FUELS FROM SOLAR ENERGY.
A DREAM OF GIACOMO CIAMICIAN, THE FATHER OF PHOTOCHEMISTRY

Margherita Venturi
Vincenzo Balzani
Maria Teresa Gandolfi
Dipartimento di Chimica "G. Ciamician"
Via Selmi, 2 – 40126 Bologna (Italy)
e-mail: margherita.venturi@unibo.it
e-mail: vincenzo.balzani@unibo.it
e-mail: mariateresa.gandolfi@unibo.it

ABSTRACT

Giacomo Ciamician was professor of Chemistry at the University of Bologna from 1889 to 1922. Inspired by the ability of plants to make use of solar energy, he was the first scientist to investigate the photochemical reactions in a systematic way, so that he is now considered a pioneer of modern photochemistry. In a famous address presented before the VIII International Congress of Applied Chemistry, held in New York in 1912, he strongly suggested to replace "fossil solar energy" (i.e, coal) with the energy that the earth receives from the sun every day. In particular, he forecasted the production of fuels by means of artificial photochemical reactions (artificial photosynthesis), which is still one of the most important goals of current research in the field of chemistry. The possibility of obtaining fuels (particularly dihydrogen) from solar energy would indeed solve two great problems of the present day society: energy and environment.

1. INTRODUCTION

At the beginning of the new millennium, re-examination of the work of scientists who lived in between the XIX and XX centuries could be an exercise of curiosity that simply leads to loss of time. This is not the case if the scientist taken into consideration is Giacomo Ciamician (Fig. 1), since most of his work looks quite interesting and even useful for present-day research in the field of chemistry. On reading his scientific papers and the texts of his talks, we have been fascinated and, sometimes, even astonished, because his assertions and intuitions often appear to be inspired by a prophetic spirit. Almost one century ago, Giacomo Ciamician realized that Chemistry is a "central" science that permeates many other fields of knowledge, and that can play an essential role in solving the four greatest problems of humanity: food, health, energy, and environment. In particular, his thoughts on the energy problem are very close to those discussed in present days.

Ciamician was born in Trieste in 1857 from an Armenian family. His career followed a quite linear "geographical" journey. After some years of study at the University of Wien, he received in 1880 his doctorate at the German University of Giessen and then went to Rome to work in the laboratory of one of the greatest Italian chemists, Stanislao Canizzaro. In 1887 Ciamician became professor of General Chemistry at the University of Padua, and two years later he moved to the University of Bologna, where he remained until the time of his death on January 2, 1922.

Fig. 1: Autographed portrait that Giacomo Ciamician (1857 – 1922) presented to students who submitted perfect examination papers

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If the geographical journey of Ciamician was simple, his scientific activity was very rich and complex. Today Ciamician is mostly known for his contribution to the development of organic chemistry; for this reason since 1979 the Division of Organic Chemistry of the Italian Chemical Society has established the Ciamician Award which is assigned to a young researcher every year. However, Ciamician was a scientist with multiple interests: he wrote about 400 papers covering various research fields, including emission spectroscopy, theory of electrolytic dissociation, chemistry of pyrrole, chemical action of light, and chemical reactions in green plants. Considering such a scientific production, it is easy to agree with the first sentence of one of the several papers dedicated to his memory (Fig. 2): *"One of the most important human talents is for sure the ability of being interested in many fields and of increasing the knowledge in all of them. Giacomo Ciamician, pioneer of the Photochemistry, is the perfect example of this definition"* (1).


CHRONIQUE

GIACOMO CIAMICIAN
CHIMISTE DE GRAND TALENT
ET PIONNIER DE LA PHOTOCHIMIE (*)

Fig. 2: The first page of the paper of M. Pfau and N.D. Heindel dedicated to Giacomo Ciamician

Ciamician was also convinced that a scientist, worthy of this name, cannot live in an ivory tower, but must be deeply involved in the social life and engaged in the spreading of science.

Ciamician social engagement is demonstrated by his long activity as a Senator of the Italian Kingdom; he was elected to the Senate in 1910 and maintained this position until the end of his life. During this period he served on many important commissions and gave several speeches in Senate on the problem of science and public education. In particular, he participated actively in the discussions on the budgets of public instruction, agriculture, industry and commerce, as well as on several other topics such as the application of international conventions and the modification of some laws. During the First World War he dedicated all his energy to solve problems of national defence: the strain connected to this activity undoubtedly hastened his premature death.

