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4-Aza-1-azoniabicyclo[2.2.2]octane eosinide

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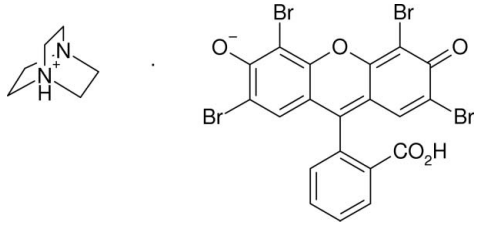
Key indicators: single-crystal X-ray study; T = 120 K; mean σ(C–C) = 0.015 Å; R factor = 0.096; wR factor = 0.149; data-to-parameter ratio = 17.2.

The title compound, $C_6H_{13}N_2^+\cdot C_{20}H_7Br_4O_5^-$, is a molecular salt of singly protonated 1,4-diazabicyclo[2.2.2]octane and the eosinide monoanion. Contrary to a handful of previous crystal structures which contain eosin in its dianionic form, here, the carboxyl group of the anion has retained its H atom. The dihedral angle between the triple ring system and the pendant benzene ring in the anion is 86.0 (2)°. In the crystal structure, the components interact by way of a bifurcated N—H···(O,Br) hydrogen bond linking cation and anion, and an O—H···O hydrogen bond which links the anions into infinite chains propagating in [001].

Related literature

For background, see: Willner *et al.* (1992); García-Granda *et al.* (1993); Jones (1997); Todd & Harrison (2007).



Experimental

Crystal data

$C_6H_{13}N_2^+\cdot C_{20}H_7Br_4O_5^-$
M_r = 760.08
Monoclinic, $P2_1/c$
a = 13.4675 (8) Å
b = 12.3257 (7) Å
c = 16.2266 (6) Å
β = 111.771 (3)°
V = 2501.4 (2) Å^3
Z = 4
Mo $K\alpha$ radiation
μ = 6.48 mm^{-1}
T = 120 (2) K
0.08 × 0.05 × 0.01 mm

Data collection

Nonius KappaCCD area-detector diffractometer
Absorption correction: multi-scan (*SADABS*; Bruker, 2003)
T_{min} = 0.625, T_{max} = 0.938
28164 measured reflections
5734 independent reflections
3468 reflections with $I > 2\sigma(I)$
R_{int} = 0.113

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.096
$wR(F^2)$ = 0.149
S = 1.36
5734 reflections
334 parameters
18 restraints
H-atom parameters constrained
$\Delta\rho_{max}$ = 1.04 e Å^{-3}
$\Delta\rho_{min}$ = −1.11 e Å^{-3}

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

D—H···A	D—H	H···A	D···A	D—H···A
N1—H1···O2	0.93	1.78	2.647 (10)	153
N1—H1···Br3	0.93	2.82	3.455 (8)	127
O5—H2···O1^{i}	0.85	1.90	2.748 (9)	177

Symmetry code: (i) $x, -y+\frac{3}{2}, z-\frac{1}{2}$.

Data collection: *COLLECT* (Nonius, 1998); cell refinement: *SCALEPACK* (Otwinowski & Minor, 1997); data reduction: *SCALEPACK* and *DENZO* (Otwinowski & Minor, 1997), and *SORTAV* (Blessing, 1995); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEP-3* (Farrugia, 1997); software used to prepare material for publication: *SHELXL97*.

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: LH2486).

References

Blessing, R. H. (1995). *Acta Cryst.* A**51**, 33–38.
Bruker (2003). *SADABS*. Bruker AXS Inc., Madison, Wisconsin, USA.
Farrugia, L. J. (1997). *J. Appl. Cryst.* **30**, 565.
García-Granda, S., Díaz, M. R., Gómez-Beltrán, F. & Blanco-Gomís, D. (1993). *Acta Cryst.* C**49**, 884–886.
Jones, W. (1997). *Organic Molecular Solids: Properties and Applications*, edited by W. Jones, p. 177. New York: CRC Press.
Nonius (1998). *COLLECT*. Nonius BV, Delft, The Netherlands.
Otwinowski, Z. & Minor, W. (1997). *Methods in Enzymology*, Vol. 276, *Macromolecular Crystallography*, Part A, edited by C. W. Carter Jr & R. M. Sweet, pp. 307–326. New York: Academic Press.
Sheldrick, G. M. (1997). *SHELXS97* and *SHELXL97*. University of Göttingen, Germany.
Todd, M. J. & Harrison, W. T. A. (2007). *Acta Cryst.* E**63**, m945–m947.
Willner, I., Eichen, Y., Rabinovitz, M., Hoffman, R. & Cohen, S. (1992). *J. Am. Chem. Soc.* **114**, 637–000.

