

2-Cyanoquinolin-1-ium nitrate

Wan-Sin Loh,‡ Madhukar Hemamalini and Hoong-Kun Fun*§

X-ray Crystallography Unit, School of Physics, Universiti Sains Malaysia, 11800 USM, Penang, Malaysia

Correspondence e-mail: hkfun@usm.my

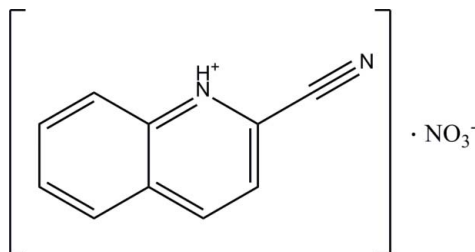
Received 30 September 2010; accepted 30 September 2010

Key indicators: single-crystal X-ray study; $T = 100$ K; mean $\sigma(\text{C}-\text{C}) = 0.002$ Å; R factor = 0.045; wR factor = 0.122; data-to-parameter ratio = 16.2.

A proton is transferred from the nitric acid to the N atom of 2-cyanoquinoline during crystallization, resulting in the formation of the title salt, $\text{C}_{10}\text{H}_7\text{N}_2^+\cdot\text{NO}_3^-$. The quinolinium ring system is approximately planar, with a maximum deviation of 0.013 (3) Å. In the crystal, a very asymmetric bifurcated $\text{N}-\text{H}\cdots(\text{O},\text{O})$ hydrogen bond to two O atoms of an adjacent nitrate anion occurs, generating an $R_2^1(4)$ ring motif. $\text{C}-\text{H}\cdots\text{O}$ hydrogen bonds link the ions into sheets stacking along the a axis.

Related literature

For background to and the biological activities of quinoline derivatives, see: Loh, Quah *et al.* (2010*a,b*); Loh *et al.* (2010); Sasaki *et al.* (1998); Reux *et al.* (2009); Morimoto *et al.* (1991); Michael (1997); Markees *et al.* (1970); Campbell *et al.* (1988). For the hydrogen-bond motif, see: Bernstein *et al.* (1995). For related structures, see: Loh, Quah *et al.* (2010*a,b*); Loh *et al.* (2010). For the stability of the temperature controller used for the data collection, see: Cosier & Glazer (1986). For bond-length data, see: Allen *et al.* (1987).



‡ Thomson Reuters ResearcherID: C-7581-2009.

§ Thomson Reuters ResearcherID: A-3561-2009.

Experimental

Crystal data

$\text{C}_{10}\text{H}_7\text{N}_2^+\cdot\text{NO}_3^-$
 $M_r = 217.19$
 Monoclinic, $P2_1/c$
 $a = 3.6969$ (1) Å
 $b = 17.7031$ (3) Å
 $c = 14.6029$ (2) Å
 $\beta = 95.802$ (1)°

$V = 950.81$ (3) Å³
 $Z = 4$
 Mo $K\alpha$ radiation
 $\mu = 0.12$ mm⁻¹
 $T = 100$ K
 $0.44 \times 0.18 \times 0.07$ mm

Data collection

Bruker SMART APEXII CCD diffractometer
 Absorption correction: multi-scan (SADABS; Bruker, 2009)
 $T_{\min} = 0.951$, $T_{\max} = 0.992$

16184 measured reflections
 2758 independent reflections
 2103 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.041$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.045$
 $wR(F^2) = 0.122$
 $S = 1.05$
 2758 reflections
 170 parameters

H atoms treated by a mixture of independent and constrained refinement
 $\Delta\rho_{\text{max}} = 0.37$ e Å⁻³
 $\Delta\rho_{\text{min}} = -0.29$ e Å⁻³

Table 1

Hydrogen-bond geometry (Å, °).