To promote science, Ciamician delivered many public lectures on important themes related to the everyday life, such as: "Chemical Problems of the New Century", "Problems and Objectives of Today's Organic Chemistry", "Cooperation of the Sciences", and "Organic Chemistry in Organisms".

During his career Ciamician received several academic honours. In 1887, when he was still very young, he was awarded with the Prize of the Royal Academy of Lincei; later on, he became a member of this academy and of the Italian National Academy of XL; he also became a correspondent member of practically all the Italian academies, a foreign member of the scientific academies of France, Prussia, Bavaria and Sweden, and of the scientific societies of Göttingen and Upsala. He was a honorary member of the American Chemical Society as well as of the Chemical Societies of France, Germany, and London. The University of Glasgow conferred on him the honorary degree of Doctor of Laws. After the reorganization of the Italian Association of General and Applied Chemistry he was elected president of the Association. Ciamician was also proposed ten times for the Nobel Prize by famous Italian and foreign scientists, in particular twice by Emil Fischer, the greatest organic chemist of his time.

Ciamician was not only a great investigator, but also equally great as a teacher. McPherson, who in 1913 had the privilege of visiting Ciamician's laboratory and attending some of his lectures, said: *"These lectures were ideal – exceedingly clear and logical. They were illustrated with numerous experiments skillfully performed. For one and one-half hours (the length of the lecture period) he poured his whole energy into this subject. At the end of his lecture he was received by an assistant with a heavy wrap – much as our modern football players who retire exhausted from the game"* (2).

2. CIAMICIAN PIONEER OF THE PHOTOCHEMISTRY

Ciamician became aware of the great potential of the utilization of solar energy for chemical purposes during his studies on the chemistry of green plants. The problem of understanding the way in which plants produce the substances that are essential to their own life was dealt with in 21 papers written in collaboration with Ciro Ravenna. Ciamician was convinced that the plants are wonderful chemical industries and that, to learn how do they work, it is necessary to go deeper and deeper in their

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structure, from the tree to the leaves, to the cells, to the chloroplasts, to the grains, to the membranes, down to reach the molecular level.

As Ciamician said in a famous address to the Italian Society for the Progress of Sciences (3), delivered some months before his death, his attention was particularly attracted by the following problem: *"Why plants produce in such great number and variety substances that look unrelated to their lives? Everybody agrees that proteins, simple and complex sugars, fats and others substances, like lecithins, and some mineral substances are essential to plants, as they are for all living organisms. But what are the others, that we called accessories, used for? I mean, the substances like glucosides, alkaloids, some dyes (of course I am not referring to the coloured substances of the flowers and plants whose purpose is clear), terpenes, camphors, tannins, resins, and some others. All these substances seem to be unnecessary and accidental; all the animals do not contain such substances or they do in a little amount. We started from the concept that plants, because of their own nature, need more chemical stimuli than the animals do.*
The chemistry of plants is more complex because it has to supply for the lack of differentiation of structures and the absence of special organs. Such additional substances, especially the alkaloids, can be considered as vegetable hormones".

In his address, Ciamician also explained in details the experiments he did and the results he got; on closing, he said: *"The conclusion is that plants make up for their organisation less differentiated than in the animals, and their wilful manifestations less expressed, by using a quite perfect chemistry. The conscience of plants is chemical in nature!"*

In systematic experiments Ciamician inoculated in the plants, or supplied to plants through their roots, organic substances pure or in solutions. He inoculated a substance (i.e, xanthine) and its methyl derivatives (theobromine, caffeine). Then he observed the toxic effect on the plant and other related reactions. He worked on hundreds of substances, with amazing results. He found, for instance, that some substances have a beneficial effect, while some others have a harmful action. These results were described by Ciamician in his admirable and suggestive talk entitled "The Photochemistry of the Future" that he delivered before the VIII International Congress of Applied Chemistry, held in New York in 1912 (4): *"More recently while studying the function of the alkaloids in the plants, we have succeeded in modifying the production of nicotine in the tobacco plant, so as to obtain a large increase or a decrease in the quantity of this alkaloid. ... In a series of experiments made in an effort to determine the physiologic function of the glucosides, we have succeeded in obtaining them from plants that usually do not produce them. We have been able, through suitable inoculations, to force maize to synthetize salicin".*

