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^{1}H NMR SULFINYL GROUP SUBSTITUENT EFFECTS OF DITHIINODIAZINE *S*-OXIDES AS A KEY FOR STRUCTURE ASSIGNMENT OF PARENT DITHIINODIAZINES

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Abstract- 1,4-Dithiinodipyridine **1** was prepared by reduction of 4-chloro-3-chlorosulfonylopyridine (**8**) with HI / H_3PO_3 system. Sulfur-assisted thermal isomerization of **1** resulted in a mixture of **1** and **2**. Treatment of dithiinodiazines **1**, **2**, **5**, and **6** with a nitrating mixture led almost selectively to respective S-monooxides **1a**, **2a**, **5a**, and **6a**. Due to the significant values of sulfinyl group substituent effects, ^{1}H NMR spectra of 1,4-dithiino-*S*-oxides **1a**, **2a**, **5a**, and **6a** permitted for structure assignment of parent dithiins **1**, **2**, **5**, and **6** and confirmed regioselectivity of the reaction of dithiins **1**, **2**, **5**, and **6** with nitrating mixture.

INTRODUCTION

3,4-Azinediyl units may be fused with 1,4-dithiin ring to form two isomeric 1,4-dithiinodiazines, *e.g*. **1** *vs* **2** or **3** *vs* **4**. Both isomers are non-distinguishable by means of ^{1}H and ^{13}C NMR spectra due to the lack of connectivity link between proton or carbon atoms of both azine units.[1-8] Moreover, structure assignment of dithiinodiquinolines[9] and dithiinodipyridines[6,7] or related structure[3,4] by means of chemical transformation may lead to incorrect conclusions, since these reactions, *e.g.* 1,4-dithiin ring opening reaction, may be accompanied by Smiles rearrangement.[4,7,8] There exist few examples for non-equivalency of azinediyl units resulting from heteroatom *N*- or *S*-oxidation,[3,4] which could be applied for the structure assignment of dithiinodipyridines or related structures.[3,4] The only method leading directly to the structure assignment of compounds **1**-**6** is X-ray diffraction of single crystals.[6,8,9]

On the other hand, some years ago we stated that treatment of 3,4-quinolinediyl bis-sulfides **3** and **4** with nitrating mixture proceeded as *S*-monooxidation to form respective mono-*S*-oxides **3a** or **4a**.[10-12] Moreover, due to the sulfinyl group substituent effects, even simple ^{1}H NMR spectra permit for

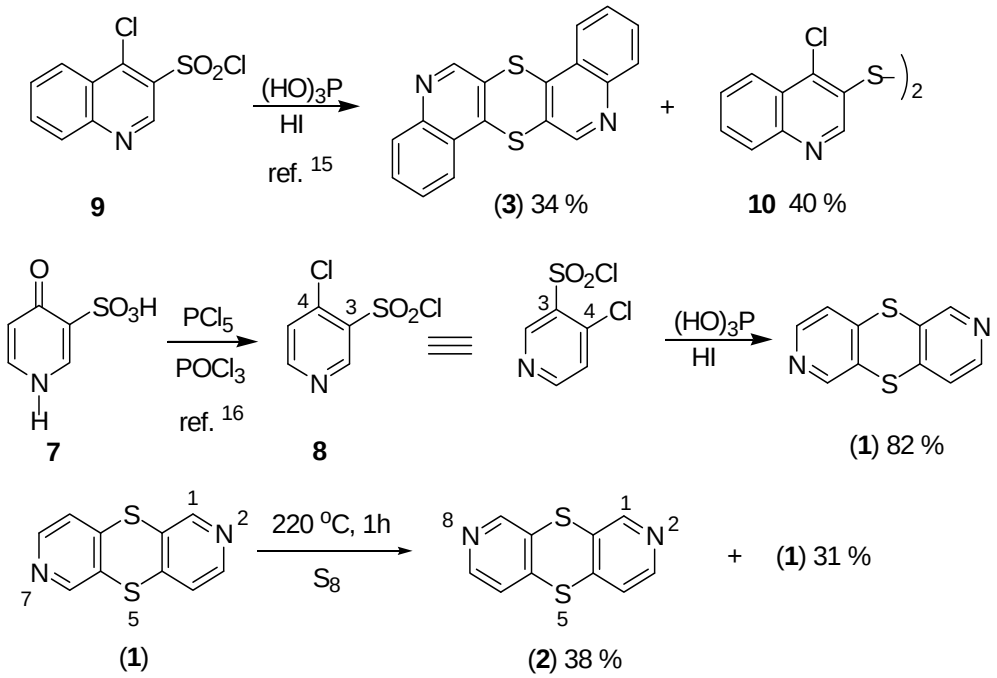
distinction between isomeric 1,4-dithiinodiquinoline S-oxides **3a** and **4a** and parent dithiinodiquinolines **3** and **4**. These observations were used to establish the structure of dithiinodiquinolines **5** and **6** as well as dithiinodipyridines **1** and **2**, as described below.

