NZIC Chemistry
IN NEW ZEALAND

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Horopito leaves from http://en.wikipedia.org/wiki/File:Pseudowinteracolorata.jpg
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New Zealand Institute of Chemistry

supporting chemical sciences

October News

Comment from the President and ICY 2011

It is now just a few months until the end of the 2010 – and that means the start of the 2011 International Year of Chemistry. I am pleased to report that the major NZIC events have been planned and a programme of events for the year written. These will all have been discussed by Council at its September 3 meeting when this is in press. We have used the services and inspiration of Glenda Lewis to develop some really exciting ideas and publicity for the IYC 2011 events will start appearing toward the end of this year, so keep a look out for that. And it is also great to see that, in addition to the larger scale national events that Council is coordinating, Branch committees have enthusiastically embraced this opportunity to promote chemistry to the public and have developed a number of their own events. Be sure to register on the IYC 2011 website and enter all your local events so the rest of the country can see what is being planned.

During our discussions we have thought very carefully about how to maximise the impact of IYC 2011. There is the need to make a big splash and capture the attention of the media and public during the year. And so our programme involves a small number of events that are designed to have high profiles for this purpose. At the same time, IYC 2011 is a good opportunity to build relationships with groups such as teachers (both high school and primary) and, in my experience, NZIC needs to demonstrate how it can have a positive impact on the teaching of chemistry in NZ for teachers to consider us a worthwhile investment of their time. Through our IYC 2011 activities, we hope to develop a range of useful resources for teachers and the general public that achieve the aims of IYC 2011 but continue to have an impact in 2012 and beyond.

We are putting plans in place to ensure that our web presence for IYC 2011 is absolutely top-shelf. In my opinion, a useful and informative web-presence is one of the keys to ensuring the growth of NZIC in the future. The NZIC tag-line is ***supporting chemical sciences*** and having an informative and authoritative NZIC website is one of the most direct methods for supporting chemical sciences in New Zealand.

Mark Waterland
President

NZIC NEWS

2010 PRIZES

Council offers its congratulations to the following recipients of its 2010 prizes:

The Maurice Wilkins Centre Prize for Chemical Science:

Prof *Keith* ***Gordon*** (Department of Chemistry, Otago University)

The Fonterra Prize for Industrial and Applied Chemistry:

A/Prof. *David* ***Harding*** (Institute of Fundamental Sciences, Massey University)

The Denis Hogan Chemical Education Award:

Dr *Jan* ***Giffney*** (St Cuthbert's College, Auckland)

NZIC MEMBERSHIP MATTERS

FNZIC

Council has elected to its Fellowship and offer its congratulations to former Members:

Dr *Gareth* ***Rowlands*** (Institute of Fundamental Sciences, Massey University)

Dr *Richard* ***Tilley*** (SCPS, Victoria University)

Dr *Peter* ***Tyler*** (Industrial Research Limited)

MNZIC

Dr *Geoff* ***Waterhouse*** (University of Auckland)

Dr *Vyacheslav* ***Fifichev*** (Massey University)

Mrs *Heather* ***Velvin*** (Freyberg High School)

Mr *Mark* ***Reynolds*** (Fonterra)

STUDENT MEMBERS

Miss *Yiwen* (*Angela*) ***Pei*** (University of Auckland)

Mr *Nicholas* ***Monahan*** (Victoria University)

Mr *Juan Olguin* ***Talavera*** (University of Otago)

BRANCH NEWS

AUCKLAND

In recent months NZIC Branch seminars in Auckland were given by NZIC President Dr *Mark* **Waterland** (May) (IFS Massey) who spoke on *Strongly absorbing and Metal-to-ligand charge-transfer states in novel* *ruthenium dipyrrin complexes: Probing ultrafast dynamics with resonance Raman spectroscopy* and Dr *Michael* **Edmonds** (August) (CPIT) on *Fluorine, Plant Nutrients and Animated Chemistry*.

University of Auckland

The second annual June Chemistry Research Showcase was a highlight for the Department, and featured PhD student presentations from *Norizah* **Abdul Rahman**, *Lauren* **Ferguson**, *Catrin* **Guenther**, *Philip* **McGill**, *Elizabeth* **McKenzie**, *Claire* **Rye**, *Zoe* **Wilson**, *Tsz Ying* **Yuen**. The day also featured a thought-provoking address by *Steve* **Wilson** (Managing Director, Talbots Plastics Ltd.) who underlined the need for the clever chemistry and thinking for industries that thrive in the NZ setting.

A different well attended event recognized several research facilities in the basement that included the Photon Factory, the Auckland Microfabrication Facility and the XRD Laboratory. They have taken up premises there over the past year or so with the NMR Centre and Free Radical Research facility. The high quality of these research facilities and their personnel was recognized, along with their importance for future research directions within the Department and wider University.

A/Prof *Yacine* **Hemar** joined the Department in July as a new member of the Food Science programme and has already been successful in gaining permission to establish a Food Microstructure Facility, based around the physical chemistry of food materials. Yacine has been appointed recently to the Editorial Board of the Elsevier *Food Hydrocolloids* journal. Dr *David* **Ware**, a well-established member of the Department, was appointed Senior Tutor with the role of Departmental Laboratory Manager. A number of our general staff have recently received Professional Development Awards and included *Min-Young* **Lee**, *Sreeni* **Pathirana**, *Anoma* **Ratnayake**, *Jan* **Robertson** and *Mike* **Wadsworth**. The awards typically support travel to courses, workshops and conferences.

A media release involving research from within Chemistry came in June, from results showing that the loss of fruity and tropical aromas in Sauvignon Blanc wines, commonly observed over the first year in the bottle, comes about, not from oxidation and wine closure issues, but from hydrolysis of a key acetate component in the wine. As with all ester hydrolyses of this type, the reaction is accelerated by lowering the pH or by raising the temperature, emphasizing the need for greater refrigeration during prolonged storage of NZ's leading export wine.

Recent seminars from visitors to Chemistry have included: Dr *Don* **Eigler** (IBM Fellow, IBM Almaden Research Center) who spoke on *Spin Excitation Spectroscopy* (and the development of a new kind of spin spectroscopy to interrogate both the energetics and dynamics of spin systems on the atomic scale); *Zvonimir* **Katancic** (Chemical Engineering and Technology, University of Zagreb), a research visitor to PERC, who spoke on *Fire retarded polymer nanocomposites*; Dr *Ashton* **Partridge** (Massey University) who gave an overview of research developments in his group in sensing and photovoltaics research and the applications of nanotechnology in a range of areas. Prof. *Kevin* **Smith** (Novel Materials Lab, Boston University) also presented a seminar on *Organic Photovoltaics*.

Prof *Peter* **Schwerdtfeger** is to chair two symposia at Pacifichem 2010 and present some of his own work.

CANTERBURY

May 12th saw a fascinating talk by *Darren* **Saunders** from ESR on *Food forensics: the application of forensic sciences to the investigation of food safety, quality and authenticity*. Branch members were enthralled (and occasionally repulsed) by cases of foreign matter, undesirable taints and false claims associated with foods that have been investigated by the ESR Food Chemistry Laboratory. On June 3, Dr *Paul* **Wyatt** (Bristol University) presented a talk entitled *Teaching innovations – using technology to enrich the traditional* to Branch members and local chemistry teachers. Paul described many of the innovative techniques used to teach practical chemistry at Bristol as part of the Chemistry School's Laboratory Sciences, known as the ChemLabS programme. It has been designated one of England's 74 Centres for Excellence in Teaching and Learning.

On July 14, Dr *Michael* **Edmonds** (Applied Sciences and Allied Health, CPIT) addressed the Branch on *Fluorine, plant nutrients and animated chemistry*. He presented material from a range of research projects that he has been involved in over the last ten years that included the synthesis of novel monofluorinated molecules, the analysis of the nutritional content of NZ edible plants, and the development of interactive chemistry animations as teaching resources. The annual Branch dinner was held at Visions restaurant, CPIT campus, on July 29 and it was enjoyed by all who attended.

On August 18, Erskine visitor to the Canterbury University's Chemistry Department, Prof. *Philip* **Doble**, presented a talk entitled *Environmental and forensic applications of hyphenated quadrupole time of flight – mass spectrometry (QTOF-MS)* to a good turn-out of NZIC members. Prof Doble gave details of a quick and cheap assay for 130 different pesticides (in 12 minutes) in vegetables developed at the Sydney University of Technology, and how the combination of capillary electrophoresis with QTOF-MS enabled the identification and quantification of minute amounts of disperse dyes extracted from single fibres and the techniques relevance to crime scene investigations.

The Canterbury Westland School's Science and Technology Fair was held over Sunday and Monday August 29/30 at the AMI stadium in Christchurch. *Darren* **Saunders** judged the projects on behalf of the Canterbury Branch and prizes for the best chemistry related exhibits were awarded to:

Thomas **Ferguson** (Year 9$^+$ category) for his project: A dairy algae industry in Canterbury, which looked at the production of algae derived bio-fuel using dairy waste.

Emma **Clucas** (Year 8 category) for her project: Polystyrene recyclene that looked at possible methods for recycling of polystyrene.

Hugh **Martin** (Year 8 category) for his project: Can seawater be made drinkable? He considered whether it could be purified by freezing it.

Tristen **Read** (Year 7 category) for his project: To pee or not to pee – compost, that looked at whether the addition of urine to compost made any improvement.

CPIT

Dr *Margaret* **Leonard** has been appointed as the new Technology Transfer Manager. This new role will have Dr Leonard oversee the interaction between CPIT and Canterbury employers, and will continue to develop the Institute's research capacity. Dr Leonard previously worked with the Wastewater group at the ESR Christchurch Science Centre.

CPIT's third annual Research Week was held over 21-27 of August. The poster and oral presentations described the various research carried out by CPIT staff and students and these included three oral presentations by chemistry staff. Dr *Barbara* **Dolamore** spoke on her work looking at *The effect of rapid chilling, time and maleimide on adrenocorticotrophic hormone (ACTH) in haemolysed blood*, Dr *David* **Hawke** described his work *Preparation of a client reference material for stable isotope analysis*, and Dr *Michael* **Edmonds** presented his preliminary findings on *Using animations as a tool for learning chemistry*.

University of Canterbury

The Prime Minister officially opened the Biomolecular Interaction Centre (BIC) on Friday May 14. Three students gave short presentations about their PhD research at a morning tea function attended by the Prime Minister and a large number of University of Canterbury staff. The UC Information Day was held in early July and lectures regarding the degree programmes on offer by the Chemistry Department were given by A/Prof *Paul* **Kruger**. Postgraduate assistants, *Dave* **Garett** and *Penel* **Cross** spoke about their undergraduate experiences and gave presentations on their current work. Following a lively question session, a guided tour of Chemistry was conducted by Dr *Chris* **Fitchett** for interested parties.

On July 28 Prof *Ian* **Shaw** gave a well received presentation to a variety of food industry representatives including producers and food scientists. His talk focussed on the newly set-up Food Safety Centre, a joint venture between Canterbury and Lincoln Universities, set up with funding from the Tertiary Education Commission. Prof Shaw has been appointed the Centre Director and aims not only to help industry and scientists become better acquainted, but to develop university courses relevant to industry that cover a range of topics including bacterial and chemical contamination to safety issues relating to the development of new food products. The centre is based at Lincoln and will have two lecturers who will draw on other food safety experts from organisations such as the Food Safety Authority and CRIs to develop a research programme and ultimately a MSc degree in food safety.

Recent Erskine visitors include Dr *Paul* **Wyatt** who completed his PhD at Cambridge and undertook postdoctoral work in Uppsala before being appointed to Bristol in 1996. His research interests are in asymmetric methods in organic chemistry, teaching and teaching innovation (especially in laboratories). Paul spent some weeks teaching CHEM408 and presented the Department with copies of his four books before his departure in June. Erskine visitor Prof *Vickie* **McKee** (Loughborough University) gave a seminar mid-May entitled *Double template effect – mechanism and manipulation*; she also left in June. Our students thoroughly enjoyed her lectures and she was of considerable help to some of the research students. Vickie is interested primarily in the synthetic and structural aspects of coordination chemistry, with particular emphasis on the use of geometric factors to control metal-metal interactions and other properties of bi- or polymetallic systems.

Other visitors have included *Katrina* **Staggemeier** (University of Alabama) who worked with *Vladimir* **Golovko** for eight weeks under a jointly funded NSF-RSNZ grant, known as the East Asia and Pacific Summer Institutes; she was one of sixteen Fellows chosen. *Alan* **Ferguson**, from Dumbarton, arrived in July to work in A/Prof *Paul* **Kruger**'s group during his 30 month stay with the Department. Alan completed his PhD at the University of Glasgow under the supervision of Dr *Mark* **Murrie**. Early in June Dr *Justin* **Hodgkiss** (MacDiarmid Institute, VUW) gave a talk on *Next generation conjugated polymers for electronic applications*. At the end of May Prof *Michael J.* **McGlinchey** (Chemistry and Chemical Biology, Dublin) gave a talk entitled *Electronic and steric barriers to molecular rearrangements in organic and organometallic chemistry: synthesis, structures and broken symmetry*. In June *Josua* **Lehr** gave his PhD seminar *Modification of surfaces with thin organic films by reaction with aryldiazonium salts*. In early August, visiting Erskine Fellow Prof *Philip* **Doble** gave a seminar on *Elemental bio-imaging: a new imaging spectrometry technique to determine the distribution of metal ions and trace elements in soft tissue samples*.

Francine **Smith** has received a travel grant from RSNZ to present a paper at the International Conference on Toxic Cyanobacteria in Istanbul in late-August; she was also awarded student support from the organizing committee of the Symposium of the International Association for Cyabophyte Research that was held in mid-August. *Sam* **Drew** received a fully-funded undergraduate scholarship and represented Canterbury at the AINSE Winter School on Applications of Nuclear Techniques at ANSTO, Lucas Heights in July. *Matt* **Poulson** has been awarded a UC Health, Safety and Wellbeing Award in recognition of his excellent improvements on the University's health and safety procedures. Matt's award will enable him to travel to other institutions in NZ to examine their approach to health and safety and to meet other people in similar roles at those institutions.

Prof *John* **Blunt** was surprised to receive the news that he and Prof *Murray* **Munro** would be joint recipients of the Norman R. Farnsworth American Society of Pharmacognosy

(ASP) Research Achievement Award in 2011. This award, made annually by the ASP since 1985, is the highest award of the Society. This is the first time the award has been made jointly and the first to anyone in the southern hemisphere. Formerly, the award was been conferred upon individuals such as K Nakanishi and M E Wall (of taxol fame) in addition to a number of previous Erskine visitors to Canterbury including K L Rinehart and D J Faulkner. The award citation reads:

Both professors have been affiliated with the Department of Chemistry at the University of Canterbury in New Zealand for 40 or more years and have been long term collaborators. They have recently shared both the UC Research Medal (2007) and the Paul J Scheuer Award (2008) as recognition of their outstanding collaborative research. Professors Blunt and Munro have co-mentored a large number of undergraduate, graduate and post-doctoral students/fellows (~120). Their >35 years of collaborative work included the discovery of many novel marine and microbial natural products with new skeletal types and potent bioactivity, for example, the mycalamides, discorhabdins, pateamine, coproverdine, spiromamakone and others. This work resulted in several leads for preclinical investigation as drug candidates. They have also fostered the development of novel methods for the rapid, microgram scale replication of natural product extracts. Professors Blunt and Munro jointly put together the marine literature database MarinLit, which is widely used worldwide by marine natural product researchers. They are also co-authors, along with three former students, of an annual review of marine natural products published in Natural Products Reports. Their first review was undertaken in 2001 and it continues to the present. Their impressive, extensive, and continuing contributions to pharmacognosy research are such that we are proud to present Professors Blunt and Monro as the joint Norman R Farnsworth ASP Research Achievement Awardees for 2011.

MANAWATU

The NZIC movie night held in late June show-cased a DVD demonstration called *It's a Gas* and a collection of funny and interesting chemistry related videos. In early July the NZIC held a mini symposium at Massey University. The excellent talks were given by a range of speakers including lectures, PhD students and high school students. The combined annual NZIC/IFS Staff *vs* Student Quiz Night was well attended at the end of August, including several teams of local high school students. Even the nibbles and drinks could not distract the staff for long enough and saw the end of the fun night with the staff beating the students.

Peter **Ting** (Palmerston North Boys High School) attended the 2010 London International Youth Science Festival in August. Peter was one of six participants from NZ. The festival is a three week programme of lectures and tours that include topics such as *Managing the warming world* and *energy – the global challenge*. One of the highlights of Peter's trip was a visit to CERN.

Massey University - IFS

Congratulation to Prof *Simon* **Hall**, a professor of electrochemistry and director of Massey University's Anzode Research Centre, who has won this year's Bayer Innovators Award for Research and Development. Prof Hall, with PhD student, Michael Liu, has invented a new zinc electrode for nickel-zinc rechargeable batteries and has taken a leading role in driving its commercialisation from the initial creative step, to formation of a start-up company, through to manufacture of prototypes. These new batteries are intended to replace environmentally unfriendly nickel-cadmium and lead-acid batteries and to compete with lithium-based systems in larger applications where lithium's safety precludes use. Through a series of creative advances, he has transformed a brilliant idea into a practical prototype. He remains closely involved with the project and has continued to make essential advances as Anzode and its partners move towards marketing and sale of the new battery chemistry. Prof Hall was awarded the 2008 Fonterra Prize for Industrial and Applied Chemistry, and a Distinguished Patent Award from the United States Energy Department in 2005. Congratulations also go to Prof Geoff Jameson who has won both the Individual Massey University Research Medal 2010 and Massey University College Research Award 2010.

Prof Simon Hall

A/Prof *Ashton* **Partridge** has announced that he will be leaving Massey University to take up a research position on Auckland University's Tamaki Campus. Ashton's group is to be renamed the *Energy and Synthesis Group* and will be supervised by Prof *Peter* **Derrick** and A/Prof *Eric* **Ainscough**. *Marziyeh* **Nazari** has recently arrived from Tehran and to commenced PhD work under the supervision of *Peter* **Derrick**.

The Plieger group has recently welcomed *Benjamin* **Roach**, a final year PhD student *on-loan* from Edinburgh University. Ben is putting the final touches to his thesis between developing new mixed oxidation state manganese oxime single molecule magnets in a combined project. *Kerry* **Betz-Stablein** is working on a related area for her honours project. *James* **Stevens** is now working hard to complete his experimental work for his masters thesis. Congratulations to *Karl* **Shaffer** who won 3rd prize in the student poster section at the ICCC39 (International Conference on Coordination Chemistry) conference in Adelaide; submission of his PhD thesis is imminent. Dr *Paul* **Plieger** took some time away from work to contest the World Triathlon Championships in Budapest in early September. Paul is representing NZ in the 35-39 age group.

A/Prof *Musa* **Shongwe** (Sultan Qaboos University, Oman), visited the institute to discuss potential collaborations with staff and presented a seminar titled *Based manganese(III) spin-crossovers exhibiting considerable zero-field splitting*. Musa spent two years from 1990 at Massey on a postdoctoral fellowship with A/Prof *Eric* **Ainscough** and Prof *Andrew* **Brodie** on the Lactoferrin project. On June 23, Dr *Nigel* **Lucas** (Chemistry Department, Otago University) gave a presentation entitled *Well-defined, soluble graphenes and graphene-metal complexes*. On August 4, A/Prof *Antony* **Fairbanks** (Canterbury University) gave a talk about *Synthetic approaches to homogenous Glycoproteins* and on September 9, as part of the 2010 RSC Australasian Lectureship Prof *Cameron* **Kepert** (Sydney University) spoke on *Achieving advanced function in metal-organic framework*.

Dr. *Mark* **Waterland** and *Tracy* **McLean** visited the laboratory of *David* **Phillips** at the University of Hong Kong to perform time-resolved Raman and fluorescence measurements on metallodipyrrin complexes. Tracey's expenses were partly funded by a Claude McCarthy Fellowship. The 2010 honours and masters students have just completed their exams and after a well earned break are now working hard on their research projects. We have been advised that chemistry professor *Brigid* ***Heywood*** (Open University, UK) has been appointed Pro-Vice-Chancellor (Research).

NZP

NZP has recently welcomed Dr *Carl* **Otter** to their product development department. Most recently Karl worked at Massey as a postdoctoral fellow with Drs *Shane* **Telfer** and *Mark* **Waterland**. In August, the company welcomed home Dr *Ghislaine* **Cousins** and *Jennifer* **Peat** who had spent the last three months at Dextra in Reading (UK), the carbohydrate and custom synthesis company that was purchased by NZP in late 2009 (see: www.dextrauk.com).

OTAGO

In July and August, the Branch sponsored three events. Firstly, it organized a tour of the Otago Museum Basement, which is normally inaccessible to the public. Attendees explored the depths of the museum, viewed interesting off-access artefacts, and learned about the museum's preservation techniques. Secondly, a well attended beer-tasting and posters event was held involving both chemists and colleagues from other Departments, especially Pharmacy. The beer-tasting was enthusiastically led by *Richard* **Emerson** of Dunedin's Emerson Brewing Company and included tastings of brews from both Emerson's and Epic Brewery. Lastly, the Branch and the Chemistry Department jointly sponsored the 2010 Arthur Campbell Lecture. Prof *Arthur* **Campbell** was a staff member in the Chemistry Department from 1948 to 1988 and was in attendance at the lecture and the after-lecture dinner. This year's speaker was Dr *Gordon* **Miskelly** from the Auckland's Chemistry Department with a seminar entitled *What you see is what you've got: using the eye or a digital camera as an analytical transducer*.

University Chemistry Department

Keith **Gordon** has been awarded a short-term FRST grant ($297 K per annum for 3 years) to study self-repair organic electronics. The aim of the research is to develop a class of organic electronic materials that can self-repair. *Keith* **Hunter** and *Sylvia* **Sander** were part of the successful FRST proposal *Management of cumulative effects of stressors on aquatic ecosystems* worth $14.5 M over 6 years, with their contribution being worth $1.2 million. The project aims to develop knowledge and science-based tools for better management of aquatic ecosystems.

