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A Sulfur-Stabilized Enol

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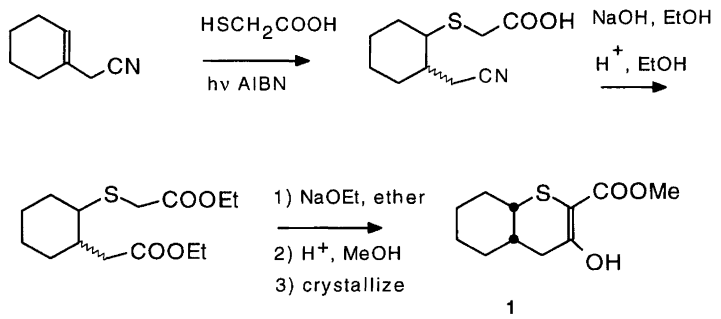
The preparation and X-ray structure of *cis*-3-hydroxy-4a,5,6,7,8,8a-hexahydro-4*H*-thiochromene-2-carboxylic acid methyl ester are described. The compound crystallizes in the orthorhombic space group $Pca2_1$ with cell parameters a/Å 11.942(9), b/Å 5.399(1), c/Å 17.503(6), V/Å^3 1129(2). The molecule is an enol with an intramolecular H-bond. NMR and IR spectra show that the main tautomer is also the enol form in solution, the enol content being 74% in $CDCl_3$. The major solution conformation is found to be similar to the solid-state conformation. Molecular mechanics calculations reproduce the conformational equilibrium well but indicate that the enol form of the title compound is strained and would be less stable than the keto form. The role of the α-sulfur as a stabilizer of the enol is investigated with *ab initio* calculations.

β-Keto esters such as ethyl acetoacetate are known to form fairly stable enols because of the stabilizing effect of the intramolecular H-bond of the enol OH to the ester carbonyl.[1] The enol content varies depending on the medium and is at greatest 20% in non-polar solvents such as toluene. We wish to report a relatively simple β-keto ester, 3-hydroxy-4a,5,6,7,8,8a-hexahydro-4*H*-thiochromene-2-carboxylic acid methyl ester (**1**), which crystallizes as an enol and is also extensively enolized in solution. Though enols of common ketones and aldehydes can be prepared, keto forms are thermodynamically favored.[2] Noticeable amounts of enol tautomers are usually seen when there is a possibility for intramolecular hydrogen bonding, such as in β-dicarbonyl compounds, when there are bulky aromatic groups in the molecule, or in polyfluorinated compounds.[1] In cyclic β-keto esters the preference for the enol tautomer is enhanced especially in six-membered rings.[3] The enhancing effect of an α-alkylthio substituent on enol stability is not widely known though Yoshida *et al.*[4] reported that such a substituent makes the β-dicarbonyls completely enolized.

Results and discussion

Preparation. The title compound **1** was prepared by Dieckmann condensation of ethyl (2-ethoxycarbonylmethylcyclohexylthio)acetate (Scheme 1). This diester was obtained by radical addition[5] of thioglycolic acid to cyclohex-1-enylacetonitrile followed by hydrolysis of the resulting nitrile and esterification. The stereochemistry of the addition product was predominantly *cis*.

Crystallographic study. Crystal data for the title compound **1** are shown in Table 1, selected bond lengths and angles in Table 2 and the positional parameters in Table 3. The numbering system of the molecule is presented in Fig. 1. The crystal consists of discrete molecules with no apparent intermolecular interactions in the solid state. There are three fused six-membered rings in the molecule (Fig. 2). The cyclohexane ring displays a chair conformation with characteristic puckering parameters[6] $Q = 0.526$ Å, $\theta = 4.8°$ and $\phi = 48.2°$, while the corresponding parameters of the dihydrothiine ring are nearly



Scheme 1.

Table 1. Crystal data and experimental details of the structure determination of the title compound.

