CRYSTALLOGRAPHIC COMMUNICATIONS

ISSN 2056-9890

Received 15 December 2014
Accepted 19 December 2014

Edited by H. Stoeckli-Evans, University of Neuchâtel, Switzerland

Keywords: crystal structure; pyridinium; styphnate; TGA/DTA studies; hydrogen bonding

CCDC reference: 1006492

Supporting information: this article has supporting information at journals.iucr.org/e

Crystal structure and thermal behaviour of pyridinium styphnate

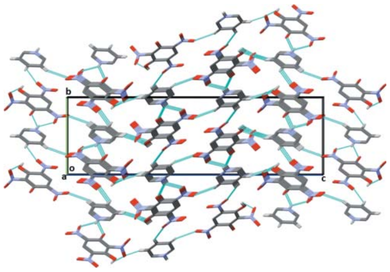
Selvarasu Muthulakshmi and Doraisamyraja Kalaivani*

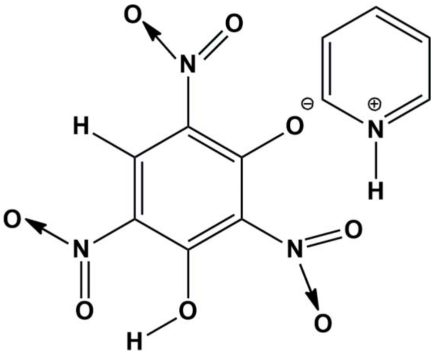
PG and Research Department of Chemistry, Seethalakshmi Ramaswami College, Tiruchirappalli 620 002, Tamil Nadu, India. *Correspondence e-mail: kalaivbalaj@yahoo.co.in

In the crystal structure of the title molecular salt, $C_5H_6N^+\cdot C_6H_2N_3O_8^-$ (systematic name: pyridinium 3-hydroxy-2,4,6-trinitrophenolate), the pyridinium cation and the 3-hydroxy-2,4,6-trinitrophenolate anion are linked through bifurcated N—H···(O,O) hydrogen bonds, forming an $R_1^2(6)$ ring motif. The nitro group *para* with respect to phenolate ion forms an intramolecular hydrogen bond with the adjacent phenolic –OH group, which results in an $S(6)$ ring motif. The nitro group flanked by the phenolate ion and the phenolic –OH group deviates noticeably from the benzene ring, subtending a dihedral angle of 89.2 (4)°. The other two nitro groups deviate only slightly from the plane of the benzene ring, making dihedral angles of 2.8 (4) and 3.4 (3)°. In the crystal, the 3-hydroxy-2,4,6-trinitrophenolate anions are linked through O—H···O hydrogen bonds, forming chains along [100]. These anionic chains, to which the cations are attached, are linked *via* C—H···O hydrogen bonds, forming a three-dimensional structure. Impact friction sensitivity tests and TGA/DTA studies on the title molecular salt imply that it is an insensitive high-energy-density material.

1. Chemical context

A number of crystalline styphnate salts with inorganic metal cations have been reported in recent years (Cui *et al.*, 2008*a*,*b*; Hu *et al.*, 2005; Liu *et al.*, 2009; Orbovic & Codoceo, 2008; Zhang *et al.*, 2011*a*,*b*; Zheng *et al.*, 2006*a*,*b*; Zhu & Xiao, 2009). In spite of the fact that styphnates with protonated organic amine cations crystallize with difficulty (Vogel, 1978), they have received attention because of their high thermal stability (Abashev *et al.*, 2001*a*,*b*; Deblitz *et al.*, 2012; Kalaivani & Malarvizhi, 2010; Kalaivani *et al.*, 2011; Kazheva *et al.*, 2002; Liu *et al.*, 2008; Refat *et al.*, 2013; Tang *et al.*, 2012; Zhang *et al.*, 2012; Wu *et al.*, 2013*a*,*b*,*c*). Amorphous pyridinium styphnate has found applications in the preparation of chloropicryl chloride (Feuer & Harban, 1954). We report herein on the crystal structure of the title molecular salt.