Sally **Brooker** attended a number of conferences mid-2010. She was an invited speaker at the Inorganic Gordon Conference (UNE, Biddeford, Maine), MOLMAT (Montpellier), ICMFC-1 (Singapore) and ICCC-39 (Adelaide). Sally also visited Oxford University briefly, touching base with Profs *Paul* **Beer** and *Stephen* **Faulkner**, and with her ex-group members, Dr *Jonathan* **Kitchen** (now an IRCSET postdoc with Profs **Gunnlaugsson** and **Faulkner**) and *Nick* **White** (now a Clarendon PhD student with Prof Beer). She then travelled to Bordeaux where her MacDiarmid Institute PhD student, *Juan* **Olguin** had already spent 10 days working with Prof *Rodolphe* **Clérac** collecting and interpreting magnetic data. Juan presented posters on his research at MOLMAT and ICMFC-1. Her PhD students *Worku* **Gobeze**, *Scott* **Cameron** and *Matthew* **Cowan** presented their research at ICCC-39. Drs *Holger* **Willms** and *Laszlo* **Mercs** completed their postdoctoral fellowships in Sally's group mid-year, and returned to Europe sightseeing en route. We were thrilled to hear from Holger that he has already secured his *dream job* in a pretty town in Bavaria. *Michael* **Juchum**, from Mainz University, has joined the Brooker Bunch to carry out 5 months research.

A number of PhD students have recently received rewards and other honours. *Anthea* **Blackburn** (*Lyall* **Hanton**'s group) received a Fulbright Award to conduct PhD study in the US. *Katie Baer* **Jones** (Keith Hunter's group) received the 2010 NZ Marine Science Society Student Research Award. *Ruma* **Ghosh** and *Karen* **Lavin** (*Kimberly* **Hageman**'s group) received 3rd Place in the Student Oral Presentation Contest at the Antarctica NZ Conference in Christchurch, and a Fulbright Travel Award to attend a conference and give presentations at two universities in the US, respectively. *Samuel* **Lind** (Keith Gordon's group) was awarded the 2010 R. H. T. Bates Postgraduate Scholarship for *the theoretically driven, rational design of high-performance organic photovoltaics*. *Daniel* **Hutchinson** (from *Lyall* **Hanton**'s group) and *Jacqeline* **Koa** (from *Keith* **Gordon**'s group) were finalists in the 3-minute thesis competition; *Daniel* **Hutchinson** received the Audience Choice Award.

The polymer and supramolecular gel group, led by *Lyall* **Hanton** and *Stephen* **Moratti**, have had several arrivals, departures, and other important events. *Remi* **Boissezon** visited for several months as a project student from Clermont-Ferrand, France, to investigate chitosan wound healing gels. *Parag* **Dhake** recently arrived from India to start a PhD on supramolecular metal complexes. *Anthea* **Blackburn** recently left after her MSc to take up her Fulbright PhD studentship in Fraser Stoddart's group at Northwestern University. *Daniel* **Hutchinson** presented a poster at the International Conference on Coordination Chemistry in Adelaide, got engaged, and published his first paper – all in one month!

WAIKATO

The annual NZIC Waikato Analytical Chemistry Competition was held in mid-June. Invitations were sent to schools in the Waikato/Bay of Plenty region as usual and 24 teams of four students representative of the entire area came to the University for the day to carry out an analysis. The task was to analyse a solution for lead content using a gravimetric and a back-titration method. This was a demanding task in the time allotted but some excellent results were achieved. The competition allowed nearly 100 enthusiastic Year-13 chemists to spend a day in the University laboratories working on an experiment that was beyond the resources of their schools. While rivalry was fierce, the main emphasis was on enjoying the experience and meeting students from other schools. Many of the Chemistry staff set up the competition and supervised the laboratories and Bryant Hall provided excellent NZIC-sponsored lunches and Hill Laboratories generously donated the prizes to:

1st Prize: ***Pukekohe High School*** (Timothy Christopher, Liam McDonald, Katie Ward-Allen, Ronnie Gong)

2nd Prize: ***Katikati College*** (Dean Ramage, Richard Sanger, Oscar Dowson, Ana Sheerin)

3rd Prize: ***St Pauls Collegiate*** (Kent Stewart, Hugh McKay, Sam Hogg, James Chancellor)

4th Prize: ***Mt Maunganui College*** (Baylee Smith, Jonathan Mayo, Kristy Toy, Nicole Toy)

5th Prize: ***John Paul College*** (Sean Bates, Emily Burnett, Elizabeth Bickerton, Anne Marie Manzano)

Pukekohe High School winners.

In the lab

University of Waikato

Dougal **Laird** successfully completed his PhD supervised by *Michael* **Mucalo** on *Reinforced sintered cancellous bovine bone as a potential bone replacement material* and is now resident in Germany where he is employed in two positions that utilise the experience he gained in biomaterials during his PhD. Two other PhD students of Michael's have just begun their PhD study: *Kethsiri* **Alwis** comes from Sri Lanka and is to look at the use of electrospray mass spectrometry to monitor electrochemical reactions, whilst *Stephen* **Gardyne** is looking at the fate of some organic waste water contaminants in the aquatic and terrestrial environment from a NZ perspective. This is being supervised by *Michael* **Mucalo**, *Alistair* **Wilkins** and *Grant* **Northcott** (Plant & Food, Ruakura).

Recently-retired *Derek* **Smith** and Lyndsay Main were inducted as Honorary Fellows of the University of Waikato at a function on August 27th in recognition of their long service and distinguished contributions to Chemistry. *Graham* **Saunders** and *Brian* **Nicholson** presented lectures at the ICCC39 meeting in Adelaide in July. Prof *Ian* **Shaw** (Canterbury University) recently visited the Department and gave a seminar entitled *Environmental estrogens – the ultimate biochemical feminists.*

NIWA

In May, through the ISAT linkages fund, *Mike* **Stewart** spent two weeks at the laboratory of Dr *Mira* **Petrovic** in Barcelona. Dr Petrovic is a world leader in developing new methods in LC/MS/MS for the detection of emerging chemicals of concern in the environment. The methods developed while there allowed for the detection and quantitation of up to 76 pharmaceuticals in environmental matrices, including sediments from around Auckland and Christchurch, and various NZ wastewater treatment plant influents and effluents.

Craig **Depree** has been working with research groups in Scion and IRL and industry partner Altex Coatings Ltd. The research has resulted in a number of potentially new antifouling paint formulations that have significant environmental advantages over existing copper-based commercial ones. Research prototype formulations being evaluated by Altex Coatings consist of ones that are copper-free and others that contain 20-40-times less copper than standard formulations. Research prototypes were the result of FRST-funded research focused on developing environmentally-friendly antifouling technologies for shipping and aquaculture applications.

WELLINGTON

The June Branch meeting comprised an address by recent *Chemistry in New Zealand* author Dr *Mattie* **Timmer** (SCPS, Victoria University) who told us about the times *When carbohydrate chemists go flat*, namely some of the work of the VUW/MIMR Immunoglycomics Platform that examines the role of planar aromatic compounds in the treatment of diseases from cancer to tuberculosis and inflammation, and as coloured reporter groups. The annual NZIC Branch dinner was held at Cafe Pasha in the city on July 14. Although it attracted fewer participants than in recent years, those present had a great evening.

Patent law features regularly in *Chemistry in New Zealand* and the August meeting featured one of its former writers, Dr *Jarrod* **Ward** of Baldwins, who spoke on *changes in New Zealand's patent law* that have come from the overhaul of the original 1953 act. The Patents Bill, presently before Parliament, represents a significant change for NZ and Jarrod very nicely described the changes likely to be adopted to a good sized audience and with a batch of well selected examples of recent and historical patents.

The September meeting was a real change for the Branch as it comprised a combined meeting with the Manawatu Branch by way of a joint visit to NZ Pharmaceutical in Palmerston North and this was followed by dinner at Bethany's Restaurant on The Square.

Victoria University

Victoria's new science building – the ***Alan MacDiarmid Building*** was officially opened by the Prime Minister, Hon. John Key, on the 26th of July. The investment in the building will allow for greater focus on research and specialised teaching in the sciences and it is now occupied predominantly by biochemists, chemists and physicists of the MacDiarmid Institute.

The building is named after Victoria alumnus and Chemistry Nobel Prizewinner, the late Professor Alan MacDiarmid. His Nobel Medal is now on display in the building together with other memorabilia donated by his family. VUW hopes that by housing the medal in the Alan MacDiarmid Building, it will inspire the students and staff that study and work there each day.

More than 150 guests attended the opening including the Hon Dr Wayne Mapp, Minister for Research, Science and Technology, Steven Joyce, Minister for Tertiary Education; and many members of the MacDiarmid Family, including Alan's widow Gayl Gentile.

Dr *Matthias* **Lein** has joined the School of Chemical and Physical Sciences as a senior lecturer in Computational Chemistry. Born and raised in Germany, Matthias gained his PhD at the University of Marburg under the supervision of Prof *Gernot* **Frenking**. His work involved the quantitative description of the coordination chemistry and bonding of transition metal compounds. After brief stints visiting the University of Auckland and Budapest Technical University in Hungary he took up a postdoctoral position as with Prof *Peter* **Schwerdtfeger** at the Institute of Fundamental Sciences at Massey (Auckland) where he later joined the NZ Institute for Advanced Study as a Research Officer. His VUW research programme will focus on the investigation of reaction mechanisms in metal catalyzed systems and the accurate description of the electronic structure in unusual bonding situations. Dr *Rod* **Weston**, who retired from IRL, has joined the SCPS as a research fellow for three months until the end of October, while Prof *Bradley* **Williams** from the University of Johannesburg (South Africa) has joined *John* **Spencer** for his sabbatical stay. His research focuses on synthesis chemistry, particularly relating to transition metal- and Lewis acid-catalyzed organic transformations and he has participated in the 400-level teaching programme.

Tony **Brewster** (Alphatech Systems) gave a presentation on the new *AB Sciex Triple TOF 5600 mass spectrometer* as the School is keen to obtain a new instrument. His presentation was one of the best that an instrument manufacturer has presented in very many years and the instrument seems to be very desirable indeed. Prof *Brigid* **Heywood** visited the School in late August and spoke on *Bioinspired molecular maps for the controlled fabrication of inorganic materials*.

MSc student and NIWA technician *Jonathan* **Wright** gave a paper *Successful aquaculture – how do we control environmental pH levels?* in the US in September whilst *Nick* **Monahan** has completed his MSc degree under Kate McGrath's supervision and taken up his Fulbright Fellowship to study for a PhD in Austin, Texas. Dave Herman of Richard Tilley's group was a finalist in the 3-minute thesis competition.

The Alan MacDiarmid Building; courtesy of Image Services, VUW

Rotaxanes as Molecular Machines – The Work of Professor David Leigh

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The concept, preparation, and development of mechanically interlocked molecules, dates back more than forty years and, as an area, has attracted increasing attention. Those who have made significant contributions include Professor David Leigh of the University of Edinburgh. His activities in working on the synthesis and applications of rotaxanes, in particular, stem from the late 1990s and are the focus of this paper. He began with the development of an active metal template synthesis that offers increased efficiency over the previously used passive template methods; supramolecular chemistry and non-covalent interactions enable the syntheses of rotaxanes in fewer steps and in greater yields. Rotaxanes are of interest to scientists because they exhibit markedly different spectroscopic responses, chemical reactivity, and mechanical properties over their non-interlocked analogues. More recently Leigh has turned to the properties of these molecules as molecular machines.

Rotaxanes are defined by the IUPAC as *molecules in which a ring encloses another rod-like molecule having end-groups too large to pass through the ring opening; the rod-like molecule is thus held in position without covalent bonding*.[1] A rotaxane is thus a mechanically locked architecture which consists of macrocyclic rings trapped on a linear unit, the thread, by two bulky constituents, the stoppers (Fig. 1).[2] This mechanical interlocking is not a chemical bond; rather, it intrinsically links the backbone components of the molecule and prevents their dissociation without the cleavage of one, or more, covalent bonds. They are named using the format [***x***]-rotaxane, where ***x*** indicates the number of components in the molecule; thus, a [2]-rotaxane would consist of one thread and one macrocyclic ring.

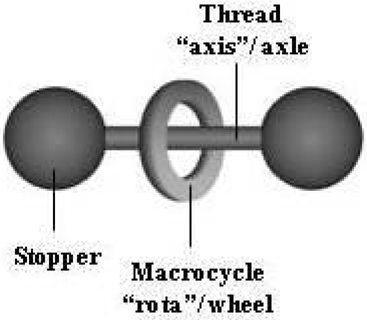


Fig. 1. Graphical representation of a [2]-rotaxane - one thread and one macrocycle.

Rotaxanes are prevalent in biology as molecular motors that produce rotary and linear motion. One such molecular machine is a bacterial flagellum. It is a tail-like structure that projects from bacterial cells and assists in locomotion via a helical motion. The bacterial flagellum is driven by a rotary engine made up of a protein anchored in the inner cell membrane. This protein has the shape of a [3]-rotaxane with one thread and two macrocyclic components as shown in Fig. 2.[3] The engine is powered by an electrochemical proton gradient across the cell membrane set up by the cell's metabolism. This turns the flagellum at a frequency of approximately 1000 Hz, propelling the bacterial cell at 100 μm/sec with an estimated 100 % fuel efficiency.[4]

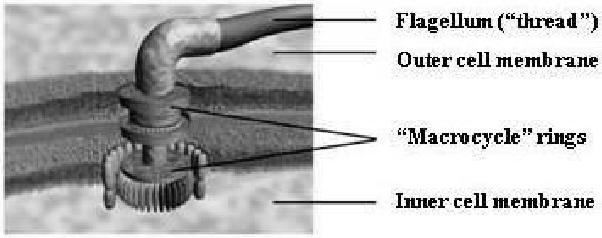


Fig. 2. Bacterial flagella motor of *E. Coli*, which is a [3]-rotaxane.

Rotaxanes are also utilized in DNA replication, including the enzyme DNA polymerase, which is used to catalyse the polymerisation of deoxyribonucleotides into a DNA strand. The polymerase binds to a single strand of DNA, and then directs the incoming deoxyribonucleotides into the correct position to form a sequence complementary to the original single strand. It also keeps the DNA strand in place to greatly reduce errors during synthesis. As the DNA chain does not have stoppers at its end, the complex is not a *true* rotaxane as it is able to separate into its independent components – such molecules are termed pseudo-rotaxanes (Fig. 3).[5] Both of these biological molecular machines utilize chemical energy through metabolism to generate motion at ambient temperatures. One of the most interesting and important functions of these biological rotaxanes is their ability to assemble in the correct arrangement without the need for an external stimulus. It is this self-assembly which Leigh is trying to replicate out of the biological world using supramolecular chemistry.

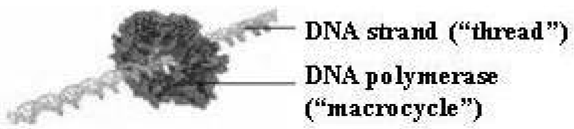


Fig. 3. Pseudo-rotaxane structure of DNA polymerase.

The self-assembly of rotaxanes is an important characteristic of their synthesis. Self-assembly is the spontaneous formation of a thermodynamically stable product from the aggregation of pre-existing components by weak supramolecular, non-covalent interactions into a particular spatial arrangement. This requires architectures that restrict the degrees of freedom of the reactants, and control their motion to encourage the desired product to form. These supramolecular interactions include hydrogen bonding, dipole and ion interactions, π-stacking, and dispersion effects. They generally have a high stability and are relatively labile. This self-assembly is also known as bottom-up assembly where smaller components are built into larger, more complex assemblies without the use of an external stimulus. This type of synthesis is beneficial as it enables the formation of complex structures with multiple functional groups in relatively few steps and in good yield. As a thermodynamically stable product is produced, it also increases the likelihood of the desired product being formed as the major product, which decreases the need for separation from side products.

There are three commonly used methods for rotaxane synthesis known as i) capping, ii) clipping, and iii) slipping as illustrated in Fig. 4.[6] In each, a metal ion complexes with the separate rotaxane components to hold them in the correct orientation for the formation of the interlocked architecture; as the metal ion is unused otherwise in the reaction, these methods are known as *passive* metal template syntheses. The capping method relies strongly on thermodynamics to hold the thread within the macrocycle by non-covalent, supramolecular interactions. The stoppers are then added onto the pseudo-rotaxane to form a rotaxane. Clipping is similar to the capping method, except that the thread and chain are complete and bound to a partial macrocycle. This macrocycle undergoes a ring-closing reaction to form the final rotaxane. The slipping method exploits the kinetic stability of the rotaxane. If the stopper molecules are of an appropriate size one can reversibly thread through the macrocycle at high temperature: that is, it is a dynamic complex. On cooling, the macrocycle becomes kinetically trapped on the thread. These are efficient synthetic methods as they generally result in good yields. However, the removal of the metal ion after the desired mechanically interlocked architecture is made is non-trivial since it has a permanent coordination site on each component. The method also requires stoichiometric quantities of the metal ion, which can be expensive.

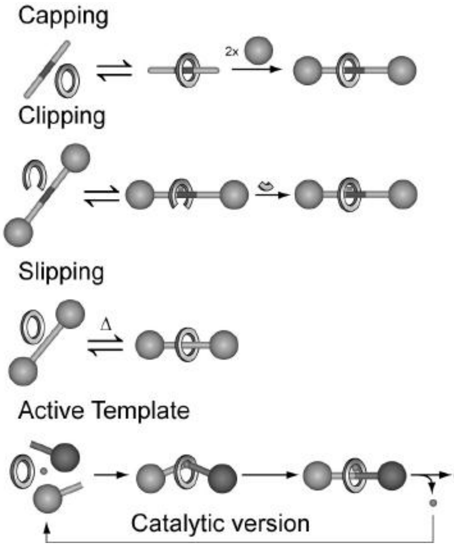


Fig. 4. Rotaxane synthesis by *passive* template mechanisms.

Active template synthesis was developed by Leigh to overcome the limitations associated with passive metal template routes. It utilizes the catalytic properties of metal ions to enhance covalent bond formation, as well as their ability to direct the bond formation; in this way the metal ion is *active* as it has dual functionality. This synthesis relies on a macrocycle that is able to bind a metal ion endotopically in its cavity, promoting the formation of a covalent bond between two *half-thread* units to form a rotaxane. As the metal ion is locked into position, the mechanical bond is selectively formed through the macrocycle as shown in Fig. 5.[7] The reaction can occur stoichiometrically with one equivalent of the template, or catalytically when the active template turns over during the reaction. This active route has the advantage over the previously used methods as it enables *traceless* syntheses: it does not require permanent recognition elements on each component of the interlocked product to enable the mechanical bond to be formed. This also enables otherwise *impossible* rotaxanes to be synthesized, as architectures that cannot otherwise be generated become possible, *viz*., greater structural diversity is achievable.

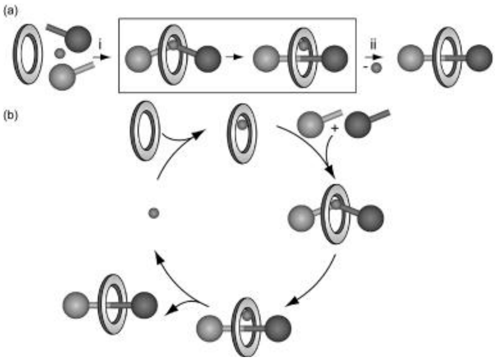
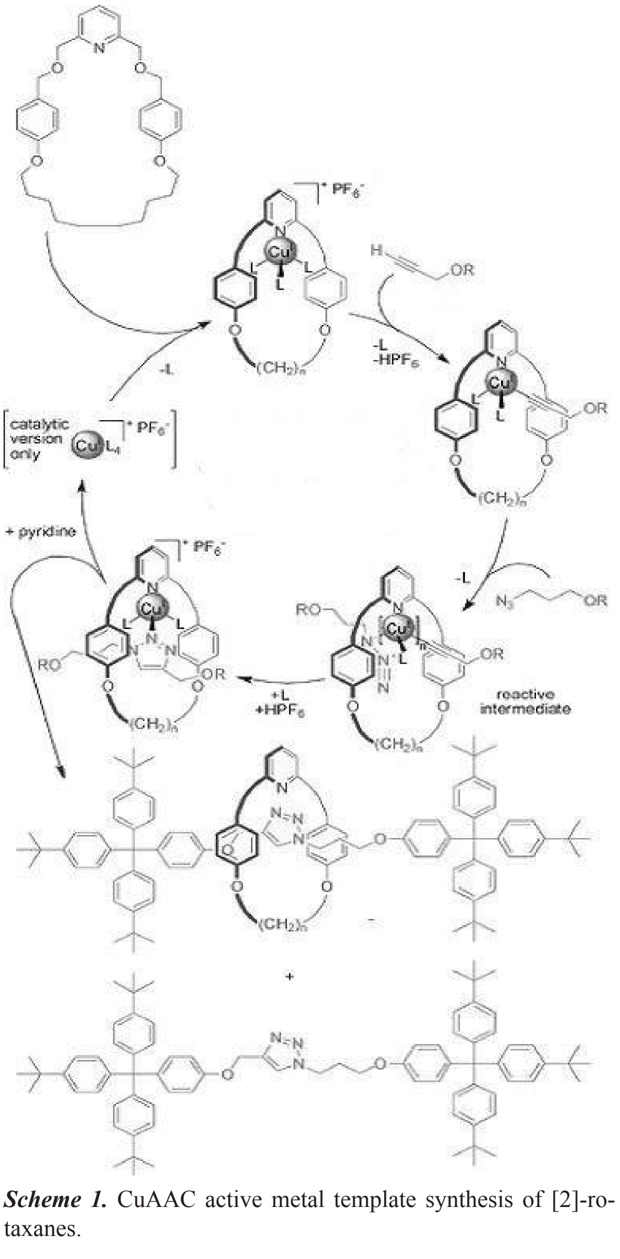


Fig. 5. (a) Non-catalytic, and (b) catalytic active metal template synthesis of a rotaxane.

