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# 2-[2-(4-Bromophenyl)hydrazinylidene]-1,3-diphenylpropane-1,3-dione

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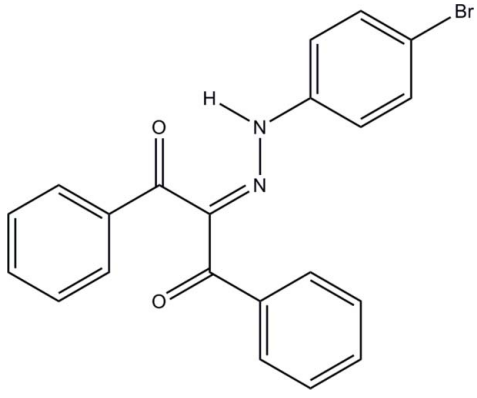
Key indicators: single-crystal X-ray study; $T$ = 150 K; mean $\sigma$(C–C) = 0.003 Å; $R$ factor = 0.030; $wR$ factor = 0.079; data-to-parameter ratio = 15.2.

The conformation of the title molecule, $C_{21}H_{15}BrN_2O_2$, is stabilized by a weak intramolecular C—H···N hydrogen bond and a strong resonance-assisted N—H···O intramolecular hydrogen bond. In the crystal, the molecules are linked by weak intermolecular C—H···O interactions, forming zigzag chains along the $b$ axis.

## Related literature

For resonance-assisted hydrogen bonds and related structures, see: Bertolasi *et al.* (1994). For details of the synthesis, see: Bustos *et al.* (2007, 2009); Yao (1964).




## Experimental

### Crystal data

$C_{21}H_{15}BrN_2O_2$ $M_r$ = 407.25
Monoclinic, $P2_1/n$
$a$ = 12.0273 (9) Å
$b$ = 10.2977 (8) Å
$c$ = 14.2626 (11) Å
$\beta$ = 96.452 (1)°
$V$ = 1755.3 (2) Å$^3$
$Z$ = 4
Mo $K\alpha$ radiation
$\mu$ = 2.36 mm$^{-1}$
$T$ = 150 K
0.44 × 0.41 × 0.12 mm

### Data collection

Bruker D8 Discover diffractometer with SMART CCD area detector
Absorption correction: multi-scan (*SADABS*; Bruker, 2000)
$T_{min}$ = 0.368, $T_{max}$ = 0.753
13742 measured reflections
3575 independent reflections
3107 reflections with $I > 2\sigma(I)$
$R_{int}$ = 0.021

### Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.030
$wR(F^2)$ = 0.079
$S$ = 1.06
3575 reflections
235 parameters
H-atom parameters constrained
$\Delta\rho_{max}$ = 0.67 e Å$^{-3}$
$\Delta\rho_{min}$ = −0.17 e Å$^{-3}$

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

| $D$—H···$A$ | $D$—H | H···$A$ | $D$···$A$ | $D$—H···$A$ |
|---|---|---|---|---|
| N2—H21···O2 | 0.88 | 1.90 | 2.592 (2) | 135 |
| C8—H8···N1 | 0.95 | 2.60 | 3.060 (3) | 110 |
| C17—H17···O2$^{i}$ | 0.95 | 2.46 | 3.382 (3) | 162 |

Symmetry code: (i) $-x-\frac{1}{2}, y-\frac{1}{2}, -z+\frac{1}{2}$.

Data collection: *SMART* (Bruker, 2001); cell refinement: *SAINT* (Bruker, 2000); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *XP* in *SHELXTL-PC* (Sheldrick, 2008); software used to prepare material for publication: *PLATON* (Spek, 2009) and *Mercury* (Macrae *et al.*, 2006).

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: PV2416).

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# supporting information

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## 2-[2-(4-Bromophenyl)hydrazinylidene]-1,3-diphenylpropane-1,3-dione

**Carlos Bustos, Luis Alvarez-Thon, Juan-Guillermo Cárcamo, Maria Teresa Garland and Christian Sánchez**

### S1. Comment

In recent years, much attention has been devoted to structural studies on heterodienic systems forming strong intramolecular hydrogen bonds, N—H···O, assisted by resonance (RAHB, Resonance Assisted Hydrogen Bond) which, *inter alia*, could have potential technological applications as bistate molecular switches (Bertolasi *et al.*, 1994; Bustos *et al.*, 2007). On the other hand, it is well known that the phenyl diazonium salts are capable of coupling with a series of *β*-diketonate anions to give *β*-diketohidrazones that contain the N—H···O core (Yao, 1964; Bustos *et al.*, 2007; Bustos *et al.*, 2009). Using this reaction (Yao, 1964) we have prepared the title compound and, in this report, we present its crystal and molecular structure determined by X-ray diffraction method.

