



# Synthesis, structure, and photoisomerization of derivatives of 2-(2-quinoly)-1,3-tropolones prepared by the condensation of 2-methylquinolines with 3,4,5,6-tetrachloro-1,2-benzoquinone

Yury A. Sayapin<sup>a</sup>, Bang Nghia Duong<sup>a</sup>, Vitaly N. Komissarov<sup>a</sup>, Igor V. Dorogan<sup>a</sup>, Nadezhda I. Makarova<sup>a</sup>, Inna O. Bondareva<sup>a</sup>, Valery V. Tkachev<sup>b</sup>, Gennady V. Shilov<sup>b</sup>, Sergey M. Aldoshin<sup>b</sup>, Vladimir I. Minkin<sup>a,\*</sup>

<sup>a</sup> Institute of Physical and Organic Chemistry, Southern Federal University, 194/2 Stachka St., 344090 Rostov on Don, Russian Federation

<sup>b</sup> Institute of Problems of Chemical Physics of Russian Academy of Sciences, 1 Akad. Semjonov N.N. Ave., 142432 Chernogolovka, Moscow region, Russian Federation

## ARTICLE INFO

### Article history:

Received 31 May 2010

Received in revised form 4 August 2010

Accepted 31 August 2010

Available online 9 September 2010

### Keywords:

1,3-Tropolones

Intermolecular hydrogen bond

Photolysis

Electrocyclic rearrangement

## ABSTRACT

A series of novel derivatives of the 1,3-tropolone ( $\beta$ -tropolone) system—2-(2-quinoly)-5,6,7-trichloro-1,3-tropolones and 2-(2-quinoly)-4,5,6,7-tetrachloro-1,3-tropolones have been prepared by the acid-catalyzed reaction of 2-methylquinolines with 3,4,5,6-tetrachloro-1,2-benzoquinone. The molecular structures of two compounds, 2-(4-chloro-6,8-dimethyl-5-nitro-2-quinoly)-5,6,7-trichloro-1,3-tropolone **8** and 2-(4-chloro-7,8-dimethyl-5-nitro-2-quinoly)-4,5,6,7-tetrachloro-1,3-tropolone **9**, have been determined using X-ray crystallography. According to the performed DFT B3LYP/6-311++G\*\* calculations the tautomeric (OH) and (NH) forms of  $\beta$ -tropolones **8** and **9** are nearly energy equivalent, the latter being more stabilized in polar media. Photolysis of 2-(2-quinoly)-1,3-tropolones in heptane solution leads to the disrotatory electrocyclic rearrangement resulting in the formation of a mixture of *E*- and *Z*-isomers of 3-[2(1*H*)-quinolinyliden]-bicyclo[3.2.0]hept-6-en-2,4-dione derivatives.

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## 1. Introduction

It has been shown that the reaction of *o*-quinones with methylene active compounds serves as a convenient method for the construction of 1,3-tropolone ( $\beta$ -tropolone) derivatives.<sup>1–5</sup> The mechanism of the reaction detailed by quantum chemical DFT calculations<sup>5</sup> involves, at its initial stage, formation of norcaradiene derivatives, which subsequently isomerize to give  $\beta$ -tropolones. It was reported<sup>1</sup> that coupling 3,4,5,6-tetrachloro-1,2-benzoquinones with acetone gives rise to the formation of an  $\alpha$ -tropolone derivative **1**, but this conclusion was later called into question by the results of a 2D NMR spectroscopic study<sup>2</sup> of the structure of the product, that attributed it to a  $\beta$ -tropolone derivative **2** (Fig. 1).

In this paper, we extend the previously studied acid-catalyzed reaction<sup>3–5</sup> of 2-methylquinolines with *o*-quinones to 3,4,5,6-tetrachloro-*o*-quinone derivative, describe a synthetic entry to novel derivatives of 2-(2-quinoly)- $\beta$ -tropolones substituted in the seven-membered ring and address the problem of the structure of the tropolones obtained by this method.

To unambiguously assign the structure to  $\alpha$  or  $\beta$ -isomeric form X-ray determinations have been performed for two compounds

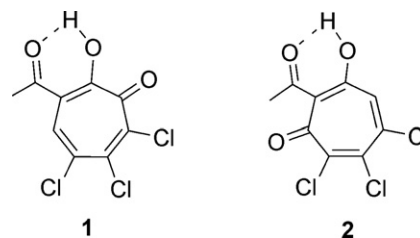


Fig. 1. Structures of  $\alpha$ -tropolone **1** and  $\beta$ -tropolone **2** derivatives.

and the relative stability of the tautomeric forms of the tropolones estimated by quantum chemical calculations using DFT B3LYP/6-311++G\*\* method with account taken for solvation.

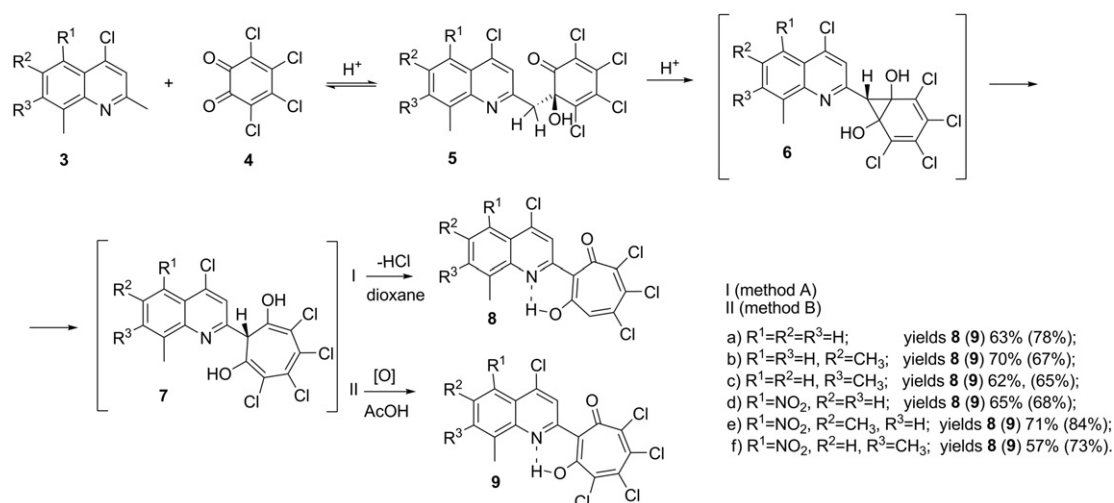
Recently, we have found that  $\beta$ -tropolones, similar to their  $\alpha$ -congeners<sup>6</sup> are susceptible to a photoinduced electrocyclic rearrangement, occurring via the intramolecular O–H $\cdots$ N $\rightarrow$ O $\cdots$ H–N excited state proton transfer followed by the disrotatory cyclization of the seven-membered ring diene fragment.<sup>7</sup> In the present work, we attempted to apply this reaction to the newly obtained polychloro- $\beta$ -tropolones and studied photolysis of their hexane solutions as well as absorption and fluorescence spectra of the initial compounds and the products of the photochemical reaction.

\* Corresponding author. Tel./fax: +7 863 243 47 00; e-mail address: minkin@ipoc.rsu.ru (V.I. Minkin).

## 2. Results and discussion

### 2.1. Synthesis and structure of 2-(2-quinolyl)-5,6,7-trichloro-1,3-tropolones and 2-(2-quinolyl)-4,5,6,7-tetrachloro-1,3-tropolones

Heating of a dioxane solution of 2-methylquinolines **3** and 3,4,5,6-tetrachloro-1,2-benzoquinone **4** at reflux over 20–30 min (method **A**) gives rise to a mixture of  $\beta$ -tropolones **8a–f** and **9a–f** with a substantial prevalence of the former. The total yields can be slightly increased and the ratio of the products reversed when running the reaction at about 50 °C for 5–6 h in the presence of acetic acid (method **B**). In this case,  $\beta$ -tropolones **9a–f** were obtained in 65–80% yield, whereas only trace amounts of compounds **8a–f** were isolated from the reaction mixture. The mechanism of the reaction based on the experimental findings (preparative isolation of an analog of the intermediate **5**) and theoretical modeling of the reaction of 2-methylquinoline with 3,5-di(*tert*-butyl)-1,2-benzoquinone<sup>5</sup> is pictured in Scheme 1. It includes four basic steps.



Scheme 1. Synthesis of 2-(2-quinolyl)-4,5,6,7-trichloro-1,3-tropolone **8** and 2-(2-quinolyl)-4,5,6,7-tetrachloro-1,3-tropolone **9**.