| $D-\text{H}\cdots A$ | $D-\text{H}$ | $\text{H}\cdots A$ | $D\cdots A$ | $D-\text{H}\cdots A$ |
|--|--------------|--------------------|-------------|----------------------|
| $\text{N1}-\text{H1N1}\cdots\text{O1}$ | 0.95 | 2.56 | 3.2376 (15) | 128 |
| $\text{N1}-\text{H1N1}\cdots\text{O3}$ | 0.95 | 1.60 | 2.5432 (14) | 172 |
| $\text{C5}-\text{H5A}\cdots\text{O3}^{\text{ii}}$ | 0.943 (16) | 2.497 (16) | 3.2835 (16) | 141.0 (15) |
| $\text{C7}-\text{H7A}\cdots\text{O2}^{\text{ii}}$ | 0.976 (16) | 2.473 (16) | 3.3641 (16) | 151.8 (12) |
| $\text{C8}-\text{H8A}\cdots\text{O2}^{\text{iii}}$ | 0.977 (18) | 2.391 (19) | 3.3355 (17) | 162.4 (15) |

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

Data collection: APEX2 (Bruker, 2009); cell refinement: SAINT (Bruker, 2009); data reduction: SAINT; program(s) used to solve structure: SHELXTL (Sheldrick, 2008); program(s) used to refine structure: SHELXTL; molecular graphics: SHELXTL; software used to prepare material for publication: SHELXTL and PLATON (Spek, 2009).

The authors thank Universiti Sains Malaysia (USM) for the Research University Grant (grant No. 1001/PFIZIK/811160). WSL thanks USM for the award of a USM fellowship. MH thanks USM for the award of a postdoctoral fellowship.

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: HB5669).

References

- Allen, F. H., Kennard, O., Watson, D. G., Brammer, L., Orpen, A. G. & Taylor, R. (1987). *J. Chem. Soc. Perkin Trans. 2*, pp. S1–19.
 Bernstein, J., Davis, R. E., Shimon, L. & Chang, N.-L. (1995). *Angew. Chem. Int. Ed. Engl.* **34**, 1555–1573.
 Bruker (2009). APEX2, SAINT and SADABS. Bruker AXS Inc., Madison, Wisconsin, USA.
 Campbell, S. F., Hardstone, J. D. & Palmer, M. J. (1988). *J. Med. Chem.* **31**, 1031–1035.
 Cosier, J. & Glazer, A. M. (1986). *J. Appl. Cryst.* **19**, 105–107.
 Loh, W.-S., Hemamalini, M. & Fun, H.-K. (2010). *Acta Cryst.* **E66**, o2709.
 Loh, W.-S., Quah, C. K., Hemamalini, M. & Fun, H.-K. (2010*a*). *Acta Cryst.* **E66**, o2357.

- Loh, W.-S., Quah, C. K., Hemamalini, M. & Fun, H.-K. (2010b). *Acta Cryst.* **E66**, o2396.
- Markees, D. G., Dewey, V. C. & Kidder, G. W. (1970). *J. Med. Chem.* **13**, 324–326.
- Michael, J. P. (1997). *Nat. Prod. Rep.* **14**, 605–608.
- Morimoto, Y., Matsuda, F. & Shirahama, H. (1991). *Synlett*, **3**, 202–203.
- Reux, B., Nevalainen, T., Raitio, K. H. & Koskinen, A. M. P. (2009). *Bioorg. Med. Chem.* **17**, 4441–4447.
- Sasaki, K., Tsurumori, A. & Hirota, T. (1998). *J. Chem. Soc. Perkin Trans. 1*, pp. 3851–3856.
- Sheldrick, G. M. (2008). *Acta Cryst.* **A64**, 112–122.
- Spek, A. L. (2009). *Acta Cryst.* **D65**, 148–155.

supplementary materials

Acta Cryst. (2010). E66, o2726-o2727 [doi:10.1107/S1600536810039243]

2-Cyanoquinolin-1-ium nitrate

W.-S. Loh, M. Hemamalini and H.-K. Fun

Comment

Recently, hydrogen-bonding patterns involving quinoline and its derivatives with organic acid have been investigated (Loh *et al.*, 2010*a,b*; Loh *et al.*, 2010). Syntheses of the quinoline derivatives were discussed earlier (Sasaki *et al.*, 1998; Reux *et al.*, 2009). Quinolines and their derivatives are very important compounds because of their wide occurrence in natural products (Morimoto *et al.*, 1991; Michael, 1997) and biologically active compounds (Markees *et al.*, 1970; Campbell *et al.*, 1988). Heterocyclic molecules containing cyano group are useful as drug intermediates. Herein we report the synthesis of 2-cyanoquinolin-1-ium nitrate.

