1444 Russian Chemical Bulletin, International Edition, Vol. 57, No. 7, pp. 1444—1450, July, 2008

Synthesis and spectral-kinetic investigation of fulgimide-based photochromic autocomplexes of the dinitroquinoline series

I. G. Ilyina,[a]* *V. V. Mel´nikov,*[a] *S. I. Luyksaar,*[b] *M. M. Krayushkin,*[b]
Yu. A. P´yankov,[c] *V. A. Barachevsky,*[c] *and I. V. Fedyanin*[d]

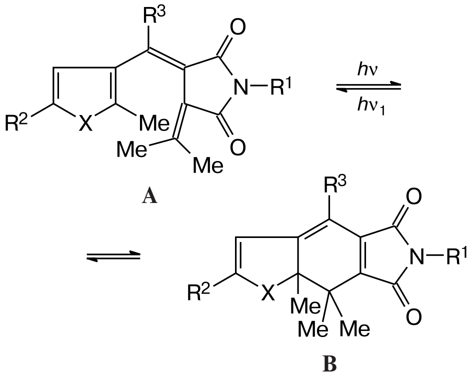
[a]*Department of Chemistry, M. V. Lomonosov Moscow State University,*
1 Leninskie Gory, 119992 Moscow, Russian Federation.
Fax: +7 (495) 939 0290. E-mail: igi@org.chem.msu.ru
[b]*N. D. Zelinsky Institute of Organic Chemistry, Russian Academy of Sciences,*
47 Leninsky prosp., 119991 Moscow, Russian Federation.
Fax: +7 (495) 137 6939. E-mail: mkray@ioc.ac.ru
[c]*Photochemistry Center, Russian Academy of Sciences,*
7a ul. Novatorov, 119421 Moscow, Russian Federation.
Fax: +7 (495) 936 1255. E-mail: barva@photonics.ru
[d]*A. N. Nesmeyanov Institute of Organoelement Compounds, Russian Academy of Sciences,*
28 ul. Vavilova, 119991 Moscow, Russian Federation.
Fax: +7 (499) 135 5085

Two new hybrid compounds, which belong to autocomplexes of the dinitroquinoline series and contain an NH spacer and fragments of photochromic fulgimides as donor components, were synthesized. These autocomplexes were used as ligands in the synthesis of cobalt-containing metal chelates. The spectral-kinetic study revealed that these compounds exhibit photochromism. The introduction of photochromic fulgimide moieties into the autocomplexes has no substantial effect on the spectral properties of the latter but influences the kinetics of photochromic transformations by decreasing their efficiency. Chelate complexes of the hybrid compounds with cobalt ions are characterized by the lowest efficiency of photochromic transformations due to a decrease in the intensity of activating radiation as a result of its absorption by the dinitroquinoline moieties, which are not conjugated with fragments of photochromic compounds.

Key words: synthesis, photochromism, autocomplexes, photochromic fulgimides, dinitroquinoline, metal chelates, cobalt, electronic spectroscopy, X-ray diffraction study.

Organic photochromic compounds have found increasing use due primarily to their interesting properties.[1] In recent years, particular attention has been given to the synthesis and investigation of the properties of thermally irreversible photochromic compounds, in particular, of fulgimides, which undergo reversible valence photoisomerization resulting in the transformation of the open form **A** into the cyclic form **B** (Scheme 1).[2—4]

Scheme 1



The colorless open form **A** is transformed into the colored cyclic form **B** under UV irradiation (*h*ν). The latter form is again transformed into the starting colorless state under visible light irradiation (*h*ν$_1$).

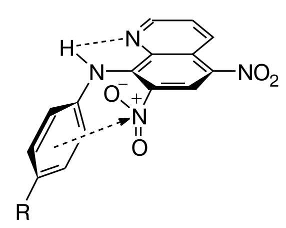
Due to thermal stability of the forms **A** and **B**, fulgimides are of particular interest for the design of different types of photoswitches, including recording media for optical memory.[3,4]

In the present study, we investigated the spectral-kinetic properties of the newly synthesized hybrid compounds, which can be assigned, according to the accepted classification,[5] to organic intramolecular charge-transfer compounds or autocomplexes. Molecules of these compounds are characterized by the simultaneous presence

Published in Russian in *Izvestiya Akademii Nauk. Seriya Khimicheskaya,* No. 7, pp. 1417—1423, July, 2008.

of electron-withdrawing and electron-releasing fragments separated by a spacer. Such structures can be considered as convenient model systems, in which the targeted change in the degree of intramolecular charge transfer is one of the possible ways of controlling the electronic properties of these compounds.

