

Available online at www.sciencedirect.com



Tetrahedron

Tetrahedron 60 (2004) 11959-11968

9-Anthroylacetone and its photodimer

Francesca Cicogna, Giovanni Ingrosso,* Fabio Lodato, Fabio Marchetti and Maurizio Zandomeneghi

Dipartimento di Chimica e Chimica Industriale, Università di Pisa, Via Risorgimento 35, 56126 Pisa, Italy

Received 4 June 2004; revised 26 August 2004; accepted 16 September 2004

Available online 27 October 2004

Abstract—9-Anthroylacetone undergoes a head-to-tail $[4\pi + 4\pi]$ photo-dimerisation reaction that leads to the formation of 5,11-bis(1,3-diketobutyl)-5,6,11,12-tetrahydro-5,12,6,11-di-*o*-benzeno-dibenzo[*a,e*]cyclooctene both in solution and in the solid state when irradiated with different sources (sunlight, tungsten lamp, xenon lamp, UV laser beam 351–364 nm), the reaction being accompanied by a colour variation from bright yellow to colourless. Quantum yields >0.023 mol/Einstein are evaluated for the solid state reaction. Interestingly, the dimer dissociates to give 9-anthroylacetone, both thermally (*T*>130 °C) and photochemically, by short UV wavelength irradiation. The single-crystal X-ray structure of 9-anthroylacetone and its dimer are reported. © 2004 Elsevier Ltd. All rights reserved.

1. Introduction

9-Anthroylacetone **1**, reported first by Evans in 1961,¹ has been the object of attention since its conjugate base, i.e. 9-anthroylacetonate **2**, gave rise to various boron² and rare earth derivatives³ showing potentially interesting photophysical properties (Scheme 1).



Scheme 1.

More recently, the self assembled compound **3** has been described in which energy and electron transfer can take place between $\text{Ru}(\text{bipy})_3^{2+}$, the donor sub-unit, and the ligand **2**, the acceptor component, under photo-activation conditions.⁴



During the last years, some of us have studied whether and how the anthrylic fluorophore communicates with different metal-ligand sub-units, like metal-\beta-ketoenolato or metal-cyclopentadienyl systems, under those conditions (chemical, photochemical, and electrochemical) that can induce the intramolecular transmission of electronic effects.⁵ In this context, we prepared **1** as reported by Evans¹ with the aim to synthesise new rhodium(I) and iridium(I) derivatives of 2.⁶ We observed that freshly prepared bright yellow solid samples of 9-anthroylacetone gave rise to a new colourless compound, when they were exposed to laboratory light in the presence of air and this drew our attention towards the photochemistry of 1. We succeeded in isolating the colourless compound and found that it has the structure 4 resulting from the $[4\pi + 4\pi]$ photo-dimensiation of **1**. To our knowledge, such a reaction of 1 has not yet reported in the literature. A similar behaviour has instead been documented for 9-benzoylanthracene.⁷

Keywords: Anthracene derivatives; Anthracene photo-dimerisation; Photochromism.

^{*} Corresponding author. Fax: +39 50 2219410/260; e-mail: vanni@dcci.unipi.it

^{0040–4020/\$ -} see front matter @ 2004 Elsevier Ltd. All rights reserved. doi:10.1016/j.tet.2004.09.070



The $[4\pi + 4\pi]$ photo-dimerisation of anthracene as well as of several anthracene derivatives is a very well known reaction that has been studied extensively since 1950.⁸ The reaction takes place both in solution,^{8,9} in a variety of organic solvents and in the solid state,^{7,9c,10} although the reaction in the solid state is less documented. Photoexcitation of *meso*-substituted anthracene derivatives in solution typically leads to the head-to-tail dimers, though evidence for the concomitant formation of the thermally more labile head-to-head dimers has been obtained in some cases (Scheme 2).^{8b,9e,10b,11} Bimolecular reactions are expected to take place in the solid state only between nearest neighbours. Thus, the molecular structure of the dimer is expected to reflect the geometric relationship lying between the neighbours in the crystal lattice.¹² As a result of these restrictions, solid state reactions are generally more selective then those in solution.



Scheme 2.

One of the most interesting features of the photo-dimerisation of anthracene derivatives is the reversibility, this being the prerequisite for the development of new logic devices that operate at the molecular level.^{9a,b,13} The photo-dimer can be reverted to the monomer by thermal and photochemical dissociation. While the first process is quantitative, a steady state mixture of monomer and dimer is obtained by photochemical dissociation, at least under the irradiation conditions used until now.^{8a} Compounds that interconvert between one form and another upon irradiation with convenient light (photo-chromic molecules)^{8b,9b,14} can be useful, at least in principle, to project various photonic devices, such as erasable optical memory media and photo-optical switch components. For this reason it is important that the direct and inverse photoreactions are not limited to the solution phase but also occur in the solid state.

All these facts prompted us to study in some detail the photochemical dimerisation of 1 to 4 and the thermal and photochemical dissociation of 4, both in solution and in the solid state. The results of this study are presented herein.

2. Result and discussion

2.1. The photo-dimerisation of 9-anthroylacetone 1

As described in the Section 4, when a d₂-dichloromethane solution of 1 (ca. 10^{-2} M) was irradiated for 3 h, under dinitrogen atmosphere, with a xenon lamp, about 50% of 1 was converted into 4. Exposure of 1 to sunlight, at the same concentration, gave 4 in about 28% yield. The photodimerisation took place also when a d₂-dichloromethane solution of 1 was irradiated with a near-UV laser beam, although in this case the conversion of 1 into 4 was about 11%. Since each experiment was carried out under very different irradiation conditions (irradiation geometries, light source, energy), it is not possible to draw any conclusion regarding the relative efficiency of the different irradiation techniques. Nevertheless, the photo-conversion of 1 into 4 appears a relatively simple clean reaction. A new, unidentified, species were formed only when the irradiation is carried out on chloroform solutions.

