

LIGHT-DRIVEN MOLECULAR MOTORS BASED ON AZOBENZENE PHOTOISOMERIZATION

Rodica-Mariana ION¹, Daniel MUNTEANU²

Rezumat. *Un motor molecular poate fi definit ca un ansamblu de un număr discret de componente moleculare concepute pentru a efectua mișcări mecanice sub controlul factorilor de producție de energie corespunzătoare.*

Abstract. *A molecular motor can be defined as an assembly of a discrete number of molecular components designed to perform mechanical movements under control of appropriate energy inputs.*

Keywords: Nanorobotics, azobenzene.

1. Introduction

A molecular motor can be defined as an assembly of a discrete number of molecular components designed to perform mechanical movements under control of appropriate energy inputs. The words *motor* and *machine* are often used interchangeably when referred to molecular systems. Molecular motors and machines operate by means of electronic and/or nuclear rearrangements and make use of thermal fluctuations (*Brownian motion*). They are characterized by the kind of energy input supplied to make them work, the type of motion (*such as translation, rotation, or oscillation*) performed by their components, causing readable changes in some chemical or physical property of the system.

Molecular photochromic switches are an intriguing class of organic molecules which allow the control of molecular structure and function with light.

For references use [³].

Consequently, this offers the possibility of effecting dramatic changes to the bulk properties of a system by irradiation. Photochemical methods are also useful for monitoring the operation of the motor. In general with respect to chemical systems photons can play the dual role of *writing (causing a change in the system)* and *reading (reporting the state of the system)*. As a matter of fact, *cis-trans*

¹Prof. Dr. Ch. Rodica-Mariana ION, ICECHIM, Bucharest, Valahia University of Targoviste, Romania, (rodica_ion2000@yahoo.co.uk)

²Drd. Ing. Daniel MUNTEANU, Valahia University of Targoviste, Romania, (daniellmunteanu@yahoo.com)

³Prof. Dr. Ch. Rodica-Mariana ION, ICECHIM, Bucharest, Valahia University of Targoviste, Romania, (rodica_ion2000@yahoo.co.uk)

photoisomerization reactions involving N=N, C=N, or C=C bonds are well known processes. The molecular tweezers based on the azobenzene unit were perhaps the first examples of lightdriven molecular machines reported in the literature. The construction of molecular rotary motors poses several challenges, particularly because it is difficult to satisfy the unidirectional rotation requirement.

For the references use [²,³].

In general, they are extremely clean and reversible reactions, the prototypical case being the *cis*–*trans* isomerization of azobenzene. See figure 1.

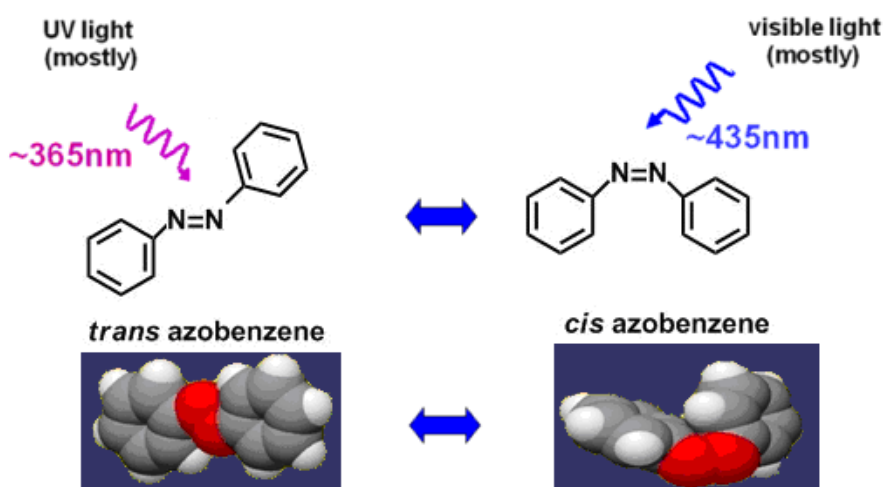


Fig.1. *Cis*–*trans* isomerization of azobenzene

Photochemical methods are also useful for operation of the motor, and *cis*–*trans* photoisomerization reactions involving N=N, C=N, or C=C bonds are discussed in this paper, and azobenzene photoisomerization, especially. The efficiency aspects (*quantum yield*) and issues in movement of a nanorobot regimes are discussed.

