β-Thioxoketones. Part 6.[1] Electronic Absorption Spectra of Aromatic β-Thioxoketones. A Study of Enol–Enethiol Tautomerism

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Aromatic β-thioxoketones exist in solution as mixtures of rapidly interconverting Z-enol and Z-enethiol tautomers. The electronic absorption spectra exhibit in general four absorption bands in the u.v.–visible region at *ca.* 265 (ArC=O, π,π^*; ArC=C π,π^*), 330 (ArC=S π,π^*; O=CC=CS π,π^*; C=O n,π^*), 415 (OC=CC=S π,π^*), and 520 nm (C=S n,π^*), respectively. The β-thioxoketones are converted by sodium hydroxide into the corresponding anions. CNDO/B Calculations predict that the negative charge in the β-thioxoketonates is delocalized over the OCCCS system, suggesting simultaneously sickles or W shaped conformations. Two characteristic absorption bands found for the β-thioxoketonates at *ca.* 275 and 400 nm are assigned to π,π^* transitions involving the Ar–C⋮C⋮C–Ar′ and S⋮C⋮C⋮C⋮O chromophores, respectively. The enol–enethiol tautomeric equilibrium has been studied by means of low temperature spectroscopy. At room temperature equilibrium constants (K_{293}) of 3—5 have been found corresponding to a 4 : 1 enol–enethiol concentration ratio. The reaction entropy (ΔS_r) has been found to be negative for the enethiol→enol conversion, reflecting the intramolecular O–H⋯S hydrogen bond to be considerably stronger than the corresponding O⋯H–S hydrogen bond. Variations in ΔS_r and K_{293} as functions of substitution in the aryl group next to oxygen are discussed.

RECENT spectroscopic studies have clearly shown that β-thioxoketones † in solution exist exclusively or preponderantly as equilibrium mixtures of the tautomeric (Z)-enol (D) and (Z)-enethiol (C) forms, which interconvert very rapidly (on the n.m.r. time scale) by intramolecular chelate proton transfer.[2,3] An alternative interpretation in terms of the existence of an electron-delocalized ' quasi-aromatic ' structure (F) has been rebutted.[4] No evidence has been found for the existence of the thioxoketone tautomeric form (B).

In connection with our current fascination with the enol–enethiol tautomeric system (D) ⇌ (C) we here report on an examination of the electronic absorption spectra of a series of aromatic β-thioxoketones (1)—(12) and the corresponding β-thioxoketonates (1G)—(12G), as well as on the thermodynamics of the enol–enethiol equilibrium for four selected β-thioxoketones (1)—(4).

β-*Thioxoketones.*—Solutions of aromatic β-thioxoketones (R¹ = Ar¹, R² = Ar²) in general exhibit four absorption maxima (λ_1—λ_4) in the u.v.–visible region, located at *ca.* 265 (λ_1), 330 (λ_2), 415 (λ_3), and 520 nm (λ_4) (Table 1). Molar absorption coefficients cannot be calculated directly as the equilibrium concentrations of the enol and enethiol forms are not known.

As a consequence of the existence of the (C) ⇌ (D) tautomeric equilibrium system, the β-thioxoketones (1)—(12) are expected to exhibit absorption bands in the u.v.—visible region arising from transitions involving the chromophores ArC=C, ArC=O, ArC=S, S–C=CC=O, and S=CC=C–O. Thioacetylacetone (13)[2] exhibits two absorption bands at 296 and 354 nm, respectively, besides the long wavelength absorption at 455 nm assigned to the C=S n,π^* transition.[1,2] The former two

absorptions correspond to λ_2 and λ_3 found for (1)—(12). Evidently, the blue shifts observed are due to lack of aromatic conjugation in compound (13). We have calculated the electronic absorption spectra of the enol

TABLE 1

Electronic absorption spectra of aromatic β-thioxoketones [a]

Compound	λ_1/nm [A_1]	λ_2/nm [A_2]	λ_3/nm [A_3]	λ_4/nm [A_4]
(1)	262 [0.276]	325 [0.370]	408 [0.488]	~515 [0.007]
(2)	271 [0.320]	328 [0.369]	409 [0.546]	~520 [0.004]
(3)	268 [0.282]	323 [0.374]	413 [0.591]	~515 [0.006]
(4)	245 [b] [0.236]	326 [0.398]	423 [0.704]	~515 [0.009]
(5)	261 [0.302]	340 [0.470]	408 [0.494]	~520 [0.008]
(6)	272 [0.333]	346 [0.496]	411 [0.574]	~520 [0.005]
(7)	268 [0.296]	339 [0.467]	413 [0.586]	~515 [0.007]
(8)	~248 [0.253]	337 [0.445]	422 [0.668]	~510 [0.009]
(9)	252 [c] [0.257]	335 [0.469]	412 [0.559]	~520 [0.005]
(10)	259 [d] [0.394]	372 [0.681]	407 [0.540]	~515 [0.008]
(11)	264 [0.329]	378 [0.669]	~410 [0.55]	~520 [0.007]
(12)	253 [0.33]	365 [0.475]	421 [0.573]	~510 [0.009]

