# Definitive Evidence for the Existence of the Hydrogen-bonding Enol Form of Non-aromatic β-Thioxoketones. *X*-Ray Crystal Structure of 1-(1-Methylcyclopropyl)-3-thioxobutan-1-one

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1-(1-Methylcyclopropyl)-3-thioxobutan-1-one, a simple non-aromatic β-thioxoketone, has been found by *X*-ray diffractometry to exist exclusively in the hydrogen-chelating (*Z*)-enol form in the crystalline state.

Recent studies of simple β-thioxoketones† have provided considerable evidence for their existence in the gas phase and in solution as equilibrium mixtures of the tautomeric hydrogen-chelating enethiol and enol forms, (**2**) and (**3**), respectively (Scheme 1).[1–4] There has been controversy concerning the exact nature of the tautomeric species involved.[5,6] On the basis of i.r. monitoring of the photolysis of matrix-isolated thioacetylacetone (**1b**) at 12 K, the exclusive existence of photolytically interconvertible rotameric forms of the (*Z*)-enethiol tautomer (**2**) was assumed. The enolic O–H stretching vibration absorption[7] in the i.r. spectra was not recognised and the (*Z*)-enol tautomer (**3**) was not considered as a co-existent species in spite of the fact that a related simple β-thioxoketone, monothiodibenzoylmethane [(**1**) $R^1 = R^2 = Ph$], is purely (*Z*)-

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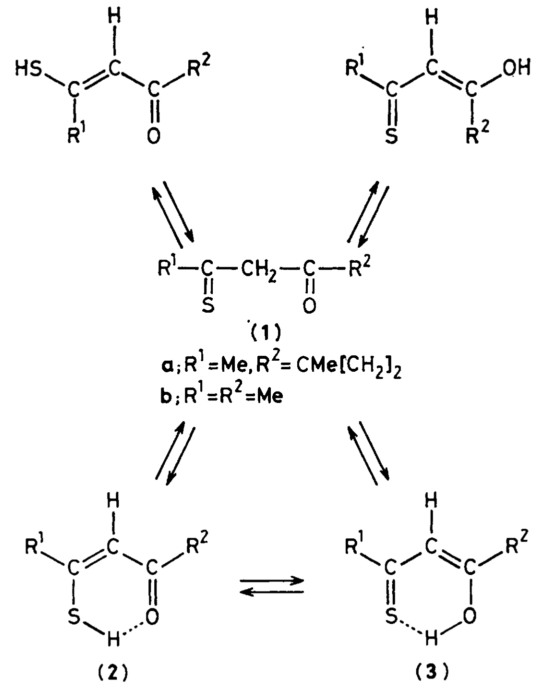
† For simplicity, the β-thioxoketones are named throughout as such, regardless of which possible tautomeric form may be predominant in the individual case. β-Thioxoketones are classified as 'simple' when they display only the n.m.r. spectral pattern of proton-chelating species at room temperature.



**Scheme 1.** Potential tautomeric forms of β-thioxoketones and probable pathways of interconversion.

**Table 1.** Diagnostic spectroscopic characteristics of 1-(1-methylcyclopropyl)-3-thioxobutan-1-one (**1a**) and thioacetylacetone (**1b**).

| | | (**1a**) | (**1b**) |
|---|---|---|---|
| $^1$H N.m.r.[a] | δ(chelated-H) | 11.77 | 11.48 |
| | δ(=CH–) | 6.40 | 6.30 |
| | δ[MeC(S)] | 2.39 | 2.35 |
| U.v.[b] | $\lambda_{max}$ (**2**)/nm[c] | 291 | 292 |
| | $\epsilon_{max}$ (**2**)[c] | 6059 | 5460 |
| | $\lambda_{max}$ (**3**)/nm[d] | 367 | 355 |
| | $\epsilon_{max}$ (**3**)[d] | 11760 | 6853 |

[a] Weighted average spectra of the (*Z*)-enol and (*Z*)-enethiol forms, (**3**) and (**2**), respectively. The spectra were measured for 0.1 M solutions (CDCl$_3$) using a Jeol FX 19Q spectrometer. [b] The u.v. spectra were measured for 8.07 × 10$^{-5}$ M (**1a**) and 10.71 × 10$^{-5}$ M (**1b**) solutions (CHCl$_3$) using a Beckman Acta III spectrophotometer. [c] $\pi \rightarrow \pi^*$ Transition of the S–C=C–C=O chromophore system. [d] $\pi \rightarrow \pi^*$ Transition of the O–C=C–C=S chromophore system.

enolic in the crystalline state.[8] In the light of recent dynamic $^1$H n.m.r. spectroscopic results,[9] we therefore found it necessary to establish unambiguously the physical existence of the (*Z*)-enol form for non-aromatic β-thioxoketones, and efforts were made to procure a crystalline non-aromatic simple β-thioxoketone [(**1**) R$^1$=R$^2$ = alkyl] suitable for an *X*-ray diffraction study.

