Acta Cryst E
CRYSTALLOGRAPHIC COMMUNICATIONS
ISSN 2056-9890

Crystal structure of a 1:1 salt of 4-aminobenzoic acid (vitamin B_{10}) with pyrazinoic acid

K. V. Drozd,[a]* S. G. Arkhipov,[b,c] E. V. Boldyreva[b,d] and G. L. Perlovich[a]

[a]G. A. Krestov Institute of Solution Chemistry of the Russian Academy of Sciences, 1, Academicheskaya, Ivanovo 153045, Russian Federation, [b]Novosibirsk State University, Pirogova str. 2, Novosibirsk, 630090, Russian Federation, [c]Institute of Solid State Chemistry and Mechanochemistry SB RAS, Kutateladze str. 18, Novosibirsk 630128, Russian Federation, and [d]G. K. Boreskov Institute of Catalysis SB RAS, Laverentiev Ave. 5, Novosibirsk 630090, Russian Federation.
*Correspondence e-mail: ksdrozd@yandex.ru

Received 24 October 2018
Accepted 23 November 2018

Edited by C. Rizzoli, Universita degli Studi di Parma, Italy

Keywords: crystal structure; 4-aminobenzoic acid; pyrazinoic acid; salt; hydrogen bonding; melting point.

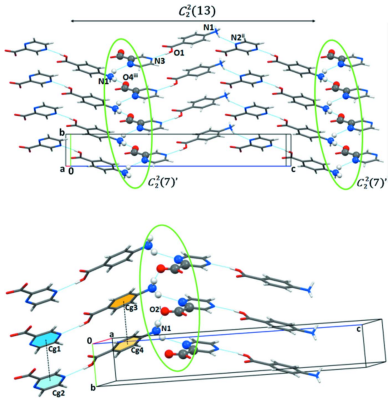
CCDC references: 1880871; 1880870

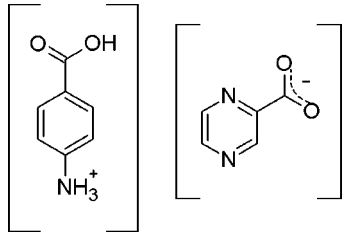
Supporting information: this article has supporting information at journals.iucr.org/e

The title 1:1 salt, $C_7H_8NO_2^+\cdot C_5H_3N_2O_2^-$ (systematic name: 4-carboxyanilinium pyrazine-2-carboxylate), was synthesized successfully by slow evaporation of a saturated solution from water–ethanol (1:1 *v*/*v*) mixture and characterized by X-ray diffraction (SCXRD, PXRD) and calorimetry (DSC). The crystal structure of the salt was solved and refined at 150 and 293 K. The salt crystallizes with one molecule of 4-aminobenzoic acid (PABA) and one molecule of pyrazinoic acid (POA) in the asymmetric unit. In the crystal, the PABA and POA molecules are associated via COOH···N_{arom} heterosynthons, which are connected by N—H···O hydrogen bonds, creating zigzag chains. The chains are further linked by N—H···O hydrogen bonds and π–π stacking interactions along the *b* axis [centroid-to-centroid distances = 3.7377 (13) and 3.8034 (13) Å at 150 and 293 K, respectively] to form a layered three-dimensional structure.

1. Chemical context

4-Aminobenzoic acid (PABA) is known as vitamin B_{10} and is involved in the production of folic acid in bacteria (Chang & Hu, 1996; Akberova, 2002). It is used as an antibacterial (Richards *et al.*, 1995), anti-inflammatory (Flindt-Hansen & Ebbesen, 1991), antioxidant (Sirota *et al.*, 2017; Galbinur *et al.*, 2009), anticoagulant (Stroeva *et al.*, 1999; Drozd *et al.*, 2000), or dermatologic agent (Rothman & Henningsen, 1947; Xavier *et al.*, 2006; Hanson *et al.*, 2006). Moreover, it is a building block used in the design of drug candidates and is frequently found as a structural moiety in drugs (Kluczyk *et al.*, 2002). PABA has been the subject of many scientific investigations, due not only to its pharmaceutical and biological properties, but also its ability to form various multi-component solid forms. PABA is a simple organic molecule with two functional groups: amine and carboxyl. This makes it unique in its ability to form various hydrogen-bonded network structures (Athimoolam & Natarajan, 2007). Among all the multi-component crystals of PABA known to date, co-crystals and salts of PABA are especially numerous.





OPEN ACCESS

Today, the formation of either salts or co-crystals of APIs is one of the promising strategies to modify the solid-state properties of pharmaceutical compounds, such as solubility, bioavailability, stability, *etc.* (Shevchenko *et al.*, 2012; Perumalla & Sun, 2013; Manin *et al.*, 2018). The main difference between a salt and a co-crystal is in the position of a proton. A salt is formed if a proton is transferred from an acid to a base (Aakeröy *et al.*, 2007). Childs *et al.* (2007) and Cruz-Cabeza (2012) have noticed a linear correlation between ΔpK_a [pK_a(base) – pK_a(acid)] of the starting compounds and the probability of the formation of either a salt or a co-crystal. It is assumed that a salt is expected to be formed if $\Delta pK_a > 3$ (Childs *et al.*, 2007) or $\Delta pK_a > 4$ (Cruz-Cabeza, 2012), whereas a co-crystal forms when $\Delta pK_a < 0$ (Childs *et al.*, 2007) or $\Delta pK_a < -1$ (Cruz-Cabeza, 2012). In the intermediate ΔpK_a range, the nature of multi-component crystal is difficult to predict – a so called 'salt–co-crystal continuum' (Childs *et al.*, 2007; Hathwar *et al.*, 2010). Several examples have been documented where both a salt and a co-crystal could be formed by the same components from the same solutions under different crystallization conditions (Fu *et al.*, 2016; Losev & Boldyreva, 2018*a*,*b*). A co-crystal can also be converted into a salt in the solid state upon temperature variations (Grobelny *et al.*, 2011).

The present study reports the synthesis and crystallization of a novel salt of 4-aminobenzoic acid with pyrazinoic acid (pyrazine-2-carboxylic acid, POA), [PABA-POA], which was characterized using single crystal and powder X-ray diffraction (SCXRD, PXRD) and different scanning calorimetry (DSC).

