

EPA NEWSLETTER

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EPA on the Internet ;: General photochemistry and EPA information (statutes, conference, announcements and calendar, membership list, EPA NL contents and articles) is available at <http://pages.unibas.ch/epa/welcome.html>

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Fabienne Wetz

***“New long chain molecules derived from Parsol[®] 1789 :
a new solar filters family absorbing on the UV domain”***

Ph.D. Thesis, October 2004, Toulouse, France.;

Research Adviser: Isabelle Rico-Lattes

*Université Paul Sabatier de Toulouse, Laboratoire des Interactions
Moléculaires et Réactivité Chimique et Photochimique, CNRS UMR 5623,
31062 Toulouse (France)*

Chairman's Letter

NEW FACES

The EPA General Assembly held in July 2004 in Granada, Spain, on the occasion of the IUPAC Symposium on Photochemistry voted to appoint me as Chairman of EPA in succession to Jacek Waluk. Needless to say, I feel greatly honoured by this, and hope to discharge the duties well in the coming years. However, I should apologise for having made a slow start. Members will have noticed the hiatus in production of the EPA Newsletter. This has been caused in part by the handover from Jacek to me, but also by the tragic illness and untimely death of Jean Kossanyi, who acted as an extremely effective Editor of EPA Newsletter, and EPA Membership Secretary. We will all miss Jean's friendship, his zest for life, his humour, and his great contributions to our science. Elsewhere in this Newsletter there is a full appreciation of Jean. In the meantime, we have a willing volunteer, recruited by Jean, to take over the Editorship. This is Mohamed Sarakha, from Universite Blaise Pascal, Clermont Ferrand, France. Please support Mohamed in his heroic efforts to keep EPA Newsletter going in difficult initial circumstances.

One of the actions taken at the Granada EPA Assembly was to increase the membership fee, which we recognise will not necessarily be a wholly popular move. However, this is the first increase for a while, and was necessary to preserve the availability to EPA members of access to the journal, Photochemical and Photobiological Sciences. Other steps are being taken to increase the number of subscribers to PPS, which should result in the price being fixed for some time, obviating the need for any further sudden hikes in EPA membership charges. We will keep you informed of progress on this front.

The EPA Newsletter is published in hard copy only once per year, but will be available more frequently on the EPA website, which is in the process of being updated. The success of the Newsletter and web-site depend upon there being material for publication, so may I urge you all to send contributions to Mohamed Sarakha [mohamed.sarakha@univ-bpclermont.fr], or to me for inclusion in forthcoming editions.

We need the usual kind of contributions; conference reports, details of forthcoming meetings, conferences, Thesis extracts, personal news, news of

scientific breakthroughs, funding opportunities, big grants won, anything in fact which will make for interesting reading, and which will bind the Photochemical community together.

May I, as the [comparatively] new Chairman, invite you to let me know what EPA should be doing to try to enhance our association. My own feeling is that we should be doing more to help young scientists, but this is contingent upon raising funds for EPA. I would welcome your sharing with me any thoughts as to how we might do this as an association, or locally in your own countries.

David Phillips [d.phillips@imperial.ac.uk]

OBITUARY

Jean KOSSANYI (1932 – 2004)



“Who of the international community of photochemists does not know of Jean in one or several of his many ways, who will not rejoice at recalling the many times of participating with him in scientific exchanges of all sorts, at collaborating on science-related organisational occasions, and at sharing with him efforts in sports (sensibly, though, he has developed second thoughts on jogging) and more vital endeavours in the fields of oenology and gastronomy? Who will not join me in congratulations and wishing him all the very best for the next decades?”

I have had the pleasure to write these lines on the occasion of Jean Kossanyi's 70th anniversary, and I had concluded that “happily we can expect to continue to enjoy his delightful company for many years to come”.¹ But unpredictable as life is so often, his wife Paulette, their three sons and families, and numerous friends including many of his chemistry friends gathered on December 28, 2004, in the *Église Sainte-Anne de la Butte aux Caille* in Paris, to wish Jean a final farewell. He had passed away on December 23, after a brave fight for almost two years against the inevitable, *viz.* the progress of an unstoppable cancer.

Jean, of Hungarian origin, was global in many ways, attitudes and interests, but had strong bonds attached to his French homeland, in particular to Paris as well as to the Burgundy-Mâcon area. He was held in highest regard both as an international photochemist and as a personality characterized by a kind human touch. He loved to help and to entertain, and very many of his colleagues and friends from all over the world will cherish the memories of warm hospitality extended to them by the Kossanyis - either in their high-rise residence above the roofs of Paris, or enjoying a glass of the mellow local crus in front of their ancient farmhouse on the bank of the river Saône, or more recently overlooking the Mâconnais hills from their charming *Château de Chavy*.