[a] Solvent, cyclohexane. The absorbances (in brackets) refer to 3×10^{-5} mol l⁻¹ solutions. [b] Shoulder at 252 nm. [c] Shoulder at 266 nm. [d] Shoulder at 233 nm.
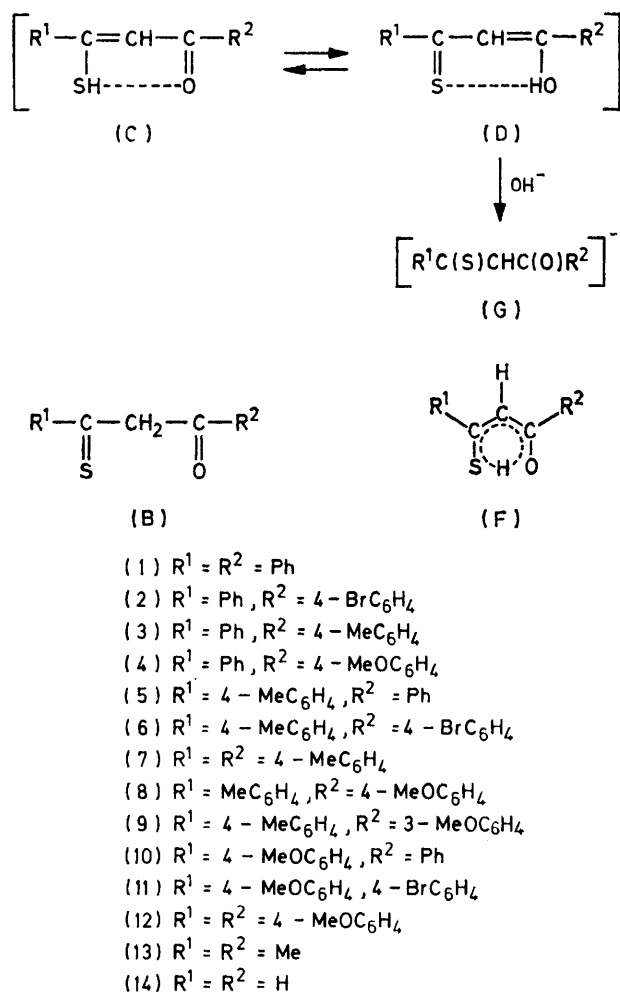
and enethiol forms of monothiomalondialdehyde (14D and C) ‡ by means of a CNDO/S-CI procedure (see Experimental section). Thus (14D and C) are predicted to exhibit absorption bands at 339 and 304 nm, respect-

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† The β-thioxoketones are named as such for simplicity, regardless of which possible tautomer is predominant. The notation of the tautomeric forms as shown in Scheme 1 is consistent with that in previous Parts.

‡ The hypothetical compound monothiomalondialdehyde has been chosen as a model in order to reduce the calculation costs (*cf.* refs. 4 and 5).

ively, originating in both cases almost exclusively from H-1, L π, π^* transitions † (Figure 1).

The composite nature of λ_1 and λ_2 suggests complicated actions of the flanking substituents R^1 and R^2 on the intensities and positions of these bands. However, λ_3, which is an absorption arising alone from the O–C= CC=S system (Figure 1), clearly shows shifts in consequence of variation in R^2, whereas practically no effect is observed by varying R^1. For comparison we have also studied the spectra of two series of monoaryl

(C)   (D)

(G)

(B)   (F)

(1) $R^1 = R^2 = Ph$
(2) $R^1 = Ph$, $R^2 = 4-BrC_6H_4$
(3) $R^1 = Ph$, $R^2 = 4-MeC_6H_4$
(4) $R^1 = Ph$, $R^2 = 4-MeOC_6H_4$
(5) $R^1 = 4-MeC_6H_4$, $R^2 = Ph$
(6) $R^1 = 4-MeC_6H_4$, $R^2 = 4-BrC_6H_4$
(7) $R^1 = R^2 = 4-MeC_6H_4$
(8) $R^1 = MeC_6H_4$, $R^2 = 4-MeOC_6H_4$
(9) $R^1 = 4-MeC_6H_4$, $R^2 = 3-MeOC_6H_4$
(10) $R^1 = 4-MeOC_6H_4$, $R^2 = Ph$
(11) $R^1 = 4-MeOC_6H_4$, $4-BrC_6H_4$
(12) $R^1 = R^2 = 4-MeOC_6H_4$
(13) $R^1 = R^2 = Me$
(14) $R^1 = R^2 = H$

