# A Mercurated Azobenzene Complex for Photoswitching between *trans* and *cis* Forms

Francesco Barigelletti,* Mauro Ghedini,† Daniela Pucci,† and Massimo La Deda†
*Istituto FRAE-CNR, V. P. Gobetti 101, I-40129 Bologna, Italy*
†*Dipartimento di Chimica, Università della Calabria, I-87030 Arcavacata (CS), Italy*

(Received December 21, 1998; CL-980947)

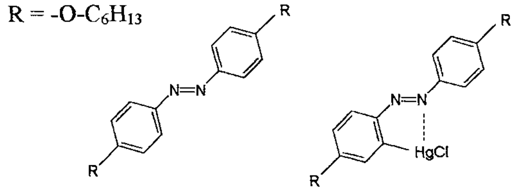
A pro-mesogenic compound based on an ortho-mercurated derivative of the azobenzene chromophore undergoes reversible *trans-cis* photoisomerization. By exploiting the spectral features of the orthometalated *cis* and *trans* isomers it is possible to produce photostationary states containing 78 and 90% of *trans* (rod-like, bright yellow) and *cis* (bent, colourless) isomers, respectively, which may be the basis for an efficient all-optical control of ON/OFF liquid crystalline behaviour.

The *trans-cis* photoisomerization in azobenzene derivatives is an extensively investigated reaction that has attracted a huge interest.[1] Concerning possible applications in the field of photoswitchable devices[2-7] it is noteworthy that liquid crystalline (LC) materials based on azobenzene derivatives can undergo an isothermal phase transition because of *trans-cis* photoisomerization.[5-7] This is a consequence of the change of the molecular shape from linear (*trans* –N=N–, ON) to bent (*cis* –N=N–, OFF) geometries, resulting in the disruption of the LC order, which is based on rod-like molecular arrangements.

A relevant drawback against the use of azobenzenes as photoswitchable materials is related to the fact the absorption spectra exhibited by the *trans* and *cis* isomers of almost all azobenzene derivatives overlap significantly.[1] As a consequence, *trans-cis* isomerization as driven by light usually leads to photostationary states (PSS) which are far from containing a predominant isomer, thus compromising the $\mathrm{ON}_{trans}/\mathrm{OFF}_{cis}$ functionality. Furthermore, given that selection of suitable excitation wavelengths proves difficult, complete recovery of the thermodynamically stable *trans* form (and of the liquid crystalline properties), is frequently achieved by protecting the material from light exposure.[5-7] This brings about the additional complication that dark-recovery occurs over time scales ranging from μs to minutes, while recovery by light pulses of suitable duration might allow to better control the timing of the process.

Within our strategy to find out ways for developing useful photoresponsive properties of azobenzene-containing compounds[8,9] we have prepared the ortho-mercurated derivative, (Azo-6)HgCl, **1**, Scheme 1.

The complex, whose cyclometallated fragment involves a weak Hg-N bond[10-12] was obtained by reacting mercury acetate with the mesogenic 4,4'-bis-(hexyloxy)azobenzene, H(Azo-6), **L**, and LiCl.[13] Elemental analysis and $^1$H NMR spectroscopy, performed with a Bruker WH-30 spectrometer, accounted for the (Azo-6)HgCl stoichiometry. Irradiation experiments were performed at selected wavelengths by using the 150 W Xenon lamp of a Spex Fluorolog II spectrofluorimeter and absorption spectra were determined with a Perkin-Elmer Lambda 5 spectrophotometer. The extinction coefficients for the *trans* form, $\varepsilon^t$, were determined from dark-incubated solutions, and those for the *cis* form, $\varepsilon^c$, were determined from solutions exposed to prolonged irradiation with $\lambda$ = 390 nm. Photoisomerization quantum yields, $\phi_c$ and $\phi_t$, for the *trans*-to-*cis* and *cis*-to-*trans* processes, respectively, were determined by using Aberchrome actinometry. Spectral changes occurring upon irradiation of dimethylformamide (DMF) solutions of **L** and **1** are illustrated in Figure 1.



L 1

**Scheme 1.**

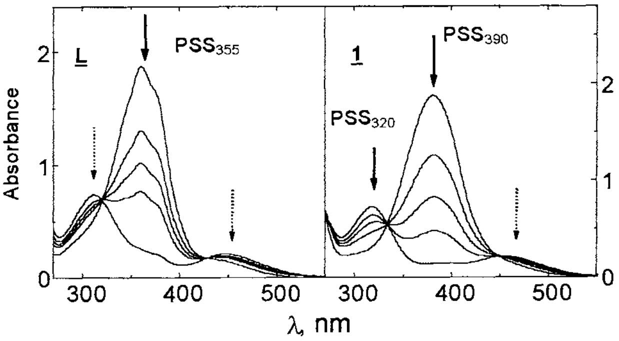


**Figure 1.** Reversible spectral changes observed upon irradiation of DMF solutions of **L** and **1**. The solid arrows indicate excitation wavelengths for production of PSS containing one predominant isomer.

The case of **L** conforms to the situation encountered for most azobenzes,[1] where the *trans*-to-*cis* conversion can be effectively driven but for the reverse path a suitable excitation wavelength is not easily available. Thus, for **L** $\phi_c$ was determined to be 0.29 by using $\lambda_{exc}$ = 355 nm, but $\phi_t$ was not measured, owing to large experimental uncertainties for the cases of excitation around the 310 and 450 nm regions, Figure 1. By contrast, for **1** a) at 390 nm the *trans* form[1] exhibits a strong absorption intensity, $\varepsilon_{390}{}^t$ = 27000 M$^{-1}$ cm$^{-1}$ in correspondence of a low absorption plateau for the *cis* form, $\varepsilon_{390}{}^c \leq$ 3000 M$^{-1}$ cm$^{-1}$ and b) the *cis* form[1] exhibits a moderately intense absorption at 320 nm, $\varepsilon_{320}{}^c$ = 11660 M$^{-1}$ cm$^{-1}$, against a low absorption intensity for the *trans* form, $\varepsilon_{320}{}^t$ = 3200 M$^{-1}$ cm$^{-1}$, see Figure 1.

