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Journal of Molecular Structure 687 (2004) 23–33
Journal of MOLECULAR STRUCTURE
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Synthesis and multinuclear NMR investigation of some mesoionic 3-phenyl-5-imino-1,2,3,4-oxatriazole imines

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Received 17 June 2003; revised 11 August 2003; accepted 13 August 2003

Abstract

Six new derivatives of mesoionic 3-phenyl-5-imino-1,2,3,4-oxatriazole imine have been obtained and investigated by ^{1}H, ^{13}C, ^{14}N, ^{15}N and ^{17}O NMR techniques. The ^{15}N and ^{17}O NMR studies reveal that mesoionic oxatriazoles imines exist in a cyclic, 'mesoionic' form. Two stable conformers of mesoionic 3-phenyl-5-imino-1,2,3,4-oxatriazole imines, *E* and *Z*, in comparable concentrations, have been detected for the first time in the solution by the use of low temperature NMR experiments. ^{1}H NMR techniques and band shape analysis were applied for estimation of *Z*–*E* interconversion barrier of mesoionic 3-phenyl-5-methylimino-1,2,3,4-oxatriazole imine **6** and 3-phenyl-5-benzylimino-1,2,3,4-oxatriazole imine **10**. Some one-bond $^{1}J(^{15}N–^{13}C)$ coupling constants have been measured using ^{15}N enriched oxatriazole and tetrazole, as a means of the C5–N^{-}6 bond characterisation.

Keywords: Oxatriazole; Mesoionic compound; Nitrogen NMR; ^{17}O NMR; *E*–*Z* interconversion

1. Introduction

Mesoionic oxatriazoles, thiatriazoles and tetrazoles, due to interesting structure, attract attention of chemistry and physical chemistry. The derivatives of mesoionic 1,2,3,4-thiatriazole imine **1** (Fig. 1) have been investigated as multicentre ligands [1–3]. Compounds containing mesoionic 1,3-diphenyl-5-imino-1,2,3,4-tetrazole moiety were investigated as high-energy molecules [4–6]. Recently, derivatives of mesoionic 5-phenylimino-1,2,3,4-oxatriazole imine **4** have been examined as nitrogen oxide carrier agent in pharmacology [7–10].

The C5–N6 bond of a mesoionic aminide exhibits a partial double bond character. The C5–N6 bond lengths of various thiatriazole imines cover the range from 1.262 to 1.290 Å [11,12]. Similar bond length, of 1.272 Å, is observed for oxatriazole imine **4** [13]. These bonds are comparable with carbon–nitrogen bond of imines or acyclic amides [14]. The C5–C^{-}6 bond lengths of thiatriazolium-5-methylides **12** and **13** (Fig. 1) cover the range from 1.398 to 1.414 Å [15,16], i.e. a range of C(sp^2)–C(sp^2) single, conjugated bond. Character of the C5–N^{-}6 (C5–C^{-}6) bond implies the possibility of hindered rotation around this bond, and existence of two stable rotamers of a compound (Fig. 2a,b). Restricted rotation was observed for 'symmetrical' 1,2,3,4-thiatriazolium-5-methylides, for example **12**, $R^1 = R^2 =$ CN, where two CN groups are non-equivalent and give two signals on ^{13}C and ^{15}N NMR spectra. On the other hand, simply one set of NMR signals, deriving from one conformer only, was observed for 'unsymmetrical' methylides ($R^1 \neq R^2$, e.g. **13**).

Ab initio MO calculations [17] suggest that one conformer of a mesoionic 5-phenylimino-1,2,3,4-thiatriazole imine **1** should exist in a solution in minority, less than 1%, due to energy difference between both forms. On the contrary, low energy difference between conformers is expected for mesoionic 5-imino-1,2,3,4-oxatriazole imine; thus both form of an oxatriazole, being in equilibrium, should exist in the solution. However, no experimental proof was found in course of previous investigations of oxatriazoles [18].

Ring-chain rearrangement (Fig. 2c) is expected for all mesoionic compounds [19,20]. Such rearrangement has been found for sydnonimines [21–23] and isothiosydnonimines [24] only. X-ray study of oxatriazole imine **4** exhibits an interesting fact that the C5–O1 bond is longer than

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doi:10.1016/j.molstruc.2003.08.017

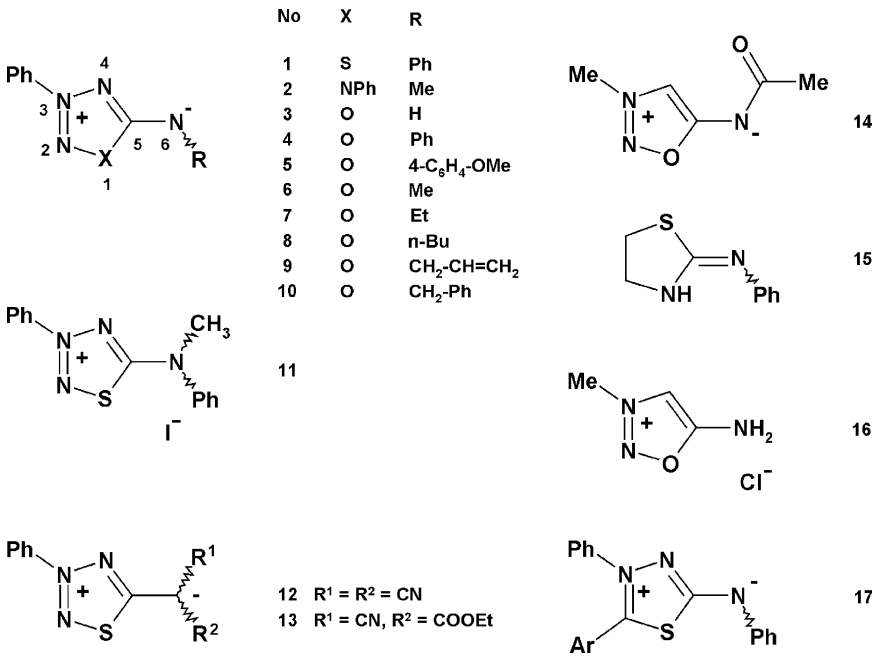


Fig. 1. The compounds discussed in the present paper. For all of compound the same numbering scheme is adopted for the comparison purposes.

the C–O bond in furan [13]. Authors conclude that the oxatriazole **4** tends to adopt an open-chain structure. It is noteworthy that pharmacological activity and nitrogen donating properties of mesoionic oxatriazoles are similar to those observed for 3-morpholino-sydnonimine, which undergoes ring-chain rearrangement [25].

The present work has been done for a following reasons: (i) synthesis of a new set of mesoionic 5-imino-1,2,3,4-oxatriazole imines, especially compounds with non-aromatic, N–CH_2–R group, with potential pharmacological interest; (ii) examination of hindered rotation around C5–N^-6 bond and founding whether two stable conformers of a compound exist; (iii) establishing if mesoionic 5-imino-1,2,3,4-oxatriazole imine exists as a linear or a cyclic valence tautomer.