Mixtures of 1 and 4 can be separated by taking advantage of their different solubility in diethyl ether.

The main pattern of the ¹H NMR spectrum of **4** (Table 1) looks like that reported in the literature for other anthracene photodimers,^{7,15} but in this spectrum a peak at $\delta = 14.8$ ppm is present due to the enolic proton of **4**. In the ¹H NMR spectrum of **1** (Table 1), the enolic peak is observed at $\delta = 16.0$ ppm, thus showing that **1** is moderately more acid than **4**. Both compounds are in their enolic form and the ketoenol equilibrium cannot be shifted by changing the solvent polarity.

As anticipated in the introduction, solid samples of **1** show the presence of increasing amounts of **4** when they are exposed to laboratory light. With the aim to better define the photo-dimerisation of **1** in the solid state some experiments were carried out. Irradiation experiments of solids are less straightforward than experiments on solutions. In particular, the irradiation geometry (i.e. the relative position and orientation of the light source and of the sample), the emission characteristics of the source and the spatial extension of its light-generating volume, the dimension of the particles being irradiated and their reflective and scattering properties and the optics make a precise evaluation of photochemical quantities difficult. However, we attempted to estimate the limit values of quantum yields of the photochemical reactions.





^a Spectra recorded in CDCl₃; s=singlet; m=multiplet; d=doublet.

A variety of irradiation experiments successfully transform 1 into 4 (see Section 4). Irradiation with a tungsten lamp (24 h), with a xenon arc lamp (4 h) or with a near-UV Argon-ion laser (2 h) produced the photo-transformation up to high conversion values: in our experiments, 70% yields were easily obtained without any detectable formation of other products. The irradiation of 50 mg of 1 with the 351–364 nm emission lines of an Argon-ion laser $(1 \rightarrow 4$ conversion, 31%) allowed us to estimate the minimum value $(\Phi_{1\rightarrow 4}>0.023 \text{ mol of } 4/\text{Einstein})$ of the quantum yield of photo-production of 4. This value was obtained on the hypothesis that all incident light was absorbed by the sample, thus ignoring scattering and reflection of light, which are more and more intense with the increasing amount of white microcrystals of 4 on the sample surface. Thus, the above calculated value is a lower limit of the true quantum yield.

The 1 to 4 transformation in the solid state (UV Argon-ion laser beam) (see Section 4.6, Experiment D) can be followed by direct analysis using front-surface absorption spectroscopy.¹⁶ Figure 1(A), that shows the spectra of pure micro-crystalline 1, registered before and after irradiation, as well as the spectrum of pure 4, demonstrates clearly that 1 photo-dimerises, at least partially, giving rise to 4. All the spectra show saturation effects¹⁶ at absorbance > 0.8 which are due to the strong absorbing features of pure 1 and 4. To avoid the saturation effects it is necessary to dilute the sample with non-absorbing powder species to lower the concentration of absorbing centres. A comparison between the spectra reported in Figure 1(A) and those of Figure 1(B), which were recorded on diluted mixtures of 1 or 4 in BaSO₄, supports the above conclusion, the spectrum of pure 4 looking like that of diluted 4, although, because of saturation at absorbance >0.8, the absorbance in the range 350-400 nm seems proportionally higher than that expected on the base of the absorbance of the band at ca. 300 nm shown by diluted 4. On the other hand, the spectrum of diluted 1 (Fig. 1(B)) clearly shows the dramatic effect of dilution, and now it looks similar to that obtained in solution (see Section 2.2, Fig. 6).

In order to gain insight into the topochemical aspects of the photo-dimerisation reaction, single crystals of 1 and 4 were analysed by X-ray diffraction. The molecular structure of 1 is shown in Figure 2. Bond distances and angles are provided in Supporting Information. The molecule lies on two planes, one being defined by the 9-anthryl moiety (max deviating atom being C(8), 0.06 Å) and the other by the 1,3diketobutyl moiety (max deviating atom being C(3), 0.002 Å). The two planes intersect each other along a line almost coincident with the C(4)-C(5) bond and make a dihedral angle of about 64.7°. The wideness of the C(2)–C(3)–C(4) angle (121.5°) and the presence of only one hydrogen maximum beside C(3) in the difference Fourier map both suggest the essential sp² nature of this carbon atom, which supports the enolic form for the 1.3-diketobutyl moiety. Anyway, the equal lengths within the C(2)–C(3)/C(3)–C(4) and C(2)–O(1)/C(4)–O(2) bonds do not establish reliably which oxygen atom carries the enolic hydrogen atom, which probably is statistically



Figure 1. Front surface absorbance spectra (absorbance vs λ , nm); (A) spectrum of pure micro-crystalline 9-anthroylacetone 1 (—); spectrum of the same sample after 5 min of irradiation (—); spectrum of pure 4 (—); (B) spectrum of 9-anthroylacetone 1 in BaSO₄ (1 mg in 5 g of BaSO₄) (—); spectrum of pure 4 in BaSO₄ (1 mg in 0.5 g of BaSO₄) (—).



Figure 2. View of the molecular structure of 1. Thermal ellipsoids of O atoms are at 30% probability, those of C atoms have been omitted for clarity.

bonded to either O(1) or O(2) atoms. However, according to the finding of a maximum in the difference Fourier map, we have introduced in our model the hydrogen atom bonded to O(1). The resulting OH group behaves as a donor in an intramolecular hydrogen bond (O(1)…O(2) distance 2.516 Å). Figure 3 suggests the crystal structure of 1 by showing the contents of the unit cell. The molecules are arranged in pairs, related by the inversion centre placed at $\frac{1}{2}$, $\frac{1}{2}$. The 9-anthryl moieties of each pair overlap each other in such a way that C(5) faces C(12') and, consequently, C(12) faces C(5'), at a distance of 3.794 Å, where the primed atoms belong to the second molecule of the pair.

