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## Dimeric Hydrogen-Bonded Structure of Bis(3-fluorophenylmethine)carbonohydrazide

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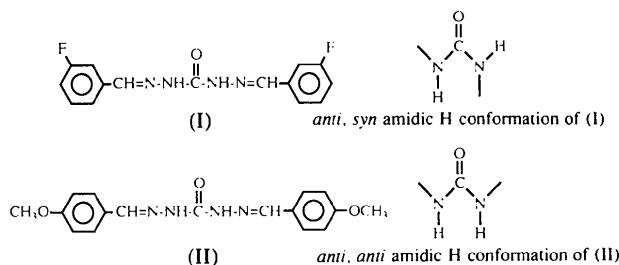
### Abstract

The title carbazone,  $C_{15}H_{12}F_2N_4O$  (I), was found to be an intermolecularly hydrogen-bonded centrosymmetric dimer. [For a discussion of CAS/IUPAC nomenclature of carbazones see Grasselli & Weast (1989). In *Handbook of Data on Organic Compounds*, 2nd edition, Vol. I, Introduction, §§190, 252. Florida: CRC Press.] This is in contrast to the only other reported X-ray structure of a related carbazone, which was a non-centrosymmetric infinite hydrogen-bonded polymeric structure. The monomer unit of compound (I) is neither planar nor symmetrical. One amidic H atom is *anti* to the carbonyl O atom while the other is *syn*. The *syn* amidic H atom and the carbonyl O atom form strong hydrogen bonds with the respective atoms of a second molecule to produce an eight-membered ring which links the two monomeric units. The intermolec-

ular N—H...O hydrogen-bond distances are 2.01 (2) Å for H...O and 2.873 (3) Å for N...O, and the N—H...O angle is 172 (2)°. The *anti* amidic H atom of compound (I) is not involved in hydrogen bonding.

### Comment

Extending the study to deduce a relationship between Raman and IR carbonyl frequencies of a series of carbazones in the solid state with variations in the nature of their intermolecular hydrogen bonding (Kolb, Janota, Dantzman, Kozenski & Strommen, 1992), we initiated an investigation of their X-ray structures (Kolb, Meyers & Robinson, 1993). Our recent report on the crystal structure of bis(4-methoxyphenylmethine)carbonohydrazide, (II), describes its non-centrosymmetric infinite hydrogen-bonded polymeric nature (Kolb, Robinson & Meyers, 1994). We now report the X-ray crystal structure of the related compound bis(3-fluorophenylmethine)carbonohydrazide, (I).



Although molecules of compounds (I) and (II) are closely related, the first striking difference exhibited by their crystal structures is seen in the fact that in (I) one of the amidic H atoms is *anti* to the carbonyl O atom and the other is *syn*, while in (II) both amidic H atoms are *anti*. This difference in monomer conformation gives rise to the second striking difference, *i.e.* the availability of one *syn* amidic H atom per molecule of (I) permits reciprocal hydrogen bonding between two molecules via their respective *syn* amidic H atoms and carbonyl O atoms, the latter bridging with a single H atom, to provide the observed dimeric crystal structure in which the common linkage is an eight-membered ring. As shown in Fig. 1, the two molecules of a dimeric pair are related by a center of symmetry. The following characteristics of the eight-membered hydrogen-bonded dimer bridge are noted: (a) the torsion angle O1—C8—N2—H6 is  $-9(2)^\circ$ ; (b) the planes O1—C8—N2 and O1<sup>i</sup>—C8<sup>i</sup>—N2<sup>i</sup> are parallel and are offset (one above the other) by 0.65 Å; (c) Atoms H6 and H6<sup>i</sup> lie between the N2—C8—O1 and N2<sup>i</sup>—C8<sup>i</sup>—O1<sup>i</sup> planes, essentially on the N2...O1 and N2<sup>i</sup>...O1<sup>i</sup> vectors, respectively; (d) the N—H...O intermolecular hydrogen bond has H...O and N...O distances of 2.01 (2) and 2.873 (3) Å, respectively, and an N—H...O bond angle of 172 (2)°. Only the *syn* amidic H atom of compound (I) is involved in hydrogen bonding, while in (II), which