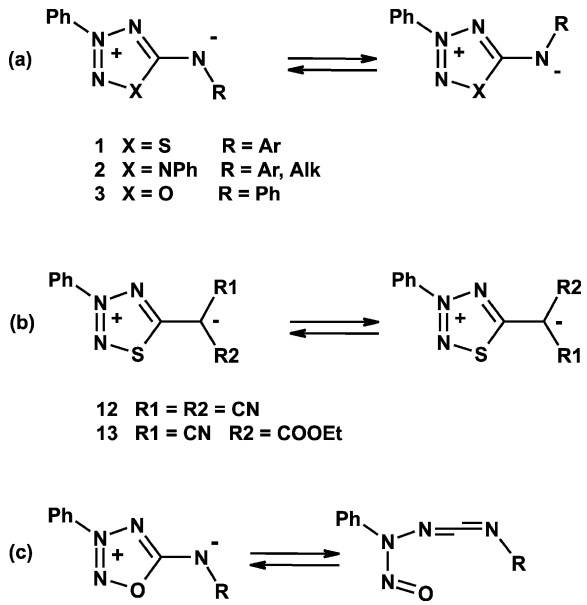


Fig. 2. Equilibriums potentially expected for mesoionic compounds in a solution. (a), (b) equilibriums between *E* and *Z* form for free mesoionic base and salt, being a consequence of hindered rotation around C5–N6 or C5–C^- bond; (c) hypothetical ring-chain valence tautomerism for mesoionic 3-phenyl-5-alkylimino-1,2,3,4-oxatriazole imine.

2. Experimental

2.1. NMR measurements

All NMR measurements were carried out on BRUKER Avance DRX 500 spectrometer. ^{1}H NMR, ^{13}C NMR, COSY, HSQC and HMBC experiments were performed using standard Bruker software with either a 5 mm dual ^{1}H/^{13}C or 5 mm triple broadband inverse gradient probes.

Chemical shifts were referred to internal TMS ($\delta = 0.00$ ppm) for ^{1}H and the central peak of acetone-d_6 ($\delta = 29.8$ ppm) for ^{13}C. Digital resolutions were 0.2 Hz per point in the ^{1}H and 0.5 Hz per point in the ^{13}C NMR spectra. Typically, a relaxation delay of 1 s, an acquisition time of ca. 1 s and pulse flip angle of 45° were applied for ^{13}C NMR experiment. Carbon-13 chemical shifts have been taken from 1D ^{13}C NMR spectra; HSQC and HMBC 2D spectra were used as a means of signals assignments only.

One-bond ^{15}N–^{13}C coupling constants were taken from ^{13}C NMR spectra, with parameter values of 0.1 s for a relaxation delay, an acquisition time of ca. 9 s, and a sweep width of ca. 1500 Hz, giving FID resolution of ca. 0.055 Hz per point, and, after zero-filling, a spectral resolution of 0.01 Hz per point. The samples 100% ^{15}N enriched at N6 position were used.

The ^{15}N NMR chemical shifts were referred with respect to the signal of external neat nitromethane ($\delta = 0$ ppm). For direct ^{15}N NMR measurement a dedicated 10 mm ^{15}N probe was utilized. A frequency of 50.689 MHz was applied with typical parameters values of 3 s for a relaxation delay, 1.6 s for an acquisition time, a flip angle of 30° and about 300–1000 scans depending on the sample concentration. The solutions with concentration of ca. 1 M were used (saturated solutions); about 1% of $Cr(acac)_3$ per one mole of substrate molecule was added as a relaxation reagent.

The ^{14}N NMR measurements were recorded at 36.136 MHz using a 5 mm broad band probe; with a typical relaxation delay of 0.001 s, an acquisition time of 0.2 s, spectral resolution of 1 Hz per point, flip angle 90° and ca. 4000 scans. Typically, diluted solutions of mesoionic heterocycles with concentration of 0.1 M, were used. The spectrometer software was applied for the ^{14}N signals deconvolution.

The ^{17}O NMR spectra were taken at 67.818 MHz using a 10 mm broad band probe with typical parameters values of 0.001 s for a relaxation delay, 0.02 s for an acquisition time, a flip angle of 90° and about 7000 scans. FID resolution of 26 Hz/point was applied, giving, after zero-filling, a spectral resolution of 13 Hz per point. The solvent signal was used as secondary reference; $\delta_{acetone} = 573.4$ ppm with respect to water signal $\delta_{water} = 0$ ppm.

Temperature-variable ^{1}H, ^{13}C and ^{15}N NMR spectra were recorded on a Bruker Avance DRX 500 instrument, equipped with BVT 3000 temperature control unit giving temperature stability of 0.1 K, and with the use of a probe fitted with thermocouple (5 mm dual ^{1}H/^{13}C probe, 5 mm triple broadband inverse gradient probe or a dedicated 10 mm ^{15}N probe). Temperatures, from 233 to 318 K, have been read from the instrument panel; no further measures for more precise temperature determinations for standard samples were taken. The measurements for band shape analysis have been made using 5 mm triple broadband inverse gradient probe; the temperature reads have been corrected by means of a calibration curve based on methanol chemical shift thermometer.

2.2. NMR data treatments

All data treatments were performed with Mathcad 2001 Professional program, running on a personal computer. ^{1}H NMR measurements at various temperatures, and the complete band shape method were applied for estimation of E–Z interconversion rate for oxatriazoles **5**, **6** and **10.** The signals of either CH_3 or CH_2 groups were used for calculations, assuming an uncoupled two-site, A and B, exchange model [26]. The spectra were recorded at various temperatures, at least six measurements for each sample, below and above of coalescence temperature. Interconversion rate k has been estimated for each temperature by means of band shape analysis. Typically, a spectrum was calculated using a normalization factor, estimated experimental values of T_2, conformers molar fractions $p1$ and $p2$, chemical shifts of both forms and guess value of exchange rate, k. Both spectra, calculated one and experimental one, have been compared on the plot. In the next step the values of chemical shifts and normalization factor were readjusted, the exchange rate k was changed in order to obtain the spectrum similar to experimental one. Then calculations were repeated. As a quantitative means of spectra fitting, mean squared error was used. On this way, it was possible to obtain the exchange rate k with accuracy of $\pm 0.2\ s^{-1}$.

The normalization factor was adjusted by the comparison of signals integral intensities for calculated and experimental spectra. The initial population ratios of conformers, p1/p2, have been calculated using signal integral intensities from a spectrum recorded at low temperature, usually 253 K. The population ratios were recalculated for each temperature by Boltzman's equation, $p1/p2 = \exp(-\Delta E/RT)$. Initial T_2 relaxation time values were calculated on the basis of signals half-width taken from the low temperature spectrum (253 K). Then, T_2 was estimated for each experiment applying the reference line method [26] with the use of central signal of residual acetone-d_6 multiplet on each spectrum as the reference line. Its half-width was found by deconvolution procedure using Bruker spectrometer software. Chemical shift drift, of ca. 0.4 Hz K^{-1}, was readjusted manually, during line shape calculation, in order to obtain the best fit of experimental and calculated line.

$\Delta H^{\#}$ and $\Delta S^{\#}$ have been obtained by a least-squares adaptation of the rate constant and corresponding temperatures to a straight line of the form $\ln(kT^{-1}) = bT^{-1} + c$, where $\Delta H^{\#} = -8.31b$ and $\Delta S^{\#} = 8.31(c - 23.76)$. Free energy of activation, $\Delta G^{\#}$, has been calculated by the equation $\Delta G^{\#} = \Delta H^{\#} - T\Delta S^{\#}$ [26].

