

Reduction of dipyrido-[3,2-*a*:2',3'-*c*]-phenazine (dppz) by photolysis in ethanol solution†

David A. McGovern,^a Ania Selmi,^a John E. O'Brien,^a John M. Kelly*^a and Conor Long^b

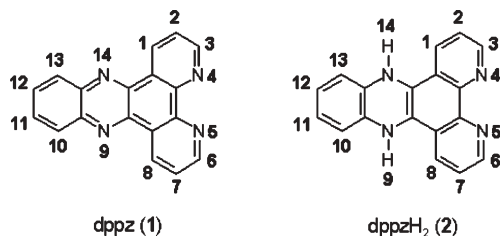
Received (in Cambridge, UK) 6th October 2004, Accepted 2nd December 2004

First published as an Advance Article on the web 27th January 2005

DOI: 10.1039/b415471a

Photolysis of dipyrido-[3,2-*a*:2',3'-*c*]-phenazine (dppz) (**1**) in ethanol solution leads to the formation of 9,14-dihydrodipyridophenazine (**2**), which has been characterised by detailed NMR analysis, UV/VIS absorption spectroscopy, and theoretical calculations which reveal that its red colour is due to a low-lying intramolecular charge transfer state.

There is great interest in dppz-containing metal complexes, especially as some of its ruthenium¹ and rhenium² complexes show a light-switching effect when bound to DNA. This behaviour is attributed to the charge distribution of the reduced ligand formally produced in the MLCT excited state. We have recently started to investigate the photophysics of the free ligand dppz, as relatively little is known about this subject.³ Our preliminary picosecond studies⁴ have indicated that the intersystem crossing takes place in *ca.* 50 ps, yielding the triplet state, which Schanze and co-workers³ had earlier identified in methanol solution using nanosecond laser flash photolysis. They had also observed a second, long-lived transient, which they tentatively assigned to a tautomer of dppz. We have confirmed these nanosecond results but we have additionally found that the reaction in alcohol leads to a stable, but oxygen sensitive, red product.



Dppz (5.5×10^{-5} mol dm⁻³) in degassed ethanol was photolysed by UV radiation ($\lambda = 365$ nm) from a filtered high-pressure Hg lamp. As can be observed in Fig. 1, **1** converts to a species showing broad bands centred at $\lambda_{\text{max}} \approx 360$ nm and at $\lambda_{\text{max}} \approx 485$ nm, the latter being responsible for the solution's red colour. A solution of this compound is stable, so long as it remains deaerated, but rapidly bleaches when air is readmitted, substantially reforming dppz.

To further study this compound we have carried out the photolysis ($\lambda > 330$ nm) in degassed perdeuterioethanol *in situ* in an NMR tube. Fig. 2 shows the spectrum (a) before, (b) after

60 min irradiation, (c) after 240 min irradiation and (d) after re-aeration. Additional NMR studies (Carbon-13, TOCSY and HMQC) (see ESI†) reveal that the structure is consistent with the formation of the reduced compound 9,14-dihydrodipyridophenazine (**2**), presumably as its 9,14-dideuterio-derivative (dppzD₂). It may also be observed (Table 1) that the signals of each of the protons in **2** are displaced markedly upfield compared to those in **1**, the effect being particularly marked for the protons in the 10, 11, 12 and 13 positions.

A similar set of results was observed for 11,12-Me₂dppz. Photolysis ($\lambda > 330$ nm) of a degassed ethanol solution yields a species exhibiting broad bands centred at $\lambda_{\text{max}} \approx 370$ nm and at $\lambda_{\text{max}} \approx 493$ nm. The NMR spectrum taken after 240 mins irradiation shows aromatic signals similarly shifted to those for the conversion of dppz, (Table 1) while the 11,12-methyl signal is shifted strongly upfield to 2.03 ppm in Me₂dppzH₂ compared to that of 2.61 in Me₂dppz.

