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A new orthorhombic phase of *N*,*N'*-diphenylguanidine

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(*Received 28 October 1998; accepted 8 February 1999*)

Abstract

A new orthorhombic phase of the title compound, $C_{13}H_{13}N_3$, is reported. There are two symmetry-independent molecules in the unit cell, as in the monoclinic phase, both having a *syn-anti* conformation of the phenyl rings with respect to the unsubstituted N atom. This orthorhombic phase differs from the monoclinic one in the hydrogen-bonding scheme and molecular packing. Bond lengths and angles within the guanidine moiety are close to those expected for a central C*sp*^{2} atom with one C=N and two C—N bonds. The *anti* ring binds to the guanidine moiety as C_{aryl}—NH—C and the *syn* ring as C_{aryl}—N=C.

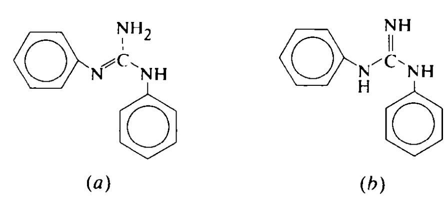
Comment

The title compound, also known as melaniline, is used as a cure accelerator in the rubber industry. It is marked under the trade name of 'Vulkazit'. Certain *N*,*N'*-diarylguanidines are potent ligands for the *N*-methyl-D-aspartate/PCP(Phencyclidine) receptor and have neuroprotective properties against glutamate-induced neuronal cell death (Olney *et al.*, 1989). *N*,*N'*-Di-*ortho*-tolylguanidine and its congeners are selective ligands for the haloperidol-sensitive σ receptor (Weber *et al.*, 1986; Largent *et al.*, 1987). As such, disubstituted guanidine compounds are of considerable interest in pharmaceutical applications, as neuroleptic and antipsychotic drugs. From the point of view of their physical properties, guanidine compounds are potentially interesting for non-linear optics applications (Zyss *et al.*, 1993).

This work is part of an on-going research project to study the structural, optical and dielectric properties of diphenylguanidine (dpg) salts. It is known that dpg is a very flexible molecule due to the low potential barrier for rotation of the phenyl rings and a number of different molecular conformations (*syn-syn*, *syn-anti* and *anti-anti*) have been found both in solution (Alagona *et al.*, 1994) and in several salts (Antolini *et al.*, 1991; Paixão *et al.*, 1997; Matos Beja *et al.*, 1998; Paixão *et al.*, 1998*a*,*b*,*c*). The effect of the counter ion of the protonated molecule on the relative stability of the different conformers has also been studied theoretically from both *ab initio* and Monte–Carlo calculations (Nagy & Durant, 1996). The dipole moment and polarizability of protonated dpg molecules, and therefore the optical and dielectric properties of dpg salts, depend on the orientation of the rings, which justifies the need to determine accurate structural data for these compounds.

The structure of monoclinic dpg was reported by Zakharov *et al.* (1980). We have found that under certain conditions, namely crystallization from weak acidic media, crystals of a new, orthorhombic phase of the free base grew from the solution. The structure of this new polymorph is reported here.

There are two symmetry-independent molecules in the asymmetric unit cell, I and II, as in the monoclinic phase. The CN_3 fragment of the guanidinium group has the planar geometry expected for a central C*sp*^{2} atom. The bond lengths C1—N1 [I 1.366 (3), II 1.367 (3) Å] and C1—N2 [I 1.356 (3), II 1.336 (3) Å] are larger than literature averages for unsubstituted and substituted guanidinium cations, 1.321 and 1.328 Å, respectively (Allen *et al.*, 1987). They are closer to the standard value of a single C—N bond than in dpg$^+$ salts, where protonation is followed by a relevant charge delocalization within the guanidine moiety. The bond length C1—N3 [I 1.278 (3), II 1.292 (3) Å] is significantly shorter than the C1—N1 and C1—N2 bonds and has a value closer to that expected for a C=N bond. This fact, and the objective localization of the H atoms on a difference Fourier map confirm the observation of Zakharov *et al.* (1980) that the tautomeric form (*a*) is preferred over form (*b*).