SCHEME 1

substituted β-thioxoketones, i.e. thioacetylacetophenones ($R^1 = Me$, $R^2 = Ar$), and thioaroylacetones ($R^1 = Ar$, $R^2 = Me$), and the same overall effect was observed (Table 2). Thus the effect due to R^2 substitution is qualitatively similar to the corresponding substitution effects observed in e.g. benzophenones and thiobenzophenones,[6] i.e. a blue shift, then a red shift by changing R^2 from p-MeOC$_6$H$_4$ to p-MeC$_6$H$_4$ and Ph to p-BrC$_6$H$_4$. To account for this observation both conjugative and

† For simplicity H = HOMO (highest occupied MO) and L = LUMO (lowest unoccupied MO). H-1 and H-2 refer to the next highest and second next highest MOs, respectively. Similarly, L + 1, L + 2, etc., designate the next lowest, the second next lowest, etc., unoccupied MOs.

inductive effects must be considered. For $R^2 = p$-BrC$_6$H$_4$, the C=CC=S π-system interacts strongly with the energetically high-lying $3p\pi$-bromine electrons; a similar interaction is also present for $R^2 = p$-MeOC$_6$H$_4$, but in

(14D)   (14C)

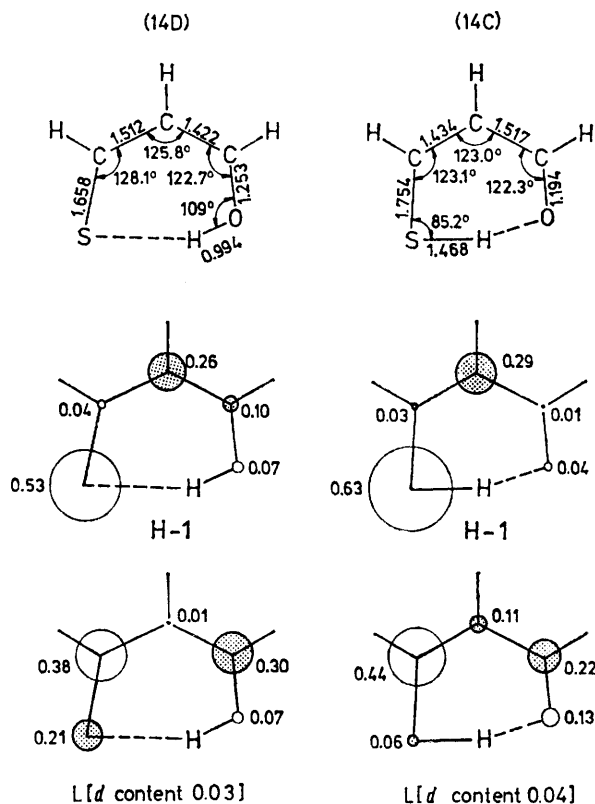L[d content 0.03]   L[d content 0.04]

FIGURE 1 Calculated geometries (CNDO/B) and population analysis (CNDO/S–CI) of the H-1 and L levels in the enol and ethaniol tautomers of monothiomalondialdehyde (14). Diameters of circles are proportional to the square of the contributing atomic orbital coefficients. U.v. (CNDO/S-CI): (14D), 339 nm [H-1, L (0.97), H-2, L + 1 (0.03)]; (14C), 304 nm [H-1, L (0.93), H, L + 2 (0.03), H, L + 3 (0.02), H-2, L + 1 (0.01)]

the latter case the effect will be weaker owing to the less effective interaction between the relatively lower lying $2p\pi$-oxygen electrons in the methoxy-function and the C=CC=S π-system. However, both of these interactions

TABLE 2

Effects of flanking groups R^1 and R^2 of $R^1CSCH=C(OH)R^2$ on the $\pi\pi,^*$ transition within the chromophore S=C–C=C–O, visualized by the shifts of λ_3 [a]

R^1	R^2				
	Me	4-BrC$_6$H$_4$	Ph	4-MeC$_6$H$_4$	4-MeOC$_6$H$_4$
Me	356	390	389	392	399
Ph	374	409	408	413	423
4-MeC$_6$H$_4$	373	411	408	413	422
4-MeOC$_6$H$_4$	377	410	407		421

[a] Solvent, cyclohexane.

are modified by the simultaneously operating electron-withdrawing inductive effects (Br > MeO), decreasing the electron density in the C=CC=S system. Hence, the net effects of both of the two substituents apparently

are qualitatively similar although quantitatively different, as reflected by the observed absorption maxima.