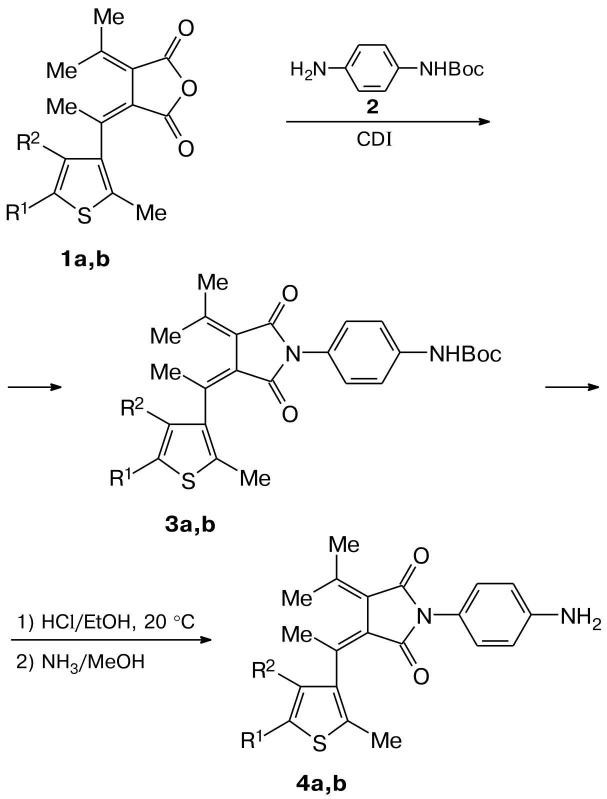
In the present study, we investigated autocomplexes of the dinitroquinoline series containing an NH spacer and fragments of photochromic fulgimides as donor components. Earlier,[6] we have reported the synthesis and investigation of the characteristic features of the donor-acceptor interactions in numerous autocomplexes of this series containing donor moieties of different nature and strength. Based on the results of the detailed spectroscopic study, it was established that the charge transfer in these compounds can occur both *via* the direct polar conjugation through the bridging nitrogen atom and through space between the closely spaced fragments of the autocomplexes.



In the present study, we used the fulgides, 3-(*Z*)-[α-(2,5-dimethyl-3-thienyl)ethylidene]-4-isopropylidenetetrahydrofuran-2,5-dione (**1a**) and its benzothiophene analog **1b**, as the starting compounds (Scheme 2). The reactions of these compounds with Boc-phenylenediamine **2** were carried out under reflux in benzene for 20 h. Then the reaction mixture was concentrated, the residue was dissolved in a mixture of dichloromethane and ethanol and filtered through silica gel, and the solvent was distilled off. The resulting mixture of amido acids was dissolved in THF, 1.1 equiv. of *N*,*N*′-carbonyldiimidazole (CDI) was added, and the reaction mixture was allowed to stand at room temperature for 24 h. The product was isolated by silica gel flash chromatography. This method was used to synthesize Boc-aminophenylfulgimides **3a,b** in 80—85% yields. In the final step of the synthesis of aminophenylfulgimides, the Boc protection was removed by the reaction with a 5 *M* ethanolic HCl solution followed by the treatment of the resulting hydrochlorides with a methanolic ammonia solution. Amines **4a,b** were obtained in 80—90% yields.

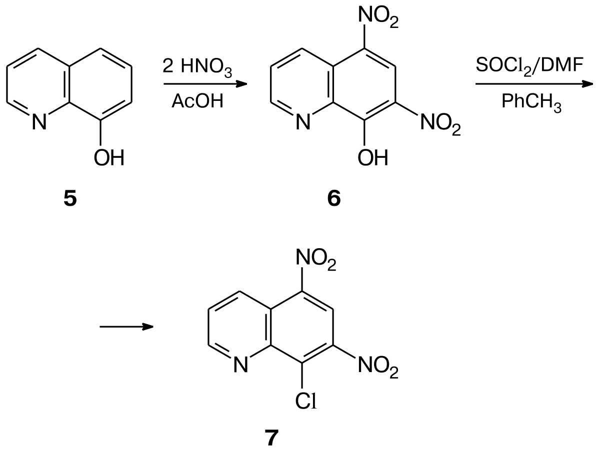
Then 8-chloro-5,7-dinitroquinoline (**7**) was synthesized starting from 8-hydroxyquinoline (**5**) by successive transformations through 8-hydroxy-5,7-dinitroquinoline (**6**) according to known procedures[7—9] (Scheme 3). The reaction of compound **7** with amines **4a,b** was carried out by refluxing equimolar amounts of the starting reagents in a mixture of acetone and ethanol. After partial evaporation of the reaction mixture, the colored precipitates of autocomplexes **8a,b** were filtered off and crystallized from an appropriate solvent.

Scheme 2

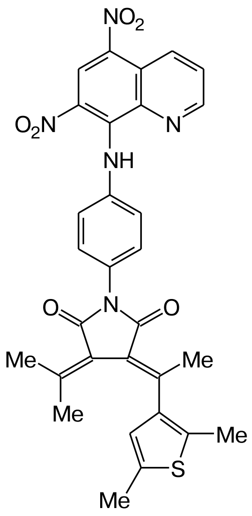


1, **3**, **4**: R^1 = Me, R^2 = H (**a**); R^1R^2 = —(CH=CH)$_2$— (**b**)
Boc = Bu^{t}OCO

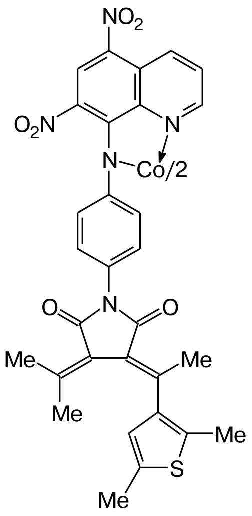
Scheme 3



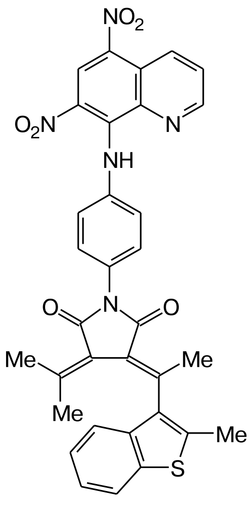
We also used autocomplex **9** as a model compound (its synthesis and spectral properties have been described in our earlier study[6]) and chelate Co^{II} complexes (**8a**·Co, **8b**·Co, and **9**·Co), which were synthesized by the reactions of autocomplexes **8a,b** and **9** as ligands with cobalt acetate in an appropriate organic solvent.



