THE MOLECULAR AND CRYSTAL STRUCTURE OF BENZAMIDINIUM BROMOACETATE

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The molecular and crystal structure of benzamidinium bromoacetate was solved on the basis of Patterson and Fourier synthesis. The positions of all the atoms were localized and the least squares method was employed to refine the coordinates of all the atoms together with their thermal vibration parameters. A final R factor value of 0·067 was obtained for 1 349 observed reflections ($I > 1·96\sigma(I)$). The substance crystallizes in the $P2_1/n$ monoclinic space group with lattice parameters of $a = 1\,145·7(2)$, $b = 1\,571·3(3)$, $c = 578·3(1)$ pm, $\gamma = 90·65(1)°$, $Z = 4$. Intramolecular hydrogen bonds form ion pairs in the structure between the nitrogen atoms of the amidinium group and the oxygen atoms of the bromoacetate. Intermolecular hydrogen bonds, also between nitrogen and oxygen atoms, connect the molecules in an infinite chain. The molecular chains are joined together by van der Waals forces. The N···O distance in the hydrogen bonds varies between 280·3(8) and 284·5(8) pm.

Study of the bonds between the amidinium group and the carboxyl in nonnative (model) molecules is important for the clarification of some biocatalytic processes. The amidinium–carboxylate complex is present in capture of a substrate containing a carboxyl group in lactate dehydrogenase[1,2], carboxypeptidase[3], adenosine triphosphatase[4], malate dehydrogenase[5], aldehydereductase[6], and other enzymes[7]. It has been pointed out by Smrčková[8] that compounds containing amidinium--carboxylate bonds can be divided into four groups: amidinium carboxylates, guanidinium (N-amidinium) carboxylates, carboxylates of S-substituted isothioureas (S-amidines), and carboxylates of O-substituted isoureas (O-amidines). The structures of guanidinium carboxylates have so far been studied most extensively, probably because guanidines are chemically closely related compounds present in living matter and N-amidinium carboxylates are fragments in the enzyme–substrate or enzyme–coenzyme interaction. Benzamidinium bromoacetate, studied in this work, is an amidinium carboxylate, for which three structures have so far been

described in the literature, bis(acetamidinium) carbonate monohydrate[9], formamide oxime oxalate[10], and benzamidinium pyruvate[11]. The structure of bis(acetamidinium)carbonate monohydrate contains hydrogen bonds between the amino groups and the water molecules acting as hydrogen donors and carbonate oxygens as acceptors. These contacts produce a pleated-sheet arrangement of the molecules of this compound. The structure of formamide oxime oxalate contains a complex system of 2-, 3-, and 4-centred hydrogen bonds between the oxalate ions and the hydroxy-formamidinium ions[10]. The benzamidinium pyruvate structure contains both intra-molecular hydrogen bonds, forming the amidinium–carboxylate attraction, and also intermolecular hydrogen bonds connecting the molecules in chains. Solution of the structure of the studied compound, benzamidinium bromoacetate, contributes to better understanding of the amidinium–carboxylate attraction mechanism and its effect in a number of substituted benzamidines.

EXPERIMENTAL

Benzamidinium bromoacetate was prepared by the reaction of potassium bromoacetate[12] with benzamidinium chloride[13]. The crystals formed were recrystallized from an ethanol–acetone mixture. For $C_9H_{11}BrN_2O_2$ (259·1) calculated: 41·72% C, 4·28% H, 30·48% Br, 10·81% N; found: 42·06% C, 4·43% H, 30·34% Br, 10·81% N. The density of the substance was measured by the flotation method in a bromoform–toluene mixture at 24°C. Preliminary values of the lattice parameters and symmetry space group were found from Weissenberg patterns (reflection absences: $kh0$: $h + k = 2n + 1$, $00l$: $l = 2n + 1$). The studied crystal with dimensions of $0·09 \times 0·25 \times 0·5$ mm was measured on a four-circle Hilger and Watts diffractometer. MoK$_\alpha$ radiation, $\lambda = 71·069$ pm, filtered through a Zr filter, was used in the measurement. The lattice parameter values were refined from a set of 25 centred reflections. The intensities were measured using the $\omega/2\Theta$ scanning technique at laboratory temperature. A total of 1 826 reflections were measured in the reciprocal space quadrants: $-13 \leqq h \leqq 13$, $0 \leqq k \leqq 18$, $0 \leqq l \leqq 6$, where the scan rate varied in dependence on the reflection intensity from 2°/min to 12°/min. The intensities of three standard reflections did not vary during the measurement. On the basis of condition $I < 1·96\sigma(I)$, only 1 349 reflections were considered observed. The corrections for absorption and extinction were negligible.

