Synthesis of New Non-Symmetrical Substituted 7,7'-Bisindolizines by the Direct Reaction of 4,4'-Bipyridinium-Ylides with Dimethyl Acetylenedicarboxylate

Alexandru V. Rotaru*, Ramona P. Danac and Ioan D. Druta

Department of Organic Chemistry, Faculty of Chemistry, "Al. I. Cuza" University,
B-dul Carol I, No.11, IASI-700506, Romania

Received March 18, 2004

We report here on the synthesis of some novel non-symmetrical substituted bisindolizines by 3+2 dipolar cycloaddition reaction. New compounds were prepared by the direct reaction of isolated non-symmetrical substituted 4,4'-bipyridinium bisylides with dimethyl acetylenedicarboxylate (DMAD). The obtained compounds can be used as precursors of fluorescent markers in fluorometric analysis.

J. Heterocyclic Chem., **41**, 893 (2004).

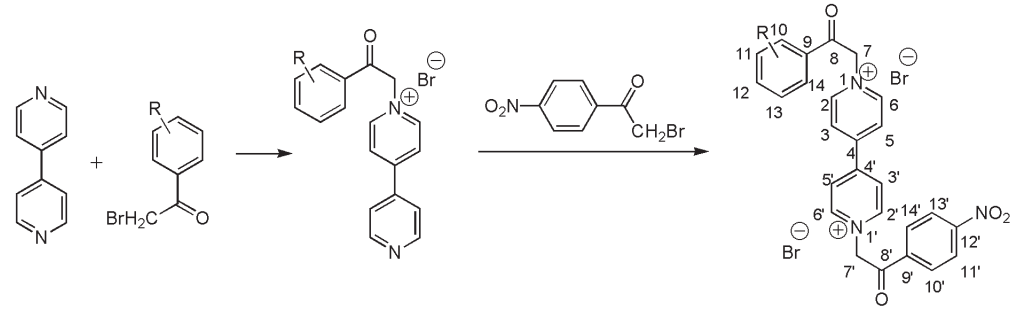
Introduction.

Our previous papers [1-3] showed that the symmetrical substituted bisindolizine could be of considerable interest due to their heterocyclic ring system. Considering the well known fluorescence properties of indolizines [4-6] and the increasing importance of fluorescence spectroscopy in both biological and environmental analysis, we were interested in the synthesis of bisindolizine systems with remarkable high quantum yields suitable for use in fluorometric analysis. Thus, related compounds that possess similar structures to those reported here proved to be highly fluorescent and with very high quantum yields [5]. In order to use these fluorescent compounds as markers in proteomics analyses, we synthesized compounds with only one nitro group, which can be reduced to the corresponding amines and then transformed to isocyanates or isothiocyanates. The cycloaddition reactions of cycloimmonium ylides to activated symmetrical or non-symmetrical alkenes and alkynes [1-3], [7-10] offered an opportunity of preparing new heterocycles difficult or impossible to be obtained otherwise.

Also, for the first time, the reaction of cycloaddition to cycloimmonium ylides was carried out directly with isolated ylides which are stable for a short period. This is a method for the preparation of the final compounds in a pure state and with better yields. The structure of final bisindolizines was proved by elemental analysis and spectral methods (^{1}H nmr, ir).

Results and Discussions.

Heterocyclic compounds, namely indolizines, have been synthesized by the 3+2 dipolar cycloaddition of isolated non-symmetrical substituted 4-(4'-pyridyl)-pyridinium-bis-ylides **13b-18b** with dimethyl acetylenedicarboxylate (DMAD). Thus, to prepare compounds **13-18** we synthesized monoquaternary salts **1-6** using previously reported data [11-13]. We chose to vary the experimental conditions (reaction time and different solvents) with the aim to find those leading to an efficient synthesis of monoquaternary salts. Therefore, the starting compound was dissolved and then reacted in anhydrous acetone and not in acetonitrile as reported [13]. We succeeded in preparing the monoquaternary salts **1-6** in an almost quantitative yield. This change in the reaction conditions permits rapid formation of salt crystals and avoids the possible formation of diquaternary salts or dimerisation processes as occurs in case of phta-