It is easy to see in these results the first attempts to develop what nowadays we call biotechnology. Ciamician himself forecasted the development of this branch of science: *"... modern industry is affiliated very intimately with pure science; the progress of one determines necessarily that of the other. ... Modern interest is concentrated on the study of the organic chemistry of organisms. This new direction in the field of pure science is bound to have its effect on the technical world and to mark out new paths for the industries to follow in the future".*

During his researches Ciamician noticed that: *"organic chemistry ... needs ... high temperature, inorganic acids and very strong bases, halogens, the most electropositive metals, some anhydrous metal chlorides and halogenated phosphorous compounds.... plants, on the contrary, by using small traces of carbonic acid obtained from the air, small amounts of salts subtracted from the ground, water found everywhere, and by exploiting solar light, are able to prepare easily many substances that we can badly reproduce"* (5, 6).

During another address to the First Congress of the Italian Society for the Progress of Sciences, Ciamician said to the authorities attending his lecture: *"For sure the request to support our studies may seem exaggerated to the Ministry of the Public Education, considering that plants can obtain so great results without needing money. But in our laboratories we have to use strong and expensive chemical reagents, because we are not capable of exploiting solar energy, as the plants do"* (7).

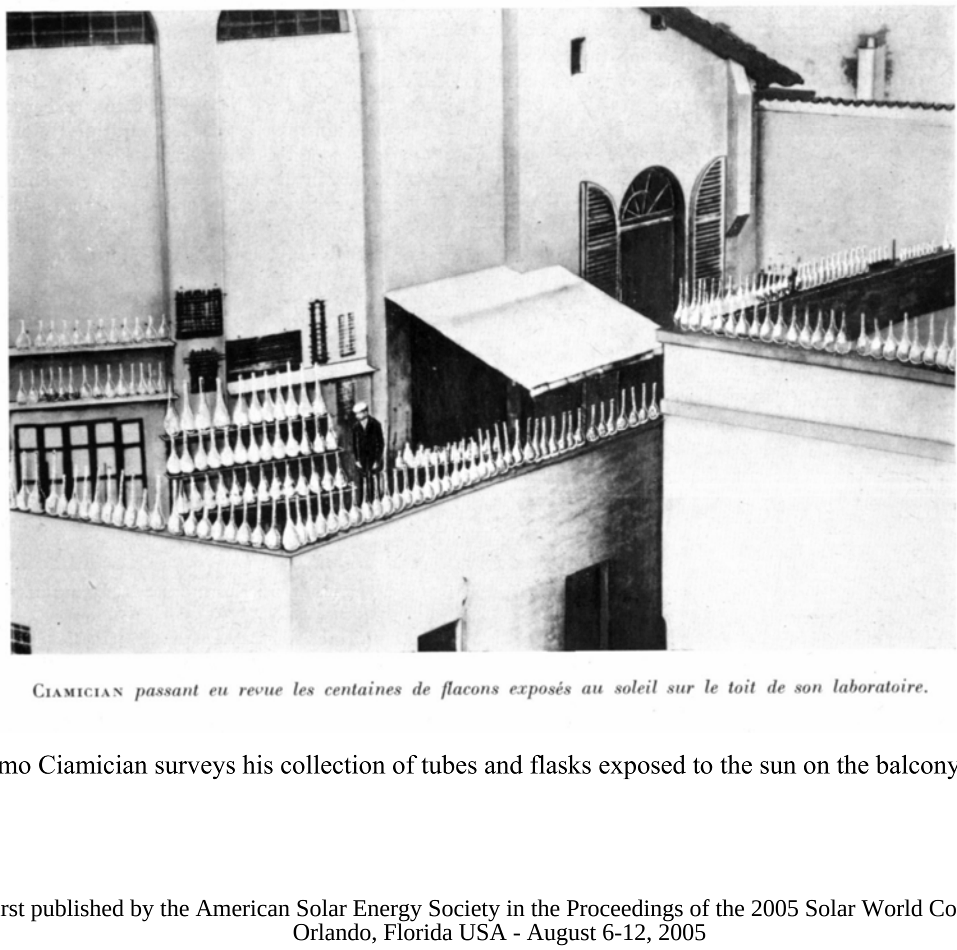
Ciamician clearly understood the importance of sunlight, as evidenced by the following words: *"there is another agent that has a profound effect on the processes of organisms and that deserves to be deeply investigated: that is light"* (8). This was indeed his greatest discovery.