The asymmetric unit of the title compound (Fig. 1) consists of one 2-cyanoquinolin-1-ium cation (C1–C10/N1/N2) and one nitrate anion (N3/O1–O3). One proton is transferred from the hydroxyl group of nitrate to the atom N1 of 2-cyanoquinoline during the crystallization, resulting in the formation of salt. The quinoline ring system (C1–C9/N1) is approximately planar with a maximum deviation of 0.013 (3) Å at atom C6. The $R_2^1(4)$ ring motif (Fig. 1; Bernstein *et al.*, 1995) indicates a bifurcated hydrogen bond from N1–H1N1 to the two acceptors (O1/O3). Bond lengths (Allen *et al.*, 1987) and angles are within the normal ranges and are comparable to the related structures (Loh *et al.*, 2010*a,b*; Loh *et al.*, 2010).

In the crystal packing (Fig. 2), intermolecular N1—H1N1···O1, N1—H1N1···O3, C5—H5A···O3, C7—H7A···O2 and C8—H8A···O2 hydrogen bonds (Table 1) link the molecules into two-dimensional planes stacking along the *a* axis.

Experimental

A few drops of nitric acid were added to a hot methanol solution (20 ml) of quinoline-2-carbonitrile (39 mg, Aldrich) which had been warmed over a magnetic stirrer hotplate for a few minutes. The resulting solution was allowed to cool slowly to room temperature. Colourless plates of (I) appeared after a few days.

Refinement

All H atoms were located from a difference Fourier map. H1N1 was fixed at its found position with bond length of N—H being 0.9481 Å. The remaining H atoms were refined freely with the bond lengths of C—H being 0.943 (17) to 0.998 (17) Å.

Figures

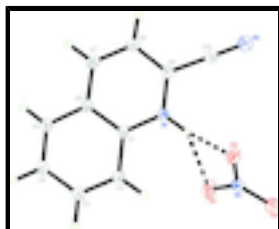


Fig. 1. The molecular structure of the title compound showing 50% probability displacement ellipsoids for non-H atoms. The $R_2^1(4)$ ring motif which indicates the bifurcated hydrogen bond is shown.

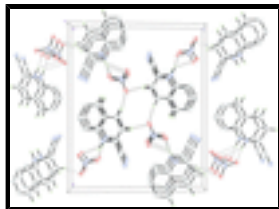


Fig. 2. The crystal structure of the title compound, viewed along the *a* axis.

2-Cyanoquinolin-1-ium nitrate

Crystal data

| | |
|--------------------------------|---|
| $C_{10}H_7N_2^+ \cdot NO_3^-$ | $F(000) = 448$ |
| $M_r = 217.19$ | $D_x = 1.517 \text{ Mg m}^{-3}$ |
| Monoclinic, $P2_1/c$ | Mo $K\alpha$ radiation, $\lambda = 0.71073 \text{ \AA}$ |
| Hall symbol: -P 2ybc | Cell parameters from 3861 reflections |
| $a = 3.6969 (1) \text{ \AA}$ | $\theta = 2.7\text{--}31.0^\circ$ |
| $b = 17.7031 (3) \text{ \AA}$ | $\mu = 0.12 \text{ mm}^{-1}$ |
| $c = 14.6029 (2) \text{ \AA}$ | $T = 100 \text{ K}$ |
| $\beta = 95.802 (1)^\circ$ | Plate, colourless |
| $V = 950.81 (3) \text{ \AA}^3$ | $0.44 \times 0.18 \times 0.07 \text{ mm}$ |
| $Z = 4$ | |