1 R = *para*-H
2 R = *para*-CH_3
3 R = *para*-OCH_3
4 R = *meta*-OCH_3
5 R = *para*-Br
6 R = *para*-Cl

7 R = *para*-H
8 R = *para*-CH_3
9 R = *para*-OCH_3
10 R = *meta*-OCH_3
11 R = *para*-Br
12 R = *para*-Cl

Figure 1. Synthesis of diquaternary salts.

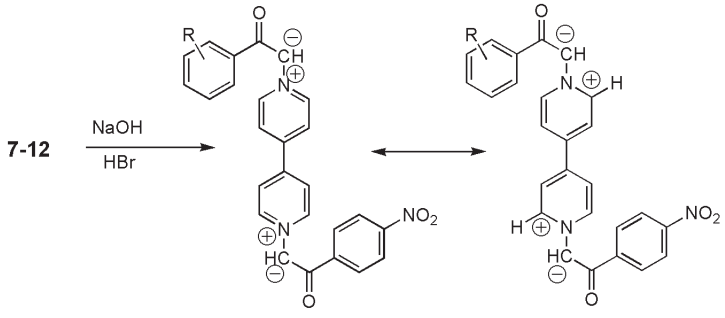
lazinium ylides [14] and some monoquaternary salts [15].

The monoquaternary salts obtained in the first step react with α-bromo-4-nitroacetophenone to afford corresponding new diquaternary salts **7-12** in good yields (Figure 1). The structure of prepared diquaternary salts was determined by ^{1}H-nmr, ir and elemental analysis.

Ylides **13b-18b** were obtained by the reaction between diquaternary salts **7-12** and aqueous solution of NaOH and then separated by centrifugation. The isolated ylides have an amphionic structure and can react in the 3+2 dipolar cycloaddition reactions as 1,3-dipole according to the structures **13b-18b** [8-10] (Figure 2).

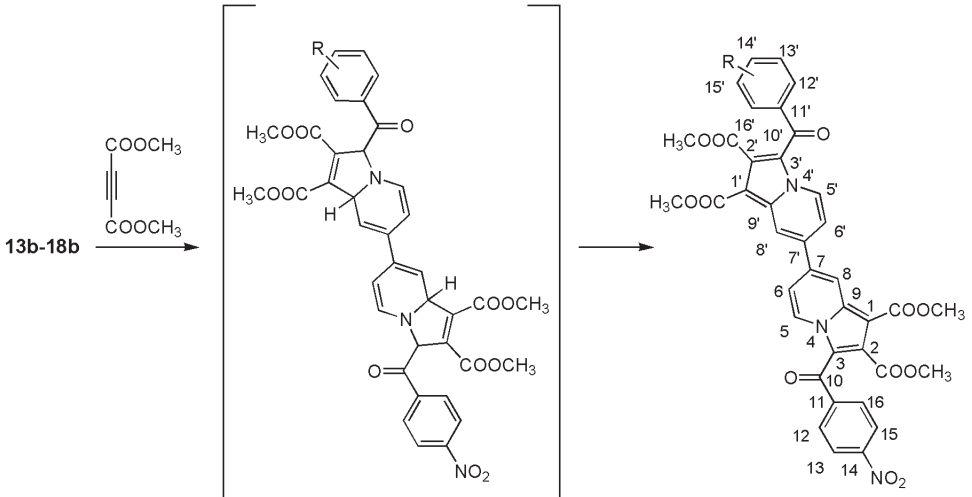
Thus, 4-(4'-pyridyl)-pyridinium-bisylides suspended in THF, react with DMAD to give cycloadducts **25-30**. The ylides, very likely form unisolable intermediate cycloadducts **19-24**, which due to stabilization tendency undergo a dehydrogenation. The reaction was carried out under ambient conditions; possibly, an oxidative dehydrogenation process may have occurred as well. Isolable cycloadducts **25-30** were obtained in a pure state and high yields (Figure 3).