At the initial stage of the reaction, the aldol condensation of 2-methylquinolines **3** with 3,4,5,6-tetrachloro-1,2-benzoquinone **4** affords the intermediate adducts—6-(2-quinolinylyl methylene)-6-hydroxy-2,4-cyclohexadiene-1-ones **5**. The essential ring-closing step (**5**→**6** in Scheme 1) must be preceded by the proton transfer from the methylene group of intermediate **5** to the heterocyclic nitrogen. The geometry of the H<sub>2</sub>C–C=N triad of **5** is unfavorable for the intramolecular proton transfer and, as in many other 1,3-hydrogen shifts,<sup>8–10</sup> the pre-formation of an adduct with a suitable carrier molecule (acetic acid in the considered reaction) is the prerequisite for the proton transfer to proceed with a sufficiently low energy barrier. The CH→N proton transfer in **5** is accompanied by the cyclization reaction to give the norcaradiene derivatives **6**, which then rearrange to the dihydrotropolone derivatives **7**. In the absence of acetic acid (method **A**) the further reaction proceeds through dehydrochlorination of **7** and results in the formation of trichloro- $\beta$ -tropolones **8**. In method **B**, one has to use a twofold excess of quinone **3** since it serves as an oxidant converting dihydrotropolone **7** into 2-(2-quinolyl)-4,5,6,7-tetrachloro-1,3-tropolone **9** as the final product. Under relatively mild conditions (heating at ~50 °C), only small amounts of trichlorotropolones **8** are formed in this reaction. The yields of **8** substantially increase

when increasing temperature of the dioxane solution, achieving 60–80% at reflux.

The structures of  $\beta$ -tropolones **8** and **9** were characterized by <sup>1</sup>H NMR, IR-spectroscopy, and mass-spectrometry as well as X-ray diffraction study of compounds **8e** and **9f**. The overall views of their molecules are shown in Figs. 2–4.

An independent part of the elementary cell of compound **8e** contains two molecules (for the second molecule, numbers of atoms are increased by 20 relative to first one). The quinoline fragment (including atoms C(8)–C(18) and atom N(1)) lie in a root-mean-square plane (deviations from the plane less than 0.03 Å). Deviations of atoms Cl(4) and C(2) from this plane are, respectively, 0.17 and 0.03 Å in the same direction, whereas that of N(2) is 0.20 Å in the opposite direction. The tropolone ring is acoplanar. It is possible to allocate four atoms laying in common planes for molecules **A**: C(2),C(3),C(6),C(7) (deviations are less than 0.02 Å) and **B**: C(22),C(23),C(26),C(27) (deviations are less than 0.04 Å).

Another plane in each molecule is formed by remaining atoms of the tropolone moieties, so that the seven-membered rings acquire bath configurations folded along the C(2)–C(7) and C(3)–C(6)

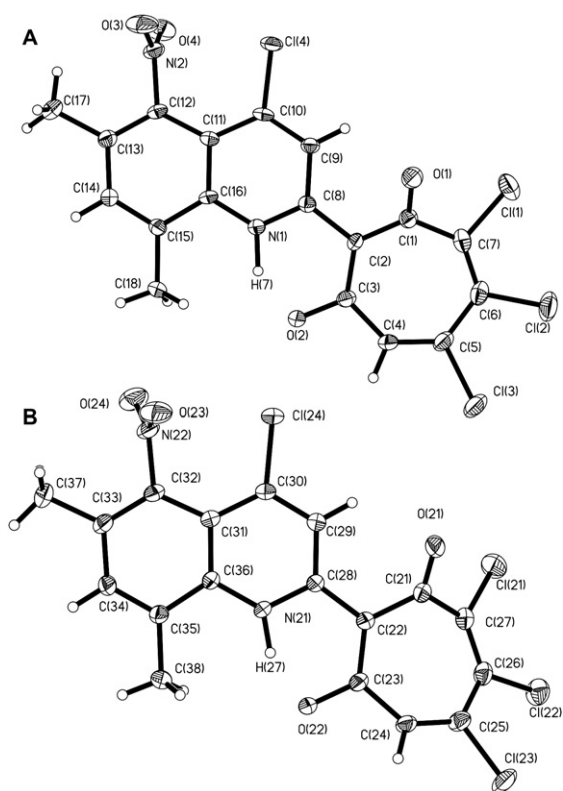
(molecule **A**) and C(22)–C(27) and C(23)–C(26) (molecule **B**) lines by the angles 32.5°, 15.6° (**A**) and 35.3°, 25.3° (**B**).

Fig. 2 represents a superimposition of two independent molecules of **8e**, so that quinoline fragments are made coincident. This picture helps to see that the tropolone moieties of molecules **A** and **B** are turned along the C(1)–C(4) line in opposite directions as well as the nitro groups with respect to the 2-methylquinoline fragments.

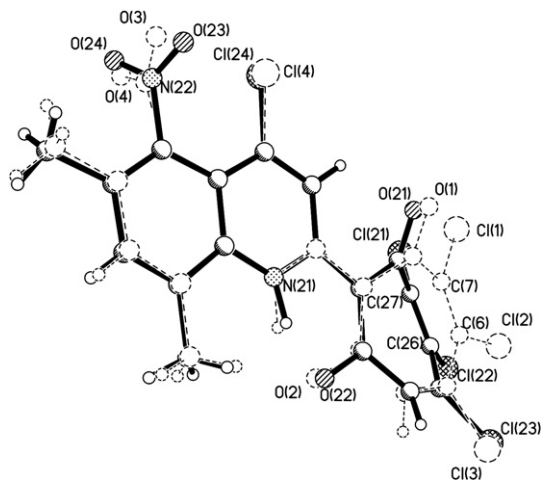
Compound **8e** exists in the NH tautomeric form with a strong intramolecular N–H···O hydrogen bond and very short N···O distance (N(1)···O(2)=2.432 (4) Å). The H(7)···O(2) distance is equal to 1.49 Å. The O(2)–C(3) carbonyl bond is significantly elongated (1.301 (5) Å) compared to the bond lengths of typical carbonyl bonds (1.21–1.23 Å). The angles N(1)–H(7)···O(2) and H(7)–O(2)–C(3) are equal to 143 (2)° and 106 (1)°, respectively. The six-membered ring closed by the intramolecular N(1)–H(7)···O(2) bond is planar with an accuracy of 0.027 Å.

As with **8e**,  $\beta$ -tropolone **9f** exists in the solid state in the NH tautomeric form with a strong intramolecular N–H···O hydrogen bond.

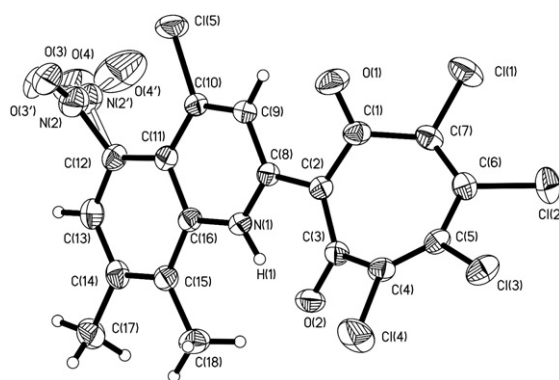
In **9f**, the N(1)···O(2) and H···N(1) distances (2.49 Å and 1.71 Å, respectively) are significantly longer than those in **8e**, while the



**Fig. 2.** Molecular structure of 2-(4-chloro-6,8-dimethyl-5-nitro-2-quinolyl)-5,6,7-trichloro-1,3-tropolone (**8e**) showing two independent molecules (**A** and **B**) in the crystal cell. Thermal ellipsoids are drawn on the 50% probability level. Selected bond lengths of the molecule **A** (Å): O(1)–C(1) 1.200(5), O(2)–C(3) 1.301(5), N(1)–C(8) 1.339(5), C(1)–C(2) 1.450(6), C(1)–C(7) 1.496(6), C(2)–C(3) 1.406(6), C(2)–C(8) 1.471(6), C(3)–C(4) 1.458(6), C(4)–C(5) 1.327(6), C(5)–C(6) 1.458(7), C(6)–C(7) 1.338(7), C(8)–C(9) 1.410(5); selected bond angles of the molecule **A** (°) O(1)–C(1)–C(2) 122.8(4), C(3)–C(2)–C(1) 123.8(4), C(3)–C(2)–C(8) 118.5(4), O(2)–C(3)–C(2) 121.9(4), N(1)–C(8)–C(2) 117.5(4), C(8)–N(1)–C(16) 123.7(3). Selected bond lengths of the molecule **B** (Å): O(21)–C(21) 1.198(5), O(22)–C(23) 1.292(5), N(21)–C(28) 1.348(5), C(21)–C(22) 1.467(6), C(21)–C(27) 1.721(5), C(22)–C(23) 1.415(6), C(22)–C(28) 1.450(6), C(23)–C(24) 1.458(6), C(24)–C(25) 1.329(6), C(25)–C(26) 1.447(7), C(26)–C(27) 1.334(6), C(28)–C(29) 1.406(6); selected bond angles of the molecule **B** (°) O(21)–C(21)–C(22) 123.7(4), C(23)–C(22)–C(21) 122.3(4), C(23)–C(22)–C(28) 120.3(4), O(22)–C(23)–C(22) 121.4(4), N(21)–C(28)–C(22) 116.5(4), C(28)–N(21)–C(36) 124.1(4).



