cinchonine can be used to resolve mandelic acid and that the higher melting (*R*)-mandelate also is the less soluble of the two diastereomeric salts. A difference between the melting enthalpies would be due to a difference in the crystal enthalpies, if the resulting liquids had very similar thermodynamic properties. The DSC measurements showed that the more soluble (*S*)-mandelate salt has the larger heat of fusion indicating a smaller crystal enthalpy for this compound relative to the *R* salt. As the two diastereomeric salts have virtually identical densities this difference in the crystal enthalpies would correspond to an equivalent difference in the crystal energies. The *S* salt has more interionic interactions in terms of hydrogen bonds than the *R* salt, as described previously. On the other hand, the (*S*)-mandelate ion is found in a conformation with an energy that is *ca* 8 kJ mol^{-1} larger than the energy of the (*R*)-mandelate ion. This difference in conformational energy would be more than compensated for by the intermolecular hydrogen bonds in the *S* salt which consequently would have a lower energy and a larger energy of fusion, as found experimentally. The *R* salt has disorder in one of the cinchoninium ions and the displacement parameters are larger than those in the *S* salt. One would expect that these differences would be reflected in a smaller entropy of fusion for the *R* salt. The experimental data supports this, as $\Delta S^{\ominus}_{\rm fus}$(*S* salt) = 97 J K^{-1} mol^{-1} and $\Delta S^{\ominus}_{\rm fus}$(*R* salt) = 80 J K^{-1} mol^{-1} at their respective melting points. Assuming correspondence between the melting and solution processes for the two salts, the difference in the solubilities of the diastereomeric salts should be caused by differences in their melting enthalpies and entropies. If the difference in solubility was due solely to a difference in enthalpy the *S* salt should be the less soluble, but the difference in entropy more than compensates for the ΔH difference, making the *R* salt the less soluble salt. This leads one to the conclusion that the difference in the solubilities of the diastereomeric cinchoninium mandelates has its origin in the difference between the crystal entropies.

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β-Alkoxy Schiff Base–Oxazolidine Tautomerism: Solid-State Structure of *N*-Diphenylmethylene-L-threonine Methyl Ester

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Abstract

The benzophenone Schiff base of methyl L-threonate, $C_{18}H_{19}NO_3$, $M_r = 297.36$, crystallized as its cyclic methyl (4*S*,5*R*)-5-methyl-2,2-diphenyl-1,3-oxazolidine-4-carboxylate tautomer, orthorhombic, $P2_12_12_1$, $a = 8.455$ (2), $b = 12.648$ (2), $c = 14.650$ (3) Å, $V = 1566.6$ (5) Å^3, $Z = 4$, $D_x = 1.26$ g cm^{-3}, λ(Mo $K\alpha$) = 0.71073 Å, $\mu = 0.8$ cm^{-1}, $F(000) = 632$, $T = 296$ K. The structure was solved by direct methods; $R = 0.040$ and $wR = 0.045$ for 1113 observed reflections. H atoms were included in the refinement, but were constrained to their attached atoms. The amine hydrogen (HN) was located from a difference map and was refined with a fixed isotropic thermal parameter. The structure confirms the existence of

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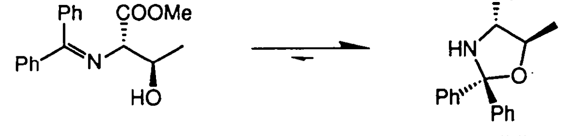
the oxazolidine tautomer in the solid state and shows that the oxazolidine nitrogen is sp^3 hybridized with a fixed Walden configuration. In the crystal there is no obvious hydrogen bonding to HN, or to the nitrogen lone pair, although the N—H bond is directed toward the center of a phenyl ring on an adjacent molecule (perpendicular H atom–ring distance 3.09 Å).

Introduction

There has been increasing interest in *N*-diphenylmethylene protection of primary amines (*i.e.* benzophenone Schiff bases, $Ph_2C{=}N$—) in organic synthesis (Greene & Wuts, 1991). Schiff bases of α-amino esters have been particularly useful as glycine anion equivalents (O'Donnell *et al.*, 1988; O'Donnell, Bennett & Wu, 1989; Genet *et al.*, 1990) and as amino-acid cation equivalents (O'Donnell, Bennett & Polt, 1985; O'Donnell & Falmagne, 1985). The basic imine lone pair (C=N:) has been used to complex metals to achieve 'chelation control' (Belokon *et al.*, 1985; Polt & Peterson, 1990) and to increase the nucleophilicity of neighboring hydroxyl groups (Szabò, Li & Polt, 1991). ^1H and ^{13}C nuclear magnetic resonance (NMR) spectra have indicated that many of these β-hydroxy-substituted benzophenone Schiff bases are fluxional (Polt, Peterson & DeYoung, 1992).

