Photochromism of Alkylisophthalaldehydes in the Solid State: Structure–Reactivity Correlations

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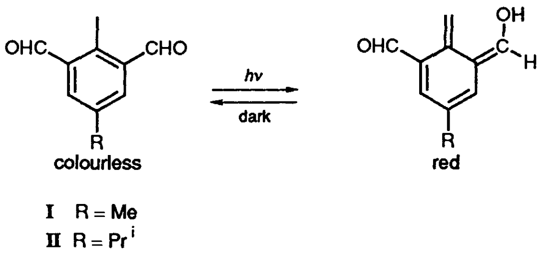
The crystal and molecular structures of the photochromic compounds 2,5-dimethylisophthalaldehyde (I) and 5-isopropyl-2-methylisophthalaldehyde (II) have been determined by single crystal X-ray analyses. The intramolecular γ-hydrogen abstraction process involved in the photoenolisation of I and II in the solid state has been rationalised in the light of relevant geometrical parameters.

Photochromism,[1] now a well known phenomenon, is a reversible change of a single chemical species between two states having distinguishably different absorption spectra, such a change being induced, at least in one direction, by the action of electromagnetic radiation. The quest for new photochromic materials has been growing in recent years since, in addition to their intrinsic interest, they have potential applications in areas such as communications, computers and display systems.[2] Several different classes of organic compounds such as anils, hydrazones, semicarbazones, stilbene derivatives, sydnones and spiro compounds have been found to be photochromic, and their properties, such as the rate of the reaction, reversibility,[3] thermal stability[4] and reusability, have been investigated.

The current study was motivated by the following serendipitous observation. Although the compounds 2,5-dimethylisophthalaldehyde (I), 5-isopropyl-2-methylisophthalaldehyde (II) and 2-methyltrimesaldehyde (III) were actually made out of synthetic interest,[5] it was discovered that the crystals of these compounds exhibit photochromism, The crystals of I and II, which are colourless in the dark, turn red in *ca.* 3–5 s upon exposure to sunlight. These red crystals become completely colourless in *ca.* 5 min at room temperature after their removal from the sunlight. Upon exposure to the sunlight the colourless crystals of III turn golden yellow in *ca.* 5 min, but in the dark, at room temperature, the reaction takes almost two days to go to completion. While the forward reaction in all of the above compounds is purely photochemical, as is evident from the fact that it proceeds equally readily even at −10 °C, the reverse reaction is thermal, the rate increasing with temperature. The colour change in all these compounds was observed clearly in the solid state, but in solutions of different concentrations, and in the melt, the colour change could not be seen. This effect may, however, be due to a fast thermal reverse reaction in the solution state as well as in the melt. The photochromic property of these solids was thought to be due to photoenolisation[6] (Scheme 1).



Scheme 1

The X-ray crystallographic study of the colourless forms of I and II was undertaken in order to establish the structure–reactivity correlations for the observed photochromic reaction in the solid state.

Certain common features of the reaction mechanisms of the compounds exhibiting photochromism by phototropic tautomerism have been discussed in literature.[7] These include an intramolecular hydrogen transfer photolysis step in *ortho* substituted aromatic structures, which occurs *via* a six-membered transition state leading to quinonoid structures. The stability of the coloured quinonoid form depends upon various factors, but it is generally observed that H-transfer reactions have a poor photochromic reversibility due to several competing side reactions. Crystalline anils are among the few groups of compounds which show a high degree of reversibility. Compounds undergoing reversible photoenolisation reactions in the literature include nitrotoluenes,[8] *o*-alkylbenzophenones[9] and *o*-alkylacetophenones.[10] The present study becomes important in that the colourless to red change in both I and II is completely reversible, and the process can be repeated several times without any fading. This is borne out by the fact that there was no noticeable difference between the oscillation photographs of the crystals of I and II before irradiation and after repeating the photochromic process five times. Further, to our knowledge structures I and II are the first examples of photochromic organic compounds involving γ-hydrogen abstraction for which X-ray structure–photoreactivity correlations have been obtained. Detailed X-ray analyses of compound III, however, could not be undertaken as good single crystals suitable for X-ray diffraction could not be obtained, even after several attempts.

