

Synthesis and structural characterization of new spiropyran containing conjugated vinyl-3*H*-indolium moiety and its hydrolysis product

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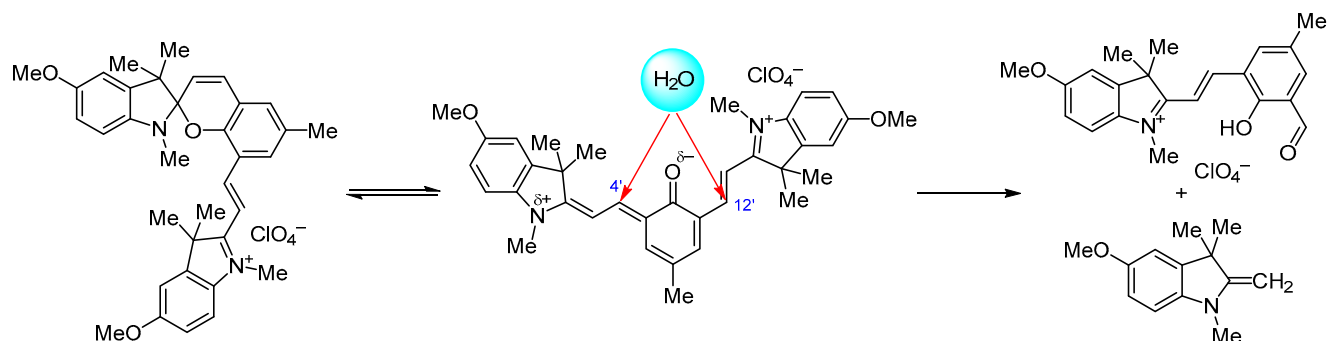
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A new spiropyran containing a cationic 3*H*-indolium substituent and methoxy groups at positions 5 and 5'' of the indoline cycles was synthesized. Hydrolysis of this compound was observed during crystallization from EtOH, leading to the formation of protonated merocyanine form of spiropyran containing a free formyl group. The hydrolysis product was characterized by X-ray structural analysis, the intermolecular interactions in crystal were studied with the CrystalExplorer 21.5 software suite. Quantum-chemical modeling based on the Fukui function distribution was used to establish the preferred site for nucleophilic attack, and a mechanism for hydrolysis was proposed.

Keywords: merocyanine, spiropyran, CrystalExplorer, density functional theory, hydrolysis, NMR spectroscopy, X-ray structural analysis.

The interest toward developing materials with tunable properties has been steadily growing over the previous decades. A striking example of the use of such materials are sensor systems,^{1,2} while one of the currently developing areas is the design of targeted drug delivery systems.³ The tuning of material properties can be provided by molecular switches, whose molecules tend to change their structure and properties in response to external factors. Such molecular systems are relevant not only as components of advanced materials: some of them are capable of functioning as molecular machines. Developments in this area have been recognized with a Nobel prize a few years ago.^{4–6} Among

molecular switches used in recent studies, spiropyran of indoline series are one of the most common types.^{7,8}

The synthesis of indoline spiropyran, as a rule, has been accomplished by the condensation of Fischer bases with *o*-hydroxyaromatic aldehydes.^{9,10} Their molecules can respond to various types of stimuli: electromagnetic radiation, changes in the temperature and acidity of the medium, pressure, solvent polarity, and other parameters,^{11,12} enabling a broad range of applications for compounds of this class. The switchable properties of spiropyran are based on reversible isomerization between the spirocyclic (SP) and several merocyanine (MC) structures (Fig. 1).

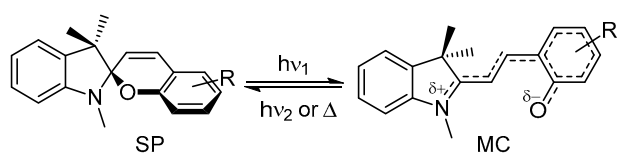


Figure 1. Reversible isomerization of spiropyrans.

The molecules of spiropyrans can be incorporated into the structure of materials as a simple physical mixture or *via* new chemical bond formation. In the latter case, the presence of reactive groups, such as formyl, hydroxy, or carboxyl is obligatory.^{13,14} Recently, there have been active developments in the synthesis of cationic spiropyrans that can be used as the basis for the design of hybrid materials containing ionic type bonds.^{15–18} In this case, the properties of systems also depend on the cationic moiety structure and the type of anion.^{19–21} Of particular interest are derivatives containing a conjugated cationic fragment in the benzopyran moiety. Such compounds can be considered as structural analogs of cyanine dyes, exhibiting the bathochromically shifted absorption maximum of MC isomer^{22,23} and, in several cases, demonstrating photoluminescence in the near IR wavelengths.^{19,24} As a rule, the presence of a sufficiently strong electron-withdrawing group at position 6' leads to partial stabilization of the MC form in similar compounds due to partial neutralization of the negative δ^- charge on the oxygen atom.^{23–26} Analogously, a stabilizing effect in the case of spiropyrans is due to the presence of electron-donating substituents at position 5 of indoline system, reducing the positive charge on the nitrogen and C-2,2' atoms.²⁷

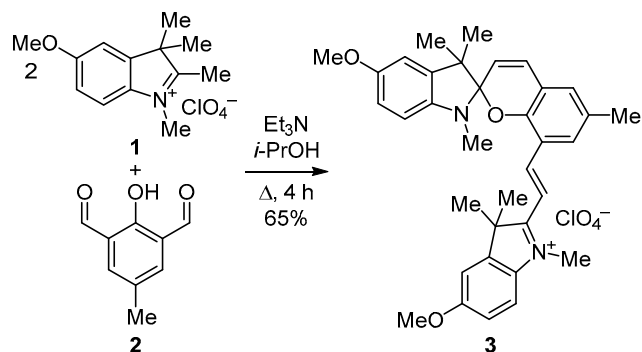
In order to examine the influence of electron-donating substituents in the indoline fragments on the structure and properties of compounds, a new spiropyran containing cationic 3*H*-indolium fragment in the benzopyran moiety and methoxy groups in both indoline cycles was obtained.

Spiropyran **3** containing a conjugated cationic fragment in the 2*H*-chromene moiety was synthesized according to a one-step procedure by a condensation reaction between 2 equiv of 5-methoxy-1,2,3,3-tetramethyl-3*H*-indolium perchlorate **1** and 2-hydroxy-5-methylisophthalic aldehyde (**2**) in the presence of an organic base (Scheme 1).²⁸

The structure of compound **3** was established from the results of NMR and high-resolution mass spectral analysis. The integrated signal intensities, chemical shifts, and the signal multiplicity in the spectrum were in complete agreement with the proposed structure. According to ¹H NMR data, compound **3** exists in CDCl₃ solution as a 10:1 mixture of SP and MC isomers (Fig. 2).

