

HETEROCYCLES, Vol. 78, No. 9, 2009, pp. 2315 - 2324. © The Japan Institute of Heterocyclic Chemistry  
Received, 16th April, 2009, Accepted, 1st June, 2009, Published online, 1st June, 2009.  
DOI: 10.3987/COM-09-11734

## REACTIONS OF RADICALS GENERATED FROM 1-ETHYL-1,4-DIAZINIUM SALTS: ADDITION TO THE C-C TRIPLE BOND VERSUS DIMERIZATION

Gennadiy L. Rusinov,\* Egor V. Verbitskiy, Pavel A. Slepukhin, Olga N. Zabelina, Mikhail I. Kodess, Marina A. Ezhikova, Valeriy N. Charushin, and Oleg N. Chupakhin

Dedicated to Professor Dr. Henk van der Plas on his 80<sup>th</sup> anniversary

I. Postovsky Institute of Organic Synthesis, 620041 Ekaterinburg, GSP-147, S. Kovalevskoy Str., 22, Russian Federation. E-mail: Rusinov@ios.uran.ru

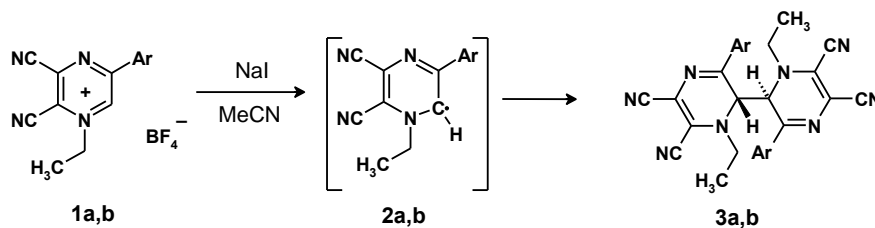
**Abstract** – Radical species generated from 5-aryl-substituted 1-ethyl-2,3-dicyano-1,4-diazinium salts by action of sodium iodide undergo dimerization into [2,2']bipyrazinyl derivatives, as evidenced by NMR and X-ray crystallography data. The pyrazinyl radicals can also be involved into the addition reaction on the C-C triple bond, thus demonstrating a new synthetic route to the structure of pyrazines. The structures of *E*- and *Z*-isomers of 1-(1',2'-dihydropyrazinyl-2')-2-iodoethenes have been proved by <sup>1</sup>H and <sup>13</sup>C NMR spectroscopy and X-ray analysis.

## INTRODUCTION

Chemistry of uncharged pyrazines is well documented in the literature.<sup>1-5</sup> Much less attention has been paid to 1-alkylpyrazinium salts, although a number of recently published papers were dedicated to the synthesis and transformations of quaternary *N*-alkyl-1,4-diazinium salts.<sup>6-11</sup> As far as synthetic aspects of the chemistry of 1,4-diazines are concerned, the reactions of pyrazines and pyrazinium salts with nucleophilic agents appear to be of great importance. Indeed, it has been shown that 1-alkyl-1,4-diazinium cations are prone to add carbo- and heteroatomic nucleophiles to give mono- and diadducts, or to be transformed into condensed tetrahydropyrazines through the tandem addition reactions with bifunctional nucleophiles.<sup>12-15</sup>

## RESULTS AND DISCUSSION

In this communication we wish to report a new approach to build the C-C bond with the pyrazine ring which is based on use of radical species (**2a,b**) generated from 5-aryl-substituted 1-ethyl-2,3-dicyano-1,4-diazinium salts (**1a,b**). The fact that radicals (**2a,b**) are easily formed under mild conditions (acetonitrile, 20 °C) in the presence of sodium iodide is substantiated by their dimerization into 1,1'-diethyl-3,3'-diaryl-1,2,1',2'-tetrahydro[2,2']bipyrazinyl-5,6,5',6'-tetracarbonitriles (**3a,b**) (Scheme 1).



Scheme 1

The structure of dimers (**3a**) and (**3b**) was proved by  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectroscopy and X-ray analysis performed for 1,1'-diethyl-3,3'-diphenyl-1,2,1',2'-tetrahydro[2,2']bipyrazinyl-5,6,5',6'-tetracarbonitrile (**3a**) (Fig. 1). As might be expected, in the  $^1\text{H}$  NMR spectra of compounds (**3a**) and (**3b**) the signals of H-2 and H-2' protons are observed as singlets at  $\delta=5.8$  and  $\delta=5.6$  ppm, respectively. All peaks observing in  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra of compounds (**3a,b**) proved to be in correspondence with the only stereostructure of diastereomers (**3a,b**). The (*R,S*/*S,R*)-configuration of diastereomers (**3a,b**) was established by X-ray crystallography (see Figure 1).