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supplementary materials

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4-Aza-1-azoniabicyclo[2.2.2]octane eosinide

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Comment

The title molecular-salt arose from our synthetic and structural studies of organic supramolecular networks (Jones, 1997).

The compound contains 4-aza-1-azoniabicyclo[2.2.2]octane ($C_6H_{13}N_2^+$) monocations and eosinide ($C_{20}H_7Br_4O_5^-$) monoanions. The eosin proton has been lost from the phenol group of the triple ring system (either O1 or O2). When deprotonated, resonance forms can be drawn which delocalize the charge and make these two O atoms equvalent, hence their equal (within experimental error) C—O bond lengths [C3—O1 = 1.266 (11) Å, C11—O2 = 1.256 (10) Å] in the crystal of (I).

Contrary to previous crystal structures containing the $C_{20}H_6Br_4O_5^{2-}$ eosin dianion (Willner *et al.*, 1992; García-Granda *et al.*, 1993), the C20/O4/O5 carboxylic acid group has retained its proton, as indicated by the strong contrast between the single [C20—O5 = 1.322 (11) Å] and double [C20—O4 = 1.201 (11) Å] bonds and the formation of an O—H···O hydrogen bond (see below). The dihedral angle between the mean planes of the triple ring system and the pendant C14–C19 benzene ring is 86.0 (2)°, indicating that they are almost perpendicular. Conversely, the C20/O4/O5 group is almost co-planar with its benzene ring [dihedral angle = 4.6 (17)°]. The $C_6H_{13}N_2^+$ cation in displays unexceptional geometrical parameters (Todd & Harrison, 2007).

The component species in are linked together by hydrogen bonds. The cation forms a bifurcated N—H···(O,Br) hydrogen bond to one side of the eosin triple ring system (bond-angle sum for H1 = 359°). Then, anions are linked into [001] chains by way of an inter-anion O—H···O link (Fig. 2) to the O atom at the other side of the fused ring. There are no significant π–π stacking interactions, as the closest separation of aromatic ring centoids is greater than 4.1 Å.

Experimental

Equimolar quantities of eosin and 1,4-diazoniabicyclo[2.2.2]octane (also known as DABCO) were each dissolved in a mixture of acetone and ethanol (2:1 *v*/*v*). The two solutions were mixed and allowed to stand at room temperature and very dark, fragile, rods of the title compound formed after four days. When smeared onto a glass slide, an orange colour was apparent.

Refinement

The tiny crystal used for data collection was a weak scatterer, which may correlate with the rather high residuals. Atoms C1, C3 and C10 gave highly aniostropic displacements and their U^{ij} values were restrained to approximate to isotropic behaviour.

The O-bound H was located in a difference map and refined as riding in its as-found relative position. The other hydrogen atoms were geometrically placed (N—H = 0.93 Å, C—H = 0.93–0.99 Å) and refined as riding. The constraint U_{iso}(H) = 1.2U_{eq}(carrier) was applied in all cases.

Figures

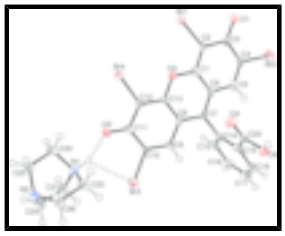

Fig. 1. View of the molecular structure showing 50% displacement ellipsoids and arbitrary spheres for the H atoms. The bifurcated N—H···(O,Br) hydrogen bond is indicated by double dashed lines.

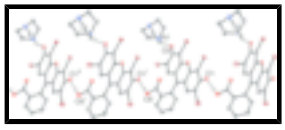

Fig. 2. Part of a [001] chain with hydrogen bonds shown as double-dashed lines and the C-bound H atoms omitted for clarity. Symmetry codes: (i) *x*, 3/2 − *y*, *z* − 1/2; (ii) *x*, *y*, *z* − 1.