¹H NMR spectrum of compound **3** contained characteristic for the SP form signals of spin-coupled protons' pair H-3' and H-4' at 5.81 and 6.86 ppm, respectively, with a spin-spin coupling constant of 10.3 Hz. The vinyl protons of 3*H*-indolium moiety appeared as doublet signals at 7.98 and 7.29 ppm with a spin-spin coupling constant of 16.4 Hz, indicating a *trans* configuration. The protons of methyl groups at the nitrogen atoms of the cationic and the hetarene moieties appeared as

Scheme 1. Synthesis of spiropyran **3**



three-proton singlets at 3.72 and 2.69 ppm, while the protons of methoxy groups – at 3.87 and 3.83 ppm, respectively. Taking into account the symmetric structure of the MC form, the H-12'/H-4' and H-13'/H-3' protons appeared as two-proton doublet signals with a spin-spin coupling constant of 16.5 Hz, providing evidence for a *transoid* configuration of the vinyl moieties. The protons of methyl groups at the indoline nitrogen atoms and the methoxy groups were observed as six-proton singlets at 4.25 ppm and 3.91 ppm, respectively.

In ¹³C NMR spectrum of compound **3**, the signal of C-2'' carbon atom appeared in the downfield region at 180.2 ppm. The signals of C-5,5'',9' carbon atoms, directly bonded to oxygen atoms, were shifted upfield relative to the signal of C-2'' atom. The signal of the spiro atom appeared in its characteristic region at 107.3 ppm. It should be also noted that the signal of C-12' atom appeared at 148.3 ppm, while the C-13' atom gave a signal at 112.0 ppm. The carbon signals of MC form were not apparent due to its low concentration.

Compound **3** existed in DMSO-*d*₆ solution entirely in its closed form, similarly to spiropyran **4** that has been studied earlier, allowing to propose that the stabilization of MC form in CDCl₃ is significantly affected by the trace amounts of hydrochloric acid that are typical for this solvent and the second form observed in the spectrum was in fact protonated merocyanine. However, its concentration was too low for allowing to detect the hydroxy group protons. The respective proton signals were shifted upfield relative to those in the case of compound **4**,²⁸ due to the electron-donating effect of the methoxy group (Table 1).

Crystals were obtained by slow evaporation of ethanol solution of compound **3**. The results of X-ray structural analysis unexpectedly revealed the structure of styryl salt **5** (Fig. 3). The hydrolysis performed under laboratory conditions (by heating spiropyran **3** as 4·10⁻³ M solution in EtOH) allowed to isolate compound **5**. The experiment was repeated under argon atmosphere, again providing compound **5** as the sole product. A reference sample of compound **5** was also obtained by a two-step procedure including the synthesis of spiropyran **6** and its subsequent protonation (Scheme 2).

¹H NMR spectrum of spiropyran **6** contained the characteristic doublet signals of H-3' and H-4' protons at 5.76 and 6.83 ppm, with a spin-spin coupling constant of