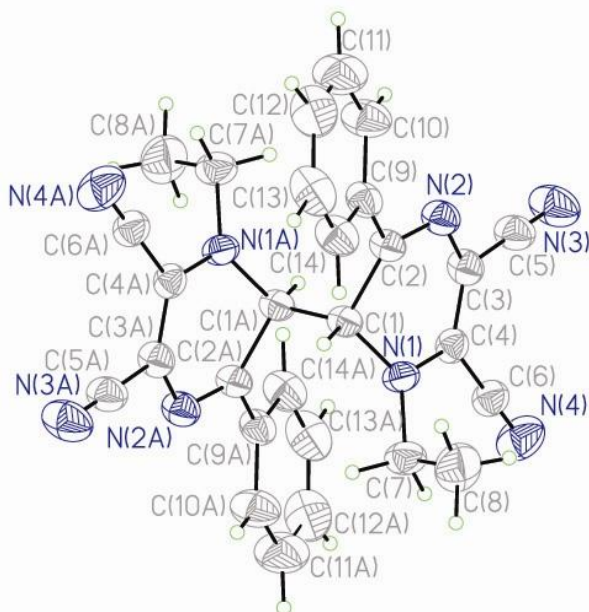


Figure 1. The X-ray structure of compound (**3a**)

The reaction appears to be initiated by a single electron transfer from the iodide anion to pyrazinium cations (**1a,b**), thus generating the radical species (**2a,b**). Recombination of these radicals affords dimeric molecules (**3a,b**). Similar examples of single electron transfer followed by dimerisation of radicals have been observed in the series of pyridines,<sup>16,17</sup> acridines,<sup>17,18</sup> and triazines.<sup>19-22</sup>

Attempts to register radical species by ESR spectroscopy failed, probably due to a very short radical's life time,  $\tau \ll 10^{-10}$  s. Sensitivity of the ESR method was  $10^{14}$  spin/G. For indirect detection of short-living radical intermediates the spin probe method was used.<sup>23</sup> A solution of 2,2-di(4-tert-octylphenyl)-1-picrylhydrazyl (DPPH) was added to the reaction mixture. The ESR spectrum of the parent DPPH solution in acetonitrile is shown in Figure 2.

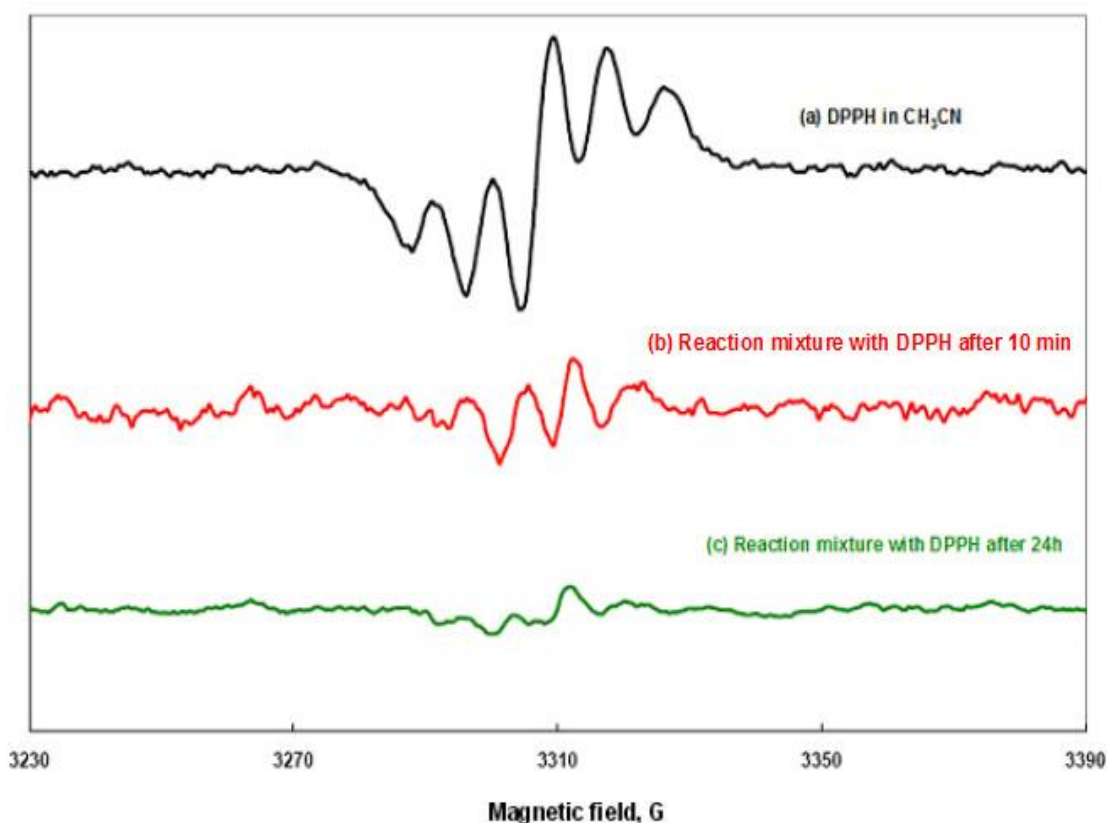


Figure 2. ESR spectra: (a) Solution of DPPH in MeCN; (b) The reaction mixture with DPPH after 10 min; (c) the same mixture after 24 h.

