Acta Crystallographica Section E
Structure Reports
Online
ISSN 1600-5368

N,*N*′-Diphenylguanidinium phthalate

P. S. Pereira Silva,[a] M. Ramos Silva,[b] A. Matos Beja[b] and J. A. Paixão[b]*

[a]Escola Superior Agrária, Instituto Politécnico de Castelo Branco, Quinta da Senhora de Mércules, Apartado 119, 6001-909 Castelo Branco, Portugal, and [b]CEMDRX, Departamento de Física, Faculdade de Ciências e Tecnologia, Universidade de Coimbra, P-3004-516 Coimbra, Portugal

Correspondence e-mail: psidonio@esa.ipcb.pt

Received 7 February 2006
Accepted 11 February 2006

The cation of the title salt, $C_{13}H_{14}N_3^+ \cdot C_8H_5O_4^-$, adopts a conformation with one of the phenyl rings lying *syn* and the other *anti* with respect to the unsubstituted N atom. The anion features a strong intramolecular hydrogen bond, with the carboxyl groups twisted out of the ring plane. Intermolecular hydrogen-bonds link anions and cations, forming chains that run parallel to the *c* axis.

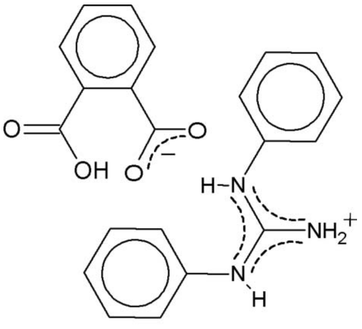
Key indicators

Single-crystal X-ray study
T = 293 K
Mean σ(C–C) = 0.004 Å
R factor = 0.038
wR factor = 0.114
Data-to-parameter ratio = 11.7

For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

Comment

Diphenylguanidine is sold under the trade name Vulkazit and is used as a cure accelerator in the rubber industry. To the solid-state physicist, diphenylguanidine is of interest as a flexible molecule due to its low energy barrier for rotation of the phenyl rings. A number of molecular conformations, *e.g.* *syn–syn*, *syn–anti* and *anti–anti*, have been found in solution (Alagona *et al.*, 1994) and in the solid state (Paixão, Matos Beja *et al.*, 1999; Paixão, Pereira Silva *et al.*, 1999; Pereira Silva *et al.*, 1999). Hydrogen phthalates (HP) can crystallize with different hydrogen-bonding motifs, even in the presence of the same cation, an observation which suggests there is a small difference between the free energy of the two main hydrogen-bonding motifs (Langkilde *et al.*, 2004), *i.e.* intra- or intermolecular carboxyl hydrogen bonds. Jessen & Küppers (1991) concluded that larger cations exert a small Coulombic force upon the HP ion which is not sufficient to twist the carboxy groups out of the plane of the phenyl group, thus favouring the formation of an intramolecular hydrogen bond. This is also the case in the title compound, (I) (Fig. 1 and Table 1).



(I)

The phthalate anion arises due to the transfer of a proton to the guanidine fragment. The remaining H atom is shared between the carboxyl groups of the phthalic anion, forming a short intramolecular hydrogen bond The O2···O3 distance is just 2.444 (3) Å, reflecting the strength of this interaction. The anion has the carboxylate and carboxylic groups twisted out of the plane of the aromatic ring with the donor and acceptor

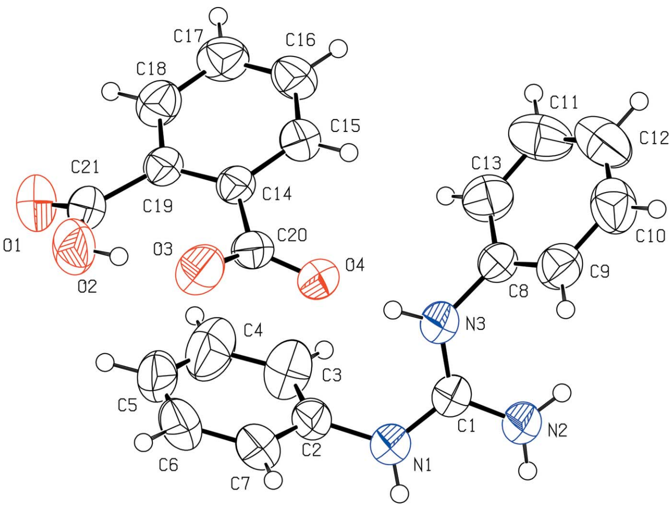


Figure 1
The asymmetric unit of (I), showing the atom-numbering scheme, with displacement ellipsoids drawn at the 50% probability level.

