SHELXL93 (Sheldrick, 1993). Molecular graphics: *ORTEP* (Johnson, 1965). Software used to prepare material for publication: MS-DOS 6.20 editor.

The authors thank the Instituto de Química de São Carlos for the data collection and CNPq, FINEP and FAPEMIG(Brazil) for financial support, and Dr Dalton L. F. Alves for helpful advice on the isolation of the title compound.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: FG1165). Services for accessing these data are described at the back of the journal.

References

Cremer, D. & Pople, J. A. (1975). *J. Am. Chem. Soc.* **97**, 1354–1358.
Enraf–Nonius (1989). *CAD-4 Software*. Version 5.0. Enraf–Nonius, Delft, The Netherlands.
Fascio, M., Mors, W. B., Gilbert, B., Mahajan, J. R., Monteiro, M. B., Santos Filho, D. & Vichnewski, W. (1976). *Phytochemistry*, **15**, 201–203.
Frenz, B. A. (1978). *The Enraf–Nonius CAD-4 SDP – a Real-Time System for Concurrent X-ray Data Collection and Crystal Structure Solution. Computing in Crystallography*, edited by H. Schenk, R. Olthof-Hazekamp, H. van Koningsveld & G. C. Bassi, pp. 64–71. Delft University Press.
Johnson, C. K. (1965). *ORTEP*. Report ORNL-3794. Oak Ridge National Laboratory, Tennessee, USA.
Mahajan, J. R. & Monteiro, M. B. (1973). *J. Chem Soc. Perkin Trans.* pp. 520–524.
Mors, W. B., Fascio, M., Monteiro, H. J., Gilbert, B. & Pellegrino, J. (1967). *Science*, **157**, 950–951.
Rubinger, M. M. M., Piló-Veloso, D., Stefani, G. M. & Alves, D. L. F. (1991). *J. Brazil. Chem. Soc.* **2**, 124–128.
Sheldrick, G. M. (1990). *Acta Cryst.* A**46**, 467–473.
Sheldrick, G. M. (1993). *SHELXL93. Program for the Refinement of Crystal Structures*. University of Göttingen, Germany.

Acta Cryst. (1997). C**53**, 984-985

N-Cyano-*N*′-(4-methoxyphenyl)guanidine

Ian D. Cunningham,[a] Nan Chi Wan,[a] David C. Povey,[a] Gallienus W. Smith[a] and Brian G. Cox[b]

[a]*Department of Chemistry, University of Surrey, Guildford GU2 5XH, England, and* [b]*Zeneca Fine Chemicals Manufacturing Organization, Huddersfield HD2 1FF, England*

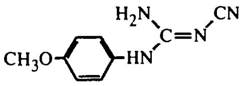
(*Received 14 September 1995; accepted 21 February 1997*)

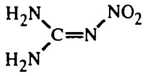
Abstract

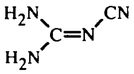
An X-ray structural analysis of the title compound, $C_9H_{10}N_4O$, shows a planar guanidine portion, the *N*-aryl group tilted *ca* 57° relative to the guanidine plane and *E* geometry about the formal 'imino' bond.

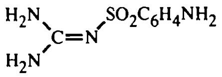
Comment

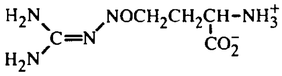
Monosubstituted guanidines such as nitroguanidine, (2), cyanoguanidine, (3), sulfaguanidine, (4), L-canavanine, (5), and *N*-methyl-*N*′-nitro-*N*-nitrosoguanidine, (6), which bear strongly electron-withdrawing groups, exist as neutral organic molecules preferring the 'imino' tautomeric form [*e.g.* $(NH_2)_2C{=}N{-}NO_2$] in solution and in the solid state (Patai & Rappoport, 1991). In a previous paper, we showed that disubstituted *N*-aryl-*N*′-cyanoguanidines in solution in Me_2SO also have the 'imino' structure seen for the title compound, (1) (Cunningham, Wan & Cox, 1994). While crystal structures have been reported for (3) (Hughes, 1940; Begley, Hubberstey & Moore, 1985; Hirshfield & Hope, 1980) and for the other guanidines listed above (Patai & Rappoport, 1991), none are known for *N*-cyano-*N*′-substituted guanidines. In this paper, we report the crystal structure of *N*-cyano-*N*′-(4-methoxyphenyl)-guanidine, (1).