In case of the radical nature of the reaction, the presence of DPPH would lead to trapping of short-living radical particles (**2a,b**) by DPPH. Indeed, the ESR spectra of the reaction mixture with DPPH taken after 10 min and 24 hours (Figure 2) indicate that intensities of the ESR signals drop down immediately after addition of DPPH and they are not restored during the next 24 hours, thus showing irreversibility of the reaction.

Acetylenes are known to react with free radicals to give addition products on the C-C triple bond. A great deal of examples for interaction of arylacetylenes with sulfanyl, selenyl or telluryl radicals are available

in the literature.<sup>24-27</sup> Also the synthesis of fluorinated acetylenes exploiting the radical addition of iodofluorocarbons to alkynes as the key step has been described.<sup>28</sup> On the other hand, the addition reactions of radicals generated from heterocyclic compounds are scarcely presented in the literature.<sup>29,30</sup> In order to explore the synthetic potential of intermediate radicals, we have generated the radical species (**2a,b**) in the presence of phenyl acetylene.

It has been established that the addition of (**2a,b**) takes place exclusively at the terminal carbon atom of phenylacetylene and is followed by interaction of radical intermediates (**5a,b**) with I (I<sub>2</sub> or I), thus resulting in the formation of 1,2-dihydropyrazines (**4a,b**) bearing the fragment of (1-iodo-vinyl)benzene (Scheme 2, Table 1). But salt (**1a,b**) does not react with phenylacetylene without sodium iodide (TLC data). As seen from the Table 1 the *E*-isomer is prevailing in the reaction mixture possibly due to steric hindrance from the aryl substituent at C-3, however a more detailed study of the reaction mechanism has to be done.

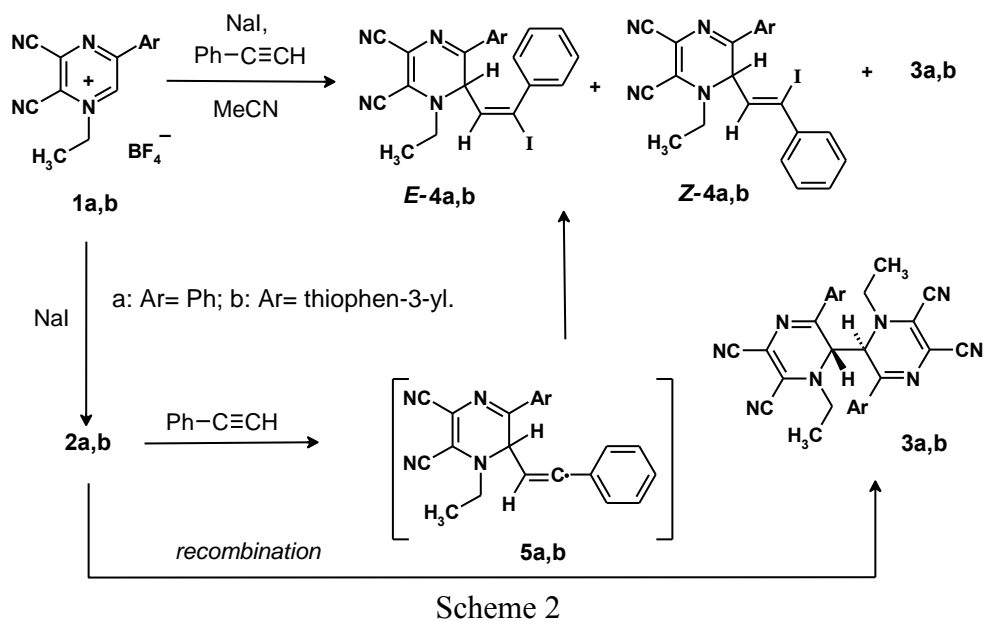


Table 1. Yields of compounds (**3a,b**) and (**4a,b**), and ratio of their *E*-/*Z*-isomers according to the <sup>1</sup>H NMR data

Starting pyrazinium salt	Products Yields, %	Ratio of <i>E</i> - : <i>Z</i> -isomers in the reaction mixture
<b>1a</b>	<i>E</i> - <b>4a</b> : <i>Z</i> - <b>4a</b> : <b>3a</b> 29 : 14 : 18	66 : 34
<b>1b</b>	<i>E</i> - <b>4b</b> : <i>Z</i> - <b>4b</b> : <b>3b</b> 19 : 10 : 55	64 : 36

Addition products **4a,b** proved to be a mixture of *E*-/*Z*-isomers, which were separated by preparative HPLC. Individual *E*- and *Z*-isomers of 1-ethyl-5-(het)aryl-6-(2-iodo-2-phenylvinyl)-

1,6-dihydropyrazine-2,3-dicarbonitrile (**4a**) and (**4b**) were identified by  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectroscopy and X-ray analysis (Figure 3 and 4).

