

SYNTHESIS AND X-RAY ANALYSIS OF ISOMERIC DIAZADITHIA-PENTACENES†

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Abstract - The isomeric diazadithiapentacenes (**3**) and (**4**) were obtained in reactions of 2-chloro-3-bromoquinoline (**5**) with selected sulfur reagents in various conditions. The 1,4-dithiin ring opening in diazadithiapentacene (**3**) led to 2,3'-diquinoliny sulfide or (*via* the Smiles rearrangement stage of the S→S type) to 3,3'-diquinoliny sulfide or to diazadithiapentacene (**4**) depending on reaction conditions. The X-Ray study of pentacenes (**3**) and (**4**) revealed non-planar and folded structures along the central sulfur-sulfur axis. The central six-membered ring is in a boat conformation.

INTRODUCTION

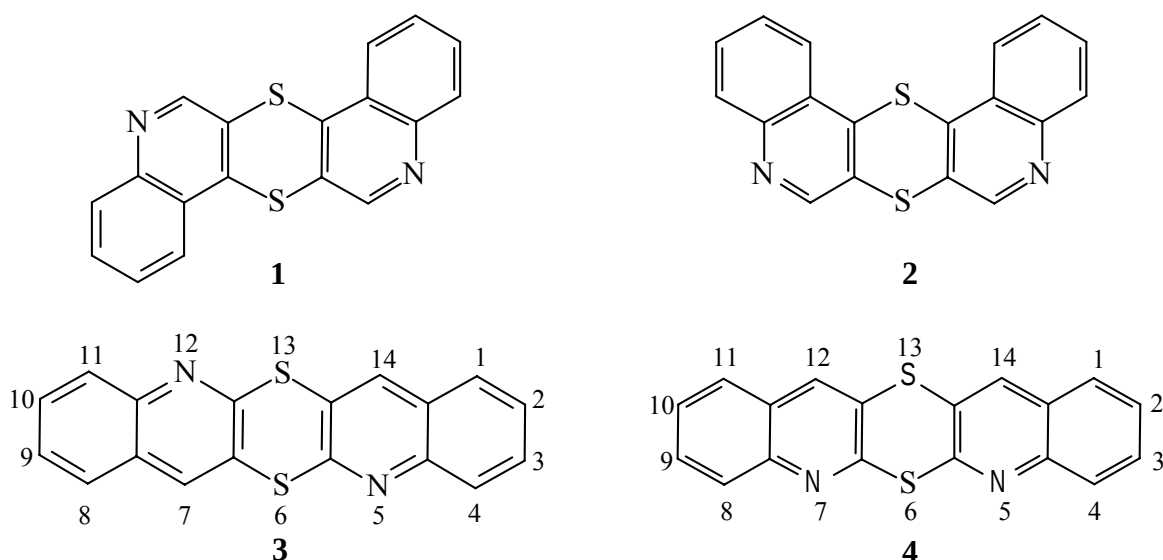
Great interest has been focused on the organic materials with interesting electronic, optoelectronic or magnetic properties. The incorporation of polarizable heteroatoms within the donor framework is regarded as an important aspect in designing new polyheterocyclic donor molecules.¹ Very few papers have appeared in the literature on the synthesis and properties of fused pentacyclic heterocycles. Some azathiapentaphenes and diazadithiapentacenes show photoelectric properties² and some diazapentacenes are considered as photodynamic therapeutic agent against cancer cell lines, bacteria and viruses.³ Recent studies demonstrated the significant conductivity enhancement of disubstituted homopentacenes.⁴ Our research group found the two angular fused pentacyclic diazadithiapentacenes (1,4-dithiinodiquinolines) (**1**) and (**2**) to be very useful substrates to obtain various thus far unknown quinoline derivatives of different types, such as disubstituted quinolines,^{5a,6} diquinolines sulfides,^{5b,7} benzoquinothiazines^{5c} and their salts,^{5d} thiazinodiquinolines and related heterocyclodiquinolines^{5e} and quinoline crown thioethers.^{5f}

RESULTS AND DISCUSSION

Synthesis

Whereas dithiinodiquinoline (**1**), possessing C_{2h} symmetry, is very easy to obtain by direct sulfurization of quinoline with elemental sulfur in good yield (64%)⁸ or by cyclization of potassium 3-bromo-4(1*H*)-quinolinethiolate in high yield (81%),⁹ a linear equivalent of dithiinodiquinoline (**1**), dithiinodiquinoline (**3**) (possessing the same C_{2h} symmetry) is difficult to obtain in good yield (reported yield of 15%¹⁰ or 27%¹¹, or 6-29% for disubstituted derivatives¹²).

In this work we report a novel synthesis method of dithiinodiquinoline (**3**), the final confirmation of the structures of dithiinodiquinolines (**3**) and (**4**) using X-Ray analysis, and a comparison of the physical and spectroscopical data of dithiinodiquinolines (**1** – **4**) with regard to the C_{2h} and C_{2v} symmetry.



