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Directed synthesis of new spiro-fused photochromes of diarylethene series

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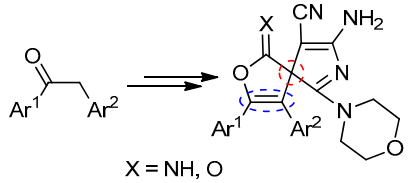


The reaction of tetracyanoethylated 1,2-diarylethanones with morpholine was used for directed synthesis of spiro-fused diarylethenes, 8-amino-1-imino(oxo)-6-morpholino-2-oxa-7-azaspiro[4.4]nona-3,6,8-triene-9-carbonitriles. The intermediates in this process were tetracyanoalkanone salts. The formation of spiranes was sensitive to the nature of aromatic substituents at the carbonyl group of 3,4-diaryl-4-oxobutane-1,1,2,2-tetracarbonitriles. The obtained spiro-fused diarylethenes exhibited photochromic properties.

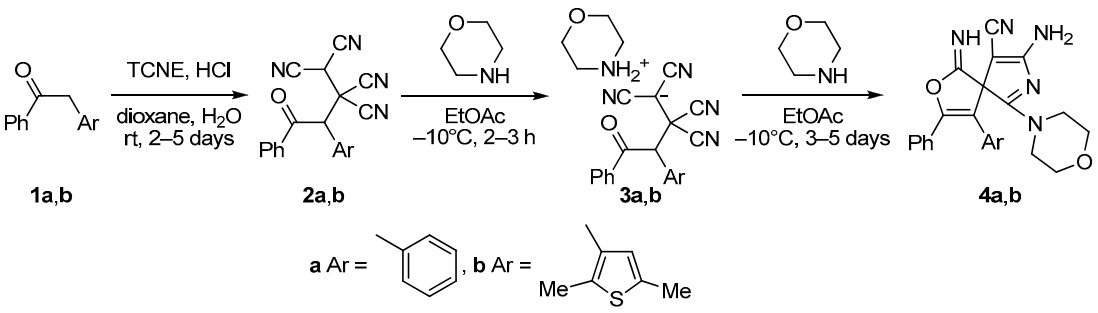
Keywords: 1,2-diarylethanones, diarylethenes, tetracyanoethylene, ethene linker, non-bonded strain, photochromes, spiro compounds, spirofusion, tetracyanoethylation.

Diarylethenes (DAE, dihetarylethenes) are subject to intense study due to the possibility of using these compounds as photosensitive components in various applications, in particular, information processing,[1–4] optical switches for organic electronics,[5–7] and biosensors.[8]

The potential for practical applications of DAE in the indicated areas motivate synthetic studies of photochromes with precisely designed photophysical parameters, such as thermal stability of the photoinduced form,[9–15] quantum yield of the forward and reverse photoreaction,[16–20] and the phototransformation cyclicity.[21–24] An important direction of study, with the goal of improving the practical characteristics of DAE, is the development of synthetic methods for obtaining DAE with intramolecular non-covalent interactions and steric hindrance.[25–31] One of the methods for creating a non-covalent interaction in DAE is the introduction of spiro-fused structures at the ethene linker. We should note that only isolated examples of spiro-fused DAE are known.[31–33] However, based on the current data, it is expected that the presence of spiro-fused moiety at the ethene linker could be used to confer certain useful properties to DAE. For example, some of the best forward quantum reaction yields have been demonstrated for spiro-fused DAE specifically due to the non-covalent interaction, caused by the presence of spirofusion.[31] By introducing or removing spirofusion it may be possible to tune the ability of DAE to undergo photochromic transformations.[32] The introduction of spirofusion may also be used for the preparation of DAE with several photoswitchable fragments.[33] The presented data show the importance of developing new approaches to the synthesis of diarylethenes featuring a rare combination of structural moieties, in particular spiro-fused systems. With this in mind, we set out to expand the range of available methods for the synthesis of DAE with spirofusion at the ethene linker.

Recently we demonstrated a new approach to the synthesis of photochromic DAE, based on the transformations of intermediates obtained by reactions of tetracyanoethylene (TCNE) with 1,2-diarylethanones, namely, 3,4-diaryl-4-oxobutane-1,1,2,2-tetracarbonitriles.[34] At the same time, it is known that 4-oxoalkane-1,1,2,2-tetracarbonitriles based on some aliphatic and alkylaromatic ketones react with amines forming spiro compounds, containing an

Scheme 1



alkylarylethene or dialkylethene fragment.[35,36] The introduction of tetracyanoethylated 1,2-diaryl ketones into these reactions allows to obtain DAE with spirofusion at the ethene linker.

Our initial objective was the preparation of tetracyanoethylated 1,2-diarylethanones **2a**,**b**. In order to achieve this, tetracyanoethylene was reacted with the simplest 1,2-diaryl ketone, deoxybenzoin (**1a**), as well as its analog, 2-(2,5-dimethylthiophen-3-yl)-1-phenylethanone (**1b**) (Scheme 1).

This reaction resulted in the formation of 3-aryl-4-oxo-4-phenylbutane-1,1,2,2-tetracarbonitriles **2a**,**b** in 83–87% yields. The selection of ketones **1a**,**b** as the starting materials for tetracyanoethylation was based on the presence of a phenyl substituent at the carbonyl group. It is known that adducts of TCNE with other 1-phenyl ketones can be converted to spiro compounds by the action of amines.[35] The next step in the synthesis of DAE with spirofusion in the ethene bridge structure was the interaction of compounds **2a**,**b** with morpholine. The final products of this reaction were identified as 8-amino-4-aryl-1-imino-6-(morpholin-4-yl) -3-phenyl-2-oxa-7-azaspiro[4.4]-nona-3,6,8-triene-9-carbonitriles **4a**,**b** (Scheme 1). The reaction was accompanied by the formation of tetracyanoalkanone salts, morpholinium 3-aryl-4-oxo-4-phenyl-1,1,2,2-tetracyanobutan-1-ides **3a**,**b**, which were produced by the initial interaction of CH acids **2a**,**b** with morpholine. These salts can be isolated as individual compounds and transformed either to the starting ketones **2a**,**b** by the action of HCl or converted to spiranes **4a**,**b** in the presence of morpholine.

