

# (1Z)-1-[(2E)-3-(4-Bromophenyl)-1-(4-fluorophenyl)prop-2-en-1-ylidene]-2-(2,4-dinitrophenyl)hydrazine

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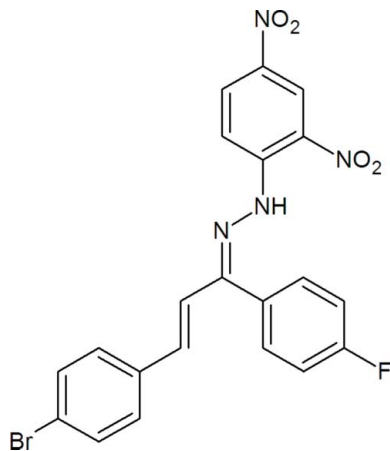
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Key indicators: single-crystal X-ray study;  $T = 293$  K; mean  $\sigma(\text{C}-\text{C}) = 0.006$  Å; R factor = 0.051;  $wR$  factor = 0.141; data-to-parameter ratio = 14.5.

In the title molecule,  $\text{C}_{21}\text{H}_{14}\text{BrFN}_4\text{O}_4$ , the mean planes of the two nitro groups form dihedral angles of 3.1 (2) and 7.1 (5)° with the benzene ring to which they are attached. The dinitro-substituted ring forms dihedral angles of 8.6 (2) and 71.9 (2)° with the bromo- and fluoro-substituted benzene rings, respectively. The dihedral angle between the bromo- and fluoro-substituted benzene rings is 80.6 (2)°. There is an intramolecular  $\text{N}-\text{H}\cdots\text{O}$  hydrogen bond. In the crystal, pairs of weak  $\text{C}-\text{H}\cdots\text{O}$  hydrogen bonds form inversion dimers. In addition,  $\pi-\pi$  stacking interactions between the bromo- and dinitro-substituted rings [centroid-centroid separation = 3.768 (2) Å] are observed.

## Related literature

For applications of hydrazone derivatives, see: Rollas *et al.* (2007); Singh *et al.* (1982). For the synthesis, see: Jasinski *et al.* (2010). For a related structure, see: Yin *et al.* (2009).



## Experimental

### Crystal data

|   |                                 |
|---|---------------------------------|
| $\text{C}_{21}\text{H}_{14}\text{BrFN}_4\text{O}_4$ | $V = 2068.5$ (2) Å <sup>3</sup> |
| $M_r = 485.27$                                      | $Z = 4$                         |
| Monoclinic, $P2_1/c$                                | Mo $K\alpha$ radiation          |
| $a = 15.0738$ (12) Å                                | $\mu = 2.03$ mm <sup>-1</sup>   |
| $b = 10.6511$ (5) Å                                 | $T = 293$ K                     |
| $c = 14.3353$ (8) Å                                 | $0.3 \times 0.2 \times 0.1$ mm  |
| $\beta = 116.010$ (9)°                              |                                 |

### Data collection

|   |  |
|---|--|
| Oxford Diffraction Xcalibur Sapphire3 diffractometer                                | 15619 measured reflections             |
| Absorption correction: multi-scan ( <i>CrysAlis PRO</i> ; Oxford Diffraction, 2010) | 4058 independent reflections           |
| $T_{\min} = 0.889$ , $T_{\max} = 1.000$   | 2232 reflections with $I > 2\sigma(I)$ |
|   | $R_{\text{int}} = 0.045$               |

### Refinement

|                                 |   |
|---------------------------------|---|
| $R[F^2 > 2\sigma(F^2)] = 0.051$ | 280 parameters                                      |
| $wR(F^2) = 0.141$               | H-atom parameters constrained                       |
| $S = 1.01$                      | $\Delta\rho_{\text{max}} = 0.30$ e Å <sup>-3</sup>  |
| 4058 reflections                | $\Delta\rho_{\text{min}} = -0.40$ e Å <sup>-3</sup> |

Table 1

Hydrogen-bond geometry (Å, °).

| $D-\text{H}\cdots A$                     | $D-\text{H}$ | $\text{H}\cdots A$ | $D\cdots A$ | $D-\text{H}\cdots A$ |
|--|--------------|--------------------|-------------|----------------------|
| $\text{N2}-\text{H21}\cdots\text{O1}$    | 0.86         | 1.95               | 2.584 (4)   | 130                  |
| $\text{C11}-\text{H11}\cdots\text{O4}^i$ | 0.93         | 2.45               | 3.316 (7)   | 154                  |

Symmetry code: (i)  $-x + 1, -y + 1, -z + 1$ .

