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(+)-(2*R*,3*S*)-3-Bromo-2-chloro-*N*,*N*-diisopropyl-3-phenylpropanamide and (+)-(2*R*,3*S*)-3-bromo-2-chloro-*N*-(4-nitrophenyl)-3-phenylpropanamide

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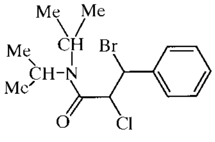
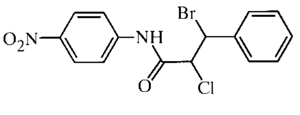
The stereochemistries at positions 2 and 3 of the title compounds, $C_{15}H_{21}BrClNO$, (I), and $C_{15}H_{12}BrClN_2O_3$, (II), have been confirmed by X-ray structural analysis. The halogen atoms adopt an antiperiplanar arrangement in each case.

Comment

The title compounds, (I) and (II), were investigated as part of a study of the stereoselective bromination of halohydrocinnamates, and the structural determinations were undertaken to determine the absolute configurations at the 2 and 3 positions in the molecules.



(I)



(II)

Compound (II) crystallizes with two unique molecules in the asymmetric unit of the orthorhombic unit cell. Small differences in bond lengths and angles between the discrete molecular units can be ascribed to crystal-packing effects. The stereochemistries at the 2 and 3 positions of both compounds were found to be *R* and *S*, respectively. The correct choice of absolute structure was confirmed by the values of the Flack parameters [0.052 (16) for (I) and 0.027 (6) for (II); Flack, 1983]. The halogen atoms were found to be antiperiplanar in both cases, with torsion angles Cl1—C2—C3—Br = −175.4 (3)° for (I), and Cl11—C12—C13—Br11 = 177.20 (16)° and Cl21—C22—C23—Br21 = 177.40 (14)° for the two unique molecules of (II).

The unit cell of (I) contains well separated molecules with the shortest intermolecular contact, not involving H atoms, being 3.301 (1) Å for C2···O1($-y + 1, x, z + \frac{1}{4}$). In contrast, the structure of (II) is stabilized by a combination of hydrogen-bond and columnar interactions. Pairs of unique molecules form *via* N—H···O intermolecular hydrogen bonds parallel to the *c* axis [H21*A*···O222($\frac{3}{2} - x, -y, -\frac{1}{2} + z$) 2.41, N21···O222 3.245 Å and N21—H21*A*···O222 158 °; see Table 3]. Columnar interactions involve the nitrophenyl and phenyl rings of both unique molecules, with mean interplanar separations C14···C19/C24···C29 3.398, C110···C115/C24···C29 3.425, C210···215/C14···C19 3.458 and C110···C115/C210···C215 3.566 Å (Spek, 1995).

Experimental

A mixture of (*S*)-2-chloro-*N*,*N*-diisopropyl-3-phenylpropanamide (500 mg, 1.86 mmol) and *N*-bromosuccinimide (331 mg, 1.86 mmol) in CCl_4 (25 ml) was heated at reflux under nitrogen. The reaction was initiated by irradiation with a 160 W mercury lamp. After 2 h, the mixture was cooled, washed with water, dried ($MgSO_4$) and the solvent removed under reduced pressure. Colourless crystals of (I) were obtained from CH_2Cl_2 (Wong *et al.*, 2000), $[\alpha]_D$ = +106.6°. Compound (II) was prepared by stirring a mixture of (2*R*,3*S*)-3-bromo-2-chloro-3-phenylpropanoic acid chloride (6.82 g, 24.2 mmol) and *p*-nitroaniline (3.34 g, 24.2 mmol) in CH_2Cl_2 (50 ml) under an anhydrous atmosphere for 2 d. The solution was washed with 1 M HCl (6 times) and dried ($MgSO_4$). The solvent was removed under reduced pressure and the product purified by column chromatography, eluting with CH_2Cl_2. The resulting solid (II) was recrytallized from hexane/CH_2Cl_2 (Wong *et al.*, 2000), $[\alpha]_D$ = +22.7°.

Compound (I)

Crystal data

$C_{15}H_{21}BrClNO$
M_r = 346.69
Tetragonal, $P4_1$
a = 8.8863 (19) Å
c = 21.299 (6) Å
V = 1681.9 (7) Å^3
Z = 4
D_x = 1.369 Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 21617 reflections
θ = 2.29–26.36°
μ = 2.596 mm^{-1}
T = 168 (2) K
Plate, colourless
0.76 × 0.34 × 0.10 mm

Data collection

CCD area-detector diffractometer
φ and ω scans
Absorption correction: empirical (*SADABS*; Bruker, 1997)
$T_{\min}$ = 0.332, $T_{\max}$ = 0.771
21 617 measured reflections
2921 independent reflections
2304 reflections with $I > 2\sigma(I)$
$R_{\rm int}$ = 0.102
$\theta_{\max}$ = 26.36°
$h = -11 \rightarrow 11$
$k = -11 \rightarrow 11$
$l = -14 \rightarrow 26$
Intensity decay: none

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.053
$wR(F^2)$ = 0.133
S = 0.992
2921 reflections
176 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0849P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} < 0.001$
$\Delta\rho_{\max}$ = 0.636 e Å^{-3}
$\Delta\rho_{\min}$ = −0.710 e Å^{-3}
Absolute structure: Flack (1983), 1168 Friedel pairs
Flack parameter = 0.052 (16)

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Table 1
Selected geometric parameters (Å, °) for (I).