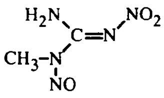

(1)


(2)


(3)


(4)


(5)


(6)

The X-ray crystal structure is shown in Fig. 1 (arbitrary numbering), where it can be seen that the imino tautomer is preferred in the solid state. The cyanoguanidine portion is essentially planar, as shown by the bond angles about C1, N1 and N2 (Table 1) and the C2—N3—C1—N1 and C2—N3—C1—N2 torsion angles. The N1—C1, N2—C1 and N3—C1 bonds which comprise the guanidine system are all of length 1.33 (1) Å; these lengths are almost identical to those seen for unsubstituted cyanoguanidine (Begley, Hubberstey & Moore, 1985) and are between the values for C—N and C=N (Allen *et al.*, 1987), indicating that the N-atom lone pairs and the C=N bond shown formally in (1) are completely delocalized over the guanidine system. The bond length (N4—C2) for the cyano group at 1.142 (3) Å is typical, suggesting that the cyano group is not involved in resonance with the guanidine system. Interestingly, the aryl group is twisted out of the guanidine plane by about 57° showing that resonance

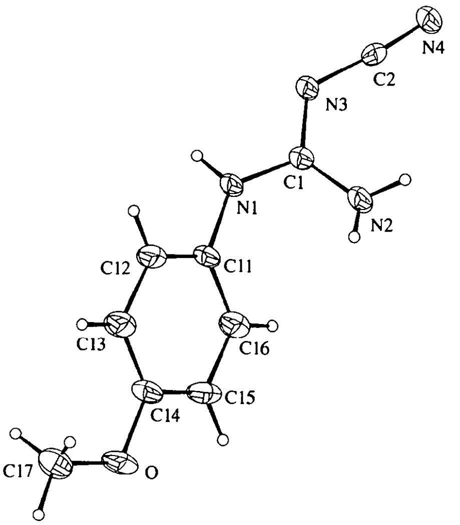


Fig. 1. The molecular structure of (1) with displacement ellipsoids drawn at the 50% probability level.

between the cyanoguanidine portion and the aromatic ring is minimal.

Fig. 1 also illustrates that the geometry about the formal C=N bond is *E*; this preference may be due to packing as much as to steric factors.

Experimental

The title compound was prepared by reaction of 4-methoxyaniline with sodium dicyanamide in aqueous hydrochloric acid and recrystallized from ethanol.

Crystal data

$C_9H_{10}N_4O$
$M_r = 190.21$
Triclinic
$P\bar{1}$
$a = 6.904\,(3)$ Å
$b = 8.431\,(3)$ Å
$c = 9.555\,(6)$ Å
$\alpha = 111.21\,(4)°$
$\beta = 92.02\,(4)°$
$\gamma = 107.74\,(4)°$
$V = 487\,(1)$ Å^3
$Z = 2$
$D_x = 1.294$ Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 25 reflections
$\theta = 7–13°$
$\mu = 0.085$ mm^{-1}
$T = 293$ K
Square prism
0.5 × 0.3 × 0.2 mm
Colourless

Data collection

Enraf–Nonius CAD-4 diffractometer
$\omega/2\theta$ scans
Absorption correction: none
2075 measured reflections
1909 independent reflections
1340 reflections with $I > 3\sigma(I)$

$\theta_{max} = 26.0°$
$h = 0 \rightarrow 8$
$k = -10 \rightarrow 9$
$l = -11 \rightarrow 11$
1 standard reflection
frequency: 60 min
intensity decay: 11.0%

