Roof, 1981) with the angle between least-squares planes C(1)C(9)C(8)C(7) (0·002 and 0·005 Å r.m.s. deviation) and H(8)C(8)C(9)H(9) (0·008 and 0·001 Å r.m.s. deviation) of 7 (1) and 6 (1)° for (2*a*) and (5*b*), respectively. The C(4)—C(5) double bond does not have the prerequisites for folding and the corresponding folding angle of 2 (1)° is not statistically different from 0·0°.

Molecular mechanics calculations (Allinger & Yuh, 1980) give heats of formation of −333·1 and −457·5 kJ mol$^{-1}$ for (2*a*) and (5*b*), respectively. The strain energy for (2*a*) is 136·4 kJ mol$^{-1}$ which is 11 kJ mol$^{-1}$ less strained than (2*b*); however, (5*b*) has a strain energy of 145·0 kJ mol$^{-1}$ which is about 7 kJ mol$^{-1}$ less strained than the major isomer (5*a*).

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# Absolute Configuration of (−)-4-Bromo-*N*-(*cis*-2-phenylcycloheptyl)benzamide

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**Abstract.** $\mathrm{C_{20}H_{22}BrNO}$, $M_r$ = 372·13, orthorhombic, $P2_12_12_1$, $a$ = 5·599 (1), $b$ = 16·888 (3), $c$ = 18·531 (3) Å, $Z$ = 4, $V$ = 1752 (1) Å$^3$, $D_x$ = 1·411 Mg m$^{-3}$, $\lambda$(Cu $K\alpha$) = 1·5418 Å, $\mu$ = 3·227 mm$^{-1}$, $F(000)$ = 776, $T$ = 293 K, final $R$ = 0·030 for 1961 observed reflections. Under enantiomeric and diastereomeric control 2-substituted cycloheptanones were converted by reductive amination and hydrogenolysis to *cis*-2-substituted cycloheptanamine hydrochlorides. The absolute configuration of one of these products, (+)-*cis*-2-phenylcycloheptanamine hydrochloride, is elucidated as (1*S*,2*S*) by X-ray structure analysis of its 4-bromo-*N*-benzamide, which corroborates the results

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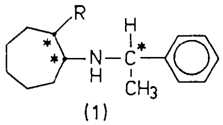
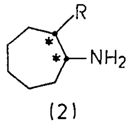
of circular-dichroism studies on the corresponding *N*-salicylidene derivates of the primary amines. There are no unusual bond angles or distances.

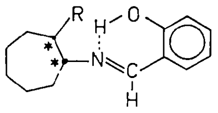
**Introduction.** Recently we have reported an efficient synthesis of optically active *cis*-2-substituted cyclopentanamines of high enantiomeric purity (Wiehl & Frahm, 1986). The absolute configurations of these compounds were predicted from circular-dichroism (CD) studies of the corresponding *N*-salicylidene derivatives of the primary amines (Wiehl & Frahm, 1986), and by comparison with the known absolute configuration of the enantiomeric *cis*-2-phenylcyclohexanamine (Knupp & Frahm, 1984). Proof was obtained by X-ray structure analysis of (−)-4-bromo-*N*-(*cis*-2-phenylcyclopentyl)benzamide (Wiehl, Frahm & Kirfel 1987). In continuation of these studies we have now synthesized optically active *cis*-2-substituted cycloheptanamines of types (1) and (2). Their absolute configurations were provisionally derived from CD studies of their corresponding *N*-salicylidene derivatives (3) (Liem & Frahm 1990).



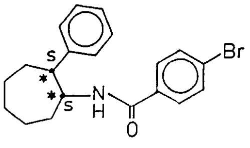
(1)



(2)



(3)



(−)-(4)

| (1)/(2)/(3) | R |
|---|---|
| a | Me |
| b | Et |
| c | Ph |
| d | Bz |

In view of the frequently observed anomalous CD behaviour due to conformational changes (Ripperger, Schreiber, Snatzke & Ponsold, 1969), particularly of cyclic amines, additional proof is now given by an X-ray structure analysis of the title compound, (−)-(4), the details of which are reported here. (−)-4 was synthesized from (+)-(2*c*) and 4-bromobenzoic acid chloride in the presence of pyridine (m.p. 425–6 K, $[\alpha]_D^{20\cdot0\,^{\circ}\mathrm{C}} = -186\cdot7^{\circ}$ [CHCl$_3$, 1·6 g dm$^{-3}$]).

