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Key indicators

Single-crystal X-ray study

$T = 297$ K

Mean $\sigma(C-C) = 0.006$ Å

R factor = 0.046

wR factor = 0.154

Data-to-parameter ratio = 6.6

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

Polyfunctionalized pyridinium *N*-benzoylguanidine: *N*²-benzoyl-*N*¹-(4-methylphenyl)-*N*³-pyridinioguanidin-3-ide

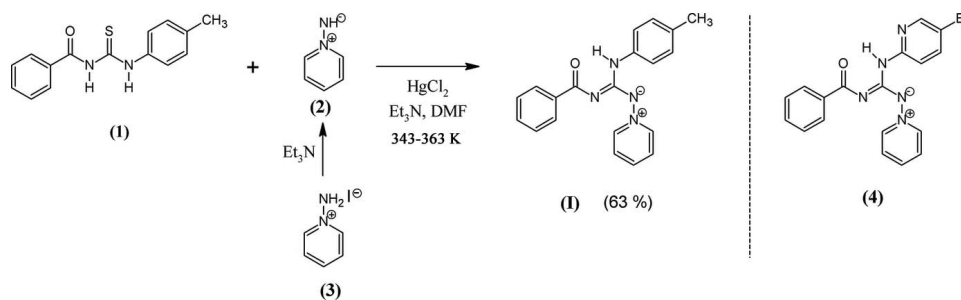
The title compound, $C_{20}H_{18}N_4O$, is an example of a recently described pyridinium *N*-benzoylguanidine. This work represents the second structural study of this kind of compound. The structure is stabilized by $C-H \cdots \pi$, $C-H \cdots N$ and $C-H \cdots O$ interactions.

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Comment

Pyridinium *N*-benzoylguanidines are a new kind of poly-substituted guanidines that can be envisioned as cycloiminium ylides (Johnson, 1996). Recently, we described the first synthesis of polysubstituted pyridinium *N*-benzoylguanidines through reaction of thioureas with a pyridinium *N*-ylide (Cunha *et al.*, 2005), being the first example of a nitrogen ylide as the nucleophilic component in the guanylation reaction. To gain insight into intra- and intermolecular interactions of such compounds, we have undertaken a structural analysis through X-ray diffraction, and here we describe the structural study of one polyfunctionalized pyridinium *N*-benzoylguanidine, namely *N*²-benzoyl-*N*¹-(4-methylphenyl)-*N*³-pyridinioguanidin-3-ide, (I).



The polysubstituted pyridinium *N*-benzoylguanidine, (I), afforded good single crystals for X-ray analysis and several structural features emerged which deserve comment. Fig. 1 shows the molecular structure of (I) with the atomic numbering scheme. Thus, the *E* configuration of (I) was unambiguously confirmed. Selected geometrical parameters are given in Table 1.

A least-squares plane through the ring $N4 \rightarrow C15 \cdots C19$ shows that atom $N3$ is 0.133 (6) Å out of that plane. This might be due to steric repulsion between the ring and the methyl group of the neighboring molecule through the short contact $H20A \cdots C17$ (2.873 Å). Comparing (I) with (4) (Cunha *et al.*, 2005), three differences are observed. The double bond distance $C2=N2$ is 1.360 (5) Å in (I) and it is shorter in (4) [1.348 (4) Å]. The distance $N1-C3$ is elongated in (I); this is mainly ascribed to the change of substituent group from

