Synthesis, crystal structure and Hirshfeld surface analysis of dimethyl 3-(3-bromophenyl)-6-methyl-7-oxo-3,5,6,7-tetrahydropyrazolo[1,2-a]pyrazole-1,2-dicarboxylate

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The title compound, C_{17}H_{17}BrN_{2}O_{5}, resulted from the 1,3-dipolar cycloaddition reaction between dimethyl acetylenedicarboxylate and (3-bromobenzylidene)-4-methyl-5-oxopyrazolidin-2-ium-1-ide in CHCl_{3}. The dihedral angle between the pyrazole rings (all atoms) is 32.91 (10)°; the oxo-pyrazole ring displays an envelope conformation whereas the other pyrazole ring adopts a twisted conformation. The bromophenyl ring subtends a dihedral angle of 88.95 (9)° with the mean plane of its attached pyrazole ring. In the crystal, the molecules are linked by C—H...O hydrogen bonds and aromatic π—π interactions with an inter-centroid distance of 3.8369 (10) Å. The Hirshfeld surface analysis and fingerprint plots reveal that the molecular packing is governed by H...H (37.1%), O...H...O (31.3%), Br...H...Br (13.5%) and C...H...C (10.6%) contacts. The energy framework indicates that dispersion energy is the major contributor to the molecular packing.

1. Chemical context

Tetrahydropyrazolo[1,2-a] pyrazolones have been studied for about forty years as analogues of penicillin and cephalosporin antibiotics (Jungheim & Sigmund, 1987; Jungheim et al., 1987; Ternansky et al., 1993; Konaklieva & Plotkin, 2003; Hanessian et al., 1997) and have been developed as herbicides and pesticides (Kosower et al., 1995), as antitumor agents and as potent drugs for the treatment of cognitive dysfunctions such as Alzheimer’s disease. Among a variety of reported synthetic approaches to these compounds (Khidre et al., 2013; Li & Zhao, 2014; Sverte, 2006), 1,3-dipolar cycloaddition has been shown to be effective (Stanley & Sibi, 2008; Kissane & Maguire, 2010; Pellissier, 2012). Until now, several 1,3-dipoles, such as azomethine ylides (El Ajlaoui et al., 2015), nitrones (Jen et al., 2000; Kano et al., 2005; Suga et al., 2005) and carbonyl ylides (Suga et al., 2007; Nambu et al., 2009; Padwa 2011), have been studied. Among them, N,N'-cyclic azomethine imines (Stanovnik et al., 1998; Qiu et al., 2014; Nájera et al., 2015; Xu & Doyle, 2014), have been increasingly employed in cycloadditions for the synthesis of pyrazolones and the related dinitrogen-fused heterocyclic derivatives with significant biological activities (Ternansky et al., 1993; Boyd, 1993; Muehlebach, et al., 2009).
As part of our studies in this area, the title compound was synthesized and its molecular and crystal structure and Hirshfeld surface analysis are reported herein.

2. Structural commentary

The molecular structure of the title compound is shown in Fig. 1. There are two stereogenic centres at C2 and C5: in the arbitrarily chosen asymmetric molecule, they have configurations of S and R, respectively, but a racemic mixture in the crystal is generated in the centrosymmetric $P\bar{1}$ space group. The structure is characterized by a disorder of the Br atom over two adjacent sites [Br Br = 0.32 (2) Å]. The dihedral angle between the fused pyrazole rings (all atoms) is 32.91 (10)$^\circ$. The C1–C3/N1/N2 oxo-pyrazole ring displays an envelope conformation on C3 whereas the C5–C7/N1/N2 pyrazole ring is twisted on N2—C5, as indicated by the following respective puckering parameters: $Q(2) = 0.2339 (19)$ Å, $\varphi(2) = 257.9$ (4)$^\circ$ and $Q(2) = 0.2127$ (16) Å, $\varphi(2) = 50.5$ (4)$^\circ$. Moreover, the mean plane passing through the oxo-pyrazole ring subtends a dihedral angle of 61.15 (10)$^\circ$ with the C12–C17 bromophenyl ring, which is practically perpendicular to the other pyrazole ring as indicated by the dihedral angle of 88.95 (9)$^\circ$. The non-H atoms of the ester groups are virtually coplanar, the maximum deviations from the mean planes being 0.017 (2) Å at C10 for the O2/O3/C10/C11 grouping and 0.013 (1) Å at O5 for the O4/O5/C8/C9 grouping. The dihedral angle between these two planes is 62.15 (12)$^\circ$.