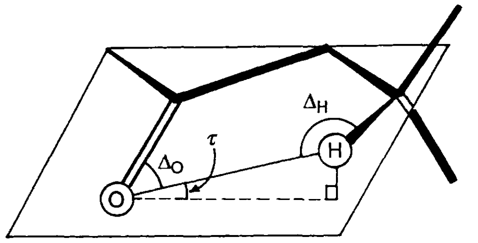


Fig. 1 Definition of the geometrical parameters referred to in Table 2

Results and Discussion

Structure–Reactivity Correlation.—The ideal geometry for a hydrogen atom to be abstracted by the oxygen atom of the carbonyl group[11] would be a short O···H distance (*i.e.*, shorter than the sum of the van der Waals radii of oxygen and hydrogen atoms (2.72 Å),[12] with the angles C–O···H and C–H···O being 90° and 180° respectively. The deviations from this ideal geometry can be specified by the angles Δ_H, Δ_O and τ (Fig. 1). Δ_H is the C–H···O angle for which a linear geometry ($\Delta_H = 180°$) seems to be favoured in a bimolecular hydrogen abstraction, but this condition can hardly be expected to be satisfied in the case of an intramolecular hydrogen abstraction

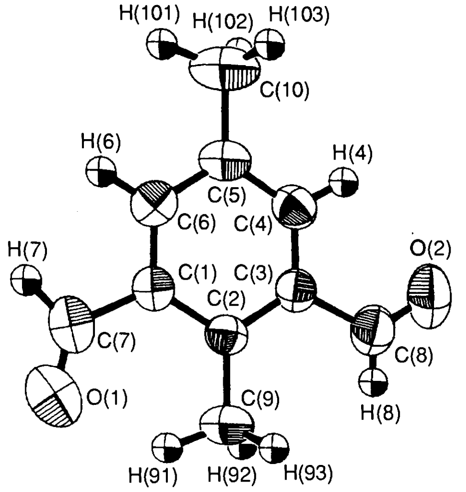


Fig. 2 The ORTEP plot of a single molecule of compound **I** with the numbering scheme

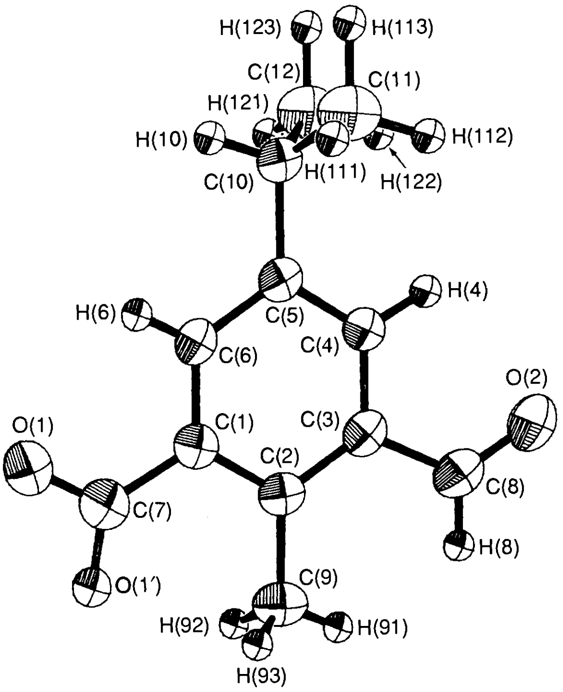


Fig. 3 The ORTEP plot of a single molecule of compound **II** with the numbering scheme

process.[13] Δ_O is the C–O ··· H angle which, in the ideal case, will be equal to 90° because the abstraction process involves an n,π* excited state in which the new O–H bond is formed using the half-occupied oxygen n-orbital which is largely 2p-like in character.[14] τ is the angle subtended by the O ··· H vector with its projection on the mean plane of the formyl group, and should have an ideal value of 0° for efficient hydrogen abstraction.