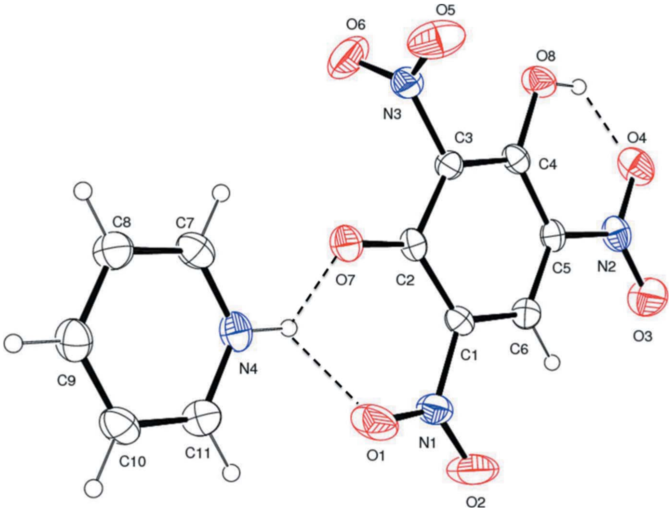


Figure 1
A view of the molecular structure of the title molecular salt, showing the atom labelling. Displacement ellipsoids are drawn at the 30% probability level. Hydrogen bonds are shown as dashed lines (see Table 1 for details).

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

D—H$\cdots$$A$	D—H	H$\cdots$$A$	$D$$\cdots$$A$	D—H$\cdots$$A$
N4—H4$A$$\cdots$O1	0.90 (2)	2.22 (4)	2.946 (4)	137 (4)
N4—H4$A$$\cdots$O7	0.90 (2)	1.88 (4)	2.625 (3)	138 (5)
O8—H8$A$$\cdots$N2	0.82	2.48	2.905 (3)	113
O8—H8$A$$\cdots$O4	0.82	1.87	2.563 (3)	141
O8—H8$A$$\cdots$O6$^{\rm i}$	0.82	2.63	3.110 (4)	119
C8—H8$\cdots$O6$^{\rm ii}$	0.93	2.58	3.352 (5)	141
C8—H8$\cdots$O8$^{\rm iii}$	0.93	2.63	3.405 (4)	141
C10—H10$\cdots$O2$^{\rm iv}$	0.93	2.43	3.139 (4)	133

Symmetry codes: (i) $x-1, y, z$; (ii) $-x+\frac{5}{2}, y+\frac{1}{2}, -z+\frac{1}{2}$; (iii) $-x+\frac{3}{2}, y+\frac{1}{2}, -z+\frac{1}{2}$; (iv) $-x+2, -y+1, -z$.

2. Structural commentary

The molecular structure of the title molecular salt is depicted in Fig. 1. The asymmetric unit is comprised of one phenolate anion and a pyridinium cation. The loss of a single proton of the styphnate anion is confirmed by the increase in the bond lengths of the C—C bonds adjacent to the phenolate ion (C1—C2 and C2—C3), which are 1.439 (4) and 1.420 (4) Å, respectively. There is an increase of the value of the bond angles C2—C1—C6 and C2—C3—C4 in the benzene ring to 122.4 (3) and 126.3 (3)°, respectively, and a decrease of the C4—C5—C6 bond angle to 120.5 (2)° compared to the values observed for free styphic acid (Pierce-Butler, 1982). The nitro group (N3/O5/O6) flanked by the phenolate ion and the phenolic –OH group deviates noticeably from the benzene ring plane, subtending a dihedral angle of 89.2 (4)°. The other two nitro groups, O1/N1/O2 and O3/N2/O4, lie close to the plane of the attached benzene ring, making dihedral angles of 2.8 (4) and 3.4 (3) °, respectively. The nitro group (N2/O3/O4) *para* with respect to the phenolate O atom, O7, forms an intramolecular hydrogen bond with the adjacent phenolic –OH group (O8—H8), which results in an $S(6)$ ring motif (Fig. 1 and Table 1).

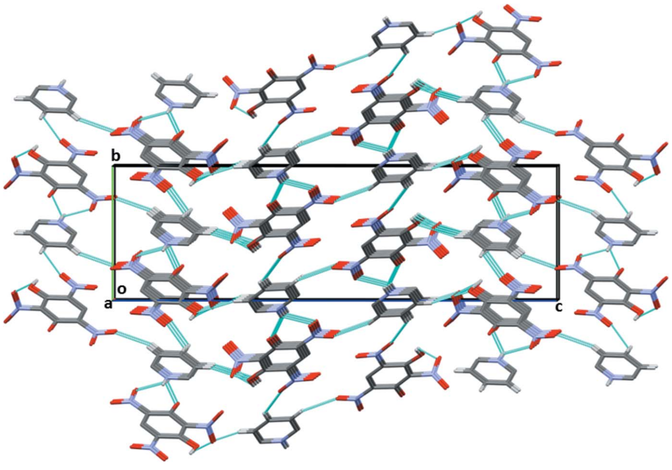


Figure 2
A view along the *a* axis of the crystal packing of the title molecular salt. Hydrogen bonds are shown as dashed lines (see Table 1 for details).

