Arylsulfochlorination of β-aminopropioamidoximes giving 2-aminospiropyrazolylammonium arylsulfonates*

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The reaction of β-(morpholin-1-yl)propioamidoxime with aromatic sulfonyl chlorides (p-$XC_6H_4SO_2Cl$; X = CH_3O, CH_3, H, Br, Cl, NO_2) in chloroform in the presence of triethylamine does not produce expected *O*-arylsulfonyl-β-(morpholin-1-yl)propioamidoximes; instead, this reaction affords isomers of the latter compounds, 2-amino-8-oxa-1,5-diazaspiro[4.5]dec-1-ene-5-ammonium arylsulfonates. The structures of the reaction products were established by physicochemical methods, spectroscopy, and X-ray diffraction.

Key words: β-(morpholin-1-yl)propioamidoxime, arylsulfochlorination, *O*-arylsulfonyl-β-(morpholin-1-yl)propioamidoximes, 2-amino-8-oxa-1,5-diazaspiro[4.5]dec-1-ene-5-ammonium arylsulfonates, IR and NMR (^1H and ^{13}C) spectroscopy, X-ray diffraction.

Sulfochlorination of structurally different amidoximes can afford *O*-sulfonyl amidoximes, ureas, and cyanamides. Stable aromatic and heteroaromatic *O*-sulfonyl amidoximes derived by the reaction of substituted benzamidoximes and pyridinecarboxylic acid amidoximes with aromatic and aliphatic sulfonyl chlorides were described.[1] Besides, resulting from the structure of the starting amidoxime and the reaction conditions, the sulfochlorination of amidoximes gives unsymmetrically substituted ureas *via* the Tiemann rearrangement. The latter products are formed after the successive treatment of amidoximes with arylsulfonyl chlorides and water.[2—4] In the presence of *N,N*-diisopropylethylamine (DIPEA) or pyridine, the sulfochlorination of amidoximes can produce substituted cyanamides.[2]

Besides, the so-called modified Tiemann rearrangement provides a preparative route to various *N*-substituted cyanamides and is accomplished *via* the treatment of a solution of amidoxime and triethylamine in dichloromethane with an equivalent amount of arylsulfonyl chloride followed by the addition of alkyl halide in a 30% NaOH solution and a phase-transfer catalyst. This is a convenient method for the transformation of amidoximes into *N,N*-disubstituted cyanamides.[5] Despite the fact that cyanamides are highly labile in an acidic medium, they are stable under basic conditions at pH >10 due to deprotonation and the formation of the cyanamide anion. A series of aromatic, aliphatic, and terpenoid amidoximes are easily transformed into disubstituted unsymmetrical cyanamides in good yields (40—90%) *via* sulfochlorination followed by the reaction with alkyl halides.

In 2014, the conditions allowing the selective formation of *N,N*-disubstituted cyanamides or monosubstituted arylureas through arylsulfochlorination of *N*-substituted amidoximes were elaborated.[6]

N-Substituted cyanamides can be produced *via* the Tiemann rearrangement of *NR*-substituted *O*-sulfoaryl amidoximes (**A**) ($R^2 \neq H$) on heating or upon the treatment with bases (Scheme 1). It was shown that *N*-substituted cyanamides or *N,N′*-disubstituted carbodiimides (**B** or **C**) are produced as intermediates in the Tiemann rearrangement. These intermediates are generally transformed into *N,N*-disubstituted cyanamides (**D**), ureas (**E**), or guanidines (**F**) and can be prepared under particular conditions indicated in Scheme 1.

Based on the spectroscopic data, we concluded that the reaction of β-aminopropioamidoximes with *p*-toluenesulfonyl chloride affords β-aminopropioamidoxime *O*-tosylates (Scheme 2).[7]

The formation of *O*-arylsulfochlorination products of β-aminopropioamidoximes would be expected based on the X-ray diffraction data on the reaction products of β-(piperidin-1-yl)propioamidoxime with substituted benzoic acid chlorides existing as *O*-aroyl-β-aminopropioamidoxime hydrochlorides.[8]

The goal of this study is to reveal the effect of the electronic properties of substituents in arylsulfonyl chlorides on the pathway of the reaction with β-(morpholin-1-yl)propioamidoxime (**1**).

We expected that the reaction of β-(morpholin-1-yl)-propioamidoxime (**1**) with substituted arylsulfonyl chlor-