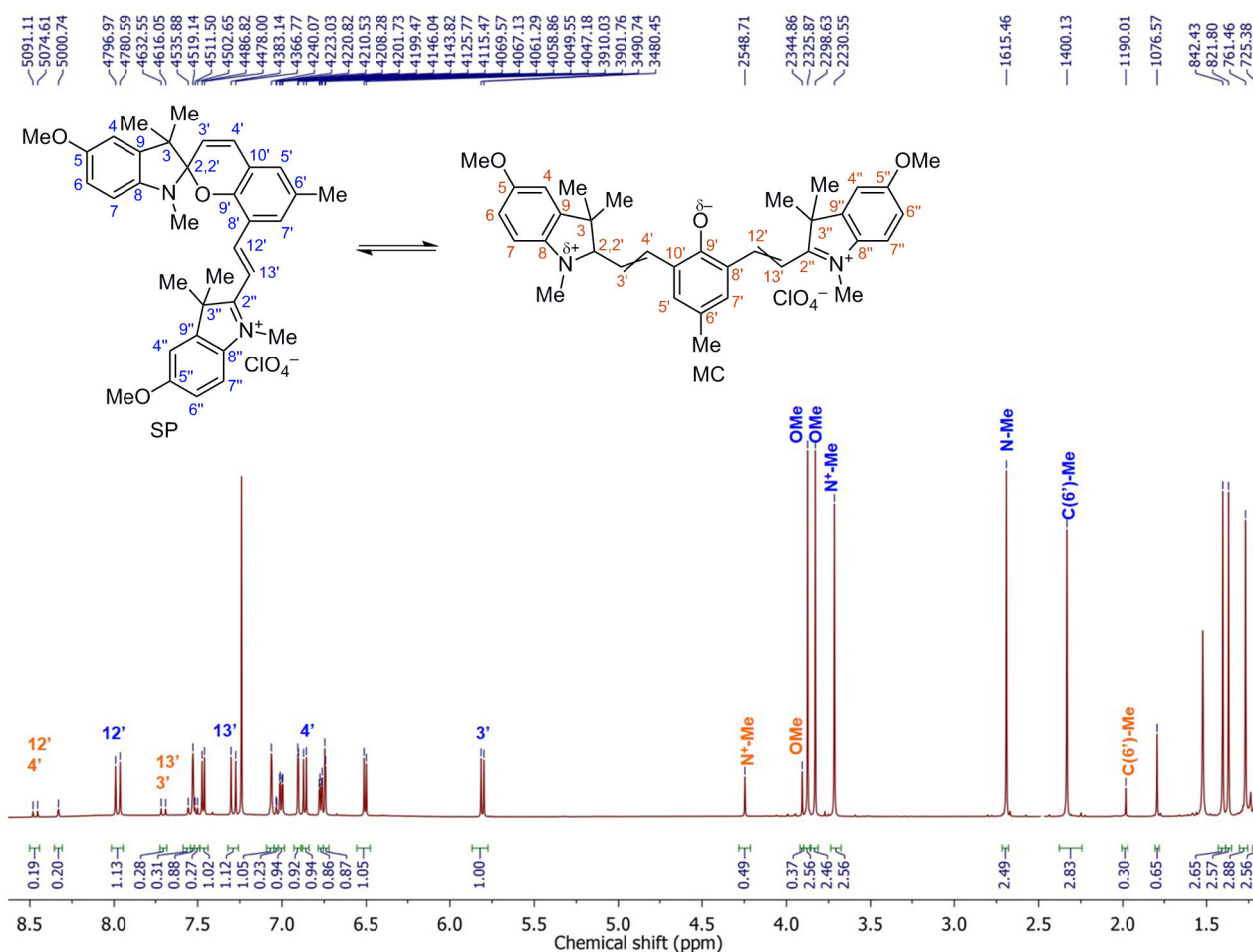


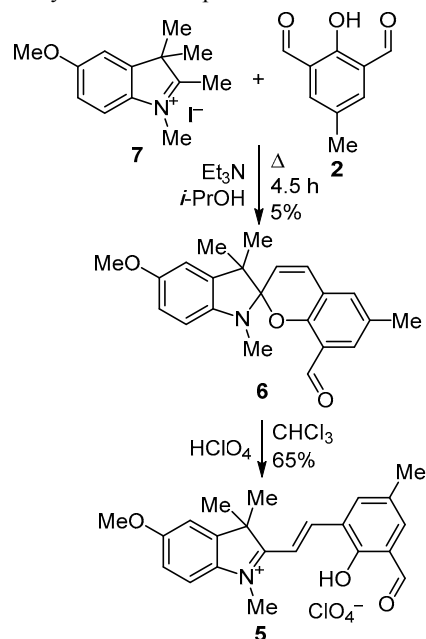
Figure 2. ^1H NMR spectrum of compound **3** in CDCl_3 .

Table 1. The characteristics of ^1H NMR signals for compounds **3** and **4** in $\text{DMSO}-d_6$ (δ , ppm; J , Hz)

Proton	Compound 3	Compound 4
N-CH ₃	2.63 (s)	2.67 (s)
N ⁺ -CH ₃	3.64 (s)	3.65 (s)
H-3'	5.94 (d, $J=10.3$)	5.97 (d, $J=10.3$)
H-4'	7.08 (d, $J=10.3$)	7.11 (d, $J=10.3$)
H-12'	7.94 (d, $J=16.5$)	8.02 (d, $J=16.5$)
H-13'	7.35 (d, $J=16.5$)	7.42 (d, $J=16.5$)
H-5'	7.29 (part of multiplet)	7.32 (d, $J=1.8$)
H-7'	7.78 (d, $J=1.2$)	7.83 (d, $J=1.3$)

10.3 Hz. The indolium protons in ^1H NMR spectrum of spiropyran **6** appeared in the same range as the analogous protons of the SP form of compound **3**, while the signal of

Scheme 2. The synthesis of compounds **5** and **6**



H-7' proton was shifted upfield (7.42 ppm) compared to the SP form of compound **3** (7.53 ppm). This upfield shift can be explained by the pronounced electron-withdrawing effect of the cationic 3*H*-indolium substituent.

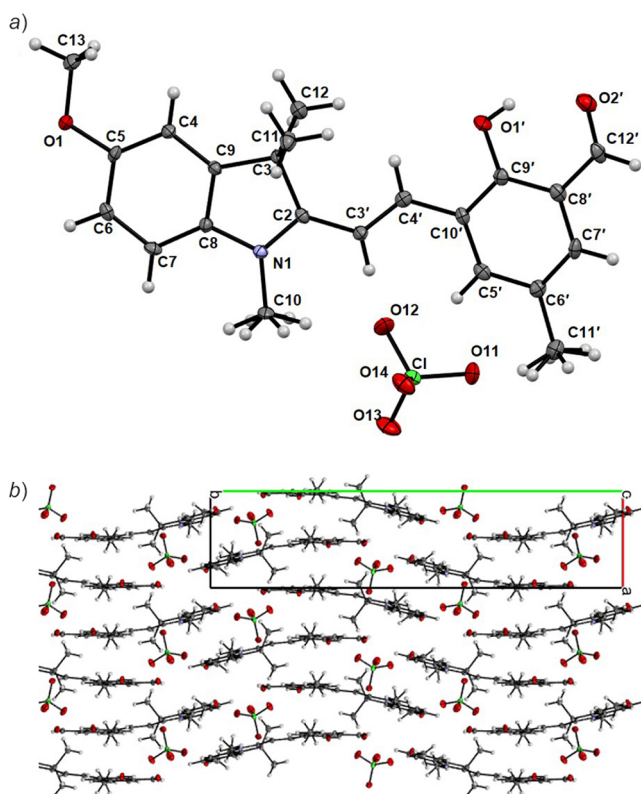


Figure 3. a) The molecular structure of compound **5** with atoms represented by thermal vibration ellipsoids of 0.5 probability. b) The molecular packing in crystal of compound **5**, a view along the axis *c*.

^1H NMR spectrum of compound **5** contained a singlet signal of the hydroxy group proton at 11.70 ppm and a formyl group proton signal at 10.08 ppm. The vinyl fragment proton signals appeared as two doublet signals at 8.32 and 7.70 ppm, with a spin-spin coupling constant of 16.6 Hz, indicating a *transoid* configuration of the C=C double bond. The protons of methyl group at the quaternary indolium nitrogen atom appeared as a three-proton singlet signal at 4.08 ppm, while the methoxy group protons gave a signal at 3.86 ppm. The proton signal of *gem*-methyl groups in the indolium moiety appeared as a six-proton singlet at 1.73 ppm, due to their magnetic equivalence.

According to the results of X-ray structural analysis, the molecule of compound **5** had a nonplanar structure: the angle between the mean square planes of rings C(9')–C(10') and C(8)–C(9) was equal to 11.66°, while the values of the torsion angles N(1)–C(2)–C(3')–C(4'), C(2)–C(3')–C(4')–C(10'), and C(3')–C(4')–C(10')–C(9') were –173.0, 173.1, and –174.4°, respectively, indicating a TTT configuration of the vinyl-3*H*-indolium moiety. The pyrrolidine ring assumed an envelope conformation, with the C(2) atom deviating from the plane of the other ring carbon atoms by 0.09 Å. The sum of valence angles at the indolium nitrogen atom was 360°, while the length of the N(1)–C(2) bond is 1.32 Å, which corresponds to the C=N bond multiplicity equal to two²⁹ and indicates the cationic nature of the indole fragment. The values of valence and torsion angles, as well as the main bond lengths are presented in Table 2.

