

ASP NEWS



Spring 2013

vol. 42(2)

Message from ASP President

The poll for the ASP election of new council members is still open but will close in a few days! Please take a few minutes to vote. You simply need to log on to the ASP web site (www.photobiology.org), read the candidates' statement, and then vote. It is important that we have a council that accurately reflects our membership and all aspects of photobiology. If you need assistance with voting, please contact **Linda Hardwick** (lhardwick@allenpress.com) or me (gaillard.beth@gmail.com)

We are also in the process of identifying division chiefs for each of the “petals” on the ASP flower. I am delighted to announce that the new chief of Phototechnology is **Alberto Diaspro** and the new chief of Photomedicine is **Heidi Jacobe**, and extend a warm welcome to both. If you would like to recommend a person for chief of one of the other divisions or if you are interested in nominating yourself, please contact me.

We continue to follow through on outreach and joint activities with other societies. We are currently negotiating with the InterAmerican Photochemical Society, the Photomedicine Society and the Society for Free Radicals in Biology and Medicine regarding joint membership rates, journal access, and meeting overlap. We are very pleased to announce that ASP will be sponsoring a session on carotenoids at the International Congress on Photosynthesis in Saint Louis, MO (Aug 11-16). We will also have a booth in the exhibitor area, so please stop by if you are attending.

-**Beth Gaillard**, Gaillard.beth@gmail.com

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ASP Candidates for Council

(Vote for 5)

Thomas Mang

Ulas Sunar

Charles B. Simone

Michael Della Vecchia

Nihal Ahmad

Frances Noonan

David Kessel

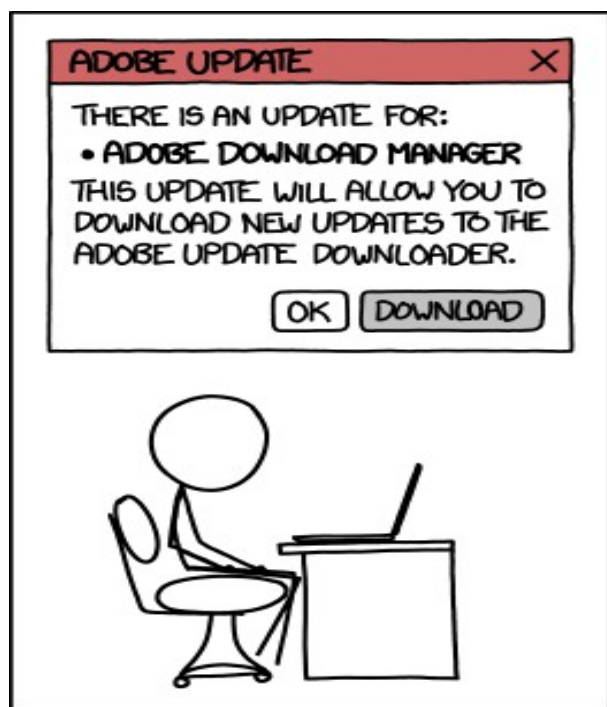
Janis T. Eells

Yu-Ying He

Johnathan F. Lovell

Zofia Drzaaga

Updates



-Reprinted with permission from **Randall Monroe** (www.xkcd.com)

15th Congress of the European Society for Photobiology

Palais des Congrès, Liège, Belgium
September 2-6, 2013

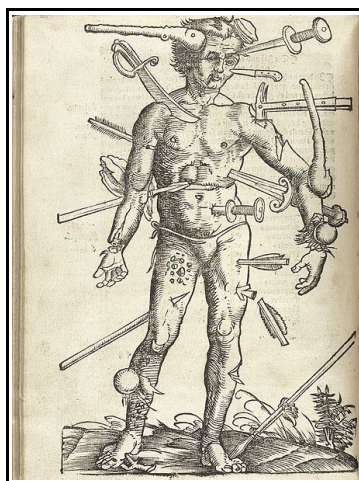
The 15th Congress of the European Society for Photobiology offers a scientific program of sessions on a wide range of topics which cover major streams of photobiological sciences. This includes highly relevant, timely, cutting edge symposia, plenary lectures, and keynote lectures on emerging topics.

