the halogen···O contact noted above, and the stacking interaction described below. A C=O carbonyl dipole, O(5′1) at (*x*,*y*,*z*−1), points down on the pyrimidine base ring, the distance of O(5′1) from the ring plane being 2·93 (3) Å; the distances from the ring atoms are given in Table 3. The distances involved in this contact here indicate that the interaction is not quite as pronounced as in AIDU, the O atom in this case being 0·1 Å further from the ring. This interaction has now appeared in four of our recent structures, the three others being AIDU, AT, and 2′,3′,5′-tri-*O*-acetyluridine (Low & Wilson, 1984), and plainly plays an important stacking role in the absence of base–base stacking interactions. The molecules stack as shown in Fig. 2.

We thank Dr J. N. Low for data collection and helpful discussion, and Dr A. G. Fitzgerald for EDX measurements.

References

CAMERMAN, A. & TROTTER, J. (1965). *Acta Cryst.* **18**, 203–211.
International Tables for X-ray Crystallography (1974). Vol. IV. Birmingham: Kynoch Press. (Present distributor D. Reidel, Dordrecht.)
KLUG, A. (1947). *Nature* (*London*), **160**, 570.
LOW, J. N. (1983). *Acta Cryst.* C**39**, 796–798.
LOW, J. N. & WILSON, C. C. (1984). *Acta Cryst.* C**40**, 1030–1032.
MOTHERWELL, W. D. S. & CLEGG, W. (1978). *PLUTO*. Program for plotting molecular and crystal structures. Univ. of Cambridge, England.
RAHMAN, A. & WILSON, H. R. (1970). *Acta Cryst.* B**26**, 1765–1775.
ROBERTS, P. & SHELDRICK, G. M. (1975). *XANADU*. Program for torsion-angle, mean-plane, and libration-correction calculations. Univ. of Cambridge, England.
SHELDRICK, G. M. (1976). *SHELX76*. Program for structure determination. Univ. of Cambridge, England.
WILSON, C. C., LOW, J. N., TOLLIN, P. & WILSON, H. R. (1984). *Acta Cryst.* C**40**, 1712–1715.
WILSON, C. C., LOW, J. N. & YOUNG, D. W. (1983). *Acta Cryst.* C**39**, 1103–1105.

Acta Cryst. (1985). C**41**, 468–470

Absolute Configuration of (−)-*cis*-2-Ethylcyclohexanamine Hydrochloride 0·39-Ethanol Solvate, $C_8H_{18}N^+.Cl^-.0{\cdot}39C_2H_6O$

BY GERD KNUPP AND AUGUST W. FRAHM*

Institut für Pharmazeutische Chemie der Universität Bonn, Kreuzbergweg 26, *D*-5300 *Bonn* 1, *Federal Republic of Germany*

AND ARMIN KIRFEL, TILL FRÖHLICH AND GEORG WILL

Lehrstuhl für Mineralogie und Kristallographie, Mineralogisches Institut der Universität Bonn, Poppelsdorfer Schloss, D-5300 *Bonn* 1, *Federal Republic of Germany*

(*Received* 20 *August* 1984; *accepted* 9 *November* 1984)

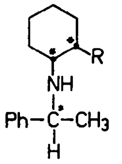
Abstract. $M_r = 181{\cdot}7$, orthorhombic, $I222$, $a = 10{\cdot}804$ (4), $b = 13{\cdot}173$ (4), $c = 15{\cdot}275$ (4) Å, $Z = 8$, $V = 2174$ Å^3, $D_m = 1{\cdot}08$, $D_x = 1{\cdot}110$ g cm^{-3}, λ(Mo $K\alpha$) = 0·71069 Å, $\mu = 3{\cdot}02$ cm^{-1}, $F(000) = 801{\cdot}12$, $T = 293$ K, final $R = 0{\cdot}031$ for 1866 observed reflections. Under enantiomeric and diastereomeric control 2-substituted cyclohexanones are converted by reductive amination and hydrogenolysis to *cis*-2-substituted cyclohexanamine hydrochlorides. The absolute configuration of one of these products, (−)-*cis*-2-ethylcyclohexanamine hydrochloride, could be elucidated as 1*R*,2*S*, which corroborates the results of circular-dichroism studies on the corresponding *N*-salicylidene derivates of the primary amines.

