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A novel photoreversible photochromic system involving a hydrogen transfer/cyclization sequence†

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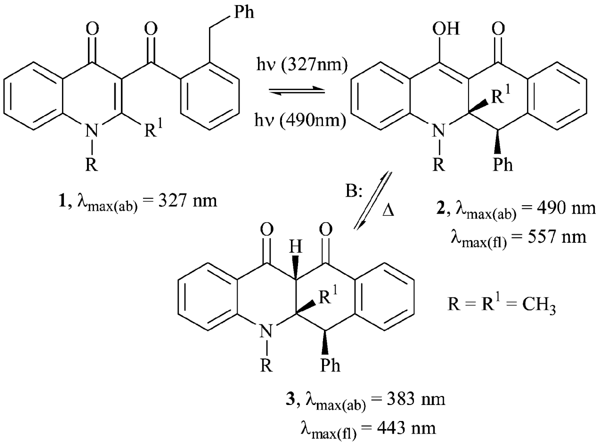
A novel photoreversible photochromic system, 3-(2-benzylbenzoyl)-1,2-R,R¹-4(1*H*)-quinolinones/12-hydroxy-5-R-5a-R¹-6-phenyl-5a,6-dihydrobenzo[*b*]acridin-11(5*H*)-ones, is described.

Photoreversible photochromic systems are currently the focus of numerous studies owing to their potential as components of optoelectronic devices.[1] Of the variety of known photochromic compounds, furylfulgides[2] and dithienylethenes[3] are the only thermally irreversible materials which can be used for optical information storage and processing. The photochromic reaction in both systems is based on the reversible hexatriene–cyclohexadiene photocyclization, one of the most intensively studied photochemical reactions. Another reversible photochemical process, the photoenolization of *o*-alkylphenylketones,[4] has been thoroughly studied during the past four decades, but these derivatives attracted little interest for photochromic applications, since the corresponding colored photoproducts, *o*-xylylenols formed upon relaxation of the initial triplet biradical, are unstable and either convert back to the starting materials or undergo fast irreversible reactions with dienophiles and oxygen.

We found that attaching a conjugated moiety to the carbonyl group of *o*-xylylenol precursors can provide access to the new type of photoreversible systems. Here we report on the photochemical behavior of 3-(2-benzylbenzoyl)-1,2-dimethyl-4(1*H*)-quinolinones (**1**, R = R¹ = Me).‡ Irradiation of degassed solutions of **1** (λ_{max} = 327 nm) in toluene (Fig. 1) led to the formation of (5a*S*,6*R*)-12-hydroxy-5,5a-dimethyl-6-phenyl-5a,6-dihydrobenzo[*b*]acridin-11(5*H*)-one (**2**).‡ Upon irradiation derivative **2** (λ_{max} = 490 nm) can be converted back into **1**. In the dark, derivative **2** is slowly converted into (5a*S*,6*R*,11a*S*)-5,5a-dimethyl-6-phenyl-5a,11a-dihydrobenzo-[*b*]acridine-11,12(5*H*,6*H*)-dione (**3**)‡ (λ_{max} = 386 nm). In the presence of catalytic amounts of a base, the equilibrium **3** $\rightleftarrows$ **2** is established rapidly and irradiation of such solutions at 490 nm led to the recovery of **1**. Both **2** and **3** are fluorescent (λ_{max} = 557 and 443 nm, quantum yields 0.08 and 0.19 in toluene, respectively). No transients were detected and two isosbestic points were observed before the photostationary state was reached. Similar behavior was observed in acetonitrile, however, formation of the colored product **2** and its dark conversion into **3** proceeded more rapidly.



The preparative experiments were carried out in toluene (xenon lamp, 300–400 nm band pass filter). The reaction mixture was separated on a silica column to afford derivative **3** as the main product (80% of reacted **1**) along with **2** (4%).

In a tentative mechanism, the initial photoenol or a biradical (formed upon irradiation, which is in fact a triplet state of the photoenol) can undergo further reversible cyclization owing to delocalization of the spin over the heterocyclic moiety (Scheme 1). In general, the hydrogen atom can be transferred to either the quinolinone (route a) or benzoyl (route b) carbonyl groups. The resulting 1,6- and 1,4-biradicals can, after rotation of the *o*-benzylphenyl fragment, cyclize affording a mixture of **2**, **5** and their respective *S*,*S*-isomers **4** and **6**. The 1,4-biradical can also relax into the usual *o*-xylylenol transient **7** (route c).[4] It is noteworthy that isomers **4–7** were not detected either spectroscopically or in preparative experiments.