Abstract submission (deadline: May 15, 2013)
liege2013.photobiology.eu/abstract_submission

Program
liege2013.photobiology.eu/programme

Further info
liege2013.photobiology.eu

Letter from the Editor



Wound man is a picture of the wounds that a soldier might experience during war in the 1400's. The picture to the left and similar pictures were common in medical text books of several hundred years ago.

I am sure that many scientists who have written journal articles feel like the *wound man* when reading feedback from the reviewers and editor. In fact, for the past 15+ years, I have worked as a language editor for thousands preclinical and clinical journal articles, so I have also inflicted my share of wounds. I believe that my work provided a significant benefit to these authors, who were mostly from Asia and Europe and spoke English as a second language. In fact, I believe that all mature writers and scientists appreciate the help of a good editor.

I also promise to inflict wounds on your newsletter contributions. But fear not! We really welcome all sorts of contributions. You can tell us about an upcoming meeting (see: "ICTPPO 2013", page 3), your new book (see: "Bioluminescence: Living Lights, Lights for Living", page 4), or about your own research (see: "A and B of Cis-Trans Photoisomerization", page 6). I look forward to hearing from you!

ASP News

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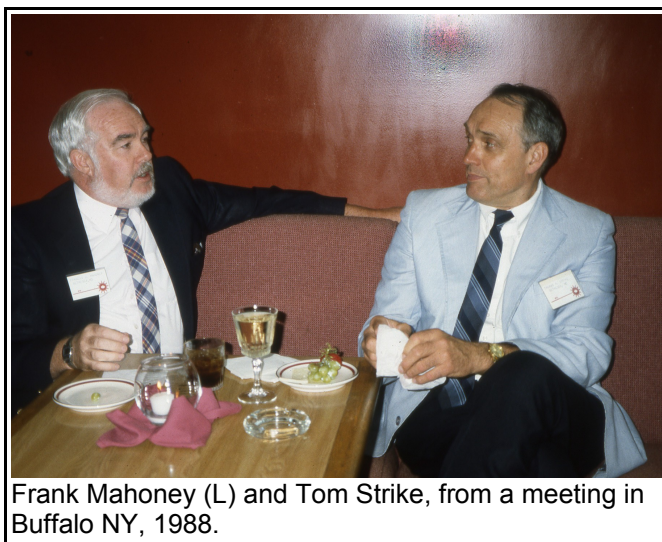
Editor

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Notes on ASP History

Photobiology and the NIH

Kendric Smith, the founder of our Society, would periodically propose that Photobiology needed a separate Study Section at the NIH. These groups evaluate grant proposals and assign priority scores for the program management to consider. Photobiology proposals would often be sent to study sections that had no appreciation or understanding of photobiology. Those dealing with photodynamic therapy generally went to RAD (now RTB: Radiation Therapeutics and Biology). In earlier days, an initial vote of assigned reviewers would identify proposals in the bottom half. To save time, these were not discussed (unscored) but the reviews were sent back to the proposers. The remaining 50% would be discussed and scored.



Frank Mahoney (L) and Tom Strike, from a meeting in Buffalo NY, 1988.

In better times, as many as half of the 'scored' proposals would be given awards. Now it's closer to 15%. My concern was that having a photobiology study section could mean that some proposals that might have been funded by other groups might not make the cut in a separate section. This assumed that the photobiology proposals were, as a group, superior to most others. The NIH never seriously considered this option, for better or worse.

Center for Scientific Review

www.nih.gov/about/almanac/organization/CSR.htm

The RAD and RTB study sections have for many years included at least two PDT reviewers which, at various times were **Tayyaba Hasan, Victor Fingar, Barbara Henderson, Brian Wilson, Al Girotti, Fred Hetzel, Nancy Oleinick, Chuck Gomer** and me. The Center for Scientific Review website shows the names of the present reviewers.

The program official responsible for RAD during the early days was **Frank Mahoney**, assisted by **Tom Strike**. **Paul Strudler** (CSR) ran the study section with a deadly sense of humor. These people were exceedingly helpful when photobiology was first making itself known to the NIH. **Rosemary Wong** (Programatic) and **Bo Hong** (CSR) are the current chiefs.