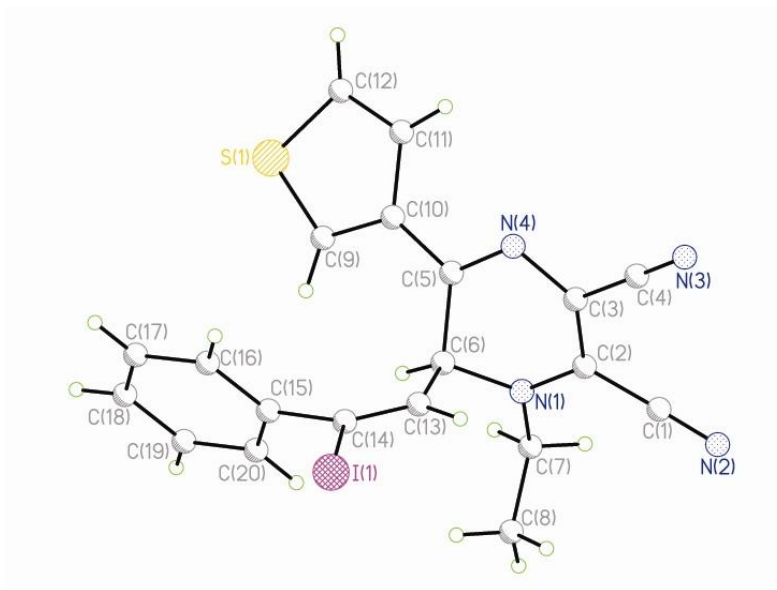


Figure 3. X-Ray crystal structure of compound (**E-4b**)

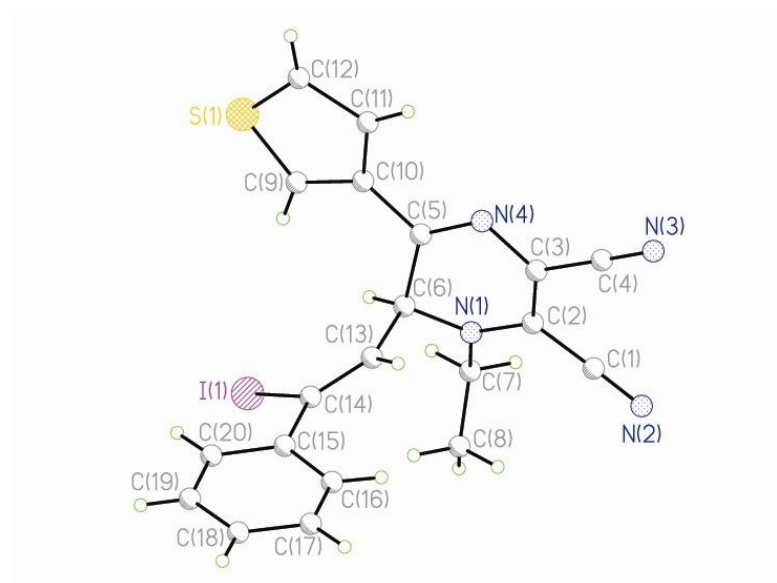


Figure 4. X-Ray crystal structure of compound (**Z-4b**)

The spin-spin coupling constants for H-6 signals for the (**4a**) and (**4b**)  $J = 9.6$  Hz (*E*-isomers) and  $J = 9.7$  Hz (*Z*-isomers) are of typical values. Because of the absence of the X-ray data for the compounds (**4a**), the configurational determinations for the corresponding isomers (**E-4a**) and (**Z-4a**) were made on the basis of NMR data.

In summary, it has been shown that 1-ethyl-5-(het)aryl-2,3-dicyanopyrazinium salts are able to undergo single electron reduction by action of sodium iodide, thus generating pyrazinyl radicals which can be trapped with acetylenes to form a mixture *Z*- and *E*-pyrazinyl iodoalkenes.

## EXPERIMENTAL

**General:** All solvents and reagents were purified and prepared according to literature procedure.<sup>31</sup> Compounds (**1a,b**) were synthesized according to procedures described in the literature.<sup>11</sup> The X-band (~9.4 GHz) EPR spectra were recorded at room temperature by using standard CW homodyne spectrometer ERS-231 with TE<sub>102</sub> microwave cavity. The experimental conditions were: central field, B<sub>0</sub>=342 mT, scan range,  $\delta B_{sr}=20$  mT ( $\delta B_{sr}>5\Delta B$ , where  $\Delta B$  is peak-to-peak EPR linewidth)<sup>32</sup>, microwave power, P= 2 mW and modulation amplitude, b<sub>mw</sub>= 0.3 mT. The g-factor was calibrated by using coal-pitch probe and CuSO<sub>4</sub>·5H<sub>2</sub>O. The EPR measurements were carried out in acetonitrile. The NMR spectra were recorded on a Bruker DRX-400 instrument with TMS as the internal standard. <sup>1</sup>H NMR spectra were recorded at 400MHz and <sup>13</sup>C NMR spectra at 100MHz, respectively. MS spectra were measured on Shimadzu LCMS-2010 quadrupole liquid GLC-mass spectrometer in MeCN at a scan rate of 0.25 mL/min using a Supelco LC-18 column (4.6 × 250 mm). Mass spectra were obtained both in positive and negative modes with APCI and ESI probe installed. Quadrupole array and curved desolvation line (CDL) were used in scan-mode according to the parameters stored in the auto-tune file. Nebulizing gas was nitrogen, at a flow rate of 2.5 L/min. Probe voltage was set to 4.5 kV. The elemental analysis was carried out on an automated Perkin Elmer PE-2400 analyzer. The melting points were determined on a combined Boetius hot-stage apparatus and are uncorrected. Flash-chromatography was performed using silica gel (0.040-0.063 mm, 230-400 mesh). The course of the reactions was monitored and the purity of the products was checked by TLC on Silufol UV-254 plates (Russia); the spots were visualized with iodine vapor and UV-radiation. X-ray diffraction analysis on single crystals was performed on an X-ray diffractometer X-calibur-3 equipped with CCD detector ( $\lambda$ MoK $\alpha$ , graphite monochromator). The structure was solved by the direct method using SHELXS-97 program and refined applying SHELXL-97 program. The X-ray crystallography data for structures (**3a**), (**E-4b**) and (**Z-4b**) reported in this paper have been deposited with Cambridge Crystallography Data Centre as supplementary publications no CCDC 714803, CCDC 714804 and CCDC 714805. Copies of these data can be obtained, free of charge, on application to the CCDC, 12 Union Road, Cambridge CB2 1 EZ, UK, (fax: +44 (0) 1223 336033 or e-mail: deposit@ccdc.cam.ac.uk).