Formula	$C_{11}H_{16}O_3S$
M_r	228.31
Space group (orthorhombic)	$Pca2_1$ (No. 29)
Cell parameters at 290(1) K	
a/Å	11.942(9)
b/Å	5.399(1)
c/Å	17.503(6)
V/Å^3	1129(2)
Calculated density/g cm^{-3}	1.344
Z	4
μ(Mo Kα)/cm^{-1}	2.59
Maximum 2θ°	50
No. of refl. measured	1211 unique
No. observations [$I > 3\sigma(I)$]	807
$R=\Sigma(\lvert F_o\rvert-\lvert F_c\rvert)/\Sigma\lvert F_o\rvert$	0.052
$R_w=[\Sigma w(\lvert F_o\rvert-\lvert F_c\rvert)^2/w\ \Sigma\lvert F_o\rvert^2]^{1/2}$	0.061
Goodness-of-fit	2.53
Least-squares weights	$w=[\sigma^2(F_o)]^{-1}$
Max./min. in final diff. map/e Å^{-3}	0.28/−0.24

Table 2. Selected bond lengths (Å) and angles (°) with their standard deviations.

S(1)–C(2)	1.768(8)	S(1)–C(2)–C(3)	124.3(5)
S(1)–C(8a)	1.822(7)	S(1)–C(2)–C(9)	117.8(4)
O(10)–C(9)	1.339(8)	C(3)–C(2)–C(9)	117.8(6)
O(12)–C(9)	1.201(9)	O(13)–C(3)–C(2)	122.8(6)
O(13)–C(3)	1.330(9)	O(13)–C(3)–C(4)	111.9(5)
O(13)–H(1)	0.65(9)	C(2)–C(3)–C(4)	125.3(6)
C(2)–C(3)	1.365(8)	C(3)–C(4)–C(4a)	115.3(5)
C(2)–C(9)	1.458(9)	C(4)–C(4a)–C(5)	116.3(6)
C(3)–C(4)	1.48(1)	C(4)–C(4a)–C(8a)	112.2(6)
C(4)–C(4a)	1.50(1)	C(5)–C(4a)–C(8a)	111.3(5)
C(4a)–C(5)	1.539(8)	C(5)–C(6)–C(7)	113.4(7)
C(4a)–C(8a)	1.527(9)	S(1)–C(8a)–C(4a)	111.1(5)
		S(1)–C(8a)–C(8)	122.4(6)
C(2)–S(1)–C(8a)	101.1(3)	O(10)–C(9)–C(2)	111.9(6)
C(9)–O(10)–C(11)	116.7(6)	O(12)–C(9)–C(2)	125.7(6)

Table 3. Atomic positional parameters and equivalent isotropic temperature factors for the non-hydrogen atoms.[a]

	x/a	y/b	z/c	U_{eq}
S(1)	0.8366(1)	0.2843(3)	0.3525(3)	0.0435(4)
O(10)	0.7488(4)	0.5029(9)	0.4849(3)	0.058(2)
O(12)	0.8237(5)	0.268(1)	0.5761(3)	0.069(2)
O(13)	0.9669(5)	−0.059(1)	0.5357(3)	0.071(2)
C(2)	0.8699(5)	0.191(1)	0.4466(4)	0.043(2)
C(3)	0.9458(5)	0.011(1)	0.4643(4)	0.046(2)
C(4)	1.0130(6)	−0.130(1)	0.4085(5)	0.056(3)
C(4a)	1.0216(5)	−0.016(1)	0.3306(5)	0.053(3)
C(5)	1.1027(5)	0.204(1)	0.3226(5)	0.058(3)
C(6)	1.1125(7)	0.288(2)	0.2414(6)	0.060(3)
C(7)	1.0033(7)	0.352(2)	0.2062(5)	0.061(3)
C(8)	0.9143(6)	0.140(2)	0.2161(5)	0.059(3)
C(8a)	0.9069(5)	0.045(1)	0.2969(4)	0.046(3)
C(9)	0.8136(5)	0.317(1)	0.5095(4)	0.045(2)
C(11)	0.6861(8)	0.638(2)	0.5427(6)	0.082(4)

[a] $U_{eq} = \frac{1}{3}\sum_i\sum_j U_{ij}a_i^*\cdot a_j^*\bar{a}_i\cdot\bar{a}_j$.

