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1-(Isopropylideneamino)guanidinium 2-nitrobenzoate: formation of corrugated sheets from $R_2^2(8)$ and $R_6^4(16)$ rings

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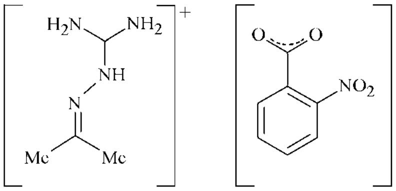
In the title compound, $C_4H_{11}N_4^+\cdot C_7H_4NO_4^-$, the guanidinium cation acts as a strong hydrogen-bonding donor *via* the guanidine NH_2 and NH groups, with the carboxy groups of the nitrobenzoate group acting as the acceptors. These hydrogen bonds lead to fused $R_2^2(8)$ and $R_6^4(16)$ rings, which form corrugated sheets perpendicular to [010].

Comment

Some of us have previously reported the supramolecular arrangements of anilinium salts of arenecarboxylates (*e.g.* Glidewell *et al.*, 2003, 2005*a*,*b*). We now report the structure and supramolecular arrangement of the title compound, $[(H_2N)_2C{-}NH{-}N{=}CMe_2]^+\cdot[2\text{-}O_2NC_6H_4CO_2]^-$, (I).



(I)

The crystal structure solution confirms the presence of a salt composed of a 2-nitrobenzoate anion and a $[(H_2N)_2CNH{-}N{=}CMe_2]^+$ cation. The adjacent positions of the carboxy and nitro groups in the nitrobenzoate anion lead to both groups twisting away from the plane; the latter is twisted at an angle of 24.72 (15)°, whereas the carboxy group is more nearly perpendicular, at 71.18°, as can be seen in Fig. 1. The 1-(isopropylideneamino)guanidinium complex is nearly planar, with an r.m.s. deviation of 0.0635 Å, and atom N4 shows the largest deviation from planarity [0.1256 (16) Å]. The angle between the plane defined by this molecule and that of the 2-nitrobenzoate ring is 72.17 (7)°. A complex strong hydrogen-bonding scheme operates between the cation and the anion (Table 1). The guanidinium N atoms act as donors, with the carboxyate O atoms the acceptors.

Two main motifs dominate the hydrogen bonding in (I). Firstly, a nearly symmetrical simple $R_2^2(8)$ ring (Bernstein *et al.*, 1995) forms from hydrogen bonding between the two molecules, involving the two guanidinium amino groups and the two carboxylate O atoms, *viz.* N2—H2*A*···O1 and N3—H3*A*···O2 (Fig. 1). These simple dimeric rings are linked by the other hydrogen bonds to form corrugated sheets (Fig. 2).

The carboxylate O atoms are central to the hydrogen-bonding scheme, and both act as multiple acceptors. As well as acting as an acceptor in the dimer described above, carboxylate atom O1 acts as a double acceptor to other guanidinium donors, *viz.* N3—H3*B*···O1^{ii} and N4—H4*A*···O1^{ii} [symmetry code: (ii) $x-\frac{1}{2}, -y+\frac{1}{2}, z+\frac{1}{2}$]. The other carboxylate O atom, O2, also is an acceptor for the guanidinium donor, *viz.* N2—H2*B*···O2^{i} [symmetry code: (i) $x-\frac{1}{2}, -y+\frac{1}{2}, z-\frac{1}{2}$]. These two chains thus form the second major motif, also shown in Fig. 2, namely an $R_6^4(16)$ ring. There is thus an alternating ladder of these two motifs, which combine to give the corrugated sheets.

The nitro O atoms do not participate in the strong hydrogen bonding described above. The only likely connection is

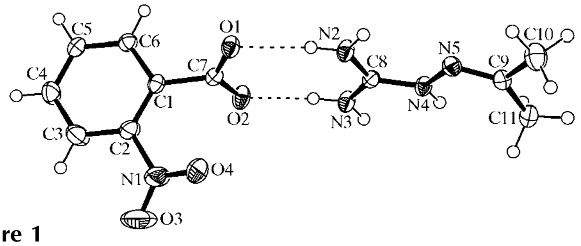


Figure 1
The molecular structure of (I), showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 50% probability level and H atoms are shown as small spheres of arbitrary radii. Dashed lines indicate hydrogen bonds.

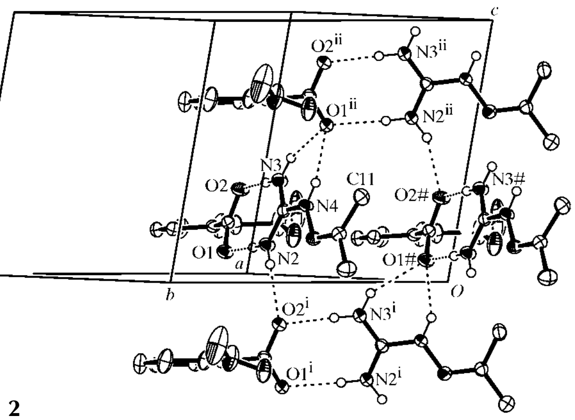


Figure 2
Part of the unit cell of (I), showing the formation of hydrogen-bonded rings. For clarity, H atoms not involved in the hydrogen bonding have been omitted. Dashed lines indicate hydrogen bonds. Atoms labelled with (i), (ii) or a hash (#) are at the symmetry positions $(x-\frac{1}{2}, -y+\frac{1}{2}, z-\frac{1}{2})$, $(x-\frac{1}{2}, -y+\frac{1}{2}, z+\frac{1}{2})$ and $(x-1, y, z)$, respectively.

