



Crystal structure of 2-[(*E*)-2-(4-bromophenyl)-diazen-1-yl]-4,5-bis(4-methoxyphenyl)-1*H*-imidazole: the first example of a structurally characterized triarylazoimidazole

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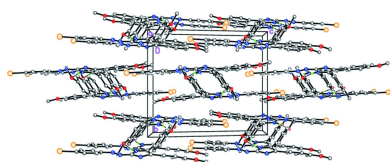
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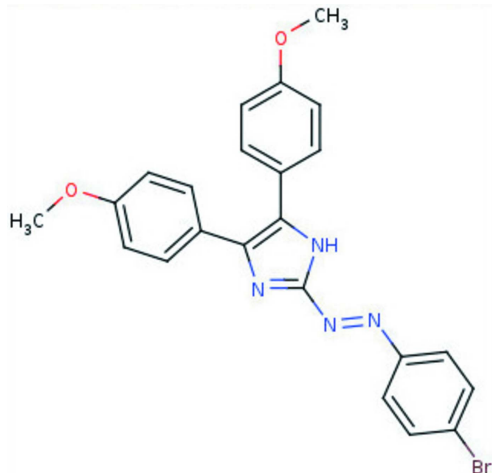
The title compound, C₂₃H₁₉BrN₄O₂, is a product of an azo coupling reaction between 3,4-bis(4-methoxyphenyl)imidazole and 4-bromophenyldiazonium tetrafluoroborate. Its crystal structure was determined using data collected at 120 K. The molecule adopts a *trans* configuration with respect to the N=N double bond. The imidazole and aryl rings attached to the azo linkage are coplanar within 12.73 (14)°, which indicates significant electron delocalization within the molecule. In the crystal, the molecules form centrosymmetric dimers *via* pairs of N—H···O hydrogen bonds.

1. Chemical context

Azoimidazoles are a class of dyes that have found widespread applications in industry, as well as in laboratory research (Eymann *et al.*, 2016; Tskhovrebov *et al.*, 2014; Liu *et al.*, 2019). They are widely used for dyeing natural and synthetic fibers. In addition, they have found applications as photoswitches and hold promise for utilization in photopharmacology (Crespi *et al.*, 2019). Azo-functionalized imidazoles have been studied intensively as ligands in coordination chemistry (Sarker, Chand *et al.*, 2007; Sarker, Sardar *et al.*, 2007; Schütt *et al.*, 2016; Das *et al.*, 1997; Misra *et al.*, 1997). They are also attractive as chelating bidentate ligands. Azoimidazole coordination compounds have been reported for numerous metals, some of them showing interesting photochromic properties (Sarker, Sardar *et al.*, 2007; Sarker, Chand *et al.*, 2007; Crespi *et al.*, 2019). Numerous publications have been devoted to the development of organic crystalline materials that contain various imidazole-based architectures (Akhriff *et al.*, 2006). Following our interest in azo dyes (Nenajdenko *et al.*, 2020; Tskhovrebov, Vasileva *et al.*, 2018), imidazole chemistry, imidazolylidenes and corresponding metal–carbene complexes (Tskhovrebov, Lingnau *et al.*, 2019; Tskhovrebov, Goddard *et al.*, 2018; Mikhaylov *et al.*, 2018; Tskhovrebov *et al.*, 2012), we report here the synthesis and crystal structure of (*E*)-2-[(4-bromophenyl)diazanyl]-4,5-bis(4-methoxyphenyl)-1*H*-imidazole. Although azoimidazoles form a widely studied class of azo compounds, triarylazoimidazoles have never been



structurally characterized. This work presents the first example of structurally characterized triarylazoimidazole.



The *PASS* program (Filimonov *et al.*, 2014) predicted the potential activity of the title compound as a thiol protease inhibitor and an aspluvinone dimethylallyltransferase inhibitor at 81% and 76% probability levels, respectively.