Standard deviations were obtained from least-square procedures [26] assuming inaccuracy of $\pm 0.2\ s^{-1}$ for interconversion rate k and ± 0.2 K for a temperature. Temperature control unit allows obtaining a temperature stability of ± 0.1 K. A systematic error of ca. ± 1.5 K between two different series of experiments arises from equipment setting itself. The temperature scale for a set of experiments can be shifted by ± 1.5 K, whereas the temperature differences within the set are given with accuracy of ± 0.1 K. A systematic error provides an inaccuracy of ± 0.5, ± 1 and ± 1.3 J mol^{-1}K^{-1} for $\Delta G^{\#}$, $\Delta H^{\#}$ and $\Delta S^{\#}$, respectively, i.e. gives the values comparable or slightly greater than standard deviations obtained from least-square methods.

2.3. Synthesis

All thiosemicarbazides were obtained from commercially available isothiocyanates and phenylhydrazine, using slightly modified, published procedure [27]. Typically, phenyhydrazine (5.5 g, 5 cm^3, 51 mmol) was dissolved in ethyl ether (100 cm^3), then suitable isothiocyanate

(51 mmol) was added. The mixture was stirred for ca. 15 min, then the solution was cooled in ice bath, the precipitate of thiosemicarbazide were filtered, washed with cold ethyl ether, and dried in vacuo. If the product did not precipitate, then the solvent was evaporated in vacuo, residual oil was diluted with small amount of ethyl ether and cooled overnight in refrigerateur. Next day crystals were filtered, washed with cold ether and dried in vacuo. Thiosemicarbazides were used for further reaction without additional purification. Following thiosemicarbazides have been obtained in this manner: 1,4-diphenyl-3-thiosemicarbazide (11.2 g, 90%); 1-phenyl-4-(4-methoxyphenyl)-3-thiosemicarbazide (13.4 g, 97%); 1-phenyl-4-methyl-3-thiosemicarbazide (6.6 g, 72%); 1-phenyl-4-ethyl-3-thiosemicarbazide (5.7 g, 57%); 1-phenyl-4-(*n*-butyl)-3-thiosemicarbazide (6.2 g, 55%); 1-phenyl-4-benzyl-3-thiosemicarbazide (10.4 g, 80%); 1-phenyl-4-allyl-3-thiosemicarbazide (5.7 g, 57%). ^{15}N enriched 1-phenyl-4-methyl-3-thiosemicarbazide was obtained from ^{15}*N*-methylisothiocyanate, which has been prepared from ^{15}*N*-methylamine (HCl salt) by means of reaction with CS_2 and $Pb(CH_3COO)_2$, followed by steam distillation [28].

Oxatriazole **4** has been obtained originally from 1,4-diphenylthiosemicarbazide by nitrosation with butylnitrite [29]. However, making use of sodium nitrite seems to be a cheaper and simpler way of synthesis. Oxatriazole **5** was also obtained by this manner. Application of sodium nitrite seems to be a general method of synthesis of oxatriazoles with aromatic group attached to 'exocyclic' nitrogen atom, that are **4** and **5**. However, the remaining oxatriazoles, **6**–**10**, need to use butylnitrite as nitrosation agent.

*2.4. Mesoionic 3-phenyl-5-phenylimino-1,2,3,4-oxatriazole imine [30] **4***

1,4-diphenylthiosemicarbazide (14 g, 58 mmol) was suspended in ethanol (350 cm^3), cooled (−10 °C) on ice bath, and acidified with concentrated hydrochloric acid (21 cm^3). The solution of sodium nitrite (6 g, 87 mmol) in water (90 cm^3) was added stepwise to the suspension of thiosemicarbazide. Then the reaction mixture was stirred at room temperature for ca. 15 min; subsequently a large excess of water (ca. 400 cm^3) was added, and the mixture was filtered in order to removal of insoluble polymeric material. The filtrate was alkalized with anhydrous sodium carbonate (ca. 35 g) and cooled overnight. Next day red crystals was filtered, washed with water and dried in vacuo. Crystallization from ethanol or *n*-hexane yielded red crystals of **4** (12 g, 88%). The compound was identified by means of NMR data, elemental analyses and MS. (Found C, 65.71; H, 4.14; N, 23.68%; M^+ 238. $C_{13}H_{10}N_4O_2$ requires C, 65.54; H, 4.23; N, 23.52%; M 238.25).

*2.5. Mesoionic 3-phenyl-5-(4-methoxyphenyl)imino-1,2,3,4-oxatriazole imine **5***

1-phenyl-4-(4-methoxyphenyl)-3-thiosemicarbazide (14.9 g, 58 mmol) and sodium nitrite (6 g, 87 mmol) was used. Crystallization of crude mesoionic base from ethanol yielded deep red crystals of **5** (8.9 g, 57%), m p. 113–115 °C. (Found C, 62.52; H, 4.55; N, 20.96%; M^+ 268. $C_{14}H_{12}N_4O_2$ requires C, 62.68; H, 4.51; N, 20.88%; M 268.28).

*2.6. Mesoionic 3-phenyl-5-methylimino-1,2,3,4-oxatriazole imine **6***

1-phenyl-4-methyl-3-thiosemicarbazide (3 g, 17 mmol) was suspended in ethanol (50 cm^3). The mixture was cooled on ice-bath (0 °C); then butyl nitrite (9 g, 10 cm^3, 87 mmol) was added. The mixture was saturated with hydrogen chloride, obtained from concentrated hydrochloric acid (20 cm^3) and concentrated sulfuric acid (30 cm^3), and stirred at room temperature for ca. 30 min. Ethanol and an excess of butyl nitrite were evaporated in vacuo; the residue was dissolved in ethanol (100 cm^3) and acidified with a few drops of hydrochloric acid. Small amount of activated carbon was added to the solution; the mixture was heated for a few minutes, filtered and cooled in an ice-bad. A large volume of diethyl ether was added stepwise to a cold, stirred filtrate. A salt of the mesoionic oxatriazole slowly precipitated; the mixture was cooled overnight in refrigerator; then a white solid of salt was filtered and dried in vacuo giving a salt of mesoionic compound (2 g, 57%). The salt was dissolved in water (50 cm^3) and alkalized with a few grams of sodium carbonate. The mixture was extracted three times with methylene chloride; extract was dried over sodium carbonate, filtered and evaporated in vacuo. The resulting yellow residue was dissolved in warm *n*-hexane, the solution was heated with small amount of activated carbon for a few minutes, filtered, concentrated in vacuo and cooled overnight in a refrigerator, at ca. −10 °C. Next day yellow crystals of the free mesoionic base were filtered and dried in vacuo (0.7 g, 4 mmol, 24%), m p 61–63 °C. (Found C, 54.89; H, 4.66; N, 31.80%; M^+, 176. $C_8H_8N_4O$ requires C, 54.54; H, 4.58; N, 31.80%; M, 176.18). ^{15}N-enriched oxatriazole has been obtained in the similar manner, by the use of ^{15}N-labelled thiosemicarbazide.