*Typical procedure for the synthesis of compounds (3a,b).* Sodium iodide (1.0 mmol) was added to a solution of salt (**1a**) or (**1b**) (1.0 mmol) in dry MeCN (7 mL). After 35 min, the resulting precipitate was filtrated off, washed with MeCN (3 × 10 mL) and water (3 × 10 mL).

**1,1'-Diethyl-3,3'-diphenyl-1,2,1',2'-tetrahydro[2,2']bipyrazinyl-5,6,5',6'-tetracarbonitrile (3a).** Orange powder, mp 209–211 °C (decomp.), yield 40%. <sup>1</sup>H & <sup>13</sup>C NMR of **3a** in DMF-*d*<sub>7</sub> (400.13 and

100.61 MHz)  $^1\text{H}$ ,  $\delta$ , ppm /  $J$ , Hz: 0.99 (t, 3H,  $\text{CH}_3$ ,  $J = 7.2$ ); 3.23 (dq, 1H,  $\text{NCH}^{\text{B}}$ ,  $J = 14.4$ , 7.2); 3.30 (dq, 1H,  $\text{NCH}^{\text{A}}$ ,  $J = 14.4$ , 7.2); 5.83 (s, 1H, H2); 7.78-7.66 (m, 3H, H $m$ , H $p$ ); 8.24 (dd, 2H, H $o$ ,  $J = 8.2$ , 1.6).  $^{13}\text{C}$ ,  $\delta$ , ppm: 15.72 ( $\text{CH}_3$ ); 50.18 ( $\text{NCH}_2$ ); 51.65 (C2); 111.62 and 113.10 (CN); 116.96 and 118.87 (C5, C6); 128.49, 129.96, 132.62 and 135.129 (Ph); 147.44 (C3).  $\text{C}_{28}\text{H}_{22}\text{N}_8 \cdot 0.3 \text{H}_2\text{O}$ : Anal. Calcd for C 70.66, H 4.79, N 23.54; Found C 70.66, H 4.67, N 23.65.

**1,1'-Diethyl-3,3'-dithiophen-3-yl-1,2,1',2'-tetrahydro[2,2']bipyrazinyl-5,6,5',6'-tetracarbonitrile (3b).** Red powder, mp 190–192 °C (decomp.), yield 37%.  $^1\text{H}$  &  $^{13}\text{C}$  NMR of **3b** in  $\text{DMF-}d_7$  (400.13 and 100.61 MHz)  $^1\text{H}$ ,  $\delta$ , ppm /  $J$ , Hz: 0.99 (t, 3H,  $\text{CH}_3$ ,  $J = 7.2$ ); 3.22 (dq, 1H,  $\text{NCH}^{\text{B}}$ ,  $J = 14.4$ , 7.2); 3.30 (dq, 1H,  $\text{NCH}^{\text{A}}$ ,  $J = 14.4$ , 7.2); 5.66 (s, 1H, H2); 7.79 (dd, 1H, H4-*thiophene*,  $J = 5.1$ , 1.3); 7.83 (dd, 1H, H5-*thiophene*,  $J = 5.1$ , 2.7); 8.65 (dd, 1H, H2-*thiophene*,  $J = 2.7$ , 1.3).  $^{13}\text{C}$ ,  $\delta$ , ppm: 15.41 ( $\text{CH}_3$ ); 50.13 ( $\text{NCH}_2$ ); 53.20 (C2); 111.92 and 113.26 (CN); 117.06 and 118.43 (C5, C6); 127.46, 129.14 and 130.71 (C4, C2, C5-*thiophene*); 139.29 (C3-*thiophene*); 143.27 (C3).  $\text{C}_{24}\text{H}_{18}\text{N}_8\text{S}_2 \cdot 0.3 \text{H}_2\text{O}$ : Anal. Calcd for C 59.07, H 3.84, N 22.96; Found: C 58.81, H 3.53, N 22.92.