3. Supramolecular features

In the crystal, the cation and anion are linked *via* bifurcated N—H$\cdots$(O,O) hydrogen bonds forming an $R_1^2(6)$ ring motif (Table 1 and Figs. 1 and 2). Inversion-related anions are connected through pairs of C—H$\cdots$O hydrogen bonds, forming dimers enclosing an $R_2^2(10)$ ring motif. The phenolate oxygen, O7, is also bifurcated and forms hydrogen bonds with the protonated nitrogen atom, N4, of the pyridinium moiety and the C—H H atom adjacent to the protonated nitrogen atom, forming an $R_2^1(5)$ ring motif. The combination of these various N—H$\cdots$O, O—H$\cdots$O and C—H$\cdots$O hydrogen bonds leads to the formation of a three-dimensional structure (Table 1 and Figs. 2 and 3).

4. Database survey

A search of the Cambridge Structural Database (Version 5.35, May 214; Groom & Allen, 2014) for 3-hydroxy-2,4,6-trinitrophenolates gave 14 hits. Six concern metal-complex cations,

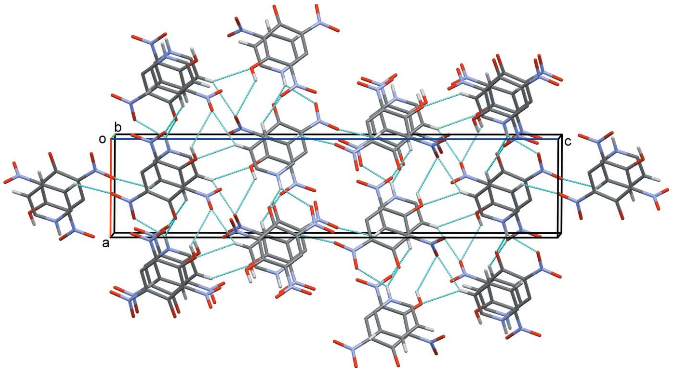


Figure 3
A view along the *b* axis of the crystal packing of the title molecular salt. Hydrogen bonds are shown as dashed lines (see Table 1 for details).

Table 2
Experimental details.

Crystal data	
Chemical formula	$C_5H_6N^+\cdot C_6H_2N_3O_8^-$
M_r	324.21
Crystal system, space group	Monoclinic, $P2_1/n$
Temperature (K)	296
a, b, c (Å)	5.9506 (2), 8.1608 (3), 27.0175 (10)
β (°)	90.379 (5)
V (Å^3)	1311.99 (8)
Z	4
Radiation type	Mo $K\alpha$
μ (mm^{-1})	0.14
Crystal size (mm)	0.35 × 0.35 × 0.30
Data collection	
Diffractometer	Bruker Kappa APEXII CCD
Absorption correction	Multi-scan (*SADABS*; Bruker, 2004)
$T_{\min}$, $T_{\max}$	0.951, 0.959
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	14733, 2296, 1771
$R_{\rm int}$	0.047
(sin $\theta/\lambda)_{\max}$ (Å^{-1})	0.595
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.059, 0.198, 1.14
No. of reflections	2296
No. of parameters	212
No. of restraints	1
H-atom treatment	H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{\max}$, $\Delta\rho_{\min}$ (e Å^{-3})	0.32, −0.34

Computer programs: *APEX2*, *SAINT* and *XPREP* (Bruker, 2004), *SIR92* (Altomare *et al.*, 1993), *SHELXL97* (Sheldrick, 2008), *ORTEP-3 for Windows* (Farrugia, 2012) and *Mercury* (Macrae *et al.*, 2008).

and the remaining eight concern organic cations. Amongst the latter are two compounds, referred to above in §1 for their high thermal stability, viz. 2-methoxyanilinium 3-hydroxy-2,4,6-trinitrophenolate (Kalaivani *et al.*, 2011) and morpholinium 3-hydroxy-2,4,6-trinitrophenolate (Kalaivani & Malarvizhi, 2010).

5. Thermal behaviour and friction sensitivity

As styphnic acid derivatives are energetic salts, the thermal behaviour of the title molecular salt has also been examined. The exothermic decomposition has been observed at four different heating rates (5 K/min, 10 K/min, 20 K/min and 40 K/min). The title molecular salt decomposes (70–80%) in two stages. For each stage, the energy of activation was determined employing Kissinger (1957) [stage I: 27.2 kcal/mol; stage II: 50.5 kcal/mol] and Ozawa (1965) methods [stage I: 28.5 kcal/mol; stage II: 51.8 kcal/mol]. The title molecular salt was observed to be insensitive towards the impact of a 2 kg mass hammer up to the height limit (160 cm) of the instrument, even at the maximum energy level of 31.392 J (Meyer & Kohler, 1993*a*). The friction sensitivity was determined under defined conditions according to the BAM method (Meyer & Kohler, 1993*b*). The title molecular salt was insensitive at the maximum force of 360 Newton. The title molecular salt is an insensitive high-energy-density material, confirmed through the impact, friction-sensitivity test, and the energy of activation from TGA/DTA curves.