2. Experimental part

2.1. Materials and apparatus

50 ml solution of azobenzene have been inserted into a quartz photoreactor. Argon is flow into the photoreactor during all reaction in order to avoid the photooxidation of azobenzene. Some samples have been prelevated time to time

² Prof. Dr. Ch. Rodica-Mariana ION, ICECHIM, Bucharest, Valahia University of Targoviste, Roumania, (rodica_ion2000@yahoo.co.uk).

³ V. Balzani, A. Credi, F. M. Raymo and J. F. Stoddard, “Artificial molecular machines”, *Angew. Chem. Int. Ed.*, vol. 39, pag. 3348-3391, 2000.

from the photoreactor and they have been registered by UV–VIS spectrophotometry. For irradiation a 250 W Hg medium pressure lamp has been used. See Figure 2.

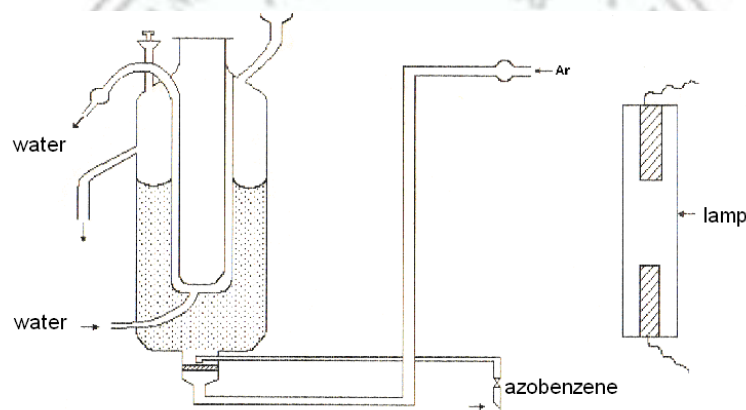


Fig. 2. The photochemical reactor

3. Results and discussion

Organic molecular photochromic switches are molecules that can be interconverted reversibly between two (meta)-stable states, A and B, by stimulus with light. See Figure 3.

This change is the result of *cis* → *trans* photoisomerization. For the switch to be useful, it should meet three criteria:

- (1) it should be thermally stable;
- (2) the states A and B should have different properties, such as a large change in molecular geometry, polarity, UV–VIS absorption, etc.;
- (3) both states of the switch should be separately addressable.

In principle, an ideal photochromic switch would exhibit perfect photocontrol. This means that irradiation at different wavelengths (k_1 and k_2) allows quantitative photoconversion to states A and B, respectively. The ability to address each isomer selectively necessitates that A and B possess significant differences in their UV–VIS absorption spectra. In many cases this change in absorption is a desirable property in itself. For de references use [⁴, ⁵].

⁴ V. Braintenberg, *Vehicles: Experiments in Synthetic Psychology*. Cambridge, MA: MIT Press, 1984.

⁵ A. M. Brower, C. Frochot, F. C. Gatti, D. A. Leigh, L. Mottier, F. Paolucci, S. Roffia and G. W. H. Wurpel, "Photoinduction of fast, reversible translational motion in a hydrogen-bonded molecular shuttle", *Science*, vol. 291, pag. 2124-2128, martie 2001.

Azobenzenes have received considerable experimental and theoretical attention because they undergo light-driven trans \rightarrow cis isomerization. Their cis- and trans-isomers have a different spatial arrangement of the aromatic moieties, and consequently show significantly different physical and chemical properties, as shown in Figure. Use Figure 3.

For de references use [⁶, ⁷, ⁸, ⁹].

A major advantage of azobenzene switches is that they are easy to synthesize. However, an important drawback is that, depending on the nature of the substituents on the aromatic groups, these switches often undergo thermal cis- \rightarrow trans isomerization at room temperature.