4-Aza-1-azoniabicyclo[2.2.2]octane eosinide

Crystal data

$C_6H_{13}N_2^+ \cdot C_{20}H_7Br_4O_5^-$	F_{000} = 1480
M_r = 760.08	D_x = 2.018 Mg m^{-3}
Monoclinic, $P2_1/c$	Mo $K\alpha$ radiation λ = 0.70173 Å
Hall symbol: -P 2ybc	Cell parameters from 5684 reflections
a = 13.4675 (8) Å	θ = 2.9–27.5º
b = 12.3257 (7) Å	μ = 6.48 mm^{-1}
c = 16.2266 (6) Å	T = 120 (2) K
β = 111.771 (3)º	Shard, orange
V = 2501.4 (2) Å^3	0.08 × 0.05 × 0.01 mm
Z = 4	

Data collection

Nonius KappaCCD area-detector diffractometer	5734 independent reflections
Radiation source: fine-focus sealed tube	3468 reflections with $I > 2\sigma(I)$
Monochromator: graphite	R_{int} = 0.113
T = 120(2) K	θ_{max} = 27.3º
ω and φ scans	θ_{min} = 2.9º
Absorption correction: multi-scan (SADABS; Bruker, 2003)	h = −17→17
T_{min} = 0.625, T_{max} = 0.938	k = −15→15
28164 measured reflections	l = −21→21

Refinement

Refinement on F^2	Secondary atom site location: difference Fourier map
Least-squares matrix: full	Hydrogen site location: difmap and geom
$R[F^2 > 2\sigma(F^2)]$ = 0.096	H-atom parameters constrained

$wR(F^2) = 0.149$	$w = 1/[\sigma^2(F_o^2) + 19.6202P]$ where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.36$	$(\Delta/\sigma)_{max} = 0.001$
5734 reflections	$\Delta\rho_{max} = 1.04$ e Å^{-3}
334 parameters	$\Delta\rho_{min} = -1.11$ e Å^{-3}
18 restraints	Extinction correction: none
Primary atom site location: structure-invariant direct methods	

Special details

Geometry. All e.s.d.'s (except the e.s.d. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell e.s.d.'s are taken into account individually in the estimation of e.s.d.'s in distances, angles and torsion angles; correlations between e.s.d.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell e.s.d.'s is used for estimating e.s.d.'s involving l.s. planes.

Refinement. Refinement of F^2 against ALL reflections. The weighted *R*-factor *wR* and goodness of fit S are based on F^2, conventional *R*-factors *R* are based on F, with F set to zero for negative F^2. The threshold expression of $F^2 > 2\text{sigma}(F^2)$ 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}
C1	0.2077 (7)	0.5378 (7)	0.4770 (6)	0.016 (2)
C2	0.2177 (7)	0.6283 (8)	0.5314 (6)	0.018 (2)
C3	0.1308 (8)	0.7015 (8)	0.5185 (6)	0.021 (2)
C4	0.0304 (8)	0.6698 (8)	0.4494 (6)	0.024 (2)
C5	0.0208 (8)	0.5828 (8)	0.3963 (6)	0.022 (2)
H5	−0.0465	0.5676	0.3510	0.027*
C6	0.1091 (8)	0.5134 (8)	0.4066 (6)	0.021 (2)
C7	0.1050 (8)	0.4252 (8)	0.3511 (6)	0.019 (2)
C8	0.1947 (7)	0.3599 (8)	0.3689 (6)	0.019 (2)
C9	0.1963 (8)	0.2659 (7)	0.3188 (6)	0.021 (2)
H9	0.1337	0.2463	0.2699	0.025*
C10	0.2849 (8)	0.2036 (7)	0.3391 (6)	0.019 (2)
C11	0.3837 (8)	0.2254 (7)	0.4122 (6)	0.018 (2)
C12	0.3815 (8)	0.3230 (7)	0.4605 (6)	0.021 (2)
C13	0.2907 (8)	0.3859 (8)	0.4410 (6)	0.021 (2)
C14	0.0028 (7)	0.3984 (8)	0.2759 (6)	0.022 (2)
C15	−0.0648 (8)	0.3250 (8)	0.2928 (6)	0.022 (2)
H15	−0.0447	0.2941	0.3503	0.027*
C16	−0.1609 (8)	0.2956 (9)	0.2279 (7)	0.031 (3)
H16	−0.2071	0.2461	0.2409	0.037*
C17	−0.1891 (8)	0.3390 (9)	0.1436 (7)	0.029 (2)
H17	−0.2544	0.3185	0.0980	0.034*
C18	−0.1215 (8)	0.4125 (8)	0.1261 (7)	0.028 (2)
H18	−0.1416	0.4421	0.0681	0.033*

