View Online / Journal Homepage / Table of Contents for this issue

Simultaneous fluorescence and redox modulation in an irreversible photochrome based on a strained dibenzo-acridinium cation†

Andrew C. Benniston* and Dorota B. Rewinska

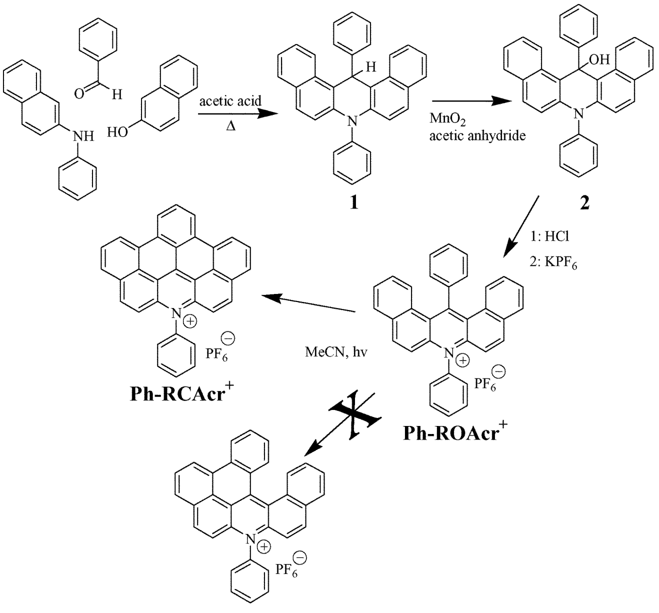
Received 1st August 2006, Accepted 12th September 2006
First published as an Advance Article on the web 28th September 2006
DOI: 10.1039/b611092d

Downloaded by Brown University on 31 July 2012
Published on 28 September 2006 on http://pubs.rsc.org | doi:10.1039/B611092D

A highly strained non-luminescent dibenzo-acridinium cationic compound is identified that undergoes in acetonitrile light-induced ring closure to create a highly fluorescent, planar, eight-ringed cationic anti-aromatic dye.

Interest in photochromic (PC) molecules that alter their colour upon exposure to light has increased in recent years as new applications have arisen in technological areas such as molecular logic gates,[1] field effect transistors[2] and bitwise volumetric data storage.[3] All these technologies rely on the fact that light activation of the PC species, at a specific wavelength, creates a molecular entity that reverts back to the original form using light of different frequency.[4] However, in general the reverse reaction is also possible thermally. This can be problematic if data need to be stored for long periods without degradation of information. Thermally irreversible PC molecules upon light activation create a new entity that not only displays dissimilar photochemical properties to the starting material but cannot revert back.[5] We have been interested not only in identifying suitable new irreversible PC molecules, but ones which also display very high fluorescent quantum yields and/or alter their redox properties. Such molecules have been identified as candidates for multilayer recording of data.[3] During our investigation into highly strained acridinium-based donor–acceptor dyads[6] the cation, **Ph-ROAcr⁺**, was prepared. Interestingly, this non-emissive compound upon illumination with white light, ring closes to generate the highly fluorescent cation, **Ph-RCAcr⁺**. The modification is also accompanied by a considerable alteration in reduction potential.

The synthetic procedure† used to prepare **Ph-ROAcr⁺** was adapted from work previously reported by Dilthey *et al.*[7] Simple refluxing of *N*-phenyl-2-naphthylamine, benzaldehyde and 2-naphthol in glacial acetic acid produced, after recrystallisation, the condensation product **1** in an unoptimised 22% yield. Oxidation of this derivative to the carbinol **2** with MnO_2 had to be performed in the dark as the product was light-sensitive. Yields of the carbinol varied (20–68%) and is attributed to unwanted photodegradation. Aromatisation to generate the desired cation was carried out by HCl acidification of **2**, followed by conversion of the chloride salt to the hexafluorophosphate derivative. Recrystallisation of the material from CH_3CN–Et_2O (1 : 4) afforded golden yellow needles. The product when stored in the dark showed no signs of degradation, but solid samples left exposed to ambient light gradually turned red. Dilthey *et al.* attributed this red product to the ring-closed form in which the 14-phenyl is fused to one side only of the benzo group (Scheme 1). We found, however, that the red solid obtained is in fact the fully closed form, **Ph-RCAcr⁺**. This identification was based on a 500 MHz ^{1}H NMR spectrum that supported a compound with only 18 protons and a high level of symmetry. The electrospray mass spectrum also revealed a cluster of peaks at $m/z = 428.3$ which matches that of the $[M - PF_6]^+$ ion.