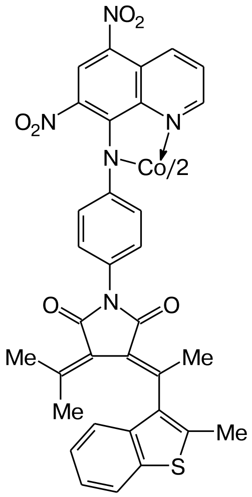
8a



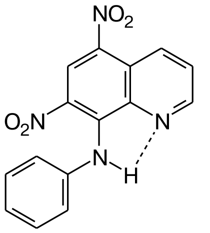
8a · Co



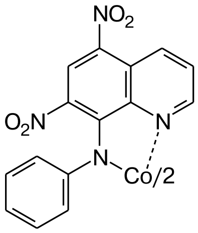
8b



8b · Co



9



9 · Co

Results and Discussion

Compound **4a** is characterized by the most intense absorption band with a maximum at 250 nm and two longer-wavelength bands at 280 (sh) and 340 nm (sh) in the UV-spectral region for the open form **A** and an absorption band with a maximum at 520 nm in the visible spectral region for the cyclic form **B** (Fig. 1). The replacement of the thiophene fragment (compound **4a**) with the benzothiophene fragment (compound **4b**) leads to a slight hypsochromic shift of the absorption band of the cyclic form (Table 1).

The absorption spectra of the open form of autocomplexes **8a,b**, which were synthesized based on compounds **4a,b**, respectively, show a new absorption band in the visible region at 425 nm (Fig. 2, curve *1*), which coincides with the absorption band of model autocomplex **9** (see Table 1). In the UV-spectral region, the absorption bands of this autocomplex and compounds **8a,b** are virtually identical (see Table 1). The UV irradiation of com-

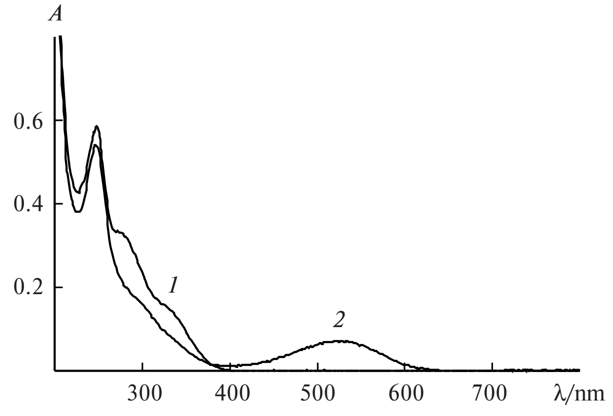


Fig. 1. Spectra of the starting (*1*) and colored (*2*) forms of amine **4a** in MeCN ($1 \cdot 10^{-4}$ mol L^{-1}). The cell path length was 2 mm.

Table 1. Spectral-kinetic characteristics of the compounds

Compound	Solvent	λ_A^{max}	λ_B^{max}	k_{AB}	k_{BA}	k_{pd}
		nm		s^{-1}		
4a	MeCN	250, 280 sh, 340 sh	522	0.010	0.0020	0.0060
4b	MeCN	220, 290 sh, 335 sh	480	0.001	0.0002	0.0003
8a	MeCN	<300, 340 sh, 425	~460—600	0.006	0.0300	0.0020
8a•Co	MeCN	<300, 350, 490	~490—540	0.030	0.0200	0.0020
8b	MeCN	220, 260, 340 sh, 420	~450—550	0.010	0.0200	0.0004
8b•Co	MeCN	330, 420, 480	~490—540	0.040	0.0200	0.0004
9	Toluene	300 sh, 380 sh, 420	—	—	—	—
9•Co	Toluene	370, 440, 500	—	—	—	—

Note. λ_A^{max} and λ_B^{max} are the absorption maxima of the starting (**A**) and photoinduced (**B**) forms; k_{AB}, k_{BA}, and k_{pd} are the rate constants of photocoloration, photobleaching, and photodegradation, respectively.

pounds **8a,b** in solution through an UFS-2 light filter causes a weak absorption in the 460—600 nm region (see Fig. 2, curve *2*, Table 1).

The corresponding chelates **8a**•Co and **8b**•Co are also characterized by insignificant photoinduced spectral changes in the visible spectral region (Fig. 3). As can be seen from a comparison of the absorption spectra presented in Fig. 3, the absorption spectrum of the starting form of the chelates is determined primarily by the absorption identical to the absorption spectrum of compound **9**•Co (see Fig. 3, curve *3*).

It was found that the slight photoinduced change in the absorbance in the visible spectral region of solutions of both hybrid compounds **8a,b** and their chelate complexes **8a**•Co and **8b**•Co is reversible. This follows from the results of investigation of the coloration kinetics of solutions under UV irradiation and the bleaching kinetics under visible light irradiation, as evidenced by the measured rate constants of these phototransformations (see Table 1). Solutions of the chelate complexes are characterized by the highest photocoloration rates (see Table 1). The rate of photoinduced bleaching of compounds **8a,b** and their chelate complexes **8a**•Co and **8b**•Co in solution under visible light irradiation in the region of photoinduced absorption of these compounds (through a ZhS-12 light filter) is substantially higher (the rate constants differ by one—two orders of magnitude) than that of photochromic fulgimides **4a,b** (see Table 1).