Data collection

| | |
|---|--|
| Bruker SMART APEXII CCD diffractometer | 2758 independent reflections |
| Radiation source: fine-focus sealed tube graphite | 2103 reflections with $I > 2\sigma(I)$ |
| φ and ω scans | $R_{\text{int}} = 0.041$ |
| Absorption correction: multi-scan (<i>SADABS</i> ; Bruker, 2009) | $\theta_{\text{max}} = 30.0^\circ$, $\theta_{\text{min}} = 1.8^\circ$ |
| $T_{\text{min}} = 0.951$, $T_{\text{max}} = 0.992$ | $h = -5 \rightarrow 5$ |
| 16184 measured reflections | $k = -24 \rightarrow 24$ |
| | $l = -20 \rightarrow 20$ |

Refinement

| | |
|---------------------------------|--|
| Refinement on F^2 | Primary atom site location: structure-invariant direct methods |
| Least-squares matrix: full | Secondary atom site location: difference Fourier map |
| $R[F^2 > 2\sigma(F^2)] = 0.045$ | Hydrogen site location: inferred from neighbouring sites |
| $wR(F^2) = 0.122$ | H atoms treated by a mixture of independent and constrained refinement |
| $S = 1.05$ | $w = 1/[\sigma^2(F_o^2) + (0.0614P)^2 + 0.2227P]$ |
| 2758 reflections | where $P = (F_o^2 + 2F_c^2)/3$ |
| 170 parameters | $(\Delta/\sigma)_{\text{max}} < 0.001$ |
| | $\Delta\rho_{\text{max}} = 0.37 \text{ e \AA}^{-3}$ |

0 restraints

$$\Delta\rho_{\min} = -0.29 \text{ e } \text{\AA}^{-3}$$

Special details

Experimental. The crystal was placed in the cold stream of an Oxford Cryosystems Cobra open-flow nitrogen cryostat (Cosier & Glazer, 1986) operating at 100.0 (1) K.

Geometry. All e.s.d.'s (except the e.s.d. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell e.s.d.'s are taken into account individually in the estimation of e.s.d.'s in distances, angles and torsion angles; correlations between e.s.d.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell e.s.d.'s is used for estimating e.s.d.'s 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 $F^2 > \sigma(F^2)$ 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)

| | <i>x</i> | <i>y</i> | <i>z</i> | $U_{\text{iso}}^*/U_{\text{eq}}$ |
|------|-------------|-------------|-------------|----------------------------------|
| O1 | 0.1851 (3) | 0.21342 (6) | 0.92466 (7) | 0.0314 (3) |
| O2 | 0.4106 (3) | 0.10064 (5) | 0.91484 (7) | 0.0255 (3) |
| O3 | 0.4296 (3) | 0.17922 (5) | 0.80150 (6) | 0.0258 (3) |
| N1 | 0.2524 (3) | 0.30942 (6) | 0.73844 (7) | 0.0144 (2) |
| H1N1 | 0.3241 | 0.2630 | 0.7672 | 0.079 (8)* |
| N2 | -0.1335 (4) | 0.17939 (7) | 0.58610 (8) | 0.0265 (3) |
| N3 | 0.3373 (3) | 0.16413 (6) | 0.88321 (7) | 0.0196 (3) |
| C1 | 0.3582 (3) | 0.37566 (7) | 0.78076 (8) | 0.0142 (3) |
| C2 | 0.5593 (4) | 0.37429 (7) | 0.86850 (8) | 0.0161 (3) |
| C3 | 0.6627 (4) | 0.44133 (7) | 0.90990 (9) | 0.0176 (3) |
| C4 | 0.5697 (4) | 0.51140 (7) | 0.86660 (9) | 0.0181 (3) |
| C5 | 0.3739 (4) | 0.51378 (7) | 0.78226 (9) | 0.0175 (3) |
| C6 | 0.2637 (3) | 0.44559 (7) | 0.73637 (8) | 0.0148 (3) |
| C7 | 0.0675 (4) | 0.44419 (7) | 0.64838 (9) | 0.0176 (3) |
| C8 | -0.0316 (4) | 0.37627 (7) | 0.60703 (9) | 0.0175 (3) |
| C9 | 0.0658 (4) | 0.30972 (7) | 0.65509 (8) | 0.0158 (3) |
| C10 | -0.0406 (4) | 0.23670 (7) | 0.61661 (9) | 0.0184 (3) |
| H2A | 0.619 (4) | 0.3267 (9) | 0.8975 (11) | 0.020 (4)* |
| H3A | 0.805 (5) | 0.4406 (9) | 0.9717 (12) | 0.023 (4)* |
| H4A | 0.649 (5) | 0.5595 (10) | 0.8975 (11) | 0.028 (4)* |
| H5A | 0.304 (5) | 0.5598 (9) | 0.7531 (11) | 0.024 (4)* |
| H7A | 0.002 (4) | 0.4918 (9) | 0.6174 (11) | 0.020 (4)* |
| H8A | -0.166 (5) | 0.3735 (10) | 0.5461 (13) | 0.030 (4)* |