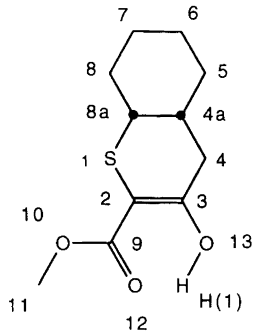


Fig. 1.

ideal for a half chair: $Q = 0.520$ Å, $\theta = 39.8°$ and $\phi = 88.1°$. A third ring contains an intramolecular hydrogen bond O(13)–H(1)···O(12). The latter is planar with the exception of hydrogen. The compound assumes the most stable conformation, i.e., the sulfur is axial with respect to the carbocyclic ring.[7] The bond distances and the bond angles appear fairly normal.[8] Comparison with the average value from known crystal structures of enolized β-keto esters[9] indicates that the C(9)–O(12) (C = O) bond is short: 1.201(9) Å compared with the average 1.227 Å. Also, the O(12)–O(13) distance 2.558(8) is shorter than the average value of 2.583 Å. The hydrogen bond distances: O(13)–H(1) 0.65 Å, O(12)–H(1) 2.21 Å, indicate hydrogen is far off from its average position:[9] O–H 1.95 Å and O···H 1.77 Å, which is undoubtedly an artifact of the X-ray method.

The molecular structure in solution. When crystals of enol **1** are dissolved in chloroform or carbon tetrachloride the resulting enol solution is stable for at least two months. Only when acid is added to the solution does equilibra-

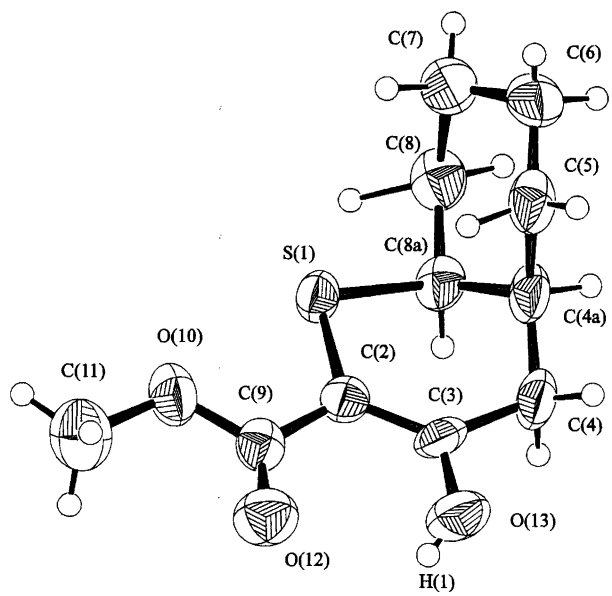


Fig. 2. ORTEP drawing of **1**. The thermal ellipsoids for the non-hydrogen atoms are drawn at the 50% probability level.

Table 4. Selected coupling constants of **1**

Protons	Hz
4*ax* 4*eq*	18.9
4*ax* 4a	6.23[a]
4*eq* 4a	5.25[a]
4a 8a	3.1
4a 5*eq*	3.1
4a 5*ax*	9.2
7*eq* 8a	3.1[a]
7*ax* 8a	5.9[a]

[a]The assignments may be reversed.