Changing the color of Petunias

Napoli C, Lemieux C, Jorgensen R (1990) Introduction of a chimeric chalcone synthase gene into *Petunia* results in reversible co-suppression of homologous genes in trans". *Plant Cell* 2: 279-89.

Photobiology continues to be of interest for both theoretical and practical (therapeutic) reasons, but the current shortage of funds will create difficulties. I can recall when budgets would permit funding of almost anything with a semblance of logic. The current tendency of study sections and program management is to look for items that appear to have an immediate pay-off. But I am reminded that siRNA was discovered by someone trying to change the color of petunias.

-David Kessel

ICTPPO 2013

**International Conference on
Tetrapyrrole Photoreceptors of
Photosynthetic Organisms
September 11-15, 2013**



The ICCTPO aims to provide a platform for photobiologists, biophysicists, biochemists, plant physiologists, and geneticists to discuss the

topics related to photosynthesis and photosensory chlorophyll and biliproteins. These topics include structure and function, signal transduction, biosynthesis and degradation of tetrapyrroles, assembly of chromophores and apoproteins, formation of photosynthetic complexes, applications in photodynamics and imaging. The conference allows exchange of research and ideas, discussion of challenges, promotion of collaborations, and facilitation of the transfer of new technologies.

ICTPPO 2013
ictppo2013.hzau.edu.cn

This conference will be in the city of Wuhan in central China, at the State Key Laboratory of Agricultural Microbiology of the Huazhong Agricultural University. Accommodations will be available on site.

The deadline for registration is July 15, 2013. In addition to the payment methods given in the registration form, payment is also possible by PayPal to zhouming321@126.com.

The deadline for the submission of abstracts is July 15, 2013. A template is provided. Abstracts are only accepted after registration.

We encourage the participation of students by a reduced registration fee. They are invited to jointly organize with the local students a special evening for young investigators.

The Organizing Committee consists of **Wolfgang Gärtner, Bernhard Grimm, Ting-Yun Kuang, Mei-Zhong Luo, Hugo Scheer, Xiao-Jing Yang, and Kai-Hong Zhao.**

-Wolfgang Gärtner

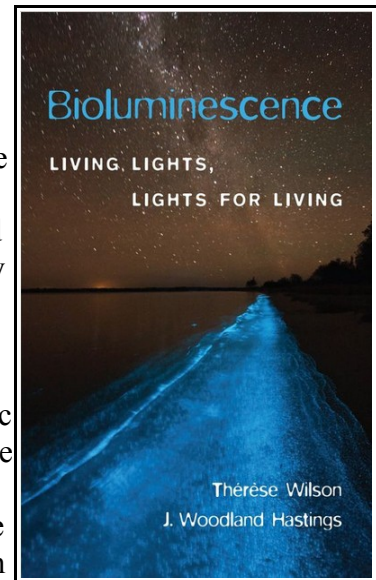
Bioluminescence: Living Lights, Lights for Living
New Book by Woody Hastings, former ASP President

Bioluminescence is everywhere on earth – most of all in the ocean, from angler fish in the depths to the flashing of dinoflagellates at the surface. Here, **Thérèse Wilson** and **Woody Hastings**

explore the natural history, evolution, and biochemistry of the diverse array of organisms that emit light.

Previously, bioluminescence was viewed as a fascinating phenomenon, whose study seemed esoteric and seemed unlikely to have any practical applications. Bioluminescence is no longer an esoteric area of research. The applications are numerous and range from rapid detection of microbial contamination in beef and water, finding the location of cancer cells, and working out circuitry in the brain.

-Harvard University Press



UV Radiation: Effects on Human Health and the Environment
Auckland New Zealand
April 15-17, 2014

The workshop will be organised along lines similar to those in the previous workshops linked to the web page below. However, the scope has been broadened to include the wider Pacific region rather than just the New Zealand region. For acceptance, papers must have specific applicability to the South Pacific region. We expect a strong focus on effects of UV on human health and the environment, as reflected in the title of the workshop.

