Excerpted from ***Chemical Demonstrations: A Handbook for Teachers of Chemistry, Volume 5*** by Bassam Z. Shakhashiri, University of WIsconsin Press, 2011

Shining Light, Shedding Light

Roald Hoffmann

FIREFLIES

At first, you're not sure it's real—it could be a passing flash on the retina, a car far off. But then you see a few lights flitting, the road bends into a spruce grove, your eyes adjust. And night strikes the screen for the pinpoint dance of fireflies chasing synchronicity.

In bright light, the beetle itself is unprepossessing. But maybe we shouldn't apply our standards of beauty to fireflies—we have enough trouble making sense of what attracts the male of our species to the female. But the phenomenon—chemiluminescence—is startling because it is relatively uncommon in the fauna and flora we see around us.

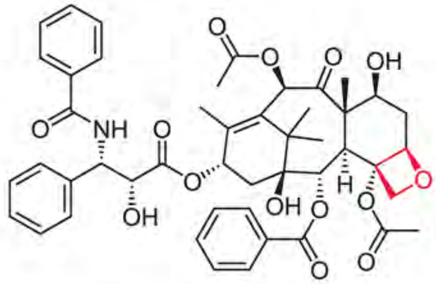
Fireflies have something to do with the appeal of color and light that is our subject. For not only do the tested demonstrations in this volume show the workings of light and color in chemistry. They also go beyond the utility of a physical phenomenon, in two ways. First they probe perception, for what the mind does with the wavelength of light that impinges on the retina is more than just register it. And second, these demonstrations touch directly on the beauty and wonder that makes chemistry more than just transforming molecules.

I will return to beauty and fireflies, but let me first delineate the special place of light absorption and emission in chemistry. Light and color in chemistry tell us of quantum mechanics at work. We use them as clues, signals from within. And light effects desired, occasionally dramatic, change.

THE QUANTUM IN CHEMISTRY

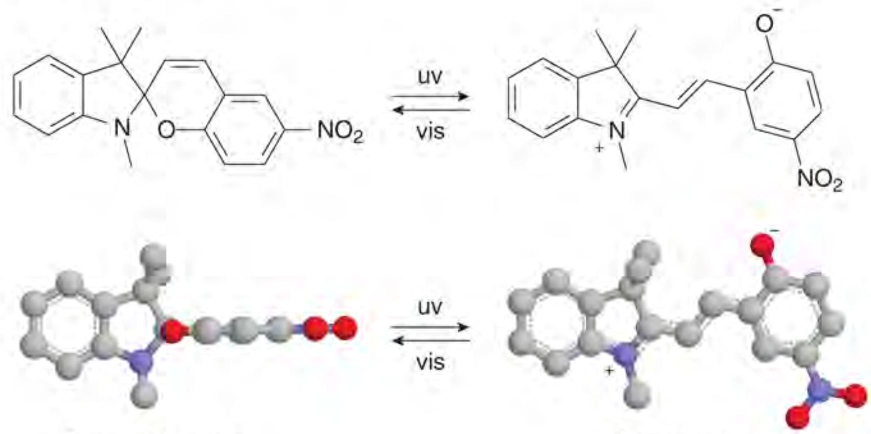
The strong, spatially expressed bonding propensities of carbon atoms imbue organic chemistry with a direct architectural sense. I have in mind the four bonds going off to the corners of a tetrahedron of a saturated C, the coplanarity of the six atoms in an ethylene.

Take taxol (paclitaxel), an important antitumor agent, a complex molecule with four rings and a number of substituents. There is much medicinal chemistry modifying the taxol structure, replacing a hydrogen by a succinate, removing an acetyl group.



taxol = paclitaxel

A simpler structure is found in the spiropyrans, molecules that figure in one lovely experiment in this volume. They are not only photochromic compounds with obvious applications in materials science, but their derivatives have been used in the treatment of hypertension and erectile dysfunction.



Benzospiropyran Merocyanine

For a variety of purposes, not the least being simple curiosity, the spiropyran and taxol structures have been man- and woman-handled. In the fascinating range of modifications seen in the literature (and many more hidden in the notes of pharma-industry chemists), the three-dimensional structure of the molecules has played a key role—the oxetane ring of taxol positioned just this way, a reaction proceeding with inversion of configuration.