Quantum yield measurements

Method I

The used formula is:

$$\Phi = \frac{A \cdot V \cdot Y}{I_0 \cdot l^2 \cdot \epsilon_t} \quad (1)$$

where:

V – sample volume;

Y_{inf} – cis izomer/total concentration in stationary state;

ϵ_t – extinction coefficient at one wavelength;

l – layer length;

I_0 – intensity of incident radiation;

A – absorbance.

The results are shown in Table 1.

⁶ S. M. Carr and M. N. Wybourne, "Elastic instability of nanomechanical beams", Appl. Phys. Lett., vol. 82, no. 5, pag. 709-711, februarie 2003.

⁷ H. A. Clark, M. Hoyer, M. A. Filbert and R. Kopelman, "Optical sensors for chemical analysis inside single living cells. 1. Fabrication, characterization, and methods for intercellular delivery of PEBBLE sensors", Anal. Chem., vol. 71, pag. 4831-4836, 1999.

⁸ H. A. Clark, R. Kopelman, R. Tjalkens and M. A. Filbert, "Optical sensors for chemical analysis inside single living cells. 2. Sensors for pH and calcium and the intercellular application of PEBBLE sensors", Anal. Chem., vol. 71, pag. 4837-4844, 1999.

⁹ J. R. Dennis, J. Howard and V. Vogel, "Molecular shuttles: directed motion of microtubules along nanoscale kinesin tracks", Nanotechnology, vol. 10, no. 3, pag. 232-236, septembrie 1999.

Table 1.

| Wavelength λ | T _{n-but} | T _{tertbut} | C |
|-------------------------|--------------------|----------------------|-------|
| 228 | 11887 | 13638 | 7653 |
| 245 | 2598 | 2680 | 15460 |
| 291 | 9543 | 13233 | 3466 |
| 316 | 19017 | 21506 | 1007 |
| 357 | 1057 | 1746 | 3698 |
| 439 | 810 | 453 | 20 |

For all calculus, A constant is decisive. This is the slope of the straight line. First is determining Y_{inf} for a stationary concentration. The ratio between cis concentration and total concentration is Y. By fitting $\ln(Y_{inf}-Y)$ vs. irradiation time a straight line – A - is determined. The measurements have been made for 348 nm, 369 nm and 375 nm and the following equations are obtained:

$$348 \text{ nm: } Y = - 3.31 \cdot 10^{-2} X - 0.476;$$

$$369 \text{ nm: } Y = - 1.87 \cdot 10^{-2} X - 1.725;$$

$$375 \text{ nm: } Y = - 1.99 \cdot 10^{-2} X - 1.050.$$

The experimental results could be resumed in the following Table 2.

Table 2.

| λ (nm) | 348 | 369 | 375 |
|---|-----------------------|------------------------|------------------------|
| A/10 ⁻² (min ⁻¹) | 3,31 | 1,87 | 1,99 |
| V/10 ⁻³ (l) | 3,5 | 3,5 | 3,5 |
| Y _{inf} | 0,58 | 0,26 | 0,38 |
| ϵ_i (l/mol*cm) | 6495 | 150 | 162,5 |
| I ₀ (Einst/min) | 1,16*10 ⁻⁶ | 34,24*10 ⁻⁶ | 1,031*10 ⁻⁶ |
| l (cm) | 1 | 1 | 1 |

Under such circumstances, the quantum yields are:

$$\Phi_{348} = 0,009;$$

$$\Phi_{369} = 0,033;$$

$$\Phi_{375} = 0,158.$$

So, the best quantum yield is obtained for 375 nm.

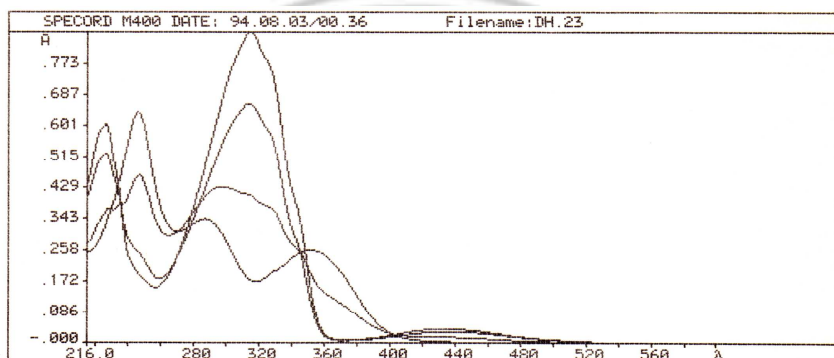


Fig. 3. Trans azobenzene spectrum in n-butyl alcohol for different irradiation time