3. Supramolecular features

In the crystal, the molecules are linked by C—H...O hydrogen bonds: O1 accepts two such bonds and O2 and O3 accept one each (Table 1 and Fig. 2). The bromophenyl rings of adjacent molecules are linked by an aromatic stacking π–π interaction with an inter-centroid distance of 3.8369 (10) Å.

4. Database survey

A search of the Cambridge Structural Database (CSD, version 5.42, update of May 2021; Groom et al., 2016) for the pyrazole-1,2-dicarboxylate unit revealed only one hit, namely refcode RICFUF: dimethyl 3-(tert-butylamino)-7-phenyl-5-oxo-1H,5H-pyrazolo[1,2-a]pyrazole-1,2-dicarboxylate (Abbasi et al., 2007). The conformations of the fused pyrazole rings present in this compound and those of the title compound are different. Furthermore, the values of the dihedral angles between the planes passing through the rings are also very different, except for the angles between the fused pyrazole

| D—H...A | D—H | H...A | D...A | D—H...A |
|---------|------|-------|-------|---------|
| C9—H9A...O1$^i$ | 0.96 | 2.42 | 3.258 (3) | 146 |
| C14—H14A...O1$^n$ | 0.93 | 2.53 | 3.418 (2) | 161 |
| C11—H11B...O2$^ii$ | 0.96 | 2.60 | 3.533 (3) | 164 |
| C3—H3B...O2$^n$ | 0.97 | 2.62 | 3.514 (3) | 154 |

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

Figure 1
The molecular structure of the title compound showing displacement ellipsoids drawn at the 50% probability level.

Figure 2
Crystal packing for the title compound showing hydrogen bonds as dashed blue lines.
rings, the difference of which does not exceed one degree, i.e. 34.13° in RICFUF and 32.91 (10)° in the title compound. It may be noted that the phenyl substituent is linked to the oxopyrazole ring and the two carboxylate groups to the other pyrazole ring in RICFUF, while in the title compound the phenyl and both carboxylate groups are linked to the same pyrazole ring.

5. Computational chemistry

**Hirshfeld surface analysis**

The Hirshfeld surface (HS) analyses (Spackman & Jayatilaka, 2009) and two-dimensional fingerprint plots (McKinnon et al., 2007) generated using CrystalExplorer17.5 (Turner et al., 2017) show the various intermolecular interactions in the crystal structure. The three-dimensional $d_{norm}$ surface of the title compound using a standard surface resolution with a fixed colour scale of $-0.21$ to $1.38$ a.u is shown in Fig. 3a. The intense red spots on the surface are due to the C—H—O hydrogen bonds and C—H···Br contacts. The bright-red spots in Fig. 3c indicate atoms with the potential to be hydrogen-bond acceptors (negative electrostatic potential), while blue regions indicate atoms with positive electrostatic potential (hydrogen-bond donors) (Spackman et al., 2008).

Two-dimensional fingerprint plots for the H···H, H···O, O···H, H···Br/Br···H and H···C/C···H contacts are presented in Fig. 4. The most important interaction is H···H ($d_i = d_e = 1.15$ Å) (Fig. 4b), contributing 37.6% to the overall crystal packing, which is reflected as widely scattered points of high density due to the large hydrogen content of the molecule. The contribution from the O···H/H···O contacts (31.4%), corresponding to C—H···O interactions, is represented by a pair of sharp spikes characteristic of a strong hydrogen-bond interaction ($d_i + d_e = 2.40$ Å, Fig. 4c). The reciprocal H···Br/Br···H interactions (12.8%) are present as two symmetrical broad wings with $d_i + d_e = 3.10$ Å (Fig. 4d). The C···H/H···C contacts contribute 10.8% to the Hirshfeld surface, featuring a wide region with $d_i + d_e = 2.95$ Å (Fig. 4e).

The smaller percentage contributions of other types of contact are listed in Table 2.

