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Short communication

Synthesis of linear bis-thiazolo[2,3-*d*][8,9-*d*]*trans*-quinacridone

Cristiana Rădulescu*, I. Ioniţă, A.M. Hossu

University Valahia Târgovişte, 18-22 Bdv. Unirii, Târgovişte, Romania

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Abstract

The paper presents the synthesis of a new heterocycles compact condensed system bis-thiazolo[2,3-*d*][8,9-*d*]*trans*-quinacridone, unquoted in speciality literature. This system was obtained for the first time by an original method, by the condensation of amino-benzothiazoles with succinyl succinic ester. The spectral analysis confirmed the structure proposed and tinctorial tests were also effected.
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Keywords: Quinacridone; Quinacridone pigment; Heterocyclic structure; Tinctorial test

1. Introduction

Quinacridonic pigments are characterized by a great thermal stability and insolubility in usual solvents. These manifest a great hydrophobic character and for this reason quinacridone and its derivates cannot be utilized for dyeing of polyester fibers by the dyeing technology with disperse dyes. For the diminution of global hydrophobic character of quinacridonic pigments the grafting on base structure the more hydrophilic thiazolic rests, has been proposed. We mentioned the fact that the compounds obtained by synthesis are not quoted in speciality literature [1–3].

2. Experimental

The original method [1] proposed by us consisted in the condensation reaction of succinyl succinic ester, **1**, with 6-aminobenzothiazol, **2**, in nitrobenzene medium, in the presence of the acetic acid, which resulted in the diesteric compound **3**. The alkaline hydrolysis of product **3** was effectuated in a 1:1 methyl alcohol:water medium and led to the generation of the dicarboxylic acid, **4**, and then, by cyclization was obtained linear bis-thiazolo[2,3-*d*][8,9-*d*]*trans*-quinacridone. These stages are presented in detail in Fig. 1.

The condensation reaction of succinyl succinic ester, **1**, with 6-aminobenzothiazol, **2**, was realized at temperature 115–125 °C, in nitrobenzene medium, in 6–7 h, with the addition of acetic acid. The role of nitrobenzene in this reaction was to oxidize the Schiff base formed as an intermediary in the reaction, to the aromatic structure, **3**.

The hydrolysis reaction of the esteric intermediary was realized at 60–70 °C, in a 1:1:1 methyl alcohol: water:NaOH system and in this case the acid salt has a total solubility. Compound **4** was isolated from the reaction mass by acidulation with HCl. The yield of hydrolysis reaction was situated between 90 and 95%.

Compound **4** was cyclized to bis-thiazolo[2,3-*d*][8,9-*d*] *trans*-quinacridone, **5**, by elimination of water, in the presence of polyphosphoric acid, at 150–180 °C or by the action of the ethylic ester, **3**, at 140–160 °C on acid **4**.

The purity of linear bis-thiazolo[2,3-*d*][8,9-*d*]*trans*-quinacridone, **5**, obtained by original organic synthesis is remarkable. In this case, polyphosphoric acid is a perfect alternative to sulphuric acid for cyclization to obtain the quinacridone system because it does not lead to secondary compounds. The use of sulphuric acid in the cyclization reaction lead to a great quantity of secondary product because of partial sulphonation and the cyclized product must be submitted to desulphonation.

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* Corresponding author. Tel./fax: +40 245 211809.
E-mail address: radulescucristiana@yahoo.com (C. Rădulescu).

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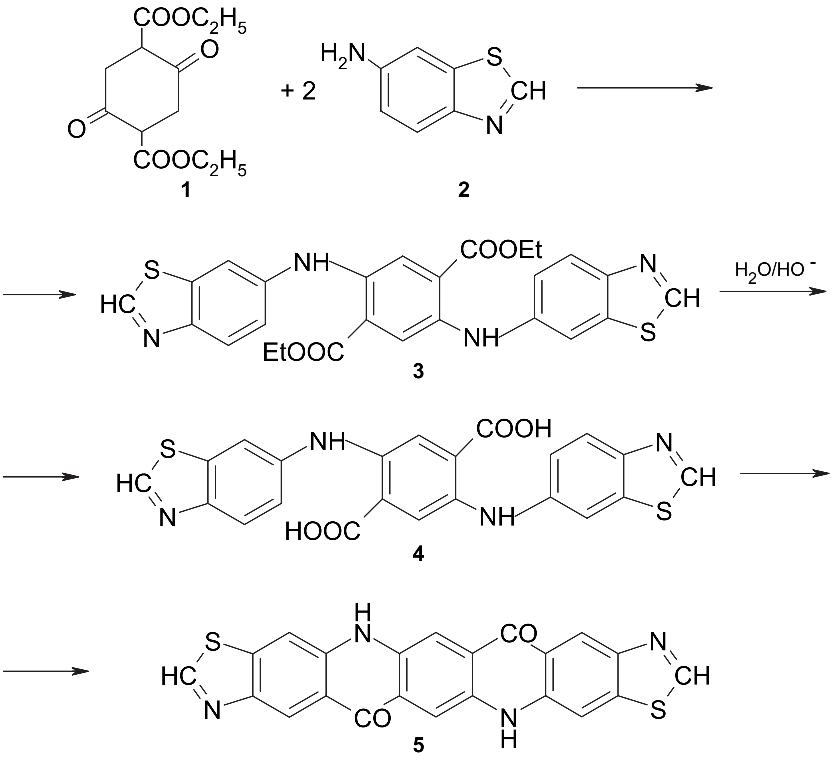