Scheme 1

Synthesis of dithiinodiquinoline (**3**) is a problem of substitution in the pyridine ring in the 2 and 3 positions. Since the direct substitution of the hydrogen atoms in quinoline in the sulfurization reaction led only to 3,4-dithiosubstituted quinolines: mainly to dithiinodiquinoline (**1**) and to some extent to dithiinodiquinoline (**2**),^{8,9} synthesis of 2,3-dithiosubstituted quinolines was based on the substitution of 2,3-haloquinolines. Although a halogen atom is much more reactive in the 2 position than in 3 in nucleophilic substitution reactions,¹³ there are a few examples of formation of 3-diquinolinyl sulfide systems: the mentioned cyclization of potassium salt of 3-bromo-4(1*H*)-quinolinethione (DMSO, 140 °C)⁹ and reactions of 3-bromoquinoline with sodium sulfide (DMSO, 150-155 °C or DMF, 153 °C).^{13,14}

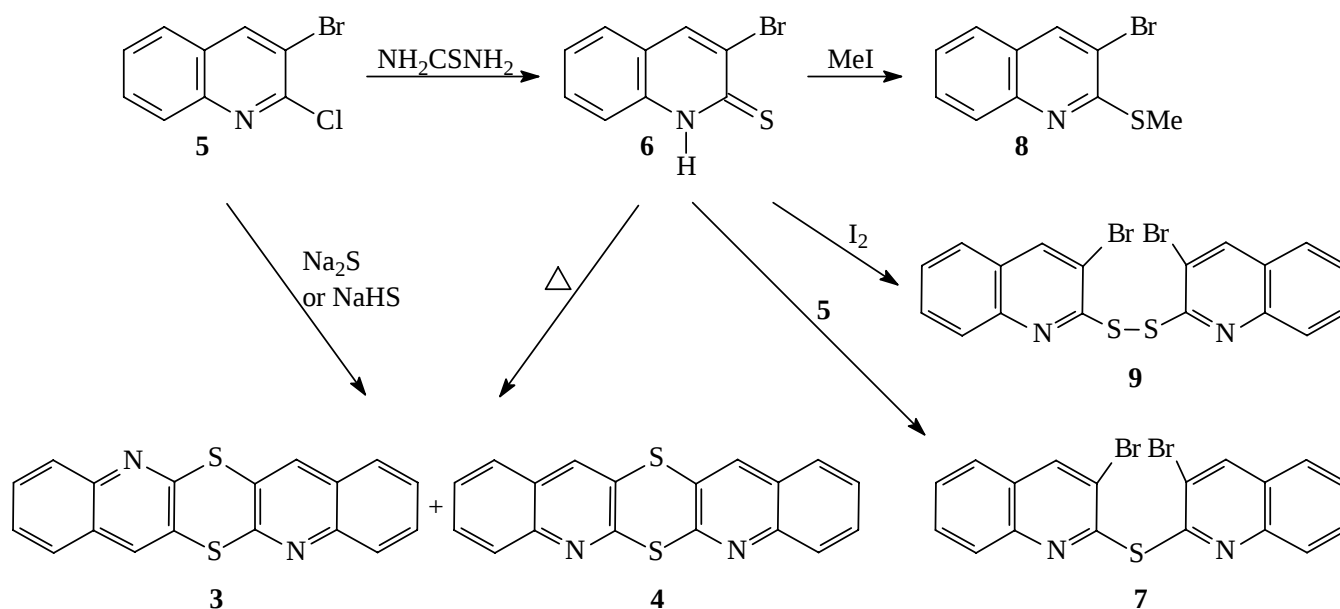
We started our synthesis of dithiinodiquinoline (**3**) with attempts at a cyclization reaction of the potassium salt of 3-bromo-2(1*H*)-quinolinethione (**6**) (obtained from 2-chloro-3-bromoquinoline (**5**)) in the above mentioned conditions but the reaction in DMSO failed even at 160 °C. Since the reaction of 2-chloro-3-bromoquinoline (**5**) with thiourea in boiling ethanol (at 78 °C) gave 3-bromo-2(1*H*)-quinolinethione (**6**) in high yield (92%), we repeated this reaction at higher temperature, i.e. in boiling DMF (at 153 °C) but quinolinethione (**6**) was the product in 83%. Next we heated neat quinolinethione (**6**) at 200 °C (without solvent) yielding dithiinodiquinolines (**3**) and (**4**) in poor yields (38% and 19%, Table 1).

Reaction of 2-chloro-3-bromoquinoline (5) with another sulfur reagent - anhydrous sodium sulfide in DMSO at 160 °C for 5 h led to dithiinodiquinolines (3) and (4) in 25% and 6% yields. Similar results (dithiinodiquinolines (3) and (4) in 25% and 19% yields) were obtained in the reaction of 2-chloro-3-bromoquinoline (5) with sodium hydrogen sulfide in DMSO at 160 °C for 1 h. Better results were obtained in the reaction of 2-chloro-3-bromoquinoline (5) with sodium hydrogen sulfide in boiling DMF for 15 h giving dithiinodiquinolines (3) and (4) in 57% and 10% yields. The best yields (57% and 19%) were obtained when this reaction was carried out in boiling 1-methyl-2-pyrrolidinone (at 202 °C).

Table 1. Reactions of bromoquinolines (5) and (6) to diazadithiapentacenes (3) and (4)

Substrate	Reaction conditions Reagent, Solvent, Temp. (°C), Time (h)	Products (%)
(5)	Na ₂ S, DMSO, 160, 5	(3) (25), (4) (6)
(5)	NaHS, DMSO, 160, 5	(3) (25), (4) (19)
(5)	NaHS, DMF, 153, 15	(3) (57), (4) (10)
(5)	NaHS, MP, 202, 1	(3) (57), (4) (19)
(6)	- neat, 200, 0.5	(3) (38), (4) (19)