In both the crystal structures there is not a single intermolecular O ··· H short contact. Therefore, only intramolecular considerations are necessary for rationalising the reactions. The atomic numbering scheme for structures **I** and **II** is shown in Figs. 2 and 3 respectively. Table 1 contains the relevant O ··· H contacts in both **I** and **II**, while Table 2 gives the intramolecular geometrical parameters, Δ_H, Δ_O and τ.

From Table 1, which lists all the distances of the oxygen atoms from the *ortho* methyl hydrogen atoms, it is obvious that the only O ··· H contacts of significance are O(1) ··· H(91) = 2.58 Å in **I** and O(1′) ··· H(92) = 2.54 Å in **II**, all the other O ··· H distances being considerably longer than the sum of the van der Waals radii of the oxygen and hydrogen atoms. The Δ_H values in **I** (96.9°) and in **II** (89.9°) deviate significantly from the ideal value of 180°. However, a large deviation from the preferred linear approach is only to be expected in the case of intramolecular hydrogen abstraction.[13] Indeed, the best possible value of the C–H ··· O angle, termed Δ_R, attainable in the two structures was obtained by rotating the methyl group so as to bring the abstractable H-atom into the plane of the formyl group. As can be seen from Table 2, the values of Δ_R in **I** and **II** are only 135.4° and 130.1° respectively, as against the Δ_H value of 180°. The corresponding values of Δ_O for these two structures are 95.3° and 100.7° which are quite close to its ideal value of 90°. The τ values of −16.6° and −19.2° for **I** and **II** respectively are also not far from the ideal value of 0°. Wagner[15] has observed that coplanar hydrogen abstraction is not a strict requirement for the Norrish type II process of ketones, which is also an intramolecular process. Examples of such non-coplanar hydrogen abstraction have indeed been reported by Ariel *et al.*,[16] Wagner *et al.*[17] and Padmanabhan *et al.*[13]

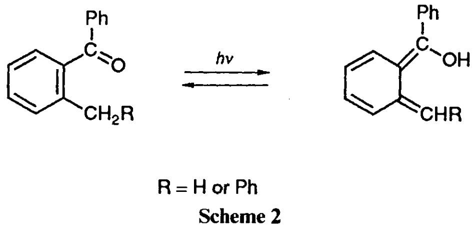
Table 1 Intramolecular distances of the oxygen atoms from the hydrogen atoms of the *o*-methyl group in **I** and **II**

Compound I		Compound II[a,b]	
O ··· H	Distance/Å	O ··· H	Distance/Å
O(1)–H(91)	2.58(3)	O(1)–H(91)	5.06(5)
O(1)–H(92)	3.06(5)	O(1)–H(92)	4.09(3)
O(1)–H(93)	3.84(4)	O(1′)–H(91)	3.64(5)
O(2)–H(91)	4.85(3)	O(1′)–H(92)	2.54(3)
O(2)–H(92)	4.48(5)	O(2)–H(91)	3.79(5)
O(2)–H(93)	3.71(4)	O(2)–H(92)	4.91(3)

[a] Since the molecule lies on the mirror plane of C2/m, H(93) and H(92) are the mirror images of one another and hence identical. [b] O(1) is the disordered oxygen with higher occupancy (90%) while O(1′) has a lower occupancy (10%).

The above considerations were further supported by the following analyses. A hypothetical point, represented by Hyp was fixed in the direction of the n-orbitals of the carbonyl group at 90° ($\mathrm{C{-}\hat{O}\cdots Hyp} = 90°$) and at a distance of 1 Å from the oxygen atom. The ideal condition for hydrogen abstraction by an n,π* excited carbonyl group would be collinearity of O-atom, Hyp and the methyl hydrogen *i.e.*, $\mathrm{O\cdots H\hat{y}p\cdots H}$ (Δ_N) should be 180°. From the values of Δ_N recorded in Table 2, it can be seen that this condition is more or less satisfied. It is interesting to observe that in the case of **II**, one of the formyl groups is disordered (see refinement). The hydrogen abstracting oxygen [O(1′)] has only 10% occupancy in the crystal.