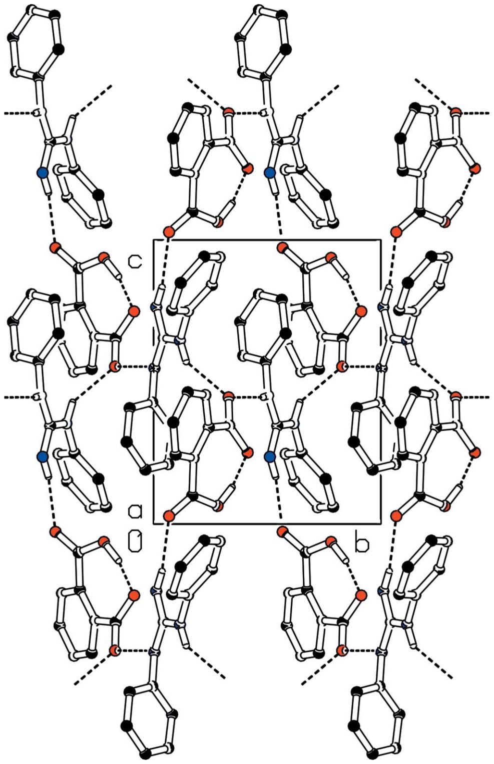


Figure 2
Packing diagram for (I). Hydrogen bonds are shown as dashed lines. H atoms not involved in hydrogen bonding have been omitted for clarity.

atoms on the same side of the ring. The C19—C14—C20—O3 and C14—C19—C21—O2 torsion angles are −31.7 (3) and −155.3 (2)°, respectively. The CN_3 fragment of the guanidinium group has a planar geometry, as expected for a central Csp^2 atom. The C1—N1 and C1—N3 bond lengths of 1.337 (3) and 1.327 (3) Å, respectively, are within the range expected for a delocalized C—N double bond and the C1—N2 distance is 1.313 (3) Å. One of the rings lies *syn* and the other *anti* with respect to the unsubstituted atom N2. The dihedral angles between the central planar guanidinium fragment and the least-squares planes of the phenyl rings are 68.55 (9) (C2—C7) and 59.92 (9)° (C8–C13), and the dihedral angle between the planes of the two phenyl rings is 46.89 (11)°.

Intermolecular hydrogen bonds (Fig. 2 and Table 2) link the anions and cations. Chains running parallel to the *c* axis are assembled *via* N2—H2*A*···O1[ii] (see Table 2 for symmetry codes) and N3—H3*A*···O4 interactions between alternating cations and anions. Additionally, N1—H1···O4[i] interactions link the chains laterally, with atom O4 accepting two protons.

Experimental

Phthalic acid (Aldrich, 98%, 1 mmol) was added to diphenylguanidine (Aldrich, 97%, 1 mmol) in a water–ethanol (1:1) solution. The solution was warmed slowly and then left to evaporate under ambient conditions. After a few days, small colourless transparent single crystals were deposited.

Crystal data

$C_{13}H_{14}N_3^+\cdot C_8H_5O_4^-$
M_r = 377.39
Monoclinic, $P2_1$
a = 10.7714 (12) Å
b = 8.440 (2) Å
c = 11.420 (3) Å
β = 112.172 (12)°
V = 961.4 (4) Å^3
Z = 2
D_x = 1.304 Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 25 reflections
θ = 8.2–12.0°
μ = 0.09 mm^{-1}
T = 293 (2) K
Prism, colourless
0.34 × 0.27 × 0.15 mm

