Acta Crystallographica Section C
**Crystal Structure Communications**
ISSN 0108-2701

# 2,4,6-Trimethylbenzamide

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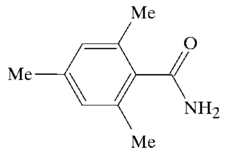
Received 27 October 2003
Accepted 19 November 2003
Online 6 December 2003

The crystal structure of the title compound, $C_{10}H_{13}NO$, displays an infinite one-dimensional network composed of primary amide molecules connected by N—H···O=C hydrogen bonds involving the *anti* NH amide H atoms, thus generating a $C(4)$ motif. This network is additionally stabilized by a weak N—H···π interaction between the *syn*-oriented amide H atom and the aromatic ring of a neighbouring molecule. The distance between the H atom and the ring centroid is 2.50 Å. The amide group and the aryl moiety are nearly perpendicular, forming an intramolecular dihedral angle of 84.69 (6)°.

## Comment

Hydrogen-bonding interactions between amide H atoms and carbonyl O atoms give rise to a variety of assembly modes in crystals of primary amides (Leiserowitz & Hagler, 1983; Bernstein *et al.*, 1994). The most common modes are the centrosymmetric cyclic $R_2^2(8)$ hydrogen-bond motif, involving the *syn*-oriented H atoms, $H_s$ (*syn* with respect to the adjacent C=O bond), and the $C(4)$ hydrogen-bond motif, engaging the *anti*-oriented H atoms, $H_a$. Depending on the symmetry operation relating the centrosymmetric dimers along the $C(4)$ chain, one- or two-dimensional hydrogen-bonded arrays can be generated in the solid state. For example, in the case of benzamide (Blake & Small, 1972), *o*-methylbenzamide (Kato *et al.*, 1979) and *m*-methylbenzamide (Orii *et al.*, 1963), formation of N—$H_a$···O hydrogen bonds between the translation-related centrosymmetric $R_2^2(8)$ dimers leads to one-dimensional networks. A similar assembly pattern was also observed in crystals of 4-methoxy-2,6-dimethylbenzamide (Mugnoli *et al.*, 1991), whereas neighbouring dimers along the $C(4)$ chain in crystals of *p*-methylbenzamide are related by a glide plane that generates a two-dimensional array of the hydrogen-bonded molecules (Kato *et al.*, 1981).

Recently, it has been shown that introduction of a bulky triphenylmethyl group at the *p*-position of the benzamide molecule leads to crystal structures in which the centrosymmetric amide dimers are connected by weak N—$H_a$···π interactions (Reddy *et al.*, 2002). We report here the crystal structure of 2,4,6-trimethylbenzamide, (I), in which a new assembly mode was found for the aromatic primary amide. This mode is characterized by strong N—$H_a$···O hydrogen bonds accompanied by weak N—$H_s$···π interactions (π denotes the aromatic ring centroid). A survey of the Cambridge Structural Database (Version 5.24, 296 427 entries; Allen, 2002) gave only three primary benzamide derivatives [HIXNIL (Pandurangi *et al.*, 1998), QELYUB (Zhang *et al.*, 1999) and TUVQIK (Kobayashi *et al.*, 2003)], in which the H···π distance and the N—H···π angle in the N—H···π interactions fall in the ranges 2.0–3.0 Å and 120–180°, respectively.



(I)

The structure of (I), with its atom-numbering scheme, is shown in Fig. 1 and selected geometric parameters are given in Table 1. The carboxamide group and benzene moiety are