MP = 1-methyl-2-pyrrolidinone

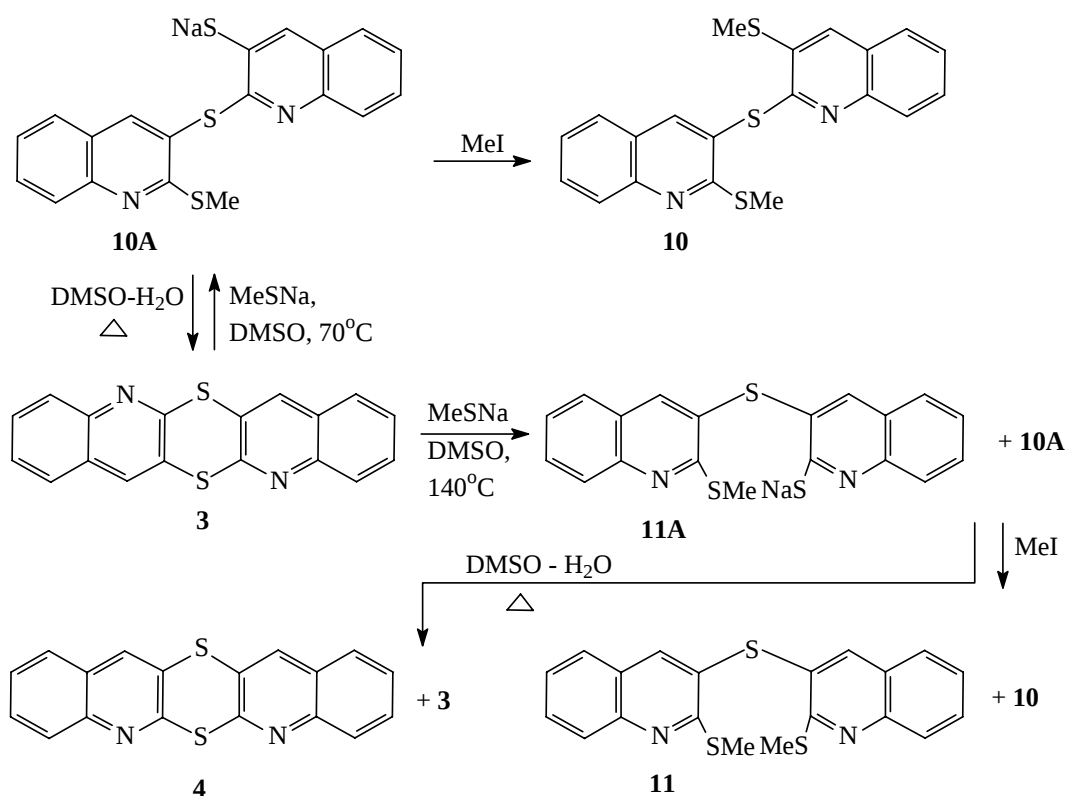


Scheme 2

Quinolinethione (6) was useful to obtain new quinoline derivatives. The reaction with the halo compounds (2-chloro-3-bromoquinoline (5) in boiling DMF and methyl iodide in aqueous solution at room temperature) led to 2-quinolinyl sulfides: 3,3'-dibromo-2,2'-diquinolinyldisulfide (7) (61%) and 2-methylthio-3-bromoquinoline (8) (63%). Oxidation of quinolinethione (6) with iodine in ethanol gave 3,3'-dibromo-2,2'-diquinolinyldisulfide (9) in 84% yield.

As mentioned above the 1,4-dithiin ring opening reactions in dithiinodiquinolines (**1**) and (**2**) with nucleophiles in DMSO or DMF was an original strategy for obtaining new quinoline derivatives.⁵⁻⁷ Under some conditions, the Smiles rearrangement of hitherto unknown type (S→S) was observed.^{6,7} The model 1,4-dithiin ring opening reaction in dithiinodiquinoline (**1**) with sodium methanethiolate led to three compounds depending on the reaction conditions. The initial product, appropriate sodium 4-quinolinylthio-3-quinolinethiolate (at 20 °C), can be isolated after S-methylation as 3',4'-dimethylthio-3,4'-diquinolyl sulfide or can be transformed *via* the Smiles rearrangement (at 70 °C) to sodium 3-quinolinylthio-4-quinolinethiolate which can be isolated after S-methylation as 4,4'-dimethylthio-3,3'-diquinolyl sulfide or can be undergone the 1,4-dithiin ring closure reaction to dithiinodiquinoline (**2**).^{6,7,15}

The 1,4-dithiin ring opening reaction in dithiinodiquinoline (**3**) with sodium methanethiolate was carried out in DMSO at 70 °C. The progress of the reaction was followed by observation of a color of the reaction mixture (a change from yellow to deep red) and dissolution of a suspension of dithiinodiquinoline (**3**) into solution during the course of the reaction (in the end of this stage the reaction mixture became a transparent solution). The reaction mixture was poured into threefold volume of 15% aqueous sodium hydroxide solution and methylated with methyl iodide to give the S-methyl derivative, 2,3'-dimethylthio-2',3'-diquinolyl sulfide (**10**), in 89% yield. When the reaction mixture was poured into aqueous sodium hydroxide solution, diluted with water and next boiled for 30 min dithiinodiquinoline (**3**) was obtained in 88% yield. These results gave no evidence of the Smiles rearrangement at 70 °C. Repeating the reaction in DMSO at 140 °C after methylation gave a mixture of sulfides, 2,3'-dimethylthio-2',3'-diquinolyl sulfide (**10**) (16%) and 2,2'-dimethylthio-3,3'-diquinolyl sulfide (**11**) (42%). The latter sul-