Data collection: *CrysAlis PRO* (Oxford Diffraction, 2010); cell refinement: *CrysAlis PRO*; data reduction: *CrysAlis PRO*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *ORTEP-3* (Farrugia, 1997); software used to prepare material for publication: *PLATON* (Spek, 2009).

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: LH5491).

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## supporting information

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**(1Z)-1-[(2E)-3-(4-Bromophenyl)-1-(4-fluorophenyl)prop-2-en-1-ylidene]-2-(2,4-dinitrophenyl)hydrazine**

**Rajni Kant, Vivek K. Gupta, Kamini Kapoor, M. Sapnakumari, B. K. Sarojini and B. Narayana**

### S1. Comment

Hydrazone derivatives are important biologically active compounds which have received attention from the synthetic community (Rollas *et al.*, 2007). Hydrazone derivatives are also used as analytical reagents (Singh *et al.*, 1982). The crystal structure of 1-(but-2-enylidene)-2-(2-nitrophenyl)hydrazine has been reported (Yin *et al.*, 2009). In order to prepare a pyrazoline derivative, (2E)-3-(4-bromophenyl)-1-(4-fluorophenyl)prop-2-en-1-one was reacted with 2,4-dinitrophenyl hydrazine as for the method of Jasinski *et al.* (2010). But, instead of a pyrazoline derivative a 2,4-dinitrophenylhydrazone compound (I) was obtained and its crystal structure is reported herein.

In (I) (Fig. 1), all bond lengths and angles are normal and correspond to those which are related in a reported structure (Yin *et al.*, 2009). The two nitro groups form dihedral angles of 3.1 (2) and 7.1 (5)° with the C16-C21 ring. The dinitro substituted ring (C16-C21) forms dihedral angles of 8.6 (2)° and 71.9 (2)° with bromo (C1-C6) and fluoro (C10-C15) substituted benzene rings, respectively. The dihedral angle between the bromo and fluoro substituted benzene rings is 80.6 (2)°. There is an intramolecular N—H···O hydrogen bond and in the crystal, pairs of weak C—H···O hydrogen bonds form inversion dimers (Table 1, Fig. 2). In addition,  $\pi$ - $\pi$  stacking interactions between the bromophenyl ring and dinitro phenyl ring are observed [centroid separation = 3.768 (2) Å, interplanar spacing = 3.410 Å, centroid shift = 1.60 Å, Symmetry =  $x, 1 + y, z$ ].

### S2. Experimental

A mixture of (2E)-3-(4-bromophenyl)-1-(4-fluorophenyl)prop-2-en-1-one (3.05 g, 0.01 mol) and 2,4-dinitrophenylhydrazine (1.98 g, 0.01 mol) in 50 ml of glacial acetic acid was refluxed for 6 hrs. The reaction mixture was cooled to produce red crystals (m.p. 414–416 K). X-ray quality crystals were obtained by slow evaporation of an acetic acid solution of (I) at room temperature.

### S3. Refinement

All H atoms were positioned geometrically and were treated as riding on their parent C/N atoms, with N—H distance of 0.86 Å and C—H distances of 0.93 Å and with  $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C}, \text{N})$ .