The next step in the hydrogen abstraction process cannot be understood from the crystallographic data, as the latter pertains to the molecule only in its ground state. Yang and Rivas[10] first reported reversible photoenolisation reactions in *ortho*-alkylbenzophenones (Scheme 2) where, although photochromism was not directly observed, the photoenol from 2-methylbenzophenone was trapped by its reaction with dimethylacetylene dicarboxylate to form a Diels–Alder adduct. From flash photolysis studies on several *o*-alkylbenzophenones[18] it has become

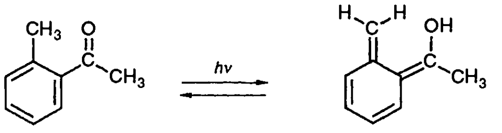


Scheme 2

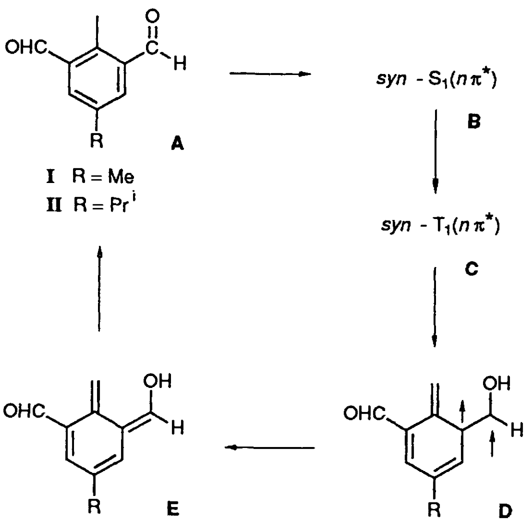
Table 2 Intramolecular geometrical parameters relevant to hydrogen abstraction in I and II

Atom pair	O···H/Å	Δ_H/°	Δ_O/°	τ/°	Δ_N/°	Δ_R/°
Compound I						
O(1)···H(91)	2.58(3)	96.92(1.8)	95.26(64)	−16.63(69)	152.21(97)	135.42(2.2)
Compound II						
O(1′)···H(92)	2.54(3)	89.86(1.9)	100.68(73)	−19.23(80)	145.13(98)	130.13(2.4)

clear that photoenolisation occurs *via* a triplet excited state rather than a singlet excited state and the mechanism of an intramolecular hydrogen abstraction reaction has been summarised.[19] From these examples as well as from the more recently reported investigation[10] on 2-methylacetophenone (Scheme 3) by nanosecond flash photolysis, which gives detailed evidence for the reaction sequence of photoenolisation, it is reasonable to postulate the reaction mechanism for compounds I and II as represented in Scheme 4 wherein, the starting compounds **A** (the aldehydes I and II), upon n,π* excitation, give first a singlet excited state **B**. By intersystem crossing **B** affords a triplet state **C** which has a sufficiently long life-time to allow γ-hydrogen abstraction. The biradical **D** then combines to form the enol **E** which, in the absence of any side reactions such as *cis–trans* isomerisation, reketonises thermally, giving back **A**. That the last step **E** ⟶ **A**, *i.e.* the conversion of the red enolic form to the colourless keto form, is thermal, is supported by the following observation. While the colourless crystals turned red almost instantaneously upon exposure to sunlight even when cooled to below 0 °C, the reverse reaction in the dark at the same temperature is much slower, needing almost two days to go to completion, clearly indicating that the forward reaction is photochemical, while the reverse reaction is thermal.