RESULTS AND DISCUSSION

Synthesis and isolation of 1,4-dithiinodiazines **1**, **2**, **5** and **6**

There are known several method of synthesizing 1,4-dithiinodipyridine **1**.[1,6,7,13,14] Except for the attempts with sulfurization of pyridine[13] or 4,4'-dipyridinyl sulfide or disulfide,[14] other methods were based on formation and transformation of 3,4-disubstituted pyridines.[1,6,7] All of them are multi-step, work consuming and low medium-effective (up to 40%). Searching for a more suitable method, a new synthesis of **1** was elaborated. As the molecule of dithiinodipyridine **1** is composed of 3,4-pyridinediyl units, our basic entry point was to find a commercially available 3,4-disubstituted pyridine. This requirement was fullfilled by 4(1*H*)-pyridinone-3-sulfonic acid (**7**). Furthermore, our previous study showed that 4-substituted 3-thioquinoline units of 4-chloro-3-chlorosulfonylquinoline (**9**) could cyclo-dimerize to 1,4-dithiinodiquinoline **3** when chloro-sulfochloride **8** was treated with hydrogen iodide / phosphorous acid system.[15] The same method applied to 4-chloro-3-chlorosulfonylpyridine (**8**) gave dithiinodipyridine **1** with 82 % yield.

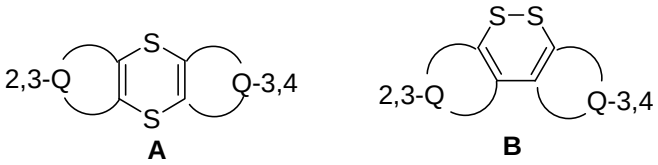
Scheme 1



Further improvement was also elaborated for the synthesis of isomeric dithiinodipyridine **2** being previously obtained by Smiles rearrangement of isomer **1** (50%).[7] As in the case of dithiinodiquinolines **3** and **4**,[17] sulfur-assisted thermal isomerization of 'trans' isomer **1** afforded the 'cis' isomer **2** (38 %).

1,4-Dithiinodiquinolines **5** and **6**, both with empirical formula $C_{18}H_{10}N_2S_2$, were isolated from quinoline sulfurization products.[18] HMBC spectra confirmed that the molecule of **5** or that of **6** is composed of 2,3- and 3,4-quinolinediyl units (see Schemes 2 and 5). Both quinoline fragments could be fused together by sulfide bridges in the form of 1,4-dithiin ring (formula **A**) or by disulfide ones in the form of a 1,2-dithiin ring (formula **B**).

Scheme 2

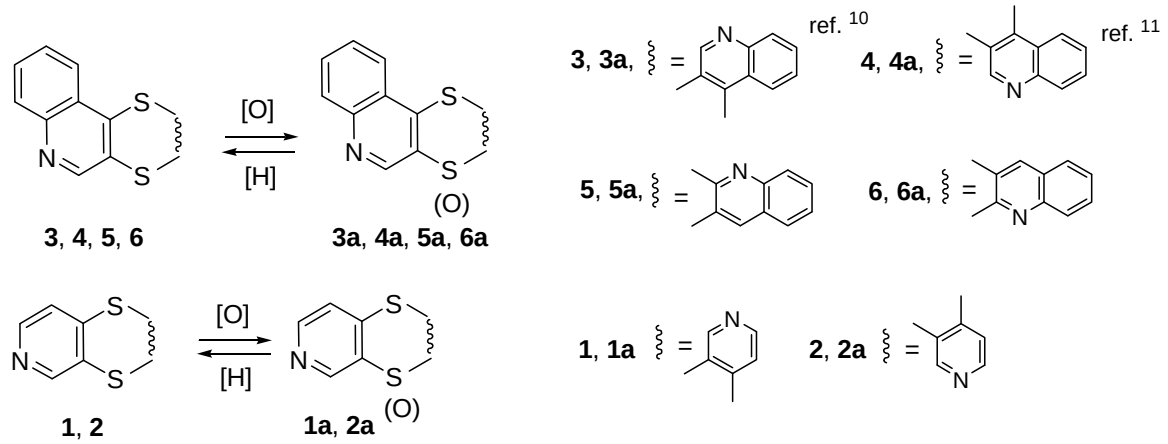


An attempt at reducing compounds **5** and **6** with hypophosporous acid[19] did not succeed. This proves that compounds **5** and **6** do not react in the way characteristic of disulfides, which excludes 1,2-dithiin structures **B**.

Reactions with nitrating mixture

When thioquinanthrene **3** or isothioquinanthrene **4** were treated (in the form of respective quinolinium salts) with nitrating mixture, the reaction gave (after dilution and neutralization) high yields of thioquinanthrene 7-oxide (**3a**) (91 %) or isothioquinanthrene 7-oxide (**4a**) (93 %), respectively.[10,11]

Scheme 3



[O] = HNO_3 (2 mol. eqv.), conc. H_2SO_4, 0-5 ^oC

[H] = KI, conc. HCl aq., rt; for **3a** and **4a** - ref.,[12].