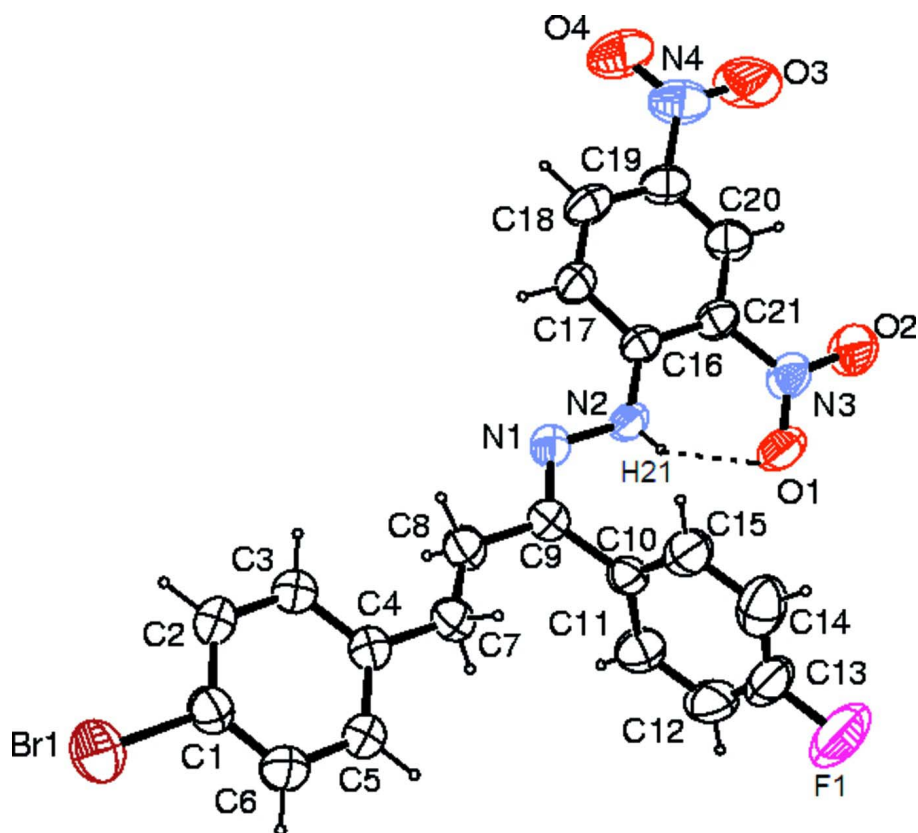
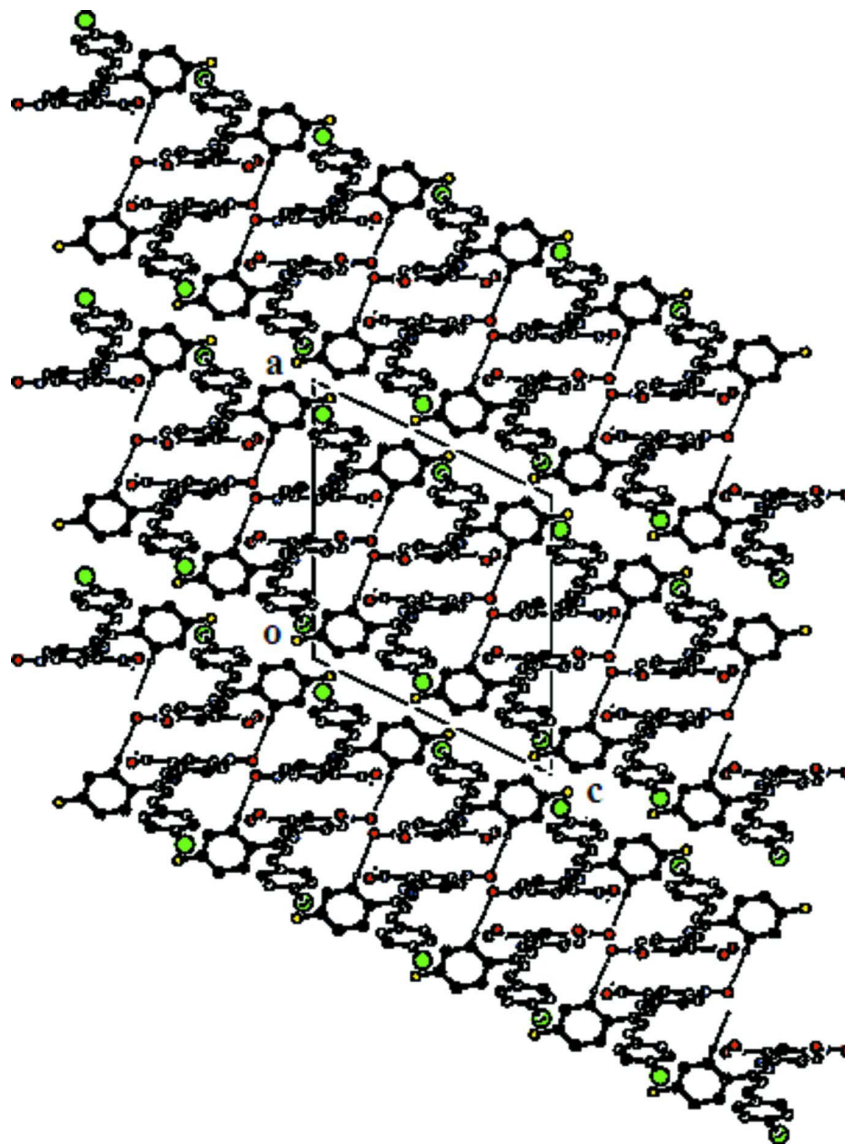


Figure 1

The molecular structure of (I) with ellipsoids drawn at the 40% probability level. H atoms are shown as small spheres of arbitrary radii. The dashed line indicates a hydrogen bond.



**Figure 2**

The packing arrangement of molecules viewed along the *b* axis. The broken lines show intermolecular C—H...O interactions.

