organic compounds

4-Nitroanilinium nitrate

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The crystal structure of the title compound, $C_6H_7N_2O_2^+ \cdot NO_3^-$, is built up from 4-nitroanilinium cations and nitrate anions. The NO_2 group is coplanar with the aryl ring, which shows significant distortion from the ideal hexagonal form. The NO_3^- anion is planar but shows distortion from the C_{3h} symmetry that is predicted by molecular orbital calculations. Two of the three O atoms of the NO_3 group are involved in hydrogen bonds as acceptors.

Comment

The present study is a continuation of our investigations characterizing the hydrogen-bonding systems formed by self-assembly of components containing complementary arrays of hydrogen-bonding sites (Janczak & Perpétuo, 2004, and references therein; Desiraju, 1990; Krische & Lehn, 2000; Sherington & Taskinen, 2001). To expand our understanding of the solid-state physical–organic chemistry of compounds containing $N-H\cdots O$ hydrogen-bonding systems, we present here the solid-state structure of p-nitroanilinium nitrate, (I), and compare the results with the structure predicted for the isolated 4-nitroanilinium cation and nitrate anion by ab initio fully optimized geometry calculations at the HF/6-31G(d,p) level (Frisch et al., 1998). The molecular orbital calculations were carried out on isolated ions corresponding to the gas phase, and the results are shown in Fig. 1.

(I)
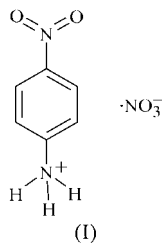
As revealed by X-ray structure analysis, the nitro group in (I) (Fig. 2) is coplanar with the aryl ring, which shows significant distortions from the ideal C_{6h} symmetry (Table 1). The $C-C$ bond lengths within the ring are consistent with those

found in other molecules of this type (Allen, 2002). Two of the internal $C-C-C$ angles in the ring, at the substituted atoms C1 and C4, are greater than $120°$, while the other four $C-C-C$ angles within the ring are smaller than $120°$. These angular differences have been attributed to the substitution effect of the NH_3^+ and NO_2 groups in the ring, respectively, at the 1- and 4-positions. The optimized geometry of the 4-nitroanilinium cation shows values similar to those found in the crystal, but the variation of the internal $C-C-C$ angles is more pronounced. The calculated $C-N_{amine}$ bond length is longer than the X-ray value, while the calculated $C-N_{nitro}$ bond is slightly shorter than the X-ray value. The $O-N-O$ angle in the NO_2 group is significantly greater than $120°$ as a result of the steric effect of the lone pair of electrons on each of the O atoms; this effect is predicted by the valence-shell electron-pair repulsion theory (Gillespie, 1963, 1992). The steric effect of the lone pairs of electrons is further evidenced in the ab initio fully optimized geometry. The X-ray geometry of the nitrate anion shows significant distortion from the D_{3h} symmetry predicted by molecular orbital calculations (the three $N-O$ bonds in the isolated NO_3^- ion are equivalent, with a distance of 1.226 Å).

The $N-O$ bonds in the nitro group are slightly shorter than those in the anion. These values indicate a bond order of 2 in the nitro group, while in the NO_3^- anion, the bond order is
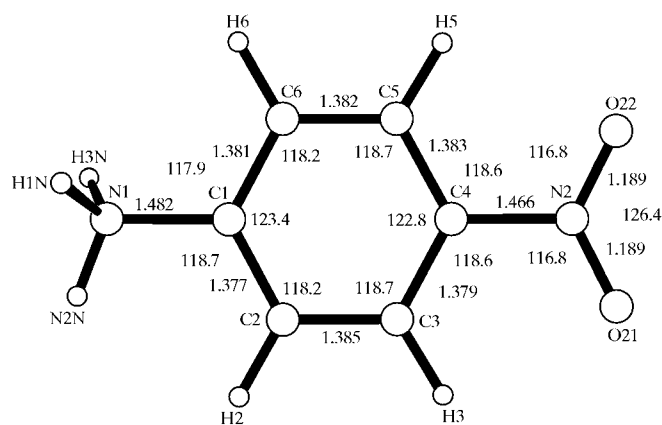