The products contain a system of extended conjugated double bonds, being similar to the highly fluorescent compounds previously reported [5]. Thus, the above-



13 R = *para*-H
14 R = *para*-CH_3
15 R = *para*-OCH_3
16 R = *meta*-OCH_3
17 R = *para*-Br
18 R = *para*-Cl

Figure 2. Zwitterionic structure of 4,4'-bipyridiniu ylides.



19 R = *para*-H
20 R = *para*-CH_3
21 R = *para*-OCH_3
22 R = *meta*-OCH_3
23 R = *para*-Br
24 R = *para*-Cl

25 R = *para*-H
26 R = *para*-CH_3
27 R = *para*-OCH_3
28 R = meta-OCH_3
29 R = *para*-Br
30 R = *para*-Cl

Figure 3. Reaction between cycloimmonium ylides and DMAD.

mentioned compounds can be used as precursors of fluorescent dyes or markers.

Conclusions.

We have obtained six new non-symmetrical heterocycles with only one nitro group by direct 3+2 cycloadition reaction of isolated 4,4'-bipyridinium ylides with DMAD. In addition, we described the synthesis of bisindolizine precursors (diquaternary salts) by a two-step synthesis. Modification of reaction conditions for synthesis of monoquaternary salts led to almost quantitative yields.

Indolizines **25-30** were characterized by spectral methods and elemental analyses, the measurements of the luminescence are under investigation as well as the conditions of nitro group transformations to corresponding isocyanates and isothiocyanates.

EXPERIMENTAL

The ^{1}H nmr spectra were recorded with BRUKER-300 spectrometer and shifts are given in ppm (internal standard TMS, coupling constants are given in Hz). The ir spectra were measured by FTIR. Melting points are uncorrected (MEL-TEMP capillary apparatus). Thin-layer chromatography (tlc) was carried out on aluminum foil coated with Silica gel 60 F_{254} (MERCK), column chromatography on ALDRICH Silica gel, 70-230 mesh, 60 Å. All reagents were obtained from commercial sources and used without further purification.

General Procedure for Synthesis of Monoquaternary salts **1-6** [13].

To a solution of 1.1 mmol of 4,4'-bipyridine in 10 mL anhydrous acetone was added 1 mmol of α-bromo-4-acetophenone derivative dissolved in 10 mL anhydrous acetone. The mixture was stirred for 3 hours at room temperature under anhydrous conditions. The blue-white crystals were collected by filtration and washed with 15 mL acetone. The final products yields vary between 89 and 96%.

General Procedure for Synthesis of Diquaternary Salts **7-12**.

To a solution of 1 mmol of monoquaternary salt in 20 mL acetonitrile and 5 mL DMF was added 1.1 mmol of α-bromo-4-nitroacetophenone in 2.5 mL acetonitrile reflux. The obtained solution was stirred under reflux for 1 hour. A yellow-greenish precipitate was collected by filtration and washed with 10-15 mL acetonitrile. The following compounds were prepared according the general method.

[*N*-Phenacyl,*N*'-(4-nitrophenacyl)-4,4'-bipyridinium Dibromide] (**7**).

This compound was obtained as green amorphous solid, mp 295-296 °C; ir (potassium bromide): CO 1691, 1643, NO_2 1527, 1348 cm^{-1}; ^{1}H nmr (DMSO-d_6): δ 9.39 (d, 4H, 2-H, 6-H, 2'-H, 6'-H, $J_{2,3}$ = 5.4 Hz), 9.01 (d, 4H, 3-H, 5-H, 3'-H, 5'-H, $J_{3,2}$ = 5.4 Hz), 8.48 (d, 2H, 11'-H, 13'-H, $J_{11',10'}$ = 8.4 Hz), 8.33 (d, 2H, 10'-H, 14'-H, $J_{10',11'}$ = 8.4 Hz), 8.10 (d, 2H, 10-H, 14-H, $J_{10,11}$ = 9.0 Hz), 7.81 (t, 1H, 12-H, $J_{12,11,13}$ = 7.2 Hz), 7.68 (t, 2H, 11-H, 13-H, $J_{11,12,10}$ = 7.2 Hz), 6.78 (s, 2H, 7'-H), 6.71 (s, 2H, 7-H).

