Profile data from ω–2θ scans	$h = -9 \rightarrow 9$
Absorption correction: none	$k = -11 \rightarrow 11$
3030 measured reflections	$l = -11 \rightarrow 1$
2510 independent reflections	3 standard reflections
2095 reflections with $I > 2\sigma(I)$	frequency: 300 min intensity decay: 1.2%

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0391P)^2 + 0.3614P]$ where $P = (F_o^2 + 2F_c^2)/3$
$R[F^2 > 2\sigma(F^2)] = 0.033$	$(\Delta/\sigma)_{max} < 0.001$
$wR(F^2) = 0.090$	$\Delta\rho_{max} = 0.210$ e Å^{-3}
$S = 1.027$	$\Delta\rho_{min} = -0.220$ e Å^{-3}
2510 reflections	Extinction correction: none
186 parameters	Scattering factors from *International Tables for Crystallography* (Vol. C)
H atoms treated by a mixture of independent and constrained refinement	

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

S1—C6	1.803 (2)	N1—C1	1.471 (2)
S1—C5	1.803 (2)	N1—C2	1.476 (2)
C6—S1—C5	90.18 (8)	C5—C4—C3	113.06 (15)
C1—N1—C2	105.84 (13)	C3—C4—C1	103.52 (13)
N1—C1—C4	107.73 (13)	C4—C5—S1	107.13 (12)
N1—C2—C3	105.20 (13)	C1—C6—S1	108.33 (12)
C4—C3—C2	102.88 (14)		
C6—C1—C4—C3	−125.73 (15)	C4—C1—C7—O1	−117.9 (2)
C6—C1—C7—O1	122.0 (2)		

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

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N1—H1···O1	0.82 (2)	2.24 (2)	2.703 (2)	115 (2)
N1—H1···O3	0.82 (2)	2.30 (2)	2.899 (2)	130 (2)
C3—H3*A*···O3	0.97	2.55	3.108 (2)	117

The H atoms of the organic moiety were placed in calculated positions and refined as riding using *SHELXL*97 defaults (Sheldrick, 1997), except for the amino H atom, which was located from a difference Fourier synthesis and refined with $U_{eq} = 1.2U_{eq}$(N1). Examination of the crystal structure with *PLATON* (Spek, 1995) showed that there were no significant empty cavities in the crystal packing. 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. Molecular graphics: *ORTEP*II (Johnson, 1976). Software used to prepare material for publication: *SHELXL*97.

We are indebted to Dr José Carlos Prata Pina for helpful assistance with our CAD-4 automatic diffractometer which enabled the experimental work to be carried out. This work was supported by project PRAXIS XXI 2/2.1/QUI/390/94 and Chymiotechnon. We thank Faculdade de Farmácia, University of Coimbra, Portugal, for the leave of absence of AMTDPVC.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: NA1332). Services for accessing these data are described at the back of the journal.

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N,*N*′-Diphenylguanidinium Nitrate

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Abstract

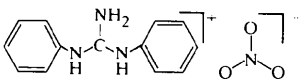
The cation of the title salt, $C_{13}H_{14}N_3^+.NO_3^-$, is found to have a conformation with both phenyl rings lying in *syn* positions with respect to the unsubstituted N atom. The geometry of the guanidinium group is close to that expected for a central C_{sp^2} atom. The structure is stabilized by a two-dimensional network of hydrogen bonds in the (100) plane, where the O atoms of the anion are acceptors from the N—H guanidinium groups.

Comment

Certain *N*,*N*′-diarylguanidines are reported to have neuroprotective properties against glutamate-induced neuronal cell depth (Olney *et al.*, 1989). *N*,*N*′-Di-*o*-tolylguanidine and its congeners were shown to be selective ligands for the haloperidol-sensitive σ receptors, and neuroleptic and antihypersensitive activities of these

compounds have been reported (Largent *et al.*, 1987; Snyder & Largent, 1989). From the structural point of view, diphenylguanidinium salts are interesting due to the different conformations exhibited by the cations, as expected from the low potential barrier of rotation of the phenyl rings (Zakharov *et al.*, 1980), and these salts might also be regarded as potential candidates for non-linear optical applications (Zyss *et al.*, 1993). We are currently engaged in a research project aimed at investigating the structures, and dielectric and optical properties of diphenylguanidine compounds.