This is the classical mechanics side of chemistry. The motions of atoms in the course of reaction certainly figure in the thinking of chemists modifying these molecules. But the chemical imagination here is dominantly architectural in feeling—a ball and stick model of the molecule, and knowledge of the stereochemical outcome of chemical reactions will get you a long way in this wonderful game.

Consider now the color of a compound—for instance the change in color at the heart of the spiropyran experiment, from colorless to deep pink or blue, back to colorless. Or the orange of Vitamin B-2, riboflavin, the bright red glow of a neon lamp, the green of chlorophyll. There is no way to explain colors of compounds classically. Molecules have definite quantum states, they have filled and unfilled orbitals. The quantization of energy levels, at the heart of quantum mechanics, is directly displayed in those energy levels. Light is emitted (by those neon atoms in a discharge tube) or absorbed (by carotene in another experiment in this volume) at quite definite energy intervals. These are the colors of molecules as they impinge on the retina and—in much more fascinating detail—the spectrum of a molecule.

Reflection of a neon tube from the surface of a compact disc.

Any spectroscopic measurement or photochemical reaction is inherently quantum mechanical. Or shall we say, quantum chemical?

SIGNALS FROM WITHIN

The determination of molecular structure is a story of knowing without seeing. It is a thrilling detective story in which meager clues to the structure of a molecule, none definitive, are assembled by the molecular detective into an incontrovertible web of evidence for what atoms there are in a molecule, how they are connected to each other, and what their three-dimensional arrangement is in space.

We did not wait for microscopes to tell us the structure of carotene, benzospiropyran, or taxol. We did it with X-ray diffraction and spectroscopies of every sort, perturbing the molecule with light and measuring its response.

The light involved in our measurements is not just visible light. It is radiation that may range from the energetic extreme of X-rays to the slightest tickling of nuclear magnetic resonance. In every case we send in a beam of the radiation and measure its absorption, or lack of it, by an interposed sample of the compound (macroscopic) = molecule (microscopic) in question. Most of the time, the probing is nondestructive and can even be done on the material in situ, for instance reflection spectroscopy of the blue pigment in a Japanese scroll. Sometimes, one needs to take a physical sample. This is okay for Vitamin B-2 coming off an assembly line, less so for the Japanese scroll.

In X-ray crystallography, currently our major technique for getting precise molecular structures, one starts with a crystal or powder and measures (it used to be photographically, now by an electronic detector) the intensities and patterns of reflection of X-radiation from layers of atoms in a molecule in that crystal. With some clever programming and hale computers, one goes from diffraction pattern to structure on the atomistic level in a matter of minutes.

In infrared spectroscopy, one puts in infrared radiation of variable wavelength and studies how much of it is absorbed by a molecule. Absorbed in what way, and why? Well, a molecule has characteristic and well-defined energy levels corresponding to the motion of atoms around their equilibrium position in the ground state of a molecule. And it has excited vibrational states, different ones corresponding to the stretching of a CO bond in a ketone (~1700 cm^{-1}) to those in an alcohol (~1100 cm^{-1}). The infrared signature of each is distinct. And, as we will see below, those vibrations really matter in the atmosphere.

I cannot imagine the incredibly detailed microscopic knowledge we have of molecular structure without the intermediate, willed exploitation of light and color. And we are beginning to "see" molecules in the act of reaction, through femtosecond spectroscopies and state-selective reactions.

ESPECIALLY IN THE ATMOSPHERE

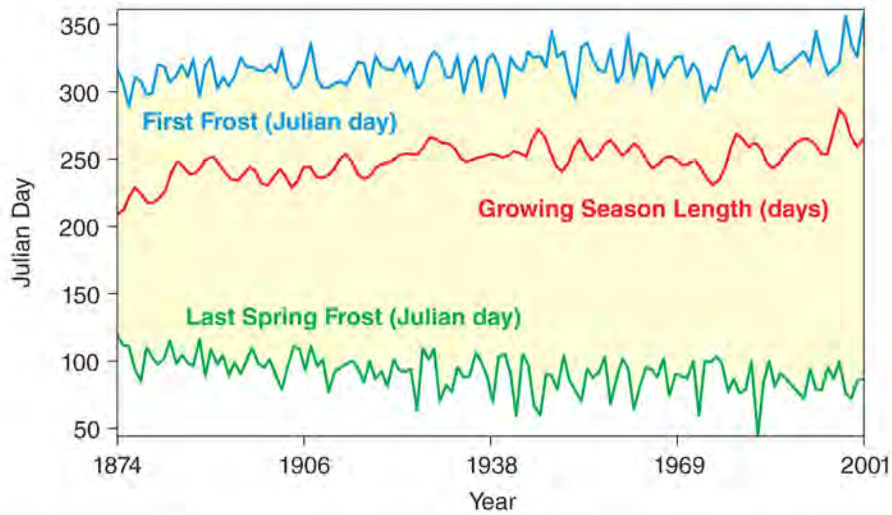
Light plays a special role in what goes on in the precious envelope that surrounds our planet. For it is the way that energy gets into molecules there, and—for better or for worse—does chemistry.

