squares planes and deviations*

(*a*) Least-squares planes
The equations are:

Plane I: $-0{\cdot}7724X + 0{\cdot}4212Y - 0{\cdot}4752Z + 2{\cdot}4999 = 0$
Plane II: $0{\cdot}7218X - 0{\cdot}4283Y - 0{\cdot}5435Z - 0{\cdot}8401 = 0$
Plane III: $0{\cdot}298X + 0{\cdot}0600Y + 0{\cdot}9525Z - 2{\cdot}7521 = 0$

where *X*, *Y*, *Z* are orthogonal coordinates in Å.

(*b*) Atomic deviations (Å) from the planes

* Indicates the atoms not included in calculating the particular plane.

	Plane I	II	III
C(1)	−0·0565	−0·3626*	−0·0995
C(2)	−0·7339*	−0·0263	−0·0369
N(1)	0·0187	−1·5852*	0·8787
N(2)	0·0188	0·3737*	−0·6222
N(3)	0·0189	0·0091	−0·6984
N(4)	−1·9373*	0·0086	1·2415
N(5)	−0·3709*	0·0086	−0·6629

The angle between Plane I and Plane II is 118·6°,
Plane I and Plane III is 131·1°
Plane II and Plane III is 109·1°.

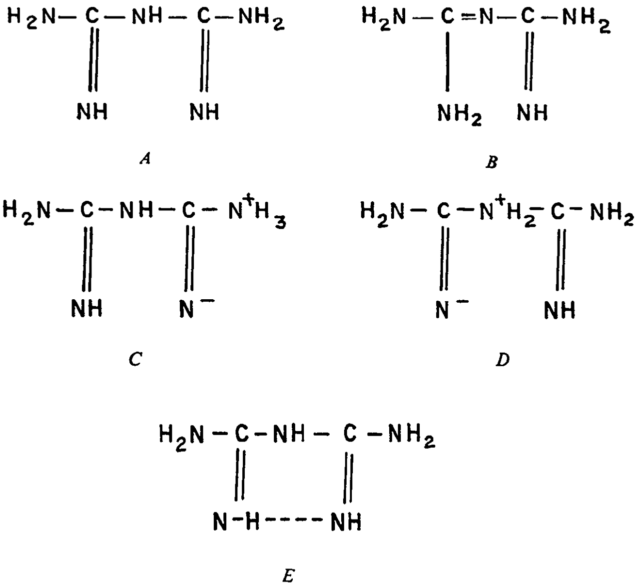

Fig. 4. Tautomeric forms of the biguanide molecule.

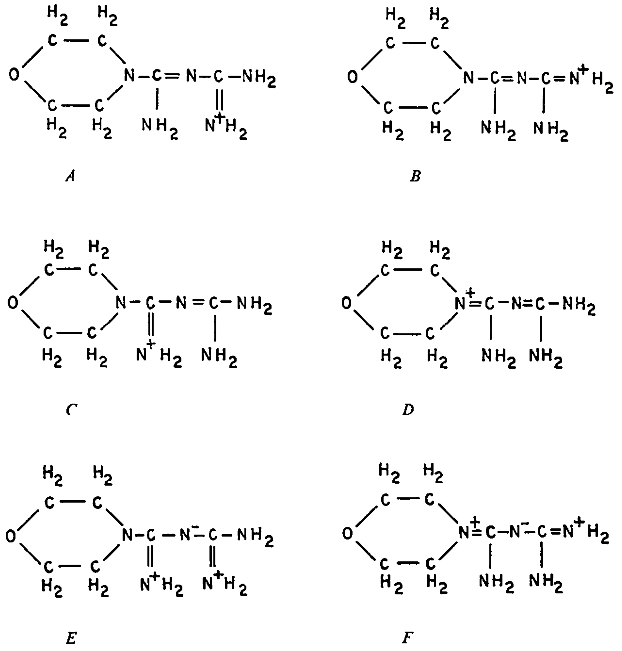

Fig. 5. Resonance forms of the morpholine biguanidium ion.

A comparison of the observed and calculated bond lengths (Table 4) shows that except for C(2)–N(5) the agreement is quite satisfactory, the average deviation being 0·006 Å. The observed discrepancy in the C(2)–N(5) bond lengths appears to be due to conjugation which occurs between the morpholine ring and the biguanide group through the C(2)–N(5) bond. Our calculation shows that the conjugation has increased the double-bond character by about 12 %, thus shortening the C(2)–N(5) bond length from the calculated value of 1·356 to 1·321 Å as obtained by our present X-ray study.

