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# (1*E*)-1-(3-Bromophenyl)ethanone 2,4-dinitrophenylhydrazone

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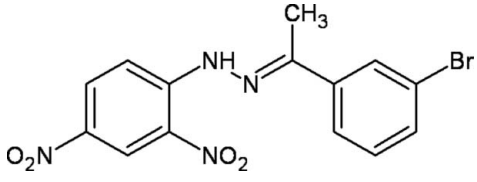
Key indicators: single-crystal X-ray study; $T$ = 100 K; mean $\sigma$(C–C) = 0.003 Å; disorder in main residue; $R$ factor = 0.040; $wR$ factor = 0.102; data-to-parameter ratio = 20.0.

The title compound, $C_{14}H_{11}BrN_4O_4$, contains 3-bromophenyl and 2,4-dinitrophenyl groups on opposite sides of a hydrazone unit and crystallizes with two molecules in the asymmetric unit. The dihedral angles between the two ring systems in each molecule are 2.0 (1) and 2.5 (4)°. Weak C—H···O hydrogen bonds and weak $\pi$–$\pi$ stacking interactions [centroid–centroid distance = 3.7269 (14) Å] help to establish the packing. Intramolecular N—H···O hydrogen bonds are also observed. On one of the rings, the Br atom is disordered over two equivalent positions of the phenyl ring [occupancy ratio 0.8734 (10):0.1266 (10).

## Related literature

For background to Schiff bases and their complexes, see: Baughman *et al.* (2004); El-Seify *et al.* (2006); Liang *et al.* (2007); Okabe *et al.* (1993); Zare *et al.* (2005). For related structures, see: Bolte & Dill, (1998); Fan *et al.* (2004); Ji *et al.* (2010); Kia *et al.* (2009); Motherwell & Ramsay, (2007); Shan *et al.* (2002). For bond-length data, see: Allen *et al.* (1987).




## Experimental

### Crystal data

$C_{14}H_{11}BrN_4O_4$
$M_r$ = 379.18
Triclinic, $P\overline{1}$
$a$ = 7.7546 (9) Å
$b$ = 13.4362 (15) Å
$c$ = 14.1884 (16) Å
$\alpha$ = 91.894 (2)°
$\beta$ = 90.553 (2)°
$\gamma$ = 97.128 (2)°
$V$ = 1466.0 (3) Å$^3$
$Z$ = 4
Mo $K\alpha$ radiation
$\mu$ = 2.83 mm$^{-1}$
$T$ = 100 K
0.55 × 0.55 × 0.24 mm

### Data collection

Bruker APEXII CCD diffractometer
Absorption correction: multi-scan (*SADABS*; Bruker, 2008)
$T_{min}$ = 0.547, $T_{max}$ = 0.746
16795 measured reflections
8581 independent reflections
6680 reflections with $I > 2\sigma(I)$
$R_{int}$ = 0.024

### Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.040
$wR(F^2)$ = 0.102
$S$ = 1.04
8581 reflections
428 parameters
2 restraints
H-atom parameters constrained
$\Delta\rho_{max}$ = 1.44 e Å$^{-3}$
$\Delta\rho_{min}$ = −0.77 e Å$^{-3}$

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

| $D$—H···$A$ | $D$—H | H···$A$ | $D$···$A$ | $D$—H···$A$ |
|---|---|---|---|---|
| N1*B*—H1*B*···O1*B* | 0.86 | 1.99 | 2.615 (2) | 129 |
| N1*A*—H1*A*···O1*A* | 0.86 | 2.00 | 2.621 (2) | 128 |
| C8*B*—H7···O2*A*$^{i}$ | 0.98 | 2.60 | 3.241 (3) | 123 |
| C12*B*—H12*B*···O3*B*$^{i}$ | 0.95 | 2.38 | 3.332 (3) | 175 |
| C8*A*—H8*A*···O3*B*$^{ii}$ | 0.98 | 2.61 | 3.369 (3) | 135 |
| C13*A*—H13*A*···O4*B*$^{iii}$ | 0.95 | 2.40 | 3.282 (3) | 154 |

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

Data collection: *APEX2* (Bruker, 2008); cell refinement: *SAINT* (Bruker, 2008); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *SHELXTL* (Sheldrick, 2008); software used to prepare material for publication: *SHELXTL*.

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: BV2160).

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# supplementary materials

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# (1*E*)-1-(3-Bromophenyl)ethanone 2,4-dinitrophenylhydrazone

**J. P. Jasinski, C. J. Guild, C. S. Chidan Kumar, H. S. Yathirajan and A. N. Mayekar**

## Comment

Schiff bases and their complexes are widely used in the fields of biology and catalysis (Liang, 2007). In particular the dinitrophenyl hydrazones exhibit good nonlinear optical (NLO) and crystalline properties (Baughman *et al.*, 2004) and are found to have versatile coordinating abilities towards different metal ions. In addition, some 2,4-dinitrophenyl hydrazone derivatives have been shown to be potentially DNA-damaging and mutagenic agents (Okabe *et al.*, 1993). As a result of their significant molecular nonlinearities and remarkable ability to crystallize in non-centrosymmetric crystal systems (Zare *et al.*, 2005; El-Seify *et al.*, 2006) many X-ray structural studies of 2,4-dinitrophenylhydrazones have been reported. Among them, the most closely related structures are (*E*)-*p*-methoxy-acetophenone 2,4-dinitrophenylhydrazone (Bolte & Dill, 1998), acetophenone (2,4-dinitrophenyl)hydrazone (Shan *et al.*, 2002), 3-chloroacetophenone 2,4-dintrophenyl-hydrazone (Fan *et al.*, 2004), 2,4-dihydroxyacetophenone 2,4-dinitrophenylhydrazone (Baughman *et al.*, 2004), *syn*-acetophenone (2,4-dinitrophenyl)hydrazone (Motherwell & Ramsay, 2007), *N*-(2,4-dinitrophenyl)-*N*'-(1-*p*-tolylethylidene)hydrazine (Kia *et al.*, 2009) and *N*-(2,4-dinitro-phenyl)-*N*'-(1-phenyl-ethylidene)- hydrazine (Ji *et al.*, 2010). In view of the importance of 2,4-dinitrophenylhydrazones, this paper reports the crystal structure of $C_{14}H_{11}N_4O_4Br$.