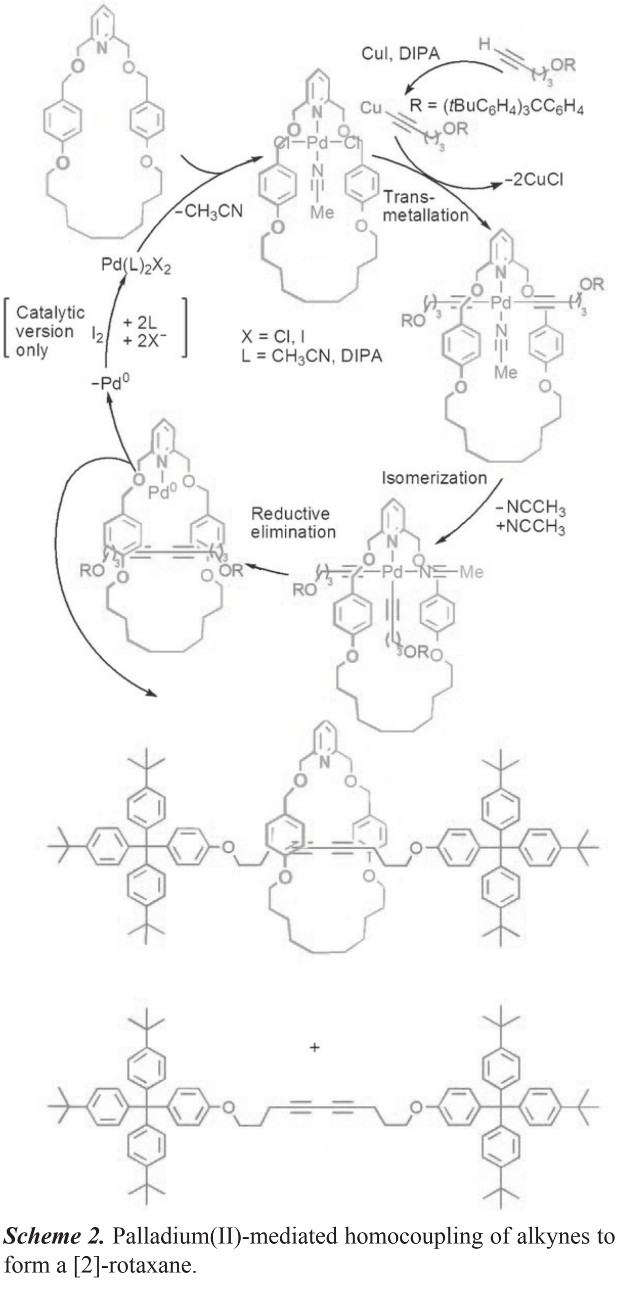
The active metal template synthesis was first developed in 2006 by Leigh using stoichiometric quantities of copper(I) as the template ion. He evolved a Cu(I)-catalysed terminal alkyne–azide 1,3-cycloaddition (CuAAC) reaction, now termed a *click* reaction,[8] which as the name suggests involves the 1,3-dipolar addition of an azide to a terminal alkyne to give a 1,2,3-triazole. Leigh used previously developed 2,6-disubstituted pyridine macrocycles in this reaction, as they contained the desired endotopic ligating nitrogen atom required to bind the metal template ion. In this case the Cu(I) source was $Cu(MeCN)_4PF_6$ as it does not contain ligands that can competitively bind with the metal (Scheme 1).[9] Sub-stoichiometric amounts of Cu(I) became possible when pyridine was added to the system. Pyridine acts as a competing ligand and prevents the Cu(I) from being sequestered by the macrocycle during the reaction, thereby allowing its use as a catalyst. The rotaxane yield was optimized by varying, the temperature, solvent, ratios of alkyne/azide to Cu(I), as well as the flexibility, size and steric properties of the macrocycle. The nature of the Cu(I) compound used also altered the kinetics of the CuAAC reaction. Thus, pyridine-based ligands facilitate the oxidation of Cu(I) to non-catalytic Cu(II). So, while they initially increase the rate of reaction, they prevent quantitative conversion because the template ion is removed from the system. The addition of a second equivalent of Cu(I) increases the rate of formation of rotaxane, suggesting that the π-activation of the copper unit is dominant; also, it suggests that the reaction involves an intermediate featuring two metal ions. This primary

Cu(I) active metal template synthesis has resulted in the development of further rotaxane syntheses using different chemistry, such as Glaser couplings,[10] which couple two alkynes together, and an Ullman biaryl ether condensation by other groups.[10]



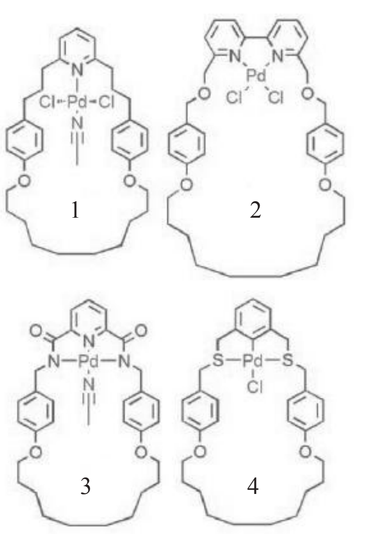
Scheme 1. CuAAC active metal template synthesis of [2]-rotaxanes.

Leigh, however, turned his focus to the use of palladium(II) as a template ion, as processes catalysed by it have led extensively to C-O, C-N, C-S and C-C bond formation. It has proved to be useful in rotaxane synthesis owing to the two-dimensional square planar coordination geometry that gives steric control over the crossover point in the third-dimension: the palladium holds the half-threads in the correct transoid position for an interlocked architecture to form. The homocoupling of half threads carrying terminal alkyne groups was used to form the rotaxane with a monopyridine macrocycle as shown in Scheme 2.[11] During the synthesis, Pd(II) is reduced to Pd(0) upon formation of a covalent bond that provides the thread molecule and, thus, the desired rotaxane. In order for the palladium to be catalytic, the Pd(0) must be oxidized back to Pd(II), a process achieved with oxygen and iodine. Optimum product yields were obtained from catalytic quantities of Pd(II), when the amount of the half thread was increased to three times that of the macrocycle, and the reaction time was increased to 72 hours. Additionally, it was found that catalytic amounts of Pd(II) gave much cleaner conversions and higher yields over use of stoichiometric Pd(II) that is likely to be a result of fewer side reactions. The method was also tested with bidentate and tridentate macrocycles, but the bidentate macrocycles gave lower yields and the tridentate macrocycles no rotaxane at all. This is most likely a result of the cisoid arrangement in which the macrocycles are held by the Pd(II) for trans-metallation to occur; it reduces the chance of two alkyne substituents coupling through the macrocycle and forming the rotaxanes (Scheme 3).[11]



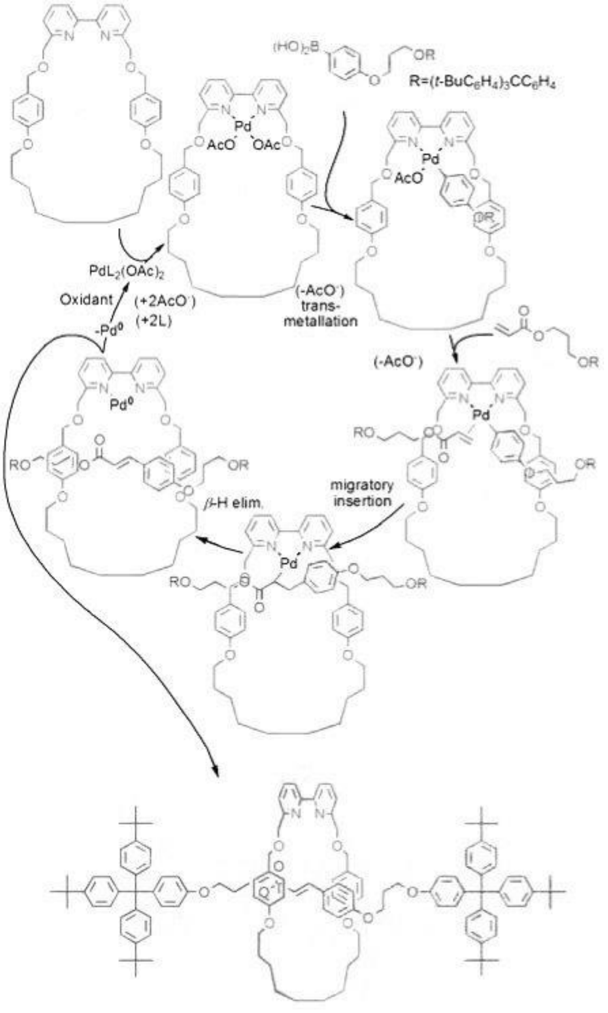
Scheme 2. Palladium(II)-mediated homocoupling of alkynes to form a [2]-rotaxane.

Catalytic quantities of Pd(II) were also used to form a [2]-rotaxane, using oxidative Heck cross-coupling to form the thread of the rotaxane. Here, migratory insertion followed by β-H elimination forms the covalent, and thus mechanical, bonds required. As in the alkyne homocoupling example, Pd(0) needs to be re-oxidized to Pd(II) and is achieved with oxygen and benzoquinone (Scheme



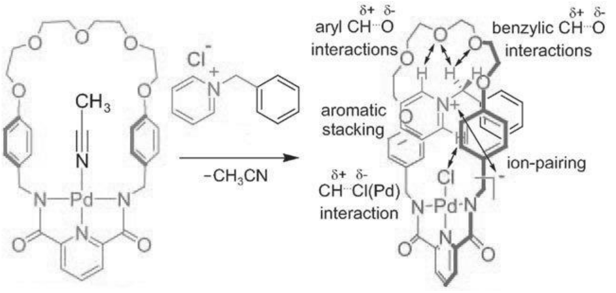
Scheme 3. Coordination geometries of **1**: free monodentate, **2**: bidentate and **3**, **4**: tridentate macrocycles to Pd(II).

4).[12] This method has an advantage over the previous ones because the cross-coupling is tolerant of a range of different partners that include vinyl ketones and styrenes as well as the alkenes already shown and, thus, gives rise to a range of rotaxanes with functionalized stoppers. It was also shown that quantitative product yields could be attained with very small amounts of Pd-template, something that had not been seen previously in the synthesis of small, complex molecules.

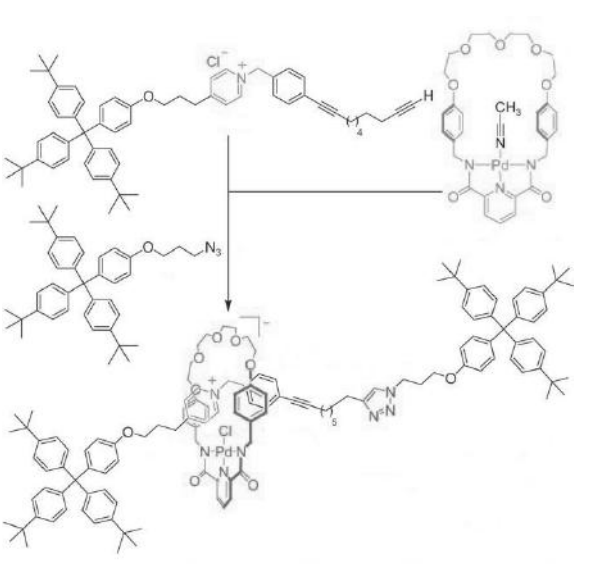


Scheme 4. [2]-Rotaxane synthesis by a Pd(II)-mediated oxidative Heck cross-coupling.

The use of Pd(II) in an ion-pair synthesis has been reported also by Leigh. Here, the Pd(II) does not act as an active template in the same manner as the previous examples. A tridentate macrocycle, which binds Pd(II) endotopically, is used and the remaining coordinative site is occupied by an acetonitrile ligand. This latter ligand is replaced by the chloride ion from benzyl pyridinium chloride in the rotaxane half thread thereby creating a positive charge in the half thread. This is now able to ion pair with the (now) negatively charged Pd(II) complex, thus holding the thread in the correct position for a mechanical bond to be formed. Aromatic π-stacking interactions, and CH···O and CH···Cl hydrogen bonding between the host and guest molecules also help hold the thread in the correct position. These interactions also stabilize the molecule and enable it to be isolated and characterised (Scheme 5).[13] As would be expected, these interactions are able to occur only in polar solvents. When the reaction is carried out in DMSO, threading, and thus rotaxane formation, did not occur. CuAAC chemistry was used to connect the two halves of the thread molecule, resulting in a quantitative yield (Scheme 6).[13] In this rotaxane synthesis, the Pd(II) is used as an anion template, rather than as a metal template; it is the ion-pair interaction between the positively charged thread and negatively charged macrocycle that is the active template component in the synthesis. The presence of charge at a single position of the thread component of the rotaxane invites the possibility for a switchable thread where the macrocycle exhibits positional preference along the thread depending on the conditions of the rotaxane system.



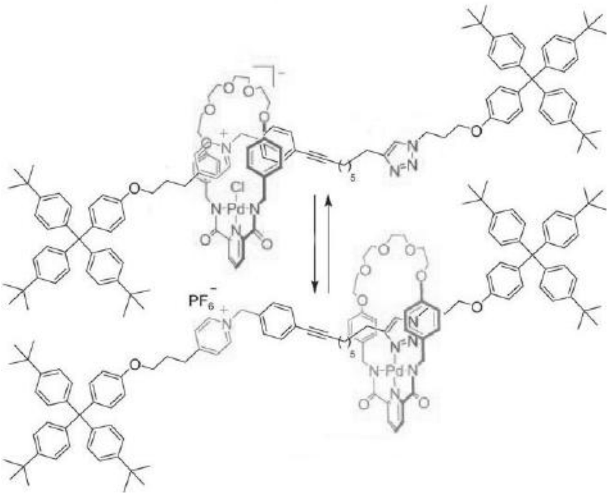
Scheme 5. Synthesis of a pseudorotaxane and the non-covalent interactions present.



Scheme 6. CuAAC synthesis of a [2]-rotaxane based on an anion template method.

Leigh used the concept of a switchable rotaxane thread in the design of a molecule that has the potential to act as a molecular machine. If two different binding sites (stations) are present on the thread of a rotaxane, the macrocycle, generally, is able to move between the positions under random thermal motion owing to its preference for one over the other. Such rotaxanes are referred to as *molecular shuttles*. The thread of Leigh's rotaxane synthesized using ion-pair interactions contains two such different ligating stations, the other of which is charged (the pyridinium station) and one which is not (the triazole station). When the rotaxane macrocycle is charged, that is, when the chloride ion is bound to the palladium, it prefers to sit over the pyridinium station because of the favourable ion-pair interaction. When $AgPF_6$ is added, the chloride ion binds to the silver ion, AgCl precipitates, and the macrocycle is uncharged; it moves to be over the neutral triazole station with the PF_6^- acting to balance the charge of the positive pyridinium station. The negative charge can be returned to the macrocycle upon the addition of tetrabutylammonium chloride, which returns the chloride ion to the palladium centre. This molecular shuttle, therefore, demonstrates motion along the rotaxane thread on changes to the macrocycle's charge; this is known as anion switching (Scheme 7)[13] Although the shuttling is reversible, it cannot be achieved quickly as solvent needs to be added to cause the anion switching and would need to be removed after each step to prevent the system from becoming too large in volume.

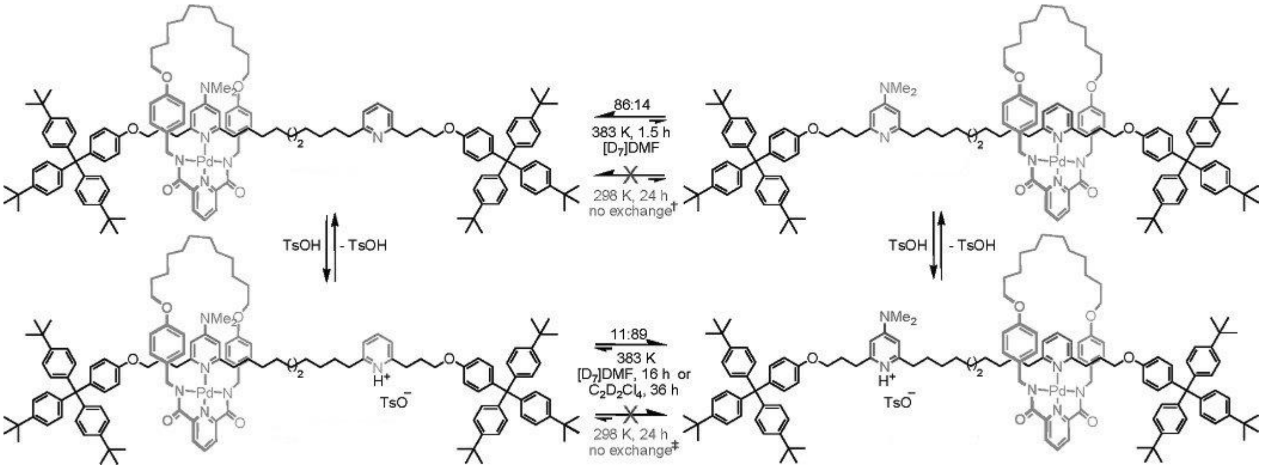
Leigh has also developed a molecular shuttle that uses reversible protonation of the rotaxane stations to drive shuttling of the macrocycle (Scheme 8).[14] The motion of this shuttle is dependent upon variations in the kinetics of binding the palladium to the nitrogen of the two stations.



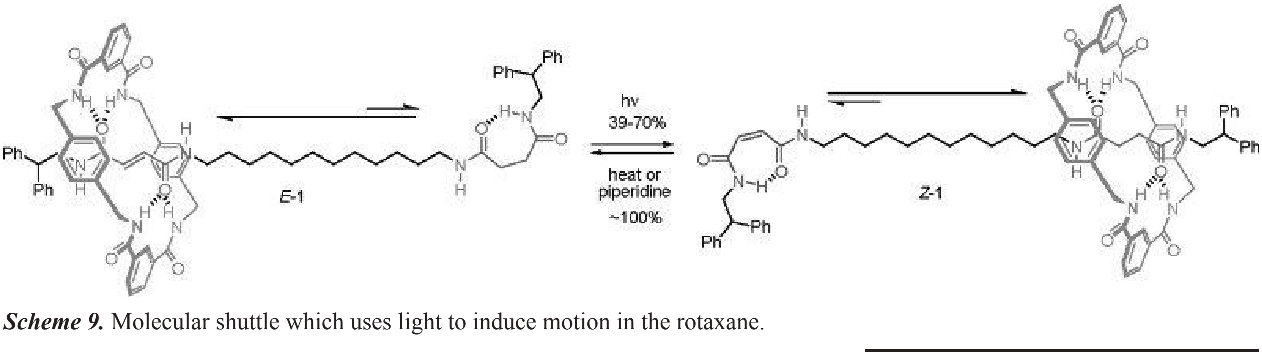
Scheme 7. Molecular shuttle using anion switching to generate motion.

In the case at hand, the macrocycle exhibits a preference for positioning over the more basic dimethylaminopyridine (DMAP). However, this preference is changed when the nitrogen of the group is protonated. Shuttling is driven by preferences in the position of the proton, rather than the palladium differentiating between the two stations, since a N-H bond is much stronger than a N-Pd bond. Therefore, this molecular shuttle could be pH-driven. However, the kinetic stability of the Pd-N bond means that protonation of the stations alone is not sufficient to induce motion; the system must be heated to 100 °C, likely limiting use as a molecular shuttle.

A change in rotaxane thread structure can be induced without the need for a chemical stimulus – light can be used instead. Photoisomerization of the favoured station



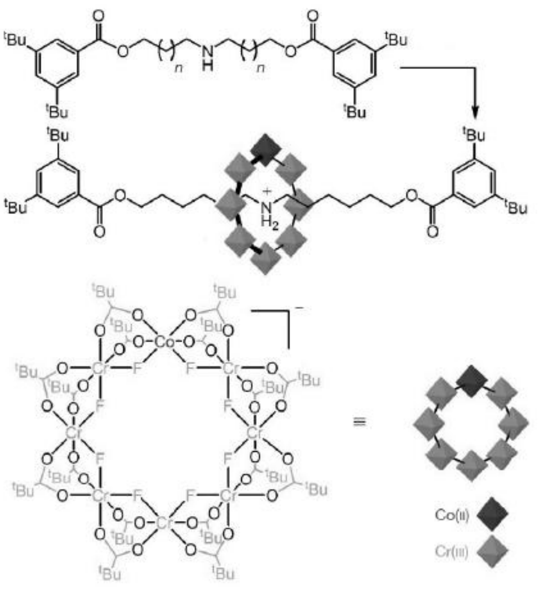
Scheme 8. Molecular shuttle driven by reversible protonation of the rotaxane stations.



Scheme 9. Molecular shuttle which uses light to induce motion in the rotaxane.

can result in a change of the station that the macrocycle prefers. Such isomerisation cannot be undone using light, however, and heat or solvent must be introduced to shuttle the macrocycle back to its original position (Scheme 9).[15] Leigh has shown also that a light stimulus can be used to form a molecular shuttle that has the ability to do work in the macroscopic world. A rotaxane containing two different stations on its thread, one hydrophilic and the other hydrophobic, was deposited as a monolayer on to a gold surface. Upon irradiation, isomerization of the hydrophilic station (the π–bond) occurred, causing the macrocycle to shuttle to the hydrophobic station, thus altering the nature of the surface of the gold film (Fig. 6).[16] This change in surface hydrophilicity can do work by moving a liquid droplet uphill. Thus, a droplet of iodomethane was moved up a gradient of 12° (Fig. 7),[16] although it remains to be seen if this gradient is the maximum at which work can be done. Regardless of this, Leigh envisages that such light-driven molecular machines have the potential to be used as energy storage devices. Alternatively, they could be employed in lab-on-a-chip devices that are being developed for use in medicinal diagnostic testing to control the flow of liquid on a microscopic scale, and enable multiple diagnostic tests on one sample, increasing throughput and lowering costs.

Leigh is also developing rotaxane shuttles as qubits (quantum bits) for quantum computers because of their mechanically linked organic and inorganic componentry (Scheme 10).[17] The inorganic macrocyclic components of such rotaxanes exhibit electronic, magnetic and paramagnetic characteristics as a result of the influence on, and potentially by, the organic portion of the molecule. The rotaxane uses a variety of supramolecular interactions, *e.g.* hydrogen bonding, ion-pair interactions and metal-to-ligand bonding, to generate motion and cause changes in the physical properties of the metals in the molecule. This is an important development in rotaxane chemistry as it successfully combines inorganic and organic chemistry by mechanical bonds and allows the formation of molecules with composite properties, a concept not previously utilized to any extent.



Scheme 10. A rotaxane with both organic and inorganic sections.