The study of photodegradation of the reaction products showed that the stability of photochromic benzothiophene-containing compounds **4b** and **8b** to photodegradation is an order of magnitude higher than that of the corresponding thiophene-substituted compounds **4a** and **8a** (see Table 1). The efficiency of photodegradation of chelate complexes **8a**•Co and **8b**•Co is virtually identical to that of compounds **8a,b** (see Table 1), which indicates that metal has no effect on the mechanism of phototransformations of these compounds.

An analysis of the spectral-kinetic data suggested the absence of conjugation between two fragments of the hybrid photochromic compounds due to the presence of the phenyl spacer between the photochromic electron-releasing fragment and the electron-withdrawing dinitroquinoline moiety. In this case, the low efficiency of photochromic transformations of the hybrid compounds and their chelates can be attributed to intense absorption of

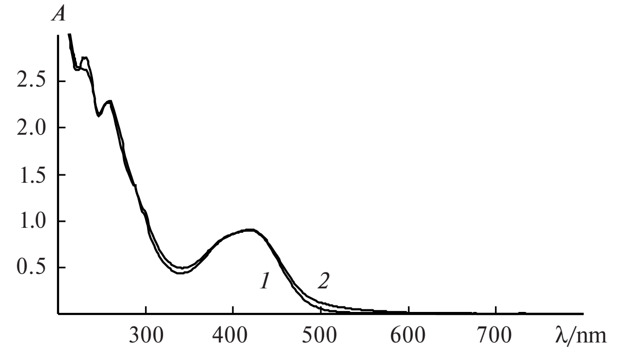


Fig. 2. Absorption spectra of the starting (*1*) and colored (*2*) forms of a solution of autocomplex **8a** in MeCN ($1 \cdot 10^{-4}$ mol L^{-1}). The cell path length was 10 mm.

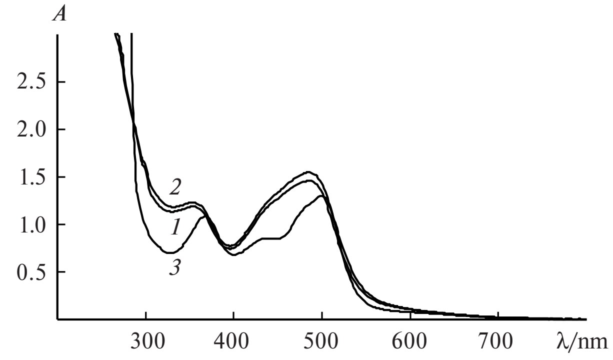


Fig. 3. Absorption spectra of the starting (*1*) and colored (*2*) forms of a solution of complex **8a**•Co and a solution of complex **9**•Co (*3*) in MeCN ($1 \cdot 10^{-4}$ mol L^{-1}). The cell path length was 10 mm.

activating radiation by the dinitroquinoline fragments showing absorption in the same UV-spectral region as the fulgimide fragments, which are not conjugated with the dinitroquinoline fragments. The intermolecular excitation energy transfer between the unconjugated but closely spaced fragments cannot be ruled out.

To confirm the three-dimensional structure and its influence on the photochromic properties, we studied compound **8a** by X-ray diffraction. The principal geometric parameters of the dinitroquinoline, *N*-phenyl-substituted maleinimide, and dimethylthiophene fragments are similar to those expected for related compounds (Fig. 4, Table 2). The conjugation between the maleinimide and phenyl substituents is absent because the rings are twisted with respect to one another by 53.4°, like in most of analogous compounds (information from the Cambridge Structural Database[10]). The conjugation between the phenyl and quinoline fragments through the N(4) atoms is also weak, if presents at all. The rings are twisted with respect to one another by 43.9°.

The observed conformation of the molecule is stabilized mainly by the following intramolecular interactions: the moderate-strength hydrogen bond N(4)—H(4N)...N(1) (N...N, 2.576(4) Å) and the shortened O(4)...C(10) and O(5)...C(23) intramolecular contacts (2.738 and 2.945 Å, respectively). There is also the shortened C(21)...C(29) distance (smaller than the sum of the van der Waals radii of the carbon atoms; 3.42 Å) between the methyl substituents of the thiophene fragment. The disordered ethanol solvent molecule is not involved in hydrogen bonding. Weak O...π and C—H...O interactions are the major intermolecular contacts.

Table 2. Selected bond lengths (*d*) and bond angles (ω) in compound **8a**

Bond	*d*/Å	Bond	*d*/Å
N(1)—C(1)	1.321(4)	N(5)—C(19)	1.400(4)
N(1)—C(9)	1.337(4)	C(16)—O(5)	1.195(4)
C(9)—C(8)	1.457(4)	C(19)—O(6)	1.207(4)
C(8)—N(4)	1.350(4)	C(17)—C(20)	1.357(4)
N(4)—C(10)	1.439(4)	C(20)—C(23)	1.483(5)
C(10)—C(11)	1.367(4)	C(22)—C(23)	1.364(5)
C(11)—C(12)	1.396(4)	C(22)—S(1)	1.715(3)
C(12)—C(13)	1.375(4)	S(1)—C(25)	1.723(4)
C(13)—N(5)	1.441(4)	C(18)—C(28)	1.339(4)
N(5)—C(16)	1.408(4)		
Angle	ω/deg	Angle	ω/deg
C(7)—C(8)—N(4)	128.4(3)	N(5)—C(19)—C(18)	106.1(3)
C(8)—N(4)—C(10)	131.0(3)	C(16)—C(17)—C(20)	122.6(3)
N(4)—C(10)—C(11)	122.5(3)	C(17)—C(20)—C(23)	122.1(3)
C(12)—C(13)—N(5)	120.3(3)	C(23)—C(22)—S(1)	111.3(3)
C(13)—N(5)—C(16)	122.7(3)	C(22)—S(1)—C(25)	92.1(2)
C(19)—N(5)—C(16)	113.3(2)	C(19)—C(18)—C(28)	122.8(3)
N(5)—C(16)—C(17)	105.5(3)		

To conclude, we synthesized four new hybrid compounds, including chelate complexes containing the dinitroquinoline and photochromic fulgimide fragments.