Refinement

Refinement on F
$R = 0.058$
$wR = 0.076$
$S = 1.026$
1340 reflections
139 parameters
$w = 1/[\sigma^2(F) + (0.5F)^2 + 5]$

$(\Delta/\sigma)_{max} = 0.16$
$\Delta\rho_{max} = 0.19$ e Å^{-3}
$\Delta\rho_{min} = -0.22$ e Å^{-3}
Extinction correction: none
Scattering factors from *International Tables for X-ray Crystallography* (Vol. IV)

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

N1—C1	1.328 (3)	N3—C2	1.314 (3)
N2—C1	1.317 (3)	N4—C2	1.142 (3)
N3—C1	1.342 (3)		
C1—N1—C11	127.9 (2)	C1—N3—C2	119.5 (2)
C1—N1—H1	117 (2)	N1—C1—N2	121.0 (2)
C11—N1—H1	115 (2)	N1—C1—N3	114.5 (2)
C1—N2—H2*A*	125 (2)	N2—C1—N3	124.6 (2)
C1—N2—H2*B*	122 (2)	N3—C2—N4	173.5 (3)
H2*A*—N2—H2*B*	112 (3)		
C1—N1—C11—C16	57 (1)	C2—N3—C1—N2	3 (1)
C2—N3—C1—N1	−178 (1)		

The structure was solved by non-default use of *MULTAN*78 (Main *et al.*, 1978) when the correct solution yielded 12 of the atoms in the molecule. A structure factor/Fourier calculation revealed the missing atoms and with H atoms included (except those on N atoms), but not refined, isotropic refinement converged slowly to $R = 0.20$. Anisotropic refinement of the non-H atoms rapidly converged to the final R of 0.058. In the final refinement, the H atoms attached to N atoms were found from a difference Fourier and were refined isotropically.

Data collection: *CAD*-4 *Software* (Enraf–Nonius, 1989). Cell refinement: *CAD*-4 *Software*. Data reduction: *SDP* (Frenz, 1983). Program(s) used to solve structure: *SDP* and *MULTAN*78. Program(s) used to refine structure: *SDP*.

The authors are grateful to Zeneca FCMO for financial support (NCW).

Supplementary data for this paper are available from the IUCr electronic archives (Reference: BM1034). Services for accessing these data are described at the back of the journal.

References

Allen, F. H., Kennard, O., Watson, D. G., Brammer, L., Orpen, A. G. & Taylor, R. (1987). *J. Chem. Soc. Perkin Trans.* 2, pp. S1–19.

Begley, M. J., Hubberstey, P. & Moore, C. H. M. (1985). *J. Chem. Res. (S)*, 378–379; *J. Chem. Res. (M)*, 4001–4034.

Cunningham, I. D., Wan, N. C. & Cox, B. G. (1994). *J. Chem. Soc. Perkin Trans.* 2, pp. 1849–1853.

Enraf–Nonius (1989). *CAD-4 Manual.* Version 5.0. Enraf–Nonius, Delft, The Netherlands.

Frenz, B. A. (1983). *Enraf–Nonius Structure Determination Package*; *SDP User's Guide.* Version of 6 January 1983. Enraf–Nonius, Delft, The Netherlands.

Hirshfield, F. L. & Hope, H. (1980). *Acta Cryst.* B**36**, 406–415.

Hughes, E. W. (1940). *J. Am. Chem. Soc.* **62**, 1258–1267.

Main, P., Hull, S. E., Lessinger, L., Germain, G., Declercq, J.-P. & Woolfson, M. M. (1978). *MULTAN78. A System of Computer Programs for the Automatic Solution of Crystal Structures from X-ray Diffraction Data.* Universities of York, England, and Louvain, Belgium.

Patai, S. & Rappoport, Z. (1991). In *The Chemistry of Amidines and Imidates*, Vol. 2. New York: Wiley.