

4-[(*E*)-2-(2,4,6-Trinitrophenyl)ethylidene]benzonitrile

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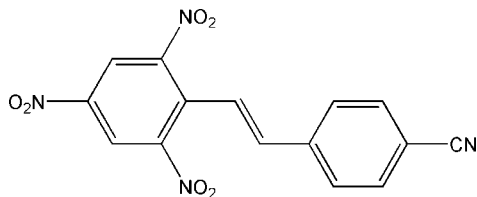
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Key indicators: single-crystal X-ray study; $T = 293$ K; mean $\sigma(\text{C}-\text{C}) = 0.003$ Å; R factor = 0.043; wR factor = 0.123; data-to-parameter ratio = 10.4.

In the crystal of the title compound, $\text{C}_{15}\text{H}_8\text{N}_4\text{O}_6$, the molecules are organized in layers due to their linkage by weak $\text{C}-\text{H}\cdots\text{N}$ hydrogen bonds. The layers are themselves interconnected by weak $\text{C}-\text{H}\cdots\text{O}$ hydrogen bonds and $\pi-\pi$ interactions [centroid-centroid distances = 3.8690 (15) and 3.9017 (16) Å]. The dihedral angle between the rings is 31.9 (1)°.

Related literature

For related nitrostilbenes, see: Hanson *et al.* (2005); Oehlke *et al.* (2007); Gérard & Hardy (1988). The title compound was synthesized as a new ligand for iron-phosphine complexes for use in non-linear optical (NLO) applications, see: Wenseleers *et al.* (1998); Garcia *et al.* (2001); Robalo *et al.* (2006); Garcia *et al.* (2007).



Experimental

Crystal data

$\text{C}_{15}\text{H}_8\text{N}_4\text{O}_6$
 $M_r = 340.25$
 Monoclinic, $P2_1/c$
 $a = 11.183$ (1) Å
 $b = 8.520$ (1) Å
 $c = 15.459$ (4) Å
 $\beta = 94.09$ (4)°

$V = 1469.2$ (4) Å³
 $Z = 4$
 Mo $K\alpha$ radiation
 $\mu = 0.12$ mm⁻¹
 $T = 293$ K
 $0.4 \times 0.4 \times 0.3$ mm

Data collection

Enraf-Nonius CAD-4
 diffractometer
 5370 measured reflections
 2689 independent reflections

1849 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.026$
 3 standard reflections every 60 min
 intensity decay: none

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.043$
 $wR(F^2) = 0.123$
 $S = 1.02$
 2689 reflections

258 parameters
 All H-atom parameters refined
 $\Delta\rho_{\text{max}} = 0.17$ e Å⁻³
 $\Delta\rho_{\text{min}} = -0.22$ e Å⁻³

Table 1

Hydrogen-bond geometry (Å, °).

| $D-H\cdots A$ | $D-H$ | $H\cdots A$ | $D\cdots A$ | $D-H\cdots A$ |
|---|----------|-------------|-------------|---------------|
| $\text{C3}-\text{H3}\cdots\text{O32}^{\text{i}}$ | 0.95 (3) | 2.50 (2) | 3.294 (3) | 142.1 (17) |
| $\text{C5A}-\text{H5A}\cdots\text{N1C}^{\text{ii}}$ | 0.96 (2) | 2.53 (2) | 3.427 (3) | 156.3 (19) |
| $\text{C7}-\text{H7}\cdots\text{O21}^{\text{iii}}$ | 0.97 (2) | 2.53 (2) | 3.354 (3) | 143.3 (19) |

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

Data collection: *CAD-4 EXPRESS* (Enraf-Nonius, 1994); cell refinement: *CAD-4 EXPRESS*; data reduction: *XCAD4* (Harms & Wocadlo, 1996); program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *ORTEP-3 for Windows* (Farrugia, 1997); software used to prepare material for publication: *WinGX* (Farrugia, 1999), *Mercury* (Macrae *et al.*, 2008) and *PLATON* (Spek, 2009).