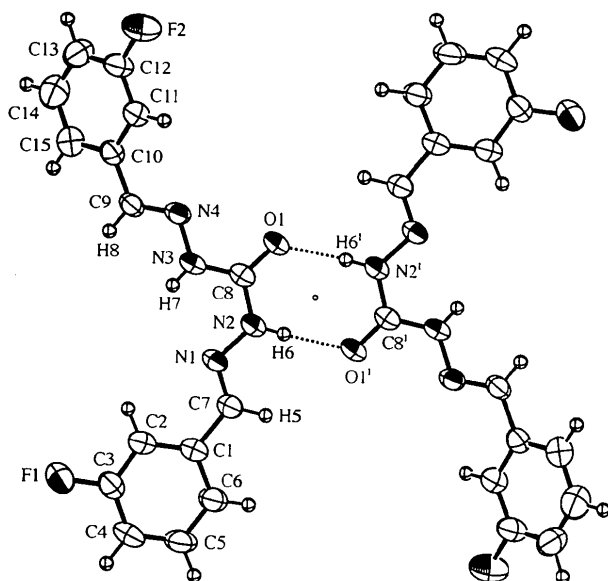


Fig. 1. Molecular configuration, hydrogen bonding and atom-numbering scheme with displacement ellipsoids at the 50% probability level. H atoms are shown as isotropic spheres of arbitrary radii. Superscripted atoms are related to their non-superscripted equivalents by a center of symmetry (shown as a small circle in the center of the figure).

does not possess a *syn* amidic H atom, both *anti* amidic H atoms are strongly hydrogen bonded to the same O atom of another molecule.

The crystal structures of related carbazones will be published shortly. The relationship between their hydrogen-bonding patterns and the carbonyl frequencies in their Raman and IR spectra will be described elsewhere.

## Experimental

A solution of *m*-fluorobenzaldehyde (694 mg, 5.6 mmol) and carbazide (252 mg, 2.8 mmol) in 20 ml of ethanol was refluxed overnight. The cooled solution yielded a mass of colorless crystals of compound (I) which were collected by filtration, recrystallized from ethanol to a constant melting point (492–494 K) and used for the X-ray study.

### Crystal data

C<sub>15</sub>H<sub>12</sub>F<sub>2</sub>N<sub>4</sub>O

*M<sub>r</sub>* = 302.28

Triclinic

*P* $\bar{1}$

*a* = 7.805 (1) Å

*b* = 15.157 (2) Å

*c* = 6.094 (1) Å

$\alpha$  = 100.90 (1)°

$\beta$  = 92.99 (1)°

$\gamma$  = 86.71 (1)°

*V* = 706.1 (4) Å<sup>3</sup>

*Z* = 2

*D<sub>x</sub>* = 1.422 Mg m<sup>-3</sup>

Mo *K*α radiation

$\lambda$  = 0.71069 Å

Cell parameters from 25 reflections

$\theta$  = 8.7–12.4°

$\mu$  = 0.105 mm<sup>-1</sup>

*T* = 296 K

Fragment

0.41 × 0.27 × 0.22 mm

Colorless

### Data collection

Rigaku AFC-5S diffractometer

$\omega$  scans (3° min<sup>-1</sup>)

Absorption correction: none

2684 measured reflections

2483 independent reflections

1814 observed reflections

[*I* > 1.5σ(*I*)]

*R*<sub>int</sub> = 0.014

$\theta_{\max}$  = 25°

*h* = 0 → 9

*k* = -18 → 18

*l* = -7 → 7

3 standard reflections

monitored every 100 reflections

intensity decay: none

### Refinement

Refinement on *F*

*R* = 0.044

*wR* = 0.051

*S* = 1.92

1814 reflections

212 parameters

H-atom parameters not refined

*w* = 4*F*<sub>o</sub><sup>2</sup>/σ<sup>2</sup>(*F*<sub>o</sub><sup>2</sup>)

(Δ/σ)<sub>max</sub> = 0.0003

Δρ<sub>max</sub> = 0.25 e Å<sup>-3</sup>

Δρ<sub>min</sub> = -0.26 e Å<sup>-3</sup>

Extinction correction:

Zachariasen (1967) Type

II, Gaussian isotropic

Extinction coefficient:

0.42 (7) × 10<sup>-5</sup>

Atomic scattering factors

from *International Tables*

for X-ray Crystallography

(1974, Vol. IV, Table

2.3.1)

Table 1. Fractional atomic coordinates and equivalent isotropic displacement parameters (Å<sup>2</sup>)

$$U_{eq} = (1/3)\sum_i\sum_j U_{ij}a_i^*a_j^*a_i \cdot a_j$$

	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> <sub>eq</sub>
F1	1.1221 (2)	0.3782 (1)	1.5520 (2)	0.076 (1)
F2	0.2851 (3)	1.0353 (1)	1.2039 (3)	0.129 (1)
O1	0.4766 (2)	0.6133 (1)	0.6525 (2)	0.054 (1)
N1	0.7487 (2)	0.4673 (1)	0.9088 (3)	0.045 (1)
N2	0.6492 (2)	0.5011 (1)	0.7474 (3)	0.050 (1)
N3	0.6013 (2)	0.6301 (1)	1.0030 (3)	0.047 (1)
N4	0.5204 (2)	0.7132 (1)	1.0697 (3)	0.045 (1)
C1	0.9207 (3)	0.3416 (1)	0.9978 (4)	0.044 (1)
C2	0.9682 (3)	0.3838 (1)	1.2137 (4)	0.047 (1)
C3	1.0712 (3)	0.3357 (2)	1.3424 (4)	0.051 (1)
C4	1.1270 (3)	0.2480 (2)	1.2718 (4)	0.061 (1)
C5	1.0794 (3)	0.2071 (2)	1.0589 (5)	0.067 (1)
C6	0.9780 (3)	0.2530 (1)	0.9211 (4)	0.057 (1)
C7	0.8133 (3)	0.3880 (1)	0.8466 (4)	0.045 (1)
C8	0.5690 (3)	0.5841 (1)	0.7943 (4)	0.043 (1)
C9	0.5132 (3)	0.7401 (1)	1.2791 (4)	0.047 (1)
C10	0.4243 (3)	0.8260 (1)	1.3681 (4)	0.049 (1)
C11	0.4007 (3)	0.8934 (2)	1.2405 (4)	0.060 (1)
C12	0.3064 (4)	0.9693 (2)	1.3262 (5)	0.077 (1)
C13	0.2330 (4)	0.9821 (2)	1.5299 (6)	0.087 (1)
C14	0.2580 (4)	0.9162 (2)	1.6554 (5)	0.084 (1)
C15	0.3544 (4)	0.8386 (2)	1.5769 (4)	0.067 (1)
H6	0.621 (3)	0.467 (2)	0.622 (4)	

Table 2. Selected geometric parameters (Å, °)

F1—C3	1.367 (3)	C3—C4	1.371 (3)
F2—C12	1.353 (3)	C4—C5	1.371 (3)
O1—C8	1.227 (2)	C5—C6	1.380 (3)
N1—N2	1.377 (2)	C9—C10	1.462 (3)
N1—C7	1.273 (3)	C10—C11	1.396 (3)
N2—C8	1.361 (3)	C10—C15	1.387 (3)
N3—N4	1.375 (2)	C11—C12	1.361 (3)
N3—C8	1.349 (3)	C12—C13	1.370 (4)
N4—C9	1.267 (3)	C13—C14	1.369 (4)
C1—C2	1.391 (3)	C14—C15	1.379 (4)
C1—C6	1.392 (3)	N2—H6	0.86 (2)
C1—C7	1.464 (3)	H6···O1'	2.01 (2)
C2—C3	1.369 (3)	N2···O1'	2.873 (3)