Anal. Calcd. For $C_{26}H_{21}Br_2N_3O_4$: C, 52.11; H, 3.53; N, 7.01. Found: C, 52.20; H, 3.48; N, 7.12.

[*N*-(4-Methylphenacyl),*N*'-(4-nitrophenacyl)-4,4'-bipyridinium Dibromide] (**8**).

This compound was obtained as green amorphous solid, mp >350 °C; ir (potassium bromide): CO 1701, 1641, NO_2 1535, 1345 cm^{-1}; ^{1}H nmr (DMSO-d_6): δ 9.33 (d, 4H, 2-H, 6-H, 2'-H, 6'-H, $J_{2,3}$ = 5.4 Hz), 8.93 (d, 4H, 3-H, 5-H, 3'-H, 5'-H, $J_{3,2}$ = 5.4 Hz), 8.49 (d, 2H, 11'-H, 13'-H, $J_{11',10'}$ = 8.1 Hz), 8.33 (d, 2H, 10'-H, 14'-H, $J_{10',11'}$ = 8.1 Hz), 8.06 (d, 2H, 10-H, 14-H, $J_{10,11}$ = 6.3 Hz), 7.49 (d, 2H, 14-H, 10-H, $J_{14,13}$ = 6.3 Hz), 6.71 (s, 2H, 7'-H), 6.61 (s, 2H, 7-H), 2.48 (s, 3H, CH_3).

Anal. Calcd. For $C_{27}H_{23}Br_2N_3O_4$: C, 52.88; H, 3.78; N, 6.85. Found: C, 52.71; H, 3.79; N, 6.61.

[*N*-(4-Methoxyphenacyl),*N*'-(4-nitrophenacyl)-4,4'-bipyridinium Dibromide] (**9**).

This compound was obtained as green amorphous solid, mp 282-283 °C; ir (potassium bromide): CO 1698, 1636, NO_2 1530, 1346, C-O 1244, 1174 cm^{-1}; ^{1}H nmr (DMSO-d_6): δ 9.32 (d, 4H, 2-H, 6-H, 2'-H, 6'-H, $J_{2,3}$ = 5.7 Hz), 8.95 (d, 4H, 3-H, 5-H, 3'-H, 5'-H, $J_{3,2}$ = 5.7 Hz), 8.49 (d, 2H, 11'-H, 13'-H, $J_{11',10'}$ = 8.4 Hz), 8.33 (d, 2H, 10'-H, 14'-H, $J_{10',11'}$ = 8.4 Hz), 8.07 (d, 2H, 10-H, 14-H, $J_{10,11}$ = 6.6 Hz), 7.20 (d, 2H, 14-H, 10-H, $J_{14,13}$ = 6.6 Hz), 6.71 (s, 2H, 7'-H), 6.58 (s, 2H, 7-H), 3.91 (s, 3H, OCH_3).

Anal. Calcd. For $C_{27}H_{23}Br_2N_3O_5$: C, 51.53; H, 3.68; N, 6.68. Found: C, 51.58; H, 3.75; N, 7.01.

[*N*-(3-Methoxyphenacyl),*N*'-(4-nitrophenacyl)-4,4'-bipyridinium Dibromide] (**10**).