The molecular structure of **4** is shown in Figure 4. Bond distances and angles are provided in Supporting Information. Compound **4** results from the cycloaddition of two molecules of **1** that are linked to each other by the new bonds C(5)-C(12') and C(12)-C(5'). As a consequence, the central rings of the two original 9-anthryl moieties lose their aromaticity and bend along the axes C(5), C(12) and C(5'), C(12'), respectively, assuming the shape of flying wings. The molecule has an inversion centre, which allows us to confine our description to only one half of compound **4**. The



Figure 3. View of the crystal packing of **1**, projected approximately along the [101] direction. The molecules of the pair are related by the inversion center at $\frac{1}{2}$, $\frac{1}{2}$, $\frac{1}{2}$, $\frac{1}{2}$, $\frac{1}{2}$, $\frac{1}{2}$, $\frac{1}{2}$.



Figure 4. View of the molecular structure of **4**. Thermal ellipsoids of O atoms are at 30% probability, those of C atoms have been omitted for clarity. '=-x+1/2, -y+1/2, -z+1.

wings derived from the bending of the 9-anthryl group make in **4** a dihedral angle of 133.1°, while the 1,3-diketobutyl moiety maintains its approximately planar conformation, and, rotating around C(4)-C(5) bond, becomes coplanar with the C(5)-C(12') bond.

Looking at Figures 3 and 4, the topological relationship between the pair of molecules in the crystal structure of 1 and the molecular structure of 4 appears evident. Moreover, it is important to underline that although the distance of 3.794 Å between C(5) and C(12') and C(5') and C(12) in the crystal structure of **1** should be thought to be too long for the cycloaddition to take place in the solid state,⁷ nevertheless such a reaction indeed occurs in the case of 1, as reported above. The cycloaddition of 1 to 4 does not follow a topotactic reaction pathway: in fact, when a single crystal of 1 was exposed to a near-UV laser the yellow colour disappeared and 4 was formed, but the crystal flaked off. This shows that the molecules of 4 cannot move in the crystal of 1 so to assemble in the packing required by the new single crystal. The occurrence of any thermal effect caused by the laser beam was discarded since the crystal was maintained at room temperature during the irradiation.

2.2. Thermal and photochemical dissociation of 4

When a solution of **4** in benzene was maintained at 80 °C for 4 h no appreciable decomposition of the sample was observed. This fact prompted us to heat solid-state samples. Thus, we observed that when a solid sample of **4** was heated at a temperature near the melting point of **1** (127–129 °C), it started to dissociate to give **1**, and, at 180 °C, it was converted almost quantitatively into **1** in about 25 min.

Since at 150 °C the reaction is slower, it can be easily followed by ¹H NMR spectroscopy. The profile of the thermal dissociation of **4** (containing a small amount of **1**, ca. 1%) as a function of time (Fig. 5) shows that, after an induction period, the reaction is fast. On the other hand, the thermal dissociation of a solid sample of **4** which did not contain any traces of **1** had a completely different course. In this case, after 200 min of heating at 150 °C, an amount of **1**



Figure 5. Thermal dissociation at 150 °C of 4 as a function of time (min): % of 1 (-),% of 4 (-).

(only 35%), smaller than that predictable based on the data reported in Figure 5, was obtained. We are inclined to conclude that small amounts of 1 in solid samples of 4 play some catalytic role in the thermal dissociation of 4. The fact that, at 150 °C, 1 is melted while 4 is still solid can favour the thermal decomposition of 4. At this temperature the thermal dissociation of crystalline 4 can be kinetically impeded; while, the solubilisation of 4 into 1 can be favoured: as a result, a new reaction pathway can be available.

The photochemical dissociation of 4 to give 1 was followed by UV-vis absorption spectroscopy and was carried out on an ethanol solution of pure 4 (4.27×10^{-6} M) which was irradiated by a medium pressure mercury lamp adopting an unusual technique (see below). Before analysing the results of these experiments it is necessary to consider the UV-vis spectra of pure 1 and 4 (Fig. 6). The spectrum of 1 is characterised by an intense absorption band at 254 nm, a shoulder at ca. 280 nm and the typical anthracene vibrational structure in the range 330-390 nm.^{4,8b} An evident feature of the UV-vis spectrum of 4 is the lack of any absorption in the spectral zone where the typical vibrational structure of anthracene is located. In involving the 9,10-positions, the photo-dimerisation interrupts the conjugation of anthracene, generating four o-xylene chromophores. This was observed first by Coulson who showed that the molar extinction coefficient at 270 and 280 nm are equal to four times that of o-xylene.¹⁷

One of the most intense emission bands of a medium pressure mercury lamp is centred at 254 nm.¹⁸ Exactly at this wavelength 9-anthroylacetone 1 has an extinction maximum significantly higher than the extinction of 4 at the same wavelength. Compound 4 has the extinction maximum at 290 nm whose value is ca. double with respect to the extinction exhibited by 1 at the same wavelength. Finally, at $\lambda < 240$ nm the extinction of **4** becomes much larger than that of 1. Then, irradiation in the $\lambda < 240$ nm zone is strongly recommended. Moreover, assuming that the quantum yield of the photodissociation of 4 is higher than the quantum yield of dimerisation of 1, as reported for most anthracene derivatives in solution,^{8a} we profited from both the quantum yield and the favourable absorption features to shift the photo-equilibrium towards 1. In this connection, it is important to underline that it is known that several anthracene photodimers partially photodissociate into two anthracene nuclei when they are irradiated in the range 250-290 nm. However, at these wavelengths the monomer can re-dimerise and a steady state mixture is obtained by prolonged irradiation,^{8a,91} characterised by the presence of high amounts of photodimer (up to 94%, under 254 nm irradiation).91

In our case, we succeeded in shifting the photo-equilibrium towards 1 taking advantage of the favourable absorption properties of 4 in the $\lambda < 240$ nm region and by adopting an unconventional use of the mercury lamp, i.e. by switching the lamp on/off at regular intervals of time to avoid the strong increase of Hg vapour pressure which parallels the warming of the lamp. Indeed, when the cool lamp is just switched on, it strongly emits at wavelengths shorter than 254 nm because of the low density of Hg vapour. In addition, the temperature of the lamp was kept as low as possible by ventilation. Finally, operating on rigorously deareated ethanol solutions, the occurrence of the photochemical reaction of anthracene with dioxygen, that leads to anthraquinone and anthracene endoperoxide,^{4,7,8b,9d,19} was avoided.