(1*Z*)-1-[(2*E*)-3-(4-Bromophenyl)-1-(4-fluorophenyl)prop-2-en-1-ylidene]-2-(2,4-dinitrophenyl)hydrazine

*Crystal data*

$C_{21}H_{14}BrFN_4O_4$

$M_r = 485.27$

Monoclinic,  $P2_1/c$

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

$a = 15.0738$  (12) Å

$b = 10.6511$  (5) Å

$c = 14.3353$  (8) Å

$\beta = 116.010$  (9)°

$V = 2068.5$  (2) Å<sup>3</sup>

$Z = 4$

$F(000) = 976$

$D_x = 1.558$  Mg m<sup>-3</sup>

Melting point = 416–414 K

Mo  $K\alpha$  radiation,  $\lambda = 0.71073$  Å

Cell parameters from 3762 reflections

$\theta = 3.6$ – $29.0$ °

$\mu = 2.03$  mm<sup>-1</sup>

$T = 293$  K

Plate, red

$0.3 \times 0.2 \times 0.1$  mm

*Data collection*

Oxford Diffraction Xcalibur Sapphire3  
diffractometer  
Radiation source: fine-focus sealed tube  
Graphite monochromator  
Detector resolution: 16.1049 pixels mm<sup>-1</sup>  
 $\omega$  scans  
Absorption correction: multi-scan  
(*CrysAlis PRO*; Oxford Diffraction, 2010)  
 $T_{\min} = 0.889$ ,  $T_{\max} = 1.000$

15619 measured reflections  
4058 independent reflections  
2232 reflections with  $I > 2\sigma(I)$   
 $R_{\text{int}} = 0.045$   
 $\theta_{\max} = 26.0^\circ$ ,  $\theta_{\min} = 3.6^\circ$   
 $h = -18 \rightarrow 18$   
 $k = -13 \rightarrow 13$   
 $l = -17 \rightarrow 17$

*Refinement*

Refinement on  $F^2$   
Least-squares matrix: full  
 $R[F^2 > 2\sigma(F^2)] = 0.051$   
 $wR(F^2) = 0.141$   
 $S = 1.01$   
4058 reflections  
280 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  
 $w = 1/[\sigma^2(F_o^2) + (0.0533P)^2 + 0.8232P]$   
where  $P = (F_o^2 + 2F_c^2)/3$   
 $(\Delta/\sigma)_{\max} = 0.001$   
 $\Delta\rho_{\max} = 0.30 \text{ e } \text{Å}^{-3}$   
 $\Delta\rho_{\min} = -0.40 \text{ e } \text{Å}^{-3}$

*Special details*

**Experimental.** *CrysAlis PRO*, Oxford Diffraction Ltd., Version 1.171.34.40 (release 27-08-2010 *CrysAlis171.NET*) (compiled Aug 27 2010, 11:50:40) Empirical absorption correction using spherical harmonics, implemented in SCALE3 ABSPACK scaling algorithm.

**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 (Å<sup>2</sup>)*

|     | <i>x</i>    | <i>y</i>    | <i>z</i>      | $U_{\text{iso}}^*/U_{\text{eq}}$ |
|-----|-------------|-------------|---------------|----------------------------------|
| Br1 | 0.10475 (5) | 1.47051 (5) | 0.45912 (4)   | 0.1080 (3)                       |
| F1  | 0.0359 (3)  | 0.6564 (3)  | -0.06938 (19) | 0.1523 (14)                      |
| N2  | 0.3279 (2)  | 0.5513 (3)  | 0.3799 (2)    | 0.0541 (7)                       |
| H21 | 0.3030      | 0.5395      | 0.3139        | 0.065*                           |
| O1  | 0.3072 (2)  | 0.3913 (3)  | 0.23628 (19)  | 0.0930 (10)                      |
| O2  | 0.3459 (3)  | 0.1980 (3)  | 0.2728 (2)    | 0.0946 (10)                      |
| O3  | 0.4846 (3)  | 0.0425 (4)  | 0.6152 (3)    | 0.1316 (16)                      |
| O4  | 0.5243 (3)  | 0.1687 (4)  | 0.7432 (3)    | 0.1200 (13)                      |
| N3  | 0.3419 (3)  | 0.3052 (4)  | 0.2993 (2)    | 0.0700 (9)                       |
| N1  | 0.3238 (2)  | 0.6688 (3)  | 0.4176 (2)    | 0.0581 (8)                       |
| N4  | 0.4898 (3)  | 0.1471 (5)  | 0.6501 (4)    | 0.0932 (12)                      |
| C1  | 0.1384 (3)  | 1.3158 (4)  | 0.4190 (3)    | 0.0624 (10)                      |
| C2  | 0.1915 (3)  | 1.2297 (4)  | 0.4951 (3)    | 0.0620 (10)                      |