The red colour of **2** initially surprised us. Therefore to understand the nature of the low-lying excited state we carried out density functional theory calculations. This involved inputting a molecular mechanics structurally optimised structure to the Gaussian 98 program suite. Initially the structure was optimised using restricted Hartree-Fock and a small basis set. This structure was then used as the starting point for the density functional calculation. Further optimisation was performed using the 6-311G basis set, expanded to include diffuse and polarisation functions. The wavefunction was checked for stability and the structure was optimised using tight convergence criteria. The Hessian matrix was checked which showed no negative elements and this confirmed that the system was in the global minimum on the potential energy surface. Application of Time-Dependent Density Functional calculations predicted that the three low energy transitions occur at 330 nm (oscillator strength $f = 0.142$); 489 nm ($f = 0.041$) and 499 nm ($f = 0.005$), within reasonable agreement of the experimental findings particularly as no effort has been made to include solvent effects. These calculations (Fig. 3) also show that the HOMO is concentrated on the quinoxaline moiety of the molecule while in the LUMO and LUMO + 1 the electron-density is localised primarily on the bipyridyl portion. This suggests therefore that the transition in the visible region involves intramolecular charge transfer.

The above experiments support a mechanism in which the dppz triplet excited state extracts a hydrogen atom from the alcoholic solvent forming a radical species dppzH•. (In agreement with this hypothesis it was observed that the formation of **2** was rapid in 2-propanol, where the α -H is more readily abstractable, but

† Electronic supplementary information (ESI) available: detailed NMR analysis of dppzD₂ in perdeuterioethanol; ¹H NMR; ¹³C-¹H COSY (HMQC); ¹³C NMR and DEPT. See <http://www.rsc.org/suppdata/cc/b4/b415471a/>

*jmkelly@tcd.ie

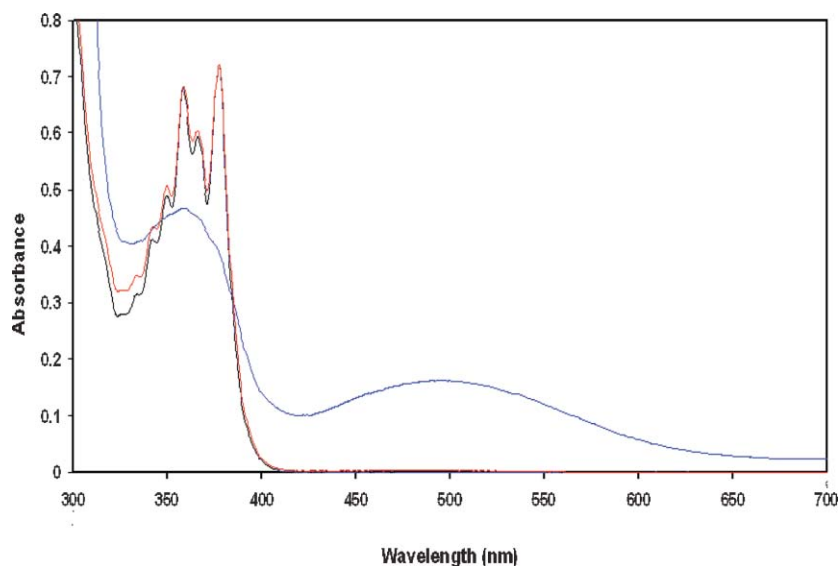


Fig. 1 UV/VIS absorption spectra of $ca. 5.5 \times 10^{-5} \text{ mol dm}^{-3}$ dppz in ethanol: before experiment (black), following 365 nm irradiation (for 360 min) (blue), following re-aeration (red).

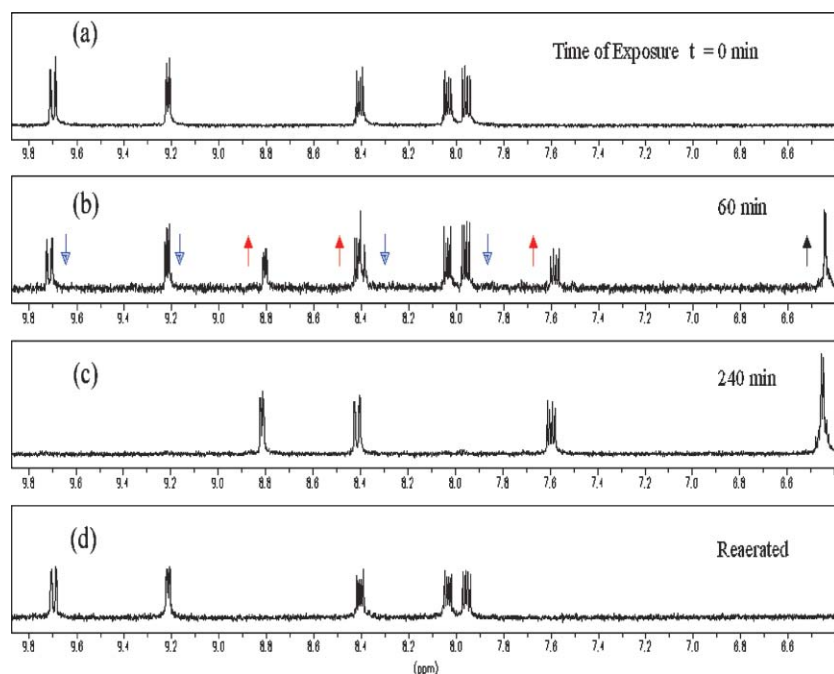
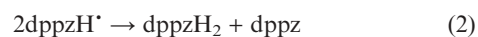