As mentioned above, the substitutional variation of R^1 is found less striking than that of R^2. It is seen (Table 2) that on changing R^2 from methyl to phenyl the absorption maximum λ_3 is red shifted by **34** nm, whereas the same change in R^1 causes only a **18** nm red shift. Similarly, shifts originating from substitution in an R^1 phenyl group are less pronounced than for similar substitution in the R^2 phenyl group. The almost total lack of change in the position of λ_3 observed by varying R^1 from p-MeOC$_6$H$_4$ to Ph is, however, still surprising.

In an attempt to explain qualitatively the different effects of the R^1 and R^2 substituents, we turn to the parent system (14D). It is seen (Figure 1) that the contributions to H-1 from the carbon atoms bearing the substituents R^1 and R^2 are 4 and 10%, respectively, which means that a substituent R^2 is able to interact more strongly with the C=CC=S π-system, than is the same substituent placed at R^1 with the C=S π-system, *i.e.* a greater change in the H-1 energy (ΔE_{H-1}) is found by varying R^2. The corresponding contributions to the LUMO are 38 and 30%, respectively (Figure 1), *i.e.* in both cases the possibility of a strong interaction between the flanking Ar π^*-systems and the S=CC=C-O π^*-system is present. If, however, the two π^*-systems are mixing only slightly due to a sizeable difference in energy, the variations in the LUMO energy (ΔE_L) with changes in R^1 and/or R^2 substitution will be small. On this basis, we tentatively suggest that ΔE_{H-1} mainly accounts for the observed shifts in λ_3 upon substitutional variation in R^2, whereas the lack of significant effects

TABLE 3

Electronic absorption spectra of anions of aromatic β-thioxoketones [a]

Anion	$\lambda_{max.}$/nm (log ε)	$\lambda_{max.}$/nm (log ε)
(1G)	257 (4.09)	400 (4.28)
(2G)	266 (4.20)	405 (4.30)
(3G)	269 (4.24)	401 (4.37)
(4G)	282 (4.13)	399 (4.34)
(5G)	256 (4.05) [b]	404 (4.22)
(6G)	265 (4.15)	400 (4.31)
(7G)	270 (4.11)	402 (4.29)
(8G)	258 (4.14)	402 (4.37)
(9G)	267 (4.03) [c]	405 (4.33)
(10G)	300 (3.92)	404 (4.33)
(11G)	266 (4.20)	411 (4.39)
(12G)	290 (4.20)	402 (4.36)

[a] Solvent, ethanol. [b] Shoulder at 280 nm (log ε 3.97). [c] Shoulder at 290 nm (log ε 3.92).

on changing R^1 from p-MeOC$_6$H$_4$ to Ph are due to a fortuitous cancelling of ΔE_{H-1} and ΔE_L.

β-*Thioxoketonates*.—The anions of the β-thioxoketones (1)—(12) are readily formed on treatment of the latter with sodium hydroxide (*cf.* Scheme 1). The electronic absorption spectra of the β-thioxoketonates are characteristically different from those of the β-thioxoketones, the four absorption maxima of the latter being replaced by two new absorption bands, λ_a (256—300 nm) and λ_b (399—411 nm) (Table 3).

Parker *et al.* have reported on the formation of the dithiodibenzoylmethane anion by stepwise electrochemical reduction of the 3,5-diphenyl-1,2-dithiolylium cation.[5] The cyclic voltammogram strongly suggests that the step associated with anion formation involves structural change. This change is probably a geometrical isomerization effected by strong coulombic repulsion between the two sulphur atoms in the Z-isomeric form.[7]

For the β-thioxoketonates several isomeric structures *a priori* have to be considered, namely the U shaped, the two sickles, and the W shaped structures, respectively (Scheme 2).[8] In order to study charge distributions,

SCHEME 2
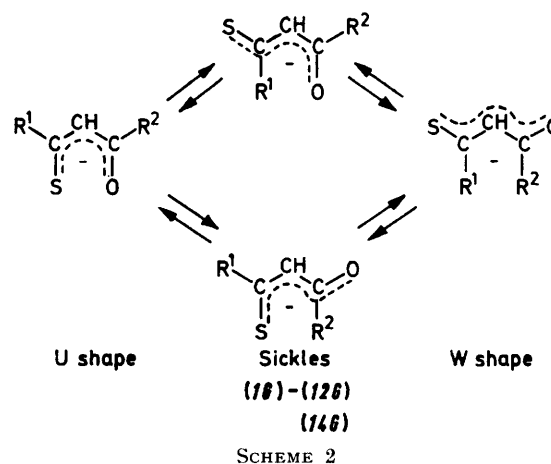
geometries, and relative stabilities of these isomers, we have carried out CNDO/B calculations on the four possible isomeric structures of the parent monothiomalondialdehyde anion (14G).

