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(+)-(4a*R*,9a*S*)-*O*-(4-Bromobenzoyl)-*N*-(3-methylanthracen-9-ylidene)hydroxylamine

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Key indicators

Single-crystal X-ray study
T = 298 K
Mean σ(C–C) = 0.035 Å
R factor = 0.063
wR factor = 0.231
Data-to-parameter ratio = 7.6

For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

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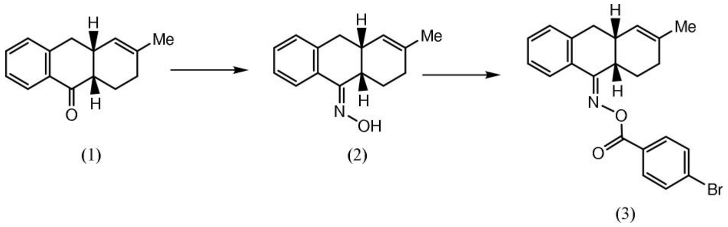
In the title compound, $C_{22}H_{20}BrNO_2$, there are two independent molecules having the same absolute configuration, although the crystal structure has a pseudo-center of symmetry. The oxime group is *anti* to the benzene ring of the 6–6–6 fused ring system.

Comment

In the research developing an entirely new asymmetric reaction, optically active 8.9-benzobicyclo[4.4.0]-2-decen-7-one, (1), is one of the expected target molecules of the reaction. In order to determine the absolute configuration of (1), one enantiomer was converted to the corresponding oxime (2), to which the *p*-bromobenzoyl group was introduced. The chiral C atoms of (1) are retained in the title compound, (3). The X-ray structure analysis of (3) has been carried out to determine the absolute configuration based on the strong anomalous scattering of Br.



In the crystal structure of (3), there are two independent molecules (Fig. 1). For both molecules, the ring junction is *cis*, and the oxime group is *anti* to the benzene ring of the ring system. Fig. 2 shows the crystal structure. The two molecules containing Br1 and Br2 are related by a pseudo-center of symmetry at nearly ($\frac{1}{4}$, 0, $\frac{1}{4}$), except for the chiral atoms C17/C22 and C39/C44.

Experimental

A racemic mixture of (1*R*,6*S*)-(1) and its enantiomer was prepared starting from *o*-bromophenylacetic acid. Details of the synthesis will be published elsewhere. The optical resolution of (1) was carried out *via* preparative high-pressure liquid chromatography using a chiral AD column (Daicel). One of the isolated optical isomers was converted to the corresponding oxime (2) by hydroxylamine. Compound (2) was then acylated with *p*-bromobenzoyl chloride to give (+)-(3), which was purified by repeated recrystallization from a methanol/diethyl ether mixture [yield 65% from (1)]. Crystals of (+)-(3) suitable for X-ray study were grown from a diethyl ether solution by slow evaporation [m.p. 353 K (decomposition)]. The specific rotation, $[\alpha]_D$, of (3) at 295 K is +84° (c = 0.038 g per 100 ml, chloroform).

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Crystal data

$C_{22}H_{20}BrNO_2$
M_r = 410.31
Monoclinic, $P2_1$
a = 10.536 (2) Å
b = 19.225 (5) Å
c = 9.500 (2) Å
β = 97.67 (2)°
V = 1907.1 (7) Å^3
Z = 4

D_x = 1.429 Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 25 reflections
θ = 10.0–11.6°
μ = 2.18 mm^{-1}
T = 298 K
Prism, colorless
0.50 × 0.45 × 0.30 mm

Data collection

Rigaku AFC-7R diffractometer
ω–2θ scans
Absorption correction: integration (Higashi, 1999)
$T_{\rm min}$ = 0.389, $T_{\rm max}$ = 0.552
3670 measured reflections
3466 independent reflections
1224 reflections with $I > 2\sigma(I)$

$R_{\rm int}$ = 0.098
$\theta_{\rm max}$ = 25.0°
$h = -12 \rightarrow 0$
$k = 0 \rightarrow 22$
$l = -11 \rightarrow 11$
3 standard reflections every 150 reflections intensity decay: 1.4%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.063
$wR(F^2)$ = 0.231
S = 0.98
3466 reflections
459 parameters
H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.1051P)^2 + 1.0533P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\rm max}$ = 0.018
$\Delta\rho_{\rm max}$ = 0.24 e Å^{-3}
$\Delta\rho_{\rm min}$ = −0.43 e Å^{-3}
Absolute structure: (Flack, 1983), no Friedel pairs
Flack parameter: −0.02 (3)

Table 1
Selected torsion angles (°).

O4—N7—C16—C17	2 (2)	C18—C17—C22—C21	−35 (2)
O6—N8—C38—C39	2 (2)	C38—C39—C44—C45	−62 (2)
C16—C17—C22—C23	−51 (2)	C40—C39—C44—C43	−47 (2)

Atoms C48 and C49 were refined isotropically to avoid abnormal deformation of the benzene ring from ideal geometry. The high $U_{\rm eq}$ values of C26 and C33, compared with those of their neighbors, and the large variation in the C—C distances of the benzene rings may be attributable to the large correlations in the atomic parameters because of the pseudo-centrosymmetry. All H atoms were positioned geometrically and refined as riding, with C—H distances of 0.95 Å and with $U_{\rm iso}$(H) = 1.2$U_{\rm eq}$(C).