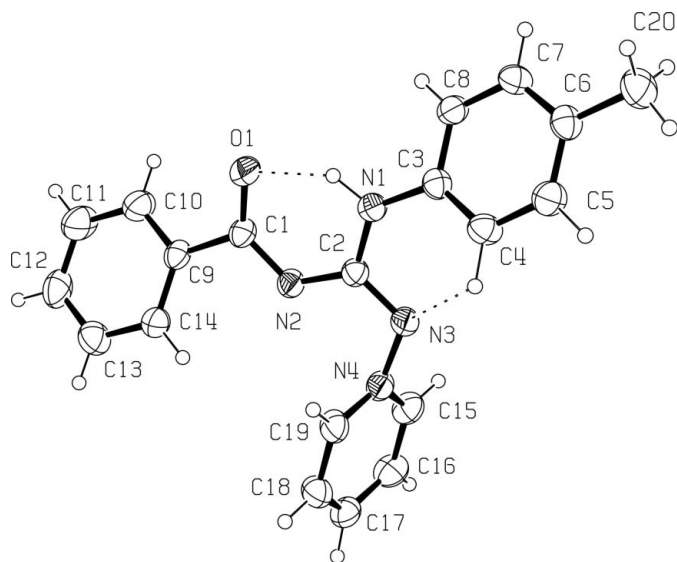


Figure 1

View of (I) with the atom-numbering scheme. Displacement ellipsoids are drawn at the 30% probability level and H atoms are shown as small spheres of arbitrary radii. Intramolecular hydrogen bonds are shown as dotted lines.

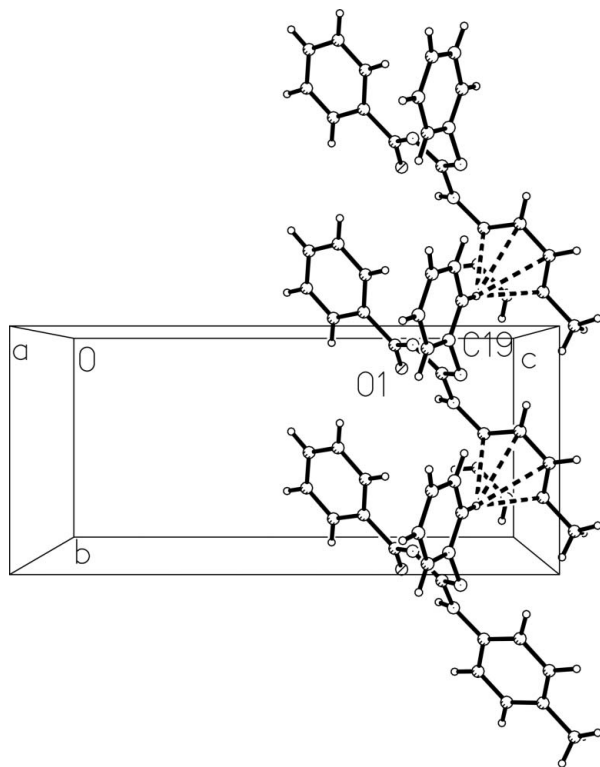


Figure 2

Projection down the *a* axis, showing the C–H··· π interactions (dashed lines).

bromopyridine to benzoyl. For the same reason, the angle C2–N1–C3 changed from 132.7 (3)° in (4) to 129.6 (3)° in (I).

One intramolecular hydrogen bond (Table 1) stabilizes the planarity through the conjugation O1–C1–N2–C2–N1. In addition, one non-classical intramolecular hydrogen bond is

observed. Concerning the orientation of the rings in relation to the least-squares plane through the guanidinium unit (O1–C1–N2–C2–N1), the ring N4→C15···C19 at N3 is rotated by 69.9 (1)° and the ring C9→C10···C14 is rotated by 27.6 (2)°. The ring C3→C4···C8 at atom N1 is not coplanar with this plane, as can be seen by the torsion angle C2–N1–C3–C8 of 154.6 (4)°.