The structure was solved by the Patterson and Fourier technique and the positions of the hydrogen atoms were obtained from the difference map. The function $\sum w(|F_o| - |F_c|)^2$ was minimized in parameter refinement by the full-matrix least squares method. The final weighting scheme had the form $w = 1·3944/(\sigma^2(F_o) + 0·0009F_o^2)$. Refinement yielded the values $R^* = 0·067$ and $wR^{**} = 0·066$ for 1 349 observed reflections. The residual maximum on the final difference map equalled $0·99$ e/(100 pm)^3. Calculations were carried out using the SHELX 76 program (ref.[14]) and the PARST program (ref.[15]) using an EC 1 033 computer.

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* $R = \sum|\Delta F|/\sum|F_o|$, ** $wR = (\sum|w \, \Delta F|^2/\sum w|F_o|)^{1/2}$

TABLE I

Basic crystallographic data, e.s.d.'s in parentheses

$a = 1\ 145 \cdot 7(2)$ pm	$\varrho_0 = 1\ 657$ kg m^{-3}
$b = 1\ 571 \cdot 3(3)$ pm	$\varrho_c = 1\ 653$ kg m^{-3}
$c = 578 \cdot 3(1)$ pm	space group: $P2_1/n$
$\gamma = 90 \cdot 65(1)$ °	$\mu(\text{MoK}_\alpha) = 3 \cdot 88$ mm^{-1}
$V = 1\ 041 \cdot 0(3) . 10^6$ pm^3	$F(000) = 520$
$Z = 4$	

TABLE II

The fractional coordinates of the nonhydrogen (. 10^4) and hydrogen (. 10^3) atoms and their equivalent and isotropic temperature parameters. $U_{eq} = (U_{11} + U_{22} + U_{33} + 2U_{12} \cos\gamma)/3$ (e.s.d.'s in parentheses)

Atom	x	y	z	U_{eq}, pm^2
Br	1 133(1)	4 300(1)	7 164(1)	601(3)
O1	2 500(5)	3 725(3)	2 932(9)	533(17)
O2	3 430(5)	4 936(3)	2 175(10)	604(18)
N1	3 554(5)	2 821(4)	−769(12)	461(21)
N2	4 522(6)	4 067(4)	−1 472(12)	467(20)
C1	2 074(9)	4 968(6)	5 087(20)	636(28)
C2	2 713(5)	4 498(4)	3 257(12)	398(21)
C3	4 353(5)	3 251(5)	−1 914(12)	375(20)
C4	5 067(5)	2 829(4)	−3 640(11)	351(20)
C5	5 451(6)	3 293(4)	−5 543(13)	437(22)
C6	6 190(7)	2 916(6)	−7 150(13)	503(25)
C7	6 531(7)	2 096(6)	−6 877(16)	556(31)
C8	6 139(6)	1 628(5)	−5 008(13)	461(23)
C9	5 398(6)	1 991(4)	−3 419(13)	421(22)
				$U_{iso} . 10^{-1}$, pm^2
H1N1	328(5)	302(4)	37(12)	26(18)
H2N1	331(6)	231(5)	−108(14)	59(23)
H1N2	411(5)	428(3)	−57(10)	12(15)
H2N2	521(7)	434(5)	−228(13)	61(23)
H1C1	188(11)	541(8)	518(23)	108(48)
H2C1	137(8)	521(6)	417(16)	71(27)
HC5	521(6)	393(5)	−587(14)	66(23)
HC6	642(6)	325(4)	−815(13)	40(21)
HC7	698(8)	188(6)	−759(15)	65(30)
HC8	642(5)	105(4)	−470(11)	34(17)
HC9	536(8)	160(6)	−226(15)	78(31)

RESULTS AND DISCUSSION

The basic crystallographic data for benzamidinium bromoacetate are given in Table I. Table II gives a survey of the final atomic coordinates together with their equivalent and isotropic temperature factors. Table III lists the interatomic distances.