The molecular structure of the title compound exhibits a strong intramolecular hydrogen bond (N2–H21···O2) and a weak intramolecular hydrogen bond (C8–H8···N1) (Fig. 1 and Tab. 1). The molecules are linked by weak intermolecular C17–H17···O2$^{i}$ interactions forming zigzag chains along the *b* axis (Fig. 2).

### S2. Experimental

In a 500 ml flask, 1,3-diphenylpropane-1,3-dione (2.24 g, 0.01 mole) was dissolved in an ethanol solution (100 ml) containing of sodium hydroxide (0.4 g, 0.01 mole) and of sodium acetate (3.65 g, 0.045 mole). The resulting *β*-diketonate solution was diluted with water to a final volume of about 220 ml, stirred and cooled at 268 K. In another 50 ml beaker a diazonium ion solution was prepared by adding 4-bromoaniline (97%) (1.77 g, 0.01 mole) in 8 ml of hydrochloric acid (5 mol/*L*), cooling at 268 K, and adding a saturated aqueous solution containing sodium nitrite (0.69 g, 0.01 mole). The diazonium salt solution was then added dropwise, with vigorous stirring, into the *β*-diketonate solution. During the addition a yellow solid precipitate of the title compound was formed which was filtered by suction and washed with an abundant quantity of water (Yield: 96% of crude product). Single crystals suitable for X-ray studies were obtained by recrystallization from a concentrated solution of the compound in ethanol.

### S3. Refinement

The H atoms were placed in geometrically idealized positions and constrained to ride on their parent atoms, with N—H = 0.88 and C—H = 0.95 Å and $U_{iso}$(H) = 1.2$U_{eq}$(C/N).

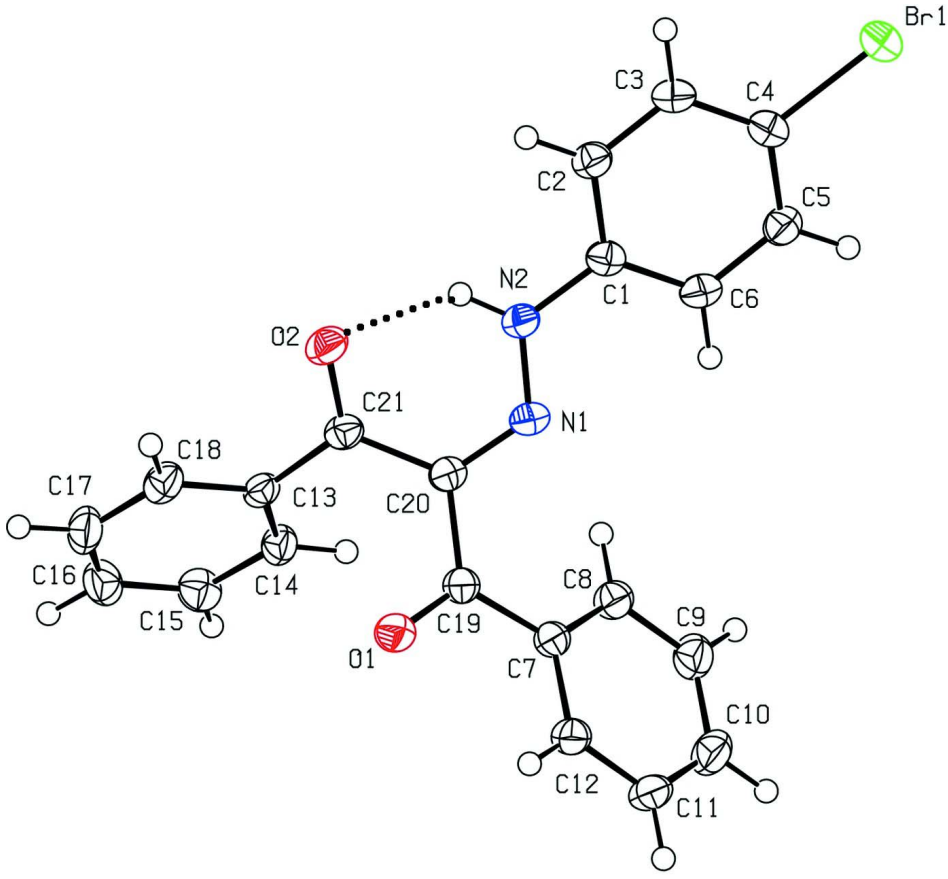


**Figure 1**

A view of the title compound with the atom numbering scheme. Displacement ellipsoids are drawn at the 50% probability level. The strong intramolecular hydrogen bond (N2–H21···O2) is depicted with dashed lines.

