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Comments on photochromism of 3-(3-pyridyl)sydnone and 4-alkenylsydnones

J. Photochem. Photobiol. A: Chem. 84 (1994) 257-264.

And *J. Photochem. Photobiol. A: Chem.* 75 (1993) 49-59.

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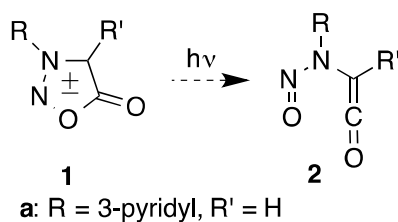
Highlights

- . Mechanism of photochromism of sydnones disputed.
- . Nitrosaminoketenes should be yellow and cannot explain the blue color.
- . Photolysis yields bicyclic azlactones (oxadiazabicyclo[2.1.0]pentanones).

Abstract. The blue photochromism of sydnones **1**, in particular 3-(3-pyridyl)sydnone **1a**, has been ascribed to the formation of nitrosaminoketenes **2** as carriers of the blue colour, allegedly supported by CNDO/S-CI and STO-3G calculations. New calculations at TD-B3LYP/6-31+G**, RM06-2X/6-311++G(d,p), CAM-B3LYP/6-311++G(d,p), and CASPT2//CASSCF(6,6)/PVDZ levels demonstrate that the nitrosaminoketenes should be yellow and cannot possibly be blue. The sydnone photochromism is not currently understood, and further experimental and computational investigation is required.

Keywords: Photochromism. Sydnones. Photochemistry.

Several sydnones **1** exhibit blue photochromism in the solid or glassy states,^{1,2} and theories to explain this phenomenon include the formation of colour centers similar to those formed by alkali metals.^{3,4} 3-(3-Pyridyl)sydnone **1a** is an almost colorless solid when pure, but a blue colour develops rapidly on exposure to UV light, daylight or fluorescent light and gives rise to a new λ_{\max} at 640 nm. This colour is bleached again by heating, by infrared irradiation, or by storing the sample at room temperature in the dark. Nespurek and co-workers have advanced the theory that *N*-nitrosaminoketenes **2** are the carriers of the blue colour in the title compounds and argued against alternate explanations (Scheme 1).^{5,6,7}



Scheme 1. The postulated photochemical formation of nitrosaminoketenes **2** as carriers of the blue color.⁵⁻⁷

The identification of **2** as the color-carrier was based on UV-vis and ESCA spectra supported by CNDO/S-CI and STO-3G calculations, respectively. This contention stands unchallenged in the literature and continues to be cited.^{8,9,10}

We wish to point out that calculations at the TD-B3LYP/6-31+G** level indicate that nitrosaminoketenes should not have absorptions in the 600 nm range.¹¹ The longest wavelength-maximum for the ketene **2a** derived from 3-(3-pyridyl)sydnone is a very weak transition at 405 nm ($f = 0.0007$) in accord with the expectation that this compound, like other nitrosamines, should be yellow, not blue. The calculated UV-vis spectrum is shown in Fig. 1.