Figure 1
The results of the optimized molecular orbital calculations (Å, °) for the p-nitroanilinium cation.
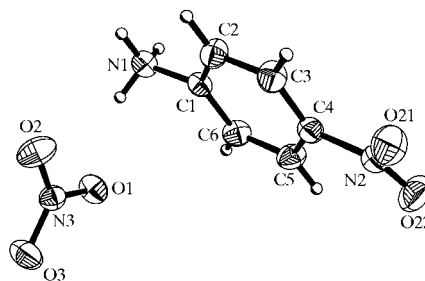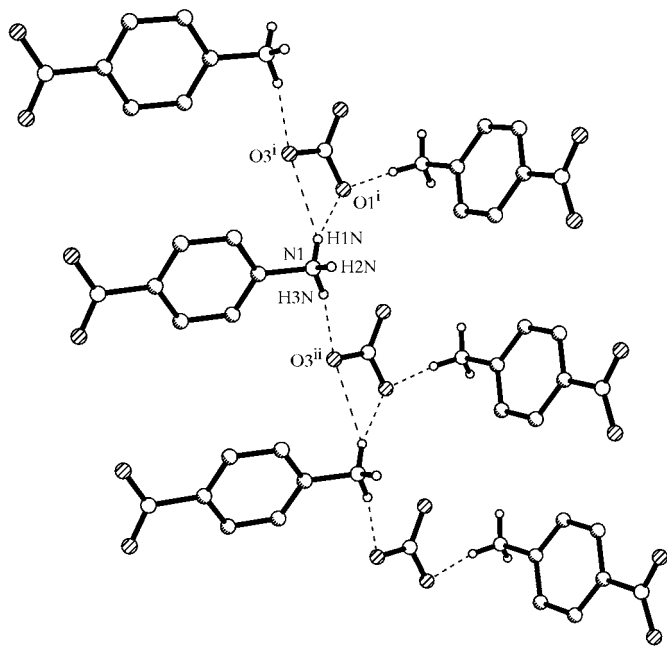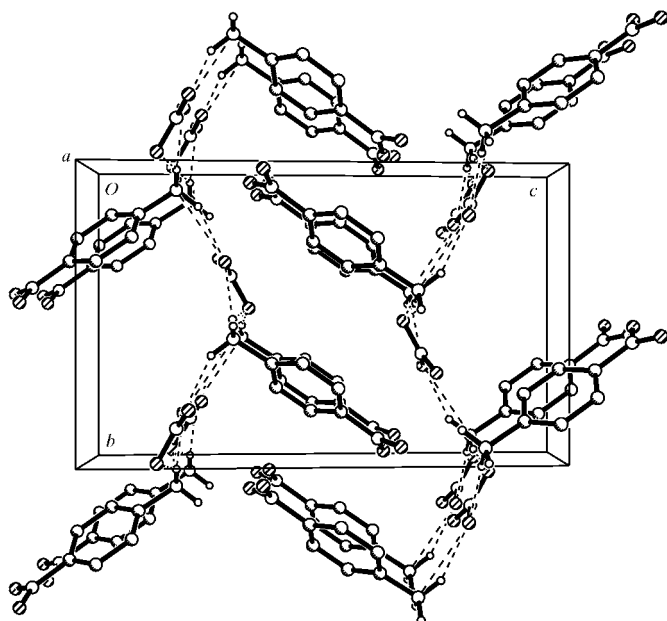

Figure 2
A view of the molecular structure of (I), showing displacement ellipsoids at the 50% probability level and H atoms as spheres of arbitrary radii.

Figure 3
A view of one [010] chain, showing the cation–anion hydrogen bonds. For the sake of clarity, H atoms bonded to C atoms have been omitted, along with the unit-cell box. The symmetry codes are as given in Table 2.

Figure 4
A view of the crystal packing, showing the interdigitated cations in adjacent chains. For the sake of clarity, H atoms bonded to C atoms have been omitted.

lated for the gas phase, since these atoms are involved as acceptors in two hydrogen bonds. The values of the third N—O bond length (to atom O2) as calculated from both X-ray and *ab initio* methods are similar, since atom O2 does not form hydrogen bonds (Fig. 3).

In the crystal structure of (I), the oppositely charged 4-nitroanilinum cations and nitrate anions related by a 2_1 screw axis interact *via* N—H⋯O hydrogen bonds, forming chains parallel to [010] (Fig. 4) in which the 4-nitroanilinium cations resemble the branches of fir trees. The cations of adjacent chains related by inversion are interdigitated, with parallel rings. The hydrogen-bonding interactions are responsible for the relatively high density of the crystal.

Experimental

4-Nitroaniline was dissolved in 10% aqueous nitric acid; after several days, colourless single crystals formed, which proved to be suitable for single-crystal X-ray diffraction analysis.