Table 2. The bond lengths, valence angles, and torsion angles in the crystal of compound **5**

Bond	<i>l</i> , Å	Angle	ω , °
C(2)–N(1)	1.320(3)	C(10)–N(1)–C(2)	126.8(2)
N(1)–C(8)	1.430(3)	C(2)–N(1)–C(8)	111.8(2)
O(1)–C(5)	1.366(2)	C(8)–N(1)–C(10)	121.4(2)
O(1)–C(13)	1.447(3)	O(2')–H(1')–O(1')	146.9
C(2)–C(3')	1.429(3)	C(13)–O(1)–C(5)–C(6)	–174.7(2)
C(3')–C(4')	1.347(3)	N(1)–C(2)–C(3')–C(4')	–173.0(2)
C(4')–C(10')	1.454(3)	C(2)–C(3')–C(4')–C(10')	173.1(2)
C(9')–O(1')	1.358(3)	C(3')–C(4')–C(10')–C(9')	–174.4(2)
O(2')–C(12')	1.238(3)		

Crystals of compound **5** had a layered structure where molecules were linked by electrostatic interactions with the anion and various nonspecific interactions, as shown by the analysis of Hirshfeld surfaces (Fig. 4a) constructed at the normalized contact distance d_{norm} . The presence of ten shortened contacts was observed for each protonated merocyanine molecule when not considering the anion and twelve contacts when analyzing the surface constructed taking into account the anion. The predominant contacts in the crystal were O⋯H (39.3%), mostly occurring between the oxygen atoms of perchlorate anion and aromatic C–H protons of merocyanine molecule, as well as H⋯H contacts (39.4%) (Fig. 4b). It should be noted that O⋯H contacts were generally energetically much more favorable than H⋯H contacts. The enrichment coefficient E_{XY} ³⁰ was equal to 1.4 and 0.96, respectively. The significant number of shortened H⋯H contacts in the given case was caused

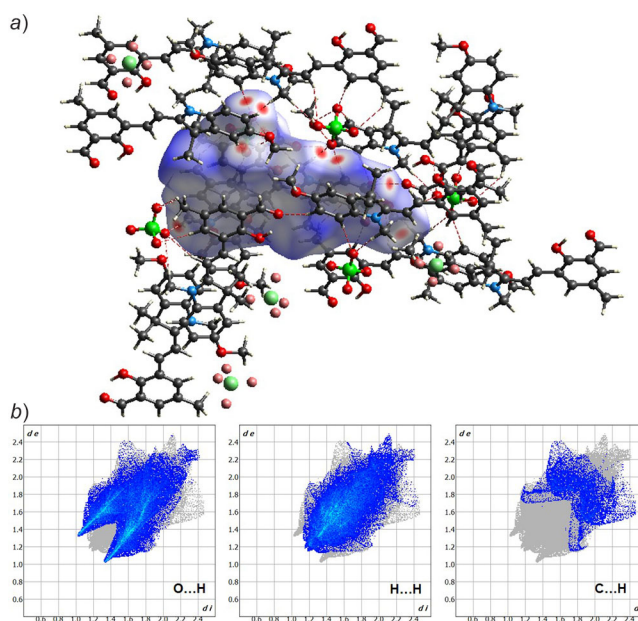


Figure 4. a) The Hirshfeld surface for compound **5**, constructed by normalized contact distance d_{norm} . b) The fingerprint surfaces for the shortened contacts O⋯H, H⋯H, and C⋯H.

Table 3. The shortened contacts in a crystal of compound **5**

Contact	<i>l</i> , Å	Contact	<i>l</i> , Å
O(1')...O(2')	2.619	H(1')C...C(11')	2.843
H(6A)...O(2')	2.541	H(1'C)...H(1'F)	2.152
C(13)...C(13)	3.206	H(12C)...O(11)	2.671
C(13)...H(13A)	2.881	H(4A)...O(14)	2.614
C(7)...C(7)	3.397	H(13B)...O(13)	2.666
O(1)...H(10C)	2.710	H(13B)...O(14)	2.718
O(1)...H(10E)	2.577	H(10C)...O(12)	2.601
H(10E)...C(13)	2.735	H(5'A)...O(14)	2.498
H(10E)...H(13B)	2.231	H(1'D)...O(11)	2.711
H(10B)...O(2')	2.674	H(1'B)...O(11)	2.624
H(10B)...C(12')	2.866	H(7A)...O(13)	2.495
C(11')...H(1'F)	2.884	H(10A)...O(13)	2.410
H(1'E)...C(11')	2.680	H(7'A)...O(11)	2.639
H(1'E)...H(1'F)	2.031	C(12')...O(12)	3.140
H(1'E)...H(1'B)	2.031	H(12D)...O(12)	2.484
H(1'C)...C(6')	2.858		

by the relatively tight packing of molecules in the crystal. Each anion interacted with three cationic organic functional groups, while each cationic site – with four anions. The structure also contained an intramolecular O(1')–H(1')...O(2') hydrogen bond (*l* 1.892 Å, with the angle O(1')–H(1')...O(2') equal to 146.9°). The shortened contacts observed in the crystal are listed in Table 3.

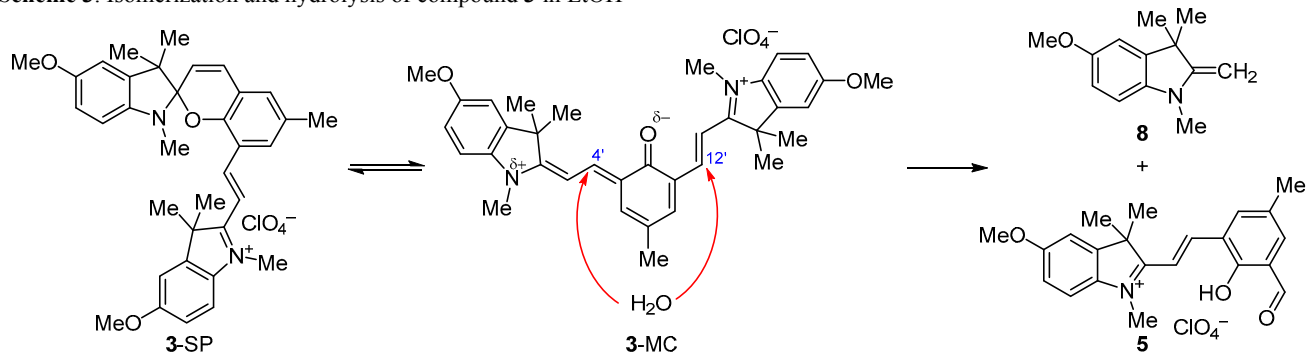
A wide range of styryl salts of indoline-substituted derivatives have been previously obtained by Seiler and coworkers *via* protonation of the corresponding spiropyrans.³¹ These compounds were also formed as intermediates during the synthesis of some other molecules.³² In the given case, compound **5** was generated by the hydrolysis of cationic spiropyran **3** in EtOH. It is well known that the condensation reaction of *ortho*-hydroxy aromatic aldehydes with Fischer bases is reversible. This fact has enabled, for example, the substitution of benzopyran moiety of a molecule incorporated in a polyphosphate chain.³³ Certain representatives of spiropyrans can undergo hydrolysis in aqueous media,^{33,34} which creates obstacles to some applications. At the same time, the possibility of spiropyran cleavage by hydrolysis or ozonolysis³⁵ with isolation of the