tion take place and the keto tautomer appear. The latter was identified as a minor component of the mixture by the carbonyl carbon signals (δ 201).[10] An estimate for the keto–enol equilibrium constant of 0.36 was obtained using proton integral signals. The IR spectrum in CCl_4 displays an OH frequency at 3000 cm^{-1}, a carbonyl frequency at 1653 cm^{-1} and a double bond at 1605 cm^{-1} indicating a strong H-bond and the absence of the keto form.[11] The low-field chemical shift of the enol OH at 12.1 ppm also supports the presence of a strong H-bond.[4] The proton coupling constants are displayed in Table 4. These confirm that the ring fusion is *cis* ($J_{4a8a} = 3.1$ Hz) and that the sulfur substituent is predominantly axial with respect to the carbocyclic ring, $J_{4a5axial} = 9.23$ Hz. Since the pure axial–axial coupling constant ought to be, in this case, 12.4 Hz[12] one can estimate that the equilibrium constant for the conformational equilibrium (Fig. 3) is ca. 2, which is similar to that for *cis*-1-thiadecalin (58:42).[7] This equilibrium constant is in reasonable agreement with the energy difference obtained from molecular mechanics calculations with MacroModel[13] $\Delta H = 0.5$ kcal mol^{-1} (roughly corresponds to $K = 2.3$). The large geminal coupling constant of 18.9 Hz on carbon 4 indicates that the plane of the neighboring double bond bisects the H–C–H angle.[14] This arrangement can be attained in a half-chair conformation in agreement with the findings of our X-ray study. In the keto form this geminal coupling is reduced to 13.25 Hz as the half-chair puckers into the normal chair form. Thus the principal conformation in solution is the same as that found in the solid state by X-ray determination. This is also confirmed by the fact that the solution and the solid state ^{13}C NMR spectra are alike.

The keto–enol tautomerism. That all the crystalline β-keto ester **1** is of enol form was verified from the solid state

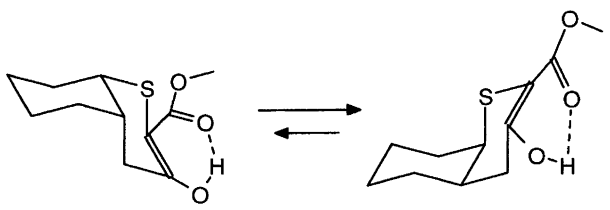


Fig. 3. Conformations of **1**.

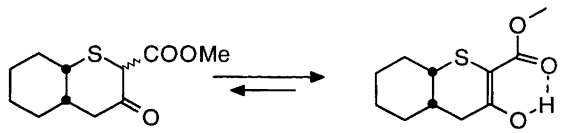


Fig. 4. Keto–enol equilibrium of **1**.

Table 5. Molecular mechanics energies (kcal mol^{-1}) calculated for isomers of **1** and 2-ethoxycarbonylcyclohexanone **2**.

	Conformation		
Compound	S	COOMe	MM2 energy
Enol **1**	axial	–	15.4
Enol **1**	equatorial	–	15.9
cis-Keto **1**	equatorial	axial	12.7
cis-Keto **1**	axial	equatorial	13.6
trans-Keto **1**	equatorial	equatorial	14.1
trans-Keto **1**	axial	axial	12.1
Compound	Conformation		
Enol **2**			0.1
Keto **2**	equatorial		1.8
Keto **2**	axial		2.0

C-13 NMR (CP/MAS) spectrum. In acidic solution the keto–enol exchange is fast. The extent of enolization of **1** in equilibrium in $CDCl_3$ is 74% (see Fig. 4). This is comparable to the enol content of 68% in CCl_4 of the parent ring 2-ethoxycarbonylthian-3-one.[15] On the other hand, the carbocyclic analogue 2-ethoxycarbonylcyclohexanone is 54.5% enolized in chloroform and 74% in benzene.[3] The acyclic parent compound ethyl acetoacetate is enolized to 5–10% in acetone[10] and 19.8% in toluene,[1] while Yoshida *et al.* do not report any keto form in their α-thio-β-dicarbonyls.[4] It seems that introduction of sulfur into an α position will shift the equilibrium in favor of enol in acyclic β-keto esters whereas the situation in a six-membered ring is less clear. The explanation offered[4] for the behavior of the sulfur-substituted β-keto carbonyl compounds is the electron-withdrawing resonance effect of divalent sulfur through pπ–dπ conjugation. On the other hand, the situation is reminiscent of the stabilization of carbanions by α-sulfur in which case the reason for the extra stability is believed to be the polarization[16] and σ*–n interaction.[17] Since there is an inconsistency in the effect of sulfur on the enol stability of acyclic and cyclic β-keto esters we decided to study this effect by computational methods. In addition, this seemed a good case in which to study the d-orbital involvement in divalent sulfur compounds.