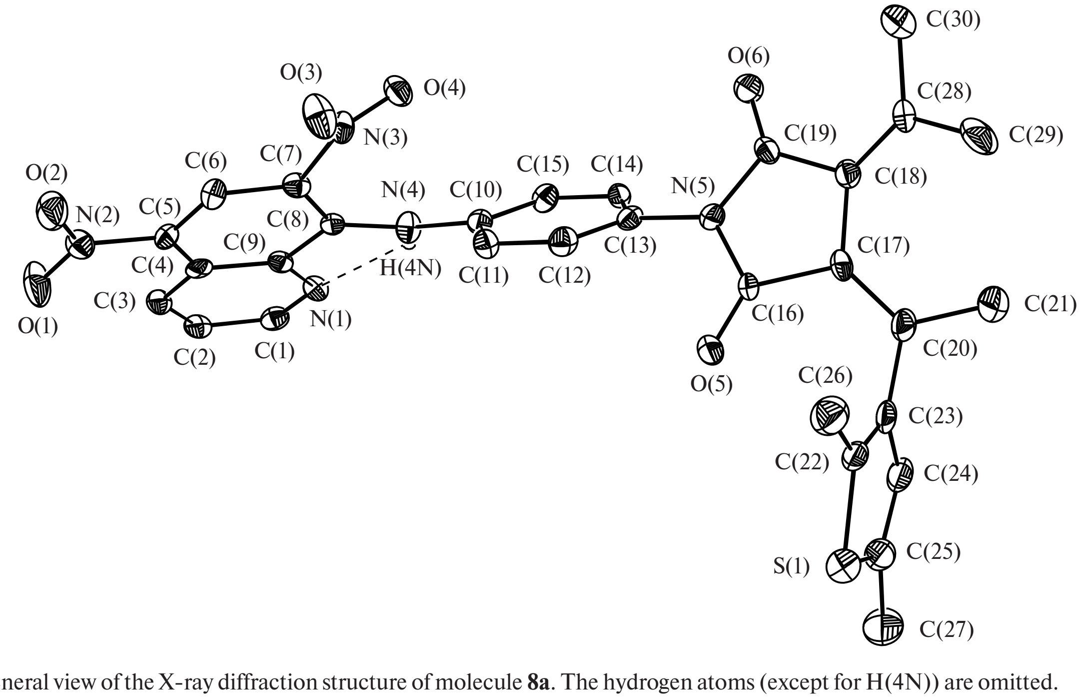


Fig. 4. General view of the X-ray diffraction structure of molecule **8a**. The hydrogen atoms (except for H(4N)) are omitted.

The X-ray diffraction study revealed that there is no conjugation between the fragments separated by the phenyl spacers. The spectral-kinetic data show that solutions of these compounds in acetonitrile are characterized by a substantially lower efficiency of photochromic transformations compared to the starting fulgimides. This fact can be responsible for a decrease in the intensity of radiation activating photochromic transformations due to radiation absorption by the dinitroquinoline fragments. The influence of the structures of the photochromic compounds under consideration on their spectral-kinetic properties was established.

Experimental

The absorption spectra were measured on a Cary 50 spectrophotometer (Varian) in 1.0-cm cells at room temperature. Toluene and acetonitrile (Aldrich) were used as the solvents. The concentrations of the solutions used for measuring the absorption spectra were $1 \cdot 10^{-4}$ mol L^{-1}. The solutions were irradiated with filtered radiation from a DRSh-250 mercury gas-discharge lamp. The light filters for isolation of mercury lines were chosen based on the positions of the absorption bands of the compounds under study.

The IR spectra were measured on an IR 200 Fourier-transform spectrophotometer (ThermoNikolet, USA) in KBr pellets at 2 cm^{-1} resolution; the number of scans was 64.

The ^1H NMR spectra were recorded on a Bruker WM-250 radiospectrometer (250 MHz) in $CDCl_3$. The EI mass spectra were obtained on a Kratos MS-30 instrument using a direct inlet system; the ionizing voltage was 70 eV; the emission current was 0.1 mA; the ionization chamber temperature was 250 °C. The melting points were measured on a Boetius hot-stage apparatus and are uncorrected.

The reaction mixtures were analyzed and the purity of the reaction products was checked by TLC on Silufol UV-254 plates.

3-(*Z*)-[1-(2,5-Dimethyl-3-thienyl)ethylidene]-4-isopropylidenetetrahydrofuran-2,5-dione (1a) was synthesized according to a known procedure.[11] The yield was 28%, pale-yellow crystals, m.p. 154—156 °C (chloroform—hexane) (*cf.* lit. data[11]: m.p. 155—156 °C).

4-Isopropylidene-3-(*Z*)-[1-(2-methyl-3-benzothienyl)ethylidene]tetrahydrofuran-2,5-dione (1b) was synthesized according to a known procedure.[12] The yield was 20%, white crystals, m.p. 174—176 °C (*cf.* lit. data[12]: m.p. 173—176 °C).

***N*-Boc-*p*-Phenylenediamine (2)** was synthesized according to a known procedure.[13] The yield was 72%, white powder, m.p. 113—114 °C (*cf.* lit. data[13]: m.p. 114—115 °C).