**Interaction energy calculations**

The intermolecular interaction energies between molecules in the title compound computed using a B3LYP/6-31G (d, p)
energy model available in Crystal Explorer 17.5 (Turner et al., 2017), where a cluster of molecules was generated within a radius of 3.8 Å by default. The total intermolecular energy \( E_{\text{tot}} \) is the sum of electrostatic \( E_{\text{ele}} \), polarization \( E_{\text{pol}} \), dispersion \( E_{\text{dis}} \), and exchange-repulsion \( E_{\text{rep}} \) energies. The energy frameworks, which provide a view of the supramolecular architecture of crystals, are represented by cylinders joining the centroids of molecular pairs using red, green and, respectively, with a cut-off value of 5 kJ mol\(^{-1} \). The nature and strength of the energies for the key identified intermolecular interactions are summarized in Table 3. The computed interaction energies for electrostatic, polarization, dispersion and exchange repulsion are 107.7 kJ mol\(^{-1} \), 33.9 kJ mol\(^{-1} \) and 185.2 kJ mol\(^{-1} \), respectively (Mackenzie et al., 2017). The natures and strengths of the energies for the key identified intermolecular interactions are summarized in Table 3. The computed interaction energies for electrostatic, polarization, dispersion and exchange repulsion are 107.7 kJ mol\(^{-1} \), 33.9 kJ mol\(^{-1} \), 185.2 kJ mol\(^{-1} \), respectively. These data reveal that the dispersive component makes the major contribution to the intermolecular interactions in the crystal. The calculations showed that the C3—H3B· · · O2 hydrogen bond has the greatest energy among all close contacts present in the crystal with its energy (–52.1 kJ mol\(^{-1} \)) having a major electrostatic contribution (−21.9 kJ mol\(^{-1} \)). The next most significant contribution, with a total energy of −34.9 kJ mol\(^{-1} \), arises from the C11—H11B· · · O2 hydrogen bond. Lower energies, compared to the above interactions, are calculated for the Br1A· · · O4, C9—H9A···· O1 and C14—H14···· O1 contacts.

### Frontier molecular orbital (FMO) calculations

The optimized structure of the title compound was established in the gas phase using density functional theory (DFT) using the B3LYP exchange correlation functional and basis-set calculations (Becke, 1993) as implanted in GAUSSIAN 09 (Frisch et al., 2009). The differences between calculated and experimental bond lengths and angles are within a few Angstroms and degrees, respectively, when compared to the experimental parameters, which indicate that our calculations are acceptable (see supplementary Tables 1 and 2). The HOMO–LUMO gap of the molecule is calculated to be about 4.16 eV.

### 6. Synthesis and crystallization

To a solution of DMAD (dimethyldiacetamidecarboxylate; 0.2 mmol, 2 equiv.) in 10 ml of CHCl\(_3\) containing a catalytic amount of DABCO (0.02 mmol, 0.2 equiv.), (3-bromobenzylidene)-4-methyl-5-oxopyrazolidin-2-ium-1-ide \( (0.10 \text{ mmol}, 1 \text{ equiv.}) \) was added (Fig. 6). The mixture was stirred at 318 K until the consumption of the azomethine imine was complete (monitored by TLC with 3:7 hexane/ethyl acetate \( v/v \)). After completion of the reaction, the residue was concentrated \( \text{in vacuo} \). The crude product was purified by column chromatography on silica gel using hexane/ethyl acetate \( (2/8 \text{ v/v}) \) as eluent. The title compound was recrystallized from ethanol solution in the form of colourless blocks (yield 68%, m.p. 383 K).

### Table 4

| Crystal data | Chemical formula | \( \text{C}_7\text{H}_7\text{BrN}_2\text{O}_5 \) |
|--------------|------------------|-----------------------------------|
| M\(_r\)       |                  | 409.23                            |
| Crystal system, space group |                  | Triclinic, \( PT \) |
| Temperature (K) |                  | 296                               |
| \( a \), \( b \), \( c \) (Å) |                  | \( 8.8579 \text{ (5)}, 10.5336 \text{ (6)}, 11.0893 \text{ (6)} \) |
| \( \alpha \), \( \beta \), \( \gamma \) (°) |                  | \( 78.282 \text{ (2)}, 75.437 \text{ (2)}, 88.241 \text{ (2)} \) |
| \( V \) (Å\(^3\)) |                  | \( 88.03 \text{ (9)} \) |
| \( Z \) |                  | 2                                 |
| Radiation type |                  | Mo Ka                             |
| \( \mu \) (mm\(^{-1}\)) |                  | 2.36                              |
| Crystal size (mm) |                  | \( 0.2 \times 0.28 \times 0.19 \) |