NIWA UV Workshop
www.niwa.co.nz/atmosphere/uv-ozone/uv-science-workshops/2014-uv-workshop

On behalf of my co-convenors (**Barbara Hegan, Robert Scragg, Peter Gies, and Robyn Lucas**), I invite you to attend and participate in this event.

Please mark the dates in your calendars and include budgeting to attend in your planning for next year. If you already know you will be attending, and would like to present a paper, it would be helpful if you could provide me with the title at your earliest convenience.

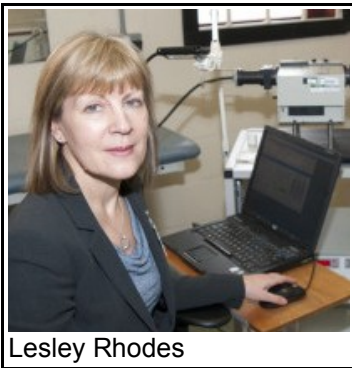


Please distribute this announcement to any of your colleagues who may be interested. A flyer is available on the web page for printing and posting at your work place.

-Richard McKenzie, Convenor

ω -3 Supplements and Skin Cancer

University of Manchester researchers report that omega-3 fish oils may protect against skin cancer



Lesley Rhodes

A team at the University of Manchester has just carried out the first clinical trial to examine the impact of the fish oils on the skin immunity of volunteers. Led by Professor **Lesley**

Rhodes, Professor of Experimental Dermatology from the Photobiology Unit Dermatology Centre at the University, the study analysed the effect of taking omega-3 fish oils on 79 healthy volunteers.

Results of the study, funded by the Association for International Cancer Research, found that taking a regular dose of fish oils boosted skin immunity to sunlight. Specifically, it also reduced sunlight-induced suppression of the immune

system (immunosuppression), which affects the body's ability to fight skin cancer and infection. The findings were published in *The American Journal of Clinical Nutrition*.

Pilkington SM, Massey KA, Bennett SP, Al-Aasswad NM, Roshdy K, Gibbs NK, Friedmann PS, Nicolaou A, Rhodes LE. (2013) Randomized controlled trial of oral omega-3 PUFA in solar-simulated radiation-induced suppression of human cutaneous immune responses. *Am J Clin Nutr* 97(3):646-52.

Professor Rhodes, who is based in the Photobiology Unit at the University's School of Medicine and Salford Royal NHS Foundation Trust, said it was the first time the research had been carried out on humans. "There has been research in this area carried out on mice in the past but this is the first time that there has been a clinical trial directly in people," she said. "It has taken a number of years to get to this stage and the findings are very exciting.

"This study adds to the evidence that omega-3 is a potential nutrient to protect against skin cancer. Although the changes we found when someone took the oil were small, they suggest that a continuous low level of chemoprevention from taking omega-3 could reduce the risk of skin cancer over an individual's lifetime."

Patients who volunteered for the trial took a 4 g dose of omega-3 (about one and a half portions of oily fish) daily and were then exposed to the equivalent of either 8, 15 or 30 minutes of summer midday sun in Manchester using a special light machine. Other patients took a placebo, before exposure to the light machine. Overall, immunosuppression was 50% lower in people who took the supplement and were exposed to 8 and 15 minutes of sun compared with those who took the placebo. The study showed little influence on those in the 30 minute group.

The findings are important in the battle against skin cancer because previous research has shown that sunscreens are often applied inadequately and only used during holiday periods. However, Professor Rhodes stressed that the omega-3 was not a substitute for sunscreen and physical protection, and that omega-3 should be regarded

as an additional small measure to help protect the skin from sun damage. Fish oil has already been shown to have many beneficial health effects, such as protection against cardiovascular disease, so taking the supplement could lead have a range of potential health benefits. Professor Rhodes' team is now continuing its research by investigation of the effect of omega-3 studies on healthy volunteers at Salford Royal. It comes as The University of Manchester, Cancer Research UK, and The Christie Cancer Hospital team up to create a Manchester Cancer Research Centre.

About 100,000 cases of non-melanoma skin cancer were diagnosed in the UK in 2010, according to the most recent figures available from Cancer Research UK, making it an extremely common cancer.