Scheme 1 Outline of the methods used in the preparation of the cation **Ph-ROAcr⁺** and the ring-closed form **Ph-RCAcr⁺**. NB: the incorrectly identified ring-closed product is also shown.

To collect detailed structural information on ring closure, 300 MHz ^{1}H NMR spectra were monitored following illumination of a sample of **Ph-ROAcr⁺** in air-equilibrated and N_2-purged P_2O_5-dried CD_3CN at 25 °C. Illustrated in Fig. 1 are a selection of ^{1}H NMR spectra collected during the course of the reaction for the N_2-purged sample. Within the first hour of irradiation four new clear doublets are visible downfield from the rest of the aromatic signals. As well as these series of new signals, clear doublet ($\delta = 6.74$) and singlet ($\delta = 6.85$) signals are visible. During irradiation these signals grow and three apparent triplets emerge at δ 7.0, 7.18 and 7.32, respectively. The spectrum in the region $\delta = 7.5$–8.0 also simplifies as resonances for the starting material disappear.

Molecular Photonics Laboratory, School of Natural Sciences (Chemistry), Bedson Building, Newcastle University, Newcastle upon Tyne, UK NE1 7RU. E-mail: a.c.benniston@ncl.ac.uk; Fax: (0191) 222 5706; Tel: (0191) 222 6929

† Electronic supplementary information (ESI) available: experimental procedures, full compound characterisation, electrochemistry, ^{1}H NMR spectra following irradiation experiments and excitation/emission spectra for final product. See DOI: 10.1039/b611092d

Published on 28 September 2006 on http://pubs.rsc.org | doi:10.1039/B611092D
Downloaded by Brown University on 31 July 2012

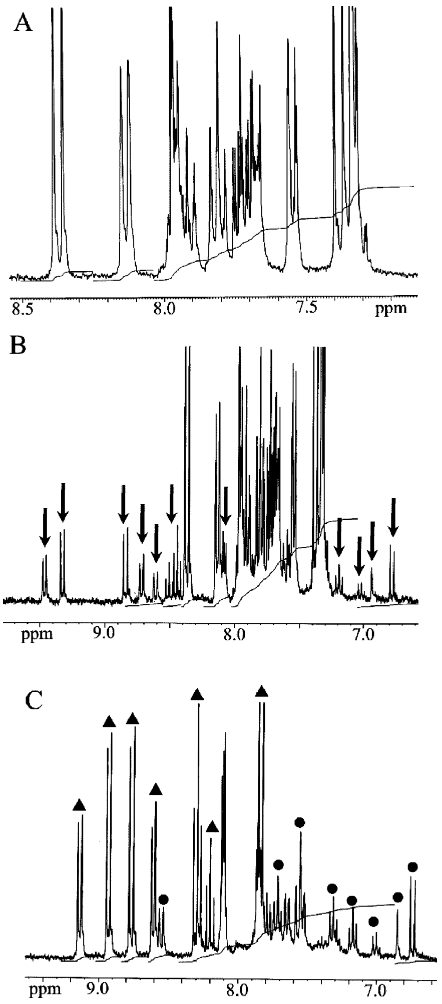


Fig. 1 Selected 300 MHz ^{1}H NMR spectra for **Ph-ROAcr$^+$** in N$_2$-purged CD$_3$CN following irradiation at time differences $t = 0$ (A), $t = 1$ h (B) and $t = 13$ h (C). Arrows in panel (B) mark new resonances. In panel (C), ▲ represent final product and ● represent intermediate product.

After a substantial irradiation time (Fig. 1C), signals associated with the final product are visible, and the other signals clearly diminish. The final spectrum at the end of the irradiation is identical to that recorded for a purified sample of **Ph-RCAcr$^+$**. Matching irradiation experiments carried out in air-equilibrated CD$_3$CN (see the ESI†) did not show identical build up and loss of resonances marked with dark circles (Fig. 1C). Instead, as well as resonances for the final product only very minor signals were observed in the δ 6.5–7.0 ppm region; these disappered after *ca.* 1 h.

