Russian Journal of General Chemistry, Vol. 75, No. 4, 2005, pp. 632–635. Translated from Zhurnal Obshchei Khimii, Vol. 75, No. 4, 2005, pp. 670–673.

Structure–Property Relationship in Bispyrrolizidine Photochromic Compounds Derived from Indolo[4,5-*e*]- and -[7,6-*g*]indoles

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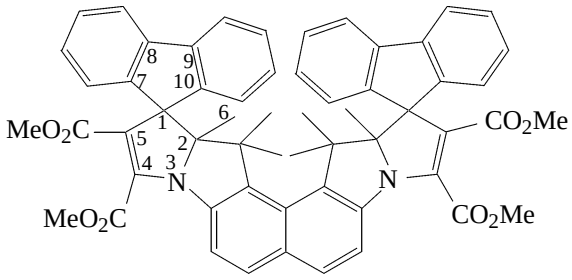
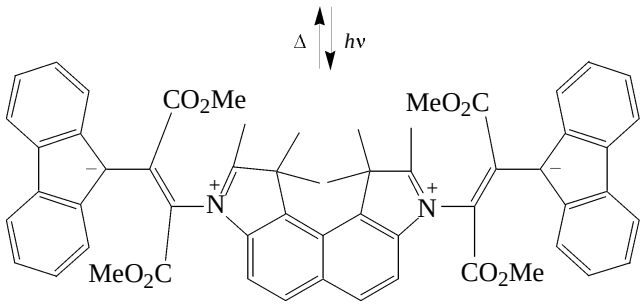
Received October 15, 2003

Abstract—The spirocyclic compounds bis[2',3'-bis(methoxycarbonyl)-5',6',6'-trimethylspirofluoren-9,4'-(1'-aza-2'-cyclopentene)][1',5'-*a*]indolino[4,5-*e*]indoline and bis[2',3'-bis(methoxycarbonyl)-5',6',6'-trimethylspirofluoren-9,4'-(1'-aza-2'-cyclopentene)][1',5'-*a*]indolino[7,6-*g*]indoline exhibit photochromic properties with various half-lifes. The AM1 method was used to correlate the structural and electronic properties, on the one hand, and photochromic properties, on the other, and to explain reasons for the difference in the photochromism of the two compounds.

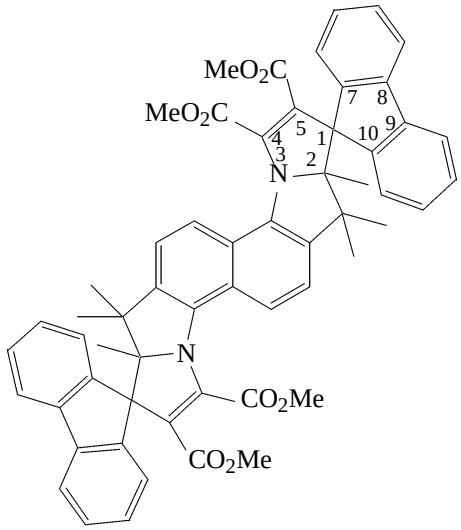
The subject of the present study were our synthesized spirocyclic compounds bis[2',3'-bis(methoxycarbonyl)-5',6',6'-trimethylspirofluoren-9,4'-(1'-aza-2'-cyclopentene)][1',5'-*a*]indolino[4,5-*e*]indoline (**I**) and bis[2',3'-bis(methoxycarbonyl)-5',6',6'-trimethylspirofluoren-9,4'(1'-aza-2'-cyclopentene)][1',5'-*a*]indolino-[7,6-*g*]indoline (**II**), that exhibit protochromic properties [1, 2].On exposure to light compound **I** passes into a colored unstable betaine form **III**. Its electronic spectra acquire absorption bands at λmax 325 and 550 nm (Fig. 1); the half-life $\tau_{0.5}$ is 1.402 s [1] (Fig. 2). Because of the fast conversion of compound **II**, absorption maxima of the corresponding betaine could not be detected [2]. We could detect the betaine formation and measure its $\tau_{0.5}$ of 0.043 s by measuring a narrower spectral region (shorter time measurements) (Fig. 3). We suggest that compound **II** is a fast converting photochromic system.



