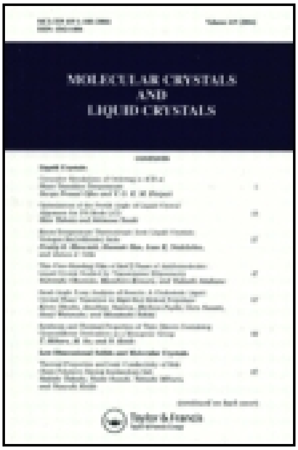

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Novel Multichromophoric Dyes for Chemical, and Physical Switching

Jörg Daub [a] , Christian Fischer [a] , Sebastian Gierisch [a] & Johann Set [a]

[a] Institut für Organische Chemie, Universitat Regensburg, Universitätsstr. 31, W-8400, Regensburg, Germany

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NOVEL MULTICHROMOPHORIC DYES FOR CHEMICAL AND PHYSICAL SWITCHING

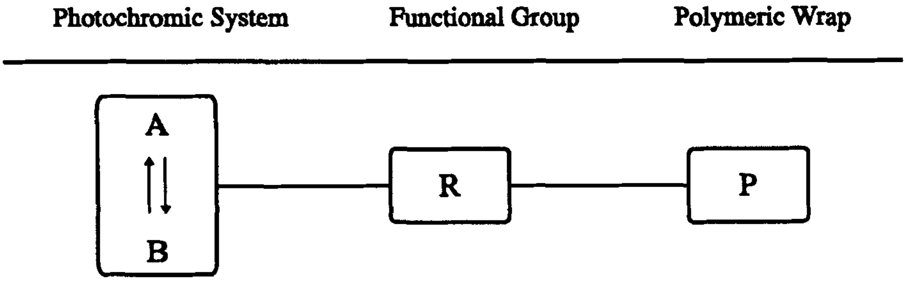
JÖRG DAUB*, CHRISTIAN FISCHER, SEBASTIAN GIERISCH
and JOHANN SIXT
Institut für Organische Chemie, Universität Regensburg, Universitätsstr. 31,
W-8400 Regensburg (Germany)

Abstract Functionalized photochromic compounds and their applications in chemical and physical switching processes are under investigation. In this report exclusive consideration is given to the dihydroazulene (DHA)/vinylheptafulvene (VHF) system **1/2**. A short description of the photochromism of **1/2** is presented. Three topics of potential switching behaviour released by the photochromism of **1/2** are pointed out: (i) change of the pk_a and of proton transfer properties in anilinium derivatives, (ii) change of the redox potential in compounds with electron transfer active subunits, (iii) increase of second-order nonlinear optical properties by irradiation of **1**.

INTRODUCTION

Colorants are compulsory to processes driven by visible light and contributing to energy transformation and the transfer and handling of information. In nature this occurs within supramolecular units comprising a reactive subunit surrounded by a polymeric bulk providing optimal efficiency. The visual process is one example within the plethora of active systems in photobiology[1].

How to create artificial systems coming in their behaviour close to natural devices ? A general scheme for a supramolecular unit is forwarded containing three subunits: (i) a central unit sustaining reversible structural changes which at least in one way must be driven by visible light (definition of photochromism)[2]; (ii) functional groups which convert structural changes into the appropriate physical or chemical properties or behaviour; (iii) a macromolecular bulk to mediate the effects and to optimize and amplify the molecular processes (Scheme 1).