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: ZL2310).

References

- Enraf-Nonius (1994). *CAD-4 EXPRESS*. Enraf-Nonius, Delft, The Netherlands.
- Farrugia, L. J. (1997). *J. Appl. Cryst.* **30**, 565.
- Farrugia, L. J. (1999). *J. Appl. Cryst.* **32**, 837–838.
- Garcia, M. H., Mendes, P. J., Robalo, M. P., Dias, A. R., Campo, J., Wenseleers, W. & Goovaerts, E. (2007). *J. Organomet. Chem.* **692**, 3027–3041.
- Garcia, M. H., Robalo, M. P., Dias, A. R., Piedade, M. F. M., Galvao, A., Wenseleers, W. & Goovaerts, E. (2001). *J. Organomet. Chem.* **619**, 252–264.
- Gérard, F. & Hardy, A. (1988). *Acta Cryst.* **C44**, 1283–1287.
- Hanson, J. R., Hitchcock, P. B. & Jones, A. B. (2005). *J. Chem. Res.* pp. 138–140.
- Harms, K. & Wocadlo, S. (1996). *XCAD4*. University of Marburg, Germany.
- 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.
- Oehlke, A., Auer, A. A., Jahre, I., Walfort, B., Ruffer, T., Zoufala, P., Lang, H. & Spange, S. (2007). *J. Org. Chem.* **72**, 4328–4339.
- Robalo, M. P., Teixeira, A. P. S., Garcia, M. H., da Piedade, M. F. M., Duarte, M. T., Dias, A. R., Campo, J., Wenseleers, W. & Goovaerts, E. (2006). *Eur. J. Inorg. Chem.* pp. 2175–2185.
- Sheldrick, G. M. (2008). *Acta Cryst.* **A64**, 112–122.
- Spek, A. L. (2009). *Acta Cryst.* **D65**, 148–155.
- Wenseleers, W., Gerbrandij, A. W., Goovaerts, E., Garcia, M. H., Robalo, M. P., Mendes, P. J., Rodrigues, J. C. & Dias, A. R. (1998). *J. Mater. Chem.* **8**, 925–930.

supplementary materials

Acta Cryst. (2010). E66, o2694 [doi:10.1107/S1600536810038584]

4-[(*E*)-2-(2,4,6-Trinitrophenyl)ethylidene]benzonitrile

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Comment

The title compound was synthesized as a new ligand for iron-phosphine complexes for use in non-linear optical (NLO) applications [Wenseleers *et al.* (1998), Garcia *et al.* (2001), Robalo *et al.* (2006), Garcia *et al.* (2007)]. The molecular structure of the title compound (Fig. 1) is mainly determined by steric factors involving the nitro groups, which force the nitro-substituted ring out of the plane of the CH=CH fragment by 54.0 (3)°. In addition, the nitro group in the 6-position is twisted by 56.6 (3)° out of the plane of the benzene ring, whereas the nitro groups in the 2- and 4-positions remain almost in the latter plane, with torsion angles of 6.2 (3)° and 3.6 (4)°, respectively. A similar conformation of the nitro-substituted ring can be seen in other trinitrostilbenes, such as MALZOP [Hanson *et al.* (2005)], PIGBAJ [Oehlke *et al.* (2007)] and GIMBOT [Gérard & Hardy (1988)]. In the case of the latter, the two rings are parallel to each other, but the ethenyl link is rotated by approximately 90° with respect to both rings.