The UV-vis absorption spectra of ethanol solutions of **4**, registered after 2, 5, 7, 12 and 15 min of irradiation, are reported in Figure 7. These spectra clearly show the progressive growth of the absorption bands due to



Figure 6. Absorption spectra (ε vs λ , nm) of: 9-anthroylacetone 1 (—) and 4 (—); the spectra were recorded in 4×10^{-6} M ethanol solutions.



Figure 7. Absorption spectra (absorbance vs λ , nm) of **4** in ethanol; successive spectra taken after 0 (\longrightarrow), 2 (\longrightarrow), 5 (\longrightarrow), 7 (\longrightarrow), 12 (\longrightarrow), and 15 min (\longrightarrow) of irradiation with a medium pressure mercury lamp.

9-anthroylacetone **1**. Since at 384 nm the photodimer **4** does not absorb and **1** exhibits an absorption maximum (ε =8300), the concentration of **1** in each sample can be calculated from absorption at this wavelength (Table 2). Interestingly, the amount of **1** formed for short irradiation times is proportionally higher than that formed for long exposure times. Evidently, the photochemical dissociation of **4** tends to a steady state with excellent yields of **1** (>80%) that can be reached in 15 min of effective irradiation.

Further evidence of the photo-dissociation of **4** to give **1** was obtained by analysing the irradiated sample by Ion Spray Mass Spectroscopy (IS-MS). The IS-MS data for pure **1** and **4** are reported in Table 3.

Both the spectra show only the pseudo molecular peaks and noteworthy in the IS-MS spectrum of **4** no peaks are present in the range m/z=263-285, where the spectrum of **1** has its pseudo molecular peaks. It is interesting to underline that rarely are the molecular peaks of anthrachene photodimers detected,^{8b} because generally the photodimer fragments to anthracene, under electron impact conditions. Only recently, by FAB(+) analysis^{9e} and by GC-MS (EI mode),^{9d} the molecular peak of a photodimer has been identified. The IS-MS spectrum of the ethanolic solution of **4**, irradiated for 15 min with the medium pressure mercury lamp, shows four pseudo molecular peaks at m/z=263(14.3%), 301 (79%), 542 (3%) and 547 (3%). The peaks at

Table 2. Concentration of 1 formed by irradiation of an ethanol solution of

 4 with a medium pressure mercury lamp

 2 min ^a	5 min ^a	7 min ^a	12 min ^a	15 min ^a
0.027 3.2×10^{-6} 37	0.037 4.5×10^{-6} 53	$0.047 \\ 5.4 \times 10^{-6} \\ 63$	$0.058 \\ 7.0 \times 10^{-6} \\ 82$	$0.060 \\ 7.2 \times 10^{-6} \\ 84$

^a Total irradiation time.

^b Absorbance at 384 nm.

Table 3. IS-MS data of compounds 1 and 4^a

Compound	$[M+H]^+$	$[M+NH_4]^+$	[M+Na] ⁺
1	263 (100)	280 (7.5)	285 (20)
4	525 (12.5)	542 (70)	547 (100)

^a m/z (% relative intensity of peak).

m/z=263 and 301 are attributable to the ions $[M(1)+H]^+$ and $[M(1)+K]^+$, respectively, M(1) being the molecular mass of 9-anthroylacetone 1 (262). The other two peaks at m/z=542 and 547 are associated with $[M(4)+NH_4]^+$ and $[M(4)+Na]^+$, respectively, M(4) being the molecular mass of 4 (524). These results clearly show that 4 photodissociates in solution, and 1 can be obtained in high yields in few minutes.

The photochemical dissociation in the solid state was carried out on a solid sample of pure **4** placed in a 1 mm optical path spectrophotometric quartz cell which was irradiated with a medium pressure mercury lamp for 30 min. During the first 15 min the lamp was switched on and off at regular intervals; whereas, during the last 15 min of irradiation the lamp was left on. The front surface absorption spectra registered after 5, 15 and 30 min of effective exposure to light are reported in Figure 8.

For the first 15 min of irradiation the amount of **1** increased whereas the spectrum registered after 30 min of irradiation was less intense than that registered after 15 min. This should be connected to the short-wavelengths emission-lines of the lamp during the cold period, i.e. the first 15 min of irradiation, with respect to the emission of the Hg stationary plasma during the last 15 min. As previously noted, at 254 and 366 nm the absorption of **1** is much higher than that of **4**. Evidently, for prolonged exposition of the sample to these wavelengths part of **1**, which is formed during the first 15 min of irradiation, reverts to **4**. The genesis of **1** was confirmed by UV–vis absorption in dichloromethane.

The definitive confirmation of the presence of **1** came once again from the IS-MS analysis of the reaction mixture that



Figure 8. Front surface absorption spectra (absorbance vs λ , nm) of a solid sample of **4**; successive spectra taken after 0 (**—**), 5 (**—**), 15 (**—**), and 30 min (**—**) of irradiation by a medium pressure mercury lamp.

^c Molar concentration of 1 calculated by Lambert–Beer law ε_1 at 384 nm = 8300.

was dissolved in dichloromethane and diluted with methanol. The IS-MS spectrum shows one peak at m/z = 263 (42.5%) attributable to $[M(1)+H]^+ (M(1))$ is the molar mass of 1) and two peaks, of the same intensity (47.5%), at m/z = 542 and 547 attributable to $[M(4)+NH_4]^+$ and $[M(4)+Na]^+ (M(4))$ is the molar mass of 4), respectively. All these results clearly show that 4 photo-dissociates to give 1 even in the solid state; although, in this case, the process takes place only at the surface level and then the overall conversion is not high.