Data collection: *WinAFC Diffractometer Control Software* (Rigaku, 1999); cell refinement: *WinAFC Diffractometer Control Software*; data reduction: *TEXSAN* (Molecular Structure Corporation, 2001); program(s) used to solve structure: *SIR92* (Altomare *et al.*, 1994) and *DIRDIF94* (Beurskens *et al.*, 1994); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEPII* (Johnson, 1976); software used to prepare material for publication: *TEXSAN*.

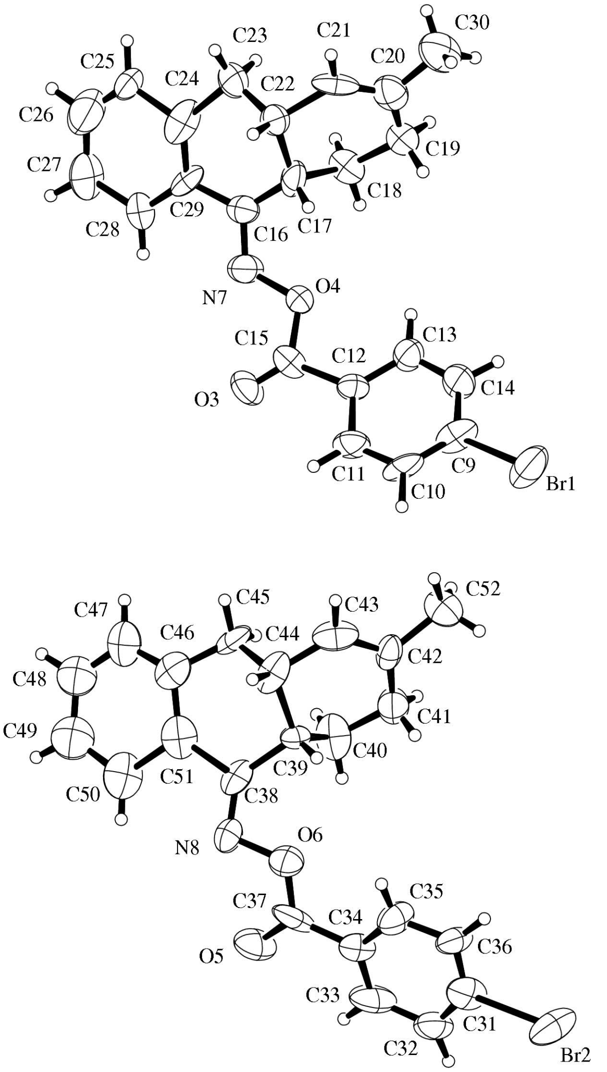

Figure 1
The structure of the two independent molecules in (3), with displacement ellipsoids plotted at the 30% probability level.

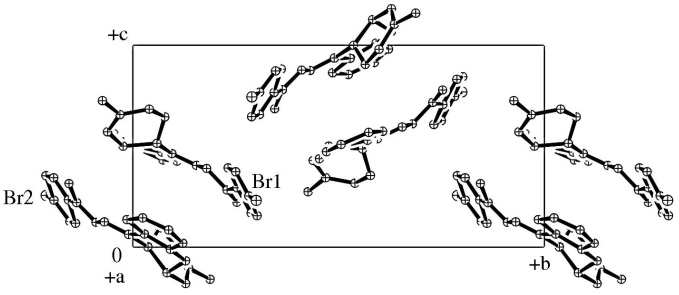

Figure 2
The projection of the crystal structure of (3) along the *a* axis. H atoms have been omitted, and non-H atoms are drawn as small spheres for clarity.

References

Altomare, A., Cascarano, G., Giacovazzo, C., Guagliardi, A., Burla, M. C., Polidori, G. & Camalli, M. (1994). *J. Appl. Cryst.* **27**, 435.

Beurskens, P. T., Admiraal, G., Beurskens, G., Bosman, W. P., de Gelder, R., Israel, R. & Smits, J. M. M. (1994). *The DIRDIF94 Program System*. Technical Report of the Crystallography Laboratory, University of Nijmegen, The Netherlands.

Flack, H. D. (1983). *Acta Cryst.* A**39**, 876–881.

Higashi, T. (1999). *ABSCOR*. Rigaku Corporation, Tokyo, Japan.

Johnson, C. K. (1976). *ORTEPII*. Report ORNL-5138. Oak Ridge National Laboratory, Tennessee, USA.

Molecular Structure Corporation (2001). *TEXSAN*. Version 1.11. MSC, 9009 New Trails Drive, The Woodlands, TX 77381-5209, USA.

Rigaku (1999). *WinAFC Diffractometer Control Software*. Rigaku Corporation, Tokyo, Japan.

Sheldrick, G. M. (1997). *SHELXL97*. University of Göttingen, Germany.