(*a*) (*b*)

The sums of the valence angles around C1 and C1' are 360.0 (4) and 359.9 (4)°, respectively, but the N—C—N angles differ considerably from the mean value of 120°. The largest deviation is that of N1—C1—N2 [I 112.9 (2), II 113.2 (2)°].

The conformation of the molecules in both polymorphs is similar, one of the rings lies *syn* and the other *anti* to the unsubstituted N atom, with the ring bonded to the imino N3 atom adopting the *syn* conformation. The C_{aryl} atoms are not coplanar with the guanidine group, and inspection of the torsion angles shows that the twist angles around the C1—N bonds differ for each ring, the largest one being that of the *anti* ring of molecule I. Also, the individual rotation angles of the phenyl rings around the C_{aryl}—N bonds are different for the two molecules of each polymorph. In the orthorhombic phase, the angles between the least-squares planes of the guanidine central fragment and the phenyl rings are 87.1 (1) (C2–C7), 22.9 (2) (C8–C13), 72.7 (1) (C2′–C7′) and 23.9 (2)° (C8′–C13′) compared with the corresponding values 73.7 (2), 34.4 (3), 64.7 (3) and 28.0 (3)° in the monoclinic phase (Zakharov *et al.*, 1980). The angles between the phenyl rings of each molecule are 74.8 (1) I and 83.6 (1)° II while in the monoclinic phase these angles are 75.2 (2) and 92.4 (3)°, respectively.

It is interesting to compare these results with the equilibrium geometry of an isolated dpg molecule. *Ab initio* Hartree–Fock Self Consistent Field (SCF)/4–31G calculations for dpg molecules both in the gas phase and in aqueous solution using the SCRF (self consistent reaction field) continuum solvent method have been reported by Alagona *et al.* (1994). Unfortunately, these calculations assumed the tautomeric form (*b*). We have repeated the calculations for the (*a*) tautomer using the quantum-chemistry package *GAMESS* (Schmidt *et al.*, 1993) with the same 4–31G basis set.

The equilibrium geometry of the isolated molecule corresponding to the energy minimum was found by the conjugate gradient method ($\Delta\rho$ at SCF cycle: 10^{-5} Bohr^{-3}; maximum and r.m.s. gradients at the last cycle: 5×10^{-6}, 2×10^{-6} Hartree Bohr^{-1} or Hartree rad^{-1}). The final energy is −662.2518 Hartree, a value substantially lower than that found for the (*b*) tautomer, −654.9901 Hartree. The calculations reproduce well the bond distances and angles (C1—N1 1.371, C1—N2 1.371, C1—N3 1.271 Å; N2—C1—N1 112.9, N3—C1—N1 122.3, N3—C1—N2 124.3°) with the exception of the angle C1—N3—C2 for which the calculated value is 123.6°. The calculated angle between the phenyl rings at equilibrium geometry is 73.8° which is close to the value observed in molecule I. The individual angles between each ring and the guanidinium CN_3 plane of the free molecule are 68.8 (C2–C7) and 5.0° (C8–C13) which differ considerably from the crystal values reported above. However, the calculations show that rotation of the rings from the equilibrium geometry in the free molecule towards the geometry found in the crystal costs only a small fraction of the solvation energy in water, estimated to be about 59 kJ mol^{-1} (Alagona *et al.*, 1994). Therefore, the orientation of the phenyl rings will be ultimately dependent on packing effects and weak intermolecular interactions. It is possible that dpg–solvent interactions during crystallization play a role in stabilizing a particular molecular conformation and crystal phase.