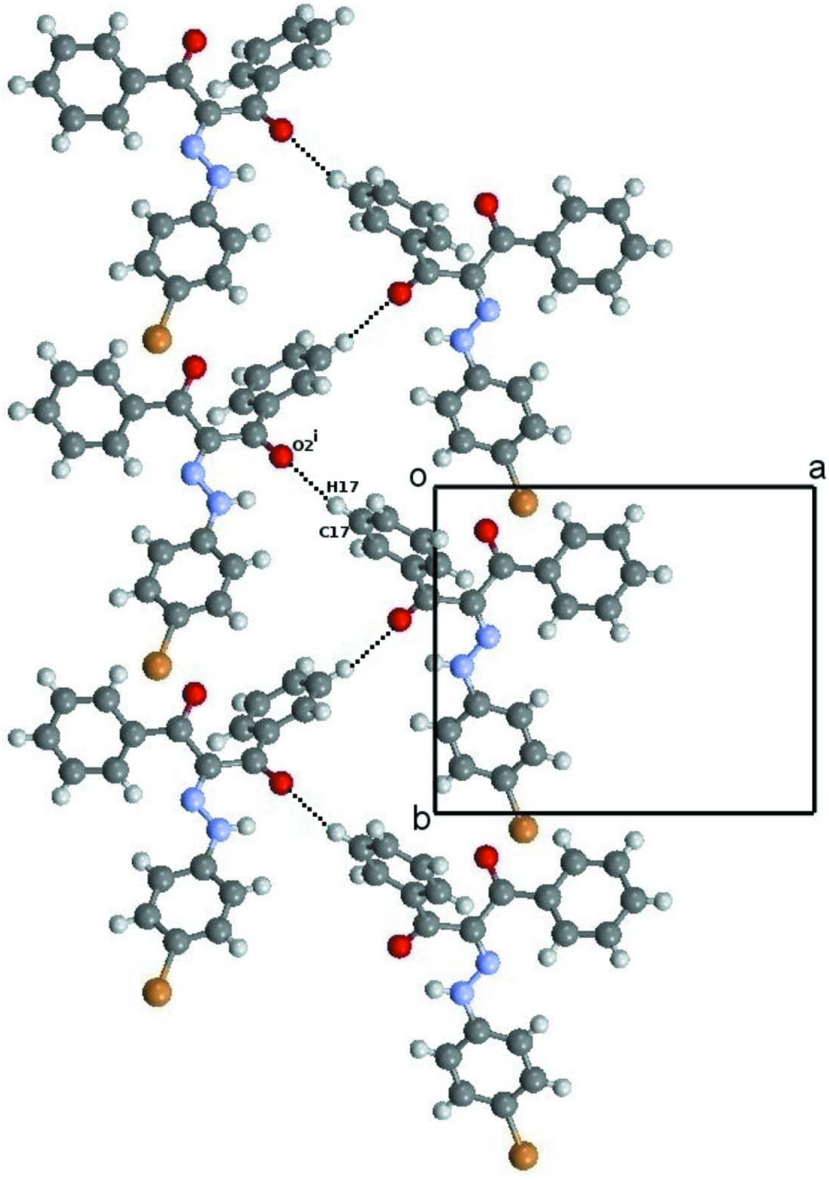


**Figure 2**

A partial view of the unit cell along the *c*-axis, showing the formation of zigzag chains of molecules along the *b* axis.

### 2-[2-(4-Bromophenyl)hydrazinylidene]-1,3-diphenylpropane-1,3-dione

*Crystal data*

$C_{21}H_{15}BrN_2O_2$
$M_r$ = 407.25
Monoclinic, $P2_1/n$
Hall symbol: -P 2yn
$a$ = 12.0273 (9) Å
$b$ = 10.2977 (8) Å
$c$ = 14.2626 (11) Å
$\beta$ = 96.452 (1)°
$V$ = 1755.3 (2) Å$^3$
$Z$ = 4

$F(000)$ = 824
$D_x$ = 1.541 Mg m$^{-3}$
Mo $K\alpha$ radiation, $\lambda$ = 0.71073 Å
Cell parameters from 999 reflections
$\theta$ = 2.1–26.4°
$\mu$ = 2.36 mm$^{-1}$
$T$ = 150 K
Polyhedron, yellow
0.44 × 0.41 × 0.12 mm

*Data collection*

Bruker D8 Discover diffractometer with SMART CCD area detector
Radiation source: fine-focus sealed tube
Graphite monochromator
$\varphi$ and $\omega$ scans
Absorption correction: multi-scan (*SADABS*; Bruker, 2000)
$T_{min}$ = 0.368, $T_{max}$ = 0.753
13742 measured reflections
3575 independent reflections
3107 reflections with $I > 2\sigma(I)$
$R_{int}$ = 0.021
$\theta_{max}$ = 26.4°, $\theta_{min}$ = 2.1°
$h$ = −14→15
$k$ = −12→12
$l$ = −17→17