Molecular mechanics calculations by MacroModel indicate that keto form should be clearly more stable than the enol. Indeed, keto forms of **1*** (see Table 5) are more stable than the enol conformers. The absolute minima

* In the equilibrium there will be two configurational isomers for the keto form as the ester group may assume a *cis* or *trans* position with respect to the ring fusion.

differ by 3.3 kcal mol^{-1} in favor of the keto form. The corresponding difference for 2-ethoxycarbonylcyclohexanone (**2**) is 1.7 kcal mol^{-1} in favor of the enol. Thus MacroModel reproduces the keto–enol tautomeric equilibrium reasonably well for **2** whereas for the *S*-containing ring **1** the calculated equilibrium is far off the experimental value. Inspection of the components of the steric energy reveals that the enol form of **1** is destabilized by strain in the dihydrothiine ring. There is also substantially less relief of torsional strain on going from the keto to the enol form in the *S*-ring than in the carbocyclic analogue. Thus molecular mechanics considerations alone would predict that, in compound **1**, the keto tautomer is preferred in contrast with the experiment. Therefore the *S*-atom stabilizes the enol form in **1** as in acyclic β-keto esters.

To evaluate the electronic contribution of various α substituents on keto–enol tautomerism, methyl acetoacetate, its α-hydroxy and α-mercapto derivatives and their corresponding enols were studied using the *ab initio* method at the STO-3G level. The keto–enol energy difference favors the keto form in all cases (see Table 6): 4.9 kcal mol^{-1} in the parent, 5.9 kcal mol^{-1} in the hydroxy and 1.8 kcal mol^{-1} in the mercapto compound. These calculations produce apparently the correct trend: in the mercapto compound the enol content is largest and is smallest in the hydroxy derivative in which the electronegative and resonance-donating OH group is expected to destabilize the enol form. When an improved basis set, STO-3G* (including the d-orbital-like functions), was used on methyl α-methylthioacetoacetate and its enol form, the enol was found to be the more stable tautomer (by 0.5 kcal mol^{-1}) in good agreement with the experiment. Compared with the keto form there is a slight increase in the electron density (Mulliken atomic population) in the methyl group of the enol *S*-methyl. The bond lengths of the optimized structures show no exceptional changes on going from keto to enol. This suggests that there exists a stabilizing interaction between the sulfur atom and the enol system.

To obtain more detailed information about the possible involvement of d-orbitals a single-point calculation was made using an extensive basis set, 6-31G*, with the X-ray structure coordinates of **1**. Natural atom and bond orbital analysis[18] was used for inspection of the results. The contribution of sulfur 3d orbitals to the bond orbitals of **1** was found to be very small. Hence, as in the case of α-thio carbanions,[16,17] the dπ–pπ conjugation is probably not implicated here. In order to check whether the calculation would produce the same geometry as the X-ray determination, compound **1** was optimized using the STO-3G* basis set starting from the X-ray geometry. Except for the hydrogens the optimized structure deviates little from the crystal structure (non-hydrogen root mean square distance 0.061). The major difference was the position of the OH hydrogen which was found to be in the same plane as other atoms of H-bonded ring. There was a slight excess of electrons on C8a (natural charge −0.09865) compared with other CH or carbons (natural charges vary from +0.00850 to −0.06557) according to NBO analysis. This situation can be interpreted in terms of polarization of the C8a–S bond. The stabilization of the enol with respect to the keto form may be rationalized as follows: there is a considerable negative charge on C4 which is stabilized by the adjacent sulfur by polarization of the C–S bond.[19]

Table 6. Ab initio energies (a.u.)[a] calculated for β-keto esters and their enol tautomers

Methyl acetoacetate	Keto	Enol	δ(keto–enol)
α-H	−413.199794	−413.192010	−4.9 kcal mol^{-1}
α-OH	−487.027741	−487.018311	−5.9 kcal mol^{-1}
α-SH	−806.370626	−806.367687	−1.84 kcal mol^{-1}
α-SCH_3	−844.992290	−844.99319	0.56 kcal mol^{-1}

[a] 1 a.u. corresponds to 627.5 kcal mol^{-1}.