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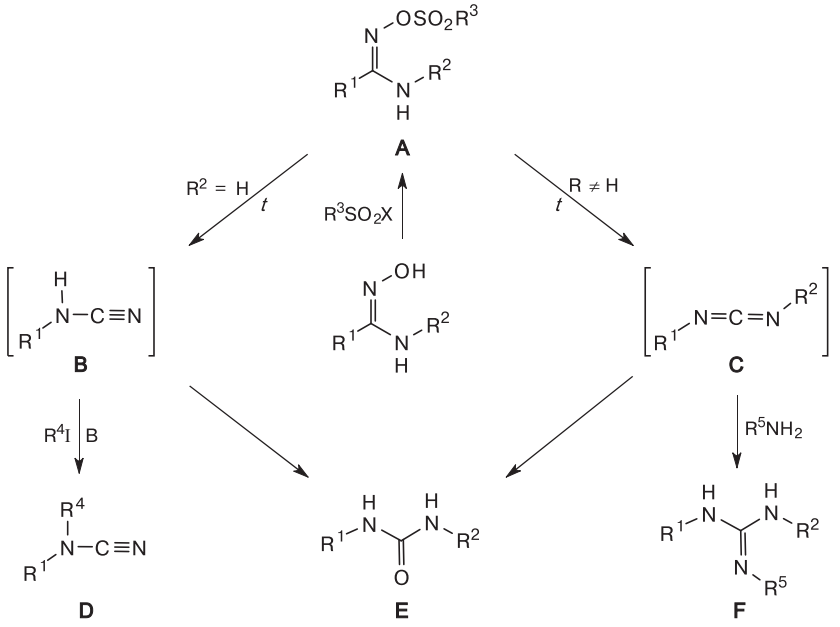
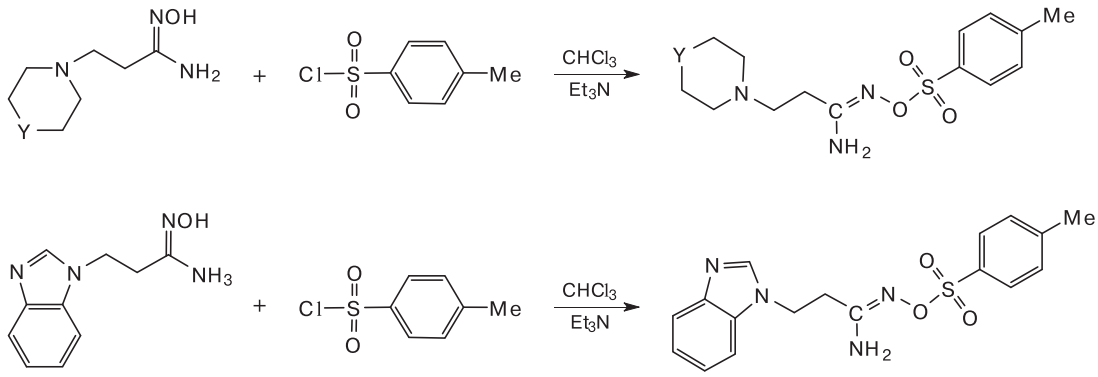
Scheme 1



R^4 = Alk; B is a base.

Scheme 2



Y = CH_2, O, S, PhN

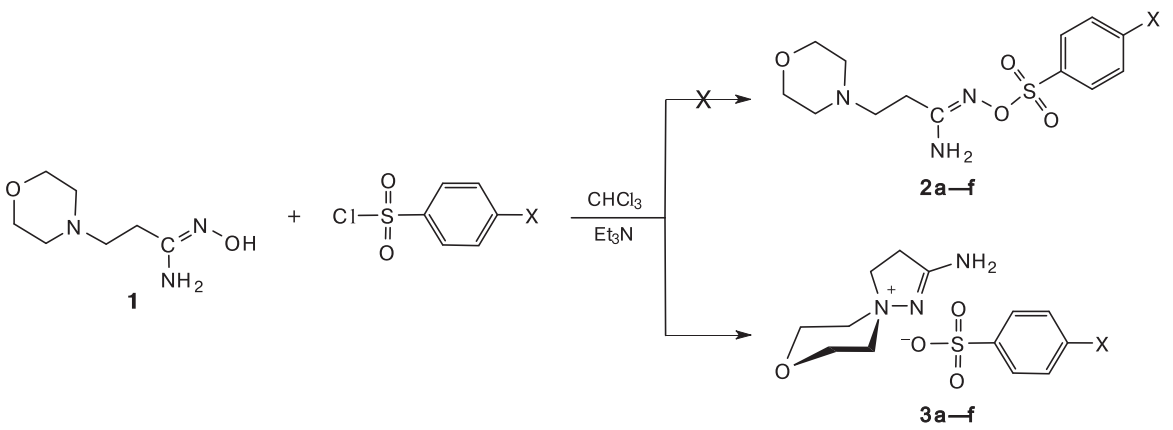
ides in the presence of triethylamine, like the reaction of a series of β-aminopropioamidoximes with *p*-toluenesulfonyl chloride, would afford *O*-arylsulfonyl-β-(morpholin-1-yl)propioamidoximes (**2a**—**f**).[7] The physicochemical and spectroscopic data are not contradictory to this assumption (Scheme 3).

Meanwhile, *O*-arylsulfonyl-β-(morpholin-1-yl)propioamidoximes **2a**—**f** and 2-amino-4,5-dihydrospiropyrazolylammonium arylsulfonates **3a**—**f** are structural isomers. The stretching bands in the recorded IR spectra and the chemical shifts of protons and carbon atoms in the NMR spectra are consistent with both structures (see Scheme 3).

However, the X-ray diffraction data provide unambiguous evidence that the reaction affords 2-aminospiropyrazolylmorpholineammonium arylsulfonates **3a**—**f**. The X-ray diffraction structures were determined for two extreme compounds of the series — sulfochlorination products with *p*-methoxy- and *p*-nitrosulfonyl chlorides (**3a** and **3f**, see Fig. 1).[9]

The IR spectra of compounds **3a**—**f** display two characteristic symmetric and asymmetric stretching bands of the SO_2 group at ν 1119—1191 and 1195—1220 cm^{-1}. The stretching bands of C=C double bonds of compounds **3a**—**f** at ν 1596—1609 cm^{-1} and stretching bands of the C_{sp^2}—H bond at >3000 cm^{-1} are also evidence of sulfochlorination

Scheme 3



X = MeO (**a**), Me (**b**), H (**c**), Br (**d**), Cl (**e**), NO_2 (**f**)

products. Other characteristic absorption bands typical of 2-amino-4,5-dihydrospiropyrazolylmorpholineammonium arylsulfonates **3a—f** are the stretching bands of C=N bonds at 1646—1664 cm^{-1}, symmetric and asymmetric stretching bands of the NH_2 group at 3176—3460 cm^{-1}, and stretching bands of C_{sp3}—H bonds at 2870—2985 cm^{-1}.