C19	−0.0257 (8)	0.4442 (8)	0.1906 (6)	0.024 (2)
C20	0.0451 (8)	0.5252 (8)	0.1720 (6)	0.021 (2)
O1	0.1412 (5)	0.7877 (5)	0.5633 (4)	0.0225 (15)
O2	0.4645 (5)	0.1652 (5)	0.4323 (4)	0.0216 (15)
O3	0.2952 (5)	0.4734 (5)	0.4927 (4)	0.0206 (15)
O4	0.1318 (5)	0.5485 (6)	0.2249 (4)	0.0296 (17)
O5	0.0031 (5)	0.5656 (6)	0.0909 (4)	0.0315 (18)
H2	0.0458	0.6093	0.0805	0.038*
Br1	0.34956 (8)	0.65689 (8)	0.62238 (6)	0.0270 (3)
Br2	−0.09106 (9)	0.75531 (9)	0.43160 (7)	0.0365 (3)
Br3	0.28147 (9)	0.08005 (9)	0.26922 (7)	0.0344 (3)
Br4	0.50931 (8)	0.36284 (8)	0.55491 (6)	0.0238 (2)
N1	0.5498 (6)	0.0147 (7)	0.3626 (5)	0.0227 (19)
H1	0.5004	0.0584	0.3745	0.027*
N2	0.6838 (7)	−0.1054 (7)	0.3322 (5)	0.028 (2)
C21	0.5153 (8)	−0.1002 (8)	0.3589 (6)	0.022 (2)
H21A	0.4448	−0.1103	0.3107	0.026*
H21B	0.5092	−0.1212	0.4157	0.026*
C22	0.6572 (8)	0.0274 (8)	0.4362 (6)	0.026 (2)
H22A	0.6535	0.0043	0.4934	0.031*
H22B	0.6801	0.1043	0.4415	0.031*
C23	0.5557 (9)	0.0482 (8)	0.2767 (6)	0.028 (2)
H23A	0.5816	0.1239	0.2802	0.033*
H23B	0.4844	0.0434	0.2285	0.033*
C24	0.6000 (10)	−0.1709 (9)	0.3418 (7)	0.039 (3)
H24A	0.6314	−0.2220	0.3918	0.047*
H24B	0.5654	−0.2140	0.2871	0.047*
C25	0.7368 (8)	−0.0440 (9)	0.4131 (7)	0.032 (3)
H25A	0.7928	0.0024	0.4055	0.039*
H25B	0.7721	−0.0948	0.4626	0.039*
C26	0.6349 (9)	−0.0305 (9)	0.2588 (7)	0.033 (3)
H26A	0.5966	−0.0724	0.2042	0.039*
H26B	0.6918	0.0120	0.2487	0.039*

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
C1	0.022 (5)	0.015 (4)	0.018 (4)	−0.002 (4)	0.014 (4)	0.005 (4)
C2	0.013 (5)	0.023 (5)	0.015 (5)	0.008 (4)	0.002 (4)	0.009 (4)
C3	0.027 (6)	0.019 (5)	0.015 (5)	0.005 (4)	0.006 (4)	0.014 (4)
C4	0.021 (5)	0.026 (6)	0.023 (5)	0.012 (4)	0.005 (4)	0.000 (4)
C5	0.018 (5)	0.024 (6)	0.024 (5)	0.008 (4)	0.007 (4)	0.012 (4)
C6	0.022 (5)	0.018 (5)	0.023 (5)	0.004 (4)	0.008 (4)	0.001 (4)
C7	0.025 (5)	0.017 (5)	0.010 (5)	0.001 (4)	0.001 (4)	0.004 (4)
C8	0.017 (5)	0.025 (6)	0.016 (5)	0.001 (4)	0.005 (4)	0.001 (4)
C9	0.030 (6)	0.015 (5)	0.015 (5)	0.001 (4)	0.004 (4)	0.001 (4)
C10	0.027 (5)	0.018 (5)	0.009 (4)	0.002 (4)	0.005 (4)	−0.006 (3)
C11	0.023 (5)	0.019 (5)	0.018 (5)	−0.002 (4)	0.016 (4)	0.000 (4)