Compounds **7**–**10** were obtained in a similar way

*2.7. Mesoionic 3-phenyl-5-ethylimino-1,2,3,4-oxatriazole imine **7***

1-phenyl-4-ethyl-3-thiosemicarbazide (3.3 g, 17 mmol) yielded slightly gray powder of hydrochloride of **7** (2.5 g, 65%). Alkalization of salt and crystallization of free base from *n*-hexane yielded yellow crystals of free mesoionic base (1.3 g, 41%), m p 34.5–36.0 °C. (Found C, 56.57; H,

5.28; N, 29.61 %; M^+, 190. $C_9H_{10}N_4O$ requires C, 56.83; H, 5.30; N, 29.46%; M, 190.21).

2.8. Mesoionic 3-phenyl-5-(n-butyl)-imino-1,2,3,4-oxatriazole imine **8**

1-phenyl-4-(*n*-butyl)-4-3-thiosemicarbazide (3.7 g, 17 mmol) yielded slightly gray powder of hydrochloride salt of oxatriazole **8** (2.0 g, 46%). Alkalization of salt and crystallization of free base from n-hexane yielded yellow crystals of free mesoionic base **8** (1.2 g, 32%), m p 39–39.5 °C. (Found C, 60.53; H, 6.59; N, 25.72%; M^+ 218. $C_{11}H_{14}N_4O$ requires C, 60.53; H, 6.47; N, 25.67%; M 218.26).

2.9. Mesoionic 3-phenyl-5-allylimino-1,2,3,4-oxatriazole imine **9**

3.5 g (17 mmol) of 1-phenyl-4-allyl-3-thiosemicarbazide (3.5 g, 17 mmol) gave slightly gray powder of hydrochloride salt (2.4 g, 60%). Alkalization of salt and crystallization of free base from *n*-hexane yielded yellow crystals of free mesoionic base **9** (1.5 g, 44%), m p 37–39 °C. (Found C, 59.28; H, 4.79; N, 27.91%; $M^+ + H$, 203. $C_{10}H_{10}N_4O$ requires C, 59.40; H, 4.98; N, 27.71%; M 202.22).

2.10. Mesoionic 3-phenyl-5-benzylimino-1,2,3,4-oxatriazole imine **10**

1-phenyl-4-benzyl-3-thiosemicarbazide (4.4 g, 17 mmol) gave hydrochloride salt of **10** (2.6 g, 52%). Alkalization of salt and crystallization of free base from *n*-hexane yielded yellow crystals of free mesoionic base **10** (1 g, 24%), m p 66–68 °C (Found C, 66.79; H, 4.69; N, 22.12%; $M^+ + H$, 253. $C_{14}H_{12}N_4O$ requires C, 66.66; H, 4.79; N, 22.21%; M, 252.28).

2.11. ^1H and ^{13}C NMR data for oxatriazoles **4–10**

Asterisk denotes a signal of a major conformer. Abbreviations: d—two signals with chemical shift difference less than 0.1 ppm; br—broad signal; m—unresolved multiplet; n.d.—signal no detected; ([a]) data from a spectrum taken at 233 K; ([b]) signal assignment can be opposite. Chemical shifts (ppm) were referred to internal TMS ($\delta = 0.00$ ppm) for ^1H and to the central peak of acetone-d_6 ($\delta = 29.8$ ppm) for ^{13}C.

2.12. Mesoionic 3-phenyl-5-phenylimino-1,2,3,4-oxatriazole imine **4**

^1H NMR: Acetone-d_6, 253 K, N3–Ph: 8.22*, 8.20 (H2′), 7.85 m (H3′, H4′). N6–Ph: 7.30 m (H2′, H3′); 7.01 (H4′). Acetone-d_6/CF_3COOH, 353 K, N3–Ph 8.49*, 8.41 (H2′); 7.93 (H3′); 8.05 (H4′). N6–Ph: 7.78 (H2′); 7.31–7.70 m (H3′, H4′).

^{13}C NMR data are taken from Ref. [18] and given for the comparison purposes: DMSO-d_6, 303 K, C5: 162.4. N3-Ph: 134.0 (C1′); 121.6 (C2′); 130.3 (C3′); 133.8 (C4′). N6-Ph: 145.1 (C1″); 122.9 (C2″); 128.9 (C3″); 122.5 (C4″).

2.13. Mesoionic 3-phenyl-5-(4-methoxyphenyl)imino-1,2,3,4-oxatriazole imine **5**

^1H NMR: Acetone-d_6, 253 K, N3–Ph: 8.23, 8.19* (H2′); 7.80 m (H3′); 7.86 m (H4′). N6-R: 7.31, 7.22* (H2″); 6.87, 6.90* (H3″); 3.76, 3.75 (CH_3). Acetone-d_6/CF_3COOH, 253 K, 8.47, 8.39* (H2′); 8.01 m (H3′); 7.89 m (H4′). N6–R: 7.65, 7.57* (H2″); 7.12*, 7.08 (H3″); 3.81*, 3.79 (CH_3). NH: 12.95*([a]), 12.76([a]), CF_3COOH: 14.19([a]).

^{13}C NMR: Acetone-d_6, 253 K, C5: 164.7*, 163.6. N3-Ph: 135.3d (C1′); 122.1, 122.0* (C2′); 130.9 (C3′); 134.3, 134.2* (C4′). N6-R: 139.7, 139.0* (C1″); 124.4d (C2″); 114.6*, 114.5 (C3″); 156.3*, 155.9 (C4″); 55.1d (CH_3). Acetone-d_6/CF_3COOH, 253 K, C5: 170.8*. 170.5. N3–Ph: 133.7, 133.6* (C1′); 123.2([b]), 123.1* (C2′); 132.0d (C3′); 137.2d (C4′). N6-R: n.d. (C1″); 123.3*([b]), 124.4 (C2″); 115.9*, 115.7 (C3″); 160.1*, 159.5 (C4″); 55.8*, 55.7 (CH_3).

2.14. Mesoionic 3-phenyl-5-methylimino-1,2,3,4-oxatriazole imine **6**

^1H NMR: Acetone-d_6, 318 K, N3–Ph: 8.11 br (H2′); 7.74 (H3′); 7.80 (H4′). N6–R: 3.03 (CH_3). Acetone-d_6, 253K, N3–Ph: 8.10*, 8.06 (H2′), 7.71 m (H3′); 7.77 m (H4′). N6-R: 2.95*; 2.91 (CH_3). Acetone-d_6/CF_3COOH, 318 K, N3–Ph: 8.36 br (H2′); 7.91 m (H3′); 8.03 (H4′). N6–R: 3.45 (CH_3). Acetone-d_6/CF_3COOH, 253 K, N3-Ph: 8.42, 8.36* (H2′); 7.92 m (H3′); 8.04 m (H4′). N6–R: 3.44 (CH_3). NH: 11.20*([a]). 10.92([a]); CF_3COOH: 13.8([a]).

^{13}C NMR: Acetone-d_6, 243 K, C5: 165.9*, 162.1. N3-Ph: 135.4, 135.3 (C1′); 121.8d (C2′); 130.8d (C3′); 134.1*, 134.0 (C4′). N6-CH_3: 35.7*, 33.7. Acetone-d_6/CF_3COOH, 303 K, C5: 172.9. N3–Ph: 134.0 (C1′); 123.3 (C2′); 131.9 (C3′); 136.9 (C4′). N6–CH_3: 31.7 br.