Let us reiterate shortly his curriculum which had been summarized in greater detail three years ago.¹ Jean did all his studies - in organic chemistry - at the *Université Pierre et Marie Curie*. He was associated with the *Centre National de Recherches Scientifiques* (CNRS) already as a doctoral student. After his promotion in 1964 (*Doctorat-ès-Sciences Physiques de l'Université de Paris*), his career continued to proceed up through the ranks at the CNRS Centre at Thiais, occasionally interruptions by postdoctoral assignments in mass spectrometry with Carl Djerassi at Stanford (1964/5) and in photochemistry with George Hammond at Caltech (1969), and by lectureships at the Ecole Nationale Supérieure in Massy (1968-78), the universities of Rouen (1970/1), Orsay (1979-81), *Pierre et Marie Curie* (1982-97), Saõ-Paulo (1984 and 1988), and Berkeley (1988). His major positions at Thiais were Director of the *Laboratoire de Photochimie Solaire* (1980-85) and the *Laboratoire des Matériaux Moléculaires* (1992-95). He was appointed President of the Centre in the years 1983/4 and 1992/3, *Directeur de Recherche de 1^{ère} Classe* in 1990, and since 1998 he had been *Directeur de Recherche Emérite*.

Trained as a graduate student in organic synthesis, Jean's research was soon broadened and complemented by his keen interest in the application of modern spectroscopy. Indeed, mass spectrometry remained a prominent subject for quite a while. His first papers in photochemistry appeared in 1970, dealing mostly with structure-dependent ketone reactivities, and with interesting applications of photoreactions to key steps of natural product syntheses. A decade later new topics surfaced, such as studies of energy and charge transfer and photochromism - witness of Jean's alertness towards the progress and ever changing focus of scientific interest. It also demonstrates his command of a growing array of state-of-the-art physical methods, which were either established in his laboratory or became accessible to him by collaboration - often over periods of many years - with his many friends worldwide.

Still broadening the horizon of his research activities, photoconductivity, photoluminescence, electroluminescence and triboluminescence of rare-earth metal-doped semiconducting zinc oxide electrodes came into play (in the 1990s), culminating, *inter alia*, in a demonstration of the electroluminescence mechanism of the inserted rare-earth metal ions with a kinetic approach to the energy transfer between two rare earth metals incorporated into the same semiconducting electrode.

Jean's involvement in photochemistry, however, reached beyond the excitement and satisfaction which he enjoyed from laboratory research and teaching. He devoted enthusiasm, energy and much of his time also to scientific organization, at the national and international level. Thus, he was involved in numerous roles with the *Groupe Français de Photochimie* (president 1993-99), the *Société Française de Chimie* (secretary of the section *Ile-de-France*), the *Comité National du C.N.R.S.* (member 1975-83), and the Academy of Sciences of Brazil (member since 2000). Of special importance to the photochemists at large, and to the members of EPA in particular, was Jean's never ending commitment to our

professional community which he served as a Secretary-General (1973-77), and as Membership Secretary and Managing Editor of the Newsletter since 1999. While most of us will also remember his merits as an organizer of the 6th International Conference on Solar Energy Conversion and Storage and the 15th International Conference of Photochemistry (both in Paris 1986 and 1992, respectively), only the more seasoned among us have had the pleasure to attend already the 6th IUPAC Symposium on Photochemistry in 1976 which Jean organised so masterfully in Aix-en-Provence.

Jean has left a large number of colleagues and students, graduates and postgraduates within the scientific community, who join me in expressing our gratitude for having had the privilege of sharing a true personal friendship with him, and expressing our appreciation of a life devoted to photochemistry as a successful researcher and teacher, and as a scientist who readily accepted the additional challenges of activities which guarantee the complex function of a scientific discipline.

We all will miss his infectious smile and warm sense of humor. Jean will be remembered!

Kurt Schaffner
Max-Planck-Institut für Bioanorganische Chemie
(former MPI für Strahlenchemie)
D-45470 Mülheim an der Ruhr

¹ K. Schaffner, 70 Years of Jean Kossanyi. *EPA Newslett.* **2002**, 76, 37 - 40.

**Recent activities of the Inter-American Photochemical Society
By Pr. Peter C. FORD**

Department of Chemistry and Biochemistry
University of California, Santa Barbara, CA 93106-9510
ford@chem.ucsb.edu <http://fordgroup.chem.ucsb.edu>



Peter C. Ford

(805) 893-2443
(fax 805-893-4120)

March 2005

Report from the *Inter-American Photochemical Society*

I am writing at the invitation of EPA Chairman David Phillips to provide some news about the recent activities of I-APS. For those who are not familiar with our organization, the Inter-American Photochemical Society was formed about 30 years ago with the goal of promoting and disseminating knowledge and encouraging development of photochemistry and allied subjects throughout North, Central and South America. The scope encompasses the numerous areas related to the interdisciplinary nature of photochemistry, from photophysics to photobiology. We have about 500 members, about ten percent of whom reside outside the Western Hemisphere. The general structure and activities of the organization are described in our website listed below, but activities I will highlight are the annual I-APS Conference, usually held in early January, and the various I-APS awards. We also publish an annual newsletter, which will be available this Spring.