Atomic displacement parameters (\AA^2)

| | U^{11} | U^{22} | U^{33} | U^{12} | U^{13} | U^{23} |
|----|------------|------------|------------|-------------|-------------|-------------|
| O1 | 0.0486 (7) | 0.0188 (5) | 0.0295 (6) | 0.0018 (5) | 0.0167 (5) | -0.0018 (4) |
| O2 | 0.0375 (6) | 0.0142 (5) | 0.0234 (5) | -0.0007 (4) | -0.0040 (4) | 0.0047 (4) |

supplementary materials

| | | | | | | |
|-----|------------|------------|------------|-------------|-------------|-------------|
| O3 | 0.0438 (7) | 0.0173 (5) | 0.0170 (5) | 0.0075 (4) | 0.0072 (4) | 0.0026 (4) |
| N1 | 0.0169 (6) | 0.0120 (5) | 0.0142 (5) | 0.0006 (4) | 0.0010 (4) | 0.0000 (4) |
| N2 | 0.0331 (7) | 0.0217 (6) | 0.0237 (6) | -0.0029 (5) | -0.0020 (5) | -0.0014 (5) |
| N3 | 0.0255 (6) | 0.0153 (5) | 0.0172 (5) | -0.0027 (4) | -0.0015 (4) | -0.0003 (4) |
| C1 | 0.0146 (6) | 0.0126 (6) | 0.0159 (6) | 0.0002 (4) | 0.0035 (5) | -0.0005 (4) |
| C2 | 0.0180 (6) | 0.0145 (6) | 0.0156 (6) | 0.0004 (5) | 0.0013 (5) | 0.0005 (4) |
| C3 | 0.0164 (6) | 0.0187 (6) | 0.0177 (6) | -0.0017 (5) | 0.0020 (5) | -0.0024 (5) |
| C4 | 0.0180 (7) | 0.0151 (6) | 0.0216 (6) | -0.0035 (5) | 0.0044 (5) | -0.0037 (5) |
| C5 | 0.0200 (7) | 0.0128 (6) | 0.0204 (6) | 0.0002 (5) | 0.0053 (5) | 0.0002 (5) |
| C6 | 0.0146 (6) | 0.0140 (6) | 0.0160 (6) | 0.0009 (4) | 0.0027 (5) | 0.0008 (4) |
| C7 | 0.0185 (7) | 0.0166 (6) | 0.0177 (6) | 0.0030 (5) | 0.0023 (5) | 0.0023 (5) |
| C8 | 0.0179 (6) | 0.0192 (6) | 0.0153 (6) | 0.0016 (5) | 0.0008 (5) | 0.0009 (5) |
| C9 | 0.0157 (6) | 0.0159 (6) | 0.0158 (6) | -0.0003 (5) | 0.0017 (5) | -0.0016 (4) |
| C10 | 0.0190 (7) | 0.0192 (6) | 0.0166 (6) | 0.0004 (5) | 0.0003 (5) | 0.0005 (5) |