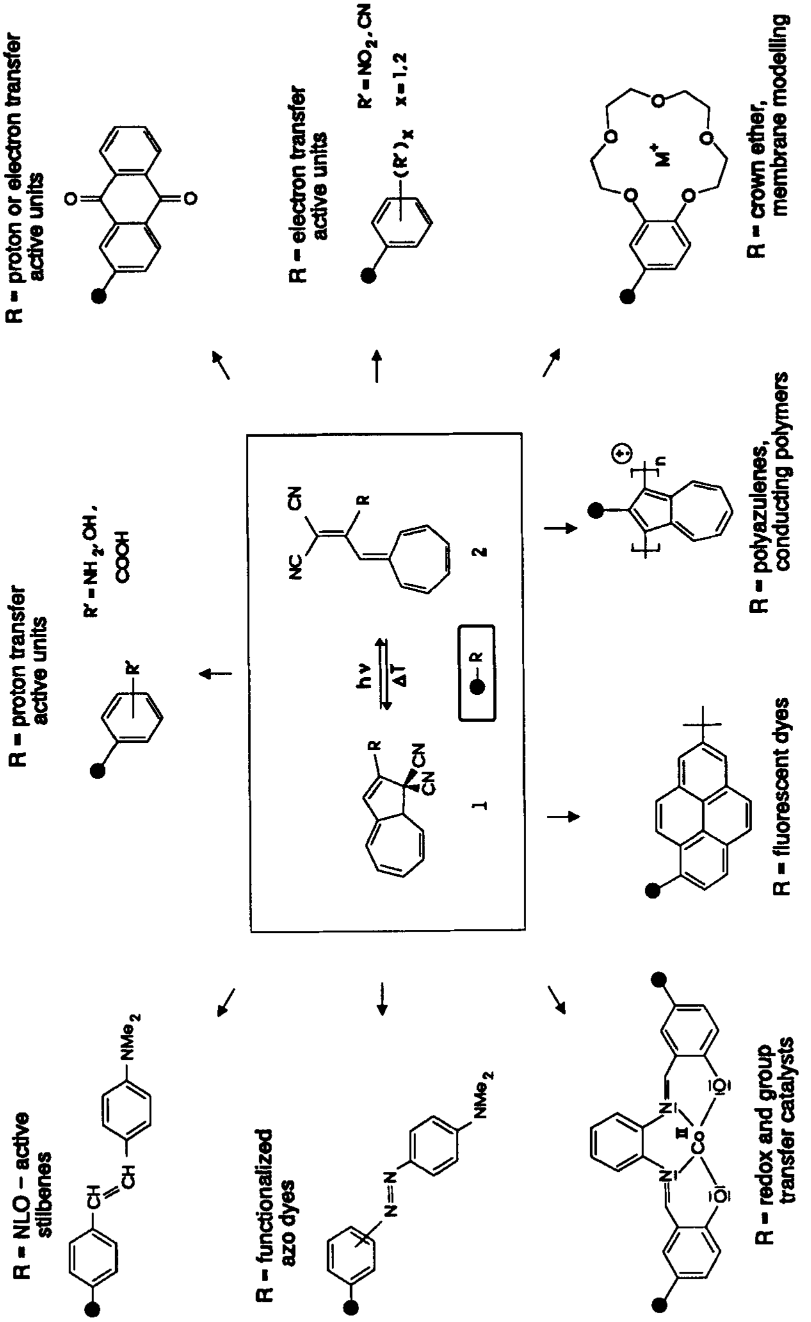
SCHEME 1

This report deals with investigations to utilize the dihydroazulene (DHA) 1/vinylheptafulvene (VHF) 2 couple as the central functional unit and its potential to stimulate chemical and physical switching processes. Main emphasis at this level of investigation is laid on the understanding of the basic photochemical and photophysical properties of the DHA/VHF photochromism and on the question of how the rearrangement 1 ⇄ 2 biases the properties of a functional group **R**. Scheme 2 surveys various domains of interest implying activation or desactivation of (i) proton or group transfer reactions, (ii) electron transfer, (iii) metal ion complexation or metal ion transport, (iv) conductivity in conducting polymers as for example polyazulenes, (v) fluorescent properties, (vi) catalytic properties, (vii) non-linear optical effects[3].

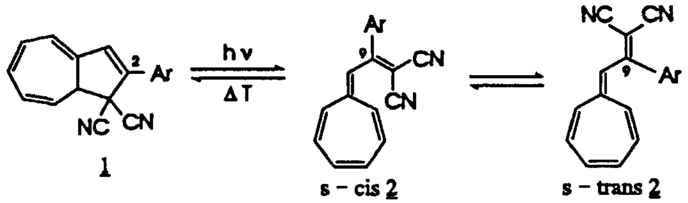
Emphasis in this account is given to discuss the mechanism of the photochemical and the thermal reaction pathways in the DHA/VHF photochromism and to point out the potential of molecular switching in functionalized systems 1 ⇄ 2 by three examples: (i) perturbation of acid/base equilibria, respectively proton or group transfer reactions, (ii) triggering of redox-potentials which stimulate heterogeneous electron transfer, and (iii) generating of molecular subunits with nonlinear optical (NLO) properties[4].