|     |            |            |            |             |
|-----|------------|------------|------------|-------------|
| H2  | 0.2122     | 1.2492     | 0.5648     | 0.074*      |
| C3  | 0.2135 (3) | 1.1146 (4) | 0.4666 (3) | 0.0615 (10) |
| H3  | 0.2490     | 1.0559     | 0.5173     | 0.074*      |
| C4  | 0.1829 (3) | 1.0855 (3) | 0.3623 (3) | 0.0574 (9)  |
| C5  | 0.1301 (3) | 1.1750 (4) | 0.2885 (3) | 0.0655 (10) |
| H5  | 0.1090     | 1.1564     | 0.2186     | 0.079*      |
| C6  | 0.1080 (3) | 1.2911 (4) | 0.3162 (3) | 0.0692 (11) |
| H6  | 0.0732     | 1.3507     | 0.2660     | 0.083*      |
| C7  | 0.2021 (3) | 0.9630 (3) | 0.3285 (3) | 0.0621 (10) |
| H7  | 0.1672     | 0.9451     | 0.2581     | 0.074*      |
| C8  | 0.2633 (3) | 0.8747 (3) | 0.3863 (3) | 0.0613 (10) |
| H8  | 0.3046     | 0.8936     | 0.4553     | 0.074*      |
| C9  | 0.2700 (3) | 0.7506 (3) | 0.3489 (3) | 0.0560 (9)  |
| C10 | 0.2108 (3) | 0.7207 (3) | 0.2368 (3) | 0.0523 (9)  |
| C11 | 0.2375 (4) | 0.7628 (4) | 0.1622 (3) | 0.0780 (12) |
| H11 | 0.2958     | 0.8080     | 0.1816     | 0.094*      |
| C12 | 0.1792 (5) | 0.7388 (5) | 0.0598 (4) | 0.0965 (17) |
| H12 | 0.1981     | 0.7659     | 0.0095     | 0.116*      |
| C13 | 0.0950 (5) | 0.6765 (5) | 0.0324 (3) | 0.0895 (16) |
| C14 | 0.0659 (3) | 0.6315 (5) | 0.1030 (4) | 0.0905 (14) |
| H14 | 0.0074     | 0.5864     | 0.0822     | 0.109*      |
| C15 | 0.1253 (3) | 0.6545 (4) | 0.2068 (3) | 0.0695 (11) |
| H15 | 0.1068     | 0.6246     | 0.2566     | 0.083*      |
| C16 | 0.3702 (2) | 0.4545 (3) | 0.4448 (2) | 0.0495 (8)  |
| C17 | 0.4066 (3) | 0.4703 (4) | 0.5530 (2) | 0.0565 (9)  |
| H17 | 0.4031     | 0.5488     | 0.5797     | 0.068*      |
| C18 | 0.4465 (3) | 0.3722 (4) | 0.6188 (3) | 0.0643 (11) |
| H18 | 0.4705     | 0.3840     | 0.6900     | 0.077*      |
| C19 | 0.4517 (3) | 0.2545 (4) | 0.5802 (3) | 0.0614 (10) |
| C20 | 0.4187 (3) | 0.2341 (4) | 0.4765 (3) | 0.0614 (10) |
| H20 | 0.4231     | 0.1549     | 0.4516     | 0.074*      |
| C21 | 0.3786 (2) | 0.3336 (4) | 0.4092 (2) | 0.0537 (9)  |

*Atomic displacement parameters (Å<sup>2</sup>)*

|     | $U^{11}$    | $U^{22}$    | $U^{33}$    | $U^{12}$    | $U^{13}$    | $U^{23}$     |
|-----|-------------|-------------|-------------|-------------|-------------|--------------|
| Br1 | 0.1532 (6)  | 0.0716 (4)  | 0.1080 (4)  | 0.0292 (3)  | 0.0652 (4)  | -0.0073 (3)  |
| F1  | 0.197 (3)   | 0.147 (3)   | 0.0548 (16) | 0.047 (3)   | 0.0025 (18) | -0.0091 (17) |
| N2  | 0.0666 (19) | 0.0520 (18) | 0.0393 (15) | 0.0087 (15) | 0.0193 (14) | 0.0017 (14)  |
| O1  | 0.145 (3)   | 0.077 (2)   | 0.0458 (15) | 0.027 (2)   | 0.0320 (17) | 0.0036 (16)  |
| O2  | 0.142 (3)   | 0.073 (2)   | 0.079 (2)   | 0.022 (2)   | 0.0581 (19) | -0.0100 (16) |
| O3  | 0.181 (4)   | 0.087 (3)   | 0.122 (3)   | 0.061 (3)   | 0.062 (3)   | 0.047 (2)    |
| O4  | 0.114 (3)   | 0.140 (3)   | 0.074 (2)   | 0.031 (2)   | 0.0118 (19) | 0.046 (2)    |
| N3  | 0.085 (2)   | 0.072 (2)   | 0.058 (2)   | 0.015 (2)   | 0.0360 (18) | -0.0049 (19) |
| N1  | 0.0656 (19) | 0.0526 (18) | 0.0520 (17) | 0.0019 (16) | 0.0219 (15) | -0.0028 (16) |
| N4  | 0.084 (3)   | 0.099 (3)   | 0.086 (3)   | 0.026 (3)   | 0.028 (2)   | 0.040 (3)    |
| C1  | 0.072 (3)   | 0.051 (2)   | 0.068 (2)   | 0.001 (2)   | 0.034 (2)   | -0.003 (2)   |
| C2  | 0.073 (3)   | 0.060 (2)   | 0.050 (2)   | -0.002 (2)  | 0.025 (2)   | -0.0078 (19) |