1-(1-Methylcyclopropyl)-3-thioxobutan-1-one (**1a**) was synthesized easily by the thio-Claisen condensation reaction[10] of 1-acetyl-1-methylcyclopropane with *O*-ethyl thioacetate using sodium amide as base.‡ As a solute (**1a**) shows spectroscopic characteristics very similar to those of thioacetylacetone (**1b**) (Table 1) which is a clear indication of the close similarity of their tautomeric species. The only deviation, not immediately accounted for by the assumption of different sites in the two (**2**)⇌(**3**) equilibrium systems, is the 12 nm red shift of the absorption arising from the $\pi \rightarrow \pi^*$ transition of the O–C=C–C=S chromophore system [(**3**)-form]. However, the observed bathochromic effect is undoubtedly due to the π-conjugative effect of the cyclopropyl group, this effect being reflected also by a relatively enhanced $\epsilon_{max}$ value, and, in the $^1$H n.m.r. spectrum, by a distinct downfield displacement of the methine proton signal of (**1a**) relative to that of (**1b**).[11]

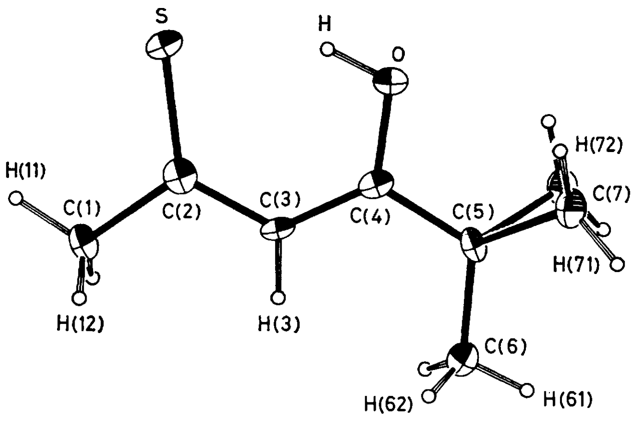


**Figure 1.** ORTEP plot (50% probability ellipsoids) for 1-(1-methylcyclopropyl)-3-thioxobutan-1-one (**1a**) revealing its purely (*Z*)-enolic molecular structure in the crystalline state. Pertinent bond distances are: S–C(2) 1.679(2), O–C(4) 1.320(3), C(1)–C(2) 1.498(3), C(2)–C(3) 1.409(3), C(3)–C(4) 1.380(3), C(4)–C(5) 1.476(3), C(5)–C(6) 1.506(3), C(5)–C(7) 1.528(2), C(7)–C(7′) 1.485(2), O–H 0.89(3), and S–H 2.05(3) Å. Principal bond angles are: C(1)–C(2)–S 118.6(2), C(1)–C(2)–C(3) 116.4(2), S–C(2)–C(3) 125.0(2), C(2)–C(3)–C(4) 126.3(2), C(3)–C(4)–O 122.7(2), C(3)–C(4)–C(5) 122.6(2), O–C(4)–C(5) 114.7(2), C(4)–C(5)–C(6) 117.9(2), C(4)–C(5)–C(7) 115.9(1), C(6)–C(5)–C(7) 117.7(1), C(7)–C(5)–C(7′) 58.1(1), C(5)–C(7)–C(7′) 60.9(1), S–H–O 156(2), and C(4)–O–H 108(2)°.

Crystals suitable for diffraction experiments were obtained by slowly evaporating an isopentane solution of (**1a**). An elongated prismatic crystal of dimensions 0.34 × 0.21 × 0.13 mm was selected for the data collection.§ The structure determined is shown in Figure 1. Evidently, the β-thioxoketone (**1a**) is purely (*Z*)-enolic in the crystalline state. The molecule is essentially planar.¶ The length of the C(2)–S bond [1.679(2) Å] clearly reflects its character as a C=S double bond with the sulphur atom strongly engaged in intramolecular hydrogen-bonding, the S · · · H distance [2.05(3) Å] being considerably shorter than the sum (3.05 Å[12]) of the van der Waals radii of the respective atoms. Interestingly, the bond distances and bond angles of the central chelate system of (**1a**) deviate only slightly from the corresponding distances and

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‡ Yield 43%; m.p. (uncorrected) 50—51 °C (recrystallised from light petroleum). A satisfactory elemental analysis was obtained.

§ *Crystal data:* C$_8$H$_{12}$OS, *M* = 156.25, orthorhombic, space group *Pnma*, cell constants at 100 K: *a* = 12.278(3), *b* = 7.296(3), *c* = 9.161(2) Å, *U* = 820.6(5) Å$^3$, $D_c$ = 1.264 g cm$^{-3}$, *Z* = 4, $\mu$(Mo-$K_\alpha$) = 3.17 cm$^{-1}$. The structure was solved and refined using the Enraf Nonius SDP programs on the basis of 1209 measured reflections with $\theta$ < 37.5° to a final *R* of 0.038 and $R_w$ of 0.030 [reflections with $I < 3\sigma(I)$ and the 0 2 0 reflections, which appeared to suffer severely from extinction, were omitted]. The thermal parameters of the hydrogen atoms were refined isotropically while all other atoms were treated anisotropically.

¶ The atomic co-ordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW. Any request should be accompanied by the full literature citation for this communication.

angles determined for monothiodibenzoylmethane [(**1**) $R^1 = R^2 = Ph$].[8] Another interesting point is the spatial arrangement of the cyclopropyl group in (**1a**); evidently a $\pi$-conjugative effect is operating (also suggested by the $^1H$ n.m.r. and u.v. data), this being reflected most clearly by the relatively short C(4)–C(5) bond length and the pertubated equilateral nature of the cyclopropane ring.

We conclude that 1-(1-methylcyclopropyl)-3-thioxobutan-1-one (**1a**) exists purely in the (*Z*)-enol form in the crystalline state. Upon dissolution, (**1a**) still preferentially populates the (*Z*)-enol form (**3**), but simultaneously, and to an appreciable extent, also populates the (*Z*)-enethiol form (**2**), a rapid interconversion between (**3**) and (**2**) taking place by intramolecular chelate proton transfer.

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