Scheme 3

fide was the sole product of the 1,4-dithiin ring opening reaction in dithiinodiquinoline (**4**).¹⁰ Boiling the aqueous DMSO solution of the initial dithiin ring opening products gave a mixture of dithiinodiquinolines (**3**) and (**4**) in 22% and 57% yields. These products are results of the Smiles rearrangement of the very unusual S→S type (the quinolinyl group migrates from one sulfur atom to another) of sodium 2-quinolinylthio-3-quinolinethiolate (**10A**) to sodium 3-quinolinylthio-2-quinolinethiolate (**11A**) proceeding with about 70% efficiency. The *ab initio* calculations using 6-31G**/STO-3G* model for all dipyridinyl sulfides suggested the possibility of the Smiles rearrangement only for 2,2'-, 2,3'- and 2,4'-dipyridinyl sulfides¹⁶ and indeed the rearrangement but of the S→N type was observed only for 2,2'- and 2,4'-dipyridinyl sulfides.¹⁷ This rearrangement is unprecedented because the nucleophilic attack of 3'-quinolinethiolate anion occurs at the position 3 in the quinoline ring in sulfide (**10A**) (a cleavage of the C3-S bond), which is not susceptible as a rule for such attack,¹³ and the more reactive position 2 remains unaffected (Scheme 3). This is the first example of such a rearrangement in a 2,3'-diazinyl sulfide system and only the third example at all (found so far in 3,4'-diazinyl sulfide system, azinyl = quinolinyl,^{6,7} pyridinyl¹⁸).

X-Ray analysis

All these isomeric 1,4-dithiinodiquinolines (**1-4**) (C₁₈H₁₀N₂S₂) have pairs of the identical 2,3- and 3,4-quinolinediyl units, therefore they are difficult to determine, the more so because in certain conditions they even isomerize.^{15,19,20} A problem of determination of the correct structures of 1,4-dithiinodiquinolines (**1-4**) was put forward by some authors.^{9,11} Since spectroscopic evidences are indirect and subtle, and chemical ones are sometimes dubious (with the regard to isomerization and rearrangement) only X-Ray analysis as a direct proof can give a final answer on the structure determination. Although dithiinodiquinoline (**1**) has been known for over a hundred years, and dithiinodiquinoline (**2**) eighty years, the correct structures as 1,4-dithiino[2,3-*c*;5,6-*c'*]diquinoline and 1,4-dithiino[2,3-*c*;6,5-*c'*]diquinoline were introduced by us only in 1980⁹ on the basis of spectroscopic and chemical properties. The structure of dithiinodiquinoline (**1**) was finally confirmed by the X-Ray analysis of its dihydrochloride in 1990.²¹ Similar to crystallizations of dithiinodiquinolines (**1**) and (**2**) also crystallization of 1,4-dithiinodiquinolines (**3**) and (**4**) from various solvents did not lead to crystals of good quality. Using horizontal vapor transport²² produced crystals appropriate for X-Ray analysis.

The X-Ray study of compounds (**3**) and (**4**) is the final confirmation of their structure as 5,12-diaza-6,13-dithiapentacene (1,4-dithiino[2,3-*b*;5,6-*b'*]diquinoline) and 5,7-diaza-6,13-dithiapentacene (1,4-dithiino[2,3-*b*;6,5-*b'*]diquinoline), respectively. Whereas dithiinodiquinoline (**3**) crystallizes in the monoclinic space group I2/a with a stacked configuration along the b-axis of 3.892 Å, dithiinodiquinoline (**4**) crystallizes in the monoclinic space group P2₁/n with two independent molecules in the unit cell (the two molecules are chemically equivalent, with molecule 1 on the inverted molecule 2 giving the best fit). In contrast to homopentacene²³ and 5,7,12,14-tetraza-6,13-dithiapentacene²⁴ but similar to our other heteropentacenes (5,7-diaza-13-thia-, 5,6,7-triaza-13-thia- and 5,7-diaza-6-selena-13-thiapentacenes) the both diazadithiapentacenes (**3**) and (**4**) are non-planar (Figure 1). The central 1,4-dithiin ring is in a boat conformation with the sulfur atoms out of the basal plane formed by the central four carbon atoms

(Table 2). The diazadithiapentacene system is folded mainly along the S-S axis and slightly along the C-C axes (the bonds linking the dithiin ring with the quinoline rings). Pentacene (3) is less folded than pentacene (4) with higher values of ring system is quite planar, the dihedral angles between the pyridine and benzene ring do not exceed 1.8° . The 2-quinolinyl-sulfur bond is slightly longer than the 3-quinolinyl-sulfur bond in both pentacenes. The C-S-C angle is larger in pentacene (3) than pentacene (4). Table 2 contains selected geometrical features of pentacenes (3) and (4).