Scheme 3



Scheme 4

It is interesting to note that since only 10% of the oxygen is in the abstracting position in compound **II**, it would be natural to expect some difference in the kinetics of compounds **I** and **II**. Since no such differences were observed at room temperature, or even at −10 °C, it indicates that the kinetic barrier to rotation is very small in the crystal. This suggests 'designing' some substituents that could hinder the rotation of the formyl group and thus yield compounds with a variety of rates in their colour changes.

Experimental

2,5-Dimethylisophthalaldehyde (**I**), 2-methyl-5-isopropylisophthaldehyde (**II**) and 2-methyltrimesaldehyde (**III**) were synthesised starting from *p*-xylene, *p*-cymene and toluene respectively, employing Birch reduction followed by Vilsmeier–Haack formylation as per the procedures developed by Krishna Rao *et al.*[5] The compounds were then purified by column chromatography and the spectral data and the m.p. were consistent with the values reported.[5]

The colourless crystals of both compounds **I** and **II** turned red upon exposure to sunlight in *ca.* 5 s. The red crystals, when kept in the dark for *ca.* 5 min at room temperature, turned colourless. The IR spectra of the colourless and the coloured forms were recorded in a Nujol mull and the absence or presence of the absorption at 3350 cm^{-1}, corresponding to the enolic O–H stretching frequency, was monitored. The absorption at 3350 cm^{-1} which was absent in the keto compound appeared in the red enolic form and disappeared again when the mull was recorded after being kept in the dark for fifteen minutes.

X-Ray Crystallographic Analyses of Compounds I *and* II.—Good single colourless crystals of **I** were obtained by slow evaporation from chloroform, while compound **II** was crystallised from a chloroform–ethanol (1:1) mixture. The crystals of both these compounds chosen for data collection were sealed in Lindeman capillary tubes so as to avoid aerial oxidation on the crystal surface. Accurate cell dimensions and intensity data were obtained from an Enraf–Nonius CAD-4 diffractometer using monochromated Cu-Kα (λ = 1.5418 Å) radiation (for the single crystal of **I**) and graphite monochromatised Mo-Kα (λ = 0.7107 Å) radiation (for the single crystal of **II**) in $\omega/2\theta$ scan mode with a scan speed of 1° min^{-1}. The stability and orientation of the crystal in both cases were monitored by measuring three standard reflections after every 3600 s of data collection; the orientation was checked after every 400 reflections and the fluctuations in their intensities were below 3%. The data were corrected for Lorentz and polarisation effects, but not for absorption.

The structure **I** was solved by direct methods using MULTAN 87.[20] Isotropic refinement followed by anisotropic least squares refinement of the non-hydrogen atoms converged to an R value of 0.162. The hydrogen atoms were located in the difference Fourier map at stereochemically reasonable positions. Full matrix refinement, using SHELX 76,[21] of the scale factor, positional and anisotropic thermal parameters of the non-hydrogen atoms and positional and isotropic thermal parameters of the hydrogen atoms converged to $R = 0.053$ and $R_w = 0.064$. The function minimised in the least squares refinement was $\Sigma(w|F_o| - |F_c|)^2$ where the weighting scheme used is given by $w = k/\sigma^2|F_o| + g|F_c|^2$ with $k = 0.4656$ and $g =$

Table 3 Crystal data for compounds I and II[a]