The structure of benzamidinium bromoacetate is very similar to that of benzamidinium pyruvate[11]. The amidinium and carboxylic parts of the molecule are connected through two intramolecular hydrogen bonds through the H1N1 and H1N2 atoms

TABLE III

The interatomic distances (pm) and angles (°). E.s.d.'s in parentheses. Symmetry code: i) x, $1/2 - y$, $z - 1/2$; ii) $1 - x$, $1 - y$, $-z$

C1—Br	191·8(10)	H1Cl—C1—Br	107(10)
C1—H1Cl	73(12)	H2Cl—C1—Br	95(5)
C1—H2Cl	104(9)	H2Cl—C1—H1Cl	56(11)
C1—C2	148·8(12)	H1Cl—C1—C2	133(10)
C2—O1	124·9(8)	H2Cl—C1—C2	102(5)
C2—O2	123·6(8)	O1—C2—O2	125·9(6)
N1—H1N1	80(7)	O1—C2—C1	119·8(6)
N1—H2N1	87(8)	O2—C2—C1	114·3(6)
N1—C3	131·1(9)	H2N1—N1—H1N1	115(7)
N2—H1N2	78(6)	H1N1—N1—C3	119(4)
N2—H2N2	101(8)	H2N1—N1—C3	126(5)
N2—C3	131·8(8)	H1N2—N2—H2N2	128(6)
C3—C4	145·6(9)	H1N2—N2—C3	117(4)
C4—C9	137·9(9)	H2N2—N2—C3	115(4)
C9—HC9	91(9)	N1—C3—C4	120·3(6)
C9—C8	137·9(10)	N2—C3—C4	119·9(6)
C8—HC8	98(6)	N1—C3—N2	119·8(6)
C8—C7	138·0(12)	C3—C4—C9	122·2(6)
C7—HC7	75(9)	C3—C4—C5	118·6(6)
C7—C6	136·0(13)		
C6—HC6	82(7)		
C6—C5	139·4(11)		
C5—HC5	105(8)		
C5—C4	138·9(10)		

Hydrogen bonds

N1···O1	284·5(8)	N1—H1N1···O1	170(6)
N1···O1^i	280·3(8)	N1—H2N1···O1^i	168(6)
N2···O2	281·4(9)	N2—H1N2···O2	165(6)
N2···O2^{ii}	283·6(9)	N2—H2N2···O2^{ii}	150(6)

(Fig. 1). The equatorial hydrogen atoms in the amidine group (H2N1 and H2N2) form intermolecular hydrogen bonds (Fig. 2) connecting the compound molecules in infinite chains lying in the [110] direction in the structure. The chains are bonded together by van der Waals forces. The length of the N···O bonds in benzamidinium bromoacetate vary in the range from 280·3(8) to 284·5(8) pm; this distance is some-
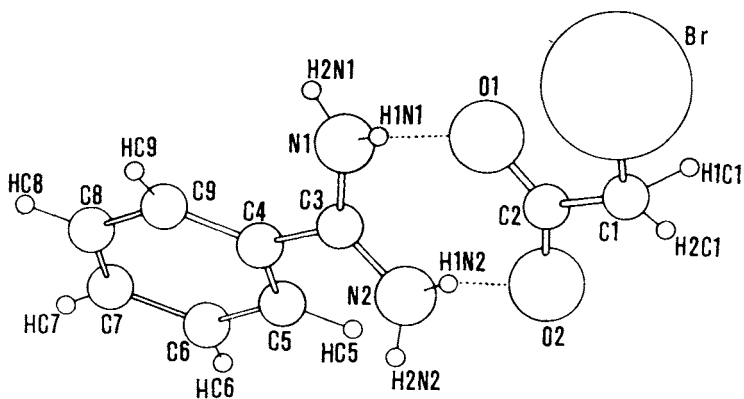