The title compound, $C_{14}H_{11}N_4O_4Br$, contains 3-bromophenyl and 2,4-dinitrophenyl groups on opposite sides of a hydrazone moiety. Two molecules (A & B) are present in the asymmetric unit (Fig. 1). The Br atom in molecule B is disordered across the *meta* positions of the benzene ring (Br2B and Br2C occupancies of 0.873 (1) and 0.127 (1), respectively). The dihedral angles between the least squares planes of the two benzene rings in each structure are 2.01° (A) and 2.58° (B), respectively. Weak C—H···O hydrogen bonds (Table 1) and weak π···π stacking interactions [$Cg1\cdots Cg2^{i}$ and $Cg1\cdots Cg3^{i}$ = 3.7269 (14)Å and where *Cg*1, *Cg*2, *Cg*3 = centroids for C1B···C6B, C9B—C14B and C9B/C10B/C11C/C12B/C13C/C14B, respectively; $^{i}$ = 1 - *x*, 1 - *y*, 1 - *x*] contribute to the stability of the crystal packing (Fig.2). In addition there are N—H···O hydrogen bonds involving the N-H and adjacent nitro O atoms.

## Experimental

A mixture of 2,4-dinitrophenylhydrazine (1.98 g) and 1-(3-bromophenyl)ethanone (1.99 g) was dissolved in methanol and refluxed for about 6 h (Fig. 3). The precipitate formed was filtered, dried and recrystallized in ethyl acetate. X-ray quality crystals of the title compound were obtained after three days by the slow evaporation of ethyl acetate solution at room temperature. (mp: 497- 499 K).

## Refinement

All of the H atoms were placed in their calculated positions and then refined using the riding model with Atom—H lengths of 0.93Å (CH), 0.96Å ($CH_3$) or 0.86Å (NH). Isotropic displacement parameters for these atoms were set to 1.2 times (NH), 1.2 (CH) or 1.5 ($CH_3$) times $U_{eq}$ of the parent atom. For one of the rings the the Br is disordered over two equivalent positions with occupancies of 0.873 (1) and 0.127 (1).

## Figures

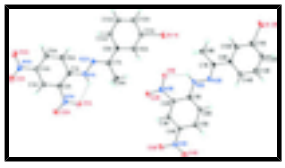

Fig. 1. Molecular structure of $C_{14}H_{11}N_4O_4Br$, showing the atom labeling scheme with 50% probability displacement ellipsoids with two molecules in the asymmetric unit. In molecule B only the major component [Br2B (0.873 (1) occupancy]) is depicted.

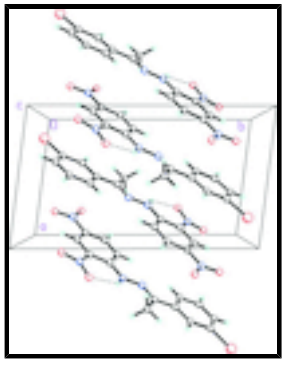

Fig. 2. Packing diagram of $C_{14}H_{11}N_4O_4Br$ viewed down the *c* axis.

## (1*E*)-1-(3-Bromophenyl)ethanone 2,4-dinitrophenylhydrazone

*Crystal data*

| | |
|---|---|
| $C_{14}H_{11}BrN_4O_4$ | $Z = 4$ |
| $M_r = 379.18$ | $F(000) = 760$ |
| Triclinic, $P\overline{1}$ | $D_x = 1.718$ Mg m$^{-3}$ |
| Hall symbol: -P 1 | Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å |
| $a = 7.7546$ (9) Å | Cell parameters from 5432 reflections |
| $b = 13.4362$ (15) Å | $\theta = 2.7$–$30.8°$ |
| $c = 14.1884$ (16) Å | $\mu = 2.83$ mm$^{-1}$ |
| $\alpha = 91.894$ (2)° | $T = 100$ K |
| $\beta = 90.553$ (2)° | Block, orange |
| $\gamma = 97.128$ (2)° | 0.55 × 0.55 × 0.24 mm |
| $V = 1466.0$ (3) Å$^3$ | |

*Data collection*

| | |
|---|---|
| Bruker APEXII CCD diffractometer | 8581 independent reflections |
| Radiation source: fine-focus sealed tube | 6680 reflections with $I > 2\sigma(I)$ |
| graphite | $R_{int} = 0.024$ |
| ω scans | $\theta_{max} = 31.3°$, $\theta_{min} = 1.4°$ |
| Absorption correction: multi-scan (*SADABS*; Bruker, 2008) | $h = -11 \rightarrow 11$ |
| $T_{min} = 0.547$, $T_{max} = 0.746$ | $k = -19 \rightarrow 19$ |
| 16795 measured reflections | $l = -20 \rightarrow 19$ |

*Refinement*

| | |
|---|---|
| Refinement on $F^2$ | Primary atom site location: structure-invariant direct methods |
| Least-squares matrix: full | Secondary atom site location: difference Fourier map |
| $R[F^2 > 2\sigma(F^2)] = 0.040$ | Hydrogen site location: inferred from neighbouring sites |
| $wR(F^2) = 0.102$ | H-atom parameters constrained |
| $S = 1.03$ | $w = 1/[\sigma^2(F_o^2) + (0.049P)^2 + 0.9159P]$ where $P = (F_o^2 + 2F_c^2)/3$ |
| 8581 reflections | $(\Delta/\sigma)_{max} = 0.002$ |
| 428 parameters | $\Delta\rho_{max} = 1.44$ e Å$^{-3}$ |
| 2 restraints | $\Delta\rho_{min} = -0.77$ e Å$^{-3}$ |

*Special details*

**Experimental**. 2010-03-28 # Formatted by publCIF

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**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.