3. Conclusions

For the first time the photodimerisation of 9-anthroylacetone 1 to give the photodimer 4 has been observed and studied. The ¹H NMR spectra and the X-ray analysis reveal that both 1 and 4 are in their enolic form in solution as well as in the solid state.

1 photodimerises in solution as well as in the solid state by irradiation with different sources, the reaction being accompanied by a colour variation from bright yellow to colourless, a manifestation of the deep spectroscopic differences between **1** and **4**. No appreciable amounts of other products are detected although, in same cases, small quantities of anthraquinone are present, probably due to the presence of oxygen.^{4,7,8a,9d,19}

The crystal structure of a 9-substituted anthracene derivative can be classified into three types according to the geometric relationship between neighbouring molecules (Fig. 9).¹² In the γ type structure the central ring of the two anthracene units are not superimposed and anthracene derivatives which crystallise with this structure hardly photodimerise in the solid state; on the other hand, when anthracene derivatives crystallise in the α or β type structure the photodimerisation can take place.^{10c} The X-ray analysis of 1 reveals that it crystallises in the α -type structure, this allowing compound 1 to undergo the photodimerisation to 4 in the solid state.



Figure 9. Main crystalline packing modes found in the case of 9-substituted anthracene derivatives.



Scheme 3.

Compound **4** dissociates to give **1**, both thermally and photochemically (Scheme 3).

The thermal dissociation is a well known phenomenon extensively documented in the literature, 7,9a,b,g,i and 4 behaves like many other anthracene photodimers although the accelerating effect on thermal dissociation played by the presence of even small amounts of 1 had not been reported previously. The photochemical dissociation of 4 is particularly interesting because it can be carried out in solution as well as in the solid state by irradiation with a medium pressure mercury lamp. Some examples of this reaction carried out in solution are reported in the literature, ^{9a,c,d,1} but in all cases the samples were irradiated at wavelengths that seem to favour the photo-recombination of monomers since a steady state is reached characterised by the prevalent presence of the photodimer. Instead, under the irradiation conditions adopted here, >80% yield of 1 can be obtained. As said, 4 in the solid state can photo-dissociate. It is noticeable that only a very few examples of photochemical dissociation in this phase are reported in the literature.^{9j,10d,20}

4. Experimental

4.1. General

All solvents were used as received. The HPLC grade or spectrophotometric grade solvents were used in the spectrophotometric measurements. Microanalyses were performed by the Laboratorio di Microanalisi, Facoltà di Farmacia, Università di Pisa, Italy. 9-Anthroylacetone was prepared as reported.¹

¹H NMR spectra were run at 200 MHz on a Varian Gemini 200 instrument. Ion Spray Mass Spectra (IS-MS) were performed on a Perkin–Elmer Sciex API III plus triple quadrupole mass spectrometer (Sciex Co., Thornhill, ONT, Canada) equipped with an API ion source and an ionspray interface. The spectra were obtained under the following experimental conditions: ionspray voltage, 5.5 kV; orifice voltage, 35 or 60 V. The samples were dissolved in a very small amount of dichloromethane and diluted with methanol to obtain a concentration ca. 10 mM. The irradiation of solid samples or solutions of **1** were carried out with a tungsten lamp (100 W), with a xenon lamp (150 W) which emits at $\lambda > 250$ nm and with a Argon-Ion laser Coherent Innova 600 ($\lambda_1 = 351$ nm; $\lambda_2 = 364$ nm, jointly). The irradiations of solid samples or solutions of **4** were carried out with a medium pressure mercury lamp (125 W).

4.2. Crystal structure determination of 1 and 4

The X-ray diffraction experiments were carried out at room temperature (T=293 K) by means of a Bruker P4 diffractometer, operating with a graphite-monochromated Mo- K_{α} radiation. The intensity data collection was carried out with the $\omega/2\theta$ scan mode, collecting a redundant set of data. Three standard reflections were measured every 97 measurements to check sample decay. The intensities were corrected for Lorentz and polarisation effects and for absorption by means of a ψ -scan method.²¹ The absorption correction was not applied due to the low absorption coefficient. The structure solutions were obtained by means of the automatic direct methods contained in SHELXS97²² programme and the refinements, based on full-matrix leastsquares on F^2 , were done by means of the SHELXL97²² programme. Some other utilities contained in the WINGX suite²³ were also used. The more relevant crystal parameters are listed in Table 4.

The crystals of compound **1** are yellow platelets flattened on (100). One of them, glued at the end of a glass fibre, was used for intensity data collection. Table 4 lists the essential collection statistics. The structure solution was obtained in the centrosymmetric $P\bar{1}$ space group. The hydrogen atoms were observed in the difference Fourier map, they was, however, introduced in idealised positions and refined letting them 'to ride' on the connected heavy atoms. The final refinement cycle gave the reliability factors listed in Table 4.