**Fig. 3.** A superimposition of the independent molecules **A** and **B** from the elementary cell of 2-(4-chloro-6,8-dimethyl-5-nitro-2-quinolyl)-5,6,7-trichloro-1,3-tropolone combined on 2-methylquinoline fragment (**8e**).



**Fig. 4.** Molecular structure of 2-(4-chloro-7,8-dimethyl-5-nitro-2-quinolyl)-4,5,6,7-tetrachloro-1,3-tropolone (**9f**). Thermal ellipsoids are drawn on the 50% probability level. Selected bond lengths (Å): O(1)–C(1) 1.221(4), O(2)–C(3) 1.251(4), N(1)–C(8) 1.339(4), C(1)–C(2) 1.462(4), C(1)–C(7) 1.494(5), C(2)–C(3) 1.423(4), C(2)–C(8) 1.440(4), C(3)–C(4) 1.501(4), C(4)–C(5) 1.329(5), C(5)–C(6) 1.448(5), C(6)–C(7) 1.335(4), C(8)–C(9) 1.416(4); selected bond angles (°) O(1)–C(1)–C(2) 123.8(3), C(3)–C(2)–C(1) 122.7(3), C(3)–C(2)–C(8) 119.3(3), O(2)–C(3)–C(2) 123.7(3), N(1)–C(8)–C(2) 117.9(3), C(8)–N(1)–C(16) 125.8(3). It must be noted that the crystal under study contained one molecule of benzene for two molecules of **9f**.

carbonyl O(2)–C(3) bond length (1.253(4) Å) is significantly shorter than that bond in **8e**. These geometric parameters definitely point to the stronger intramolecular N–H···O hydrogen bond realized in **8e**. As seen from Fig. 3, the NO<sub>2</sub>-group in **9f** is disordered on two independent positions (the population of two rotameric forms is 0.6: 0.4).

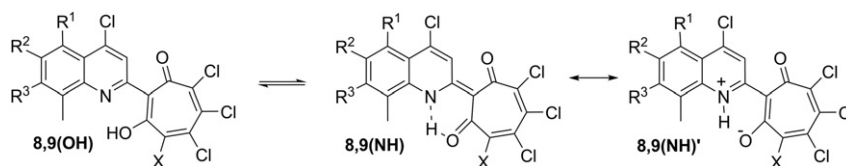
As in the case of the previously studied derivatives of 2-(2-quinolyl)-β-tropolone,<sup>5</sup> the O···N distances in β-tropolones **8e** and **9f** are approximately 0.5 Å shorter than the corresponding van der Waals contact. Such the geometry is characteristic of a very strong intramolecular N–H···O hydrogen bond belonging to the so-called resonance assisted hydrogen bonds.<sup>11</sup> Correspondingly, the protons in hydrogen bridges of compounds **8** and **9** are characterized by the unusually high downfield chemical shifts in the <sup>1</sup>H NMR spectra: 18–19 ppm (**8a–f**) and 17–18 ppm (**9a–f**). The proton signals in these compounds are significantly broadened, which testifies the occurrence of the rapid N–H⇌H–O transfer of a proton within the intramolecular N–H···O hydrogen bond bridge (Scheme 2).

For a theoretical estimate of the geometries of the tautomeric forms of β-tropolones **8e** and **9f** in the gas phase and in a polar solvent (DMSO), and the relative stabilities of the NH and OH tautomers, DFT B3LYP/6-311++G\*\* calculations have been carried out, the results of which are given in Table 1. The calculations sufficiently reproduce the experimentally determined geometries of β-tropolones as well as their main structural features such as the very short O···N distances and the folding of the seven-membered rings. The largest difference between the experimental and calculated bond lengths does not exceed 0.02 Å (see Supplementary data).

According to the theoretical estimations in the gas phase and in solution the OH and NH tautomeric forms of **8e** are nearly energy equivalent with a slight domination of the latter. Introduction of an additional acceptor substituent to the tropolone ring (**9f**) leads to stabilization of the more polar NH form. This stabilization becomes more pronounced in a polar solvent.

## 2.2. Electronic absorption spectra of β-tropolones **8, 9**

Results of the study of the absorption and fluorescence spectra of 2-quinolyl-β-tropolones **8, 9** are illustrated in Figs. 5 and 6 (see also Tables S2, S3 (Supplementary data)). Electronic absorption spectra of 2-(2-quinolyl)-5,6,7-trichloro-1,3-tropolone **8a–f** and



Scheme 2. Intramolecular proton transfer in compounds **8** and **9**.

Table 1

Total energies with zero-point energy correction ( $E_{\text{tot}}+\text{ZPE}$ , a.e.) and relative energies ( $\Delta E$ , kcal mol<sup>-1</sup>) of the NH and OH tautomers of **8e** and **9f** calculated by the B3LYP/6-311++G\*\* method in the gas phase and DMSO solution

Structure	$E_{\text{tot}}+\text{ZPE}$ (gas)	$\Delta E_{\text{gas}}$	$E_{\text{tot}}+\text{ZPE}$ (sol)	$\Delta E_{\text{sol}}$
<b>8e</b> (OH)	-2943.145135	0	-2943.154053	0
<b>8e</b> (NH)	-2943.145203	-0.04	-2943.155485	-0.90
<b>9f</b> (OH)	-3402.760878	0	-3402.770004	0
<b>9f</b> (NH)	-3402.764127	-2.04	-3402.774915	-3.08

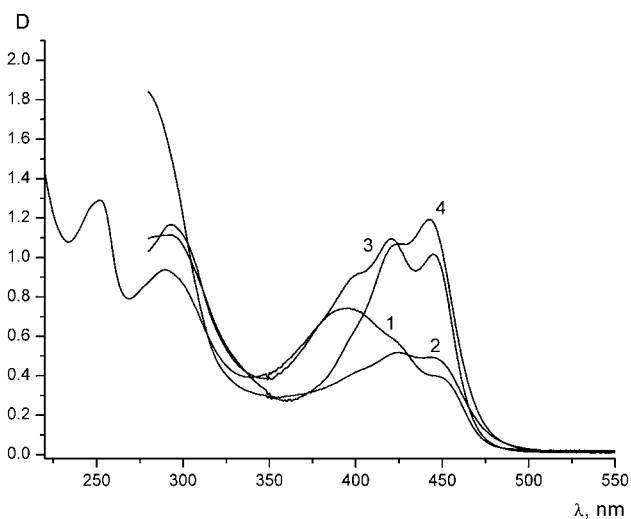


Fig. 5. Electronic absorption spectra of 2-(4-chloro-6,8-dimethyl-5-nitro-2-quinolyl)-5,6,7-trichloro-1,3-tropolone **8e** and 2-(4-chloro-6,8-dimethyl-2-quinolyl)-5,6,7-trichloro-1,3-tropolone **8b** in heptane (1, 3) and in dimethylsulfoxide (2, 4) solutions at 293 K for a layer in 1 cm ( $C=2.5 \times 10^{-5}$  mol  $\times$  l<sup>-1</sup>).

2-(2-quinolyl)-4,5,6,7-tetrachloro-1,3-tropolones **9a–f** in heptane solution have the structured long-wave band with maxima at 391–448 nm, the position of which depends on the substitution in the quinoline and tropolone fragments.

The main impact on the spectral pattern of compounds **8** and **9** has the introduction of a nitro group in the quinoline and an additional chlorine atom to the tropolone rings as shown in Fig. 5.

In order to get a closer insight into the origin of the electronic transitions responsible for the observed absorption spectra, theoretical TD B3LYP/6-311++G\*\* calculations were performed (see Supplementary data).