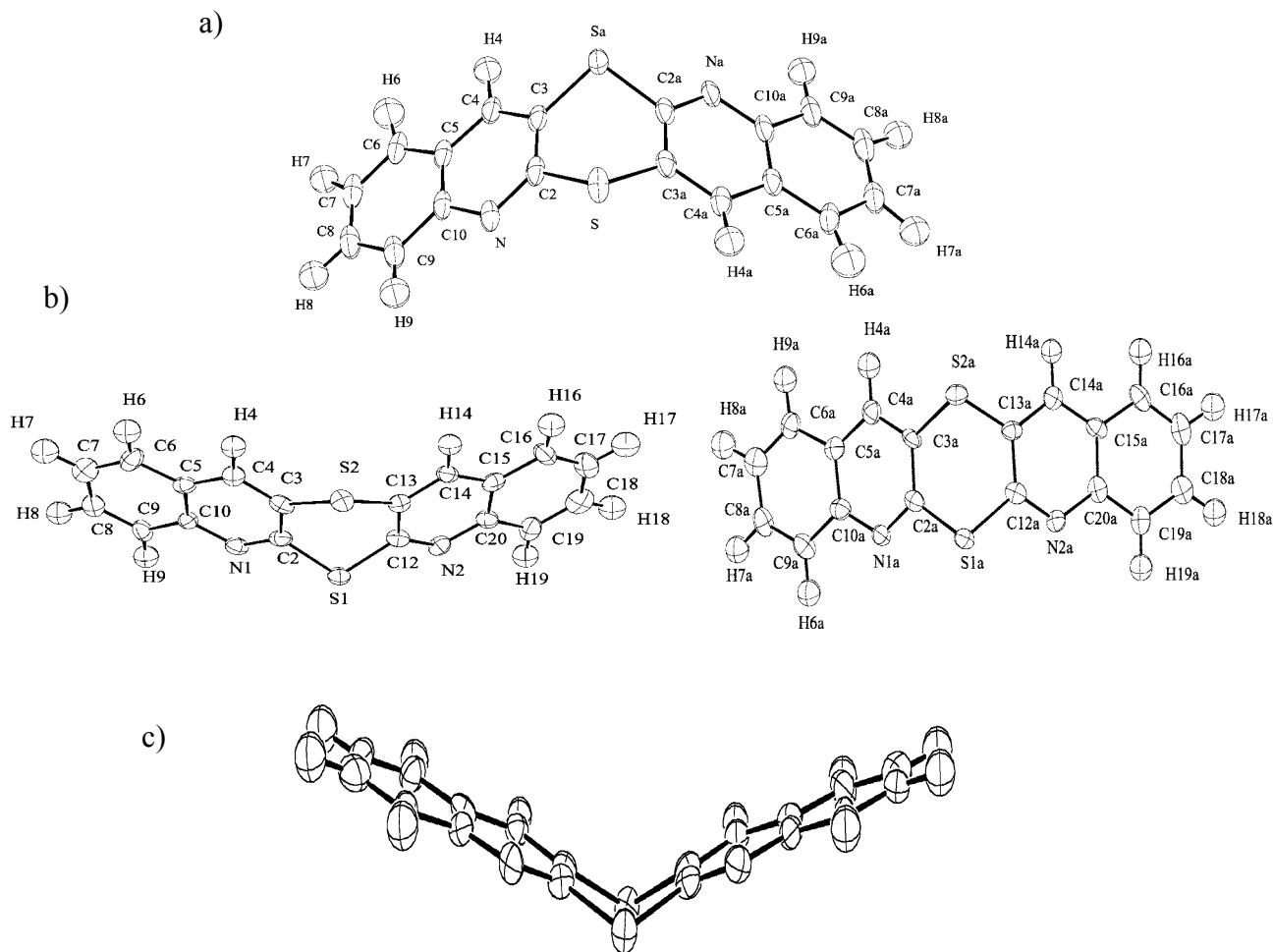


Figure 1. ORTEP drawings of diazadithiapentacenes (3) (a) and (4) (b,c)

Comparison of 1,4-dithiinodiquinolines (1-4).

Pentacyclic 1,4-dithiinodiquinolines (1-4) represent two classes of symmetry: point groups C_{2h} and C_{2v} . Both compound classes revealed some regularities in physical and spectroscopic data which enables their differentiation (Table 3). Dithiinodiquinolines with the C_{2h} symmetry (1 and 3) show higher melting points, higher R_f values, higher chemical shift of a singlet signal of the pyridinyl proton in 1H NMR spectra and lower intensities of fragment ions $[M-S]^{+\bullet}$ and $[M-CS]^{+\bullet}$ (formed by elimination of the sulfur atom and the thiocarbonyl group) than the isomers with the C_{2v} symmetry (2 and 4). Higher melting point and R_f of the isomers (1) and (3) are a result of their higher thermal stability observed during synthesis at

high temperatures^{8,9} (including this paper) and their reduced polarity as is apparent from their structures. The intensities of the fragment ions in the mass spectra depend on a cleavage of the 2-, 3- and 4-quinolinyl-sulfur bonds. The X-Ray study of diquinolinyl sulfides and disulfides showed the 3-quinolinyl-sulfur bond to be shorter²⁵⁻²⁷ (including the data in Table 2) than the 2- and 4-quinolinyl-sulfur bonds,^{28,29} and therefore the former bonds are expected to be more resistant to a cleavage. The angular isomers (**1**) and (**2**) and the linear isomers (**3**) and (**4**) differ in spot color (Table 3).

Table 2. Selected details of the molecular geometry of heteropentacenes (**3**) and (**4**)

Geometrical feature	pentacene (3)	pentacene (4)	
		molecule 1	molecule 2
2-quinolinyl-sulfur bond (Å)	1.785(9)	1.771(11), 1.771(11)	1.781(12), 1.766(11)
3-quinolinyl-sulfur bond (Å)	1.777(9)	1.756(11), 1.767(11)	1.757(11), 1.763(11)
C-S-C angle (°)	100.0(4)	103.7(5), 102.3(5)	103.1(5), 102.3(5)
Dihedral angle between the halves of the dithiin ring (°)	128.0(5)	46.8(5)	44.9(4)
Dihedral angle between the quinoline rings (°)	48.2(5)	35.24(21)	35.66(21)
Dihedral angle between the pyridine and benzene rings (°)	1.0(4)	1.8(4), 1.1(4)	1.7(4), 1.2(4)
Displacement of the sulfur atoms from the central CCCC plane (Å)	0.666(15)	0.529(16), 0.661(15)	0.582(16), 0.640(15)

Table 3. Comparison of the physical and spectroscopic data of 1,4-dithiinodiquinolines (**1-4**)