6. Synthesis and crystallization

Styphnic acid (2.45 g, 0.01 mol) dissolved in 25 mL of absolute alcohol was mixed with pyridine (0.79 g, 0.01 mol) and stirred continuously for 6 hrs and then kept aside for 2 h. The yellow-coloured amorphous solid obtained was filtered, washed with 30 ml of dry ether and recrystallized from ethylene glycol. Yellow crystals formed in an ethylene glycol solution after slow evaporation at 298 K over a period of 2 weeks (m.p: 455 K; yield: 80%).

7. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 2. The NH H atom was located from a difference Fourier map and freely refined. The OH and C-bound H atoms were included in calculated positions and treated as riding atoms: O—H = 0.82, C—H = 0.93 Å, with $U_{\rm iso}$(H) = 1.5$U_{\rm eq}$(O) for the hydroxyl H atom and = 1.2$U_{\rm eq}$(C) for the other H atoms.

Acknowledgements

The authors are grateful to the UGC for financial support and the SAIF, IIT Madras, for the data collection.

References

Abashev, G. G., Gritsenko, V. V., Kazheva, O. N., Tenishev, A. G., Canadell, E. & Dyachenk, O. A. (2001*b*). *Z. Kristallogr.* **216**, 623–628.

Abashev, G. G., Kazheva, O. N., Dyachenk, O. A., Gritsenko, V. V., Tenishev, A. G., Nishimura, K. & Saito, G. (2001*a*). *Mendeleev Commun.* **4**, 125–127.

Altomare, A., Cascarano, G., Giacovazzo, C. & Guagliardi, A. (1993). *J. Appl. Cryst.* **26**, 343–350.

Bruker (2004). *APEX2*, *SAINT*, *XPREP* and *SADABS*. Bruker AXS Inc., Madison, Wisconsin, USA.

Cui, Y., Zhang, T. L., Zhang, J. G. & Yang, L. (2008*a*). *Chin. J. Chem.* **26**, 2021–2028.

Cui, Y., Zhang, T. L., Zhang, J. G., Yang, L., Hu, X. C. & Zhang, J. (2008*b*). *J. Mol. Struct.* **889**, 177–185.

Deblitz, R., Hrib, C. G., Plenikowski, G. & Edelmann, F. T. (2012). *Crystals*, **2**, 34–42.

Farrugia, L. J. (2012). *J. Appl. Cryst.* **45**, 849–854.

Feuer, H. & Harban, A. A. (1954). US Patent 2679538 A.

Groom, C. R. & Allen, F. H. (2014). *Angew. Chem. Int. Ed.* **53**, 662–671.

Hu, R., Chen, S., Gao, S., Zhao, F., Luo, Y., Gao, H., Shi, Q., Zhao, H., Yao, P. & Li, J. (2005). *J. Hazard. Mater.* **117**, 346–350.

Kalaivani, D. & Malarvizhi, R. (2010). *Acta Cryst.* E**66**, o2698.

Kalaivani, D., Malarvizhi, R., Thanigaimani, K. & Muthiah, P. T. (2011). *Acta Cryst.* E**67**, o686.

Kazheva, O. N., Canadell, E., Shilov, G. V., Abashev, G. G., Tenishev, A. G. & Dyachenk, O. A. (2002). *Phys. E Low Dimens. Syst. Nanostruct.* **13**, 1268–1270.

Kissinger, H. E. (1957). *Anal. Chem.* **29**, 1702–1706.

Liu, Z. H., Ao, G. J., Zhang, T. L., Yang, L., Zhang, J. G. & Zhang, Y. (2008). *Wuji Huaxue Xuebao*, **24**, 1155–1159.

Liu, J. W., Zhang, J. G., Zhang, T. L., Zheng, H., Yang, L. & Yu, K. B. (2009). *Struct. Chem.* **20**, 387–392.

Macrae, C. F., Bruno, I. J., Chisholm, J. A., Edgington, P. R., McCabe, P., Pidcock, E., Rodriguez-Monge, L., Taylor, R., van de Streek, J. & Wood, P. A. (2008). *J. Appl. Cryst.* **41**, 466–470.