It was found that both NH and OH isomers of **8b** in heptane must have intensive long-wave absorption bands corresponding to the  $S_0 \rightarrow S_1$  transitions of  $\pi \rightarrow \pi^*$  origin with the excitation energies of 2.994 eV and 3.123 eV, respectively. The comparison with the experimental data allows correlation of the longest-wave absorption band of **8b** with the absorption of the NH isomer, whereas the next shorter-wavelength band should be assigned to the long-wave band of the OH form. It must be noted that the calculated transitions energies exceed the experimentally observed ones in the average of 0.2 eV. Such a difference is in the range of accuracy of the method.<sup>12</sup>

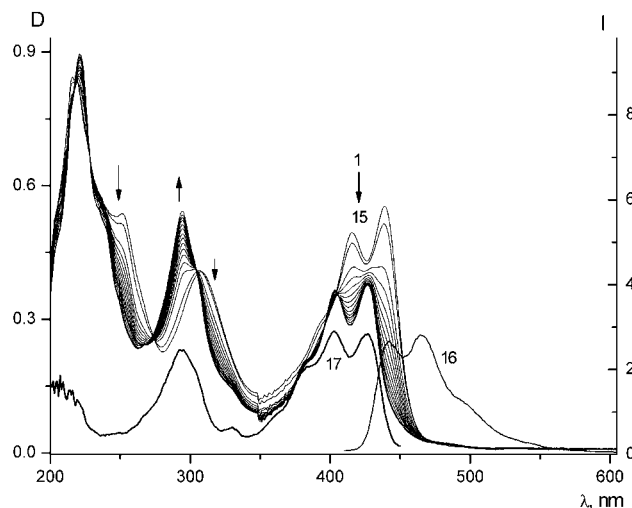


Fig. 6. Photoinduced changes of electronic absorption spectra (shown in 10 min intervals, 1–15) of 2-(4-chloro-8-methyl-2-quinolyl)-4,5,6,7-tetrachloro-1,3-tropolone **9a** ( $C=2.5 \times 10^{-5}$  mol  $\times$  l<sup>-1</sup>) occurring under irradiation with the filtered light ( $\lambda_{\text{irr}}=436$  nm); fluorescence spectra (16) and excitation of fluorescence spectra (17) of the photoproduct **11a** in heptane solution at 293 K.

According to the calculations, the broad absorption band of **8e** with a maximum at 394 nm (3.147 eV) represents a superposition of  $S_0 \rightarrow S_1$  transition of the OH isomer (main contribution) and the near in energy  $S_0 \rightarrow S_2$  transition of the NH form associated with the charge transfer to the nitro group. The absorption band with a maximum at 445 nm (2.787 eV) is caused by the  $S_0 \rightarrow S_1$  transition of the NH tautomer. In DMSO solution, the intensity of the long-wave absorption band at 445 nm is notably increased due to the increase of the relative content of the polar NH tautomeric form of **8e**. The next absorption band of **8e** at 424 nm (2.921 eV) is a superposition of  $S_0 \rightarrow S_1$  and  $S_0 \rightarrow S_2$  (the main contribution) electronic transitions in the OH tautomer and  $S_0 \rightarrow S_2$  transition in the NH form. These assignments are in line with the enhancement of relative stability of the more polar NH tautomer upon passing from heptane to DMSO solution (Table 1), and explain the observed bathochromic shift (solvatochromic effect) and substantial decrease in the intensity of the absorption band at 394 nm (3.147 eV) of **8e** with the increase of polarity of the solvent.

At room temperature, heptane solutions of compounds **8** and **9** do not exhibit measurable luminescence.

### 2.3. Photoinduced rearrangement

The irradiation of heptane solutions of 2-(2-quinolyl)-5,6,7-trichloro-1,3-tropolones **8** and 2-(2-quinolyl)-4,5,6,7-tetrachloro-1,3-tropolones **9** ( $\lambda=365$  or 436 nm,  $t=150$ –280 min) leads to the irreversible rearrangements manifested by the evolution of the spectral patterns as shown in Fig. 6. The growth of the new long wavelength absorption band is accompanied by the appearance of intensive structured fluorescence of the formed products ( $\lambda_{\text{max}}=438$ –498 nm).

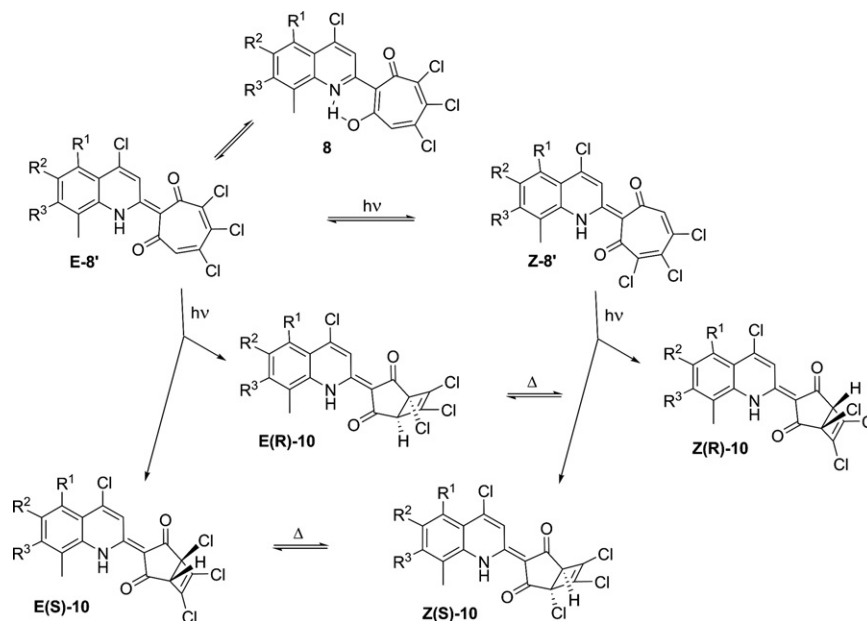


The observed photoinduced changes are determined by the disrotatory electrocyclic rearrangement, the mechanism of which has been previously studied for the case of the transformation of 2-(2-quinoliny)- $\beta$ -tropolones into derivatives of 3-[2(1*H*)-quinolinyden]-bicyclo[3.2.0]hept-6-en-2,4-diones.<sup>7</sup>

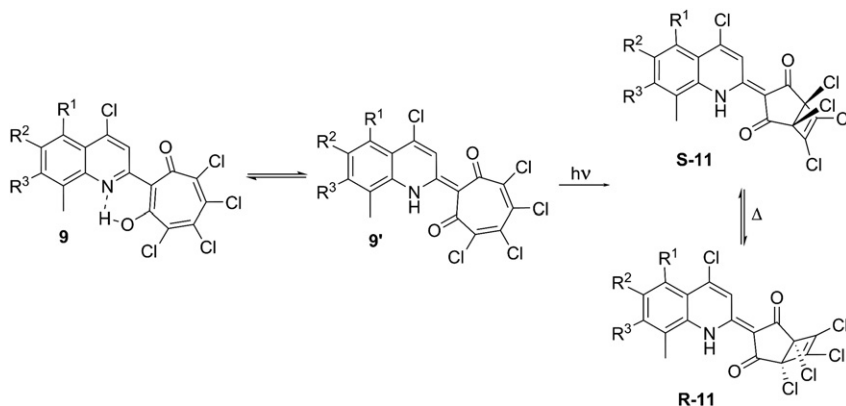
The reaction mechanisms responsible for the **8**→**10** and **9**→**11** transformations are depicted by Schemes 3–5.

The data on spectral and luminescent properties of the photo-products **10a–f** and **11a–f** are given in Supplementary data.

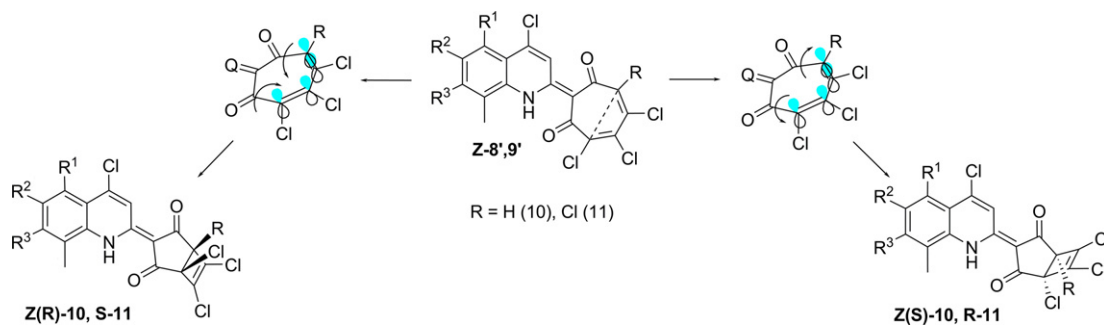
The photolysis of heptane solutions 2-(2-quinoliny)-5,6,7-trichloro-1,3-tropolones **8** and 2-(2-quinoliny)-4,5,6,7-tetrachloro-1,3-tropolones **9** containing equilibrium amounts of the OH and NH tautomeric forms is accompanied by the disrotatory electrocyclic rearrangement resulted in the formation of derivatives



Scheme 3. Photoisomerization of 2-(2-quinoliny)-4,5,6,7-trichloro-1,3-tropolone **8**.