Physical and spectroscopic data	Pairs of isomers with the C _{2h} and C _{2v} symmetry	
	angular (1)/(2)	linear (3)/(4)
Melting point (° C)	314-315 ¹⁹ /270-271 ¹⁵	287-289 ¹¹ /258-259 ¹¹
TLC (R _f , spot color)		
a. silica gel, CHCl ₃ -MeOH	0.53 orange/0.45 orange	0.63 blue/0.57 blue
b. aluminum oxide, CH ₂ Cl ₂	0.57 orange/0.26 orange	0.77 blue/0.47 blue
¹ H NMR, δ H _{pyridinyl} (ppm)	8.89 ³⁰ /8.86 ³⁰	8.24/8.17 ¹⁰
MS 70 eV, m/z (%)		
a. 318 (M)	100 ³¹ /100	100/100
b. 286 (M-S)	15.5 ³¹ /18.4	15.6/19.3
c. 274 (M-CS)	7.5 ³¹ /10.0	9.6/11.2

Conclusion

We report here effective synthesis of pentacyclic diazadithiapentacenes (**3**) and (**4**) and disubstituted 2,2'-, 2,3'- and 3,3'-diquinolinyl sulfides (**7**, **10** and **11**). The structures of isomeric diazadithiapentacenes (**3**)

and (**4**) were confirmed by the X-Ray analysis. Under some reaction conditions the Smiles rearrangement of the S→S type of sodium salt of 2-methylthio-3'-mercapto-2',3-diquinoliny sulfide (**10A**) to 3-methylthio-2'-mercapto-3,3'- diquinoliny sulfide (**11A**) was observed.

EXPERIMENTAL

Melting points were determined in open capillary tubes on a Boetius melting point apparatus and are uncorrected. The ¹H NMR spectra were recorded on a Varian Unity-Inova 300 spectrometer 300 MHz in deuteriochloroform and dimethyl sulfoxide-d₆ with tetramethylsilane as the internal standard. EI MS spectra were run on a LKB 9000S at 70 eV and a chemical ionization mass spectrum (CI MS) was run on a Finnigan MAT 95 spectrometer. The thin layer chromatography of 1,4-dithiinodiquinolines (**1-4**) were performed on silica gel 60 F₂₅₄ (Merck 1.05735) with chloroform-methanol (95:5 v/v) and on aluminum oxide 60 F₂₅₄ neutral (type E) (Merck 1.05581) with methylene chloride as eluent.

Synthesis

1,4-Dithiinodiquinoline (**1**) was obtained by exhaustive sulfuration of quinoline with elemental sulfur⁸ and 1,4-dithiinodiquinoline (**2**) was obtained from compound (**1**) via the ring opening - ring closure reactions.¹⁵ 2-Chloro-3-bromoquinoline (**5**) was obtained from 3-bromoquinoline by oxidation with 3-chloroperbenzoic acid to 3-bromoquinoline *N*-oxide followed by rearrangement and chlorination with phosphoryl chloride according to the described procedures.^{32,33}

3-Bromo-2(1*H*)-quinolinethione (**6**)

- a) A solution of sulfide (**5**) (2.4 g, 10 mmol) and thiourea (1.5 g, 20 mmol) in 30 mL was stirred for 1 h at ambient temperature and then refluxed for 2h. After cooling the reaction mixture was poured into 90 mL of water and alkalinized with 20% aqueous sodium hydroxide to pH = 8. The resulting solid was filtered off, washed with ethanol and air-dried to give 3-bromo-2(1*H*)-quinolinethione (**6**) (2.2 g, 92%), mp 231-233 °C (ethanol). ¹H NMR (DMSO-d₆) δ: 7.39 (m, 1H, **H6**), 7.66 (m, 1H, **H7**), 7.67 (m, 1H, **H5**), 7.80 (m, 1H, **H8**), 8.64 (s, 1H, **H4**), 14.14 (s, 1H, **NH**). EI MS (70 eV) m/z: 241 (M, Br⁸¹, 88.4), 239 (M, Br⁷⁹, 84.2), 160 (M-Br, 100). *Anal.* Calcd for C₉H₆NBrS: C 45.02, H 2.52, N 5.83. Found: C 44.89, H 2.67, N 5.72.
- b) The same reaction in DMF at ambient temperature for 1 h and in reflux for 2 h gave (**6**) in 83% yield.

Diazadithiapentacenes (**3**) and (**4**)

A. From 3-Bromo-2(1*H*)-quinolinethione (**6**)

Bromoquinolinethione (**6**) (0.24 g, 1 mmol) was heated in a test tube on an oil bath at 200 °C for 30 min. After cooling the reaction mixture was extracted with chloroform (4 x 5 mL). The insoluble solid was filtered off and the filtrate was concentrated and purified by column chromatography (silica gel, chloroform) to give:

- (1) diazadithiapentacene (**3**) (0.06 g, 38%), mp 287-288 °C (lit.,¹³ mp 287-289 °C). ¹H NMR (CDCl₃) δ: 7.54 (m, 2H, **H2** and **H9**), 7.72 (m, 2H, **H3** and **H10**), 7.74 (m, 2H, **H1** and **H8**), 8.04 (m, 2H, **H4** and **H11**), 8.24 (s, 2H, **H7** and **H14**). EI MS (70 eV) m/z: 318 (M⁺, 100), 286(M-S, 15.6), 274(M-CS, 9.6).