Fig. 1. The stages of synthesis *bis*-thiazolo[2,3-*d*][8,9-*d*]*trans*-quinacridone, **5**.

3. Results and discussions

Theoretically, the cyclization of compound **4** can lead to angular thiazolo-quinacridone products in accordance with Fig. 2. These products, **6** and **7**, cannot be emphasized by experimental research.

The purification of linear bis-thiazolo[2,3-*d*][8,9-*d*] *trans*-quinacridone, **5**, was realized by three recrystallization from a 1:1:1 (volume) DMF:DMSO:Py mixture. Its purity was emphasized by interdependence of the emission spectrum as wavelength of excitation light. This method is very sensible and this fact is quoted.

The cyclization reaction of compound **4** to **5** was analyzed, in comparison with other analogous systems [4,5] and the conclusion was: the exclusive formation of linear bis-thiazolo[2,3-*d*][8,9-*d*]*trans*-quinacridone can be justified by the greatest electron density in 5 position in rapport with 6 position in thiazolic system; this fact favoured the electrophilic attack in 5 position of the acidic carbocation generated in the system.

3.1. The IR spectrum of linear bis-thiazolo[2,3-d] [8,9-d]trans-quinacridone

Compound **5** is practically insoluble in usual solvents and for this reason the IR spectrum was realized in KBr pastille [7,8].

The bands produced were:

- ν_{CO} is situated at $1618\,\mathrm{cm}^{-1}$ in comparison with $1625\,\mathrm{cm}^{-1}$ which is the frequency in linear *trans*-quinacridone. This value is very small in comparison with that registered in the case of diphenylketone, where the frequency $\nu_{CO} = 1670\,\mathrm{cm}^{-1}$. This fact confirmed the diminution of the double bond index in case of the C=O group and can be attributed to the formation of the intermolecular hydrogen bonds N–H···O=C.

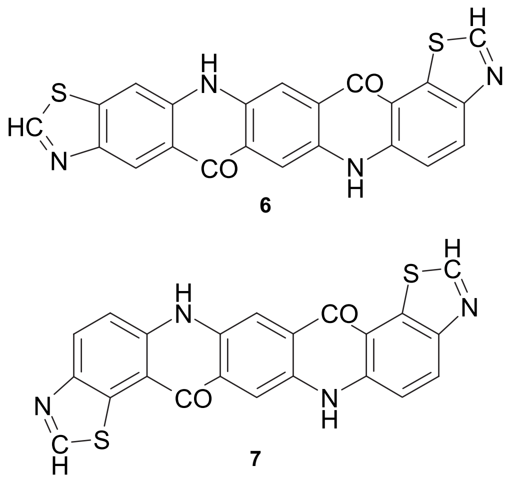

Fig. 2. The angular thiazolo-quinacridone products.