The same treatment of dithiinodipyridines **1** and **2** as well as s*emi-linear* 1,4-dithiinodiquinolines **5** and **6** led to the respective *S*-monooxides **1a** (90 %), **2a** (88 %), **5a** (80 %) and **6a** (82 %) as deduced from elemental analysis, IR and ^{1}H NMR spectral data. Their IR spectra have shown new strong bands due to sulfinyl groups at *ca.* 1050 cm^{-1}. Positioning of introduced oxygen atom was estabilished from ^{1}H NMR spectra as discussed in detail below.

As discussed recently[20] on the basis of competitive experiments and quantum mechanical calculations, reactions of compounds **3** and **4** and related β- and γ-quinolinyl sulfides with NO_2^+ ion (formed from nitrating mixture) occurred at the most electron donating β-quinolinyl-sulfur atom. Formation of *S*-oxides of type **3a** and **4a**, which should exist as quinolinium and sulfonium species, significantly reduces the electron donating properties of non-oxidized sulfur atom and makes impossible its further oxidation to the *S*,*S*'-dioxide. The same reactivity and regioselectivity was also noted in the case of dithiins **1**, **2**, **5** and **6**, which underwent mono-oxidation at β-azinyl (pyridinyl or quinolinyl) sulfide sulfur atom only.

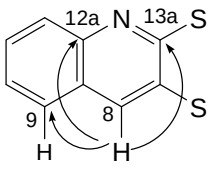
NMR study

All of the ^{1}H and ^{13}C NMR signals were unquestionably assigned using 1D and 2D NMR techniques (including COSY, HMQC and HMBC).

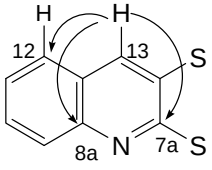
In the case of dithiinodiquinolines **5** and **6** and theirs *S*-oxides **5a** and **6a**, the analytical steps are as follows: x) Presence of two proton singlets indicates two different pyridine-ring disubstituted quinoline moieties; xx) The more deshielded proton singlet was assigned to α-quinolinyl proton of 3,4-quinolinediyl unit because it exhibited lack of proton-proton correlation and showed one-bond C-H correlation (with C-6) and three-bond C-H correlation with downfield-shifted α-aza-influenced carbons (C-6 and C-4a). The values of chemical shifts are very close and the proton-carbon one-bond and long-range correlation are the same as reported for 3,4-quinolinediyl bis-sulfides **3** and **4**.[5] xxx) The less deshielded proton singlet was assigned to γ-quinolinyl proton of 2,3-quinolinediyl unit since it exhibited three-bond proton-carbon correlation with tertiary 5-quinolinyl carbon (C-9 for **5** or C-12 for **6**) and showed two three-bond C-H correlation with quaternary α-aza-influenced carbons (C-12a and C-13a for **5** and C-7 and C-8a for **6**, respectively). ix) Spectral position of H-1 (*i.e.* 5-quinolinyl) proton multiplet was deduced from long range proton-carbon correlations as shown on Scheme 4.

Scheme 4

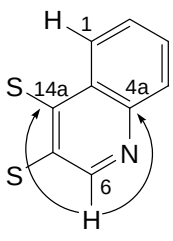
Crucial C-H correlation used in the NMR assignment of dithiinodiquinolines (**5**, **5a**, **6** and **6a**)

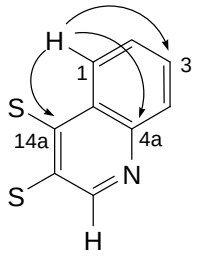


for **5** and **5a**



for **6** and **6a**





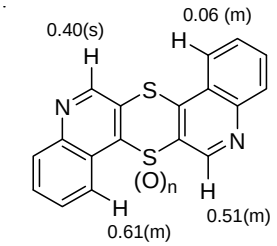
for compounds **5**, **5a**, **6** and **6a**

As compared to the respective sulfide group, sulfinyl group strongly affected the ^{1}H NMR spectral positions of *ortho*- and *peri* protons of aromatic and heteroaromatic systems, both being shifted downfield

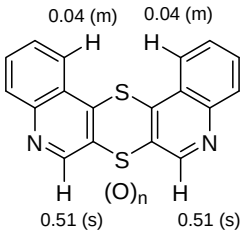
up to 0.68 ppm or 0.61 ppm, respectively.[21,10-12] (see also Scheme 5) Additionally, due to the *pseudo-axial* arrangement of sulfinyl oxygen at 1,4-dithiin ring, deshielded are also (up to 0.40 ppm) the *ortho* protons at the sulfide fragment of mono-*S*-oxides of 1,4-dithiinodiquinoline **3a** and its nitroderivatives.[10-12] All these effects were observed for the newly prepared couples of dithiinodiazines and theirs *S*-oxides: **1** vs **1a**, **2** vs **2a**, **5** vs **5a** and **6** vs **6a**.