**Experimental.** Enantiomeric excess 99·5% by means of high-pressure liquid chromatography. Colourless needles from methanol–water. Crystal dimensions 0·26 × 0·37 × 0·54 mm. Enraf–Nonius CAD-4 diffractometer, Cu $K\alpha$ radiation, graphite monochromator. Lattice parameters from angular settings of 25 independent reflections ($60 < 2\theta < 113^{\circ}$). Intensity measurements by $\theta$–$2\theta$ scans for $h, \pm k, l$ up to $h = 7$, $k = 21$, $l = 23$, $2\theta_{\max} = 150^{\circ}$, $(\sin\theta/\lambda)_{\max} = 0\cdot626$ Å$^{-1}$. Empirical absorption correction ($\psi$ scans); max. and min. transmission factors 0·99, 0·52. Two standard measurements after every 2 h, standard intensity variation over measuring period 0·9%. 3443 reflections measured, 86 unobserved [$I < 3\sigma(I)$, unmerged data]. 2039 unique observed reflections after merging in the Laue group, $R_{\text{int}} = 0\cdot037$ (based on intensities). Structure solution by direct methods. Structure refinement on $|F|$ by block matrix calculations (max. 155 parameters) using anisotropic atomic displacement parameters for the non-H atoms. Scattering factors for neutral atoms and anomalous-dispersion corrections taken from *International Tables for X-ray Crystallography* (1974). H atoms from difference Fourier syntheses and refined for positional parameters and isotropic atomic displacement parameters. Isotropic extinction correction factors $g$ (Becker & Coppens formalism, Lorentzian distribution) included as variable, final value $g = 1\cdot45 \times 10^{-4}$.

Refinement of 289 parameters converged at $R = 0\cdot030$, $wR = 0\cdot044$ (omitting unobs.), $S = 1\cdot09$, $w = [\sigma^2(|F|) + (0\cdot04|F|)^2]^{-1}$; final $\Delta/\sigma = 0\cdot30$, $\Delta\rho_{\max} = 0\cdot34$, $\Delta\rho_{\min} = -0\cdot42$ e Å$^{-3}$.

In order to establish the absolute configuration of the molecule both enantiomorphs were refined separately using the unmerged data set. Refinements yielded identical atomic parameters, however, $R = 0\cdot039$, $wR = 0\cdot055$, $S = 1\cdot28$ [350 reflections with $w|\Delta F| > 3\sigma(F)$ given zero weight] for the (+)-antipode, and $R = 0\cdot032$, $wR = 0\cdot048$, $S = 1\cdot09$ (96 zero weight) for the (−)-antipode. The decision in favour of the (−)-antipode may also be illustrated by the general reflections $4\bar{5}5$, $1,\bar{2},14$, $2,\overline{10},11$, $3,2,15$, $2,\bar{7},14$, $1,\overline{13},7$, $1,\overline{10},10$ with ratios $F(h)_{\text{obs}}/F(\bar{h})_{\text{obs}}$: 1·17, 1·15, 1·10, 0·82, 1·15, 0·91, 1·08. The corresponding ratios $F(h)_{\text{calc}}/F(\bar{h})_{\text{calc}}$ for the chosen enantiomer are 1·09, 1·13, 1·11, 0·85, 1·10, 0·91, 1·09, and 0·92, 0·88, 0·90, 1·16, 0·90, 1·10, 0·92 for the optical antipode. Data reduction and absorption correction with *CAD*-4 software (Enraf–Nonius, Delft, The Netherlands), all ensuing calculations with local crystallographic program system *CRYSTAL* installed at HASYLAB/DESY (Hamburg).