A dilute sample of the L-threonine-derived Schiff base (1*a*) in $CDCl_3$ (5 mg/0.5 ml) exists as a 1:60 mixture of equilibrating structures (1*a*) and (1*b*) at 203 K (see scheme below). This equilibrium has implications for many synthetic processes. Since there are few monocyclic oxazolidines with a free N—H bond described in the literature, an X-ray analysis of the 'Schiff base' was performed. There is one example of a polycyclic oxazolidine bearing a free N—H bond (Lindeman, Shklover, Struchkov, Turuta & Kamernitzky, 1982), several examples of monocyclic *N*-substituted oxazolidines (Andreetti, Bocelli & Sgarabotto, 1979; Bellan *et al.*, 1978; Godfrey, Gordon, Von Langen, Engebrecht & Pluscec, 1986; Roques, Bellan, Rossi, Declercq & Germain, 1979; Skarzynski, 1982; Skarzynski, Derewenda, Brzozowski & Mloston, 1982) and three examples of polycyclic *N*-substituted oxazolidines (Alcaide *et al.*, 1986; Faure, Loiseleur, Alvernhe & Laurent, 1984; Meyers, Lefker, Wanner & Aitken, 1986).



β-Hydroxy Schiff base (1*a*)

Oxazolidine (1*b*)

Experimental

Compound (1*a*)/(1*b*) was synthesized from methyl-L-threonate.HCl and diphenyl ketimine (Balsamini, Duranti, Mariani, Salvatori & Spandoni, 1990; Szabò *et al.*, 1991), chromatographed on SiO_2 with 5% EtOAc/hexane and recrystallized from 30% EtOAc/hexane using solvent diffusion with pure hexane. This provided colorless block crystals. A crystal of approximate dimensions 0.3 × 0.5 × 0.5 mm was mounted on a glass fiber in a random orientation. Data were collected on a Syntex $P2_1$ diffractometer using the θ–2θ scan technique. Cell constants and an orientation matrix for data collection were obtained from a least-squares refinement using 25 reflections in the range $20 < 2\theta < 27°$. Data were collected at a maximum of 50° in 2θ, from the $+h+k+l$ quadrant ($h_{\max} = 11$, $k_{\max} = 16$, $l_{\max} = 18$). A total of 1648 reflections were collected, of which 1599 were unique and not systematically absent. As a check on crystal and electronic stability two reflections were measured after every 98 reflections. The intensities of these standards remained constant within experimental error throughout data collection. No decay correction was applied. Lorentz and polarization corrections were applied to the data. The linear absorption coefficient is $0.8\ \text{cm}^{-1}$ for Mo $K\alpha$ radiation. No absorption correction was made. Intensities of equivalent reflections were averaged. The agreement factors for the averaging of the 43 observed and accepted reflections were 3.7% based on intensity and 2.3% based on F_o. The structure was solved by direct methods. 21 atoms were located using *SHELXS*86 (Sheldrick, 1985), the remaining non-H atom was found in a difference map. With the exception of the amine H atom (HN), H atoms were included at idealized positions and constrained to ride on the atom to which they are bonded. The HN atom was found from a difference map. This H atom was refined with a fixed isotropic thermal parameter.

The structure was refined in full-matrix least squares (Frenz, 1978), where the function minimized was $\sum w(|F_o| - |F_c|)^2$. The weights for each reflection were calculated using the counter-weighting scheme. The standard deviation on intensities is defined as $\sigma(F^2) = [\sigma^2(I) + (pF^2)^2]^{1/2}$ and the uncertainty factor, p, was set to the value 0.040. Only the 1113 reflections with $I > 3\sigma(I)$ were used in the refinements. The final cycle of refinement included 202 variable parameters and converged, $(\Delta/\sigma)_{\max} = 0.00$, with agreement factors of $R = 0.040$, $wR = 0.045$ and $S = 1.61$. The highest peak in the final difference Fourier map had a height of $(\Delta\rho)_{\max} = 0.22\,(5)\ \text{e}\ \text{Å}^{-3}$, the minimum negative peaks had a height of $(\Delta\rho)_{\min} = -0.22\,(5)\ \text{e}\ \text{Å}^{-3}$ (Cruickshank, 1949). Scattering factors were taken from *International Tables for X-ray*

Crystallography (1974, Vol. IV, Table 2.2B). Anomalous-dispersion effects were included in F_c (Ibers & Hamilton, 1964) the values for f' and f'' were those given in *International Tables for X-ray Crystallography* (1974, Vol. IV, Table 2.3.1).