### 5. Experimental details

- **Data collection**
  - Bruker D8 VENTURE Super DUO
- **Absorption correction**
  - Multi-scan (SADABS; Krause et al., 2015)

**Data collection**

- **Crystal data**
  - \( \text{C}_7\text{H}_7\text{BrN}_2\text{O}_5 \)
  - \( M_r = 409.23 \)
- **Crystal system, space group**
  - Triclinic, \( PT \)
- **Temperature (K)**
  - 296
- **\( a \), \( b \), \( c \) (Å)**
  - \( 8.8579 \text{ (5)}, 10.5336 \text{ (6)}, 11.0893 \text{ (6)} \)
- **\( \alpha \), \( \beta \), \( \gamma \) (°)**
  - \( 78.282 \text{ (2)}, 75.437 \text{ (2)}, 88.241 \text{ (2)} \)
- **\( V \) (Å\(^3\))**
  - \( 88.03 \text{ (9)} \)
- **\( Z \)**
  - 2
- **Radiation type**
  - Mo Ka
- **\( \mu \) (mm\(^{-1}\))**
  - 2.36
- **Crystal size (mm)**
  - \( 0.2 \times 0.28 \times 0.19 \)

**Absorption correction**

- **Data collection**
  - Bruker D8 VENTURE Super DUO
- **Absorption correction**
  - Multi-scan (SADABS; Krause et al., 2015)

**Data collection**

- **\( T_{\text{min}}, T_{\text{max}} \)**
  - 0.617, 0.746
- **No. of measured, independent and observed \([I > 2\sigma(I)]\) reflections**
  - 27467, 3884, 3257
- **\( R_{\text{int}} \)**
  - 0.027
- **\( \sin \theta/\lambda_{\text{max}} \) (Å\(^{-1}\))**
  - 0.641

**Refinement**

- **\( R[F^2 > 2\sigma(F^2)] \), \( \omega R(F^2) \), \( S \)**
  - 0.027, 0.078, 1.04
- **No. of reflections**
  - 3882
- **No. of parameters**
  - 235
- **H-atom treatment**
  - H-atom parameters constrained
- **\( \Delta \sigma_{\text{max}}, \Delta \sigma_{\text{min}} \) (Å\(^{-1}\))**
  - 0.23, –0.26

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Figure 6

Scheme showing the synthesis of the title compound.
7. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 4. Four reflections affected by the beamstop were omitted from the refinement. All H atoms were placed geometrically (C—H = 0.93–0.98 Å) and refined as riding atoms with $U_{	ext{iso}}(H) = 1.2 U_{eq}(C)$ or $1.5 U_{eq}$(methyl C). The Br atom was modelled as disordered over adjacent sites in a 0.5862:0.4138 ratio.

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Synthesis, crystal structure and Hirshfeld surface analysis of dimethyl 3-(3-bromophenyl)-6-methyl-7-oxo-3,5,6,7-tetrahydropyrazolo[1,2-a]pyrazole-1,2-dicarboxylate

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Computing details

Data collection: APEX3 (Bruker, 2016); cell refinement: SAINT (Bruker, 2016); data reduction: SAINT (Bruker, 2016); program(s) used to solve structure: SHELXT2014/5 (Sheldrick, 2015a); program(s) used to refine structure: SHELXL2018/3 (Sheldrick, 2015b); molecular graphics: WinGX and ORTEP-3 for Windows (Farrugia, 2012); software used to prepare material for publication: Mercury (Macrae et al., 2020) and publCIF (Westrip, 2010).

Dimethyl 3-(3-bromophenyl)-6-methyl-7-oxo-3,5,6,7-tetrahydropyrazolo[1,2-a]pyrazole-1,2-dicarboxylate

Crystal data

C17H17BrN2O5  Z = 2  
Mr = 409.23  
Triclinic, P1  
a = 8.8579 (5) Å  
b = 10.5336 (6) Å  
c = 11.0893 (6) Å  
α = 62.282 (2)°  
β = 75.437 (2)°  
γ = 88.241 (2)°  
V = 882.03 (9) Å³

Data collection

Bruker D8 VENTURE Super DUO diffractometer  
Radiation source: INCOATEC μS micro-focus source  
HELIOS mirror optics monochromator  
Detector resolution: 10.4167 pixels mm⁻¹  
φ and ω scans  
(SADABS; Krause et al., 2015)