The DAE with 1,2-dithienyl fragments is known to have particularly promising practical properties.[3] For this reason, our next objective was to convert 3,4-bis(2,5-dimethylthiophen-3-yl)-4-oxobutane-1,1,2,2-tetracarbonitrile **2c**, the synthesis of which we have described previously,[34] to the spiro compound **4c**. We found that in this case the process stopped at the stage of morpholinium 3,4-bis(2,5-dimethylthiophen-3-yl)-1,1,2,2-tetracyano-4-oxobutan-1-ide **3c** (Scheme 2).

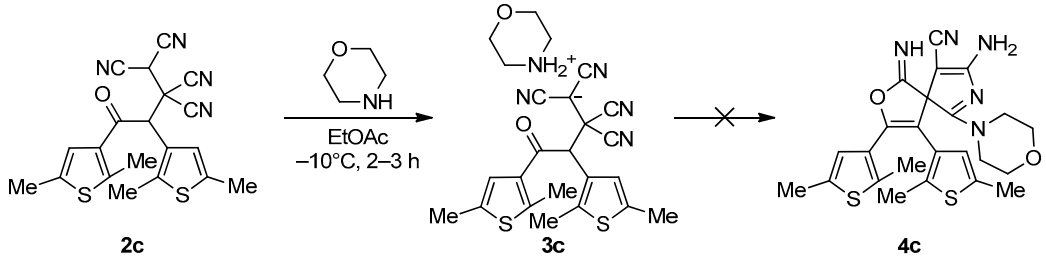
It should be noted that salts similar to compound **3** can rarely be isolated and characterized. For example, such salts are known for cations of copper and silver, as well as ammonium.[37] This is the first case when salts of this type with organic cations have been isolated and characterized, although their presence has been implied at the initial stage of many transformations of 4-oxoalkane-1,1,2,2-tetracarbonitriles in basic media.[35,38–41]

Compounds **3a**–**c** were found to be unstable in solutions, therefore suitable NMR spectra could not be acquired. The actual spectra contained a multitude of signals, which could not be assigned. The structure of salts could be confirmed by IR spectroscopy, mass spectrometry, and X-ray structural analysis. The IR spectra contained carbonyl group absorption bands at 1689–1694 cm^{-1}, strong cyano group bands of the $C^-(CN)_2$ fragment in the region of 2149–2155 cm^{-1}, and unconjugated CN group bands at 2243–2247 cm^{-1}. Mass spectral fragment ions corresponding to the loss of cyanide and hydride from the structure of anion ($[M–O(CH_2)_2NH–HCN]^+$) were detected with 19–41% intensity.

The structure of salts **3a**–**c** was unequivocally proved by monocrystal X-ray structural analysis, using the salt **3c** as example (Fig. 1). The crystal structure featured an association between morpholinium cation and two neutral morpholine molecules, as shown in Figure 2. The molecular triad was linked with strong hydrogen bonds: N(5)–H(51)···N(6^i) (1+*x*, *y*, *z*) and N(5)–H(5) ···N(7^{ii}) (1–*x*, 1–*y*, –*z*). Taking into account the possibility of proton transfer in the crystalline state from one morpholine molecule to another, the cation in this compound can be assigned with the structure $[O(CH_2)_2NH]_3H^+$ (Fig. 2).

A possible reason why spirane **4c** was not formed might be the deactivation of carbonyl group by electron-donating 2,5-dimethylthienyl fragment, adjacent to the carbonyl group of ketone **2c**. In the case of analogous structure **2b**, containing a phenyl substituent instead of 2,5-dimethylthienyl fragment at position 4, the formation of spirane **4b** was observed. This fact demonstrated the sensitivity of

Scheme 2



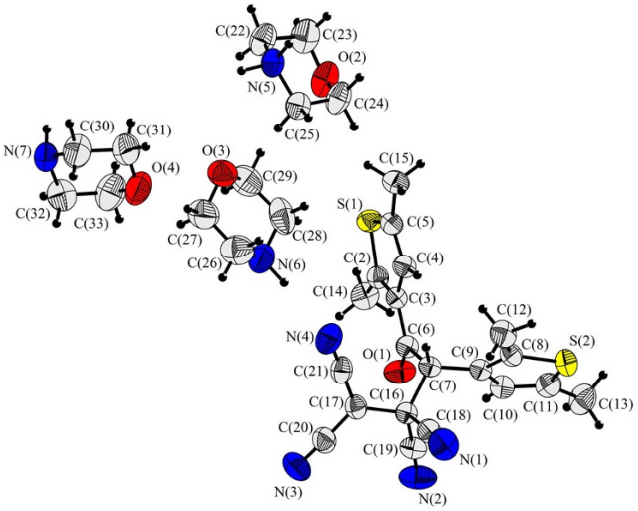


Figure 1. Molecular structure of compound **3c** with atoms represented by thermal vibration ellipsoids of 50% probability.

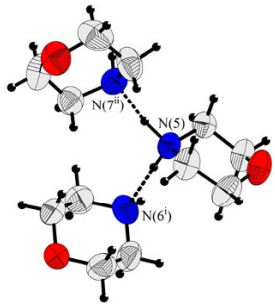


Figure 2. The structure of cation $[O(CH_2)_2NH]_3H^+$ in crystal of compound **3c** with atoms represented by thermal vibration ellipsoids of 50% probability.