The 2005 I-APS Winter Conference was held in early January in Clearwater Beach, Florida and was organized by *Phil Castellano* (Bowling Green U.) and *Dirk Guldí* (U. Erlangen-Neurenberg). Both the content and the organization of the organization were excellent with about 120 in attendance, and this meeting again demonstrated the vitality of photochemical research and of I-APS. There were a number of students and first-time attendees as well as quite a few regulars. A wonderful range of speakers participated, from *Lakshmi Kaanumalle* of Tulane University (the **Closs Student Awardee**) and *Alvaro Delgadillo* of Pontifical Catholic University of Chile (the **Cilento Awardee**) to *Michael Kasha* (Florida State), who chided some of us on our relative youth. The mixture of talks illustrated the highly interdisciplinary character of photochemistry as it is practiced today.

During 2005 conference, the **I-APS Award in Photochemistry** was presented to *Devens Gust* (Arizona State U.) and the **Young Investigator Award** to *Igor Alabugin* (Florida State U), and *David Schuster* (New York U) and *Kerry Thomas* (U. Notre Dame) were inducted as new **I-APS Fellows**. Other I-APS news is that officers for 2004-2006 were elected last Fall, and the new I-APS Vice President (President-Elect) is *Cornelia Bohne* (U. Victoria). Newly elected Advisory Board members are *Claudia Turro* (Ohio State U.), *Lisa Kelly* (U. MD, Baltimore County) and *Teresa Atvars* (U. Campinas, Brazil).

The next I-APS Conference will be held in Salvador, Bahia, BRAZIL, in late May or early June 2006, and you should keep this in mind when scheduling meetings for next year. A preliminary announcement for this conference will appear on the I-APS web site, <http://www.chemistry.mcmaster.ca/~iaps/> once more details are available. Past I-APS conferences in South America have been very rewarding and I am very much looking forward to the 2006 meeting.

Sincerely,

Peter C. Ford
I-APS President (2004-06)



Conference report

4th International Symposium on Photochromism

ISOP'04

Photoswitchable materials and devices

Arcachon (France), September 12-15, 2004.

The 4th International Symposium on Photochromism (ISOP'04) was held in Arcachon (France) from 12 to 15 september 2004. This series of symposia was initiated by Professor Robert Guglielmetti (Université de la Méditerranée at Luminy, France) who organized the first one in Les Embiez, France in 1993. The second one was organized by Dr Crano at Clearwater, Florida in 1996. The third one was organized by Professor Masahiro Irie at Fukuoka, Japan in 1999. The present one was co-chaired by Professors Jean Pierre Desvergne and Jean-Luc Pozzo from the Université Bordeaux 1. The number of participants from University and Industry was around 170, from more than 20 countries. Nowadays, photochromism is one of the most active branch in photochemistry and photophysics. In the early 1990s, this field received a strong impulse from the successful commercial development of organic photochromic ophthalmic lenses and the anticipation of applications in many areas. Since then, fundamental and applied research on photochromics has known an increasing activity with the finding of new molecular architectures exhibiting various optical properties and new potential applications in different domains extending from optical data processing and storage to optical computing, magnetism, astrophysics, chemical analysis, medicine and biology. Indeed, as photochromism is accompanied by the change of several physical and chemical properties, this light-driven process – generally very fast – provides a convenient way to switch or trigger changes of measurable physical quantities or to induce changes of conformation or reactivity of molecular assemblies.

The opening lecture was given by Professor Irie on the photochromism of diarylethene single crystals and single molecules. Since their discovery in 1988 by Professor Irie, *diarylethene derivatives* have clearly emerged as one of the most attractive photochromic families for applications which do not need thermal reversibility, mainly because of their excellent thermal stability. The large number of

posters (28) and oral contributions (9) dealing with different aspects of these compounds gives some idea of their importance. New related chemical structures have been proposed (M. Irie, V. Barachevsky, A. Samat, Y. Yokoyama, M. Krayushkin). Photochromism of *diarylethene derivatives* was also investigated in polymers (E. Kim, K. Uchida), in polysilicate hybrids (K. Takagi) or in nanolayered structures (S. Kobatake). Different functional groups have been attached to *diarylethenes* in order to provide new properties which can be triggered by photochromism: photoelectron transfer (D. Gust), photoemission (R.T.F. Jukes), NLO properties (A. Léaustic), molecular electronics (T. Tsujioka, C. Chiorboli, C. Coudret, V. Rodriguez and J.-L. Pozzo, T. Kudernaca), magnetism (P. Yu, N. Tanifuji), holography (C. Bertarelli), liquid crystals (G. H. Mehl), organogels (J.-L. Pozzo), optical recording and non destructive readout (K. Uchida, F. Hartl, A. Bianco), chemical reactivity (N. Branda). Finally, during the last lecture, I. Colombier presented a new photomechanical effect in photochromic *diarylethene crystals* which jump away from the laser beam.