This compound was obtained as green amorphous solid, mp 232-233 °C; ir (potassium bromide): CO 1699, 1641, NO_2 1529, 1349, C-O 1264, 1199 cm^{-1}; ^{1}H nmr (DMSO-d_6): δ 9.36 (d, 4H, 2-H, 6-H, 2'-H, 6'-H, $J_{2,3}$ = 5.7 Hz), 8.93 (d, 4H, 3-H, 5-H, 3'-H, 5'-H, $J_{3,2}$ = 5.7 Hz), 8.49 (d, 2H, 11'-H, 13'-H, $J_{11',10'}$ = 8.4 Hz), 8.34 (d, 2H, 10'-H, 14'-H, $J_{10',11'}$ = 8.4 Hz), 7.71-7.83 (m, 3H, 10-H, 13-H, 14-H), 7.65 (m, 1H, 12-H), 6.71 (s, 2H, 7'-H), 6.62 (s, 2H, 7-H), 3.73 (s, 3H, CH_3).

Anal. Calcd. For $C_{27}H_{23}Br_2N_3O_5$: C, 51.53; H, 3.68; N, 6.68. Found: C, 51.61; H, 3.77; N, 6.54.

[*N*-(4-Bromophenacyl),*N*'-(4-nitrophenacyl)-4,4'-bipyridinium Dibromide] (**11**).

This compound was obtained as green amorphous solid, mp >350 °C; ir (potassium bromide): CO 1698, 1641, NO_2 1529, 1345 cm^{-1}; ^{1}H nmr (DMSO-d_6): δ 9.36 (d, 4H, 2-H, 6-H, 2'-H, 6'-H, $J_{2,3}$ = 5.4 Hz), 8.94 (d, 4H, 3-H, 5-H, 3'-H, 5'-H, $J_{3,2}$ = 5.4 Hz), 8.49 (d, 2H, 11'-H, 13'-H, $J_{11',10'}$ = 8.4 Hz), 8.33 (d, 2H, 10'-H, 14'-H, $J_{10',11'}$ = 8.4 Hz), 8.10 (d, 2H, 10-H, 14-H, $J_{10,11}$ = 6.3 Hz), 7.30 (d, 2H, 14-H, 10-H, $J_{14,13}$ = 6.3 Hz), 6.62 (s, 2H, 7'-H), 6.58 (s, 2H, 7-H).

Anal. Calcd. For $C_{26}H_{20}Br_3N_3O_4$: C, 46.05; H, 2.97; N, 6.20. Found: C, 45.98; H, 3.04; N, 6.28.

[*N*-(Clorophenacyl),*N*'-(4-nitrophenacyl)-4,4'-bipyridinium Dibromide] (**12**).

This compound was obtained as green amorphous solid, mp >350 °C; ir (potassium bromide): CO 1699, 1643, NO_2 1531, 1347 cm^{-1}; ^{1}H nmr (DMSO-d_6): δ 9.36 (d, 4H, 2-H, 6-H, 2'-H, 6'-H, $J_{2,3}$ = 5.4 Hz), 8.94 (d, 4H, 3-H, 5-H, 3'-H, 5'-H, $J_{3,2}$ = 5.4 Hz),

8.49 (d, 2H, 11'-H, 13'-H, $J_{11',10'}$ = 8.4 Hz), 8.33 (d, 2H, 10'-H, 14'-H, $J_{10',11'}$ = 8.4 Hz), 8.10 (d, 2H, 10-H, 14-H, $J_{10,11}$ = 6.3 Hz), 7.30 (d, 2H, 14-H, 10-H, $J_{14,13}$ = 6.3 Hz), 6.62 (s, 2H, 7'-H), 6.58 (s, 2H, 7-H).

Anal. Calcd. For $C_{26}H_{20}Br_2N_3O_4$: C, 49.28; H, 3.18; N, 6.63. Found: C, 49.32; H, 3.34; N, 6.56.

General Procedure for Synthesis of Bisindolizines **25-30**.

