

2-(2,4-Dinitrobenzyl)pyridinium 2-hydroxy-3,5-dinitrobenzoate

Graham Smith,^{a*} Urs D. Wermuth^a and David J. Young^b

^aFaculty of Science and Technology, Queensland University of Technology, GPO Box 2434, Brisbane, Queensland 4001, Australia, and ^bSchool of Biomolecular and Physical Sciences, Griffith University, Nathan, Queensland 4111, Australia

Correspondence e-mail: g.smith@qut.edu.au

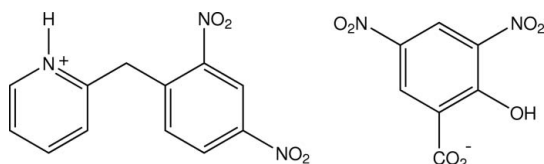
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Key indicators: single-crystal X-ray study; $T = 200$ K; mean $\sigma(\text{C}-\text{C}) = 0.003$ Å; R factor = 0.051; wR factor = 0.153; data-to-parameter ratio = 12.2.

In the structure of the title salt, $\text{C}_{12}\text{H}_{10}\text{N}_3\text{O}_4^+ \cdot \text{C}_7\text{H}_3\text{N}_2\text{O}_7^-$, the cations and the anions are linked by a single $\text{N}^+ \cdots \text{H} \cdots \text{O}_{\text{carboxyl}}$ hydrogen bond, the discrete cation–anion unit having no intermolecular associations other than weak cation–anion aromatic ring π – π interactions [ring centroid separation = 3.7320 (14) Å] and a number of weak inter-unit aromatic C–H \cdots O contacts. An intramolecular C–H \cdots O hydroxyl–carboxyl hydrogen bond occurs in the anion.

Related literature

For structural data on 2-(2,4-dinitrobenzyl)pyridine and related compounds, see: Seff & Trueblood (1968); Scherl *et al.* (1996); Naumov *et al.* (2002, 2005); Smith, Wermuth & Young (2010). For some structures of 3,5-dinitrosalicylic acid salts of Lewis bases, see: Smith *et al.* (2002, 2003, 2007); Smith, Cotton *et al.* (2010).



Experimental

Crystal data

$\text{C}_{12}\text{H}_{10}\text{N}_3\text{O}_4^+ \cdot \text{C}_7\text{H}_3\text{N}_2\text{O}_7^-$
 $M_r = 487.34$
 Monoclinic, $P2_1/c$
 $a = 7.1550$ (2) Å
 $b = 21.7356$ (5) Å
 $c = 13.2080$ (4) Å
 $\beta = 104.424$ (3)°

$V = 1989.34$ (10) Å³
 $Z = 4$
 Mo $K\alpha$ radiation
 $\mu = 0.14$ mm⁻¹
 $T = 200$ K
 $0.40 \times 0.35 \times 0.18$ mm

Data collection

Oxford Diffraction Gemini-S CCD-detector diffractometer

Absorption correction: multi-scan (SADABS; Sheldrick, 1996)
 $T_{\text{min}} = 0.960$, $T_{\text{max}} = 0.982$

13759 measured reflections
 3910 independent reflections

2865 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.025$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.051$
 $wR(F^2) = 0.153$
 $S = 1.08$
 3910 reflections

320 parameters
 H-atom parameters constrained
 $\Delta\rho_{\text{max}} = 0.75$ e Å⁻³
 $\Delta\rho_{\text{min}} = -0.32$ e Å⁻³

Table 1

Hydrogen-bond geometry (Å, °).

$D-H \cdots A$	$D-H$	$H \cdots A$	$D \cdots A$	$D-H \cdots A$
$\text{N1}-\text{H1} \cdots \text{O11A}$	0.91	1.72	2.627 (3)	172
$\text{O2A}-\text{H2A} \cdots \text{O12A}$	0.93	1.61	2.476 (3)	152
$\text{C3}-\text{H3} \cdots \text{O11A}^{\text{i}}$	0.93	2.48	3.246 (3)	140
$\text{C5}-\text{H5} \cdots \text{O31A}^{\text{ii}}$	0.93	2.56	3.051 (4)	114
$\text{C6}-\text{H6} \cdots \text{O31A}^{\text{ii}}$	0.93	2.48	3.020 (4)	117
$\text{C51}-\text{H51} \cdots \text{O51A}^{\text{iii}}$	0.93	2.55	3.137 (4)	122
$\text{C61}-\text{H61} \cdots \text{O51A}^{\text{iii}}$	0.93	2.54	3.141 (3)	123
$\text{C71}-\text{H72} \cdots \text{O11A}$	0.97	2.55	3.247 (3)	129