**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 $F^2 > 2\text{sigma}(F^2)$ 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$^2$)*

| | *x* | *y* | *z* | $U_{iso}$*/$U_{eq}$ | Occ. (<1) |
|---|---|---|---|---|---|
| C11B | 0.3320 (3) | 0.11977 (16) | 0.42870 (18) | 0.0279 (5) | 0.8734 (10) |
| C13B | 0.4862 (3) | 0.17310 (18) | 0.56961 (15) | 0.0281 (5) | 0.8734 (10) |
| H13B | 0.5206 | 0.1596 | 0.6319 | 0.034* | 0.8734 (10) |
| C11C | 0.3320 (3) | 0.11977 (16) | 0.42870 (18) | 0.0279 (5) | 0.1266 (10) |
| H11C | 0.2387 | 0.0610 | 0.3838 | 0.034* | 0.1266 (10) |
| C13C | 0.4862 (3) | 0.17310 (18) | 0.56961 (15) | 0.0281 (5) | 0.1266 (10) |
| Br2B | 0.19142 (4) | 0.02208 (2) | 0.36023 (3) | 0.04126 (11) | 0.8734 (10) |
| Br2C | 0.5634 (3) | 0.13884 (16) | 0.68483 (14) | 0.0364 (7) | 0.1266 (10) |
| O1B | 0.7504 (2) | 0.67942 (12) | 0.30264 (11) | 0.0236 (3) | |
| O2B | 0.9336 (2) | 0.81206 (12) | 0.32857 (12) | 0.0291 (4) | |
| O3B | 1.2253 (2) | 0.88614 (12) | 0.61872 (12) | 0.0276 (4) | |
| O4B | 1.2248 (2) | 0.77225 (13) | 0.72350 (11) | 0.0265 (3) | |
| N1B | 0.7215 (2) | 0.53546 (13) | 0.42320 (12) | 0.0171 (3) | |
| H1B | 0.6906 | 0.5510 | 0.3677 | 0.021* | |
| N2B | 0.6603 (2) | 0.44461 (13) | 0.45865 (13) | 0.0178 (3) | |

| | | | | |
|---|---|---|---|---|
| N3B | 0.8600 (2) | 0.73102 (13) | 0.35350 (12) | 0.0196 (4) |
| N4B | 1.1765 (2) | 0.80244 (14) | 0.64777 (13) | 0.0198 (4) |
| C1B | 0.8319 (3) | 0.60103 (15) | 0.47668 (14) | 0.0159 (4) |
| C2B | 0.9025 (3) | 0.69629 (15) | 0.44510 (14) | 0.0161 (4) |
| C3B | 1.0139 (3) | 0.76242 (15) | 0.50129 (15) | 0.0172 (4) |
| H3B | 1.0591 | 0.8263 | 0.4793 | 0.021* |
| C4B | 1.0576 (3) | 0.73365 (15) | 0.58945 (15) | 0.0175 (4) |
| C5B | 0.9929 (3) | 0.64026 (15) | 0.62373 (15) | 0.0180 (4) |
| H5B | 1.0254 | 0.6220 | 0.6849 | 0.022* |
| C6B | 0.8825 (3) | 0.57554 (15) | 0.56820 (14) | 0.0171 (4) |
| H6B | 0.8386 | 0.5120 | 0.5915 | 0.021* |
| C7B | 0.5594 (3) | 0.38472 (15) | 0.40366 (15) | 0.0176 (4) |
| C8B | 0.5111 (3) | 0.41146 (17) | 0.30597 (16) | 0.0245 (5) |
| H6 | 0.4551 | 0.4730 | 0.3090 | 0.037* |
| H7 | 0.4306 | 0.3566 | 0.2772 | 0.037* |
| H8 | 0.6161 | 0.4223 | 0.2679 | 0.037* |
| C9B | 0.4959 (3) | 0.28630 (15) | 0.44326 (16) | 0.0189 (4) |
| C10B | 0.3893 (3) | 0.21275 (16) | 0.39073 (17) | 0.0225 (4) |
| H10B | 0.3554 | 0.2248 | 0.3295 | 0.027* |
| C12B | 0.3816 (3) | 0.10017 (17) | 0.52082 (19) | 0.0291 (5) |
| H12B | 0.3434 | 0.0379 | 0.5482 | 0.035* |
| C14B | 0.5455 (3) | 0.26506 (16) | 0.53498 (16) | 0.0226 (4) |
| H14B | 0.6185 | 0.3133 | 0.5724 | 0.027* |
| Br1A | 0.46515 (3) | 0.585783 (17) | 0.117323 (18) | 0.02724 (7) |
| O1A | 1.1072 (2) | 1.23013 (12) | 0.17885 (11) | 0.0250 (3) |
| O2A | 1.2017 (2) | 1.38349 (12) | 0.14856 (12) | 0.0279 (4) |
| O3A | 1.1250 (2) | 1.52151 (13) | −0.14936 (13) | 0.0300 (4) |
| O4A | 0.9604 (3) | 1.43670 (13) | −0.25602 (12) | 0.0320 (4) |
| N1A | 0.9017 (2) | 1.11916 (13) | 0.05847 (13) | 0.0191 (3) |
| H1A | 0.9406 | 1.1219 | 0.1156 | 0.023* |
| N2A | 0.8042 (2) | 1.03459 (13) | 0.02230 (13) | 0.0199 (4) |
| N3A | 1.1202 (2) | 1.30168 (14) | 0.12536 (13) | 0.0200 (4) |
| N4A | 1.0306 (3) | 1.44583 (15) | −0.17722 (14) | 0.0241 (4) |
| C1A | 0.9364 (3) | 1.19896 (16) | 0.00283 (15) | 0.0185 (4) |
| C2A | 1.0392 (3) | 1.28937 (16) | 0.03282 (15) | 0.0179 (4) |
| C3A | 1.0704 (3) | 1.37046 (16) | −0.02584 (16) | 0.0201 (4) |
| H3A | 1.1401 | 1.4304 | −0.0047 | 0.024* |
| C4A | 0.9983 (3) | 1.36193 (16) | −0.11485 (16) | 0.0210 (4) |
| C5A | 0.8957 (3) | 1.27486 (17) | −0.14749 (16) | 0.0233 (4) |
| H5A | 0.8470 | 1.2710 | −0.2094 | 0.028* |
| C6A | 0.8655 (3) | 1.19486 (17) | −0.09004 (15) | 0.0223 (4) |
| H6A | 0.7960 | 1.1356 | −0.1127 | 0.027* |
| C7A | 0.7589 (3) | 0.96430 (16) | 0.08055 (15) | 0.0204 (4) |
| C8A | 0.8080 (5) | 0.9730 (2) | 0.18295 (19) | 0.0453 (8) |
| H8A | 0.7673 | 1.0332 | 0.2114 | 0.068* |
| H8B | 0.9347 | 0.9780 | 0.1898 | 0.068* |
| H8C | 0.7543 | 0.9136 | 0.2148 | 0.068* |
| C9A | 0.6534 (3) | 0.87396 (16) | 0.03918 (15) | 0.0183 (4) |
| C10A | 0.6164 (3) | 0.78681 (16) | 0.09002 (15) | 0.0200 (4) |