*Refinement*

Refinement on $F^2$
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.030
$wR(F^2)$ = 0.079
$S$ = 1.06
3575 reflections
235 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
$w = 1/[\sigma^2(F_o^2) + (0.0456P)^2 + 0.6227P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = 0.002
$\Delta\rho_{max}$ = 0.67 e Å$^{-3}$
$\Delta\rho_{min}$ = −0.17 e Å$^{-3}$

*Special details*

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

**Refinement**. Refinement on $F^2$ for ALL reflections except those flagged by the user for potential systematic errors. Weighted *R*-factors *wR* and all goodnesses 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 observed criterion of $F^2 > \sigma(F^2)$ is used only for calculating -*R*-factor-obs *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 (Å²)*

| | *x* | *y* | *z* | $U_{iso}$*/$U_{eq}$ |
|---|---|---|---|---|
| Br1 | 0.23271 (2) | 1.04855 (2) | 0.59316 (1) | 0.0359 (1) |
| O1 | 0.13462 (11) | 0.13416 (13) | 0.33354 (11) | 0.0333 (4) |
| O2 | −0.09408 (11) | 0.40741 (15) | 0.32404 (10) | 0.0329 (4) |
| N1 | 0.13907 (13) | 0.45872 (14) | 0.37523 (11) | 0.0244 (5) |
| N2 | 0.07047 (14) | 0.55054 (14) | 0.39738 (12) | 0.0259 (5) |
| C1 | 0.11110 (16) | 0.66570 (18) | 0.44103 (13) | 0.0244 (5) |
| C2 | 0.03445 (16) | 0.74538 (19) | 0.47975 (14) | 0.0275 (6) |
| C3 | 0.07041 (16) | 0.85857 (19) | 0.52624 (14) | 0.0283 (6) |
| C4 | 0.18176 (17) | 0.89302 (18) | 0.53100 (13) | 0.0272 (6) |
| C5 | 0.25851 (16) | 0.81515 (19) | 0.49182 (14) | 0.0294 (6) |
| C6 | 0.22285 (16) | 0.70074 (19) | 0.44637 (13) | 0.0280 (6) |
| C7 | 0.29704 (16) | 0.25718 (18) | 0.31885 (13) | 0.0255 (5) |
| C8 | 0.34273 (16) | 0.3676 (2) | 0.28233 (14) | 0.0294 (6) |
| C9 | 0.45584 (17) | 0.3718 (2) | 0.27136 (16) | 0.0358 (7) |
| C10 | 0.52336 (18) | 0.2658 (2) | 0.29719 (16) | 0.0402 (7) |
| C11 | 0.47871 (18) | 0.1550 (2) | 0.33354 (16) | 0.0370 (7) |

| | | | | |
|---|---|---|---|---|
| C12 | 0.36607 (17) | 0.1503 (2) | 0.34456 (14) | 0.0304 (6) |
| C13 | −0.05567 (15) | 0.24899 (18) | 0.21378 (13) | 0.0241 (5) |
| C14 | 0.00727 (16) | 0.23913 (18) | 0.13846 (14) | 0.0277 (6) |
| C15 | −0.03124 (18) | 0.1653 (2) | 0.05974 (14) | 0.0332 (6) |
| C16 | −0.13105 (19) | 0.0989 (2) | 0.05795 (16) | 0.0369 (7) |
| C17 | −0.19298 (18) | 0.1058 (2) | 0.13385 (17) | 0.0373 (7) |
| C18 | −0.15682 (16) | 0.1820 (2) | 0.21102 (15) | 0.0306 (6) |
| C19 | 0.17494 (16) | 0.24228 (18) | 0.32685 (13) | 0.0250 (6) |
| C20 | 0.09791 (15) | 0.35573 (18) | 0.32905 (13) | 0.0245 (5) |
| C21 | −0.02208 (15) | 0.33948 (18) | 0.29325 (13) | 0.0251 (5) |
| H2 | −0.04240 | 0.72210 | 0.47430 | 0.0330* |
| H3 | 0.01900 | 0.91180 | 0.55450 | 0.0340* |
| H5 | 0.33500 | 0.83990 | 0.49600 | 0.0350* |
| H6 | 0.27470 | 0.64690 | 0.41910 | 0.0340* |
| H8 | 0.29640 | 0.44040 | 0.26480 | 0.0350* |
| H9 | 0.48690 | 0.44720 | 0.24620 | 0.0430* |
| H10 | 0.60090 | 0.26910 | 0.28990 | 0.0480* |
| H11 | 0.52540 | 0.08250 | 0.35080 | 0.0440* |
| H12 | 0.33530 | 0.07460 | 0.36960 | 0.0360* |
| H14 | 0.07700 | 0.28290 | 0.14060 | 0.0330* |
| H15 | 0.01100 | 0.16070 | 0.00740 | 0.0400* |
| H16 | −0.15730 | 0.04810 | 0.00440 | 0.0440* |
| H17 | −0.26070 | 0.05800 | 0.13290 | 0.0450* |
| H18 | −0.20080 | 0.18880 | 0.26210 | 0.0370* |
| H21 | −0.00220 | 0.53940 | 0.38450 | 0.0310* |