ISOP'04 was a showcase of all the last developments of molecular engineering, structural and dynamic studies and applications of the different classes of photochromic systems. New spiropyrans and spirooxazines have been synthesized (V. Lokshin and A. Samat, V.I. Minkin, A. Shimkin, A. Metelitsa, N.L. Zaichenko, O.A. Fedorova) with different objectives : to find ecologically friendly methods, to increase stability of the open form, to add fluorescent groups or complexing cavities for the selective entrapping of ions...The creation of new hybrid materials based on spiropyrans salts and metal oxalates opens the way to photoswitching of magnetic properties (S.M. Aldoshin). Different contributions dealt with chromenes, an old class of photochromic compounds which has been deeply revisited because of their application for ophthalmic lenses (O. Breyne). These new developments include new chemistry (A. Samat, C. Moustrou, J.-L. Pozzo, M.-J. Queiroz, M. Oliveira, P.J. Coelho, C. Gabbut), new theoretical, photophysical and NMR studies (F. Maurel, J. Aubard, G. Favaro, G. Vermeersch).

Although less developed than diarylethenes, *fulgides* represent another class of photochromic substances whose colored form is thermally stable. They are developed for the possibility of fluorescence photoswitching (H. Port), or for optical memories (Y. Chen, H. Miyasaka).

It would be tedious to enumerate all the old and new photochromic compounds presented along the oral and poster sessions. Among them, are the *dimethyldihydropyrenes* (C. Bohne) and the *tetrahydropyrenes* (M. Takeshita), the *dihydroazulenes* (J. Daub), the *tetracenes* (H. Bouas-Laurent, J.-P. Desvergne, A. Del Guerzo), the *quinolones* (A. Samat), the α -*thioxoketones* (J. Waluk), the *dinitrobenzyl pyridines* (A. Samat), the *bis-imidazoles* (J. Abe, Y. Nagasawa), the *salicylidene anilines* (K. Nakatani), the *triphenylmethane derivatives* (R.M. Uda). Natural *photochromic systems* like *bacteriorhodopsin* (N. Hampp, O.V. Demina) or others mimicking natural *phototropin* (J. Daub) have also been presented. It should be noted that, besides all the applications mentioned above, a large effort has been made to develop chemosensors by coupling different complexing units like azacrown ethers with photochromic subunits, such as naphthopyrans (O. Fedorova), spiropyrans (A.A. Khodonov), hetarylphenylethenes (E.N. Andryukhina), or butadienyl dyes (S. Zaitsev).

The conference was held in the "Palais des Congrès" of Arcachon, located along the picturesque bay named "Bassin d'Arcachon". The delegates were welcomed by the chairmen and the mayor of Arcachon who gave a substantial oysters tasting party. This was the starter of a welcome mixer where the veterans of ISOP joyfully met each other and welcomed the new comers. The atmosphere of the conference was very lively and the talks and presentations were followed with great interest by all the participants, including a memorable evening poster session accompanied by a buffet washed down with excellent Bordeaux wines, that made easier the understanding of the posters. Last but not least, an exhibition of equipment and photochromic materials nicely completed the Symposium. In spite of an unusually unpleasant weather, the participants enjoyed the place, with so many excellent sea food restaurants. The excursion to St Emilion, the visit of a famous vineyard and the banquet in Château La Couspaude with the sampling of different "Saint Emilion Grand Crus " will certainly remain as one of the most pleasant recollection of ISOP'04. The next Symposium (ISOP 07) will be organized by Professor Neil Branda, in Vancouver Canada, in 2007.

Conference report

8th International Conference on Solar Energy and Applied Photochemistry

SOLAR '05 and Enpho'05

20-25 February 2005, Luxor, Egypt

Klaas A. Zachariasse

-Spectroscopy and Photochemical Kinetics-

Max-Planck-Institute for biophysical Chemistry,

37070 Göttingen, Germany

The conference SOLAR '05 is the eighth in this very successful series organized by the Chairman Professor Sabry Abdel-Mottaleb, accompanied now for the fifth time by the international workshop on environmental photochemistry Enpho'05. The large and continuing interest of the scientific community for this conference is documented by the attendance of 203 participants (69 from Egypt) from 32 countries. The program contained 63 lectures and 90 posters.

The opening ceremony of the Conference was attended by Prof. Dr. Ali Al-Abd, the Vice President for research and higher studies of Ain Shams University (Cairo) and the president of the steering committee of the Photoenergy Center, an Institute founded by Prof. Abdel-Mottaleb.

