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4-Methoxy-*N*,*N*′-diphenylbenzamidine

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Key indicators

Single-crystal X-ray study
T = 293 K
Mean σ(C–C) = 0.003 Å
R factor = 0.043
wR factor = 0.126
Data-to-parameter ratio = 14.3

For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

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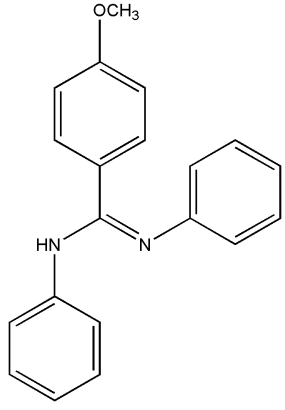
The crystal structure of the title compound, $C_{20}H_{18}N_2O$, reveals lengthened C=N [1.283 (2) Å] and shortened C—N [1.372 (2) Å] bonds, showing *n*-π conjugation, which is a feature of amidines. The secondary amino N atom and the phenyl substituent at the C=N double bond are in an *E* configuration. The molecules are linked into chains by a single N—H···N hydrogen bond parallel to the *c* axis.

Comment

The biological and pharmaceutical activities of amidines have been studied (Genestra *et al.*, 2003; Croft & Coombs, 2003; Pinto *et al.*, 2004). These properties depend on the molecular structure of amidines, particularly on their conformation. Amidines can exist in *E* (*trans*) or *Z* (*cis*) configurations (Kinasiewicz *et al.*, 1988), in addition to the possibility of intermolecular hydrogen bond (N—H···N) formation, which is an important property of these compounds. We present here the crystal and molecular structure of a new amidine, (I), which was characterized as having the *E* configuration by X-ray analysis.



(I)

The crystal structure of (I) shows lengthened C1=N2 [1.283 (2) Å] and shortened C1—N1 [1.372 (2) Å] bonds, a feature of *n*-π conjugation. It is already known that the difference between the C—N and C=N distances is related to the degree of delocalization in the N—C=N skeleton. This is the most important feature of this moiety (Ciszak *et al.*, 1988). The difference is 0.089 Å in the title compound (Fig. 1), 0.06 Å in *N*,*N*′-di(*p*-tolyl)benzamidine (Alcock *et al.*, 1994), 0.046 Å in acetamidine (Norrestam *et al.*, 1983) and 0.058 Å in *N*,*N*′-diphenylbenzamidine (Alcock *et al.*, 1988). This correlation shows that the degree of delocalization clearly depends on the substituents on the phenyl rings bonded to the N and C atoms; as one can observe, the methoxy substituent strongly affects the *n*-π conjugation in (I) (0.089 Å) when compared with the

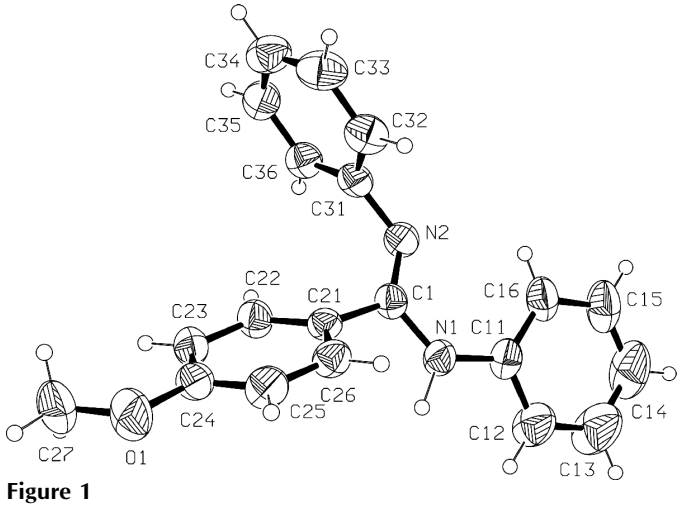


Figure 1
The molecular structure of (I), with the labeling scheme. Displacement ellipsoids are shown at the 40% probability level.

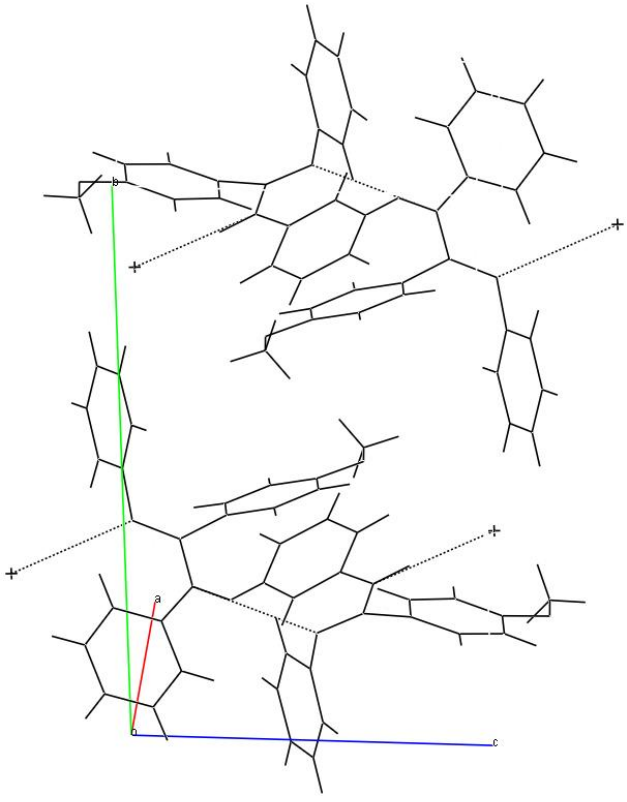


Figure 2
Hydrogen bonding (dotted lines) in the packing of (I) (Bruno *et al.*, 2002). The + symbols indicate the next N atoms (donors or acceptors) that form the infinite zigzag hydrogen-bonded chain.

unsubstituted compound *N*,*N*′-diphenylbenzamidine (0.058 Å).