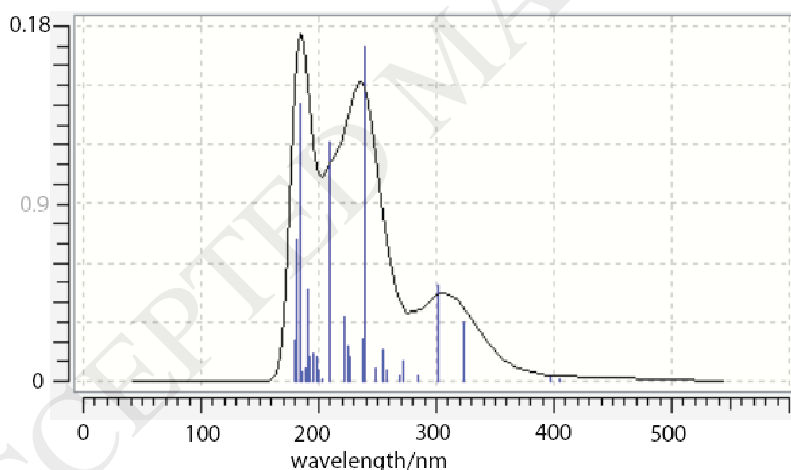
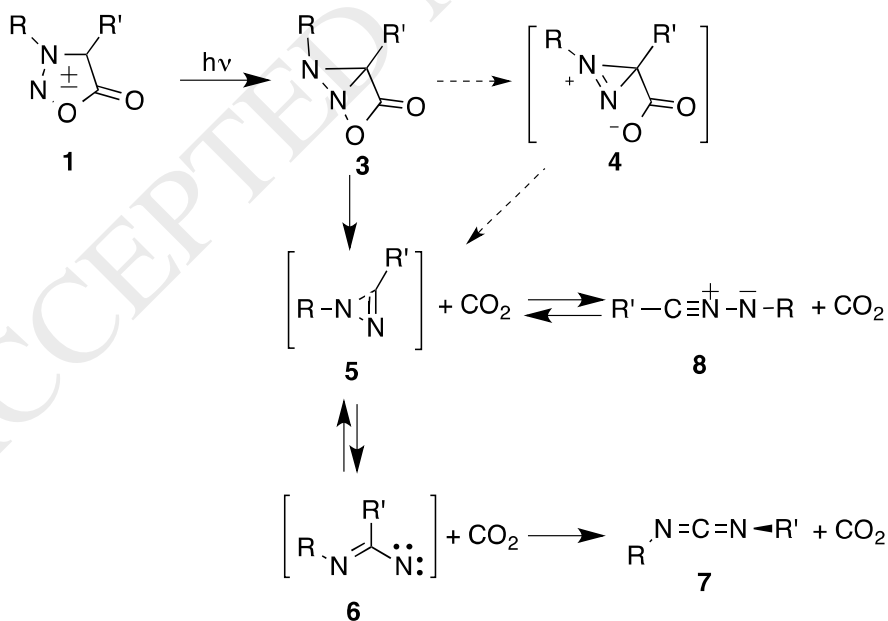


Fig. 1. UV-vis transitions calculated for *N*-nitrosamino-*N*-(3-pyridyl)ketene **2a** at the TD-B3LYP/6-31+G** level. Ordinate: oscillator strengths.

In addition, we calculated the UV-vis spectrum of **2a** at the RM06-2X/6-311++G(d,p) level, where the longest wavelength maximum corresponds to a very weak transition at 439 nm

($f = 0.0013$). At the CAM-B3LYP/6-311++G(d,p) level the longest wavelengths are 401 nm ($f = 0.0000$) and 369 nm ($f = 0.0017$). At the CASPT2//CASSCF(6,6)/PVDZ level, this transition is at 406 nm ($f = 0.0055$). All these results reinforce the conclusion that the *N*-nitrosaminoketenes **2** can only be yellow.

We have shown that sydnones **1**, including 3-(3-pyridyl)sydnone **1a**, are converted to the directly observable bicyclic azlactones **3** on photolysis in argon or xenon matrices (Scheme 2), but there was no evidence for the formation of ketenes.¹¹ The azlactones undergo further photochemical elimination of CO₂ and formation of carbodiimides **7**.¹¹ This reaction is likely to proceed via 1*H*-diazirines **5**, which may be formed directly from **3** or from diaziridinium carboxylates **4** (Scheme 2). The latter are akin to 1-amino-3-alkylthio-diazirinium-3-carboxylate zwitterions proposed by Gotthardt and Reiter.¹² A different kind of diazonium carboxylate zwitterions RN=N⁺=CH-COO⁻ proposed by Trozzolo et al.¹³ has been discounted.⁶ Solution photolysis of sydnones is known to afford nitrile imines **8**, which are probably also formed from the diazirines **5**, and finally nitrile imines **8** rearrange both thermally and photochemically to the lower-energy carbodiimides **7**.¹⁴ The first 1*H*-diazirines **5** have been reported recently,¹⁵ whereas imidoynitrenes **6** (open-shell singlets with triplet ground states) remain so far as unobserved intermediates.¹¹



Scheme 2. Observed and postulated transformations of sydnones. Postulated intermediates are in square brackets.

In conclusion, nitrosaminoketenes like **2** cannot explain the photochromism observed for many sydnones. Azlactones **3** are definitely formed on matrix photolysis of sydnones, but they cannot themselves be the carriers of the blue photochromism.¹¹ Systematic experimental investigation of sydnone photochromism is lacking, and the phenomenon of photochromism is currently not understood. Further computational studies of known and postulated intermediates in sydnone photochemistry and their potential involvement in photochromism will be published.