| | | | | |
|---|---|---|---|---|
| H10A | 0.6583 | 0.7845 | 0.1530 | 0.024* |
| C11A | 0.5178 (3) | 0.70347 (16) | 0.04771 (16) | 0.0204 (4) |
| C12A | 0.4544 (3) | 0.70369 (17) | −0.04363 (16) | 0.0237 (4) |
| H12A | 0.3871 | 0.6460 | −0.0713 | 0.028* |
| C13A | 0.4918 (3) | 0.79094 (17) | −0.09411 (16) | 0.0232 (4) |
| H13A | 0.4496 | 0.7928 | −0.1570 | 0.028* |
| C14A | 0.5887 (3) | 0.87411 (17) | −0.05387 (15) | 0.0212 (4) |
| H14A | 0.6127 | 0.9328 | −0.0894 | 0.025* |

*Atomic displacement parameters (Å$^2$)*

| | $U^{11}$ | $U^{22}$ | $U^{33}$ | $U^{12}$ | $U^{13}$ | $U^{23}$ |
|---|---|---|---|---|---|---|
| C11B | 0.0214 (11) | 0.0159 (10) | 0.0454 (15) | −0.0015 (8) | −0.0004 (10) | −0.0014 (9) |
| C13B | 0.0296 (12) | 0.0218 (11) | 0.0332 (13) | 0.0029 (9) | 0.0039 (10) | 0.0080 (9) |
| C11C | 0.0214 (11) | 0.0159 (10) | 0.0454 (15) | −0.0015 (8) | −0.0004 (10) | −0.0014 (9) |
| C13C | 0.0296 (12) | 0.0218 (11) | 0.0332 (13) | 0.0029 (9) | 0.0039 (10) | 0.0080 (9) |
| Br2B | 0.03745 (18) | 0.01748 (14) | 0.0650 (2) | −0.00971 (11) | −0.01999 (15) | −0.00010 (13) |
| Br2C | 0.0462 (13) | 0.0301 (11) | 0.0300 (11) | −0.0101 (8) | −0.0098 (9) | 0.0181 (8) |
| O1B | 0.0299 (8) | 0.0207 (8) | 0.0189 (7) | −0.0016 (6) | −0.0053 (6) | 0.0013 (6) |
| O2B | 0.0428 (10) | 0.0198 (8) | 0.0217 (8) | −0.0101 (7) | −0.0024 (7) | 0.0078 (6) |
| O3B | 0.0326 (9) | 0.0194 (8) | 0.0283 (9) | −0.0068 (6) | −0.0036 (7) | −0.0008 (6) |
| O4B | 0.0268 (8) | 0.0307 (9) | 0.0207 (8) | −0.0016 (7) | −0.0068 (6) | 0.0010 (7) |
| N1B | 0.0200 (8) | 0.0139 (8) | 0.0165 (8) | −0.0017 (6) | −0.0017 (7) | 0.0031 (6) |
| N2B | 0.0185 (8) | 0.0137 (8) | 0.0205 (9) | −0.0011 (6) | 0.0012 (7) | 0.0023 (6) |
| N3B | 0.0252 (9) | 0.0164 (8) | 0.0167 (8) | 0.0007 (7) | 0.0006 (7) | 0.0010 (7) |
| N4B | 0.0167 (8) | 0.0199 (9) | 0.0217 (9) | −0.0012 (6) | −0.0006 (7) | −0.0029 (7) |
| C1B | 0.0162 (9) | 0.0152 (9) | 0.0159 (9) | 0.0004 (7) | 0.0021 (7) | 0.0004 (7) |
| C2B | 0.0191 (9) | 0.0149 (9) | 0.0140 (9) | 0.0001 (7) | −0.0004 (7) | 0.0025 (7) |
| C3B | 0.0174 (9) | 0.0140 (9) | 0.0197 (10) | −0.0005 (7) | 0.0021 (7) | 0.0005 (7) |
| C4B | 0.0160 (9) | 0.0167 (9) | 0.0187 (10) | −0.0012 (7) | −0.0006 (7) | −0.0017 (7) |
| C5B | 0.0189 (9) | 0.0177 (9) | 0.0173 (9) | 0.0015 (7) | 0.0000 (7) | 0.0023 (7) |
| C6B | 0.0188 (9) | 0.0146 (9) | 0.0176 (9) | 0.0004 (7) | 0.0003 (7) | 0.0021 (7) |
| C7B | 0.0166 (9) | 0.0153 (9) | 0.0204 (10) | 0.0001 (7) | 0.0007 (7) | 0.0020 (7) |