**Discussion.** The atomic positional and equivalent isotropic displacement parameters are given in Table 1.* Table 2 summarizes the bond distances and

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* Lists of structure factors, anisotropic atomic displacement parameters, H-atom parameters and least-squares-planes data have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 52584 (14 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. *Fractional atomic coordinates* ($\times 10^4$) *and equivalent isotropic thermal parameters* ($Å^2$) (*Hamilton,* 1965) *with e.s.d.'s in parentheses*

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

| | $x$ | $y$ | $z$ | $U_{eq}$ |
|---|---|---|---|---|
| C(1) | −2652 (4) | 150 (1) | 1193 (1) | 0·050 (1) |
| C(2) | −1471 (3) | 966 (1) | 1024 (1) | 0·045 (1) |
| C(3) | 1119 (4) | 1029 (1) | 1278 (1) | 0·055 (1) |
| C(4) | 1421 (5) | 1270 (2) | 2073 (1) | 0·067 (1) |
| C(5) | 773 (6) | 667 (2) | 2642 (1) | 0·070 (1) |
| C(6) | −1692 (6) | 314 (2) | 2556 (1) | 0·074 (2) |
| C(7) | −1887 (8) | −237 (1) | 1899 (1) | 0·079 (2) |
| C(α′) | −4118 (3) | −776 (1) | 269 (1) | 0·044 (1) |
| C(1′) | −3440 (3) | −1342 (1) | −318 (1) | 0·041 (1) |
| C(2′) | −1337 (4) | −1280 (1) | −709 (1) | 0·051 (1) |
| C(3′) | −866 (4) | −1802 (1) | −1273 (1) | 0·055 (1) |
| C(4′) | −2503 (4) | −2383 (1) | −1433 (1) | 0·049 (1) |
| C(5′) | −4585 (4) | −2473 (1) | −1046 (1) | 0·051 (1) |
| C(6′) | −5067 (3) | −1941 (1) | −491 (1) | 0·045 (1) |
| C(1″) | −1744 (4) | 1179 (1) | 231 (1) | 0·048 (1) |
| C(2″) | −87 (4) | 937 (1) | −288 (1) | 0·057 (1) |
| C(3″) | −385 (6) | 1129 (2) | −1007 (1) | 0·067 (1) |
| C(4″) | −2354 (6) | 1566 (2) | −1226 (1) | 0·070 (1) |
| C(5″) | −3980 (5) | 1826 (2) | −719 (2) | 0·068 (1) |
| C(6″) | −3668 (4) | 1636 (1) | 3 (1) | 0·057 (1) |
| N | −2306 (3) | −426 (1) | 618 (1) | 0·048 (1) |
| O | −6245 (3) | −654 (1) | 416 (1) | 0·060 (1) |
| Br | −1880 (1) | −3058 (0) | −2228 (0) | 0·077 (0) |
| H(N) | −1064 (73) | −549 (16) | 550 (14) | 0·025 (6) |

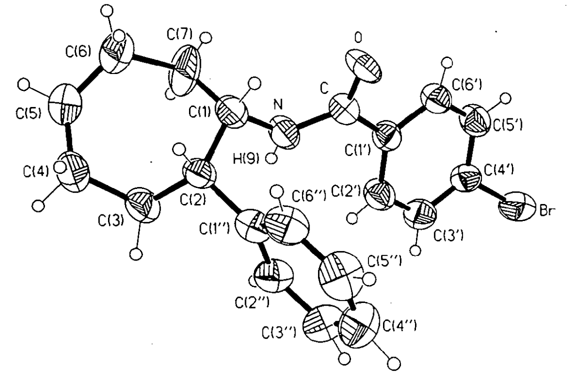

Fig. 1. *ORTEP* (Johnson, 1965) drawing of the (−)-enantiomer.

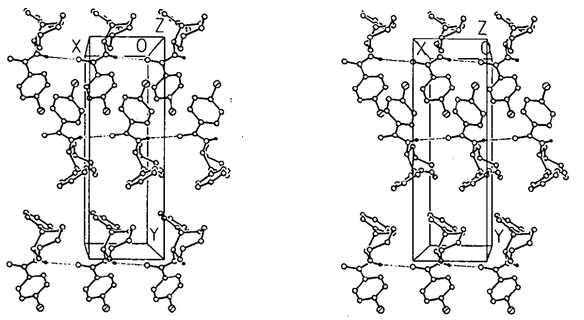

Fig. 2. Stereoscopic view of an arrangement of (−)-(4) molecules in the unit cell showing N—H···O hydrogen bonds along [100].