respective aldehyde allows to use spiro structures as effective protecting groups. Even though cationic spiropyran related to compound **3** are usually quite resistant to hydrolysis,^{19,26,28} in some cases there are precedents where the cationic group has been cleaved³⁶ or the hetarene system has been substituted,³⁷ using a molecule of Fischer base in the role of a nucleophile.

Compound **3** showed the presence of MC form in EtOH solution, as evidenced by the characteristic broadened absorption band with a maximum at 668 nm in the absorption spectrum. Under analogous conditions in aprotic MeCN, the longest wavelength absorption maximum was at 433 nm, corresponding to the SP form of compound containing a conjugated cationic vinyl-3*H*-indolium motif. Since polar and, in particular, protic solvents such as EtOH are known to stabilize the MC form of spiropyran,³⁸ the nucleophilic attack by H₂O during the hydrolysis occurred most likely at one of the two sites – at the C-4' or C-12' atom (Scheme 3). We have performed a quantum-chemical study in order to gain a more detailed understanding of the hydrolysis process.

First, the structure of product **5** was used as the reference for proposing a structure for the starting merocyanine **3**-MC. Since the stable merocyanine forms for the majority of spiropyran are isomers with TTC and TTT configurations of the vinylindolium fragment,^{39,40} we considered both of these conformations and selected the configuration of the second fragment on the basis of X-ray structural analysis data. The distribution of Fukui function, determined as the difference of electron density distribution between the starting molecule and ions obtained by adding or removing a certain number of electrons, was evaluated as a criterion for the reactivity estimation.⁴¹ The spatial distribution of Fukui function f^+ for two forms of **3**-MC characterized by different configuration of the vinylindolium fragment obtained *via* spirocycle cleavage, is shown in Figure 5a.

Quantitative description of the electrophilicity or nucleophilicity of a potential reactive site, as a rule, can be obtained by comparing the atomic populations calculated by the Hirschfeld method.^{42,43} A higher value of f^+ (equation (1)) points to the preferred site of nucleophilic attack, while f^- – to the preferred site of electrophilic attack (equation (2)). The calculated values of f^+ for **3**-MC were equal to 0.049 and 0.056 for the C-4' and C-12' atoms, respectively, in the TTC–TTT form or 0.054 and 0.056 for

Scheme 3. Isomerization and hydrolysis of compound **3** in EtOH

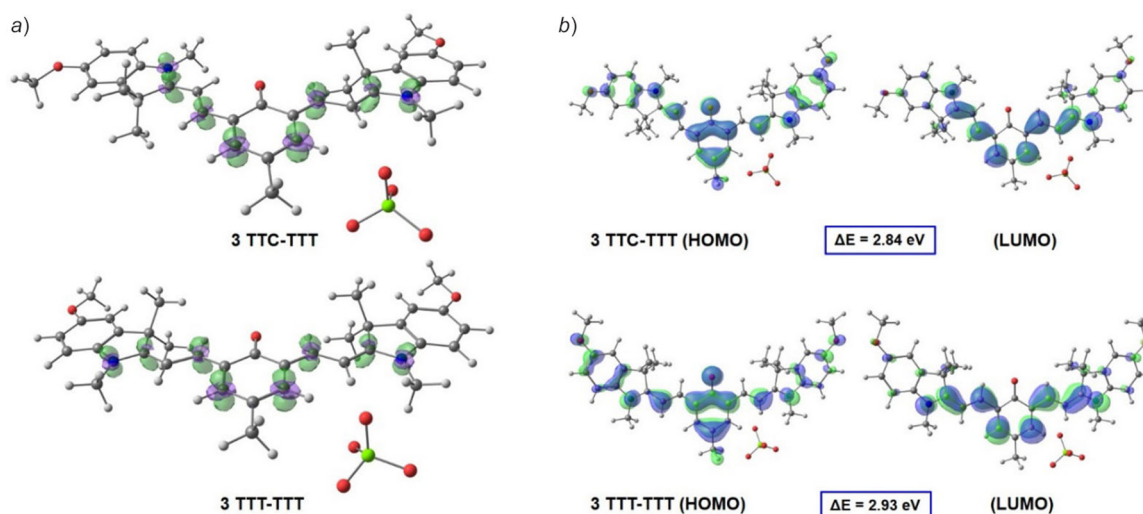


Figure 5. a) The distribution of Fukui function f^+ and b) frontier molecular orbitals in merocyanine **3-MC**.

the TTT–TTT form. Despite the fact that in the case of symmetric TTT–TTT isomer the activity of the two considered sites became practically equivalent, the calculation of Gibbs free energy indicated that the isomer TTC–TTT was more stable by 0.4 kcal·mol⁻¹. At the same time, this isomer was slightly more reactive according to the analysis of frontier orbitals' energies (Fig. 5b). In such a case, the C-12' atom became the preferred site of nucleophilic attack, while the mechanism likely included a quaternization of the previously neutral indoline fragment through redistribution of electron density in the molecule