THE DIHYDROAZULENE/VINYLHEPTAFULVENE PHOTOCHROMISM

The photochemically induced rearrangement of dihydroazulene 1 into vinylheptafulvene 2 is accompanied by a change of colour from yellow to red as exemplified by the phenyl derivative 1a resulting from a decrease of the absorption band at 350 nm (in acetonitrile) and an increase of the long wave length absorption of 2a at 468 nm. The photoreaction occurs from the excited singlet state (quantum yield of the reaction: 0.55). The rate constant for the thermal backreaction[5] at 25°C is $7 \cdot 10^{-5}$ sec^{-1} . The complete cycle exhibits good long term stability[6].


R = proton or electron transfer active units
R = electron transfer active units
R' = NO2, CN
x = 1,2
(R')x
M+
R = crown ether, membrane modelling
R = proton transfer active units
R' = NH2, OH, COOH
R'
NC
CN
R
hν
ΔT
R
1
2
R = polyazulenes, conducting polymers
n
R = fluorescent dyes
R = NLO – active stilbenes
CH
CH
NMe2
R = functionalized azo dyes
N=N
NMe2
Co
II
N
O
R = redox and group transfer catalysts

SCHEME 2



1 s - cis 2 s - trans 2

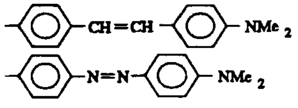
Ar = a : Ph

b : 4' - MeO C_6H_4 e : 4' - $NH_2C_6H_4$

c : 4' - $H_3\overset{+}{N}$ C_6H_4 f : 3' - $NH_2C_6H_4$

d : 3' - $H_3\overset{+}{N}$ C_6H_4 g : 2',4' - $(NO_2)_2C_6H_3$

h : i :



FORMULA 1

The photochromic property depends strongly on structure and medium. On comparison, systems as for example 1b/2b which are photochromic in solution are completely inert in the crystalline state. Obviously, crystal packing prevents the photochemical ring opening process. This completely changes if 1b is embedded in polymethylmethacrylate (PMMA) by radical polymerization (α,α' - azoisobutyronitrile as initiator) of a solution of 1b in methylmethacrylate (24 h, 60°C; afterwards 24 h at 100°C). Irradiation of a casted block of the polymer leads to the rearrangement of 1b into 2b (figure 1) which in 1 h by heating at 80°C is completely reverted to 1b. These results indicate that in the polymeric material the cavities are large enough to allow rotation of the bulky groups during the transformation 1 ⇄ 2.

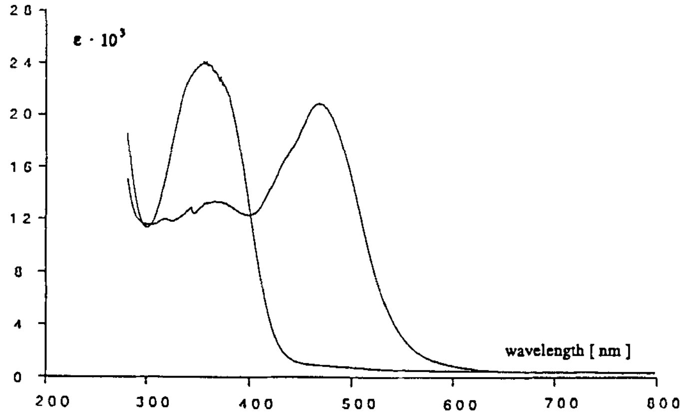


FIGURE 1: UV/VIS-Spectra of 1b and 2b in PMMA-matrix (c = 10^{-4} M, T = 25°C)

PHOTOCHROMISM IN AQUEOUS SOLUTION - MOLECULAR SWITCHING OF PROTON TRANSFER PROCESSES

The ring-opening reaction leading to photocolouration during rearrangement of DHA **1** into VHF **2** leads to severe changes in the electronic structure of the π-system. The alternant conjugated π-system in **1** is converted into a nonalternant topology in **2** which furthermore has strong acceptor character due to the dicyanovinyl subunit. This specially influences functional groups at C-9 as for example in **1c-d**/**2c-d**. In particular **1c** should experience a dramatic change of N-H acidity on rearrangement to **2c** and therefore allowing light-induced switching of the thermodynamic acidity (pK_a) of the anilinium subgroup. This may be of interest in proton transfer processes and in proton catalysis. The following results confine themselves on the photochromism of **1c-d** and the corresponding neutral species **1e-f**.