The crystals of compound 2 are colourless prisms. The intensity data collection was done on one of them, glued on

Table 4. Crystal data and structure refinements

1	4
C ₁₈ H ₁₄ O ₂	C ₃₆ H ₂₈ O ₄
262.29	524.58
Triclinic	Monoclinic
<i>P</i> 1 (no. 2)	C2/c (no. 15)
8.521(2)	23.784(3)
8.980(2)	9.180(1)
10.079(2)	16.553(2)
71.34(1)	
68.67(1)	132.13(1)
74.24(2)	
670.0(2)	2680.3(6)
2	4
1.300	1.300
0.084	0.084
2864	2186
2346 [0.0259]	1749 [0.0168]
183	237
0.0550, 0.1254	0.0399, 0.1022
1.032	0.961
	$\begin{array}{c} 1 \\ \mathbf{C}_{18}\mathbf{H}_{14}\mathbf{O}_2 \\ 262.29 \\ \text{Triclinic} \\ P\bar{1} (no. 2) \\ 8.521(2) \\ 8.980(2) \\ 10.079(2) \\ 71.34(1) \\ 68.67(1) \\ 74.24(2) \\ 670.0(2) \\ 2 \\ 1.300 \\ 0.084 \\ 2864 \\ 2346 [0.0259] \\ 183 \\ 0.0550, 0.1254 \\ 1.032 \end{array}$

 $R_1 = \sum ||F_o| - |F_c|| / \sum F_o; wR_2 = [\sum [w(F_o^2 - F_c^2)^2] / \sum [w(F_o^2)^2]]^{1/2}; w = 1/[\sigma^2(F_o^2) + BQ] \text{ where } Q = [MAX(F_o^2, 0) + 2F_c^2]/3; \text{ Goodness-of-fit} = [\sum [w(F_o^2 - F_c^2)^2] / (N - P)]^{1/2}, \text{ where } N, P \text{ are the numbers of observations and parameters, respectively.}$

the tip of a glass fibre, giving the results summarised in Table 4. The structure solution was found in the centrosymmetric C2/c space group. The asymmetric unit resulted to be done by one half molecule placed beside an inversion centre. The hydrogen atoms were localised in the difference Fourier map and refined without constraints. The reliability factors resulting from the final refinement cycle are listed in Table 4.

Further details of crystal characterisations and structure refinements have been deposited in the form of CIF files with the Cambridge Crystallographic Data Centre. Deposition references: CCDC 237079 and CCDC 237080 for **1** and **4**, respectively. Copies of the data can be obtained, free of charge, on application to the CCDC, 12 Union Rd, Cambridge CB21EZ UK (fax: +44 1223 336 033); e-mail: deposit@ccdc.cam.ac.uk. Bond distances and angles for both **1** and **4** are provided in Supporting Information.

4.3. Spectrophotometric measurements

The UV-vis absorption spectra were measured at room temperature in ethanol or dichloromethane solutions using a Perkin–Elmer UV/VIS LAMDA EZ 201 spectrophotometer with a spectral bandwidth of 1 nm. Front-surface absorbance measurements in the UV-vis spectral region (250-500 nm) were performed on powder samples of 1 and 4 using the method reported by one of us.¹⁶ Experiments were carried out on a conventional spectrofluorimeter (ISA Fluoromax II with photon counting detection) suitably set to detect light scattered from powder samples. The samples, ca. 1 mm thick, were enclosed in a cell-holder suitably designed to avoid specular reflections into the emission monochromator in measurements on powders.²⁴ Thus, the incident angle was 35° . Powdered BaSO₄ was used as reference light scatterer.²⁵ The front-surface absorbance measurements reported in Figure 1(A) were performed on powder samples of 1 and 4 obtained by mixing a dichloromethane solution of 1 or 4 with BaSO₄. The slurries so obtained were dried under vacuum, re-powdered by a mortar and examined. The relative ratios were of 1 mg 1/5 gof $BaSO_4$ and 1 mg 4/0.5 g of $BaSO_4$, respectively.

4.4. Purification of 4

To 200 mg of a mixture of 1 (about 60%) and 4 (about 40%) was added of diethyl ether (20 mL). The resulting suspension was stirred for 1 min and decanted. The residual solid was treated twice with diethyl ether (5 mL). The ethereal extracts contains 1 with minor amounts of 4 and the solid residue is constituted by almost pure 4. A further amount of 4 was recovered by drying the ethereal extracts under reduced pressure and then suspending the resulting solid residue in 10 mL of diethyl ether. The ethereal solution was collected and dried under reduced pressure. The solid so obtained was further extracted with 5 mL of diethyl ether and, once again, the solution was separated from the solid and dried. The last sequence was repeated 2 times. All residual solid phases were dissolved in dichloromethane and dried under reduced pressure. About 100 mg almost pure 4 was so obtained which can be further purified by two methods. (A) 1 mL of a benzenic solution of impure 4 was purified by column (internal diameter, 15 mm; length,

150 mm) chromatography on silica gel 60 (230-400 mesh, Merck) using benzene as eluant, the first band eluted was collected and dried. The obtained solid is colourless and very pure. By this method a small amount of 4 can be obtained because 4 is slightly soluble in benzene. (B) About 100 mg of impure 4 was dissolved in about 25 mL of dichloromethane. The solution was extracted with portions of aqueous NaOH 2% (3×25 mL). The organic phase was discarded. Each aqueous phase was acidified with a few drops of HCl 35%, which caused the precipitation of a white solid. The resulting suspensions were extracted $(2 \times 20 \text{ mL})$ with dichloromethane. The organic extracts were then dried over anhydrous Na₂SO₄, then concentrated to 2 mL under reduced pressure (17 mmHg), and finally, chromatographated over a column (internal diameter, 5 mm; length, 30 mm) of silica gel 60 (230-400 mesh, Merck), using dichloromethane as eluant. A colourless solution was collected and dried under reduced pressure (17 mmHg) to give pure **4**. Anal. Calcd for $C_{36}H_{28}O_4$ (524) C, 82.4; H, 5.3%. Found: C, 82.4; H, 5.2%.

4.5. Photo-dimerisation of 1 in solution

Three ¹H NMR tubes, each containing 3 mg of **1** in 0.5 mL of d_2 -dichloromethane, were irradiated with three different sources and analysed by ¹H NMR. Sample A was irradiated with a xenon lamp for 3 h: the analysis of the sample indicated the conversion of 50% of **1** to **4**. Sample B was exposed to sun light for 3 h: the conversion of **1** to **4** was about 28%. Sample C was exposed to the near-UV Argonion laser beam (0.010 W) for 4 h: the conversion of **1** to **4** was about 11%.