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

| | | | |
|---|---|---|---|
| C(1)—C(2) | 1·560 (3) | C(4′)—C(5′) | 1·377 (3) |
| C(2)—C(3) | 1·528 (3) | C(5′)—C(6′) | 1·392 (3) |
| C(3)—C(4) | 1·538 (4) | C(6′)—C(1′) | 1·399 (3) |
| C(4)—C(5) | 1·510 (4) | C(2)—C(1″) | 1·521 (3) |
| C(5)—C(6) | 1·512 (5) | C(1″)—C(2″) | 1·397 (3) |
| C(6)—C(7) | 1·536 (4) | C(2″)—C(3″) | 1·381 (4) |
| C(7)—C(1) | 1·524 (3) | C(3″)—C(4″) | 1·387 (4) |
| C(1)—N | 1·456 (3) | C(4″)—C(5″) | 1·380 (4) |
| N—C(α′) | 1·340 (3) | C(5″)—C(6″) | 1·387 (4) |
| C(α′)—C(1′) | 1·487 (3) | C(6″)—C(1″) | 1·391 (3) |
| C(1′)—C(2′) | 1·387 (3) | C(α′)—O | 1·239 (3) |
| C(2′)—C(3′) | 1·392 (3) | C(4′)—Br | 1·895 (2) |
| C(3′)—C(4′) | 1·375 (3) | N—H(N) | 0·74 (4) |

| | | | |
|---|---|---|---|
| C(1)—C(2)—C(3) | 113·7 (2) | C(2′)—C(3′)—C(4′) | 119·2 (2) |
| C(2)—C(3)—C(4) | 114·7 (2) | C(3′)—C(4′)—C(5′) | 122·0 (2) |
| C(3)—C(4)—C(5) | 117·6 (2) | C(4′)—C(5′)—C(6′) | 118·5 (2) |
| C(4)—C(5)—C(6) | 114·3 (2) | C(5′)—C(6′)—C(1′) | 120·7 (2) |
| C(5)—C(6)—C(7) | 112·8 (3) | C(6′)—C(1′)—C(2′) | 119·2 (2) |
| C(6)—C(7)—C(1) | 116·1 (2) | Br—C(4′)—C(3′) | 118·3 (2) |
| C(7)—C(1)—C(2) | 115·6 (2) | Br—C(4′)—C(5′) | 119·6 (2) |
| N—C(1)—C(2) | 112·8 (2) | C(1)—C(2)—C(1″) | 111·1 (2) |
| N—C(1)—C(7) | 107·7 (2) | C(3)—C(2)—C(1″) | 112·1 (2) |
| C(1)—N—H | 116 (2) | C(2)—C(1″)—C(2″) | 121·9 (2) |
| C(1)—N—C(α′) | 123·2 (2) | C(2)—C(1″)—C(6″) | 120·2 (2) |
| H—N—C(α′) | 123 (2) | C(1″)—C(2″)—C(3″) | 121·0 (2) |
| N—C(α′)—O | 123·2 (2) | C(2″)—C(3″)—C(4″) | 120·2 (3) |
| N—C(α′)—C(1′) | 116·1 (2) | C(3″)—C(4″)—C(5″) | 119·6 (2) |
| O—C(α′)—C(1′) | 120·6 (2) | C(4″)—C(5″)—C(6″) | 120·0 (2) |
| C(α′)—C(1′)—C(2′) | 123·2 (2) | C(5″)—C(6″)—C(1″) | 121·3 (2) |
| C(α′)—C(1′)—C(6′) | 117·6 (2) | C(6″)—C(1″)—C(2″) | 117·9 (2) |
| C(1′)—C(2′)—C(3′) | 120·3 (2) | | |

| | | | |
|---|---|---|---|
| C(2)—C(1)—C(7)—C(6) | 42·5 (3) | C(3)—C(4)—C(5)—C(6) | −52·0 (3) |
| C(7)—C(1)—C(2)—C(3) | 35·2 (2) | C(4)—C(5)—C(6)—C(7) | 70·0 (3) |
| C(1)—C(2)—C(3)—C(4) | −84·5 (2) | C(5)—C(6)—C(7)—C(1) | −90·5 (3) |
| C(2)—C(3)—C(4)—C(5) | 71·6 (3) | | |

| | |
|---|---|
| N—H(N)···O$^{i}$ with N···O$^{i}$ | 3·436 (2) Å |
| H(N)···O$^{i}$ 2·72 (4) Å | N—H(N)···O 166° |