It is seen (Figure 2) that all four isomers exhibit a delocalized electronic structure of the SCCCO system with negative charges on the heteroatoms and the central carbon atom, whereas the flanking carbon atoms are positively charged. The delocalized nature of the anion is furthermore reflected in the calculated geometries, the CC, CO, and CS bond lengths being intermediate between the lengths of the respective single and double bonds.

On the basis of the existence of electron-delocalized structures for the β-thioxoketonates (1G)—(12G), their electronic absorption spectra are easily explained. The long wavelength absorption, at *ca.* 400 nm (λ_b), must be assigned to a π,π^* transition involving the S⋯C⋯C⋯C⋯O chromophore, the short wavelength band (λ_a) to a π,π^* transition involving the Ar^1–C⋯C⋯C–Ar^2 chromophore. This assignment is justified from a CNDO/S-CI investigation on (14G). The calculated first absorption bands are predicted to be centred around 308, 303, 302, and 297 nm (π,π^*) for the U shaped, the two sickles, and the W shaped isomers, respectively (Figure 2). The first absorption band for the thioacetylacetonate anion (13G) is found at 355 nm.[9] It is worthy of mention that neither the enolate structure, nor the enethiolate

structure, can account for the electronic absorption spectra of the β-thioxoketonates, since both structures would exhibit π,π*-transitions at *ca.* 330 nm originating from ArC=S and O=CC=CS chromophores, respectively.

Our calculations on the anion (14G) do not enable us to draw any final conclusion concerning the actual geometry

forms, *i.e.* only the temperature dependent variation in the absorption band λ_3 can be used directly to evaluate the enethiol–enol equilibrium parameters ΔH_r, ΔG_r, and ΔS_r. Assuming that the reaction enthalpy (ΔH_r) and the reaction entropy (ΔS_r) are constants within the temperature range 213—293 K [10] we may rewrite the
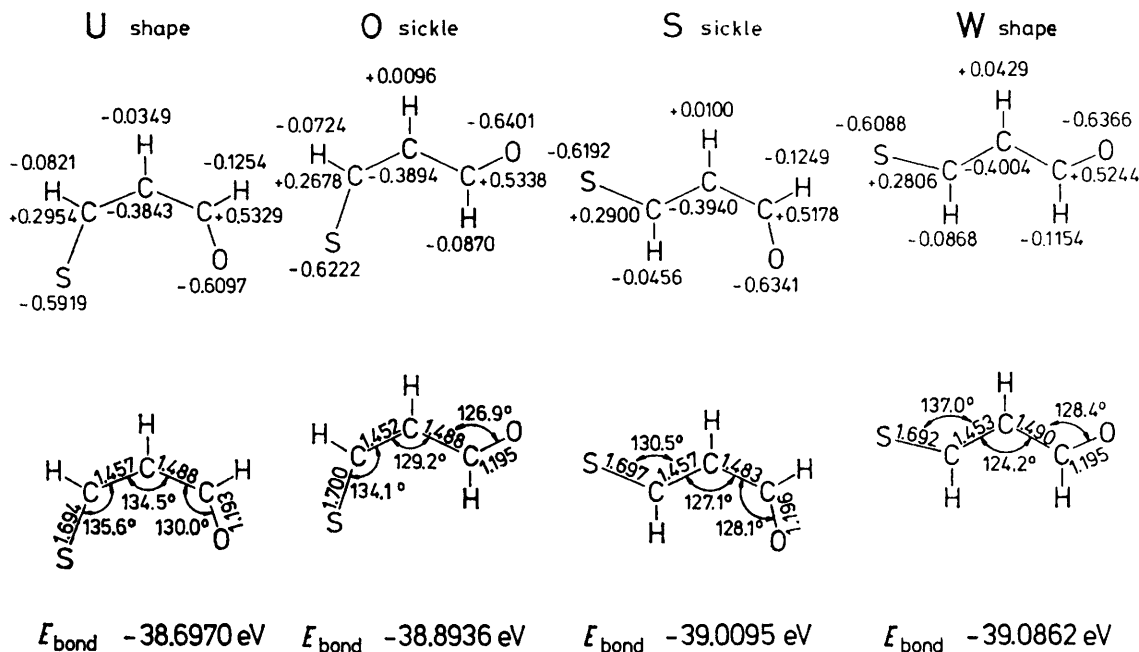