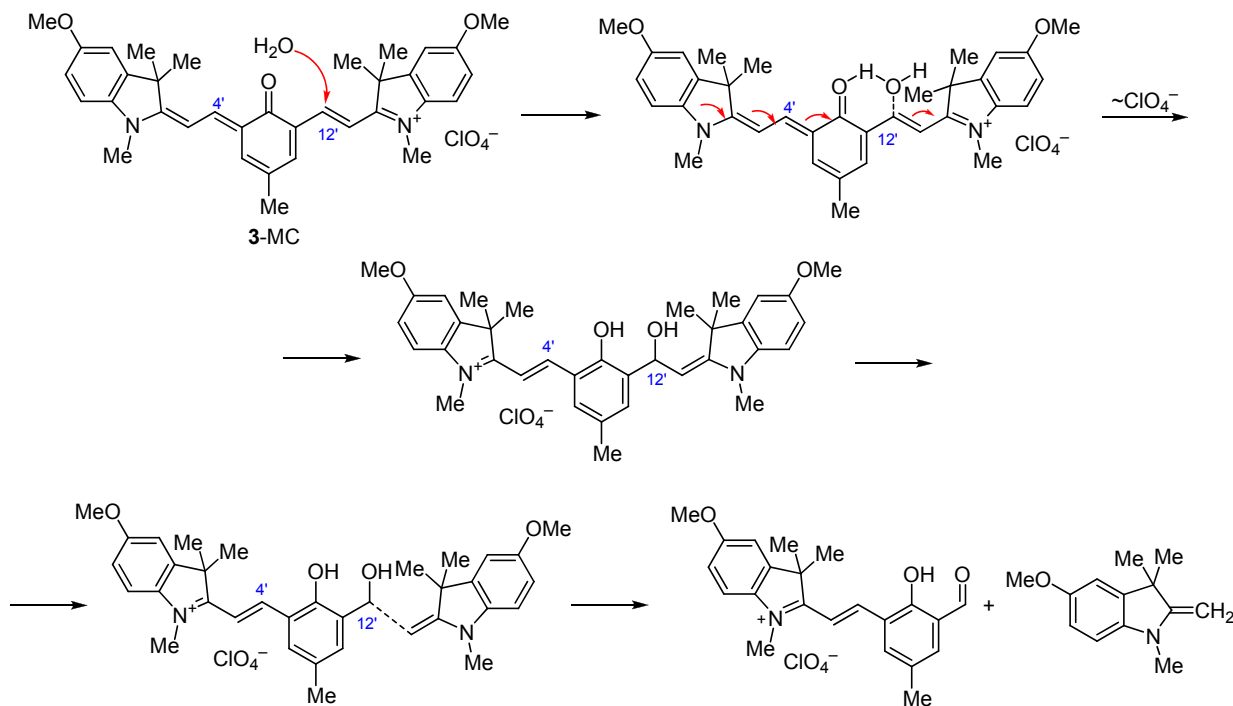
$$f_A^+ = q_N^A + q_{N+1}^A \quad (1)$$

$$f_A^- = q_{N-1}^A - q_N^A \quad (2)$$

upon hydrogen addition to the phenolate oxygen atom and the transfer of anion to it (Scheme 4). This process was enabled by the localization of extended conjugation chain in this area of the molecule (Fig. 5b).

Thus, within the scope of this work, we obtained a new cationic spiroopyran containing methoxy groups in its indolium rings. According to NMR spectra acquired in CDCl₃, the merocyanine form of the compound was partially stabilized. During the attempts to grow crystals from EtOH, hydrolysis of the compound was observed, resulting in the formation of protonated merocyanine containing a free formyl group. According to the calculations of Fukui function values, the preferred site of nucleophilic attack by a molecule of H₂O was the C-12' atom of the cationic vinyl-3*H*-indolium moiety.

Scheme 4. The proposed mechanism for the hydrolysis of compound **3-MC**



Experimental

IR spectra were recorded on a Varian Excalibur 3100 FT-IR spectrometer using the ATR technique. ^1H and ^{13}C NMR spectra were acquired on a Bruker AVANCE 600 instrument (at 600 and 151 MHz, respectively). The residual signals of deuterated solvents were used as internal standards (7.26 ppm (CDCl_3) and 2.50 ppm ($\text{DMSO-}d_6$) for ^1H nuclei; 77.2 ppm (CDCl_3) and 39.5 ppm ($\text{DMSO-}d_6$) for ^{13}C nuclei). High-resolution mass spectra were recorded on a Bruker maXis mass spectrometer, electrospray ionization, $\text{HCO}_2\text{Na-HCO}_2\text{H}$ system was used for calibration. Melting points were determined on a Fisher–Johns apparatus (Thermo Fisher Scientific, USA).

5-Methoxy-1,2,3,3-tetramethyl-3H-indolium iodide (7). A solution of *p*-methoxyhydrazine hydrochloride (3.49 g, 20 mmol) in EtOH (20 ml) was treated by adding 3-methylbutan-2-one (2.15 ml, 20 mmol) and concd HClO_4 (1.2 ml, 20 mmol). The mixture was heated at reflux for 3 h then 2/3 of the solvent were distilled off, the residue was neutralized with 20% NaOH solution, and the product was extracted with CHCl_3 . The extract was washed with distilled H_2O , dried over anhydrous Na_2SO_4 , and the solvent was removed by evaporation. Yield 3.15 g (83%), brown oil with a characteristic odor. The product was used in the next step without additional purification.

A solution of 5-methoxy-3,3-dimethyl-2-methyleneindole (3.15 g, 16.7 mmol) and MeI (1.56 ml, 25 mmol) in MeCN (10 ml) was heated at reflux for 3.5 h. The solution was then cooled, the precipitate that formed was filtered off and washed with cold MeCN. Yield 2.36 g (43%), pale-pink powder, mp 231–232°C. IR spectrum, ν , cm^{-1} : 1617 (C=C), 1290 (C–N Ar), 1019 (C–O–C Ar). ^1H NMR spectrum ($\text{DMSO-}d_6$), δ , ppm (J , Hz): 7.80 (1H, d, $J = 8.8$, H-7); 7.45 (1H, d, $J = 2.5$, H-4); 7.13 (1H, dd, $J = 8.8$, $J = 2.5$, H-6); 3.91 (3H, s, $\text{N}^+\text{-CH}_3$); 3.84 (3H, s, OCH_3); 2.68 (3H, s, C(2)– CH_3); 1.49 (6H, s, 2C(3)– CH_3). Found, %: C 47.17; H 5.51; N 4.18; I 38.35. $\text{C}_{13}\text{H}_{18}\text{INO}$. Calculated, %: C 47.13; H 5.44; N 4.23; I 38.37.