The fact that the nitro group in the 6-position is twisted so much more than the other two may be linked to the weak intermolecular hydrogen bond involving O32 of the nitro group and H3 of the neighbouring molecule (Table 1). As a consequence of this twist, the second oxygen atom of this nitro group, O31, comes quite close to O12 of a neighbouring molecule within the layer depicted in Fig. 2 [O31...O12^{iv}, 2.821 (3) Å, symm. code $iv = x, 1+y, z$], but this should not be seen as a stabilizing contact. In fact, these layers are rather formed by the weak hydrogen bond involving H5A and the nitrogen atom N1C of the nitrile group (Table 1). The layers display a typical herringbone structure and extend along the [-1 0 2] plane. A final weak hydrogen bond, involving H7 and an oxygen atom of the nitro group in the 4-position (O21), is responsible for the organization of the molecules in the direction perpendicular to these layers (Table 1). Finally, the crystal structure displays two π - π interactions. The first involves two nitrile-substituted rings (1) of neighbouring molecules contacting each other: Cg(1)...Cg(1)^v, 3.8690 (15) Å, 25.01°, symm. code $v = 2-x, -y, 1-z$. The second involves a nitrile- (1) of one and a nitro-substituted ring (2) of another molecule: Cg(1)...Cg(2)^{vi}, 3.9017 (16) Å, 26.52°, symm. code $vi = 2-x, 1/2+y, 1/2-z$.

Experimental

2,4,6-Trinitrotoluene (2.2 g, 0.0096 mol) and 4-cyanobenzaldehyde (1.3 g, 0.0096 mol) were dissolved in benzene (50 ml). Ten drops of piperidine were added, and the mixture was refluxed overnight. After cooling, the precipitate was collected by filtration. The crude product was refluxed for 4 h in *p*-xylene (25 ml) in the presence of a catalytic amount of iodine. After cooling, a mixture of yellow powder and orange-red crystals was collected, and both powder and crystals turned out to be the desired product. The yield was 12%. M.p. (uncorrected) 490–491 K. ¹H NMR (400 MHz, CDCl₃, TMS): δ 6.72 (d, 16.33 Hz, 1H, H7), 7.46 (d, 16.33 Hz, 1H, H8), 7.57 (d, 8.32 Hz, 2H, H2 and H6), 7.70 (d, 8.32 Hz, 2H, H3 and H5), 8.93 (s, 2H, H13 and H15) p.p.m. ¹³C NMR (100 MHz, CDCl₃, TMS): δ 113.31 (C4), 118.24 (CN), 120.54 (C7), 122.42 (C2 and C6), 127.85 (C3 and C5), 132.78 (C13 and C15), 133.01 (C11), 135.83 (C8), 138.91 (C1), 150.32 (C14) p.p.m.

Refinement

All the H atoms have been observed in the difference electron density map and were left to refine freely.

Figures

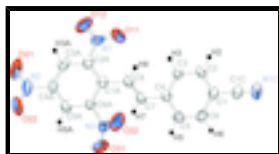


Fig. 1. Molecular structure of the title compound showing the numbering scheme. Displacement ellipsoids are drawn at the 50% probability level; hydrogen atoms are represented by spheres with an arbitrary radius.

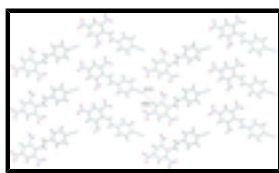


Fig. 2. Representation of one layer of the title compound, showing the herringbone arrangement of the molecules and the associated weak hydrogen bond.