Refinement

Refinement on F²  
Least-squares matrix: full  
R[F² > 2σ(F²)] = 0.027  
wR(F²) = 0.078

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[https://doi.org/10.1107/S2056989021013621]
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
\[ w = 1/(\sigma(F_o^2) + (0.0411P)^2 + 0.1854P) \]
where \( P = (F_o^2 + 2F_c^2)/3 \)

\( \Delta(\sigma)_{max} < 0.001 \)
\( \Delta \rho_{max} = 0.23 \text{ e } \AA^{-3} \)
\( \Delta \rho_{min} = -0.26 \text{ e } \AA^{-3} \)

Special details

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.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²)

|    | x     | y     | z     | Uiso*/Ueq | Occ. (<1) |
|----|-------|-------|-------|-----------|-----------|
| C1 | 0.59723 (18) | 0.82071 (16) | 0.63241 (16) | 0.0400 (3) | 0.0400 (3) |
| C2 | 0.73763 (18) | 0.89402 (17) | 0.50667 (16) | 0.0426 (3) | 0.0426 (3) |
| H2 | 0.747329 | 0.997326 | 0.477490 | 0.051 | 0.051 |
| C3 | 0.69585 (19) | 0.8717 (2) | 0.39196 (17) | 0.0543 (4) | 0.0543 (4) |
| H3A | 0.734473 | 0.955697 | 0.300247 | 0.065* | 0.065* |
| H3B | 0.741502 | 0.788389 | 0.387941 | 0.065* | 0.065* |
| C4 | 0.8868 (2) | 0.8311 (3) | 0.5424 (2) | 0.0678 (5) | 0.0678 (5) |
| H4A | 0.974476 | 0.879267 | 0.461016 | 0.102* | 0.102* |
| H4B | 0.902100 | 0.844121 | 0.618805 | 0.102* | 0.102* |
| H4C | 0.877991 | 0.730075 | 0.570107 | 0.102* | 0.102* |
| C5 | 0.45427 (17) | 0.73166 (15) | 0.41577 (15) | 0.0372 (3) | 0.0372 (3) |
| H5 | 0.533031 | 0.664725 | 0.413900 | 0.045* | 0.045* |
| C6 | 0.32540 (17) | 0.65778 (15) | 0.55378 (15) | 0.0377 (3) | 0.0377 (3) |
| C7 | 0.35203 (17) | 0.69677 (15) | 0.64608 (15) | 0.0374 (3) | 0.0374 (3) |
| C8 | 0.27063 (18) | 0.64773 (17) | 0.79956 (16) | 0.0418 (3) | 0.0418 (3) |
| C9 | 0.2384 (3) | 0.4599 (2) | 1.03001 (19) | 0.0738 (6) | 0.0738 (6) |
| H9A | 0.270856 | 0.365515 | 1.078206 | 0.111* | 0.111* |
| H9B | 0.273764 | 0.521748 | 1.061323 | 0.111* | 0.111* |
| H9C | 0.126110 | 0.453518 | 1.050550 | 0.111* | 0.111* |
| C10 | 0.21152 (18) | 0.54235 (16) | 0.58279 (16) | 0.0423 (3) | 0.0423 (3) |
| C11 | −0.0089 (2) | 0.3797 (2) | 0.7483 (2) | 0.0690 (5) | 0.0690 (5) |
| H11A | −0.084012 | 0.361710 | 0.835157 | 0.103* | 0.103* |
| H11B | −0.062337 | 0.398430 | 0.677267 | 0.103* | 0.103* |
| H11C | 0.047778 | 0.296859 | 0.763103 | 0.103* | 0.103* |
| C12 | 0.40315 (17) | 0.79230 (15) | 0.28093 (14) | 0.0367 (3) | 0.0367 (3) |
| C13 | 0.4618 (2) | 0.7461 (2) | 0.18122 (18) | 0.0517 (4) | 0.0517 (4) |
| H13 | 0.533604 | 0.677727 | 0.196652 | 0.062* | 0.062* |
| C14 | 0.4127 (3) | 0.8027 (2) | 0.05800 (19) | 0.0644 (6) | 0.0644 (6) |
| H14 | 0.453637 | 0.772789 | −0.009399 | 0.077* | 0.077* |
| C15 | 0.3053 (2) | 0.9015 (2) | 0.03454 (17) | 0.0610 (5) | 0.0610 (5) |
| H15 | 0.271768 | 0.937716 | −0.047350 | 0.073* | 0.073* |
| C16 | 0.2476 (2) | 0.94653 (18) | 0.13404 (16) | 0.0484 (4) | 0.0484 (4) |
| C17 | 0.29670 (17) | 0.89409 (16) | 0.25580 (15) | 0.0394 (3) | 0.0394 (3) |
supporting information