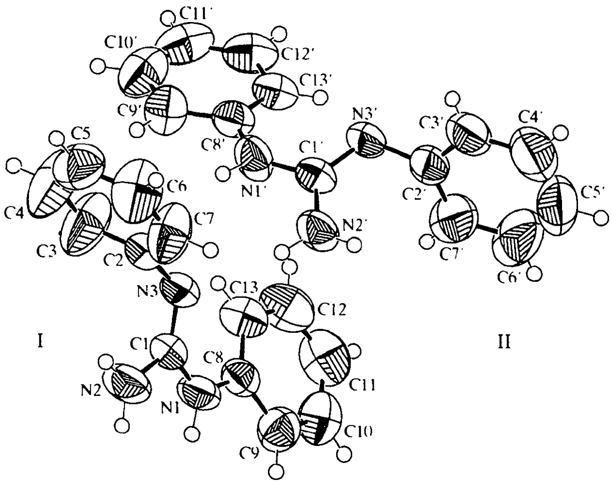


Fig. 1. *ORTEP*II (Johnson, 1976) plot of the title compound. Displacement ellipsoids are drawn at the 50% level.

Hydrogen bonding is markedly different in the two polymorphs. In the orthorhombic phase, molecules I and II are linked by hydrogen bonds in infinite chains running along [100]. The hydrogen-bonding functionality of the two symmetry-independent molecules is similar. The imino N3 atom of one molecule accepts two protons from the other, one donated by the NH_2 group and the other by the NH group. In the monoclinic phase, the imino N atom of each molecule accepts a single proton, donated either by the NH_2 or NH groups of the other symmetry-independent molecule. Therefore, and in contrast to the orthorhombic phase, the NH group acts as a donor in one molecule and as an acceptor in the other. Another difference in the hydrogen bonding of the two polymorphs concerns the role of the NH_2 groups. In the monoclinic phase, one molecule donates its two protons and the other is only involved in very weak hydrogen bonds, the shortest N···N distance being 3.520 (2) Å. Interestingly, although the hydrogen-bonding network is more extensive in the orthorhombic than in the monoclinic crystals, the full potential for hydrogen bonding of the dpg molecules is not fulfilled in either polymorph. Indeed, in the orthorhombic phase, one of the two H atoms of NH_2 is apparently not involved in hydrogen bonding. This contrasts with the situation commonly found in dpg$^+$ salts where a full saturation of hydrogen-bonding capability of the N atoms is usually observed.

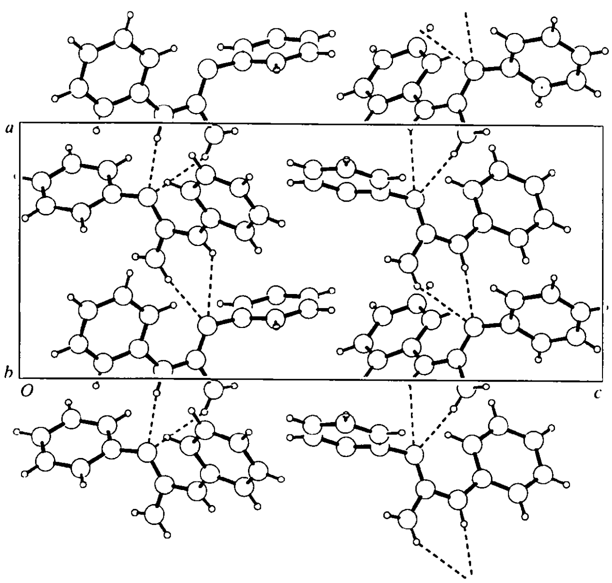


Fig. 2. Projection of the packing diagram along **b**, showing the hydrogen-bonding scheme as dashed lines.

Experimental

Crystals of orthorhombic dpg grew from water/ethanol solutions of *N*,*N*′-diphenylguanidine (98%, Aldrich) acidified by either boric or acetic acid. The crystal used in the data collection was grown from a boric acid solution.