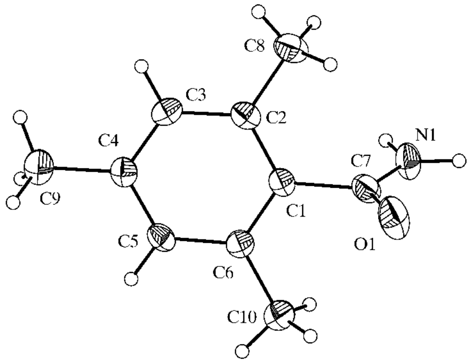


**Figure 1**
The molecule of (I), with displacement ellipsoids at the 50% probability level for non-H atoms.

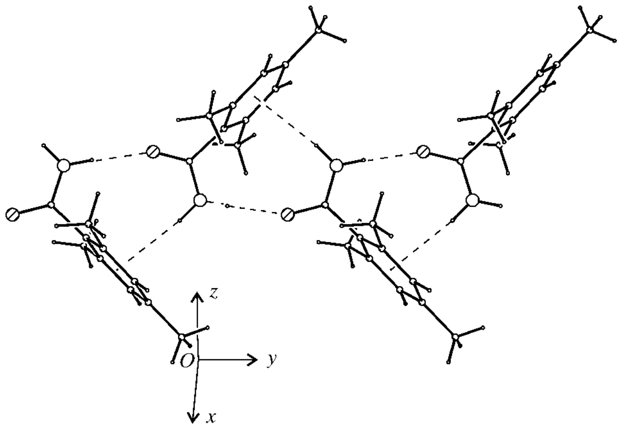


**Figure 2**
A hydrogen-bonded chain in (I), with N—H···O and N—H···π interactions shown by dashed lines.

nearly perpendicular to one another, as shown by the dihedral angle between their planes [84.69 (6)°], whereas the corresponding dihedral angles in 4-methoxy-2,6-dimethylbenzamide (Mugnoli *et al.*, 1991) and 2,4,6-trimethylbenzoic acid (Benghiat & Leiserowitz, 1972) were only 56.7 (1) and 48.7°, respectively. The molecules of (I) are connected by $\mathrm{N-H}_a\cdots\mathrm{O{=}C}$ interactions that lead to an infinite one-dimensional network characterized by a *C*(4) hydrogen-bond motif and extending along the [010] direction (Fig. 2 and Table 2). The amide $\mathrm{H}_s$ atoms within this chain are involved in $\mathrm{N-H}\cdots\pi$ interactions with the aryl ring of the amide molecules related by the $2_1$ axis (Table 2). Malone *et al.* (1997) have analyzed $X\mathrm{-H}\cdots\pi$ interactions in small-molecule crystal structures and indicated six possible forms of interaction between an H atom and an aromatic ring. Interactions classified as type I correspond to classical T-shaped geometry and are characterized by the geometric parameters indicated in Fig. 3. The approach geometry of the $\mathrm{N-H}_a$ group to the phenyl ring [with the parameters $\mathrm{H}\cdots\pi = 2.50$ Å, $\alpha = 173°$, $\theta = 84°$ and $d = 0.27$ Å] allows us to classify the $\mathrm{N-H}\cdots\pi$ interaction in (I) as typical type I.

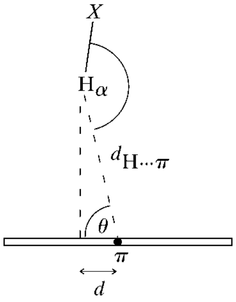


**Figure 3**
Geometric parameters describing the $X\mathrm{-H}\cdots\pi$ interaction according to Malone *et al.* (1997). For a type I interaction, $\mathrm{H}\cdots\pi < 3.05$ Å, $\alpha$ is in the range 150–180°, $\theta > 53°$ and $d < 0.5$ Å.

## Experimental

The title compound was obtained by reaction of 2,4,6-trimethylbenzoylamide with aqueous ammonia [m.p. 461–462 K (toluene–hexane); literature m.p. 462 K (Hantzsch & Lucas, 1895)].

*Crystal data*

$C_{10}H_{13}NO$
$M_r = 163.21$
Orthorhombic, *Pbca*
$a = 14.2587$ (9) Å
$b = 8.5369$ (6) Å
$c = 14.9245$ (10) Å
$V = 1816.7$ (2) Å$^3$
$Z = 8$
$D_x = 1.193$ Mg m$^{-3}$
Mo $K\alpha$ radiation
Cell parameters from 3457 reflections
$\theta = 4$–25°
$\mu = 0.08$ mm$^{-1}$
$T = 130$ (2) K
Plate, colorless
0.22 × 0.15 × 0.02 mm

*Data collection*

Kuma KM-4-CCD $\kappa$-geometry diffractometer
$\omega$ scans
8742 measured reflections
1597 independent reflections
1096 reflections with $I > 2\sigma(I)$
$R_{\mathrm{int}} = 0.049$
$\theta_{\max} = 25.0°$
$h = -9 \rightarrow 16$
$k = -9 \rightarrow 10$
$l = -17 \rightarrow 17$

*Refinement*

Refinement on $F^2$
$R[F^2 > 2\sigma(F^2)] = 0.043$
$wR(F^2) = 0.090$
$S = 1.03$
1597 reflections
122 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0363P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} < 0.001$
$\Delta\rho_{\max} = 0.13$ e Å$^{-3}$
$\Delta\rho_{\min} = -0.18$ e Å$^{-3}$

**Table 1**
Selected geometric parameters (Å, °).

| | | | |
|---|---|---|---|
| O1—C7 | 1.238 (2) | C1—C7 | 1.498 (2) |
| N1—C7 | 1.331 (2) | | |
| | | | |
| O1—C7—N1 | 123.03 (18) | N1—C7—C1 | 116.46 (16) |
| O1—C7—C1 | 120.50 (17) | | |

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

| $D\mathrm{-H}\cdots A$ | $D\mathrm{-H}$ | $\mathrm{H}\cdots A$ | $D\cdots A$ | $D\mathrm{-H}\cdots A$ |
|---|---|---|---|---|
| $\mathrm{N1-H1N}\cdots\mathrm{O1}^{\mathrm{i}}$ | 0.90 | 1.97 | 2.868 (2) | 177 |
| $\mathrm{N1-H2N}\cdots\pi^{\mathrm{ii}}$ | 0.90 | 2.50 | 3.393 (18) | 173 |

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

All H atoms were located from difference maps. Distances involving H atoms were standardized to 0.90 and 0.96 Å for N—H and C—H bonds, respectively. The isotropic displacement parameters were allowed to refine.

Data collection: *CrysAlis CCD* (Oxford Diffraction, 2000); cell refinement: *CrysAlis CCD*; data reduction: *CrysAlis RED* (Oxford Diffraction, 2000); program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *Stereochemical Workstation Operation Manual* (Siemens, 1989); software used to prepare material for publication: *SHELXL*97.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: FA1038). Services for accessing these data are described at the back of the journal.

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