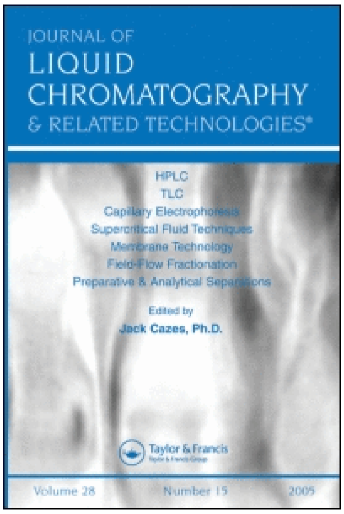

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TLC Separation of Isomeric Diazinodithiins and Diazinyl Sulfides as the Smiles Rearrangement Products

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Abstract: The reactions of diazinodithiins **1**, **5**, and **9** with sodium methanethiolate in DMSO, followed by methylation with methyl iodide, proceed with or without the Smiles rearrangement to give isomeric diazinodithiins **4**, **8**, and **12** and diazinyl sulfides **2**, **3**, **6**, **7**, **10**, and **11**. The aim of this was to find TLC conditions to follow the rearrangement, to separate and identify thioazines **1–12**. The retention parameter R_F was measured and next calculated as separation factors ΔR_F, R_S, and α. The R_F values were correlated with the dipole moments of thioazines **1–12** and the symmetry (C_{2h} and C_{2v}) of diazinodithiins **1**, **4**, **5**, **8**, **9**, and **12**.

Keywords: Dipyridodithiins, Diquinodithiins, Diquinolinyl sulfides, Dipyridinyl sulfides, Retention and separation factors, The Smiles Rearrangement

Part CVIII in the series of Azinyl sulfides

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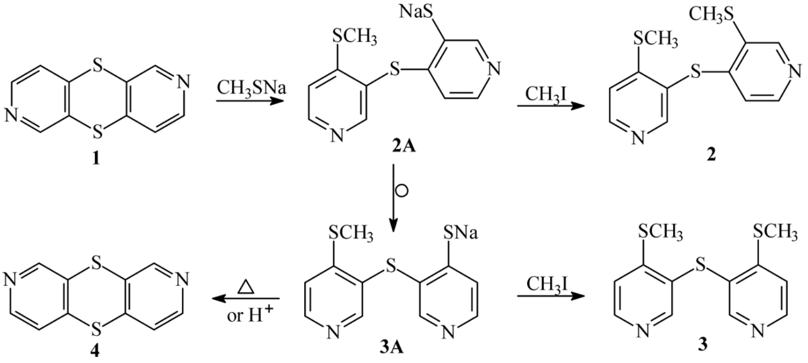
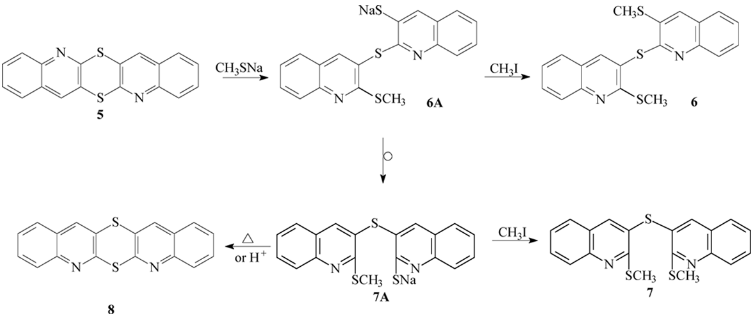
INTRODUCTION

Multicyclic thia- and azaheterocycles are considered as the new type of electron donor,[1–4] show photoelectric properties,[5] and are the active layer in a FET device.[6] During our study on the multicyclic heterocycles containing nitrogen and sulfur atoms we found unprecedented Smiles rearrangement of the S → S type (heterocyclic unit migrates from one sulfur atom to another sulfur atom).[7–10] Diquinodithiins turned out to be excellent substrates in the search of new quinoline derivatives via the 1,4-dithiin ring opening reactions.[7–9,11]