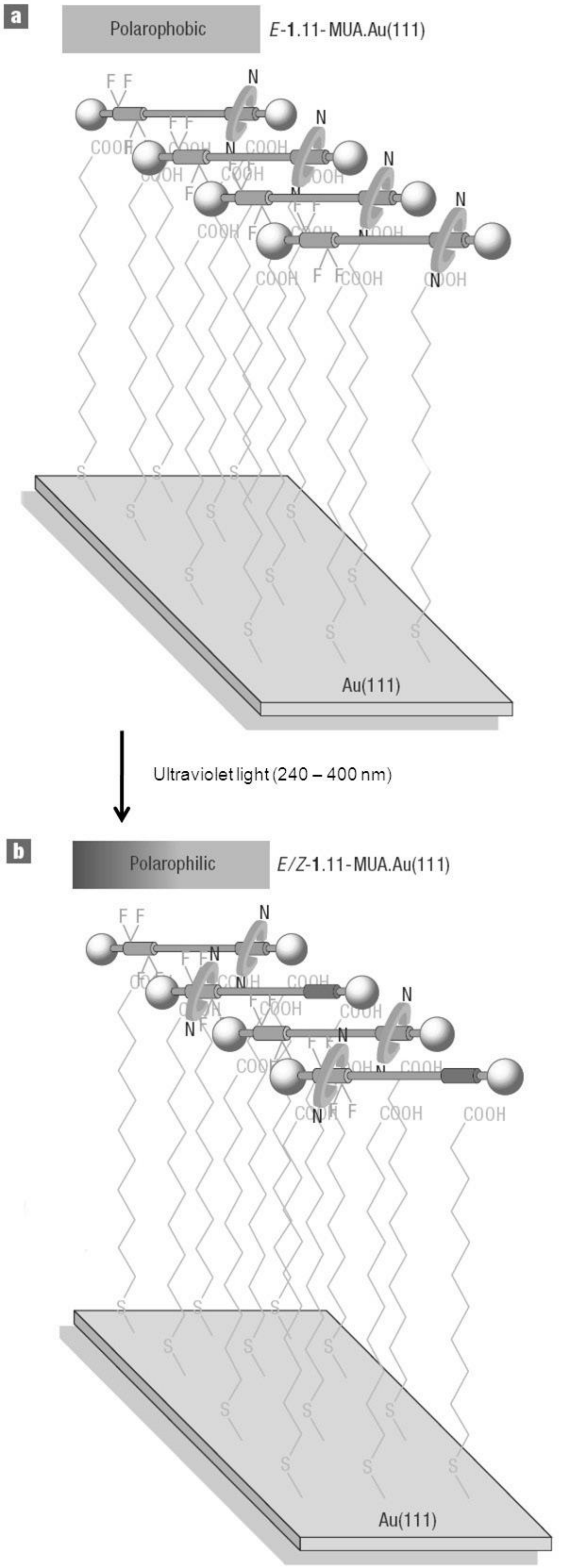


Fig. 6. Photoswitching of surface a. hydrophilicity (polarophilic)/ b. hydrophobicity (polarophobic) of arotaxane macrocycle. Copyright Nature Publishing Group and reproduced with permission from *Nature Materials* - see ref.16.

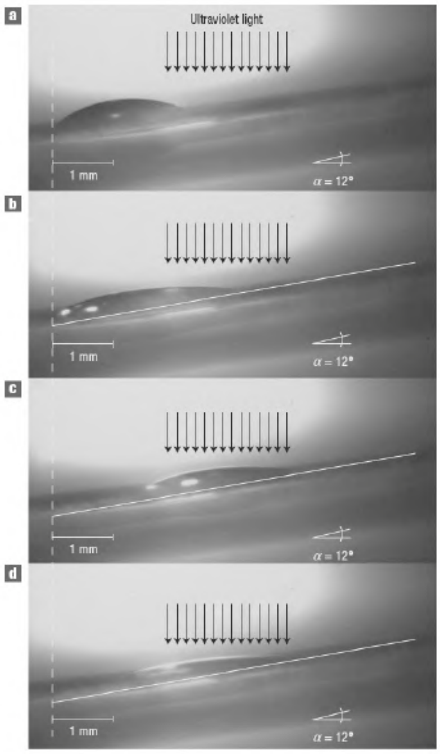


Fig. 7. Movement of a droplet of iodomethane up a gradient of 12°. Copyright Nature Publishing Group and reproduced with permission from *Nature Materials* - see ref.16.

The development of alternative active metal template methods to the original *passive* template methods by Professor David Leigh has been an important step in the synthesis of rotaxanes. The dual functionality of the metal ion in directing covalent bond formation, and catalysing the formation of a rotaxane, allows efficient synthesis with the possibility of synthesizing otherwise inaccessible rotaxane architectures. This success results from combining supramolecular chemistry and non-covalent interactions. The increased efficiency has allowed Leigh to focus on applications of these rotaxanes as molecular shuttles and the design of such molecular motors with potential in, amongst others, medicine and technology.

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NZIC Annual General Meeting

The NZIC AGM will take place at Victoria University of Wellington in the Laby Building, Room LB408 at 5.30 pm for a 6 pm start on Wednesday 17 November 2010 prior to the Branch Lecture entitled ***From Vine to Wine: The Chemistry of Grapes*** by Dr. Rob Keyzers.

Entry to the Laby Building is from car park off the roundabout at the top of Kelburn Parade. Proceed to the SPCS Office at the southern end of the long walkway and follow the signs and take the evevator to Level 4.

Agenda

1. Apologies
2. Minutes of 2009 AGM held at the Victoria University 11 November 2009
3. Matters arising
4. Financial Report – including auditor's report
5. Election of Officers
    - President
    - 1st Vice-President
    - 2nd Vice-President
    - Treasurer
    - Honorary General Secretary
6. Other Business

Nominations for the Officers of Council close with NZIC administration on 31 October 2010. Email: ***NZIC.office@nzic.org.nz***

Hydrated Complexes in Earth's Atmosphere

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Introduction

In recent years, a number of global environmental problems have arisen due to anthropogenic atmospheric emissions. The release of sulfur dioxide (SO_2) from fossil fuel combustion has been found to increase the acidity of rain, causing widespread foliar damage in Europe and North America. The use of chlorofluorocarbons (CFCs) as a major component of refrigerants significantly perturbed the atmospheric budget of chlorine, causing ozone depletion in the stratosphere. Probably the most topical global environmental problem of the present time is that of anthropogenic climate change. This results largely from the release of greenhouse gases (GHGs); in particular carbon dioxide (CO_2) from burning fossil fuels and deforestation but also from methane (CH_4) owing to the intensification of agricultural processes. In all of these atmospheric processes, the role of sunlight is of great importance as it provides energy for reactions, producing reactive free radical intermediate species and affecting Earth's energy balance. Thus, to understand fully the chemistry of atmospheric processes, one must understand the interaction of light with molecules, radicals and complexes present in the atmosphere.

Water vapour makes up about 1% by volume of the Earth's atmosphere. Water vapour is one of the major absorbers of both solar and terrestrial radiation. It is one of the most important GHGs in the atmosphere as it traps a large amount of the energy in the 4-20 μm spectral range, contributing to an overall warming of the planet.[1] Extensive spectroscopic experimentation has been conducted on water vapour to determine the exact role that it plays in this absorption. Tens of thousands of rovibrational (coupled rotational and vibrational) lines of H_2O have been measured and characterised. Despite this effort, there is considerable excess absorption that cannot solely be attributed to monomeric H_2O.[2] This excess absorption is well-established and is referred to as the water vapour continuum, although debate is still rife over the exact cause of the absorption.[3] Part of the continuum absorption exhibits a dependence on the square of the water vapour partial pressure, suggesting that it is partly due to bound pairs of H_2O molecules.[2]

The high abundance of water in the atmosphere and its ability to form intermolecular hydrogen bonds means H_2O can form complexes readily with itself and other atmospheric molecules. These are collectively referred to as *hydrated complexes* and the strength of interaction varies from < 1 kcal/mol for weakly-bound van der Waals complexes such as $H_2O\cdots O_2$ and $H_2O\cdots Ar$, to 6–12 kcal/mol for strong hydrogen bonded complexes,[4-6] such as $H_2O\cdots NH_3$ and $H_2O\cdots HNO_3$. Complex formation causes changes in the geometries and physicochemical properties of the individual monomers that can lead to shifts in the absorption spectra and changes in chemical relativities compared to those of the constituent monomers. Often, new features, such as intermolecular modes that are unique to the complex, arise upon complex formation. The most conceptually simple hydrated complex is the binary complex of water, the water dimer ($H_2O\cdots H_2O$), the structure of which is shown in Fig. 1. Knowledge of its vibrational spectrum is essential in elucidating the role of complexes in the water vapour continuum, and hence the absorption of solar and terrestrial radiation.

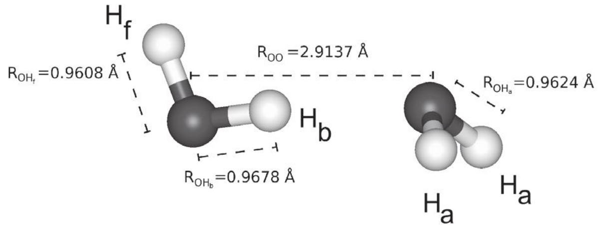

Fig. 1. CCSD(T)/aug-cc-pVTZ calculated structure of $H_2O\cdots H_2O$.

The formation of a hydrated complex $H_2O\cdots X_{(g)}$, where $X_{(g)}$ is any other species, can be expressed by:

$$H_2O_{(g)} + X_{(g)} \rightleftarrows H_2O\cdots X_{(g)}$$

The relatively weak binding of the hydrated complexes means that the partial pressure of $H_2O\cdots X_{(g)}$ is low, *e.g.* the $H_2O\cdots H_2O$ equilibrium constant of dimerization is *ca.* ~0.05/atm, which corresponds to approximately one water dimer for every 1000 water monomers.[7] It follows, therefore, that experimental detection of hydrated complexes is inherently very difficult, no hydrated complex has been unequivocally identified in the atmosphere. There are several techniques that can enhance complex formation in laboratory experiments that include matrix isolation and jet expansions. Such techniques have been used successfully to record vibrational spectra of hydrated complexes.[8] However, these techniques require low temperature and can perturb transitions and, therefore, offer little information on the vibrational spectra at atmospherically relevant conditions. There have been two laboratory experiments conducted on $H_2O\cdots H_2O$ at ambient temperatures, but only in low-energy spectral regions.[7,9] An alternative approach to obtaining spectroscopic information of hydrated complexes is to use theoretical calculations. With the recent advance in computational methods and hardware, it is now possible to calculate many molecular properties of small systems to near-experimental accuracy.[10] What follows is a discussion of recent theoretical advances from our research in calculating the vibrational spectra of hydrated complexes, with application to $H_2O\cdots H_2O$.

Structure and Spectroscopy of $H_2O\cdots H_2O$

The structure of $H_2O\cdots H_2O$ (Fig. 1) consists of two H_2O units, one a symmetric proton acceptor unit (H_aOH_a) and the other an asymmetric proton donor unit (H_fOH_b) that are held together by a near-linear hydrogen bond. Upon complex formation, the O−H_b bond is elongated with respect to the free H_2O monomer. $H_2O\cdots H_2O$ has twelve vibrational degrees of freedom, six attributable to the intramolecular modes of the two H_2O units and six arising from the low frequency intermolecular modes. An exact solution of this twelve dimensional problem presently is not possible and one must use approximations. In the overtone region, the vibrational spectrum of $H_2O\cdots H_2O$ is dominated by OH–stretching and HOH–bending vibrations and the low-frequency motion is expected to have relatively little effect on the position and intensity of the dominant transitions. Thus, it is reasonable to employ an approximation in which only high-frequency OH–stretching and HOH–bending motion is included. Our research has focussed on the use of the local mode model of vibration of harmonically coupled anharmonic oscillators (HCAO) to describe the dominant transitions in overtone spectra.[11]

In 1999, our group first utilized a two-dimensional (2D) HCAO model to calculate the vibrational spectrum of $H_2O\cdots H_2O$. In this model, coupling between each of the OH–stretching modes on the donor and acceptor unit were included.[12] Input parameters were obtained from *ab initio* calculations with empirical scaling factors derived from comparison of calculated and observed parameters for H_2O monomer. Fig. 2 shows the frequencies and intensities of transitions in the fundamental OH–stretching region, calculated using the 2D and subsequent (*vide infra*) models; and from experiment.[13] The 2D calculation showed very good agreement with experiment for the fundamental OH–stretching transitions of both the proton donor and proton acceptor unit.

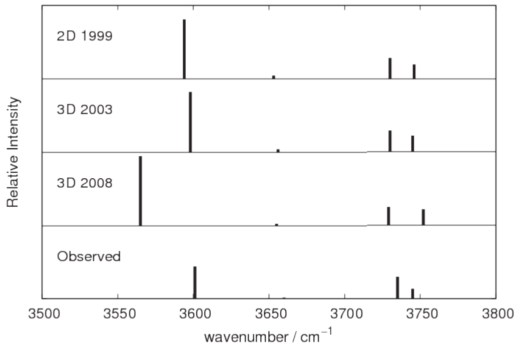

Fig. 2. Frequencies and relative intensities of fundamental OH–stretching transitions in $H_2O\cdots H_2O$, calculated using various HCAO approaches.

In 2003 these calculations were extended by using a three-dimensional (3D) HCAO model that included HOH–bending motion of both proton donor and acceptor units.[14] The major advantage of this model is that HOH–bending and stretch-bend combination transitions could be calculated; they, too, were found to be in good agreement with experiment. Inclusion of the bending mode caused the calculated frequency of the fundamental OH_b–stretching mode to be shifted to slightly higher energy, in better agreement with experiment. The remaining OH–stretching modes showed little change upon inclusion of the bending mode, and remained in good agreement with experiment.

Both of these early HCAO calculations used empirical scaling factors, derived from experimentally observed H_2O transitions. Although this approach gives good results, it is desirable to have a vibrational model that can be used entirely *ab initio*, with no reliance on experimental data. In 2008, a 3D HCAO model was again used to calculate frequencies and intensities of vibrational transitions in $H_2O\cdots H_2O$, but this time employing high-level *ab initio* parameters without empirical scaling.[15] As Fig. 2 shows, the agreement with experiment for the three higher energy OH–stretching transition is somewhat lower than the earlier calculations. However, calculated frequency of the OH_b–stretching transition is lower somewhat than the previous calculations, and in the worse agreement with experiment.

The 2008 HCAO calculations have been compared to a normal mode second-order vibrational perturbation theory (VPT2) calculation that includes all 12 vibrational modes.[15] The results for the fundamental OH–stretching transitions are given in Table 1 and it follows that, for the OH_f– and OH_a–stretching modes, the HCAO 3D calculation is in better agreement with experiment than the VPT2 calculation. For the OH_b–stretching transition, the VPT2 calculated frequency is in very good agreement with experiment. Likely, there is coupling between the OH_b–stretching mode and the low-frequency modes that is included in the VPT2 method, but absent in the HCAO model; this could explain the worse agreement with experiment for this transition calculated using HCAO. Overall, the HCAO local mode model can accurately predict the frequencies and intensities of vibrational transitions in $H_2O\cdots H_2O$, and the calculations can be performed at relatively modest cost.

Table 1. Calculated wavenumbers (cm^{-1}) of fundamental OH–stretching transitions in $H_2O\cdots H_2O$.

Transition	VPT2	HCAO 3D	Expt.[a]
OH_b	3591	3565	3601
OH_a sym.	3634	3655	3660
OH_f	3711	3729	3735
OH_a asym.	3725	3752	3745

[a] See ref. 13.

Band Profiles of $H_2O\cdots H_2O$

In addition to their frequency and intensity, the shape and widths of individual absorption bands are important. Simulations have shown that the absorption of solar radiation by $H_2O\cdots H_2O$ varies significantly as the band profile is varied.[16] Most of the vibrational spectroscopy of $H_2O\cdots H_2O$ is limited to non-equilibrium jet-cooled and matrix isolation experiments and, as such, provides limited information on the shape and width of the absorption bands at ambient temperatures. To shed additional light on the ambient $H_2O\cdots H_2O$ spectra, the band profiles of the OH-stretching transitions in $H_2O\cdots H_2O$ have been investigated. Numerous experimental and theoretical spectroscopic studies of molecules such as toluene and peroxynitrous acid exist and contain high-frequency CH– or OH–stretching vibrations as well as low-frequency internal rotation or torsional modes.[17] In all cases, the XH–stretching bands exhibit rich structure owing to the vibrations of the low frequency modes. This structure has been successfully modelled by considering an adiabatic separation of the high- and low-frequency modes, and a similar approach was used to calculate the band profiles of OH–stretching transitions in $H_2O\cdots H_2O$.

A local mode model that assumes an adiabatic separation between the high-frequency OH–stretching vibration and the low-frequency OO–stretching intermolecular vibration was used.[18] The adiabatic separation is treated in a similar manner to the Born-Oppenheimer separation of electronic and vibrational motion, with the OO–stretching motion taking place in an effective potential that varies significantly with the OH–stretching state. Fig. 3 shows the effective OO–stretching potentials associated with the various OH_b– and OH_f– stretching states and those associated with the OH_b–stretching mode change significantly with quantum number v_b. In contrast, the OO–stretching potentials associated with the different v_f states are almost identical. This is not too surprising as the O−H_f bond is uninvolved in the intermolecular interaction. Transitions between OO−stretching states (with quantum label n) in the ground and excited OH−stretching states were allowed as depicted in Fig. 4. The result is that the OH−stretching band appears as a series of OO−stretching transitions spread over a large wavenumber range, much like vibronic structure in an electronic spectrum. The intensity of each OO−stretching transition is dependent on the overlap of the wavefunctions.

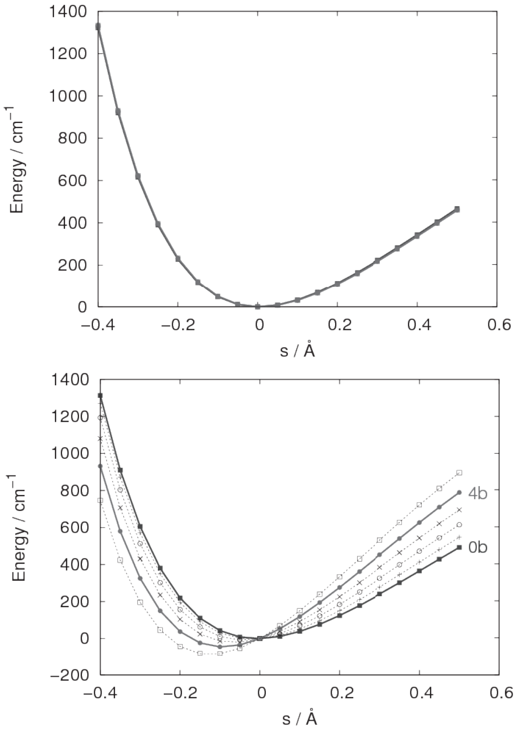

Fig. 3. Effective OO-stretching potentials for OH_f– (upper) and OH_b–stretching (lower) states. ■, $V^{(0)}_{OO} + V^{(1)}_{OO}$; ○, $V^{(2)}_{OO}$; ×, $V^{(3)}_{OO}$; ●, $V^{(4)}_{OO}$; □, $V^{(5)}_{OO}$.; superscripts refer to the number of quanta (v) in the OH–stretching mode.

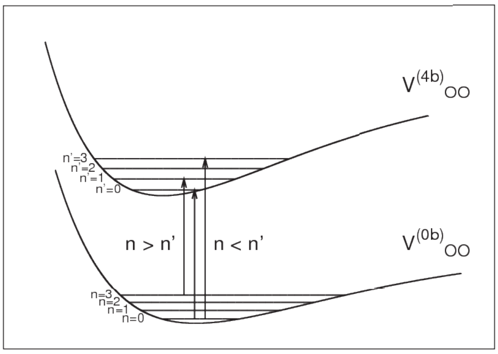

Fig. 4. Schematic of OO-stretching transitions within the 3rd overtone OH_b–stretching transition in $H_2O\cdots H_2O$.

The calculated OO−stretching transitions within the fundamental OH_b− and OH_f−stretching transitions appear in Fig. 5. The effective potentials for the ground and excited states are very similar and only OO−stretching transitions $n' \leftarrow n$, where $\Delta n = 0$, are significantly intense. Adding rotational structure to these transitions and recalculating gives the spectra of Fig. 6 that show limited OO−stretching vibrational structure in the fundamental OH−stretching spectra and, consequently, the OH−stretching band profiles are dominated by rotational structure. The overall width of both bands is ~35 cm^{-1}. Recently, the fundamental region of the $H_2O\cdots H_2O$ spectrum has been recorded in the gas phase under atmospherically relevant conditions.[7,9] Two main peaks due to $H_2O\cdots H_2O$ were observed, with the lower energy one assigned to the fundamental OH_b−stretching transition, and that at higher energy to the OH_f −stretching and asymmetric acceptor stretching modes.[9] At slightly higher energy, weaker combination peaks are observed.[7] Both the observed main peaks were found to have FWHM band widths of ~50-60 cm^{-1}. These results are in good agreement with our calculated widths.

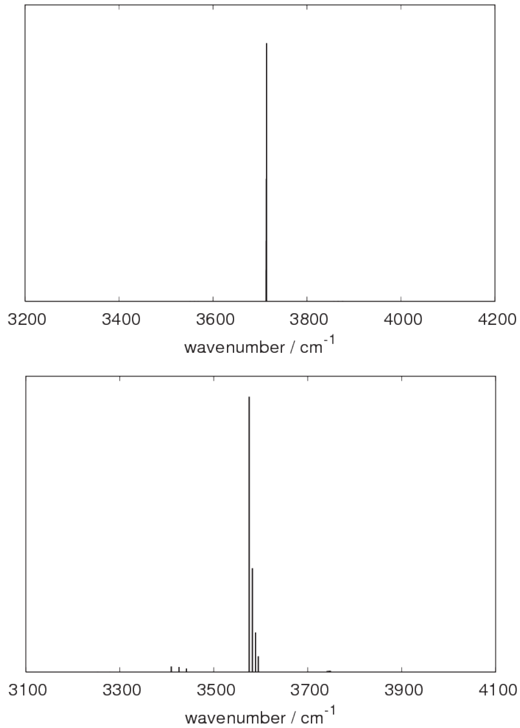

Fig. 5. Calculated OO–stretching transitions within the fundamental OH_f– (upper) and OH_b–stretching (lower) transitions in $H_2O\cdots H_2O$.