Meyer, R. & Kohler, J. (1993*a*). Editors. *Explosives*, 4th ed., revised and extended, p. 149. New York: VCH Publishers.

Meyer, R. & Kohler, J. (1993*b*). Editors. *Explosives*, 4th ed., revised and extended, p. 197. New York: VCH Publishers.

Orbovic, N. & Codoceo, C. L. (2008). *Prop. Explos. Pyrotech.* **33**, 459–466.

Ozawa, T. (1965). *Bull. Chem. Soc. Jpn*, **38**, 1881–1886.

Pierce-Butler, M. A. (1982). *Acta Cryst.* B**38**, 3097–3100.

Refat, M. S., Saad, H. A., EI-Sayed, M. Y., Adam, A. M. A., Yeşilel, O. Z. & Taş, M. (2013). J. Chem. 2013, article ID 107515, 8 pages. doi: 10.1155/2013/107515.

Sheldrick, G. M. (2008). *Acta Cryst.* A**64**, 112–122.

Tang, Z., Yang, L., Qiao, X. J., Wu, B. D., Zhang, T. L., Zhou, Z. N. & Yu, K. B. (2012). *Chem. Res. Chin. Univ.* **28**, 4-8.

Vogel, A. I. (1978). *Textbook of Practical Organic Chemistry*, 4th ed., p. 1093. London: Longman.

Wu, J. T., Zhang, J. G., Sun, M., Yin, X. & Zhang, T. L. (2013*b*). *New Trends Res. Energ. Mater.* pp. 433–440.

Wu, J. T., Zhang, J. G., Sun, M., Yin, X. & Zhang, T. L. (2013*c*). *Cent. Eur. J. Energ. Mater.* **10**, 481–493.

Wu, J. T., Zhang, J. G., Yin, X., Sun, M. & Zhang, T. L. (2013*a*). *Z. Anorg. Allg. Chem.* **639**, 2354–2358.

Zhang, J. G., Liang, Y. H., Feng, J. L., Wang, K., Zhang, T. L., Zhou, Z. N. & Yang, L. (2012). *Z. Anorg. Allg. Chem.* **638**, 1212–1218.

Zhang, J. G., Wang, K., Li, Z. M., Zheng, H., Zhang, T. L. & Yang, L. (2011*a*). *Main Group Chem.* **10**, 205–213.

Zhang, J., Wei, L., Cui, Y., Zhang, T., Zhou, Z. & Yong, L. (2011*b*). *Z. Anorg. Allg. Chem.* **637**, 1527–1532.

Zheng, H., Zhang, T. L., Zhang, J. G., Qiao, X. L., Yang, L. & Yu, K. B. (2006*a*). *Wuji Huaxue Xuebao* **22**, 346–350.

Zheng, H., Zhang, T. L., Zhang, J. G., Qiao, X. L., Yang, L. & Yu, K. B. (2006*b*). *Chin. J. Chem.* **24**, 845–848.

Zhu, W. & Xiao, H. (2009). *J. Phys. Chem. B*, **113**, 10315–10321.

supporting information

Acta Cryst. (2015). E**71**, 117-120   [doi:10.1107/S2056989014027704]

Crystal structure and thermal behaviour of pyridinium styphnate

Selvarasu Muthulakshmi and Doraisamyraja Kalaivani

Computing details

Data collection: *APEX2* (Bruker, 2004); cell refinement: *APEX2* and *SAINT* (Bruker, 2004); data reduction: *SAINT* and *XPREP* (Bruker, 2004); program(s) used to solve structure: *SIR92* (Altomare *et al.*, 1993); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *ORTEP-3 for Windows* (Farrugia, 2012) and *Mercury* (Macrae *et al.*, 2008); software used to prepare material for publication: *SHELXL97* (Sheldrick, 2008).

Pyridinium 3-hydroxy-2,4,6-trinitrophenolate

Crystal data

$C_5H_6N^+\cdot C_6H_2N_3O_8^-$
$M_r = 324.21$
Monoclinic, $P2_1/n$
Hall symbol: -P 2yn
$a = 5.9506$ (2) Å
$b = 8.1608$ (3) Å
$c = 27.0175$ (10) Å
$\beta = 90.379$ (5)°
$V = 1311.99$ (8) Å^3
$Z = 4$
$F(000) = 664$
$D_x = 1.641$ Mg m^{-3}
Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
Cell parameters from 5354 reflections
$\theta = 2.6$–26.1°
$\mu = 0.14$ mm^{-1}
$T = 296$ K
Block, yellow
0.35 × 0.35 × 0.30 mm