2. Structural commentary

The molecular structure of the title compound is shown in Fig. 1. Overall, bond dimensions within the molecule are similar to those reported for structurally relevant azo compounds (Tskhovrebov *et al.*, 2014, 2015; Liu *et al.*, 2019; Eymann *et al.*, 2016; Nenajdenko *et al.*, 2020). The molecule adopts a *trans* configuration with respect to the azo double bond. The N=N bond distance of 1.274 (3) Å is slightly longer than that in azobenzene. The imidazole and aryl rings attached to the azo group are coplanar within 12.73 (14)°, which indicates significant electron delocalization within the molecule. The two other aromatic rings, C4–C9 and C11–C16, form dihedral angles with the plane of the imidazole ring of 60.64 (14) and 22.38 (13)°, respectively.

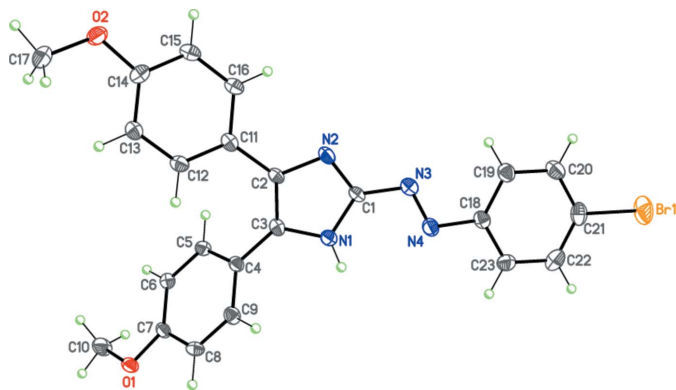


Figure 1
Molecular structure of the title compound. Displacement ellipsoids are shown at the 50% probability level. The hydrogen atoms are presented as small spheres of arbitrary radius.

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

<i>D</i> –H··· <i>A</i>	<i>D</i> –H	H··· <i>A</i>	<i>D</i> ··· <i>A</i>	<i>D</i> –H··· <i>A</i>
N1–H1···O1 ⁱ	0.80 (3)	2.17 (3)	2.963 (3)	169 (3)

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

3. Supramolecular features

In the crystal, the title molecules form centrosymmetric dimers *via* pairs of N–H···O hydrogen bonds (Fig. 2, Table 1). A similar supramolecular motif has previously been observed by our group (Repina *et al.*, 2020; Tskhovrebov, Novikov *et al.*, 2019). The crystal packing involves some π – π stacking interactions (Fig. 3) with a shortest intercentroid separation of 3.792 (2) Å between two imidazole rings related by the symmetry operation $1 - x, 1 - y, 1 - z$.

4. Database survey

A search of the Cambridge Structural Database (CSD version 5.41, update of March 2020; Groom *et al.*, 2016) revealed that this is the first example of a structurally characterized triarylazomidazole. At the same time, the CSD search revealed

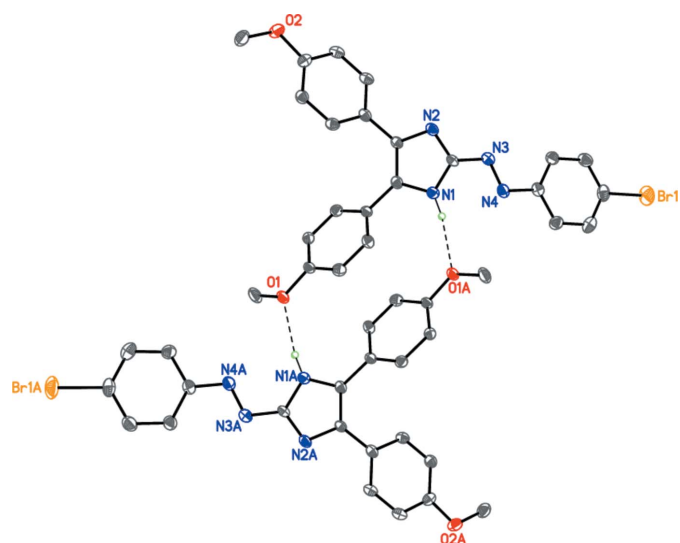


Figure 2
The hydrogen-bonded centrosymmetric dimer. Dashed lines indicate the N–H···O hydrogen bonds.