The Conference then started with four plenary lectures (40 minutes), in a joint session with the 1st Conference on Nanotechnology, which was held simultaneously at the same location, the Pyramisa Hotel. The lectures and their titles were: *K. Müllen (Mainz, Germany)*: Putting the Molecules into Molecular Electronics. *G.Q. Max Lu (Brisbane, Australia)*: Novel Method of Synthesis of Mesoporous and Nanocrystalline TiO₂ for Dye-Sensitized Solar Cells. *P.K. Hansma (Santa Barbara, USA)*: Lessons for New Nanotechnology from Nature's Nanotechnology. *C. Levy-Clément (Paris-Thiais, France)*: A New Eta-Solar Cell Based on Free-Standing ZnO/CdSe Nanowires.

The topics discussed at the SOLAR'05 and Enpho '05 were largely grouped into two main categories: (a) (solar) photocatalysis and atmospheric photochemistry and (b)

photochemistry, photophysics and photobiology, including electron and energy transfer.

The titles of the following 12 Plenary Lectures (40 minutes) show the wide scope of the topics treated at the Conference: *R. E. Baier (Buffalo, USA)*, Solar-Activated Photocatalytic Purification of the Clinical Air Circulating in a Dental Hospital. *I.R. Bellabono (Milan, Italy)*, Photocatalytic Membrane Processes and Plants for Purification of Water and Air; State of the Art and Industrial Issues. *G. Kaup (Oldenburg, Germany)*, SNOM: a New Photophysical Tool for Chemistry and Life Sciences. *S. Lis (Poznan, Poland)*, Photophysical Characterization of Chosen Ln(III) Macromolecular Complexes with Inorganic and Organic Ligands in Solution and Solid. *K.A. Zachariasse (Göttingen, Germany)*, Intramolecular Charge Transfer in the Excited State. *V. Vaida (Boulder, USA)*, Sunlight Initiated Reactions in Atmospheric Chemistry. *K. Hashimoto (Tokyo, Japan)*, Environmental Preservation Technologies with TiO₂ Using Solar Light. *D. Bahnemann (Hannover, Germany)*, Solar Photocatalysis: Cleaning Polluted Water, Air and Surfaces with Sunlight. *M.A. Aegerter (Saarbrücken, Germany)*, Electrochromic Devices Made by the Sol-Gel Process: State of the Art and Issues. *A. Vlček (London, UK/Prague, Czech Republic)*, Ultrafast Photochemical Electron and Energy Transfer in Complexes $fac-[Re^1(L)(CO)_3(2,2'-bipyridine)]^{n+}$. *R. Loutfy (Tucson, USA)*, Fullerene Nanoparticles and Applications. *N. Russo (Calabria, Italy)*, Time-Dependent Density Functional Theory and Photodynamic Therapy.

Besides the plenary lectures, 15 Keynote Contributions (30 minutes) were presented, about evenly divided over the two main Conference topics: (a) water treatment (*J.-M. Herrmann (France)*, *M. Mehrvar (Canada)*, *V. Loddo (Italy)*, *O. Zahraa (France)*), photodegradation (*A. Zarkadis (Greece)*, *P. Mazellier (France)*, *M. Sarakha (France)*) and photocatalysis (*J. Blanco (Spain)*, *C. Guillard (France)*) and (b) intramolecular charge transfer (*W. Rettig, Germany*), long-lived charge transfer states (*J.W. Verhoeven, Netherlands*), chemical sensors (*G. Orellana, Spain*), artificial light-harvesting (*S. Balaban, Germany*), luminescent materials (*A.M. Klonkowski, Poland*) and a photorechargeable cell (*T. Miyasaka, Japan*).

An important part of the oral contributions consisted of 32 short lectures (20 minutes) on water treatment, photodegradation, ultrastable fluorescent dyes, photocatalysis,

photochemistry, photobiology, nanoparticles, solar energy conversion, long range electron transfer, excited state relaxation and luminescent microcrystals. These lectures were delivered by B. Legube (France), J. Correia de Oliveira (Portugal), C. Pulgarin (Switzerland), L. Österlund (Sweden), S.Y. AlQaradawi (Qatar), W.M. Nau (Germany), B. Sánchez (Spain), P. Kurz (Switzerland), K. Akutari (Switzerland), J.P. Da Silva (Portugal), B.S. Lukyanov (Russia), S. Szarska (Poland), D. Bahnemann (Germany), J. Dussaud (France), J. Yu (HongKong), J.S. Lee (Korea), I. Pastoriza (Spain), E. Selli (Italy), J.C.S. Wu (Taiwan), S. Zálíš (Czech Republic), S. Ali (USA), N. Sakai (Japan), C.-S. Kim (Korea), K.-J. Kim (Korea), V. Jovanovski (Slovenia), L. Brohan (France), M.A. Rampi (Italy), B.M. Uzhinov (Russia), S. Fery-Forgues (France) and T. D. Karapantsios (Greece).

Besides the lectures, 90 Posters were presented in two evening sessions. The lively discussions that often arose in front of the posters underline the important contribution made by the poster authors to the scientific success of the Conference.

