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# Stereochemical Studies. 114.* Structure of *cis*-2-(*p*-Chlorophenyl)-4a,5,8,8a-tetrahydro-4*H*-3,1-benzoxazine

BY ALAJOS KÁLMÁN AND GYULA ARGAY

*Central Research Institute of Chemistry, Hungarian Academy of Sciences, Budapest*-114, *POB* 17, *H*-1525, *Hungary*

AND GÁBOR BERNÁTH AND GÉZA STÁJER

*Institute of Pharmaceutical Chemistry, University Medical School, Szeged, POB* 21, *H*-7601, *Hungary*

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**Abstract.** $C_{14}H_{14}ClNO$, $M_r = 247{\cdot}73$, monoclinic, $P2_1/c$, $a = 5{\cdot}227(1)$, $b = 10{\cdot}416(1)$, $c = 22{\cdot}182(3)$ Å, $\beta = 93{\cdot}49(1)°$, $V = 1205{\cdot}5(5)$ Å$^3$, $Z = 4$, $D_x = 1{\cdot}365$ Mg m$^{-3}$, $\lambda$(Cu $K\alpha$) = 1·54184 Å, $\mu = 2{\cdot}7$ mm$^{-1}$, $F(000) = 520$, $T = 295(2)$ K, $R = 0{\cdot}039$ for 1889 unique observed reflections. The same sign of the endocyclic torsion angles about the C—C bond in the ring junction substantiates the stereospecificity of the reaction in which a *cis*-amino alcohol (obtained by reduction from *cis*-2-amino-4-cyclohexene-1-carboxylic acid) is cyclized by an imidate [*p*-$ClC_6H_4C(NH)OC_2H_5$] to bicyclic tetrahydro-4*H*-3,1-benzoxazine. Owing to the lone pair of the N atom delocalized on the planar $>C-C\lessdot^{O-}_{N-}$ moiety possessing a C=N double bond [1·266 (2) Å], the hetero ring exhibits an almost perfect $^5E$ conformation. The cyclohexene ring retains its half-chair shape with a local pseudo-twofold symmetry axis which bisects the C—C bond at the ring junction.

**Experimental.** Colourless crystal (0·08 × 0·3 × 0·5 mm) of the title compound mounted on a glass fiber by its long axis. Enraf–Nonius CAD-4 computer-controlled diffractometer equipped with a graphite-crystal incident-beam monochromator. $0{\cdot}017 \le \sin\theta/\lambda \le 0{\cdot}626$ Å$^{-1}$. $\omega$–$2\theta$ scan, $h$ 0 to 6, $k$ 0 to 13 and $l$ −27 to 27. Cell parameters by least-squares fit for 25 centred reflections. Systematic absences: $l = 2n + 1$ in $h0l$, $k = 2n + 1$ in $0k0$. Of 2489 unique reflections 600 with $I < 3\sigma(I)$ were taken as unobserved. Three standard reflections, intensity variation ±2%. Solved by Patterson and subsequent structure-factor and Fourier calculations. Empirical absorption correction (Walker & Stuart, 1983) (min. absorption correction 0·557, max. 1·338) improved $R$ from 0·115 to 0·082. The H-atom positions were generated from assumed geometries and were refined in isotropic mode in the final cycles of the anisotropic least-squares treatment of non-H atoms. The full-matrix least-squares procedure minimized $\sum w(\Delta F)^2$ using the weighting scheme $w = [\sigma^2(F_o) + 0{\cdot}25(pF_o)^2]^{-1}$ with $p = 0{\cdot}09$ for 155 parameters. Final $R = 0{\cdot}039$, $wR = 0{\cdot}067$, $R_{tot} = 0{\cdot}047$, $S = 1{\cdot}31$. Extinction coefficient (Zachariasen, 1963): $1{\cdot}3741 \times 10^{-6}$. Max. peak height in final $\Delta\rho = 0{\cdot}4$ e Å$^{-3}$. Max. $\Delta/\sigma = 0{\cdot}21$. Scattering factors from *International Tables for X-ray Crystallography* (1962). Program system applied: Enraf–Nonius (1982) *SDP* with local modification adapted to a PDP11/34 minicomputer (64 K). The structure is defined in Tables 1 and 2 and Fig. 1.†

* Part 113: Stájer, Bernáth, Szabó & Sohár (1986).