2.15. Mesoionic 3-phenyl-5-ethylimino-1,2,3,4-oxatriazole imine **7**

^1H NMR: Acetone-d_6, 253K, N3–Ph: 8.14, 8.11 (H2′), 7.82 m (H3′); 7.76 m (H4′). N6-R: 3.32, 3.27 (CH_2); 1.15, 1.12 (CH_3). Acetone-d_6/CF_3COOH, 303 K, N3-Ph: 8.34 br (H2′); 7.88 (H3′); 7.99 (H4′). N6–R: 3.84 (CH_2); 1.44 (CH_3). Acetone-d_6/CF_3COOH, 253 K, N3–Ph: 8.53*, 8.41 (H2′); 8.03 m (H3′); 7.92 m (H4′). N6–R: 3.84 (CH_2); 1.40 (CH_3). NH: 10.95*([a]), 10.67([a]). CF_3COOH 14.0([a]).

^{13}C NMR: Acetone-d_6, 243 K, C5: 160.8, 164.9. N3–Ph: 135.4, 135.3 (C1′); 121.8d (C2′); 130.8 (C3′); 134.1, 133.9 (C4′). N6–R: 43.9, 41.8 (CH_2); 16.7, 16.6 (CH_3). Acetone-d_6/CF_3COOH, 303 K, C5: 172.4. N3–Ph: 134.1 (C1′); 123.3

(C2′); 131.9 (C3′); 137.0 (C4′). N6–R: 41.7 (CH_2); 14.0 (CH_3).

2.16. Mesoionic 3-phenyl-5-(n-butyl)-imino-1,2,3,4-oxatriazole imine **8**

^{1}H NMR: Acetone-d_6, 253 K, N3–Ph: 8.13, 8.10 (H2′); 7.44 m (H3′); 7.80 m (H4′); N6–R: 3.29*, 3.23 (NCH_2); 1.50 m (NCH_2CH_2); 1.37 m (CH_2CH_3); 0.89, 0.88 (CH_3). Acetone-d_6/CF_3COOH, 253 K, N3–Ph: 8.38, 8.32* (H2′); 7.89 m (H3′); 8.00 m (H4′). N6–R: 3.79 m (NCH_2); 1.76 m (NCH_2CH_2); 1.45 m (CH_2CH_3); 0.92 (CH_3). NH 10.85*([a]), 10.59([a]). CF_3COOH 14.52([a]).

^{13}C NMR: Acetone-d_6, 253 K, C5: 164.7, 160.7. N3–Ph: 135.5d (C1′); 121.9*, 121.8 (C2′); 130.8d (C3′); 134.0*, 133.9 (C4′). N6–R: 49.2, 47.1 (NCH_2); 34.1*, 34.0 (NCH_2CH_2); 20.9d (CH_2CH_3); 14.2d (CH_3). Acetone-d_6/CF_3COOH, 253 K, C5: 171.3, 171.1*. N3–Ph: 132.8, 132.7 (C1′); 122.1, 122.0* (C2′); 130.8 (C3′); 135.8 (C4′). N6–R: 44.9, 43.6* (NCH_2); 30.1*, 29.9 (NCH_2CH_2); 19.1*, 19.0 (CH_2CH_3); 12.7 (CH_3).

2.17. Mesoionic 3-phenyl-5-allylimino-1,2,3,4-oxatriazole imine **9**

^{1}H NMR: Acetone-d_6, 318 K, N3–Ph: 8.12 br (H2′); 7.74 m (H3′); 7.80 m (H4′). N6–R: 5.99 m (–CH=); 5.27 br (=CH_2); 5.02 br (=CH_2); 3.99 br (–CH_2–). Acetone-d_6, 253 K, N3=Ph: 8.14 m (H2′); 7.77 m (H3′); 7.83 m (H4′). N6–R: 5.97 m (–CH=); 5.30, 5.25 (=CH_2); 5.03, 5.01 (=CH_2); 3.94, 3.90 (–CH_2–). Acetone-d_6/CF_3COOH, 253 K, N3=Ph: 8.41, 8.36* (H2′); 7.91 m (H3′); 8.03 m (H4′). N6=R: 6.04 m (–CH=); 5.50, 5.48* (=CH_2); 5.34*, 5.32 (=CH_2); 4.46 m (–CH_2–). NH: 10.97([a]), 10.24*([a]). CF_3-COOH 10.2([a]).^{13}C NMR: Acetone-d_6, 243 K, C5: 165.6, 161.6. N3–Ph: 135.3, 135.2 (C1′); 121.9, 121.8 (C2′); 130.8d (C3′); 134.1, 134.0 (C4′). N6–R: 137.6, 137.2 (–CH=); 114.1, 113.9 (=CH_2); 51.6, 49.4 (–CH_2–). Acetone-d_6/CF_3COOH, 303 K, C5: 172.6. N3–Ph: 134.1 (C1′); 123.3 (C2′); 131.9 (C3′); 136.9 (C4′). N6–R: 131.7 (–CH=); 119.4 (=CH_2); 47.5 (–CH_2).

2.18. Mesoionic 3-phenyl-5-benzylimino-1,2,3,4-oxatriazole imine **10**

^{1}H NMR: Acetone-d_6, 318 K, N3–Ph: 8.14 br (H2′); 7.74 (H3′); 7.81 (H4′). N6–R: 7.47 (H2″); 7.31 (H3″); 7.20 (C4″); 4.56 (CH_2). Acetone-d_6, 253 K, N3–Ph: 8.18 m (H2′); 7.71 m (H3′); 7.84 m (H4′). N6–R: 7.44 m (H2″); 7.33 m (H3″); 7.23 m (H″); 4.55, 4.51 (CH_2). Acetone-d_6/CF_3COOH 253 K, N3–Ph: 8.44, 8.36* (H2′); 7.9m (H3′); 8.1m (H4′). N6–R: 7.5m (H2″); 7.45 m (H3″, H4″); 5.02 br (CH_2). NH: 11.65*([a]), 11.36([a]). CF_3COOH 14.4([a]).

^{13}C NMR: Acetone-d_6, 243 K, C5 166.1, 161.9. N3–Ph: 135.3d (C1′); 121.9d (C2′); 130.8 (C3′); 134.1, 134.0 (C4′). N6–R: 141.9, 141.6 (C1″); 127.7d (C2″); 128.7d (C3″); 126.9d (C4″);52.8, 50.6 (CH_2). Acetone-d_6/CF_3COOH, 303 K, C5: 172.7. N3–Ph: 134.1 (C1′); 123.3 (C2′); 131.9 (C3′); 137.0 (C4′). N6–R: 135.6 (C1″); 129.1 (C2″); 129.8 (C3″); 129.4 (C4″); 49.7 (CH_2).