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

Data collection: *CrysAlis PRO* (Oxford Diffraction, 2009); cell refinement: *CrysAlis PRO*; data reduction: *CrysAlis PRO*; program(s) used to solve structure: *SIR92* (Altomare *et al.*, 1994); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *PLATON* (Spek, 2009); software used to prepare material for publication: *PLATON*.

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: EZZ2219).

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supplementary materials

Acta Cryst. (2010). E66, o1895 [doi:10.1107/S1600536810024888]

2-(2,4-Dinitrobenzyl)pyridinium 2-hydroxy-3,5-dinitrobenzoate

G. Smith, U. D. Wermuth and D. J. Young

Comment

The Lewis base 2-(2,4-dinitrobenzyl)pyridine (DNBP) is unusual because of its photochromic properties, undergoing a reversible solid-state colour change from colourless to deep blue on irradiation with light of wavelength 400 nm or less. This is due to two-photon excitation giving nitro-assisted proton transfer (NAPT) involving an oxygen of the *o*-nitro substituent group and the pyridine N atom (Naumov *et al.*, 2002). The structures of both the colourless form (Seff & Trueblood, 1968; Scherl *et al.*, 1996) and the blue form (Naumov *et al.*, 2002), have been determined as well, as that of the chloride (Naumov *et al.*, 2005).

Our reaction of DNBP with a number of aromatic carboxylic and sulfonic acids in aqueous ethanol has previously provided only one crystalline compound: bis[2-(2,4-dinitrobenzyl)pyridinium] biphenyl-4,4'-disulfonate trihydrate, for which the structure was reported (Smith, Wermuth & Young, 2010). A second crystalline compound was subsequently obtained from the reaction of DNBP with 3,5-dinitrosalicylic acid (DNSA), the title compound anhydrous $C_{12}H_{10}N_3O_4^+ \cdot C_7H_3N_2O_7^-$ (I), the structure of which is reported here. DNSA has been very useful as an acid capable of producing crystalline salts with a range of both aliphatic and aromatic Lewis bases and the structures of a large number of these are reported in the crystallographic literature, *e.g.* Smith *et al.* (2002, 2003, 2007) and Smith, Cotton *et al.* (2010).

With compound (I) (Fig. 1), a single cation–anion $N^+ \cdots H \cdots O_{\text{carboxyl}}$ hydrogen bond together with a weak aliphatic $C-H \cdots O_{\text{carboxyl}}$ association (C71–H \cdots O11A) (Table 1), form discrete cation–anion units. These units have no intermolecular interactions other than mostly weak aromatic C–H \cdots O contacts [one is strong: C6–H \cdots O31Aⁱⁱⁱ; symmetry code (iii), $-x + 1, -y + 1, -z + 1$], and also weak cation–anion π – π aromatic ring associations [ring centroid separation for C11–C61 to C1A–C6A, 3.7320 (14) Å] down the *a* axial direction (Fig. 2).

With the DNBP cation both nitro groups are rotated out of the plane of the benzene ring [torsion angles C11–C21–N21–O22, -151.4 (2)° and C31–C41–N41–O42, 149.9 (2)°]. In the DNSA anion, within the intramolecular hydroxyl–carboxyl hydrogen bond, the H atom is located on the hydroxyl group rather than being *anti*-related on the carboxyl group. (I) is only one of the *ca* 30% of the known examples of DNSA salts having this (Smith *et al.*, 2007). The carboxyl group, as expected, is close to planar with the benzene ring [torsion angle C2A–C1A–C11A–O11A, 175.0 (2)°], while one nitro group is close to coplanar [torsion angle C4A–C5A–C51A–O52A, 177.6 (2)°], the other being rotated out of the plane [torsion angle C2A–C3A–C31A–O32A, -159.1 (2)°]. In the structure there is a short nonbonded contact across an inversion centre [O42 \cdots O42^{iv}, 2.897 (3) Å; symmetry code (iv) $-x + 1, -y, -z + 1$], this O atom being associated with the large electron density maximum ($0.75 \text{ e } \text{Å}^{-3}$).