C12	0.029 (6)	0.012 (5)	0.019 (5)	0.003 (4)	0.006 (4)	−0.002 (4)
C13	0.027 (6)	0.019 (5)	0.016 (5)	−0.005 (4)	0.008 (4)	−0.007 (4)
C14	0.019 (5)	0.023 (6)	0.026 (6)	0.007 (4)	0.012 (4)	−0.002 (4)
C15	0.024 (6)	0.017 (5)	0.026 (5)	0.003 (4)	0.010 (4)	0.004 (4)
C16	0.030 (6)	0.025 (6)	0.045 (7)	−0.010 (5)	0.023 (5)	−0.007 (5)
C17	0.018 (5)	0.035 (6)	0.029 (6)	−0.013 (5)	0.004 (4)	−0.009 (5)
C18	0.027 (6)	0.021 (5)	0.032 (6)	0.001 (5)	0.006 (5)	0.001 (5)
C19	0.025 (6)	0.023 (6)	0.028 (6)	0.002 (4)	0.013 (5)	−0.002 (4)
C20	0.025 (6)	0.018 (5)	0.019 (5)	0.001 (4)	0.008 (4)	0.001 (4)
O1	0.023 (4)	0.018 (4)	0.028 (4)	0.004 (3)	0.012 (3)	0.002 (3)
O2	0.021 (4)	0.020 (4)	0.026 (4)	0.008 (3)	0.011 (3)	−0.001 (3)
O3	0.023 (4)	0.025 (4)	0.013 (3)	0.007 (3)	0.006 (3)	0.001 (3)
O4	0.021 (4)	0.037 (5)	0.030 (4)	−0.008 (3)	0.008 (3)	−0.001 (3)
O5	0.027 (4)	0.037 (5)	0.027 (4)	−0.009 (3)	0.005 (3)	0.006 (3)
Br1	0.0270 (6)	0.0228 (6)	0.0250 (5)	0.0056 (5)	0.0026 (4)	−0.0046 (4)
Br2	0.0321 (6)	0.0345 (7)	0.0409 (7)	0.0097 (5)	0.0115 (5)	−0.0064 (5)
Br3	0.0304 (6)	0.0299 (6)	0.0374 (6)	0.0042 (5)	0.0063 (5)	−0.0100 (5)
Br4	0.0217 (5)	0.0220 (5)	0.0241 (5)	0.0031 (4)	0.0042 (4)	−0.0020 (4)
N1	0.020 (5)	0.025 (5)	0.020 (4)	0.001 (4)	0.004 (4)	0.002 (3)
N2	0.034 (5)	0.022 (5)	0.027 (5)	0.003 (4)	0.011 (4)	−0.002 (4)
C21	0.025 (6)	0.023 (6)	0.019 (5)	−0.002 (4)	0.010 (4)	0.000 (4)
C22	0.031 (6)	0.018 (5)	0.030 (6)	−0.005 (5)	0.013 (5)	−0.004 (4)
C23	0.041 (7)	0.020 (6)	0.030 (6)	0.002 (5)	0.022 (5)	0.002 (4)
C24	0.055 (8)	0.019 (6)	0.042 (7)	0.007 (6)	0.017 (6)	−0.005 (5)
C25	0.026 (6)	0.035 (7)	0.034 (6)	0.013 (5)	0.010 (5)	−0.003 (5)
C26	0.031 (6)	0.037 (7)	0.032 (6)	0.001 (5)	0.016 (5)	−0.004 (5)

Geometric parameters (Å, °)

C1—O3	1.364 (10)	C17—C18	1.387 (13)
C1—C2	1.398 (13)	C17—H17	0.9500
C1—C6	1.426 (13)	C18—C19	1.382 (13)
C2—C3	1.429 (13)	C18—H18	0.9500
C2—Br1	1.874 (9)	C19—C20	1.486 (13)
C3—O1	1.266 (11)	C20—O4	1.201 (11)
C3—C4	1.454 (13)	C20—O5	1.322 (11)
C4—C5	1.352 (13)	O5—H2	0.8497
C4—Br2	1.876 (9)	N1—C21	1.485 (12)
C5—C6	1.423 (13)	N1—C23	1.485 (12)
C5—H5	0.9500	N1—C22	1.504 (12)
C6—C7	1.401 (13)	N1—H1	0.9300
C7—C8	1.389 (13)	N2—C24	1.441 (14)
C7—C14	1.500 (12)	N2—C25	1.453 (12)
C8—C9	1.421 (13)	N2—C26	1.457 (13)
C8—C13	1.422 (12)	C21—C24	1.540 (14)
C9—C10	1.352 (13)	C21—H21A	0.9900
C9—H9	0.9500	C21—H21B	0.9900
C10—C11	1.442 (12)	C22—C25	1.538 (13)
C10—Br3	1.889 (9)	C22—H22A	0.9900