|     | u\(^{11}\) | u\(^{22}\) | u\(^{33}\) | u\(^{12}\) | u\(^{13}\) | u\(^{23}\) |
|-----|------------|------------|------------|-----------|-----------|-----------|
| C1  | 0.0449 (8) | 0.0403 (8) | 0.0409 (8) | 0.0084 (6) | −0.0182 (6) | −0.0210 (6) |
| C2  | 0.0429 (8) | 0.0422 (8) | 0.0438 (8) | 0.0011 (6) | −0.0158 (6) | −0.0188 (7) |
| C3  | 0.0417 (8) | 0.0765 (12) | 0.0409 (8) | −0.0126 (8) | −0.0039 (7) | −0.0272 (8) |
| C4  | 0.0453 (10) | 0.0867 (15) | 0.0733 (13) | 0.0103 (9) | −0.0232 (9) | −0.0359 (11) |
| C5  | 0.0362 (7) | 0.0378 (7) | 0.0373 (7) | 0.0047 (5) | −0.0116 (6) | −0.0168 (6) |
| C6  | 0.0399 (7) | 0.0346 (7) | 0.0349 (7) | 0.0042 (6) | −0.0137 (6) | −0.0117 (6) |
| C7  | 0.0356 (7) | 0.0366 (7) | 0.0359 (7) | 0.0069 (5) | −0.0108 (6) | −0.0134 (6) |
| C8  | 0.0396 (8) | 0.0439 (8) | 0.0382 (8) | 0.0050 (6) | −0.0104 (6) | −0.0167 (7) |
| C9  | 0.0947 (16) | 0.0698 (13) | 0.0363 (9) | 0.0047 (11) | −0.0136 (9) | −0.0103 (9) |
| C10 | 0.0438 (8) | 0.0374 (7) | 0.0412 (8) | 0.0031 (6) | −0.0168 (7) | −0.0121 (6) |
| C11 | 0.0573 (11) | 0.0614 (12) | 0.0733 (13) | −0.0196 (9) | −0.0058 (10) | −0.0241 (10) |
| C12 | 0.0371 (7) | 0.0409 (7) | 0.0307 (7) | −0.0047 (6) | −0.0057 (6) | −0.0171 (6) |
| C13 | 0.0526 (10) | 0.0586 (10) | 0.0471 (9) | −0.0028 (8) | −0.0030 (7) | −0.0322 (8) |
| C14 | 0.0738 (13) | 0.0832 (14) | 0.0400 (9) | −0.0215 (11) | 0.0041 (9) | −0.0400 (10) |
| C15 | 0.0740 (13) | 0.0699 (12) | 0.0313 (8) | −0.0236 (10) | −0.0151 (8) | −0.0154 (8) |
| C16 | 0.0523 (9) | 0.0460 (8) | 0.0394 (8) | −0.0105 (7) | −0.0199 (7) | −0.0095 (7) |
| C17 | 0.0414 (8) | 0.0450 (8) | 0.0320 (7) | −0.0012 (6) | −0.0116 (6) | −0.0173 (6) |
| N1  | 0.0387 (6) | 0.0437 (7) | 0.0328 (6) | 0.0016 (5) | −0.0103 (5) | −0.0173 (5) |
| N2  | 0.0428 (7) | 0.0424 (6) | 0.0310 (6) | −0.0011 (5) | −0.0130 (5) | −0.0144 (5) |
| O1  | 0.0644 (8) | 0.0741 (8) | 0.0392 (6) | 0.0039 (6) | −0.0209 (5) | −0.0274 (6) |
| O2  | 0.0767 (9) | 0.0566 (7) | 0.0574 (7) | −0.0117 (6) | −0.0126 (6) | −0.0297 (6) |
| O3  | 0.0482 (7) | 0.0557 (7) | 0.0564 (7) | −0.0121 (5) | −0.0033 (6) | −0.0245 (6) |
| O4  | 0.0697 (9) | 0.0660 (8) | 0.0554 (7) | 0.0218 (7) | −0.0032 (6) | −0.0297 (7) |
| O5  | 0.0660 (8) | 0.0486 (6) | 0.0363 (6) | 0.0124 (5) | −0.0126 (5) | −0.0128 (5) |
| Br1A| 0.0563 (3) | 0.0541 (3) | 0.0611 (2) | 0.0139 (2) | −0.0361 (2) | −0.0164 (2) |
| Br1B| 0.1041 (15) | 0.0955 (10) | 0.1272 (17) | 0.0249 (8) | −0.0824 (13) | −0.0302 (9) |