The central guanidine fragment of the cation of the title salt, (I), is planar and the geometry is close to that expected for a central C_{sp^2} atom. The bond lengths C1—N1 [1.328 (3) Å] and C1—N3 [1.348 (3) Å] are within the range expected for a delocalized C=N bond, while the C1—N2 bond length is slightly shorter [1.310 (3) Å]. These values can be compared with the average values reported for substituted and unsubstituted guanidinium cations of 1.321 and 1.328 Å, respectively (Allen *et al.*, 1987).



(I)

The geometry of the guanidine fragment of the cation is similar to that observed in other diphenylguanidinium salts (Paixão *et al.*, 1997, 1998; Antolini *et al.*, 1991), but different to that of diphenylguanidine molecules, where one of the bonds has double-bond character and is much shorter than the other two (Zakharov *et al.*, 1980). In the X-ray study of the unprotonated species, one H atom was assigned to the N atom having the longer N—phenyl bond and the remaining two H atoms of the guanidine group were assigned to the unsubstituted N2 atom. In the cationic form, the N—C bond distances suggest that a H atom is bonded to the N1 and N3 atoms, and this was confirmed by analysis of a difference Fourier synthesis.

The bond lengths N1—C2 and N3—C8 are similar to those observed in the free base and in other diphenylguanidinium salts. The phenyl rings are flat within 0.01 Å and have a *syn,syn* conformation with respect to the unsubstituted N2 atom. The dihedral angle between the two phenyl rings is 81.49 (10)°, and the dihedral angles between the ring planes and the plane defined by the central guanidine fragment are 35.71 (12) (C2–C7) and 45.92 (14)° (C8–C13). This conformation is similar to that observed in both *N,N'*-diphenylguanidinium hydrogenselenite monohydrate (Paixão *et al.*, 1997) and *N*-(adamant-1-yl)-*N'*-(2-iodophenyl)guanidinium chloride (Weakley *et al.*, 1990). In the molecular crystal of diphenylguanidine, one of the rings lies *syn* and the other *anti* to the N2 atom, and such a conformation was also found in both diphenylguanidinium chlorobenzeneseleninate (Antolini *et al.*, 1991) and diphenylguanidinium perchlorate (Paixão *et al.*, 1998).

With regard to the geometry of the anion, there is a slight dissymmetry in the N—O bond lengths; the N4—O2 bond is significantly shorter than the other two. This probably reflects the fact that the O2 atom is involved in a weaker hydrogen bond than the other O atoms (see below). The bond angles do not differ significantly from the ideal value and the anion remains almost planar [maximum deviation from the least-squares plane is 0.007 (2) Å].

The anions and cations are linked by a two-dimensional network of hydrogen bonds in the (100) plane (Fig. 2). Each of the N—H groups is involved in a hydrogen bond with the bare O atoms of the anion.

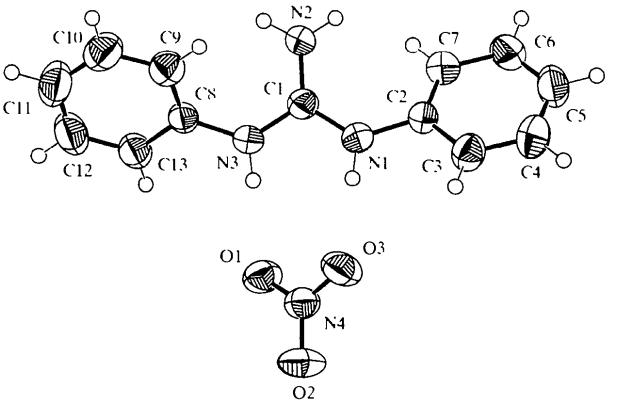


Fig. 1. *ORTEP*II (Johnson, 1976) plot of the title compound. Displacement ellipsoids are drawn at the 50% probability level.