Dr. **Helen Rippon**, Head of Science at AICR, said: "Skin cancer has been one of the fastest growing types of cancer, and numbers will likely continue to increase. It is always exciting to see research that AIRC has funded generating such promising results, and we look forward to seeing future developments in this area."

-adapted with permission from **Alison Barbuti** (Media Relations Officer, The University of Manchester)

A and B of Cis-Trans Photoisomerization

(reprinted from *EPA Newsletter*, June 2012)

The focus of this contribution is on the photoisomerization mechanism of the first three members of the α,ω -diphenylpolyene series, $C_6H_5(C=C)_n C_6H_5$, $n = 1-3$, long studied as models for retinyl polyenes related to vitamin A and the visual pigments. Experimental evidence shows that the doubly excited singlet state, 2^1A_g , is not involved in shaping the potential energy surface for the reaction and its formation does not facilitate photoisomerization. It is likely that torsional relaxation leading to photoisomerization occurs entirely in the 1^1B_u excited singlet state.

In 1967 I proposed that cis-trans stilbene photoisomerization involves torsional relaxation to $1^1t^* \rightarrow 1^1p^*$ process in *trans*-stilbene (*t*-St) and case

and decay from a global energy minimum (the phantom singlet, 1^1p^*) in S_1 .¹ The complementarity of *trans*-stilbene, 1^1t^* , fluorescence and photoisomerization quantum yields and 1^1t^* lifetimes, over a wide T -range, were thus accounted for.² Fine tuning of the energetics of the potential energy curve, was accomplished when fluorescence studies revealed a small (0.2%) T -independent adiabatic pathway to 1^1t^* from the cis isomer, 1^1c^* .³ Soon after Hudson and Kohler assigned the anomalous fluorescence of the vinylogous α,ω -diphenylpolyenes to emission from a forbidden doubly excited singlet state, 2^1A_g , lower in energy than the one-photon allowed 1^1B_u state,⁴ Orlandi and Siebrand (OS) postulated a central role for that state in cis-trans photoisomerization.⁵ OS attributed the intrinsic $1^1t^* \rightarrow 1^1p^*$ torsional barrier to crossing of the 1^1B_u and 2^1A_g potential energy surfaces and Birks extended this model to the higher members of the vinylogous series.⁶

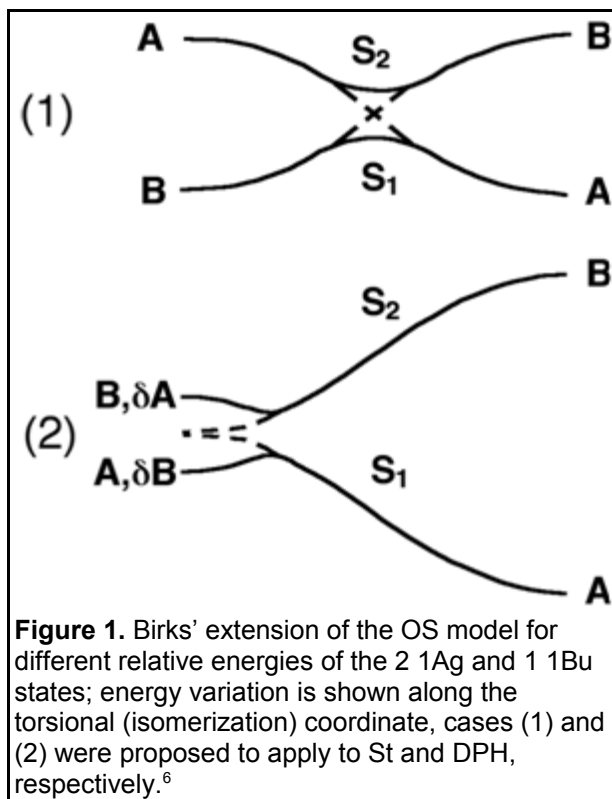


Figure 1. Birks' extension of the OS model for different relative energies of the 2^1A_g and 1^1B_u states; energy variation is shown along the torsional (isomerization) coordinate, cases (1) and (2) were proposed to apply to St and DPH, respectively.⁶

