Fig. 2. Stereoscopic view of the crystal structure.

A stereoscopic view of the crystal structure is shown in Fig. 2. The packing contacts are van der Waals type.

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Absolute Configuration of (−)-4-Bromo-N-cis-2′-phenylcyclopentylbenzamide

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Abstract. $C_{18}H_{18}BrNO$, $M_r = 344 \cdot 10$, orthorhombic, $P2_12_12_1$, $a = 5 \cdot 311$ (1), $b = 16 \cdot 815$ (3), $c = 17 \cdot 420$ (3) Å, $Z = 4$, $V = 1555 \cdot 6$ (6) Å^3, $D_x = 1 \cdot 468$ g cm^{-3}, λ (Mo $K\alpha$) = 0·71069 Å, $\mu = 3 \cdot 02$ cm^{-1}, $F(000) = 704$, $T = 293$ K, final $R = 0 \cdot 039$ for 1819 observed reflections. Under enantiomeric and diastereomeric control 2-substituted cyclopentanones are converted by reductive amination and hydrogenolysis to cis-2-substituted cyclopentylamine hydrochlorides. The absolute configuration of one of these products, (+)-cis-2-phenylcyclopentylamine hydrochloride, could be elucidated as (1S, 2S) via its 4-bromo-N-benzamide,

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which corroborates the results of circular-dichroism studies on the corresponding N-salicylidene derivatives of the primary amines. There are no unusual bond angles or distances.

Introduction. Recently we have reported an efficient synthesis of optically active cis-2-substituted cyclopentylamines of types (1) and (2) with high enantiomeric purity (Wiehl & Frahm, 1986). The absolute configurations of these compounds were predicted from circular-dichroism (CD) studies of the corresponding N-salicylidene derivatives (3) of the primary amines (2) (Wiehl & Frahm, 1986), and by comparison with the known absolute configuration of the enantiomeric cis-2-phenylcyclohexylamine (Knupp & Frahm, 1984).

(1)/(2)/(3)	R
a	Me
b	Et
c	i-Prop
d	Ph
e	Bz
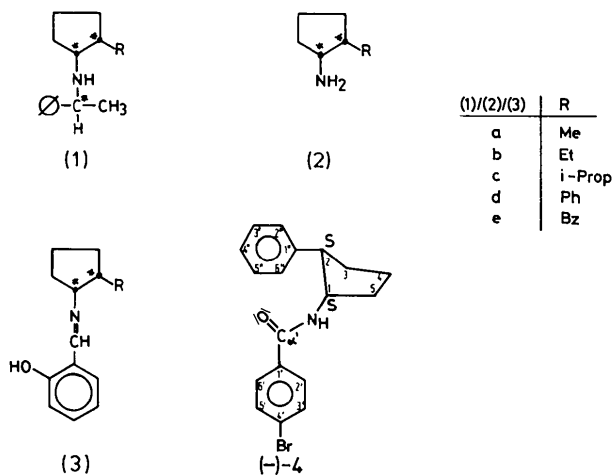
In view of frequently observed anomalous CD behaviour, particularly of cyclic amines, which is due to conformational change (Ripperger, Schreiber, Snatzke & Ponsold, 1969) additional proof is now given by X-ray structure analysis of the title compound, (—)-(4), the details of which are reported here. (—)-(4) was synthesized from (+)-(2d) and 4-bromobenzoyl chloride in the presence of pyridine (m.p. 429–430 K, $[\alpha]_D^{20°C} = -39.9°, c = 1.6, CHCl_3$).

Experimental. Enantiomeric purity 98% by means of high-pressure liquid chromatography. Colourless needles from methanol–water. Crystal dimensions $0.2 \times 0.2 \times 0.25$ mm. Syntex $P2_1$ diffractometer, Mo $K\alpha$ radiation, graphite monochromator. Lattice parameters from angular settings of 25 independent reflections ($0 < 2\theta \le 25°$). Intensity measurements by θ–2θ scan for hkl, $\bar{h}k\bar{l}$ up to $h = 6$, $k = 20$, $l = 20$, $2\theta_{max} = 50°$, $(\sin\theta/\lambda)_{max} = 0.595$ Å^{-1}. Empirical absorption correction (ψ scans); max. and min. transmission factors 0.94, 0.89. One standard measurement after every 33 records, standard intensity variation over measuring period 1.5%. 3328 reflections measured,