Conclusion. *cis*-3-Hydroxy-4a,5,6,7,8,8a-hexahydro-4*H*-thiochromene-2-carboxylic acid methyl ester, a simple β-keto ester, crystallizes as an enol. The enol is also the main tautomer in solution, in contrast with expectation. It may be concluded that the α sulfur atom stabilizes the enol form and that the origin of this stabilization is probably polarization.

Experimental

Fifty ml (0.39 mol) of cyclohexenylacetonitrile and 40 ml of 80% aqueous thioglycolic acid in acetic acid, were irradiated with a UV-lamp for a few hours in the presence of a catalytic amount of α,α′-azoisobutyronitrile. The slow reaction was allowed to proceed until no further addition appeared to take place (NMR). The reaction mixture was poured into 450 ml of water and the organic layer was separated and dried. The product was distilled until no more cyclohexenylacetonitrile came over (b.p. 105°C/20 mm). The residue, a brownish oil, (2-cyanomethylcyclohexylthio)acetic acid, 56.2 g (67% yield based on the recovery of 19 ml of nitrile) was hydrolyzed by being refluxed in a solution of 40 g NaOH and 100 ml of water and 50 ml of ethanol for 4 days. The ethanol was removed by distillation and the residue was acidified (HCl). The separated oil was taken up in dichloromethane and the aqueous solution was extracted with dichloromethane. The solvent was removed and the residue was dried by distillation with added toluene. Absolute ethanol (100 ml) and 50 ml of acetyl chloride were added (with cooling) and the solution was left to stand for one week. The excess of HCl was removed *in vacuo* and absolute ethanol and cyclohexane and a little *p*-toluenesulfonic acid were added and the solution was refluxed in a Dean–Stark apparatus. The product solution was stirred with solid K_2CO_3, filtered and evaporated to afford 74.7 g (98%) of crude diester, ethyl 2-ethoxycar-

bonylmethylcyclohexylthioacetate which appeared reasonably pure by GC.

*3-Hydroxy-4a,5,6,7,8,8a-hexahydro-4*H*-thiochromene-2-carboxylic acid methyl ester.* Sodium (6.5 g) was allowed to react with 15 ml of absolute ethanol in a three-necked flask under nitrogen. Octanethiol (1 ml) and 2 ml of ethanol were added and the mixture was stirred for several hours. Then 74.5 g (0.25 mol) of diester in 150 ml of dry ether was added dropwise to the stirred ice-cold mixture (1.5 h). Stirring was continued overnight while the temperature was allowed to reach ambient. The reaction mixture was acidified by addition of 30 ml (0.5 mol) of acetic acid and 100 ml of water. The organic layer was washed with 50 ml of brine, the combined aqueous solution was extracted once with ether. The ether extracts were dried over Na_2SO_4 and concentrated, to give a dark brown oil. Distillation was interrupted at bath temperature 190°C/0.1 mmHg, since the mixture appeared to decompose. The product was dissolved in methanol and stored in a freezer (−19°C several months). The large crystals isolated, 12.7 g (30%) m.p. 70–71°C, proved to be the *cis*-fused isomer. NMR: δ_H (500 MHz; $CDCl_3$) 1.42 (m, 3 H 6–8 *axial*), 1.72 (m, 5 H 5–8), 2.18 (m, $J = 6.23$, $J = 5.25$, $J = 3.1$, $J = 3.1$, $J = 9.2$, 1 H 4a), 2.28 (dd, $J = 18.87$, $J = 5.25$, 1 H 4), 2.51 (dd, $J = 18.87$, $J = 6.23$, 1 H 4), 3.33 (m, $J = 3.1$, $J = 3.1$, $J = 5.9$, 1 H 8a), 3.81 (s, 3 H Me), 12.1 (s, 1 H OH). δ_C (200 MHz; $CDCl_3$) 21.92 (t 6,7), 23.67 (t 6,7), 28.02 (t 5,8), 29.54 (t 5,8), 33.58 (t 4), 34.53 (d 4a), 40.59 (d 8a), 51.76 (q Me), 91.32 (s 2), 164.93 (s 3), 169.98 (s ester C = O). CP/MAS spectrum δ_C (200 MHz) 21.13 (6 and 7), 28.14 (5 and 8), 30.91 (4), 36.90 (4a), 42.89 (8a), 52.10 (Me), 92.27 (2), 167.80 (3), 171.60 (C = O). IR (KBr): ν_{max}/cm^{-1} 3439 (OH), 1713.5 (C = O intermol. H-bond), 1645 (C = O intramol. H-bonded), 1601 (enol C = C). (CCl_4): 3009 (OH), 1653 (enol C = O), 1605 (enol C = C). Mass spectrum (EI) m/z 229 ($M + 1^+$, 9%), 228 (M^+, 58%), 210 (17), 198 (7), 197 (16), 196 (100), 168 (21), 167 (10), 165 (12), 163 (9), 157 (7), 151 (10), 140 (9), 139 (7), 123 (10), 95 (19), 93 (8), 85 (14), 83 (16), 81 (28), 79 (10), 77 (7), 67 (14), 55 (9), 53 (7), 45 (8). For NMR assignments off-resonance decoupling, HETCOR and analysis by LAOCOON III[20] were used.