The crystal packing of (I), in analogy of compound (4), does not show any strong hydrogen bonds, and the above-discussed intramolecular interactions of the new poly-substituted guanidinium derivative (I) are somewhat similar to the previous structural study of (4) (Cunha *et al.*, 2005). However, several differences in the intermolecular interactions are observed. Only one *ortho* H atom of the pyridinium ring, C19–H19, of (I) is involved in one weak intermolecular C–H··· π interaction, linking adjacent molecules in columns parallel to the [010] direction, as shown in Fig. 2; this is in contrast to compound (4) where the two *ortho* H atoms of the pyridinium ring are involved in two weak intermolecular C–H···O and C–H··· π interactions (Cunha *et al.*, 2005). There is another main difference in the packing interaction of (I) and (4) involving this weak C–H··· π interaction. In compound (I), the ring which behaves as a π acceptor in the intermolecular interaction is attached to N1, whereas in compound (4), the acceptor aromatic ring is the benzoyl group at C1. This can be related to the electronic nature of each compound. From a chemical point of view, in compound (I) the aromatic ring at N1 is more electron-rich than the ring at C1 because the former has an electron-releasing group (the methyl substituent at C6) and the second an electron-withdrawing one (the carbonyl C1=O1). In contrast, compound (4) has two electron-poor rings at N1 and C1, but the presence of a bromo-substituted pyridine ring at N1 confers a lower electron density than the benzoyl group, which justifies the C–H··· π interaction with the phenyl ring of the benzoyl group at C1 in (I).

Additionally, two other intermolecular weak interactions make contributions to the stabilization of the molecular packing (Table 2), resulting in a linear chain along the [102] direction, as can be seen in Fig. 3. Here again, the interaction involving atoms C17–H17 of the pyridinium ring is another difference in the solid-state behavior of (I), since it is not observed in (4).

Experimental

To a solution of 0.5 mmol of thiourea (1) in 4 ml of DMF was added 1 mmol of *N*-aminopyridinium iodide, (3); 1.5 mmol of Et₃N and 0.5 mmol of HgCl₂ were then added to the solution with vigorous magnetic stirring and ice-bath cooling. The suspension became black after a few minutes and was left stirring at 343–363 K. After 24 h, the thiourea was consumed and 20 ml of CH₂Cl₂ was added and the suspension filtered through a pad of Celite. The filtrate was extracted with water (4 × 15 ml) and dried over anhydrous MgSO₄. After filtration, the solvent was evaporated and the crude residue was recrystallized from CH₂Cl₂/petroleum ether (m.p. 500–501 K).

Crystal data

C₂₀H₁₈N₄O
M_r = 330.38
 Orthorhombic, *Pna*2₁
a = 17.182 (3) Å
b = 6.660 (1) Å
c = 14.730 (3) Å
V = 1685.6 (5) Å³
Z = 4
D_x = 1.302 Mg m⁻³

Cu Kα radiation
 Cell parameters from 25 reflections
 θ = 16.1–36.7°
 μ = 0.67 mm⁻¹
T = 297 (2) K
 Prism, colorless
 0.35 × 0.25 × 0.18 mm

Data collection

Enraf–Nonius CAD-4 diffractometer
 $\omega/2\theta$ scans
 Absorption correction: none
 1690 measured reflections
 1586 independent reflections
 1513 reflections with *I* > 2σ(*I*)
R_{int} = 0.038

θ_{\max} = 67.9°
h = -1 → 20
k = -8 → 0
l = 0 → 17
 2 standard reflections
 frequency: 120 min
 intensity decay: <1%

Refinement

Refinement on *F*²
R [*F*² > 2σ(*F*²)] = 0.046
wR (*F*²) = 0.154
S = 1.20
 1586 reflections
 240 parameters
 H atoms treated by a mixture of independent and constrained refinement

$w = 1/[\sigma^2(F_o^2) + (0.0865P)^2 + 0.6464P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 (Δ/σ)_{max} < 0.001
 $\Delta\rho_{\max} = 0.21 \text{ e \AA}^{-3}$
 $\Delta\rho_{\min} = -0.30 \text{ e \AA}^{-3}$
 Extinction correction: *SHELXL97*
 Extinction coefficient: 0.054 (5)

Table 1

Selected geometric parameters (Å, °).