The N1—C1—N2 bond angle [121.9 (2)°; Table 1] is close to the ideal value for sp^2 hybridization (120°), indicating the delocalization of the π electrons over the N1—C1═N2 region of the molecule of (I), but is somewhat larger than the same angle in *N*,*N*′-diphenylbenzamidine (120.4°), *N*,*N*′-di(*p*-tolyl)acetamidine (120.7°), *N*,*N*′-di(*p*-tolyl)benzamidine (120.8°) and others. Intermolecular forces seem to be the reason for this widening of the angle.

The C21—C1—N2—C31 [10.9 (3)°] and N1—C1—N2—C31 [172.1 (2)°] torsion angles demonstrate that atom N1 atom and the phenyl substituent at N2 are in an *E* (*trans*) configuration with respect to the C1═N2 bond. The arrangement of the atoms in the molecular structure of (I) indicates that the imine lone pair and the N1—H bond are on opposite sides of the molecule. This orientation hinders self-association to give cyclic dimer formation (Bureiko & Chernyshova, 1991), as observed in *N*,*N*′-di(*p*-tolyl)formamidine and *N*,*N*′-di(*p*-chlorophenyl)formamidine (Cotton *et al.*, 1997). However, this orientation results in an infinite zigzag chain formed from intermolecular N1—H···N2^{i} hydrogen bonds parallel to the *c* axis (Fig. 2 and Table 2).

Experimental

The preparation of (I) was performed according to the method of Echevarria *et al.* (1996), starting with *p*-methoxybenzamide and phosphorus pentachloride (PCl_5), giving *p*-methoxybenzimidoyl chloride *in situ*; aniline was then added to afford the target compound (I). Crystals of (I) suitable for single-crystal X-ray diffraction were obtained by recrystallization from methanol (m.p. 406 K, yield 90%). MS EI (70 eV) *m*/*z* (%): 302 (M^+,13), 210 (100), 195 (1), 167 (4), 77 (15), 65 (5), 51 (9).

Crystal data

$C_{20}H_{18}N_2O$
M_r = 302.36
Monoclinic, $P2_1/c$
a = 12.547 (2) Å
b = 14.366 (2) Å
c = 9.353 (2) Å
β = 100.18 (3)°
V = 1659.3 (5) Å^3
Z = 4
D_x = 1.210 Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 25 reflections
θ = 6.7–12.3°
μ = 0.08 mm^{-1}
T = 293 (2) K
Irregular block, pale yellow
0.50 × 0.33 × 0.33 mm

Data collection

Enraf–Nonius CAD-4 diffractometer
ω–2θ scans
Absorption correction: none
3105 measured reflections
2967 independent reflections
1722 reflections with $I > 2\sigma(I)$
R_{int} = 0.014
θ_{max} = 25.2°
$h = -15 \rightarrow 0$
$k = 0 \rightarrow 17$
$l = -11 \rightarrow 11$
3 standard reflections
every 200 reflections
intensity decay: 1%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.043
$wR(F^2)$ = 0.126
S = 1.01
2967 reflections
208 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0602P)^2 + 0.0955P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max}$ = 0.12 e Å^{-3}
$\Delta\rho_{min}$ = −0.15 e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

N1—C1	1.372 (2)	N2—C1	1.283 (2)
N1—C11	1.407 (2)	N2—C31	1.416 (2)
C1—N1—C11	130.0 (2)	N2—C1—C21	126.7 (2)
C1—N2—C31	119.6 (2)	N1—C1—C21	111.3 (2)
N2—C1—N1	121.9 (2)		

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

D—H···A	D—H	H···A	D···A	D—H···A
N1—H1N···N2^{i}	1.01	2.35	3.353 (2)	169

Symmetry code: (i) $x, \frac{1}{2}-y, \frac{1}{2}+z$.

H atoms were placed in idealized positions and refined using a riding model, with C—H distances of 0.96 and 0.93 Å, and with U_{iso}(H) fixed at 1.5 and 1.2 times U_{eq} of the parent atom for CH_3 and $CH_{aromatic}$, respectively. The H atom of the amine group was found in a Fourier map and treated as riding, with the U_{iso}(H) value fixed at $1.2U_{eq}$(N1).

Data collection: *CAD*-4 *EXPRESS* (Enraf–Nonius, 1994); cell refinement: *SET*4 in *CAD*-4 *EXPRESS*; data reduction: *HELENA* (Spek, 1996); program(s) used to solve structure: *SIR*97 (Altomare *et al.*, 1999); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *ORTEP*-3 (Farrugia, 1997); software used to prepare material for publication: *SHELXL*97.

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