*Typical procedure for the synthesis of compounds (4a,b).* Sodium iodide (0.6 mmol) was added to a solution of salt (**1a**) or (**1b**) (0.5 mmol) and phenyl acetylene (0.5 mmol) in dry MeCN (7 mL). After 35 min the resulting precipitate of dimer (**3a**) or (**3b**) was filtrated off, washed with MeCN (3  $\times$  5 mL) and water (3  $\times$  5 mL). For yields of compounds (**3a,b**) see Table 1. The filtrate was distilled off under reduced pressure and the residue was purified on silica gel column using  $\text{CHCl}_3$ . The obtained mixture of *E*-/*Z*-isomers was fractionated by preparative HPLC (ZORBAX Eclipse XDB-C18 PrepHT (21.2 $\times$ 150 mm, 5  $\mu\text{m}$ ) column). Mixture of MeCN :  $\text{H}_2\text{O} = 4 : 1$  was used as mobile phase. Yields of (**4a,b**) are given in Table 1.

**1-Ethyl-6-(2-iodo-2-phenyl-vinyl)-5-phenyl-1,6-dihydropyrazine-2,3-dicarbonitrile (4a).** Compound *E*-**4a**: yellow powder, mp 138–140 °C., compound (*Z*-**4a**): yellow powder, mp 56–58 °C.  $^1\text{H}$  &  $^{13}\text{C}$  NMR of (**4a**) in  $\text{CDCl}_3$  (400.13 and 100.61 MHz): *E*-isomer:  $^1\text{H}$ ,  $\delta$ , ppm /  $J$ , Hz: 1.12 (t, 3H,  $\text{CH}_3$ ,  $J = 7.2$ ); 3.39 (dq, 1H,  $\text{NCH}^{\text{B}}$ ,  $J = 14.5$ , 7.2); 3.62 (dq, 1H,  $\text{NCH}^{\text{A}}$ ,  $J = 14.5$ , 7.2); 5.05 (d, 1H, H6,  $J = 9.7$ ); 6.38 (d, 1H, H1',  $J = 9.7$ ); 7.20 (m, 2H, Ph); 7.31 (m, 2H, Ph); 7.43-7.49 (m, 6H, Ph).  $^{13}\text{C}$ ,  $\delta$ , ppm: 14.87 ( $\text{CH}_3$ ); 47.80 ( $\text{NCH}_2$ ); 52.44 (C6); 103.16 (C2'); 110.52 and 111.13 (CN); 115.76 (C3); 118.15 (C2); 127.54, 127.86, 128.84, 129.00 and 129.50 (Ph); 131.78 and 131.82 (Ph, C1'); 133.03 (Ph); 141.14 (C2'-*Cl*); 146.48 (C5).  $\text{C}_{22}\text{H}_{17}\text{N}_4\text{I} \cdot 0.4\text{H}_2\text{O}$ : Anal. Calcd for C 56.04, H 3.81, N 11.88; Found: C 56.07, H 3.49, N 11.48. MS (in MeCN, Q-array scan):  $m/z$  (%) = 463 (100)  $[\text{M}-\text{H}]^+$ , 464 (17)  $[\text{M}]^+$ , 465 (4)  $[\text{M}+\text{H}]^+$ . *Z*-isomer:  $^1\text{H}$ ,  $\delta$ , ppm /  $J$ , Hz: 1.40 (t, 3H,  $\text{CH}_3$ ,  $J = 7.2$ ); 3.69 (dq, 1H,  $\text{NCH}^{\text{B}}$ ,  $J = 14.5$ , 7.2); 3.80 (dq, 1H,  $\text{NCH}^{\text{A}}$ ,  $J = 14.5$ , 7.2); 5.64 (d, 1H, H6,  $J = 9.6$ ); 5.99 (d, 1H, H1',  $J = 9.6$ ); 7.30-7.34 (m, 2H, Ph); 7.31 (m, 2H, Ph); 7.40-7.53 (m, 6H, Ph); 8.05 (m, 2H, Ph).  $^{13}\text{C}$ ,  $\delta$ , ppm: 15.31 ( $\text{CH}_3$ ); 48.69 ( $\text{NCH}_2$ ); 60.13 (C6); 109.69 (CN); 111.09 and 111.13 (CN, C2'); 116.02 and 118.87 (C3, C2); 127.94, 128.20, 128.58, 128.79, 129.04,

129.93, 132.05 and 133.70 (Ph, C1'); 141.26 (Ci-C2'); 146.90 (C5). C<sub>22</sub>H<sub>17</sub>N<sub>4</sub>I·0.4H<sub>2</sub>O: Anal. Calcd for C 56.04, H 3.81, N 11.88; Found: C 56.07, H 3.49, N 11.48. MS (in MeCN, Q-array scan): m/z (%)= 463 (100) [M-H]<sup>+</sup>, 464 (17) [M]<sup>+</sup>, 465 (4) [M+H]<sup>+</sup>.