O1–C1	1.250 (5)	N2–C2	1.360 (5)
N1–C2	1.365 (5)	N3–C2	1.321 (5)
N1–C3	1.413 (5)	N3–N4	1.406 (5)
N2–C1	1.340 (5)		
C2–N1–C3	129.6 (3)	N3–C2–N2	122.9 (3)
C1–N2–C2	121.7 (3)	N3–C2–N1	116.9 (3)
C2–N3–N4	112.3 (3)	N2–C2–N1	120.2 (3)
C2–N2–C1–O1	-1.8 (7)	C3–N1–C2–N3	-4.0 (6)
N4–N3–C2–N2	-5.9 (6)	C3–N1–C2–N2	177.2 (4)
N4–N3–C2–N1	175.3 (4)	C2–N1–C3–C4	-28.0 (7)
C1–N2–C2–N3	-178.7 (4)	O1–C1–C9–C10	27.0 (6)
C1–N2–C2–N1	0.1 (6)		

Table 2

Hydrogen-bond geometry (Å, °).

<i>D</i> –H... <i>A</i>	<i>D</i> –H	H... <i>A</i>	<i>D</i> ... <i>A</i>	<i>D</i> –H... <i>A</i>
N1–H1...O1	0.95 (5)	1.78 (5)	2.592 (4)	142 (4)
C4–H4...N3	1.05 (5)	2.39 (5)	2.895 (6)	108 (4)
C5–H5...N2 ⁱ	1.03 (6)	2.51 (6)	3.535 (6)	172 (4)
C17–H17...O1 ⁱⁱ	0.93 (6)	2.54 (6)	3.465 (6)	172 (5)
C19–H19...C8 ⁱⁱⁱ	0.93	2.48	3.37	161

Symmetry codes: (i) $-x + \frac{1}{2}, y + \frac{1}{2}, z + \frac{1}{2}$; (ii) $x + \frac{1}{2}, -y - \frac{1}{2}, z$; (iii) $x, y + 1, z$. Cg is the centroid of the C3–C8 ring.

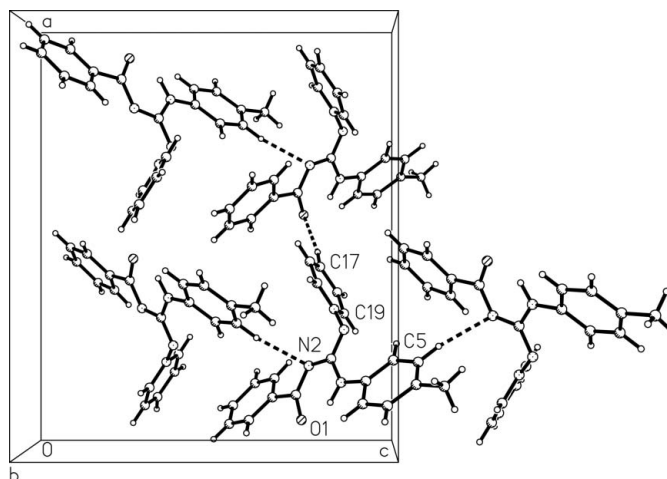


Figure 3

View down the *b* axis, with the intermolecular C–H...O and C–H...N hydrogen bonds shown as dashed lines.

All H atoms, except H1, H4, H5 and H17, were positioned geometrically and allowed to ride on their parent atoms, with C–H = 0.93–0.97 Å and *U*_{iso}(H) = 1.5*U*_{eq}(C) for methyl H atoms and 1.2*U*_{eq}(C) for other atoms. The H atoms on the N1, C4, C5 and C17 atoms were located in a difference Fourier map, and were refined with *U*_{iso}(H) = 1.2*U*_{eq}(N,C). No Friedel pairs were measured.

Data collection: *CAD-4/PC Software* (Enraf–Nonius, 1993); cell refinement: *CAD-4/PC Software*; data reduction: *XCAD4* (Harms & Wocadlo, 1995); 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: *WinGX* (Farrugia, 1999).

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