1509 unobserved [$I < 2\sigma(I)$, unmerged data]. 1439 unique reflections after merging, $R_{int} = 0.0135$ (based on intensities). Structure solution by direct methods. Structure refinement on $|F|$ by block-matrix calculations (max. 100 parameters) using anomalous-dispersion corrections and anisotropic temperature factors. Scattering factors for neutral atoms and dispersion corrections taken from *International Tables for X-ray Crystallography* (1974). H atoms treated as riding on carrier atoms with fixed isotropic temperature factors $B(H) = 1.2B(C)$. H atom bonded to N located from difference Fourier synthesis and refined for positional parameters and isotropic temperature factor. Isotropic extinction correction factor g included as variable, final value $g = 0.00026$. Refinement on 195 parameters converged at $R = 0.039$, $wR = 0.028$ (omitting unobs.), $S = 1.22$, $w = [\sigma^2(F) + 0.00007F^2]^{-1}$; final $\Delta/\sigma < 0.30$, $\Delta\rho_{max} = 0.40$, $\Delta\rho_{min} = -0.35$ e Å^{-3}.

In order to establish the absolute configuration of the molecule both enantiomorphs were refined separately using the unmerged data set. Refinement yielded identical atomic parameters; however, $R = 0.059$, $wR = 0.051$, $S = 2.22$ for the (+)-antipode. The decision in favour of the (—)-antipode may also be illustrated by the general reflections 115, 131, 221, 185, 153, 332, 146 with ratios $F(h)_{obs}/F(\bar{h})_{obs}$: 0.89, 1.09, 1.07, 0.88, 0.91, 1.17, 0.87. The corresponding ratios $F(h)_{calc}/F(\bar{h})_{calc}$ for the chosen enantiomer are 0.90, 1.09, 1.07, 0.90, 0.92, 1.14, 0.89, and 1.11, 0.92, 0.94, 1.11, 1.09, 0.88, 1.12 for the optical antipode.

All calculations were performed with *SHELX*76 (Sheldrick, 1976).

Discussion. The atomic coordinates and equivalent isotropic temperature factors are given in Table 1.* Table 2 summarizes the bond distances and angles. The values lie within the normal range as given by general literature data (*International Tables for X-ray Crystallography*, 1974), and compared with those of acetamide (Jeffrey, Ruble, McMullan, De Frees, Binkley & Pople, 1980).

An *ORTEP* drawing (Johnson, 1965) of a single molecule of (—)-(4) is depicted in Fig. 1, clearly showing it to possess the (1S,2S)-cis configuration in agreement with the absolute configuration deduced from CD data (Wiehl & Frahm, 1986).

The cyclopentane ring is in the envelope conformation† with a tendency to twist. Moreover it is seen that the amido group is in a bisectional and the phenyl

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* Lists of structure factors, anisotropic thermal parameters, H-atom parameters and least-squares-plane data have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 43288 (15 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

† C(3) 0.60 Å out of plane through C(1), C(2), C(4), C(5).

Table 1. *Fractional coordinates* (× 10⁴) *and equivalent isotropic thermal parameters* (*Hamilton*, 1965) (Å² × 10³) *with e.s.d.'s in parentheses*

U_{eq} is defined as one third of the trace of the orthogonalized U tensor.

	x	y	z	U_{eq}
Br	11010 (1)	16 (1)	10268 (1)	71 (1)
N	10362 (9)	3426 (2)	8099 (2)	35 (2)
O	6223 (7)	3146 (2)	8235 (2)	52 (1)
C(1)	10022 (9)	4130 (3)	7611 (2)	38 (2)
C(2)	10695 (10)	4009 (2)	6758 (2)	36 (2)
C(3)	13274 (9)	4389 (3)	6669 (3)	53 (2)
C(4)	13137 (9)	5107 (3)	7191 (3)	54 (2)
C(5)	11765 (11)	4806 (2)	7879 (2)	72 (3)
C(α')	8432 (12)	2977 (3)	8346 (3)	34 (2)
C(1')	9130 (10)	2254 (2)	8813 (2)	31 (2)
C(2')	11298 (12)	1820 (3)	8667 (3)	41 (2)
C(3')	11850 (10)	1145 (3)	9101 (3)	44 (2)
C(4')	10244 (8)	935 (2)	9677 (2)	38 (2)
C(5')	8090 (9)	1358 (2)	9837 (3)	43 (2)
C(6')	7550 (9)	2023 (2)	9395 (2)	39 (2)
C(1")	10454 (9)	3163 (3)	6445 (2)	32 (2)
C(2")	12189 (10)	2570 (3)	6636 (2)	42 (2)
C(3")	11857 (11)	1807 (3)	6356 (2)	44 (2)
C(4")	9880 (10)	1623 (3)	5890 (3)	52 (2)
C(5")	8185 (11)	2206 (3)	5688 (3)	52 (2)
C(6")	8470 (10)	2964 (3)	5973 (2)	39 (2)