Exclusive formation of **2** can be rationalized by the results of quantum mechanical calculations,§ which showed that the bent conformation of **1**, in which hydrogen atom transfer to the quinolinone carbonyl is possible (C···O distance 3.50 Å, typical of C–H···O hydrogen bonds,[5] Fig. 2), corresponds to the equilibrium geometry, and is more stable than conformations enabling hydrogen transfer to the benzoyl carbonyl. The longest wavelength absorption band of **1** (calc. λ_{max} = 342 nm, *f* =

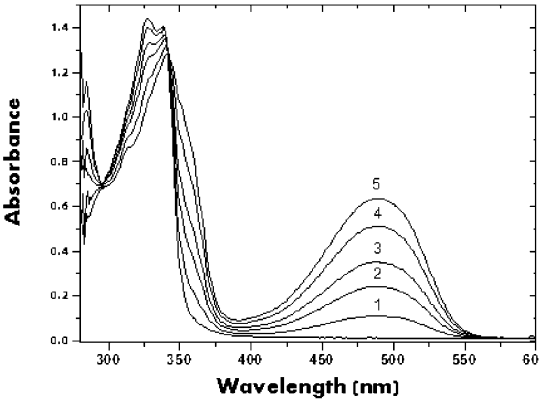


Fig. 1 Irradiation of a solution of **1** in toluene: 1, 1 min; 2, 3 min; 3, 5 min; 4, 9 min; 5, 15 min (saturation).

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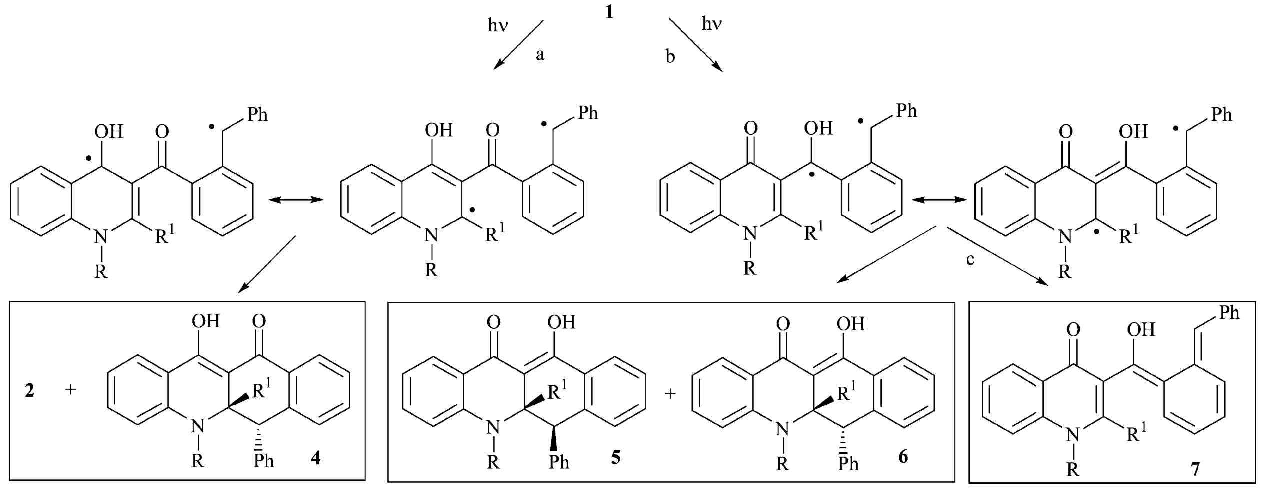
† Electronic supplementary information (ESI) available: supporting data for **2** and **3**. See http://www.rsc.org/suppdata/cc/b3/b304861f/



Scheme 1

0.0032) corresponds to the HOMO–LUMO transition within the quinolinone moiety and involves the CH_2 group (Fig. 2). The second peak observed at 327 nm should involve the benzoyl carbonyl group and corresponds to predominantly HOMO^{-1}–LUMO^{+1} transition (calc. 323 nm, $f = 0.0002$). Note also that the triplet 1,6-biradical is 3.2 kcal mol^{-1} more stable than the 1,4-biradical. In fact to the best of our knowledge formation of the 1,6-biradicals, in contrast to the 1,4-biradicals, is unprecedented, although the possibility of direct 1,7-hydrogen abstraction giving rise to the 1,5-biradicals has been discussed.[6] We also cannot exclude the possibility that the excited state intramolecular proton transfer mechanism,[7] which should give rise to the same products, is involved. Mechanistic aspects of the reaction are currently under study.

Assuming direct hydrogen transfer to the quinolinone carbonyl as shown in Fig. 2 can explain not only the absence of isomer **5**, but also the predominant formation of the *S*,*R*-isomer **2** over the *S*,*S*-isomer **4**. Indeed, the triplet biradical, which can form from this conformation and is the precursor of **2**, is indicated by the calculations to be more stable than the biradical precursor of **4** by 3.9 kcal mol^{-1} (whose formation requires additional rotation over the CH–CPh bond). Moreover, the calculations showed that within the series of 5a*S*,6*R* isomers, derivative **3** is the most stable. Thus, isomers **2** and **5** are 6 and 7 kcal mol^{-1} less stable than **1** and 8–9 kcal mol^{-1} less stable than **3**, which accounts for the thermal conversion of **2** into **3**. The 5a*S*,6*R*,11a*R* isomer of **3** is the least stable (11 kcal mol^{-1} less than **1**).