Crystal data

$C_{13}H_{13}N_3$
M_r = 211.27
Orthorhombic
$P2_12_12_1$
a = 9.003 (5) Å
b = 12.699 (3) Å
c = 20.522 (8) Å
V = 2346.3 (17) Å^3
Z = 8
D_x = 1.196 Mg m^{-3}
D_m not measured

Mo *Kα* radiation
λ = 0.71073 Å
Cell parameters from 25 reflections
θ = 10.49–13.77°
μ = 0.074 mm^{-1}
T = 293 (2) K
Block
0.51 × 0.37 × 0.23 mm
Colourless

Data collection

Enraf–Nonius CAD-4 diffractometer
Profile data from ω–2θ scans
Absorption correction: none
3366 measured reflections
3006 independent reflections
2165 reflections with $I > 2\sigma(I)$

R_{int} = 0.014
θ_{max} = 24.97°
h = −6 → 10
k = −9 → 15
l = −24 → 24
3 standard reflections frequency: 180 min intensity decay: 1.1%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.036
$wR(F^2)$ = 0.109
S = 1.030
3006 reflections
290 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0539P)^2 + 0.3312P]$ where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{max}$ < 0.001
$\Delta\rho_{max}$ = 0.135 e Å^{-3}
$\Delta\rho_{min}$ = −0.116 e Å^{-3}
Extinction correction: *SHELXL*97 (Sheldrick, 1997)
Extinction coefficient: 0.0036 (10)
Scattering factors from *International Tables for Crystallography* (Vol. C)

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

N1—C1	1.366 (3)	N1′—C1′	1.367 (3)
N1—C8	1.402 (3)	N1′—C8′	1.400 (4)
N2—C1	1.356 (3)	N2′—C1′	1.336 (3)
N3—C1	1.278 (3)	N3′—C1′	1.292 (3)
N3—C2	1.421 (3)	N3′—C2′	1.412 (3)
C1—N1—C8	130.0 (2)	C1′—N1′—C8′	129.7 (2)
C1—N3—C2	118.3 (2)	C1′—N3′—C2′	118.5 (2)
N3—C1—N2	124.7 (3)	N3′—C1′—N2′	125.1 (3)
N3—C1—N1	122.4 (2)	N3′—C1′—N1′	121.6 (2)
N2—C1—N1	112.9 (2)	N2′—C1′—N1′	113.2 (2)
C2—N3—C1—N2	−2.2 (4)	C2′—N3′—C1′—N2′	10.7 (4)
C8—N1—C1—N2	173.6 (3)	C8′—N1′—C1′—N2′	−157.6 (3)
C1—N3—C2—C7	97.3 (4)	C1′—N3′—C2′—C7′	69.2 (4)
C1—N1—C8—C13	−19.4 (4)	C1′—N1′—C8′—C13′	1.3 (5)

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

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N2—H2*B*···N3′ⁱ	0.86	2.52	3.279 (3)	147.2
N1—H1···N3′ⁱ	0.86	2.16	3.016 (3)	170.6
N1′—H1′···N3	0.86	2.60	3.273 (4)	136.2
N2′—H2*B*′···N3	0.86	2.23	3.062 (3)	162.0

Symmetry code: (i) *x* − 1, *y*, *z*.

The structure was solved by direct methods using *SHELXS*97 (Sheldrick, 1990). H atoms were clearly observed in a Fourier difference synthesis. They were placed at calculated positions and refined as riding using the *SHELXL*97 (Sheldrick, 1997) defaults: C_{aryl}—H = 0.93, N—H = 0.86 Å, $U(H)_{eq} = 1.2U_{eq}$ of the parent atom. A planar trigonal geometry was assumed for the N—H bonds.

Examination of the crystal structure with *PLATON* (Spek, 1995) showed that there are no solvent-accessible voids in the crystal lattice. All calculations were performed on a Pentium 150 MHz PC running LINUX.

Data collection: *CAD*-4 *Software* (Enraf–Nonius, 1989). Cell refinement: *CAD*-4 *Software*. Data reduction: *SDP-Plus* (Frenz, 1985). Program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1990). Program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997). Molecular graphics: *ORTEP*II (Johnson, 1976). Software used to prepare material for publication: *SHELXL*97.

The authors are indebted to Dr J. C. Prata Pina for his invaluable assistance in the maintenance of the CAD-4 diffractometer. This work was supported by Fundação Ciência e Tecnologia (FCT).

Supplementary data for this paper are available from the IUCr electronic archives (Reference: NA1391). Services for accessing these data are described at the back of the journal.

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