During the closing session of SOLAR '05/Enpho'05, the speakers R.E. Baier, J. Blanco, J.-M. Herrmann, S. Lis, B. Uzhinov, J.W. Verhoeven, V. Vaida and K.A. Zachariasse expressed their compliments and gratitude to the Chairman M.S.A. Abdel-Mottaleb and his team for the excellent organization of the Conference and made it clear that this Conference plays a very important role in the development of solar energy and applied photochemistry. The fact that the new Nano-Tech Conference was being held simultaneously in the same location, can offer for the attendees of both meetings the unparalleled opportunity to 'look over the fence' and extend their scientific interest with new vistas, even further than was already offered by the joint starting session of both Conferences. For a full list of *the speakers at the Conference on Nanotechnology*, www.nanoinsight.net may be visited.

The social program of the SOLAR '05/Enpho'05 consisted of two excursions for all participants and the Conference Banquet. On the Monday afternoon, a visit was organized to Karnak, the Temple of Amun. Even for those who had visited Karnak before, the vast size and artistic excellence of the ancient temples, constructed mainly during the New Kingdom (1550-1075 BC), exerted an unforgettable impression. The last day of the meeting (Friday) was reserved for a full-day excursion to the west bank: the Memnon Colossi, the famous mortuary temple Deir el-Bahri of

the female pharaoh Hatsheput (1503-1482 BC), of a surprisingly modern architecture, and the Valley of the Kings, where the pharaohs of the New Kingdom, such as Tutankhamun (1333-1323 BC), Seti I (1289-1279 BC) and Ramses II (1279-1212 BC) have been entombed. The excursion was concluded with a visit to the huge temple Medinet Habu, constructed for Ramses III (1184-1153 BC). Besides the impact of the historic importance and architectonic excellence of the temples and tombs, the scenery on the west bank of the Nile, opposite to Luxor, is of impressive beauty. In addition to the excursions for all participants, an extensive program was organized for the accompanying persons, with visits to the museum and bazars in Luxor and the temple of Dendera.

The Conference Banquet, an Oriental Evening, was held on the Wednesday in the Khan El-Khalili Hall of the Pyramisa Hotel. The excellent selection from the Egyptian cuisine was further enlivened by a Nubian folklore program, including a sufi dancer. This program was followed by the performance of a belly-dancer, who induced many participants to show their mastery of this kind of dynamic art.

An important number of participants extended their exposure to Egypt by taking part in the post-conference excursion to Aswan, with visits to the temples of Edfu, Esna and Kom-Ombo on the way.

In conclusion, I am sure to speak in the name of all attendees when I congratulate Prof. Sabry Abdel-Mottaleb and his staff with a highly successful and enjoyable SOLAR '05/Enpho'05 and we all look forward to the following meeting in this series.

Klaas A. Zachariasse

-Spectroscopy and Photochemical Kinetics-

Max-Planck-Institute for biophysical Chemistry,

37070 Göttingen, Germany

Abstracts of thesis

Fabienne Wetz (France)

Université Paul Sabatier de Toulouse, Laboratoire des Interactions Moléculaires et Réactivité Chimique et Photochimique, CNRS UMR 5623, 31062 Toulouse.

***New long chain molecules derived from Parsol[®] 1789 :
a new solar filters family absorbing on the UV domain***

Ph.D. Thesis, October 2004, Toulouse, France.

Research Adviser: Isabelle Rico-Lattes

4-*tert*-butyl-4'-methoxydibenzoylmethane (called BM-DBM) is a UVA filter currently used in cosmetic preparations like sunscreens. It absorbs solar energy and filters UVA rays with a maximum efficiency near 340 nm^[1]. This absorbance is due to resonance throughout a large part of the molecule owing to a hydrogen bond that creates a six-bond pseudo-cycle between the carbonyl and the enol group. Two tautomers of the molecule exist: enol and diketone forms (Figure 1). The enol is the most stable form of the molecule.

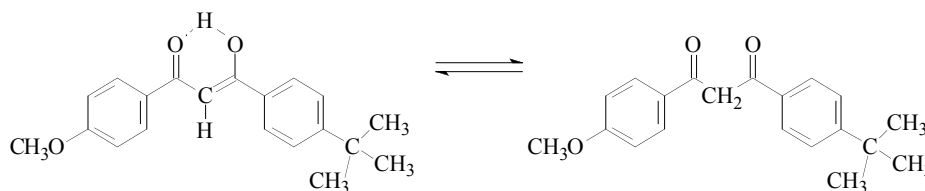


Figure 1. Tautomeric equilibrium of BM-DBM.