† Lists of structure factors, anisotropic thermal parameters, bond lengths involving H atoms, torsion angles, and H-atom parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 43244 (17 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. *Atomic coordinates and equivalent isotropic temperature factors for the non*-H *atoms with e.s.d.'s in parentheses*

$B_{eq} = \frac{4}{3}$trace($B$G) where G is the direct metric tensor.

| | $x$ | $y$ | $z$ | $B_{eq}$(Å$^2$) |
|---|---|---|---|---|
| N(1) | 0·9290 (4) | 0·2691 (2) | 0·1651 (1) | 4·15 (5) |
| C(2) | 0·9056 (3) | 0·1732 (2) | 0·1994 (1) | 3·72 (5) |
| O(3) | 1·0151 (3) | 0·0559 (1) | 0·1957 (1) | 4·42 (5) |
| C(4) | 1·1794 (4) | 0·0349 (2) | 0·1468 (1) | 4·44 (7) |
| C(4a) | 1·0998 (3) | 0·1169 (2) | 0·0928 (1) | 3·92 (6) |
| C(5) | 0·8413 (4) | 0·0756 (2) | 0·0638 (1) | 4·22 (6) |
| C(6) | 0·7272 (4) | 0·1739 (3) | 0·0214 (1) | 5·22 (8) |
| C(7) | 0·8023 (5) | 0·2944 (3) | 0·0215 (1) | 5·52 (9) |
| C(8) | 1·0108 (5) | 0·3478 (2) | 0·0636 (1) | 5·14 (8) |
| C(8a) | 1·0961 (4) | 0·2552 (2) | 0·1144 (1) | 4·21 (6) |
| C(9) | 0·7355 (3) | 0·1790 (2) | 0·2506 (1) | 3·58 (5) |
| C(10) | 0·7375 (4) | 0·0828 (2) | 0·2943 (1) | 4·18 (6) |
| C(11) | 0·5734 (4) | 0·0908 (2) | 0·3412 (1) | 4·50 (7) |
| C(12) | 0·4096 (4) | 0·1940 (2) | 0·3436 (1) | 3·94 (6) |
| C(13) | 0·4024 (4) | 0·2898 (2) | 0·3006 (1) | 4·23 (6) |
| C(14) | 0·5673 (4) | 0·2817 (2) | 0·2548 (1) | 4·10 (6) |
| Cl(15) | 0·2076 (1) | 0·2058 (1) | 0·4033 (0) | 5·12 (1) |

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Table 2. *Bond lengths* (Å) *and angles* (°) *with their e.s.d.'s in parentheses*

| | | | |
|---|---|---|---|
| N(1)–C(2) | 1·266 (3) | C(7)–C(8) | 1·498 (3) |
| N(1)–C(8a) | 1·472 (3) | C(8)–C(8a) | 1·529 (3) |
| C(2)–O(3) | 1·354 (2) | C(9)–C(10) | 1·394 (3) |
| C(2)–C(9) | 1·486 (3) | C(9)–C(14) | 1·391 (3) |
| O(3)–C(4) | 1·441 (3) | C(10)–C(11) | 1·391 (3) |
| C(4)–C(4a) | 1·509 (3) | C(11)–C(12) | 1·377 (3) |
| C(4a)–C(5) | 1·523 (3) | C(12)–C(13) | 1·379 (3) |
| C(4a)–C(8a) | 1·519 (3) | C(12)–Cl(15) | 1·748 (2) |
| C(5)–C(6) | 1·490 (3) | C(13)–C(14) | 1·374 (3) |
| C(6)–C(7) | 1·315 (4) | | |