Scheme 5

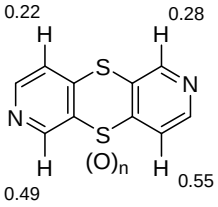
The values of the sulfinyl group substituent effects $\Delta\delta_H$ [ppm] = δ_H(sulfoxide)-δ_H(sulfide) in the structure assignment of compounds **1** / **1a**, **2** / **2a**, **5** / **5a** and **6** / **6a**



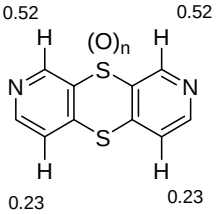
3, n=0
3a, n=1
ref. [10]



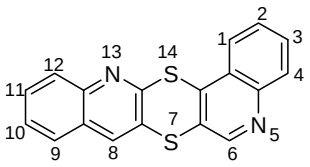
4, n=0
4a, n=1
ref. [11]



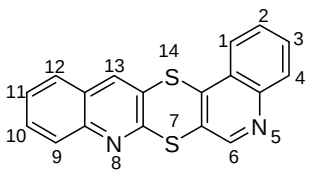
1, n=0
1a, n=1



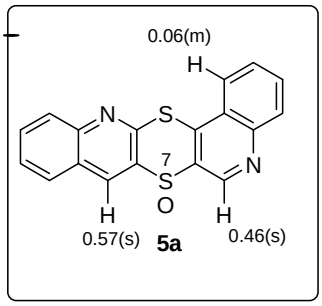
2, n=0
2a, n=1

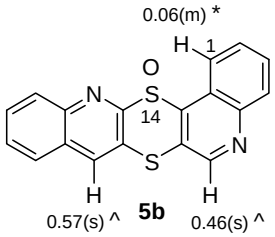


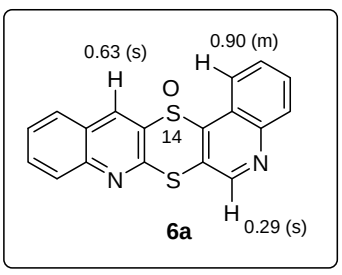
5

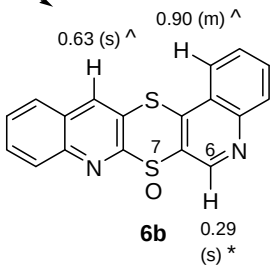


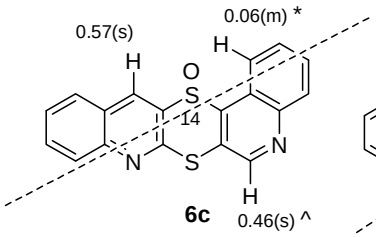
6

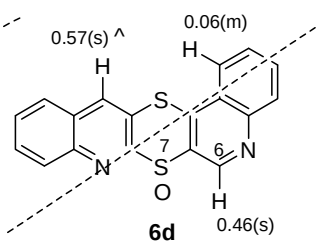


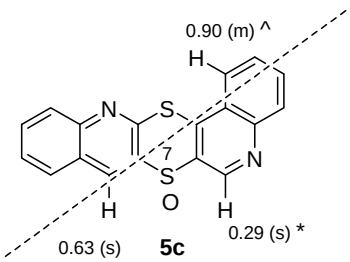


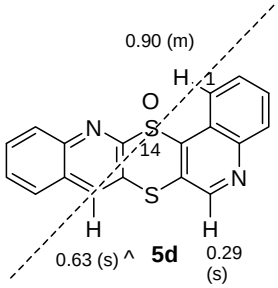












* too low value of $\Delta\delta_H$, ^ too high value of $\Delta\delta_H$.

^{1}H and ^{13}C NMR spectra of **1** showed three proton signals and five carbon signals, whereas the same spectra of *S*-oxide **1a** showed, due to non-identical substituent effects of sulfide *vs* sulfoxide group, six and ten signals, respectively. As oxidation of **2** to **2a** does not changes the symmetrical arrangement of **2a**, *i.e.* protons and carbons of the same type are affected by the same substituent, thus number of ^{1}H and ^{13}C NMR signals in **2** and **2a** remains unchanged.