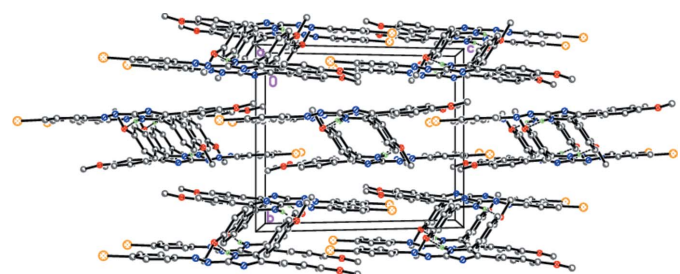


Figure 3
Crystal packing projected along the *a* axis direction.

Table 2
Experimental details.

Crystal data	
Chemical formula	C ₂₃ H ₁₉ BrN ₄ O ₂
<i>M_r</i>	463.32
Crystal system, space group	Monoclinic, <i>P</i> 2 ₁ / <i>c</i>
Temperature (K)	120
<i>a</i> , <i>b</i> , <i>c</i> (Å)	10.7812 (9), 12.7877 (11), 15.4575 (13)
β (°)	109.635 (2)
<i>V</i> (Å ³)	2007.2 (3)
<i>Z</i>	4
Radiation type	Mo <i>K</i> α
μ (mm ⁻¹)	2.08
Crystal size (mm)	0.33 × 0.21 × 0.08
Data collection	
Diffractometer	Bruker APEXII CCD
Absorption correction	Multi-scan (<i>SADABS</i> ; Krause <i>et al.</i> , 2015)
<i>T_{min}</i> , <i>T_{max}</i>	0.597, 0.746
No. of measured, independent and observed [<i>I</i> > 2 σ (<i>I</i>)] reflections	22147, 6069, 3449
<i>R_{int}</i>	0.084
(<i>sin</i> θ / λ) _{max} (Å ⁻¹)	0.714
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, <i>S</i>	0.052, 0.122, 1.00
No. of reflections	6069
No. of parameters	276
H-atom treatment	H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{\max}$, $\Delta\rho_{\min}$ (e Å ⁻³)	0.44, -0.62

Computer programs: *APEX3* (Bruker, 2018), *SAINTE* (Bruker, 2013), *SHELXT* (Sheldrick, 2015a), *SHELXL* (Sheldrick, 2015b) and *SHELXTL* (Sheldrick, 2008).

several examples of structurally similar azoimidazoles, which contain a proton at the imidazolic N atom, *viz.* 2-[(4-bromophenyl)diazanyl]-1*H*-imidazole (Pramanik *et al.*, 2010), 2-(1-naphthylidiazanyl)-1*H*-imidazole (Pramanik *et al.*, 2010), 2-[4-(*N,N*-dihydroxyethylamino)phenylazo]-4,5-dicyanoimidazole (Carella *et al.*, 2004), phenylazoimidazole (Fun *et al.*, 1999), 4-(4,5-dicyano-1*H*-imidazolylazo)-*N,N*-diethylaniline (Zhang *et al.*, 2007), 2-(*p*-tolylazo)imidazole (Bhunia *et al.*, 2006) and 3,3'-({4-[4,5-dicyano-1*H*-imidazol-2-yl]diazanyl}phenyl)imino) dipropionic acid (Centore *et al.*, 2013).

5. Synthesis and crystallization

Triaryloimidazole was prepared according to the literature method (Fun *et al.*, 1999) *via* azo coupling of *p*-bromophenyldiazonium tetrafluoroborate with di(*p*-anisyl)imidazole and isolated in 84% yield as a red solid. Crystals suitable for X-ray analysis were obtained by slow evaporation of a saturated MeOH solution.