To a suspension of 1 mmol of 4,4'-bipyridinium diquaternay salts **7-12** in water (50 mL) was added 10 mL 0.2 *N* aqueous NaOH and the mixture was stirred for 5 minutes. The obtained deep-blue suspension was centrifuged at 2500 rot/min for 10 min. Then, the upper water layer was decanted and 70 mL of THF was added together with 2 mmoles (0.142 g, 0.123 mL) of DMAD. The mixture was stirred for 5 hours at room temperature. The obtained yellow precipitate was collected by filtration, washed with ethanol, and then purified by column chromatography benzene:acetone (19:1). The following compounds were prepared according the general method.

1,2,1',2'-Tetra(methoxycarbonyl)-3-(4-nitrobenzoyl)-3'-(benzoyl)-7,7'-bisindolizine (**25**).

This compound was obtained as yellow solid (365 mg, 51%), mp 291-292 °C; ir (potassium bromide): CO 1739, 1700, 1628, 1601, NO_2 1522, 1347, C-O 1252, 1213, 1160, 1096 cm^{-1}; ^1H nmr (DMSO-d_6): δ 9.44 (d, 1H, 5-H, $J_{5,6}$ = 6.3 Hz,), 9.35 (d, 1H, 5'-H, $J_{5',6'}$ = 7.1 Hz,), 8.62 (s, 2H, 8-H, 8'-H), 7.83 (m, 4H, 12-H, 13-H, 15-H, 16-H), 7.43 (m, 2H, 6-H, 6'-H), 7.32 (d, 2H, 12'-H, 16'-H, $J_{12',13'}$ = 6.4 Hz), 7.14 (m, 3H, 13'-H, 14'-H, 15'-H), 3.57 (s, 3H, $1CH_3$), 3.51 (s, 3H, $1CH_3$), 3.15 (s, 3H, $1CH_3$), 3.01 (s, 3H, $1CH_3$).

Anal. Calcd. For $C_{38}H_{27}N_3O_{12}$: C, 63.60; H, 3.79; N, 5.86. Found: C, 63.52; H, 3.90; N, 5.82.

1,2,1',2'-tetra(methoxycarbonyl)-3-(4-nitrobenzoyl)-3'-(4-methylbenzoyl)-7,7'-bisindolizine (**26**).

This compound was obtained as yellow solid (350 mg, 48%), mp 273-274 °C; ir (potassium bromide): CO 1742, 1704, 1627, 1602, NO_2 1521, 1344, C-O 1251, 1214, 1180, 1159 cm^{-1}; ^1H nmr (DMSO-d_6): δ 9.55 (d, 1H, 5-H, $J_{5,6}$ = 6.4 Hz), 9.35 (d, 1H, 5'-H, $J_{5',6'}$ = 6.2 Hz,), 8.54 (s, 2H, 8-H, 8'-H), 8.33 (d, 2H, 13-H, 15-H, $J_{13,12}$ = 7.52 Hz), 7.83 (d, 2H, 12-H, 16-H $J_{12,13}$ = 7.52 Hz), 7.70 (d, 1H, 6-H, $J_{6,5}$ = 6.4 Hz), 7.61 (d, 1H, 6'-H $J_{6',5'}$ = 6.4 Hz), 7.52 (d, 2H, 12'-H, 16'-H, $J_{12',13'}$ = 6.3 Hz), 7.29 (d, 2H, 13'-H, 15'-H $J_{13',12'}$ = 6.3 Hz), 3.84 (s, 6H, $2CH_3$), 3.28 (s, 6H, $2CH_3$), 2.40 (s, 3H, $1CH_3$).

Anal. Calcd. for $C_{39}H_{29}N_3O_{12}$: C, 64.02; H, 4.00; N, 5.74. Found: C, 63.98; H, 4.03; N, 5.78.

1,2,1',2'-Tetra(methoxycarbonyl)-3-(4-nitrobenzoyl)-3'-(4-methoxybenzoyl)-7,7'-bisindolizine (**27**).