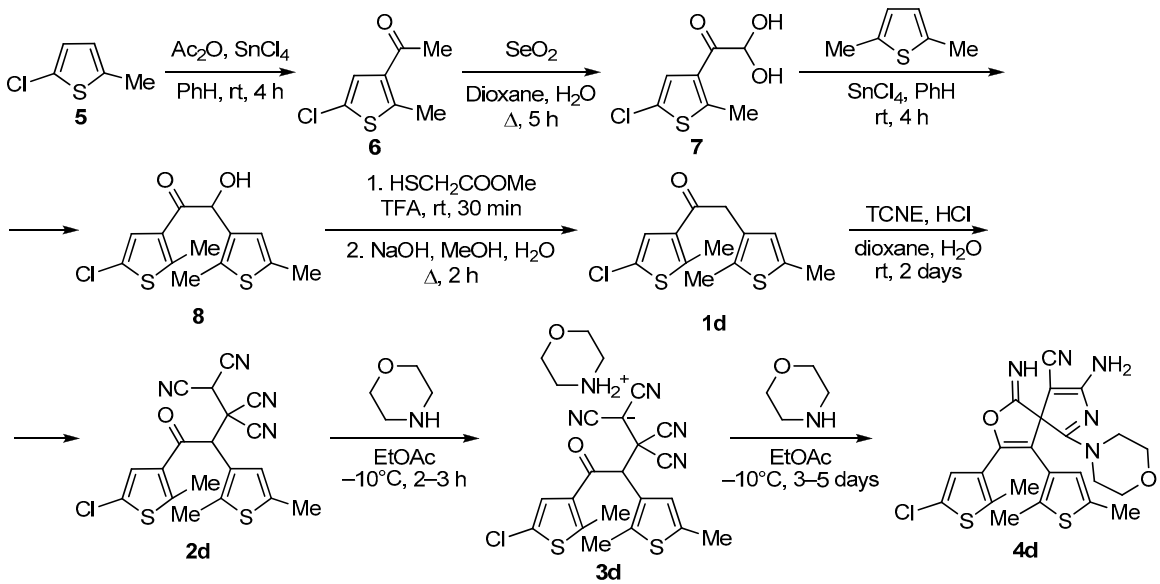
reactions leading to spiranes **4** to the nature of aromatic substituent at the carbonyl group of compounds **2**.

It has been proposed that the presence of electron-withdrawing substituents in the thiophene ring adjacent to the CO group of compounds **2** should facilitate the formation of spiranes with the structure **4**. For this reason, reaction with morpholine was performed with the custom synthesized 4-(5-chloro-2-methylthiophen-3-yl)-3-(2,5-dimethylthiophen-3-yl)-4-oxobutane-1,1,2,2-tetracarbonitrile **2d**, containing a chlorine atom at position 5 of the thiophene ring at the CO group (Scheme 3). As expected, the ketone **2d** could be converted to an analog of spiranes **4a**,**b**, 8-amino-3-(5-chloro-2-methylthiophen-3-yl)-4-(2,5-dimethylthiophen-3-yl)-1-imino-6-(morpholin-4-yl)-2-oxa-7-azaspiro[4.4]nona-3,6,8-triene-9-carbonitrile **4d**, albeit at lower yield (44%).

We obtained the ketone **1d** for the first time according to Scheme 3 from 2-chloro-5-methylthiophene (**5**). Compound **5** was acylated in anhydrous benzene in the presence of $SnCl_4$, leading to the known[42] 1-(5-chloro-2-methylthiophen-3-yl)-ethanone (**6**). The next stage was synthesis of 1-(5-chloro-2-methylthiophen-3-yl)-2,2-dihydroxyethanone (**7**) by the action of selenium oxide in 1,4-dioxane on acetylthiophene **6**. The subsequent reaction of glyoxal **7** with 2,5-dimethylthiophene in anhydrous benzene in the presence of $SnCl_4$ led to 1-(5-chloro-2-methylthiophen-3-yl)-2-hydroxy-2-(2,5-dimethylthiophen-3-yl)ethanone (**8**). The acyloin **8** was then converted to 1-(5-chloro-2-methylthiophen-3-yl)-2-(2,5-dimethylthiophen-3-yl)ethanone (**1d**) by the action of methyl thioglycolate in trifluoroacetic acid with subsequent treatment of reaction mixture with aqueous methanol solution of NaOH. The interaction of ketone **1d** with tetracyanoethylene leading to the formation of adduct **2d** was accomplished in 1,4-dioxane analogously to the preparation of compounds **2a**–**c**.

The structure of spiranes **4a**,**b**,**d** was confirmed by IR spectroscopy, ^1H and ^{13}C NMR spectroscopy, as well as mass spectrometry. The mass spectra contained characteristic molecular ion peaks with 2–100% intensity. According to IR spectra, the structures contained amino and imino groups (bands at 3130–3343 cm^{-1}) and conjugated cyano groups (strong bands at 2165–2171 cm^{-1}). According to the obtained data, there was duplication of ^1H and ^{13}C NMR signals. It was found that ^1H NMR spectra contained amino group singlets at 7.05–7.21 ppm and imine proton

Scheme 3



peaks at 9.09–9.41 ppm. A notable feature in the ^{1}H NMR spectra was the broadening of morpholine ring proton signals in the region of 3.30–3.90 ppm. The ^{13}C NMR signals of the CN group carbon were observed in the spectrum of compound **4b** at 119.0 and 119.2 ppm, while the signals of the C=NH group and C atoms at positions 2 and 5 of the 3*H*-pyrrole ring were in the region of 163.8–172.2 ppm. The duplication of NMR signals was explained by *E*- and *Z*-configuration of the C=NH bond, in which the proton at the nitrogen atom can assume various positions. A similar situation was earlier described by us for analogs of compounds **4**.[35,36]

The synthesized spiranes **4b**,**d**, containing a potentially photosensitive 1,2-diarylethene fragment, were found to be photochromic (Scheme 4). The irradiation of colorless solutions in MeCN with UV light at 312 nm caused the formation of colored photoinduced form **9b**,**d**. The opposite transition, fading of the color, occurred under irradiation of the solution with visible light.

Compounds **4b**,**d**, compared to known photochromes,[1] were characterized by a low number of cycles: by-product absorption bands appeared in the spectra after 2–3 cycles of reversible phototransformations. A possible reason for the poor photochromic properties may be molecular contact between the morpholine fragment and aromatic substituent at position 4 of the spiro system **4**.