4-[(E)-2-(2,4,6-Trinitrophenyl)ethylidene]benzonitrile

Crystal data

$C_{15}H_8N_4O_6$

$M_r = 340.25$

Monoclinic, $P2_1/c$

Hall symbol: -P 2ybc

$a = 11.183 (1) \text{ \AA}$

$b = 8.520 (1) \text{ \AA}$

$c = 15.459 (4) \text{ \AA}$

$\beta = 94.09 (4)^\circ$

$V = 1469.2 (4) \text{ \AA}^3$

$Z = 4$

$F(000) = 696$

$D_x = 1.538 \text{ Mg m}^{-3}$

Melting point: 490 K

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

Cell parameters from 25 reflections

$\theta = 5.7\text{--}20.3^\circ$

$\mu = 0.12 \text{ mm}^{-1}$

$T = 293 \text{ K}$

Prism, orange

$0.4 \times 0.4 \times 0.3 \text{ mm}$

Data collection

Enraf–Nonius CAD-4
diffractometer

Radiation source: fine-focus sealed tube
graphite

non-profiled $\omega/2\theta$ scans

5370 measured reflections

2689 independent reflections

1849 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.026$

$\theta_{\text{max}} = 25.3^\circ$, $\theta_{\text{min}} = 1.8^\circ$

$h = -13 \rightarrow 13$

$k = 0 \rightarrow 10$

$l = -18 \rightarrow 18$

3 standard reflections every 60 min

intensity decay: none

Refinement

Refinement on F^2

Primary atom site location: structure-invariant direct
methods

Least-squares matrix: full

$$R[F^2 > 2\sigma(F^2)] = 0.043$$

$$wR(F^2) = 0.123$$

$$S = 1.02$$

2689 reflections

258 parameters

0 restraints

Secondary atom site location: difference Fourier map

Hydrogen site location: inferred from neighbouring sites

All H-atom parameters refined

$$w = 1/[\sigma^2(F_o^2) + (0.0596P)^2 + 0.3738P]$$

$$\text{where } P = (F_o^2 + 2F_c^2)/3$$

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

$$\Delta\rho_{\max} = 0.17 \text{ e } \text{\AA}^{-3}$$

$$\Delta\rho_{\min} = -0.22 \text{ e } \text{\AA}^{-3}$$

Special details

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> | $U_{\text{iso}}^*/U_{\text{eq}}$ |
|-----|--------------|-------------|--------------|----------------------------------|
| H2 | 1.241 (2) | -0.019 (3) | 0.4595 (14) | 0.054 (6)* |
| H8 | 0.935 (2) | -0.129 (3) | 0.2627 (13) | 0.053 (6)* |
| H3 | 1.0738 (19) | -0.105 (3) | 0.3753 (14) | 0.056 (6)* |
| H7 | 0.800 (2) | 0.102 (3) | 0.3391 (14) | 0.059 (6)* |
| H5A | 0.530 (2) | -0.005 (3) | 0.1028 (15) | 0.067 (7)* |
| H5 | 0.922 (2) | 0.319 (3) | 0.4044 (16) | 0.073 (7)* |
| H3A | 0.5894 (19) | -0.444 (3) | 0.1969 (14) | 0.060 (6)* |
| H6 | 1.093 (2) | 0.408 (3) | 0.4864 (16) | 0.081 (8)* |
| C3 | 1.07779 (17) | -0.0016 (2) | 0.39786 (13) | 0.0451 (5) |
| C4 | 0.98073 (17) | 0.0976 (2) | 0.37989 (12) | 0.0423 (4) |
| C1 | 1.18268 (18) | 0.1991 (2) | 0.47949 (12) | 0.0465 (5) |
| C2 | 1.17765 (18) | 0.0471 (2) | 0.44706 (13) | 0.0467 (5) |
| C6A | 0.67988 (18) | -0.0359 (2) | 0.17933 (13) | 0.0471 (5) |
| C2A | 0.71612 (18) | -0.2887 (2) | 0.23434 (12) | 0.0457 (5) |
| C8 | 0.86810 (18) | -0.0745 (2) | 0.27531 (13) | 0.0473 (5) |
| C5 | 0.9867 (2) | 0.2489 (3) | 0.41437 (14) | 0.0537 (5) |
| C3A | 0.6117 (2) | -0.3410 (3) | 0.19242 (14) | 0.0535 (5) |
| N1 | 0.7863 (2) | -0.4074 (2) | 0.28671 (11) | 0.0619 (5) |
| C1C | 1.2883 (2) | 0.2523 (3) | 0.52933 (14) | 0.0558 (5) |
| C7 | 0.87283 (18) | 0.0455 (2) | 0.32863 (13) | 0.0479 (5) |
| N3 | 0.7162 (2) | 0.1266 (2) | 0.16228 (15) | 0.0732 (6) |
| C5A | 0.57307 (19) | -0.0814 (3) | 0.13789 (14) | 0.0546 (5) |
| C1A | 0.75697 (17) | -0.1337 (2) | 0.22990 (12) | 0.0429 (5) |