Molar fractions of the major conformer in the solution one can calculated on the basis of signal integrations on ^{1}H NMR spectra (253 K). Energy differences between forms, calculated using Arrhenius equation (J mol^{-1}, at 253 K), are given in parenthesis. The suitable values for free mesoionic bases (acetone-d_6 solution), are: 0.63 (1150) for **4**, 0.61 (900) for **5**, 0.54 (340) for **6**, 0.53 (270) for **7**, 0.53 (270) for **8**, 0.52 (130) for **9** and 0.51 (90) for **10**. The values for mesoionic salts (acetone-d_6/CF_3COOH solution) are: 0.77 (2500) for **4**, 0.69 (1700) for **5**, 0.61 (940) for **6**, 0.65 (1300) for **7**, 0.65 (1300) for **8**, 0.65 (1300) for **9** and 0.69 (1700) for **10**.

3. Results and discussion

3.1. Synthesis

All mesoionic 3-phenyl-5-imino-1,2,3,4-oxatriazole imines were obtained from suitable thiosemicarbazide, via nitrosation by butyl nitrite in ethanol with presence of gaseous hydrochloride, and by alkalization of salt with sodium bicarbonate. This method was also used originally for synthesis of 3-phenyl-5-phenylimino-1,2,3,4-oxatriazole imine **4** [13]. However, the oxatriazoles **4** and **5,** i.e. the compounds with N^-Ar group at C5 position, we obtained by nitrosation of thiosemicarbazide with sodium nitrite, which seems to be a simpler method of synthesis.

Mesoionic 3-phenyl-5-arylimino-1,2,3,4-oxatriazole imines containing aromatic R group directly bonded to N^-6 atom, **4** and **5**, are relatively stable. In contrast, oxatriazoles **6–10,** with CH_2-R group attached to N^-6 atom, are unstable, and decompose within 24 h at room temperature. These compounds can be stored at dry ice temperature for a long time. All of these compounds form colour crystals, deep red (**4** and **5**, R = Ar) or yellow (**6–10**, R = CH_2R). The salt of these compound are white or slightly yellow. Generally, the salts of mesoionic oxatriazole imines are more stable than free bases.

3.2. ^{1}H and ^{13}C NMR

^{1}H and ^{13}C NMR data for mesoionic oxatriazoles **4–10**, taken at various temperatures, are given in the experimental part of work. The compounds were investigated both as free bases (acetone-d_6 solutions) and as salts (acetone-d_6 solutions with addition of trifluoroacetic acid). The signal assignments were done by means of common NMR procedures: coupling constant pattern, NOE experiments, 2D COSY, HSQC and HMBC spectra.

The ^{1}H NMR spectra of a free mesoionic base, acquired at low temperature, contain two sets of signals, resulting

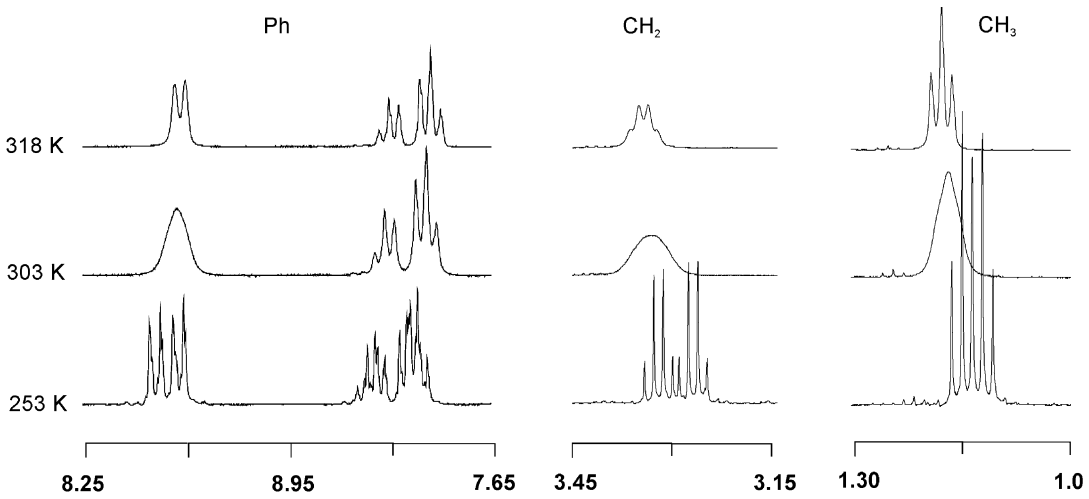


Fig. 3. ^{1}H NMR spectra of mesoionic 3-phenyl-5-ethylimino-1,2,3,4-oxatriazole imine **7** at various temperatures.

from two forms of a compound, *Z* and *E*. Broad signals are observed at room temperature, 303 K, and only one set of signals is observed at 318 K. Molar ratio of two conformers, estimated from signal integral intensities, varies from 1:0.7 to 1:1 The ^{1}H NMR spectra of **7** (R = CH_2CH_3) at various temperatures are shown as an example (Fig. 3). The same is true for ^{13}C NMR spectra. At low temperature, one can see two sets of signals, while the average signals are observed at high temperature (318 K).

Protonation of a free base results in changes of all ^{1}H and ^{13}C chemical shifts. As an example, one can consider NMR spectra of oxatriazole **6** (R = CH_3), taken at 318 K. The high frequency shift of ca. 0.3 ppm was observed for ^{1}H signals of N3–Ph group; the larger change, of 0.5 ppm, was found for CH_3 group. The low field shift of the ^{13}C signal, of ca. 10 ppm, was noted for the C5 atom, while remaining ^{13}C signals move from 1 to 3 ppm only. The shift of the C5 signal is larger than that observed for the methyl group, probably due to fact that the C5 atom is attached directly to the centre of protonation via conjugated CN bond

The spectra of mesoionic salts, taken at low temperature, contain also two sets of signals. The molar ratio of conformers ranges from 1:0.3 to 1:0.6. At low temperature, on ^{1}H NMR spectra, one can observe separately the N6–H signals of both forms, and the signal of CF_3COOH.

The signal dispersion, defined as a chemical shift difference between *E* and *Z* form, is large for the atoms neighbouring to the N6, while the effect vanishes with increasing the distance from the N6 atom. Oxatriazole **8** (R = n–Bu), is an example: ^{13}C signal dispersion of 2.1 ppm is observed for N–CH_2 signal, while less than 0.1 ppm are found for the remaining ^{13}C signals of n-Bu group. The largest dispersion, of 4 ppm, is noted for the signals of C5 atom. Dispersions are observed also for the ^{13}C signals of N3-Ph group, located far from N6 atom.

Our NMR data do not allow choosing which form of a compound, *E* or *Z*, is more stable, and which one exists as a major component in the solution. According to ab initio MO calculation of electronic energy [17], a conformer with R group at *Z* position in relation to oxygen atom is preferred. However, all calculations were made using as an input the simplified structures, containing hydrogen atoms instead of groups at 3 and 6 positions, with no consideration of solvent effects.

3.3. ^{14}N, ^{15}N and ^{17}O NMR

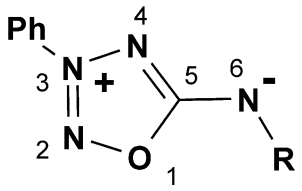
The ^{14}N, ^{15}N and ^{17}O NMR data (Table 1) are the most diagnostic ones. A ^{15}N spectrum of a mesoionic 3-phenyl-5-imino-1,2,3,4-oxatriazle imine, taken on at 318 K, includes four signals, at ca. −20 (N2), −73 (N3), −150 (N4) and −220 ppm (N6). The signal assignments are obvious by using simple comparison with previously collected data for similar structures, and by using selectively ^{15}N labelled compounds [18]. On ^{15}N spectra, at low temperature, there are two sets of signals, arising from two conformers of a mesoionic compound (Fig. 4).