The ^1H NMR spectra of 2-amino-4,5-dihydrospiropyrazolylmorpholineammonium arylsulfonates **3a—f** show doublets of protons of the *p*-substituted phenyl group at δ_H 6.84—8.19 and a signal of the *p*-methoxy and *p*-methyl substituents at δ_H 3.75 and 3.36 for compounds **3a** and **3f**, respectively, which are evidence that the sulfochlorination takes place. A broadened signal of the amino group NH_2 of compounds **3a—f** appears at δ_H 7.30—7.48. The interacting groups of methylene protons of the ethylene moiety $CCH_2CH_2N^+$ of the pyrazoline ring give two signals at δ_H 3.13—3.17 and 3.88—3.99. The former signal is a triplet. The latter one overlaps with the signal of methylene protons at the morpholine oxygen atom with an integral intensity of six protons.

The methylene protons at the nitrogen atom of the six-membered heterocycle of compounds **3a—f** exhibit a diastereotopic effect and appear as two multiplets each at δ_H 3.40—3.41 and δ_H 3.64—3.68 with two-proton intensity. The diastereotopicity of these geminal protons is primarily associated with asymmetry due to the presence of the spirocyclic system. Besides, the diastereotopicity of geminal protons should include the dynamic contribution due to retarded rotation of the morpholine heterocycle. These signals can be assigned to axial and equatorial protons, respectively. The effect of retarded inversion of six-membered heterocycles, with a chair-like conformer with fixed positions of the axial and equatorial protons being predominant, in the ^1H NMR spectra is a known fact reported in reference data.[10,11]

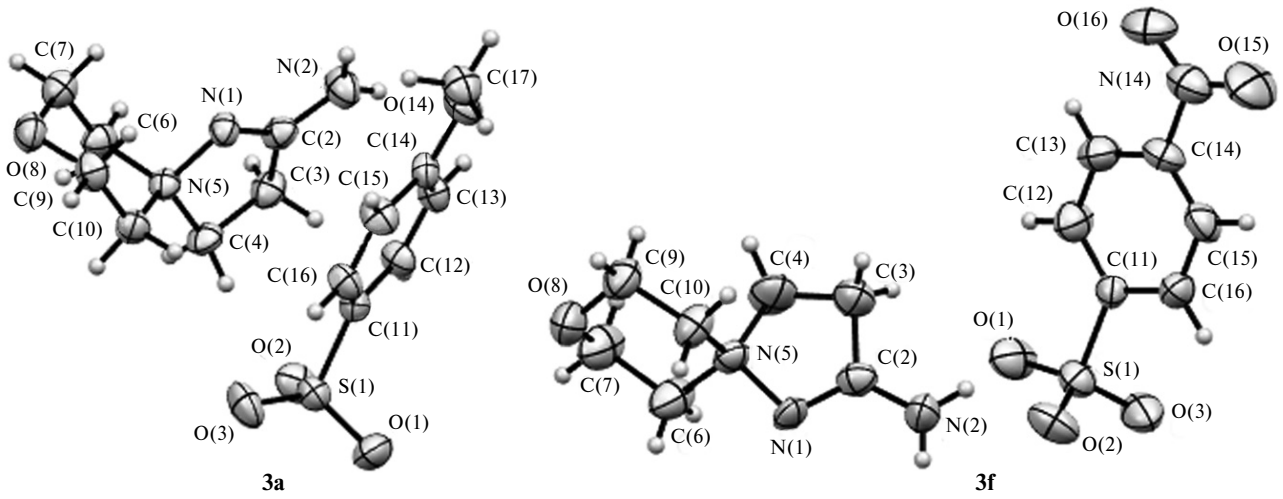


Fig. 1. Molecular geometry of salts **3a** and **3f** in the crystals with thermal displacement ellipsoids drawn at the 50% probability level.

The ^{13}C NMR spectra show characteristic signals of carbon atoms corresponding to the structure of 2-amino-4,5-dihydrospiropyrazolylmorpholineammonium arylsulfonates **3a—f**: signals of carbon atoms of the *p*-$\underline{C}H_3O$-$C_6H_4SO_3^-$ group at δ_C 55.64 and the *p*-$\underline{C}H_3C_6H_4SO_3^-$ group at δ_C 21.25 and signals of sp^2-hybridized phenyl carbon atoms at δ_C 113.20—159.65; signals of carbon atoms of the C=N bond of products **3a—f** at δ_C 169.09—169.11; signals of methylene carbon atoms of the ethylene moiety $CC(3)H_2C(4)H_2N^+$ of the pyrazoline ring at δ_C 31.43—31.49 and 62.02—62.13, respectively; signals of methylene carbon atoms at the morpholine nitrogen atom $N^+(\underline{C}H_2)_2$ of compounds **3a—f** at δ_C 62.08—62.46; signals of methylene groups at the oxygen atom at δ_C 63.23—63.35.

The presumptive mechanism of the reaction of β-(morpholin-1-yl)propioamidoxime (**1**) with arylsulfonyl chlorides is shown in Scheme 4.