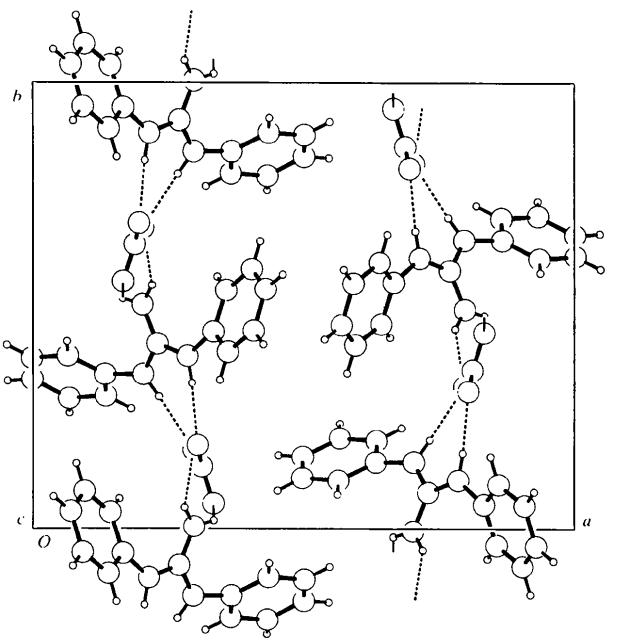


Fig. 2. Projection of the crystal structure down the *c* axis showing the hydrogen-bond network as dashed lines.

The O1 atom is an acceptor of two protons, the other O atoms accept a proton each. There is, in addition, a short intramolecular contact between atoms C7 and N2 [C7···N2 3.069 (4) Å and C7—H···N2 110.6°].

It should be noted that because none of the atoms is a strong enough anomalous scatterer at the characteristic molybdenum wavelength, the absolute structure determination, *i.e.* the determination of the orientation of the structure with respect to the polar axis, could not be performed.

Experimental

The title compound was prepared by adding nitric acid dropwise to a water solution of *N,N'*-diphenylguanidine (98%, Aldrich) until complete neutralization was achieved. Small crystals grew from the solution over a period of a few weeks.

Crystal data

$C_{13}H_{14}N_3^+.NO_3^-$
M_r = 274.28
Orthorhombic
$Pna2_1$
a = 17.020 (4) Å
b = 13.906 (3) Å
c = 5.811 (1) Å
V = 1375.3 (5) Å^3
Z = 4
D_x = 1.325 Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
λ = 0.71073 Å
Cell parameters from 25 reflections
θ = 9–15°
μ = 0.097 mm^{-1}
T = 293 (2) K
Tabular
0.30 × 0.23 × 0.13 mm
Clear pale brown

Data collection

Enraf–Nonius CAD-4 diffractometer
Profile data from ω–2θ scans
Absorption correction: none
3521 measured reflections
2061 independent reflections (including Friedel pairs)
1548 reflections with $I > 2\sigma(I)$

R_{int} = 0.024
θ_{max} = 24.97°
$h = -20 \rightarrow 18$
$k = 0 \rightarrow 16$
$l = -6 \rightarrow 6$
3 standard reflections
frequency: 180 min
intensity decay: 1.5%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.031
$wR(F^2)$ = 0.098
S = 0.916
2061 reflections
182 parameters
H atoms constrained
$w = 1/[\sigma^2(F_o^2) + (0.0631P)^2 + 0.2366P]$ where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max}$ = 0.15 e Å^{-3}
$\Delta\rho_{min}$ = −0.13 e Å^{-3}
Extinction correction: *SHELXL*93
Extinction coefficient: 0.016 (3)
Scattering factors from *International Tables for Crystallography* (Vol. C)

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

O1—N4	1.252 (3)	N1—C2	1.417 (3)
O2—N4	1.224 (3)	N2—C1	1.310 (3)
O3—N4	1.260 (3)	N3—C1	1.348 (3)
N1—C1	1.328 (3)	N3—C8	1.416 (3)
C1—N1—C2	130.3 (2)	O1—N4—O3	120.5 (2)
C1—N3—C8	128.2 (2)	N2—C1—N1	123.7 (3)
O2—N4—O1	119.9 (3)	N2—C1—N3	120.6 (2)
O2—N4—O3	119.5 (3)	N1—C1—N3	115.7 (2)
C1—N1—C2—C3	152.3 (3)	C1—N3—C8—C9	−34.2 (4)