6. Refinement

Crystal data, details of data collection, and results of structure refinement are summarized in Table 2. The X-ray diffraction study was performed using the equipment of the Center for Molecular Studies of INEOS RAS. The hydrogen atom of the NH group was localized in the difference-Fourier map and

refined with a fixed isotropic displacement parameter [$U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{N})$]. The other hydrogen atoms were placed in calculated positions with C–H = 0.95–0.98 Å and refined using a riding model with fixed isotropic displacement parameters [$U_{\text{iso}}(\text{H}) = 1.5U_{\text{eq}}(\text{C})$ for CH₃ groups and $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$ for other groups].

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supporting information

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Crystal structure of 2-[(*E*)-2-(4-bromophenyl)diazen-1-yl]-4,5-bis(4-methoxyphenyl)-1*H*-imidazole: the first example of a structurally characterized triaryl-azoimidazole

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Computing details

Data collection: *APEX3* (Bruker, 2018); cell refinement: *SAINT* (Bruker, 2013); data reduction: *SAINT* (Bruker, 2013); program(s) used to solve structure: *SHELXT* (Sheldrick, 2015a); program(s) used to refine structure: *SHELXL* (Sheldrick, 2015b); molecular graphics: *SHELXTL* (Sheldrick, 2008); software used to prepare material for publication: *SHELXTL* (Sheldrick, 2008).

2-[(*E*)-2-(4-Bromophenyl)diazen-1-yl]-4,5-bis(4-methoxyphenyl)-1*H*-imidazole

Crystal data

C₂₃H₁₉BrN₄O₂

M_r = 463.32

Monoclinic, *P2₁/c*

a = 10.7812 (9) Å

b = 12.7877 (11) Å

c = 15.4575 (13) Å

β = 109.635 (2)°

V = 2007.2 (3) Å³

Z = 4

F(000) = 944

D_x = 1.533 Mg m⁻³

Mo *Kα* radiation, λ = 0.71073 Å

Cell parameters from 2288 reflections

θ = 2.6–25.4°

μ = 2.08 mm⁻¹

T = 120 K

Plate, orange

0.33 × 0.21 × 0.08 mm

Data collection

Bruker APEXII CCD
diffractometer

φ and ω scans

Absorption correction: multi-scan
(SADABS; Krause *et al.*, 2015)

T_{min} = 0.597, *T_{max}* = 0.746

22147 measured reflections

6069 independent reflections

3449 reflections with *I* > 2σ(*I*)

R_{int} = 0.084

θ_{max} = 30.5°, θ_{min} = 2.0°

h = -14→15

k = -18→18

l = -21→21

Refinement

Refinement on *F*²

Least-squares matrix: full

R [*F*² > 2σ(*F*²)] = 0.052

wR (*F*²) = 0.122

S = 1.00

6069 reflections

276 parameters

0 restraints

Primary atom site location: difference Fourier
map

Secondary atom site location: difference Fourier
map

Hydrogen site location: mixed

H atoms treated by a mixture of independent
and constrained refinement
 $w = 1/[\sigma^2(F_o^2) + (0.0498P)^2]$
where $P = (F_o^2 + 2F_c^2)/3$

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

$$\Delta\rho_{\max} = 0.44 \text{ e } \text{\AA}^{-3}$$

$$\Delta\rho_{\min} = -0.61 \text{ e } \text{\AA}^{-3}$$

Special details

Experimental. SADABS-2014/5 (Bruker, 2014/5) was used for absorption correction. $wR2(\text{int})$ was 0.0815 before and 0.0536 after correction. The Ratio of minimum to maximum transmission is 0.8000. The $\lambda/2$ correction factor is 0.00150.

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 (\AA^2)