An *ORTEP*II drawing (Johnson, 1976) of oxazolidine (1*b*) is shown in Fig. 1. Final atomic coordinates are given in Table 1.* Bond lengths and bond angles are shown in Table 2. All calculations were performed on a VAX computer using *SDP*/*VAX* (Frenz, 1978) and *SHELXS*86 (Sheldrick, 1985).

Table 1. *Positional parameters and their e.s.d.'s*

$$B_{eq} = (8\pi^2/3)(U_{11} + U_{22} + U_{33}).$$

	x	*y*	*z*	B_{eq} (Å^2)
O1	0.2231 (3)	0.7595 (2)	0.4407 (1)	4.23 (5)
O2	0.4408 (3)	0.7840 (3)	0.3571 (2)	5.43 (6)
O3	0.1665 (3)	0.8629 (2)	0.1565 (1)	3.75 (5)
N	0.0432 (3)	0.8009 (2)	0.2864 (2)	2.89 (5)
C1	0.3142 (5)	0.7746 (4)	0.5229 (2)	6.2 (1)
C2	0.3012 (4)	0.7676 (3)	0.3626 (2)	3.53 (7)
C3	0.1945 (4)	0.7463 (3)	0.2809 (2)	3.00 (6)
C4	0.2682 (4)	0.7811 (3)	0.1897 (2)	3.28 (7)
C5	0.2761 (6)	0.6947 (3)	0.1190 (3)	5.3 (1)
C6	0.0627 (4)	0.8941 (2)	0.2295 (2)	2.99 (6)
C7	−0.0928 (4)	0.9290 (2)	0.1893 (2)	3.31 (7)
C8	−0.1056 (5)	0.9587 (3)	0.0981 (2)	4.41 (9)
C9	−0.2505 (6)	0.9919 (4)	0.0639 (3)	5.69 (9)
C10	−0.3814 (5)	0.9983 (3)	0.1193 (3)	5.7 (1)
C11	−0.3692 (5)	0.9688 (3)	0.2101 (3)	4.78 (9)
C12	−0.2261 (4)	0.9351 (3)	0.2439 (3)	3.93 (8)
C13	0.1388 (4)	0.9847 (2)	0.2828 (2)	2.75 (6)
C14	0.1176 (5)	0.9958 (3)	0.3761 (2)	3.92 (8)
C15	0.1842 (5)	1.0803 (3)	0.4226 (3)	5.04 (9)
C16	0.2700 (5)	1.1549 (3)	0.3756 (3)	4.85 (9)
C17	0.2904 (4)	1.1457 (3)	0.2831 (3)	4.49 (8)
C18	0.2246 (4)	1.0610 (3)	0.2371 (3)	3.62 (7)

Table 2. *Bond distances* (Å) *and bond angles* (°)

O1—C1	1.441 (4)	C7—C8	1.392 (5)
O1—C2	1.325 (4)	C7—C12	1.384 (5)
O2—C2	1.200 (4)	C8—C9	1.389 (6)
O3—C4	1.430 (4)	C9—C10	1.374 (7)
O3—C6	1.440 (4)	C10—C11	1.385 (6)
N—C3	1.456 (4)	C11—C12	1.375 (5)
N—C6	1.453 (4)	C13—C14	1.387 (4)
C2—C3	1.524 (5)	C13—C18	1.380 (4)
C3—C4	1.538 (4)	C14—C15	1.387 (5)
C4—C5	1.507 (5)	C15—C16	1.374 (6)
C6—C7	1.507 (4)	C16—C17	1.372 (5)
C6—C13	1.528 (4)	C17—C18	1.382 (5)
C1—O1—C2	116.4 (3)	C7—C6—C13	110.3 (2)
C4—O3—C6	108.2 (2)	C6—C7—C8	112.1 (5)
C3—N—C6	104.7 (2)	C6—C7—C12	120.0 (3)
O1—C2—O2	124.2 (3)	C8—C7—C12	118.5 (3)
O1—C2—C3	111.7 (3)	C7—C8—C9	119.7 (4)
O2—C2—C3	124.0 (3)	C8—C9—C10	121.0 (4)
N—C3—C2	113.1 (2)	C9—C10—C11	119.4 (4)
N—C3—C4	105.6 (2)	C10—C11—C12	119.6 (4)
C2—C3—C4	113.1 (3)	C7—C12—C11	121.7 (3)
O3—C4—C3	105.0 (2)	C6—C13—C14	121.6 (3)
O3—C4—C5	108.5 (3)	C6—C13—C18	119.9 (3)
C3—C4—C5	114.0 (3)	C14—C13—C18	118.4 (3)
O3—C6—N	105.8 (2)	C13—C14—C15	120.6 (4)
O3—C6—C7	108.8 (2)	C14—C15—C16	119.9 (4)
O3—C6—C13	109.2 (3)	C15—C16—C17	120.2 (4)
N—C6—C7	111.3 (3)	C16—C17—C18	119.8 (4)
N—C6—C13	111.3 (2)	C13—C18—C17	121.1 (3)