Geometric parameters (\AA , $^\circ$)

| | | | |
|-------------|--------------|-------------|-------------|
| O1—N3 | 1.2301 (15) | C3—H3A | 0.998 (17) |
| O2—N3 | 1.2347 (14) | C4—C5 | 1.3646 (19) |
| O3—N3 | 1.3015 (14) | C4—H4A | 0.993 (18) |
| N1—C9 | 1.3370 (16) | C5—C6 | 1.4203 (17) |
| N1—C1 | 1.3642 (15) | C5—H5A | 0.943 (17) |
| N1—H1N1 | 0.9481 | C6—C7 | 1.4104 (18) |
| N2—C10 | 1.1466 (18) | C7—C8 | 1.3784 (18) |
| C1—C2 | 1.4152 (17) | C7—H7A | 0.976 (17) |
| C1—C6 | 1.4243 (16) | C8—C9 | 1.3998 (18) |
| C2—C3 | 1.3686 (18) | C8—H8A | 0.977 (18) |
| C2—H2A | 0.959 (16) | C9—C10 | 1.4480 (18) |
| C3—C4 | 1.4188 (18) | | |
| C9—N1—C1 | 120.45 (10) | C3—C4—H4A | 119.9 (10) |
| C9—N1—H1N1 | 120.2 | C4—C5—C6 | 120.01 (12) |
| C1—N1—H1N1 | 119.3 | C4—C5—H5A | 122.1 (10) |
| O1—N3—O2 | 123.76 (12) | C6—C5—H5A | 117.9 (10) |
| O1—N3—O3 | 118.74 (11) | C7—C6—C5 | 122.77 (11) |
| O2—N3—O3 | 117.50 (11) | C7—C6—C1 | 118.63 (11) |
| N1—C1—C2 | 119.72 (11) | C5—C6—C1 | 118.60 (12) |
| N1—C1—C6 | 119.68 (11) | C8—C7—C6 | 120.25 (12) |
| C2—C1—C6 | 120.60 (11) | C8—C7—H7A | 120.5 (10) |
| C3—C2—C1 | 118.87 (12) | C6—C7—H7A | 119.2 (10) |
| C3—C2—H2A | 121.7 (10) | C7—C8—C9 | 118.10 (12) |
| C1—C2—H2A | 119.4 (10) | C7—C8—H8A | 122.1 (10) |
| C2—C3—C4 | 121.13 (12) | C9—C8—H8A | 119.8 (10) |
| C2—C3—H3A | 119.1 (9) | N1—C9—C8 | 122.87 (11) |
| C4—C3—H3A | 119.8 (9) | N1—C9—C10 | 116.40 (11) |
| C5—C4—C3 | 120.79 (12) | C8—C9—C10 | 120.72 (12) |
| C5—C4—H4A | 119.3 (10) | N2—C10—C9 | 178.33 (15) |
| C9—N1—C1—C2 | -179.23 (11) | C2—C1—C6—C7 | 179.11 (11) |
| C9—N1—C1—C6 | 1.04 (18) | N1—C1—C6—C5 | 179.37 (11) |
| N1—C1—C2—C3 | -179.94 (12) | C2—C1—C6—C5 | -0.36 (18) |

| | | | |
|-------------|--------------|--------------|--------------|
| C6—C1—C2—C3 | -0.21 (19) | C5—C6—C7—C8 | 179.86 (12) |
| C1—C2—C3—C4 | 0.39 (19) | C1—C6—C7—C8 | 0.40 (19) |
| C2—C3—C4—C5 | 0.0 (2) | C6—C7—C8—C9 | 0.44 (19) |
| C3—C4—C5—C6 | -0.6 (2) | C1—N1—C9—C8 | -0.16 (19) |
| C4—C5—C6—C7 | -178.69 (12) | C1—N1—C9—C10 | -178.81 (11) |
| C4—C5—C6—C1 | 0.76 (19) | C7—C8—C9—N1 | -0.6 (2) |
| N1—C1—C6—C7 | -1.15 (18) | C7—C8—C9—C10 | 177.99 (12) |