In this case, the state of the N—O bond plays a crucial role. The cleavage of this bond is facilitated by the formation of hydrochloride $Et_3N \cdot HCl$ and the stable arylsulfonate anion as a good leaving group in transition states **A** and **B**. The attack on the nitrogen atom of the heterocycle by the ammonium nitrogen resulted in the ring closure giving a spiropyrazoline structure, in which the arylsulfonate anion is a counterion for the bridging ammonium nitrogen.

The ease of the formation of spiro compounds is consistent with the fact that *O*-arylsulfonyl-β-(morpholin-1-yl)propioamidoximes **2a—f** are evidently thermodynamically less stable than 2-amino-4,5-dihydrospiropyrazolylmorpholineammonium arylsulfonates **3a—f** and with the fact that arylsulfonate anions are good leaving groups.[12]

The formation of spiropyrazolinium structures *via* the Boulton—Katritzky rearrangement of 5-aryl-3-β-aminoethyl-1,2,4-oxadiazoles (the β-amino group: thiomorpholin-1-yl, 4-phenylpiperazin-1-yl) in the presence of HCl and H_2O was reported in our previous studies and was established by X-ray diffraction.[13—15]

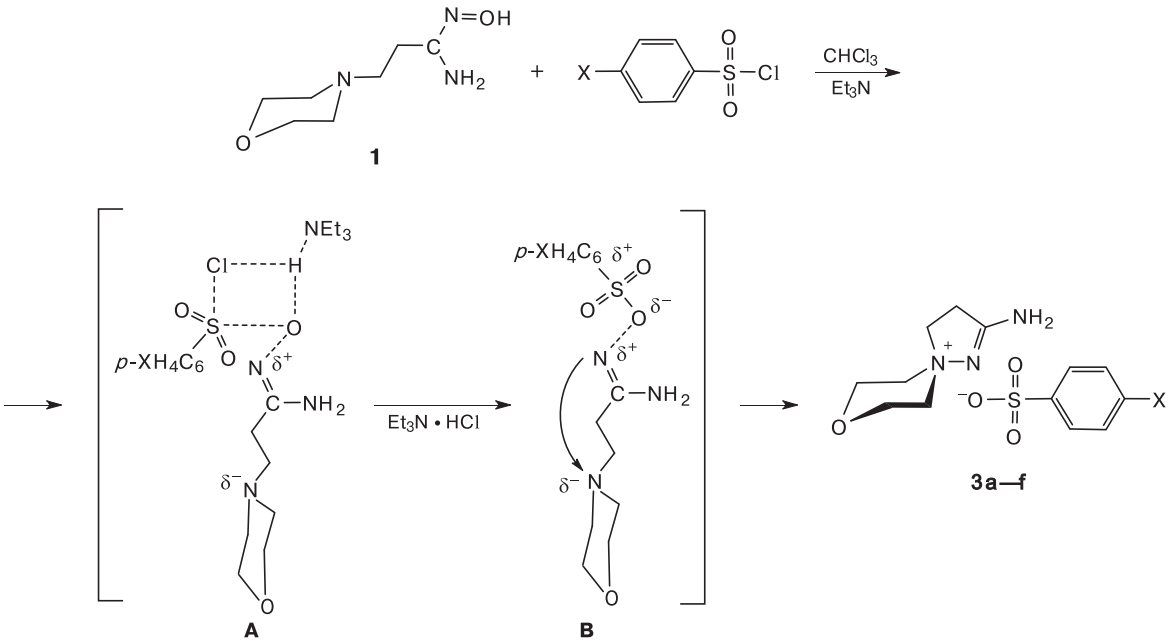
According to the single-crystal X-ray diffraction study of **3a** and **3f**, the cations in these compounds have the same structure and the six-membered morpholine rings adopt a chair conformation. The five-membered rings adopt an envelope conformation, with the C(4) atom deviating from the mean plane of the N(5)—N(1)=C(2)—C(3) atoms. The nitro group at the C(2) atom has a planar configuration and lies in the plane of the base of the five-membered ring. The arylsulfonyl anions have a standard geometry. Thus, the methoxy group in compound **3a** and the nitro group in compound **3f** lie in the planes of the benzene rings. The sulfonate groups are deprotonated and the S—O bond lengths in these groups are equalized, which is indicative of the negative charge delocalization.

The bond lengths, bond angles, and torsion angles in compounds **3a** and **3f** are typical of such structures.

The crystal structures of compounds **3a** and **3f** are mainly determined by hydrogen bonds. Thus, a closed dimeric associate in the crystal of **3a** is formed by two cations and two anions linked by hydrogen bonds (Fig. 2).

In the crystal of **3a**, one hydrogen atom of the amino group is linked to the oxygen atom of the morpholine ring

Scheme 4



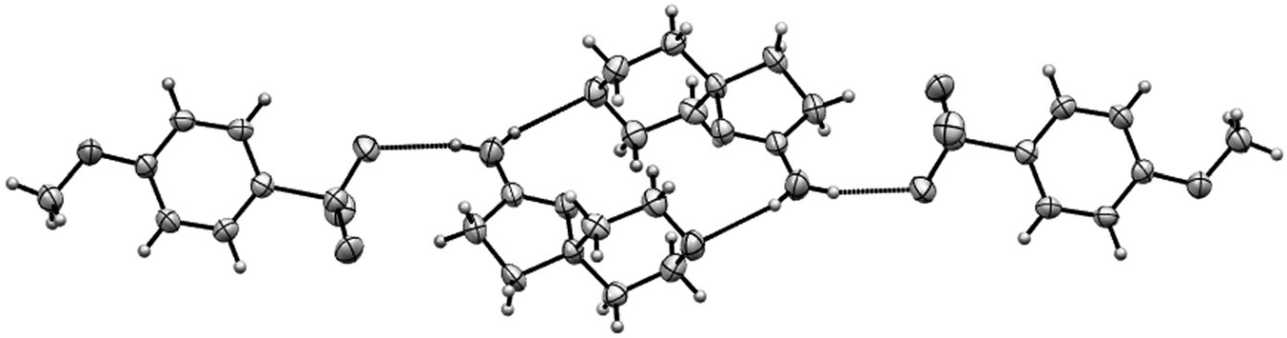


Fig. 2. Hydrogen-bonding network in the crystal of **3a**.

