

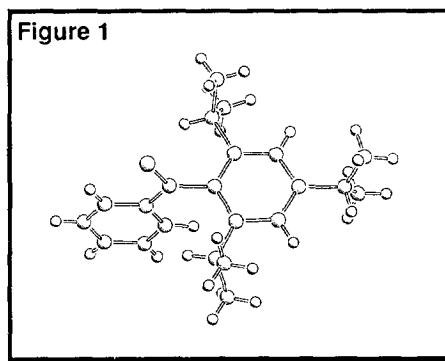
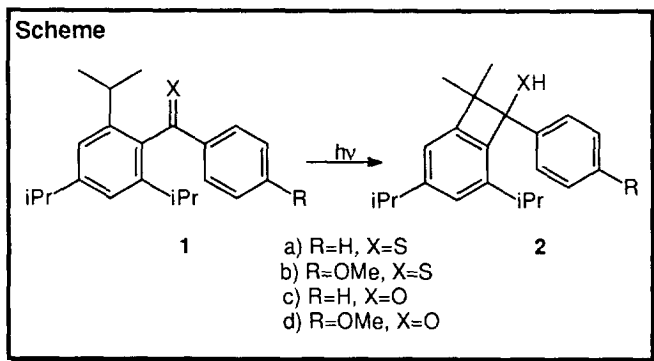
CRYSTAL STRUCTURE-REACTIVITY RELATIONSHIPS IN THE SOLID STATE PHOTOCHEMISTRY OF 2,4,6-TRIIISOPROPYLTHIOBENZOPHENONE: C=O...H VERSUS C=S...H ABSTRACTION GEOMETRY

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Abstract X-ray crystal structure - solid state photoreactivity correlations are reported for 2,4,6-triisopropylthiobenzophenone (**1a**) and its *p*-methoxy derivative **1b**. The results reveal interesting differences in the geometry of γ -hydrogen atom abstraction for ketones and thiones.

Unlike their oxygen analogues, which abstract hydrogen more rapidly from their n, π^* excited states,¹ *thioketones* undergo hydrogen atom abstraction reactions more efficiently from their π, π^* excited states.² Since n, π^* and π, π^* excited states differ in the spatial properties of the orbitals involved in abstraction,³ and since the larger sulfur atom should be capable of abstraction over greater distances than oxygen, it follows that ketones and thiones should exhibit significantly different hydrogen atom abstraction geometries. In this paper we report our attempts to detect such differences experimentally by the crystal structure-reactivity correlation method—a method whereby the hydrogen abstraction is studied in the *solid state* and correlated with geometric data determined by X-ray crystallography.

The compounds chosen for study were 2,4,6-triisopropylthiobenzophenone (**1a**, Scheme) and its *p*-methoxy derivative **1b**. In analogy to the known photochemistry of their oxygen analogues **1c** and **1d**,⁴ these thiones were expected to undergo γ -hydrogen atom abstraction-initiated photocyclization to form the benzocyclobutenethiol derivatives **2a** and **2b**. Thiones **1a** and **1b** were prepared in ca. 65% yield as beautiful blue crystalline solids, mp 97.5-98.5° and 116.5-117°, respectively, by the reaction of ketones **1c** and **1d** with Lawesson's reagent.⁵ Along with the photochemical studies described below, the crystal and molecular structures of thioketones **1a** and **1b** were determined by direct method, single crystal X-ray diffraction studies.⁶ The conformation of thioketone **1a** in the crystalline state is shown in Figure 1; a nearly identical conformation was found for thione **1b**.



Like thiobenzophenone, thiones **1a** and **1b** show well separated absorption maxima in the visible (600 nm, n,π^*) and UV (320 nm, π,π^*) regions of the spectrum, and selective and extended irradiation of these compounds in the visible region under conditions of rigorous exclusion of oxygen led to no detectable reaction, either in solution (benzene) or the crystalline state. In contrast, photolysis of freeze-pump-thaw-deoxygenated solutions of thiones **1a** and **1b** in benzene through Pyrex ($\lambda > 290$ nm) afforded excellent chemical yields (ca. 70% following column chromatography) of the benzocyclobutenethiol derivatives **2a** and **2b**. The same photoreaction could be brought about in the crystalline state, albeit at a much reduced rate. Photoproducts **2a** and **2b** were identified through comparison of their spectra with those of alcohols **2c** and **2d**. A characteristic feature of all four compounds was the large difference in chemical shift between the singlets due to the two methyl groups on the four membered ring (ca. 0.8 vs 1.6 ppm).

The photochemical results indicate that it is the π,π^* excited state of thiones **1a** and **1b** that is responsible for the photocyclization, most likely of singlet multiplicity.² The sluggishness of n,π^* (triplet) excited states of thiones towards γ -hydrogen atom abstraction has been noted previously.² Four parameters serve to define the geometry of intramolecular hydrogen atom abstraction: **d**, the C=X...H distance; Δ , the C=X...H angle; θ , the C-H...X angle and ω , the angle by which the abstracted hydrogen lies above or below the mean plane of the carbonyl group.⁷ For abstractions involving the n -orbital of the n,π^* excited state (which lies in the carbonyl plane), the ideal value of ω is expected to be 0° ; for π,π^* abstraction, which utilizes a π -orbital that is orthogonal to the carbonyl plane, the optimum value of ω should be 90° . The angle Δ (the C=X...H angle) is also expected to differ for the two excited states. Adopting the Kasha model of the n,π^* excited state ($2p$ n -orbital),⁸ the ideal value of Δ should be 90° . For π,π^* abstraction, Δ should be less than 90° , since the π -electrons do not lie directly above the heteroatom, but are displaced towards carbon. The C-H...X angle θ is expected to be optimum at 180° for both types of excited states⁹ and, finally, it is likely that the ideal value of **d** is independent of excited state configuration and should be close to the sum of the van der Waals radii for X and H: 2.72 Å for X = O and 3.00 Å for X = S.