Data collection

Enraf–Nonius CAD-4 diffractometer
profile data from ω–2θ scans
Absorption correction: none
5916 measured reflections
2999 independent reflections
1803 reflections with $I > 2\sigma(I)$
$R_{\rm int}$ = 0.031
$\theta_{\rm max}$ = 30.1°
$h = -15 \rightarrow 15$
$k = 0 \rightarrow 11$
$l = -16 \rightarrow 16$
3 standard reflections
frequency: 180 min
intensity decay: 3%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.038
$wR(F^2)$ = 0.114
S = 1.00
2999 reflections
256 parameters
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0647P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\rm max} < 0.001$
$\Delta\rho_{\rm max}$ = 0.16 e Å^{-3}
$\Delta\rho_{\rm min}$ = −0.22 e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

N1—C2	1.417 (3)	O3—C20	1.262 (3)
N3—C8	1.429 (3)	O2—C21	1.299 (3)
O4—C20	1.229 (2)	O1—C21	1.205 (3)
N2—C1—N1	118.47 (18)	O4—C20—O3	122.7 (2)
N3—C1—N1	119.24 (18)	O1—C21—O2	120.7 (2)
C8—N3—C1—N2	6.7 (4)	C2—N1—C1—N2	−163.0 (3)
C8—N3—C1—N1	−173.4 (2)	C2—N1—C1—N3	17.1 (4)

o1068 Pereira Silva *et al.* • $C_{13}H_{14}N_3^+\cdot C_8H_5O_4^-$ *Acta Cryst.* (2006). E**62**, o1067–o1069

Table 2
Hydrogen-bond geometry (Å, °).

D—H···A	D—H	H···A	D···A	D—H···A
N1—H1···O4$^{\rm i}$	0.86	2.01	2.799 (2)	152
N2—H2A···O1$^{\rm ii}$	0.86	2.08	2.861 (3)	151
N3—H3A···O4	0.86	2.10	2.861 (3)	147
O2—H2···O3	0.95 (4)	1.51 (4)	2.444 (3)	167 (4)

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

The carboxyl H atom was refined [O—H = 0.95 (4) Å]. The other H atoms were placed at calculated positions and refined as riding [N—H = 0.86 Å and C—H = 0.93 Å, and $U_{\rm iso}$(H) = 1.2$U_{\rm eq}$(parent atom)]. In the absence of significant anomalous scattering effects, Friedel pairs were merged in the final refinement.

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: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEPII* (Johnson, 1976); software used to prepare material for publication: *SHELXL97*.

This work was supported by Fundação para a Ciência e a Tecnologia (FCT) under project POCI/FIS/58309/2004.

References

Alagona, G., Ghio, C., Nagy, P. & Durant, G. (1994). *J. Phys. Chem.* **98**, 5422–5430.

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

Frenz, B. A. (1985). *Enraf-Nonius SDP-Plus Structure Determination Package*. Version 3.0. Enraf–Nonius, Delft, The Netherlands.

Jessen, S. M. & Küppers, H. (1991). *J. Mol. Struct.* **263**, 247–265.

Johnson, C. K. (1976). *ORTEPII*. Report ORNL-5138. Oak Ridge National Laboratory, Tennessee, USA.

Langkilde, A., Madsen, D. & Larsen, S. (2004). *Acta Cryst.* B**60**, 502–511.

Paixão, J. A., Matos Beja, A., Pereira Silva, P. S., Ramos Silva, M. & Alte da Veiga, L. (1999). *Acta Cryst.* C**55**, 1037–1040.

Paixão, J. A., Pereira Silva, P. S., Matos Beja, A., Ramos Silva, M., de Matos Gomes, E. & Belsley, M. (1999). *Acta Cryst.* C**55**, 1287–1290.

Pereira Silva, P. S., Paixão, J. A., Matos Beja, A., Ramos Silva, M. & Alte da Veiga, L. (1999). *Acta Cryst.* C**55**, 1096–1099.

Sheldrick, G. M. (1997). *SHELXS97* and *SHELXL97*. University of Göttingen, Germany.

Acta Cryst. (2006). E**62**, o1067–o1069 Pereira Silva *et al.* • $C_{13}H_{14}N_3^{+}\cdot C_8H_5O_4^{-}$ **o1069**