8-Hydroxy-5,7-dinitroquinoline (6) was synthesized according to a known procedure.[7] The yield was 64%, yellow-green powder, m.p. 276—277 °C (with decomp.) (*cf.* lit. data[8]: m.p. 276—279 °C).

8-Chloro-5,7-dinitroquinoline (7) was synthesized according to a known procedure.[9] The yield was 87%, large transparent crystals, m.p. 157 °C (*cf.* lit. data[8]: m.p. 158 °C; *cf.* lit. data[9]: m.p. 154 °C). ^1H NMR (DMSO-d_6), δ:[9] 9.27 (dd, 1 H, H(2), $J_{2,3}$ = 4.0 Hz, $J_{2,4}$ = 1.5 Hz); 9.03 (s, 1 H, H(6)); 8.93 (d, 1 H, H(4), $J_{3,4}$ = 8.9 Hz); 8.02 (d, 1 H, H(3), $J_{3,4}$ = 8.9 Hz).

Compound **9** has been described in our earlier study.[6]

1-{4-[(*tert*-Butoxycarbonyl)amino]phenyl}-3-[(*Z*)-1-(2,5-dimethyl-3-thienyl)ethylidene]-4-isopropylidenepyrrolidine-2,5-dione (3a). A mixture of fulgide **1a** (2 g, 7.2 mmol) and *p*-(*tert*-butoxycarbonylamino)aniline (**2**) (1.57 g, 7.54 mmol) was refluxed in benzene (50 mL) for 20 h. Then benzene was distilled off on a rotary evaporator. The residue was dissolved in dichloromethane, SiO_2 (15 g) was added, and dichloromethane was distilled off on a rotary evaporator. The reaction mixture immobilized on silica gel was transferred onto a 8-cm glass filter, which was packed with silica gel (40—63 μm) to a height of 4 cm and placed into a round-bottom flask connected to a water-jet vacuum pump through a pipe. A mixture of amido acids was washed from silica gel *in vacuo*, and a mixture of dichloromethane and ethanol (40 : 1) was poured portionwise (100 mL) onto a filter. The fractions were collected in individual flasks. The fractions containing amido acids were combined (TLC monitoring; a dichloromethane—ethanol mixture, 40 : 1, as the eluent; R_f for amide acids was ~0.3), and the eluent was distilled off on a rotary evaporator. The residue was dissolved in THF (50 mL), and CDI (1.28 g, 7.9 mmol) was added. The reaction mixture was stirred at room temperature for 24 h, and THF was distilled off on a rotary evaporator. After silica gel flash chromatography (hexane—ethyl acetate mixture, 5 : 1, as the eluent), fulgimide **3a** was obtained in a yield of 2.87 g (85%) as pale-yellow crystals, m.p. 208—211 °C. ^1H NMR, δ: 1.49 (s, 9 H, $C(CH_3)_3$); 2.02, 2.12, 2.33, 2.39, and 2.47 (all s, 3 H each, CH_3); 6.48 (s, 1 H, NH); 6.54 (s, 1 H, H_{Ar}); 6.97 (d, 1 H, H_{Ar}, J = 6.8 Hz); 7.24 (d, 1 H, H_{Ar}, J = 7.5 Hz); 7.30 (t, 1 H, H_{Ar}, J = 8.3 Hz); 7.41 (s, 1 H, H_{Ar}). MS, m/z (I_{rel} (%)): 467 $[M + 1]^+$ (3), 466 $[M]^+$ (18), 411 (9), 307 (22), 306 (100), 224 (12). Found (%): C, 67.04; H, 6.55; N, 6.04. $C_{26}H_{30}N_2O_4S$. Calculated (%): C, 66.93; H, 6.48; N, 6.00.

1-(4-Aminophenyl)-3-[(*Z*)-1-(2,5-dimethyl-3-thienyl)ethylidene]-4-isopropylidenepyrrolidine-2,5-dione (4a). Fulgimide **3a** (1 g, 2.14 mmol) was dissolved with stirring in a 5 *M* ethanolic HCl solution (75 mL) and kept at room temperature for 12 h. Then the reaction mixture was concentrated to dryness on a rotary evaporator, the residue was dissolved in methanol (30 mL), and a 5 *M* methanolic NH_3 solution (10 mL) was added. The mixture was concentrated to dryness on a rotary evaporator, diethyl ether (30 mL) was added to the residue, and the precipitate was filtered off and washed on a filter with diethyl ether (2×20 mL). The filtrate was concentrated on a rotary evaporator. Fulgimide **4a** was obtained in a yield of 0.71 g (91%) as colorless crystals, m.p. 150—151 °C. IR, ν/cm^{-1}: 3369 (NH_2), 3056 (CH arom.), 2984—2856 (CH_3), 1695 (CO of amide). ^1H NMR, δ: 2.01, 2.10, 2.31, 2.38, and 2.44 (all s, 3 H each, CH_3); 3.70 (s, 2 H, NH_2); 6.52 (s, 1 H, H_{Ar}); 6.76 (d, 2 H, H_{Ar}, J = 7.4 Hz); 7.10 (d, 2 H, H_{Ar}, J = 8.0 Hz). MS, m/z (I_{rel} (%)): 367 $[M + 1]^+$ (11), 366 $[M]^+$ (24), 351 (83), 217 (90), 189 (100). Found (%): C, 69.14; H, 6.22; N, 7.57. $C_{21}H_{22}N_2O_2S$. Calculated (%): C, 68.83; H, 6.05; N, 7.64.