Introduction. Recently we have reported an efficient synthesis of optically active *cis*-2-substituted cyclohexanamines of types (1) and (2) with high enantiomeric purity (Knupp & Frahm, 1981, 1984). 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) (Knupp & Frahm, 1984) and by comparison with the known absolute configuration of the enantiomeric *cis*-2-phenylcyclohexanamine (Verbit & Price, 1972). In view of known 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, (−)-(2*b*).HCl (4), the details of which are reported here.

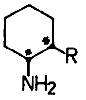
---

* To whom correspondence should be addressed.

0108-2701/85/030468-03$01.50

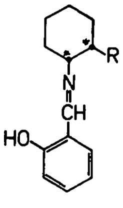


(1)

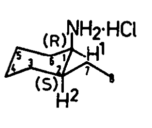


(2)

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



(3)



(–)-(2*b*).HCl (4)

Experimental. Enantiomeric purity 97% by means of high-pressure liquid chromatography. Colourless needles from ether–ethanol. Crystal 0·3 × 0·3 × 0·2 mm. D_m pyknometrically. Syntex $P2_1$ diffractometer, Mo *Kα* radiation, graphite monochromator. Lattice constants from angular settings of 25 independent reflections ($0 < 2\theta \leq 30°$). Empirical absorption correction (ψ scans). $\sin\theta_{max}/\lambda = 0{\cdot}595$ Å^{-1}; *hkl* range: $0 < 2\theta \leq 20°$ full sphere, $20 < 2\theta \leq 50°$ $hk\pm l$. One standard measurement after every 33 records, intensity variation ±2·5%. 2402 reflections measured, 1866 observed, 536 unobserved ($I < 3\sigma_I$), 921 unique, $R_{int} = 0{\cdot}024$ (based on intensities). Structure solution by direct methods. Structure refinement on *F*. H atoms treated riding on carrier atoms with fixed isotropic $B(\mathrm{H}) = 1{\cdot}2B(\mathrm{C})$. H atoms bonded to N were located from a difference Fourier map, and their positional parameters and temperature factors were refined. 127 parameters refined; refinement converged at $R = 0{\cdot}033$, $wR = 0{\cdot}042$ (omitting unobserveds), $S = 1{\cdot}37$; $w = [\sigma^2(F) + 0{\cdot}00046F^2]^{-1}$; final $\Delta/\sigma < 0{\cdot}5$; $\Delta\rho_{max} = 0{\cdot}34$, $\Delta\rho_{min} = -0{\cdot}35$ e Å^{-3}. No secondary-extinction correction. Atomic scattering factors from *International Tables for X-ray Crystallography* (1974). All calculations performed with *SHELX*76 (Sheldrick, 1976).

The structure was initially solved by direct methods and refined by full-matrix least-squares calculations using dispersion corrections and anisotropic temperature factors for the non-hydrogen atoms, but without inclusion of ethanol molecules. With this model the refinement converged to $R = 0{\cdot}078$ only. Inspection of the difference density distribution showed significant residual peaks which could be associated with less than 1 mol of disordered ethanol molecules. With inclusion of a variable amount of ethanol in the model the refinement readily converged to $R = 0{\cdot}031$ and $wR = 0{\cdot}038$ (GOF = 1·226) for the merged data set. (The refined amount of 0·39 mol ethanol is corroborated by the ensuing theoretical density, $D_x = 1{\cdot}110$ g cm^{-3}, compared to the experimental $D_m = 1{\cdot}08$ g cm^{-3}.) In order to establish the absolute configuration of the molecule both enantiomorphs were refined with the unmerged data set yielding identical atomic parameters, but $R = 0{\cdot}0335$, $wR = 0{\cdot}0422$, GOF = 1·366 for the present configuration compared to $R = 0{\cdot}0345$, $wR = 0{\cdot}0436$, GOF = 1·412 for the (+)-antipode. Though the differences between the agreement factors are small owing to both the space-group symmetry and the small anomalous-dispersion effects of Cl, they are significant at all levels of *R*-value statistical analysis. According to the Hamilton (1965) test the *wR* ratio of 1·03 implies that the present enantiomorph is correct with a probability exceeding 99·5%.