*Atomic displacement parameters (Å²)*

| | $U^{11}$ | $U^{22}$ | $U^{33}$ | $U^{12}$ | $U^{13}$ | $U^{23}$ |
|---|---|---|---|---|---|---|
| Br1 | 0.0364 (1) | 0.0287 (1) | 0.0424 (1) | −0.0006 (1) | 0.0032 (1) | −0.0091 (1) |
| O1 | 0.0286 (7) | 0.0262 (7) | 0.0452 (8) | 0.0008 (6) | 0.0049 (6) | 0.0005 (6) |
| O2 | 0.0243 (7) | 0.0386 (8) | 0.0362 (8) | 0.0060 (6) | 0.0050 (6) | −0.0053 (7) |
| N1 | 0.0248 (8) | 0.0254 (8) | 0.0234 (8) | 0.0059 (6) | 0.0041 (6) | 0.0006 (6) |
| N2 | 0.0227 (8) | 0.0264 (8) | 0.0285 (8) | 0.0039 (6) | 0.0027 (7) | −0.0031 (6) |
| C1 | 0.0285 (10) | 0.0237 (9) | 0.0207 (8) | 0.0033 (7) | 0.0019 (7) | 0.0018 (7) |
| C2 | 0.0249 (10) | 0.0280 (10) | 0.0302 (10) | 0.0026 (7) | 0.0053 (8) | 0.0007 (8) |
| C3 | 0.0301 (10) | 0.0260 (9) | 0.0297 (10) | 0.0063 (8) | 0.0076 (8) | −0.0003 (8) |
| C4 | 0.0334 (11) | 0.0233 (9) | 0.0250 (9) | 0.0013 (8) | 0.0038 (8) | −0.0012 (8) |
| C5 | 0.0240 (10) | 0.0312 (10) | 0.0332 (10) | 0.0012 (8) | 0.0036 (8) | 0.0003 (8) |
| C6 | 0.0267 (10) | 0.0284 (10) | 0.0293 (10) | 0.0067 (8) | 0.0056 (8) | −0.0007 (8) |
| C7 | 0.0247 (9) | 0.0277 (10) | 0.0233 (9) | 0.0026 (7) | −0.0001 (7) | −0.0049 (7) |
| C8 | 0.0270 (10) | 0.0314 (10) | 0.0297 (10) | 0.0023 (8) | 0.0027 (8) | −0.0021 (8) |
| C9 | 0.0290 (11) | 0.0394 (12) | 0.0396 (12) | −0.0045 (9) | 0.0060 (9) | −0.0046 (9) |
| C10 | 0.0235 (10) | 0.0536 (14) | 0.0435 (13) | 0.0021 (10) | 0.0038 (9) | −0.0133 (11) |
| C11 | 0.0292 (11) | 0.0385 (12) | 0.0416 (12) | 0.0121 (9) | −0.0034 (9) | −0.0095 (10) |
| C12 | 0.0293 (10) | 0.0299 (10) | 0.0308 (10) | 0.0052 (8) | −0.0013 (8) | −0.0056 (8) |
| C13 | 0.0202 (9) | 0.0232 (9) | 0.0284 (9) | 0.0030 (7) | 0.0008 (7) | 0.0041 (7) |
| C14 | 0.0227 (9) | 0.0289 (10) | 0.0314 (10) | −0.0029 (8) | 0.0030 (8) | 0.0013 (8) |

| | | | | | | |
|---|---|---|---|---|---|---|
| C15 | 0.0368 (11) | 0.0349 (11) | 0.0279 (10) | 0.0005 (9) | 0.0035 (8) | −0.0016 (8) |
| C16 | 0.0394 (12) | 0.0319 (11) | 0.0363 (11) | −0.0022 (9) | −0.0096 (10) | −0.0028 (9) |
| C17 | 0.0260 (10) | 0.0335 (11) | 0.0502 (13) | −0.0074 (8) | −0.0051 (9) | 0.0049 (10) |
| C18 | 0.0236 (9) | 0.0324 (11) | 0.0359 (11) | −0.0002 (8) | 0.0040 (8) | 0.0074 (9) |
| C19 | 0.0255 (10) | 0.0250 (10) | 0.0241 (9) | 0.0021 (7) | 0.0005 (7) | −0.0017 (7) |
| C20 | 0.0238 (9) | 0.0256 (9) | 0.0239 (9) | 0.0033 (7) | 0.0025 (7) | −0.0002 (7) |
| C21 | 0.0240 (9) | 0.0239 (9) | 0.0277 (9) | 0.0024 (7) | 0.0049 (7) | 0.0035 (8) |