As the molecules of **5** and **6** are composed of 3,4- and 2,3-quinolinediyl units, the starting distinction between the formulae **5** and **6** may be reverse. Therefore, beside isomeric *S*-oxides **5a** and **5b**, also the formulae **6c** and **6d** were taken into consideration for the structure assignment of the oxidation product of **5**. However, as compared to the spectral pictures of **5**, data of its oxidation product **5a** showed that both singlets of α-quinolinyl proton H6 and γ-quinolinyl proton H-8 are shifted downfield by 0.46 ppm or 0.57 ppm, respectively, but the H-1 proton multiplet is only little affected by Δδ ~0.06 ppm. Other possible formulae (**5b** , **6c** and **6d**) do not match the structural relationship with **5** as the values of the $\Delta\delta_H$ substituent effects are too low (*) or too high (^) (see Scheme 5). The same analysis performed for the structure assignment of **6** *vs* **6a** excludes a structural relationship of **6** with formulae **6b**, **5c** and **5d**. It confirms the structure of **6** deduced previously from chemical transformations.[18]

CONCLUSIONS

S-Oxidation affected NMR spectral positions of protons and carbons from both azinediyl units in dithiinodiazine *S*-oxides **1-6** in two manners. Firstly, in the same manner for both azinediyl units in the case when azinediyl units were coupled with 1,4-dithiin ring by the same position of azine, or secondly, non-equivalently, when azinediyl units were coupled by different positions of azine unit. This enabled a distinction between both types of dithiinodiazine derivatives based on sulfinyl group substituent effects as presented on Scheme 5 and as mentioned previously for 1,4-dithiino[2,3-b;5,6-b']dipyridine.[3] Structural relationships in the dithiinodiazine set could be additionally confirmed as *S*-oxides (**1a**, **2a,** **5a**, and **6a**) could be back deoxygenated to the parent dithiinodiazines (**1**, **2**, **5**, and **6**).

Convenient entry-point for structure assignment mentioned above is high regioselectivity in the *S*-oxidation of β-quinolinyl or β-pyridinyl sulfur bridge in the 1,4-dithiin ring of dithiinodiazines to respective mono-*S*-oxides.

EXPERIMENTAL

All melting points are uncorrected. All NMR spectra were recorded on a Bruker AVANS 400 spectrometer operating at 400.22 MHz and 100.64 MHz for ^{1}H and ^{13}C nuclei, respectively, in deuterochloroform or in hexadeuterodimethyl sulfoxide solutions with tetramethylsilane (δ 0.0 ppm) as internal standard. Two-dimensional ^{1}H-^{13}C HSQC and HMBC experiments were performed using

standard Bruker software HSQCGP and HMBCGP, respectively, and the following parameters: the spectral widths in F_2 and F_1 were *ca* 5 kHz for ^{1}H and 16.7 kHz for ^{13}C, the relaxation delay was 1.5 s, the refocusing in the HSQC experiment was 1.7 ms and the delay for long-range evolutions was 50 ms in ^{1}H / ^{13}C HMBC. 2D spectra were acquired as 2048 x 1024 hypercomplex files, with 1-4 transients.

IR spectra were recorded with a Magma – IR 500 (Nicolet) spectrometer in potassium bromide pellets. TLC analyses were performed employing Merck's silicagel 60 F_{254} plates and a solution of carbon-tetrachloride-acetone (9 : 1, v/v) as eluent (system I) or Merck's aluminium oxide 60 F_{254} neutral (type E) plates using chloroform as eluent (system II).

1,4-Dithiino[2,3-*b*:5,6-*c*']diquinoline (**5**) and 1,4-dithiino[2,3-*b*:6,5-*c*']diquinoline (**6**) were isolated from mother-liquor (*i.e*. n-3 fraction) obtained after separation of thioquinanthrene (**3**) from products of exhaustive quinoline sulfurization[18] by column chromatography on neutral aluminium oxide (activity I according to Brockman) using carbon tetrachloride as eluent. The separation was repeated again and crude dithiins **5** and **6** were twice recrystallized from methanol.

1,4-Dithiino[2,3-*b*:5,6-*c*']diquinoline (**5**)

mp 246-247.5 ºC (EtOH). R_f=0.70 (system I). ^{1}H NMR ($CDCl_3$), δ: [δ_C for carbons from single bond and / long-range proton-carbon correlations]: 7.56 [(ddd, 1H, *J*=8.1 Hz, *J*=1.1 Hz, H-10); 127.6 (C-10) / 127.1 (C-8a), 128.6 (C-12)], 7.65 [(ddd, 1H, *J*=8.3 Hz, *J*=7.0 Hz, *J*=1.3 Hz, H-2); 127.9 (C-2) / 126.6 (C-14b), 130.0 or 130.1 (C-4)], 7.72 [(ddd, 1H, *J*=8.2 Hz, *J*=7.1 Hz, *J*=1.0 Hz, H-11); 130.6 (C-11) / 127.1 (C-9), 146.7 or 146.8 (C-12a)], 7.77 [(ddd, 1H, *J*=8.3 Hz, *J*=7.0 Hz, *J*=1.3 Hz, H-3); 130.0 or 130.1 (C-3) / 123.6 (C-1), 146.7 or 146.8 (C-4a)], 7.79 [(m, 1H, H-12); 127.1 (C-9) / 130.6 (C-11), 135.0 (C-8), 146.7 or 146.8 (C-12a)], 8.03-8.05 [(m, 1H, H-12); 128.6 (C-12) / 127.1 (C-8a), 127.6 (C-10)], 8.09-8.11 [(m, 1H, H-4); 130.0 or 130.1 (C-4) / 126.6 (C-14b), 127.9 (C-2)], 8.23 [(s, 1H, H-8); 135.0 (C-8) / 127.1 (C-9), 146.7 or 146.8 (C-12a), 155.7 (C-13a)], 8.37-8.39 [(m, 1H, H-1); 123.6 (C-1) / 130.0 or 130.1 (C-3), 142.6 (C-14a), 146.7 or 146.8 (C-4a)], 8.85 [(s, 1H, H-6); 147.7 (C-6) / 126.0 (C-6a), 142.6 (C-14a), 146.7 or 146.8 (C-4a)], 126.3 (C-7a) (do not show any proton-carbon correlations). *Anal.* Calcd for $C_{18}H_{10}N_2S_2$: C 67.90; H 3.17; N 8.80; S 20.14. Found: C 67.69; H 3.05; N 8.60; S 19.65.

