

2,2'-*o*-Phenylenebis(1,3-dimethylguanidine)Masatoshi Kawahata,^a Kentaro Yamaguchi,^{a*} Tomoya Ito^b and Tsutomu Ishikawa^b^aFaculty of Pharmaceutical Sciences at Kagawa Campus, Tokushima Bunri University, 1314-1 Shido, Sanuki-shi, Kagawa 769-2193, Japan, and ^bGraduate School of Pharmaceutical Sciences, Chiba University, 1-33 Yayoi-cho, Inage-ku, Chiba-shi, Chiba 263-8522, JapanCorrespondence e-mail:
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Key indicators

Single-crystal X-ray study
T = 150 K
Mean $\sigma(\text{C}-\text{C}) = 0.002 \text{ \AA}$
R factor = 0.047
wR factor = 0.137
Data-to-parameter ratio = 19.3For details of how these key indicators were automatically derived from the article, see <http://journals.iucr.org/e>.

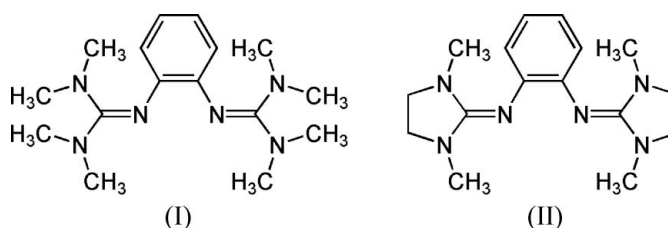
The title compound, $\text{C}_{16}\text{H}_{28}\text{N}_6$, was obtained from the reaction of *o*-phenylenediamine with *N,N,N',N'*-tetramethylformamidinium chloride. The two guanidyl groups are almost coplanar with the benzene ring. Both C—N bonds adjacent to the benzene ring were found to be double bonds, while the others were identified as single bonds, based on their bond distances.

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Comment

We have developed guanidine chemistry (Ishikawa *et al.*, 2006) focusing on the potential abilities of the guanidyl groups to act, for example, as chiral auxiliaries (Kitani *et al.*, 2005). Recently, we have reported interesting cocrystal properties based on the cluster formation of bisguanidine (II) and benzoic acid (Kawahata *et al.*, 2005; Kawahata *et al.*, 2006). As a part of our investigation into guanidine chemistry, in this paper we report the title compound (I).



The molecular structure and atom-numbering scheme of (I) are shown in Fig. 1. Selected geometric parameters are presented in Table 1. The two guanidyl groups are *anti* relative to the benzene ring. The sum of angles around each guanidyl group (group 1: N1—C7—N2, N1—C7—N3 and N2—C7—N3; group 2: N4—C12—N5, N4—C12—N6 and N5—C12—N6) are both almost 360°. The largest deviations from the mean planes are for atoms C7 [0.0143 (1) Å] in group 1 and C12 [0.0083 (10) Å] in group 2. These indicate that each guanidyl group is planar. The C—N bonds adjacent to the benzene rings are short (see Table 1), exhibiting C=N double-bond character, while the remaining four C—N bonds around C7 and C12 (N2—C7, N3—C7, N4—C12 and N5—C12) are longer [1.3765 (16) Å to 1.3893 (15) Å].

Experimental

2-Chloro-1,1,3,3-tetramethylformamidinium chloride was prepared from *N,N,N',N'*-tetramethylurea (Ohno *et al.*, 2003). A mixture of *N,N,N',N'*-tetramethylurea (6.0 ml, 50.0 mmol) and oxalyl chloride (21.2 ml, 247.2 mmol, 4.9 equivalents) in anhydrous chloroform (30 ml) was refluxed for 15 h. After evaporating the chloroform, the residual solid was washed with dry diethyl ether to give 2-chloro-

1,1,3,3-tetramethylformamidinium chloride (9.08 g, 106%, 91% purity). This was dissolved in dichloromethane (42 ml) and added dropwise to a solution of *o*-phenylenediamine (2.46 g, 21.8 mmol) and triethylamine (13 ml, 93.3 mmol, 4.3 equivalents) in dichloromethane (84 ml) at 273 K. The mixture was stirred at 273 K for 1 h and extracted with 10% aq. HCl. The aqueous solution was washed with dichloromethane, then 20% aq. NaOH was added and the mixture extracted with toluene. The toluene solution was washed with water and brine, dried over K₂CO₃ and concentrated *in vacuo*. The residue was recrystallized from *n*-hexane to give *N,N,N',N'*-tetramethyl-1,2-phenylenebis(*N,N,N',N'*-tetramethyl)guanidine as colorless prisms (6.0 g, 90%). The purified product was recrystallized from *n*-hexane and colorless single crystals were formed (m.p. 350–352 K). Analysis calculated for C₁₆H₂₈N₆: C 63.12, H 9.27, N 27.61%; found: C 63.09, H 9.32, N 27.77%.