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
Br1	0.27445 (4)	0.40711 (3)	-0.14822 (2)	0.04431 (14)
O1	-0.01642 (18)	0.55364 (14)	0.68807 (12)	0.0212 (4)
O2	0.84035 (18)	0.33604 (14)	0.90163 (12)	0.0249 (4)
N1	0.2914 (2)	0.39235 (17)	0.42224 (15)	0.0191 (5)
H1	0.222 (3)	0.410 (2)	0.387 (2)	0.023*
N2	0.5047 (2)	0.35277 (17)	0.47136 (14)	0.0194 (5)
N3	0.4041 (2)	0.36812 (17)	0.30966 (15)	0.0204 (5)
N4	0.2927 (2)	0.38470 (16)	0.24827 (15)	0.0215 (5)
C1	0.3985 (3)	0.36862 (19)	0.39831 (17)	0.0176 (5)
C2	0.4641 (3)	0.37005 (19)	0.54552 (17)	0.0162 (5)
C3	0.3314 (3)	0.39603 (19)	0.51634 (17)	0.0178 (5)
C4	0.2423 (3)	0.43346 (19)	0.56408 (17)	0.0163 (5)
C5	0.2757 (3)	0.5239 (2)	0.61663 (17)	0.0192 (6)
H5	0.3570	0.5577	0.6235	0.023*
C6	0.1921 (3)	0.56603 (19)	0.65933 (17)	0.0177 (6)
H6	0.2161	0.6281	0.6949	0.021*
C7	0.0742 (3)	0.51714 (19)	0.64976 (17)	0.0175 (5)
C8	0.0393 (3)	0.4255 (2)	0.59788 (18)	0.0203 (6)
H8	-0.0416	0.3915	0.5918	0.024*
C9	0.1230 (3)	0.38447 (19)	0.55551 (17)	0.0190 (6)
H9	0.0990	0.3223	0.5202	0.023*
C10	0.0165 (3)	0.6508 (2)	0.7369 (2)	0.0321 (7)
H10A	0.0296	0.7048	0.6958	0.048*
H10B	0.0978	0.6422	0.7895	0.048*
H10C	-0.0552	0.6717	0.7588	0.048*
C11	0.5584 (3)	0.36163 (19)	0.64007 (17)	0.0175 (5)
C12	0.5186 (3)	0.34390 (19)	0.71556 (18)	0.0195 (6)
H12	0.4273	0.3382	0.7065	0.023*
C13	0.6090 (3)	0.3342 (2)	0.80404 (18)	0.0201 (6)
H13	0.5800	0.3203	0.8545	0.024*
C14	0.7421 (3)	0.34526 (19)	0.81732 (17)	0.0199 (6)
C15	0.7843 (3)	0.3655 (2)	0.74336 (18)	0.0208 (6)
H15	0.8753	0.3754	0.7531	0.025*