Scheme 4. Photoisomerization of 2-(2-quinoliny)-4,5,6,7-tetrachloro-1,3-tropolone **9**.



Scheme 5. Photoinduced electrocyclicization of  $\beta$ -tropolones **8** and **9**.

of 3-[2(1*H*)-quinolinyliden]-bicyclo[3.2.0]hept-6-en-2,4-dione system. As shown in Scheme 5, the disrotatory photoinduced electrocyclicization of  $\beta$ -tropolones **8** and **9** can occur in two possible ways allowed by the orbital symmetry rules giving rise to a mixture of trans- and cis-isomers and subsequently formed mixture of the enantiomers *E*(*S*)-**10**, *E*(*R*)-**10** and *Z*(*R*)-**10**, *Z*(*S*)-**10**, and *S*-**11**, *R*-**11**.

The photoproducts **10a** and **11a** have been preparatively isolated and their structure confirmed by NMR <sup>1</sup>H, IR-spectroscopy, mass-spectrometry, and elemental analysis.

In CDCl<sub>3</sub> solution, the <sup>1</sup>H NMR spectrum of compound **10**, displays two signals (3.87 and 3.92 ppm) of the vinyl protons and two signals (15.10 and 15.23 ppm) of the protons in the intramolecular N–H⋯O hydrogen bond appearing in the 45:55 ratio corresponding to the ratio of the *E* and *Z* (or *Z* and *E*) isomers. In DMSO-*d*<sub>6</sub> solution, these signals coalesce at 30 °C, revealing a rapid dynamic isomerization *E*-**10**⇌*Z*-**10** associated with rotation of the bicyclic moiety of **10** around the double C=C bond. Energetic parameters of the critical points on PES (potential energy surface) of this reaction calculated by B3LYP/6-311++G\*\* method in DMSO solution are given in Table 2.

**Table 2**

Total energies with zero-point energy correction (*E*<sub>tot</sub>+ZPE, a.e.) and relative energies ( $\Delta E$ , kcal mol<sup>-1</sup>) of the *E*(*S*) and *Z*(*S*) tautomeric forms of **10** and transition state **Ts-EZ** calculated by the B3LYP/6-311++G\*\* method in DMSO solution

Structure	<i>E</i> <sub>tot</sub> +ZPE	$\Delta E$
<i>E</i> ( <i>S</i> )- <b>10</b>	-2699.321952	0
<b>Ts-EZ</b>	-2699.292807	18.3
<i>Z</i> ( <i>S</i> )- <b>10</b>	-2699.321689	0.2

The experimentally estimated energy barrier  $\Delta G^{\ddagger}_{303}$ =15.6 kcal mol<sup>-1</sup> is in satisfactory agreement with the calculated one (18.3 kcal mol<sup>-1</sup>). Similar type dynamic intramolecular processes occur also in solutions of other compounds **10a** and **11a** as is witnessed by doubling their N–H⋯O proton signals in the <sup>1</sup>H NMR spectra.

### 3. Conclusion

The acid-catalyzed ring expansion of the 3,4,5,6-tetrachloro-1,2-benzoquinones occurring under coupling with 2-methylquinolines can proceed through two reaction channels. Reaction in dioxane solution leads to the formation of mainly 2-quinolyl derivatives of 5,6,7-trichloro-1,3-tropolones, while heating the initial components with a twofold excess of 3,4,5,6-tetrachloro-1,2-benzoquinone gives rise to 2-quinolyl derivatives of 4,5,6,7-tetrachloro-1,3-tropolones.

As elucidated by X-ray crystallography and DFT B3LYP/6-311++G\*\* calculations of the (OH) and (NH) tautomeric forms of  $\beta$ -tropolones in the gas phase and solution the obtained 1,3-tropolones exist in the aminoenone form in a crystal phase, which is also a prevailing form in solution in polar solvents. Experimental dependencies of absorption spectra **8b** and **8e** on solvent polarity in conjunction with TD DFT calculation results are in accord with these assignments.

Photolysis of heptane solutions of 1,3-tropolones **8** and **9** results in the disrotatory electrocyclic rearrangement that affords derivatives of 3-[2(1*H*)-quinolinyliden]-bicyclo[3.2.0]hept-6-en-2,4-dione.

## 4. Experimental

### 4.1. General

<sup>1</sup>H NMR spectra were recorded on a 'Varian Unity-300' (300 MHz) spectrometer. Infrared (IR) spectra were recorded on

a Varian 3100FT-IR Excalibur Series with an attenuate total reflection accessory (ATR). The electronic absorption spectra were recorded on a 'Cary 100' (Varian) spectrophotometer. Photolysis was carried out by irradiation with monochromatic light after passing it through a water IR filter and an interference light filter to select the lines at 365 nm and 436 nm of the mercury spectrum of a DRSh 250 lamp. Fluorescence measurements were carried out on a 'Cary Eclipse' (Varian) spectrofluorimeter. The fluorescence quantum yields were determined by the Parker–Rees method<sup>13</sup> with the use of 3-methoxybenzanthrone in toluene ( $\phi=0.1$ ,  $\lambda_{\text{rad}}=365$  nm) as the reference luminophore.<sup>14</sup> Mass spectra were measured on a Finnigan MAT INOS 50 spectrometer. Melting points were determined in glass capillaries and are uncorrected. Al<sub>2</sub>O<sub>3</sub> (II–III activity of Brockman) was used for chromatographic separations.

### 4.2. X-ray crystal data

The unit cell parameters of the crystal and three-dimensional set of reflection intensities for  $\beta$ -tropolone **8e** were measured on an Enraf-Nonius CAD-4 autodiffractometer (Mo *K*<sub>α</sub>—radiation, graphite monochromator). Yellow transparent crystals **8e**—triclinic system: C<sub>18</sub>H<sub>10</sub>Cl<sub>4</sub>N<sub>2</sub>O<sub>4</sub>, *M*=460, *a*=7.6440(10), *b*=9.547(3), *c*=25.771(5) Å,  $\alpha=87.03(2)^\circ$ ,  $\beta=82.41(2)^\circ$ ,  $\gamma=77.23(2)^\circ$ . *V*=1817.6(7) Å<sup>3</sup>, *Z*=4,  $\rho_{\text{calcd}}=1.681$  g cm<sup>-3</sup>,  $\mu(\text{Mo } K_{\alpha})=0.68$  mm<sup>-1</sup>, sp.gr. *P*-1. The intensities of 6820 reflexes were measured ( $2\theta \leq 50$ ) by  $\omega/2\theta$  scanning method from a single crystal of dimensions 0.52×0.45×0.05 mm. After averaging of the equivalent reflexes intensity a working file of the measured *F*<sup>2</sup>(*hkl*) and  $\sigma(F^2)$  contained 6401 independent reflexes, from which 4143 with  $F^2 > 4\sigma(F^2)$ . The structure was solved by direct methods and refined by the full-matrix least-squares method with anisotropic displacement parameters for nonhydrogen atoms against *F*<sup>2</sup> using the SHELXL\_97.<sup>15</sup> In the crystal structure **8e** all hydrogen atoms were located in fourier synthesis of difference electron density maps. Coordinates and isotropic thermal parameters of all hydrogen atoms (except H(7) and H(27) for which these parameters were refined using isotropic approximation) were refined using a riding model.<sup>15</sup> At the last cycle of full-matrix refinement absolute shifts of all 505 variables for the compound **8e** were less than 0.001  $\sigma$ . The final refinement parameters: *R*<sub>1</sub>=0.068 for observed reflexes with  $I \geq 2\sigma(i)$ ; *R*<sub>1</sub>=0.108 for all measured reflexes, GOF is equal to 0.999.

Experimental data for **9f** were obtained under the analogous conditions, yellow transparent crystals—monoclinic system: C<sub>21</sub>H<sub>12</sub>Cl<sub>5</sub>N<sub>2</sub>O<sub>4</sub>, *M*=533.58, *a*=13.195(3), *b*=9.0010(11), *c*=19.073(4) Å,  $\beta=103.64(3)^\circ$ . *V*=2201.3(6) Å<sup>3</sup>, *Z*=4,  $\rho_{\text{calcd}}=1.610$  g cm<sup>-3</sup>,  $\mu(\text{Mo } K_{\alpha})=0.69$  mm<sup>-1</sup>, sp.gr. *P*<sub>2</sub>/c. The intensities of 4320 reflexes were measured ( $2\theta \leq 50.4^\circ$ ) by  $\omega/2\theta$  scanning method from a single crystal of dimensions 0.45×0.40×0.40 mm. After averaging of the equivalent reflexes intensity a working file of the measured *F*<sup>2</sup>(*hkl*) and  $\sigma(F^2)$  contained 3340 independent reflexes, from which 2717 with  $F^2 > 4\sigma(F^2)$ . The structure was solved by direct methods and refined by the full-matrix least-squares method with anisotropic displacement parameters for nonhydrogen atoms against *F*<sup>2</sup> using the SHELXL\_97.<sup>15</sup> In the crystal structure **9f** all hydrogen atoms were located in fourier synthesis of difference electron density maps. Coordinates and isotropic thermal parameters of all H atom and refined using a riding model<sup>15</sup> (except H(1) those parameters were refined using isotropic approximation). At the last cycle of full-matrix refinement absolute shifts of all 292 variables of compound **9f** were less than 0.001  $\sigma$ . The final refinement parameters: *R*<sub>1</sub>=0.068, for observed reflexes with  $I \geq 2\sigma(i)$ ; *R*<sub>1</sub>=0.063 for all measured reflexes, GOF is equal to 1.030.