This assumption was confirmed by the broadening of morpholine ring proton ^{1}H NMR signals, which appeared as one significantly broadened signal at 3.30–3.90 ppm. Morpholine proton signals would typically exist as two triplets or two broadened singlets.[43] The possibility of steric contact between the NCH_2 proton of the morpholine ring and the neighboring substituents was also confirmed by X-ray structural analysis data for an analog of compounds **4**.[39]

The structure of spiranes **4** also allowed to propose the existence of equilibrium between the enol **4'** and ketone **4''** forms in solution phase (Scheme 5). This assumption was supported by the fact that we have previously described compounds of type **4''** for structures that are analogous to spiranes **4**.[39,40] This equilibrium may be the reason for the less pronounced photochromic properties of spiranes **4**.

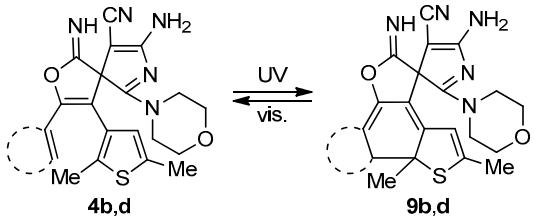
In order to exclude the processes presented in Scheme 5, we hydrolyzed the imino group in compounds **4a**,**b**,**d** with dilute HCl (Scheme 6). As a result, we obtained 8-amino-3,4-diaryl-(6-morpholin-4-yl)-1-oxo-2-oxa-7-azaspiro[4.4]-nona-3,6,8-triene-9-carbonitriles **10a**,**b**,**d**.

The structure of spiranes **10a**,**b**,**d** was confirmed by IR spectroscopy, ^{1}H and ^{13}C NMR spectroscopy, and mass spectrometry. The mass spectra contained molecular ion peaks with 8–76% intensity. The most informative IR absorption bands were at 1785–1791 cm^{-1}, corresponding to the stretching vibrations of C=O bonds in the γ-lactone moiety, as well as amino group absorption bands at 3154–3345 cm^{-1}, and strong bands due to conjugated cyano groups at 2165–2173 cm^{-1}. In contrast to ^{1}H and ^{13}C spectra of imines **4a**,**b**,**d**, ^{1}H and ^{13}C NMR signals of spiranes **10a**,**b**,**d** were not duplicated due to the absence of *E*/*Z*-isomerism after the C=NH→C=O conversion. There were ^{1}H NMR signals due to amino groups and aromatic protons at 7.23–7.46 ppm. Importantly, morpholine ring proton signals, similarly to the case of spiranes **4a**,**b**,**d**, appeared as broadened peaks at 3.20–3.80 ppm. This observation indicated the presence of a steric contact between the morpholine fragment and aromatic substituent also in the case of hydrolyzed derivatives **10a**,**b**,**d**. In the case of spiranes **10a**,**b**,**d**, ^{13}C NMR signals had similar chemical shifts to the respective ^{13}C NMR signals of compounds **4b**, indicating the preservation of carbon atom skeleton during the treatment of imines **4** with hydrochloric acid.

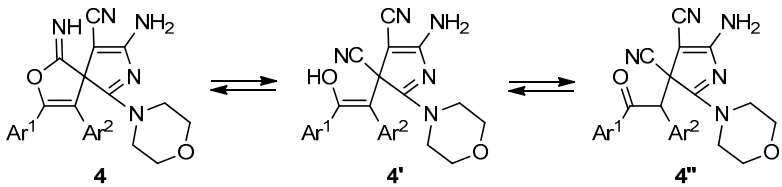
The structure of spiranes **10a**,**b**,**d** was unequivocally proved by X-ray structural analysis in the case of compound **10a** (Fig. 3). The X-ray structural data for compound **10a** showed the presence of non-bonded strain in the molecule, caused by the position of the proton at the morpholine C(9) carbon relative to the *o*-H atom at the phenyl ring C(20) carbon, located within 2.23 Å of each other. This distance was less than the sum of van der Waals radii for these atoms. We should also note that the morpholine fragment in the crystal of spirane **10a** was disordered.

The tautomeric processes described in Scheme 5 are impossible for compounds **10**. The structures **10**, similarly

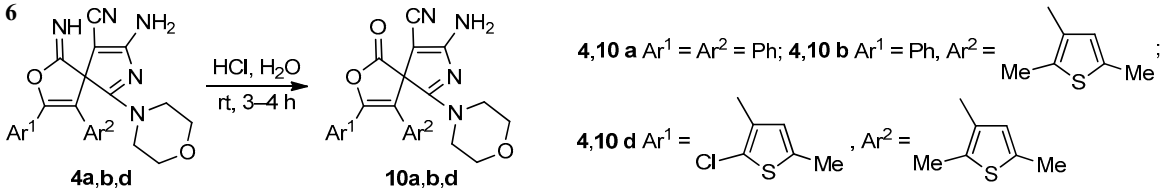
Scheme 4



Scheme 5



Scheme 6



to their analogs **4**, had unremarkable photochromic properties: substantial photodegradation was observed already after 2–3 cycles of phototransformations. This fact pointed to the key importance of steric contact between morpholine and the aryl substituent, likely hindering the phototransformations according to Scheme 4. The assumption that spirofusion at the ethene linker may create obstacles to photochromism in 1,2-dithienyl-substituted DAE was confirmed by literature data.[32] Other examples of molecules with steric contacts between substituents in the aryl group and substituents at the ethene linker also show the absence of photochromism.[44]

Thus, we have developed a new method for the synthesis of diarylethenes with spirofusion at ethene linker. Non-bonded strain has been found in the molecules of these compounds, caused by steric contact between atoms of the spiro-fused systems. The presence of such intramolecular contact may be one of the reasons for poor photochromic properties of the obtained diarylethenes.