Fig. 1. *ORTEP* (Johnson, 1965) drawing of the (−)-enantiomer.

o - H   ⊕ - c
⦿ - N   ⊛ - o
                 ○ - Br
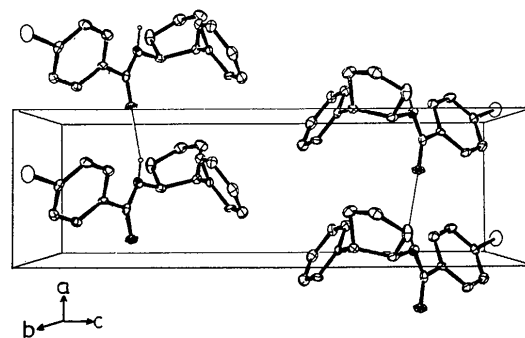
Fig. 2. Arrangement of (−)-(4) molecules in the unit cell showing N—O···O hydrogen bonds along [100].

Table 2. *Interatomic distances* (Å) *and angles* (°) *with e.s.d.'s in parentheses*

C(1)—C(2)	1·542 (6)	C(1)—C(2)—C(3)	104·6 (4)
C(2)—C(3)	1·520 (7)	C(2)—C(3)—C(4)	103·3 (4)
C(3)—C(4)	1·513 (7)	C(3)—C(4)—C(5)	103·7 (4)
C(4)—C(5)	1·490 (7)	C(4)—C(5)—C(1)	107·5 (4)
C(5)—C(1)	1·539 (7)	C(5)—C(1)—C(2)	104·5 (4)
C(1)—N	1·468 (6)	N—C(1)—C(2)	115·0 (3)
N—C(α')	1·344 (7)	N—C(1)—C(5)	110·3 (4)
C(α')—C(1')	1·509 (6)	C(1)—N—H	120·4 (26)
C(1')—C(2')	1·387 (8)	C(1)—N—C(α')	123·0 (5)
C(2')—C(3')	1·396 (6)	H—N—C(α')	116·1 (26)
C(3')—C(4')	1·363 (6)	N—C(α')—O	123·4 (4)
C(4')—C(5')	1·376 (6)	N—C(α')—C(1')	116·0 (5)
C(5')—C(6')	1·387 (6)	O—C(α')—C(1')	120·6 (5)
C(6')—C(1')	1·372 (6)	C(α')—C(1')—C(2')	121·9 (4)
C(2)—C(1")	1·528 (6)	C(α')—C(1')—C(6')	118·5 (4)
C(1")—C(2")	1·398 (7)	C(1')—C(2')—C(3')	120·2 (5)
C(2")—C(3")	1·384 (6)	C(2')—C(3')—C(4')	118·5 (5)
C(3")—C(4")	1·363 (8)	C(3')—C(4')—C(5')	122·4 (4)
C(4")—C(5")	1·377 (7)	C(4')—C(5')—C(6')	118·4 (4)
C(5")—C(6")	1·375 (7)	C(5')—C(6')—C(1')	120·8 (4)
C(6")—C(1")	1·378 (7)	C(6')—C(1')—C(2')	119·6 (4)
C(α')—O	1·233 (7)	Br—C(4')—C(3')	118·4 (3)
C(4')—Br	1·901 (4)	Br—C(4')—C(5')	119·2 (3)
N—H(N)	0·874 (42)	C(1)—C(2)—C(1")	116·6 (3)
		C(3)—C(2)—C(1")	115·5 (4)
		C(2)—C(1")—C(2")	121·6 (4)
		C(2)—C(1")—C(6")	120·2 (4)
		C(1")—C(2")—C(3")	119·6 (4)
		C(2")—C(3")—C(4")	121·3 (5)
		C(3")—C(4")—C(5")	119·6 (5)
		C(4")—C(5")—C(6")	119·7 (5)
		C(5")—C(6")—C(1")	121·7 (5)
		C(6")—C(1")—C(2")	118·1 (4)

Hydrogen bonds

	N···O^i	H(N)···O^i
N—H(N)···O^i	3·157	2·32

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

group in a pseudoequatorial position. The packing of the molecules is shown in Fig. 2; adjacent molecules related by one translation a_0 are connected *via* N—H···O hydrogen bonds (H···O = 2·32 Å) yielding infinite chains of molecules running along [100]. The hydrogen bond is indicated.

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