Fig. 2 400 MHz ^1H NMR spectra of a solution of dppz in $\text{C}_2\text{D}_5\text{OD}$ ($ca. 1.9 \times 10^{-3} \text{ mol dm}^{-3}$): (a) before irradiation (degassed), (b) after 60 min exposure (c) after 240 min exposure to UV radiation ($\lambda > 330 \text{ nm}$) (degassed) and (d) after aeration of the photolysed sample.

Table 1 Chemical shifts in $\text{C}_2\text{D}_5\text{OD}$ of aromatic protons of dppz, Me_2dppz and Redppz $\{[\text{Re}(\text{CO})_3(\text{dppz})(\text{py})]\text{Cl}\}$ (py protons not shown)

Compound	H 1,8	H 2,7	H 3,6	H 10,13	H 11,12
Dppz	9.70	7.96	9.21	8.03	8.41
DppzD ₂	8.41	7.59	8.81	6.45	6.45
Me ₂ dppz	9.63	7.91	9.17	8.06	—
Me ₂ dppzD ₂	8.40	7.60	8.81	6.32	—
Redppz	10.06	8.45	9.85	8.18	8.52
RedppzD ₂	8.75	7.98	9.39	6.37	6.45

significantly slower in methanol.) We further propose that the long-lived species observed in nanosecond flash photolysis experiments of **1** is dppzH^+ , which disproportionates to yield **2**, a mechanism similar to that proposed for the photoreduction of phenazine and related compounds.⁵ Further studies are in progress to confirm this.



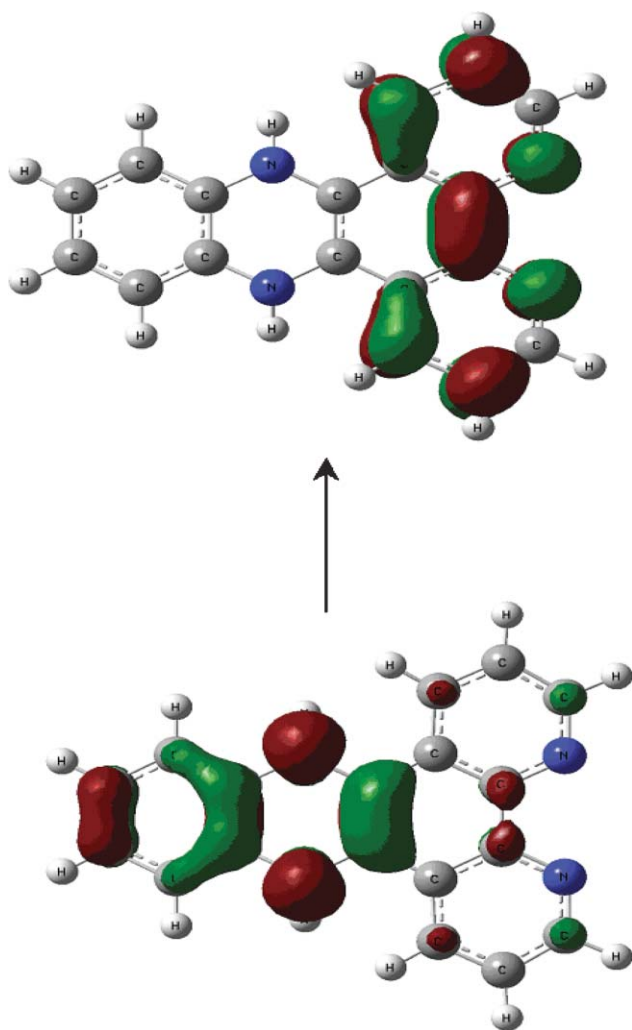


Fig. 3 Graphical representation of the lowest energy transition from the 'HOMO' to the 'LUMO' + 1.