By starting from the consideration that the "secret" of the complex chemistry of plants resides in the use of light, and that the interaction between light and matter represents the most important and oldest natural phenomenon, Ciamician decided to study in a systematic way what he called "the chemical action of light". During such studies, performed in collaboration with Paul Silber and published in 49 papers, Ciamician not only obtained several important results, but also enjoyed very much by working with light. Indeed, at the already mentioned Congress of New York in 1912 he joked about the unexpected behaviour of some photochemical reactions – *"In ordinary ... chemistry the reactions take place in some definite way, but the photochemical reactions often furnish surprises ..."* – and about one of the possible applications of the phototropic (nowadays called photochromic) compounds – *"Such substances might well attract the attention of fashion ... The dress of a lady, so prepared, would change its color according to the intensity of light. Passing from darkness to light the* *colors would brighten up, thus conforming automatically to the environment: the last word of fashion for the future"* (4).

Of course, the interpretation of such surprising and funny results was not easy at all, particularly because at that time the analytical techniques were very rudimental, and the (trivial for us) concepts of molecular ground and excited states, radiative and radiationless deactivations, spin multiplicity, etc. had not yet been elaborated. Even the concept of photon was not yet fully accepted and the so called "law of the photochemical equivalent" proposed by Einstein (9) was in some way misleading. In the attempt to formulate some hypothesis on the mechanism of the photochemical reactions, Ciamician, indeed, used the theory of Planck and Einstein on the photoelectric effect and a model proposed by Plotnikov, another famous scientist of that time, reaching an uncorrected interpretation: *"According to a brilliant idea of Plotnikow, luminous radiations produce a different ionization from that due to electrolytic dissociation; the separation of an ion requires a quantity of light which is determined by the theory of Planck and Einstein. The problem is therefore related to the most recent and profound speculations of mathematical physics"* (4).

During his researches Ciamician met also an experimental difficulty. In order to perform photochemical experiments, a suitable light source is of course essential. Nowadays scientists engaged in this research field use powerful halogen, mercury and tungsten lamps with light filters that allow the selection of almost monochromatic light beams. In most cases, also continuous or pulsed laser sources are now routine equipment in photochemical laboratories. At the beginning of the last century, however, halogen, mercury and laser light sources were not yet available and the light emitted by the tungsten lamps was too faint and too "red" to induce photochemical reactions. Since the sun was the only convenient light source for his photochemical experiments, the balconies of the institute where Ciamician worked were the most suitable place for his laboratory (Fig. 3), and he was quite happy about that: *"Whoever saw Ciamician in his laboratory balcony, where hundreds of bottles and glass pipes containing various substances and mixtures were exposed to the sun rays, and heard him speaking of his results and projects, can say how happy he was. But only who worked with him can know how much work he had to do, how much patience he had to have, how able he had to be, how much nose he had to have, ... to isolate and characterize the products of very complex reactions ..."* (10)

In spite of the theoretical and experimental difficulties, Ciamician and his friend and co-worker Paolo Silber performed the first systematic study of the behaviour of organic compounds upon irradiation. By looking at their extensive photochemical investigations, one does not get the impression that they had in mind any particular application; nevertheless it is certain that Ciamician forested a hope that these researches might lead ultimately to the utilization of solar energy.



CIAMICIAN *passant eu revue les centaines de flacons exposés au soleil sur le toit de son laboratoire.*

Fig. 3: Giacomo Ciamician surveys his collection of tubes and flasks exposed to the sun on the balcony of his institute

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3. FUELS FROM SOLAR ENERGY: CIAMICIAN'S DREAM

Most of the Ciamician's considerations and predictions on the utilization of solar energy are contained in the already mentioned "The Photochemistry of the Future" address (4).