Atomic coordinates, full tables of bond lengths, bond angles and thermal parameters have been deposited at the Cambridge Crystallographic Data Center (CCDC 767561 (**8e**), CCDC 767562 (**9f**)).

### 4.3. Synthesis

3,4,5,6-Tetrachloro-1,2-benzoquinone was obtained from Fluka (Switzerland). Quinolines **3a–f** were prepared according to the known procedures.<sup>16,17</sup>

**4.3.1. General procedure for the synthesis of 2-(2-quinolyl)-5,6,7-trichloro-1,3-tropolone **8a–f**.** A solution of 2-methylquinoline **3** (5 mmol), 3,4,5,6-tetrachloro-1,2-benzoquinone **4** (5 mmol) in dioxane (10 mL) was heated for 20–30 min. The deposited crystals of  $\beta$ -tropolones **8a–f** were filtered off, washed with dioxane (10 mL) and hexane (20–30 mL). The solid was recrystallized from benzene.

**4.3.1.1. 2-(4-Chloro-8-methyl-2-quinolyl)-5,6,7-trichloro-1,3-tropolone **8a**.** Yield: 63%. Yellow crystals (mp: 229–231 °C). <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$  2.79 (3H, s, Me), 7.08 (1H, s, CH<sub>trop</sub>), 7.55 (1H, t, J=7.5 Hz, CH<sub>quinol</sub>), 7.71 (1H, d, J=7.5 Hz, CH<sub>quinol</sub>), 8.09 (1H, d, J=7.5 Hz, CH<sub>quinol</sub>), 8.55 (1H, s, CH<sub>quinol</sub>), 18.85 (1H, s, OH). IR:  $\nu$ =3121, 3043, 1627, 1590, 1535, 1485, 1245, 1378, 1319, 1292, 1231, 1171, 1124, 1096, 1077, 1006, 875, 836, 800, 783, 760, 737, 699 cm<sup>-1</sup>. MS: *m/z* (%): 373 (M<sup>+</sup>-CO, 26), 336 (5), 309 (8), 273 (10), 236 (10), 202 (20), 188 (12), 176 (8), 147 (28), 140 (17), 126 (33), 119 (47), 113 (20), 101 (26), 84 (90), 77 (48), 63 (100), 51 (50), 39 (65). Anal. Calcd for C<sub>17</sub>H<sub>9</sub>Cl<sub>4</sub>NO<sub>2</sub> (M=401.07): C 50.91; H 2.26; Cl 35.36; N 3.49. Found: C 50.74; H 2.08; Cl 34.92; N 3.16.

**4.3.1.2. 2-(4-Chloro-6,8-dimethyl-2-quinolyl)-5,6,7-trichloro-1,3-tropolone **8b**.** Yield: 70%. Yellow crystals (mp: 234–236 °C). <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$  2.56 (3H, s, Me), 2.75 (3H, s, Me), 7.08 (1H, s, CH<sub>trop</sub>), 7.54 (1H, s, CH<sub>quinol</sub>), 7.85 (1H, s, CH<sub>quinol</sub>), 8.54 (1H, s, CH<sub>quinol</sub>), 18.83 (1H, s, OH). IR:  $\nu$ =3127, 3058, 1623, 1591, 1531, 1471, 1439, 1387, 1318, 1293, 1235, 1123, 1103, 1067, 1032, 871, 818, 780, 752, 712, 695, 647 cm<sup>-1</sup>. MS: *m/z* (%): 387 (M<sup>+</sup>-CO, 24), 366 (2), 350 (4), 323 (4), 287 (7), 252 (7), 215 (10), 202 (10), 168 (16), 147 (29), 119 (45), 99 (25), 84 (95), 77 (55), 62 (100), 51 (57), 39 (78). Anal. Calcd for C<sub>18</sub>H<sub>11</sub>Cl<sub>4</sub>NO<sub>2</sub> (M=415.10): C 52.08; H 2.67; Cl 34.16; N 3.37. Found: C 52.02; H 2.52; Cl 34.06; N 3.08.

**4.3.1.3. 2-(4-Chloro-7,8-dimethyl-2-quinolyl)-5,6,7-trichloro-1,3-tropolone **8c**.** Yield: 62%. Yellow crystals (mp: 246–248 °C). <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$  2.59 (3H, s, Me), 2.69 (3H, s, Me), 7.07 (1H, s, CH<sub>trop</sub>), 7.50 (1H, d, J=8.5 Hz, CH<sub>quinol</sub>), 7.98 (1H, d, J=8.5 Hz, CH<sub>quinol</sub>), 8.50 (1H, s, CH<sub>quinol</sub>), 18.70 (1H, s, OH). IR:  $\nu$ =3126, 3056, 1634, 1599, 1533, 1503, 1430, 1383, 1313, 1294, 1238, 1178, 1085, 1005, 946, 908, 878, 855, 835, 817, 766, 711, 698 cm<sup>-1</sup>. MS: *m/z* (%): 415 (M<sup>+</sup>, 4), 412 (4), 387 (M<sup>+</sup>-CO, 100), 350 (20), 321 (12), 287 (15), 251 (12), 215 (15), 168 (20), 143 (20), 127 (20), 107 (28), 77 (15), 63 (18), 51 (10), 36 (15). Anal. Calcd for C<sub>18</sub>H<sub>11</sub>Cl<sub>4</sub>NO<sub>2</sub> (M=415.10): C 52.08; H 2.67; Cl 34.16; N 3.37. Found: C 51.92; H 2.58; Cl 34.04; N 3.12.

**4.3.1.4. 2-(4-Chloro-8-methyl-5-nitro-2-quinolyl)-5,6,7-trichloro-1,3-tropolone **8d**.** Yield: 65%. Yellow crystals (mp: 201–203 °C). <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$  2.81 (3H, s, Me), 7.19 (1H, s, CH<sub>trop</sub>), 7.67–7.74 (2H, m, CH<sub>quinol</sub>), 8.44 (1H, s, CH<sub>quinol</sub>), 18.95 (1H, s, OH). IR:  $\nu$ =3106, 3047, 1626, 1584, 1533, 1497, 1399, 1364, 1327, 1293, 1221, 1121, 1099, 1073, 1019, 948, 879, 839, 814, 783, 758, 734, 698 cm<sup>-1</sup>. MS: *m/z* (%): 418 (M<sup>+</sup>-CO, 45), 381 (11), 372 (6), 351 (14), 336 (22), 307 (15), 272 (14), 236 (15), 201 (15), 188 (14), 147 (28), 135 (11), 126 (15), 114 (28), 99 (16), 87 (25), 75 (22), 63 (40), 52 (9), 44 (25), 36 (18). Anal. Calcd for C<sub>17</sub>H<sub>8</sub>Cl<sub>4</sub>N<sub>2</sub>O<sub>4</sub> (M=446.07): C 45.77; H 1.81; Cl 31.79; N 6.28. Found: C 45.75; H 1.79; Cl 31.76; N 6.24.

**4.3.1.5. 2-(4-Chloro-6,8-dimethyl-5-nitro-2-quinolyl)-5,6,7-trichloro-1,3-tropolone **8e**.** Yield: 71%. Yellow crystals (mp: 205–207 °C). <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$  2.46 (3H, s, Me), 2.77 (3H, s, Me), 7.18 (1H, s, CH<sub>trop</sub>), 7.60 (1H, s, CH<sub>quinol</sub>), 8.43 (1H, s, CH<sub>quinol</sub>), 19.00

(1H, s, OH). IR:  $\nu$ =3122, 3051, 1621, 1585, 1538, 1496, 1462, 1434, 1385, 1362, 1320, 1289, 1260, 1199, 1127, 1110, 1069, 1027, 1006, 945, 880, 840, 782, 756, 741, 712, 699 cm<sup>-1</sup>. MS: *m/z* (%): 432 (M<sup>+</sup>-CO, 85), 395 (16), 386 (37), 365 (17), 350 (18), 337 (16), 314 (13), 286 (25), 250 (25), 214 (31), 188 (23), 166 (30), 147 (62), 139 (50), 119 (58), 99 (37), 84 (87), 77 (57), 62 (100), 50 (57), 38 (77). Anal. Calcd for C<sub>18</sub>H<sub>10</sub>Cl<sub>4</sub>N<sub>2</sub>O<sub>4</sub> (M=460.10): C 46.99; H 2.19; Cl 30.82; N 6.09. Found: C 46.90; H 2.12; Cl 30.70; N 6.02.