Experimental

The title compound was synthesized by heating together under reflux for 10 minutes, 1 mmol quantities of 2-(2,4-dinitrobenzyl)pyridine and 3,5-dinitrosalicylic acid in 50 ml of 50% ethanol–water. After concentration to *ca* 30 ml, partial

room temperature evaporation of the hot-filtered solution gave yellow plates (m.p. 383 K) having 90° yellow–colourless orientational dichroism in the crystals.

Refinement

The two hydrogen atoms involved in hydrogen-bonding interactions were located by difference methods and were constrained in the refinement with the other H atoms at calculated positions [C–H = 0.93 Å (aromatic) and 0.97 Å (aliphatic)] and with $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$, using a riding-model approximation. There is a larger than normal maximum residual electron density peak ($0.75 \text{ e } \text{Å}^{-3}$) which is located *ca* 1.56 Å from the nitro O atom O42).

Figures

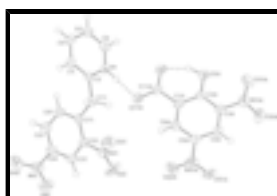


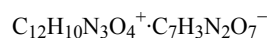
Fig. 1. Molecular configuration and atom naming scheme for the DNBP cation and the DNSA anion in the asymmetric unit of (I), with the hydrogen bonds shown as a dashed lines. Displacement ellipsoids are drawn at the 50% probability level.



Fig. 2. The packing of the cation–anion pairs in the unit cell viewed down the *a* cell direction. Non-interactive H atoms are omitted.

2-(2,4-Dinitrobenzyl)pyridinium 2-hydroxy-3,5-dinitrobenzoate

Crystal data



$M_r = 487.34$

Monoclinic, $P2_1/c$

Hall symbol: $-P\ 2_1/c$

$a = 7.1550(2) \text{ Å}$

$b = 21.7356(5) \text{ Å}$

$c = 13.2080(4) \text{ Å}$

$\beta = 104.424(3)^\circ$

$V = 1989.34(10) \text{ Å}^3$

$Z = 4$

$F(000) = 1000$

$D_x = 1.627 \text{ Mg m}^{-3}$

Melting point: 383 K

Mo $K\alpha$ radiation, $\lambda = 0.71073 \text{ Å}$

Cell parameters from 6248 reflections

$\theta = 3.1\text{--}28.7^\circ$

$\mu = 0.14 \text{ mm}^{-1}$

$T = 200 \text{ K}$

Plate, yellow

$0.40 \times 0.35 \times 0.18 \text{ mm}$

Data collection

Oxford Diffraction Gemini-S CCD-detector diffractometer

Radiation source: Enhance (Mo) X-ray source graphite

ω scans

Absorption correction: multi-scan

3910 independent reflections

2865 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.025$

$\theta_{\text{max}} = 26.0^\circ$, $\theta_{\text{min}} = 3.1^\circ$

$h = -8 \rightarrow 5$

(SADABS; Sheldrick, 1996)

$T_{\min} = 0.960$, $T_{\max} = 0.982$

13759 measured reflections

$k = -26 \rightarrow 26$

$l = -16 \rightarrow 16$

Refinement

Refinement on F^2

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.051$

$wR(F^2) = 0.153$

$S = 1.08$

3910 reflections

320 parameters

0 restraints

Primary atom site location: structure-invariant direct methods

Secondary atom site location: difference Fourier map

Hydrogen site location: inferred from neighbouring sites

H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0819P)^2 + 0.673P]$

where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\max} < 0.001$

$\Delta\rho_{\max} = 0.75 \text{ e } \text{\AA}^{-3}$

$\Delta\rho_{\min} = -0.32 \text{ e } \text{\AA}^{-3}$

Special details

Geometry. Bond distances, angles *etc.* have been calculated using the rounded fractional coordinates. All su's are estimated from the variances of the (full) variance-covariance matrix. The cell e.s.d.'s are taken into account in the estimation of distances, angles and torsion angles