**1-Ethyl-6-(2-iodo-2-phenyl-vinyl)-5-thiophen-3-yl-1,6-dihydropyrazine-2,3-dicarbonitrile (4b).**

Compound (**E-4b**): yellow powder, mp 62–64 °C., compound (**Z-4b**): yellow powder, mp 171–173 °C (decomp.). <sup>1</sup>H & <sup>13</sup>C NMR of (**4b**) in CDCl<sub>3</sub> (400.13 and 100.61 MHz): **E-isomer**: <sup>1</sup>H, δ, ppm / J, Hz: 1.15 (t, 3H, CH<sub>3</sub>, J= 7.2); 3.43 (dq, 1H, NCH<sup>B</sup>, J= 14.5, 7.2); 3.62 (dq, 1H, NCH<sup>A</sup>, J= 14.5, 7.2); 4.90 (d, 1H, H<sub>6</sub>, J= 9.7); 6.38 (d, 1H, H1', J= 9.7); 6.89 (dd, 1H, H2-thiophene, J= 2.8, 1.4); 7.26 (dd, 1H, Ho, J= 7.3, 1.2); 7.30 (dd, 1H, H5-thiophene, J= 5.2, 2.8); 7.45 (dd, 1H, H4-thiophene, J= 5.2, 1.4); 7.45-7.51 (m, 3H, Hm, Hp) <sup>13</sup>C, δ, ppm: 14.76 (CH<sub>3</sub>); 47.73 (NCH<sub>2</sub>); 53.71 (C6); 102.79 (C2'); 110.59 and 111.19 (CN); 115.78 (C3); 117.80 (C2); 127.14 (C5-thiophene); 127.35(C4-thiophene); 127.51 (Co); 128.24 (C2-thiophene); 129.19 (Cm); 129.59 (Cp); 131.88 (C1'); 137.04 (C4-thiophene); 141.21 (Ci); 142.16 (C6). C<sub>20</sub>H<sub>15</sub>N<sub>4</sub>IS·1.5H<sub>2</sub>O: calcd C 48.30, H 3.65, N 11.27; found C 48.51, H 3.59, N 11.27. MS (in MeCN, Q-array scan): m/z (%) = 469 (100) [M-H]<sup>+</sup>, 470 (22) [M]<sup>+</sup>, 471 (6) [M+H]<sup>+</sup>. **Z-isomer**: <sup>1</sup>H, δ, ppm / J, Hz: 1.40 (t, 3H, CH<sub>3</sub>, J= 7.2); 3.66 (dq, 1H, NCH<sup>B</sup>, J= 14.5, 7.2); 3.75 (dq, 1H, NCH<sup>A</sup>, J= 14.5, 7.2); 5.49 (d, 1H, H<sub>6</sub>, J= 9.6); 5.96 (d, 1H, H1', J= 9.6); 7.32-7.35 (m, 3H); 7.39-7.43 (m, 3H); 7.43 (dd, 1H, H4-thiophene, J= 5.1, 1.3); 8.10 (dd, 1H, H2-thiophene, J= 2.8, 1.3). C<sub>20</sub>H<sub>15</sub>N<sub>4</sub>IS·1.5H<sub>2</sub>O: Anal. Calcd for C 48.30, H 3.65, N 11.27; Found: C 48.51, H 3.59, N 11.27. MS (in MeCN, Q-array scan): m/z (%)= 469 (100) [M-H]<sup>+</sup>, 470 (22) [M]<sup>+</sup>, 471 (6) [M+H]<sup>+</sup>.

## ACKNOWLEDGEMENTS

This work was financially supported by the Russian Foundation for Basic Research (grants no. 07-03-12112-ofi, 07-03-96113-r\_ural\_a, and 07-03-96123-r\_ural\_a), the State Program for Supporting of Leading Scientific Schools of the Russian Federation (grants NSh 3758.2008.3 and NSh 3257.2008.2) and the Program of Presidium RAS №11). We thank to Dr. Yuriy N. Shvachko and Mr. Denis V. Starichenko from the Institute of Metal Physics (Ekaterinburg, Russia) for recording ESR spectra.

## REFERENCES

1. G. W. Cheesman and H. Werstiuk, *Adv. Heterocycl. Chem.*, 1972, **14**, 99.
2. G. B. Barlin, 'The Pyrazines', Wiley Interscience: New York, 1982.
3. N. Sato, '[Comprehensive Heterocyclic Chemistry II](#)' ed. by A. R. Katritzky, C. W. Rees and A. J. Boulton, Elsevier, Oxford, 1996, **6**, 233.
4. D. J. Brown, '[The Pyrazines: Supplement I](#)' (Ser. The Chemistry of Heterocyclic Compounds)', Wiley Interscience, New York, 2002, **58**.