Experimental

UV spectra were recorded on an SF-2000 spectrophotometer for MeCN solutions. IR spectra were obtained on an FSM-1202 FT-IR spectrometer for thin film samples (suspensions in Nujol). ^{1}H and ^{13}C NMR spectra were acquired on a Bruker DRX-500 instrument (500 and 125 MHz, respectively) in acetone-d_6 (compounds **2b**,**d**) and DMSO-d_6 (the rest of the compounds), with TMS as internal standard. Mass spectra were recorded on a Finnigan MAT INCOS-50 instrument (electron impact energy 70 eV). Elemental analysis was performed on a vario MICRO cube CHN-analyzer. Melting points were determined on an M-560 apparatus. The reaction progress and purity of the obtained compounds were controlled by TLC on Sorbfil PTSH-AF-A-UF plates (eluent 9:1 EtOAc–hexane), visualization under UV light, with iodine vapor, or thermal decomposition. Tetracarbonitriles **2a**,**c** were synthesized according to a published procedure.[34]

Preparation of 4-aryl-3-(2,5-dimethylthiophen-3-yl)-4-oxobutane-1,1,2,2-tetracarbonitriles 2b,d (General method). TCNE (0.64 g, 5 mmol) and two drops of conc. HCl were added to a solution of the corresponding 1,2-diarylethanone **1b**,**d** (5 mmol) in 1,4-dioxane (20 ml). The obtained colored solution was stirred for 2–3 min at 35–40°C, until complete dissolution of TCNE. The reaction mixture was left in a sealed vessel for 2–5 days at room temperature, while checking for the presence of TCNE (formation of a blue hydroquinone complex). After the disappearance of TCNE, the solution was cooled to 0–5°C, treated with ice water (100 ml), and stirred until the formation of homogeneous suspension. The obtained precipitate was filtered off, washed with water and cold 5:1 water–isopropanol mixture.

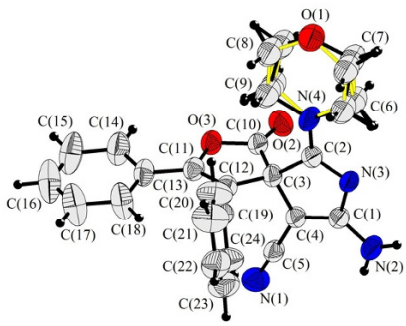


Figure 3. Molecular structure of compound **10a** with atoms represented by thermal vibration ellipsoids of 50% probability.

3-(2,5-Dimethylthiophen-3-yl)-4-oxo-4-phenylbutane-1,1,2,2-tetracarbonitrile (2b). Yield 1.49 g (83%), light-beige powder, mp 68–69°C (decomp.). IR spectrum, ν, cm^{-1}: 2252 (C≡N), 1692 (C=O). ^{1}H NMR spectrum, δ, ppm: 2.32 (3H, s, CH_3); 2.76 (3H, s, CH_3); 5.79 (1H, s, CH); 5.94 (1H, s, CH); 6.63 (1H, s, CH); 7.62–7.71 (3H, m, H Ph); 7.50–7.57 (2H, m, H Ph). Found, %: C 67.09; H 3.90; N 15.67. $C_{20}H_{14}N_4OS$. Calculated, %: C 67.02; H 3.94; N 15.63.

4-(5-Chloro-2-methylthiophen-3-yl)-3-(2,5-dimethylthiophen-3-yl)-4-oxobutane-1,1,2,2-tetracarbonitrile (2d). Yield 1.79 g (87%), light-beige powder, mp 86–87°C (decomp.). IR spectrum, ν, cm^{-1}: 2250 (C≡N), 1696 (C=O). ^{1}H NMR spectrum, δ, ppm: 2.37 (3H, s, CH_3); 2.72 (3H, s, CH_3); 2.73 (3H, s, CH_3); 5.61 (1H, s, CH); 5.73 (1H, s, CH); 6.67 (1H, s, CH); 7.11 (1H, s, CH). Found, %: C 55.30; H 3.13; N 13.59. $C_{19}H_{13}N_4ClOS_2$. Calculated, %: C 55.27; H 3.17; N 13.57.

Preparation of salts 3a–d (General method). Morpholine (0.13 g, 1.5 mmol) was added to a vigorously stirred and cooled (–10°C) solution of the respective 3,4-diaryl-4-oxobutane-1,1,2,2-tetracarbonitrile **1** (0.5 mmol) in EtOAc (2 ml). The stirring was continued for 30–60 min. The precipitate started to form during stirring, and the precipitation of salts was complete after 2–3 h. The solid product was filtered off, washed with cooled Et_2O, and dried in a vacuum desiccator until constant mass.

Morpholinium 4-oxo-3,4-diphenyl-1,1,2,2-tetracyanobutan-1-ide (3a). Yield 0.174 g (86%), light-brown powder, mp 89–90°C (decomp.). IR spectrum, ν, cm^{-1}: 2246 (C≡N), 2151 (C≡N), 1694 (C=O). Mass spectrum, *m/z* (I_{rel}, %): 297 [M–O(CH$_2$)$_2$NH–HCN]$^+$ (23), 105 (100). Found, %: C 70.13; H 5.17; N 16.90. $C_{24}H_{21}N_5O_2$. Calculated, %: C 70.06; H 5.14; N 17.02.

Morpholinium 3-(2,5-dimethylthiophen-3-yl)-4-oxo-4-phenyl-1,1,2,2-tetracyanobutan-1-ide (3b). Yield 0.160 g (72%), light-brown powder, mp 86–87°C (decomp.). IR spectrum, ν, cm^{-1}: 2243 (C≡N), 2149 (C≡N), 1691 (C=O). Mass spectrum, *m/z* (I_{rel}, %): 331 [M–O(CH$_2$)$_2$NH–HCN]$^+$ (19), 105 (100). Found, %: C 64.76; H 5.23; N 15.63. $C_{24}H_{23}N_5O_2S$. Calculated, %: C 64.70; H 5.20; N 15.72.

Morpholinium 3,4-bis(2,5-dimethylthiophen-3-yl)-4-oxo-1,1,2,2-tetracyanobutan-1-ide (3c). Yield 0.160 g (67%), light-brown powder, mp 92–93°C (decomp.). IR spectrum, ν, cm^{-1}: 2247 (C≡N), 2155 (C≡N), 1689 (C=O). Mass spectrum, *m/z* (I_{rel}, %): 365 [M–O(CH$_2$)$_2$NH–HCN]$^+$ (41), 139 (100). Found, %: C 60.17; H 5.28; N 14.49. $C_{24}H_{25}N_5O_2S_2$. Calculated, %: C 60.10; H 5.25; N 14.60.