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 $F^2 > \sigma(F^2)$ 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 (\AA^2)

	x	y	z	$U_{\text{iso}}^*/U_{\text{eq}}$
O21	1.2566 (3)	0.22969 (10)	0.63986 (18)	0.0562 (8)
O22	1.1932 (4)	0.18930 (12)	0.48691 (19)	0.0733 (10)
O41	0.7828 (4)	0.00564 (10)	0.43481 (18)	0.0635 (9)
O42	0.6790 (3)	-0.02169 (9)	0.56819 (19)	0.0577 (8)
N1	0.6649 (3)	0.32238 (8)	0.69232 (15)	0.0274 (6)
N21	1.1587 (3)	0.19783 (10)	0.57118 (18)	0.0365 (7)
N41	0.7462 (3)	0.01652 (11)	0.5177 (2)	0.0458 (8)
C2	0.7755 (3)	0.28074 (10)	0.75516 (18)	0.0267 (7)
C3	0.7361 (4)	0.26743 (11)	0.84941 (19)	0.0316 (7)
C4	0.5867 (4)	0.29735 (12)	0.87819 (19)	0.0345 (8)
C5	0.4801 (4)	0.34101 (12)	0.8133 (2)	0.0376 (8)
C6	0.5212 (4)	0.35297 (12)	0.7190 (2)	0.0359 (8)
C11	0.8856 (3)	0.19180 (10)	0.65949 (17)	0.0250 (7)
C21	0.9877 (3)	0.16655 (10)	0.59134 (18)	0.0268 (7)
C31	0.9395 (3)	0.11127 (11)	0.5400 (2)	0.0322 (8)
C41	0.7909 (4)	0.07812 (11)	0.5632 (2)	0.0353 (8)

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C51	0.6845 (4)	0.10000 (12)	0.6292 (2)	0.0359 (8)
C61	0.7296 (3)	0.15746 (11)	0.67349 (19)	0.0307 (7)
C71	0.9381 (3)	0.25231 (10)	0.7169 (2)	0.0308 (7)
O2A	0.7053 (3)	0.51546 (8)	0.39374 (15)	0.0389 (6)
O11A	0.7728 (2)	0.34274 (8)	0.51916 (13)	0.0363 (6)
O12A	0.6246 (3)	0.43376 (8)	0.50643 (15)	0.0404 (6)
O31A	0.8926 (3)	0.60447 (8)	0.32114 (17)	0.0482 (7)
O32A	1.0404 (4)	0.57457 (11)	0.20856 (19)	0.0703 (10)
O51A	1.4121 (3)	0.38998 (10)	0.28140 (17)	0.0514 (7)
O52A	1.3387 (3)	0.32069 (9)	0.38239 (19)	0.0536 (7)
N31A	0.9667 (3)	0.56457 (10)	0.28107 (17)	0.0388 (7)
N51A	1.3139 (3)	0.37048 (10)	0.33857 (18)	0.0375 (7)
C1A	0.8825 (3)	0.42179 (10)	0.42470 (17)	0.0254 (6)
C2A	0.8508 (3)	0.48139 (11)	0.38128 (18)	0.0276 (7)
C3A	0.9808 (4)	0.50221 (10)	0.32341 (18)	0.0293 (7)
C4A	1.1287 (3)	0.46614 (11)	0.30776 (18)	0.0296 (7)
C5A	1.1555 (3)	0.40898 (11)	0.35306 (18)	0.0278 (7)
C6A	1.0358 (3)	0.38671 (10)	0.41266 (18)	0.0268 (7)
C11A	0.7494 (3)	0.39730 (11)	0.48798 (18)	0.0294 (7)
H1	0.69100	0.32880	0.62900	0.0330*
H3	0.80970	0.23840	0.89370	0.0380*
H4	0.55830	0.28790	0.94140	0.0410*
H5	0.38170	0.36210	0.83300	0.0450*
H6	0.44980	0.38210	0.67380	0.0430*
H31	1.00440	0.09700	0.49180	0.0390*
H51	0.58490	0.07680	0.64350	0.0430*
H61	0.65290	0.17380	0.71420	0.0370*
H71	1.04700	0.24550	0.77630	0.0370*
H72	0.97850	0.28120	0.67050	0.0370*
H2A	0.64800	0.49380	0.43920	0.0470*
H4A	1.20920	0.48020	0.26720	0.0350*
H6A	1.05890	0.34830	0.44430	0.0320*