The keto–enol equilibrium was determined by adding a drop of trifluoroacetic acid to the $CDCl_3$ solution of the enol and following the development of the proton NMR spectrum. The ratio of keto to enol was determined from the integrals of signals of one of the C-4 protons of the keto and the 8a-proton of both the keto and enol tautomers. The equilibrium 263:737 was reached in four days in ambient temperature.

X-Ray structure determination. Details of the crystal analysis, data collection and structure refinement are given in Table 1. A suitable colorless single crystal (0.20 × 0.37 × 0.38 mm) was selected for the measurements. The unit cell parameters were obtained by least-squares refinement of 25 automatically centered reflections in the range $17.7 < 2\theta < 33.7°$. Based on the systematic absences the space group was determined to be $Pca2_1$ (No. 29). The intensity data were collected with a Rigaku AFC5S diffractometer in the ω–2θ scan mode with the θ scan rate of 4.0° min^{-1} (in ω) and a scan width of $1.68 + 0.30 \tan\theta$ using graphite monochromated Mo-Kα radiation ($\lambda = 0.71069$ Å). The weak reflections [$I < 10\sigma(I)$] were rescanned up to two times. Of 1211 unique reflections, 807 with $I > 3\sigma(I)$ were used in the refinement. The data were corrected for Lorentz and polarization effects. Since three representative reflections measured after every 150 reflections did not show any significant variation, no decay correction was applied. An empirical absorption correction, based on azimuthal scans of several reflections, was applied which resulted in transmission factors ranging from 0.62 to 1.00. Also a correction for secondary extinction was made (coefficient = 0.11407×10^{-5}). The structure was solved by direct methods and refined by standard full-matrix least-squares techniques and Fourier procedures. The hydrogen atom H(1) was found from a difference map. All the hydrogen atoms were refined isotropically with fixed temperature factors (1.2 times the temperature factor of the host atom), except the methyl hydrogens, which were included in the calculated positions. The residual density varied from 0.28 to −0.24 e $Å^{-3}$. Neutral atomic scattering and dispersion factors were taken from ref. 18.[21] Calculations were performed using the TEXSAN crystallographic software[22] installed on a VAXSTATION 3520 computer. The molecular illustration (Fig. 2) is an ORTEP[23] drawing.

The *ab initio* calculations were carried out using the GAUSSIAN 92 program[24] on Convex 3840 and Cray X-MP computers of the Center of Scientific Computing of Finland. The structure optimizations were considered complete when the largest component of the gradient in a given nucleus was less than 0.001 hartree $bohr^{-1}$.

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