FIGURE 2 Calculated charge densities, geometries, and bonding energies (CNDO/B) for the four possible isomeric structures of the monothiomalondialdehyde anion (14G). U.v. (CNDO/S-CI): **U** shape, 308 nm [H, L (0.99), H, L + 1 (0.01)]; **O** sickle, 303 nm [H, L (0.98), H, L + 1 (0.02)], **S** sickle, 302 nm [H, L (0.96), H, L + 1 (0.03), H-1, L + 2 (0.01)], **W** shape, 297 nm [H, L (0.96), H, L + 1 (0.03), H-1, L + 2 (0.01)]

of the aromatic β-thioxoketonates discussed here, except that the **U** shaped structure can hardly be of importance. The isomerization of the **U** shaped isomer of (14G) into the two sickle isomers is predicted (CNDO/B; Figure 2) to result in energy gains of 19.0 and 30.2 kJ mol⁻¹, respectively. The small energy gains (18.6 and 7.4 kJ mol⁻¹) involved in the isomerization of sickles to the **W** shape may well be overshadowed by energy contributions originating from sterical effects on substituting the flanking hydrogen atoms in (14G) by aromatic groups.

Enol–Enethiol Equilibrium.—The electronic absorption spectra of the β-thioxoketones (1)—(12) have been interpreted in terms of the coexistence of the tautomeric enol and enethiol forms (D) and (C), respectively (Scheme 1). The equilibrium concentrations of the two tautomeric forms are reflected in the band intensities, however, in a complicated way, and information on the (D) : (C) concentration ratios is not immediately extractable. To study the thermodynamics of the enol–enethiol tautomeric equilibrium (D) ⇌ (C), we have investigated the spectra of the β-thioxoketones (1)—(4) at different temperatures.†

As mentioned above the absorption bands λ_1 and λ_2 originate from transitions in enol as well as enethiol

common Gibbs–Helmholtz equation (1) as (2), from which ΔH_r, ΔS_r, and ε_3 can be calculated (c = bulk

$$\Delta G = \Delta H - T\Delta S \qquad (1)$$

$$RT_i \cdot \log_e(c \cdot \varepsilon_3/A_i - 1) + T_i\Delta S_r = \Delta H_r \qquad (2)$$

concentration of the β-thioxoketone, ε_3 = molar absorption coefficient of the λ_3 absorption, A_i = absorbance of λ_3 at the temperature T_i). The equilibrium constant at temperature T_i (K_{T_i}) can be calculated from the van't Hoff equation [equation (3)].

$$K_{T_i} = \exp[-\Delta G_r(T_i)/RT_i] \qquad (3)$$

The equilibrium data for the β-thioxoketones (1)—(4) are given in Table 4. CNDO/B Calculations predict ΔH_r —40.2 kJ mol⁻¹ for the enethiol–enol conversion of monothiomalondialdehyde (14), a value that is lowered to —32.6 kJ mol⁻¹ upon introduction of two flanking vinyl groups.[4] A further lowering of ΔH_r is anticipated when the vinyl groups are replaced by phenyl groups,[4] as reflected by the experimentally determined reaction enthalpy for (1C) ⟶ (1D), ΔH_r

† These four compounds were selected for low temperature studies with the intention of obtaining results representative of aromatic β-thioxoketones, and to elucidate the effects of aromatic substitution in R².

-12.3 kJ mol^{-1} (Table 4). Fabian [9] has estimated very roughly the equilibrium data for the enethiol–enol conversion (13C) $\longrightarrow$ (13D) to be ΔH_r -4.2 kJ mol^{-1} and ΔS_r -6.3 J mol^{-1} K^{-1}.

In all cases investigated we have found, in agreement with our previous theoretical study,[4] that the enolic

TABLE 4

Equilibrium parameters associated with the enethiol–enol conversion (C) $\longrightarrow$ (D) of aromatic β-thioxoketones (1)—(4) at 293 K

Compound	ΔH_r/ kJ mol^{-1}	ΔS_r/ J mol^{-1} K^{-1}	ΔG_r/ kJ mol^{-1}	K_{293}	X_{enol}
(1)	-12.3	-28.6	-3.94	5.03	0.83
(2)	-33.3	-105.3	-2.43	2.71	0.73
(3)	-16.7	-43.1	-4.07	5.32	0.84
(4)	-16.2	-44.0	-3.25	3.80	0.79

structure (D) represents the more stable state of existence. It is of interest to note that although *para*-substitution (with electron-donating as well as electron-withdrawing substituents) in the R^2 phenyl groups apparently effects increased relative stabilization of the enol tautomer, the reverse trend is found for the equilibrium constant K_{T_i} (Table 4). A striking variation in ΔS_r accounts for this apparent discrepancy (Table 4). However, before discussing the variation in ΔS_r, a comment on the negative sign of ΔS_r for the enethiol–enol conversion (C) $\longrightarrow$ (D) should be made.