Data collection

Bruker Kappa APEXII CCD diffractometer
Radiation source: fine-focus sealed tube
Graphite monochromator
ω and φ scan
Absorption correction: multi-scan (*SADABS*; Bruker, 2004)
$T_{\min} = 0.951$, $T_{\max} = 0.959$
14733 measured reflections
2296 independent reflections
1771 reflections with $I > 2\sigma(I)$
$R_{\text{int}} = 0.047$
$\theta_{\max} = 25.0°$, $\theta_{\min} = 2.6°$
$h = -5\rightarrow7$
$k = -9\rightarrow9$
$l = -32\rightarrow32$

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)] = 0.059$
$wR(F^2) = 0.198$
$S = 1.14$
2296 reflections
212 parameters
1 restraint
Primary atom site location: structure-invariant direct methods
Secondary atom site location: difference Fourier map
Hydrogen site location: inferred from neighbouring sites
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.1017P)^2 + 0.9268P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} < 0.001$
$\Delta\rho_{\max} = 0.32$ e Å^{-3}
$\Delta\rho_{\min} = -0.34$ e Å^{-3}

Special details

Geometry. All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds involving l.s. planes.

Refinement. Refinement of F^2 against ALL reflections. The weighted R-factor wR and goodness of fit S are based on F^2, conventional R-factors R are based on F, with F set to zero for negative F^2. The threshold expression of $F^2 > 2\text{sigma}(F^2)$ is used only for calculating R-factors(gt) etc. and is not relevant to the choice of reflections for refinement. R-factors based on F^2 are statistically about twice as large as those based on F, and R- factors based on ALL data will be even larger.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²)

	x	*y*	*z*	U_{iso}*/U_{eq}
C1	0.5386 (5)	0.1613 (3)	0.08054 (10)	0.0338 (6)
C2	0.6344 (5)	0.1587 (3)	0.12957 (10)	0.0335 (6)
C3	0.5003 (5)	0.0711 (3)	0.16385 (10)	0.0330 (6)
C4	0.3031 (4)	−0.0084 (3)	0.15364 (10)	0.0331 (6)
C5	0.2257 (4)	−0.0036 (3)	0.10427 (10)	0.0342 (7)
C6	0.3424 (5)	0.0820 (4)	0.06890 (10)	0.0372 (7)
H6	0.2873	0.0862	0.0366	0.045*
C7	1.2035 (5)	0.4297 (4)	0.17352 (12)	0.0451 (8)
H7	1.1200	0.3709	0.1964	0.054*
C8	1.3941 (6)	0.5094 (4)	0.18837 (12)	0.0485 (8)
H8	1.4407	0.5063	0.2213	0.058*
C9	1.5148 (6)	0.5936 (4)	0.15407 (12)	0.0476 (8)
H9	1.6461	0.6474	0.1635	0.057*
C10	1.4438 (6)	0.5993 (4)	0.10590 (12)	0.0488 (8)
H10	1.5250	0.6577	0.0825	0.059*
C11	1.2528 (6)	0.5186 (4)	0.09267 (12)	0.0471 (8)
H11	1.2027	0.5209	0.0600	0.057*
N1	0.6481 (5)	0.2501 (3)	0.04118 (9)	0.0477 (7)
N2	0.0254 (4)	−0.0877 (3)	0.09001 (10)	0.0445 (7)
N3	0.5834 (4)	0.0636 (3)	0.21455 (9)	0.0436 (7)
N4	1.1371 (4)	0.4356 (3)	0.12684 (10)	0.0419 (6)
O1	0.8179 (5)	0.3281 (4)	0.04960 (9)	0.0730 (9)
O2	0.5667 (5)	0.2440 (5)	0.00022 (10)	0.0953 (12)
O3	−0.0431 (5)	−0.0774 (4)	0.04783 (9)	0.0732 (8)
O4	−0.0736 (4)	−0.1705 (3)	0.12168 (9)	0.0589 (7)
O5	0.5195 (6)	0.1641 (3)	0.24370 (9)	0.0800 (10)
O6	0.7049 (5)	−0.0493 (5)	0.22574 (10)	0.0913 (11)
O7	0.8146 (3)	0.2234 (3)	0.14326 (8)	0.0493 (6)
O8	0.1994 (4)	−0.0845 (3)	0.19071 (8)	0.0478 (6)
H8A	0.0816	−0.1247	0.1805	0.072*
H4A	1.006 (6)	0.388 (7)	0.1186 (18)	0.118 (19)*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
C1	0.0332 (15)	0.0309 (14)	0.0374 (15)	−0.0026 (12)	0.0065 (12)	−0.0001 (11)