The above experimental and computational results imply that the outcome of the photoreaction of **1** and its reversibility should strongly depend on the nature of substituents R and R^1, in particular their bulkiness, since the differences in stability of isomers **2–6** that stem mostly from steric strain, do not exceed 10 kcal mol^{-1}. Indeed, whereas derivative **1** (R = Et, R^1 = Me) behaves similarly to **1** (R = R^1 = Me), different chemistry was observed in cases when R^1 = Ph. These results will be published elsewhere.

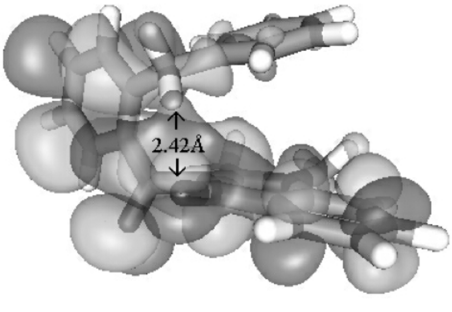


Fig. 2 Equilibrium geometry and LUMO of **1**.

Reversible regio- and stereoselective photocyclization of derivatives **1** affords not only colored but also, unlike furylfulgides and dithienylethenes,[2] fluorescent products, which is important for non-destructive readout. Another particularly promising potential application is to utilize the ability of the photoproducts to form complexes with heavy metal ions.

Notes and references

‡ **1** was synthesized using a modified procedure;[8] colorless crystals, m.p. 161–162 °C, the structure was confirmed by X-ray technique. **2**: red oil, ^{1}H NMR: δ (500 MHz, CD_2Cl_2): 17.19 (1H, s, OH), 8.10 (1H, dd, $J^1 = 7.7$, $J^2 = 1.5$, C10-H), 7.78 (1H, dd, $J^1 = 7.7$, $J^2 = 1.8$, C1-H), 7.45 (2H, m, *o*-Ph-H), 7.44 (1H, td, $J^1 = 7.4$, $J^2 = 1.5$, C8-H), 7.36 (1H, td, $J^1 = 7.5$, $J^2 = 1.3$, C9-H), 7.32 (1H, d, $J = 7.5$, C7-H), 7.27 (1H, ddd, $J^1 = 8.6$, $J^2 = 7.1$, $J^3 = 1.7$, C3-H), 7.18 (2H, m, *m*-Ph-H), 7.12 (1H, m, *p*-Ph-H), 6.69 (1H, ddd, $J^1 = 7.8$, $J^2 = 7.1$, $J^3 = 0.9$, C2-H), 6.47 (1H, d, $J = 8.6$), 4.48 (1H, s, C6-H), 2.76 (3H, s, NMe), 1.51 (3H, s, CMe). **3**: yellowish crystals, m.p. 191–192 °C. ^{1}H NMR: δ (500 MHz, 213 K, CD_2Cl_2): 7.96 (1H, d, $J = 7.8$, C10-H), 7.76 (1H, dd, $J^1 = 7.8$, $J^2 = 1.5$, C1-H), 7.58 (1H, td, $J^1 = 7.5$, $J^2 = 1.0$, C8-H), 7.39 (2H, m, *o*-Ph-H), 7.36 (1H, t, $J = 6.9$, C3-H), 7.37 (1H, td, $J^1 = 7.7$, $J^2 = 1.7$, C9-H), 7.27 (1H, d, $J = 7.7$), 7.24 (3H, m, *m*,*p*-Ph-H), 6.73 (1H, t, $J = 7.3$, C2-H), 6.69 (1H, d, $J = 8.7$, C4), 4.82 (1H, s, C11a-H), 3.60 (1H, s, C6-H), 2.76 (3H, s, NMe), 1.11 (3H, s, CMe). NMR spectra of **2** and **3** are temperature dependent and were assigned using the COSY and HMBC techniques. These results will be discussed elsewhere. *Crystal data* for $C_{25}H_{21}NO_2$ (**3**): $M = 367.43$, monoclinic, space group $P2_1/n$, $a = 7.3820(10)$, $b = 28.831(4)$, $c = 9.2480(10)$ Å, $\beta = 97.670(10)°$, $V = 1950.6(4)$ Å^3, $Z = 4$, $\mu = 0.079$ mm^{-1}, $T = 25$ °C. 2253 independent reflections were used in the refinement. Refinement of 338 parameters gave $wR2 = 0.26$ (all data) and $R1 = 0.0423$ for 952 data with $I > 2\sigma I$. CCDC 197132. See http://www.rsc.org/suppdata/cc/b3/b304861f/ for crystallographic data in CIF or other electronic format.

§ The equilibrium geometries were found by molecular dynamics simulations (Hyperchem, ver. 5.0) at the PM3 level and further optimized at the HF/6-31G(d) level. The spectra were calculated using the TD B3LYP/6-31G(d)//HF/6-31G(d) model chemistry (M. J. Frisch, *et al.*, Gaussian 98, Revision A.7, Gaussian, Inc., Pittsburgh, PA, 1998).

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