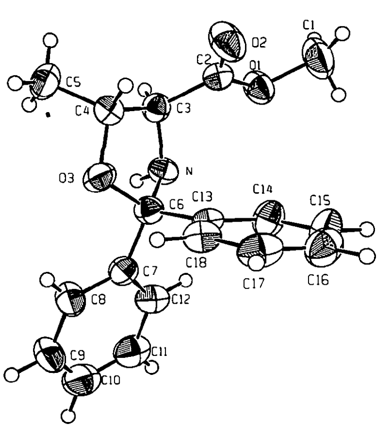


Fig. 1. *ORTEP* view of molecule (1*b*) showing labeling.

Discussion

Walden inversion of secondary amines is normally a very fast process, and rigidity in five-membered rings is exceptional (*cf. puckering* or *pseudorotation*; Davies, 1978, pp. 160–161). In this structure, we found that the oxazolidine ring was relatively rigid, and that the HN refined well, resulting in a normal N—H distance (0.93 Å) with a tetrahedral (*sp*^{3}) N atom for structure (1*b*). A comparison of this structure with the other oxazolidine structures shows that the bond lengths and angles (Table 2) are quite unexceptional. Lindeman *et al.* (1982) also found a tetrahedral (*sp*^{3}) N—H in a more complex steroidal oxazolidine structure, and invoked an intermolecular hydrogen bond (O···H—N). The O···N distance was 3.256 (3) Å, and the O···H distance was 2.36 (3) Å in that case. A stereo cell-packing diagram and nonbonding distances were examined to determine if a similar phenomenon was occurring with (1*b*). Clearly, there was no hydrogen bond between the N—H and any O or N atom. Interestingly, the N—H bond is directed toward the center of an adjacent phenyl ring (see Fig. 2). The distance between the H atom and the phenyl ring is marked with a line in Fig. 2. This distance is ~3.1 Å – probably too long to represent an intramolecular N—H···Ph hydrogen bond. Intramolecular hydrogen bonds [N:···H12 (2.65 Å) and N:···H14 (2.56 Å)] were considered as well, but these are still long. A more reasonable explanation for the configuration of the N—H is that the nitrogen inverts in order to avoid a severe nonbonded interaction between the HN and these same hydrogens, H12 and H14.

Molecular-mechanics energy calculations on a single molecule of the oxazolidine in the X-ray con-

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* Lists of structure factors, anisotropic thermal parameters, H-atom parameters, and details of data collection and refinement have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 55511 (15 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: HH0625]

formation were conducted to assess the interactions stabilizing this geometry. Calculations using the *MM*2 force-field parameter set (Allinger, 1977) were achieved with the modelling package *MACROMODEL* (Mohamadi *et al.*, 1990). All atoms of the oxazolidine were explicitly treated with inclusion of the N-atom lone pair. These calculations were compared with a similar analysis of the X-ray conformation with the tetrahedral N-atom center inverted such that the positions of HN and the N-atom lone pair were interchanged.

The strain energies of these structures indicated a relative energy difference between the oxazolidine configurations of greater than 12.6 kJ mol^{-1} in favor of the observed X-ray conformation. However, to gain a more realistic estimate of the relative energies of these structures within the *MM*2 force field, both were minimized using an initial 250 iterations of steepest decent refinement, followed by exhaustive minimization to an r.m.s. gradient of less than 0.004 kJ Å^{-1} mol^{-1} with the full-matrix Newton–Raphson method. The resulting strain energies (E) are shown in Table 3. The key reason for the higher energy of the inverted configuration is the steric compression between HN and the aromatic hydrogens H12 and H14, which leads to increased strain in the five-membered ring.