The atmosphere is tenuous, the pressure falling off exponentially with altitude. And much of the atmosphere is quite cold. Low pressure, low temperature means that there are fewer and fewer collisions per unit time as one goes to higher altitudes. And you can't have chemistry without collisions.

To put it another way, at the surface of the earth we may provide heat (from gas, coal, electricity) to some reagents in an enclosed vessel and thereby effect desired change. This happens in the Haber-Bosch process for making NH_3 from N_2 and H_2. Or in baking a meringue. In the upper atmosphere, the "vessel" is immense, with a low density of molecules in it. And there is no equivalent of a Bunsen burner or electric mantle to put energy into the atmosphere.

What the atmosphere has is light, a surfeit of it beamed to it from our sun. And the atmosphere cannot avoid reflected and emitted radiation from the earth. The way energy is traded in the atmosphere is mainly through the absorption and emission of light.

Let's take a topic of substantive current interest—global warming. No question the warming is there—I can show you a timeline of first and last frost in Atlantic City that goes back to 1874.



Growing season length and freeze dates at Atlantic City, New Jersey. The red line represents the annual length of the growing season, while the yellow area represents the growing season, the time between the last frost of spring (green line) and the first frost (blue line) of fall. From 1874 to 2001, the growing season has lengthened by 19 percent [*1*].

There be fluctuations, big ones. But there is also a trend that is clear—the growing season in Atlantic City has increased by over a month over 136 years. If this continues, there will be palms along the Boardwalk.

How does it happen? How does the atmosphere warm? Let's look at the energy of sunlight as it passes into the atmosphere. The atoms, ions, and molecules in the atmosphere absorb light. But not light of any wavelength. This is where quantum mechanics, as mentioned above, comes in, providing not only a set of quantized levels setting the color, but also a set of rules for what light will or will not be absorbed. Especially important for humans and for life as it has evolved is the absorption of the sun's light by a tenuous layer of ozone in the stratosphere. If concentrated at $P = 1$ atm, all the ozone in the atmosphere would be a layer a few millimeters thick. And you had better run—ozone, a lovely blue when concentrated—is very explosive.

The ozone molecules in the stratosphere absorb out of the sun's broad spectrum radiation a region in the ultraviolet that we have evolved to tolerate. I put it this way, for it is perfectly possible to envisage life without an ozone layer. But it would not be the life we know.

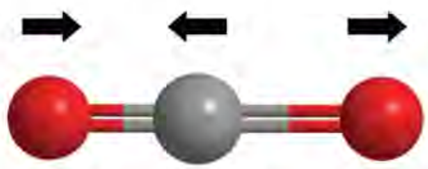
Of the sunlight impinging on the atmosphere 35 percent is reflected, 17.5 percent is absorbed by molecules in the atmosphere, 47.5 percent reaches the earth one way or another—directly or scattered by clouds and blue sky. What gets down here is absorbed—the greens, blues, and browns of the earth are testimony to that. Some of the energy of the absorbed sunlight is harnessed by photosynthetic systems, eventually leading to the local defeat of entropy represented by dandelion flowers and a poem.

Most of the energy that is absorbed by brown earth or blue water or green plant is degraded by a process called "intersystem crossing," by which an excited electronic state is transformed into a vibrationally excited ground state. The vibrationally hot molecules emit infrared radiation, and this high-wavelength, low-frequency light augments the so-called black-body radiation of the earth at its fluctuating surface temperature.