Morpholinium 4-(5-chloro-2-methylthiophen-3-yl)-3-(2,5-dimethylthiophen-3-yl)-4-oxo-1,1,2,2-tetracyanobutan-1-ide (3d). Yield 0.167 g (63%), light-brown powder, mp 81–82°C (decomp.). IR spectrum, ν, cm^{-1}:

2249 (C≡N), 2153 (C≡N), 1686 (C=O). Mass spectrum, *m/z* (I_{rel}, %): 387 [M(^{37}Cl)–O(CH$_2$)$_2$NH–HCN]$^+$ (9), 385 [M(^{35}Cl)–O(CH$_2$)$_2$NH–HCN]$^+$ (28), 161 (35), 159 (100). Found, %: C 55.33; H 4.48; N 13.92. $C_{24}H_{25}N_5O_2S_2$. Calculated, %: C 55.25; H 4.43; N 14.01.

Preparation of spiranes 4a,b,d (General method). Morpholine (0.13 g, 1.5 mmol) was added to a stirred and cooled (–10°C) solution of the respective 3,4-diaryl-4-oxobutane-1,1,2,2-tetracarbonitrile **1** (0.5 mmol) in EtOAc (4 ml). The process was accompanied by the formation of yellow-orange solution. The reaction mixture was left in a sealed vessel at –10°C. The solids that formed after 3–5 days were filtered off and washed with cold EtOAc.

8-Amino-1-imino-6-(morpholin-4-yl)-3,4-diphenyl-2-oxa-7-azaspiro[4.4]nona-3,6,8-triene-9-carbonitrile (4a). Yield 0.156 g (76%), light-beige powder, mp 155–156°C (decomp.). IR spectrum, ν, cm^{-1}: 3146–3343 (NH, NH$_2$), 2169 (C≡N). UV spectrum, λ_{max}, nm (log ε): 339 (3.80). ^{1}H NMR spectrum, δ, ppm: 3.35–3.80 (8H, m, H morpholine); 7.10 (1.1H, s) and 7.17 (0.9H, s, NH$_2$); 7.18–7.22 (10H, m, H Ph); 9.18 (0.55H, s) and 9.41 (0.45H, s, NH); isomer ratio 55:45. Mass spectrum, *m/z* (I_{rel}, %): 411 [M]$^+$ (4), 105 (45), 77 (100). Found, %: C 70.11; H 5.11; N 17.09. $C_{24}H_{21}N_5O_2$. Calculated, %: C 70.06; H 5.14; N 17.02.

8-Amino-1-imino-4-(2,5-dimethylthiophen-3-yl)-6-(morpholin-4-yl)-3-phenyl-2-oxa-7-azaspiro[4.4]nona-3,6,8-triene-9-carbonitrile (4b). Yield 0.154 g (69%), light-beige powder, mp 131–132°C (decomp.). IR spectrum, ν, cm^{-1}: 3130–3339 (NH, NH$_2$), 2165 (C≡N). UV spectrum, λ_{max}, nm (log ε): 316 (3.96). ^{1}H NMR spectrum, δ, ppm: 1.92 (1.62H, s) and 1.94 (1.38H, s, CH$_3$); 2.37 (1.38H, s) and 2.39 (1.62H, s, CH$_3$); 3.30–3.90 (8H, m, H morpholine); 6.44 (0.46H, s) and 6.48 (0.54H, s, H thiophene); 7.05 (1.08H, s) and 7.15 (0.92H, s, NH$_2$); 7.30–7.40 (5H, m, H Ph); 9.16 (0.54H, s) and 9.38 (0.46H, s, NH); isomer ratio 54:46. ^{13}C NMR spectrum, δ, ppm: 13.8; 13.9; 15.1; 45.4; 46.5; 60.5; 65.5; 65.6; 66.5; 68.5; 110.1; 110.4; 119.0; 119.2; 124.9; 125.1; 126.2; 126.7; 126.8; 128.7; 128.8; 129.8; 135.3; 136.2; 136.3; 148.6; 149.0; 163.8; 168.4; 169.9; 170.3; 171.3; 172.2. Mass spectrum, *m/z* (I_{rel}, %): 445 [M]$^+$ (100), 340 (20), 105 (15), 77 (19). Found, %: C 64.74; H 5.17; N 15.74. $C_{24}H_{23}N_5O_2S$. Calculated, %: C 64.70; H 5.20; N 15.72.

8-Amino-3-(5-chloro-2-methylthiophen-3-yl)-1-imino-4-(2,5-dimethylthiophen-3-yl)-6-(morpholin-4-yl)-2-oxa-7-azaspiro[4.4]nona-3,6,8-triene-9-carbonitrile (4d). Yield 0.101 g (44%), light-beige powder, mp 125–127°C (decomp.). IR spectrum, ν, cm^{-1}: 3151–3322 (NH, NH$_2$), 2171 (C≡N). UV spectrum, λ_{max}, nm (log ε): 303 (3.85). ^{1}H NMR spectrum, δ, ppm: 1.81 (1.71H, s) and 1.82 (1.29H, s, CH$_3$); 2.02 (1.71H, s) and 2.03 (1.29H, s, CH$_3$); 2.33 (1.29H, s) and 2.35 (1.71H, s, CH$_3$); 3.30–3.85 (8H, m, H morpholine); 6.39 (0.43H, s) and 6.43 (0.57H, s, H thiophene); 6.87 (0.57H, s) and 6.89 (0.43H, s, H thiophene); 7.11 (1.14H, s) and 7.21 (0.86H, s, NH$_2$); 9.09 (0.57H) and 9.36 (0.43H, s, NH); isomer ratio 57:43. Mass spectrum, *m/z* (I_{rel}, %): 499 [M(Cl^{35})]$^+$ (2), 161 (33), 159 (100). Found, %: C 55.29; H 4.41; N 14.09. $C_{23}H_{22}N_5ClO_2S_2$. Calculated, %: C 55.25; H 4.43; N 14.01.