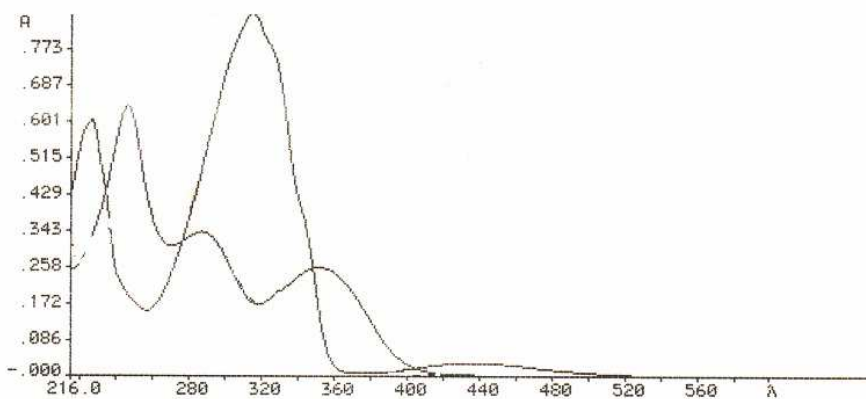


Fig. 4. Trans azobenzene spectrum compared with cis azobenzene

Method II

The quantum yield was determined knowing fraction of cis isomer, y , from the mixture of both isomers. We presumed that initially was only trans isomer. We determined the molar extinction coefficients for both isomers, as shown in Table 3.

Table 3.

| λ | <i>trans</i> | <i>cis</i> |
|-----------|--------------|------------|
| 228 | 11887 | 7653 |
| 245 | 2598 | 15461 |
| 291 | 9543 | 3466 |
| 316 | 19017 | 1007 |
| 357 | 1057 | 3698 |
| 439 | 810 | 20 |

Could be seen that the photoisomerization of trans isomer at irradiation with 348 nm, 369 nm and 375 nm and concentration of $2,5 \cdot 10^{-5}$ M, the stationary state is different for each wavelength. In order to calculate the quantum yield, we used the following equation:

$$\frac{dy}{dt} = \frac{I_o \cdot l}{V \cdot F} [\Phi_t \cdot \varepsilon_t (l - y)] - \frac{I_o \cdot l}{V \cdot F} [\Phi_c \cdot \varepsilon_c \cdot y] - k \cdot y \quad (2)$$

where:

l – sample length, cm;

$\Phi_{t,c}$ – quantum yield for trans – cis, respectively cis – trans;

$\varepsilon_{t,c}$ – absorption molar coefficients;

V – sample volume, l;

D – optical density, as in eq. (3):

$$\ln\left(\frac{I_o}{I}\right) = D = cl[\varepsilon_t + (\varepsilon_c - \varepsilon_t)y] \quad (3)$$

$$F = D/(1 - \exp(-D)). \quad (4)$$

The first two terms from the right side of eq.1 reveal the rate of photochemical reaction and the third is the rate of thermal reaction cis – trans. Knowing that $dy/dt = 0$ for $t \rightarrow \infty$, we could solve the equation for Φ_c and then introducing into (1) could be obtained:

$$\begin{aligned} dy/dt &= A/F(y_f - y) - ky(F_t/F - 1) \\ A &= I_o l^2 \Phi_t \varepsilon_t / V y_f \end{aligned} \quad (5)$$

We could neglect the last term from (2), and the eqs could result:

$$\begin{aligned} z &= (y_f - y) \\ I(z) &= \int F dz / z \end{aligned} \quad (6)$$

By integrating vs. z and t, results:

$$I(z) = -At + \text{constant} \quad (7)$$

where $I(z)$ is calculated under the hypothesis that $F = 1$.