Geometric parameters (Å, °)

|     |         |         |         |         |         |         |
|-----|---------|---------|---------|---------|---------|---------|
| C1—O1 | 1.2062 (18) | C9—H9A | 0.9600 |
| C1—N1 | 1.3765 (19) | C9—H9B | 0.9600 |
| C1—C2 | 1.507 (2) | C9—H9C | 0.9600 |
| C2—C4 | 1.519 (2) | C10—O2 | 1.202 (2) |
| C2—C3 | 1.527 (2) | C10—O3 | 1.329 (2) |
| Bond          | Length (Å)  | Bond          | Length (Å)  |
|---------------|-------------|---------------|-------------|
| C2—H2         | 0.9800      | C11—O3        | 1.447 (2)   |
| C3—N2         | 1.481 (2)   | C11—H11A      | 0.9600      |
| C3—H3A        | 0.9700      | C11—H11B      | 0.9600      |
| C3—H3B        | 0.9700      | C11—H11C      | 0.9600      |
| C4—H4A        | 0.9600      | C12—C17       | 1.381 (2)   |
| C4—H4B        | 0.9600      | C12—C13       | 1.387 (2)   |
| C4—H4C        | 0.9600      | C13—C14       | 1.392 (3)   |
| C5—N2         | 1.4903 (19) | C13—H13       | 0.9300      |
| C5—C12        | 1.5110 (19) | C14—C15       | 1.367 (3)   |
| C5—C6         | 1.523 (2)   | C14—H14       | 0.9300      |
| C5—H5         | 0.9800      | C15—C16       | 1.375 (3)   |
| C6—C7         | 1.338 (2)   | C15—H15       | 0.9300      |
| C6—C10        | 1.466 (2)   | C16—C17       | 1.380 (2)   |
| C7—N1         | 1.3801 (19) | C16—Br1B      | 1.754 (3)   |
| C7—C8         | 1.507 (2)   | C16—Br1A      | 1.961 (2)   |
| C8—O4         | 1.190 (2)   | C17—H17       | 0.9300      |
| C8—O5         | 1.3131 (19) | N1—N2         | 1.4444 (16) |
| C9—O5         | 1.447 (2)   |                |             |
| O1—C1—N1      | 124.11 (15) | H9A—C9—H9C    | 109.5       |
| O1—C1—C2      | 129.17 (14) | H9B—C9—H9C    | 109.5       |
| N1—C1—C2      | 106.72 (12) | O2—C10—O3     | 124.51 (15) |
| C1—C2—C4      | 110.91 (14) | O2—C10—C6     | 122.90 (15) |
| C1—C2—C3      | 103.61 (12) | O3—C10—C6     | 112.54 (14) |
| C4—C2—C3      | 114.19 (15) | O3—C11—H11A   | 109.5       |
| C1—C2—H2      | 109.3       | O3—C11—H11B   | 109.5       |
| C4—C2—H2      | 109.3       | H11A—C11—H11B | 109.5       |
| C3—C2—H2      | 109.3       | O3—C11—H11C   | 109.5       |
| N2—C3—C2      | 106.03 (12) | H11A—C11—H11C | 109.5       |
| N2—C3—H3A     | 110.5       | H11B—C11—H11C | 109.5       |
| C2—C3—H3A     | 110.5       | C17—C12—C13   | 119.18 (14) |
| N2—C3—H3B     | 110.5       | C17—C12—C5    | 120.30 (12) |
| C2—C3—H3B     | 110.5       | C13—C12—C5    | 120.52 (15) |
| H3A—C3—H3B    | 108.7       | C12—C13—C14   | 119.69 (18) |
| C2—C4—H4A     | 109.5       | C12—C13—H13   | 120.2       |
| C2—C4—H4B     | 109.5       | C14—C13—H13   | 120.2       |
| H4A—C4—H4B    | 109.5       | C15—C14—C13   | 121.00 (16) |
| C2—C4—H4C     | 109.5       | C15—C14—H14   | 119.5       |
| H4A—C4—H4C    | 109.5       | C13—C14—H14   | 119.5       |
| H4B—C4—H4C    | 109.5       | C14—C15—C16   | 118.90 (16) |
| N2—C5—C12     | 110.97 (11) | C14—C15—H15   | 120.5       |
| N2—C5—C6      | 101.25 (11) | C16—C15—H15   | 120.5       |
| C12—C5—C6     | 116.58 (12) | C15—C16—C17   | 121.17 (17) |
| N2—C5—H5      | 109.2       | C15—C16—Br1B  | 115.19 (16) |
| C12—C5—H5     | 109.2       | C17—C16—Br1B  | 123.57 (16) |
| C6—C5—H5      | 109.2       | C15—C16—Br1A  | 121.65 (14) |
| C7—C6—C10     | 127.27 (14) | C17—C16—Br1A  | 117.17 (13) |
| C7—C6—C5      | 109.39 (13) | Br1B—C16—Br1A | 7.44 (12)   |
Hydrogen-bond geometry (Å, °)