Based on these spectral properties, and according to $[cis]/[trans] = (\phi_c\, \varepsilon^t)/(\phi_t\, \varepsilon^c)$, the photostationary state obtained by irradiation of **1** at 390 nm (PSS$_{390}$, the measured $\phi_c$ was 0.31) is evaluated to contain more than 90% of *cis* isomer. On the other hand, $PSS_{320}$ ($\phi_t$ = 0.32) contains 78% of the *trans* form. For **1**, $PSS_{390}$ is nearly colourless and $PSS_{320}$ is bright yellow. On this basis an all-optical control of the molecular shape proves feasible which makes **1** an interesting model for azobenzene-based $ON_{trans}/OFF_{cis}$ liquid crystalline materials.[5-7] To notice that dark recovery of the *trans* form in a $2\times10^{-5}$ M DMF solution irradiated at 390 nm for 40 min occurs with $t_{1/2}$ = 176 min, which indicates a satisfactory temporal stability of the unirradiated *cis* form.

The peculiar behaviour of **1** with respect to most members of the azobenzene family[1] is likely related to the steric and electronic properties of the HgCl group which affect the role of the excited states involved in the photoconversion. For azobenzene, the two lowest-lying excited states that can be directly populated from the ground state are $S_1$ (of $n\pi^*$ nature) and $S_2$ (of $\pi\pi^*$ nature, with bands for the *trans* and *cis* forms peaking around 355 and 310 nm, respectively).[1] The $S_1$ level is usually associated with the inversion mechanism, described as an in-plane "lateral shift" of one of the two rings,[1,14] and the $S_2$ excited level is generally thought to be involved in the out-of-plane rotation mechanisms, which implies breaking of the -N=N- double bond and occurs in unhindered systems. Remarkably, for the case of **1** steric hindrance by the HgCl group does not allow rotation around the –N=N– double bond and it is known that in hindered or constrained systems inversion may be the only active path.[15] In conclusion, for **1** the *trans-cis* interconversion might take place according to the inversion mechanism, as depicted in Figure 2.

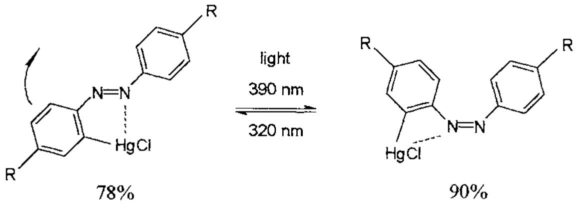


**Figure 2.** Phototoisomerization of the ortho-metalated azomercury complex in terms of in-plane inversion mechanism.

It should be further noticed that the HgCl group is known to form both five and four-member rings through weak interactions with the N positions,[10-12] Figure 2. Thus, besides steric factors, also electronic factors might contribute to facilitate the "in-plane-locking" of the two rings.

Acknowledgements are due to Dr. Sandra Monti for discussions on the interplay of the excited states of azobenzene.

## References and Notes

1 H. Rau, in "Photochromism",ed. by H. Dürr and H. Bouas-Laurent, Elsevier, Amsterdam (1990), p. 165.
2 H.-B. Mekelburger, K. Rissanen, and F. Vögtle, *Chem. Ber.*, **126**, 1161 (1993).
3 D. M. Junge and D. V. Mc Grath, *Chem. Commun.*, **1997**, 857.
4 G. Sudesh Kumar and D. C. Neckers, *Chem. Rev.*, **89**, 1915 (1989).
5 T. Ikeda and O. Tsutsumi, *Science*, **268**, 1873 (1995).
6 H.-K. Lee, A. Kanazawa, T. Shiono, T. Ikeda, T. Fujisawa, M. Aizawa and B. Lee, *Chem. Mater.*, **10**, 1402 (1998).
7 J. L. Serrano, "Metallomesogens", VCH, Weinheim (1996).
8 M. Ghedini, D. Pucci, F. Neve, *Chem. Commun.*, **1996**, 137.
9 M. Ghedini, D. Pucci, G. Calogero and F. Barigelletti, *Chem. Phys. Letters*, **267**, 341 (1997).
10 G. M. Gruter, G. P. M. van Klink, O. S. Akkerman, and F. Bickelhaupt, *Chem. Rev.*, **95**, 2405 (1995).
11 L. G. Kuz'mina and Y. T. Struchkhov, *Croat. Chem. Acta*, **57**, 701 (1984).
12 K. Ding, Y. Wu, H. Hu, L. Shen, and X. Wang, *Organometallics*, **11**, 3849 (1992).
13 a) P. V. Roling, D. D. Kirt, J. L. Aill, S. Hall, C. Hollstrom and R. A. Pickering, *J. Organomet. Chem.*, **122**, 289 (1976). b) A. Omenat and M. Ghedini, *J. Chem. Soc., Chem. Commun.*, **1994**, 1309.
14 S. Monti, G. Orlandi, and P. Palmieri, *Chem. Phys.*, **71**, 87 (1982).
15 P. Bortolus and S. Monti, *J. Phys. Chem.*, **91**, 5046 (1987).