|     |           |             |             |              |             |              |
|-----|-----------|-------------|-------------|--------------|-------------|--------------|
| C3  | 0.070 (3) | 0.054 (2)   | 0.054 (2)   | 0.002 (2)    | 0.0223 (19) | 0.0022 (19)  |
| C4  | 0.066 (2) | 0.049 (2)   | 0.054 (2)   | -0.0019 (19) | 0.0235 (19) | -0.0034 (18) |
| C5  | 0.084 (3) | 0.055 (2)   | 0.051 (2)   | -0.001 (2)   | 0.024 (2)   | -0.0016 (19) |
| C6  | 0.081 (3) | 0.062 (3)   | 0.057 (2)   | 0.010 (2)    | 0.023 (2)   | 0.005 (2)    |
| C7  | 0.079 (3) | 0.051 (2)   | 0.055 (2)   | -0.004 (2)   | 0.028 (2)   | -0.0027 (19) |
| C8  | 0.072 (3) | 0.050 (2)   | 0.056 (2)   | -0.004 (2)   | 0.022 (2)   | -0.0055 (19) |
| C9  | 0.062 (2) | 0.051 (2)   | 0.057 (2)   | -0.0016 (19) | 0.0279 (19) | 0.0011 (19)  |
| C10 | 0.066 (2) | 0.0431 (19) | 0.050 (2)   | 0.0094 (18)  | 0.0277 (19) | 0.0034 (16)  |
| C11 | 0.102 (3) | 0.075 (3)   | 0.069 (3)   | -0.005 (3)   | 0.049 (3)   | 0.003 (2)    |
| C12 | 0.165 (6) | 0.078 (3)   | 0.064 (3)   | 0.017 (4)    | 0.066 (4)   | 0.011 (3)    |
| C13 | 0.120 (4) | 0.080 (3)   | 0.042 (3)   | 0.036 (3)    | 0.011 (3)   | -0.003 (2)   |
| C14 | 0.073 (3) | 0.096 (4)   | 0.081 (3)   | 0.009 (3)    | 0.013 (3)   | -0.014 (3)   |
| C15 | 0.072 (3) | 0.077 (3)   | 0.058 (2)   | 0.003 (2)    | 0.026 (2)   | 0.001 (2)    |
| C16 | 0.045 (2) | 0.057 (2)   | 0.0428 (19) | 0.0024 (17)  | 0.0162 (16) | 0.0023 (17)  |
| C17 | 0.058 (2) | 0.061 (2)   | 0.046 (2)   | -0.0004 (19) | 0.0180 (18) | -0.0017 (18) |
| C18 | 0.051 (2) | 0.091 (3)   | 0.0410 (19) | -0.002 (2)   | 0.0110 (17) | 0.006 (2)    |
| C19 | 0.050 (2) | 0.071 (3)   | 0.058 (2)   | 0.013 (2)    | 0.0180 (19) | 0.019 (2)    |
| C20 | 0.058 (2) | 0.061 (2)   | 0.065 (2)   | 0.0100 (19)  | 0.0274 (19) | 0.007 (2)    |
| C21 | 0.054 (2) | 0.062 (2)   | 0.047 (2)   | 0.0077 (19)  | 0.0236 (17) | 0.0017 (18)  |