C16	0.6935 (3)	0.3714 (2)	0.65562 (18)	0.0200 (6)
H16	0.7232	0.3822	0.6050	0.024*
C17	0.7997 (3)	0.3123 (2)	0.97884 (18)	0.0289 (7)
H17A	0.7433	0.2501	0.9652	0.043*
H17B	0.7506	0.3716	0.9911	0.043*
H17C	0.8775	0.2989	1.0329	0.043*
C18	0.2974 (3)	0.38963 (19)	0.15723 (18)	0.0198 (6)
C19	0.4131 (3)	0.3895 (2)	0.13582 (18)	0.0234 (6)
H19	0.4961	0.3872	0.1835	0.028*
C20	0.4069 (3)	0.3928 (2)	0.04512 (19)	0.0270 (7)
H20	0.4851	0.3907	0.0298	0.032*
C21	0.2842 (3)	0.3992 (2)	-0.02354 (18)	0.0272 (7)
C22	0.1682 (3)	0.4025 (2)	-0.0033 (2)	0.0294 (7)
H22	0.0853	0.4075	-0.0508	0.035*
C23	0.1765 (3)	0.3983 (2)	0.08831 (19)	0.0250 (6)
H23	0.0984	0.4014	0.1037	0.030*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Br1	0.0599 (3)	0.0551 (2)	0.01949 (15)	0.01172 (18)	0.01531 (15)	0.00843 (14)
O1	0.0173 (10)	0.0258 (10)	0.0236 (10)	-0.0033 (8)	0.0110 (8)	-0.0072 (8)
O2	0.0192 (11)	0.0302 (11)	0.0220 (10)	-0.0016 (8)	0.0025 (8)	0.0041 (8)
N1	0.0171 (12)	0.0223 (12)	0.0187 (11)	0.0021 (10)	0.0073 (10)	0.0012 (9)
N2	0.0197 (13)	0.0231 (12)	0.0192 (11)	0.0024 (9)	0.0116 (10)	0.0030 (9)
N3	0.0207 (13)	0.0200 (11)	0.0223 (11)	0.0010 (9)	0.0098 (10)	0.0001 (9)
N4	0.0229 (13)	0.0228 (12)	0.0212 (11)	-0.0008 (9)	0.0105 (10)	-0.0023 (9)
C1	0.0159 (14)	0.0201 (13)	0.0200 (13)	0.0009 (10)	0.0103 (11)	-0.0004 (10)
C2	0.0165 (14)	0.0168 (12)	0.0180 (12)	-0.0010 (10)	0.0096 (11)	0.0015 (9)
C3	0.0200 (14)	0.0182 (13)	0.0170 (12)	0.0008 (11)	0.0089 (11)	0.0011 (10)
C4	0.0156 (14)	0.0189 (13)	0.0157 (12)	0.0033 (10)	0.0068 (11)	0.0025 (9)
C5	0.0158 (14)	0.0244 (14)	0.0180 (12)	-0.0027 (11)	0.0062 (11)	0.0012 (10)
C6	0.0177 (14)	0.0189 (13)	0.0167 (12)	-0.0004 (10)	0.0062 (11)	-0.0008 (9)
C7	0.0159 (14)	0.0224 (14)	0.0162 (12)	0.0029 (11)	0.0080 (11)	0.0024 (10)
C8	0.0159 (14)	0.0224 (14)	0.0235 (13)	-0.0059 (10)	0.0080 (11)	-0.0009 (10)
C9	0.0214 (15)	0.0171 (14)	0.0204 (13)	0.0001 (10)	0.0095 (12)	-0.0023 (10)
C10	0.0271 (18)	0.0387 (18)	0.0361 (18)	-0.0066 (14)	0.0181 (15)	-0.0197 (14)
C11	0.0213 (15)	0.0138 (12)	0.0204 (13)	0.0017 (10)	0.0108 (11)	0.0014 (10)
C12	0.0167 (14)	0.0206 (14)	0.0228 (13)	0.0000 (11)	0.0087 (11)	0.0022 (10)
C13	0.0216 (15)	0.0205 (14)	0.0200 (13)	0.0005 (11)	0.0094 (12)	0.0015 (10)
C14	0.0197 (15)	0.0154 (13)	0.0210 (13)	-0.0009 (10)	0.0021 (11)	0.0008 (10)
C15	0.0176 (15)	0.0185 (13)	0.0289 (14)	0.0020 (11)	0.0112 (12)	0.0030 (11)
C16	0.0179 (15)	0.0199 (13)	0.0251 (14)	0.0019 (11)	0.0112 (12)	0.0025 (10)
C17	0.0272 (17)	0.0354 (17)	0.0201 (14)	-0.0006 (13)	0.0027 (13)	0.0011 (12)
C18	0.0239 (16)	0.0168 (13)	0.0215 (13)	-0.0027 (11)	0.0113 (12)	0.0003 (10)
C19	0.0246 (16)	0.0261 (15)	0.0205 (13)	0.0041 (12)	0.0087 (12)	0.0030 (11)
C20	0.0264 (17)	0.0315 (16)	0.0271 (15)	0.0039 (13)	0.0141 (13)	0.0044 (12)
C21	0.0401 (19)	0.0242 (15)	0.0184 (13)	0.0012 (13)	0.0113 (13)	0.0024 (11)

C22	0.0322 (18)	0.0274 (16)	0.0235 (14)	-0.0054 (13)	0.0028 (13)	-0.0007 (12)
C23	0.0203 (15)	0.0297 (16)	0.0245 (14)	-0.0048 (12)	0.0069 (12)	-0.0008 (12)

Geometric parameters (Å, °)