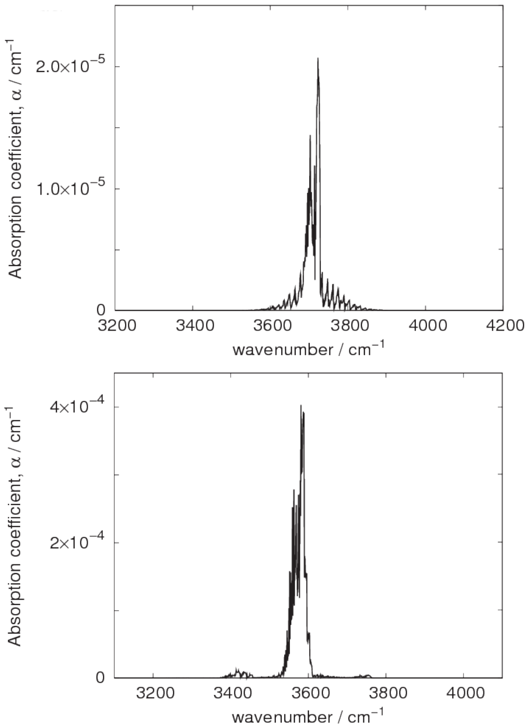

Fig. 6. Simulated spectra of fundamental OH_f– (upper) and OH_b–stretching (lower) transitions in $H_2O\cdots H_2O$.

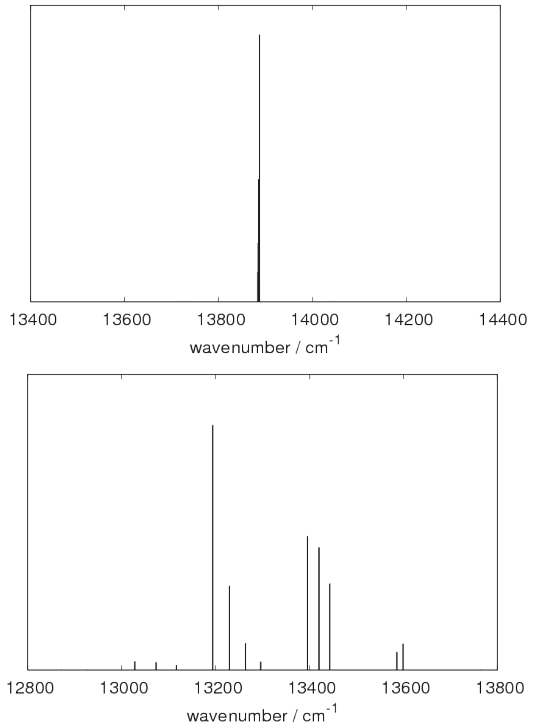

Fig. 7. Calculated OO-stretching transitions within the 3rd overtone OH_f– (upper) and OH_b–stretching (lower) transitions in $H_2O\cdots H_2O$.

The calculated OO–stretching transitions within the third overtone OH_b– and OH_f–stretching transitions are collected in Fig. 7. Again, the only OO-stretching transitions with significant intensity for the OH_f–stretching transition are those with $\Delta n = 0$. In contrast, the ground and excited state OO–stretching effective potentials associated with the OH_b–stretching transitions are displaced such that transitions with $\Delta n \neq 0$ also have some intensity. The resultant spectra, with rotational structure added, appear in Fig. 8. The OH_b–stretching band appears as several peaks spread over a substantial wavenumber range, and the overall profile is significantly widened compared to the third overtone OH_f–stretching transition. The intensities of the third overtone OH_f– and OH_b– stretching transition are similar and, thus, as the width of the band increases, the maximum absorption decreases. This is one of the reasons why detection of OH_b–stretching overtone transitions in $H_2O\cdots H_2O$ is so difficult.

In 2003, a signal due to $H_2O\cdots H_2O$ was reported in an atmospheric spectrum.[19] It was very close in position and overall intensity to that predicted by our early HCAO calculations and it exhibited the corrected dependence on the partial pressure of water due to $H_2O\cdots H_2O$. The observed band had a full width at half maximum of 19.4 cm^{-1} and this was challenged as being too narrow but with no quantification.[20] Our results show that the observed band is up to an order of magnitude too narrow to be due to the OH_b–stretching transition in $H_2O\cdots H_2O$ and highlight the importance of knowledge not only of the position and intensity but also of the shape and width of absorption bands for detection of hydrated complexes in Earth's atmosphere.

Radiative transfer models can be used to quantify the absorption of solar radiation by a given hydrated complex.[7,16]

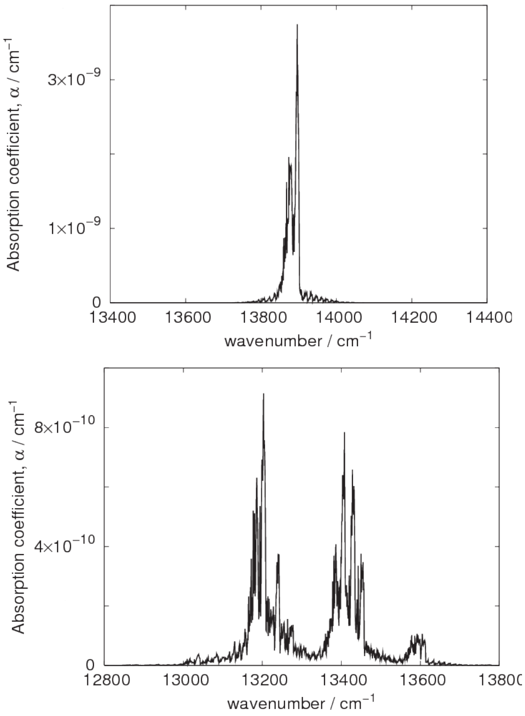

Fig. 8. Simulated spectra of 3rd overtone OH_f– (upper) and OH_b–stretching (lower) transitions in $H_2O\cdots H_2O$.

Such programs require knowledge of many factors such as the absorption by other atmospheric species, Rayleigh scattering and albedo (the measure of how strongly light is reflected), and also require accurate vibrational spectra and atmospheric abundances.[21] Our calculated vibrational spectra are useful inputs for radiative transfer models. In previous simulations of the absorption of solar radiation by hydrated complexes, various estimates of the shape and width of absorption bands were used.[16,21,22] The results of these are shown in Fig. 9, with the band width varying from 20 to 250 cm^{-1} FWHM. The total absorption of solar radiation by each complex increased by an order of magnitude[21] because, as the absorption is spread further from the band centre, the overlap with H_2O monomer transitions is less and the absorption by the complex increases. The absorption bands in $H_2O\cdots H_2O$ likely are even wider than previously suggested. Consequently, the absorption of solar radiation by $H_2O\cdots H_2O$ could be greater than previously thought.

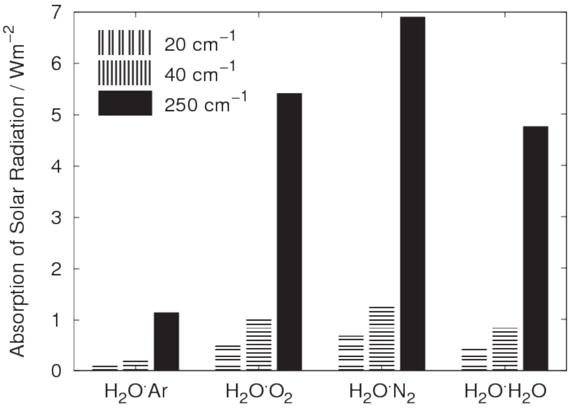

Fig. 9. Total absorption of solar radiation as a function of Lorentzian band width; data taken from ref. 21.

The current band profile model used by us includes only one OH–stretching mode and the OO–stretching intermolecular mode rather than all twelve vibrational modes. An harmonic frequency calculation on $H_2O\cdots H_2O$ indicates that two of the intermolecular normal modes involve OO–stretching motion mixed with the acceptor unit wag and, to a lesser extent, the donor unit rock. These intermolecular vibrations likely will contribute also to the OH–stretching band profile, and essentially *fill in the gaps* in our calculated spectra.

Our results show that simple local mode vibrational models, in conjunction with high level *ab initio* calculations, can be used to calculate vibrational spectra of accuracy useful for laboratory and atmospheric detection. Moreover, $H_2O\cdots H_2O$ and other hydrated complexes likely play an important role in absorption of solar radiation, and impact on Earth's energy balance and climate.

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Healthy Harbour Watchers: Community-Based Water Quality Monitoring and Chemistry Education in Dunedin

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Introduction

Healthy Harbour Watchers is a community-based programme that enables students and volunteers to perform independent investigations into chemical and biological processes in Otago Harbour, while also contributing to an ongoing water-quality data set. The programme began in 2004 when one of the authors (AI) received a Science, Mathematics and Technology Teacher Fellowship from RSNZ. The intention of the Healthy Harbour Watchers programme is to develop community knowledge and skills related to the chemical analysis of seawater. To that end, the programme has involved hundreds of volunteers, including high-school and university students, children, parents, and members of the general public in the collection and analysis of water samples from Otago Harbour over the past six years. The students and volunteers meet at the Otago University Chemistry Department and then work in groups to collect data and water samples from nine standard sites around Otago Harbour using the latitude/longitude data to accurately locate their allocated site (Table 1). Temperature, salinity, pH, and dissolved O_2 are measured in the field prior to the samples being brought to the Chemistry Department where students and volunteers determine concentrations of dissolved reactive phosphorus (DRP), nitrate/nitrite nitrogen (NNN), chlorophyll-*a* (chl-*a*), dissolved O_2, and counts of *Enterococci* bacteria using a suite of spectrophotometric, titrimetric, and microbiological techniques.

Table 1. Latitude and longitude positions of the Healthy Harbour Watchers' nine standard sampling sites.

Site No.	Name	Latitude/Longitude
1	Pulling Point	45° 47.720'S 170° 39.385'E
2	Back Beach-Port Chalmers	45° 49.089'S 170° 37.553'E
3	Mussel Bay-Port Chalmers	45° 49.249'S 170° 36.958'E
4	Ravensbourne Boat Club	45° 52.069'S 170° 32.978'E
5	Leith River Mouth	45° 52.300'S 170° 31.555'E
6	MacAndrew Bay Marina	45° 52.150'S 170° 35.710'E
7	MacAndrew Bay Stormwater Outfall	45° 52.175'S 170° 35.795'E
8	Sommerville Creek	45° 53.554'S 170° 31.680'E
9	Andersons Bay Outlet	45° 53.536'S 170° 31.233'E

The Healthy Harbour Watchers programme allows students and volunteers to perform independent investigations into water-quality parameters using a range of quantitative analysis methods. Students and volunteers are encouraged to design their own experiments and think independently to solve problems in a laboratory setting. Teachers and experienced volunteers give guidance about the sort of experiments that might be the most useful or appropriate. Not every student performs every analysis, but at the end of each session, all of the participants work together to assemble their data into a meaningful report, which is archived for future reference. The results of all the analyses performed are stored in Excel spreadsheets. The students and volunteers are introduced to a range of instrumental techniques for chemical analysis of natural water while working in a laboratory-centred learning environment at the University of Otago.

The programme provides the opportunity for analysis of water samples from several standard sampling sites six times per year, with the analyses having produced sufficient information to define a baseline for water quality in the harbour on the basis of the concentrations of nutrients, dissolved oxygen, and *Enterococci* counts. Because sampling and analyses are performed consistently over the course of each year, the data can be used also to answer questions about spatial and temporal trends in water quality parameters. As the programme continues, this collection of experimental results will provide an increasingly valuable record that may be used for development of a nutrient-based predictive model for water quality in our harbour, and to inform local government, the general public, and other stakeholders interested in the more effective management of Dunedin's water resources. Herein, data collected by the Healthy Harbour Watchers during the 2009 calendar year is presented as it demonstrates the synergy between community-based water quality monitoring and chemistry education in Dunedin.

Sampling Sites and Methods of Analysis

Nine standard sampling sites around Otago Harbour were selected (see Fig. 1 and Table 1) to represent a cross section of the types of water found within the harbour that range from pristine seawater in the lower harbour at Pulling Point, to terrestrially-influenced urban runoff in some areas of the upper harbour. Students and volunteers use Yellow Springs Instruments model 556 digital handheld multi-probe meters to collect information about temperature, salinity, and dissolved O_2 in the field. They then corroborate their field readings using a Mohr-Knudsen titration technique for salinity and a modified Winkler titration for dissolved oxygen.[1] The measurement of pH is by use of battery-powered pH meters, which the students calibrate using standard buffer solutions.

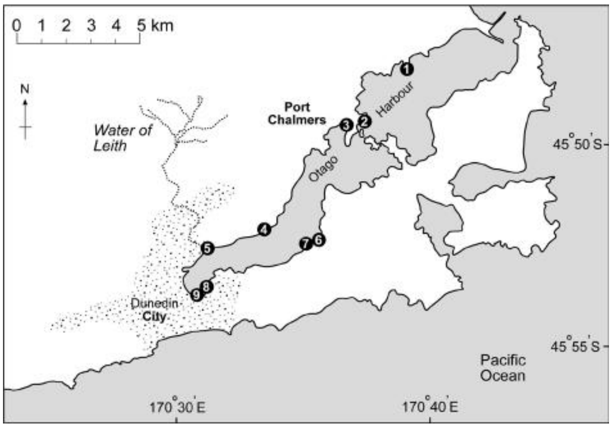

Fig. 1. Otago Harbour showing the locations of the Healthy Harbour Watchers' standard sampling sites (map designed by Lisa Bucke); the latitude/longitude of the sites appear in Table 1.

Concentrations of dissolved reactive phosphorus (DRP) are determined from the reaction of ammonium molybdate with inorganic phosphate in acidified samples and subsequent reduction of the complex to molybdenum blue. The optical density of the complex is determined by absorbance at 885 nm, and is directly proportional to the concentration of DRP in the original sample.[2] Concentrations of nitrate/nitrite nitrogen (NNN) are determined by first reducing nitrate to nitrite using a copper-cadmium column, followed by diazotisation of nitrite and subsequent formation of a pink azo dye, which is quantified by optical absorbance at 543 nm and is proportional to the sum of the concentrations of nitrate and nitrite ions present in the original sample.[3] Concentrations of chlorophyll-*a* in the water samples are determined by spectrophotometric analysis of the homogenate of material filtered from a known volume of sample water and extracted into acetone.[3] This is often the students' first experience with spectrophotometric analysis, and it provides an opportunity to introduce the Beer-Lambert Law and to explain the operation of an absorbance spectrophotometer. Concentrations of *Enterococci* are determined using a two-step membrane filtration method.[4] This microbiological analysis exposes the students to the concept of sterile techniques and introduces basic concepts related to microbial culture. Although the students do not prepare the growth medium themselves, they are responsible for filtering the water samples, aseptically introducing the filter membrane to the growth medium, and counting the colonies after a 48 hour incubation period.

2009 Results and Discussion

Temperature

Students and volunteers made 49 measurements of water temperature during the 2009 programme (Fig. 2). Temperature serves as a broad indicator of water quality, and has a direct bearing on chemical and biological processes that occur in the harbour, including nutrient cycling, and the population and distribution cycles of aquatic species. The minimum temperature measured in Otago Harbour was 7.5 C° at the mouth of the Leith River (site 5) on 23 May 2009, while the maximum temperature was 15.5 C° at the same site on 12 December (day 346). The mean of all of the temperature measurements was 10.8 C° and the data display the expected seasonal pattern and are shown in Fig. 2.

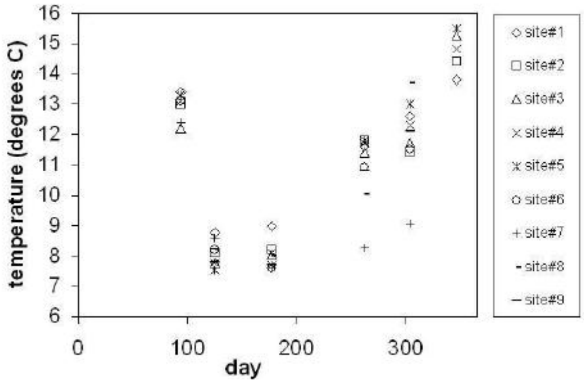

Fig. 2. Temperature variation at the 9 sites during 2009; samples were collected and analysed on 4 Apr, 23 May, 26 Jun, 19 Sep, 31 Oct, and 12 Dec 2009.

Salinity

Salinity in Otago Harbour fluctuates owing to rainfall, river flow, and tidal cycles. Salinity is expressed without units using the practical salinity scale.[5] The measured salinities ranged from 0.16 in MacAndrew Bay Stormwater (site 7) on 31 October (day 304) to 33.6 at Pulling Point (site 1) on 12 December (day 346) (Fig. 3). The vast majority of the samples had salinities between 29 and 33. However, samples collected from the mouth of the Leith River (site 5), MacAndrew Bay Stormwater Outfall (site 7), Sommerville Creek (site 8) and Anderson's Bay Outlet (site 9) sometimes had decreased salinity because of the proximity of the sampling sites to freshwater inputs.

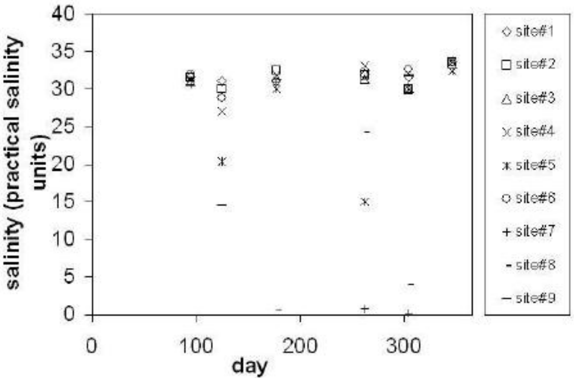

Fig. 3. Salinity variation at each site during 2009.

pH

In total, 37 pH measurements were made during 2009. Logistical constraints and limited availability of equipment meant that it was not possible to measure every parameter at every site during every meeting of the Watchers. However, all of the pH measurements recorded during 2009 are shown in Fig.4 and all of the measured pH values were within the guideline range of 6.5 to 9 with the single exception of the sample collected from the MacAndrew Bay Stormwater Outfall (site 7) on 31 October (day 304), which had a pH of 9.13. It is interesting to note that pH values appeared to decrease in response to the heavy rain event that occurred on 23 May (day 125).

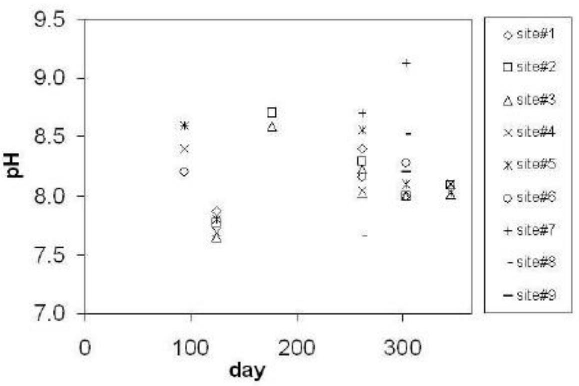

Fig. 4. pH variation at each site during 2009; the decrease on 23 May (day 125) is a result of heavy rain.

Dissolved Oxygen

Dissolved O_2 concentrations are an important indicator of eutrophication. When concentrations become depleted, the likelihood of algal blooms increases and the water becomes uninhabitable for fish and other heterotrophic organisms; the results appear in Fig. 5.

All of the dissolved O_2 concentrations measured in Otago Harbour were above 7 mg/L. Furthermore, no dead fish or dense algal blooms, which can be evidence of anoxia, were observed in any of the samples. Occasionally, samples collected from the mouth of the Water of Leith (site 5) and from the MacAndrew Bay Stormwater Outfall (site 7) were supersaturated with O_2, probably caused by turbulence resulting in entrainment of air into the water.

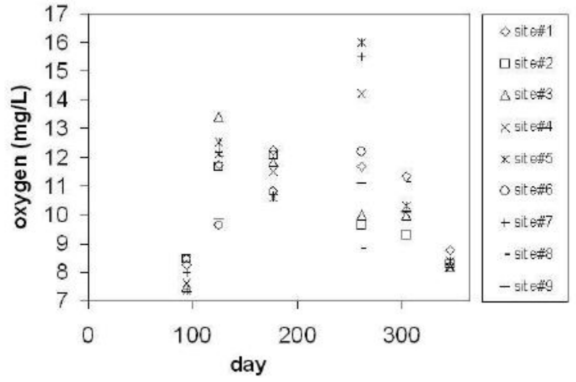

Fig. 5. Dissolved O_2 variation at each site during 2009.

Dissolved Reactive Phosphorus

Concentrations of DRP ranged from a maximum of 5.15 µM in Sommerville Creek (site 8) on 23 May (day 125), when the sample was collected during a severe rain event, to a minimum of 0.33 µM at Pulling Point (site 1) in the lower harbour on 12 December (day 346). Concentrations of DRP always exceeded the guideline value of 0.97 µM in the MacAndrew Bay Stormwater Outfall (site 7) and in Sommerville Creek (site 8), and occasionally exceeded the guideline value at all of the other sampling sites, with the exception of Pulling Point (Site 1) where the maximum measured concentration was 0.84 µM.

Phosphorus is the main cause of eutrophication in estuaries and is frequently a key indicator of water quality deterioration. Because phosphorus is often the limiting nutrient for plant growth in estuaries, even relatively small inputs of it can lead to algal blooms that, upon dying and decomposing, deplete oxygen to levels that can threaten aquatic life. A guideline value of 0.97 µM dissolved reactive phosphorus has been established for the Ruamahanga River near Wellington,[6] consistent with the UN Economic Commission for Europe and The Ontario Ministry of Environment and Energy guideline concentration values of 0.81 to 0.97 µM for phosphorus in surface water. The Healthy Harbour Watchers use a guideline value of 0.97 µM dissolved reactive phosphorus in surface water, with which the data from the sites are compared in Fig. 6. Much of the phosphorus present in estuarine waters is adsorbed on to particles and thereby sequestered from the dissolved phase. As a result, soils act as reservoirs of phosphorus and restrict the immediate impact of phosphorus inputs. However, when phosphorus-rich sediment is re-suspended, for example during a severe weather event, particle-adsorbed phosphorus may redissolve, leading to elevated concentrations of dissolved phosphorus in the water.