1,4-Dithiino[2,3-*b*:6,5-*c*']diquinoline (**6**)

mp 256-257 ºC (EtOH), no mp depression with the sample prepared previously was observed.[18] R_f=0.66 (system I) and spot color are identical with the sample prepared previously.[18] ^{1}H NMR ($CDCl_3$), δ: [δ_C for carbons from single bond and / long range proton-carbon correlations]: 7.54 [(ddd, 1H, *J*=8.0 Hz, *J*=7.0 Hz, *J*=1.0 Hz, H-11); 127.4 (C-11) / 127.1 (C-12a), 128.7 (C-9)], 7.66 [(ddd, 1H, *J*=8.2 Hz, *J*=7.0 Hz, *J*=1.2 Hz, H-2); 127.8 (C-2) / 126.9 (C-14b), 130.2 (C-4)], 7.72 [(ddd, 1H, *J*=8.4 Hz, *J*=7.0 Hz, *J*=1.4

Hz, H-10); 130.7 (C-10) / 127.1 (C-12), 147.1 (C-8a)], 7.75 [(ddd, 1H, *J*=8.2 Hz, *J*=7.0 Hz, *J*=1.3 Hz, H-3); 129.9 (C-3) / 123.6 (C-1), 147.0 (C-4a)], 7.76 [(dd, 1H, *J*=8.0 Hz, *J*=1.4 Hz, H-12); 127.1 (C-12) / 130.7 (C-10), 135.1 (C-13), 147,1 (C-8a)], 8.02-8.05 [(m, 1H, H-9); 128.7 (C-9) / 127.1 (C-12a), 127.4 (C-11)], 8.10-8.13 [(m, 1H, H-4); 130.2 (C-4) / 126.9 (C-14b), 127.8 (C-2)], 8.26 [(s, 1H, H-13); 135.1 (C-13) / 124.8 (C-13a), 127.1 (C-12), 147.1 (C-8a), 157.3 (C-7a)], 8.31 [(dd, 1H, *J*=8.2 Hz, *J*=1.3 Hz, H-1); 123.6 (C-1) / 129.9 (C-3), 141.0 (C-14a), 147.0 (C-4a)], 8.85 [(s, 1H, H-6); 148.4 (C-6) / 127.9, (C-6a), 141.0 (C-14a), 147.0 (C-4a)].

Synthesis of 1,4-dithiino[2,3-*c*;5,6-*c*']dipyridine (**1**)

A mixture of 4.1 g (50 mmol) of phosphorous acid (H_3PO_3), 5 mL of water, 0.27 mL (2 mmol) of 57 % aqueous hydroiodic acid and 20 mL of benzene was refluxed on stirring for 15-30 min until the mixture turned to yellow. 4-Chloro-3-pyridinesulfonyl chloride (**8**)[16] (2.12 g, 10 mmol) in the form of solution in 5 mL of benzene was subsequently added portionwise. Every next portion of **8** was added when the color of the reaction mixture turned from violet to yellow. The mixture was cooled to rt and poured into 50 mL of water. The benzene layer was separated. Aqueous layer was alkalized with conc. aqueous ammonia at 5 ºC. The creamy solid was filtered off and dried on air to give 0.82 g (82 %) of dithiinodipyridine **1** with mp 171-175 ºC. It was recrystallized from EtOH to give pure **1** with mp 174-175 ºC, ref.,[1,7] mp 174-175 ºC. R_f=0.72 (system II).

Isomerization of 1,4-dithiino[2,3-*c*;5,6-*c*']dipyridine **1** to 1,4-dithiino[2,3-*c*;6,5-*c*']dipyridine (**2**)

1,4-Dithiino[2,3-*c*;5,6-*c*']dipyridine **1** (436 mg, 2 mmol) was finely powdered with elemental sulfur (320 mg, 10/8 mmol of S_8), and then kept at 200 ºC for 2 h. The mixture was cooled down to rt, powdered and then extracted with boiling $CHCl_3$ (10 mL). The extract was hot filtered and evaporated to dryness. The residue was subjected to chromatographic separation on aluminium oxide with methylene chloride to give 135 mg (31 %) of starting compound **1** and 166 mg (38 %) of 1,4-dithiino[2,3-*c*;6,5-*c*']dipyridine **2** with mp 146-147 ºC, R_f=0.61 (system II), ref.,[7] mp 146-147 ºC.