Table 1 summarizes the ideal values of **d**, Δ , θ and ω for each type of excited state along with the crystallographically-derived experimental values for compounds **1a** - **1b**. Included in the table are the values of these parameters for cyclooctadecan-1,10-dione and α -cyclohexyl-*p*-chloroacetophenone, prototypical ketones that undergo solid state intramolecular γ -hydrogen atom abstraction from their n,π^* excited states.^{10,11} Also included in the table are data derived from the crystallographic results of Ito et al.⁴ for ketones **1c** and **1d**, the oxygen analogues of thiones **1a** and **1b**. Ketones **1c** and **1d** crystallize in conformations that are virtually identical to those of **1a** and **1b**, conformations in which the ketone or thione group bisects the triisopropylphenyl ring (Figure 1). As a result, there are two potentially abstractable γ -hydrogen atoms in each case, one with a somewhat longer abstraction distance than the other.

Table 1. Ideal Versus Experimental Values of **d**, Δ , θ and ω

Entry	Compound	$d_o(\text{\AA})$	$d_s(\text{\AA})$	$\Delta(^{\circ})$	$\theta(^{\circ})$	$\omega(^{\circ})$
1	n,π^* (ideal)	2.72	3.00	90	180	0
2	π,π^* (ideal)	2.72	3.00	<90	180	90
3	1a		3.06	52	118	51
4	1a		3.28	47	119	46
5	1b		3.07	52	125	50
6	1b		3.27	50	108	49
7	1c	2.90		57	^a	55
8	1c	2.94		52	^a	52
9	1d	2.88		55	^a	55
10	1d	2.97		59	^a	58
11	^b	2.78		82	114	53
12	^c	2.60		90	115	42

^aValue not reported. ^bData for cyclooctadecan-1,10-dione. See reference 10.

^cData for α -cyclohexyl-p-chloroacetophenone. See reference 11.

As can be seen from the table, the abstraction distance **d** is indeed significantly greater for sulfur than for oxygen, a conclusion that is supported by the recent work of Sakamoto *et al.*,¹² who documented C=S...H abstractions in the crystalline state with **d** ~ 3.80 Å. Work from our own laboratory has shown that abstraction fails for C=S...H distances of ~ 5 Å.¹³ Also noteworthy is a comparison of the "typical" n,π^* data in Table 1 (entries 11 and 12) with the π,π^* data (entries 3-6). Both excited states are able to tolerate ω angles that diverge from ideal by 40-50°. This is not unreasonable, however, if as suggested by Wagner,¹ the abstraction rate is proportional to $\cos^2(\omega_{\text{ideal}} - \omega_{\text{expt}})$, a relationship that predicts a rate diminution of a factor of only 2 for a 45° divergence from ideal. The major angular difference between the n,π^* and π,π^* geometrical parameters lies in the values of Δ , which are much closer to 90° for the n,π^* abstractions. As mentioned above, Δ may be more acute for π,π^* abstractions owing to the localization of π -electron density in this case closer to the *center* of the C=X bond.

Finally, we note that, except for the values of **d**, the geometric data for thiones **1a** and **1b** and ketones **1c** and **1d** are virtually identical. It is tempting to infer from this that ketones **1c** and **1d** also abstract hydrogen from their π,π^* excited states, a conclusion reached earlier by Ito *et al.*⁴ on the basis of not only topochemical considerations, but the fact that the solid state and solution phase quantum yields for ketones **1c** and **1d** are *greater* than those of 2,4,6-trisopropylbenzophenone derivatives bearing electron-withdrawing substituents in the *para* position - a trend opposite to that expected for n,π^* abstraction, but consistent with involvement of a π,π^* excited state.

Arguing against the involvement of π,π^* states in the case of ketones **1c** and **1d**, however, is the fact that the solution phase hydrogen abstraction rate constant for **1c** is $9 \times 10^6 \text{ sec}^{-1}$,¹⁴ seemingly too large for involvement of this type of excited state. For example, 1-benzoyl-8-benzyl-naphthalene undergoes a geometrically favorable δ -hydrogen abstraction from its $(\pi,\pi^*)^3$ excited state with a rate constant of only 7

$\times 10^3 \text{ sec}^{-1}$.¹⁵ By way of comparison, δ -hydrogen atom abstraction in the case of *o*-*tert*-butylbenzophenone occurs from an $(n,\pi^*)^3$ excited state with $k_H \cong 10^9 \text{ sec}^{-1}$.¹⁶ Although the question is by no means settled, we tend to agree with Wagner^{1b} that it is likely that ketones **1c** and **1d** react from $(n,\pi^*)^3$ excited states, and that their diminished reactivity stems in part from their less than ideal hydrogen abstraction geometry, particularly in the values of the abstraction distance **d** and the angle Δ (Table 1).

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References and Footnotes

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6. Compound **1a**: $P2_1/n$; $a = 9.218(2) \text{ \AA}$, $b = 16.055(4) \text{ \AA}$, $c = 13.804(2) \text{ \AA}$; $\beta = 94.89(2)^\circ$; $Z = 4$; $R = 5.1\%$. Compound **1b**: $P2_1/n$; $a = 11.336(1) \text{ \AA}$, $b = 13.136(2) \text{ \AA}$, $c = 14.240(2) \text{ \AA}$; $\beta = 96.667(8)^\circ$; $Z = 4$; $R = 4.5\%$. Full details will be published separately.
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