C11—O2	1.256 (10)	C22—H22B	0.9900
C11—C12	1.442 (12)	C23—C26	1.547 (14)
C12—C13	1.382 (13)	C23—H23A	0.9900
C12—Br4	1.896 (9)	C23—H23B	0.9900
C13—O3	1.354 (10)	C24—H24A	0.9900
C14—C15	1.381 (13)	C24—H24B	0.9900
C14—C19	1.410 (13)	C25—H25A	0.9900
C15—C16	1.380 (13)	C25—H25B	0.9900
C15—H15	0.9500	C26—H26A	0.9900
C16—C17	1.384 (14)	C26—H26B	0.9900
C16—H16	0.9500		
O3—C1—C2	118.2 (8)	C18—C19—C14	117.8 (9)
O3—C1—C6	120.7 (8)	C18—C19—C20	121.7 (9)
C2—C1—C6	121.1 (8)	C14—C19—C20	120.5 (9)
C1—C2—C3	121.9 (8)	O4—C20—O5	124.4 (9)
C1—C2—Br1	119.2 (7)	O4—C20—C19	122.9 (9)
C3—C2—Br1	118.8 (7)	O5—C20—C19	112.6 (8)
O1—C3—C2	122.3 (9)	C13—O3—C1	120.7 (7)
O1—C3—C4	122.8 (9)	C20—O5—H2	111.4
C2—C3—C4	114.9 (9)	C21—N1—C23	110.7 (7)
C5—C4—C3	123.1 (9)	C21—N1—C22	109.0 (7)
C5—C4—Br2	118.4 (7)	C23—N1—C22	110.2 (8)
C3—C4—Br2	118.5 (7)	C21—N1—H1	109.0
C4—C5—C6	121.6 (9)	C23—N1—H1	109.0
C4—C5—H5	119.2	C22—N1—H1	109.0
C6—C5—H5	119.2	C24—N2—C25	109.7 (8)
C7—C6—C5	124.0 (9)	C24—N2—C26	108.0 (8)
C7—C6—C1	118.7 (9)	C25—N2—C26	109.3 (8)
C5—C6—C1	117.2 (9)	N1—C21—C24	107.8 (8)
C8—C7—C6	119.5 (8)	N1—C21—H21A	110.2
C8—C7—C14	120.4 (8)	C24—C21—H21A	110.2
C6—C7—C14	120.0 (8)	N1—C21—H21B	110.2
C7—C8—C9	123.4 (8)	C24—C21—H21B	110.2
C7—C8—C13	119.8 (9)	H21A—C21—H21B	108.5
C9—C8—C13	116.9 (9)	N1—C22—C25	107.4 (8)
C10—C9—C8	121.5 (9)	N1—C22—H22A	110.2
C10—C9—H9	119.2	C25—C22—H22A	110.2
C8—C9—H9	119.2	N1—C22—H22B	110.2
C9—C10—C11	123.8 (8)	C25—C22—H22B	110.2
C9—C10—Br3	119.2 (7)	H22A—C22—H22B	108.5
C11—C10—Br3	117.0 (7)	N1—C23—C26	106.4 (8)
O2—C11—C10	123.4 (8)	N1—C23—H23A	110.4
O2—C11—C12	122.8 (8)	C26—C23—H23A	110.4
C10—C11—C12	113.9 (8)	N1—C23—H23B	110.4
C13—C12—C11	122.5 (8)	C26—C23—H23B	110.4
C13—C12—Br4	120.0 (7)	H23A—C23—H23B	108.6
C11—C12—Br4	117.4 (7)	N2—C24—C21	111.4 (8)
O3—C13—C12	118.2 (8)	N2—C24—H24A	109.3
O3—C13—C8	120.4 (8)	C21—C24—H24A	109.3

