Acta Crystallographica Section C
Crystal Structure Communications
ISSN 0108-2701

Cocrystal of *cis*- and *trans*-*N*-phenylformamide

Bernard Omondi, Manuel A. Fernandes, Marcus Layh and Demetrius C. Levendis*

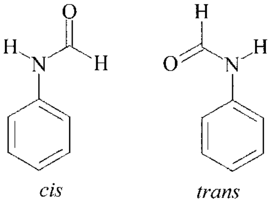
Molecular Sciences Institute, School of Chemistry, University of the Witwatersrand, PO Wits 2050, South Africa
Correspondence e-mail: demetrius.levendis@wits.ac.za

Received 18 December 2007
Accepted 24 January 2008
Online 9 February 2008

N-Phenylformamide, C_7H_7NO, crystallizes with two molecules in the asymmetric unit which have different conformations of the formylamino group, one being *cis* and the other *trans*. This is the first example of an arylformamide crystal containing both conformational isomers and it may thus be considered a cocrystal of the two conformers. The two molecules in the unit cell are linked through N—H···O hydrogen bonding to two other molecules, thereby forming hydrogen-bonded tetramers within the crystal structure.

Comment

The study of the title compound, (I), has attracted considerable interest in recent years. However, no crystallographic studies on *N*-phenylformamide have been reported previously.



(I)

Previous studies of the compound have been largely theoretical (Moreno *et al.*, 2006; Moisan & Dannenberg, 2003; Kobko & Dannenberg, 2003; Vargas *et al.*, 2001; Bock *et al.*, 1996; Manea *et al.*, 1997), including density functional theory (DFT) studies (Doerksen *et al.*, 2004), and experimental investigations on resonant two-photon ionization spectroscopy (Federov & Cable, 2000) and laser-induced fluorescence excitation (Dickinson *et al.*, 1999). The study of (I) has also been important as a model for the understanding of the structure, folding and stability of proteins. This understanding has typically been gained from an interpretation of IR, Raman or NMR spectra of model systems such as formamide (the simplest representative of this class of compounds) and *N*-alkyl- or *N*-phenylamide–water clusters, either isolated in a matrix or dispersed in an aqueous solution (Dickinson *et al.*, 1999). The solution NMR spectrum of a powdered sample of (I) in $CDCl_3$ showed equal concentrations of the *cis* and *trans* isomers, which is in agreement with the dynamic solution behaviour of amide systems reported previously (Siddall *et al.*, 1968, and references therein; Omondi *et al.*, 2005).

N-Phenylformamide crystallizes with two molecules in the asymmetric unit (Fig. 1). One of the molecules adopts a *cis* conformation, while the other shows a *trans* conformation. The formation of a cocrystal of the two conformations is unusual as *N*-phenylformamides and *N*-phenylthioamides usually crystallize as only one of these isomers (Omondi, 2007; Omondi *et al.*, 2005), even though both conformers exist in solution. The two conformers show similar bond lengths and angles that compare well with those of related compounds in the literature. The N—C(=O) and C—O bond lengths are, as expected for conjugated π-systems, in the region of 1.33 and 1.22 Å, respectively. Both molecules adopt the almost planar geometry that would be preferred in order to extend π-conjugation from the ring system to the formamide group. This, in turn, shortens the N—C_{ar} single-bond length. The shortening of this bond is, however, not very significant. A notable difference between the two conformers is in the angle between the plane defined by the phenyl ring (C11–C16 or C21–C26) and the plane defined by the formamide group (C11—N11—C17—O11 or C21—N21—C27—O21). In the *cis* isomer, the angle between the two mean planes is approximately equal to zero, whereas in the *trans* isomer the formamide group is slightly out of the plane of the phenyl ring by about 9.1 (1)°. This angle varies in related compounds, such as acetanilide, and also in the calculated structures of the *cis* and *trans* isomers of *N*-phenylformamide. The gas-phase conformation of the *trans* isomer is reported to be nonplanar (Manea