The 1,4-dithiin ring opening reactions of diazinodithiins **1**, **5**, and **9** with sodium methanethiolate in DMSO can proceed with or without the Smiles rearrangement, depending on the reaction conditions (temperature and time). Initially formed sulfides **2A**, **6A**, and **10A** can be isolated after methylation with methyl iodide as diazinyl sulfides **2**, **6**, and **10** or can rearrange to sulfides **3A**, **7A**, and **11A**, which can be further transformed to diazinodithiins **4**, **8**, and **12** via dithiin ring closure reaction, or can be isolated after methylation as diazinyl sulfides **3**, **7**, and **11** (Schemes 1–3). Sulfides **2A**, **3A**, **6A**, **7A**, **10A**, and **11A** as sodium salts are soluble in DMSO and they cannot be isolated by acidification because it induces the dithiin ring closure reactions. It is very important to follow these transformations with TLC analysis by taking a sample from the reaction mixture to determine the end of rearrangement and to identify the resulting products. Whereas diazinyl sulfides **2**, **3**, **6**, **7**, **10**, and **11** are easy to identify by ^{1}H NMR spectra (because of the symmetry of sulfides **3**, **7**, and **11**, they show only half of proton signals in comparison with unsymmetrical sulfides **2**, **6**, and **10**); the identifications of diazinodithiins **1**, **4**, **5**, **8**, **9**, and **12** only on the basis of ^{1}H NMR spectra are impossible. All these pairs of diazinodithiins consist of the same azinediyl units: 3,4-pyridinediyl,



Scheme 1. The 1,4-dithiin ring opening reaction in dipyridodithiin **1** leading to dipyridodithiin **4** and dipyridinyl sulfides **2** and **3**.



Scheme 2. The 1,4-dithiin ring opening reaction in diquinodithiin **5** leading to diquinodithiin **8** and diquinolinyl sulfides **6** and **7**.

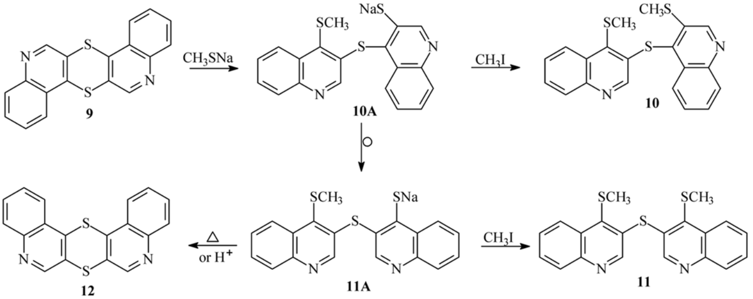
2,3-, and 3,4-quinolinediyl, but they differ with a class of symmetry: C_{2h} (diazinodithiins **1**, **5**, and **9**) and C_{2v} (diazinodithiins **4**, **8**, and **12**).

The aim of these investigations is to find the TLC conditions to separate all the reaction products on the standard adsorbents (aluminum oxide and silica gel) in order to follow the Smiles rearrangement by taking samples from the reaction mixture, to answer a question on whether the reaction is finished or should be continued, and to determine the pairs of diazinodithiins and diazinyl sulfides on the TLC data.

EXPERIMENTAL

Materials

Dipyrido-1,4-dithiins (**1** and **4**), diquino-1,4-dithiins (**5**, **8**, **9**, and **12**) dipyridinyl sulfides (**2** and **3**) and diquinolinyl sulfides (**6**, **7**, **10**, and **11**) were obtained according to the described procedures.[7–10]



Scheme 3. The 1,4-dithiin ring opening reaction in diquinodithiin **9** leading to diquinodithiin **12** and diquinolinyl sulfides **10** and **11**.