Br1—C21	1.897 (3)	C10—H10A	0.9800
O1—C7	1.382 (3)	C10—H10B	0.9800
O1—C10	1.435 (3)	C10—H10C	0.9800
O2—C14	1.381 (3)	C11—C12	1.390 (4)
O2—C17	1.435 (3)	C11—C16	1.400 (4)
N1—C1	1.360 (3)	C12—C13	1.393 (4)
N1—C3	1.372 (3)	C12—H12	0.9500
N1—H1	0.80 (3)	C13—C14	1.387 (4)
N2—C1	1.326 (3)	C13—H13	0.9500
N2—C2	1.375 (3)	C14—C15	1.389 (4)
N3—N4	1.274 (3)	C15—C16	1.382 (4)
N3—C1	1.392 (3)	C15—H15	0.9500
N4—C18	1.427 (3)	C16—H16	0.9500
C2—C3	1.388 (4)	C17—H17A	0.9800
C2—C11	1.477 (4)	C17—H17B	0.9800
C3—C4	1.474 (4)	C17—H17C	0.9800
C4—C5	1.390 (3)	C18—C23	1.383 (4)
C4—C9	1.397 (4)	C18—C19	1.393 (4)
C5—C6	1.392 (4)	C19—C20	1.382 (4)
C5—H5	0.9500	C19—H19	0.9500
C6—C7	1.379 (4)	C20—C21	1.392 (4)
C6—H6	0.9500	C20—H20	0.9500
C7—C8	1.399 (3)	C21—C22	1.388 (5)
C8—C9	1.384 (4)	C22—C23	1.389 (4)
C8—H8	0.9500	C22—H22	0.9500
C9—H9	0.9500	C23—H23	0.9500
C7—O1—C10	115.6 (2)	C12—C11—C2	122.6 (2)
C14—O2—C17	116.8 (2)	C16—C11—C2	119.6 (2)
C1—N1—C3	107.6 (2)	C11—C12—C13	121.8 (3)
C1—N1—H1	125 (2)	C11—C12—H12	119.1
C3—N1—H1	127 (2)	C13—C12—H12	119.1
C1—N2—C2	105.0 (2)	C14—C13—C12	119.0 (2)
N4—N3—C1	113.0 (2)	C14—C13—H13	120.5
N3—N4—C18	113.9 (2)	C12—C13—H13	120.5
N2—C1—N1	111.8 (2)	O2—C14—C13	123.9 (2)
N2—C1—N3	121.8 (2)	O2—C14—C15	115.7 (2)
N1—C1—N3	126.2 (2)	C13—C14—C15	120.4 (2)
N2—C2—C3	110.5 (2)	C16—C15—C14	119.9 (3)
N2—C2—C11	120.5 (2)	C16—C15—H15	120.1
C3—C2—C11	129.1 (2)	C14—C15—H15	120.1
N1—C3—C2	105.0 (2)	C15—C16—C11	121.1 (2)
N1—C3—C4	121.1 (2)	C15—C16—H16	119.4