Case (1) in Fig. 1 depicts the OS model for the

(2) shows the Birks extension of this model to photoisomerization of all-*trans*-1,6-diphenyl-1,3,5-hexatriene (*ttt*-DPH) and higher members of the series. Stronger vibronic coupling between the 1^1B_u and 2^1A_g states at the planar geometry was presumed to create the barrier along the torsional coordinate in case (2).⁶ In the following we reject the OS model and its extension by Birks, at least for the three lowest members of the diphenylpolyene series. We begin with *t*-St for which the 1^1B_u state is S_1 , continue with *ttt*-DPH whose S_1 state is 2^1A_g and conclude with *trans,trans*-1,4-diphenyl-1,3-butadiene (*tt*-DPB) for which the 1^1B_u and 2^1A_g states are close to isoenergetic.

***t*-St:** The wide acceptance of the OS model is evident in the prominent role attributed to the 2^1A_g state in current literature.⁷ Early objections to the OS model were based on theory: (1) For an A_g state to be involved in stilbene photoisomerization, it would have to be higher in energy than the 2^1A_g state.⁸ (2) The torsional barrier could be a property of the 1^1B_u state.⁹ Scrutiny of the OS model reveals that it is not consistent with experimentally determined torsional barriers in S_1 of *t*-St in solution and in the gas phase.¹⁰ The 1^1B_u state is stabilized preferentially with increasing solvent polarizability.¹¹ The expected stabilization of the 1^1B_u state relative to the 2^1A_g state on moving from the gas phase to a hydrocarbon solvent is ~5 kcal/mol. A 5 kcal/mol upward displacement of curve B in case (1) requires an earlier torsional transition state in the gas phase corresponding to a lower torsional energy barrier in S_1 for *t*-St, but the barrier, if anything, increases from an intrinsic value of 2.8 kcal/mol (based on ΔH , equivalent to a 3.3 kcal/mol Arrhenius activation energy)^{2,3b} in solution to 3.4 kcal/mol in the gas phase.¹² Congruence between theory and experiment was achieved recently in a high level theoretical paper that found no role for the 2^1A_g state in St

photoisomerization.¹³

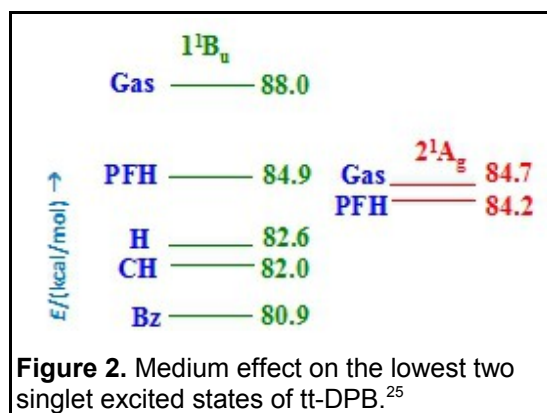


Figure 2. Medium effect on the lowest two singlet excited states of *tt*-DPB.²⁵

***ttt*-DPH:** The small torsional barrier expected from the interaction in case (2) is inconsistent with the longer fluorescence lifetimes of *ttt*-DPH (ns scale)¹⁴ relative to *t*-St (ps scale)¹² in solution. Furthermore, Birks' assumption,⁶ by analogy with the stilbenes, that all radiationless decay in the higher vinylogues involves torsional relaxation along photoisomerization coordinates is inconsistent with very small photoisomerization quantum yields.¹⁵ In *ttt*-DPH, $1^1B_u/2^1A_g$ equilibration is complete in the sub-ps time scale,¹⁶ *trans*→*cis* photoisomerization activation energies far exceed the $1^1B_u/2^1A_g$ energy gap^{15b} and there is no significant change in photoisomerization efficiency when the $1^1B_u/2^1A_g$ energy order is reversed in a rigid DPH analogue.¹⁷ Easy access to the 2^1A_g state does not facilitate photoisomerization and, if anything, impedes it.