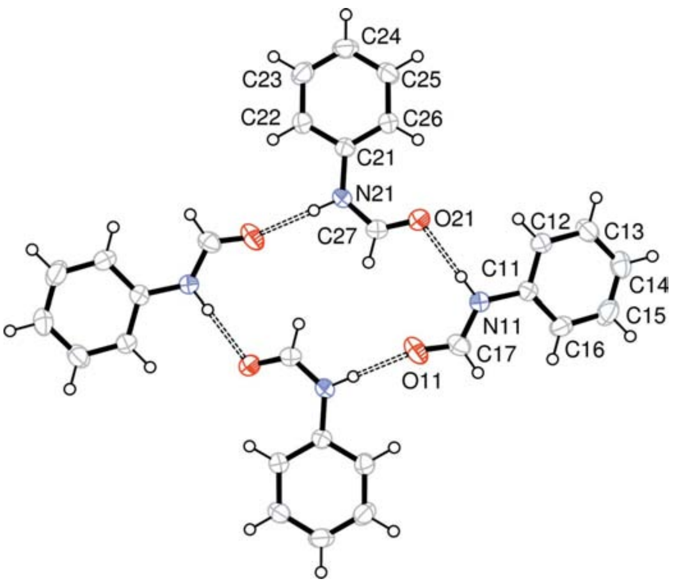


Figure 1
View of (I) down the *a* axis, showing an N—H···O hydrogen-bonded tetramer (50% probability displacement ellipsoids).

doi:10.1107/S0108270108002746

et al., 1997), in contrast to what is observed here in the crystalline phase.

The two molecules in the unit cell have a dihedral angle of 19.07 (6)° between their mean planes. Each molecule of a particular conformation (*cis* or *trans*) is related to its nearest neighbour of the same conformation through a glide plane.

Each molecule is connected to another molecule of a different conformation through N—H···O hydrogen bonding, resulting in a tetrameric arrangement [graph-set $R_4^4(16)$], with each tetramer containing two molecules of each conformation. Due to the nearly planar backbone of the molecule, the hydrogen bonds are almost linear, with N—H···O angles of 178 and 176° for the two isomers, respectively. The intramolecular N···O distances are slightly shorter than those in acetanilide and related acetamides, such as paracetamol (2.894–2.967 Å; Wasserman *et al.*, 1985; Johnson *et al.*, 1995), all of which adopt only the *trans* conformation in the solid state.

Experimental

N-Phenylformamide was synthesized according to the procedure of Ugi *et al.* (1965). Commercially available aniline (Aldrich, purity > 95%) was heated in a tenfold excess of formic acid for a period of 15 h at 363 K. The excess formic acid was removed under vacuum to give a brown liquid which was treated with dilute hydrochloric acid (0.1 *M* HCl) and ethyl acetate. The organic layer was separated from the aqueous layer, dried over magnesium sulfate and distilled under vacuum. An off-white solid was obtained in good yield. The first suitable single crystals of *N*-phenylformamide were obtained by crystallization from ethyl acetate on work-up of the reaction mixture. Only subsequent to their growth, which took almost a year, was it possible to grow the same crystals (as established by X-ray powder diffraction) from various solvents by slow evaporation (chloroform, ethanol, dichloromethane, ethyl acetate, dimethyl sulfoxide and tetrahydrofuran). The powder was recrystallized from a variety of solvents, giving crystals suitable for single-crystal X-ray diffraction studies. ^{1}H NMR (DMSO): δ 7.02, 7.22, 7.47 (*m*; *cis* and *trans*, *para*, *meta* and *ortho* Ar—H; *trans*, NH), 8.37 (*d*, *trans*, CHO, $J_{\rm H-H}$ = 1.13 Hz), 8.70 (*d*, *cis*, CHO, $J_{\rm H-H}$ = 11.38), 8.46 (*s*, broad, *cis*, NH).

Crystal data

C_7H_7NO
M_r = 121.14
Monoclinic, $C2/c$
a = 31.177 (3) Å
b = 6.1229 (5) Å
c = 14.3335 (12) Å
β = 113.771 (2)°
V = 2504.1 (4) Å^3
Z = 16
Mo $K\alpha$ radiation
μ = 0.09 mm^{-1}
T = 173 (2) K
0.53 × 0.20 × 0.14 mm

Data collection

Bruker SMART CCD area-detector diffractometer
7327 measured reflections
2732 independent reflections
1953 reflections with $I > 2\sigma(I)$
$R_{\rm int}$ = 0.026

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.040
$wR(F^2)$ = 0.110
S = 1.03
2732 reflections
163 parameters
H-atom parameters constrained
$\Delta\rho_{\rm max}$ = 0.19 e Å^{-3}
$\Delta\rho_{\rm min}$ = −0.18 e Å^{-3}

Table 1
Hydrogen-bond geometry (Å, °).