supplementary materials

| | | | | |
|-----|--------------|-------------|--------------|------------|
| O11 | 0.88345 (18) | -0.3743 (2) | 0.31976 (14) | 0.0890 (6) |
| C6 | 1.0866 (2) | 0.2992 (3) | 0.46302 (14) | 0.0569 (6) |
| C4A | 0.54232 (17) | -0.2368 (3) | 0.14446 (14) | 0.0534 (5) |
| O12 | 0.7390 (3) | -0.5339 (2) | 0.29474 (15) | 0.1157 (9) |
| N2 | 0.43278 (19) | -0.2919 (3) | 0.09634 (17) | 0.0789 (7) |
| O32 | 0.8093 (2) | 0.1460 (2) | 0.12878 (15) | 0.1011 (7) |
| O31 | 0.6471 (2) | 0.2295 (2) | 0.18090 (18) | 0.1197 (9) |
| O22 | 0.37527 (18) | -0.2012 (3) | 0.05063 (17) | 0.1101 (8) |
| N1C | 1.37272 (19) | 0.2969 (3) | 0.56717 (15) | 0.0788 (7) |
| O21 | 0.4056 (2) | -0.4286 (3) | 0.10513 (19) | 0.1266 (9) |

Atomic displacement parameters (\AA^2)

| | U^{11} | U^{22} | U^{33} | U^{12} | U^{13} | U^{23} |
|-----|-------------|-------------|-------------|--------------|--------------|--------------|
| C3 | 0.0469 (11) | 0.0378 (11) | 0.0491 (11) | 0.0004 (8) | -0.0065 (9) | -0.0040 (9) |
| C4 | 0.0451 (10) | 0.0411 (10) | 0.0397 (9) | 0.0012 (8) | -0.0041 (8) | -0.0012 (8) |
| C1 | 0.0503 (11) | 0.0514 (12) | 0.0366 (9) | -0.0088 (9) | -0.0047 (8) | -0.0014 (8) |
| C2 | 0.0440 (11) | 0.0485 (11) | 0.0465 (10) | 0.0030 (9) | -0.0059 (9) | 0.0007 (9) |
| C6A | 0.0514 (11) | 0.0383 (10) | 0.0498 (11) | -0.0012 (9) | -0.0104 (9) | -0.0035 (8) |
| C2A | 0.0546 (12) | 0.0432 (10) | 0.0387 (9) | 0.0006 (9) | -0.0007 (9) | -0.0016 (8) |
| C8 | 0.0420 (11) | 0.0511 (12) | 0.0475 (11) | 0.0035 (10) | -0.0068 (9) | -0.0040 (9) |
| C5 | 0.0591 (13) | 0.0443 (11) | 0.0553 (12) | 0.0106 (10) | -0.0119 (10) | -0.0083 (9) |
| C3A | 0.0590 (13) | 0.0495 (13) | 0.0526 (12) | -0.0124 (10) | 0.0072 (10) | -0.0040 (10) |
| N1 | 0.0905 (15) | 0.0464 (11) | 0.0474 (10) | 0.0094 (10) | -0.0049 (10) | -0.0008 (8) |
| C1C | 0.0575 (13) | 0.0616 (13) | 0.0471 (11) | -0.0099 (11) | -0.0046 (10) | -0.0048 (10) |
| C7 | 0.0425 (11) | 0.0510 (12) | 0.0484 (11) | 0.0042 (9) | -0.0085 (9) | -0.0049 (9) |
| N3 | 0.0892 (16) | 0.0438 (12) | 0.0799 (14) | -0.0076 (11) | -0.0406 (13) | 0.0026 (10) |
| C5A | 0.0505 (12) | 0.0550 (13) | 0.0557 (12) | 0.0062 (10) | -0.0136 (10) | -0.0084 (10) |
| C1A | 0.0453 (10) | 0.0443 (11) | 0.0383 (10) | -0.0002 (8) | -0.0018 (8) | -0.0035 (8) |
| O11 | 0.0780 (13) | 0.0843 (13) | 0.1003 (14) | 0.0135 (10) | -0.0249 (11) | 0.0245 (11) |
| C6 | 0.0695 (14) | 0.0422 (12) | 0.0568 (12) | 0.0000 (10) | -0.0104 (11) | -0.0118 (10) |
| C4A | 0.0395 (10) | 0.0625 (14) | 0.0576 (12) | -0.0098 (10) | -0.0015 (9) | -0.0139 (10) |
| O12 | 0.180 (2) | 0.0462 (11) | 0.1130 (17) | -0.0147 (13) | -0.0469 (16) | 0.0161 (10) |
| N2 | 0.0495 (12) | 0.0910 (18) | 0.0940 (16) | -0.0141 (12) | -0.0099 (11) | -0.0279 (14) |
| O32 | 0.1167 (18) | 0.0734 (13) | 0.1105 (17) | -0.0391 (12) | -0.0114 (14) | 0.0248 (11) |
| O31 | 0.1395 (19) | 0.0462 (11) | 0.165 (2) | 0.0184 (12) | -0.0491 (17) | -0.0185 (12) |
| O22 | 0.0677 (12) | 0.1224 (19) | 0.1324 (19) | 0.0063 (12) | -0.0469 (13) | -0.0296 (15) |
| N1C | 0.0676 (13) | 0.0894 (16) | 0.0764 (14) | -0.0197 (12) | -0.0161 (11) | -0.0150 (12) |
| O21 | 0.0924 (16) | 0.1044 (18) | 0.177 (3) | -0.0517 (14) | -0.0298 (15) | -0.0160 (17) |