*Geometric parameters (Å, °)*

|           |           |             |           |
|-----------|-----------|-------------|-----------|
| Br1—C1    | 1.886 (4) | C7—H7       | 0.9300    |
| F1—C13    | 1.352 (5) | C8—C9       | 1.447 (5) |
| N2—C16    | 1.347 (4) | C8—H8       | 0.9300    |
| N2—N1     | 1.376 (4) | C9—C10      | 1.491 (5) |
| N2—H21    | 0.8600    | C10—C15     | 1.363 (5) |
| O1—N3     | 1.231 (4) | C10—C11     | 1.372 (5) |
| O2—N3     | 1.213 (4) | C11—C12     | 1.365 (6) |
| O3—N4     | 1.209 (5) | C11—H11     | 0.9300    |
| O4—N4     | 1.223 (5) | C12—C13     | 1.330 (7) |
| N3—C21    | 1.455 (4) | C12—H12     | 0.9300    |
| N1—C9     | 1.298 (4) | C13—C14     | 1.356 (7) |
| N4—C19    | 1.463 (5) | C14—C15     | 1.381 (5) |
| C1—C6     | 1.363 (5) | C14—H14     | 0.9300    |
| C1—C2     | 1.381 (5) | C15—H15     | 0.9300    |
| C2—C3     | 1.378 (5) | C16—C21     | 1.411 (5) |
| C2—H2     | 0.9300    | C16—C17     | 1.411 (4) |
| C3—C4     | 1.393 (5) | C17—C18     | 1.359 (5) |
| C3—H3     | 0.9300    | C17—H17     | 0.9300    |
| C4—C5     | 1.386 (5) | C18—C19     | 1.386 (5) |
| C4—C7     | 1.464 (5) | C18—H18     | 0.9300    |
| C5—C6     | 1.384 (5) | C19—C20     | 1.361 (5) |
| C5—H5     | 0.9300    | C20—C21     | 1.381 (5) |
| C6—H6     | 0.9300    | C20—H20     | 0.9300    |
| C7—C8     | 1.324 (5) |             |           |
| C16—N2—N1 | 120.9 (3) | C15—C10—C11 | 118.9 (4) |

|              |            |                 |            |
|--------------|------------|-----------------|------------|
| C16—N2—H21   | 119.5      | C15—C10—C9      | 119.1 (3)  |
| N1—N2—H21    | 119.5      | C11—C10—C9      | 121.9 (4)  |
| O2—N3—O1     | 122.3 (3)  | C12—C11—C10     | 120.4 (5)  |
| O2—N3—C21    | 119.1 (3)  | C12—C11—H11     | 119.8      |
| O1—N3—C21    | 118.6 (3)  | C10—C11—H11     | 119.8      |
| C9—N1—N2     | 115.6 (3)  | C13—C12—C11     | 119.6 (4)  |
| O3—N4—O4     | 123.0 (4)  | C13—C12—H12     | 120.2      |
| O3—N4—C19    | 120.1 (4)  | C11—C12—H12     | 120.2      |
| O4—N4—C19    | 116.9 (5)  | C12—C13—F1      | 119.3 (6)  |
| C6—C1—C2     | 122.0 (4)  | C12—C13—C14     | 122.3 (4)  |
| C6—C1—Br1    | 119.4 (3)  | F1—C13—C14      | 118.3 (6)  |
| C2—C1—Br1    | 118.6 (3)  | C13—C14—C15     | 118.2 (5)  |
| C3—C2—C1     | 119.2 (3)  | C13—C14—H14     | 120.9      |
| C3—C2—H2     | 120.4      | C15—C14—H14     | 120.9      |
| C1—C2—H2     | 120.4      | C10—C15—C14     | 120.6 (4)  |
| C2—C3—C4     | 120.5 (3)  | C10—C15—H15     | 119.7      |
| C2—C3—H3     | 119.8      | C14—C15—H15     | 119.7      |
| C4—C3—H3     | 119.8      | N2—C16—C21      | 122.7 (3)  |
| C5—C4—C3     | 118.4 (3)  | N2—C16—C17      | 120.4 (3)  |
| C5—C4—C7     | 119.4 (3)  | C21—C16—C17     | 116.9 (3)  |
| C3—C4—C7     | 122.2 (3)  | C18—C17—C16     | 120.8 (4)  |
| C6—C5—C4     | 121.7 (3)  | C18—C17—H17     | 119.6      |
| C6—C5—H5     | 119.2      | C16—C17—H17     | 119.6      |
| C4—C5—H5     | 119.2      | C17—C18—C19     | 120.3 (3)  |
| C1—C6—C5     | 118.3 (4)  | C17—C18—H18     | 119.9      |
| C1—C6—H6     | 120.9      | C19—C18—H18     | 119.9      |
| C5—C6—H6     | 120.9      | C20—C19—C18     | 121.5 (3)  |
| C8—C7—C4     | 127.6 (3)  | C20—C19—N4      | 118.0 (4)  |
| C8—C7—H7     | 116.2      | C18—C19—N4      | 120.5 (4)  |
| C4—C7—H7     | 116.2      | C19—C20—C21     | 118.6 (4)  |
| C7—C8—C9     | 124.0 (3)  | C19—C20—H20     | 120.7      |
| C7—C8—H8     | 118.0      | C21—C20—H20     | 120.7      |
| C9—C8—H8     | 118.0      | C20—C21—C16     | 122.0 (3)  |
| N1—C9—C8     | 116.9 (3)  | C20—C21—N3      | 116.1 (3)  |
| N1—C9—C10    | 123.7 (3)  | C16—C21—N3      | 121.9 (3)  |
| C8—C9—C10    | 119.3 (3)  |                 |            |
|              |            |                 |            |
| C16—N2—N1—C9 | -171.1 (3) | F1—C13—C14—C15  | -178.6 (4) |
| C6—C1—C2—C3  | -0.8 (6)   | C11—C10—C15—C14 | -0.8 (6)   |
| Br1—C1—C2—C3 | 177.7 (3)  | C9—C10—C15—C14  | 176.3 (4)  |
| C1—C2—C3—C4  | 0.3 (6)    | C13—C14—C15—C10 | 0.0 (6)    |
| C2—C3—C4—C5  | 0.0 (6)    | N1—N2—C16—C21   | -178.0 (3) |
| C2—C3—C4—C7  | -178.1 (4) | N1—N2—C16—C17   | 3.5 (5)    |
| C3—C4—C5—C6  | 0.3 (6)    | N2—C16—C17—C18  | 177.9 (3)  |
| C7—C4—C5—C6  | 178.4 (4)  | C21—C16—C17—C18 | -0.7 (5)   |
| C2—C1—C6—C5  | 1.1 (6)    | C16—C17—C18—C19 | -0.3 (5)   |
| Br1—C1—C6—C5 | -177.4 (3) | C17—C18—C19—C20 | 1.0 (6)    |
| C4—C5—C6—C1  | -0.9 (6)   | C17—C18—C19—N4  | -176.7 (3) |