N2—N1—C7	115.0 (2)	O1—C8—N3	124.2 (2)
N1—N2—C8	120.8 (2)	N2—C8—N3	114.9 (2)
N4—N3—C8	119.3 (2)	N4—C9—C10	120.3 (2)
N3—N4—C9	115.8 (2)	C9—C10—C11	120.8 (2)
C2—C1—C6	119.4 (2)	C9—C10—C15	119.5 (2)
C2—C1—C7	122.0 (2)	C11—C10—C15	119.6 (2)
C6—C1—C7	118.6 (2)	C10—C11—C12	118.1 (2)
C1—C2—C3	118.0 (2)	F2—C12—C11	118.1 (3)
F1—C3—C2	117.9 (2)	F2—C12—C13	118.7 (3)
F1—C3—C4	118.5 (2)	C11—C12—C13	123.2 (3)
C2—C3—C4	123.6 (2)	C12—C13—C14	118.5 (3)
C3—C4—C5	117.9 (2)	C13—C14—C15	120.4 (3)
C4—C5—C6	120.8 (2)	C10—C15—C14	120.2 (3)
C1—C6—C5	120.3 (2)	N1—N2—H6	121 (2)
N1—C7—C1	122.1 (2)	C8—N2—H6	117 (2)
O1—C8—N2	120.9 (2)	N2—H6...O1 <sup>†</sup>	172 (2)

Symmetry code: (i)  $1 - x, 1 - y, 1 - z$ .

Weak reflections [ $I < 10\sigma(I)$ ] were rescanned (maximum of 3 rescans) and the counts accumulated to improve accuracy. The positional parameters of the non-aromatic H atoms were refined. The aromatic H atoms were placed at assumed positions (C,N—H = 0.95 Å,  $U = 1.2U_{eq}$  of the associated atom) and fixed.

Data collection: *MSC/AFC Diffractometer Control Software* (Molecular Structure Corporation, 1988). Cell refinement: *MSC/AFC Diffractometer Control Software*. Data reduction: *TEXSAN PROCESS* (Molecular Structure Corporation, 1985). Program(s) used to solve structure: *MITHRIL* (Gilmore, 1984). Program(s) used to refine structure: *TEXSAN LS*. Molecular graphics: *ORTEP* (Johnson, 1965). Software used to prepare material for publication: *TEXSAN FINISH*.

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates, complete geometry, including bond distances and angles involving H atoms, and torsion angles have been deposited with the IUCr (Reference: CR1090). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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## 2-Methylthio-10,11-dihydro-11-(4-methylpiperazin-1-yl)dibenzo[*b,f*]thiepine Maleic Acid (Metitepine Maleate)<sup>†</sup>

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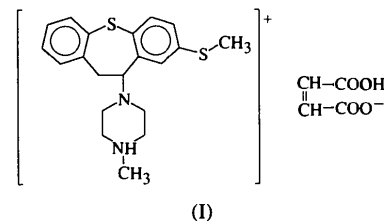
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## Abstract

The crystal structure of metitepine maleate, a mixed 5-HT<sub>1</sub>/5-HT<sub>2</sub> antagonist, has been determined from diffractometer data. The seven-membered ring has a boat–sofa conformation and folds about a line through the S atom and the opposite methylene group. The dihedral angle between the least-squares planes of the aromatic rings is 123.1 (1)°. The piperazine ring has the normal chair conformation and its mean plane is roughly parallel to the plane of one of the benzene rings.

## Comment

As part of our structural study on serotonin antagonists (ketanserine: Peeters, Blaton & De Ranter, 1982; cinanserin: Peeters, Blaton & De Ranter, 1986; pirenperone: Blaton, Peeters & De Ranter, 1985, 1995), we present here the crystal structure of metitepine, (I), a (6,7,6)-tricyclic dibenzo[*b,f*]thiepine derivative with mixed 5-HT<sub>1</sub>/5-HT<sub>2</sub> receptor antagonistic properties (Janssen, 1983). The conformation of the molecule and the atomic numbering are shown in Fig. 1.



The structure is similar to those of octoclotheptin (Jaunin, Petcher & Weber, 1977) and oxyprothepine (Koch & Evrard, 1974). Least-squares-planes calculations through the aromatic rings show that benzo ring A is more planar than the benzo ring B [maximum deviations 0.009 (4) and 0.030 (4) Å, respectively]. The dihedral angle between these planes is 123.1 (1)° and

<sup>†</sup> Internal code of the Janssen Research Foundation: R27199.