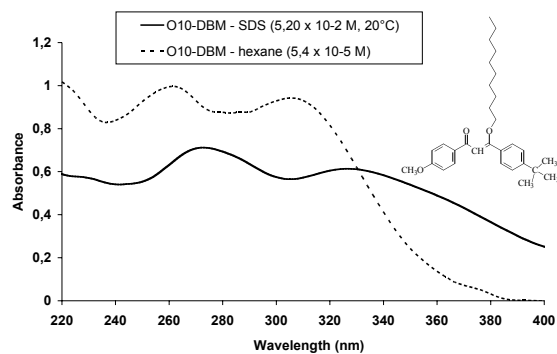
Like most dibenzoylmethane derivatives, BM-DBM undergoes rapid keto-enol photoisomerisation by proton transfer. The diketone absorbs UVB and UVC rays. For longer irradiation times, the diketone form undergoes α -photocleavage by way of the Norrish type I mechanism. Our aim was to design a more stable molecule derived from BM-DBM. Our strategy was to stabilize the enol form.

The environment has an important impact on the tautomeric equilibrium of dibenzoylmethanes and may cause equilibrium shifts. It seems that a non-polar environment would favour strong intramolecular hydrogen bonding, thus the enol form. A long aliphatic chain chemically grafted onto BM-DBM should induce the

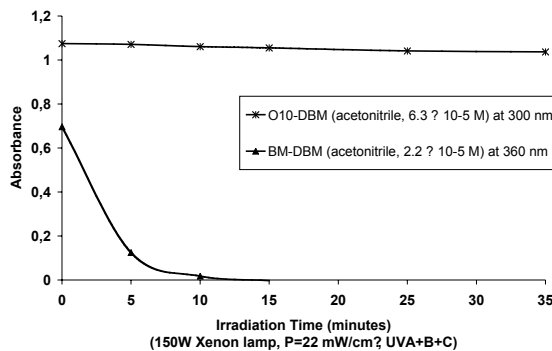
migration of the molecule into a more apolar environment in complex preparations such as cosmetic preparation. It should thus favour the enol form and limit photodegradation.

A new UVA filter, the 1-(4-*tert*-butylphenyl)-2-decyl-3-(4'-methoxyphenyl)propane-1,3-dione (C10-DBM), was prepared by grafting a ten-carbon aliphatic chain to the α -carbonyl position of BM-DBM^[2]. The 3-(4-*tert*-butylphenyl)-3-decyloxy-1-(4'-methoxyphenyl)prop-2-ene-1-one (O10-DBM) was prepared too^[2]. C10-DBM and O10-DBM were obtained according to a modified Clark and Miller^[3] procedure and a global yield of 93% was reached, 42% for the C-alkylation and 51% for the O-alkylation^[4].

The molecular structure of O10-DBM was ascertained with NMR spectroscopy. O10-DBM is obtained as four isomers : two positional isomers (the aliphatic chain can be grafted on either of the two carbonyl oxygens) which have two geometric isomers (cis/trans). O10-DBM absorbs UVB+A rays in organic and organized media (Figure 2 (a)). In organic solvents, O10-DBM absorbed in the UVA+B domain with two maxima absorption near 260 and 306 nm ($\epsilon_{306 \text{ nm}} = 17\,400 \text{ M}^{-1} \text{ cm}^{-1}$ in hexane). When O10-DBM was incorporated in an organized environment, a micellar solution of SDS, the UV spectrum showed large absorption band with ϵ_{max} at 274 nm and 328 nm. An organized environment induced a bathochromic shift. Under irradiation, O10-DBM exhibits photostable behaviour even under strong conditions (35 minutes under a 150 W xenon lamp irradiation, UVA+B+C, P=22 mW/cm², Figure 2 (b)).



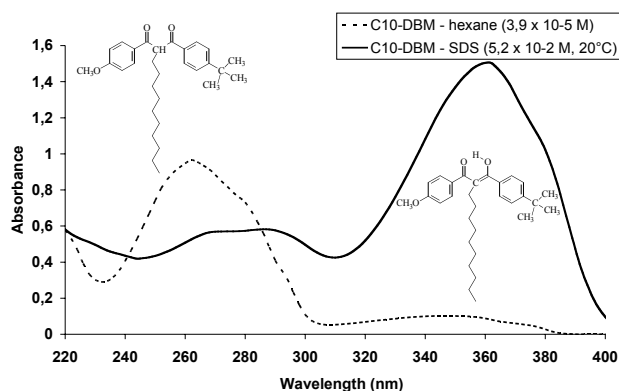
(a)



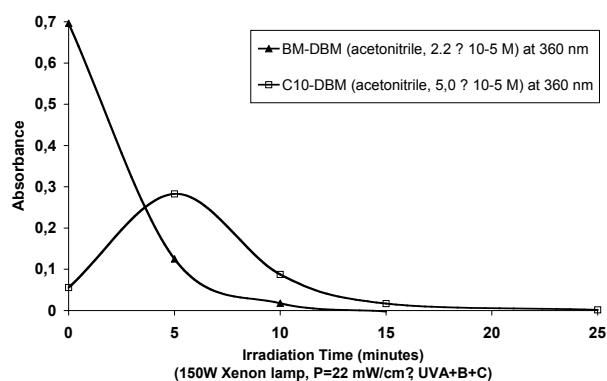
(b)

Figure 2. (a) UV spectra of O10-DBM in hexane and in a micellar solution of SDS. (b) Absorbance variation of solutions of BM-DBM and O10-DBM in acetonitrile under a 150 W xenon lamp irradiation.