2. Elucidation of the multi-component crystal nature

4-Aminobenzoic acid is an ampholyte molecule with basic (–NH_2) and acidic (–COOH) functional groups, and its pK_a values are 2.46 and 4.62 (Avdeef, 2017) respectively. Pyrazinoic acid is a weak acid with a pK_a of 2.9 (Zhang *et al.*, 1999). According to the ΔpK_a of PABA and POA, the two-component crystal is within the range of the 'salt–co-crystal continuum'. Both a salt and a co-crystal can be expected to crystallize.

The crystal structure of the title compound was solved and refined at 150 K (**Ia**) and 293 K (**Ib**). The nature of the crystal form (salt/co-crystal) was identified from the structural characteristics, namely the C—N bond length of PABA and the C—O bond lengths of the carboxylic/carboxylate groups of PABA and POA at both temperatures to eliminate the possibility of salt–co-crystal transition. In a neutral pure PABA molecule, the length of the C—N bond between the N atom of the amine group and the C atom of the benzene ring is *ca* 1.37–1.4 Å. In the title compound, the protonation of the PABA amine group results in a significantly longer C—N bond [1.455 (5) Å at 150 K and 1.467 (3) Å at 293 K]. To define the deprotonation site, the C—O bond lengths of both PABA and POA were compared. In a neutral carboxylic group, C—O is longer than C═O by 0.08 Å, or more. Deprotonation of a –COOH group leads to a decrease in this difference to 0.03 Å or less (Childs *et al.*, 2007; Chen *et al.*, 2012). In the title compound, the difference d(C—O) is 0.104 (6) or 0.102 (8) Å for PABA and 0.007 (6) or 0.012 (6) Å for POA at 150 K and 293 K, respectively, indicating deprotonation of the POA –COOH group and the formation of a salt.

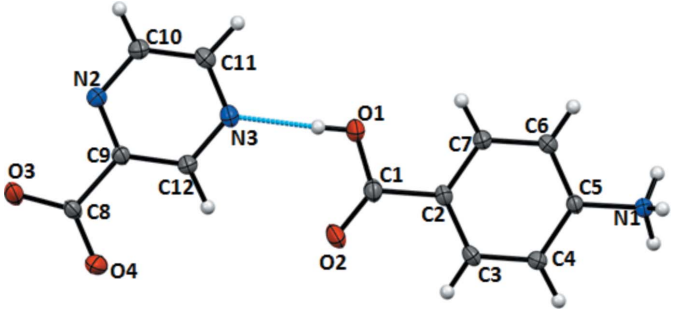


Figure 1
The asymmetric unit of the title compound at 150 K, with displacement ellipsoids drawn at the 50% probability level for non-H atoms. H atoms are shown as spheres of arbitrary radii.

3. Structural commentary

The title compound crystallizes in the monoclinic non-centrosymmetric space group *Pc* with one molecule of each component per asymmetric unit (Fig. 1). The carboxyl planes of PABA and POA are slightly twisted from the aromatic ring

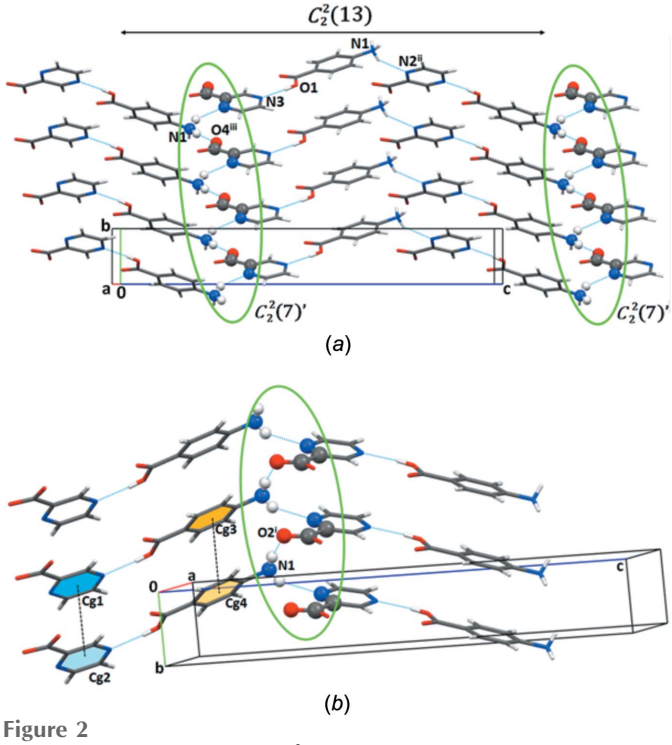


Figure 2
(*a*) The formation of zigzag $C_2^2(13)$ chains through O1—H1···N3 and N1—H1*B*···N2^{ii} interactions joined by an N1—H1*C*···O4^{iii} hydrogen bond [$C_2^2(7)$' chain motif] to generate the two-dimensional structure. (*b*) Layered arrangements of the salt via N1—H1*A*···O3^{i} interactions [$C_2^2(7)$'' chain motif] and aromatic π–π stacking interactions (dotted black lines) to generate the three-dimensional structure. Symmetry codes are in Table 1.

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

D—H···A	D—H	H···A	D···A	D—H···A
N1—H1A···O3^{i}	0.89 (4)	1.83 (4)	2.707 (3)	167 (3)
N1—H1B···N2^{ii}	0.79 (4)	2.21 (4)	2.907 (3)	148 (4)
N1—H1C···O4^{iii}	0.87 (4)	1.88 (4)	2.732 (3)	167 (4)
O1—H1···N3	0.80 (5)	1.87 (6)	2.670 (3)	175 (5)

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

Table 2
Hydrogen-bond geometry (Å, °) for **Ib**.

D—H···A	D—H	H···A	D···A	D—H···A
O1—H1···N3	0.82	1.87	2.677 (3)	167
N1—H1A···O3^{i}	0.89	1.85	2.716 (3)	164
N1—H1B···N2^{ii}	0.89	2.13	2.920 (3)	148
N1—H1C···O4^{iii}	0.89	1.87	2.732 (3)	163

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

planes [2.76 (16) and 8.4 (2)° for **Ia**; 2.89 (19) and 9.2 (3)° for **Ib**], which is a characteristic feature found in almost all known multi-component complexes of both compounds. No phase transitions occur in the temperature range between 293 and 150 K.