| D—H···A  | D—H | H···A | D···A  | D—H···A |
|----------|------|-------|--------|---------|
| C9—H9A···O1^i | 0.96  | 2.42  | 3.258 (3) | 146     |
| C14—H14···O1^ii | 0.93  | 2.53  | 3.418 (2) | 161     |
| C11—H11B···O2^iii | 0.96  | 2.60  | 3.533 (3) | 164     |
| C3—H3B···O2^iv  | 0.97  | 2.62  | 3.514 (3) | 154     |

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

Comparison of the selected experimental and calculated geometric parameters (Å, °)

| Bond lengths          | X-ray     | DFT     |
|-----------------------|-----------|---------|
| O1—C1                 | 1.206 (2) | 1.209   |
| C1—N1                 | 1.377 (2) | 1.384   |
| N1—N2                 | 1.444 (2) | 1.438   |
| N1—C7                 | 1.380 (2) | 1.374   |
| C3—N2                 | 1.481 (2) | 1.470   |
| C5—N2                 | 1.490 (2) | 1.484   |
| C8—O4                 | 1.190 (2) | 1.199   |
| C8—O5                 | 1.313 (2) | 1.334   |
| C10—O2                | 1.202 (2) | 1.212   |
| C10—O3                | 1.329 (2) | 1.351   |
| O3—C11                | 1.447 (2) | 1.438   |
| O5—C9                 | 1.447 (2) | 1.443   |
| C16—Br1A/Br1B         | 1.961 (2)/1.754 (3) | 1.922 |

Angles

|          | X-ray     | DFT     |
|----------|-----------|---------|
| O1—C1—N1 | 124.1 (2) | 125.7   |
| O1—C1—C2 | 129.2 (2) | 129.2   |
| N1—C1—C2 | 106.7 (2) | 105.1   |
| C1—N1—C7 | 130.6 (2) | 133.8   |
| C1—N1—N2 | 114.1 (2) | 113.1   |
| C3—N2—C5 | 116.3 (2) | 119.8   |
| C7—C8—O4 | 123.1 (2) | 122.9   |
| C7—C8—O5 | 110.4 (2) | 110.8   |
| O4—C8—O5 | 126.5 (2) | 126.3   |
### Quantum chemical parameters of the title compound calculated by B3LYP/6-311G (d, p)

| Parameter                  | Value  |
|----------------------------|--------|
| $E_f$(eV)                  | 101131.745 |
| $E_{\text{HOMO}}$(eV)      | -6.026 |
| $E_{\text{LUMO}}$(eV)      | -1.868 |
| $D_{\text{LUMO-HOMO}}$(eV) | 4.158 |
| Chemical hardness ($\eta$) | 2.079 |
| Chemical Softness ($\xi$)  | 0.241 |
| Chemical potential ($\mu$) | 3.947 |
| Electrophilicity ($\psi$)  | 3.754 |
| Electronegativity ($\chi$) | -3.947 |
| Dipole moment (D)          | 3.847 |

$\eta = 1/2[E_{\text{LUMO}}-E_{\text{HOMO}}], \xi = 1/2\eta, \mu = [1/2(E_{\text{LUMO}}+E_{\text{HOMO}})], \psi = \mu^2/2\eta, \chi = -\mu$