|                 |            |                 |            |
|-----------------|------------|-----------------|------------|
| C5—C4—C7—C8     | 168.4 (4)  | O3—N4—C19—C20   | -5.6 (6)   |
| C3—C4—C7—C8     | -13.6 (6)  | O4—N4—C19—C20   | 175.9 (4)  |
| C4—C7—C8—C9     | 172.9 (4)  | O3—N4—C19—C18   | 172.3 (5)  |
| N2—N1—C9—C8     | 179.3 (3)  | O4—N4—C19—C18   | -6.3 (6)   |
| N2—N1—C9—C10    | 3.5 (5)    | C18—C19—C20—C21 | -0.6 (6)   |
| C7—C8—C9—N1     | -171.1 (4) | N4—C19—C20—C21  | 177.2 (3)  |
| C7—C8—C9—C10    | 4.9 (6)    | C19—C20—C21—C16 | -0.5 (5)   |
| N1—C9—C10—C15   | 75.0 (5)   | C19—C20—C21—N3  | -178.2 (3) |
| C8—C9—C10—C15   | -100.7 (4) | N2—C16—C21—C20  | -177.4 (3) |
| N1—C9—C10—C11   | -108.0 (4) | C17—C16—C21—C20 | 1.1 (5)    |
| C8—C9—C10—C11   | 76.3 (5)   | N2—C16—C21—N3   | 0.2 (5)    |
| C15—C10—C11—C12 | 0.1 (6)    | C17—C16—C21—N3  | 178.7 (3)  |
| C9—C10—C11—C12  | -176.9 (4) | O2—N3—C21—C20   | 1.9 (5)    |
| C10—C11—C12—C13 | 1.4 (7)    | O1—N3—C21—C20   | -178.6 (3) |
| C11—C12—C13—F1  | 177.9 (4)  | O2—N3—C21—C16   | -175.8 (4) |
| C11—C12—C13—C14 | -2.3 (8)   | O1—N3—C21—C16   | 3.7 (5)    |
| C12—C13—C14—C15 | 1.6 (7)    |                 |            |

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

| $D-H\cdots A$                    | $D-H$ | $H\cdots A$ | $D\cdots A$ | $D-H\cdots A$ |
|----------------------------------|-------|-------------|-------------|---------------|
| N2—H21 $\cdots$ O1               | 0.86  | 1.95        | 2.584 (4)   | 130           |
| C11—H11 $\cdots$ O4 <sup>i</sup> | 0.93  | 2.45        | 3.316 (7)   | 154           |

Symmetry code: (i)  $-x+1, -y+1, -z+1$ .