4. Supramolecular features

In the crystal, the O1—H1···N3 hydrogen bond involving the carboxyl group of PABA and the pyridine one of POA forms an acid···pyridine heterosynthon (COOH···N$_{arom}$, Tables 1 and 2). The neighboring two-component units are linked by N1—H1B···N2^{ii} hydrogen bonds, forming a zigzag $C_2^2(13)$ chain motif. Adjacent chains are linked to each other via N1—H1C···O4^{iii} hydrogen bonds [$C_2^2(7)$' chain motif] to form a 2D structure [Fig. 2(*a*)]. The crystal packing is stabilized by stacking of the parallel 2D structures along the *b*-axis direction through π–π interactions between neighboring benzene and pyrazine rings [$Cg1\cdots Cg2 = Cg3\cdots Cg4$ = 3.7377 (13) and 3.8034 (13) for **Ia** and **Ib**, respectively; $Cg1$ and $Cg2$ are centroids of the POA N2–C9 pyrazine ring, $Cg3$ and $Cg4$ are centroids of the PABA C2–C7 benzene ring], forming a 3D structure supported via N1—H1A···O3^{i} hydrogen bonds [$C_2^2(7)$'' chain motif] [Fig. 2(*b*)].

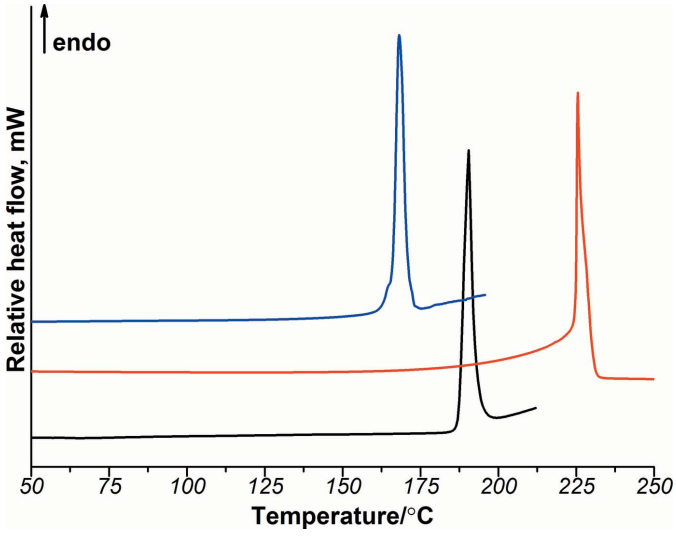


Figure 3
DSC curves of PABA (black), POA (red) and [PABA+POA] (blue).

5. Thermal analysis

The thermal behavior of the title compound was investigated by DSC techniques. The DSC curve [PABA+POA] is shown in Fig. 3. For a comparison, the DSC curves of the starting compounds are also plotted. PABA and POA show single endothermic peaks at 188.5 and 224.8°C, respectively. [PABA+POA] exhibits a sharp endothermic peak at 166.1°C. The melting temperature of the salt is *ca* 20 and 60°C lower than that of the starting compounds, suggesting the formation of a new crystalline phase. A single endothermic peak for the salt indicates that the solid state is homogeneous, and also suggests that there is no solvent in the crystal.

6. Database survey

A search of the Cambridge Structural Database (CSD version 5.39, May 2018 update; Groom *et al.*, 2016) for organic multi-component crystals (salts/co-crystals, their polymorphs and solvates) gave 88 structures for PABA and only five structures for POA. Analysis of the PABA crystal structures showed that the two most typical hydrogen-bonded motifs for them are: the acid···pyridine (COOH···N$_{arom}$) heterosynthon as in the title compound and the acid···acid (COOH···COOH)

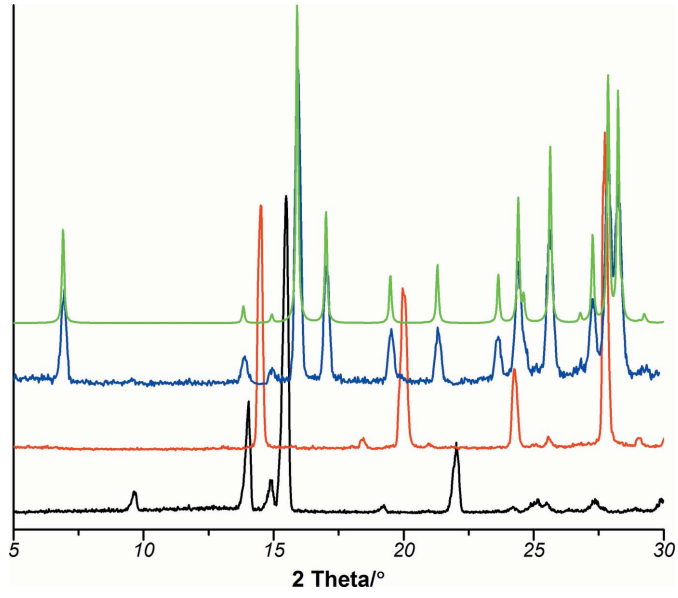


Figure 4
Comparison of the experimental PXRD patterns of [PABA+POA] prepared by liquid-assisted grinding (blue) of PABA (black) and POA (red) and calculated (green) using single-crystal X-ray diffraction data.

Table 3
Experimental details.

	150 K	293 K
Crystal data		
Chemical formula	$C_7H_8NO_2^+\cdot C_5H_3N_2O_2^-$	$C_7H_8NO_2^+\cdot C_5H_3N_2O_2^-$
M_r	261.24	261.24
Crystal system, space group	Monoclinic, *Pc*	Monoclinic, *Pc*
a, *b*, *c* (Å)	5.95842 (16), 3.73769 (10), 25.5943 (6)	5.95233 (16), 3.80345 (11), 25.6879 (7)
β (°)	95.362 (2)	95.037 (2)
V (Å^3)	567.51 (3)	579.31 (3)
Z	2	2
Radiation type	Mo *Kα*	Mo *Kα*
μ (mm^{-1})	0.12	0.12
Crystal size (mm)	0.24 × 0.19 × 0.18	0.24 × 0.19 × 0.18
Data collection		
Diffractometer	Rigaku Oxford Diffraxction Xcalibur Ruby Gemini ultra	Rigaku Oxford Diffraction Xcalibur Ruby Gemini ultra
Absorption correction	Multi-scan (*CrysAlis PRO*; Rigaku OD, 2018)	Multi-scan (*CrysAlis PRO*; Rigaku OD, 2018)
T_{min}, T_{max}	0.933, 1.000	0.822, 1.000
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	9340, 3426, 3244	8036, 2981, 2746
R_{int}	0.024	0.033
$(\sin \theta/\lambda)_{max}$ (Å^{-1})	0.727	0.694
Refinement		
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, *S*	0.044, 0.131, 1.13	0.049, 0.145, 1.11
No. of reflections	3426	2981
No. of parameters	216	174
No. of restraints	2	2
H-atom treatment	All H-atom parameters refined	H-atom parameters constrained
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.39, −0.28	0.29, −0.28

Computer programs: *CrysAlis PRO* (Rigaku OD, 2018), *SHELXT2014* (Sheldrick, 2015*a*), *SHELXL2017* (Sheldrick, 2015*b*) and *OLEX2* (Dolomanov *et al.*, 2009).

homosynthon between PABA molecules or PABA and conformer molecules with carboxylic functional group.