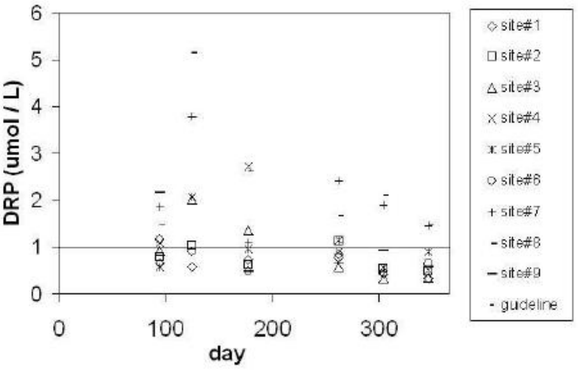

Fig. 6. Dissolved reactive phosphorus variation at each site during 2009.

Nitrate/Nitrite Nitrogen

Our programme has set a guideline concentration of 11.3 µM nitrogen present as nitrate and nitrite (NNN), consistent with the ANZ Environment and Conservation Council trigger value.[7] The measured concentrations of NNN varied from 0.34 µM to 63.4 µM (Fig. 7) and of the 52 samples analysed, 15 had concentrations of NNN above the guideline value. Samples collected from the mouth of the Water of Leith (site 5) and from the MacAndrew Bay Stormwater Outfall (site 7) consistently had concentrations higher than the guideline value.

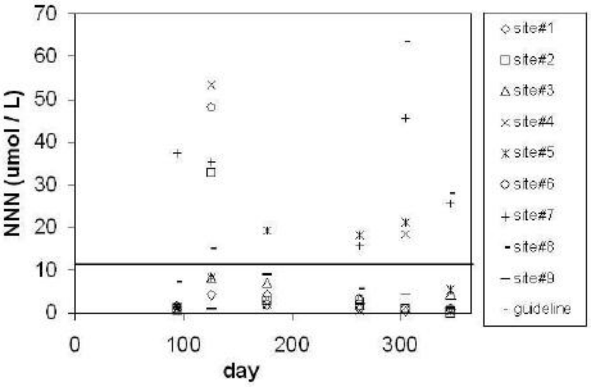

Fig. 7. Nitrate/nitrite nitrogen variation at each site during 2009.

Chlorophyll-a

The measured chl-*a* concentrations were below 4 µg/L with two exceptions, both of which occurred on 23 May (day 125) when the MacAndrew Bay Stormwater Outfall (site 7) was 15.2 µg/L, and that at Mussel Bay, Port Chalmers (site 3) was 7.80 µg/L (Fig. 8). While the concentration of 4 µg/L is not a benchmark concentration or trigger value per se, it is a convenient baseline value for chl-*a* concentrations in Otago Harbour, against which students and volunteers may compare their data to assist with the identification of anomalous measurements. During the 23 May (day 125) sampling trip, it is likely that heavy rain and wind suspended solids in the water that may have interfered with the analysis, leading to anomalously high concentrations of chl-*a* in the samples. Overall, the measured concentrations of chl-*a* ranged from a maximum of 15.2 µg/L in the MacAndrew Bay Stormwater Outfall (site 7) during the 23 May (day 125) sampling trip to a minimum of 0.26 µg/L at the MacAndrew Bay Marina (site 6) during the December sampling on day 346.

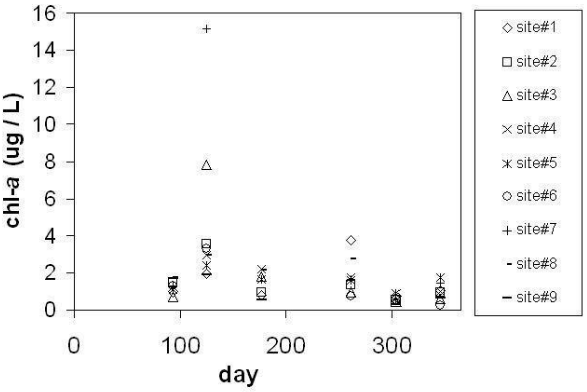

Fig. 8. Measured chlorophyll-*a* concentration variations at each site during 2009.

Enterococci Counts

Enterococci are bacteria often found in the feces of humans and other warm blooded animals.[4] Not all strains of *Enterococci* are related to fecal pollution, but the presence of *Enterococci* in marine water is a widely accepted indicator of the possible presence of pathogens.[4] The guideline for *Enterococci* concentration was set as 140 colonies/100 mL, which is the same as the recreational water quality guideline used by the Otago Regional Council.[8] The measured concentrations exceeded this guideline in only three out of the 35 samples that were analysed (Fig. 9). The sample from Sommerville Creek (site 8) and the sample from the Leith River Mouth (site 5) had high *Enterococci* counts during the May sampling trip (day 125), which coincided with a heavy rain event. In addition, the sample from Sommerville Creek contained 176 Enterococci colonies/100 mL on 31 October 2009 (day 304).

Conclusion

Healthy Harbour Watchers guideline values for concentrations of nutrients and bacteria are not intended to be applied directly as regulatory criteria or limits, but are factors for students and volunteers to consider when making decisions about future investigations. While the need to define guideline values for nutrients is debatable,[7] some indication of nutrient concentrations that constitute a threat are needed in order to assist students with data interpretation and experimental design. When students and volunteers measure values that are within the range prescribed by the guidelines, they are monitored and recorded, and when the measured values are outside of the guidelines, students are encouraged to perform more detailed investigations into the reasons for the deviations observed and suggest possible remedies.

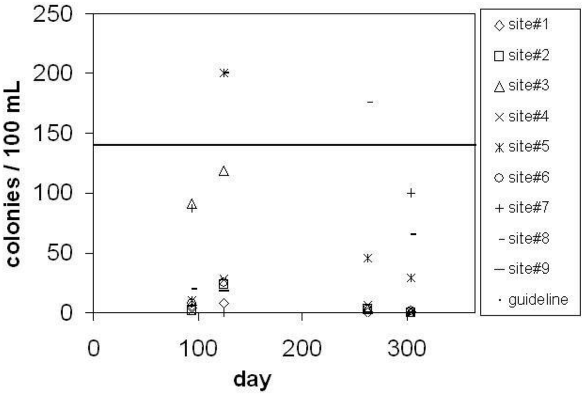

Fig. 9. *Enterococci* count variation at each site during 2009; samples with colonies too numerous to measure are shown as 200 colonies/100 mL.

There are many anthropogenic sources of nutrients around Otago Harbour. Wastewater discharges, terrestrial runoff, fertilizers, and atmospheric deposition can all contribute to elevated concentrations of nitrate and dissolved reactive phosphorus. The data collected by us generally suggest that further site-specific investigations are necessary to determine if special action is required to limit nutrient and bacterial input into Otago Harbour. No evidence of anoxia or excessive eutrophication was found in the data reported here, and chl-*a* concentrations suggest that excessive algal growth did not occur at any of the sampling sites. However, concentrations of nitrate/nitrite nitrogen and dissolved reactive phosphorus were frequently above the guideline values, particularly at the MacAndrew Bay Stormwater Outfall and at the mouth of the Water of Leith, where terrestrial inputs and anthropogenic sources are likely to have influenced nutrient concentrations.

Most importantly, the Healthy Harbour Watchers programme has transfered chemistry knowledge and analytical skills to students and volunteers, while also providing information about baseline water quality in the harbour. The students are encouraged to perform independent investigations into water quality parameters and, throughout, the Chemistry Department provide them with access to a range of quantitative analysis methods and practical experiences that are not available in high school laboratories. In the future, the Healthy Harbour Watchers programme hopes to involve students and volunteers in the development of a nutrient-based predictive model for water quality in Otago Harbour continue to engage them in the collection and analysis of water samples from the harbour.

Acknowledgements

We thank Otago area school teachers, students, volunteers and helpers for making the programme possible, especially David Patchett, Murray Vickers, and Kate Gnoth for continuing support. We are indebted to Ian Billinghurst, Rob Alumbaugh, and Ben Durrant for laboratory assistance. The RSNZ is thanked for its Science, Mathematics and Technology Teacher Fellowship (to AI).

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Hot Chemistry from Horopito

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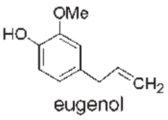
Introduction: The New Zealand Pepper Tree

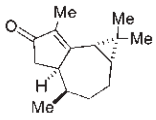
Many will be familiar with horopito, *Pseudowintera colorata*. This shrub is often found in disturbed bush and along track margins. It is readily recognised by its red blotched leaves (see front cover and dark spots in Fig. 1), and by using one of our chemical senses, namely taste. A cautious nibble on a horopito leaf shows why it is called pepper tree, as the pungent, burning sensation develops on one's tongue. Past and present research on this unique NZ plant is discussed and brings together its hot and colourful chemistry.

Fig. 1. Blotched leaves of horopito, *Pseudowintera colorata* (courtesy of Luke Youard, Botany Dept., Otago University); see front cover for colour illustration.

Horopito has traditionally been used by Māori and European settlers for a variety of ailments, including toothache (by chewing) and skin diseases (by external application).[1] The first chemical studies were reported in 1958 by Corbett and Grant on a steam distilled oil from horopito leaves.[2] A range of mono- and sesquiterpenes were identified, together with the phenylpropanoid, eugenol. Eugenol, from clove oil, has been used as a local antiseptic and anaesthetic, but is not present in horopito in sufficiently high levels leaves to explain the medicinal activities. Corbett and his colleagues also found (and named) the sesquiterpene cyclocolorenone in their steam distillate, and correctly established its unusual structure.[3] This was achieved by chemical transformations without access to the NMR spectroscopy or X-ray crystallography that now we rely upon so heavily for structure determination.



eugenol



cyclocolorenone

Pungent Polygodial

An Anti-Candida Agent

Screening of NZ plants for antibiotic activity by Canterbury University researchers showed that a horopito leaf extract stood out for its activity against *Candida albicans*, a yeast that can cause thrush infections.[4] Bioactivity-directed isolation work gave the main active compound identified as the sesquiterpene dialdehyde polygodial (**1**, Chart 1).[5] US researchers later found that the anti-*Candida* activity of polygodial was strongly increased by the presence of anethole,[6] a phenyl propanoid natural product that gives the characteristic flavour of anise. An NZ company, Forest Herbs Research in Golden Bay, is growing horopito and marketing a range of medicinal products based on these results. Forest Herbs and IRL have patented a process for extracting **1** from horopito using supercritical carbon dioxide.[7]

Polygodial (**1**) was known before it was found in horopito. It was first reported from, and named after, the water pepper *Polygonum hydropiper* by Australian chemists.[8] Water pepper, now classified as *Persicaria hydropiper*, is used in some Japanese dishes because of the pungency of polygodial.[9] Polygodial was also reported at the same time from the Australian mountain pepper, *Tasmannia* (earlier *Drimys*) *lanceolata*.[10] It is the most widely occurring sesquiterpene dialdehyde, having been found in flowering plants, ferns, liverworts, fungi, and marine molluscs from all around the world.[11] The drimane skeleton of **1**, and many of the other dialdehydes, is named after the plant genus *Drimys*, also in the family Winteraceae, the source of medicinal winter's bark from the South American *Drimys winteri*. The presence of **1** in horopito leaves is high as simple $CDCl_3$ extraction shows the two obvious aldehydic protons in the ^{1}H NMR spectrum of **1**, allowing quantitative analyses, with levels up to 40 mg/g of dry leaf.[12] The earlier work on steam-distilled leaf oil probably missed polygodial because of its low volatility and high reactivity.

An Insect Antifeedant

The attention of the Plant & Food Research group at Otago was drawn to horopito because tests run at AgResearch in Hamilton on leaf extracts showed strong antifeedant activity against insects. Bioactivity-directed isolation work showed that the main antifeedant compounds were **1** and **2**, the closely related 9-deoxymuzigadial (**2**, Chart 1).[13] Dial **2**, with its rare rearranged drimane skeleton, had only been reported once before this discovery, from a Caribbean plant *Cannela winterana* (family Canellaceae).[14] It was not reported in the Canterbury work,[5] and the Plant & Food Research group found out why when they analyzed different horopito collections from around the South Island, using HPLC and by quantitative 1H NMR spectroscopy. The ratio of dialdehydes **1** to **2** varied regionally with West Coast and Nelson horopito leaves dominated by **1**, whereas Otago and Canterbury leaves contained almost equal levels of **1** and **2**.[12]

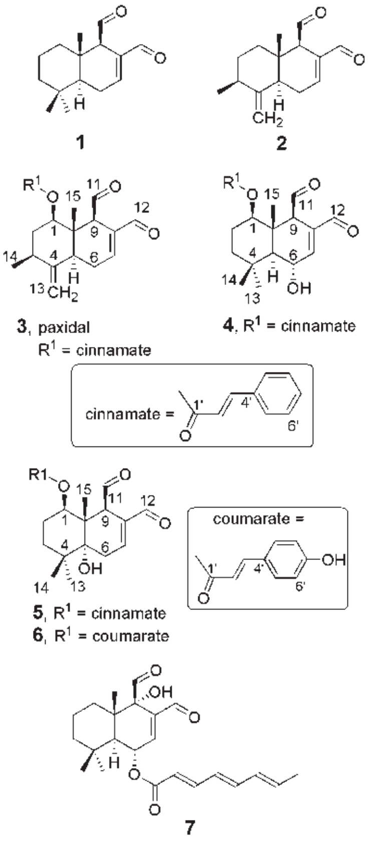
Dialdehydes **1** and **2** had similar insect antifeedant activity against the two pests tested by AgResearch, namely caterpillars of the webbing clothes moth and larvae of the Australian carpet beetle.[13] However, storage trials on wool treated with dialdehyde showed that the protective antifeedant activity was lost after a few weeks and so no commercial development was possible.

A Chemical Sensor of Electrophiles

Polygodial was also found to have other biological activities by the Plant & Food Research group. Thus, anthelmintic activity (the expulsion of parasitic worms) against the sheep parasite *Trichostrongylus colubriformis* was found in collaboration with AgResearch,[15] and anti-inflammatory activity in a mouse model of gout by working with the Malaghan Institute and NIWA.[16] Others have found cytotoxicity, plant growth inhibition, and piscicidal and molluscicidal activities for **1** and other unsaturated dialdehydes.[11]

The broad, non-selective range of biological activities of **1** is ascribed to its electrophilic reactivity[11] that binds it to thiols and amines in proteins. Italian researchers showed that the reactivity of 1,4-dialdehydes with methylamine (under conditions mimicking cellular systems) correlated with their hot taste, and they found that stable pyrrole derivatives were formed.[17] More specifically, polygodial has been shown to activate an ion channel receptor TRPA1 (transient receptor potential A1) involved in inflammatory pain signalling.[18] This receptor is present in vertebrates and invertebrates, and acts as a chemical sensor for toxic electrophiles.[19] Other pungent compounds such as allyl isothiocyanate (responsible for the *hit* of wasabi) and cinnamaldehyde are active at this receptor, which is unusual; receptors generally respond to particular molecular shapes rather than chemical reactivity. The cysteines within TRPA1 are covalently modified by electrophiles, causing channel activation and rapidly signalling potential tissue damage through the pain pathway.[20]

Chart 1. Structures of sesquiterpene dialdehydes from *Pseudowintera* and other organisms.



Red Hot

The other chemical characteristic of horopito that we can study directly with our senses is the red marking of its leaves (front cover), which gives the specific name *colorata*. This coloration is a response to damage, which can be induced if you find horopito on a favourite bush walk – simply select a leaf close to the growing tip at the end of a branch, mark your initials (or those of some significant other) on this with a finger nail. Within a few days the initials will be highlighted in red.

The red pigments were identified as anthocyanins by IRL's Ken Markham when he worked on this wounding response with plant physiologists at Auckland University.[21] They used real-time imaging of hydrogen peroxide to show that mechanical injury elicited an oxidative burst from chloroplasts. H_2O_2 accumulated in green leaf portions for 10 minutes, and then decreased slowly. By contrast, red regions recovered rapidly and maintained consistently low levels of H_2O_2. The red regions were enriched in anthocyanins, flavonols, dihydroflavonols, and hydroxycinnamic acids, all of which are antioxidants, but only the anthocyanins were suitably located to account for enhanced rates of H_2O_2 scavenging. The data support the hypothesis that red cells have elevated antioxidant capabilities *in vivo*, protecting the leaves from further damage from reactive oxygen species.

Red Alert?

The combination of the results on insect antifeedant activity and on inducible red coloration led Gould and Perry to speculate that the two observations might be linked. Youard, in his Otago PhD work, found that that the redder horopito leaves contained greater polygodial levels.[22] This led to the question of whether horopito was an example of a plant using colour to warn approaching herbivores that it is chemically well-defended.

Aposematic (warning) colouration is a well-known phenomenon in animals, but has only recently been considered in plants. Nevertheless, there are plants from all terrestrial biomes whose leaves are pigmented red rather than green, and the possibility that their bright colours are involved in defence has begun to attract keen theoretical support. The hues of autumn foliage, for example, are postulated to serve as an honest signal of defensive commitment against colonising insect pests. The implications of this hypothesis are profound. However, foliar aposematism lacks solid experimental proof.

A Marsden funded project is now underway in our laboratories to test for aposematism directly using horopito.[23] Our multidisciplinary team combines expertise in native plant biochemistry, anthocyanin function, plant-insect interactions and community ecology, based at Victoria and Plant & Food Research at Otago universities. There is also collaboration with Martin Schaefer (University of Freiburg) who has expertise on the evolutionary ecology of visual communication in distinct signalling systems. Combining these skills to study the ecological biochemistry of horopito and its predators will engender a significant contribution to the understanding of the role of plant colouration in ecosystems. There are also implications for agriculture with proof of aposematism presenting the possibility of using leaf colour as a novel tool to mitigate crop damage, thereby reducing the increasingly evident ecotoxicological problems associated with pesticide use.

Cooler, Greener Plant Protection

There is another plant protection opportunity offered by another *Pseudowintera* species. The shrub know as *P. axillaris* is also called horopito. It grows throughout the NZ North Island but only at the top of the South Island, whereas *P. colorata* is found throughout most of NZ including Stewart Island. The two species can readily be distinguished by appearance and taste since *P. axillaris* has larger leaves with no red blotching and *axillaris* is much less pungent than *colorata*. The two species also showed up quite differently in various screening assays as *P. axillaris* extracts show much less biological activity than *P. colorata* extracts. However, screening in an agrochemical discovery collaboration with Dow AgroSciences showed good activity for an extract of *P. axillaris* against *Phytophthora infestans*,[24] the plant pathogen that caused the Irish potato famine.

Bioactivity-directed fractionation of an extract of *P. axillaris* provided the main active compound with a ^{1}H NMR spectrum with aldehydic signals akin to those of **1** and **2** and signals consistent with a cinnamate group. 2D NMR spectra indicated that the structure was **3** (Chart 1), a new structure named paxidal.[24] This was available at quite high levels from leaves, allowing preparation of a series of derivatives for further antifungal testing. Structure-activity studies showed that both the dialdehyde and the bulky cinnamate groupings were important for the fungicidal activity. [24] However, none of the derivatives met the stability requirements for commercial development

The switch in biological activity provided by the cinnamate substituent is interesting. Cinnamate **3** was not active against *Candida albicans*, in contrast to the strong activity of **1** and **2**, but neither **1** nor **2** showed any activity against the plant pathogens tested. The lower pungency of *P. axillaris* suggests a lowered electrophilic reactivity of the unsaturated dialdehyde moiety owing to the bulky cinnamate substituent, at least towards TRPA1.

New Species, New Chemistry

The genus *Pseudowintera* is endemic to NZ, with *P. axillaris*, *P. colorata* and the Nelson species *P. traversii* long known. Recently, Conservation Department and Landcare botanists proposed a new species, *P. insperata*.[25] This is a threatened species known only from 46 mature individuals confined to the volcanic plugs above the Whangarei Harbour. In view of results on the other species, it seemed likely that *P. insperata* would also contain sesquiterpene dialdehydes and possibly new ones.

DoC provided samples of *P. insperata* leaves from cultivated plants. These were found to be much less pungent than leaves of *P. colorata*, implying low levels of **1**. Crude extracts from the leaves showed the characteristic ^{1}H NMR signals of unsaturated 1,4-dialdehydes, and two were isolated. The minor component, dialdehyde **5** (Chart 1), showed ^{1}H NMR signals characteristic of a polygodial derivative with a cinnamate moiety at C-1, similar to cinnamate **4** that is found in fruits of *P. colorata*.[26] Mass spectrometry on **5** suggested a molecular formula isomeric with **4**, but the 2D NMR data placed an α-OH group at C-5. This led to the proposed structure of **5**, namely the previously unknown (*E*)-1β-cinnamoyl-5α-hydroxypolygodial. However, prior to the *P. insperata* results being written up, the structure of **5** was published as occurring in *Zygozynum* spp. (also in the family Winteraceae) from New Caledonia.[27]

The major new dialdehyde was identified as **6** and differed from **5** only by having ^{1}H NMR signals characteristic of a coumarate moiety at C-1. The structure was assigned as

(*E*)-1β-*p*-coumaroyl-5α-hydroxypolygodial (insperadial, **6**, Chart 1). This structure remained unreported until this year when the *P. insperata* results were published.[28] Thus, the new species did yield new chemistry.

We extended this study by analysing multiple samples of *P. axillaris*, *P. colorata* and *P. insperata* collected from around the North Island by DoC staff. HPLC analyses showed that the main dialdehydes in the leaves conformed to the species boundaries. Thus, *P. insperata* individuals all had high levels (3.0–6.9% of leaf dry wt.) of coumarate **6**, *P. axillaris* had high levels (2.2–6.9%) of paxidal (**3**), and *P. colorata* from different regions of NZ contained varying levels of polygodial (**1**) (1.4–2.9%) and 9-deoxymuzigadial (0–2.9%) (**2**),[28] as previously found for South Island collections.[12] Therefore, the sesquiterpene dialdehydes are good species markers in *Pseudowintera*, but potential hybrids with different chemical composition were also found.[28]

Hot Questions

We have shown how the natural products chemistry and bioactivity of horopito and polygodial (**1**) has interested, and brought together, researchers from many of NZ's universities and research institutes. However, questions remain to be answered, most particularly the wide-spread occurrence, both geographical and biological, of **1**.