Further elucidation of the ring closure processes within **Ph-ROAcr$^+$** were obtained by UV-visible spectroscopy. A solution of **Ph-ROAcr$^+$** in acetonitrile at 25 °C was illuminated with white light ($\lambda_{max} > 300$ nm) for fixed time periods and the resultant spectra recorded. Samples were irradiated following substantial purging with either nitrogen, oxygen or air-equilibration. Illustrated in Fig. 2 is a typical set of spectra obtained during an irradiation experiment in air-equilibrated acetonitrile. The absorption band associated with **Ph-ROAcr$^+$** (445 nm) gradually diminished and a new absorption band grew at 505 nm, which is characteristic of **Ph-RCAcr$^+$**. Close inspection of the overlayed spectra revealed there are no clean isosbestic points, which suggests conversion of **Ph-ROAcr$^+$** to **Ph-RCAcr$^+$** proceeds *via* at least one intermediate. Rather surprisingly, the ring closure carried out in N$_2$-purged acetontrile proceeded just as well as the O$_2$-containing solutions. Moreover, the cyclisation reaction proceeded faster when carried out in N$_2$-purged acetonitrile solution containing a few drops of distilled water. This finding seems to suggest that during ring closure a H-atom abstraction process is required.

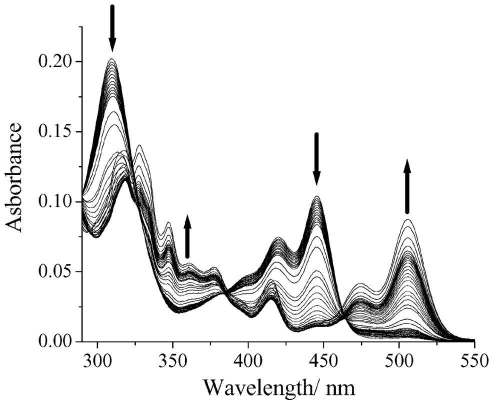


Fig. 2 Alterations in absorption spectra for **Ph-ROAcr$^+$** in dry air-equilibrated acetonitrile following irradiation with white light.

The basic absorption spectrum for **Ph-ROAcr$^+$** in acetonitrile is dominated by three major intense bands located at 446 (log $\varepsilon = 4.39$), 421 (log $\varepsilon = 4.24$) and 310 nm (log $\varepsilon = 4.65$), respectively. In contrast, the absorption spectrum of **Ph-RCAcr$^+$** is rich and contains a number of bands, the most prominant being at 505 (log $\varepsilon = 4.29$) and 328 nm (log $\varepsilon = 4.47$). Extremely weak fluorescence from **Ph-ROAcr$^+$** is observed in acetonitrile solution at 25 °C, though dependence of the band shape on the excitation wavelength strongly supports this is an artifact caused by minute traces of an impurity. By contrast, fluorescence from **Ph-RCAcr$^+$** in N$_2$-purged acetonitrile solution was readily observed centred at 530 nm, the band shape being insensitive to excitation wavelength. The excitation and absorption spectra were in good agreement (ESI†), and the small Stokes' shift (SS) of 934 cm^{-1} indicates a modest change in structure after relaxation from the initially produced Franck–Condon state. Considering the rigidity of the cation this is not too surprising since only the *N*-phenyl group is free to rotate in fluid solution. The radiative lifetime (τ_r) calculated using the Strickler–Berg[8] expression is 9.8 ns, whereas the measured lifetime (τ_s) is 7 ns. Hence, the corresponding quantum yield of fluorescene (τ_s/τ_r) for **Ph-RCAcr$^+$** is a respectable 0.71.

The redox chemistry of acridinium-based compounds is generally well understood.[9] Lacking any subsitituent in the 10-position the reductive electrochemistry of, for example, the 9-methylacridinium cation is irreversible because of chemical breakdown of the generated radical.[10] In contrast, the reductive electrochemistry of 10-phenyl-9-methylacridinium is well behaved consisting of a reversible reduction wave at −0.55 *vs.* SCE.[11] In view of these previous findings, cyclic voltammograms for **Ph-ROAcr$^+$** were obtained in dry CH$_3$CN. Upon oxidative scanning an irreversible wave is observed just around the solvent cut-off at *ca.* +2.4 V *vs.* SCE. The reduction portion of the cyclic voltammogram is dominated by a reversible one-electron wave at

$E_1 = -0.50$ V (65 mV) *vs.* SCE, an irreversible one-electron wave at $E_2 = -1.03$ V *vs.* SCE and an irreversible two-electron wave at $E_3 = -2.36$ V *vs.* SCE. The similarity of E_1 to that of the first reduction potential for the 10-methyl-9-methylacridinium cation supports one-electron addition to the central acridinium ring to create the neutral radical. Further addition of an electron to create the anion presumably breaks conjugation throughout the molecule to produce two isolated naphthalene units that are simultaneously reduced. Cyclic voltammograms collected following steady-state visible light illumination of an air-saturated solution of **Ph-ROAcr⁺**, followed by N_2-purging, were very different and are assigned to **Ph-RCAcr⁺**. The cyclic voltammogram in the oxidatative portion is more resolved and contains a main irreversible wave at 2.1 V *vs.* SCE that supports a slight shoulder at *ca.* 1.75 V *vs.* SCE. Thus, ring closure makes it easier to remove an electron from the conjugated π-system as expected because of lowering of the HOMO orbital energy. In contrast, the reductive segment of the cyclic voltammogram contains only two main waves. The first is a quasi-reversible wave situated at −0.81 V (140 mV) *vs.* SCE, with a second quasi-reversible wave at −1.5 V (80 mV) *vs.* SCE. Identical electrochemical behaviour was observed for a synthesised and purified sample of **Ph-RCAcr⁺**. In light of the electrochemical investigations it can be concluded that **Ph-ROAcr⁺** is a better one-electron acceptor than **Ph-RCAcr⁺** by *ca.* 300 mV.