4.6. Photo-dimerisation of 1 in the solid state

Experiment A. 2 mg of **1** was placed in a ¹H NMR tube under dinitrogen atmosphere and was irradiated for 24 h by a 100 W tungsten lamp, at 15 °C, the distance between the sample and the lamp being about 10 cm. At the end of irradiation, the solid sample was dissolved in d_1 -chloroform and the ¹H NMR spectrum was registered. **4** was formed in a 35% yield.

Experiment B. **1** (ca. 5 mg) was placed between two thin glass slides and irradiated by a 150 W xenon lamp (collocated at about 15 cm from the sample) for 4 h. The ¹H NMR analysis of the irradiated sample, dissolved in d_1 -chloroform, revealed the presence of 70% of **4**.

Experiment C. 50 mg of **1**, containing ca. 7% of **4**, was placed in a watch glass horizontally disposed and irradiated with a vertical UV laser beam (0.088 W) that was enlarged by means of a quartz lens up to 2 cm diameter. The sample was periodically stirred in order to expose to radiation fresh portions of solid. During irradiation the well shaped yellow crystals of **1** turned opaque white and flaked off. After 2 h of irradiation, ¹H NMR analysis of the sample in d₁-chloroform showed the presence of 38% of **4**. The temperature of the sample remained practically unchanged by irradiation.

Experiment D. About 100 mg of 1, placed in a quartz spectrophotometric cuvette (1 mm optical path), was exposed perpendicular to the UV laser beam (0.005 W)

whose spot was about 2 mm^2 , at the centre of the cell window. During the irradiation the cell was vertically moved. After 5 min, the portion exposed to laser beam showed a well defined white strip. The reaction was monitored by front surface absorption spectroscopy with illumination of the above strip.

4.7. Thermal dissociation of 4

All tests were run on 2 mg of 4 placed in a ¹H NMR tube which was heated at various temperatures as shown in the Section 2. Analysis of the samples, dissolved in d_1 -chloroform, were performed by ¹H NMR.

4.8. Photochemical dissociation of 4 in solution

Three millilitres of an ethanol solution $(4.27 \times 10^{-6} \text{ M})$ of 4 was placed, under dinitrogen atmosphere, in a quartz 10×10 mm spectrophotometric cuvette and irradiated by a medium pressure mercury lamp. The sample was placed about 3 cm far from the lamp in an equatorial position and oriented so to optimise the interception of the light rays. Both sample and lamp were cooled by a ventilator. The lamp was switched on for 30 s, then switched off for at least 1 min. After 2, 5, 7, 12 and 15 min of effective irradiation, the sample was analysed by UV-vis absorption spectra. At the end of the experiment the sample was analysed by IS MS.

4.9. Photochemical dissociation of 4 in the solid state

About 130 mg of pure 4 were placed in a 1 mm thick spectrophotometric cell and irradiated in the same geometric arrangement as above, with the only difference that the distance from the plasma source was larger (ca. 6 cm). The sample was irradiated as before, the lamp being switched on and off at regular intervals during the first 15 min of irradiation; finally, during the last 15 min, the lamp was left on. After 5, 15 and 30 min of irradiation the sample was analysed by front surface absorption spectroscopy. Spectral bandwidths of 0.25 and 4 mm were employed for the excitation and emission slits, respectively. The integration time was 0.5 s. 10 mg of the irradiated sample was used to prepare a 3.85×10^{-3} M dichloromethane solution which was analysed by UV-vis spectroscopy. The irradiated sample was also analysed by IS MS.

Acknowledgements

We are grateful to Dr. A. Raffaelli (C.N.R., Pisa, Italy) for the measurement of the mass spectra. Financial supports from the M.I.U.R. (Rome, Italy) and from the University of Pisa are gratefully acknowledged.

Supplementary data

Supplementary data associated with this article can be found in the online version, at 10.1016/j.tet.2004.09.070

References and notes

- 1. Evans, D. F. J. Chem. Soc. 1961, 1987–1993.
- Hartmann, H. J. Prakt. Chem. 1986, 328, 755–762. (b) Ilge, H.-D.; Birckner, E.; Fassler, D.; Kozmenko, M. V.; Kuz'min, M. G.; Hartmann, H. J. Photochem. 1986, 32, 177–189. (c) Ilge, H.-D.; Fassler, D.; Hartmann, H. Z. Chem. 1984, 24, 218–219.
- Akutsu, B.; Nakano, Y.; Usui, Y. Anal. Sci. 1990, 6, 827–831.
 (b) Sato, S.; Wada, M. Bull. Chem. Soc. Jpn 1970, 43, 1955–1962. (c) Sato, S.; Wada, M.; Seki, T. Jpn. J. Appl. Phys. 1968, 7, 7–13.
- Kercher, M.; König, B.; Zieg, H.; De Cola, L. J. Am. Chem. Soc. 2002, 124, 11541–11551.
- Carano, M.; Cicogna, F.; D'Ambra, I.; Gaddi, B.; Ingrosso, G.; Marcaccio, M.; Paolucci, D.; Paolucci, F.; Pinzino, C.; Roffia, S. Organometallics 2002, 21, 5583–5593. (b) Carano, M.; Cicogna, F.; Houben, J. L.; Ingrosso, G.; Marchetti, F.; Mottier, L.; Paolucci, F.; Pinzino, C.; Roffia, S. Inorg. Chem. 2002, 41, 3396–3409. (c) Carano, M.; Careri, M.; Cicogna, F.; D'Ambra, I.; Houben, J. L.; Ingrosso, G.; Marcaccio, M.; Paolucci, F.; Pinzino, C.; Roffia, S. Organometallics 2001, 20, 3478–3490. (d) Cicogna, F.; Colonna, M.; Houben, J. L.; Ingrosso, G.; Marchetti, F. J. Organomet. Chem. 2000, 593–594, 251–266.
- 6. Cicogna, F.; Ingrosso, G. Unpublished results.
- Becker, H.-D.; Langer, V.; Becker, H.-C. J. Org. Chem. 1993, 58, 6394–6396.
- Bouas-Laurent, H.; Castellan, A.; Desvergne, J.-P.; Lapouyade, R. *Chem. Soc. Rev.* 2001, *30*, 248–263.
 (b) Bouas-Laurent, H.; Castellan, A.; Desvergne, J.-P.; Lapouyade, R. *Chem. Soc. Rev.* 2000, *29*, 43–55. (c) Becker, H.-D. *Chem. Rev.* 1993, *93*, 145–172.
- Nakatsuji, S.; Ojima, T.; Akutsu, H.; Yamada, J. J. Org. Chem. 2002, 67, 916–921. (b) McSkimming, G.; Tucker, J. H. R.; Bouas-Laurent, H.; Desvergne, J.-P. Angew. Chem., Int. Ed. 2000, 39, 2167–2169. (c) Mori, Y.; Maeda, K. J. Chem. Soc., Perkin Trans. 2 1996, 113–119. (d) Schottelius, M. J.; Chen, P. J. Am. Chem. Soc. 1996, 118, 4896–4903. (e) Becker, H.-D.; Langer, V. J. Org. Chem. 1993, 58, 4703–4708. (f) Becker, H.-D.; Amin, K. A. J. Org. Chem. 1989, 54, 3182–3188. (g) Becker, H.-D.; Elebring, T.; Sandros, K. J. Org. Chem. 1982, 47, 1064–1068. (h) Castellan, A.; Desvergne, J.-P.; Bouas-Laurent, H. Chem. Phys. Lett. 1980, 76, 390–397. (i) Bergmark, W. R.; Jones, G. II; Reinhardt, T. E.; Halpern, A. M. J. Am. Chem. Soc. 1978, 100, 6665–6673. (j) Ferguson,