	I	II
Molecular formula	$C_{10}H_{10}O_2$	$C_{12}H_{14}O_2$
Mr	162	190
Space group	$P2_1/c$	$C2/m$
a/Å	7.749(3)	18.312(1)
b/Å	9.312(2)	6.810(1)
c/Å	11.794(2)	8.309(1)
α/°	90.00	90.00
β/°	93.08(2)	93.89(1)
γ/°	90.00	90.00
V/Å^3	849.8(3)	1045.1(4)
Z	4	4
D_m/Mg m^{-3}	1.25	1.20
D_x/Mg m^{-3}	1.27	1.21
μ/cm^{-1}	6.29	0.46
$F(000)$	344	408
Crystal size/mm	0.3 × 0.2 × 0.10	0.4 × 0.2 × 0.08
θ limit/°	60.0	27.0
Mode of data collection	$\omega/2\theta$	$\omega/2\theta$
No. of intensity controls	3	3
No. of reflections collected	1472	1358
No. of observed reflections	967 ($\|F_o\| > 3\sigma\|F_o\|$)	867 ($\|F_o\| > 3\sigma\|F_o\|$)
Final R^b	0.0527	0.0561
Weighted R (R_w)^b	0.0635	0.0561
Weighting function	$0.466/(\sigma^2\|F_o\| + 0.002\|F_o\|^2)$	$1/(\sigma^2\|F_o\| + \|F_o\|^2)$
Number of variables	137	114

[a] Anisotropic thermal parameters of non-hydrogen atoms, positional parameters, bond lengths and angles involving hydrogen atoms have been deposited at the Cambridge Crystallographic Data Centre. See instructions to authors, *J. Chem. Soc., Perkin Trans. 2*, 1991, Issue 1. [b] $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$, $R_w = \Sigma(w^{\frac{1}{2}}|F_o| - |F_c|)/\Sigma(w^{\frac{1}{2}}|F_o|)$.

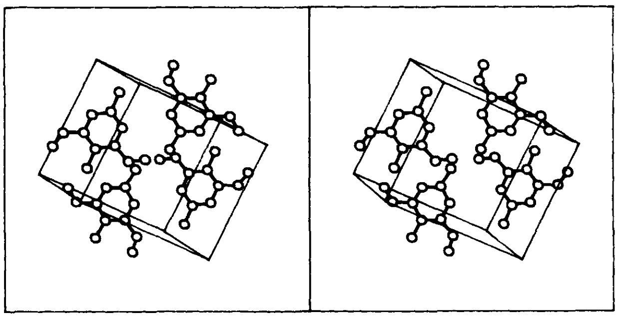


Fig. 4 A stereo view of the molecules of I in the unit cell

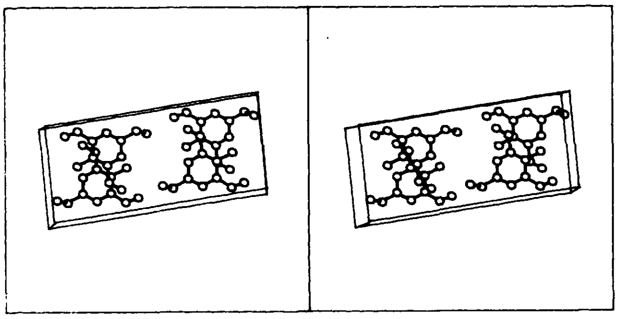


Fig. 5 A stereo view of the molecules of II in the unit cell

0.00201. The positional and temperature factors of the C(10) methyl hydrogens were kept fixed in the final cycles of refinement. There were no significant features in the difference Fourier map when the refinement was complete. The maximum and minimum values were 0.24 and −0.16 Δe Å^{-3}.

The structure II was also solved by direct methods using MULTAN 87. While the preliminary oscillation and Weissenberg photographs of the crystal had indicated the space group to be $C2$, Cm or $C2/m$ with $Z = 4$, the statistical distribution of E values showed a centric distribution. Therefore $C2/m$ was chosen as the correct space group which is of course justified by the satisfactory refinement of the structure. An E-map computed with the best set of phases (combined figure of merit = 2.94) revealed all the non-hydrogen atoms. All these atoms except the two methyl carbon atoms of the isopropyl group were found to be on the crystallographic mirror plane ($y = 0$). Full matrix refinement using SHELX 76 of the scale factor, positional and anisotropic thermal parameters of the non-hydrogen atoms and isotropic thermal parameters of hydrogen atoms converged to an $R = 0.057$. Unit weighting scheme was used, and the function minimised was $\Sigma(|F_o| - |F_c|)^2$. Careful examination of the values of different parameters at this stage resulted in the following important observation.