Atomic displacement parameters (\AA^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
O21	0.0376 (11)	0.0622 (13)	0.0758 (15)	-0.0202 (10)	0.0272 (11)	-0.0216 (12)
O22	0.0767 (17)	0.0939 (18)	0.0687 (15)	-0.0332 (14)	0.0546 (14)	-0.0196 (14)
O41	0.0775 (17)	0.0640 (14)	0.0585 (14)	-0.0200 (12)	0.0349 (13)	-0.0309 (12)
O42	0.0637 (14)	0.0356 (11)	0.0721 (15)	-0.0054 (10)	0.0135 (12)	0.0012 (11)
N1	0.0292 (10)	0.0257 (9)	0.0297 (10)	-0.0008 (8)	0.0120 (9)	0.0026 (8)
N21	0.0322 (12)	0.0356 (11)	0.0477 (13)	-0.0004 (10)	0.0212 (11)	0.0017 (11)
N41	0.0363 (13)	0.0420 (13)	0.0597 (16)	-0.0027 (10)	0.0132 (12)	-0.0135 (12)
C2	0.0264 (12)	0.0207 (10)	0.0338 (13)	-0.0042 (9)	0.0093 (10)	-0.0031 (10)
C3	0.0344 (13)	0.0284 (12)	0.0306 (13)	-0.0009 (10)	0.0057 (11)	0.0015 (10)
C4	0.0373 (14)	0.0405 (14)	0.0283 (13)	-0.0064 (11)	0.0133 (11)	-0.0037 (11)
C5	0.0367 (14)	0.0408 (14)	0.0391 (14)	0.0066 (12)	0.0164 (12)	-0.0033 (12)
C6	0.0341 (13)	0.0337 (13)	0.0412 (14)	0.0074 (11)	0.0121 (12)	0.0054 (11)

C11	0.0219 (11)	0.0259 (11)	0.0270 (12)	0.0036 (9)	0.0055 (9)	0.0055 (9)
C21	0.0223 (11)	0.0304 (12)	0.0289 (12)	0.0020 (9)	0.0087 (9)	0.0049 (10)
C31	0.0296 (13)	0.0357 (13)	0.0335 (13)	0.0058 (10)	0.0121 (11)	-0.0016 (11)
C41	0.0301 (13)	0.0322 (13)	0.0440 (15)	0.0014 (10)	0.0098 (11)	-0.0072 (12)
C51	0.0292 (13)	0.0363 (13)	0.0455 (15)	-0.0065 (11)	0.0153 (12)	-0.0050 (12)
C61	0.0277 (12)	0.0289 (12)	0.0393 (13)	0.0007 (10)	0.0158 (11)	-0.0019 (11)
C71	0.0284 (12)	0.0265 (12)	0.0396 (14)	-0.0002 (10)	0.0123 (11)	0.0002 (11)
O2A	0.0345 (10)	0.0364 (10)	0.0512 (11)	0.0054 (8)	0.0209 (9)	0.0012 (8)
O11A	0.0406 (10)	0.0372 (10)	0.0350 (9)	-0.0063 (8)	0.0169 (8)	0.0018 (8)
O12A	0.0391 (10)	0.0429 (10)	0.0475 (11)	-0.0027 (8)	0.0266 (9)	-0.0072 (9)
O31A	0.0479 (12)	0.0313 (10)	0.0636 (13)	0.0026 (9)	0.0108 (11)	0.0013 (9)
O32A	0.101 (2)	0.0591 (14)	0.0630 (15)	-0.0014 (13)	0.0434 (15)	0.0203 (12)
O51A	0.0386 (11)	0.0653 (13)	0.0604 (13)	0.0026 (9)	0.0311 (10)	-0.0076 (11)
O52A	0.0403 (11)	0.0374 (11)	0.0861 (16)	0.0093 (9)	0.0215 (11)	0.0020 (11)
N31A	0.0385 (12)	0.0389 (12)	0.0385 (12)	-0.0018 (10)	0.0087 (10)	0.0062 (10)
N51A	0.0249 (11)	0.0425 (13)	0.0475 (13)	0.0001 (9)	0.0133 (10)	-0.0094 (11)
C1A	0.0254 (11)	0.0286 (11)	0.0228 (11)	-0.0030 (9)	0.0073 (9)	-0.0043 (10)
C2A	0.0258 (12)	0.0325 (12)	0.0255 (12)	-0.0010 (10)	0.0082 (10)	-0.0051 (10)
C3A	0.0316 (13)	0.0290 (12)	0.0274 (12)	-0.0018 (10)	0.0074 (10)	0.0015 (10)
C4A	0.0262 (12)	0.0385 (13)	0.0265 (12)	-0.0069 (10)	0.0113 (10)	-0.0032 (11)
C5A	0.0226 (11)	0.0327 (12)	0.0288 (12)	-0.0007 (10)	0.0076 (10)	-0.0091 (10)
C6A	0.0265 (12)	0.0273 (12)	0.0266 (11)	-0.0024 (9)	0.0065 (10)	-0.0019 (10)
C11A	0.0285 (12)	0.0352 (13)	0.0264 (12)	-0.0073 (10)	0.0104 (10)	-0.0061 (10)