I



III



II

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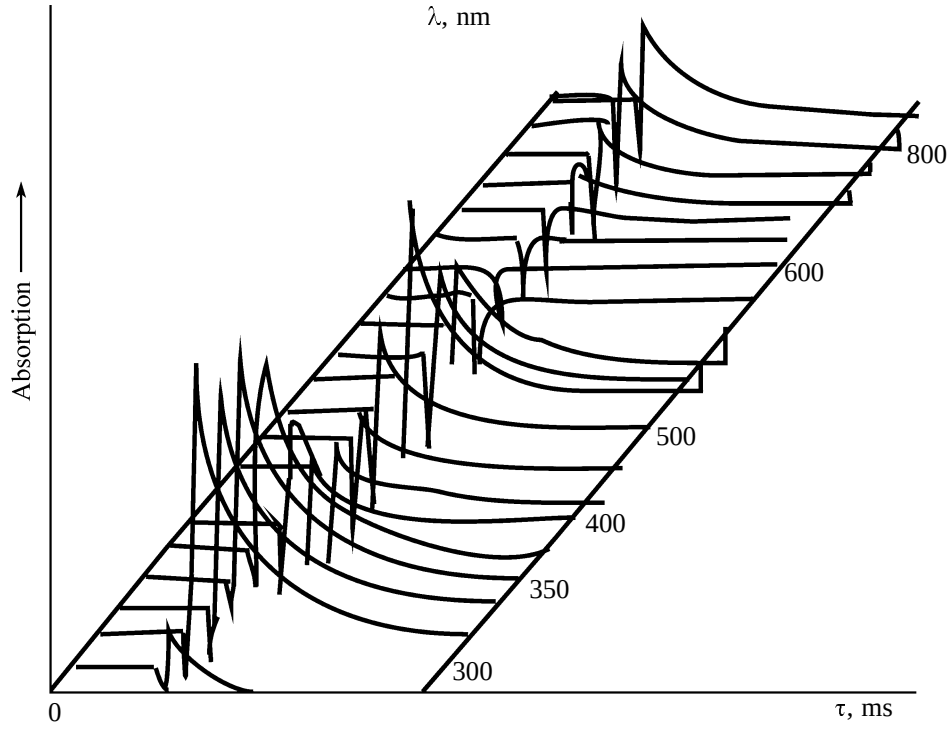

Fig. 1. Decay curves for betaine form **III** of compound **I** at various wavelengths (300–750 nm, step 25 nm) in CH_2Cl_2 at 20°C.

To correlate the photochromic properties of compounds **I** and **II** with their electronic and geometric structures, we performed a quantum-chemical study. The AM1 procedure [3] with full geometry optimization was used to calculate the energy characteristics, atomic charges, bond orders, and geometries of structures **I** and **II**. The transfer to the colored betaine form involves fission of the C^1–C^2 bond and doubling of the C^2–N^3 bond [1], the nitrogen atom acquires excess positive charge, and the spiro atom, negative.

The energy diagram (Fig. 4) depicts the enthalpies of molecules **I** and **II** and enthalpy changes ($\Delta\Delta H$) along the $S_0 > S_{FC}$ coordinate; $\Delta H(S_0)$ is the enthalpy of the ground state of the photochromic structures, and $\Delta H(S_{FC})$ is the enthalpy of the Franck–Condon excited state. As seen from the diagram, the enthalpies $\Delta\Delta H$ of the transition into the Franck–Condon excited state on absorption for compounds **I** and **II** are almost equal to each other. It would make no sense to calculate the betaine form as an isolated system, since