| C8B | 0.0285 (11) | 0.0208 (11) | 0.0221 (11) | −0.0059 (8) | −0.0054 (9) | 0.0047 (8) |
| C9B | 0.0160 (9) | 0.0152 (9) | 0.0255 (11) | 0.0012 (7) | 0.0027 (8) | 0.0009 (8) |
| C10B | 0.0186 (10) | 0.0168 (10) | 0.0314 (12) | 0.0001 (8) | −0.0006 (8) | −0.0012 (8) |
| C12B | 0.0275 (12) | 0.0163 (10) | 0.0437 (15) | 0.0014 (8) | 0.0060 (10) | 0.0070 (10) |
| C14B | 0.0231 (10) | 0.0182 (10) | 0.0260 (11) | −0.0001 (8) | 0.0016 (9) | 0.0017 (8) |
| Br1A | 0.02909 (13) | 0.01787 (11) | 0.03320 (13) | −0.00395 (8) | −0.00194 (9) | 0.00412 (9) |
| O1A | 0.0301 (9) | 0.0221 (8) | 0.0220 (8) | −0.0007 (6) | −0.0029 (6) | 0.0035 (6) |
| O2A | 0.0280 (9) | 0.0207 (8) | 0.0326 (9) | −0.0055 (6) | −0.0078 (7) | −0.0011 (7) |
| O3A | 0.0301 (9) | 0.0219 (8) | 0.0375 (10) | −0.0004 (7) | 0.0038 (7) | 0.0078 (7) |
| O4A | 0.0447 (11) | 0.0289 (9) | 0.0232 (9) | 0.0065 (8) | 0.0014 (8) | 0.0064 (7) |
| N1A | 0.0214 (9) | 0.0170 (8) | 0.0177 (8) | −0.0024 (7) | −0.0026 (7) | −0.0003 (7) |
| N2A | 0.0196 (9) | 0.0176 (8) | 0.0213 (9) | −0.0016 (7) | −0.0006 (7) | −0.0016 (7) |
| N3A | 0.0177 (8) | 0.0205 (9) | 0.0215 (9) | 0.0016 (7) | −0.0003 (7) | −0.0005 (7) |
| N4A | 0.0260 (10) | 0.0228 (9) | 0.0247 (10) | 0.0061 (7) | 0.0072 (8) | 0.0046 (8) |
| C1A | 0.0183 (9) | 0.0169 (9) | 0.0201 (10) | 0.0016 (7) | 0.0033 (8) | 0.0003 (8) |

| | | | | | | |
|---|---|---|---|---|---|---|
| C2A | 0.0174 (9) | 0.0188 (10) | 0.0174 (10) | 0.0020 (7) | −0.0001 (7) | −0.0007 (7) |
| C3A | 0.0186 (10) | 0.0174 (10) | 0.0243 (11) | 0.0022 (7) | 0.0037 (8) | 0.0000 (8) |
| C4A | 0.0216 (10) | 0.0194 (10) | 0.0227 (11) | 0.0034 (8) | 0.0049 (8) | 0.0052 (8) |
| C5A | 0.0254 (11) | 0.0249 (11) | 0.0195 (10) | 0.0026 (8) | 0.0014 (8) | 0.0007 (8) |
| C6A | 0.0246 (11) | 0.0208 (10) | 0.0205 (10) | −0.0010 (8) | 0.0005 (8) | −0.0008 (8) |
| C7A | 0.0245 (11) | 0.0171 (10) | 0.0194 (10) | 0.0025 (8) | −0.0028 (8) | −0.0003 (8) |
| C8A | 0.088 (2) | 0.0196 (12) | 0.0236 (13) | −0.0116 (13) | −0.0209 (14) | 0.0033 (10) |
| C9A | 0.0182 (9) | 0.0169 (9) | 0.0198 (10) | 0.0025 (7) | −0.0006 (8) | −0.0014 (8) |
| C10A | 0.0206 (10) | 0.0194 (10) | 0.0197 (10) | 0.0016 (8) | −0.0021 (8) | 0.0008 (8) |
| C11A | 0.0193 (10) | 0.0170 (10) | 0.0245 (11) | 0.0006 (7) | 0.0013 (8) | 0.0006 (8) |
| C12A | 0.0203 (10) | 0.0230 (11) | 0.0268 (11) | 0.0001 (8) | −0.0018 (8) | −0.0038 (9) |
| C13A | 0.0235 (11) | 0.0279 (11) | 0.0175 (10) | 0.0016 (8) | −0.0040 (8) | −0.0023 (8) |
| C14A | 0.0248 (10) | 0.0203 (10) | 0.0185 (10) | 0.0024 (8) | −0.0012 (8) | 0.0016 (8) |