5-Methoxy-1,2,3,3-tetramethyl-3H-indolium perchlorate (1). Aqueous lead(II) perchlorate solution (498 mg, 1.23 mmol, 6 ml of solution) and an excess of HClO_4 were gradually added with stirring to a solution of indolium iodide (812 mg, 2.5 mmol) in MeCN (10 ml). The precipitate of lead iodide was removed by filtration, the solvent was partially evaporated, and the solution was left until the precipitation of product. Yield 362 mg (48%), bordeaux-colored crystals, mp 178–179°C. IR spectrum, ν , cm^{-1} : 1608 (C=C), 1293 (C–N Ar), 1016 (C–O–C Ar), 1069 (ClO_4^-). ^1H NMR spectrum ($\text{DMSO-}d_6$), δ , ppm (J , Hz): 7.79 (1H, d, $J = 8.8$, H-7); 7.45 (1H, d, $J = 2.4$, H-4); 7.13 (1H, dd, $J = 8.8$, $J = 2.5$, H-6); 3.91 (3H, s, $\text{N}^+\text{-CH}_3$); 3.84 (3H, s, OCH_3); 2.67 (3H, s, C(2)– CH_3); 1.48 (6H, s, 2C(3)– CH_3). Found, %: C 51.37; H 5.95; N 4.58; Cl 11.63. $\text{C}_{13}\text{H}_{18}\text{INO}_5$. Calculated, %: C 51.40; H 5.93; N 4.61; Cl 11.70.

(E)-5-Methoxy-2-[2-(5-methoxy-1,3,3,6'-tetramethylspiro[chromene-2',2'-indolin]-8'-yl)vinyl]-1,3,3-trimethyl-3H-indolium perchlorate (3). 2-Hydroxy-5-methylisophthalic aldehyde **2** (0.164 g, 1 mmol) was dissolved in *i*-PrOH

(10 ml), indolium perchlorate **1** (0.605 g, 2 mmol) was added and then Et_3N (0.1 ml, 1 mmol) was added dropwise. The mixture was heated at reflux for 4 h. The precipitate was recrystallized from EtOH and washed with cold EtOH. Yield 0.415 g (65%), orange-red powder, mp 247–248°C. IR spectrum, ν , cm^{-1} : 1605 (C=C), 1297 (C–N Ar), 1100 (ClO_4^-), 932 (C–O). Found, m/z : 535.2947 [$\text{M}]^+$. $\text{C}_{35}\text{H}_{39}\text{N}_2\text{O}_3$. Calculated, m/z : 535.2955. Found, %: C 66.10; H 6.19; N 4.38; Cl 5.51. $\text{C}_{35}\text{H}_{39}\text{ClN}_2\text{O}_7$. Calculated, %: C 66.19; H 6.15; N 4.41; Cl 5.59.

SP form of compound 3. ^1H NMR spectrum (CDCl_3), δ , ppm (J , Hz): 7.98 (1H, d, $J = 16.4$, H-12'); 7.53 (1H, s, H-7'); 7.47 (1H, d, $J = 8.8$, H-7''); 7.29 (1H, d, $J = 16.4$, H-13'); 7.06 (1H, s, H-5'); 7.01 (1H, dd, $J = 8.8$, $J = 2.3$, H-6''); 6.90 (1H, d, $J = 2.2$, H-4''); 6.86 (1H, d, $J = 10.3$, H-4'); 6.77 (1H, dd, $J = 8.4$, $J = 2.3$, H-6); 6.74 (1H, d, $J = 2.4$, H-4); 6.51 (1H, d, $J = 8.3$, H-7); 5.81 (1H, d, $J = 10.3$, H-3'); 3.87 (3H, s, OCH_3); 3.83 (3H, s, OCH_3); 3.72 (3H, s, $\text{N}^+\text{-CH}_3$); 2.69 (3H, s, N-CH_3); 2.33 (3H, s, CH_3); 1.40 (3H, s, C(3,3'')– CH_3); 1.37 (3H, s, C(3,3'')– CH_3); 1.27 (3H, s, C(3,3'')– CH_3); 1.21 (3H, s, C(3,3'')– CH_3). ^1H NMR spectrum ($\text{DMSO-}d_6$), δ , ppm (J , Hz): 7.94 (1H, d, $J = 16.5$, H-12'); 7.78 (1H, d, $J = 1.2$, H-7'); 7.75 (1H, d, $J = 8.8$, H-7''); 7.35 (1H, d, $J = 16.5$, H-13'); 7.29 (2H, m, H-5',4''); 7.13 (1H, dd, $J = 8.8$, $J = 2.5$, H-6''); 7.08 (1H, d, $J = 10.3$, H-4'); 6.85 (1H, d, $J = 2.6$, H-4); 6.77 (1H, dd, $J = 8.4$, $J = 2.6$, H-6); 6.57 (1H, d, $J = 8.4$, H-7); 5.94 (1H, d, $J = 10.3$, H-3'); 3.87 (3H, s, OCH_3); 3.78 (3H, s, OCH_3); 3.64 (3H, s, $\text{N}^+\text{-CH}_3$); 2.63 (3H, s, N-CH_3); 2.29 (3H, s, CH_3); 1.35 (3H, s, C(3,3'')– CH_3); 1.34 (3H, s, C(3,3'')– CH_3); 1.23 (3H, s, C(3,3'')– CH_3); 1.15 (3H, s, C(3,3'')– CH_3). ^{13}C NMR spectrum (CDCl_3), δ , ppm: 180.2 (C-2''); 161.4 (C-5''); 154.4 (C-5); 153.6 (C-9''); 148.3 (C-12''); 144.9 (C-9''); 142.2 (C-8); 138.2 (C-9); 134.9 (C-8''); 133.5 (C-5''); 131.6 (C-7''); 130.8 (C-6''); 129.4 (C-4''); 120.1 (C-8''); 119.8 (C-3', C-10''); 115.8 (C-7''); 114.3 (C-6''); 112.0 (C-13''); 111.9 (C-6); 109.6 (C-4); 108.8 (C-4''); 107.8 (C-7); 107.3 (C-2,(2'')); 56.1 (OCH_3); 52.3 (C-3''); 51.8 (C-3); 34.1 ($\text{N}^+\text{-CH}_3$); 29.5 (N-CH_3); 26.8 (C(3,3'')– CH_3); 26.6 (C(3,3'')– CH_3); 25.4 (C(3,3'')– CH_3); 20.2 (CH_3); 20.0 (C(3,3'')– CH_3).

MC form of compound 3. ^1H NMR spectrum (CDCl_3), δ , ppm (J , Hz): 8.47 (2H, d, $J = 16.5$, H-4',12''); 8.33 (2H, s, H Ar); 7.70 (2H, d, $J = 16.5$, H-3',13''); 7.56 (2H, s, H Ar); 7.51 (2H, d, $J = 8.8$, H Ar); 7.03 (2H, d, $J = 2.2$, H Ar); 4.25 (6H, s, $2\text{N}^+\text{-CH}_3$); 3.91 (6H, s, 2OCH_3); 1.98 (3H, s, CH_3); 1.79 (12H, s, $2\text{C}(3,3'')\text{-CH}_3$).