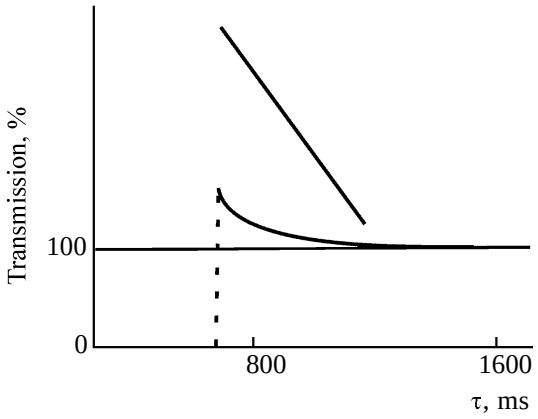

Fig. 2. Decay curve for half-life determination for betaine form **III** of compound **I** at 25°C.

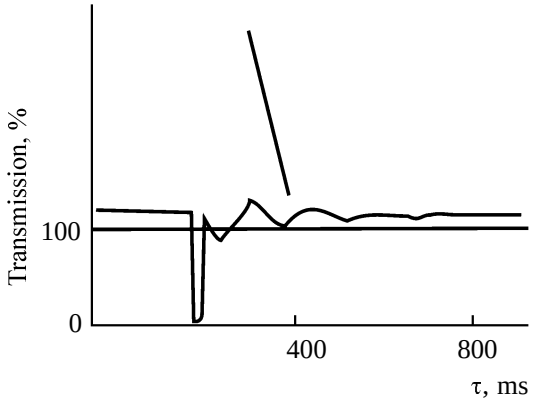

Fig. 3. Decay curve for half-life determination for the betaine form of compound **II** at 25°C.

the energy gap between the colored and colorless forms is so large that an appreciable amount of the colored form in equilibrium with colorless is hardly imaginable [4].

Searching for factors favoring faster transition into the betaine form was performed via revealing the strongest differences in the electronic and geometric characteristics of compounds **I** and **II** (Tables 1 and 2).

As seen from Table 1, the C^1–C^2 and C^2–N^3 bonds are longer than normal C–C and C–N bonds; this finding may explain the facility of C^1–C^2 bond fission in molecules **I** and **II**. Bond angles in this opening ring vary only slightly. However, the φ($C^8C^7C^1C^2$) angle in **II** is ~19° larger than in **I**. It is known that at the spiro C1 atom the rings are arranged in mutually perpendicular planes, as suggested by its sp^3 hybridization. In system **II**, however, the dihedral angle in turned by 34° out of the orthogonal direction, which should facilitate change of the dihedral angle at the spiro atom and transition to the betaine form.

As seen from Table 1, the N^3–C^4 bond order in compound **II** is smaller by 0.033 than in compound **I**.

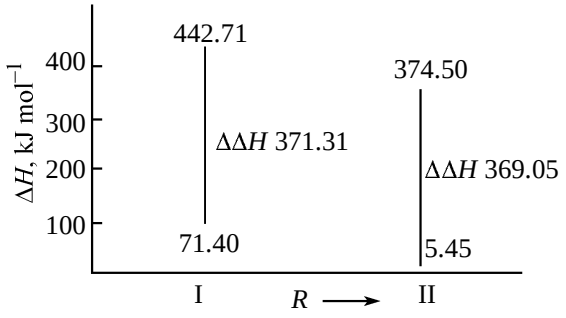

Fig. 4. Energy diagram for the transition of compounds **I** and **II** from the ground (S_0) to excited (S_{FC}) state (*R* is reaction coordinate).