Hydrogen-bond geometry (\AA , $^\circ$)

| <i>D</i> —H \cdots <i>A</i> | <i>D</i> —H | H \cdots <i>A</i> | <i>D</i> \cdots <i>A</i> | <i>D</i> —H \cdots <i>A</i> |
|-----------------------------------|-------------|---------------------|----------------------------|-------------------------------|
| N1—H1N1 \cdots O1 | 0.95 | 2.56 | 3.2376 (15) | 128 |
| N1—H1N1 \cdots O3 | 0.95 | 1.60 | 2.5432 (14) | 172 |
| C5—H5A \cdots O3 ⁱ | 0.943 (16) | 2.497 (16) | 3.2835 (16) | 141.0 (15) |
| C7—H7A \cdots O2 ⁱⁱ | 0.976 (16) | 2.473 (16) | 3.3641 (16) | 151.8 (12) |
| C8—H8A \cdots O2 ⁱⁱⁱ | 0.977 (18) | 2.391 (19) | 3.3355 (17) | 162.4 (15) |

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

Fig. 1

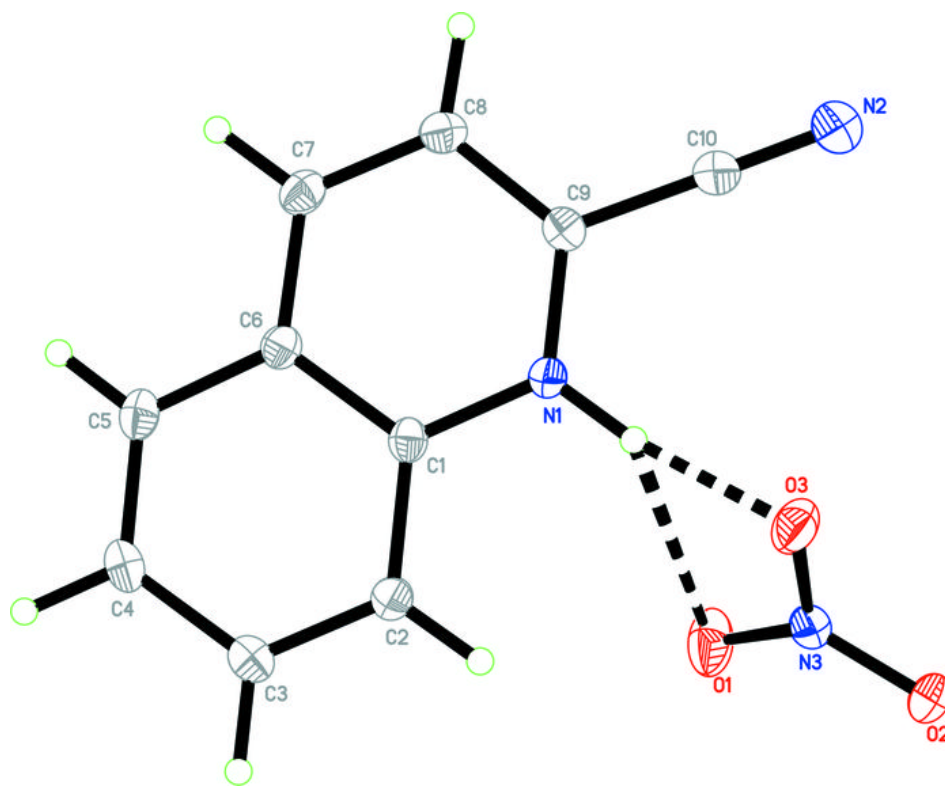


Fig. 2