This compound was obtained as yellow solid (306 mg, 41%), mp 286-288 °C; ir (potassium bromide): CO 1741, 1703, 1624, 1600, NO_2 1521, 1341, C-O 1256, 1226, 1147, 1099 cm^{-1}; ^1H nmr (DMSO-d_6): δ 9.55 (d, 1H, 5-H, $J_{5,6}$ = 7.5 Hz), 9.26 (d, 1H, 5'-H, $J_{5',6'}$ = 7.5 Hz), 8.56 (s, 2H, 8-H, 8'-H), 8.33 (d, 2H, 13-H, 15-H, $J_{13,12}$ = 8.4 Hz), 7.83 (d, 2H, 12-H, 16-H, $J_{12,13}$ = 8.4 Hz), 7.77 (dd, 1H, 6-H, $J_{6,5}$=7.4 Hz, $J_{6,8}$=1.7 Hz), 7.63 (d, 3H, 6'-H, 12'-H, 16'-H, $J_{12',13'}$ = 8.7 Hz), 7.02 (d, 2H, 13'-H, 15'-H, $J_{13',12'}$ = 8.7 Hz), 3.86 (s, 3H, $1CH_3$), 3.85 (s, 3H, $1CH_3$), 3.84 (s, 3H, $1CH_3$), 3.66 (s, 3H, $1CH_3$), 3.26 (s, 3H, $1CH_3$).

Anal. Calcd. for $C_{39}H_{29}N_3O_{13}$: C, 62.65; H, 3.91; N, 5.62. Found: C, 62.68; H, 3.88; N, 5.65.

1,2,1',2'-Tetra(methoxycarbonyl)-3-(4-nitrobenzoyl)-3'-(3-methoxybenzoyl)-7,7'-bisindolizine (**28**).

This compound was obtained as yellow solid (313 mg, 42%), mp 234-235 °C; ir (potassium bromide): CO 1743, 1705, 1623, 1601, NO_2 1522, 1341, C-O 1258, 1229, 1146, 1099 cm^{-1}; ^1H nmr (DMSO-d_6): δ 9.84 (d, 1H, 5-H, $J_{5,6}$ = 7.4 Hz), 9.68 (d, 1H, 5'-H, $J_{5',6'}$ = 7.4 Hz), 8.80 (s, 2H, 8-H, 8'-H), 8.33 (d, 2H, 13-H, 15-H, $J_{13,12}$ = 6.7 Hz), 7.85 (d, 2H, 12-H, 16-H, $J_{12,13}$ = 6.7 Hz), 7.61 (d, 1H, 6-H, $J_{6,5}$ = 7.5 Hz), 7.52 (d, 1H, 6'-H, $J_{6',5'}$ = 7.5 Hz), 7.39-7.14 (m, 4H, 12'-H, 13'-H, 14'-H, 16'-H), 3.93 (s, 3H, $1CH_3$), 3.91 (s, 3H, $1CH_3$), 3.88 (s, 3H, $1CH_3$), 3.39 (s, 3H, $1CH_3$), 3.38 (s, 3H, $1CH_3$).

Anal. Calcd. for $C_{39}H_{29}N_3O_{13}$: C, 62.65; H, 3.91; N, 5.62. Found: C, 62.67; H, 3.89; N, 5.66.

1,2,1',2'-tetra(methoxycarbonyl)-3-(4-nitrobenzoyl)-3'-(4-bromobenzoyl)-7,7'-bisindolizine (**29**).

This compound was obtained as yellow solid (397 mg, 50%), mp >300 °C; ir (potassium bromide): CO 1741, 1702, 1626, 1601, NO_2 1523, 1346, C-O 1250, 1215, 1182, 1161 cm^{-1}; ^1H nmr (DMSO-d_6): δ 9.61 (d, 1H, 5-H, $J_{5,6}$ = 6.1 Hz,), 9.47 (d, 1H, 5'-H, $J_{5',6'}$ = 6.0 Hz,), 8.67 (s, 2H, 8-H, 8'-H), 8.35 (d, 2H, $J_{13,12}$ = 7.2 Hz, 13-H, 15-H), 7.85 (m, 3H, 6-H, 12-H, 16-H), 7.63 (m, 5H, 6'-H, 12'-H, 13'-H, 15'-H, 16'-H), 3.86 (s, 6H, $2CH_3$), 3.31 (s, 6H, $2CH_3$).