(2) diazadithiapentacene (**4**) (0.03 g, 19%), mp 257-258 °C (lit.,¹¹ mp 258-259 °C). ¹H NMR (CDCl₃) as described in ref.¹⁰ EI MS (70 eV) m/z: 318 (M⁺, 100), 286 (M-S, 19.3), 274 (M-CS, 11.2).

B. From 2-Chloro-3-bromoquinoline (**5**)

a) A solution of 2-chloro-3-bromoquinoline (**5**) (0.24 g, 1 mmol) in dry DMSO (2 mL) was heated with anhydrous sodium sulfide (0.12 g, 1.5 mmol) on an oil bath at 160 °C for 5 h. After cooling the reaction mixture was poured into water (6 mL) and the resulting solid was filtered off, washed with water and air-dried. Separation by column chromatography gave diazadithiapentacene (**3**) (0.04 g, 25%) and diazadithiapentacene (**4**) (0.01 g, 6%).

b) Similar reaction of 2-chloro-3-bromoquinoline (**5**) (0.24 g, 1 mmol) in DMSO (2 mL) with commercial sodium hydrogen sulfide (NaSH x nH₂O, Aldrich, 0.18 g, ca. 2 mmol,) at 160 °C for 1 h gave diazadithiapentacene (**3**) (0.04 g, 25%) and diazadithiapentacene (**4**) (0.03 g, 19%).

c) A solution of 2-chloro-3-bromoquinoline (**5**) (0.24 g, 1 mmol) in dry DMF (2 mL) was boiled with commercial sodium hydrogen sulfide (NaSH x nH₂O, 0.18 g, ca. 2 mmol) for 15 h. After cooling the resulting solid was filtered off, boiled in water (10 mL) and air-dried. Purification by column chromatography gave diazadithiapentacene (**3**) (0.09 g, 57%). The organic filtrate was diluted with water (6 mL) and the resulting solid was filtered off, washed with water and air-dried. Purification by column chromatography gave diazadithiapentacene (**4**) (0.016 g, 10%).

d) A solution of 2-chloro-3-bromoquinoline (**5**) (0.24 g, 1 mmol) in dry 1-methyl-2-pyrrolidinone (2 mL) was boiled with commercial sodium hydrogen sulfide (NaSH x nH₂O, 0.18 g, ca. 2 mmol) for 1 h. After cooling the resulting solid was filtered off, boiled with water (10 mL) and air-dried. Purification by column chromatography gave diazadithiapentacene (**3**) (0.05 g, 31%). The organic filtrate was diluted with water (6 mL) and the resulting solid was filtered off, washed with water and air-dried. Separation by column chromatography gave diazadithiapentacene (**3**) (0.04 g, 25%) and diazadithiapentacene (**4**) (0.03 g, 19%).

C. From Isomerization

To a suspension of diazadithiapentacene (**3**) (0.32 g, 1 mmol) in dry DMSO (10 mL) at 140 °C was added sodium methanethiolate (0.21 g, 3 mmol) and the mixture was stirred for 30 min. After cooling the reaction mixture was poured into 15% aqueous sodium hydroxide (30 mL). Possibly unreacted substrate was filtered off and the filtrate was diluted with water (40 mL) and boiled for 1 h. The resulting solid was filtered off and separated by column chromatography to give diazadithiapentacene (**3**) (0.07 g, 22%) and diazadithiapentacene (**4**) (0.18 g, 57%).

When this reaction was carried out at 70 °C diazadithiapentacene (**3**) (0.28 g, 88%) was obtained as a sole product.

3,3'-Dibromo-2,2'-diquinolinyl Sulfide (7**)**

A solution of 2-chloro-3-bromoquinoline (**5**) (0.24 g, 1 mmol) and bromoquinolinethione (**6**) (0.24 g, 1 mmol) in dry DMF (3 mL) was boiled for 1.5 h. After cooling the reaction mixture was poured into water (10 mL) and the resulting solid was filtered off, washed with water and air-dried. Purification by column chromatography (silica gel, chloroform) gave sulfide (**7**) (0.27 g, 61%), mp 136-137 °C. ¹H NMR (CDCl₃) δ: 7.54 (m, 2H, **2H**₆), 7.64 (m, 2H, **2H**₇), 7.75 (m, 2H, **2H**₅), 7.82 (m, 2H, **2H**₈), 8.39 (s, 2H,

2H4). EI MS (70 eV) m/z : 446 (M, Br⁷⁹, Br⁸¹, 0.5), 367 (M-Br⁷⁹, 100), 365 (M-Br⁸¹, 96.2), 286 (M-2Br, 16.5). *Anal.* Calcd for C₁₈H₁₀N₂Br₂S: C 48.46, H 2.26, N 6.28. Found: C 48.28, H 2.35, N 6.16.

2-Methylthio-3-bromoquinoline (8)

A solution of bromoquinolinethione (**6**) (0.24 g, 1 mmol) in DMSO (1 mL) and 25% aqueous sodium hydroxide (3 mL) was stirred with methyl iodide (0.1 mL, 1.6 mmol) at ambient temperature for 1 h. The resulting solid was filtered off, washed with water, air-dried and purified by column chromatography (silica gel, chloroform) to give sulfide (**8**) (0.16 g, 63%), mp 30-31 °C. ¹H NMR (CDCl₃) δ : 2.68 (s, 3H, SCH₃), 7.45 (m, 1H, **H6**), 7.66 (m, 1H, **H7**), 7.68 (m, 1H, **H5**), 7.95 (m, 1H, **H8**), 8.18 (s, 1H, **H4**). EI MS (70 eV) m/z : 255 (M, Br⁸¹, 56.0), 253 (M, Br⁷⁹, 50.7), 174 (M-Br, 100). *Anal.* Calcd for C₁₀H₈NBrS: C 47.26, H 3.17, N 5.51. Found: C 47.13, H 3.27, N 5.39.