7. Synthesis and crystallization

A commercial sample of PABA (Merck, 99%) was co-crystallized with POA (Acros organics, 99%) by either liquid-assisted grinding, or by slow evaporation from solution under ambient conditions. Single crystals of [PABA+POA] were grown at room temperature by slow evaporation of a water–ethanol (1:1 *v*/*v*) solution in a 1:1 stoichiometric ratio. The powder sample of the title compound for DSC analysis was obtained by liquid-assisted grinding of the physical mixture in the presence of ethanol using a planetary micro mill. The ground material was characterized using PXRD to verify the formation of a new phase by comparing the diffraction pattern with the powder pattern calculated based on the single crystal X-ray diffraction data obtained in this work (Fig. 4).

8. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 3. The positions of all H atoms at 293 K were optimized geometrically and refined using a riding model, with the following assumptions and restraints: N—H = 0.89 Å, C—H = 0.93 Å and O—H = 0.82 Å with U_{iso}(H) = 1.5U_{eq}(O) for the hydroxyl groups, and 1.2U_{eq}(C, N) otherwise. The positions of the H atoms at 150 K were refined freely in an isotropic approximation.

Acknowledgements

KD thanks Dr Alex Manin and Dr Denis Rychkov for their interest in this work and helpful discussions.

Funding information

Funding for this research was provided by: RFBR (grant No. 17-33-50073 mol_nr).

References

Aakeröy, C. B., Fasulo, M. E. & Desper, J. (2007). *Mol. Pharm.* **4**, 317–322.
Akberova, S. I. (2002). *Biol. Bull. Russ. Acad. Sci.* **29**, 390–393.
Athimoolam, S. & Natarajan, S. (2007). *Acta Cryst.* C**63**, o283–o286.
Avdeef, A. (2017). *Eur. J. Pharm. Sci.* **110**, 2–18.
Chang, T.-Y. & Hu, M.-L. (1996). *J. Nutr. Biochem.* **7**, 408–413.
Chen, J.-M., Wang, Z.-Z., Wu, C.-B., Li, S. & Lu, T.-B. (2012). *CrystEngComm*, **14**, 6221–6229.
Childs, S. L., Stahly, G. P. & Park, A. (2007). *Mol. Pharm.* **4**, 323–338.
Cruz-Cabeza, A. J. (2012). *CrystEngComm*, **14**, 6362–6365.
Dolomanov, O. V., Bourhis, L. J., Gildea, R. J., Howard, J. A. K. & Puschmann, H. (2009). *J. Appl. Cryst.* **42**, 339–341.
Drozd, N. A., Makarov, V. T., Miftakhova, N. A., Kalugin, S. G., Stroeva, O. & Akberova, S. I. (2000). *Eksp. Klin. Farmakol.* **63**, 40–44.
Flindt-Hansen, H. & Ebbesen, P. (1991). *Br. J. Dermatol.* **125**, 222–226.
Fu, X., Li, J., Wang, L., Wu, B., Xu, X., Deng, Z. & Zhang, H. (2016). *RSC Adv.* **6**, 26474–26478.

Galbinur, T., Obolensky, A., Berenshtein, E., Vinokur, V., Chowers, I., Chevion, M. & Banin, E. (2009). *J. Ocul. Pharmacol. Ther.* **25**, 475–482.

Grobelny, P., Mukherjee, A. & Desiraju, G. R. (2011). *CrystEngComm*, **13**, 4358–4364.

Groom, C. R., Bruno, I. J., Lightfoot, M. P. & Ward, S. C. (2016). *Acta Cryst.* B**72**, 171–179.

Hanson, K. M., Gratton, E. & Bardeen, C. J. (2006). *Free Radic. Biol. Med.* **41**, 1205–1212.

Hathwar, V. R., Pal, R. & Guru Row, T. N. (2010). *Cryst. Growth Des.* **10**, 3306–3310.

Kluczyk, A., Popek, T., Kiyota, T., de Macedo, P., Stefanowicz, P., Lazar, C. & Konishi, Y. (2002). *Curr. Med. Chem.* **9**, 1871–1892.

Losev, E. & Boldyreva, E. (2018*a*). *CrystEngComm*, **20**, 2299–2305.

Losev, E. & Boldyreva, E. (2018*b*). *Acta Cryst.* C**74**, 177–185.

Manin, A. N., Voronin, A. P., Drozd, K. V., Churakov, A. V. & Perlovich, G. L. (2018). *Acta Cryst.* C**74**, 797–806.

Perumalla, S. R. & Sun, C. C. (2013). *CrystEngComm*, **15**, 5756–5759.

Richards, R. M. E., Xing, D. K. L. & King, T. P. (1995). *J. Appl. Bacteriol.* **78**, 209–215.

Rigaku OD (2018). *CrysAlis PRO*. Rigaku Oxford Diffraction, Yarnton, England.

Rothman, S. & Henningsen, A. B. (1947). *J. Invest. Dermatol.* **9**, 307–313.

Sheldrick, G. M. (2015*a*). *Acta Cryst.* A**71**, 3–8.

Sheldrick, G. M. (2015*b*). *Acta Cryst.* C**71**, 3–8.

Shevchenko, A., Bimbo, L. M., Miroshnyk, I., Haarala, J., Jelínková, K., Syrjänen, K., van Veen, B., Kiesvaara, J., Santos, H. A. & Yliruusi, J. (2012). *Int. J. Pharm.* **436**, 403–409.

Sirota, T. V., Lyamina, N. E. & Weisfeld, L. I. (2017). *Biophysics* **62**, 691–695.