C10-DBM in organic solvent only occurs in its beta-diketone form. The long aliphatic chain of the new molecule prevents the equilibrium with its steric-hindrance. C10-DBM absorbs UVB rays in organic solutions ($\lambda_{\text{max}} = 263 \text{ nm}$, $\epsilon_{\text{max}} = 25000 \text{ M}^{-1} \text{ cm}^{-1}$ in hexane). When C10-DBM was placed in an organized environment, a micellar solution of sodium dodecyl sulfate (SDS), the UV spectrum showed two absorption bands: a first band corresponding to the diketone form with an absorbance maximum at 288 nm and a second corresponding to the enol form at 360 nm. An organized environment seemed to favour the enol form which absorbed UVA rays (Figure 3 (a)).



(a)



(b)

Figure 3. (a) UV spectra of C10-DBM in hexane and in a micellar solution of SDS. (b) Absorbance variation of solutions of BM-DBM and C10-DBM in acetonitrile under a 150 W xenon lamp irradiation.

The UVA absorption efficiency of organic solutions containing C10-DBM was tested and compared to identical solutions containing BM-DBM with or without irradiation (xenon lamp). The originality of this new filter is that its UVA absorbance appeared during irradiation of the molecule (Figure 3 (b)). We demonstrated that C10-DBM was a precursor of BM-DBM (enol isomer) by means of high-performance liquid chromatography followed by mass spectrometry^[4]. Indeed, we showed that the UVA absorption of C10-DBM solutions appearing during the irradiation of the molecule was due to a Norrish type II reaction (α -cleavage) which induced the release of the BM-DBM enol form and 1-decene (Figure 4). This mechanism was confirmed and its efficiency was estimated with the help of a kinetic model^[4]. The photochemical behaviour of C10-DBM shows an important benefit for cosmetic applications.

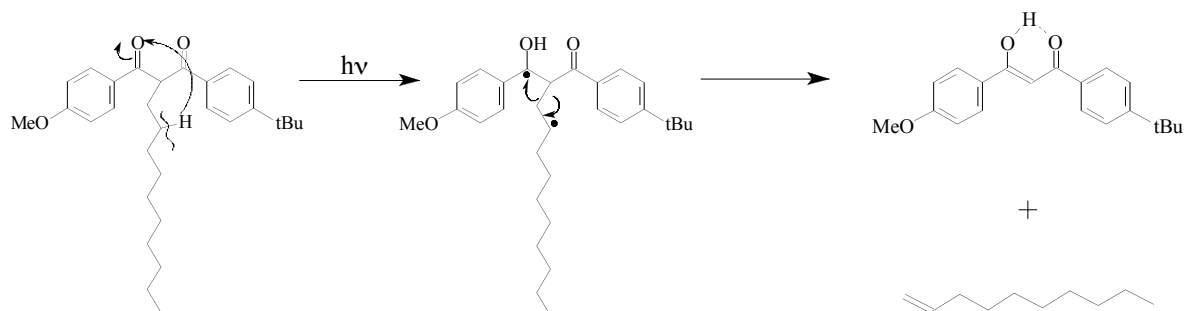


Figure 4. Proposed mechanism for the photodegradation of C10-DBM.

UVA absorption efficiency of UVA sunscreen preparations containing C10-DBM or O10-DBM in water-in-oil preparations similar to those currently used in cosmetics, were tested and compared to an identical preparation containing BM-DBM. The three preparations were irradiated under a 150 W xenon lamp or exposed to natural sunlight. Moreover, although the molar absorption coefficients of C10-DBM and O10-DBM in the UVA domain were lower than that of BM-DBM, its absorption showed much more photostable behaviour under both methods of irradiation. After 2 hours of sunlight exposure, the preparation containing the BM-DBM lost 85% of its

UVA absorbance whereas the UVA absorbance of the preparation containing O10-DBM remained stable. The UVA absorbance of the preparation containing C10-DBM showed a decrease of 3% in comparison to the maximum absorbance obtained after 30 minutes of irradiation. Besides, after 2 hours of exposure to natural sunlight, the UVA absorbance of the preparation containing C10-DBM remained above its initial value (before the irradiation began)^[5]. The use of both filters together, BM-DBM and C10-DBM, the first one for its high UVA absorption and the second one for its ability to supply BM-DBM under irradiation, results in good stability of the UVA protection. Moreover, cosmetic preparations containing both C10-DBM, O10-DBM and BM-DBM exhibit UVA absorbance which remains, under irradiation, at useful levels for longer than cosmetic preparations containing only BM-DBM.

References

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