All the compounds exhibit photochromic behaviour in acetonitrile (neutral forms) and in aqueous protic solution (protonated forms) (Table 1, Figure 2). However the protonated species showed irreversible side reactions after extended irradiation. Compared to the unprotonated forms the VHF's of the anilinium salts have strong bathochromic shifts of the long-wavelength absorptions. Table 1 summarizes the absorption spectra of **1c-d** and **2c-d** in acetonitrile and in acidic aqueous solution.

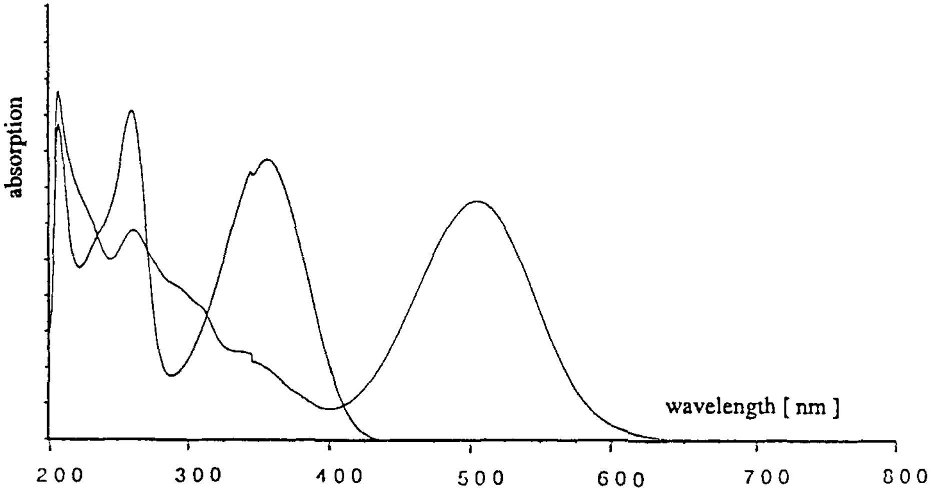


FIGURE 2: Photochromism of **1d** ⇄ **2d** in aqueous solution (2 N HCl)

	1 λ_{max} [nm]	**2** λ_{max} [nm]
c	350	501
d	355	505
e	388	456
f	359	470

TABLE 1: Long-wavelength absorptions of amino substituted compounds **1c-f** and **2c-f**

MOLECULAR SWITCHING OF ELECTRON TRANSFER PROCESSES

DHA/VHF photochromism allows photomodulation of an electric current if compounds with appropriate subunits R are subjected to pulse irradiation (photomodulation amperometry)[3]. Electron transfer active functional groups **R** are essential as probes. Again the severe change of the electronic structure by rearranging **1** into **2** shifts the redox potential. This is demonstrated by **1g** which is sensitive to electrochemical reduction due to the nitroaryl substituent. In a photoelectrochemical cell (transparent electrodes, indium oxide/tin oxide) a solution of compound **1g** in acetonitrile was irradiated with a pulsed light-beam under constant voltage conditions set at a slightly less negative potential than that necessary for the reduction of **1g** however sufficient to reduce **2g**. The experimental set-up is described in ref. 7. The resulting current/time response-signal pattern is given in figure 3.