Crystal data

$C_6H_7N_2O_2{}^+\cdot NO_3{}^-$	D_m measured by flotation in a
$M_r = 201.15$	mixture of $CHCl_3$ and $CHBr_3$
Monoclinic, $P2_1/n$	Mo $K\alpha$ radiation
$a = 5.644\ (1)$ Å	Cell parameters from 1950
$b = 9.682\ (2)$ Å	reflections
$c = 15.662\ (3)$ Å	$\theta = 2.9$–$29°$
$\beta = 95.23\ (2)°$	$\mu = 0.14$ mm^{-1}
$V = 852.3\ (3)$ Å^3	$T = 293\ (2)$ K
$Z = 4$	Parallelepiped, pink
$D_x = 1.568$ Mg m^{-3}	$0.37 \times 0.28 \times 0.22$ mm
$D_m = 1.56$ Mg m^{-3}	

Data collection

Kuma KM-4 CCD area-detector diffractometer	2254 independent reflections
	1950 reflections with $I > 2\sigma(I)$
ω scans	$R_{int} = 0.014$
Absorption correction: analytical face-indexed (*SHELXTL*; Sheldrick, 1990)	$\theta_{max} = 29.0°$
	$h = -7 \rightarrow 7$
	$k = -13 \rightarrow 13$
$T_{min} = 0.941,\ T_{max} = 0.958$	$l = -20 \rightarrow 20$
11 065 measured reflections	

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0691P)^2]$
$R[F^2 > 2\sigma(F^2)] = 0.041$	where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.113$	$(\Delta/\sigma)_{max} < 0.001$
$S = 1.00$	$\Delta\rho_{max} = 0.18$ e Å^{-3}
2254 reflections	$\Delta\rho_{min} = -0.16$ e Å^{-3}
129 parameters	Extinction correction: *SHELXL*97
H-atom parameters constrained	Extinction coefficient: 0.032 (5)

smaller than 2 because of the delocalization of the two π bonds over three N—O bonds. The experimental and calculated N—O bond lengths in the nitro group are comparable, since in the crystal the nitro O atoms do not form any hydrogen bonds. Two of the N—O bonds of the anion (to atoms O1 and O3) are longer in the crystal than those calcu-

Table 1
Selected geometric parameters (Å, °).

N1—C1	1.4590 (14)	C5—C6	1.3770 (17)
C1—C6	1.3672 (16)	N2—O21	1.2182 (14)
C1—C2	1.3766 (15)	N2—O22	1.2287 (14)
C2—C3	1.3797 (16)	N3—O2	1.2212 (12)
C3—C4	1.3719 (16)	N3—O3	1.2396 (13)
C4—C5	1.3726 (16)	N3—O1	1.2502 (12)
C4—N2	1.4707 (15)		
C6—C1—C2	121.19 (10)	C1—C6—C5	119.75 (10)
C1—C2—C3	119.48 (11)	O21—N2—O22	123.65 (11)
C4—C3—C2	118.74 (10)	O2—N3—O3	121.15 (11)
C3—C4—C5	122.02 (10)	O2—N3—O1	121.09 (10)
C4—C5—C6	118.81 (10)	O3—N3—O1	117.75 (10)

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All H atoms were treated as riding atoms, with C—H distances of 0.93 Å and N—H distances of 0.89 Å, and with U_{iso}(H) values of $1.2U_{eq}$(C) or $1.3U_{eq}$(N).

Data collection: *KM-4 Software* (Kuma, 2001); cell refinement: *KM-4 Software*; data reduction: *KM-4 Software*; program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *SHELXTL* (Sheldrick, 1990); software used to prepare material for publication: *SHELXL*97.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: GD1344). Services for accessing these data are described at the back of the journal.

References

Allen, F. H. (2002). *Acta Cryst.* B**58**, 380–388.
Desiraju, G. R. (1990). In *Crystal Engineering: The Design of Organic Solids.* Amsterdam: Elsevier.
Frisch, J. M., Trucks, G. W., Schlegel, H. B., Scuseria, G. E., Robb, M. A., Cheeseman, J. R., Zakrzewski, V. G., Montgomery, J. A. Jr, Stratmann, R. E., Burant, J. C., Dapprich, S., Millam, J. M., Daniels, A. D., Kudin, K. N., Strain, M. C. *et al.* (1998). *GAUSSIAN*98. Revision A3. Gaussian Inc., Pittsburgh, PA, USA.
Gillespie, R. J. (1963). *J. Chem. Educ.* **40**, 295–301.
Gillespie, R. J. (1992). *Chem. Soc. Rev.* **21**, 59–69.
Janczak, J. & Perpétuo, G. J. (2004). *Acta Cryst.* C**60**, o211–o214.
Krische, M. J. & Lehn, J. M. (2000). *Struct. Bonding*, **96**, 3–29.
Kuma (2001). *KM-4 Software.* Kuma Diffraction, Wrocław, Poland.
Sheldrick, G. M. (1990). *SHELXTL.* Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.
Sheldrick, G. M. (1997). *SHELXS*97 and *SHELXL*97. University of Göttingen, Germany.
Sherington, D. C. & Taskinen, K. A. (2001). *Chem. Soc. Rev.* **30**, 83–91.