of the adjacent cation. The parameter of the N(2)—H(2A)...O(8′) (1 − *x*, −*y*, 1 −*z*) hydrogen bond are *d*(N(2)—H(2A)) = 0.86 Å, *d*(H(2A)...O(8′) = 2.28 Å, *d*(N(2)...O(8′) = 3.099(5) Å, ∠N(2)—H(2A)...O(8) = 160°. The second hydrogen atom of the amino group forms a bond with the anion through an oxygen atom of the sulfonate group. The parameters of the (N(2)—H(2B)...O(2″) (1/2 + *x*, 1/2 − *y*, 1/2 + *z*) hydrogen bond are *d*(N(2)—H(2B)) = 0.86 Å, *d*(H(2B)...O(2″)) = 2.10 Å, *d*(N(2)...O(2″)) = 2.941(5) Å, ∠N(2)—H(2B)...O(2″) = 166°.

A different hydrogen-bonding network exists in the crystal of **3f** (Fig. 3). The cations are linked through centrosymmetric dimers by N(2)—H(2A)...N(1′) (2 − *x*, 1 − *y*, 1 − *z*) hydrogen bonds. The hydrogen-bond parameters are as follows: N(2)—H(2A), 0.86 Å; H(2A)...N(1′), 2.17 Å; N(2)...N(1′), 3.018(5) Å; the N(2)—H(2a)...N(1′) angle is 170°. The second hydrogen atom of the amino group forms a bond with the anion through the sulfonate oxygen atom, like in the crystal of **3a**. The parameters of the N(2)—H(2B)...O(1) hydrogen bond are as follows: N(2)—H(2B), 0.86 Å; H(2B)...O, 2.10 Å; N(2)...O(1), 2.931(5) Å; the N(2)—H(2B)...O(1) angle is 162°.

To summarize, we established that the reaction of β-aminopropioamidoximes with *p*-substituted arylsulfonyl chlorides in chloroform in the presence of an equivalent of triethylamine affords spiropyrazolinium arylsulfonates rather than expected *O*-sulfoaryl-β-aminopropioamidoximes regardless of the electronic properties of substituents in arylsulfonyl chlorides.

Experimental

The IR spectra were recorded on a Thermo Scientific Nicolet 5700 FTIR spectrometer as KBr pellets. The ^{1}H and ^{13}C NMR spectra were measured on a Bruker Avance III NMR 500 MHz spectrometer (500 and 126 MHz, respectively). The elemental

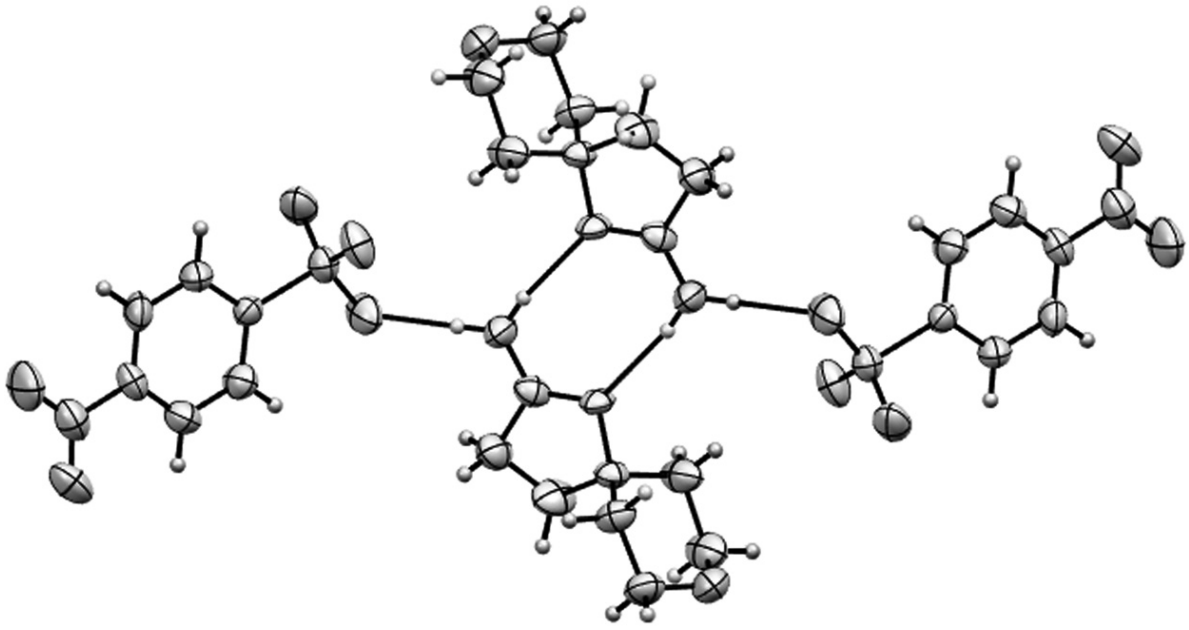


Fig. 3. Hydrogen-bonding network in the crystal of **3f**.

analysis was performed on a CE-440 elemental analyzer (Exeter Analytical, Inc., China). The melting points were measured on a TPL melting-point apparatus (Khimlabpribor, Russia). The course of reactions was monitored by TLC on Sorbfil plates (Sorbpolymer, Russia) pre-coated with STKh-1A silica gel with a particle size of 5—17 μm using a fluorescent indicator UV-254. A 1 : 3 benzene—EtOH mixture was used as the eluent.