5'-Methoxy-1',3',3',6'-tetramethylspiro[chromene-2',2'-indoline]-8-carbaldehyde (6). 5-Methoxy-1,2,3,3-tetramethylindolium iodide **7** (331 mg, 1 mmol) was added to a solution of 2,6-diformyl-4-methylphenol **2** (164 mg, 1 mmol) in *i*-PrOH, followed by slow dropwise addition of Et_3N (0.1 ml, 1 mmol). The mixture was heated at reflux for 4.5 h, then cooled. The product was extracted with CHCl_3 and dried over anhydrous Na_2SO_4 . After the residual solvent was evaporated, the crude product was separated by silica gel column chromatography using CHCl_3 as eluent. The product was recrystallized from petroleum ether. Yield 0.018 g (5%), yellow crystals, mp 152–

153°C. IR spectrum, ν , cm^{-1} : 1675 (C=O), 1296 (C–N Ar), 919 (C–O). ^1H NMR spectrum (CDCl_3), δ , ppm (J , Hz): 10.10 (1H, s, CHO); 7.42 (1H, d, $J = 1.9$, H-7); 7.07 (1H, d, $J = 1.9$, H-5); 6.83 (1H, d, $J = 10.3$, H-4); 6.67 (2H, m, H-4',6'); 6.40 (1H, d, $J = 8.0$, H-7'); 5.76 (1H, d, $J = 10.3$, H-3); 3.77 (3H, s, OCH_3); 2.67 (3H, s, N– CH_3); 2.25 (3H, s, CH_3); 1.29 (3H, s, C(3)– CH_3); 1.18 (3H, s, C(3)– CH_3). ^{13}C NMR spectrum (CDCl_3), δ ppm: 188.4; 155.1; 153.5; 141.5; 137.4; 132.8; 128.6; 128.2; 126.8; 121.7; 119.7; 119.5; 110.8; 109.0; 106.5; 105.3; 55.4; 51.6; 28.8; 25.1; 19.7 (2C). Found, %: C 75.57; H 6.59; N 3.95. $\text{C}_{35}\text{H}_{39}\text{ClN}_2\text{O}_7$. Calculated, %: C 75.62; H 6.63; N 4.01.

(E)-2-[2-(3-Formyl-2-hydroxy-5-methylphenyl)vinyl]-5-methoxy-1,3,3-trimethyl-3H-indolium perchlorate (5). A solution of spiropyran **6** (18 mg, $5 \cdot 10^{-5}$ mol) in CHCl_3 was treated with 1 drop (~ 0.01 ml) of concd HClO_4 . The solvent was evaporated under ambient atmosphere. Yield 0.015 g (65%), orange crystals, mp 244–245°C. IR spectrum, ν , cm^{-1} : 1642 (C=O), 1601 (C=C), 1294 (C–N Ar), 1065 (ClO_4^-). ^1H NMR spectrum ($\text{DMSO}-d_6$), δ , ppm (J , Hz): 11.70 (1H, s, OH); 10.08 (1H, s, CHO); 8.32 (1H, d, $J = 16.6$, H-12'); 8.29 (1H, d, $J = 1.9$, H-7'); 7.81 (2H, d, $J = 8.8$, H-5',7"); 7.70 (1H, d, $J = 16.6$, H-13'); 7.49 (1H, d, $J = 2.4$, H-4"); 7.16 (1H, dd, $J = 8.8$, $J = 2.4$, H-6"); 4.08 (3H, s, N^+-CH_3); 3.86 (3H, s, OCH_3); 2.37 (3H, s, CH_3); 1.73 (6H, s, 2C(3)– CH_3). ^{13}C NMR spectrum ($\text{DMSO}-d_6$), δ , ppm: 196.1 (CHO); 179.4 (C-2"); 161.0 (C-5"); 158.1 (C-9"); 145.6 (C-10"); 143.5 (C-12"); 137.6 (C-5'); 136.6 (C-7"); 135.1 (C-8"); 129.7 (C-6'); 122.9 (C-8'); 122.1 (C-9"); 116.4 (C-7"); 114.8 (C-6"); 114.1 (C-13"); 108.6 (C-4"); 56.1 (OCH_3); 52.0 (C-3"); 34.6 (N^+-CH_3); 25.6 (C(3)– CH_3); 19.6 (CH_3). Found, %: C 58.62; H 5.78; N 3.05; Cl 7.64. $\text{C}_{22}\text{H}_{24}\text{ClNO}_7$. Calculated, %: C 58.73; H 5.34; N 3.11; Cl 7.90.

X-ray structural analysis of compound 5. The unit cell parameters for the crystal and the three-dimensional array of intensities were determined on an Xcalibur automatic diffractometer (MoK α radiation, graphite monochromator, EOS detector). Absorption was accounted for empirically according to the Multiscan procedure. The structure was solved by direct method and refined according to full-matrix method of least squares by F^2 using the SHELXTL program in anisotropic approximation for non-hydrogen atoms. The majority of H atoms were located in the crystal structure by difference Fourier synthesis of the electron density, then the coordinates and isotropic temperature parameters of all H atoms were calculated by the method of least squares using the riding model.⁴⁴ The analysis and visualization of X-ray crystallography results were performed by using the Mercury software suite.⁴⁵ The complete crystallographic dataset was deposited at the Cambridge Crystallographic Data Center (deposit CCDC 2182739).

The Hirschfeld surfaces were calculated at the DFT-B3LYP level with 6-311G(d,p) basis set, using the CrystalExplorer v21.5 program.⁴⁶

Quantum-chemical modeling was performed with the Orca 5.0.3 software^{47,48} at the density functional theory level, using a three-parameter Lee–Yang–Parr functional

(B3LYP)⁴⁹ and 6-311G(d,p) basis set.⁵⁰ The C-PCM solvation model was applied (EtOH). The character of the identified critical points was established by analytical calculation of the matrix of constants. The Hirschfeld analysis of atomic populations was performed with the Multiwfn software.⁵¹ Visualization of the results was achieved with the Chemcraft program.⁵²

Supplementary information file containing ^1H and ^{13}C NMR, COSY, $^1\text{H}-^{13}\text{C}$ HSQC, $^1\text{H}-^{13}\text{C}$ HMBC spectra, as well as the high-resolution mass spectrum of compound **3** and X-ray structural analysis results for compound **5** is available at the journal website <http://link.springer.com/journal/10593>.

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^1H and ^{13}C NMR spectra were acquired at the Molecular Spectroscopy Collective Use Center of the Southern Federal University.

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