3,3'-Dibromo-2,2'-diquinolinyl Disulfide (9)

To a stirring solution of bromoquinolinethione (**6**) (0.24 g, 1 mmol) in ethanol (30 mL) at ambient temperature was added portionally iodine until the violet color of the iodine persisted. The solvent was evaporated under reduced pressure and the residue was extracted with chloroform (2 x 3 mL). The insoluble solid was identified as disulfide (**9**) (0.20 g, 84%), mp 200-201 °C (ethanol). ¹H NMR (CDCl₃) δ : 7.43 (m, 2H, **2H6**), 7.57 (m, 2H, **2H7**), 7.67 (m, 2H, **2H5**), 7.81 (m, 2H, **2H8**), 8.26 (s, 2H, **2H4**). EI MS (70 eV) m/z : 478 (M, Br⁷⁹, Br⁸¹, 9.2), 399 (M-Br⁷⁹, 100), 397 (M-Br⁸¹, 93.5). *Anal.* Calcd for C₁₈H₁₀N₂Br₂S₂: C 45.21, H 2.11, N 5.86. Found: C 45.11, H 2.22, N 5.75.

2,3'-Dimethylthio-2',3-diquinolinyl Sulfide (10)

To a suspension of diazadithiapentacene (**3**) (0.32 g, 1 mmol) in dry DMSO (10 mL) at 70 °C was added sodium methanethiolate (0.084 g, 1.2 mmol). The mixture was stirred for 30 min. After cooling the reaction mixture was poured into 15% aqueous sodium hydroxide (30 mL). Possibly unreacted substrate was filtered off and the filtrate was stirred with methyl iodide (0.1 mL, 1.6 mmol). The resulting solid was filtered off, washed with water, air-dried and purified by column chromatography (silica gel, chloroform) to give sulfide (**10**) (0.34 g, 89%), mp 153-154 °C. ¹H NMR (CDCl₃) δ : 2.59 and 2.67 (2s, 6H, 2SCH₃), 7.90 and 8.31 (2s, 2H, **H4** and **H4'**), 8.02 (d, $J=8.7$ Hz, 1H, **H_{arom}**), 7.36-7.55 (m, 4H, **H_{arom}**), 7.65-7.78 (m, 3H, **H_{arom}**). CI MS (70 eV) m/z : 381 (M+1, 100), 333 (M-SCH₃, 41.3), 319 (M-S(CH₃)₂+1, 12.6). *Anal.* Calcd for C₂₀H₁₆N₂S₃: C 63.13, H 4.24, N 7.36. Found: C 63.04, H 4.29, N 7.27.

2,2'-Dimethylthio-3,3'-diquinolinyl Sulfide (11)

To a suspension of diazadithiapentacene (**3**) (0.32 g, 1 mmol) in dry DMSO (10 mL) at 140 °C was added sodium methanethiolate (0.21 g, 3 mmol). The mixture was stirred for 30 min. After cooling the reaction mixture was poured into 15% aqueous sodium hydroxide (30 mL). Possibly unreacted substrate was filtered off and the filtrate was stirred with methyl iodide (0.1 mL, 1.6 mmol). The resulting solid was filtered off, washed with water, air-dried and separated by column chromatography (silica gel, methylene chloride) to give:

(1) sulfide (**10**) (0.06 g, 16%), mp 153-154 °C.

(2) sulfide (**11**) (0.160 g, 42%), mp 188-189 °C (lit.,¹⁰ mp 188-189 °C).

X-Ray analysis

Single crystals of diazadithiapentacenes (**3**) and (**4**) were grown by a horizontal vapor transport in a flow of argon gas at 1 atm. The evaporation zone was kept at 250 °C and the growth zone at rt. Crystals nucleated spontaneously on the wall of the furnace tube and grown in a temperature gradient between evaporation zone and room temperature zone. Details of the experimental apparatus have been reported in ref.²² Single crystal X-Ray studies were carried out using an Enraf-Nonius kappa-axis diffractometer with either graphite monochromated molybdenum ($\lambda = 0.70930 \text{ \AA}$) or copper ($\lambda = 1.54056 \text{ \AA}$) K α radiation. All calculations were carried out using the NRCVAX suite of programs.³⁴

Crystal data for diazadithiapentacene (**3**): C₁₈H₁₀N₂S₂, M = 318.41, monoclinic, a = 12.928(3), b = 3.8920(10), c = 28.355(8), $\beta = 98.11(5)$, space group I2/a, Z = 4, V = 1412.4(6) Å³, $\mu(\text{Cu K}\alpha) = 3.31 \text{ mm}^{-1}$. 3602 reflections were collected of which 1053 were unique and 828 with $I > 2.5\sigma(I)$ ($R_{\text{int}} = 0.040$). The structure was refined to R = 0.081 and $R_w = 0.086$.

Crystal data for diazadithiapentacene (**4**): C₁₈H₁₀N₂S₂, M = 318.41, monoclinic, a = 21.615(6), b = 6.1212(8), c = 23.458(6), $\beta = 113.470(20)$, space group P2₁/n, Z = 8, V = 2846.9(11) Å³, $\mu(\text{Mo K}\alpha) = 0.35 \text{ mm}^{-1}$. 5393 reflections were collected of which 4493 were unique and 1756 with $I > 2.5\sigma(I)$ ($R_{\text{int}} = 0.026$). The structure was refined to R = 0.057 and $R_w = 0.033$.

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