The starting β-(morpholin-1-yl)propioamidoxime (**1**) was prepared in the following two steps: 1) the reaction of morpholine with acrylonitrile, which were distilled before use (EtOH as the solvent); 2) the resulting aminopropionitrile was distilled *in vacuo* and introduced into the reaction with commercial hydroxylamine hydrochloride, which was used as received (EtOH as the solvent). β-(Morpholin-1-yl)propioamidoxime (**1**) that was isolated from the reaction mixture was recrystallized from Pr^{i}OH (benzene as the solvent for the extraction of amidoxime **1**).[16]

β-(Morpholin-1-yl)propioamidoxime (**1**) was subjected to arylsulfochlorination with substituted arylsulfonyl chlorides, which were purchased from Sigma-Aldrich and used as received (chloroform as the solvent, triethylamine distilled before use as the base).

The solvents for the synthesis, recrystallization, extraction, and TLC (EtOH, Pr^{i}OH, benzene, chloroform) were purified according to standard procedures described for each solvent.[17]

Synthesis of 2-amino-8-oxa-1,5-diazospiro[4.5]dec-1-ene-5-ammonium arylsulfonates (3a—f) (general procedure). Triethylamine (0.28 g, 0.0028 mol) was added to a solution of β-(morpholin-1-yl)propioamidoxime (**1**) (0.5 g, 0.0028 mol) in chloroform (10 mL). The reaction mixture was cooled to 0 °C. A solution of arylsulfonyl chloride (0.55 g, 0.0028 mol) in chloroform (2 mL) was added dropwise with stirring. Then the reaction mixture was allowed to warm to room temperature and stirred for several days until the completion of the reaction. The course of the reaction was monitored by TLC. The resulting white precipitates of arylsulfonates **3a—f** were filtered off and recrystallized from Pr^{i}OH.

2-Amino-8-oxa-1,5-diazospiro[4.5]dec-1-ene-5-ammonium 4-methoxybenzenesulfonate (3a). The reaction time was 2 days. The yield of **3a** was 0.4 g (41.4%); m.p. 225—227 °C, R_f = 0.16. IR, ν/cm^{-1}: 3377 ν^{as}(NH_2), 3312 ν^{s}(NH_2), 1650 (C=N), 1597 (C=C), 1205 ν^{as}(SO_2), 1119 ν^{s}(SO_2). ^{1}H NMR, δ: 3.14 (t, 2 H, CC$\underline{H}_2$CH_2N$^+$, J = 7.0 Hz); 3.41, 3.64 (both m, 2 H each, H_{ax} and H_{eq}, N$^+$(C$\underline{H}_2$)$_2$); 3.75 (s, 3 H, OCH_3); 3.93 (m, 6 H, CCH$_2$C$\underline{H}_2$N$^+$);* 3.93(m, 6 H, O(C$\underline{H}_2$)$_2$);* 6.84 (d, 2 H, CH_{sp^2}, J = 7.0 Hz); 7.30 (br, 2 H, NH_2); 7.53 (d, 2 H, CH_{sp^2}, J = 7.0 Hz). ^{13}C NMR, δ: 31.47 (C$\underline{C}$H$_2$CH$_2$N$^+$), 55.64 (CH_3O), 62.02 (CCH$_2$$\underline{C}H_2N^+$), 63.35 (N$^+$($\underline{C}H_2$)$_2$, 62.42 (O($\underline{C}H_2$)$_2$), 113.20 (2 C); 127.51 (2 C), 141.89 (1 C), 159.65 (1 C), 169.10 (C=N). Found (%): C, 48.75; H, 5.93; N, 12.70; S, 9.02. $C_{14}H_{21}N_3O_5S$. Calculated (%): C, 48.97; H, 6.16; N, 12.24; S, 9.34.

2-Amino-8-oxa-1,5-diazospiro[4.5]dec-1-ene-5-ammonium 4-tosylate (3b). The reaction time was 2 days. The yield of 2-aminospiropyrazolylammonium tosylate (**3b**) was 0.44 g (47.8%); m.p. 220—222 °C, R_f 0.14. IR, ν/cm^{-1}: 3422 ν^{as}(NH_2), 3367 ν^{s}(NH_2), 1654 (C=N), 1601 (C=C), 1195 ν^{as}(SO_2), 1120 ν^{s}(SO_2). ^{1}H NMR, δ: 3.14 (t, 2 H, CC$\underline{H}_2$CH_2N$^+$, J = 7.0 Hz); 3.36 (s, 3 H, CH_3); 3.40, 3.65 (both m, 2 H each, H_{ax} and H_{eq}, N$^+$(C$\underline{H}_2$)$_2$); 3.93 (m, 6 H, CCH$_2$C$\underline{H}_2$N$^+$);* 3.93 (m, 6 H, O(C$\underline{H}_2$)$_2$);* 7.11 (d, 2 H, CH_{sp^2}, J = 7.0 Hz); 7.35 (br.s, 2 H, NH_2); 7.48 (d, 2 H, CH_{sp^2}, J = 7.0 Hz). ^{13}C NMR, δ: 21.25 (CH_3), 31.43 (C$\underline{C}$H$_2$CH$_2$N$^+$), 62.02 (CCH$_2$$\underline{C}H_2N^+$), 62.42 (N$^+$($\underline{C}H_2$)$_2$), 63.23 (O($\underline{C}H_2$)$_2$), 125.95 (2 C); 128.55 (2 C), 138.13 (1 C), 146.16 (1 C), 169.10 (C=N). Found (%): C, 51.81; H, 6.59; N, 13.25; S, 9.37. $C_{14}H_{21}N_3O_4S$. Calculated (%): C, 51.36; H, 6.47; N, 12.83; S, 9.79.