Geometric parameters (Å, °)

O21—N21	1.215 (3)	C11—C61	1.393 (3)
O22—N21	1.213 (3)	C11—C71	1.518 (3)
O41—N41	1.211 (3)	C21—C31	1.381 (3)
O42—N41	1.235 (3)	C31—C41	1.381 (4)
O2A—C2A	1.321 (3)	C41—C51	1.377 (4)
O11A—C11A	1.253 (3)	C51—C61	1.383 (4)
O12A—C11A	1.262 (3)	C3—H3	0.9300
O31A—N31A	1.206 (3)	C4—H4	0.9300
O32A—N31A	1.222 (3)	C5—H5	0.9300
O51A—N51A	1.228 (3)	C6—H6	0.9300
O52A—N51A	1.219 (3)	C31—H31	0.9300
O2A—H2A	0.9300	C51—H51	0.9300
N1—C6	1.343 (4)	C61—H61	0.9300
N1—C2	1.344 (3)	C71—H71	0.9700
N21—C21	1.481 (3)	C71—H72	0.9700
N41—C41	1.470 (3)	C1A—C6A	1.377 (3)
N1—H1	0.9100	C1A—C11A	1.512 (3)
N31A—C3A	1.460 (3)	C1A—C2A	1.412 (3)
N51A—C5A	1.459 (3)	C2A—C3A	1.417 (4)
C2—C71	1.511 (3)	C3A—C4A	1.373 (4)
C2—C3	1.374 (3)	C4A—C5A	1.372 (3)
C3—C4	1.383 (4)	C5A—C6A	1.387 (3)
C4—C5	1.375 (4)	C4A—H4A	0.9300