It is interesting to speculate whether this photoreduction process may also occur for dppz-containing metal complexes. To test this we have photolysed $[\text{Re}(\text{CO})_3(\text{dppz})(\text{py})]\text{Cl}$ (py = pyridine) under similar conditions to those used with the free ligands. This complex was chosen as it is known to have a long-lived dppz-centred excited state.^{2a} UV radiation ($\lambda > 330$ nm) converts the complex to a pale green-coloured species showing broad bands centred at $\lambda_{\text{max}} \approx 370$ nm and at $\lambda_{\text{max}} \approx 600$ nm. Irradiation in degassed perdeuterioethanol caused shifts in the aromatic protons consistent

with those observed for the reduction of the free ligand (Table 1), and this assignment is further confirmed by additional NMR measurements. Aeration of the solution induces a reversal to the starting material, although this process is significantly slower than that observed with dppzH_2 itself. Studies are in progress to scale up this reaction and to attempt to isolate $[\text{Re}(\text{CO})_3(\text{dppzH}_2)(\text{py})]\text{Cl}$.

The above studies show that the activation of dppz excited states (either as free ligands or in metal complexes) can lead to two electron photoreduction. It is possible therefore that dppz-derivatives may be able to play similar roles to binuclear metal complexes, where irradiation into MLCT states in the presence of a sacrificial electron donor has recently been shown to cause multi-electron reductions.⁶

Financial support through the HEA PRTLII (Materials) programme and the EU scheme for access to the Rutherford Appleton Laboratories is acknowledged. Mr Kevin McCarthy is thanked for his help with the Me_2dppz studies. We also thank Professor T. Brian H. McMurry and Dr Susan Quinn for helpful discussions.

David A. McGovern,^a Ania Selmi,^a John E. O'Brien,^a John M. Kelly^{*a} and Conor Long^b

^aChemistry Department, Trinity College, University of Dublin, Dublin 2, Republic of Ireland. E-mail: jmkelly@tcd.ie; Fax: 353 1 671 2826; Tel: 353 1 608 1726

^bSchool of Chemical Sciences, Dublin City University, Dublin 9, Ireland. E-mail: conor.long@dcu.ie; Fax: 353 1 7005503; Tel: +353 1 7008001

Notes and references

- (a) M. K. Brennaman, J. H. Alstrum-Acevedo, C. N. Fleming, P. Jang, T. J. Meyer and J. M. Papanikolas, *J. Am. Chem. Soc.*, 2002, **124**, 15094; (b) B. Önfelt, J. Olofsson, P. Lincoln and B. Nordén, *J. Phys. Chem. A*, 2003, **107**, 1000; (c) E. J. C. Olson, D. Hu, A. Hörmann, A. M. Jonkman, M. R. Arkin, E. D. A. Stemp, J. K. Barton and P. F. Barbara, *J. Am. Chem. Soc.*, 1997, **119**, 11458; (d) I. Ortmans, B. Elias, J. M. Kelly, C. Moucheron and A. Kirsch-De Mesmaeker, *Dalton Trans.*, 2004, 668.
- (a) J. Dyer, W. J. Blau, C. G. Coates, C. M. Creely, J. D. Gavey, M. W. George, D. C. Grills, S. Hudson, J. M. Kelly, P. Matousek, J. J. McGarvey, J. McMaster, A. W. Parker, M. Towrie and J. A. Weinstein, *Photochem. Photobiol. Sci.*, 2003, **2**, 542; (b) V. W. Yam, K. K. W. Lo, K. K. Cheung and R. Y. C. Kong, *J. Chem. Soc., Dalton Trans.*, 1999, 2067.
- H. D. Stoeffler, N. B. Thornton, S. L. Temkin and K. S. Schanze, *J. Am. Chem. Soc.*, 1995, **117**, 7119.
- C. M. Creely, J. M. Kelly, A. M. Selmi, D. A. McGovern, W. J. Blau, P. Matousek, M. Towrie and A. W. Parker, *Proc. SPIE*, 2003, **4991**, 482.
- H. Görner, D. Döpp and A. Dittmann, *J. Chem. Soc., Perkin Trans. 2*, 2000, 1723 and references therein.
- R. Konduri, H. Ye, F. M. MacDonnell, S. Serroni, S. Campagna and K. Rajeshwar, *Angew. Chem., Int. Ed.*, 2002, **41**, 3815.