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

angles. The values vary in the normal range compared to general literature data (*International Tables for X-ray Crystallography*, 1974), and to 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 (1′*S*,2′*S*)-*cis* configuration. This is in agreement with the absolute configuration deduced from CD data (Liem & Frahm, 1990).

The cycloheptane ring is in the twist chair conformation (see Table 2). Moreover, it is seen that the amido group is in a bisectional and the phenyl group in a pseudoequatorial position. The packing of the molecules is shown in Fig. 2; adjacent molecules related by one translation $\mathbf{a}_o$ are connected *via* very weak N—H···O hydrogen bonds [2·72 (4) Å] yielding infinite chains of molecules running along [100]. The hydrogen bond is indicated.

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*Acta Cryst.* (1990). C**46**, 1271–1273

# Structure of Dimethyl (±)-1,2,3,4,4aα,4b,9,10-Octahydro-6,7-bis(trimethylsilyl)-2β,10aβ-ethanophenanthrene-12,12-dicarboxylate

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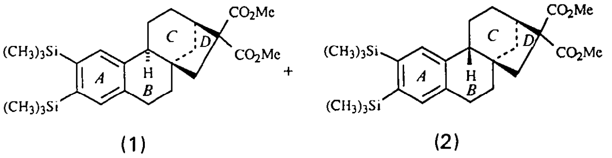
**Abstract.** $C_{26}H_{40}O_4Si_2$, $M_r = 472{\cdot}8$, monoclinic, $P2_1/c$, $a = 16{\cdot}432\,(2)$, $b = 9{\cdot}597\,(3)$, $c = 17{\cdot}029\,(2)$ Å, $\beta = 93{\cdot}73\,(1)°$, $V = 2680\,(1)$ Å$^3$, $Z = 4$, $D_x = 1{\cdot}17$ g cm$^{-3}$, $\lambda(\text{Cu }K\bar{\alpha}) = 1{\cdot}5424$ Å, $\mu = 13{\cdot}9$ cm$^{-1}$, $F(000) = 1024$, $T = 295$ K, $R = 0{\cdot}042$ for 4337 unique observed reflections. The title compound has a phyllocladane-type framework. One of the two Si atoms is out of the mean-square plane of the phenyl ring [$d_{\rm Si} = 0{\cdot}234\,(1)$ Å]. This feature can explain the different reactivity of the two trimethylsilyl groups.

**Introduction.** Kaurane and phyllocladane are two families of naturally occurring tetracyclic diterpenes exhibiting very important biological activities (Hanson, 1988). They have very close structural features with a bicyclo[3.2.1]octane arrangement of *CD* rings and a spiro *BD* ring junction in common; the only difference in structure arises from the stereochemistry of the *BC* ring junction: *cis* for the kaurane, *trans* for the phyllocladane. Two of us have recently disclosed (Gotteland & Malacria, 1989) a strategy based upon a sequence of three consecutive cycloaddition reactions, allowing a straightforward access, in high yields, to the basic skeleton of these related families of natural products (see scheme).



(1) (2)

In our model study this synthetic approach gave rise to a major (90%) phyllocladane stereoisomer (1) and a minor (10%) kaurane stereoisomer (2) whose structural determination turned out to be quite difficult by NMR. We report in this paper the molecular structure of the title compound (1) having a phyllocladane-type framework. To the best of our knowledge, no structural investigations have been carried out for such a compound.

**Experimental.** The synthesis of the compound has been previously reported (Gotteland & Malacria, 1989). Transparent crystal from benzene/methanol (50/50), 0·25 × 0·40 × 0·40 mm. Enraf–Nonius CAD-4 diffractometer, graphite monochromator,

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