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through a very weak aryl C5—H5$\cdots$O4^{iii} bond [symmetry code: (iii) $x + 1$, y, z], which would contribute to the sheet structure, forming chains along [100].

Experimental

Solutions of aminoguanidinium carbonate, $[HN{=}C(NH_2){-}NH{-}NH_2]{\cdot}H_2CO_3$ (3 mmol), in MeOH (20 ml) and 2-nitrobenzoic acid (3 mmol) in MeOH (20 ml) were mixed. After the effervescence had subsided, the reaction solution was maintained at 313 K for 30 min, left overnight at room temperature and then reduced on a rotary evaporator to leave crude $[(H_2N)_2C{-}NH{-}NH_2]^+{\cdot}[2{-}O_2NC_6H_4{-}CO_2]^-$. Attempts to obtain suitable crystals of $[(H_2N)_2C{-}NH{-}NH_2]^+{\cdot}[2{-}O_2NC_6H_4CO_2]^-$ for X-ray study from EtOH and MeOH solutions failed. The crude material was dissolved in acetone, and the solution was left to produce crystals of (I) slowly (m.p. 449–451 K).

Crystal data

$C_4H_{11}N_4^+{\cdot}C_7H_4NO_4^-$
$M_r = 281.28$
Monoclinic, $P2_1/n$
$a = 7.8683$ (4) Å
$b = 19.4979$ (12) Å
$c = 9.1273$ (5) Å
$\beta = 98.968$ (3)°
$V = 1383.15$ (13) Å^3

$Z = 4$
$D_x = 1.351$ Mg m^{-3}
Mo $K\alpha$ radiation
$\mu = 0.11$ mm^{-1}
$T = 120$ (2) K
Cut plate, colourless
0.28 × 0.12 × 0.02 mm

Data collection

Nonius KappaCCD area-detector diffractometer
φ and ω scans
Absorption correction: multi-scan (*SADABS*; Sheldrick, 2003)
$T_{min} = 0.623$, $T_{max} = 0.928$ (expected range = 0.670–0.998)

18434 measured reflections
3163 independent reflections
2158 reflections with $I > 2\sigma(I)$
$R_{int} = 0.087$
$\theta_{max} = 27.5°$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.058$
$wR(F^2) = 0.133$
$S = 1.06$
3163 reflections
183 parameters
H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.044P)^2 + 0.8011P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 0.23$ e Å^{-3}
$\Delta\rho_{min} = -0.32$ e Å^{-3}

Table 1
Hydrogen-bond geometry (Å, °).

$D{-}H\cdots A$	$D{-}H$	$H\cdots A$	$D\cdots A$	$D{-}H\cdots A$
N2—H2*A*$\cdots$O1	0.88	2.04	2.912 (2)	174
N3—H3*A*$\cdots$O2	0.88	1.90	2.774 (2)	175
N2—H2*B*$\cdots$O2^{i}	0.88	2.12	2.926 (2)	152
N3—H3*B*$\cdots$O1^{ii}	0.88	2.22	2.994 (2)	146
N4—H4*A*$\cdots$O1^{ii}	0.88	2.06	2.863 (2)	151

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

All H atoms were located in difference maps and then treated as riding atoms, with C—H distances of 0.95 (aryl) or 0.98 Å (methyl) and N—H distances of 0.88 Å, with U_{iso}(H) values of $1.2U_{eq}$(aryl or NH) or $1.5U_{eq}$(methyl). The displacement ellipsoid for nitro atom O3 was large, with a high U_{33} value. Attempts to split the position of O3 over two sites were unsuccessful, simply leading to one dominant large ellipsoid, and one even larger ellipsoid with very low occupancy. Hence, despite the large value obtained, the single-site model was retained for the final refinement.

Data collection: *COLLECT* (Nonius, 1998); cell refinement: *DENZO* (Otwinowski & Minor, 1997) and *COLLECT*; data reduction: *DENZO* and *COLLECT*; program(s) used to solve structure: *OSCAIL* (McArdle, 2003) and *SHELXS97* (Sheldrick, 1997*a*); program(s) used to refine structure: *OSCAIL* and *SHELXL97* (Sheldrick, 1997*a*); molecular graphics: *ORTEP-3 for Windows* (Farrugia, 1997); software used to prepare material for publication: *CIFTAB* (Sheldrick, 1997*b*) and *PLATON* (Spek, 2003).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: FG3021). Services for accessing these data are described at the back of the journal.

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