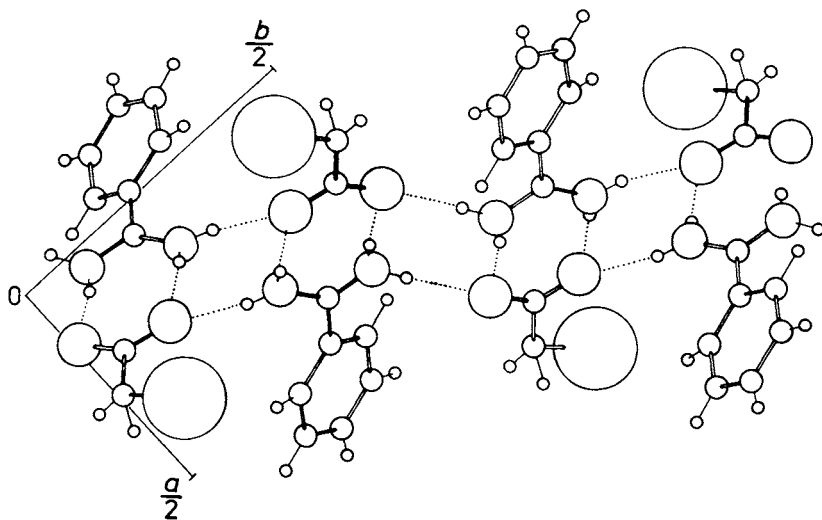FIG. 1

The benzamidinium bromoacetate molecule

FIG. 2

Projection of the structure onto the *xy* plane. Dotted lines correspond to hydrogen bonds

TABLE IV

Optimal least squares planes fitted through the atoms in the molecule. Each plane is defined as: $AX + BY + CZ + D = 0$. E.s.d.'s in parentheses

Atom	Deviation from the plane, pm	Atom	Deviation from the plane, pm	Atom	Deviation from the plane, pm
	Plane I[a]		Plane II[b]		Plane III[c]
C4	$-1 \cdot 0(6)$	C3	$-0 \cdot 1(6)$	O1	$-0 \cdot 4(6)$
C5	$0 \cdot 7(7)$	N1	$0 \cdot 2(6)$	C2	$0 \cdot 9(6)$
C6	$0 \cdot 4(8)$	N2	$0 \cdot 0(7)$	O2	$-0 \cdot 6(6)$
C7	$-0 \cdot 6(9)$	H1N1	$-16(7)$	H1N1	$2(7)$
C8	$-0 \cdot 4(7)$	H1N2	$4(6)$	H1N2	$19(6)$
C9	$-1 \cdot 3(7)$				

[a] $-0 \cdot 792(2) X - 0 \cdot 306(3) Y - 0 \cdot 529(3) Z - 4 \cdot 79(2) = 0$; $\chi^2 = 8 \cdot 25$; [b] $-0 \cdot 682(7) X + 0 \cdot 234(7) Y - 0 \cdot 692(9) Z - 1 \cdot 40(3) = 0$; $\chi^2 = 5 \cdot 95$; [c] $-0 \cdot 724(6) X + 0 \cdot 248(6) Y - 0 \cdot 644(8) Z - 1 \cdot 66(4) = 0$; $\chi^2 = 13 \cdot 80$.

what greater in benzamidinium pyruvate, and equals $277 \cdot 9(3) - 289 \cdot 8(3)$ pm. Three optimal planes can be drawn through the atoms in the benzamidinium bromoacetate molecule (Table IV). Plane I passes through the atoms of the benzene ring, plane II passes through the amidine group and includes the C3, N1, N2, H1N1 and H1N2 atoms, and plane III contains the carboxyl C2, O1, O2 and H1N1 and H1N2 atoms. Plane I is rotated by $33 \cdot 4(4)°$ relative to plane II (in benzamidinium pyruvate this angle equals $35 \cdot 2(3)°$). The angle of rotation of planes I and II corresponds closely to the appropriate torsion angles C9—C4—C3—N1: $33 \cdot 5(1 \cdot 0)°$ and C5—C4—C3—N2: $32 \cdot 9(9)°$. The angle between the II and III planes equals $3 \cdot 7(6)°$. The value $5 \cdot 6(3)°$ was found for this angle in the benzamidinium pyruvate structure[11]. Both of these values are in good agreement with quantum chemical calculations[16]. Geometrically, the amidinium–carboxylate contact appears slightly "bent" along the H1N1—N1N2 connecting line in both compounds. The O1—C2—C1—Br and O2—C2—C1—Br torsion angles have values of $9 \cdot 7(1 \cdot 0)°$ and $9 \cdot 7(6)°$, respectively. It follows from comparison of the geometric characteristics of the amidinium–carboxylate contact in benzamidinium bromoacetate and benzamidinium pyruvate that there are no great differences between these two compounds.

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