supplementary materials

C5—C6	1.374 (4)	C6A—H6A	0.9300
C11—C21	1.405 (3)		
C2A—O2A—H2A	106.00	C5—C4—H4	120.00
C2—N1—C6	122.9 (2)	C3—C4—H4	120.00
O21—N21—C21	118.4 (2)	C6—C5—H5	121.00
O22—N21—C21	117.5 (2)	C4—C5—H5	120.00
O21—N21—O22	124.1 (3)	N1—C6—H6	120.00
O41—N41—O42	123.9 (2)	C5—C6—H6	120.00
O42—N41—C41	117.8 (2)	C41—C31—H31	121.00
O41—N41—C41	118.3 (2)	C21—C31—H31	121.00
C6—N1—H1	121.00	C41—C51—H51	121.00
C2—N1—H1	116.00	C61—C51—H51	121.00
O31A—N31A—O32A	122.6 (2)	C11—C61—H61	119.00
O31A—N31A—C3A	119.7 (2)	C51—C61—H61	119.00
O32A—N31A—C3A	117.6 (2)	H71—C71—H72	108.00
O51A—N51A—C5A	117.7 (2)	C2—C71—H72	109.00
O52A—N51A—C5A	118.2 (2)	C11—C71—H71	109.00
O51A—N51A—O52A	124.1 (2)	C2—C71—H71	109.00
C3—C2—C71	124.5 (2)	C11—C71—H72	109.00
N1—C2—C3	118.6 (2)	C2A—C1A—C6A	120.9 (2)
N1—C2—C71	116.9 (2)	C2A—C1A—C11A	119.2 (2)
C2—C3—C4	119.8 (2)	C6A—C1A—C11A	119.9 (2)
C3—C4—C5	120.0 (2)	O2A—C2A—C3A	122.1 (2)
C4—C5—C6	119.0 (3)	C1A—C2A—C3A	116.8 (2)
N1—C6—C5	119.7 (2)	O2A—C2A—C1A	121.0 (2)
C61—C11—C71	120.3 (2)	N31A—C3A—C2A	120.7 (2)
C21—C11—C71	123.7 (2)	C2A—C3A—C4A	122.2 (2)
C21—C11—C61	116.0 (2)	N31A—C3A—C4A	117.0 (2)
N21—C21—C11	121.4 (2)	C3A—C4A—C5A	118.7 (2)
C11—C21—C31	123.3 (2)	N51A—C5A—C6A	118.9 (2)
N21—C21—C31	115.3 (2)	C4A—C5A—C6A	121.7 (2)
C21—C31—C41	117.2 (2)	N51A—C5A—C4A	119.4 (2)
N41—C41—C51	118.4 (2)	C1A—C6A—C5A	119.6 (2)
N41—C41—C31	119.1 (2)	O11A—C11A—C1A	117.7 (2)
C31—C41—C51	122.6 (2)	O12A—C11A—C1A	117.3 (2)
C41—C51—C61	118.2 (2)	O11A—C11A—O12A	125.0 (2)
C11—C61—C51	122.6 (2)	C3A—C4A—H4A	121.00
C2—C71—C11	113.96 (18)	C5A—C4A—H4A	121.00
C2—C3—H3	120.00	C1A—C6A—H6A	120.00
C4—C3—H3	120.00	C5A—C6A—H6A	120.00
C6—N1—C2—C3	2.1 (3)	C71—C11—C61—C51	-175.1 (2)
C6—N1—C2—C71	-177.0 (2)	C21—C11—C71—C2	160.2 (2)
C2—N1—C6—C5	-1.4 (4)	C61—C11—C71—C2	-20.4 (3)
O21—N21—C21—C11	29.4 (3)	C11—C21—C31—C41	-4.3 (4)
O21—N21—C21—C31	-149.7 (2)	N21—C21—C31—C41	174.8 (2)
O22—N21—C21—C11	-151.4 (2)	C21—C31—C41—N41	-174.5 (2)
O22—N21—C21—C31	29.5 (3)	C21—C31—C41—C51	4.2 (4)
O41—N41—C41—C31	-27.8 (4)	C31—C41—C51—C61	0.0 (4)