**4.3.1.6. 2-(4-Chloro-7,8-dimethyl-5-nitro-2-quinolyl)-5,6,7-trichloro-1,3-tropolone **8f**.** Yield: 57%. Yellow crystals (mp: 214–216 °C). <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$  2.62 (3H, s, Me), 2.72 (3H, s, Me), 7.16 (1H, s, CH<sub>trop</sub>), 7.60 (1H, s, CH<sub>quinol</sub>), 8.40 (1H, s, CH<sub>quinol</sub>), 19.02 (1H, s, OH). IR:  $\nu$ =3127, 3052, 1620, 1587, 1531, 1504, 1478, 1401, 1383, 1362, 1315, 1296, 1245, 1135, 1092, 1011, 925, 881, 771, 719, 701 cm<sup>-1</sup>. MS: *m/z* (%): 460 (M<sup>+</sup>, 3), 432 (M<sup>+</sup>-CO, 100), 395 (31), 386 (37), 365 (57), 350 (35), 314 (18), 286 (28), 250 (35), 215 (33), 188 (20), 166 (21), 147 (48), 139 (36), 119 (43), 99 (22), 84 (53), 77 (42), 63 (64), 51 (41), 39 (53). Anal. Calcd for C<sub>18</sub>H<sub>10</sub>Cl<sub>4</sub>N<sub>2</sub>O<sub>4</sub> (M=460.10): C 46.99; H 2.19; Cl 30.82; N 6.09. Found: C 46.84; H 2.10; Cl 30.66; N 6.00.

**4.3.2. General procedure for the synthesis of 2-(2-quinolyl)-4,5,6,7-tetrachloro-1,3-tropolone **9a–f**.** A solution of 2-methylquinoline **3** (5 mmol), 3,4,5,6-tetrachloro-1,2-benzoquinone **4** (10 mmol) in AcOH (10 mL) was heated at 50 °C for 4–5 h or allowed to stand at room temperature for 50 h (from compounds **9d–f**). The solutions were diluted with water and the formed precipitate was filtered off, washed with water (50 mL) and propanol-2 (10–15 mL). The solid was recrystallized from benzene.

**4.3.2.1. 2-(4-Chloro-8-methyl-2-quinolyl)-4,5,6,7-tetrachloro-1,3-tropolone **9a**.** Yield: 78%. Yellow crystals (mp: 239–241 °C). <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$  2.82 (3H, s, Me), 7.59 (1H, t, J=7.7 Hz, CH<sub>quinol</sub>), 7.73 (1H, d, J=7.7 Hz, CH<sub>quinol</sub>), 8.09 (1H, d, J=7.7 Hz, CH<sub>quinol</sub>), 8.51 (1H, s, CH<sub>quinol</sub>), 17.33 (1H, s, OH). IR:  $\nu$ =3120, 1680, 1635, 1612, 1594, 1561, 1527, 1492, 1469, 1428, 1394, 1353, 1300, 1284, 1233, 1205, 1151, 1098, 1028, 1002, 950, 900, 875, 844, 799, 761, 749 cm<sup>-1</sup>. MS: *m/z* (%): 435 (M<sup>+</sup>, 3), 420 (5), 407 (M<sup>+</sup>-CO, 75), 392 (27), 383 (10), 372 (25), 357 (5), 343 (18), 335 (10), 307 (27), 272 (25), 236 (35), 216 (5), 202 (16), 188 (22), 176 (10), 167 (9), 153 (40), 141 (15), 127 (18), 118 (65), 87 (27), 77 (10), 63 (15), 47 (7), 39 (7). Anal. Calcd for C<sub>17</sub>H<sub>8</sub>Cl<sub>5</sub>NO<sub>2</sub> (M=435.52): C 46.88; H 1.85; Cl 40.70; N 3.22. Found: C 46.78; H 1.74; Cl 40.54; N 3.14.

**4.3.2.2. 2-(4-Chloro-6,8-dimethyl-2-quinolyl)-4,5,6,7-tetrachloro-1,3-tropolone **9b**.** Yield: 67%. Yellow crystals (mp: 227–229 °C). <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$  2.59 (3H, s, Me), 2.77 (3H, s, Me), 7.56 (1H, s, CH<sub>quinol</sub>), 7.86 (1H, s, CH<sub>quinol</sub>), 8.50 (1H, s, CH<sub>quinol</sub>), 17.38 (1H, s, OH). IR:  $\nu$ =3124, 1680, 1636, 1595, 1561, 1533, 1474, 1428, 1402, 1352, 1284, 1236, 1203, 1175, 1147, 1103, 1028, 1001, 948, 900, 874, 858, 837, 793, 759, 735, 717 cm<sup>-1</sup>. MS: *m/z* (%): 421 (M<sup>+</sup>-CO, 7) 412 (3), 394 (3), 385 (3), 250 (5), 214 (8), 202 (7), 190 (14), 181 (12), 167 (13), 153 (20), 140 (12), 127 (13), 118 (65), 103 (13), 95 (10), 87 (40), 77 (14), 63 (20), 44 (30), 36 (12). Anal. Calcd for C<sub>18</sub>H<sub>10</sub>Cl<sub>5</sub>NO<sub>2</sub> (M=449.54): C 48.09; H 2.24; Cl 39.43; N 3.12. Found: C 47.90; H 2.10; Cl 39.28; N 3.06.

**4.3.2.3. 2-(4-Chloro-7,8-dimethyl-2-quinolyl)-4,5,6,7-tetrachloro-1,3-tropolone **9c**.** Yield: 65%. Yellow crystals (mp: 234–236 °C). <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$  2.60 (3H, s, Me), 2.72 (3H, s, Me), 7.51 (1H, d, J=8.5 Hz, CH<sub>quinol</sub>), 7.99 (1H, d, J=8.5 Hz, CH<sub>quinol</sub>), 8.45 (1H, s, CH<sub>quinol</sub>), 17.26 (1H, s, OH). IR:  $\nu$ =3131, 1624, 1601, 1540, 1505, 1434, 1389, 1361, 1344, 1295, 1239, 1202, 1115, 1108, 1083, 1020, 999, 946, 875, 841, 816, 799, 766, 710, 681 cm<sup>-1</sup>. MS: *m/z* (%): 449 (M<sup>+</sup>, 25), 421 (M<sup>+</sup>-CO, 100), 386 (35), 349 (15), 321 (20), 286 (20), 259

(11), 236 (10), 205 (20), 193 (50), 175 (20), 162 (60), 153 (75), 124 (60), 95 (28), 83 (68), 77 (50), 63 (60), 57 (35), 51 (50), 36 (58). Anal. Calcd for  $C_{18}H_{10}Cl_5NO_2$  ( $M=449.54$ ): C 48.09; H 2.24; Cl 39.43; N 3.12. Found: C 47.96; H 2.14; Cl 39.34; N 3.02.

4.3.2.4. 2-(4-Chloro-8-methyl-5-nitro-2-quinolyl)-4,5,6,7-tetrachloro-1,3-tropolone **9d**. Yield: 68%. Yellow crystals (mp: 210–212 °C).  $^1H$  NMR ( $CDCl_3$ ):  $\delta$  2.87 (3H, s, Me), 7.70–7.77 (2H, m,  $CH_{quinol}$ ), 8.51 (1H, s,  $CH_{quinol}$ ), 17.80 (1H, s, OH). IR:  $\nu=3113, 1643, 1595, 1570, 1533, 1487, 1467, 1410, 1390, 1358, 1296, 1163, 1140, 1100, 1037, 949, 903, 881, 847, 797, 763, 680\text{ cm}^{-1}$ . MS:  $m/z$  (%): 452 ( $M^+-CO$ , 17), 418 (10), 406 (6), 387 (10), 371 (5), 351 (5), 343 (6), 334 (10), 307 (8), 271 (9), 236 (10), 201 (7), 188 (10), 174 (5), 166 (3), 153 (24), 140 (10), 126 (15), 114 (25), 99 (13), 87 (22), 78 (45), 63 (28), 44 (32). Anal. Calcd for  $C_{17}H_7Cl_5N_2O_4$  ( $M=480.51$ ): C 42.49; H 1.47; Cl 36.89; N 5.83. Found: C 42.36; H 1.44; Cl 36.74; N 5.72.