The decision in favour of the (–)-antipode may be additionally illustrated by the general reflections 211, 121, 112 with ratios $F(\mathbf{h})_{obs}/F(\bar{\mathbf{h}})_{obs}$: 0·994, 0·984, 1·009. The corresponding ratios $F(\mathbf{h})_{calc}/F(\bar{\mathbf{h}})_{calc}$ for the chosen enantiomer are: 0·995, 0979, 1·006, whereas the optical antipode yields: 1·005, 1·021, 0·994.

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

$$U_{eq} = \tfrac{1}{3}\textstyle\sum_i\sum_j U_{ij}a^*_i a^*_j \mathbf{a}_i.\mathbf{a}_j.$$

	x	*y*	*z*	U_{eq}
Cl	1641 (1)	6196 (1)	1017 (1)	55 (1)
N	1313 (2)	3810 (2)	1040 (2)	52 (1)
C(1)	2122 (3)	3119 (2)	1564 (2)	54 (1)
C(2)	1719 (3)	3076 (2)	2519 (2)	56 (1)
C(3)	533 (3)	2487 (2)	2636 (2)	67 (1)
C(4)	589 (4)	1446 (2)	2222 (3)	84 (1)
C(5)	932 (4)	1517 (3)	1265 (3)	89 (1)
C(6)	2151 (3)	2079 (3)	1146 (3)	80 (1)
C(7)	1668 (4)	4137 (2)	2928 (2)	73 (1)
C(8)	1625 (6)	4122 (3)	3923 (2)	133 (2)

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

C(1)–C(2)	1·524 (4)	N–C(1)–C(2)	111·6 (2)
C(1)–C(6)	1·512 (4)	N–C(1)–C(6)	109·8 (2)
C(1)–N	1·494 (4)	C(2)–C(1)–C(6)	112·2 (2)
C(2)–C(3)	1·509 (4)	C(1)–C(2)–C(3)	112·0 (2)
C(2)–C(7)	1·531 (4)	C(1)–C(2)–C(7)	111·5 (2)
C(3)–C(4)	1·511 (5)	C(3)–C(2)–C(7)	113·0 (3)
C(4)–C(5)	1·511 (6)	C(2)–C(3)–C(4)	112·6 (3)
C(5)–C(6)	1·522 (5)	C(3)–C(4)–C(5)	111·0 (3)
C(7)–C(8)	1·520 (4)	C(4)–C(5)–C(6)	111·0 (3)
N–H(1N)	0·92 (3)	C(5)–C(6)–C(1)	111·8 (3)
N–H(2N)	0·91 (3)	C(2)–C(7)–C(8)	113·4 (3)
N–H(3N)	0·83 (2)		

Hydrogen bonds

				∠N–H···Cl
N···Cl	3·162 (3)	H(1N)···Cl	2·27 (3)	165 (2)
N···Cl^{i}	3·192 (2)	H(3N)···Cl^{i}	2·40 (2)	160 (2)
N···Cl^{ii}	3·162 (2)	H(2N)···Cl^{ii}	2·25 (3)	172 (3)

Symmetry code: (i) $-x, 1-y, z$; (ii) $x, 1-y, -z$.

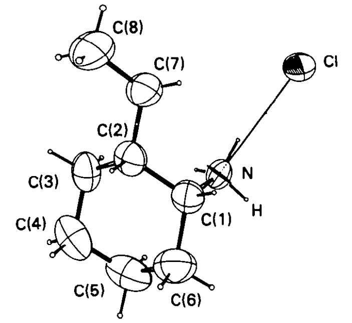


Fig. 1. *ORTEP* drawing (Johnson, 1965) of (–)-(2*b*).HCl.

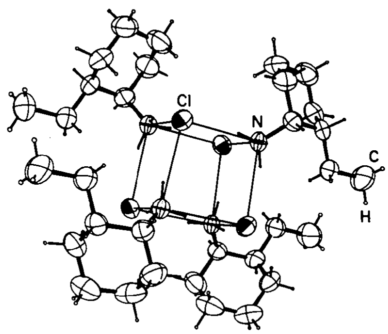


Fig. 2. Salt cluster arrangement of four molecules of (–)-(2*b*).HCl.