Anal. Calcd. for $C_{38}H_{26}BrN_3O_{12}$: C, 57.30; H, 3.29; N, 5.28. Found: C, 57.36; H, 3.25; N, 5.31.

1,2,1',2'-Tetra(methoxycarbonyl)-3-(4-nitrobenzoyl)-3'-(4-chlorobenzoyl)-7,7'-bisindolizine (**30**).

This compound was obtained as yellow solid (398 mg, 53%), mp >300 °C; ir (potassium bromide): CO 1741, 1703, 1625, 1601, NO_2 1524, 1345, C-O 1250, 1213, 1181, 1160 cm^{-1}; ^1H nmr (DMSO-d_6): δ 9.60 (d, 1H, 5-H, $J_{5,6}$ = 6.2 Hz), 9.46 (d, 1H, 5'-H, $J_{5',6'}$ = 6.0 Hz), 8.65 (s, 2H, 8-H, 8'-H), 8.34 (d, 2H, 13-H, 15-H, $J_{13,12}$ = 7.2 Hz), 7.83 (m, 3H, 6-H, 12-H, 16-H), 7.64 (m, 3H, 6'-H, 12'-H, 16'-H), 7.6 (d, 2H, 13'-H, 15'-H, $J_{13',12'}$ = 6.1 Hz), 3.85 (s, 6H, $2CH_3$), 3.28 (s, 6H, $2CH_3$).

Anal. Calcd. for $C_{38}H_{26}ClN_3O_{12}$: C, 60.69; H, 3.48; N, 5.59. Found: C, 60.72; H, 3.44; N, 5.64.

REFERENCES AND NOTES

* Corresponding author: Dr. Rotaru Alexandru e-mail rotaru_a@yahoo.com or rdanac@uaic.ro

[1] R. Dinica, I. Druta and C. Pettinari, *Synlett*, 1013 (2000),

[2] I. Druta, M. Andrei and P. Aburel, *Tetrahedron*, **54**, 2107 (1998).

[3] I. Druta, R. Dinica, E. Bacu and I. Humelnicu, *Tetrahedron*, **54**, 10811 (1998).

[4] H. Sonnenschein, G. Hennrich, U. Resch-Genger and B. Schulz, *Dyes and Pigments*, **46**, 23 (2000).

[5] A. Vlahovici, I. Druta, M. Andrei, M. Cotlet and R. Dinica, *Journal of Luminescence*, **82**, 155 (1999).

[6] A. Vlahovici, M. Andrei and I. Druta, *Journal of Luminescence*, **96**, 279 (2002).

[7] R. Danac, A. Rotaru, G. Drochioiu and I. Druta, *J. Heterocyclic Chem*., **40**, 283 (2003).

[8] I. Zugravescu and M. Petrovanu, *N-Ylide-Chemistry*, Mc.Graw Hill: London, 1976.

[9] I. Zugravescu and M. Petrovanu, Cicloaditii 3+2 Dipolare, Ed. Acad. R.S.R.: Bucharest, 1987.

[10] A. Pawda, 1,3-Dipolar Cycloaddition Chemistry, John Wiley & Sons: New York, 1984.

[11] F. Krohnke, *Angew. Chem.*, 181 (1963).

[12] F. Krohnke, *Angew. Chem*., 605 (1953).

[13] I. Druta, L. Smau, C. Cuciac and R. Dinica, *An. St. Univ. "Al.I.Cuza"Iasi*, **3**, 117 (1995).

[14] M. Caprosu, M. Petrovanu, I. Druta and I. Zugravescu, *Bull. Soc. Chim. France*, 1834 (1971).

[15] C. Cuciac, PhD Thesis, "Al. I. Cuza" University, Iasi, Romania (2003).