C2—C3—C4	133.5 (2)	C11—C16—H16	119.4
C5—C4—C9	118.6 (2)	O2—C17—H17A	109.5
C5—C4—C3	118.6 (2)	O2—C17—H17B	109.5
C9—C4—C3	122.8 (2)	H17A—C17—H17B	109.5
C4—C5—C6	121.2 (3)	O2—C17—H17C	109.5
C4—C5—H5	119.4	H17A—C17—H17C	109.5
C6—C5—H5	119.4	H17B—C17—H17C	109.5
C7—C6—C5	119.6 (2)	C23—C18—C19	120.3 (2)
C7—C6—H6	120.2	C23—C18—N4	115.2 (2)
C5—C6—H6	120.2	C19—C18—N4	124.4 (2)
C6—C7—O1	124.0 (2)	C20—C19—C18	119.9 (3)
C6—C7—C8	120.1 (2)	C20—C19—H19	120.0
O1—C7—C8	115.9 (2)	C18—C19—H19	120.0
C9—C8—C7	119.8 (2)	C19—C20—C21	119.0 (3)
C9—C8—H8	120.1	C19—C20—H20	120.5
C7—C8—H8	120.1	C21—C20—H20	120.5
C8—C9—C4	120.8 (2)	C22—C21—C20	121.8 (3)
C8—C9—H9	119.6	C22—C21—Br1	118.8 (2)
C4—C9—H9	119.6	C20—C21—Br1	119.4 (2)
O1—C10—H10A	109.5	C21—C22—C23	118.3 (3)
O1—C10—H10B	109.5	C21—C22—H22	120.8
H10A—C10—H10B	109.5	C23—C22—H22	120.8
O1—C10—H10C	109.5	C18—C23—C22	120.6 (3)
H10A—C10—H10C	109.5	C18—C23—H23	119.7
H10B—C10—H10C	109.5	C22—C23—H23	119.7
C12—C11—C16	117.8 (2)		
C1—N3—N4—C18	177.1 (2)	C3—C4—C9—C8	-176.7 (2)
C2—N2—C1—N1	-1.7 (3)	N2—C2—C11—C12	-158.2 (2)
C2—N2—C1—N3	173.7 (2)	C3—C2—C11—C12	22.9 (4)
C3—N1—C1—N2	2.4 (3)	N2—C2—C11—C16	21.6 (3)
C3—N1—C1—N3	-172.7 (2)	C3—C2—C11—C16	-157.2 (3)
N4—N3—C1—N2	180.0 (2)	C16—C11—C12—C13	-1.1 (4)
N4—N3—C1—N1	-5.3 (4)	C2—C11—C12—C13	178.8 (2)
C1—N2—C2—C3	0.4 (3)	C11—C12—C13—C14	1.7 (4)
C1—N2—C2—C11	-178.7 (2)	C17—O2—C14—C13	0.8 (4)
C1—N1—C3—C2	-2.0 (3)	C17—O2—C14—C15	-178.4 (2)
C1—N1—C3—C4	171.9 (2)	C12—C13—C14—O2	-179.2 (2)
N2—C2—C3—N1	1.0 (3)	C12—C13—C14—C15	-0.1 (4)
C11—C2—C3—N1	180.0 (2)	O2—C14—C15—C16	177.1 (2)
N2—C2—C3—C4	-171.7 (3)	C13—C14—C15—C16	-2.1 (4)
C11—C2—C3—C4	7.2 (5)	C14—C15—C16—C11	2.7 (4)
N1—C3—C4—C5	-115.9 (3)	C12—C11—C16—C15	-1.2 (4)
C2—C3—C4—C5	55.9 (4)	C2—C11—C16—C15	179.0 (2)
N1—C3—C4—C9	61.2 (3)	N3—N4—C18—C23	174.5 (2)
C2—C3—C4—C9	-127.0 (3)	N3—N4—C18—C19	-7.5 (4)
C9—C4—C5—C6	-0.6 (4)	C23—C18—C19—C20	-3.2 (4)
C3—C4—C5—C6	176.6 (2)	N4—C18—C19—C20	178.9 (2)

C4—C5—C6—C7	0.2 (4)	C18—C19—C20—C21	1.8 (4)
C5—C6—C7—O1	-178.9 (2)	C19—C20—C21—C22	0.1 (4)
C5—C6—C7—C8	0.4 (4)	C19—C20—C21—Br1	178.5 (2)
C10—O1—C7—C6	2.6 (4)	C20—C21—C22—C23	-0.6 (4)
C10—O1—C7—C8	-176.7 (2)	Br1—C21—C22—C23	-179.0 (2)
C6—C7—C8—C9	-0.6 (4)	C19—C18—C23—C22	2.8 (4)
O1—C7—C8—C9	178.7 (2)	N4—C18—C23—C22	-179.2 (2)
C7—C8—C9—C4	0.1 (4)	C21—C22—C23—C18	-0.8 (4)
C5—C4—C9—C8	0.4 (4)		

Hydrogen-bond geometry (Å, °)

<i>D</i> —H... <i>A</i>	<i>D</i> —H	H... <i>A</i>	<i>D</i> ... <i>A</i>	<i>D</i> —H... <i>A</i>
N1—H1...O1 ⁱ	0.80 (3)	2.17 (3)	2.963 (3)	169 (3)

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