Discussion. The atomic coordinates and equivalent isotropic thermal parameters are given in Table 1.* Table 2 summarizes the bond distances and angles. The values vary in the normal range in comparison to literature data (*International Tables for X-ray Crystallography*, 1974). Moreover it is seen that the amino group is in an axial and ethyl group in an equatorial position. This conformation is in contrast to that of the free base in solution (Knupp & Frahm 1984).

An *ORTEP* drawing (Johnson, 1965) of a single molecule of (–)-(2*b*).HCl is depicted in Fig. 1, clearly showing it to possess the (1*R*,2*S*)-*cis* configuration. This is in agreement with the absolute configuration deduced from CD data (Knupp & Frahm, 1984). The cyclohexane ring is in the chair conformation. The packing of the molecules is shown in Fig. 2, with four molecules and four Cl atoms forming a salt cluster *via* $H_2N{\cdots}H{-}Cl$ hydrogen bonds. The somewhat distorted cubic arrangement of the Cl and N atoms is clearly seen. The ethanol molecules between the cubes are omitted.

This work was supported by the Fonds der Chemischen Industrie.

References

Hamilton, W. C. (1965). *Acta Cryst.* **18**, 502–510.
International Tables for X-ray Crystallography (1974). Vol. IV. Birmingham: Kynoch Press. (Present distributor D. Reidel, Dordrecht.)
Johnson, C. K. (1965). *ORTEP*. Report ORNL-3794. Oak Ridge National Laboratory, Tennessee.
Knupp, G. & Frahm, A. W. (1981). *Tetrahedron Lett.* **22**, 2633–2636.
Knupp, G. & Frahm, A. W. (1984). *Chem. Ber.* **117**, 2076–2098.
Ripperger, H., Schreiber, K., Snatzke, G. & Ponsold, K. (1969). *Tetrahedron*, **25**, 827–836.
Sheldrick, G. M. (1976). *SHELX76*. Program for crystal structure determination. Univ. of Cambridge, England.
Verbit, L. & Price, H. C. (1972). *J. Am. Chem. Soc.* **94**, 5143–5152.

---

* Lists of structure factors, anisotropic thermal parameters, H-atom parameters, interatomic distances and angles and least-squares-plane data have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 39894 (11 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Acta Cryst. (1985). C**41**, 470–472

α-Fluoro-*trans*-cinnamoyl Peroxide, $C_{18}H_{12}F_2O_4$

By Donald Bethell, Derek J. Chadwick, Marjorie M. Harding, Guy Q. Maling and Michael D. Wiley

Departments of Organic and Inorganic Physical and Industrial Chemistry, University of Liverpool, Liverpool L69 3BX, England

(*Received* 17 *September* 1984; *accepted* 22 *November* 1984)

Abstract. $M_r = 330{\cdot}29$, monoclinic, $C2/c$, $a = 18{\cdot}78\ (3)$, $b = 10{\cdot}91\ (2)$, $c = 7{\cdot}50\ (1)$ Å, $\beta = 94{\cdot}4\ (2)^\circ$, $U = 1532{\cdot}1$ Å^3, $Z = 4$, $D_x = 1{\cdot}43$ Mg m^{-3}, λ(Cu $K\alpha$) $= 1{\cdot}5418$ Å, $\mu = 1{\cdot}014$ mm^{-1}, $F(000) = 680$, $T = ca$ 293 K, final $R = 0{\cdot}062$ for 607 unique reflexions. As for *trans*-cinnamoyl peroxide, the molecule adopts an extended conformation with the two acyloxy groups in orthogonal planes, *s-cis* stereochemistry in the α,β-unsaturated carbonyl moiety, and unusually short C=O bond lengths [1·185 (11) Å].

Introduction. As part of our program aimed at relating structure and reactivity in diacyl peroxide thermolysis, the structure of the title compound (1) has been

0108-2701/85/030470-03$01.50