The isotropic temperature factor of one of the hydrogens H(7) was 0.02(1) Å^2, much lower than that of the corresponding hydrogen H(8) of the other formyl group *viz.*, 0.07(1) Å^2, Further, the anisotropic thermal parameters, $U_{i,j}$s for O(1) [$U_{11} = 0.061(2)$, $U_{22} = 0.143(3)$, $U_{33} = 0.063(2)$] are in general higher than those of O(2) [$U_{11} = 0.067(2)$, $U_{22} = 0.109(3)$ and $U_{33} = 0.037(1)$]. Also, the C(7)–H(7) bond length [1.06(3) Å] is longer than than that of C(8)–H(8) [0.95(4) Å]. These observations led us to suspect that the formyl group attached to C(1) may be disordered. This is supported primarily by the occurrence of the photoreaction itself. In fact, without the disorder of the kind proposed, this compound could not exhibit the photochromic effect. H(7) is designated as O(1′). The atoms O(1) and O(1′) were refined only isotropically for different values of their occupancies and finally an occupancy value of 0.90 for O(1) and 0.10 for O(1′) was found reasonable. Atom O(1) was then refined anisotropically. The C(7)–O(1′) bond length was fixed at 1.15 Å but the isotropic temperature factor of O(1′) was refined. The refinement finally converged to $R = 0.056$ (unit weighting scheme) with the maximum and the minimum values of residual peaks being 0.24 and −0.20 Δe Å^{-3}.

The details of the crystallographic data of I and II are given in Table 3. The final positional parameters of the atoms are listed in Table 4, relevant bond lengths and bond angles in Tables 5 and 6 respectively. Figs. 2 and 3 are drawn using ORTEP.[22] No intermolecular hydrogen bonds are observed in I or II. Both the

Table 4 The fractional atomic coordinates ($\times 10^4$) of the non-hydrogen atoms of **I** and **II** with their esds in parentheses

Atom	*x*	*y*	*z*
Compound **I**			
C(1)	3 153(2)	4 710(2)	10 844(2)
C(2)	2 337(2)	3 994(2)	9 899(1)
C(3)	1 713(2)	4 877(2)	9 010(1)
C(4)	1 865(3)	6 350(2)	9 063(2)
C(5)	2 659(3)	7 060(2)	9 979(2)
C(6)	3 290(3)	6 186(2)	10 861(2)
C(7)	3 905(3)	3 968(4)	11 858(2)
O(1)	3 946(3)	2 715(2)	12 062(2)
C(8)	785(3)	4 270(4)	7 979(2)
O(2)	162(3)	4 975(2)	7 222(1)
C(9)	2 181(2)	2 396(3)	9 863(2)
C(10)	2 822(4)	8 659(3)	10 019(3)
Compound **II**			
C(1)	7 249(2)	0(0)	2 114(4)
C(2)	7 173(2)	0(0)	3 789(4)
C(3)	7 812(2)	0(0)	4 802(4)
C(4)	8 485(2)	0(0)	4 148(4)
C(5)	8 564(2)	0(0)	2 502(4)
C(6)	7 932(2)	0(0)	1 509(4)
C(7)	6 605(2)	0(0)	929(5)
O(1)	6 641(2)	0(0)	−485(4)
O(1′)	6 008(0)	0(0)	1 214(0)
C(8)	7 810(2)	0(0)	6 587(5)
O(2)	8 351(2)	0(0)	7 469(3)
C(9)	6 426(2)	0(0)	4 444(6)
C(10)	9 304(2)	0(0)	1 805(4)
C(11)	9 729(2)	1 838(6)	2 301(4)

Table 5 Selected bond lengths involving non-hydrogen atoms with their esds in parentheses