The earth shines in the infrared. Over 99 percent of the atmosphere, the recipient of this emission, couldn't care less. N_2, O_2, and Ar do not absorb infrared radiation to any significant amount. Why? Quantum mechanics again! The subject here is selection rules for vibrational spectroscopy: molecules whose dipole moment does not change in the course of a vibration will not absorb in the IR.

So H_2O, CO_2, CO, CH_4, NO do absorb infrared radiation, in different regions of the spectrum, some overlapping well, some badly, the spectrum of impinging IR radiation from the earth. They are "greenhouse gases." But wait, the story, a story of trading energies, is not quite over. How do the molecules that do absorb in the IR heat the atmosphere? Their own motions are enhanced by the energy of the infrared light they have absorbed—they vibrate like crazy. But these molecules are a tiny, trace part of the atmosphere. The temperature of the atmosphere is set by the velocities and collisions of the majority molecules—N_2, O_2, Ar. And these are not excited by IR radiation.

Not yet. The mechanism for heating the atmosphere is vibrational to translational energy transfer, from, say, CO_2 to N_2. The effect is quantum mechanical, but one can understand it semi-classically. While a CO_2 molecule is doing, say, an energetic asymmetric stretch, it collides with a relatively slow moving N_2 molecule.



asymmetric stretch
2346.3 cm^{-1}

The vibration of the CO_2 delivers a kick to the N_2; the CO_2 vibrates less violently thereafter, the N_2 moves off with great velocity. Do it a billion times, you have made the N_2 molecules move faster, on average. The N_2 is hotter. And N_2 is 78 percent of the atmosphere.

The anthropomorphic language I use is imprecise. But it serves to make us less afraid of the quantum logic that governs the microworld. That energy is conserved does not mean that life (or the atmosphere) is static. Energy is traded continually. There is balance, dynamic balance. Or that balance is perturbed. By us.

BEAUTY

Now that was a slog through the intricacies of trading energy in the atmosphere. A necessary excursion, given the importance of the precious envelope of our planet. What does it have to do with the wonder of the clear, dark June night on which we first see fireflies? Or, in another season, seeing the aurora borealis? Or the rapidly moving clouds in clearest air the day after the hurricane spent itself?

What is the relationship of the facts and mechanisms, as best as we may discern them, to the emotion that comes over us when the sky, in its incredible range of presentations, presents such beauty?

One point of view is that knowing about things, here color and light, in the way chemists work diligently to gain such knowledge, detracts in some way from the gut feeling that beauty is before us. I don't think so. Philosophers have thought about beauty for over 2,500 years. Here, for instance, is what Immanuel Kant (who lived before and after Lavoisier) wrote about beauty:

> He who feels pleasure in the mere reflection upon the form of an object . . . justly claims the agreement of all men, because the ground of this pleasure is found in the universal, although subjective, condition of reflective judgments, viz. the purposive harmony of an object (whether a product of nature or of art) with the mutual relations of the cognitive faculties (the imagination and the understanding) [*2*].

A sentence Kantian in complexity, so let me try to unpack its meaning. Kant says that while beauty is in the eye of the beholder, there are also universals in the idea. That an object is beautiful derives from two sources—the immediate, emotional appeal of its harmony, coupled to our thinking about it, trying to understand, seeing the relations of an object to everything else in the world.

To see the fireflies, to love their light, links to our desire to understand—chemically and biologically—how and why they flash. That knowledge does not detract from but augments our appreciation of the fireflies. More of that anon. But let's return to doing things with lights.

PHOTODYNAMIC

It is one thing to measure, another to effect transformation. The absorption of light, using mechanisms honed by evolution, plays an essential role in biochemistry. And cultural evolution (science and technology) have introduced into our lives a variety of active photochemical devices—the phosphors on the display of your computer, the neon sign, the sensors in your camera, the silver halides in our old friend, photography.

The difference from spectroscopy, from using light to spy on molecular secrets, is that with photochemistry we aim to achieve change. And do it with large dollops of energy.