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

D—H···A	H···A	D···A	D—H···A
N1—H1···O3	1.97	2.822 (3)	173.8
N3—H3···O1	2.00	2.860 (3)	177.3
N2—H2A···O1^i	2.27	3.056 (3)	151.9
N2—H2A···O2^i	2.68	3.186 (4)	119.3

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

The H atoms of the organic moiety were located from a difference Fourier synthesis, placed at calculated positions and refined as riding using *SHELXL*97 (Sheldrick, 1997) defaults. Examination of the crystal structure with *PLATON* (Spek, 1995) showed that there was a small potential solvent volume of 39.1 Å^{-3} in the crystal lattice at (0.559,0.722,0.208) and symmetry-equivalent positions. However, the small residual electron density at this position excluded the possibility of occupation by a water molecule. 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. Molecular graphics: *ORTEP*II (Johnson, 1976). Software used to prepare material for publication: *SHELXL*97.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: NA1354). Services for accessing these data are described at the back of the journal.

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Irbesartan Crystal Form B

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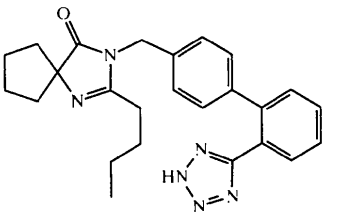
Abstract

Irbesartan (2-butyl-3-{[2′-(2*H*-tetrazol-5-yl)biphenyl-4-yl]methyl}-1,3-diazaspiro[4.4]non-1-en-4-one, $C_{25}H_{28}N_6O$), a highly selective angiotensin II receptor (AT_1) antagonist was found to exist in two distinct crystal forms (A and B). This paper describes the crystal structure of irbesartan form B.

Comment

Irbesartan, (I), belongs to a new class of antihypertensive agents which interfere with the renin angiotensin system. It is a highly selective non-peptide antagonist of angiotensin II AT_1 receptors, which has shown clinical benefits in the treatment of hypertension.



(I)

Irbesartan exists in the solid state as two distinct forms. It provides a rare example of desmotropy (Lempert *et al.*, 1973) in which tautomeric equilibrium exists in the liquid state, and individual tautomers can be isolated in the solid state, each with unique and stable crystal forms. Each crystal form exhibits unique properties when examined by optical microscopy, differential scanning calorimetry (DSC), Fourier-transform infrared (FTIR) spectroscopy and powder X-ray diffraction (XRDP). A thorough examination of the crystallographic data is an essential component in our understanding of not only pharmaceutical activity, but also the physicochemical and solid-state NMR data.

It is known from the literature (Elguero *et al.*, 1976) that a monosubstituted tetrazole ring can undergo a tautomeric process according to the scheme below. If both tautomers can be crystallized then we face a case of desmotropy (Foces-Foces *et al.*, 1994), which seems to be a very rare phenomenon.

The crystal structure determination proved unambiguously that form B is a 2*H*-tautomer, *i.e.* the tetrazole ring carries the H atom at the N25 atom (Fig. 1). Difference–Fourier calculations indicated the presence

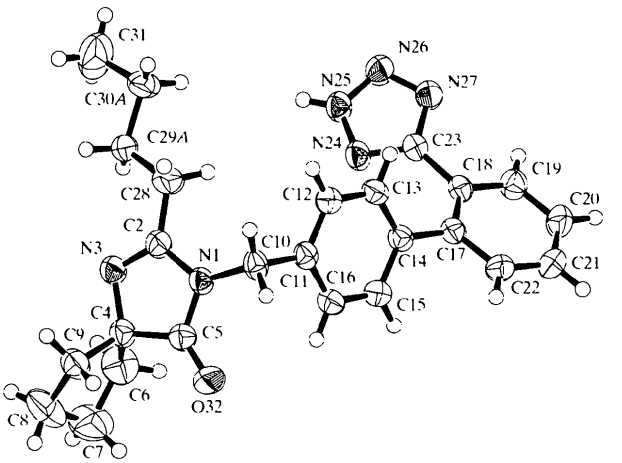


Fig. 1. The molecular structure and atomic numbering for irbesartan.

† Deceased.