4.3.2.5. 2-(4-Chloro-6,8-dimethyl-5-nitro-2-quinolyl)-4,5,6,7-tetrachloro-1,3-tropolone **9e**. Yield: 84%. Yellow crystals (mp: 225–227 °C).  $^1H$  NMR ( $CDCl_3$ ):  $\delta$  2.46 (3H, s, Me), 2.83 (3H, s, Me), 7.63 (1H, s,  $CH_{quinol}$ ), 8.45 (1H, s,  $CH_{quinol}$ ), 17.84 (1H, s, OH). IR:  $\nu=3119, 1680, 1632, 1595, 1559, 1536, 1476, 1438, 1356, 1346, 1315, 1295, 1241, 1204, 1159, 1107, 1083, 1029, 1002, 946, 899, 881, 795, 759, 736, 716, 677\text{ cm}^{-1}$ . MS:  $m/z$  (%): 466 ( $M^+-CO$ , 13), 431 (7), 420 (5), 401 (4), 384 (6), 348 (8), 320 (8), 285 (12), 249 (12), 214 (10), 181 (10), 166 (11), 153 (26), 139 (19), 118 (40), 101 (7), 87 (21), 78 (20), 63 (18), 44 (19). Anal. Calcd for  $C_{18}H_9Cl_5N_2O_4$  ( $M=494.54$ ): C 43.72; H 1.83; Cl 35.84; N 5.66. Found: C 43.64; H 1.74; Cl 35.70; N 5.48.

4.3.2.6. 2-(4-Chloro-7,8-dimethyl-5-nitro-2-quinolyl)-4,5,6,7-tetrachloro-1,3-tropolone **9f**. Yield: 73%. Yellow crystals (mp: 236–238 °C).  $^1H$  NMR ( $CDCl_3$ ):  $\delta$  2.63 (3H, s, Me), 2.76 (3H, s, Me), 7.60 (1H, s,  $CH_{quinol}$ ), 8.45 (1H, s,  $CH_{quinol}$ ), 17.66 (1H, s, OH). IR:  $\nu=3126, 1680, 1646, 1637, 1594, 1560, 1536, 1504, 1428, 1402, 1359, 1331, 1284, 1250, 1207, 1163, 1118, 1091, 1029, 1002, 944, 900, 870, 792, 771, 736, 670\text{ cm}^{-1}$ . MS:  $m/z$  (%): 466 ( $M^+-CO$ , 85), 431 (50), 420 (30), 401 (50), 384 (20), 365 (15), 348 (24), 320 (21), 285 (30), 272 (10), 249 (28), 236 (7), 214 (20), 183 (25), 166 (23), 153 (57), 139 (40), 127 (32), 118 (84), 87 (62), 77 (27), 63 (43), 51 (24), 39 (27). Anal. Calcd for  $C_{18}H_9Cl_5N_2O_4$  ( $M=494.54$ ): C 43.72; H 1.83; Cl 35.84; N 5.66. Found: C 43.58; H 1.78; Cl 35.76; N 5.54.

4.3.3. General procedure for the photosynthesis of (2(1H)-quinolinylidene)bicyclo[3.2.0]hept-6-ene-2,4-dione **10a** and **11a**. Compounds **10a** and **11a** were synthesized by irradiation of a solution of compound **8a** or **9a** (0.15 mmol) in heptane (500 mL) in a quartz photoreactor with the use of a DRT-230 mercury lamp for 150 min (for **9a**—250 min). The course of the reaction was monitored by UV spectroscopy. After completion of irradiation, the solvent was evaporated and the residue was recrystallized from heptane. A mixture of *E*-**10a** (45%) and *Z*-**10a** (55%) was obtained as yellow crystals.

4.3.3.1. 1,6,7-Trichloro-3-[4-chloro-8-methyl-2(1H)-quinolinylidene]-bicyclo[3.2.0]hept-6-ene-2,4-dione **10a**. Yield: 93%. Yellow crystals (mp: 248–250 °C with decomposition).  $^1H$  NMR ( $CDCl_3$ ):  $\delta$  2.78, 2.79 (3H, s,s, Me)<sub>E,Z</sub>, 3.87,3.92 (1H, s,s,  $CH_{bic}$ )<sub>E,Z</sub>, 7.58 (1H, t,  $J=7.5$  Hz,  $CH_{quinol}$ )<sub>E,Z</sub>, 7.73 (1H, d,  $J=7.5$  Hz,  $CH_{quinol}$ )<sub>E,Z</sub>, 8.11 (1H, d,  $J=7.5$  Hz,  $CH_{quinol}$ )<sub>E,Z</sub>, 8.89, 8.92 (1H, s,s,  $CH_{quinol}$ )<sub>E,Z</sub>, 15.10, 15.23 (1H, s,s, NH)<sub>E,Z</sub>.  $^1H$  NMR (DMSO- $d_6$ ):  $\delta$  2.70 (3H, s, Me)<sub>E,Z</sub>, 4.29 (1H, s,  $CH_{bic}$ )<sub>E,Z</sub>, 7.72 (1H, d,  $J=7.5$  Hz,  $CH_{quinol}$ )<sub>E,Z</sub>, 7.92 (1H, d,  $J=7.5$  Hz,  $CH_{quinol}$ )<sub>E,Z</sub>, 8.08 (1H, t,  $J=7.5$  Hz,  $CH_{quinol}$ )<sub>E,Z</sub>, 8.64 (1H, s,  $CH_{quinol}$ )<sub>E,Z</sub>, 14.82 (1H, s, NH)<sub>E,Z</sub>. IR:  $\nu=3100, 3330, 1733, 1674, 1597, 1519, 1442, 1391, 1323, 1276, 1238, 1183, 1127\text{ cm}^{-1}$ . Anal. Calcd for  $C_{17}H_9Cl_4NO_2$  ( $M=401.07$ ): C 50.91; H 2.26; Cl 35.36; N 3.49. Found: C 50.84; H 2.10; Cl 34.98; N 3.24.

4.3.3.2. 1,5,6,7-Tetrachloro-3-[4-chloro-8-methyl-2(1H)-quinolinylidene]-bicyclo[3.2.0]hept-6-ene-2,4-dione **11a**. Yield: 95%. Yellow crystals (mp: >300 °C with decomposition).  $^1H$  NMR ( $CDCl_3$ ):  $\delta$  2.80 (3H, s, Me), 7.62 (1H, t,  $J=7.5$  Hz,  $CH_{quinol}$ ), 7.76 (1H, d,  $J=7.5$  Hz,  $CH_{quinol}$ ), 8.14 (1H, d,  $J=7.5$  Hz,  $CH_{quinol}$ ), 8.92 (1H, s,  $CH_{quinol}$ ), 15.09 (1H, s, NH). IR:  $\nu=3100, 3357, 1733, 1686, 1596, 1518, 1441, 1386, 1323, 1275, 1239, 1180, 1157\text{ cm}^{-1}$ . Anal. Calcd for  $C_{17}H_8Cl_5NO_2$  ( $M=435.52$ ): C 46.88; H 1.85; Cl 40.70; N 3.22. Found: C 46.62; H 1.68; Cl 40.28; N 3.06.

#### 4.4. Computational methods

The calculations were performed using the B3LYP hybrid functional, which comprises the Becke<sup>18,19</sup> three-parameter exchange and Lee–Yang–Parr<sup>20</sup> correlation functionals with 6-311++G\*\* basis set using the GAUSSIAN 03<sup>21</sup> set of programs. Calculations in solution were performed using the CPCM model.<sup>22</sup> The nature of the stationary points on the PES was characterized by analyzing the Hessian force constant matrices. Absorption spectra were calculated using time dependent density functional methods (TD DFT) at the same level of theory.

#### Acknowledgements

This work was supported by the program (No.7P) of Russian Academy of Sciences, NSch.-3233.2010.3 of Ministry of Higher Education and Science of RF and Federal Target Program 'Research and scientific-pedagogical personnel of innovation in Russia' for 2009–2013 years (No: 02.740.11.0456).

#### Supplementary data

Crystallographic data for **8e**; calculated geometries of the compounds **8e** and **9f** in their OH and NH tautomeric forms in the gas phase; absorption and fluorescence spectra of compound **8a–f**, **9a–f** and their photoisomers **10a–f**, **11a–f** in heptane solution; calculated excitation energies and oscillator strengths of the singlet transitions of (OH) and (NH) isomers of **8b** and **8e** in heptane and DMSO solution; calculated geometries of the compound **10** in their *E*(S) and *Z*(S) tautomeric forms and transition state **Ts-EZ** in DMSO solution. Supplementary data associated with this article can be found in online version at doi:10.1016/j.tet.2010.08.077. These data include MOL files and InChIKeys of the most important compounds described in this article.

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