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N11—H11···O21	0.88	1.97	2.844 (2)	176
N21—H21···O11$^{\rm i}$	0.88	1.94	2.821 (2)	178

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

H atoms were positioned geometrically and allowed to ride on their respective parent atoms, with bond lengths of 0.95 (C—H) and 0.88 Å (N—H), and isotropic displacement parameters 1.2 times $U_{\rm eq}$ of the parent atom.

Data collection: *SMART-NT* (Bruker, 1998); cell refinement: *SAINT-Plus* (Bruker, 1999); data reduction: *SAINT-Plus*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *PLATON* (Spek, 2003) and *ORTEP-3* (Farrugia, 1997); software used to prepare material for publication: *WinGX* (Farrugia, 1999).

The authors thank the IUCr for a PhD grant (to BO), NRF for financial support (No. GUN2069064) and the University of Witwatersrand for providing the experimental facilities.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: GD3183). Services for accessing these data are described at the back of the journal.

References

Bock, H., Van, T. T. H., Solouki, B., Schödel, H., Artus, G., Herdtweck, E. & Herrmann, W. A. (1996). *Liebigs Ann.* pp. 403–407.
Bruker (1998). *SMART-NT*. Version 5.050. Bruker AXS Inc., Madison, Wisconsin, USA.
Bruker (1999). *SAINT-Plus*. Version 6.02 (including *XPREP* and *SADABS*). Bruker AXS Inc., Madison, Wisconsin, USA.
Dickinson, J. A., Hockridge, M. R., Robertson, E. V. & Simons, J. P. (1999). *J. Phys. Chem. A*, **103**, 6938–6949.
Doerksen, R. J., Chen, B., Liu, D., Tew, G. N., DeGrado, W. F. & Klein, M. L. (2004). *Chem. Eur. J.* **10**, 5008–5016.
Farrugia, L. J. (1997). *J. Appl. Cryst.* **30**, 565.
Farrugia, L. J. (1999). *J. Appl. Cryst.* **32**, 837–838.
Federov, A. V. & Cable, J. R. (2000). *J. Phys. Chem. A*, **104**, 4943–4952.
Johnson, S. W., Eckert, J., Barthes, M., McMullan, R. K. & Muller, M. (1995). *J. Phys. Chem.* **99**, 16253–16290.
Kobko, N. & Dannenberg, J. J. (2003). *J. Phys. Chem. B*, **107**, 6688–6697.
Manea, V. P., Wilson, K. J. & Cable, J. R. (1997). *J. Am. Chem. Soc.* **119**, 2033–2039.
Moisan, S. & Dannenberg, J. J. (2003). *J. Phys. Chem. B*, **107**, 12842–12846.
Moreno, J.-R. A., Petitprez, D. & Huet, T. R. (2006). *Chem. Phys. Lett.* **419**, 411–416.
Omondi, B. (2007). PhD thesis, University of the Witwatersrand, South Africa.
Omondi, B., Fernandes, M. A., Layh, M., Look, J., Levendis, D. C. & Mkwizu, T. (2005). *CrystEngComm*, **7**, 1–12.
Sheldrick, G. M. (2008). *Acta Cryst.* A**64**, 112–122.
Siddall, T. H. III, Stewart, W. E. & Marston, A. L. (1968). *J. Phys. Chem.* **72**, 2135–2141.
Spek, A. L. (2003). *J. Appl. Cryst.* **36**, 7–13.
Ugi, I., Fetzer, U., Eholzer, U., Knuffer, H. & Offermason, K. (1965). *Angew. Chem. Int. Ed. Engl.* **4**, 472–481.
Vargas, R., Garza, J., Friesna, R. A., Stern, H., Hay, B. P. & Dixon, D. A. (2001). *J. Phys. Chem. A*, **105**, 4963–4968.
Wasserman, H. J., Ryan, R. R. & Layne, S. P. (1985). *Acta Cryst.* C**41**, 783–785.