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References

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- ¹ (a) J. M. Tien and I. M. Hunsberger, A Phototropic Heterocyclic Derivative of a Sydnone: a new Synthesis of an N-Substituted Glycine; and a General Synthesis of Mono-Substituted Hydrazines, *Chem. Ind. (London)* (1955) 119-120. (b) J. M. Tien and I. M. Hunsberger, The Preparation of Substituted Hydrazines. 11. 3-Pyridylhydrazine via the Phototropic N-(3-Pyridyl)-Sydnone, *J. Am. Chem. Soc.* 77 (1955) 6604-6607. (c) H. S. Gutowski, R. L. Rutledge and I. M. Hunsberger, Electron Spin Resonance Studies of Photochromic solids, *J. Chem. Phys.* 29 (1958) 1183-1184. (d) C. V. Greco and B. P. O'Reilly, Mesoionic Compounds VIII. Synthesis of 3-Phenylsydnonyl Substituted Alkenes. Some new Photochromic Sydnones, *J. Heterocycl. Chem.* 9 (1972) 207-213.

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- ² M. Sorm and S. Nespurek, Mesoionic Compounds. Sydnones and their Photochromic Properties. *Coll. Czech. Chem. Commun.* **40** (1975) 3459-3468.
- ³ T. Mill, A. van Roggen and F. C. Wahlig, Photochromism of N-3-Pyridylsydnone, *J. Chem. Phys.* **35** (1961) 1139-1140.
- ⁴ F. I. Metz, W. C. Servoss, F. E. Welsh, Photochromic Behavior of Sydnones, *J. Phys. Chem.* **66** (1962) 2446-2448.
- ⁵ S. Nespurek, S. Böhm, J. Kuthan, Photochromism of Sydnones: Structural Evidence for the Blue Colored Species from 3-(3-Pyridyl)sydnone, *J. Mol. Struct. (Theochem)* **136** (1986) 261-273.
- ⁶ S. Nespurek, J. Lukas, S. Böhm, and Z. Bastl, Photochromism of 3-(3-Pyridyl)sydnone: An Investigation by Electron Spectroscopy for Chemical Analysis (ESCA) and Molecular Orbital Calculations, *J. Photochem. Photobiol. A: Chem.* **84** (1994) 257-264.
- ⁷ S. Nespurek, J. Obrda, and J. Lipinski, A Possible Explanation for the Photochromism of two 4-Alkenyl-sydnones, *J. Photochem. Photobiol. A: Chem.* **75** (1993) 49-59.
- ⁸ R. Giovanni and U. Chiacchio, Oxadiazoles, in: *Modern Heterocyclic Chemistry*, J. Alvarez-Builla, J. J. Vaquero, J. Barluenga (Eds.), Wiley-VCH, Weinheim, 2011, Vol 2, Chapter 13, pp. 1047-1252.
- ⁹ S. Nakamura, Molecular Modeling Calculations, in: J. J. Crano and R. J. Guglielmetti (Eds.), *Organic Photochromic and Thermochromic Compounds*, Kluwer, New York 2002, Vol. 2, Physicochemical Studies, Chapter 5, pp. 241-295.
- ¹⁰ T. M. Cooper, B. C. Hall, D. G. McLean, J. E. Rogers, A. R. Burke, K. Turnbull, A. Weisner, A. Fratini, Y. Liu, K. S. Schanze, Structure-Optical Property Relationships in Organometallic Sydnones, *J. Phys. Chem. A* **109** (2005) 999-1007.
- ¹¹ R. N. Veedu, D. Kvaskoff, C. Wentrup, Sydnone Photochemistry: Direct Observation of Earl's Bicyclic Lactone Valence Isomers (Oxadiazabicyclo[2.1.0]pentanones), Formation of Carbodiimides, Reaction Mechanism, and Photochromism, *Aust. J. Chem.* **67** (2014) 457-468.
- ¹² H. Gotthardt, F. Reiter, Neue, Ungewöhnliche Photochemische Reaktionen von 3-Aminosydnonen. *Chem. Ber.* **114** (1981) 1737-1745.
- ¹³ A. M. Trozzolo, T. M. Leslie, A. S. Sarpotdar, R. D. Small and G. J. Ferraudi, Photochemistry of some 3-Membered Heterocycles, *Pure Appl. Chem.* **51** (1979) 261-270.

¹⁴ D. Bégué, G. G. Qiao and C. Wentrup, Nitrile Imines: Matrix Isolation, IR Spectra, Structures, and Rearrangement to Carbodiimides, *J. Am. Chem. Soc.* *134* (2012) 5339-5350.

¹⁵ C. M. Nunes, C. Araujo-Andrade, R. Fausto and I. Reva, Generation and Characterization of a 4 π -Electron Three-Membered Ring 1*H*-Diazirine: an Elusive Intermediate in Nitrile Imine – Carbodiimide Isomerization, *J. Org. Chem.* *79* (2014) 3641-3646 , and references therein.

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