1-(5-Chloro-2-methylthiophen-3-yl)ethanone (6). Solution of $SnCl_4$ (31.8 g, 0.122 mol) in anhydrous benzene (30 ml) was added dropwise to a solution of 2-chloro-5-methylthiophene (**5**) (13.2 g, 0.1 mol) and Ac_2O (10.2 g, 0.1 mol) in anhydrous benzene (100 ml), while keeping the temperature not higher than 15–20°C. The reaction mixture was stirred for 4 h at room temperature, then poured into a mixture of ice water (220 ml) and conc. HCl (55 ml). The organic layer was separated, washed with water (100 ml), saturated $NaHCO_3$ solution (100 ml), and again with water (100 ml). The solvent was removed by evaporation and the residue was distilled at reduced pressure, collecting the fraction with bp 140–150°C (25 mmHg). Care should be taken to prevent crystallization of the product in the condenser. Yield 13.6 g (78%), transparent crystals, mp 30–31°C. IR spectrum, ν, cm^{-1}: 1695 (C=O). ^{1}H NMR spectrum, δ, ppm: 2.45 (3H, s, CH$_3$); 2.60 (3H, s, COCH$_3$); 7.51 (1H, s, H thiophene). Mass spectrum, *m/z* (I_{rel}, %): 176 [M(Cl^{37})]$^+$ (18), 174 [M(Cl^{35})]$^+$ (51), 161 [M(Cl^{37})–CH$_3$]$^+$ (42), 159 [M(Cl^{35})–CH$_3$]$^+$ (98), 133 [M(Cl^{37})–Ac]$^+$ (6), 131 [M(Cl^{35})–Ac]$^+$ (18), 43 [CH$_3$CO]$^+$ (100), 15 [CH$_3$]$^+$ (59). Found, %: C 48.09; H 4.11. C_7H_7ClOS. Calculated, %: C 48.14; H 4.04.

1-(5-Chloro-2-methylthiophen-3-yl)-2,2-dihydroxyethanone (7). A solution of SeO_2 (7.7 g, 0.070 mol) in a mixture of 1,4-dioxane (50 ml) and water (3 ml) was stirred, heated to 50–55°C, and treated by the addition of acetylthiophene **6** (10.2 g, 0.059 mol). The obtained mixture was stirred and refluxed for 5 h, then cooled to room temperature, and the precipitated selenium was removed by filtration. The filtrate was evaporated under reduced pressure (25 mmHg), the residue was recrystallized from distilled water. Yield 7.65 g (63%), transparent crystals, mp 117–118°C. IR spectrum, ν, cm^{-1}: 3453 (OH), 1695 (CO). ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 2.63 (3H, s, CH$_3$); 5.36 (1H, t, *J* = 6.5, CH); 5.71 (2H, d, *J* = 6.5, 2OH); 7.58 (1H, s, H thiophene). Mass spectrum, *m/z* (I_{rel}, %): 208 [M(Cl^{37})]$^+$ (1), 206 [M(Cl^{35})]$^+$ (3), 161 [M(Cl^{37})–CH(OH)$_2$]$^+$ (41), 159 [M(Cl^{35})–CH(OH)$_2$]$^+$ (100). Found, %: C 40.58; H 3.44. $C_7H_7ClO_3S$. Calculated, %: C 40.69; H 3.41.

1-(5-Chloro-2-methylthiophen-3-yl)-2-hydroxy-2-(2,5-dimethylthiophen-3-yl)ethanone (8). 2,5-Dimethylthiophene (1.85 g, 0.016 mol) was added to a solution of glyoxal hydrate **7** (3.10 g, 0.015 mol) in anhydrous benzene (75 ml), followed by slow dropwise addition of $SnCl_4$ (3.92 g, 0.015 mol). The obtained solution was stirred for 4 h at room temperature. The mixture was then poured into ice water (150 ml), phases were separated, the aqueous layer was extracted with Et_2O (3×30 ml). The combined organic phases were washed with water (100 ml), saturated $NaHCO_3$ solution (100 ml), water (100 ml) and dried over anhydrous $MgSO_4$. The solvents were removed under vacuum, the residue was crystallized from *n*-C_6H_{14}. IR spectrum, ν, cm^{-1}: 1691 (C=O). Yield 3.36 g (75%), beige powder, mp 83–84°C. ^{1}H NMR spectrum, δ, ppm: 2.28 (3H, s, CH$_3$); 2.35 (3H, s, CH$_3$); 2.57 (3H, s, CH$_3$); 5.65 (1H, s, CH); 6.48 (1H, s, H thiophene); 7.40 (1H, s, H thiophene); OH was exchanged. Mass spectrum, *m/z* (I_{rel}, %): 302 [M(Cl^{37})]$^+$ (1), 300 [M(Cl^{35})]$^+$ (3), 161 (6), 159 (18), 141 (100), 113 (53).

Found, %: C 51.84; H 4.39. $C_{13}H_{13}ClO_2S_2$. Calculated, %: C 51.91; H 4.36.

1-(5-Chloro-2-methylthiophen-3-yl)-2-(2,5-dimethylthiophen-3-yl)ethanone (1d). Acyloin **8** (1.38 g, 0.0046 mol) was added to a stirred mixture of trifluoroacetic acid (6 ml) and methyl thioglycolate (2.4 g, 0.023 mol). The obtained dark-green solution was stirred for 30 min at room temperature, then carefully diluted while stirring with cold (5°C) solution of NaOH (9.0 g) in a mixture of MeOH (25 ml) and water (25 ml). The obtained mixture was refluxed for 2 h, then cooled to room temperature and diluted with ice water (200 ml). The obtained precipitate was filtered off under vacuum, washed with ice water until the washes became neutral. Yield 1.08 g (83%), beige powder, mp 38–39°C. IR spectrum, ν, cm^{-1}: 2247 (C≡N), 1697 (C=O). ^{1}H NMR spectrum, δ, ppm: 2.22 (3H, s, CH_3); 2.32 (3H, s, CH_3); 2.59 (3H, s, CH_3); 4.02 (2H, s, CH_2); 6.48 (1H, s, H thiophene); 7.62 (1H, s, H thiophene). Mass spectrum, *m*/*z* (I_{rel}, %): 286 $[M(Cl^{37})]^+$ (19), 284 $[M(Cl^{35})]^+$ (45), 161 (35), 159 (100). Found, %: C 54.89; H 4.54. $C_{13}H_{13}ClOS_2$. Calculated, %: C 54.82; H 4.60.

