Acta Crystallographica Section C
Crystal Structure Communications
ISSN 0108-2701

Benzdiamidine

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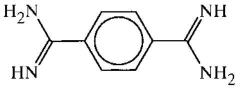
Received 18 June 2001
Accepted 3 September 2001

The molecule of benzene-1,4-dicarboxamidine or benzdiamidine, $C_8H_{10}N_4$, reveals C_i symmetry. Hydrogen bonds utilize the amino groups as double donors, whereas the imino groups act as double acceptors. The network formed is similar to that observed in the crystal packing of terephthalamide.

Comment

In the successful design of molecular solids, it is of primary interest to identify molecular functionalities that will generate predictable intermolecular interactions (Nguyen *et al.*, 1998). Many functional groups have been analysed with respect to their ability to form recognizable structural patterns (Desiraju, 1995). Among these, the amidine group appears to possess a very good functionality for hydrogen bonding, generating supramolecular aggregates. A high predominance of the protonated form has been detected in crystal structures. In the light of this, the molecular and crystal structures of benzdiamidine, (I), are presented here.



(I)

The molecule of (I) has C_i symmetry with *anti*-disposed amidine groups (Fig. 1). The dihedral angle between the benzene ring and the amidine group is 24.52 (9)°, close to the value observed in benzamidine, (II) (22.71°; Barker *et al.*, 1996). In both molecules, deviations from planarity are a consequence of an overcrowding effect, *i.e.* steric hindrances between the H atoms of the aromatic ring and the amidine moieties.

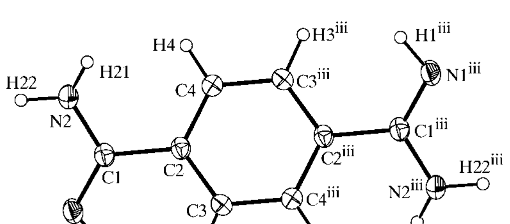


Figure 1
The molecular structure of (I) with the atom-numbering scheme and 30% probability displacement ellipsoids (Johnson, 1976). H atoms are shown as small spheres of arbitrary radii [symmetry code: (iii) $1 - x, 1 - y, 1 - z$].

In the crystal structure of (I), the molecules are connected into an infinite two-dimensional hydrogen-bonding network (Fig. 2). In forming the hydrogen bonds, the H atoms donated to the imino group are oriented toward its lone pairs (Ermer & Eling, 1994). Thus, the hybridization of the atomic orbitals of nitrogen N1 should also possess some sp^3 character. As shown in Fig. 2, all the bonds of the imino N atom, together with its hydrogen bonds, are oriented towards the vertices of a distorted tetrahedron. The C1—N1—H1 angle of 111.0 (15)° is close to the sp^3-hybridization value (Table 1). A similar situation has been observed in the crystal structures of acetamidine (Norrestam *et al.*, 1983) and (II).

The amino N atoms are double donors, while the imino N atoms are double acceptors, and the H atoms of the imino groups are not involved in any hydrogen bonds. Generally, there are two types of hydrogen bonds in the three structures, N_{amino}—*anti*-H$\cdots N_{imino}$ and N_{amino}—*syn*-H$\cdots N_{imino}$ (Table 2). Motifs generated by the first type of hydrogen bond have different characters in these three structures. In the structure of acetamidine, the motif is a helical chain with a $C(4)$ graph-set descriptor (Etter *et al.*, 1990). In the structure of (II), the motif is a ring pattern, graph-set descriptor $R_4^4(16)$, and in (I), it is a centrosymmetrical ring, graph-set descriptor $R_2^2(8)$ (Fig. 2). Benzamidine, (II), does not form a centrosymmetrical $R_2^2(8)$ ring pattern; its imino H atom is in an *anti* position and it would be very close to the *anti*-amino H atom of a neigbouring molecule, so the formation of an $R_2^2(8)$ motif is not favoured.

The second type of hydrogen bond (with a *syn*-amino H atom) for (I) and (II) is characterized by a one-dimensional $C(4)$ chain. The combined first-level graph-set descriptor of the hydrogen-bonding network in (I) is $C(4)R_2^2(8)$, typical of primary amides (Etter *et al.*, 1990). From this analogy, it can be expected that the hydrogen-bonding network in (I) is similar to that in the crystal structure of terephthalamide (Cobbledick & Small, 1972). In these two structures, the combined first-

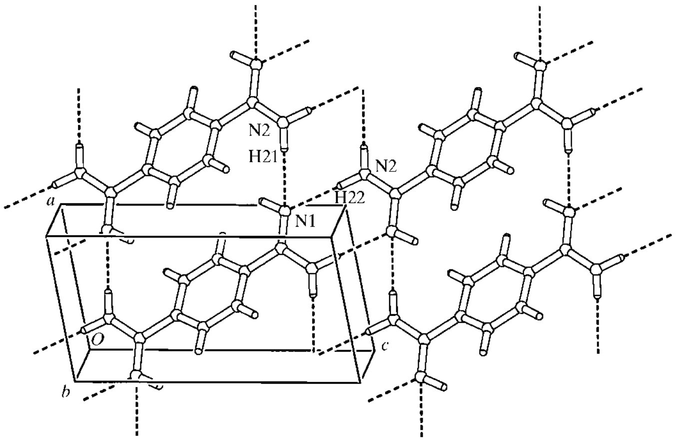


Figure 2
Part of the crystal structure of (I) showing the formation of the two-dimensional hydrogen-bonding network.