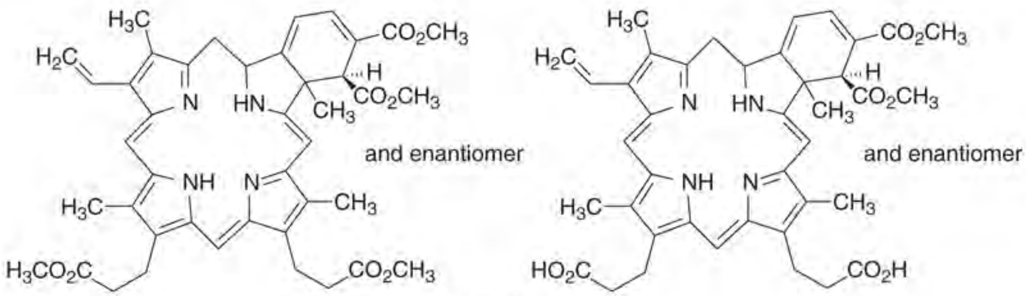
The photons of visible light absorbed by the photosynthetic assemblages of nature carry 40–80 kcal/mole. To introduce the same amount of energy into a cell through heating would necessitate heating to 200–1000°C, a process that would certainly destroy the cell. The lovely molecular machines in a leaf of a green plant take in that sunlight in one fell swoop. And then the energy is cleverly, rapidly (and efficiently, ~40 percent) shuttled by a cascade of fast reactions from biomolecule to biomolecule, effecting the transfer of protons across a cell membrane.

I want to tell you the story of another use of light, in healing. Though, in the nicely complicated way the world has of complicating our simplistic categorizations, that healing is accomplished by destruction. This is photodynamic therapy, and the particular use of porphyrins in it.

As it is, there are in our body destructive molecules—NO, and the singlet form of oxygen, an excited state of normal triplet state diatomic oxygen molecules. These destructive small molecules attack tissue components in a number of ways, and there have evolved ways for their controlled production in the body, for, if you like, housecleaning tasks. The generation and disposal of these internal reagents is nicely controlled. Singlet oxygen is essentially "biodisposable"—in water it has just a couple of microseconds to do its dastardly deeds. The idea of photodynamic therapy is simple: why not generate a multitude of such molecules, singlet oxygen in particular, at a desired place and time to destroy tumor cells and other tissue?

Outside the body, in the laboratory, we have come up with ways to "sensitize" oxygen, convert the ground triplet state of the molecule to the excited singlet state. The sensitizer is a usually more complex molecule that absorbs light, then undergoes another kind of "intersystem crossing" to an excited triplet state. With a proper match of energies and orbital shapes, that triplet state of the photosensitizer can interact with normal triplet oxygen and transform it to the highly reactive singlet form. Trading energies again, controlled by quantum mechanics.

David Dolphin of the University of British Columbia was and is an expert on the lovely class of molecules called porphyrins. They, or molecules related to them, play important biochemical roles—witness hemoglobin, coenzyme B-12, and chlorophyll. Some synthetic porphyrins are photosensitizers of singlet oxygen formation. Taking account of the biological constraints, Dolphin synthesized a set of porphyrin structures that are effective at the task. One of these, verteporfin = visudine[R], a mixture of two regioisomers and their mirror images, is widely used for treatment of one form of macular degeneration.

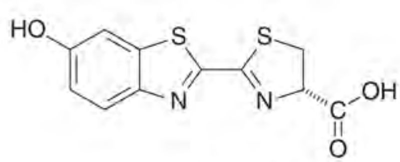


verteporfin

How nice that here a photochemical reaction is used for curing a disorder of our most prominent photochemical organ!

FIREFLIES

What makes them flash? It's luciferin, three rings of carbon, sulfur, and nitrogen, reacting with oxygen and ATP to a stressed molecule that gives off light with 100 percent efficiency.



luciferin

There's more to the story here, of reflecting uric acid crystals to make the light brighter. And how it's all for sex: male signals, the delay of the female flash back counts. I could tell you of the femme fatale of *Photuris*, imitating the flash pattern to poor male *Photinus* fireflies, promptly eaten to get a parcel of chemicals warding off spiders. But here and now I see the spruce's mass traced by fireflies, not falling like the dark angel, but in their criss-crossing outshining stars, imposing piecewise order.

Beautiful, physical, chemical, beautiful.

REFERENCES

1. Adam Markham and Cameron Wake, *Indicators of Climate Change in the Northeast*, Clean Air—Cool Planet: Durham, New Hampshire (2005).
2. Immanuel Kant, *Critique of Judgment*, trans. J.H. Bernard, p. 28, Hafner: New York (1951).