Stroeva, O. G., Akberova, S. I., Drozd, N. N., Makarov, V. A., Miftakhova, N. T. & Kalugin, S. S. (1999). *Izv. Akad. Nauk Ser. Biol.* **26**, 329–336.

Xavier, S., Macdonald, S., Roth, J., Caunt, M., Akalu, A., Morais, D., Buckley, M. T., Liebes, L., Formenti, S. C. & Brooks, P. C. (2006). *Int. J. Radiat. Oncol. Biol. Phys.* **65**, 517–527.

Zhang, Y., Scorpio, A., Nikaido, H. & Sun, Z. (1999). *J. Bacteriol.* **181**, 2044–2049.

supporting information

Acta Cryst. (2018). E**74**, 1923-1927 [https://doi.org/10.1107/S2056989018016663]

Crystal structure of a 1:1 salt of 4-aminobenzoic acid (vitamin B_{10}) with pyrazinoic acid

K. V. Drozd, S. G. Arkhipov, E. V. Boldyreva and G. L. Perlovich

Computing details

For both structures, data collection: *CrysAlis PRO* (Rigaku OD, 2018); cell refinement: *CrysAlis PRO* (Rigaku OD, 2018); data reduction: *CrysAlis PRO* (Rigaku OD, 2018); program(s) used to solve structure: SHELXT2014 (Sheldrick, 2015a); program(s) used to refine structure: *SHELXL2017* (Sheldrick, 2015b); molecular graphics: *OLEX2* (Dolomanov *et al.*, 2009); software used to prepare material for publication: *OLEX2* (Dolomanov *et al.*, 2009).

4-Carboxyanilinium pyrazine-2-carboxylate (Ia)

Crystal data

$C_7H_8NO_2^+\cdot C_5H_3N_2O_2^-$
M_r = 261.24
Monoclinic, *Pc*
a = 5.95842 (16) Å
b = 3.73769 (10) Å
c = 25.5943 (6) Å
β = 95.362 (2)°
V = 567.51 (3) Å^3
Z = 2
F(000) = 272
D_x = 1.529 Mg m^{-3}
Mo $K\alpha$ radiation, λ = 0.71073 Å
Cell parameters from 5674 reflections
θ = 3.2–30.9°
μ = 0.12 mm^{-1}
T = 150 K
Block, light colourless
0.24 × 0.19 × 0.18 mm

Data collection

Rigaku Oxford Diffraction Xcalibur Ruby Gemini ultra diffractometer
Radiation source: fine-focus sealed X-ray tube, Enhance (Mo) X-ray Source
Graphite monochromator
Detector resolution: 10.3457 pixels mm^{-1}
ω scans
Absorption correction: multi-scan (CrysAlis PRO; Rigaku OD, 2018)
T_{min} = 0.933, T_{max} = 1.000
9340 measured reflections
3426 independent reflections
3244 reflections with $I > 2\sigma(I)$
R_{int} = 0.024
θ_{max} = 31.1°, θ_{min} = 3.2°
h = −8→8
k = −5→5
l = −36→36

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.044
$wR(F^2)$ = 0.131
S = 1.13
3426 reflections
216 parameters
2 restraints
Hydrogen site location: difference Fourier map
All H-atom parameters refined
$w = 1/[\sigma^2(F_o^2) + (0.0925P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = 0.001
$\Delta\rho_{max}$ = 0.39 e Å^{-3}
$\Delta\rho_{min}$ = −0.28 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.

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

	x	*y*	*z*	U_{iso}*/U_{eq}
O3	0.3138 (3)	0.3939 (5)	0.25476 (7)	0.0243 (4)
O4	0.6224 (3)	0.5432 (6)	0.30735 (7)	0.0277 (4)
O1	0.4407 (3)	0.5831 (6)	0.53444 (8)	0.0294 (4)
O2	0.7570 (4)	0.7455 (6)	0.50022 (7)	0.0315 (5)
N2	0.1012 (3)	0.1876 (5)	0.33842 (7)	0.0188 (4)
N1	0.9340 (3)	1.2049 (5)	0.74469 (7)	0.0168 (3)
N3	0.2855 (3)	0.3515 (6)	0.43916 (8)	0.0216 (4)
C8	0.4243 (4)	0.4341 (6)	0.29860 (8)	0.0182 (4)
C5	0.8626 (3)	1.0835 (6)	0.69173 (8)	0.0158 (4)
C9	0.3040 (4)	0.3411 (6)	0.34657 (8)	0.0166 (4)
C6	0.6482 (4)	0.9450 (6)	0.68152 (8)	0.0183 (4)
C1	0.6445 (4)	0.7247 (6)	0.53737 (9)	0.0215 (4)
C7	0.5784 (3)	0.8259 (6)	0.63124 (8)	0.0186 (4)
C2	0.7220 (4)	0.8505 (6)	0.59139 (8)	0.0176 (4)
C3	0.9376 (4)	0.9931 (7)	0.60225 (9)	0.0200 (4)
C12	0.3970 (4)	0.4200 (6)	0.39723 (8)	0.0188 (4)
C4	1.0095 (4)	1.1100 (6)	0.65252 (9)	0.0187 (4)
C10	−0.0077 (4)	0.1148 (6)	0.38037 (9)	0.0208 (4)
C11	0.0822 (4)	0.1982 (6)	0.43081 (9)	0.0210 (4)
H7	0.437 (6)	0.717 (10)	0.6221 (13)	0.021 (8)*
H10	−0.150 (8)	−0.003 (11)	0.3727 (18)	0.037 (10)*
H4	1.156 (6)	1.214 (9)	0.6619 (14)	0.020 (8)*
H3	1.033 (6)	1.003 (9)	0.5770 (15)	0.021 (8)*
H12	0.550 (6)	0.517 (9)	0.4054 (14)	0.020 (8)*
H1A	1.046 (7)	1.362 (10)	0.7450 (15)	0.028 (9)*
H11	0.005 (6)	0.147 (10)	0.4628 (15)	0.027 (9)*
H1B	0.978 (7)	1.037 (11)	0.7611 (17)	0.034 (10)*
H6	0.553 (6)	0.919 (9)	0.7079 (14)	0.020 (7)*
H1C	0.823 (7)	1.291 (9)	0.7600 (15)	0.026 (8)*
H1	0.399 (8)	0.505 (14)	0.506 (2)	0.046 (12)*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
O3	0.0226 (8)	0.0359 (9)	0.0146 (7)	0.0076 (7)	0.0026 (6)	−0.0009 (7)
O4	0.0201 (8)	0.0422 (10)	0.0210 (8)	−0.0057 (7)	0.0034 (6)	0.0067 (7)
O1	0.0264 (9)	0.0470 (11)	0.0151 (8)	−0.0116 (8)	0.0028 (6)	−0.0063 (8)
O2	0.0337 (10)	0.0464 (11)	0.0157 (8)	−0.0122 (9)	0.0085 (7)	−0.0059 (7)
N2	0.0165 (8)	0.0229 (9)	0.0171 (8)	0.0001 (7)	0.0014 (6)	−0.0016 (7)