The results described herein have shown the chemotaxonomic links between the two vascular plant families Canellaceae and Winteraceae, which both consistently contain sesquiterpene dialdehydes, from plants growing in the Caribbean, South America, Africa, Australia, New Caledonia and New Zealand. However, **1** has also been found in other, unrelated organisms from all around the world – ferns from NZ and South America;[29,30] liverworts from NZ, Europe and Japan;[29,31] and in marine molluscs from the Mediterranean and Pacific.[32] At the microbial level, polygodial derivative **7** (Chart 1) has been reported from a fungal mold *Aspergillus* species, from a soil sample cultured in Japan.[33]

The diverse and potent biological activities of the sesquiterpene dialdehydes described herein presumably offer evolutionary advantages to all of these organisms. What is not known is how the same secondary metabolites, with quite complex structures, arise in so many different life forms. Could this be from parallel evolution, production by a symbiotic microorganism, or even horizontal gene transfer? More research and increased levels of funding are needed, as we scientists like to tell anyone who will listen.

Acknowledgements

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Jan Romuald Zdysiewicz, FRACI (1943-2010)*

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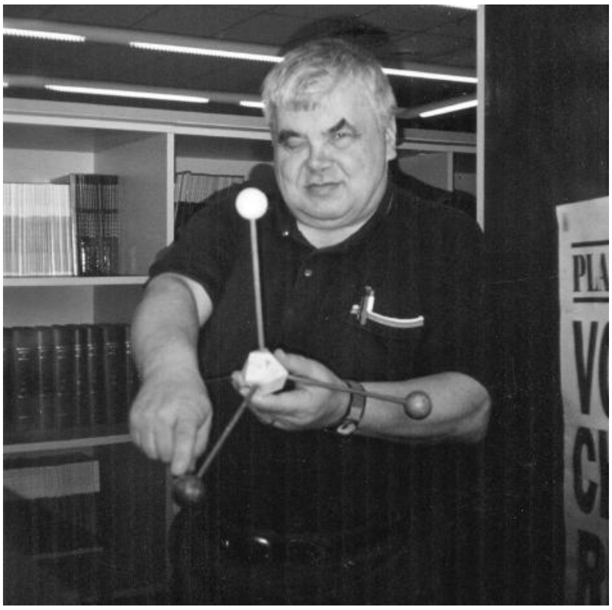
Jan Zdysiewicz, known to most of us as John Z, former Managing Editor of the *Australian Journal of Chemistry*, died in the Royal Melbourne Hospital on 10 March 2010, followed by family burial in Adelaide.

John was born in Laukischken, East Prussia, on 12 April 1943. His parents were Polish, from Mosty, near Lwow, now part of Ukraine. They had been taken to Germany as forced labour during World War II two months prior to John's birth. For several years after the war, they were shifted from camp to camp as displaced persons. Eventually they were accepted for migration to Australia, and the family arrived by ship at Port Melbourne in December 1950. More camp dwelling followed, including time spent at the large immigration centre at Bonegilla, until they were able to settle in Adelaide. John attended Adelaide Boys High School and in 1962 became an Australian citizen. As a child, he was interested in photography and sport, and he displayed a great fondness and talent for music.

By 1965 John had completed BSc (Hons.) in physical and inorganic chemistry at the University of Adelaide, gaining a First. He continued there on to the PhD, which he completed in 1968, under the supervision of Tom Kurucsev. Then followed postdoctoral work at the University of Lancaster, where he was a Leverhulme Visiting Fellow. In 1970, he came to Melbourne as a Postdoctoral Fellow in the CSIRO Division of Protein Chemistry. For his final postdoctoral appointment, he went abroad again in 1973, to the University of Western Ontario. Up to that point his research was broadening with each successive appointment, and he published several papers in the primary chemical literature. His interests included work on oriented DNA films, ESR studies on radical anions, interaction of fluorescent whitening agents with wool components, and photochemical reactions involving radical ions. In 1974 he married Joan; there were no children.

In 1975 John made a change that was to dominate the second half of his life. He moved into scientific publishing to another part of CSIRO, as Assistant Editor of the *Australian Journal of Chemistry*, where he was mentored by Bob Schoenfeld. As strong, independent folk, Bob and John had very different personalities but they shared great respect, the one for the other. They had other things in common, too. Against the odds, both succeeded professionally despite having their early lives blighted by wartime disruption; and each in succession could be considered to have become the Australian arbiter in matters of good chemical communication, possessing enviable skill in English, despite not having English as his first language. When Bob retired in 1985, John became Managing Editor of the *Journal*, where he remained until his retirement at the end of 2000.



John Z in his office at CSIRO PUBLISHING, 1998.

As Managing Editor over a timeframe when scientific publishing saw many technological changes, John was very much hands-on. He brought meticulous accuracy to every aspect of the editorial process and took creative pride doing so. But he was also a very visible participant in the corporate life of Australian chemistry, known widely, never losing an opportunity to engage with established authors and referees or to drum up new ones, giving and sponsoring lectures, visiting departments, attending conferences, and awarding prizes, particularly as a means of encouraging student participation.

John's exceptional patience for his work, and the respect he showed to members of the chemical community, earned him much admiration from his colleagues. He was a scrupulous and supportive mentor, and placed equal value on both a solid work ethic and the necessity to treat people with great respect. He demonstrated particular kindness and encouragement to students and young scientists at the beginning of their careers. Those lucky enough to be invited will never forget the outstanding Christmas lunches that he hosted at the Macedonian Restaurant. Many will remember his booming laugh that punctuated refreshment sessions after lectures and symposia.

John was a member of the Royal Australian Chemical Institute for 40 years, becoming a Fellow in 1994. In 1998 he was awarded an Institute Citation for his contribution to the promotion of Australian chemistry nationally and internationally. From 1987 to 1997 he served on the IUPAC Commission III 2 (on Physical Organic Chemistry), first as a National Representative and then as an Associate Member. Outside of chemistry, he possessed one particular talent, of which he rarely spoke. He was a first-rate accordion player (in 1961 he was Grand Australian Accordion Champion), something that, in later years, those of us who were privileged to hear him in action could vouch for. In retirement, he was set to take satisfaction honing this skill. Sadly, the onset of debilitating illness allowed him little opportunity to do so.

John was a shy person but one who possessed sharp intellect, broad knowledge, and strong views. His professional life revolved around the *Australian Journal of Chemistry*, maintaining its editorial standards and integrity at exceptionally high level. Relaxing with his many friends, though, he was socially ebullient, great company, and extraordinarily generous. He was an outstanding human being, and a true friend. Early in 2006 he successfully underwent surgery for prostate cancer. But that was followed by severe symptoms of Parkinson's disease that greatly impeded the remainder of his life. During that time, in and out of hospital, he was helped by his younger sister, Janina. At the end, he never regained consciousness following a cardiac arrest at home, and he died a few days later. We deeply regret his passing.

Jenny Bennett, a PhD graduate from the University of Melbourne, is Publisher of the chemical sciences journals within ***CSIRO*** *PUBLISHING. Don Cameron was Professor of Organic Chemistry at the University of Melbourne from 1968 to 2000 and a member of the Editorial Advisory Committee for the Australian Journal of Chemistry from 1978 to 1983, and was the Committee's Chairman from 1990 to 1995; he lives in retirement in Melbourne.*

Earthquakes and Chemistry

Anthea Lees

Like many other residents of Christchurch and Canterbury, my family and I were awoken in the most terrifying manner at 4.35 am on Saturday 4th September 2010 by a 7.1 magnitude earthquake. The major quake had a focal depth of 10 km and was situated 10 km south of Darfield (*ca* 40 km west of Christchurch). Our house felt as though it was placed on a surf board riding on very large waves, accompanied by the noise of a passing train.

An earthquake is the result of a sudden release of energy in the Earth's crust that creates seismic waves. These waves, which travel through the earth, are primary (P-waves) and secondary (S-waves) waves. The low rumbling noise you hear is associated with the P-wave and this is quickly followed by the S-wave, which is what you feel under your feet. P-waves travel at about 5 km/s while S-waves are slightly slower; travelling at 3 km/s. The earthquake was a strike-slip quake which means that it occurred on an approximately vertical fault plane as the rock on one side of the fault slid horizontally past the other. The fault ruptured east to west away from Christchurch and was previously unknown.

Geologists, including Dr. Mark Quigley from the University of Canterbury (UC), have appeared regularly on the news and on the children's TV2 programme *What Now* explaining the concepts behind earthquakes and the phenomenon known as liquefaction. Soil liquefaction describes the action of soils suddenly moving from a solid to a liquefied state, when stressed by some external force. A number of houses in Christchurch and surrounding areas were affected in this way. Soil liquefaction can cause rigid structures, like buildings and bridges, to tilt or sink into liquefied soil deposits.

In the aftermath of the earthquake, work is now focused on the assessment of damaged buildings and monitoring their structural integrity. It is thought that more than 500 buildings in the city were damaged with over 90 of those in the central city area. Thankfully no-one was killed or seriously injured. What impact has the earthquake had on the Department of Chemistry at UC? Department Head, Professor Alison Downard, kindly provided this statement:

On 4th September at 4.35 am, the Canterbury region suffered a magnitude 7.1 earthquake. There has been no loss of life and few injuries, but a lot of damage to some parts of Christchurch and nearby areas. We know of no injuries to members of the Chemistry Department and most of us suffered only very minor damage to property. Unfortunately there are exceptions and several people have had serious damage to their homes.

Many university staff and students live close to the campus and this part of the city was relatively lightly hit. However, the Department of Chemistry, housed in the eight storey Rutherford building, did get a big shake-up, with increasingly dramatic results going up the floors. Over the past week, a great team of mainly technical staff, along with other University personnel, were involved in an initial assessment of risks, identifying and dealing with physical and chemical hazards and cleaning-up. Now that order has been restored and the building made safe, we can see that things could have been much, much worse.

Staff and some research students are at work in the Department this week and it's a hive of activity, testing and assessing equipment and instruments, and assessing loss of samples. With teaching re-starting next week, academic staff are also getting on with teaching preparation and their usual administrative tasks. We hope that at least some researchers will be back in their laboratories next week (three weeks after the earthquake). Morale is high and we're making fast progress towards 'business-as-usual'.

During the past week we have received numerous messages of concern and offers of assistance from friends, colleagues and chemistry departments from New Zealand and around the world. It is heart-warming to experience such support and generosity and to know we really are part of an international community of chemists. Thank you for your emails and phone calls. 14/9/2010

Green is the New Black

Katherine Hebditch and Tim Stirrup

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Inventions in the field of Green Technologies (or *Green Tech*) seem to be one of the hot topics in the patent world at the moment. Can we save the world one patent at a time?

Initiatives by Patent Offices to promote Green Tech

A patent application can be filed in most countries in the world but in most cases a patent will not be granted until it has undergone examination to determine if it contains patentable subject matter. In a number of countries the time between the filing of a patent application and the start of the examination process can be two years or more.

Driven by fears of climate change and limited natural resources, many developed countries are trying to encourage and accelerate the development of innovation in the field of Green Tech. With this goal in mind, some Patent Offices have initiated schemes to allow patent applications related to Green Tech to be examined ahead of the rest. Where these schemes are in place, the wait for examination of a patent application can be reduced from years to a few months.

Patent offices currently offering or planning schemes like this include Australia, Israel, Japan, Korea, the UK and the United States.

Some of these schemes (such as in Australia and the UK) are straight-forward to apply for and are providing great benefits for applicants who wish to have a patent granted quickly.

Pilot Scheme in the United States

The initial uptake of the pilot scheme in the US has been slow. When the pilot scheme was started in December 2009, the patent office announced it intended to accelerate the examination of the first 3000 eligible applications to apply for the scheme. However, from the beginning of the scheme until May 2010, only 342 applications were accepted.

In May 2010, the office announced they would expand the scheme to encompass a broader classification of what they considered to be a Green Tech invention (and therefore potentially eligible for the scheme). Previously, only a very limited range of technologies was eligible, which was found to be the main reason applications were being denied.

As of 26 August 2010, 716 applications have been accepted onto the scheme out of a total of 1477 applications. There is still some way to go before the full allocation of 3000 is filled. It is likely the scheme will receive diminishing applications, and may not meet its full allocation, as one of the main criteria is that the patent application must be currently pending. Patent applications filed after 8 December 20092 are not eligible to enter the scheme. Therefore as these pending applications move towards being examined by the normal process, there will be less reason to apply and fewer applicants will who want to accelerate examination.

Problems of classification

What is Green Tech? The United States Patent and Trade Mark Office initially used a very narrow definition of the technology. In contrast, under the UK Patent Office scheme any patent application which relates to an invention in the *green* or *environmentally-friendly* technology space can request accelerated examination. Examples of patent applications in the scheme range from a hip prosthesis system which can allow a hospital to carry less stock and parts[2] to production of butanol using thermophilic Bacillaceae.[3]

It is clearly hard to define what Green Tech is. It can also be hard to search for previous patents in the area as the field can be very broad. In order to avoid infringing existing patents and to search for ideas that could be licensed from the patentee, it is essential that patent databases can be searched quickly and easily. However, traditional classification codes for Green Tech inventions are in some cases inadequate as the technology has moved on but the classification has not kept step.

The European Patent Office is responding to this problem by introducing new classification codes for patents in the Green Tech area. All patent applications are currently coded for searching purposes by their area of content. However, Green Tech can be found in so many areas that range over many of the current classification codes. Accordingly, the current codes may not group together technologies in areas of current research.

The new codes already up and running are for inventions relating to *Greenhouse gases – capture or storage/sequestration or disposal* and *Greenhouse gases – emissions reduction technologies related to energy generation, transmission or distribution*. Each of these codes encompass subclasses for more specific searches. More classification codes will be added as the project moves forward.

What effect will these schemes have?

These types of programs are designed to encourage development of technologies and businesses with products that protect or at least do less damage to the environment. They could also stimulate investment in companies with great ideas. However, since a large proportion of the cost of gaining a patent is incurred during the examination stage, bringing such costs forward can be a high financial burden. In situations where exploration of commercial opportunities is ongoing and cash is short, delaying examination can be more preferable. These schemes can provide options for applicants, but it should be considered on a case by case basis whether they will be beneficial in each situation.

The improvements in classification of inventions by the major patent offices would appear to have more concrete benefits. By knowing what has already been achieved in an area, further ideas can be developed rather than repeating the work of others. It can also be a very important commercial tool. Patent searching gives information on what your competitors are doing.

The World Intellectual Property Organisation has opened up discussions for further options including reduction of fees for patent applications in the field of Green Tech. With the current financial climate this option would be well received by applicants. We will keep you informed if these discussions eventuate into further initiatives in this area.

References

1. Either the International filing date or the filing date in the US must be before 8 December 2009.
2. Patent application publication number GB2467261
3. Patent application publication number GB2458818.

A reminder: if you have any queries regarding intellectual property related matters (including patents, trademarks, copyright or licensing), please contact:

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Katherine Hebditch and Tim Stirrup of Baldwins Intellectual Property in Auckland specialise in chemistry and biotechnology patents. Katherine obtained her PhD in organic chemistry from the University of Manchester in the UK in 2004. She is currently working towards registration as a patent attorney. Tim obtained his PhD in molecular biology from the University of Southampton in the UK in 2007. He is also working towards registration as a patent attorney.

ChemScrapes

- Monthly report? Heck no!
This is just the hazard assessment for my first experiement.

Brendan Burkett

Dates of Note

In the July issue we labelled *John* **Kidd** (b. 10 Sep 1775; d. 17 Sep 1851) as the first ***Aidrichian*** professor of Chemistry at Oxford University. Emeritus Professor Brian Davis, an astute reader, has pointed out the error of our ways. The chair is correctly the ***Aldrichian*** chair named for George Aldrich (d. 1797), a graduate of Merton and medical practitioner in Nottingham who bequeathed monies for professorships in anatomy and physiology, the practice of medicine, and chemistry - and long before the days of the Aldrich catalogue! Thank you Brian.

Sir *Ernest* ***Rutherford*** died on Oct 19, 1937, the same date as Sir *Charles* ***Wheatstone*** (of Wheatstone bridge fame) in 1875 and Lewis Urry the Canadian-American chemical engineer (who invented the ubiquitous alkaline batteries and, later, lithium batteries) followed him just six years ago. *Paul A. M.* ***Dirac***, the English physicist and mathematician who originated quantum mechanics and the spinning electron theory, and shared the 1933 Nobel Prize for Physics with the Austrian physicist Erwin Schrödinger, died on Oct. 20, 1984. In 1970 this day American agricultural pioneer *Norman* ***Borlaug*** received the Nobel Peace Prize for his contribution to the *green revolution* that increased grain production throughout the Third World. *Alfred* ***Nobel*** was born on Oct 21, 1833 and died on Dec 10, 1896.

Georg Ernst ***Stahl*** was born 350 years ago on Oct 21, 1660. He was the German physician and chemist, born in Ansbach, who developed the phlogiston theory of combustion and of such related biological processes as respiration, fermentation, and decay. Combustible objects, he said, *were rich in phlogiston, and during combustion, it is lost. The remaining ash, now having no phlogiston, could no longer burn*. It was this day in 1879 that *Thomas A.* ***Edison*** successfully demonstrated the first durable and commercially practical electric light; it lasted 40 hours before burning out. *Charles Glen* ***King*** was born this same day in 1896. He discovered vitamin C in 1932 after five years of painstaking research extracting components from lemon juice. Finally, on Oct 21, 225 years ago was born (1785) *Henry Miller* ***Schreve***, the American steamboat designer and builder who helped develop the commercial potential of the inland waterways of the Mississippi River system.

Felix ***Bloch***, the Swiss-born American physicist who shared (with independent discoverer, E.M. Purcell) the Nobel Prize for Physics in 1952 for developing nuclear magnetic resonance (NMR) was born on Oct 23, 1905. *G(ilbert) N(ewton)* ***Lewis*** was an American chemist who collaborated with Langmuir in developing an atomic theory; he was born on Oct 23, 1875. On the same day in 1803, at a meeting of the Manchester Literary and Philosophical Society, *John* ***Dalton*** presented an essay on the absorption of gases by water, at the conclusion of which he gave a series of atomic weights for 21 simple and compound elements.

In 1990, on Oct 25, the first transplant operation of a lung from a live donor to a recipient was performed by Dr. *Vaughn A.* ***Starnes*** at Stanford University Medical Center, California. *E(dward) R(obinson)* ***Squibb*** died on Oct 25, 1900. He became a US chemist and pharmaceutical manufacturer who improved the purity and reliability of drugs. While in the US Navy as a medical officer, he convinced the authorities to manufacture their own drugs to ensure better quality. October 27 marks the day in 1938 that Du Pont announced a name for its new synthetic fibre yarn: *nylon*. *Richard Errett* ***Smalley***, known as the father of nanotechnology, who shared the 1996 Nobel Prize for Chemistry with Robert F. Curl, Jr., and Sir Harold W. Kroto for their joint 1985 discovery of C_{60}, died on Oct 28, 2005.

Gustav ***Hertz*** died 30 Oct 30, 1975. He was the German quantum physicist who, with James Franck, received the Nobel Prize for Physics in 1925 for confirming experimentally the quantum theory for energy to be absorbed by an atom only in definite amounts. *John A.* ***Pople*** was the British mathematician and chemist who, with Walter Kohn, received the 1998 Nobel Prize in Chemistry for his work on computational methodology to study the quantum mechanics of molecules, their properties and how they act together in chemical reactions. He died six years ago but was born on Oct 31, 1925. Sir *William Jackson* ***Pope***, who broadened understanding of stereoisomerism, was born on the same day in 1870. Perhaps more importantly, it marks the 175th anniversary of the birth of the noted organic chemist *Adolf von* ***Baeyer*** and 195 years since Sir *Humphrey* ***Davy*** patented the miner's safety lamp.

Eugen ***Baumann*** was the German chemist who discovered that the thyroid gland was rich in iodine. At that time iodine was recognised as occurring naturally in animal tissue; he died on Nov 3, 1896. *Marie* ***Curie***, whose 100th anniversary for the Nobel Prize in Chemistry is next year, was born on Nov 7, 1867. On Nov 8, 1895 *Wilhelm* ***Röntgen*** discovered X-rays during an experiment at Würzburg University. *Chaim* ***Weizmann*** (b. Nov 27, 1874), the noted Russian-British-Israeli chemist who did much to establish science in Israel, died on Nov 9, 1952. *Ernst Otto* ***Fischer***, who received the 1973 Nobel Prize with Sir Geoffry Wilkinson for *organometallic sandwich compounds*, was born on Nov 10, 1918; he died in 2007.

Nov 14 marks the 25th anniversary of the discovery of the fullerene*s*. In 1985, *Robert F.* ***Curl***, Jr. and *Richard E.* ***Smalley***, colleagues at Rice, met with Sir *Harry* ***Kroto*** of the University of Sussex, England, and published their discovery in *Nature*. Sir Harry will visit NZ next February. *James W.* ***Mitchell***, born on Nov 16, 1943, is the African-American chemist best known for advancing the accuracy of trace element analyses. With his collaborators at Bell Labs, he pioneered the development of X-ray fluorescence methods for ppb trace element analysis and his research contributions enhanced the knowledge-base of characterization science. The research units he directed gave innovated technology to enhance the bottom-line of what is now Lucent Technologies. *Henry* ***Taube***, the

Canadian-born American chemist who in 1983 won the Nobel Prize for Chemistry for his extensive research into the properties and reactions of dissolved inorganic substances, died on Nov, 16, 2005.

William Merriam ***Burton*** devised the first thermal cracking process that more than doubled the proportion of the gasoline yield from crude oil. He was born on Nov 17, 1865. Fifteen years earlier, on the same day in 1850, Sir *George Thomas* ***Beilby***, the Scottish industrial chemist who developed (1890) the process of manufacturing potassium cyanide, was born. Even earlier, on Nov. 17, 1790 *August* ***Möbius*** was born; he is remembered especially as one of the discoverers of the strip now named after him - molecules with a twist within them have now been synthesized.

Nov 18 marks 40 years since 1970 Nobel Prize winner, *Linus* ***Pauling*** declared that large doses of Vitamin C could ward off the common cold; NZ's *Brian* ***Shorland*** (d. June 6, 1999) was a great believer in this. *Rudolf* ***Fittig***, the German organic chemist famous for his extensive work synthesizing of organic compounds in the late 19th century, died 100 years ago on Nov 19 (he was born 175 years ago on Dec. 6, 1835). *Francis William* ***Aston*** died on Nov 20, 1945; he was the British physicist awarded the 1922 Nobel Prize for Chemistry for his development of the mass spectrograph. Sir *Chandrasekhara Venkata* ***Raman*** died on Nov 21, 1970. As a physicist, he was an influential in advancing science in India. He received the 1930 Nobel Prize for Physics for his 1928 discovery now called Raman scattering.