Atoms	Distance/Å	Atoms	Distance/Å
Compound **I**			
C(1)–C(2)	1.418(3)	C(3)–C(8)	1.490(3)
C(1)–C(6)	1.378(3)	C(4)–C(5)	1.383(3)
C(1)–C(7)	1.474(3)	C(5)–C(6)	1.389(3)
C(2)–C(3)	1.398(2)	C(5)–C(10)	1.495(3)
C(2)–C(9)	1.494(3)	C(7)–O(1)	1.192(4)
C(3)–C(4)	1.378(3)	C(8)–O(2)	1.189(3)
Compound **II**			
C(1)–C(2)	1.408(5)	C(5)–C(6)	1.384(5)
C(1)–C(6)	1.393(5)	C(5)–C(10)	1.523(5)
C(1)–C(7)	1.494(5)	C(7)–O(1)	1.182(5)
C(2)–C(3)	1.405(5)	C(7)–O(1′)	1.145(4)
C(2)–C(9)	1.520(5)	O(1)–O(1′)	1.895(3)
C(3)–C(4)	1.394(5)	C(8)–O(2)	1.199(5)
C(3)–C(8)	1.483(5)	C(10)–C(11)	1.521(4)
C(4)–C(5)	1.385(5)		

crystal structures are stabilised by van der Waals forces. The stereo packing arrangements of the molecules in **I** and **II**, obtained using PLUTO,[23] are presented in Figs. 4 and 5 respectively.

Conclusion

The crystallographic analyses of the colourless forms of **I** and **II** allow us to identify the specific hydrogen atom abstracted in the crystals of these compounds upon excitation. The geometrical requirements derived from the X-ray studies described here would be of general validity wherever γ-hydrogen abstraction is implicated. Also by combining our own results with those obtained from the ns flash photolysis study of 2-methylacetophenone and related compounds,[10] it is reasonable to postulate the complete reaction sequence of the reversible photoenolisation reaction as shown in Scheme 4.

Table 6 Selected bond angles involving non-hydrogen atoms with their esds in parentheses

Atoms	Angle/°	Atoms	Angle/°
Compound **I**			
C(2)–C(1)–C(7)	123.9(2)	C(3)–C(4)–C(5)	123.0(2)
C(6)–C(1)–C(7)	115.4(2)	C(4)–C(5)–C(6)	115.5(2)
C(1)–C(2)–C(3)	115.8(1)	C(4)–C(5)–C(10)	122.3(2)
C(1)–C(2)–C(9)	121.5(2)	C(6)–C(5)–C(10)	122.3(2)
C(3)–C(2)–C(9)	122.7(2)	C(1)–C(6)–C(5)	123.3(2)
C(2)–C(3)–C(4)	121.7(2)	C(1)–C(7)–O(1)	128.9(3)
C(2)–C(3)–C(8)	121.4(2)	C(3)–C(8)–O(2)	124.2(2)
Compound **II**			
C(2)–C(1)–C(6)	120.7(3)	C(4)–C(5)–C(10)	122.2(3)
C(2)–C(1)–C(7)	121.5(3)	C(6)–C(5)–C(10)	121.2(3)
C(6)–C(1)–C(7)	117.8(3)	C(1)–C(6)–C(5)	122.4(3)
C(1)–C(2)–C(3)	117.1(3)	C(1)–C(7)–O(1)	124.0(3)
C(1)–C(2)–C(9)	120.5(3)	C(1)–C(7)–O(1′)	127.0(3)
C(3)–C(2)–C(9)	122.3(3)	O(1)–C(7)–O(1′)	109.0(3)
C(2)–C(3)–C(4)	120.4(3)	C(7)–O(1)–O(1′)	34.8(2)
C(2)–C(3)–C(8)	122.7(3)	C(3)–C(8)–O(2)	123.5(3)
C(4)–C(3)–C(8)	116.9(3)	C(5)–C(10)–C(11)	111.1(3)
C(3)–C(4)–C(5)	122.8(3)	C(7)–O(1′)–O(1)	36.1(2)
C(4)–C(5)–C(6)	116.6(3)		

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