2-Amino-8-oxa-1,5-diazospiro[4.5]dec-1-ene-5-ammonium benzenesulfonate (3c). The reaction time was 4 days. The yield of **3c** was 0.37 g (42.5%); m.p. 192—195 °C, R_f 0.75. IR, ν/cm^{-1}: 3326 ν^{as}(NH_2), 3176 ν^{s}(NH_2), 1656 (C=N), 1604 (C=C), 1220 ν^{as}(SO_2), 1181 ν^{as}(SO_2). ^{1}H NMR, δ: 3.13 (t, 2 H, CC$\underline{H}_2$CH_2N$^+$, J = 7.0 Hz); 3.40, 3.65 (both m, 2 H each, H_{ax} and H_{eq}, N$^+$(C$\underline{H}_2$)$_2$); 3.92 (m, 6 H, CCH$_2$C$\underline{H}_2$N$^+$);*2 3.92 (m, 6 H, O(C$\underline{H}_2$)$_2$);*2 7.48—7.61 (m, 5 H, CH_{sp^2}); 7.48 (br.s, NH_2). ^{13}C NMR, δ: 31.43 (C$\underline{C}$H$_2$CH$_2$N$^+$), 62.08 (CCH$_2$$\underline{C}H_2N^+$), 62.08 (N$^+$($\underline{C}H_2$)$_2$), 63.23 (O($\underline{C}H_2$)$_2$), 125.93 (2 C); 128.10 (2 C), 128.84 (1 C), 148.87 (1 C), 169.10 (C=N). Found (%): C, 49.29; H, 5.97; N, 13.87; S, 9.91. $C_{13}H_{19}N_3O_4S$. Calculated (%): C, 49.83; H, 6.11; N, 13.41; S, 10.23.

2-Amino-8-oxa-1,5-diazospiro[4.5]dec-1-ene-5-ammonium 4-bromobenzenesulfonate (3d). The reaction time was 4 days. The yield of **3d** was 0.58 g (53.2%); m.p. 230—232 °C, R_f 0.30. IR, ν/cm^{-1}: 3392 ν^{as}(NH_2), 3336 ν^{s}(NH_2), 1646 (C=N), 1609 (C=C), 1225 ν^{as}(SO_2), 1191 ν^{s}(SO_2). ^{1}H NMR, δ: 3.16 (t, 2 H, CC$\underline{H}_2$CH_2N$^+$, J = 7.0 Hz); 3.40, 3.67 (both m, 2 H each, H_{ax} and H_{eq}, N$^+$(C$\underline{H}_2$)$_2$); 3.87—3.98 (m, 6 H, CCH$_2$C$\underline{H}_2$N$^+$);* 3.87—3.98 (m, 6 H, O(C$\underline{H}_2$)$_2$);* 7.50 (d, 2 H, CH_{sp^2}, J = 7.0 Hz); 7.39 (br.s, 2 H, NH_2); 7.54 (d, 2 H, CH_{sp^2}, J = 7.0 Hz). ^{13}C NMR, δ: 31.48 (C$\underline{C}$H$_2$CH$_2$N$^+$), 62.07 (CCH$_2$$\underline{C}H_2N^+$), 62.46 (N$^+$($\underline{C}H_2$)$_2$), 63.34 (O($\underline{C}H_2$)$_2$), 122.00 (1 C); 128.23 (2 C), 131.04 (2 C), 148.33 (1 C), 169.11 (C=N). Found (%): C, 40.25; H, 4.85; Br, 19.89; N, 10.28; S, 8.17. $C_{13}H_{18}BrN_3O_4S$. Calculated (%): C, 39.80; H, 4.63; Br, 20.37; N, 10.71; S, 8.17.