level graph-set descriptors and all higher level graph-set descriptors are identical. In spite of this, these two structures are not isostructural; terephthalamide crystallizes in space group $P\overline{1}$ and (I) crystallizes in $P2_1/c$. This example shows that identical graph-set descriptors for all levels of hydrogen-bonding patterns in two crystal structures do not necessarily imply isostructural crystals.

According to the concept of saturated hydrogen bonding (SHB) and complementarity in the number of donors and acceptors (Ermer & Eling, 1994; Loehlin *et al.*, 1998), it is evident that, for molecules having amidine groups only, hydrogen-bond donors prevail. This implies that some donors (imino N) are not saturated, as observed in the crystal structures of acetamidine, (I) and (II). Only with additional acceptors in the molecule or in cocrystallized molecules is the imino H atom activated as a hydrogen-bond donor, as in the structure of the cocrystal of (II) with 2,6-diisopropyl-5,5-dimethyl-4-carboxymethoxide (Marsura *et al.*, 1984).

Experimental

Crystals of (I) suitable for X-ray diffraction were grown from a solution of benzdiamidine hydrochloride (150 mg, 0.64 mmol) in water (5 ml) after addition of 1,8-diazabicyclo[5.4.0]undec-7-ene (0.2 ml). The benzdiamidine hydrochloride was prepared according to the procedure described by Felix *et al.* (1997).

Crystal data

$C_8H_{10}N_4$
$M_r = 162.20$
Monoclinic, $P2_1/c$
$a = 5.0570$ (4) Å
$b = 7.9646$ (5) Å
$c = 9.7226$ (9) Å
$\beta = 100.702$ (7)°
$V = 384.79$ (5) Å^3
$Z = 2$
$D_x = 1.400$ Mg m^{-3}
Cu $K\alpha$ radiation
Cell parameters from 23 reflections
$\theta = 40.1$–$45.5°$
$\mu = 0.74$ mm^{-1}
$T = 293$ K
Prism, colourless
0.20 × 0.15 × 0.10 mm

Data collection

Enraf–Nonius CAD-4 diffractometer
$\omega/2\theta$ scans
Absorption correction: ψ scan (*PLATON*; Spek, 1999)
$T_{\min} = 0.885$, $T_{\max} = 0.973$
870 measured reflections
783 independent reflections
657 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.015$
$\theta_{\max} = 74°$
$h = 0 \rightarrow 6$
$k = 0 \rightarrow 9$
$l = -12 \rightarrow 11$
3 standard reflections
frequency: 120 min
intensity decay: 2%

Refinement

Refinement on F^2
$R(F) = 0.040$
$wR(F^2) = 0.118$
$S = 1.03$
783 reflections
76 parameters
All H-atom parameters refined
$w = 1/[\sigma^2(F_o^2) + (0.0747P)^2 + 0.0747P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} < 0.001$
$\Delta\rho_{\max} = 0.24$ e Å^{-3}
$\Delta\rho_{\min} = -0.20$ e Å^{-3}
Extinction correction: *SHELXL*97 (Sheldrick, 1997)
Extinction coefficient: 0.011 (4)

Table 1
Selected geometric parameters (Å, °).

N1—C1	1.283 (2)	C1—C2	1.4981 (15)
N2—C1	1.3491 (18)		
C1—N1—H1	111.0 (15)	N1—C1—C2	124.40 (12)
N1—C1—N2	119.54 (11)	N2—C1—C2	116.05 (13)
N1—C1—C2—C3	−25.3 (2)	N2—C1—C2—C4	−23.8 (2)

Table 2
Hydrogen-bonding geometry (Å, °).

D—H···A	D—H	H···A	D···A	D—H···A
N2—H21···N1$^{\rm i}$	0.88 (3)	2.49 (3)	3.298 (2)	153 (2)
N2—H22···N1$^{\rm ii}$	0.934 (19)	2.082 (19)	3.0154 (15)	178 (2)

Symmetry codes: (i) $1 + x, y, z$; (ii) $-x, 1 - y, -z$.

Data collection: *CAD*-4 *EXPRESS* (Enraf–Nonius, 1992); cell refinement: *CAD*-4 *EXPRESS*; data reduction: *HELENA* (Spek, 1997); program(s) used to solve structure: *SIR*97 (Altomare *et al.*, 1999); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *PLATON* (Spek, 1999); software used to prepare material for publication: *PLATON*.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: AV1083). Services for accessing these data are described at the back of the journal.

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