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

| | | | |
|-------|-----------|---------|-----------|
| C3—C2 | 1.370 (3) | C8—H8 | 0.91 (2) |
| C3—C4 | 1.389 (3) | C5—C6 | 1.371 (3) |
| C3—H3 | 0.95 (2) | C5—H5 | 0.94 (3) |
| C4—C5 | 1.395 (3) | C3A—C4A | 1.363 (3) |
| C4—C7 | 1.464 (3) | C3A—H3A | 0.92 (2) |
| C1—C6 | 1.381 (3) | N1—O11 | 1.200 (3) |
| C1—C2 | 1.388 (3) | N1—O12 | 1.211 (3) |

| | | | |
|-----------------|--------------|-----------------|--------------|
| C1—C1C | 1.437 (3) | C1C—N1C | 1.139 (3) |
| C2—H2 | 0.91 (2) | C7—H7 | 0.97 (2) |
| C6A—C5A | 1.370 (3) | N3—O32 | 1.206 (3) |
| C6A—C1A | 1.397 (3) | N3—O31 | 1.217 (3) |
| C6A—N3 | 1.472 (3) | C5A—C4A | 1.374 (3) |
| C2A—C3A | 1.369 (3) | C5A—H5A | 0.96 (2) |
| C2A—C1A | 1.401 (3) | C6—H6 | 1.00 (3) |
| C2A—N1 | 1.484 (3) | C4A—N2 | 1.464 (3) |
| C8—C7 | 1.312 (3) | N2—O22 | 1.202 (3) |
| C8—C1A | 1.472 (3) | N2—O21 | 1.213 (3) |
| C2—C3—C4 | 121.39 (19) | C2A—C3A—H3A | 120.2 (14) |
| C2—C3—H3 | 120.1 (13) | O11—N1—O12 | 123.6 (2) |
| C4—C3—H3 | 118.5 (13) | O11—N1—C2A | 119.96 (19) |
| C3—C4—C5 | 118.13 (18) | O12—N1—C2A | 116.4 (2) |
| C3—C4—C7 | 121.71 (18) | N1C—C1C—C1 | 178.3 (3) |
| C5—C4—C7 | 120.14 (18) | C8—C7—C4 | 124.83 (19) |
| C6—C1—C2 | 119.91 (18) | C8—C7—H7 | 119.5 (13) |
| C6—C1—C1C | 120.16 (19) | C4—C7—H7 | 115.5 (13) |
| C2—C1—C1C | 119.92 (19) | O32—N3—O31 | 125.8 (2) |
| C3—C2—C1 | 119.59 (19) | O32—N3—C6A | 117.7 (2) |
| C3—C2—H2 | 121.1 (14) | O31—N3—C6A | 116.5 (3) |