5. A. E. A. Porter, 'Pyrazines and their Benzo Derivatives In Comprehensive Heterocyclic Chemistry II' ed. by A. R. Katritzky and C. W. Rees, Pergamon Press, New York, 1984, **3**, 191.
6. G. L. Rusinov, P. A. Slepukhin, V. N. Charushin and O. N. Chupakhin, [\*Mendeleev Commun.\*, 2001, \*\*11\*\*, 78.](#)
7. P. A. Slepukhin, D. G. Kim, G. L. Rusinov, V. N. Charushin and O. N. Chupakhin, [\*Chem. Heterocycl. Compounds\*, 2002, \*\*38\*\*, 1142.](#)
8. P. A. Slepukhin, G. L. Rusinov, V. N. Charushin, M. I. Kodess and O. N. Chupakhin, [\*Russ. Chem. Bull.\*, 2003, \*\*52\*\*, 689.](#)
9. P. A. Slepukhin, G. L. Rusinov, V. N. Charushin, V. I. Filyakova, N. S. Karpenko, D. B. Krivolapov and I. A. Litvinov, [\*Russ. Chem. Bull.\*, 2004, \*\*53\*\*, 1272.](#)
10. E. V. Verbitskiy, G. L. Rusinov, P. A. Slepukhin, A. I. Matern, Yu. N. Shvachko, D. V. Starichenko, V. N. Charushin and O. N. Chupakhin, [\*Russ. Chem. Bull.\*, 2006, \*\*55\*\*, 2114.](#)
11. E. V. Verbitskii, G. L. Rusinov, P. A. Slepukhin, A. N. Grishakov, M. A. Ezhikova, M. I. Kodess and V. N. Charushin, [\*Russ. J. Org. Chem.\*, 2008, \*\*44\*\*, 302.](#)
12. O. N. Chupakhin, V. N. Charushin and H. C. van der Plas, 'Nucleophilic Aromatic Substitution of Hydrogen', Academic Press, San Diego, New York, 1994.
13. V. N. Charushin, O. N. Chupakhin and H. C. van der Plas, [\*Adv. Heterocycl. Chem.\*, 1988, \*\*43\*\*, 301.](#)
14. V. N. Charushin and O. N. Chupakhin, [\*Pure Appl. Chem.\*, 2004, \*\*76\*\*, 1621.](#)
15. V. N. Charushin and O. N. Chupakhin, [\*Mendeleev Commun.\*, 2007, \*\*17\*\*, 249.](#)
16. R. Lai, S. Le Bot and F. Djafri, [\*J. Organomet. Chem.\*, 1991, \*\*410\*\*, 335.](#)
17. A. I. Matern, V. N. Charushin and O. N. Chupakhin, [\*Russ. Chem. Rev.\*, 2007, \*\*76\*\*, 23.](#)
18. J. Preuss, V. Zanker and A. Gieren, *Acta Crystallogr.*, [\*Sect. B: Struct. Crystallogr. Cryst. Chem.\*, 1977, \*\*33\*\*, 2317.](#)
19. B. V. Rudakov, S. G. Alexeev, V. N. Charushin, O. N. Chupakhin, V. A. Chertkov, G. G. Alexandrov and E. S. Klimov, *Russ. J. Org. Chem.*, 1992, **28**, 479.
20. D. K. Krass and W. W. Paudler, [\*J. Heterocycl. Chem.\*, 1974, \*\*11\*\*, 43.](#)
21. D. K. Krass, Teh-Kuei-Chen and W. W. Paudler, [\*J. Heterocycl. Chem.\*, 1973, \*\*10\*\*, 343.](#)
22. J. Laweka, E. Olender, P. Piszcz and A. Rykowski, [\*Tetrahedron Lett.\*, 2008, \*\*49\*\*, 723.](#)
23. A. N. Kuznetsov, 'Metod spinovogo zonda' (Method of spin probe), Nauka, Moscow, 1976.
24. N. O. Brace, [\*Journal of Fluorine Chemistry\*, 1993, \*\*62\*\*, 217.](#)
25. D. Melandri, P. C. Montevecchi and M. L. Navacchia, [\*Tetrahedron\*, 1999, \*\*55\*\*, 12227.](#)
26. K. Tsuchii and A. Ogawa, [\*Tetrahedron Lett.\*, 2003, \*\*44\*\*, 8777.](#)
27. A. Ogawa, K. Yokoyama, R. Obayashi, L.-B. Han, N. Kambe and N. Sonoda, [\*Tetrahedron\*, 1993, \*\*49\*\*, 1177.](#)

28. K. Baum, C. D. Bedford and R. J. Hundai, [\*J. Org. Chem.\*, 1982, \*\*47\*\*, 2251.](#)
29. H. J. Shine, B. K. Bandlish, S. R. Mani and A. G. Padilla, [\*J. Org. Chem.\*, 1979, \*\*44\*\*, 915.](#)
30. A. Albertazzi, R. Leardini, G. F. Pedulli, A. Tundo and G. Zanardi, [\*J. Org. Chem.\*, 1984, \*\*49\*\*, 4482.](#)
31. L. F. Tietze and T. Eicher, '[Reaktionen und Synthesen im organisch-chemischen Praktikum und Forschungslaboratorium](#)', Georg Thieme Verlag, Stuttgart, New York, 1991.
32. C. P. Poole, Jr. and H. A. Farach, Theory of Magnetic Resonance, 2nd Edition Wiley, New York, 1987.