Preparation of spiranes 10a,b,d (General method). Suspension of the respective spirane **4a**,**b**,**d** (0.2 mmol) in 5:1 water–isopropanol mixture (2 ml) was treated with 2–3 drops of concentrated hydrochloric acid. The obtained suspension was stirred for 3–4 h at room temperature until the reaction was complete (TLC control), the precipitate that formed was filtered off, washed with water and isopropanol.

8-Amino-6-(morpholin-4-yl)-1-oxo-3,4-diphenyl-2-oxa-7-azaspiro[4.4]nona-3,6,8-triene-9-carbonitrile (10a). Yield 75 mg (91%), white powder, mp 294–295°C (decomp.). IR spectrum, ν, cm^{-1}: 3154–3320 (NH_2), 2165 (C≡N), 1788 (C=O). UV spectrum (MeCN), λ_{max}, nm (log ε): 332 (3.62). ^{1}H NMR spectrum, δ, ppm: 3.40–3.75 (8H, m, H morpholine); 7.23–7.45 (12H, m, H Ph, NH_2). ^{13}C NMR spectrum, δ, ppm: 46.3; 57.2; 65.7; 66.8; 110.8; 118.2; 126.1; 126.6; 127.0; 127.5; 128.8; 129.4; 129.6; 130.4; 148.7; 170.5; 171.1; 173.8. Mass spectrum, *m*/*z* (I_{rel}, %): 412 $[M]^+$ (17), 105 (92), 77 (100). Found, %: C 69.81; H 4.83; N 13.68. $C_{24}H_{20}N_4O_3$. Calculated, %: C 69.89; H 4.89; N 13.58.

8-Amino-4-(2,5-dimethylthiophen-3-yl)-6-(morpholin-4-yl)-1-oxo-3-phenyl-2-oxa-7-azaspiro[4.4]nona-3,6,8-triene-9-carbonitrile (10b). Yield 77 mg (86%), white powder, mp 275–276°C (decomp.). IR spectrum, ν, cm^{-1}: 3161–3339 (NH_2), 2170 (C≡N), 1791 (C=O). UV spectrum (MeCN), λ_{max}, nm (log ε): 318 (3.82). ^{1}H NMR spectrum, δ, ppm: 1.94 (3H, s, CH_3); 2.39 (3H, s, CH_3); 3.40–3.80 (8H, m, H morpholine); 6.50 (1H, s, H thiophene); 7.34–7.44 (7H, m, H Ph, NH_2). ^{13}C NMR spectrum, δ, ppm: 14.0; 15.7; 46.6; 57.4; 65.7; 66.9; 111.0; 118.7; 124.9; 125.2; 126.8; 128.9; 129.8; 135.1; 135.7; 136.4; 149.3; 170.3; 170.9; 173.7. Mass spectrum, *m*/*z* (I_{rel}, %): 446 $[M]^+$ (79), 105 (100), 77 (98). Found, %: C 64.65; H 4.90; N 12.64. $C_{24}H_{22}N_4O_3S$. Calculated, %: C 64.56; H 4.97; N 12.55.

8-Amino-3-(5-chloro-2-methylthiophen-3-yl)-4-(2,5-dimethylthiophen-3-yl)-6-(morpholin-4-yl)-1-oxo-2-oxa-7-azaspiro[4.4]nona-3,6,8-triene-9-carbonitrile (10d). Yield 89 mg (89%), white powder, mp 266–267°C (decomp.). IR spectrum, ν, cm^{-1}: 3151–3345 (NH_2), 2173 (C≡N), 1785 (C=O). UV spectrum (MeCN), λ_{max}, nm (log ε): 307 (3.83). ^{1}H NMR spectrum, δ, ppm: 1.83 (3H, s, CH_3); 2.00 (3H, s, CH_3); 2.36 (3H, s, CH_3); 3.20–3.80 (8H, m, H morpholine); 6.44 (1H, s, H thiophene); 7.02 (1H, s, H thiophene); 7.46 (2H, s, NH_2). ^{13}C NMR spectrum, δ, ppm: 13.7; 14.9; 15.2; 46.5; 57.5; 65.7; 66.8; 111.4; 118.2; 125.3; 125.4; 129.1; 131.2; 134.3; 135.5; 135.8; 139.8; 149.7; 170.2; 171.0; 173.5. Mass spectrum, *m*/*z* (I_{rel}, %): 502 $[M(Cl^{37})]^+$ (3), 500 $[M(Cl^{35})]^+$ (8), 161 (35), 159 (100). Found, %: C 55.23; H 4.16; N 11.28. $C_{23}H_{21}ClN_4O_3S_2$. Calculated, %: C 55.14; H 4.22; N 11.18.

X-ray structural investigation of salt 3c. Crystals suitable for X-ray structural analysis were obtained by slow evaporation of reaction mixture without stirring. Monocrystal X-ray structural analysis of salt **3c** was performed on a STOE StadiVari Pilatus 100K diffractometer, using MoKα radiation. The data collection and processing, determination and refinement of unit cell parameters were performed with the STOE X-Area software suite. The structure was solved by direct method, using the SHELXS-97 software suite.[45] The visual rendering of molecule in crystalline state was performed with the DIAMOND program.[46] The complete X-ray structural data set for compound **3c** was deposited at the Cambridge Crystallographic Data Center (deposit CCDC 1059042).

X-ray structural investigation of spirane 10a. Crystals suitable for X-ray structural analysis were obtained by slow evaporation of compound **10a** solution in a 5:1 mixture of isopropanol–conc. HCl. Monocrystal X-ray structural analysis of spirane **10a** was performed on an Enraf-Nonius CAD4 diffractometer. The complete X-ray structural data set for compound **10a** was deposited at the Cambridge Crystallographic Data Center (deposit CCDC 1058585).

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