These preliminary results support the basic tenet that light-induced ring closure in a highly-strained acridinium cation effectively modulates its luminscent and redox properties. That the ring opening reaction appears irreversible means that any ‘information’ written into the molecule is permanently stored, and in addition can be read out by two different means, *i.e.* electrochemically or photochemically. Furthermore, the work also throws up some interesting basic questions regarding the actual ring closure process and the subsequent mechanism. For example, why is no apparent oxidant required to complete the ring closure reaction?[12] Follow-up experiments are currently underway to obtain a comprehensible picture of the pericyclic reaction.

Published on 28 September 2006 on http://pubs.rsc.org | doi:10.1039/B611092D
Downloaded by Brown University on 31 July 2012

Acknowledgements

This work was supported by the University of Newcastle. We also thank the EPSRC sponsored Mass Spectrometry Service at Swansea for the electrospray mass spectra.

Notes and references

1 J. Andréasson, Y. Terazono, B. Albinsson, T. A. Moore, A. L. Moore and D. Gust, *Angew. Chem., Int. Ed.*, 2005, **44**, 7591; X. Guo, D. Zhang, T. Wang and D. Zhu, *Chem. Commun.*, 2003, 914; D. Gust, T. A. Moore and A. L. Moore, *Chem. Commun.*, 2006, 1169.

2 M. Frigoli and G. H. Mehl, *Angew. Chem., Int. Ed.*, 2005, **44**, 5048; X. Guo, L. Huang, S. O’Brien, P. Kim and C. Nuckolls, *J. Am. Chem. Soc.*, 2005, **127**, 15045.

3 T. D. Milster and Y. Zhang, *MRS Bull.*, 2006, **31**, 318.

4 G. Berkovic, V. Krongauz and V. Weiss, *Chem. Rev.*, 2000, **100**, 1741.

5 Y. Yokoyama, S. M. Shrestha and Y. Yokoyama, *Mol. Cryst. Liq. Cryst.*, 2005, **431**, 133; M. Irie and M. Mohri, *J. Org. Chem.*, 1988, **53**, 903; S. Nakamura and M. Irie, *J. Org. Chem.*, 1988, **53**, 6136; Y. Nakayama, K. Hayashi and M. Irie, *J. Org. Chem.*, 1990, **55**, 2592; T. Yamaguchi, Y. Fujita and M. Irie, *Chem. Commun.*, 2004, 1010; M. Hanazawa, R. Sumiya, Y. Horikawa and M. Irie, *J. Chem. Soc., Chem. Commun.*, 1992, 206.

6 A. C. Benniston, A. Harriman, P. Li, J. P. Rostron, H. J. van Ramesdonk, M. M. Groeneveld, H. Zhang and J. W. Verhoeven, *J. Am. Chem. Soc.*, 2005, **127**, 16054.

7 W. Dilthey, F. Quint and J. Heinen, *J. Prakt. Chem.*, 1939, **152**, 49.

8 S. J. Strickler and R. A. Berg, *J. Chem. Phys.*, 1962, **37**, 814.

9 P. Hapiot, J. Moiroux and J.-M. Savéant, *J. Am. Chem. Soc.*, 1990, **112**, 1337.

10 S. Fukuzumi, T. Kitano and K. Mochido, *J. Chem. Soc., Chem. Commun.*, 1990, 1236.

11 N. W. Koper, S. A. Jonker, J. W. Verhoeven and C. van Dijk, *Recl. Trav. Chim. Pays-Bas*, 1985, **104**, 296; S. Fukuzumi, K. Ohkub, T. Suenobu, K. Kato, M. Fujitsuka and O. Ito, *J. Am. Chem. Soc.*, 2001, **123**, 8459.

12 If the reaction proceeded in an analogous manner for the conversion of stilbene to phenanthrene, molecular oxygen would be required in order to remove the two hydrogen atoms of the intermediate.

This journal is © The Royal Society of Chemistry 2006