Separation of Thioazines 1–4, 5–8, and 9–12

TLC was performed on the plates precoated with silica gel 60 F_{254} (Merck, #1.05735) and aluminum oxide 60 F_{254} (type E, Merck, #1.05581). Solutions of thioazines **1–12** (2.0 mg mL^{-1}) in ethanol were prepared and spotted on a plate in 1 µL volume. Before development of plates, chromatographic chamber was saturated with the mobile phase for 0.5 hour. The chromatograms were developed at room temperature using as a mobile phases: A1. CH_2Cl_2 and A2. C_6H_6-$CHCl_3$ (1:1 v/v) for aluminum oxide, B1. $CHCl_3$-C_2H_5OH (10:1 v/v) and B2. $CHCl_3$ for silica gel. The development distance was 9 cm. After development the plates were dried at room temperature in a fume cupboard and the spots were observed under UV light at $\lambda = 254$ and 365 nm.

At least three chromatograms were developed for each group of thioazines and the R_F values were averaged. The separation factors ΔR_F, R_S and α were calculated by use of the equations:

$$\Delta R_F = R_{F1} - R_{F2} \tag{1}$$

$$R_S = \frac{d_1 - d_2}{0.5(w_1 + w_2)} \tag{2}$$

where d_1 and d_2 are the distances between the centers of the spots and the starting points, w_1 and w_2 are the widths of the spots.

$$\alpha = \frac{[(1/R_{F1}) - 1]}{[(1/R_{F2}) - 1]} \tag{3}$$

The separation of neighboring pairs of thioazines is regarded as effective when the values of the separation factors are $\Delta R_F \geq 0.05$, $R_S > 1$, and $\alpha > 1$.

Examination of the Smiles Rearrangement in the Reaction of Diazinodithiins 1, 5, and 9 with Sodium Methanethiolate – General Procedure

To a suspension of diazinodithiins **1**, **5**, or **9** (1 mmol) in dry DMSO (5 mL) at 20–170°C sodium methanethiolate (0.084 g; 1.2 mmol) was added. The mixture was stirred for 10 minutes to 7 days depending on the diazinodithiin nature. After some time, a sample (0.05 mL) was taken from the reaction mixture and poured into 15% aqueous sodium hydroxide solution (0.15 mL). Methyl iodide (0.02 mL) was added and the mixture was shaken for a minute. Next water (2 mL) was added to the mixture and the mixture was shaken with chloroform (2 mL) also for a minute. The separated chloroform extract was dried with anhydrous sodium sulfate. A sample (1 μL) was taken from the chloroform solution and spotted on the chromatographic plate to observe the Smiles rearrangement. When the rearrangement was considered as finished, the reaction mixture was cooled down to room temperature and poured into 15% aqueous sodium hydroxide solution (15 mL). Methyl iodide (0.1 mL, 1.6 mmol) was added and the reaction mixture was stirred at room temperature for 1 hour. The resulting solid was filtered off, washed with water, air-dried, and separated by column chromatography (silica gel, chloroform) to give thioazines **1–4**, **5–8** and **9–12**.

Calculation of Dipole Moments

Values of the molecular dipole moments of thioazines **1–12** were calculated using a commercial software PQS.[12] The following methods were employed: two semiempirical (AM1[13] and PM3[14,15]), and two *ab initio*: the popular hybrid potential B3LYP[16,17] of the density functional theory (DFT),[18] and the second order Mϕller-Plesset perturbation theory (MP2).[19] Both *ab initio* methods were used in combination with two split-valence basis sets: the polarized[20,21] 6–31G*, and the diffusive[22] 6–31 + G*.

Geometries of all the molecules studied were optimized. In the case of sulfides **2**, **3**, **6**, **7**, **10**, and **11** the rotational freedom around the C–S–C bonds connecting more rigid aromatic rings was taken into account by performing relaxed potential energy scans of the respective torsional angles. Geometries of these molecules were additionally reoptimized for all identified energy minima. The values of the dipole moment for these molecules were assumed to be mean values over all such conformers.