According to the distribution of bond lengths, the six C–N bonds in the biguanide part of the molecule may be classified under three groups, the longest (~1·379 Å) being C(1)–N(1) and C(2)–N(4), the shortest (~1·319 Å) being C(1)–N(3) and C(2)–N(3), and in between (~1·356) these two groups are the C(1)–N(2) and C(2)–N(5) bonds.

The sum of three N–C–N angles around C(1), *i.e.* N(1)–C(1)–N(2) (121·9°), N(1)–C(1)–N(3) (119·7°) and N(2)–C(1)–N(3) (117·4°) is 359° and that around C(2), *i.e.* N(3)–C(2)–N(4) (123·3°), N(3)–C(2)–N(5) (118·6°) and N(4)–C(2)–N(5) (117·7°) is 359·6°. This indicates the planarity of each of the individual guanidine groups of the biguanide.

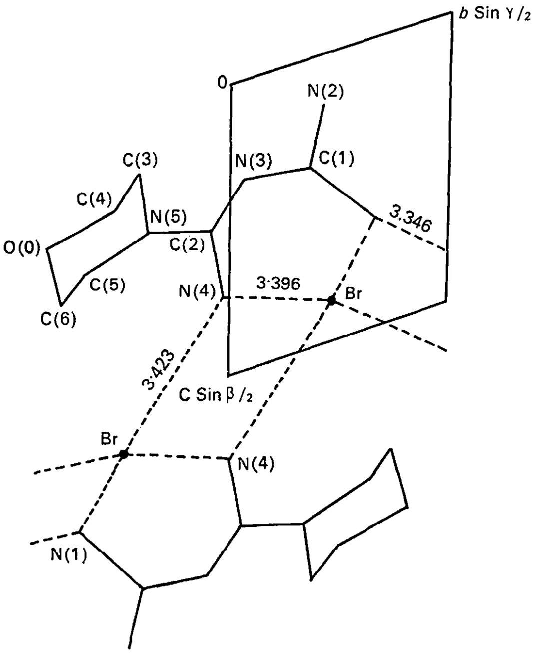

Fig. 6. Intermolecular packing viewed down the *a* axis.

The equations of the least-squares planes, calculated on an IBM 1130 using the *MPLN* program of Ahmed–Vickery, through each of the two guanidine groups and the biguanide as a whole, *i.e.* plane I defined by C(1), N(1), N(2) and N(3), plane II defined by C(2), N(3), N(4) and N(5) and plane III defined by C(1), C(2), N(1), N(2), N(3), N(4) and N(5) atoms, are given in Table 5 together with the deviations (Å) of the individual atoms from the planes. The atoms which are not included in defining the particular plane are marked with asterisks.

The sum of three C–N–C angles around N(5), *i.e.* C(2)–N(5)–C(3) (119·8°), C(2)–N(5)–C(5) (124·6°), C(3)–N(5)–C(5) (114·9°) is 359·3°. Of these three angles, the angle C(3)–N(5)–C(5) is of particular interest because of its occurrence within the morpholine ring. The values of the corresponding angle in some other compounds are: 115·1° in cycloalliin (Palmer & Lee, 1960), 112·3° in piperidine (Dutta Gupta & Saha, 1970, 1971), and 114·3° in MBHCl (Handa & Saha, 1971). The fact that the C(3)–N(5)–C(5) angle, [which, incidentally, is opposite the exocyclic bond C(2)–N(5)], is the smallest of the three angles around N(5) indicates the relatively higher double bond character of C(2)–N(5) which, in fact, has been obtained by us.

Two N–C–C angles, N(5)–C(3)–C(4) (108·0°) and N(5)–C(5)–C(6) (110·8°) are close enough to the tetrahedral value (109·5°). For comparison, the values of the corresponding N–C–C angles of similar rings in some other compounds are given, *e.g.* 110·1 and 112·1° in cycloalliin (Palmer *et al.*, 1960), 109·2 and 111·0° in α-prodine (Kartha, Ahmed & Barnes, 1960), 110·0 and 110·0° in piperazine (Schwarzenbach, 1968) and 108·0 and 109·5° in MBHCl (Handa & Saha, 1971). The two C–C–O angles, C(3)–C(4)–O(1) and C(5)–C(6)–O(1), have been found to be 108·5 and 106·1° respectively, the corresponing values in MBHCl being 109·5 and 110·0°. The value of the angle C(4)–O(1)–C(6) (112·5°) compares well with the C–O–C angle in α-glucose (111·0°) (McDonald & Beevers, 1952) and