***tt*-DPB.** As for DPH, Birks assumed complementarity between fluorescence and photoisomerization pathways in applying the OS model to DPB.^{6,18} With one notable exception,¹⁹ subsequent investigators followed that practice,²⁰⁻²³ despite early low photoisomerization quantum yields that suggest the presence of competing unreactive radiationless pathways.^{24,25} *t*-St and *tt*-DPB photoisomerizations were used as probes for testing theories on medium effects on large amplitude motions. Discrepancies emerged in the interpretation of the influence of the medium on what appeared to be similar motions in the two

molecules. tt -DPB \rightarrow ct -DPB quantum yields, $\phi_{tt\rightarrow ct}$ in hexane (H), cyclohexane (CH), benzene (Bz) and perfluorohexane (PFH) confirmed our suspicion that the discrepancies could be traced to assignment of all radiationless decay in tt -DPB to torsional relaxation. The $\phi_{tt\rightarrow ct}$ values at 20 °C range from a high of 0.25 in Bz to a low of 0.07₆ in PFH.²⁶ Figure 2 gives the relative energies of the 1^1B_u and 2^1A_g states in the four solvents. The changes reflect preferential stabilization of the 1^1B_u state with increasing medium polarizability. Photoisomerization is most efficient in the highly polarizable Bz in which the 1^1B_u state is the lowest excited singlet state and the ΔE_{ab} gap is largest, and is least efficient in PFH where the 2^1A_g state is the lowest excited singlet state.²⁶ If the 2^1A_g state were involved, photoisomerization would be most, not least, efficient in PFH whose radiationless decay is dominated by the $1^1B_u \rightarrow 2^1A_g$ process. Here too, the Birks extension of the OS mechanism fails.

Conclusion. The 2^1A_g state plays no role in the $trans \rightarrow cis$ photoisomerization of the three lowest members of the α,ω -diphenylpolyene series. Photoisomerization occurs in the 1^1B_u state in all three. Beyond those generalities, the behaviour of each of the three is unique. Strict complementarity between fluorescence and photoisomerization via torsional relaxation in S_1 applies only to t -St. Significant radiationless decay channels not leading to photoisomerization compete in the excited singlet state decay of tt -DPB and ttt -DPH. But, even tt -DPB and ttt -DPH exhibit strikingly different behaviour. In solution, and that also applies to PFH in which S_1 is the 2^1A_g state, all tt -DPB fluorescence is from the 1^1B_u state. Vibronic coupling between the tt -DPB 1^1B_u and 2^1A_g states is not sufficiently strong to allow observation of the radiative decay of a mainly-A $2^1A_g/1^1B_u$ mixed state. The opposite is true for ttt -DPH. Here

2^1A_g and 1^1B_u fluorescences are observed simultaneously from the equilibrated mixture of these two vibronically coupled states.¹⁰

Acknowledgment. This work was supported by the National Science Foundation, most recently by Grant No. CHE-0846636.

-Jack Saltiel (Department of Chemistry & Biochemistry, Florida State University, Tallahassee, FL)

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Photobiology Events



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Vision: A Platform for Linking Circuits, Perception and Behavior

Cold Spring Harbor, NY (USA)

Web site: meetings.cshl.edu/courses/2013/c-sfvs13.shtml

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Easton, MA (USA)

Web site: www.grc.org

Jul 20-24, 2013

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Providence, RI (USA)

Web site: aspb.org/calendar

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16th International Congress on Photosynthesis
St. Louis, MO (USA)

Web site: www.ps16stlouis.wustl.edu

Sep 2-6, 2013

ESP 2013
Liège (Belgium)

Web site: www.liege2013.photobiology.eu

Sep 11-15, 2013

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Wuhan, China

Web site: ictpo2013.hzau.edu.cn

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6th Asia and Oceania Conference on
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Sydney (Australia)

Web site: www.aocp2013.org.au

Apr 14-17, 2014

SPIE Photonics Europe 2014

Brussels, Belgium

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NIWA UV Workshop

Auckland, New Zealand

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- Environmental and antimicrobial applications of photosensitised processes
- UV damage to biomolecules



- DNA repair – skin cancer
- UV and melanoma
- Photoresponses in skin cells



- UVR sources and VitD

- Photoimmunology
- Photoprotection
- Photomedicine



- Optogenetics
- Visual pigments
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