RESULTS AND DISCUSSION

In order to follow the Smiles rearrangement of the S → S type we looked for chromatographic conditions to separate the reaction products. The discussed rearrangement proceeded smoothly in the reaction of diquinodhiin **9** (at 20°C but for 7 days or at 70°C for 10 minutes[7,8]) and slowly for diquinodithiin **5** (at 140°C for 0.5 hour[9]) and dipyridodithiin **1** (at 170°C for 0.5 hour[10]). The examined reaction of diazinodithiins **1**, **5**, and **9** consists of four stages:

1. the 1,4-dithiin ring opening process with sodium methanethiolate to sulfides **2A**, **6A**, and **10A**,

2. the rearrangement process of sulfides **2A**, **6A**, and **10A** to sulfides **3A**, **7A**, and **11A**,
3. the methylation process of sulfides **2A**, **3A**, **6A**, **7A**, **10A**, and **11A** with methyl iodide to sulfides **2**, **3**, **6**, **7**, **10**, and **11**,
4. the 1,4-dithiin ring closure process of sulfides **2A**, **3A**, **6A**, **7A**, **10A**, and **11A** to diazinodithiins **1**, **4**, **5**, **8**, **9**, and **12** in some reaction conditions (Scheme 1–3).

Since the ring closure reaction is not rapid and proceeds in some reaction conditions, especially at high temperature (the best preparative results were obtained when the reaction mixture was diluted with sodium hydroxide solution and boiled for 1 hour[23]), the methylation is a more useful process because it gives the methylated products after a few seconds. The presence of sulfides **3**, **7**, and **11** in the reaction products gives evidence for the rearrangement process. A ratio of sulfides **3** to **2** + **3**, **7** to **6** + **7**, and **11** to **10** + **11** can be regarded as the progress of the rearrangement. A sample taken from the reaction mixture without the following methylation gives evidence, first of all, for the presence of remaining unconsumed diazinodithiins **1**, **5**, and **9** as starting material and the presence of diazinodithiins **4**, **8**, and **12** gives evidence, to less extent, for the progress of rearrangement.

In order to follow this rearrangement we looked for the appropriate mobile phase to separate well all four thioazines (**1–4**, **5–8**, and **9–12**) in the reaction. In some cases there were difficulties to find conditions to separate sulfides **2** from **3** and **6** from **7**, and dipyridodithiins **1** from **4**. From the developed chromatograms, we calculated the R_F values and further separation factors: ΔR_F, R_S, and α values. There is no one mobile phase to separate all 12 thioazines but each azinediyl system needs another solvent system. We elaborated 4 mobile phases, which separated quite well thioazines **1–4**, **5–8**, and **9–12**. The best separation of thioazines **1–4** was achieved using $CH_2Cl_2/Al_2\ O_3$, of thioazines **5–8** using $CHCl_3/SiO_2$ and of thioazines **9–12** using CH_2Cl_2/Al_2O_3 and C_6H_6-$CHCl_3$ (1:1 v/v, Table 1). We tried by trials and errors other mobile systems (CCl_4, $CHCl_3$, $CHCl_3$-EtOH-$C_6\ H_{12}$ 10:1:0.5 v/v, for Al_2O_3 and ethyl acetate, acetone, and C_2H_5OH for SiO_2 but neither pairs of diazinodithiins nor sulfides were separated well. We observed different colors of the spots of thioazines **1–12**, not only for different azinyl systems (3,4-pyridinediyl, 2,3- and 3,4-quinolinediyl), but also for the type of products which enable to distinguish diazinodithiins from diazinyl sulfides (Table 2). In our examination we observed such a regularity of the R_F values in diazinodithiins:

$$\underset{(\mathbf{1},\mathbf{5},\text{and }\mathbf{9})}{\text{diazinodithiins of } C_{2h} \text{ symmetry}} > \underset{(\mathbf{4},\mathbf{8},\text{and }\mathbf{12})}{\text{diazinodithiins of } C_{2v} \text{ symmetry}}$$