Snyder *et al.*[11] used the Schroeder–Lippincott potential function model of the hydrogen bond [12] to study the properties of intramolecular O–H $\cdots$ S and O $\cdots$ H–S hydrogen bonds, comparable experimental results being obtained from an i.r. spectroscopic study on 1-hydroxy-2-mercaptobenzene. Their results strongly indicate that sulphur may be a better acceptor than oxygen in intramolecular hydrogen bonds. The calculated potential energy of the O $\cdots$ H–S bond (-1.59 kJ mol^{-1}) is considerably less than that calculated for the intramolecular O–H $\cdots$ S hydrogen bond (-10.04 kJ mol^{-1}). On this basis a negative reaction entropy can be expected for the (C) $\longrightarrow$ (D) conversion, in agreement with our experimental results (Table 4). We conclude that the difference in the strengths of the hydrogen bonds in the two tautomeric forms [(C) and (D)] is directly reflected by the sign of ΔS_r, whereas the absolute value of ΔS_r is conditional on the aromatic substituents.

The distances between the sulphur and the oxygen atoms in the enol and enethiol tautomeric forms [calculated to be 3.08 and 2.86 Å for (14D and C), respectively] are considerably longer than the sum of the OH and SH bond lengths (Figure 1), consistent with an interpretation in terms of a double minimum potential energy surface of the enol–enethiol system.[4] This strongly indicates that the two hydrogen bonds involved are essentially electrostatic.[13] The electron densities on the heteroatoms, which are decisive for the hydrogen bond strengths, are determined by inductive as well as conjugative contributions from the aryl substituents. In the enethiol tautomer (C) both inductive and conjugative effects arising from R^2 substitution will operate

on the oxygen atom. Thus, for R^2 = *p*-BrC$_6$H$_4$ and *p*-MeOC$_6$H$_4$, increased positive charges are accumulated on oxygen due to the inductively electron-withdrawing effect of these substituents (σ_I^{Br} 0.44, σ_I^{OMe} 0.27),[14] effecting a reduction of the O $\cdots$ H–S hydrogen bond strength. For R^2 = *p*-MeC$_6$H$_4$ electrons are weakly donated by induction (σ_I^{Me} -0.04)[14] resulting in a small increase in the O $\cdots$ H–S hydrogen bond strength. However, the O $\cdots$ H–S hydrogen bond strength is increased by conjugation, since all three substituents donate electrons to oxygen (σ_R^{OMe} -0.61, σ_R^{Br} -0.19, σ_R^{Me} -0.11).[15] In the enol tautomer (D) the inductive effects of R^2 still operate significantly merely on the oxygen atom, whereas the conjugative effects operate on the sulphur atom. Hence, by induction, R^2 = *p*-BrC$_6$H$_4$ and *p*-MeOC$_6$H$_4$ increase the positive charge on oxygen, weakening the O–H bond and thus probably increasing the strength of the O–H $\cdots$ S hydrogen bond; methyl substitution operates weakly in the opposite direction. However, the effect of conjugation is in all cases an accumulation of electrons on the sulphur atom, hence giving rise to a strengthening of the O–H $\cdots$ S hydrogen bond.

Although the above effects are qualitatively consistent with the experimentally observed increases in the O–H $\cdots$ S hydrogen bond strengths relative to the O $\cdots$ H–S hydrogen bond strength conditional on R^2 substitution, a more quantitative evaluation is not directly possible without any knowledge of the relative importance of the inductive and conjugative contributions.

However, it is possible to attain a quantitative description of the (C) $\rightleftharpoons$ (D) equilibrium system based on a discussion of the equilibrium constants K_{293} (Table 4) within the Hammett correlation framework. Owing to the lability of the vinylic double bond, inductive and conjugative effects should be considered separately. For changes in R^2 (R^1 unchanged) the Hammett correlation can be formulated as a sum of inductive and conjugative contributions [equation (4) where K and

$$\log_{10}(K/K^0) = \sigma_I \rho_I + \sigma_R \rho_R \qquad (4)$$

K^0 refer to the tautomeric equilibrium constants for the aryl-substituted and unsubstituted systems, respectively, σ_I and σ_R are the Hammett constants for the pure induction and conjugation contributions, respectively,[14,15] and ρ_I and ρ_R are the corresponding Hammett ρ-values]. The treatment gives ρ_I -0.59 ± 0.07 and ρ_R -0.04 ± 0.05, indicating hence a very small conjugational influence on the enol $\rightleftharpoons$ enethiol equilibrium.

The in-plane enethiol $\longrightarrow$ enol conversion (as well as the opposite process) can be classified, according to Lemal *et al.*,[16] as a pseudo-pericyclic reaction, since a bonding *p*-orbital and a 'non-bonding' lone pair orbital switch roles at the sulphur atom, while a complementary interchange occurs at the oxygen atom. However, it is important to note that these interchanges occur within the σ-component, which is persistently orthogonal to the π-component, *i.e.* no coupling occurs

between the σ and the π components. Since the inductive and conjugative effects operate through the σ- and π-skeletons, respectively, it is understandable that inductive effects only can have a significant influence on the site of the enol–enethiol equilibrium.