Oxidation of 1,4-dithiinodiazines **1**, **2**, **5**, **6** to 1,4-dithiinodiazines *S*-oxides **1a**, **2a**, **5a**, **6a**

1,4-Dithiinodiazine (2 mmol) was dissolved upon stirring in conc. sulfuric acid (6 mL) at 0 ºC. Then nitrating mixture (fum. nitric acid, d=1.50 g/mL, 0.32 mL, *ca*. 24 mmol of HNO_3 and 0.32 mL of conc. sulfuric acid) was added dropwise at 0-5 ºC. The mixture was maintained at 0-5 ºC for 90 min. and then poured onto 100 g of ice and neutralized at 0 ºC with conc. aqueous ammonia up to pH 5.5. The solid was filtered off, washed twice with cold water and air-dried to give yellow crude products. In the case of pyridine derivatives **1a** and **2a**, the filtrate was extracted with 2 x 5 mL of CH_2Cl_2. Combined extracts

were dried with anhydrous $CaCl_2$ and evaporated to dryness to give the second crop of product. Both crops were combined and recrystallized from EtOH.

1,4-Dithiino[2,3-*c*;5,6-*c*']dipyridine 5-oxide (**1a**)

mp 191-192 ºC (EtOH). R_f=0.46 (system II). ^{1}H NMR ($CDCl_3$) [ppm], δ: [δ_c for carbon single bond and / long range correlations]: 7.62 [(d, 1H, *J*=5.1 Hz, H-9); 123.1 (C-9) / 150.6 (C-8), 134.9 (C-5a)], 7.95 [(d, 1H, *J*=5.0 Hz, H-4); 118.9 (C-4) / 150.0 (C-3), 122.9 (C-10a)], 8.70 [(d, 1H, *J*=5.1 Hz, H-8); 150.6 (C-8) / 146.0 (C-6), 137.9 (C-9a), 123.1 (C-9)], 8.85 [(d, 1H, *J*=5.0 Hz, H-3); 150.0 (C-3) / 150.0 (C-4a), 148.4 (C-1), 118.9 (C-4)], 8.86 [(s, 1H, H-1); 148.4 (C-1) / 150.0 (C-3, C-4a), 122.9 (C-10a), 118.9 (C-4)], 9.07 [(s, 1H, H-6); 146.0 (C-6) / 150.6 (C-8), 137.9 (C-9a), 134.9 (C-5a)]. IR: υ_{SO}=1051 cm^{-1}. ***Anal.*** Calcd for $C_{10}H_6N_2OS_2$: C 51.26; H 2.58; N 11.96; S 27.37. Found: C 51.06; H 2.49; N 11.80; S 27.07.

1,4-Dithiino[2,3-*c*:6,5-*c*']dipyridine 10-oxide (**2a**)

mp 194-196 ºC (EtOH). R_f=0.32 (system II). ^{1}H NMR ($CDCl_3$) [ppm], δ: [δ_c for carbons single bond and / long range proton-carbon correlations]: 7.61 [(d, 2H, *J*=5.1 Hz, H-4 and H-6); 122.7 (C-4 and C-6) / 134.0 (C-9a and C-10a)], 8.71 [(d, 2H, *J*=5.1 Hz, H-3 and H-7); 151.0 (C-3 and C-7) / 147.8 (C-1 and C-9), 138.3 (C-4a and C-5a), 122.7 (C-4 and C-6)], 9.15 [(s, 2H, H-1 and H-9); 147.8 (C-1 and C-9) / 151.0 (C-3 and C-7), 138.3 (C-4a and C-5a), 134.0 (C-9a and C-10a)]. IR: υ_{SO}=1056 cm^{-1} ***Anal.*** Calcd for $C_{10}H_6N_2OS_2$: C 51.26; H 2.58; N 11.96; S 27.37. Found: C 51.01; H 2.39; N 11.81; S 26.97.