Table 1. The retention and separation factors of thioazines **1–12**

Mobile phase	Neibouring pairs of thioazines	R_F	ΔR_F	R_S	α
A1	**1/4**	0.55/0.48	0.07	2.10	1.32
	4/2	0.48/0.34	0.14	4.20	1.80
	2/3	0.34/0.26	0.08	2.40	2.64
	6/7	0.84/0.84	0.0	0.0	0.0
	6/5 and **7/5**	0.84/0.77	0.07	1.58	1.57
	5/8	0.77/0.47	0.30	6.75	3.89
	11/10	0.71/0.62	0.09	2.02	1.49
	10/9	0.62/0.57	0.05	1.12	1.24
	9/12	0.57/0.26	0.31	6.98	3.79
A2	**1/4**	0.34/0.26	0.08	2.40	1.47
	4/2	0.26/0.12	0.14	4.20	2.57
	2/3	0.12/0.09	0.03	0.90	1.38
	6/7	0.82/0.79	0.03	0.68	1.21
	7/5	0.79/0.69	0.10	2.25	1.66
	5/8	0.69/0.37	0.32	7.25	3.78
	9/11	0.51/0.39	0.12	2.75	1.63
	11/12	0.39/0.33	0.06	1.35	1.30
	12/10	0.33/0.23	0.10	2.25	1.65
B1	**1/4**	0.54/0.50	0.04	1.20	1.18
	4/2	0.50/0.41	0.09	2.70	1.44
	2/3	0.41/0.34	0.07	2.10	1.35
	6/7	0.84/0.84	0.0	0.0	0.0
	6/5 and **7/5**	0.84/0.76	0.08	1.80	1.66
	5/8	0.76/0.70	0.06	1.35	1.36
	11/9	0.81/0.78	0.03	0.68	1.23
	9/12	0.78/0.75	0.03	0.68	1.15
	12/10	0.75/0.70	0.05	1.13	1.30
B2	**1/4**	0.32/0.31	0.10	0.30	1.03
	4/2	0.31/0.10	0.21	6.30	2.79
	2/3	0.10/0.80	0.02	0.60	1.28
	7/6	0.86/0.81	0.05	1.13	1.45
	6/5	0.81/0.53	0.28	6.30	3.77
	5/8	0.53/0.33	0.20	4.50	2.28
	11/9	0.52/0.48	0.04	0.90	1.18
	9/12	0.48/0.42	0.06	1.35	1.28
	12/10	0.42/0.35	0.07	1.58	1.35

A1 = CH_2Cl_2/Al_2O_3, A2 = C_6H_6-$CHCl_3$ 1:1/Al_2O_3, B1 = $CHCl_3$-C_2H_5OH 10:1/SiO_2, B2 = $CHCl_3/SiO_2$

Table 2. The color of the spots of thioazines **1-12** at $\lambda = 254\,\text{nm}$

No	Thioazines	Color of the spot
1	Dipyridodithiins **1** and **4**	pale pink
2	Dipyridinyl sulfides **2** and **3**	pink
3	Diquinodithiins **5** and **8**	blue
4	Diquinolinyl sulfides **6** and **7**	blue-grey
5	Diquinodithiins **9** and **12**	orange
6	Diquinolinyl sulfides **10** and **11**	bluish

But we did not observe such a regularity of the R_F values in diazinyl sulfides. Whereas the unrearranged dipyridinyl sulfide **2** has a higher R_F value than the rearranged sulfide **3**, the unrearranged diquinolinyl sulfide **10** has a lower R_F value than the rearranged sulfide **11**. In the case of diquinolinyl sulfides **6** and **7**, their values depend on the chromatographic conditions (adsorbent and mobile phase).