So, $I(z) = \ln(z)$.

By graphical representation of $I(z)$ vs. time, results a straight with slope A, and finally could be calculated the quantum yield.

The quantum yields are:

$$\Phi_{348} = 0,172;$$

$$\Phi_{369} = 0,100;$$

$$\Phi_{375} = 0,120.$$

Both quantum yields obtained by both methods, are quite similar. The photoisomerization could be considered as a transfer of one electronic excited

molecule on a higher vibrational level belonging to the ground state. Also, the photoisomerization involves a common state for trans and cis isomers. Between these levels there does not exist an energy barrier, the transfer between them being spontaneous.

For the references use: [¹⁰, ¹¹].

Photoisomerization could be considered as a “thermal reaction” of one excited level as an interconversion of excited molecules trans and cis over an energetic hypothetical barrier very small able to allow the interconversion in a very short lifetime of excited state (10^{-9} s). Such barrier would be smaller for N-N bond than the rotation with 180° at N-N-C bond. Studying the planar configuration of both isomers, we can conclude that the trans isomer is planar, the non-participating electron of nitrogen being in the nodal plane of π electrons of benzene and the double bond. See Figure 5.

For cis azobenzene the benzene rings are perpendicular to the -N=N- plane. See Figure 6.

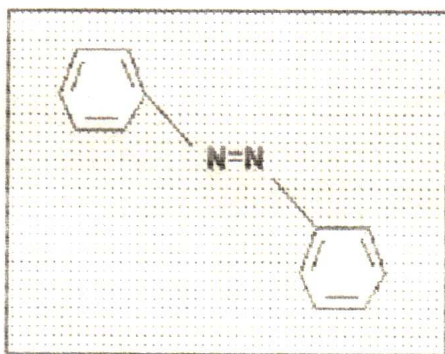


Fig. 5. The planar configuration of trans azobenzene

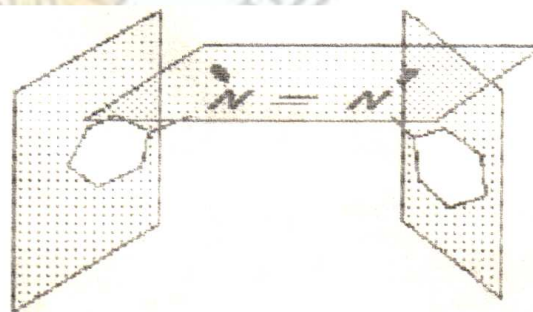


Fig. 6. The configuration of cis azobenzene

¹⁰ K. E. K. Eric Drexler, *Nanosystems: Molecular Machinery, Manufacturing and Computation*. New York: Wiley, 1992.

¹¹ B. L. Feringa, N. Koumura, R. A. van Delden and M. K. J. ter Wiel, “Light-driven molecular switches and motors”, *Appl. Phys. A*, vol. 75, pag.301-308, 2002.

The principle aspect in context to artificial nanorobot is also presented in this paper. See Figure 7.

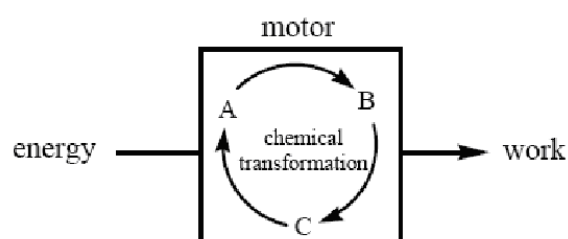


Fig. 7. The principle of molecular motor

A molecular motor is molecular motions of its component parts. The motor responds to an input (energy) with an output (work) and must produce a unidirectional, cyclic process.

See Figure 8.