N1	0.0163 (8)	0.0204 (8)	0.0138 (8)	0.0004 (7)	0.0013 (6)	−0.0006 (6)
N3	0.0238 (10)	0.0272 (9)	0.0138 (8)	−0.0024 (7)	0.0021 (7)	−0.0009 (7)
C8	0.0174 (9)	0.0237 (10)	0.0140 (9)	0.0042 (8)	0.0042 (7)	0.0021 (7)
C5	0.0174 (9)	0.0183 (9)	0.0118 (8)	0.0014 (7)	0.0017 (7)	−0.0003 (7)
C9	0.0166 (9)	0.0196 (9)	0.0138 (9)	0.0021 (7)	0.0018 (7)	−0.0008 (7)
C6	0.0166 (9)	0.0243 (10)	0.0144 (9)	−0.0017 (7)	0.0036 (7)	0.0005 (7)
C1	0.0253 (11)	0.0242 (10)	0.0147 (9)	−0.0018 (8)	0.0005 (8)	−0.0011 (8)
C7	0.0172 (9)	0.0243 (10)	0.0142 (8)	−0.0033 (8)	0.0017 (7)	−0.0005 (7)
C2	0.0191 (9)	0.0216 (10)	0.0122 (8)	0.0001 (7)	0.0018 (7)	−0.0002 (7)
C3	0.0208 (10)	0.0271 (10)	0.0128 (9)	−0.0017 (8)	0.0057 (7)	−0.0019 (8)
C12	0.0161 (9)	0.0242 (10)	0.0161 (9)	−0.0029 (8)	0.0015 (7)	−0.0004 (8)
C4	0.0160 (9)	0.0243 (10)	0.0161 (9)	−0.0033 (7)	0.0034 (7)	−0.0015 (7)
C10	0.0183 (9)	0.0248 (10)	0.0193 (10)	−0.0035 (8)	0.0027 (7)	−0.0017 (8)
C11	0.0214 (10)	0.0255 (10)	0.0168 (10)	−0.0019 (8)	0.0050 (8)	0.0015 (8)

Geometric parameters (Å, º)

O3—C8	1.256 (3)	C5—C4	1.395 (3)
O4—C8	1.249 (3)	C9—C12	1.393 (3)
O1—C1	1.320 (3)	C6—C7	1.388 (3)
O1—H1	0.80 (5)	C6—H6	0.93 (4)
O2—C1	1.216 (3)	C1—C2	1.492 (3)
N2—C9	1.336 (3)	C7—C2	1.394 (3)
N2—C10	1.334 (3)	C7—H7	0.95 (4)
N1—C5	1.455 (3)	C2—C3	1.394 (3)
N1—H1A	0.89 (4)	C3—C4	1.388 (3)
N1—H1B	0.79 (4)	C3—H3	0.90 (4)
N1—H1C	0.87 (4)	C12—H12	0.99 (4)
N3—C12	1.338 (3)	C4—H4	0.97 (4)
N3—C11	1.340 (3)	C10—C11	1.386 (3)
C8—C9	1.519 (3)	C10—H10	0.96 (5)
C5—C6	1.380 (3)	C11—H11	0.99 (4)
C1—O1—H1	114 (4)	O2—C1—C2	124.0 (2)
C10—N2—C9	117.57 (18)	C6—C7—C2	120.38 (19)
C5—N1—H1A	112 (2)	C6—C7—H7	123 (2)
C5—N1—H1B	108 (3)	C2—C7—H7	116 (2)
C5—N1—H1C	112 (2)	C7—C2—C1	119.9 (2)
H1A—N1—H1B	108 (4)	C7—C2—C3	119.75 (19)
H1A—N1—H1C	111 (3)	C3—C2—C1	120.30 (19)
H1B—N1—H1C	107 (4)	C2—C3—H3	120 (2)
C12—N3—C11	117.6 (2)	C4—C3—C2	120.2 (2)
O3—C8—C9	116.57 (19)	C4—C3—H3	120 (2)
O4—C8—O3	127.4 (2)	N3—C12—C9	121.5 (2)
O4—C8—C9	116.05 (19)	N3—C12—H12	115 (2)
C6—C5—N1	118.57 (18)	C9—C12—H12	124 (2)
C6—C5—C4	121.47 (19)	C5—C4—H4	118 (2)
C4—C5—N1	119.95 (19)	C3—C4—C5	119.0 (2)

N2—C9—C8	117.39 (18)	C3—C4—H4	123 (2)
N2—C9—C12	120.8 (2)	N2—C10—C11	122.0 (2)
C12—C9—C8	121.83 (19)	N2—C10—H10	115 (3)
C5—C6—C7	119.17 (19)	C11—C10—H10	123 (3)
C5—C6—H6	121 (2)	N3—C11—C10	120.7 (2)
C7—C6—H6	119 (2)	N3—C11—H11	116 (2)
O1—C1—C2	112.5 (2)	C10—C11—H11	124 (2)
O2—C1—O1	123.6 (2)		

O3—C8—C9—N2	7.2 (3)	C5—C6—C7—C2	−0.9 (3)
O3—C8—C9—C12	−171.1 (2)	C9—N2—C10—C11	0.9 (3)
O4—C8—C9—N2	−172.9 (2)	C6—C5—C4—C3	−0.2 (3)
O4—C8—C9—C12	8.7 (3)	C6—C7—C2—C1	−179.4 (2)
O1—C1—C2—C7	−2.9 (3)	C6—C7—C2—C3	0.5 (4)
O1—C1—C2—C3	177.2 (2)	C1—C2—C3—C4	−180.0 (2)
O2—C1—C2—C7	178.0 (2)	C7—C2—C3—C4	0.1 (3)
O2—C1—C2—C3	−1.9 (4)	C2—C3—C4—C5	−0.2 (3)
N2—C9—C12—N3	−1.3 (3)	C12—N3—C11—C10	0.0 (3)
N2—C10—C11—N3	−1.1 (4)	C4—C5—C6—C7	0.7 (3)
N1—C5—C6—C7	−179.6 (2)	C10—N2—C9—C8	−178.14 (19)
N1—C5—C4—C3	−179.9 (2)	C10—N2—C9—C12	0.2 (3)
C8—C9—C12—N3	177.0 (2)	C11—N3—C12—C9	1.1 (3)