Ciamician began his address as follows: *"Modern civilization is the daughter of coal, for this offers to mankind the solar energy in its most concentrated form; that is, in a form in which it has been accumulated in along series of centuries. Modern man uses it with increasing eagerness and thoughtless prodigality for the conquest of the world and, like the mythical gold of Rhine, coal is to-day the greatest source of energy and wealth. The earth still holds enormous quantities of it, but coal is not inexhaustible. The problem of the future begins to interest us ... Is fossil solar energy the only one that may be used in modern life and civilization? That is the question"*. If the word "coal", which was the only fuel used at that time, is replaced by "fossil fuels", such a statement holds even today.

Ciamician estimated that: *"... the solar energy that reaches a small tropical country ... is equal annualy to the energy produced by the entire amount of coal mined in the world!"*. It is interesting to note that the disproportion between the solar energy that reaches the surface of the earth and the human energy needs still holds today, even if the energy consumption has remarkably increased. A recent estimate has indeed proved that the amount of solar energy that arrives on the earth is 10,000 times more than that we need.

Ciamician goes on noticing that: *"The enormous quantity of energy that the earth received from the sun, in comparison with which the part which has been stored by the plants in the geological periods is almost neglegible, is largely wasted"*.

Ciamician also wonders whether and how this energy could be used: *"Is it possible or, rather, is it conceivable that this production of organic matter may be increased in general and intensified in special places, and that the cultivation of plants may be so regulated as to make them produce abundantly such substances as can become sources of energy ... I believe that this is possible. ...For the problem we are now considering the quality of the plants is of secondary importance ...; the essential point is that they grow fast or that their growth may be intensified. It would be like realizing the desire of Faust: Und Bäume die sich täglich neu begrünen!"*. It is interesting to note that nowadays several countries have set up programs dealing with the development of biomass to convert solar energy into fuels. Even on this topic, Ciamician gives advices that we still try to follow: *"The harvest, dried by the sun, ought to be converted, in the most economical way, entirely into gaseous fuel ..."*.

Then, Ciamician deals with the main aspect of the energy problem, wondering: *"... whether there are not other methods of production which may rival the photochemical processes of the plants. ... For our purposes the fundamental problem from the technical point of view is how to fix the solar energy through suitable photochemical reactions. ... By using suitable catalyzers, it should be possible to transform the mixture of water and carbon dioxide into oxygen and methane, or to cause other endo-energetic processes"*. It is clear that Ciamician was thinking about the possibility of obtaining an artificial photosynthetic process capable of converting solar energy into fuels. What this great scientist foresaw more than 90 years ago is the most ambitious goal of today's photochemistry (11,12). The possibility of obtaining fuels (particularly dihydrogen) from solar energy would indeed solve two great problems of the present day society: energy and environment.

The final part of the Ciamician address is wonderful and is worth to be reported almost completely: *"Where vegetation is rich, photochemistry may be left to the plants and by rational cultivation, as I have already explained, solar radiation may be used for industrial purposes. In the desert regions, unadapted to any kind of cultivation, photochemistry will artificially put their solar energy to practical uses. On the arid lands there will spring up industrial colonies without smoke and without smokestacks; forests of glass tubes will extend over the plants and glass buildings will rise everywhere; inside of these will take place the photochemical processes that hitherto have been the guarded secret of the plants, but that will have been mastered by human industry which will know how to make them bear even more abundant fruit than nature, for nature is not in a hurry and mankind is. And if in a distant future the supply of coal becomes completely exhausted, civilization will not be checked by that, for life and civilization will continue as long as the sun shines! If our black and nervous civilization, based on coal, shall be followed by a quieter civilization based on the utilization of solar energy, that will not be harmful to progress and to human happiness"*.

4. CONCLUSIONS

There is no doubt that Ciamician, considering his impressive work, ideas and intuitions, was a scientist a century ahead of his time. In his famous "Photochemistry of the Future" address (4) he raised problems on the use of energy resources that are the same as those we have to cope with at the beginning of the third millennium. He indicated the advantages provided by the use of solar energy, and suggested that the more convenient way to exploit solar energy is its conversion into fuels. In an attempt to solve the present day energy crisis, we should follow the suggestion of this great scientist.

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