*Geometric parameters (Å, °)*

| | | | |
|---|---|---|---|
| C11B—C10B | 1.400 (3) | Br1A—C11A | 1.896 (2) |
| C11B—C12B | 1.401 (4) | O1A—N3A | 1.239 (2) |
| C11B—Br2B | 1.843 (2) | O2A—N3A | 1.231 (2) |
| C11B—H11C | 1.1703 | O3A—N4A | 1.229 (3) |
| C13B—C12B | 1.358 (3) | O4A—N4A | 1.234 (3) |
| C13B—C14B | 1.372 (3) | N1A—C1A | 1.354 (3) |
| C13B—H13B | 0.9500 | N1A—N2A | 1.366 (2) |
| O1B—N3B | 1.238 (2) | N1A—H1A | 0.8599 |
| O2B—N3B | 1.229 (2) | N2A—C7A | 1.294 (3) |
| O3B—N4B | 1.227 (2) | N3A—C2A | 1.446 (3) |
| O4B—N4B | 1.232 (2) | N4A—C4A | 1.455 (3) |
| N1B—C1B | 1.357 (3) | C1A—C2A | 1.418 (3) |
| N1B—N2B | 1.367 (2) | C1A—C6A | 1.419 (3) |
| N1B—H1B | 0.8604 | C2A—C3A | 1.392 (3) |
| N2B—C7B | 1.288 (3) | C3A—C4A | 1.372 (3) |
| N3B—C2B | 1.444 (3) | C3A—H3A | 0.9500 |
| N4B—C4B | 1.454 (3) | C4A—C5A | 1.394 (3) |
| C1B—C2B | 1.417 (3) | C5A—C6A | 1.369 (3) |
| C1B—C6B | 1.418 (3) | C5A—H5A | 0.9500 |
| C2B—C3B | 1.386 (3) | C6A—H6A | 0.9500 |
| C3B—C4B | 1.373 (3) | C7A—C9A | 1.478 (3) |
| C3B—H3B | 0.9500 | C7A—C8A | 1.496 (3) |
| C4B—C5B | 1.397 (3) | C8A—H8A | 0.9800 |
| C5B—C6B | 1.366 (3) | C8A—H8B | 0.9800 |
| C5B—H5B | 0.9500 | C8A—H8C | 0.9800 |
| C6B—H6B | 0.9500 | C9A—C10A | 1.396 (3) |
| C7B—C9B | 1.483 (3) | C9A—C14A | 1.408 (3) |
| C7B—C8B | 1.499 (3) | C10A—C11A | 1.390 (3) |
| C8B—H6 | 0.9800 | C10A—H10A | 0.9500 |
| C8B—H7 | 0.9800 | C11A—C12A | 1.382 (3) |
| C8B—H8 | 0.9800 | C12A—C13A | 1.395 (3) |
| C9B—C10B | 1.397 (3) | C12A—H12A | 0.9500 |
| C9B—C14B | 1.402 (3) | C13A—C14A | 1.372 (3) |

| | | | |
|---|---|---|---|
| C10B—H10B | 0.9299 | C13A—H13A | 0.9500 |
| C12B—H12B | 0.9500 | C14A—H14A | 0.9500 |
| C14B—H14B | 0.9500 | | |
| C10B—C11B—C12B | 119.6 (2) | C9B—C14B—H14B | 120.7 |
| C10B—C11B—Br2B | 121.40 (19) | C1A—N1A—N2A | 118.89 (18) |
| C12B—C11B—Br2B | 118.98 (17) | C1A—N1A—H1A | 120.3 |
| C10B—C11B—H11C | 119.1 | N2A—N1A—H1A | 120.8 |
| C12B—C11B—H11C | 121.2 | C7A—N2A—N1A | 116.76 (18) |
| C12B—C13B—C14B | 124.4 (2) | O2A—N3A—O1A | 121.74 (19) |
| C12B—C13B—H13B | 117.8 | O2A—N3A—C2A | 118.64 (18) |
| C14B—C13B—H13B | 117.8 | O1A—N3A—C2A | 119.62 (18) |
| C1B—N1B—N2B | 119.14 (17) | O3A—N4A—O4A | 123.5 (2) |
| C1B—N1B—H1B | 120.2 | O3A—N4A—C4A | 119.0 (2) |
| N2B—N1B—H1B | 120.6 | O4A—N4A—C4A | 117.6 (2) |
| C7B—N2B—N1B | 116.20 (18) | N1A—C1A—C2A | 123.4 (2) |
| O2B—N3B—O1B | 121.78 (18) | N1A—C1A—C6A | 119.72 (19) |
| O2B—N3B—C2B | 118.60 (18) | C2A—C1A—C6A | 116.92 (19) |
| O1B—N3B—C2B | 119.62 (17) | C3A—C2A—C1A | 121.85 (19) |
| O3B—N4B—O4B | 123.68 (18) | C3A—C2A—N3A | 116.29 (19) |
| O3B—N4B—C4B | 118.75 (18) | C1A—C2A—N3A | 121.84 (18) |
| O4B—N4B—C4B | 117.56 (18) | C4A—C3A—C2A | 118.5 (2) |
| N1B—C1B—C2B | 122.79 (18) | C4A—C3A—H3A | 120.8 |
| N1B—C1B—C6B | 120.28 (18) | C2A—C3A—H3A | 120.8 |
| C2B—C1B—C6B | 116.93 (18) | C3A—C4A—C5A | 121.8 (2) |
| C3B—C2B—C1B | 121.79 (18) | C3A—C4A—N4A | 119.2 (2) |
| C3B—C2B—N3B | 116.10 (17) | C5A—C4A—N4A | 119.0 (2) |
| C1B—C2B—N3B | 122.10 (18) | C6A—C5A—C4A | 119.8 (2) |
| C4B—C3B—C2B | 118.59 (18) | C6A—C5A—H5A | 120.1 |
| C4B—C3B—H3B | 120.7 | C4A—C5A—H5A | 120.1 |
| C2B—C3B—H3B | 120.7 | C5A—C6A—C1A | 121.1 (2) |
| C3B—C4B—C5B | 121.95 (19) | C5A—C6A—H6A | 119.4 |
| C3B—C4B—N4B | 118.55 (18) | C1A—C6A—H6A | 119.4 |
| C5B—C4B—N4B | 119.49 (19) | N2A—C7A—C9A | 115.38 (19) |
| C6B—C5B—C4B | 119.20 (19) | N2A—C7A—C8A | 122.9 (2) |
| C6B—C5B—H5B | 120.4 | C9A—C7A—C8A | 121.8 (2) |
| C4B—C5B—H5B | 120.4 | C7A—C8A—H8A | 109.5 |
| C5B—C6B—C1B | 121.53 (19) | C7A—C8A—H8B | 109.5 |
| C5B—C6B—H6B | 119.2 | H8A—C8A—H8B | 109.5 |
| C1B—C6B—H6B | 119.2 | C7A—C8A—H8C | 109.5 |
| N2B—C7B—C9B | 115.24 (19) | H8A—C8A—H8C | 109.5 |
| N2B—C7B—C8B | 122.65 (19) | H8B—C8A—H8C | 109.5 |
| C9B—C7B—C8B | 122.10 (19) | C10A—C9A—C14A | 118.40 (19) |
| C7B—C8B—H6 | 109.5 | C10A—C9A—C7A | 121.57 (19) |
| C7B—C8B—H7 | 109.5 | C14A—C9A—C7A | 120.02 (19) |
| H6—C8B—H7 | 109.5 | C11A—C10A—C9A | 119.4 (2) |
| C7B—C8B—H8 | 109.5 | C11A—C10A—H10A | 120.3 |
| H6—C8B—H8 | 109.5 | C9A—C10A—H10A | 120.3 |
| H7—C8B—H8 | 109.5 | C12A—C11A—C10A | 122.2 (2) |
| C10B—C9B—C14B | 118.6 (2) | C12A—C11A—Br1A | 118.45 (16) |