*Geometric parameters (Å, º)*

| | | | |
|---|---|---|---|
| Br1—C4 | 1.8985 (19) | C13—C21 | 1.488 (3) |
| O1—C19 | 1.222 (2) | C14—C15 | 1.392 (3) |
| O2—C21 | 1.232 (2) | C15—C16 | 1.379 (3) |
| N1—N2 | 1.317 (2) | C16—C17 | 1.383 (3) |
| N1—C20 | 1.315 (2) | C17—C18 | 1.382 (3) |
| N2—C1 | 1.402 (2) | C19—C20 | 1.494 (3) |
| N2—H21 | 0.8800 | C20—C21 | 1.485 (3) |
| C1—C6 | 1.385 (3) | C2—H2 | 0.9500 |
| C1—C2 | 1.394 (3) | C3—H3 | 0.9500 |
| C2—C3 | 1.386 (3) | C5—H5 | 0.9500 |
| C3—C4 | 1.380 (3) | C6—H6 | 0.9500 |
| C4—C5 | 1.387 (3) | C8—H8 | 0.9500 |
| C5—C6 | 1.389 (3) | C9—H9 | 0.9500 |
| C7—C8 | 1.389 (3) | C10—H10 | 0.9500 |
| C7—C19 | 1.494 (3) | C11—H11 | 0.9500 |
| C7—C12 | 1.402 (3) | C12—H12 | 0.9500 |
| C8—C9 | 1.387 (3) | C14—H14 | 0.9500 |
| C9—C10 | 1.385 (3) | C15—H15 | 0.9500 |
| C10—C11 | 1.386 (3) | C16—H16 | 0.9500 |
| C11—C12 | 1.382 (3) | C17—H17 | 0.9500 |
| C13—C14 | 1.386 (3) | C18—H18 | 0.9500 |
| C13—C18 | 1.395 (3) | | |
| | | | |
| Br1···C17$^{i}$ | 3.700 (2) | C4···H18$^{iii}$ | 3.0500 |
| Br1···C18$^{i}$ | 3.433 (2) | C5···H14$^{viii}$ | 2.9000 |
| Br1···C13$^{i}$ | 3.5778 (19) | C6···H16$^{vi}$ | 3.0100 |
| Br1···H11$^{ii}$ | 3.2300 | C6···H14$^{viii}$ | 2.9500 |
| Br1···H18$^{iii}$ | 3.2500 | C14···H6$^{iv}$ | 2.9900 |
| O1···C13 | 2.945 (2) | C14···H5$^{iv}$ | 3.0300 |
| O1···C14 | 3.209 (2) | C15···H6$^{iv}$ | 3.0700 |
| O1···C8$^{iv}$ | 3.231 (2) | C19···H14 | 2.8100 |
| O1···C9$^{iv}$ | 3.218 (3) | C20···H14 | 2.7700 |
| O1···C3$^{iii}$ | 3.346 (2) | C20···H8 | 2.7900 |
| O2···N1 | 2.866 (2) | C20···H2$^{iii}$ | 3.0600 |
| O2···C2$^{iii}$ | 3.220 (2) | C21···H21 | 2.4300 |
| O2···C17$^{v}$ | 3.382 (3) | H2···H21 | 2.3600 |
| O2···N2 | 2.592 (2) | H2···C20$^{iii}$ | 3.0600 |
| O1···H8$^{iv}$ | 2.6300 | H3···O1$^{iii}$ | 2.6200 |