| C1—C2—H2 | 119.3 (13) | C6A—C5A—C4A | 116.9 (2) |
| C5A—C6A—C1A | 125.10 (19) | C6A—C5A—H5A | 117.8 (14) |
| C5A—C6A—N3 | 115.15 (18) | C4A—C5A—H5A | 125.1 (14) |
| C1A—C6A—N3 | 119.60 (17) | C6A—C1A—C2A | 113.55 (17) |
| C3A—C2A—C1A | 123.62 (19) | C6A—C1A—C8 | 121.90 (17) |
| C3A—C2A—N1 | 115.90 (18) | C2A—C1A—C8 | 124.53 (18) |
| C1A—C2A—N1 | 120.48 (18) | C5—C6—C1 | 120.1 (2) |
| C7—C8—C1A | 124.16 (19) | C5—C6—H6 | 121.8 (15) |
| C7—C8—H8 | 122.3 (13) | C1—C6—H6 | 118.1 (15) |
| C1A—C8—H8 | 113.6 (13) | C3A—C4A—C5A | 122.16 (19) |
| C6—C5—C4 | 120.9 (2) | C3A—C4A—N2 | 119.4 (2) |
| C6—C5—H5 | 118.5 (15) | C5A—C4A—N2 | 118.4 (2) |
| C4—C5—H5 | 120.7 (15) | O22—N2—O21 | 123.7 (2) |
| C4A—C3A—C2A | 118.6 (2) | O22—N2—C4A | 119.0 (2) |
| C4A—C3A—H3A | 121.2 (14) | O21—N2—C4A | 117.2 (3) |
| C2—C3—C4—C5 | -0.8 (3) | N3—C6A—C5A—C4A | 173.1 (2) |
| C2—C3—C4—C7 | -178.91 (19) | C5A—C6A—C1A—C2A | 0.9 (3) |
| C4—C3—C2—C1 | -0.3 (3) | N3—C6A—C1A—C2A | -174.5 (2) |
| C6—C1—C2—C3 | 0.9 (3) | C5A—C6A—C1A—C8 | -177.5 (2) |
| C1C—C1—C2—C3 | -178.44 (19) | N3—C6A—C1A—C8 | 7.2 (3) |
| C3—C4—C5—C6 | 1.4 (3) | C3A—C2A—C1A—C6A | 0.9 (3) |
| C7—C4—C5—C6 | 179.5 (2) | N1—C2A—C1A—C6A | -178.91 (18) |
| C1A—C2A—C3A—C4A | -0.9 (3) | C3A—C2A—C1A—C8 | 179.2 (2) |
| N1—C2A—C3A—C4A | 178.93 (18) | N1—C2A—C1A—C8 | -0.6 (3) |
| C3A—C2A—N1—O11 | 174.0 (2) | C7—C8—C1A—C6A | 53.8 (3) |
| C1A—C2A—N1—O11 | -6.2 (3) | C7—C8—C1A—C2A | -124.3 (2) |
| C3A—C2A—N1—O12 | -7.4 (3) | C4—C5—C6—C1 | -0.9 (3) |