Table 1. Bond lengths (*d*, A), bond (ω, deg) and dihedral (φ, deg) angles, and bond orders (*P*) in the opening five-membered ring of compounds **I** and **II**

Parameter	Compound **I**	Compound **II**
Bond	*d*	
C^1–C^2	1.596	1.593
C^2–N^3	1.523	1.593
N^3–C^4	1.423	1.435
C^4–C^5	1.369	1.364
C^5–C^1	1.516	1.525
C^2–C^6	1.529	1.525
Bond angle	ω	
$C^1C^2N^3$	103.0	104.4
$C^2N^3C^4$	106.5	104.9
$N^3C^4C^5$	112.4	113.9
$C^4C^5C^1$	110.4	110.0
$C^5C^1C^2$	101.7	100.8
Dihedral angle	φ	
$C^8C^7C^1C^2$	105.4	124.3
$C^9C^{10}C^1C^2$	–113.2	–123.5
Bond	*P*	
C^1–C^2	0.916	0.919
C^2–N^3	0.917	0.921
N^3–C^4	1.032	0.999
C^4–C^5	1.752	1.810
C^5–C^1	0.950	0.939
C^2–C^6	0.957	0.977

Transition to the betaine form occurs via fission of the C^1–C^2 bond and torsion about the N^3–C^4 bond, and decreased bond orders should favor these processes.

Let us consider the total atomic charges and π- and *n*-electron densities on C^1–C^6 and N^3 both in the ground (S_0) and Franck–Condon excited state (S_{FC}) in compounds **I** and **II** (Table 2). Considerable dif-

Table 2. Total atomic charges and π- and *n*-electron densities[a] in the opening five-membered ring of compounds **I** and **II** in the S_0 and S_{FC} states

Comp. no.	State	C^1	C^2	N^3	C^4	C^5	C^6
I	S_0	0.095	0.045	–0.135	0.030	–0.128	–0.208
		(0.899)	(0.970)	(1.302)	(0.909)	(1.018)	(0.915)
	S_{FC}	0.094	0.044	–0.117	0.027	–0.128	–0.208
		(0.899)	(0.970)	(1.287)	(0.906)	(1.018)	(0.914)
II	S_0	0.072	0.047	–0.144	–0.041	–0.135	–0.205
		(0.922)	(0.918)	(1.306)	(0.903)	(0.944)	(0.996)
	S_{FC}	0.074	0.042	–0.111	–0.049	–0.138	–0.207
		(0.920)	(0.921)	(1.277)	(0.896)	(0.945)	(0.996)

[a] Electron densities are given in parentheses.

ference relate to N^3 whose *n*-electron density decreases along the $S_0 > S_{FC}$ coordinate by 0.015 and 0.029 for compounds **I** and **II**, respectively. In compound **II**, the ground-state total and π-electron densities are higher by 0.023 compared to compound **I**. The increased electron density on C^1 in the S_0 and S_{FC} states and decrease of the electron density on N^3 on excitation ($S_0 > S_{FC}$) render the electronic structure of compound **II** close to the electronic structure of the betaine form, which probably explains the fast transition into betaine.

We suggest that the above factors, such as turn by 34° of the dihedral angle at the spiro C^1 atom out of the orthogonal direction, decreased N^3–C^4 bond order, increased electron density on C^1, and similarity of the electronic structure to the betaine form, should facilitate transition into the unstable betaine form and thus decrease the half-life of compound **II**.

REFERENCES

1. Samsoniya, Sh.A., Dyurr, G., Trapaidze, M.V., Chkhaidze, E.R., and Gogrichiani, E.O., *Khim. Geterotsikl. Soedin.*, 2001, no. 10, p. 1423.
2. Samsoniya, Sh.A., Trapaidze, M.V., Machaidze, N.N., and Dyurr, G., *Khim. Geterotsikl. Soedin.*, 2002, no. 4, p. 461.
3. Dewar, M.J.S., Zoebish, E.G., Healy, E.F., and Stewart, J.J.P., *J. Am. Chem. Soc.*, 1985, vol. 107, no. 13, p. 3902.
4. Dzhaparidze, K.G., *Spirokhromeny* (Spirochromenes), Tbilisi: Metsniereba, 1979, p. 11.