| | | | |
|---|---|---|---|
| O1···H12 | 2.4900 | H3···C3$^{vii}$ | 2.7900 |
| O1···H3$^{iii}$ | 2.6200 | H3···H3$^{vii}$ | 2.4000 |
| O1···H9$^{iv}$ | 2.6000 | H5···C14$^{viii}$ | 3.0300 |
| O2···H18 | 2.6900 | H5···H14$^{viii}$ | 2.3900 |
| O2···H17$^{v}$ | 2.4600 | H6···N1 | 2.5600 |
| O2···H21 | 1.9000 | H6···C14$^{viii}$ | 2.9900 |
| N1···O2 | 2.866 (2) | H6···C15$^{viii}$ | 3.0700 |
| N1···C8 | 3.060 (3) | H6···H14$^{viii}$ | 2.4900 |
| N2···O2 | 2.592 (2) | H6···H16$^{vi}$ | 2.4400 |
| N1···H8 | 2.6000 | H8···N1 | 2.6000 |
| N1···H16$^{vi}$ | 2.9000 | H8···C20 | 2.7900 |
| N1···H6 | 2.5600 | H8···O1$^{viii}$ | 2.6300 |
| C2···O2$^{iii}$ | 3.220 (2) | H9···O1$^{viii}$ | 2.6000 |
| C2···C20$^{iii}$ | 3.469 (3) | H10···H18$^{xi}$ | 2.6000 |
| C2···C21$^{iii}$ | 3.373 (3) | H11···Br1$^{ii}$ | 3.2300 |
| C3···O1$^{iii}$ | 3.346 (2) | H12···O1 | 2.4900 |
| C3···C3$^{vii}$ | 3.410 (3) | H14···C19 | 2.8100 |
| C3···C21$^{iii}$ | 3.386 (3) | H14···C20 | 2.7700 |
| C8···O1$^{viii}$ | 3.231 (2) | H14···C5$^{iv}$ | 2.9000 |
| C8···N1 | 3.060 (3) | H14···C6$^{iv}$ | 2.9500 |
| C9···O1$^{viii}$ | 3.218 (3) | H14···H5$^{iv}$ | 2.3900 |
| C13···O1 | 2.945 (2) | H14···H6$^{iv}$ | 2.4900 |
| C13···Br1$^{ix}$ | 3.5778 (19) | H16···N1$^{xii}$ | 2.9000 |
| C14···C19 | 3.173 (3) | H16···C6$^{xii}$ | 3.0100 |
| C14···O1 | 3.209 (2) | H16···H6$^{xii}$ | 2.4400 |
| C17···O2$^{x}$ | 3.382 (3) | H17···O2$^{x}$ | 2.4600 |
| C17···Br1$^{ix}$ | 3.700 (2) | H18···O2 | 2.6900 |
| C18···Br1$^{ix}$ | 3.433 (2) | H18···H10$^{xiii}$ | 2.6000 |
| C19···C14 | 3.173 (3) | H18···Br1$^{iii}$ | 3.2500 |
| C20···C2$^{iii}$ | 3.469 (3) | H18···C4$^{iii}$ | 3.0500 |
| C21···C2$^{iii}$ | 3.373 (3) | H21···O2 | 1.9000 |
| C21···C3$^{iii}$ | 3.386 (3) | H21···C21 | 2.4300 |
| C3···H3$^{vii}$ | 2.7900 | H21···H2 | 2.3600 |

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| N2—N1—C20 | 119.24 (16) | C19—C20—C21 | 119.06 (16) |
| N1—N2—C1 | 121.18 (16) | N1—C20—C19 | 116.22 (16) |
| N1—N2—H21 | 119.00 | C13—C21—C20 | 120.18 (16) |
| C1—N2—H21 | 119.00 | O2—C21—C13 | 119.06 (16) |
| N2—C1—C2 | 117.45 (17) | O2—C21—C20 | 120.55 (17) |
| N2—C1—C6 | 122.17 (17) | C1—C2—H2 | 120.00 |
| C2—C1—C6 | 120.38 (17) | C3—C2—H2 | 120.00 |
| C1—C2—C3 | 120.00 (18) | C2—C3—H3 | 120.00 |
| C2—C3—C4 | 119.26 (18) | C4—C3—H3 | 120.00 |
| C3—C4—C5 | 121.19 (18) | C4—C5—H5 | 120.00 |
| Br1—C4—C3 | 120.03 (15) | C6—C5—H5 | 120.00 |
| Br1—C4—C5 | 118.78 (15) | C1—C6—H6 | 120.00 |
| C4—C5—C6 | 119.59 (18) | C5—C6—H6 | 120.00 |
| C1—C6—C5 | 119.56 (18) | C7—C8—H8 | 120.00 |

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| C12—C7—C19 | 117.24 (17) | C9—C8—H8 | 120.00 |
| C8—C7—C12 | 119.53 (18) | C8—C9—H9 | 120.00 |
| C8—C7—C19 | 123.12 (17) | C10—C9—H9 | 120.00 |
| C7—C8—C9 | 120.13 (19) | C9—C10—H10 | 120.00 |
| C8—C9—C10 | 119.89 (19) | C11—C10—H10 | 120.00 |
| C9—C10—C11 | 120.5 (2) | C10—C11—H11 | 120.00 |
| C10—C11—C12 | 119.8 (2) | C12—C11—H11 | 120.00 |
| C7—C12—C11 | 120.12 (19) | C7—C12—H12 | 120.00 |
| C14—C13—C21 | 120.75 (17) | C11—C12—H12 | 120.00 |
| C14—C13—C18 | 119.50 (18) | C13—C14—H14 | 120.00 |
| C18—C13—C21 | 119.50 (17) | C15—C14—H14 | 120.00 |
| C13—C14—C15 | 120.28 (18) | C14—C15—H15 | 120.00 |
| C14—C15—C16 | 119.73 (19) | C16—C15—H15 | 120.00 |
| C15—C16—C17 | 120.3 (2) | C15—C16—H16 | 120.00 |
| C16—C17—C18 | 120.3 (2) | C17—C16—H16 | 120.00 |
| C13—C18—C17 | 119.92 (19) | C16—C17—H17 | 120.00 |
| O1—C19—C20 | 117.28 (17) | C18—C17—H17 | 120.00 |
| O1—C19—C7 | 120.11 (17) | C13—C18—H18 | 120.00 |
| C7—C19—C20 | 122.60 (16) | C17—C18—H18 | 120.00 |
| N1—C20—C21 | 124.02 (17) | | |