1-{4-[(*tert*-Butoxycarbonyl)amino]phenyl}-4-isopropylidene-3-[(*Z*)-1-(2-methyl-3-benzothienyl)ethylidene]pyrrolidine-2,5-dione (3b). A mixture of (2.26 g, 7.2 mmol) fulgide **1b** and *p*-(*tert*-butoxycarbonylamino)aniline (**2**) (1.57 g, 7.54 mmol) was refluxed in benzene (50 mL) for 20 h and then worked up as described above to prepare compound **3a**. After silica gel flash chromatography (hexane—ethyl acetate mixture, 5 : 1, as the eluent), fulgimide **3b** was obtained in a yield of 2.90 g (80%), m.p. 219—220 °C. ^1H NMR, δ: 1.52 (s, 9 H, $C(CH_3)_3$); 2.16, 2.24, 2.46, and 2.53 (all s, 3 H each, CH_3); 6.51 (s, 1 H, NH); 6.59 (d, 2 H, H_{Ar}, J = 7.5 Hz); 7.00 (d, 2 H, H_{Ar}, J = 7.8 Hz); 7.12—7.48 (m, 3 H, H_{Ar}); 7.75 (d, 1 H, H_{Ar}, J = 9.1 Hz). MS, m/z: 502 $[M]^+$. Found (%): C, 69.54; H, 6.03; N, 5.81. $C_{29}H_{30}N_2O_4S$. Calculated (%): C, 69.30; H, 6.02; N, 5.57.

1-(4-Aminophenyl)-3-isopropylidene-4-[(*Z*)-1-(2-methyl-3-benzothienyl)ethylidene]pyrrolidine-2,5-dione (4b). Compound **3b** (1 g, 2 mmol) was worked up as described above in the synthesis of compound **4a**. Fulgimide **4b** was obtained in a yield of 0.65 g (82%) as colorless crystals, m.p. 239—241 °C. IR, ν/cm^{-1}: 3374 (NH_2), 3057 (CH arom.), 2990—2852 (CH_3), 1703 (CO of amide). ^{1}H NMR, δ: 2.15, 2.21, 2.45, and 2.52 (all s, 3 H each, CH_3); 3.58 (s, 2 H, NH_2); 6.59 (d, 2 H, H_{Ar}, J = 7.5 Hz); 7.00 (d, 2 H, H_{Ar}, J = 7.8 Hz); 7.12—7.48 (m, 3 H, H_{Ar}); 7.75 (d, 1 H, H_{Ar}, J = 9.1 Hz). MS, m/z (I_{rel} (%)): 402 $[M]^+$. Found (%): C, 71.65; H, 5.53; N, 6.80. $C_{24}H_{22}N_2O_2S$. Calculated (%): C, 71.62; H, 5.51; N, 6.96.

Synthesis of autocomplexes 8a,b. A solution of equimolar amounts of dinitrochloroquinoline **7** and the corresponding amine **4a,b** in chloroform was heated to reflux, cooled, and concentrated by a factor of 2—3. The colored precipitates that formed were filtered off and crystallized from the appropriate solvent (acetonitrile or ethanol).

3-[(*Z*)-1-(2,5-Dimethyl-3-thienyl)ethylidene]-1-{4-[(5,7-dinitro-8-quinolyl)amino]phenyl}-4-isopropylidenepyrrolidine-2,5-dione (8a). The yield was 80%, orange crystals, m.p. 253—255 °C (MeCN). IR, ν/cm^{-1}: 3242 (NH), 3110—3056 (CH arom.), 2986—2858 (CH_3), 1702 (CO of amide), 1336—1315 (ν_s NO_2), 1595—1542 (ν_{as} NO_2). Found (%): C, 61.03; H, 4.28; N, 12.05. $C_{30}H_{25}N_5O_6S$. Calculated (%): C, 61.74; H, 4.32; N, 12.00.

1-{4-[(5,7-Dinitro-8-quinolyl)amino]phenyl}-4-isopropylidene-3-[(*Z*)-1-(2-methyl-1-benzothiophen-3-yl)ethylidene]-pyrrolidine-2,5-dione (8b). The yield was 82%, bright-yellow powder, m.p. 250—253 °C. IR, ν/cm^{-1}: 3195 (NH), 3108—3049 (CH arom.), 2988—2839 (CH_3), 1712 (CO of amide), 1330—1312 (ν_s NO_2), 1570—1540 (ν_{as} NO_2). Found (%): C, 63.93; H, 3.99; N, 10.90. $C_{33}H_{25}N_5O_6S$. Calculated (%): C, 63.96; H, 4.07; N, 11.30.

Synthesis of chelate compounds (general procedure). A solution of the corresponding autocomplex in acetone was added to a hot methanolic solution of cobalt acetate tetrahydrate in a ratio of 1 : 2 using a small excess with respect to **8a,b** or **9**. The reaction mixture was heated to reflux and then allowed to slowly cool and evaporate in air. The crystals were filtered off and successively washed with methanol and water.

Bis{3-[(*Z*)-1-(2,5-dimethyl-3-thienyl)ethylidene]-1-{4-[(5,7-dinitro-8-quinolyl)amino]phenyl}-4-isopropylidenepyrrolidine-2,5-dionato}diaquacobalt(II) hexahydrate (8a • Co). The yield was 80%, red-brown powder, m.p. >300 °C (with decomp.). IR, ν/cm^{-1}: 3110—3070 (CH arom.), 2987—2858 (CH_3), 1710 (CO of amide), 1320—1274 (ν_s NO_2), 1597—1526 (ν_{as} NO_2). Found (%): C, 52.26; H, 3.97; N, 9.71. $C_{60}H_{64}CoN_{10}O_{20}S_2$. Calculated (%): C, 52.67; H, 4.70; N, 10.24.