C4—C3	1.498 (9)	C2—Cl1	1.905 (6)
C3—C2	1.525 (8)	C1—O1	1.213 (7)
C3—Br1	2.013 (7)	C1—N1	1.363 (7)
C2—C1	1.551 (8)		
C4—C3—C2	117.7 (5)	C1—C2—Cl1	106.1 (4)
C4—C3—Br1	109.9 (4)	O1—C1—N1	124.2 (5)
C2—C3—Br1	102.7 (4)	O1—C1—C2	115.9 (5)
C3—C2—C1	111.1 (5)	N1—C1—C2	119.8 (5)
C3—C2—Cl1	107.7 (4)		

Compound (II)

Crystal data

$C_{15}H_{12}BrClN_2O_3$
M_r = 383.63
Orthorhombic, $P2_12_12_1$
a = 13.900 (4) Å
b = 14.648 (5) Å
c = 15.553 (5) Å
V = 3166.8 (17) Å^3
Z = 8
D_x = 1.609 Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 40975 reflections
θ = 1.96–26.47°
μ = 2.778 mm^{-1}
T = 170 (2) K
Block, pale yellow
0.64 × 0.30 × 0.20 mm

Data collection

CCD area-detector diffractometer
φ and ω scans
Absorption correction: empirical (*SADABS*; Bruker, 1997)
$T_{\min}$ = 0.371, $T_{\max}$ = 0.574
40 975 measured reflections
6487 independent reflections
5023 reflections with $I > 2\sigma(I)$
$R_{\rm int}$ = 0.071
$\theta_{\max}$ = 26.47°
$h = -17 \rightarrow 17$
$k = -18 \rightarrow 16$
$l = -19 \rightarrow 19$
Intensity decay: none

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.033
$wR(F^2)$ = 0.066
S = 0.967
6487 reflections
397 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0309P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} < 0.001$
$\Delta\rho_{\max}$ = 0.362 e Å^{-3}
$\Delta\rho_{\min}$ = −0.652 e Å^{-3}
Absolute structure: Flack (1983), 2852 Friedel pairs
Flack parameter = 0.027 (6)

Table 2
Selected geometric parameters (Å, °) for (II).

C14—C13	1.498 (4)	C24—C23	1.498 (4)
C13—C12	1.513 (4)	C23—C22	1.519 (4)
C13—Br11	1.988 (3)	C23—Br21	1.986 (3)
C12—C11	1.524 (4)	C22—C21	1.532 (4)
C12—Cl11	1.796 (3)	C22—Cl21	1.805 (3)
C11—O11	1.210 (4)	C21—O21	1.211 (4)
C11—N11	1.364 (4)	C21—N21	1.366 (4)
N11—C110	1.405 (4)	N21—C210	1.402 (4)
C14—C13—C12	115.9 (3)	C24—C23—C22	115.2 (3)
C14—C13—Br11	109.6 (2)	C24—C23—Br21	109.9 (2)
C12—C13—Br11	105.1 (2)	C22—C23—Br21	105.51 (19)
C13—C12—C11	112.8 (3)	C23—C22—C21	113.3 (3)
C13—C12—Cl11	109.3 (2)	C23—C22—Cl21	107.9 (2)
C11—C12—Cl11	104.6 (2)	C21—C22—Cl21	105.3 (2)
O11—C11—N11	124.6 (3)	O21—C21—N21	125.1 (3)
O11—C11—C12	122.6 (3)	O21—C21—C22	120.9 (3)
N11—C11—C12	112.7 (3)	N21—C21—C22	114.0 (3)
C11—N11—C110	128.9 (3)	C21—N21—C210	127.9 (3)

Table 3
Hydrogen-bonding geometry (Å, °) for (II).

D—H···A	D—H	H···A	D···A	D—H···A
N11—H11A···O121$^{\rm i}$	0.88	2.00	2.847 (4)	162

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

For both compounds, data collection: *SMART* (Siemens, 1994); cell refinement: *SMART*; data reduction: *SHELXTL/PC* (Sheldrick, 1990); program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); software used to prepare material for publication: *SHELXL*97.

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