| | | | |
|---|---|---|---|
| C10B—C9B—C7B | 121.6 (2) | C10A—C11A—Br1A | 119.39 (17) |
| C14B—C9B—C7B | 119.75 (19) | C11A—C12A—C13A | 118.2 (2) |
| C9B—C10B—C11B | 120.9 (2) | C11A—C12A—H12A | 120.9 |
| C9B—C10B—H10B | 120.3 | C13A—C12A—H12A | 120.9 |
| C11B—C10B—H10B | 118.8 | C14A—C13A—C12A | 120.7 (2) |
| C13B—C12B—C11B | 117.9 (2) | C14A—C13A—H13A | 119.6 |
| C13B—C12B—H12B | 121.1 | C12A—C13A—H13A | 119.6 |
| C11B—C12B—H12B | 121.1 | C13A—C14A—C9A | 121.1 (2) |
| C13B—C14B—C9B | 118.6 (2) | C13A—C14A—H14A | 119.4 |
| C13B—C14B—H14B | 120.7 | C9A—C14A—H14A | 119.4 |
| C1B—N1B—N2B—C7B | −178.38 (18) | C1A—N1A—N2A—C7A | −172.92 (19) |
| N2B—N1B—C1B—C2B | 179.47 (18) | N2A—N1A—C1A—C2A | −178.63 (19) |
| N2B—N1B—C1B—C6B | −0.2 (3) | N2A—N1A—C1A—C6A | 2.5 (3) |
| N1B—C1B—C2B—C3B | 179.45 (19) | N1A—C1A—C2A—C3A | −179.2 (2) |
| C6B—C1B—C2B—C3B | −0.9 (3) | C6A—C1A—C2A—C3A | −0.3 (3) |
| N1B—C1B—C2B—N3B | 0.7 (3) | N1A—C1A—C2A—N3A | 2.1 (3) |
| C6B—C1B—C2B—N3B | −179.63 (18) | C6A—C1A—C2A—N3A | −179.05 (19) |
| O2B—N3B—C2B—C3B | 5.3 (3) | O2A—N3A—C2A—C3A | 4.2 (3) |
| O1B—N3B—C2B—C3B | −174.14 (19) | O1A—N3A—C2A—C3A | −175.28 (19) |
| O2B—N3B—C2B—C1B | −175.93 (19) | O2A—N3A—C2A—C1A | −176.97 (19) |
| O1B—N3B—C2B—C1B | 4.6 (3) | O1A—N3A—C2A—C1A | 3.5 (3) |
| C1B—C2B—C3B—C4B | 0.7 (3) | C1A—C2A—C3A—C4A | 0.3 (3) |
| N3B—C2B—C3B—C4B | 179.46 (18) | N3A—C2A—C3A—C4A | 179.14 (19) |
| C2B—C3B—C4B—C5B | −0.1 (3) | C2A—C3A—C4A—C5A | 0.0 (3) |
| C2B—C3B—C4B—N4B | 179.09 (18) | C2A—C3A—C4A—N4A | −179.65 (19) |
| O3B—N4B—C4B—C3B | 4.4 (3) | O3A—N4A—C4A—C3A | 1.7 (3) |
| O4B—N4B—C4B—C3B | −174.42 (19) | O4A—N4A—C4A—C3A | −178.3 (2) |
| O3B—N4B—C4B—C5B | −176.35 (19) | O3A—N4A—C4A—C5A | −178.0 (2) |
| O4B—N4B—C4B—C5B | 4.8 (3) | O4A—N4A—C4A—C5A | 2.1 (3) |
| C3B—C4B—C5B—C6B | −0.2 (3) | C3A—C4A—C5A—C6A | −0.3 (3) |
| N4B—C4B—C5B—C6B | −179.38 (18) | N4A—C4A—C5A—C6A | 179.3 (2) |
| C4B—C5B—C6B—C1B | −0.1 (3) | C4A—C5A—C6A—C1A | 0.3 (3) |
| N1B—C1B—C6B—C5B | −179.74 (19) | N1A—C1A—C6A—C5A | 178.9 (2) |
| C2B—C1B—C6B—C5B | 0.6 (3) | C2A—C1A—C6A—C5A | 0.0 (3) |
| N1B—N2B—C7B—C9B | 179.45 (17) | N1A—N2A—C7A—C9A | 179.93 (18) |
| N1B—N2B—C7B—C8B | 0.4 (3) | N1A—N2A—C7A—C8A | 0.2 (3) |
| N2B—C7B—C9B—C10B | −178.26 (19) | N2A—C7A—C9A—C10A | 170.6 (2) |
| C8B—C7B—C9B—C10B | 0.8 (3) | C8A—C7A—C9A—C10A | −9.7 (4) |
| N2B—C7B—C9B—C14B | 0.7 (3) | N2A—C7A—C9A—C14A | −8.8 (3) |
| C8B—C7B—C9B—C14B | 179.8 (2) | C8A—C7A—C9A—C14A | 170.9 (2) |
| C14B—C9B—C10B—C11B | 0.3 (3) | C14A—C9A—C10A—C11A | 0.0 (3) |
| C7B—C9B—C10B—C11B | 179.3 (2) | C7A—C9A—C10A—C11A | −179.5 (2) |
| C12B—C11B—C10B—C9B | 0.3 (3) | C9A—C10A—C11A—C12A | 0.0 (3) |
| Br2B—C11B—C10B—C9B | −179.97 (17) | C9A—C10A—C11A—Br1A | −179.19 (16) |
| C14B—C13B—C12B—C11B | 0.5 (4) | C10A—C11A—C12A—C13A | 0.1 (3) |
| C10B—C11B—C12B—C13B | −0.6 (4) | Br1A—C11A—C12A—C13A | 179.22 (17) |
| Br2B—C11B—C12B—C13B | 179.58 (18) | C11A—C12A—C13A—C14A | −0.1 (3) |
| C12B—C13B—C14B—C9B | 0.0 (4) | C12A—C13A—C14A—C9A | 0.1 (3) |
| C10B—C9B—C14B—C13B | −0.4 (3) | C10A—C9A—C14A—C13A | 0.0 (3) |