In our opinion, the obtained R_F values in thioazines **1–12** are dependent, most of all, on the polarity of these compounds. We calculated the dipole moments (μ) by semi-empirical (AM1 and PM3) and *ab intio* (B3LYP/6-31G*, B3LYP/6-31 + G*, MP2/6-31G*, and MP2/6-31 + G*) quantum chemical methods and the values are listed in Table 3. All these calculations show that the dipole moment values of diazinodithiins of C_{2v} symmetry (**4**, **8**, and **12**) are higher than the values of diazinodithiins of C_{2h} symmetry (**1**, **5**,

Table 3. Calculated dipole moments (μ) of thioazines **1–12** with the use of quantum chemical methods

Thioazine	AM1 [D]	PM3 [D]	B3LYP/6-31G* [D]	B3LYP/6-31 + G* [D]	MP2/6-31G* [D]	MP2/6-31 + G* [D]
1	0.01	0.36	0.09	0.09	0.13	0.08
2	3.12	2.50	2.26	2.62	2.41	2.77
3	3.98	3.55	2.20	4.82	1.84	1.95
4	1.98	1.98	2.28	2.43	2.37	2.51
5	0.96	1.57	1.63	1.60	2.17	2.18
6	2.67	3.38	2.63	2.68	4.10	4.16
7	1.28	3.52	3.07	2.81	3.24	2.97
8	3.55	3.73	3.73	3.90	4.10	4.26
9	0.01	0.67	0.51	0.34	0.69	0.50
10	2.90	2.29	2.30	2.35	1.66	1.66
11	3.31	4.78	2.11	2.10	3.25	3.49
12	2.64	2.90	3.12	3.17	3.22	3.28

Table 4. Relationship between the R_F values and calculated dipole moment values ($R_F = a\mu + b$) for the thioazines **1–12**

Thioazines	Mobile phase	Calculation method	Correlation a	b	r
1–4	A1	AM1	−0.0739	0.5753	0.9642
1–4	A2	AM1	−0.0668	0.3541	0.9721
1–4	B1	AM1	−0.0498	0.5606	0.9502
1–4	B2	AM1	−0.0672	0.3550	0.8849
5–8	A1	B3LYP/6-31G*	−0.1467	1.1198	0.7140
9–12	A2	B3LYP/6-31 + G*	−0.0767	0.5173	0.7801

and **9**). This fact can be ascribed to the contribution of electronegative nitrogen atoms in the appropriate places in the ring systems. As diazinodithiins of C_{2h} symmetry show the higher R_F values, but lower dipole moments values than isomeric diazinodithiins of C_{2v} symmetry, this observation can be used in the future to identify other pairs of isomeric diazinodithiins. Although there are over 20 known different types of diazinodithiins (azine = pyridine pyridazine, pyrimidine, pyrazine, quinoline, quinoxaline, and pteridine) only a few diazinodithiins were unequivocally identified by X-ray analyses (dithiins **1**, **4**, **5**, **8**, **9**, and **12** are non-planar, folded along the S−S axis,[9,10,24,25] dipyrazinodithiin,[26] and diquinoxalinodithiin,[27] are planar).

Calculations of dipole moments of the pairs of isomeric sulfides **2**/**3**, **6**/**7**, and **10**/**11** were more complicated because of the rotational freedom around the C−S−C bonds and the influence of the resulted conformations on the polarity.

We tried to find a relationship between the obtained R_F values for used mobile phases and the dipole moment (μ) values obtained by quantum chemical methods:

$$R_F = a\mu + b \tag{4}$$

for each thioazine groups (**1–4**, **5–8**, and **9–12**). In some cases, the correlations were significant (Table 4), for other cases, the correlation coefficients were low or very low.

CONCLUSIONS

On the basis of the examined separations of thioazines **1–12**, it can be concluded that TLC analysis is a convenient method to examine the Smiles rearrangement of the S → S type occurring during the dithiin ring opening in diazinodithiins. This is the first example to use TLC analysis in this rearrangement and opens possibilities to investigate such a rearrangement in other diazinodithiins. We found regularity between the symmetry of diazinodithiins (C_{2h} and C_{2v}) and the R_F parameter and the polarity. Diazinodithiins of C_{2h} symmetry have the higher R_F and lower dipole moments values than diazinodithiins of C_{2v} symmetry. This enables the identification of these diazinodithiins.

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