2-Amino-8-oxa-1,5-diazospiro[4.5]dec-1-ene-5-ammonium 4-chlorobenzenesulfonate (3e). The reaction time was 6 days. The yield of **3e** was 0.36 g (37%); m.p. 160—162 °C, R_f 0.19. IR, ν/cm^{-1}: 3405 ν^{as}(NH_2), 3305 ν^{s}(NH_2), 1647 (C=N), 1596 (C=C), 1220 ν^{as}(SO_2), 1191 ν^{s}(SO_2). ^{1}H NMR, δ: 3.17 (t, 2 H, CC$\underline{H}_2$CH_2N$^+$, J = 7.0 Hz); 3.40, 3.67 (both m, 2 H each, H_{ax} and H_{eq}, N$^+$(C$\underline{H}_2$)$_2$); 3.88—3.98 (m, 6 H, CCH$_2$C$\underline{H}_2$N$^+$);* 3.88—3.98 (m, 6 H, O(C$\underline{H}_2$)$_2$);* 7.37 (d, 2 H, CH_{sp^2}, J = 7.0 Hz); 7.44 (br.s, 2 H, NH_2); 7.61 (d, 2 H, CH_{sp^2}, J = 7.0 Hz). ^{13}C NMR, δ: 31.49 (C$\underline{C}$H$_2$CH$_2$N$^+$), 62.04 (CCH$_2$$\underline{C}H_2N^+$), 62.46 (N$^+$($\underline{C}H_2$)$_2$), 63.33 (O($\underline{C}H_2$)$_2$), 127.93 (2 C); 128.11 (2 C), 133.38 (1 C), 147.89 (1 C), 169.11 (C=N). Found (%): C, 44.68; H, 5.47; Cl, 10.47; N, 12.50; S, 8.85. $C_{13}H_{18}ClN_3O_4S$. Calculated (%): C, 44.89; H, 5.22; Cl, 10.19; N, 12.08; S, 9.22.

2-Amino-8-oxa-1,5-diazospiro[4.5]dec-1-ene-5-ammonium 4-nitrobenzenesulfonate (3f). The reaction time was 3 days. The yield of **3f** was 0.49 g (48.5%); m.p. 192—195 °C, R_f 0.17. IR, ν/cm^{-1}: 3405 ν^{as}(NH_2), 3305 ν^{s}(NH_2), 1664 (C=N), 1601 (C=C), 1204 ν^{as}(SO_2), 1120 ν^{s}(SO_2). ^{1}H NMR, δ: 3.14 (t, 2 H, CC$\underline{H}_2$CH_2N$^+$, J = 7.0 Hz); 3.41, 3.64 (both m, 2 H each, H_{ax} and H_{eq}, N$^+$(C$\underline{H}_2$)$_2$); 3.88—3.99 (m, 6 H, CCH$_2$C$\underline{H}_2$N$^+$);* 3.88—3.99 (m, 6 H, O(C$\underline{H}_2$)$_2$);* 7.29 (br.s, 2 H, NH_2); 7.85 (d, 2 H, C_{sp^2}H, J = 7.0 Hz); 8.19 (d, 2 H, C_{sp^2}H, J = 7.0 Hz). ^{13}C NMR, δ: 31.47 (C$\underline{C}$H$_2$CH$_2$N$^+$), 62.13 (CCH$_2$$\underline{C}H_2N^+$), 62.44 (N$^+$($\underline{C}H_2$)$_2$), 63.35 (O($\underline{C}H_2$)$_2$), 123.71 (2 C); 127.39 (2 C), 147.79 (1 C), 155.00 (1 C), 169.09 (C=N). Found (%): C, 43.96; H, 5.29; N, 16.01; S, 9.28. $C_{13}H_{18}N_4O_6S$. Calculated (%): C, 43.57; H, 5.06; N, 15.63; S, 8.95.

* Hereinafter, the overlapping signals of protons in the ^{1}H NMR spectra of compounds **3a—f** are marked with an asterisk.

Table 1. Crystallographic data and the X-ray diffraction data collection and structure refinement statistics for compounds **3a** and **3f**

Parameter	**3a**	**3f**
Molecular formula	$C_{14}H_{21}N_3O_5S$	$C_{13}H_{18}N_4O_6S$
M	343.40	358.37
Color	Colorless	Colorless
Crystal habit	Prismatic	Prismatic
Crystal system	Monoclinic	Monoclinic
Space group	$P2_1/n$	$P2_1/c$
a/deg	9.2401(14)	15.706(3)
b/deg	18.448(2)	6.6935(10)
c/deg	9.5149(14)	16.144(2)
β/Å	100.361(6)	111.884(8)
V/Å^3	1595.5(4)	1574.9(4)
Z	4	4
d_{calc}/g cm^{-3}	1.430	1.512
μ(Mo)/mm^{-1}	0.233	0.245
θ-Scan range/deg	2.20—28.30	3.30—26.00
Number of reflections		
measured	9873	11400
unique	3959	3046
with $I \geq 2\sigma(I)$	1746	1319
Final *R* factor		
based on all reflections	3959	3046
R	0.1660	0.1598
R_w	0.2280	0.1414
based on observed reflections with $F > 2\sigma(F^2)$		
R	0.0669	0.0581
R_w	0.1541	0.1060
GOOF	0.926	0.906
CCDC	1957795	1957796

X-ray diffraction study. Crystals of compounds **3a** and **3f** suitable for X-ray diffraction were grown from Pr^{i}OH. The X-ray diffraction data were collected from the crystals of compounds **3a** and **3f** on a Bruker Kappa APEX II CCD automated diffractometer equipped with a graphite monochromator (λ(Mo-Kα) = 0.71073 Å; ω- and φ-scanning technique) at 100 K. Semiempirical absorption corrections were applied with the SADABS program.[18] The structures were solved by direct methods using the SHELXT 2014/4 program package[19] and refined first with isotropic and then with anisotropic displacement parameters using the SHELXL-2018/3 program package.[20]

Hydrogen atoms were positioned geometrically and refined using a riding model. All calculations were carried out with the WinGX[21] and APEX2 programs.[22] All figures were prepared and intermolecular interactions were analyzed with the PLATON[23] and ORTEP programs.[21]

The crystallographic data and the X-ray diffraction data collection and structure refinement statistics for compounds **3a** and **3f** are given in Table 1.

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