Table 1
The position of bands O–O (cm^{-1}) for linear bis-thiazolo[2,3-*d*][8,9-*d*] *trans*-quinacridone

Solvent	DMF	H_2SO_4 100%
Excitation	19 036	18 929
Emission	18 160	18 962
(O–O)	876	167

- The formation of these bonds was suggested by the frequency ν_{NH} from the quinacridonic rest which in this case was situated at 3220 cm^{-1}, in comparison with the value 3280 cm^{-1} in classic quinacridone. This value is unusually diminished.
- The bands situated at 1420, 1038, 946, 835 and 780 cm^{-1} are characteristic of thiazolic ring.
- In case of compound **5** the value δ_{NH} was situated at 1495 cm^{-1}, a very close position as that registered for classic quinacridone, at 1495 cm^{-1}.
- The linear bis-thiazolo[2,3-*d*][8,9-*d*]*trans*-quinacridone presented the value 1620 cm^{-1} for C=N bond vibration, in comparison with that situated at 1660–1620 cm^{-1} frequency in quinacridone and with that presented at 1645 cm^{-1} in aminothiazol.
- The spectral data registered for linear bis-thiazolo [2,3-*d*][8,9-*d*]*trans*-quinacridone suggested the fact that in solid phase this compound was presented under associate form (intermolecular hydrogen bonds).

3.2. The excitation and emission spectra

The excitation and emission spectra for quinacridone system was studied very attentively by Zaharia C.Z. and Tărăbăşănu [6].

The band positions O–O for linear bis-thiazolo[2,3-*d*][8,9-*d*]*trans*-quinacridone are presented in Table 1.

Examination of these data (presented in Table 1) ascertained a diminution of Δ_{O-O} from value 876 cm^{-1} by the utilization of DMF solvent, to 167 cm^{-1}, in case of sulphuric acid 100% solvent. The dependence of excitation and emission spectra on the solvent character was due probably to the changing of ratio between compound **5** and its enolic tautomer, **8** (Fig. 3).

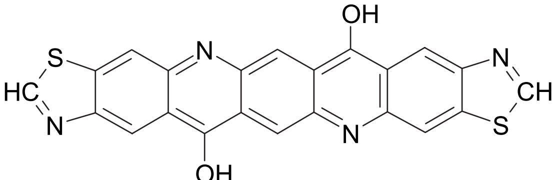

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Fig. 3. Enolic tautomere of linear *bis*-thiazolo[2,3-*d*][8,9-*d*]*trans*-quinacridone.

3.3. The tinctorial tests

The dyeing of polyester fibers [9–11] was realized at 140 °C, by the utilization of a dye bath which contained 1% DMF in water. To a concentration of the dye **5** situated between 1 and 6%, in ratio with the fiber, shades between red and brown were registered, with a remarkable light fastness (situated between 5 and 6 in grey scale) and a good cool water fastness situated between 4 and 5 in grey scale.

4. Conclusions

In this work, was conceived and synthesized a new dye of thiazolo-quinacridone class, unquoted in speciality literature by the utilization of a simple and original method, realized by the condensation reaction between amino-benzothiazoles and succinyl succinic ester. The hydrolysis reaction of ester **3** and then the cyclization reaction of compound **4** led to the *trans*-quinacridone thiazolic dyes. For the moment this method was applied to a single amino-benzothiazole, but the proposed alternative permitted the realization of diverse structures by the utilization of amino-benzothiazoles or the other heterocyclic structures.

The linear bis-thiazolo[2,3-*d*][8,9-*d*]*trans*-quinacridone was used successfully for the dyeing of polyester fibers due to its hydrophilic character, with remarkable tinctorial fastness.

References

[1] Radulescu C. Ph. Dr. Faculty of Industrial Chemistry, Bucharest, Romania; 2003.
[2] Radulescu C, Tarabasanu CM. Chem Rev 2004;55(2):102–5. [Bucharest].
[3] Radulescu C, Tarabasanu Mihaila C. Chem Rev 2004;55(1): 25–30. [Bucharest].
[4] Zaharia CZ. Rev Chim 1975;26:255. [Bucharest].
[5] Altiparmakian RH. Helv Chim Acta 1972;58:85.
[6] Zaharia CZ, Tărăbăşanu CM. Rev Roum Phys 1976;25:359.
[7] Avram M, Mateescu Gh. IR spectroscopy. Applications in organic chemistry, Bucharest; 1966.
[8] Balaban AT, Banciu M, Pogany I. The applications of physic methods in organic chemistry. Bucharest: Scientific and Encyclopedic; 1983.
[9] Radulescu C, Tarabasanu CM, Ionita I, Hossu AM. The First International Conference of Moldavian Chemical Society. Chisinau, Republic of Moldova; 2003. p. 189.
[10] Radulescu C, Ionita I, Hossu AM. 10th International Conférence COLORCHEM'04, may 23–27. Pardubice, Czerny Republic; 2004, P24, ISBN 80-85119-01-3.
[11] Radulescu C, Tarabasanu CM, Ionita I, Irimescu L. Anal Univ Ovidius 2003;14:113–7. [Constanta].