C2	0.0283 (14)	0.0298 (13)	0.0424 (15)	0.0001 (11)	0.0028 (12)	−0.0035 (11)
C3	0.0324 (15)	0.0339 (14)	0.0327 (14)	−0.0014 (12)	−0.0003 (11)	−0.0011 (11)
C4	0.0317 (15)	0.0281 (13)	0.0397 (15)	−0.0009 (11)	0.0066 (12)	−0.0007 (11)
C5	0.0261 (14)	0.0323 (14)	0.0441 (16)	−0.0023 (11)	−0.0006 (12)	−0.0039 (12)
C6	0.0367 (16)	0.0374 (15)	0.0374 (15)	0.0010 (12)	−0.0014 (12)	−0.0043 (12)
C7	0.0468 (19)	0.0385 (16)	0.0503 (18)	−0.0043 (14)	0.0104 (14)	0.0022 (13)
C8	0.053 (2)	0.0475 (18)	0.0455 (17)	−0.0064 (16)	−0.0028 (15)	0.0011 (14)
C9	0.0424 (18)	0.0414 (17)	0.059 (2)	−0.0093 (14)	−0.0024 (15)	−0.0018 (15)
C10	0.0491 (19)	0.0419 (17)	0.055 (2)	−0.0082 (15)	0.0100 (15)	0.0081 (14)
C11	0.053 (2)	0.0450 (17)	0.0432 (17)	−0.0018 (15)	−0.0018 (15)	0.0019 (14)
N1	0.0497 (16)	0.0525 (16)	0.0408 (15)	−0.0080 (13)	0.0037 (12)	0.0065 (12)
N2	0.0343 (14)	0.0446 (14)	0.0544 (16)	−0.0056 (12)	0.0010 (12)	−0.0080 (12)
N3	0.0395 (15)	0.0515 (16)	0.0398 (14)	−0.0069 (12)	0.0005 (11)	0.0036 (12)
N4	0.0349 (14)	0.0362 (13)	0.0547 (16)	−0.0041 (11)	0.0008 (12)	−0.0050 (11)
O1	0.0702 (18)	0.091 (2)	0.0575 (15)	−0.0443 (16)	0.0055 (13)	0.0103 (14)
O2	0.092 (2)	0.147 (3)	0.0465 (15)	−0.054 (2)	−0.0129 (15)	0.0350 (17)
O3	0.0594 (17)	0.102 (2)	0.0584 (16)	−0.0280 (15)	−0.0190 (13)	−0.0023 (15)
O4	0.0472 (14)	0.0603 (15)	0.0692 (16)	−0.0234 (12)	0.0075 (12)	−0.0048 (12)
O5	0.133 (3)	0.0616 (16)	0.0453 (14)	0.0037 (17)	−0.0071 (15)	−0.0118 (13)
O6	0.089 (2)	0.124 (3)	0.0600 (17)	0.052 (2)	−0.0210 (15)	0.0014 (17)
O7	0.0364 (12)	0.0594 (14)	0.0521 (13)	−0.0177 (10)	−0.0026 (10)	0.0031 (10)
O8	0.0440 (13)	0.0533 (13)	0.0464 (12)	−0.0163 (10)	0.0059 (10)	0.0059 (10)

Geometric parameters (Å, º)

C1—C6	1.369 (4)	C8—H8	0.9300
C1—C2	1.439 (4)	C9—C10	1.366 (4)
C1—N1	1.445 (4)	C9—H9	0.9300
C2—O7	1.249 (3)	C10—C11	1.359 (5)
C2—C3	1.420 (4)	C10—H10	0.9300
C3—C4	1.367 (4)	C11—N4	1.339 (4)
C3—N3	1.454 (4)	C11—H11	0.9300
C4—O8	1.333 (3)	N1—O2	1.206 (4)
C4—C5	1.409 (4)	N1—O1	1.215 (4)
C5—C6	1.376 (4)	N2—O3	1.211 (3)
C5—N2	1.426 (4)	N2—O4	1.242 (3)
C6—H6	0.9300	N3—O5	1.200 (4)
C7—N4	1.320 (4)	N3—O6	1.208 (4)
C7—C8	1.366 (5)	N4—H4A	0.90 (2)
C7—H7	0.9300	O8—H8A	0.8200
C8—C9	1.362 (5)		
C6—C1—C2	122.4 (3)	C7—C8—H8	120.6
C6—C1—N1	117.1 (3)	C8—C9—C10	120.3 (3)
C2—C1—N1	120.5 (2)	C8—C9—H9	119.9
O7—C2—C3	120.3 (3)	C10—C9—H9	119.9
O7—C2—C1	126.9 (3)	C11—C10—C9	119.1 (3)
C3—C2—C1	112.8 (2)	C11—C10—H10	120.4