Nov 25 sees the 35th anniversary of the first US patent for a whole-body X-ray (CAT) scanner issued to *Robert S.* ***Ledley*** (US 3,922,552). *Thomas* ***Andrews*** died 125 years ago on Nov 26. He was the Irish chemist and physicist who demonstrated the continuity of the gaseous and liquid states discovering the critical temperature for carbon dioxide (1861). He wrote: *We may yet live to see...such bodies as oxygen and hydrogen in the liquid, perhaps even in the solid state*.

Richard ***Kuhn*** was the Austrian biochemist awarded the 1938 Nobel Prize for Chemistry for work on carotenoids and vitamins; he was born on Dec 3, 1900. Sir *George* ***Porter***, the English chemist who was awarded a share of the 1967 Nobel Prize for Chemistry (with Norrish and Eigen) for studies of extremely fast reactions, was born on Dec 6, 1920, the same day as noted German organic chemist, *Rudolf* ***Fittig*** (see above). *Walter Karl Friedrich* ***Noddack*** was a German chemist who discovered the element rhenium (June 1925) in collaboration with his wife Ida Tacke; he died on Dec 7, 50 years ago. This same day in 1995, the *Galileo* spacecraft arrived at Jupiter and entered orbit after 6 years of travel including a flyby of Venus and two asteroids, Gaspra and Ida.

Fritz ***Haber***, the German physical chemist and winner of the 1918 Nobel Prize for Chemistry for his development of a method of synthesizing ammonia (1909), was born on Dec 9, 1868. *Joseph* ***Needham*** was an English biochemist, embryologist, and historian of science who wrote and edited the landmark history *Science and Civilisation in China* (a multivolume study of nearly every branch of Chinese medicine, science, and technology over some 25 centuries). As head of the British Scientific Mission in China (1942-46) he worked to assure adequate liaison between Chinese scientists and technologists and their colleagues in the West. He also was born on Dec 9, but in 1900. On this same day in 1935 died *Lafayette Benedict* ***Mendel***, the American biochemist whose discoveries concerning the value of vitamins and proteins helped establish modern concepts of nutrition. This same day 50 years ago saw the first electronic computer to employ thin-film memory announced - Sperry Rand Corporation unveiled the Univac 1107.

Alfred Bernhard ***Nobel*** died on Dec 10, 1896 and the anniversary of his death is the day that the major Prizes are awarded in Stockholm, with ***Rutherford*** gaining his on this day in 1908. The 1910 Nobel Prize in Chemistry was awarded to *Otto* ***Wallach*** in recognition of his pioneering work in the field of alicyclic compounds, and his services to organic chemistry and the chemical industry; he was born in 1847 and died in 1931.

Ludwig ***Mond*** was the German-born British chemist and industrialist who perfected a method of soda manufacture by improving the Solvay alkali process in 1890 (the Mond Process); he died on Dec 11, 1909. *William* ***Henry***, the English physician and chemist who, in 1803, proposed what is now called Henry's law, was born on Dec 12, 1775. This same day in 1900 was born *Maria* ***Telkes*** who was an Hungarian-born American physical chemist who pioneered the application of solar energy to water distillation and home heating. *Johann Wolfgang* ***Döbereiner*** was a German chemist who, in 1829, observed that when certain triads of elements were arranged in order of increasing atomic mass. The mass of the central member was approximately the average of the other two, and intermediate in chemical properties between the other two elements. The triads are consecutive members of the groups of the periodic table, such as Li, Na, K, and Cl, Br, I. He was born on Dec 13, 1780. On this same day in 1930 died *Fritz* ***Pregl***, the Austrian chemist awarded the 1923 Nobel Prize for Chemistry for developing techniques in the microanalysis of organic compounds. Five years later (1935) this same day died *Victor* ***Grignard***, the discoverer of alkyl magnesium halides in 1901.

On Dec 14 in 1900, *Max* ***Planck*** made public his ideas on quantum physics at a meeting of the German Physics Society. Planck demonstrated that in certain situations energy exhibits characteristics of physical matter, something unthinkable at the time, which he called *quanta*. NZ's Sir *Ernest* ***Marsden*** died 40 years ago on Dec 15, 1970, the day in 2000 that the ill-fated Chernobyl nuclear plant in the Ukraine was ceremoniously permanently shut down. On Dec 16, 1935, the use of eye prints, the pattern of capillaries in the retina, was described in an article in *Time* magazine as a new scientific method for identification because an individual's eye pattern is as unique as fingerprints.

Sir *J. J.* ***Thomson*** was born on Dec 18, 1856; he helped revolutionize the knowledge of atomic structure by his discovery of the electron in 1897. The following day (Dec 19) six years ago saw the death of *Herbert C.* ***Brown***. Dec 19, 1950 saw *Rose Marie* ***Reid*** of Los Angeles received a US patent for a one-piece bathing suit *embodying a novel construction for causing it to snugly fit the body of a wearer in a flattering manner* using elastic fabric. It would *shape and support portions of the body of the wearer in areas of the bust and abdomen in a flattering manner without discomfort or impedance to free movements of the body*. The elastic fabric and elastic securing bands were designed to enable the garment to be put on without having buttoned openings which would *detract from the appearance of the garment*. On this same day in 1910, rayon was first commercially produced, in Marcus Hook, PA, by the American Viscose Company.

Jaroslav ***Heyrovský*** was the Czech chemist who received the 1959 Nobel Prize for Chemistry for his 1922 discovery and development of the polarographic methods of analysis; he was born on Dec 20, 1890, the same day as *Thomas* ***Graham*** in 1805. On Dec 23 1750, *Benjamin* ***Franklin*** was severely shocked while electrocuting a turkey (Christmas dinner?). *William Hayward* ***Pickering***, the engineer and physicist who was head of the team that developed the first US satellite, was born on Dec 24, 1910.

Born on Christmas day in 1906, *Ernst August Friedrich* ***Ruska*** was the German physicist and electrical engineer who invented the first electron microscope and won the Nobel Prize in Physics in 1986 for his work. Christmas day was also Sir *Isaac* ***Newton***'s birth date in 1642. *Dian* ***Fossey*** was the American zoologist who, for years, made a daily study of the mountain forest gorillas of Rwanda; she died 25 years ago on Dec 26. One hundred years ago on Dec 27 was the birth of *Ian* ***Donald***, the English physician who first successfully applied ultrasound reflection imaging for medical diagnosis. *Charles* ***Goodyear***, who baked rubber mixed with sulfur and discovered the vulcanization process, was born on Dec 29, 1800. On Dec 30, 1924, *Edwin* ***Hubble*** announced the existence of another galactic system in addition to the Milky Way, and on the same day in 1930, 80 years ago, a photograph showing the curvature of the Earth was exhibited in Cleveland, Ohio, at the AAAS annual convention; according to the *New York Times*, it was the first photograph to show the Earth's curvature. On the last day of the year in 1935, a patent was issued for the game of *Monopoly* that is now 75 years old.

2011

Donald B. ***Keck***, the American research physicist, who with his colleagues at Corning Glass invented fused silica optical waveguide - optical fibre, was born on Jan 2, 1941. Jan 4 marks 50 years since the death of theoretical physicist *Erwin* ***Schrödinger*** whilst the 5th sees the 30th anniversary of the death of *Harold C.* ***Urey***, the American scientist awarded the Nobel Prize for Chemistry in 1934 for his 1932 discovery of deuterium. 115 years ago on Jan 5 (1896), an Austrian newspaper (*Wiener Presse*), published the first public account of Röentgen's discovery of the radiation that became known as X-rays.

John E(rnest) ***Walker*** celebrates his 70th birthday on Jan 7; he is the British chemist who won a share of the 1997 Nobel Prize for his pioneering work on how the enzyme ATP synthase catalyses the formation of the ATP. *Melvin* ***Calvin*** died on Jan 8, 1997 and *Kenichi* ***Fukui*** on Jan 9, 1998. Calvin needs no introduction while Fukui was the theoretician of orbital symmetry fame. Jan 9, 1901 marks 110 years since first application for Meccano was submitted as *improvements in toy or educational devices for children and young people*; who would have thought that molecular *meccano* was a force in synthesis 110 years later. Jan 10 marks 100 years since the first photograph to be taken in the US from an airplane was made and 110 years since the first major discovery of oil in Texas.

Jan 11 marks the 100th anniversary of the founding of the ***Kaiser Wilhelm Society for the Advancement of Science***; it is now known as the Max Planck Society that comprises some 80 research institutes. Jan 12 marks 10 years since the death of *William* ***Hewlett***, the American electrical engineer who co-founded the Hewlett-Packard Company. *David* ***Wesson***, the American chemist who purified cotton seed oil and developed a system (in 1900) to make the pure oil palatable, was born 150 years ago on Jan 14. He formed the Southern Oil Company to market Wesson Oil. Cottonseed oil was the first vegetable oil used in the US and remains versatile, prized by chefs for its ability to allow food flavour to come through. British metallurgist, *Henry Livingstone* ***Sulman***, one of the originators of the froth flotation process for concentrating ores preliminary to the extraction of metal, was born 150 years ago on Jan 15, 1861.

75 years ago on Jan 16 (1936), the first photo-finish camera was installed at the Hialeah, Florida racetrack. *Charles Thurstan* ***Holland*** died on Jan 16 in 1941; he was the English radiologist who pioneered the clinical use of X-rays in the UK, beginning shortly after Röentgen announced their discovery. He was present at the first clinical use of X-rays in England, (Feb 7, 1896) in the laboratory of Oliver Lodge, head of Physics at Liverpool University. The American chemist who devised the first oxyhydrogen blowpipe for the purpose of producing great heat, *Robert* ***Hare***, was born on Jan 17, 1781. *Hans* ***Goldschmidt*** was the German chemist who invented the thermite (aluminothermic) process that was adopted worldwide for welding railroad and streetcar rails. It is still in use for on-site welding with the first track so welded in Essen. He was born 150 years ago on Jan 18, 1861.

The final date of note in this issue recognises the Jan 23, 1911 rejection of *Marie* ***Curie*** to a vacant seat for a physicist in the French Academy of Sciences. Despite her winning the 1903 Nobel Prize in Physics, the Academy's all-male membership turned her down. There was clearly a healthy dose of sexism, racism and chauvinism as she won the 1911 Nobel Prize in Chemistry, and was the only woman at the Dec 10/11 ceremonies. The Academy seat was awarded instead to Edouard Branly, a radio pioneer with the distinct advantage of being more French, more Catholic and, most importantly, more male than Marie Curie.

Conferences

Faraday Discussion 150: Frontiers in Spectroscopy, Basel, Switzerland, 6 - 8 April 2011

FD150 will review recent advances in spectroscopy from several areas with the aim to identify current frontiers of research and future directions. The meeting is addressed at both experimentalists and theoreticians and aims to bring together scientists from different fields including chemistry, physics, the biosciences and related disciplines

Poster abstract deadline - 4 February 2011

www.rsc.org/ConferencesAndEvents/RSCConferences/FD150/index.asp

EICC-1: First EuCheMS Inorganic Chemistry Conference, University of Manchester, UK, 11-14 April 2011

The Dalton Division of the RSC is joining together with the EuCheMS Inorganic Division (EID) to host the first edition in a new European conference series in Inorganic Chemistry. Themes include: Supramolecular and Co-ordination Chemistry,

Organometallic and Catalysis, Reaction Mechanisms, Inorganic Materials, Energy and Photochemistry, Bioinorganic and Metallic Enzymes, Main Group Chemistry and Solid State Chemistry

Call for oral abstracts deadline - 1 October 2010

http://www.rsc.org/ConferencesAndEvents/RSCConferences/EICC1/

5th International Congress of Chemistry and Environment (ICCE 2011),Kuching, Sarawak, Malaysia, 27-29 May 2011

www.chemistry-conferences.com/2011/05/27%20-%2029%20Conference%20of%20Chemistry%20and%20Environment%20(Kuching%20-%20MY).htm

6th International Symposium on Macrocyclic and Supramolecular Chemistry (6-ISMSC), University of Sussex, Brighton, UK, 3 – 7 July 2011

This will cover all aspects of macrocyclic and supramolecular chemistry. The meeting will include a mix of established and younger speakers and will offer the chance for students to present their work in the form of short oral presentations and posters. Themes include:Imaging and sensing, Molecular machines and self-assembly, Macrocycles in the 21st Century, Biological supramolecular chemistry, Systems chemistry and complexity, Functional materials and devices.

Call for papers opens September 2010.

www.ISMSC2011.org

10th International Conference on Materials Chemistry (MC10), University of Manchester, United Kingdom, 4-7 July 2011

Themes will include:Advanced technologies and nanomaterials, Energy and sustainability, Life and health, Soft matter and Crystalline solids

Oral abstract submission by 22 October 2010

Poster abstract submission by 6 May 2011

www.rsc.org/ConferencesAndEvents/RSCConferences/MC10/

22nd International Symposium: Synthesis in Organic Chemistry, Churchill College, University of Cambridge, United Kingdom, 11-14 July 2011

The Synthesis in Organic Chemistry Symposium traditionally provides an international showcase for the core area of organic chemistry - synthesis - covering all aspects of contemporary organic synthesis and providing a forum for the ever more exciting methodologies and strategies that continue to emerge.

www.rsc.org/ConferencesAndEvents/RSCConferences/OrganicSynthesis2011/index.asp

3rd Asian Conference on Coordination Chemistry (ACCC-3)

The 3rd Asian Conference on Coordination Chemistry (ACCC-3) will be held during October 17-20, 2011 at the India Habitat Centre, New Delhi.

www.accc3.org/home

2012 International Symposium on Macrocyclic and Supramolecular Chemistry (ISMSC-2012), University of Otago, Dunedin, Sunday 29 January to Thursday 2 February 2012.

Please register your interest via our website *www.otago.ac.nz/ismsc2012/*

Grants and Scholarships

Ramsay Memorial Fellowships for Chemical Research (Postdoctoral)

The Ramsay Trustees will, in February 2011, consider applications for the award of one or more General (British) Ramsay Memorial Fellowships.

The Fellowship(s) will normally be tenable in the United Kingdom for two years from 1 October 2011. Candidates will generally be expected to have had already some postdoctoral experience of research, although this should normally not have exceeded two years.

Although the Fellowship(s) may be fully funded by the Trust, the expectation is that they will normally be co-sponsored and jointly funded either by a university department, an industrial company or another body approved by the Trustees. Where this is the case, the Trust will contribute 50% towards the total salary costs of the Fellowship(s), up to a maximum of £15,000 per annum, with the balance of all other costs to be paid by the co-sponsor. In addition, a grant of up to £1,000 per annum may be requested for (non-travel) expenses.

Further information and application forms are available online at *http://www.ucl.ac.uk/ramsay-trust/* or from the Executive Secretary, Ramsay Memorial Fellowships Trust, c/o Academic Services, University College London, 2 Taviton Street, London WC1E 6BT, UK; telephone (0207) 679 8592; fax (0207) 679 8595; email *g.hawes@ucl.ac.uk*

Completed application forms must be received by no later than 15 November 2010.

2011 Dumont d'Urville NZ/France S&T Support Programme

Applications for the 2011 Dumont d'Urville NZ/France S&T Support Programme are now being called for to promote and support scientific and technological cooperation between New Zealand and French researchers in the public, non-government and private sectors in the fields of renewable energy, biotechnology, and nanosciences.

Closing Date: 7 October 2010

http://www.royalsociety.org.nz/programmes/funds/international-relationships/durville/

International mobility fund

The programme facilitates bilateral research through the provision of funding for New Zealand researchers to travel overseas or overseas researchers to travel to New Zealand to work on joint research projects. Funding under this programme generally supports travel related costs. It supports new, emerging and existing international relationships for the following countries – Australia; Canada; China; Europe; India; Japan; Korea; Latin America; and the USA but countries may also be included.

Closing date: 5 October 2010

www.royalsociety.org.nz/programmes/funds/international-relationships/mobility/

Sarah Beanland Memorial Scholarship - call for applications

A prestige scholarship for PhD study in the areas of earth, physical, biological and social sciences.

Applications must be received by 20 October 2010.

For more information on eligibility and to apply:see http://*www.gns.cri.nz/news/fellowships/sarahbeanland.html*

Charles Fleming Fund Travel Award

Up to $6,000 (total fund) available annually and this is split between a number of applicants to provide partial funding support to scientists or technologists to travel and attend scientific congresses, assemblies, or committees for the furtherance of science or technology. The fund will give preference to those who do not normally have access to travel funds through their place of employment and who will be actively involved in the activity. Examples include expenses for:

- presenting a paper or a poster
- participating in a summer school or workshop
- representing New Zealand at an international committee meeting

Closing date: 31 March 2011

www.royalsociety.org.nz/programmes/funds/fleming/travel/

Charles Fleming Fund Senior Scientist Award

Up to $10,000 p.a. is available to support the research of a senior scientist at a university in New Zealand, and that of their research group. The fund will give preference to requests for research expenses over and above those that a university would normally be expected to cover. Examples include expenses to:

- cover a visit to an institution in New Zealand or overseas,
- expenses related to specialist assays or methodologies,
- research assistance to carry out a specific task or
- expenses relating to a visit to the research group of a visitor

Closing date: 31 March 2011

www.royalsociety.org.nz/programmes/funds/fleming/senior-scientist/

Charles Fleming Fund Publishing Award

Approximately $2,000 is available annually to support the preparation of scientific books and relevant publications.

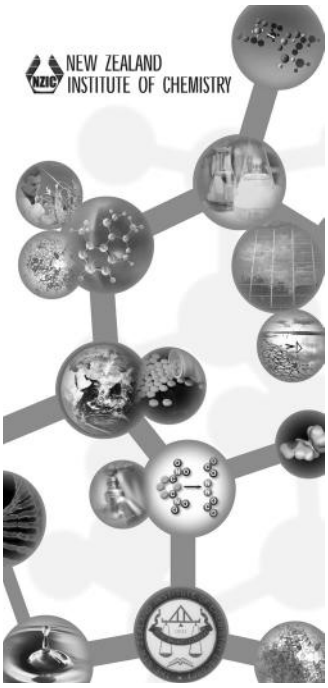
The fund will give preference to those who do not normally have access to funds through their place of employment for assisting with the writing and publication of their research or a review of a particular area of scientific endeavour.

Closing date: 31 March 2011

At the conclusion of the project, a brief report (500 words maximum) explaining how the objectives have been met, should be submitted.

www.royalsociety.org.nz/programmes/funds/fleming/publishing/

Chemistry—our life, our future



As you must know by now, 2011 is the International Year of Chemistry (IYC 2011). It is set to be a worldwide celebration of the achievements of chemistry and its contributions to the well-being of all. Under the unifying theme ***Chemistry—our life, our future***, IYC 2011 will offer a range of interactive, entertaining, and educational activities for all ages. The Year of Chemistry is intended to reach across the globe, with opportunities for public participation at the local, regional, and national level.

New Zealand is a keen participant with the NZIC and RSNZ determined, in partnership, to make the year very special. Our opening event will occur on February 9 ahead of a public lecture by ***Prof. Sir Richard Friend*** (one of the AMN5 conference plenary speakers – 2011 is also the centenary of the discovery of superconductivity) in Wellington's Michael Fowler Centre. This will be a fashion display of garments involving gold and silver nanoparticle-impregnated wools as developed by Prof. Jim Johnston's group at Victoria University and designed by Massey University's School of Design students. Some of the research team that developed the wool are to address senior chemistry and physics students under the chairmanship of John Watt who fronts the TVNZ ***Ever Wondered*** programme. Then, in March, Prof. Robin Clark (University College, London), one of the January 2011 Chemistry in New Zealand authors (Raman Microscopy as a Structural, Analytical and Forensic Tool in Art and Archaeology), will open the ***Science and Art*** exhibition at the National Portrait Gallery. Robin will then undertake a lecture tour of the country as the 2011 RSNZ Distinguished Speaker.

The goals of IYC 2011 are to increase public appreciation of chemistry in its efforts to meet world needs, to stimulate interest in chemistry among young people, and to enthuse the creative nature of chemistry into the future. In this context, the 2011 ***ChemEd*** conference (Palmerston North, July 24-27) will have focus; and the ***NZIC National Conference*** (Hamilton, 27 Nov – Dec 1) will see five distinguished overseas speakers and (likely) the awards from the various NZIC competitions being presented. Furthermore, as stated in the ***Dates of Note***, December 2011 will mark the 100th anniversary of the Chemistry Nobel Prize awarded to Marie Curie and this gives an opportunity to celebrate and highlight the contributions of women to science in NZ. Thus, a series of lectures will be given in the main centres by some of this country's leading women scientists under the auspices of RSNZ.

IYC 2011 events are set to emphasize that chemistry is a creative science essential for sustainability and improvements to our way of life. The NZ activities are expected to involve regional finalists competing in a national quiz for secondary students in Wellington, involvement of *e.g.* quilters/artists/schools in designing novel periodic tables, chemistry as art, the production of a choreographed *molecular reaction video*, schools pupils being involved in what has evolved as the *colour of water*, and a range of Branch activities.

The year also marks the 100th anniversary of the founding of the International Association of Chemical Societies when delegates nominated by the French, German, and English Chemical Societies met and ratified the statutes of the association, providing a chance to highlight the benefits of international scientific collaboration. In 1919 it became the *International Union of Pure and Applied Chemistry* (IUPAC).

Some of the international events include:

- A pre-launch publicity event at the Pacifichem congress on Dec 16, 2010 in Honolulu.
- Chemistry – the key to Africa's future as the South African Chemical Institute Convention in mid-January 2011.
- Networking Breakfast Jan 18, Brisbane, Australia *Women Sharing a Chemical Moment in Time* that will be mirrored in France, the Netherlands and Poland.
- ***The official IYC2011 Launching Ceremony on Jan 27 - Jan 28 at the UNESCO headquarters in Paris.***
- Chemistry exhibition ***Elemental Matters: Artists Imagine Chemistry*** in Philadelphia, PA for most of the year.
- The Science Behind It Presents... The Chemistry Between Us on Feb 8 in Calgary, Canada.

To see the current year-long listing visit:
http://www.chemistry2011.org/participate/events/

Brian Halton, Editor

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