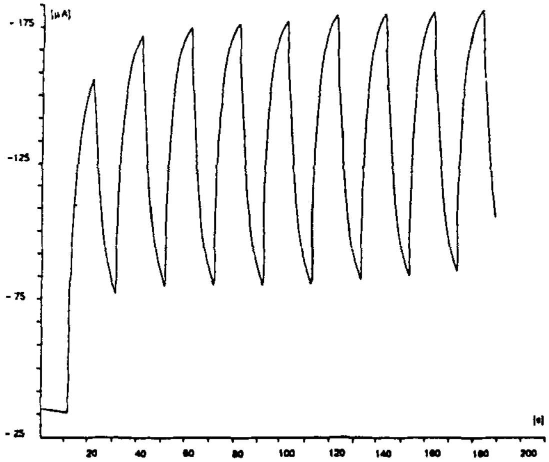


FIGURE 3: Photomodulation of an electric current by **1g**/**2g** rearrangement

PHOTOCHROMIC PROPERTIES OF MOLECULAR SWITCHES TO ACTIVATE SECOND-ORDER NONLINEARITIES

Macroscopic nonlinearity depends on the magnitude of the molecular hyperpolarizability (β) and on the orientation of the chromophores[8]. We expect that the system **1**/**2** if organized in macroscopic assemblies might provide a good model system for activating NLO properties by light induced molecular switching. This again is delineated from structural considerations: By irradiation, the weakly polarized dihydroazulene **1** rearranges into **2** which - as proven by solvatochromism[6] - comprises a highly polarized π-system with a cycloheptatrienylidene electron donor and a dicyanovinyl electron-acceptor. Compounds of structure **2** were classified as heptafulvenes with normal ring polarization[9]. By appropriate additional groups R the polarisation in **2** may be even more enhanced. Therefore, we started to investigate compounds **1h-i**/**2h-i**, containing azobenzene and stilbene subunits covalently attached.

Experimental details on the synthesis of **1h-i** will be reported elsewhere. The stilbene moiety in **1h** has (E)-configuration as demonstrated by ^{1}H-NMR-spectroscopy. Irradiation (λ_{irr} = 366 nm) of **1h** (in acetonitrile at room temperature) leads to a new absorption at 476 nm which is assigned to the heptafulvene chromophore (figure 4).

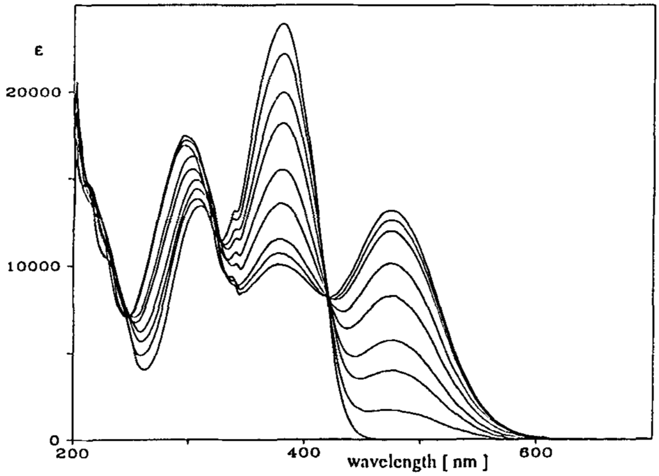


FIGURE 4: UV/VIS-spectra of **1h** and **2h** in acetonitrile

The rate of the thermal back reaction was measured in the range from 14°C to 40°C leading to an enthalpy of activation of 97 kJ mol^{-1} (± 9 kJ mol^{-1}). The half-life of **2h** at 25°C is 3.3 h. Isosbestic points clearly prove the reversibility of the photochromic cycle. Compounds **1h** and **2h** represent an interesting combination of two intrinsic photochromic subunits: The dihydroazulene/vinylheptafulvene subunit and the stilbene chromophore. Under the irradiation conditions described before (E)/(Z)-isomerization could not be observed. This follows from the absorption spectra and from the finding that thermal back reaction gives exclusively dihydroazulene with (E)-**1h** configuration.

On irradiation the azobenzene derivative **1i** behaves completely different. No spectral changes are observed in the UV/VIS-spectrum neither by irradiation at different wavelengths nor at lower temperature to prevent fast thermal back reaction **2**→**1**. Obviously the azobenzene chromophore which contributes mainly to the long wavelength absorption at λ_{max} = 467 nm totally quenches the energy presumably by fast rotation about the N-N double bond preventing energy transfer to the dihydroazulene subunit.

Investigations to elucidate the photophysics of the compounds **1h-i**/**2h-i** as well as investigations to apply these compounds in switching devices are in progress.

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