Bis{1-{4-[(5,7-dinitro-8-quinolyl)amino]phenyl}-4-isopropylidene-3-[(*Z*)-1-(2-methyl-1-benzothiophen-3-yl)ethylidene]-pyrrolidine-2,5-dionato}diaquacobalt(II) (8b • Co). The yield was 65%, red-brown powder, m.p. >300 °C (with decomp.). IR, ν/cm^{-1}: 3104—3064 (CH arom.), 2986—2850 (CH_3), 1710 (CO of amide), 1320—1280 (ν_s NO_2), 1596—1525 (ν_{as} NO_2). Found (%): C, 60.48; H, 3.86; N, 9.77. $C_{66}H_{52}CoN_{10}O_{14}S_2$. Calculated (%): C, 59.50; H, 3.93; N, 10.50.

Bis[5,7-dinitro-8-(phenyl)aminoquinolinato]cobalt(II) (9 • Co). The yield was 81%, black crystals with green luster, m.p. 239—241 °C. IR, ν/cm^{-1}: 3117—3074 (CH arom.), 1597—1527 (ν_{as} NO_2), 1320—1269 (ν_s NO_2). Found (%): C, 53.28; H, 2.90; N, 16.40. $C_{30}H_{18}CoN_8O_8$. Calculated (%): C, 53.19; H, 2.68; N, 16.54.

X-ray diffraction study of compound 8a. The crystals ($C_{30}H_{25}N_5O_6S$, M = 583.636) are monoclinic, at 110 K, a = 10.153(4) Å, b = 8.165(3) Å, c = 35.72(1) Å, β = 90.002(1)°, V = 2961.3(18) Å^3, d_{calc} = 1.412 g cm^{-3}, space group $P2_1/c$, Z = 4. The intensities of 20017 reflections were measured on an automated Smart 1000 CCD diffractometer at 110 K (Mo-Kα radiation, graphite monochromator, ω-scanning technique, $2\theta_{max}$ = 54°), of which 6447 observed reflections (R_{int} = 0.160) were used in the calculations. The monoclinic angle β is close to 90°, but R_{int} for the orthorhombic system is 0.575, which is indicative of the monoclinic system. The refinement of the occupancies of two possible twin components (TWIN instructions, BASF) gave 0.00 for the second component. The structure was solved by direct methods and refined by the full-matrix least-squares method with anisotropic and isotropic displacement parameters based on F^2. The hydrogen atoms were positioned geometrically. The H(4N) atom was located in a difference Fourier map. All hydrogen atoms were refined using a riding model. The positions of the atoms of the disordered ethanol solvent molecule were refined using a rigid-body model with the fixed geometric parameters determined for the crystal structure of ethanol. The lowest reliability factors were obtained by superposing three components with an occupancy ratio of 0.55 : 0.25 : 0.2. The final R factors were R_1 = 0.0674 (based on F^2_{hkl} for 2531 observed reflections with $I > 2\sigma(I)$), wR_2 = 0.1094, GOF = 0.907. All calculations were carried out with the use of the SHELXTL PLUS 5.1 program package.[14]

This study was financially supported by the Russian Foundation for Basic Research (Project No. 04-03-32845).

References

1. V. A. Barachevskii, *Khim. Vysok. Energii*, 2003, **37**, 10 [*High Energy Chem.*, 2003, **37** (Engl. Transl.)].
2. B. Otto, K. Ruck-Braun, *Eur. J. Org. Chem.*, 2003, 2409.
3. R. Matsushima, H. Sakaguchi, *J. Photochem. Photobiol. A*, 1997, **108**, 239.
4. Y. Yokoyama, *Chem. Rev.*, 2000, **100**, 1717.
5. Ya. F. Freimanis, *Organicheskie soedineniya s vnutrimolekulyarnym perenosom zaryada* [*Organic Compounds with Intramolecular Charge Transfer*], Zinatne, Riga, 1985, 190 pp. (in Russian).
6. I. G. Ilyina, V. V. Mel´nikov, B. N. Tarasevich, K. P. Butin, *Zh. Org. Khim.*, 2006, **42**, 1016 [*Russ. J. Org. Chem.*, 2006, **42**, 996 (Engl. Transl.)].
7. R. P. Dikshoorn, *Recl. Trav. Chim. Pays-Bas*, 1929, **48**, 550.
8. H. Hennig, J. Tauchnitz, K. Schone, *Z. Chem.*, 1971, 267.
9. N. L. Khilkova, V. N. Knyazev, N. S. Patalakha, V. N. Drozd, *Zh. Org. Khim.*, 1992, **28**, 1048 [*Russ. J. Org. Chem.*, 1992, **28** (Engl. Transl.)].
10. F. H. Allen, *Acta Crystallogr.*, 2002, **B58**, 380.
11. A. P. Glaze, S. A. Harris, H. G. Heller, W. Johncock, S. N. Oliver, P. J. Strydom, J. Whittall, *J. Chem. Soc., Perkin Trans. 1*, 1985, 957.
12. M. Kose, E. Orhan, *J. Photochem. Photobiol. A*, 2006, **177**, 170.
13. F. Troisi, A. Russo, C. Gaeta, G. Bifulco, P. Neri, *Tetrahedron Lett.*, 2007, **48**, 7986.
14. G. M. Sheldrick, *SHELXTL v. 5.10, Structure Determination Software Suite*, Bruker AXS, Madison, Wisconsin, USA.

Received July 20, 2007;
in revised form May 14, 2008