A better indication of the effect of this interaction on the relative populations of the two configurations was gained by calculating their approximate vibrational entropies at 300 K ($T\Delta S$, Table 3) using the 'free energy' option in *MACROMODEL* and using these to estimate their configurational free energies, ΔG (Table 3). This gave a relative free energy difference of 7.1 kJ mol^{-1}, corresponding to a population ratio of 94:6 in favor of the X-ray configuration, which is consistent with our experimental observations.

Since we have observed products arising from both the imine form (Szabò *et al.*, 1991) and the oxazolidine form (Polt *et al.*, 1992) of these tautomers, a more complete study of the factors affecting these equilibria is in order. Although this tautomerism can be viewed as a problem, successful trapping of the oxazolidines (Polt *et al.*, 1992) or the related oxazolidinones (*cf.* Seebach, Juaristi, Miller, Schickli & Weber, 1987) can provide useful synthetic protocols.

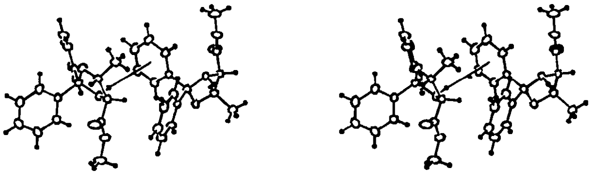

Fig. 2. Stereo packing view of two (*1b*) molecules.

Table 3. *Molecular-mechanics energies* (kJ mol^{-1})

	E	$T\Delta S$*	ΔG†
Minimized X-ray structure	113	107	6.3
Minimized X-ray structure with N-atom center inverted	118	105	13

* $T = 300$ K.
† $\Delta G = E - T\Delta S$.

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Structural Studies of Cyclohexane IV*

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Abstract

We report an extensive neutron powder diffraction study of the high-pressure phase IV of cyclohexane-d_{12}. Using constrained Rietveld refinement we deduce approximate atomic positions for this phase which are found to be in close accord with the predictions of energy-minimization calculations. The likely relationship between the unit cell of phase IV and that of the ambient-pressure phase II is also presented. We further demonstrate, by means of an X-ray powder diffraction study of cyclohexane-h_{12}, that phase IV can be produced in a metastable state at ambient pressure by rapid quenching to 77 K from the liquid. This finding contradicts a previous report [Burns & Dacol (1984). *Solid State Commun.* **51**, 773–775] claiming that the ambient-pressure metastable phase is an orientational glass.

1. Introduction and background

Although a relatively simple organic molecular system, cyclohexane is characterized by a high degree of structural polymorphism in quite modest ranges of temperature and pressure (Schulte & Würflinger, 1987). It therefore represents an ideal system for studies of the processes governing structural polymorphism in organic molecular crystals. Indeed a thorough understanding of phase formation in such a simple system is a prerequisite for a wider elucidation of the generic factors governing structural phase changes in other (more complex) organic molecular materials. With this motivation, cyclohexane has been the subject of a number of detailed structural investigations.

The bulk of previous structural studies has concentrated solely on the phases obtainable at *ambient* pressure. Under these conditions, cyclohexane is known to exhibit two stable solid phases. Phase I, the plastic phase, lies between 186.1 K and the melting point at 279.82 K. It is cubic [$a = 8.61$ (2) Å; $Z = 4$; space group $Fm3m$] and from NMR studies is known to be characterized by a large degree of dynamic molecular disorder, the molecules undergoing rapid reorientations on the lattice sites (Andrew & Eades, 1953). Below 186.1 K an order–disorder transition takes place to an orientationally ordered structure (phase II). Single-crystal X-ray diffraction measurements performed by Kahn, Fourme, André & Renaud (1973) have shown that phase II possesses a monoclinic unit cell [$a = 11.23$ (2), $b = 6.44$ (2), $c = 8.20$ (2) Å, $\beta = 108.83°$; $Z = 4$; space group $C2/c$]. In the same work, a determination of the molecular positions and atomic coordinates also revealed that the molecules have the so-called 'chair-like' conformation.

In addition to the stable ambient-pressure phases, cyclohexane is also known to exhibit a *metastable* phase. This phase was discovered by Renaud &

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