Addition of trifluoroacetic acid to a solution of free mesoionic base causes a significant shift of the N2 and N6 signals, of ca. +15 and −80 ppm, respectively. The similar behaviour of ^{15}N signals has been observed during protonation of thiatriazole imine, **1** [1,2], proving the proton location at the N6 atom. The one-bond $^{1}J(^{15}N–^{1}H)$ coupling observed for the N6 signalis also an evidence of protonation site.

Similarly to ^{1}H and ^{13}C experiments, the ^{15}N spectra of oxatriazole salts contain the signals of two forms of a compound, *E* and *Z*. The signal dispersion on ^{15}N NMR spectra varies from 1 to ca. 10 ppm.

A ^{14}N NMR spectra of oxatriazolium free bases, **4**–**10**, contain broad signals, with half-width in order of thousands Hz, with exception of one narrow signal of the N3 atom, of ca. 100 Hz. The signal of N3 atom consists of three components: the peaks of two rotamers of oxatriazole, and the signal of N_2, dissolved in a solvent [31]. Deconvolution

Table 1
^{14}N, ^{15}N and ^{17}O NMR data for some mesoionic 3-phenyl-5-imino-1,2,3,4-oxatriazole imines



R group	O1	N2	N3	N4	N6	Remarks
Mesoionic oxatriazole (free bases)						
4[a] C_6H_5	[b]	−16.6; −20.8	−73.5; −74.1	−149.6; −139.6	−210.8; −220.2	[c]
	[b]	−18.2	−72.4 (450)	−143.3	−210.0	[d]
5 p−C_6H_4 (OCH_3)	303 (O1) (900)	−17.6*; −22.7	−74.0; −74.9 (140)	−139.2; −150.3	−210.8; −219.3	[c,e]
6 CH_3	308 (750)	−17.0*; −23.6 (1500)	−73.0; −74.2 (110)	−142.2*; −150.9 (1230)	−226.1*; −223.9 (580)	[f]
	[b]	−17.6; −23.4	−74.1; −75.2	−143.6; −151.6	−231.5; −239.4	[c]
7 CH_2CH_3	308 (820)	−17.8*; −24.4 (2200)	−73.1*; −74.4 (90)	−143.1*; −150.9 (870)	−210.8*; −216.6 (580)	[f]
8 $CH_2(CH_2)_2CH_3$	[b]	−17.1*; −19.8 (2000)	−73.2*; −73.7 (110)	−143.2; −148.9 (1160)	−222.0; −226.2 (920)	[f]
9 CH_2-CH = CH_2	310 (800)	−16.5*; −23.0 (1250)	−72.8; −74.0 (100)	−142.1*; −150.0 (1360)	−217.6; −225.1 (660)	[f]
10 CH_2−C_6H_5	310 (900)	−16.8*; −23.0 (2000)	−72.9; −74.1 (120)	−142.8*; −150.2 (1800)	−219.0; −226.3 (750)	[f]
Salts of mesoionic oxatriazole						
4 C_6H_5	[b]	−5.4*; −5.0	−69.0*; −69.3	−140.8*; −135.9	−282.8*; −280.3	[g]
5 p−C_6H_4(OCH_3)		−5.6*; −5.8	−69.1*; −69.4	−141.6*; −137.1	−284.5[h]	[g]
6 CH_3		−1.6*; −3.0	−68.2*; −67.5	−141.0*; −138.3	−306.9*; −304.3	[i]
		−4.0*; −5.1	−69.6*; −68.9	−143.0*; −140.3	−309.2*; −306.5	[g]
7 CH_2CH_3		−2.9*; −4.0	−68.5*; −67.9	−141.7*; −138.4	−290.1*; −287.8	[i]
8 $CH_2(CH_2)_2CH_3$		−2.4*; −3.5	−68.4*; −67.8	−141.2*; −138.3	−291.7; −293.8	[i]
9 CH_2−CH = CH_2		−2.0; −3.2	−68.4; −67.5	−141.2; −137.9	−296.1; −293.8	[i]
10 CH_2 − C_6H_5		−1.2; −2.6	−68.1; −67.2	−140.8; −137.8	−293.7; −291.6	[g]

^{15}N chemical shifts (ppm) referred to external neat nitromethane ($\delta = 0$ ppm). ^{17}O chemical shifts (ppm) referred to external neat water ($\delta = 0$ ppm). The ^{14}N and ^{17}O line widths are reported in parenthesis [Hz] as the full width at half the vertical height of the signal. A relaxating agent, $Cr(acac)_3$ was added to all of the samples used for ^{15}N NMR measurements. A signal of major component, if identified, is marked with asterisks.

[a] Some ^{15}N NMR data for **4** were published in Ref. [18].
[b] Not measured.
[c] Measurement carried out in CD_3OD solution, at 253 K.
[d] Measurement carried out in dmso-d_6 solution, at 303 K. Data taken from Ref. [18].
[e] ^{17}O signal of OCH_3 group at 44 ppm; with line width of 780 Hz.
[f] The measurements were carried out in acetone-d_6 solution either at 253 K (^{15}N NMR) or at 303 K (^{14}N and ^{17}O NMR).
[g] Measurement carried out in CD_3OD solution with addition of CF_3COOH, at 253 K.
[h] Second signal not detected, probably due to broadening.
[i] Measurement carried out in acetone-d_6 solution with addition of CF_3COOH, at 253 K.

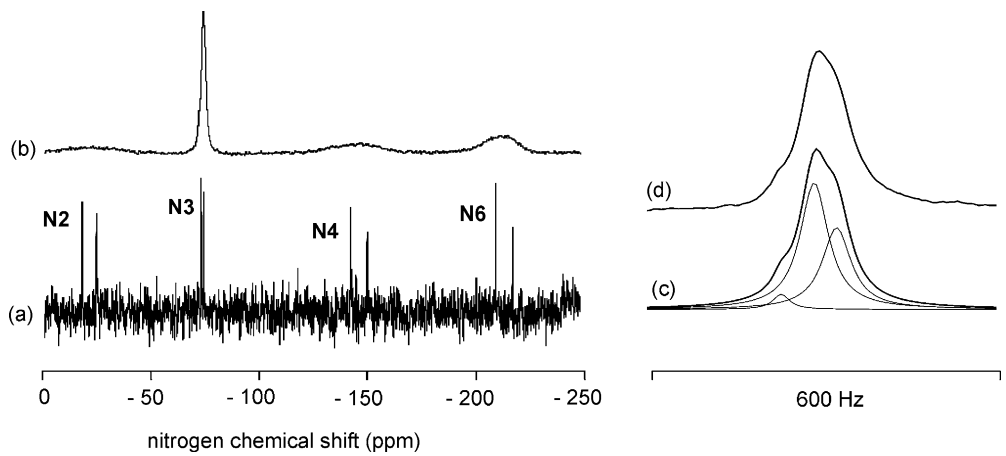


Fig. 4. (a) ^{15}N NMR spectrum of oxatriazole **6**, at 233 K. Two set of signals result from two forms, *Z* and *E*, of the compound (b) ^{14}N NMR spectrum of **6**, at 303 K. The narrow signal at *ca.* −74 ppm indicates location of positive charge within molecule. (c) deconvolution of ^{14}N signal at −74 ppm. The signal contains three components: a signal at −73.8 ppm, with linewith of 58 Hz, a signal at −74.9 ppm (59 Hz), and the small signal at −72.2 ppm (34 Hz), caused by the presence of N_2, dissolved in sample [31]. Bold trace means a calculated spectrum. (d) experimental spectrum.