C12—C13—C8	121.3 (8)	N2—C24—H24B	109.3
C15—C14—C19	119.9 (9)	C21—C24—H24B	109.3
C15—C14—C7	117.2 (8)	H24A—C24—H24B	108.0
C19—C14—C7	122.9 (9)	N2—C25—C22	111.4 (8)
C16—C15—C14	121.3 (9)	N2—C25—H25A	109.3
C16—C15—H15	119.3	C22—C25—H25A	109.3
C14—C15—H15	119.3	N2—C25—H25B	109.3
C15—C16—C17	119.3 (9)	C22—C25—H25B	109.3
C15—C16—H16	120.3	H25A—C25—H25B	108.0
C17—C16—H16	120.3	N2—C26—C23	112.2 (8)
C16—C17—C18	119.6 (9)	N2—C26—H26A	109.2
C16—C17—H17	120.2	C23—C26—H26A	109.2
C18—C17—H17	120.2	N2—C26—H26B	109.2
C19—C18—C17	122.0 (9)	C23—C26—H26B	109.2
C19—C18—H18	119.0	H26A—C26—H26B	107.9
C17—C18—H18	119.0		
O3—C1—C2—C3	178.6 (8)	Br4—C12—C13—C8	178.1 (7)
C6—C1—C2—C3	−1.1 (13)	C7—C8—C13—O3	0.4 (14)
O3—C1—C2—Br1	0.1 (11)	C9—C8—C13—O3	−179.1 (8)
C6—C1—C2—Br1	−179.6 (7)	C7—C8—C13—C12	−179.8 (9)
C1—C2—C3—O1	−174.9 (8)	C9—C8—C13—C12	0.7 (14)
Br1—C2—C3—O1	3.6 (12)	C8—C7—C14—C15	85.0 (11)
C1—C2—C3—C4	4.5 (13)	C6—C7—C14—C15	−91.8 (11)
Br1—C2—C3—C4	−177.0 (7)	C8—C7—C14—C19	−94.7 (12)
O1—C3—C4—C5	174.3 (9)	C6—C7—C14—C19	88.5 (12)
C2—C3—C4—C5	−5.1 (14)	C19—C14—C15—C16	−0.5 (15)
O1—C3—C4—Br2	−4.4 (13)	C7—C14—C15—C16	179.7 (9)
C2—C3—C4—Br2	176.2 (7)	C14—C15—C16—C17	1.3 (15)
C3—C4—C5—C6	2.1 (15)	C15—C16—C17—C18	−1.1 (16)
Br2—C4—C5—C6	−179.2 (7)	C16—C17—C18—C19	0.2 (16)
C4—C5—C6—C7	−177.0 (9)	C17—C18—C19—C14	0.6 (15)
C4—C5—C6—C1	1.6 (14)	C17—C18—C19—C20	−178.4 (9)
O3—C1—C6—C7	−3.2 (13)	C15—C14—C19—C18	−0.4 (14)
C2—C1—C6—C7	176.6 (8)	C7—C14—C19—C18	179.3 (9)
O3—C1—C6—C5	178.2 (8)	C15—C14—C19—C20	178.6 (9)
C2—C1—C6—C5	−2.1 (13)	C7—C14—C19—C20	−1.7 (14)
C5—C6—C7—C8	−177.6 (9)	C18—C19—C20—O4	−174.8 (10)
C1—C6—C7—C8	3.9 (13)	C14—C19—C20—O4	6.2 (15)
C5—C6—C7—C14	−0.8 (14)	C18—C19—C20—O5	3.5 (13)
C1—C6—C7—C14	−179.3 (8)	C14—C19—C20—O5	−175.4 (8)
C6—C7—C8—C9	176.9 (9)	C12—C13—O3—C1	−179.4 (8)
C14—C7—C8—C9	0.1 (14)	C8—C13—O3—C1	0.4 (13)
C6—C7—C8—C13	−2.6 (14)	C2—C1—O3—C13	−178.7 (8)
C14—C7—C8—C13	−179.4 (8)	C6—C1—O3—C13	1.0 (12)
C7—C8—C9—C10	−179.1 (9)	C23—N1—C21—C24	61.7 (10)
C13—C8—C9—C10	0.4 (14)	C22—N1—C21—C24	−59.6 (9)
C8—C9—C10—C11	0.5 (15)	C21—N1—C22—C25	62.4 (10)
C8—C9—C10—Br3	−179.7 (7)	C23—N1—C22—C25	−59.2 (10)
C9—C10—C11—O2	177.7 (9)	C21—N1—C23—C26	−57.7 (10)