1,4-Dithiino[2,3-b:5,6-c']diquinoline 7-oxide (**5a**)

mp=293-294.5 ºC (ethanol). R_f=0.41 (system I). ^{1}H NMR ($CDCl_3$), δ: [δ_c for carbons from single bond and / long range proton-carbon correlations]: 7.70 [(ddd, 1H, *J*=8.1 Hz, *J*=7.0 Hz, H-10); 128.3 or 128.4 (C-10) / 127.0 (C-8a), 128.9 (C-12)], 7.76 [(ddd, 1H, *J*=8.2 Hz, *J*=7.0 Hz, *J*=1.2 Hz, H-2); 128.5 (C-2) / 125.4 (C-14b), 130.6 (C-4)], 7.87-7.91 [(m, 2H, H3, H-11); 131.8 (C-3), 132.5 (C-11) / 124.4 (C-1), 128.3 or 128.4 (C-9), 148.2 (C-4a, C-12a)], 8.02-8.04 [(m, 1H, H-9); 128.3 or 128.4 (C-9) / 132.5 (C-11), 135.1 (C-8), 148.2 (C-12a)], 8.16-8.18 [(m, 1H, H-12); 128.9 (C-12) / 127.0 (C-8a), 128.3 or 128.4 (C-10)], 8.22-8.24 [(m, 1H, H-4); 130.6 (C-4) / 125.4 (C-14b), 128.5 (C-2)], 8.45 [(ddd, 1H, *J*=8.3 Hz, *J*=1.3 Hz, *J*=0.5 Hz, H-1); 124.4 (C-1) / 131.8 (C-3), 138.4 (C-14a), 148.2 (C-4a)], 8.81 [(s, 1H, H-8); 135.1 (C-8) / 128.3 or 128.4 (C-9), 132.9 (C-7a), 148.2 (C-12a and C-13a)], 9.31 [(s, 1H, H6); 144.4 (C-6) / 130.4 (C-6a), 138.4 (C-14a), 148.2 (C-4a)]. IR (KBr pellet): υ_{SO} = 1081 cm^{-1}. ***Anal.*** Calcd for $C_{18}H_{10}N_2S_2O$: C 64.65; H 3.01; N 8.38; S 19.18. Found: C 64.69; H 3.33; N 8.44; S 18.82.

1,4-Dithiino[2,3-*c*:5,6-*b*']diquinoline 14-oxide (**6a**)

mp 261-263 ºC (EtOH). R_f=0.50 (system I). ^{1}H NMR ($CDCl_3$), δ: [δ_c for carbons from single bond and / long range proton-carbon correlations]: 7.69 [(ddd, 1H, *J*=8.1 Hz, *J*=7.0 Hz, *J*=1.1 Hz, H-11); 128.0 (C-11) / 126.8 (C-12a), 128.8 (C-9)], 7.77 [(ddd, 1H, *J*=8.3 Hz, *J*=7.0 Hz, *J*=1.3 Hz, H-2); 128.8 (C-2) / 125.6 (C-14b), 130.5 (C-4)], 7.84 [(ddd, 1H, *J*=8.4 Hz, *J*=7.0 Hz, *J*=1.4 Hz, H-3); 130.4 (C-3) / 122.5 (C-1), 147.9 (C-4a)], 7.92 [(ddd, 1H, *J*=8.4, *J*=7.0, *J*=1.4, H-10); 132.9 (C-10) / 128.5 (C-12), 148.6 (C-8a)], 8.01-8.04 [(m, 1H, H-12); 128.5 (C-12) / 132.9 (C-10), 137.4 (C-13), 148.6 (C-8a)], 8.16-8.19 [(m, 1H, H-9); 128.8 (C-9) / 126.8 (C-12a), 128.0 (C-11)], 8.21 [(dd, 1H, *J*=8.4 Hz, *J*=1.3 Hz, H-4); 130.5 (C-4) / 125.6 (C-14b), 128.8 (C-2)], 8.89 [(s, 1H, H-13); 137.4 (C-13) / 128.5 (C-12), 130.9 (C-13a), 148.6 (C-8a), 150.3 (C-7a)], 9.14 [(s, 1H, H-6); 149.1 (C-6) / 124.2 (C-6a), 140.5 (C-14a), 147.9 (C-4a)], 9.21 [(ddd, 1H, *J*=8.3 Hz, *J*=1.4 Hz, *J*=0.4 Hz, H-1); 122.5 (C-1) / 130.4 (C-3), 140.5 (C-14a), 147.9 (C-4a)]. IR (KBr pellet): ν_{SO} = 1080 cm^{-1}. *Anal.* Calcd for $C_{18}H_{10}N_2OS_2$: C 64.45; H 3.01; N 8.38; S 19.18. Found: C 64.23; H 2.90; N8.32; S 18.91.

Deoxygenation of dithiinodiazine S-oxides **1a**, **2a**, **5a**, **6a** to dithiinodiazines **1a**, **2a**, **5a**, **6a**

Previous procedure[12] was modified as follows:

Solution of dithiinodiazine-*S*-oxide (1 mmol) in conc. hydrochloric acid (3.5 mL) was treated with potassium iodide (0.4 g, 2.4 mmol) at 20 °C for 15 min and then diluted with water (5 mL). Iodine was removed with a saturated sodium thiosulfate solution and the mixture was neutralized on cold with 10 % aqueous NaOH up to pH~6. The solid was filtered off, washed with small amount of cold water and dried on air. It almost quantitatively led to homogenous (one spot in TLC) dithiinodiazine, identical with the material used for oxidation to *S*-oxide.

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