EXPERIMENTAL

U.v. spectra were recorded on a Beckmann Acta III spectrophotometer (β-thioxoketones) or on a Pye–Unicam SP 1800 spectrophotometer (β-thioxoketonates). The β-thioxoketonate anions were generated in the cuvettes by addition of sufficient sodium hydroxide to the alcoholic solutions of the corresponding β-thioxoketones. Low temperature u.v. spectra were recorded on a SM-Brückl HRS 4001-C instrument equipped with thermostattable quartz cuvettes (Hellma)[17] The measured absorbances were corrected for solvent contraction induced by temperature decrease. Relevant data are given in Table 5.

TABLE 5

Measured absorbances at λ_3 of aromatic β-thioxoketones (1)—(4) at 293 (A_{293}), 253 (A_{253}), and 213 K (A_{213}).[a] Calculated molar absorption coefficients (ε_3)

Compound	Concentration (10^{-5} mol l^{-1})	A_{293}	A_{253}	A_{213}	ε_3
(1)	6.092	0.990	1.090	1.153	19 500
(2)	5.746	1.045	1.374	1.428	24 920
(3)	5.052	0.995	1.111	1.165	23 400
(4)	3.651	0.857	0.991	1.059	29 640

[a] Solvent, methylcyclohexane–methylbutane, 1 : 5.

The aromatic β-thioxoketones (1)—(12) were synthesized by thio-Claisen condensation reactions between appropriately substituted acetophenones and ethyl thionobenzoates.[18] The purity of the compounds was checked by elemental analysis, t.l.c., and ^{1}H n.m.r.* Compounds (1)—(3) and (5)—(8) have been described previously.[18] Yields and m.p.s (uncorrected) for new compounds (4) and (9)—(12) are given below. Elemental analyses were performed by the microanalytical laboratory of the Department of General and Organic Chemistry, University of Copenhagen.

1-(4-Methoxyphenyl)-3-phenyl-3-thioxopropan-1-one (4) was formed in 77% yield, m.p. 134 °C (from cyclohexane) (Found: C, 71.25; H, 5.25; S, 11.55. $C_{16}H_{14}O_2S$ requires C, 71.1; H, 5.2; S, 11.85%), 1-(3-methoxyphenyl)-3-(4-methylphenyl)-3-thioxopropan-1-one (9) in 75% yield, m.p. 72 °C (petroleum) (Found: C, 71.75; H, 5.6; S, 11.3. $C_{17}H_{16}O_2S$ requires C, 71.8; H, 5.65; S, 11.25%), 3-(4-methoxyphenyl)-1-phenyl-3-thioxopropan-1-one (10) in 50% yield, m.p. 72—73 °C (from cyclohexane) (Found: C, 70.95; H, 5.1; S, 11.8. $C_{16}H_{14}O_2S$ requires C, 71.0; H, 5.2; S, 11.85%), 1-(4-bromophenyl)-3-(4-methoxyphenyl)-3-thioxopropan-1-one (11) in 48% yield, m.p. 146 °C (from petroleum) (Found: C, 55.2; H, 3.75; S, 9.1; Br, 22.95. $C_{16}H_{13}BrO_2S$ requires C, 55.0; H, 3.75; S, 9.2; Br, 22.9%), and 1,3-bis-(4-methoxyphenyl)-3-thioxopropan-1-one (12) in 64% yield, m.p. 122—124 °C (from cyclohexane) (Found: C, 67.7; H, 5.4; S, 10.5. $C_{17}H_{16}O_3S$ requires C, 68.0; H, 5.35; S, 10.65%).

Semiempirical MO Calculations.—The calculated geo-

metries, electron densities, and bonding energies of (14) and (14G) were determined by application of the Boyd–Whitehead CNDO/B procedure,[19] which was parameterized to give geometries and energies in accord with experimental data. The bonding energies were minimized with respect to all internal valence co-ordinates.

The theoretical electronic absorption spectra were calculated by a CNDO/S-CI procedure using the CNDO/B energy-minimized structures. CNDO/S-CI is a semi-empirical SCF parameterization including sulphur d orbitals and configurational interaction (CI), and is designed specifically for the calculation of absorption spectra of sulphur-containing compounds.[20] MO Population analyses were carried out on the basis of the CNDO/S-CI calculations.

* The ^{1}H n.m.r. spectra of the β-thioxoketones will be published separately, F. Duus, L. Carlsen, and O. Lang Rasmussen, in preparation.

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