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N1—H1*A*···O3^{i}	0.89 (4)	1.83 (4)	2.707 (3)	167 (3)
N1—H1*B*···N2^{ii}	0.79 (4)	2.21 (4)	2.907 (3)	148 (4)
N1—H1*C*···O4^{iii}	0.87 (4)	1.88 (4)	2.732 (3)	167 (4)
O1—H1···N3	0.80 (5)	1.87 (6)	2.670 (3)	175 (5)

Symmetry codes: (i) *x*+1, −*y*+2, *z*+1/2; (ii) *x*+1, −*y*+1, *z*+1/2; (iii) *x*, −*y*+2, *z*+1/2.

4-Carboxyanilinium pyrazine-2-carboxylate (Ib)

Crystal data

$C_7H_8NO_2^+\cdot C_5H_3N_2O_2^-$
M_r = 261.24
Monoclinic, *Pc*
a = 5.95233 (16) Å
b = 3.80345 (11) Å
c = 25.6879 (7) Å
β = 95.037 (2)°
V = 579.31 (3) Å^3
Z = 2

F(000) = 272
D_x = 1.498 Mg m^{-3}
Mo *Kα* radiation, *λ* = 0.71073 Å
Cell parameters from 4235 reflections
θ = 3.2–29.2°
μ = 0.12 mm^{-1}
T = 293 K
Block, light colourless
0.24 × 0.19 × 0.18 mm

Data collection

Rigaku Oxford Diffraction Xcalibur Ruby Gemini ultra diffractometer

Radiation source: fine-focus sealed X-ray tube, Enhance (Mo) X-ray Source
Graphite monochromator

Detector resolution: 10.3457 pixels mm^{-1}
ω scans
Absorption correction: multi-scan
(CrysAlis PRO; Rigaku OD, 2018)
T_{min} = 0.822, T_{max} = 1.000
8036 measured reflections
2981 independent reflections
2746 reflections with $I > 2\sigma(I)$
R_{int} = 0.033
θ_{max} = 29.6°, θ_{min} = 1.6°
$h = -7 \rightarrow 8$
$k = -5 \rightarrow 5$
$l = -35 \rightarrow 33$

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.049
$wR(F^2)$ = 0.145
S = 1.11
2981 reflections
174 parameters
2 restraints
Hydrogen site location: inferred from
neighbouring sites
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0973P)^2]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = 0.001
$\Delta\rho_{max}$ = 0.29 e Å^{-3}
$\Delta\rho_{min}$ = −0.28 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.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2)

	x	y	z	U_{iso}*/U_{eq}
O3	0.3114 (4)	0.4159 (6)	0.25493 (8)	0.0428 (6)
O4	0.6195 (4)	0.5580 (8)	0.30677 (9)	0.0505 (6)
O1	0.4431 (4)	0.5870 (8)	0.53404 (9)	0.0547 (7)
H1	0.415003	0.501947	0.504859	0.082*
O2	0.7585 (5)	0.7517 (8)	0.50073 (10)	0.0588 (7)
N2	0.1020 (4)	0.2017 (6)	0.33869 (9)	0.0328 (5)
N1	0.9323 (4)	1.1834 (6)	0.74503 (8)	0.0282 (5)
H1A	1.042185	1.341470	0.744245	0.034*
H1B	0.982136	0.999337	0.764065	0.034*
H1C	0.815616	1.279554	0.759180	0.034*
N3	0.2877 (4)	0.3635 (7)	0.43878 (10)	0.0383 (6)
C8	0.4229 (4)	0.4514 (8)	0.29826 (10)	0.0314 (6)
C5	0.8611 (4)	1.0681 (7)	0.69163 (9)	0.0262 (5)
C9	0.3039 (4)	0.3555 (7)	0.34649 (10)	0.0273 (5)
C6	0.6491 (4)	0.9282 (8)	0.68141 (10)	0.0312 (6)
H6	0.552972	0.909327	0.707932	0.037*
C1	0.6453 (5)	0.7272 (9)	0.53745 (10)	0.0365 (6)
C7	0.5796 (4)	0.8159 (8)	0.63147 (11)	0.0319 (6)
H7	0.436812	0.718844	0.624423	0.038*
C2	0.7226 (4)	0.8473 (8)	0.59157 (10)	0.0301 (5)
C3	0.9362 (5)	0.9920 (8)	0.60255 (11)	0.0356 (6)
H3	1.032069	1.014408	0.576030	0.043*
C12	0.3970 (5)	0.4333 (8)	0.39670 (11)	0.0335 (6)
H12	0.538987	0.536543	0.401120	0.040*