J.; Morita, M.; Puza, M. Chem. Phys. Lett. 1976, 42, 288–292.
(k) Bradshaw, A. W.; Chapman, O. L. J. Am. Chem. Soc. 1967, 89, 2372–2375.
(l) Livingston, R.; Wei, K. S. J. Am. Chem. Soc. 1967, 89, 3098–3100.

- Ihmels, H.; Leusser, D.; Pfeiffer, M.; Stalke, D. Tetrahedron 2000, 56, 6867–6875. (b) Ito, Y.; Olovsson, G. J. Chem. Soc., Perkin Trans. 1 1997, 127–133. (c) Kaupp, G. Angew. Chem. Int. Ed. 1992, 31, 595–598. (d) Chandross, E. A.; Ferguson, J. J. Chem. Phys. 1966, 45, 3564–3567. (e) Ito, Y.; Craig, D. P.; Sarti-Fantoni, P. Chem. Commun. 1966, 20, 742–743.
- Wu, D.-Y.; Zhang, L.-P.; Wu, L.-Z.; Wang, B.-J.; Tung, C.-H. *Tetrahedron Lett.* 2002, 43, 1281–1283. (b) Grimme, S.; Peyerimhoff, S. D.; Bouas-Laurent, H.; Desvergne, J.-P.; Becker, H.-D.; Sarge, S. M.; Dreeskamp, H. *Phys. Chem. Chem. Phys.* 1999, 1, 2457–2462. (c) Tung, C.-H.; Guan, J.-Q. *J. Org. Chem.* 1998, 63, 5857–5862.
- 12. Cohen, M. D. Angew. Chem., Int. Ed. Engl. 1975, 14, 386-393.
- Trouts, T. D.; Tyson, D. S.; Pohl, R.; Kozlov, D. V.; Waldron, A. G.; Castellano, F. N. *Adv. Funct. Mater.* **2003**, *13*, 398–402.
 (b) Hiraga, H.; Morozumi, T.; Nakamura, H. *Tetrahedron Lett.* **2002**, *43*, 9093–9095. (c) Ojima, T.; Akutsu, H.; Yamada, J.; Nakatsuji, S. *Polyhedron* **2001**, *20*, 1335–1338.
- Irie, M. Chem. Rev. 2000, 100, 1683–1684. (b) Irie, M. Chem. Rev. 2000, 100, 1685–1716.
- 15. Becker, H.-D.; Andersson, K. J. Org. Chem. 1983, 48, 4542–4549.
- Zandomeneghi, M.; Festa, C.; Carbonaro, L.; Galleschi, L.; Lenzi, A.; Calucci, L. J. Agric. Food Chem. 2000, 48, 2216–2221.
- 17. Coulson, C. A.; Orgel, L. E.; Taylor, W.; Weiss, J. J. Chem. Soc. 1955, 2961–2962.
- Calvert, J. G.; Pitts, J. N., Jr. *Photochemistry*; Wiley: New York, 1966; p. 297.
- Toshima, N.; Sugano, T.; Hirai, H. Can. J. Chem. 1984, 62, 2047–2053.
- Anderson, B. F.; Ferguson, J.; Morita, M.; Robertson, G. B. J. Am. Chem. Soc. 1979, 101, 1832–1840.
- North, C. T.; Phillips, C.; Mathews, F. S. Acta Crystallogr. A 1968, 24, 351–359.
- 22. Sheldrick, G. M. *SHELXTL-Plus*, Rel. 5.1; Brucker A.X.S. Instruments Inc.: Madison, Wisconsin, USA, 1997.
- 23. Farrugia, L. J. J. Appl. Crystallogr. 1999, 32, 837-838.
- 24. Zandomeneghi, M. J. Agric. Food Chem. 1999, 47, 878-882.
- Hapke, B. In *Theory of Reflectance and Emittance Spectroscopy*; Arvidson, R. E., Rycroft, M. J., Eds.; Cambridge University Press: Cambridge, UK, 1993; Chapters 10 and 11.