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| C20—N1—N2—C1 | −175.78 (17) | C8—C9—C10—C11 | 0.3 (3) |
| N2—N1—C20—C21 | 4.7 (3) | C9—C10—C11—C12 | −0.3 (3) |
| N2—N1—C20—C19 | −165.54 (16) | C10—C11—C12—C7 | 0.2 (3) |
| N1—N2—C1—C6 | 13.0 (3) | C18—C13—C14—C15 | 1.4 (3) |
| N1—N2—C1—C2 | −166.92 (17) | C21—C13—C18—C17 | 174.85 (18) |
| N2—C1—C6—C5 | −179.01 (18) | C14—C13—C21—O2 | 135.6 (2) |
| C2—C1—C6—C5 | 0.9 (3) | C14—C13—C21—C20 | −39.1 (3) |
| N2—C1—C2—C3 | 178.10 (18) | C18—C13—C21—O2 | −38.7 (3) |
| C6—C1—C2—C3 | −1.8 (3) | C18—C13—C21—C20 | 146.63 (18) |
| C1—C2—C3—C4 | 2.0 (3) | C21—C13—C14—C15 | −172.87 (18) |
| C2—C3—C4—C5 | −1.3 (3) | C14—C13—C18—C17 | 0.5 (3) |
| C2—C3—C4—Br1 | 179.34 (15) | C13—C14—C15—C16 | −1.8 (3) |
| C3—C4—C5—C6 | 0.4 (3) | C14—C15—C16—C17 | 0.2 (3) |
| Br1—C4—C5—C6 | 179.76 (14) | C15—C16—C17—C18 | 1.7 (3) |
| C4—C5—C6—C1 | −0.2 (3) | C16—C17—C18—C13 | −2.1 (3) |
| C19—C7—C8—C9 | −175.90 (19) | O1—C19—C20—N1 | 141.39 (18) |
| C8—C7—C12—C11 | 0.0 (3) | C7—C19—C20—C21 | 151.86 (17) |
| C8—C7—C19—O1 | 159.27 (19) | O1—C19—C20—C21 | −29.4 (3) |
| C8—C7—C19—C20 | −22.0 (3) | C7—C19—C20—N1 | −37.4 (3) |
| C19—C7—C12—C11 | 176.17 (18) | N1—C20—C21—O2 | −17.5 (3) |
| C12—C7—C8—C9 | 0.1 (3) | N1—C20—C21—C13 | 157.07 (18) |
| C12—C7—C19—C20 | 161.96 (18) | C19—C20—C21—O2 | 152.44 (18) |
| C12—C7—C19—O1 | −16.8 (3) | C19—C20—C21—C13 | −33.0 (3) |
| C7—C8—C9—C10 | −0.2 (3) | | |

Symmetry codes: (i) $x+1/2, -y+3/2, z+1/2$; (ii) $-x+1, -y+1, -z+1$; (iii) $-x, -y+1, -z+1$; (iv) $-x+1/2, y-1/2, -z+1/2$; (v) $-x-1/2, y+1/2, -z+1/2$; (vi) $x+1/2, -y+1/2, z+1/2$; (vii) $-x, -y+2, -z+1$; (viii) $-x+1/2, y+1/2, -z+1/2$; (ix) $x-1/2, -y+3/2, z-1/2$; (x) $-x-1/2, y-1/2, -z+1/2$; (xi) $x+1, y, z$; (xii) $x-1/2, -y+1/2, z-1/2$; (xiii) $x-1, y, z$.

*Hydrogen-bond geometry (Å, º)*

| *D*—H···*A* | *D*—H | H···*A* | *D*···*A* | *D*—H···*A* |
|---|---|---|---|---|
| N2—H21···O2 | 0.88 | 1.90 | 2.592 (2) | 135 |
| C8—H8···N1 | 0.95 | 2.60 | 3.060 (3) | 110 |
| C17—H17···O2$^{x}$ | 0.95 | 2.46 | 3.382 (3) | 162 |

Symmetry code: (x) −*x*−1/2, *y*−1/2, −*z*+1/2.