C4	1.0070 (4)	1.1027 (8)	0.65257 (11)	0.0330 (6)
H4	1.149948	1.198795	0.659963	0.040*
C10	−0.0051 (5)	0.1270 (8)	0.38076 (13)	0.0376 (6)
H10	−0.144761	0.016045	0.376452	0.045*
C11	0.0861 (5)	0.2102 (9)	0.43080 (12)	0.0390 (7)
H11	0.005353	0.158345	0.459237	0.047*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
O3	0.0390 (12)	0.0655 (15)	0.0241 (10)	0.0140 (10)	0.0039 (8)	−0.0003 (9)
O4	0.0356 (12)	0.0830 (18)	0.0336 (12)	−0.0103 (11)	0.0068 (9)	0.0122 (11)
O1	0.0491 (13)	0.0908 (18)	0.0241 (10)	−0.0236 (13)	0.0034 (9)	−0.0131 (11)
O2	0.0618 (16)	0.0920 (19)	0.0244 (10)	−0.0238 (15)	0.0149 (10)	−0.0122 (12)
N2	0.0273 (10)	0.0424 (12)	0.0285 (11)	−0.0009 (9)	0.0011 (8)	−0.0052 (9)
N1	0.0288 (10)	0.0343 (11)	0.0211 (10)	0.0011 (8)	0.0007 (7)	−0.0007 (8)
N3	0.0429 (14)	0.0498 (14)	0.0221 (11)	−0.0049 (10)	0.0027 (9)	−0.0028 (10)
C8	0.0295 (12)	0.0427 (14)	0.0226 (12)	0.0078 (10)	0.0059 (9)	0.0036 (10)
C5	0.0292 (12)	0.0305 (13)	0.0190 (11)	0.0026 (9)	0.0022 (9)	0.0009 (9)
C9	0.0269 (12)	0.0331 (12)	0.0218 (11)	0.0028 (9)	0.0022 (9)	−0.0011 (9)
C6	0.0288 (12)	0.0441 (15)	0.0215 (12)	−0.0042 (10)	0.0067 (9)	0.0011 (10)
C1	0.0420 (15)	0.0458 (15)	0.0217 (12)	−0.0049 (12)	0.0033 (11)	−0.0035 (11)
C7	0.0278 (12)	0.0429 (14)	0.0253 (12)	−0.0056 (11)	0.0045 (10)	−0.0015 (10)
C2	0.0339 (13)	0.0363 (14)	0.0202 (11)	0.0010 (10)	0.0028 (9)	−0.0004 (9)
C3	0.0349 (14)	0.0514 (16)	0.0218 (12)	−0.0053 (11)	0.0092 (10)	−0.0024 (11)
C12	0.0287 (12)	0.0443 (16)	0.0274 (13)	−0.0059 (11)	0.0017 (10)	−0.0027 (11)
C4	0.0265 (12)	0.0441 (15)	0.0286 (13)	−0.0065 (10)	0.0042 (9)	−0.0035 (11)
C10	0.0303 (13)	0.0466 (16)	0.0364 (15)	−0.0082 (12)	0.0061 (10)	−0.0033 (12)
C11	0.0413 (16)	0.0484 (16)	0.0285 (14)	−0.0042 (12)	0.0109 (11)	−0.0001 (11)

Geometric parameters (Å, º)

O3—C8	1.252 (3)	C5—C4	1.390 (4)
O4—C8	1.240 (4)	C9—C12	1.390 (4)
O1—H1	0.8200	C6—H6	0.9300
O1—C1	1.313 (4)	C6—C7	1.380 (4)
O2—C1	1.210 (4)	C1—C2	1.497 (4)
N2—C9	1.336 (4)	C7—H7	0.9300
N2—C10	1.332 (4)	C7—C2	1.394 (4)
N1—H1A	0.8900	C2—C3	1.391 (4)
N1—H1B	0.8900	C3—H3	0.9300
N1—H1C	0.8900	C3—C4	1.382 (4)
N1—C5	1.467 (3)	C12—H12	0.9300
N3—C12	1.336 (4)	C4—H4	0.9300
N3—C11	1.334 (4)	C10—H10	0.9300
C8—C9	1.524 (4)	C10—C11	1.388 (4)
C5—C6	1.374 (3)	C11—H11	0.9300

C1—O1—H1	109.5	O2—C1—C2	123.6 (3)
C10—N2—C9	117.4 (2)	C6—C7—H7	119.8
H1A—N1—H1B	109.5	C6—C7—C2	120.3 (2)
H1A—N1—H1C	109.5	C2—C7—H7	119.8
H1B—N1—H1C	109.5	C7—C2—C1	119.9 (2)
C5—N1—H1A	109.5	C3—C2—C1	120.6 (2)
C5—N1—H1B	109.5	C3—C2—C7	119.4 (2)
C5—N1—H1C	109.5	C2—C3—H3	119.8
C11—N3—C12	117.3 (3)	C4—C3—C2	120.5 (2)
O3—C8—C9	116.7 (2)	C4—C3—H3	119.8
O4—C8—O3	127.6 (3)	N3—C12—C9	121.7 (3)
O4—C8—C9	115.7 (2)	N3—C12—H12	119.1
C6—C5—N1	118.7 (2)	C9—C12—H12	119.1
C6—C5—C4	121.4 (2)	C5—C4—H4	120.5
C4—C5—N1	120.0 (2)	C3—C4—C5	118.9 (2)
N2—C9—C8	117.3 (2)	C3—C4—H4	120.5
N2—C9—C12	120.8 (2)	N2—C10—H10	119.1
C12—C9—C8	121.8 (2)	N2—C10—C11	121.8 (3)
C5—C6—H6	120.2	C11—C10—H10	119.1
C5—C6—C7	119.5 (2)	N3—C11—C10	121.0 (3)
C7—C6—H6	120.2	N3—C11—H11	119.5
O1—C1—C2	113.0 (2)	C10—C11—H11	119.5
O2—C1—O1	123.3 (3)		

O3—C8—C9—N2	8.0 (4)	C5—C6—C7—C2	−0.7 (4)
O3—C8—C9—C12	−170.1 (3)	C9—N2—C10—C11	1.1 (5)
O4—C8—C9—N2	−172.4 (3)	C6—C5—C4—C3	−0.3 (4)
O4—C8—C9—C12	9.5 (4)	C6—C7—C2—C1	−179.6 (3)
O1—C1—C2—C7	−2.3 (4)	C6—C7—C2—C3	0.2 (4)
O1—C1—C2—C3	177.9 (3)	C1—C2—C3—C4	180.0 (3)
O2—C1—C2—C7	178.7 (3)	C7—C2—C3—C4	0.2 (4)
O2—C1—C2—C3	−1.0 (5)	C2—C3—C4—C5	−0.2 (4)
N2—C9—C12—N3	−1.1 (5)	C12—N3—C11—C10	0.1 (5)
N2—C10—C11—N3	−1.2 (5)	C4—C5—C6—C7	0.7 (4)
N1—C5—C6—C7	−179.6 (3)	C10—N2—C9—C8	−178.1 (2)
N1—C5—C4—C3	180.0 (3)	C10—N2—C9—C12	0.0 (4)
C8—C9—C12—N3	176.9 (3)	C11—N3—C12—C9	1.1 (5)

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O1—H1···N3	0.82	1.87	2.677 (3)	167
N1—H1*A*···O3^{i}	0.89	1.85	2.716 (3)	164
N1—H1*B*···N2^{ii}	0.89	2.13	2.920 (3)	148
N1—H1*C*···O4^{iii}	0.89	1.87	2.732 (3)	163

Symmetry codes: (i) *x*+1, −*y*+2, *z*+1/2; (ii) *x*+1, −*y*+1, *z*+1/2; (iii) *x*, −*y*+2, *z*+1/2.