supplementary materials

| | | | |
|-----------------|-------------|-----------------|-------------|
| C1A—C2A—N1—O12 | 172.4 (2) | C2—C1—C6—C5 | -0.3 (3) |
| C6—C1—C1C—N1C | -71 (9) | C1C—C1—C6—C5 | 179.0 (2) |
| C2—C1—C1C—N1C | 109 (9) | C2A—C3A—C4A—C5A | -0.9 (3) |
| C1A—C8—C7—C4 | 174.55 (19) | C2A—C3A—C4A—N2 | 177.55 (19) |
| C3—C4—C7—C8 | -20.7 (3) | C6A—C5A—C4A—C3A | 2.4 (3) |
| C5—C4—C7—C8 | 161.3 (2) | C6A—C5A—C4A—N2 | -176.0 (2) |
| C5A—C6A—N3—O32 | -119.2 (2) | C3A—C4A—N2—O22 | -176.2 (2) |
| C1A—C6A—N3—O32 | 56.6 (3) | C5A—C4A—N2—O22 | 2.3 (3) |
| C5A—C6A—N3—O31 | 58.5 (3) | C3A—C4A—N2—O21 | 3.6 (3) |
| C1A—C6A—N3—O31 | -125.7 (2) | C5A—C4A—N2—O21 | -177.9 (2) |
| C1A—C6A—C5A—C4A | -2.5 (3) | | |

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

| $D-H\cdots A$ | $D-H$ | $H\cdots A$ | $D\cdots A$ | $D-H\cdots A$ |
|------------------------------------|----------|-------------|-------------|---------------|
| C3—H3 \cdots O32 ⁱ | 0.95 (3) | 2.50 (2) | 3.294 (3) | 142.1 (17) |
| C5A—H5A \cdots N1C ⁱⁱ | 0.96 (2) | 2.53 (2) | 3.427 (3) | 156.3 (19) |
| C7—H7 \cdots O21 ⁱⁱⁱ | 0.97 (2) | 2.53 (2) | 3.354 (3) | 143.3 (19) |

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

Fig. 1

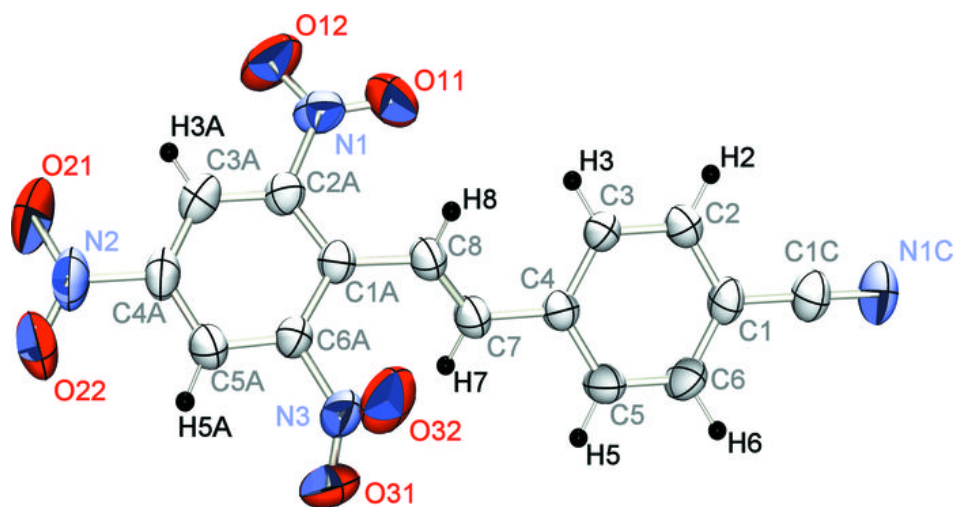


Fig. 2