C4—C3—C2	126.3 (3)	C9—C10—H10	120.4
C4—C3—N3	117.1 (2)	N4—C11—C10	119.8 (3)
C2—C3—N3	116.5 (2)	N4—C11—H11	120.1
O8—C4—C3	118.1 (2)	C10—C11—H11	120.1
O8—C4—C5	125.0 (2)	O2—N1—O1	121.5 (3)
C3—C4—C5	116.9 (2)	O2—N1—C1	118.3 (3)
C6—C5—C4	120.5 (2)	O1—N1—C1	120.2 (3)
C6—C5—N2	118.8 (3)	O3—N2—O4	121.9 (3)
C4—C5—N2	120.7 (3)	O3—N2—C5	119.8 (3)
C1—C6—C5	120.9 (3)	O4—N2—C5	118.4 (3)
C1—C6—H6	119.5	O5—N3—O6	123.2 (3)
C5—C6—H6	119.5	O5—N3—C3	118.8 (3)
N4—C7—C8	120.4 (3)	O6—N3—C3	117.8 (3)
N4—C7—H7	119.8	C7—N4—C11	121.7 (3)
C8—C7—H7	119.8	C7—N4—H4A	118 (3)
C9—C8—C7	118.7 (3)	C11—N4—H4A	120 (3)
C9—C8—H8	120.6	C4—O8—H8A	109.5

C6—C1—C2—O7	178.0 (3)	N2—C5—C6—C1	−178.3 (3)
N1—C1—C2—O7	−2.3 (4)	N4—C7—C8—C9	−0.6 (5)
C6—C1—C2—C3	−2.0 (4)	C7—C8—C9—C10	0.8 (5)
N1—C1—C2—C3	177.7 (2)	C8—C9—C10—C11	−0.7 (5)
O7—C2—C3—C4	−178.4 (3)	C9—C10—C11—N4	0.3 (5)
C1—C2—C3—C4	1.6 (4)	C6—C1—N1—O2	−3.0 (5)
O7—C2—C3—N3	0.6 (4)	C2—C1—N1—O2	177.3 (3)
C1—C2—C3—N3	−179.4 (2)	C6—C1—N1—O1	177.1 (3)
C2—C3—C4—O8	−179.9 (3)	C2—C1—N1—O1	−2.6 (4)
N3—C3—C4—O8	1.1 (4)	C6—C5—N2—O3	−2.8 (4)
C2—C3—C4—C5	0.3 (4)	C4—C5—N2—O3	177.3 (3)
N3—C3—C4—C5	−178.7 (2)	C6—C5—N2—O4	177.0 (3)
O8—C4—C5—C6	178.3 (3)	C4—C5—N2—O4	−2.9 (4)
C3—C4—C5—C6	−1.9 (4)	C4—C3—N3—O5	−87.2 (4)
O8—C4—C5—N2	−1.8 (4)	C2—C3—N3—O5	93.7 (3)
C3—C4—C5—N2	178.0 (2)	C4—C3—N3—O6	89.1 (4)
C2—C1—C6—C5	0.6 (4)	C2—C3—N3—O6	−90.0 (4)
N1—C1—C6—C5	−179.2 (3)	C8—C7—N4—C11	0.2 (5)
C4—C5—C6—C1	1.5 (4)	C10—C11—N4—C7	0.0 (5)

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N4—H4*A*···O1	0.90 (2)	2.22 (4)	2.946 (4)	137 (4)
N4—H4*A*···O7	0.90 (2)	1.88 (4)	2.625 (3)	138 (5)
O8—H8*A*···N2	0.82	2.48	2.905 (3)	113
O8—H8*A*···O4	0.82	1.87	2.563 (3)	141
O8—H8*A*···O6^{i}	0.82	2.63	3.110 (4)	119
C8—H8···O6^{ii}	0.93	2.58	3.352 (5)	141

C8—H8···O8$^{\text{iii}}$	0.93	2.63	3.405 (4)	141
C10—H10···O2$^{\text{iv}}$	0.93	2.43	3.139 (4)	133

Symmetry codes: (i) $x-1, y, z$; (ii) $-x+5/2, y+1/2, -z+1/2$; (iii) $-x+3/2, y+1/2, -z+1/2$; (iv) $-x+2, -y+1, -z$.