Table 6. *Intermolecular bond distances and bond angles*

C(1)–N(1)–H(1)···Br^{i}	3·416±0·015	C(1)–N(1)–Br^{i}	142·7±1·17°
C(1)–N(1)–H(2)···Br^{ii}	3·346±0·015	C(1)–N(1)–Br^{ii}	114·9±1·12
C(2)–N(4)–H(5)···Br^{iii}	3·423±0·015	C(2)–N(4)–Br^{iii}	133·8±1·09
C(2)–N(4)–H(6)···Br^{iv}	3·296±0·015	C(2)–N(4)–Br^{iv}	125·9±1·08

Superscripts refer to coordinates of atoms in molecules 1 to 4; namely:

i	$1-x$	$1-y$	$1-z$
ii	x	y	z
iii	$1+x$	y	z
iv	$1-x$	$-y$	$1-z$

is not significantly different from that of MBHCl (109·6°).

Hydrogen bonds and intermolecular packing

The structure of MBHBr projected along the *a* axis is shown diagramatically in Fig. 6. The intermolecular bond distances involving hydrogen atoms are given in Table 6. The molecules are linked together by a three-dimensional network of hydrogen bonds of the type N–H···Br, lengths varying from $3{\cdot}346 \pm 0{\cdot}015$ to $3{\cdot}423 \pm 0{\cdot}015$ Å.

There are six hydrogen atoms in the molecule available for hydrogen bond formation *e.g.* two each at N(1), N(2) and N(4). It has been found that only four, two at N(1) and two at N(4), take part in forming hydrogen bonds with the Br ions. It may be noted that there is no acceptor available within the hydrogen bond forming distances of N(2). The distances $\mathrm{N(1)\cdots Br^{i}}$ and $\mathrm{N(1)\cdots Br^{ii}}$ are 3·416 and 3·346 Å respectively, while the angles $\mathrm{C(1)–N(1)–Br^{i}}$ and $\mathrm{C(1)–N(1)–Br^{ii}}$ are 142·7 and 114·9° respectively. The hydrogen atoms at N(4) form hydrogen bonds of lengths 3·423 and 3·396 Å with $\mathrm{Br^{iii}}$ and $\mathrm{Br^{iv}}$ respectively and the angles $\mathrm{C(2)–N(4)–Br^{iii}}$ and $\mathrm{C(2)–N(4)–Br^{iv}}$ and 113·8 and 128·9° respectively.

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Structure Cristalline de $C_6H_{12}SnSO_2$, Composé d'Insertion d'Anhydride Sulfureux dans une Liaison Carbone–Etain

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$C_6H_{12}SnSO_2$ crystallizes in space group $P2_1/n$, with $a=9{\cdot}72$, $b=11{\cdot}24$, $c=9{\cdot}18$ Å; $\beta=95{\cdot}33°$ and $Z=4$. The structure was solved by the heavy-atom technique. X-ray intensity data were collected with a manual diffractometer and refined by the full-matrix least-squares method to a final *R* of 0·065 for 509 reflexions. The crystal structure consists of infinite chains parallel to [101]. These chains are formed by oxygen bridges linking tin and sulphur atoms. The tin atoms are five-coordinated.

Introduction

Le composé $(CN_3)_3Sn–O–S(O)–CH_2–C{\equiv}CH$ fait partie de la série des produits d'insertion étudiés par Fong & Kitching (1970). A partir d'études de spectroscopie infrarouge, ces auteurs ont avancé plusieurs hypothèses structurales possibles.

Nous avons entrepris l'étude cristallographique du composé pour lever l'indétermination qui subsistait sur sa conformation moléculaire. Ce composé fait partie d'une série qui a été synthétisé au laboratoire de Chimie Organique de l'Ecole Nationale Supérieure de Chimie de Paris.

Partie expérimentale

Les cristaux sont obtenus par recristallisation dans le méthanol; ce sont des parallèlépipèdes transparents et instables. Voici les principales données cristallographiques:

Formule brute	$C_6H_{12}SnSO_2$
Masse moléculaire	266,91
Système cristallin	Monoclique
Groupe spatial	$P2_1/n$
a	9,72 (1) Å
b	11,24 (2)