O41—N41—C41—C51	153.4 (3)	N41—C41—C51—C61	178.7 (2)
O42—N41—C41—C31	149.9 (2)	C41—C51—C61—C11	-4.5 (4)
O42—N41—C41—C51	-28.8 (4)	C6A—C1A—C2A—O2A	-179.2 (2)
O31A—N31A—C3A—C2A	24.4 (4)	C6A—C1A—C2A—C3A	1.4 (3)
O31A—N31A—C3A—C4A	-153.3 (2)	C11A—C1A—C2A—O2A	-1.1 (3)
O32A—N31A—C3A—C2A	-159.1 (2)	C11A—C1A—C2A—C3A	179.5 (2)
O32A—N31A—C3A—C4A	23.2 (3)	C2A—C1A—C6A—C5A	-3.0 (3)
O51A—N51A—C5A—C4A	-3.5 (3)	C11A—C1A—C6A—C5A	178.9 (2)
O51A—N51A—C5A—C6A	176.6 (2)	C2A—C1A—C11A—O11A	175.0 (2)
O52A—N51A—C5A—C4A	177.6 (2)	C2A—C1A—C11A—O12A	-5.8 (3)
O52A—N51A—C5A—C6A	-2.3 (3)	C6A—C1A—C11A—O11A	-6.9 (3)
C71—C2—C3—C4	178.3 (2)	C6A—C1A—C11A—O12A	172.3 (2)
N1—C2—C71—C11	-94.0 (2)	O2A—C2A—C3A—N31A	4.4 (4)
C3—C2—C71—C11	86.9 (3)	O2A—C2A—C3A—C4A	-178.0 (2)
N1—C2—C3—C4	-0.8 (4)	C1A—C2A—C3A—N31A	-176.2 (2)
C2—C3—C4—C5	-1.1 (4)	C1A—C2A—C3A—C4A	1.4 (3)
C3—C4—C5—C6	1.7 (4)	N31A—C3A—C4A—C5A	175.2 (2)
C4—C5—C6—N1	-0.5 (4)	C2A—C3A—C4A—C5A	-2.5 (4)
C61—C11—C21—N21	-178.8 (2)	C3A—C4A—C5A—N51A	-179.0 (2)
C61—C11—C21—C31	0.2 (3)	C3A—C4A—C5A—C6A	0.9 (4)
C71—C11—C21—N21	0.6 (3)	N51A—C5A—C6A—C1A	-178.2 (2)
C71—C11—C21—C31	179.6 (2)	C4A—C5A—C6A—C1A	1.9 (4)
C21—C11—C61—C51	4.3 (3)		

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...O11A	0.91	1.72	2.627 (3)	172
O2A—H2A...O12A	0.93	1.61	2.476 (3)	152
C3—H3...O11A ⁱ	0.93	2.48	3.246 (3)	140
C5—H5...O31A ⁱⁱ	0.93	2.56	3.051 (4)	114
C6—H6...O31A ⁱⁱ	0.93	2.48	3.020 (4)	117
C51—H51...O51A ⁱⁱⁱ	0.93	2.55	3.137 (4)	122
C61—H61...O51A ⁱⁱⁱ	0.93	2.54	3.141 (3)	123
C71—H72...O11A	0.97	2.55	3.247 (3)	129

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

Fig. 1

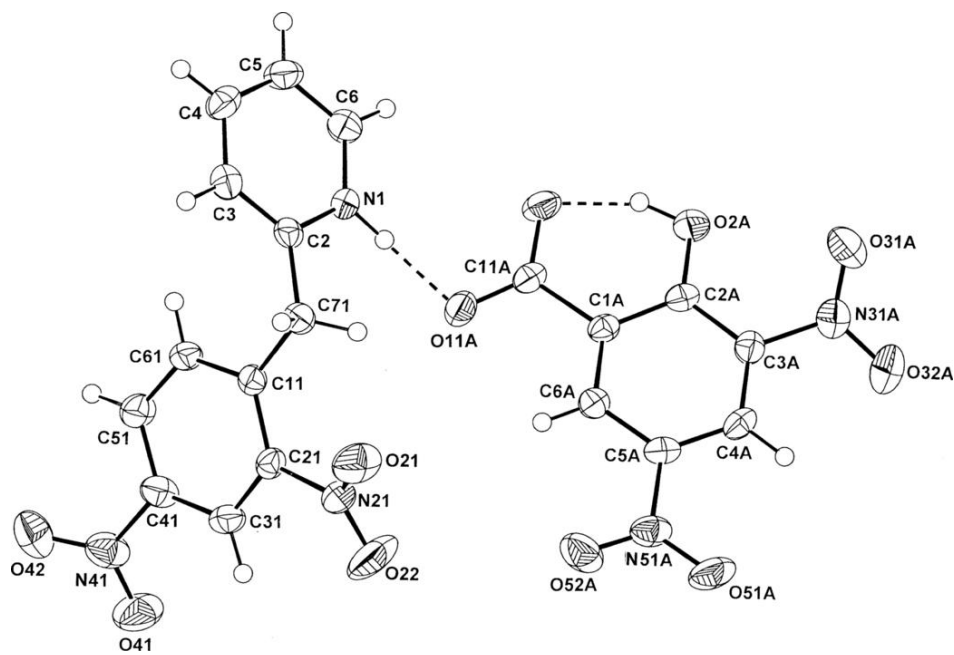


Fig. 2