| | | | |
|---|---|---|---|
| C7B—C9B—C14B—C13B | −179.4 (2) | C7A—C9A—C14A—C13A | 179.5 (2) |

*Hydrogen-bond geometry (Å, °)*

| *D*—H···*A* | *D*—H | H···*A* | *D*···*A* | *D*—H···*A* |
|---|---|---|---|---|
| N1B—H1B···O1B | 0.86 | 1.99 | 2.615 (2) | 129 |
| N1A—H1A···O1A | 0.86 | 2.00 | 2.621 (2) | 128 |
| C8B—H7···O2A$^{i}$ | 0.98 | 2.60 | 3.241 (3) | 123 |
| C12B—H12B···O3B$^{i}$ | 0.95 | 2.38 | 3.332 (3) | 175 |
| C8A—H8A···O3B$^{ii}$ | 0.98 | 2.61 | 3.369 (3) | 135 |
| C13A—H13A···O4B$^{iii}$ | 0.95 | 2.40 | 3.282 (3) | 154 |

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

**Fig. 1**

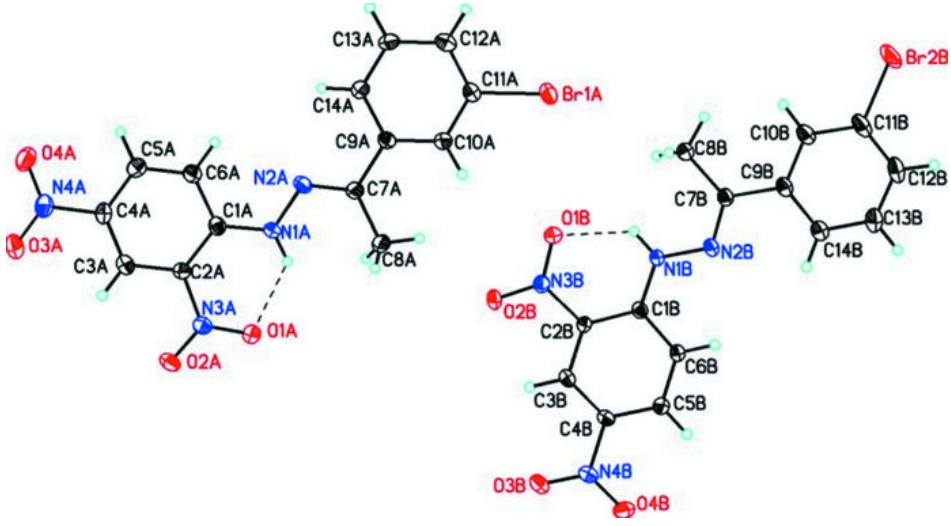
C13A
C12A
C11A
Br1A
C14A
C9A
C10A
O4A
C5A
C6A
N2A
N4A
C4A
C1A
C7A
O3A
N1A
C3A
C2A
C8A
N3A
O1A
O2A
Br2B
C10B
C11B
C8B
C9B
C12B
C7B
O1B
N2B
C13B
C14B
N3B
N1B
O2B
C1B
C2B
C6B
C3B
C5B
C4B
N4B
O3B
O4B

**Fig. 2**