Crystal data

C₁₆H₂₈N₆
M_r = 304.44
 Monoclinic, *P*2₁/*c*
a = 7.6337 (12) Å
b = 8.5800 (13) Å
c = 27.199 (4) Å
 β = 97.000 (2)°
V = 1768.2 (5) Å³
Z = 4
D_x = 1.144 Mg m⁻³
 Mo Kα radiation
 μ = 0.07 mm⁻¹
T = 150 K
 Prism, colorless
 0.50 × 0.40 × 0.30 mm

Data collection

Bruker SMART 1000 CCD area detector diffractometer
 φ and ω scans
 Absorption correction: none
 10296 measured reflections
 3996 independent reflections
 3015 reflections with *I* > 2σ(*I*)
R_{int} = 0.055
 θ_{max} = 27.5°

Refinement

Refinement on *F*²
R[*F*² > 2σ(*F*²)] = 0.047
wR(*F*²) = 0.137
S = 1.04
 3996 reflections
 207 parameters
 H-atom parameters constrained
 $w = 1/[\sigma^2(F_o^2) + (0.0671P)^2 + 0.1667P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 (Δ/σ)_{max} < 0.001
 Δρ_{max} = 0.24 e Å⁻³
 Δρ_{min} = -0.22 e Å⁻³

Table 1

Selected geometric parameters (Å, °).

N1–C7	1.2996 (16)	N4–C12	1.2910 (16)
N2–C7	1.3808 (18)	N5–C12	1.3893 (15)
N3–C7	1.3765 (16)	N6–C12	1.3798 (16)
N1–C7–N2	118.78 (12)	N4–C12–N5	119.00 (11)
N1–C7–N3	127.03 (12)	N4–C12–N6	126.66 (11)
N2–C7–N3	114.13 (11)	N5–C12–N6	114.32 (11)

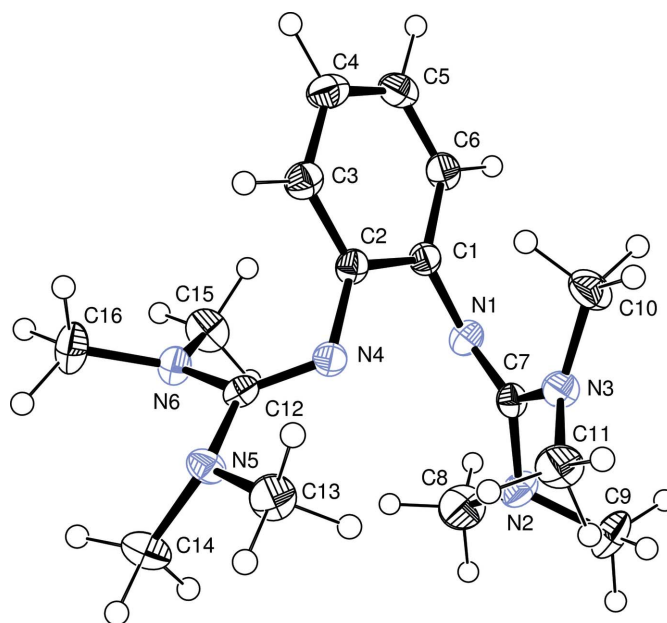


Figure 1

The molecular structure of (I). Displacement ellipsoids are drawn at the 50% probability level.

H atoms were positioned geometrically (C–H = 0.95–0.98 Å) and refined as riding, with *U*_{iso}(H) = 1.2*U*_{eq}(C).

Data collection: SMART (Bruker, 1998); cell refinement: SAINT (Bruker, 1998); data reduction: SAINT program(s) used to solve structure: SHELXS97 (Sheldrick, 1997); program(s) used to refine structure: SHELXL97 (Sheldrick, 1997); molecular graphics: ORTEP-3 for Windows (Farrugia, 1997); software used to prepare material for publication: SHELXL97 (Sheldrick, 1997).

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