| | | | |
|---|---|---|---|
| C(2)–N(1)–C(8a) | 117·7 (3) | N(1)–C(8a)–C(4a) | 110·7 (3) |
| N(1)–C(2)–O(3) | 128·2 (3) | N(1)–C(8a)–C(8) | 109·9 (3) |
| N(1)–C(2)–C(9) | 120·8 (3) | C(4a)–C(8a)–C(8) | 112·0 (3) |
| O(3)–C(2)–C(9) | 111·0 (3) | C(2)–C(9)–C(10) | 121·5 (3) |
| C(2)–O(3)–C(4) | 117·1 (3) | C(2)–C(9)–C(14) | 119·5 (3) |
| O(3)–C(4)–C(4a) | 111·3 (3) | C(10)–C(9)–C(14) | 119·0 (3) |
| C(4)–C(4a)–C(5) | 111·7 (3) | C(9)–C(10)–C(11) | 119·9 (3) |
| C(4)–C(4a)–C(8a) | 107·1 (3) | C(10)–C(11)–C(12) | 119·3 (3) |
| C(5)–C(4a)–C(8a) | 111·9 (3) | C(11)–C(12)–C(13) | 121·9 (3) |
| C(4a)–C(5)–C(6) | 112·5 (3) | C(11)–C(12)–Cl(15) | 119·3 (3) |
| C(5)–C(6)–C(7) | 123·1 (4) | C(13)–C(12)–Cl(15) | 118·7 (3) |
| C(6)–C(7)–C(8) | 124·1 (4) | C(12)–C(13)–C(14) | 118·3 (3) |
| C(7)–C(8)–C(8a) | 113·2 (3) | C(9)–C(14)–C(13) | 121·6 (3) |

**Related literature.** The synthesis and $^1H$ and $^{13}C$ NMR studies of this and other related compounds are discussed by Bernáth, Stájer, Szabó, Fülöp & Sohár (1985). The structure determination of a related compound with a *trans* ring junction is reported in Argay, Kálmán, Ribár & Bernáth (1986).

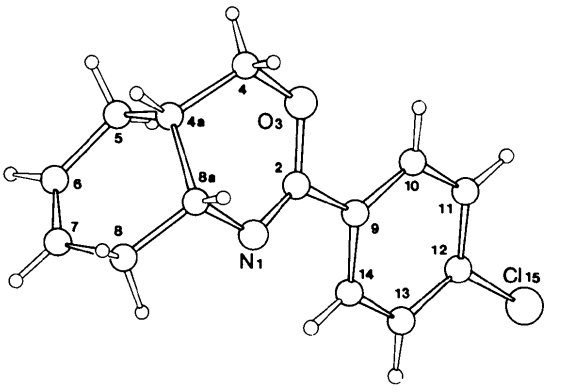


Fig. 1. A perspective view of the molecule with the numbering scheme. Numbers refer to C atoms unless otherwise indicated.

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# Stereochemical Studies. 115.* Structure of *trans*-2-(*p*-Chlorophenyl)-1,2,4a,5,8,8a-hexahydro-4*H*-3,1-benzoxazine


BY GYULA ARGAY AND ALAJOS KÁLMÁN

*Central Research Institute of Chemistry, Hungarian Academy of Sciences, Budapest*-114, *POB* 17, *H*-1525, *Hungary*

BÉLA RIBÁR

*Institute of Physics, Faculty of Sciences, Ilije Djuricica* 4, 21000 *Novi Sad, Yugoslavia*

AND GÁBOR BERNÁTH

*Institute of Pharmaceutical Chemistry, University Medical School, Szeged, POB* 21, *H*-6701, *Hungary*


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**Abstract.** $C_{14}H_{16}ClNO$, $M_r = 249·74$, orthorhombic, $P2_12_12_1$, $a = 16·725$ (4), $b = 12·833$ (4), $c = 5·939$ (1) Å, $V = 1274·7$ (9) Å$^3$, $Z = 4$, $D_x = 1·301$ Mg m$^{-3}$, $\lambda$(Mo $K\alpha$) = 0·71073 Å, $\mu = 0·28$ mm$^{-1}$, $F(000) = 528$, $T = 293$ (2) K, $R = 0·061$ for 1063 unique observed reflections. The opposite signs of the endocyclic torsion angles about the C–C bond in the ring junction substantiate the stereospecificity of the reaction in which a *trans*-amino alcohol (obtained by reduction from *trans*-2-amino-


* Part 114: Kálmán, Argay, Bernáth & Stájer (1986).

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