Br3—C10—C11—O2	−2.1 (12)	C22—N1—C23—C26	62.9 (10)
C9—C10—C11—C12	−2.4 (13)	C25—N2—C24—C21	60.5 (11)
Br3—C10—C11—C12	177.9 (6)	C26—N2—C24—C21	−58.4 (11)
O2—C11—C12—C13	−176.6 (9)	N1—C21—C24—N2	−1.6 (11)
C10—C11—C12—C13	3.5 (13)	C24—N2—C25—C22	−57.3 (11)
O2—C11—C12—Br4	2.6 (12)	C26—N2—C25—C22	60.8 (11)
C10—C11—C12—Br4	−177.4 (6)	N1—C22—C25—N2	−3.5 (11)
C11—C12—C13—O3	177.0 (8)	C24—N2—C26—C23	62.4 (11)
Br4—C12—C13—O3	−2.1 (12)	C25—N2—C26—C23	−56.8 (11)
C11—C12—C13—C8	−2.8 (15)	N1—C23—C26—N2	−4.2 (12)

Hydrogen-bond geometry (Å, °)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N1—H1···O2	0.93	1.78	2.647 (10)	153
N1—H1···Br3	0.93	2.82	3.455 (8)	127
O5—H2···O1^{i}	0.85	1.90	2.748 (9)	177

Symmetry codes: (i) *x*, −*y*+3/2, *z*−1/2.

Fig. 1

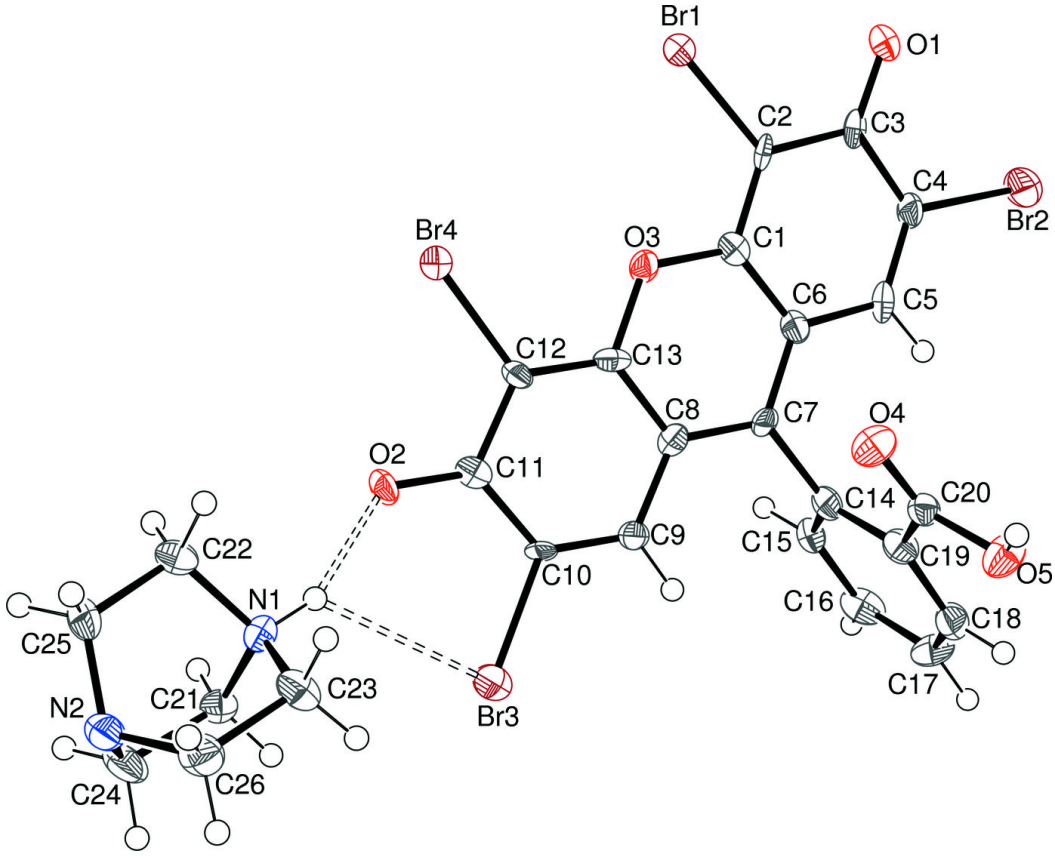
Br1
O1
C2
C3
C4
Br2
Br4
O3
C1
C6
C5
C12
C13
C8
C7
O4
O2
C11
C14
C20
C22
C9
C15
C19
O5
N1
C10
C16
C18
C25
C21
C23
Br3
C17
N2
C24
C26

Fig. 2