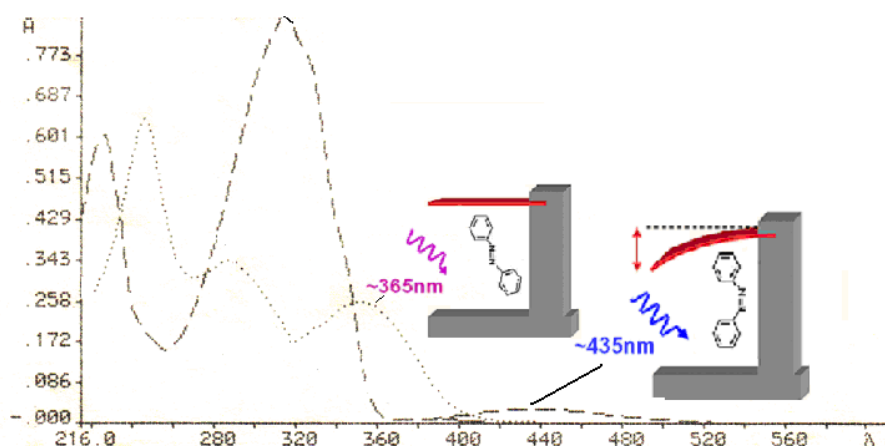


Fig. 8. Action of azobenzene molecular motor (exposure to 365-nm light causes the backbone to contract, pulling on the cantilever (right)).

Conclusions

Photochemical methods are also useful for monitoring the operation of the motor. *Cis-trans* photoisomerization reactions involving N=N, C=N, or C=C bonds are well known processes. The molecular tweezers based on the azobenzene unit were perhaps the first examples of lightdriven molecular machines reported in the literature. The construction of molecular rotary motors poses several challenges, particularly because it is difficult to satisfy the unidirectional rotation requirement. These are ideal processes to obtain lightdriven operation of molecular machines because they bring about evident structural

changes that can be exploited to cause large amplitude motions in suitably designed molecular and supramolecular systems. In the present work, the highlight review focused on selected recent examples where light-driven molecular motors based on azobenzene have been used for some switching behaviour.

REFERENCES

- [1] R.M. Ion, D. Munteanu, “*Nanotechnology-Nanorobotics-Nanomedicine*”, Metalurgia International, XVI, 2, 34 (2009);
- [2] Rodica Mariana Ion, “*Materiale nanocristaline*”, Editura Științifică Fundația Metalurgia Română, București, 2003;
- [3] V. Balzani, A. Credi, F. M. Raymo and J. F. Stoddard, “*Artificial molecular machines*”, Angew. Chem. Int. Ed., vol. 39, pag. 3348-3391, 2000;
- [4] V. Braintenberg, *Vehicles: Experiments in Synthetic Psychology*. Cambridge, MA: MIT Press, 1984;
- [5] M. Brower, C. Frochot, F. C. Gatti, D. A. Leigh, L. Mottier, F. Paolucci, S. Roffia and G. W. H. Wurpel, “*Photoinduction of fast, reversible translational motion in a hydrogen-bonded molecular shuttle*”, Science, vol. 291, pag. 2124-2128, martie 2001;
- [6] S. M. Carr and M. N. Wybourne, “*Elastic instability of nanomechanical beams*”, Appl. Phys. Lett., vol. 82, no. 5, pag. 709-711, februarie 2003;
- [7] H. A. Clark, M. Hoyer, M. A. Filbert and R. Kopelman, “*Optical sensors for chemical analysis inside single living cells. 1. Fabrication, characterization, and methods for intercellular delivery of PEBBLE sensors*”, Anal. Chem., vol. 71, pag. 4831-4836, 1999;
- [8] H. A. Clark, R. Kopelman, R. Tjalkens and M. A. Filbert, “*Optical sensors for chemical analysis inside single living cells. 2. Sensors for pH and calcium and the intercellular application of PEBBLE sensors*”, Anal. Chem., vol. 71, pag. 4837-4844, 1999;
- [9] J. R. Dennis, J. Howard and V. Vogel, “*Molecular shuttles: directed motion of microtubules along nanoscale kinesin tracks*”, Nanotechnology, vol. 10, no. 3, pag. 232-236, septembrie 1999;
- [10] K. E. K. Eric Drexler, *Nanosystems: Molecular Machinery, Manufacturing and Computation*. New York: Wiley, 1992;
- [11] B. L. Feringa, N. Koumura, R. A. van Delden and M. K. J. ter Wiel, “*Light-driven molecular switches and motors*”, Appl. Phys. A, vol. 75, pag. 301-308, 2002.