procedure reveals that overlapped signals of N3 atoms have half-width from 34 to 59 Hz. (Fig. 4). A ^{14}N NMR signal line-width depends on the symmetry of chemical environment of atom under consideration, on a molecule reorientational correlation times, and on electric field gradient at the nucleus. The latter depends on density of electric charge [32]. Thus, the nuclei having a positive charge are expected to produce narrow signals on ^{14}N NMR spectrum. Because of a few factors controlling ^{14}N signal width, any conclusions on charge distribution within molecule should be taken with care. However, for a rigid molecule containing a similar type of nitrogen atoms, one can assume that the presence of narrow peak indicates the location of positive charge. In the case of mesoionic oxatriazoles, **4**–**10**, positive charge is located mainly at N3 atom. These findings agree with previously obtained results for mesoionic thiatriazoles and tetrazoles [33].

^{17}O NMR spectra of oxatriazoles **4**–**10** contain one signal at ca. 300 ppm. In some cases the signal can be deconvoluted. For example, the signal of **6**, at 308 ppm, results in two signals at 305 and 308 ppm, with half-widths of 610 and 450 Hz, respectively. The ^{17}O chemical shifts of **4**–**10** are comparable with the values observed for aromatic oxazole [34].

^{15}N and ^{17}O NMR results clearly indicate that mesoionic 3-phenyl-5-imino-1,2,3,4-oxatriazole imines adopts a cyclic, 'mesoionic' form (Fig. 2c). A hypothetical linear valence tautomer of a 5-imino-1,2,3,4-oxatriazole imine contains a nitroso group, which is expected to have a ^{17}O NMR signal within the range from 650 to 700 ppm [34], and ^{15}N NMR signal within the range from 155 to 200 ppm [35]. In fact, there are not ^{15}N and ^{17}O NMR signals on the spectra of oxatriazoles **4**–**10,** fitting these ranges. Instead of that, the observed chemical shift pattern is comparable with the NMR data of analogous compounds, derivatives of mesoionic thiatriazole **1**. On the other hand, our NMR data cannot exclude occurrence of the linear form of oxatriazole in low concentration, being in equilibrium with the cyclic form.

It is obvious that ^{1}H and ^{13}C NMR experiments reveal the existence of two components in the solution, but does not provide an answer which kind of equilibrium is observed, i.e. equilibrium between *E* and *Z* form, or an equilibrium between cyclic and linear forms of a compound. In contrast, ^{15}N and ^{17}O NMR techniques offer insight into a backbone of a mesoionic heterocycle, and allow denoting the type of equilibrium.

For the comparison purposes, some NMR measurements at various temperatures of thiatriazole **1** and tetrazole **2** have been made. The ^{15}N NMR spectra of thiatriazole **1**, taken at various temperatures, from 213 to 318 K, contain only one set of signal, deriving from one form only. Some broadening of ^{1}H signal has been observed on ^{1}H NMR spectrum; however, the signals of second conformer were not noted at 213 K. Similarly, ^{1}H NMR spectrum of **2**, taken at low temperature, 253 K, contains only one signal of CH_3 group. Presumably, the concentrations of less stable conformers are too low to be detected.

3.4. $^{15}N-^{13}C$ one bond coupling, $^{1}J(^{15}N-^{13}C)$

One bond ^{15}N–^{13}C coupling constants have been applied sporadically as a parameter describing a character of the C5–N6 bond of a mesoionic molecule [36–38]. A small number of data did not provide general conclusions. As a contribution to these investigations, the ^{1}J(^{15}N–^{13}C) coupling constants across the C5–N6 bond for mesoionic tetrazole **2** and oxatriazole **6** have been measured. Available reference data [36,38,39] concerning mesoionic heterocycles are quoted for the comparison purposes (Table 2).

The absolute value of ^{1}J(N6–C5) coupling constant for a mesoionic free base cover the range from ca. 10 Hz for the tetrazole **2** to ca. 16 Hz for one conformer of oxatriazole **6** (Table 2). The value of 11.3 Hz was found for oxadiazole **14** [36], an example of another class of mesoionic heterocycles, acetylsydnonimines.

Imines, $(R^1)(R^2)C{=}NR$, are expected to be a reference model of mesoionic C5–N6 bond. The suitable coupling constant across the N=C bond does not exceed a value of 5 Hz [40]. The largest value of 14.5 Hz is observed for imine **15** containing heteroatoms attached to the carbon

Table 2
Absolute values of ^{1}J(^{15}N-^{13}C) coupling constants for some mesoionic compounds and related structures.

Number of compound and *R* group	^{1}J(^{15}N–^{13}C) [Hz]		Solvent, temperature
	^{1}J(N6–C5)	^{1}J(N6-R)	
1[a]	12.6	N6–C_{Ph} 4.9	303 K, acetone-d_6
1[a] (HCl salt)	24.0	N6–C_{Ph} 13.3	303 K, acetone-d_6
11[a]	26.9	N6–C_{Ph} 15.7 N6–CH_3 5.3	303 K, acetone-d_6
2	10.3	N6–CH_3 0.3[b]	303 K, dmso-d_6
2 (CF_3COOH salt)	26.9	N6–CH_3 9.5	303 K, dmso-d_6 with CF_3COOH
6	16.1 11.9[c]	N6–CH_3 1.2[b,c] 1.0[b]	243 K, $CDCl_3$
	15.8 11.4	N6–CH_3, 1[d]	243 K, acetone-d_6
6(CF_3COOH salt)	30.1 30.1[c]	N6–CH_3 9.0	243 K, acetone-d_6 with CF_3COOH
14[e]	11.3	N6–CO 0.9	r.t., CD_3OD
14[e] (HCl salt)	23.7	N6–CO 9.1	r.t., CD_3OD
15[f]	14.5		
16[g] (HCl salt)	23.5		
17[h]	30		$CDCl_3$
17[h] (HCl salt)	23		dmso-d_6

[a] Data from Ref. [37].
[b] Only residual signal splitting is observed; coupling constant was estimated by signal deconvolution using spectrometer software.
[c] Major component.
[d] Singlet; maximum value of ^{1}J was estimated assuming that ^{1}J does not exceed the signal half width.
[e] Data from Ref. [36].
[f] Data from Ref. [40].
[g] Data from Ref. [38].
[h] Data from Ref. [39].

atom [35]. The values of ^{1}J(NC) with similar magnitude have been also noted for compounds containing formally single, but conjugated carbon nitrogen bond, such as aromatic amines and amides.

Protonation or methylation of mesoionic aminides, occurring at N6 atom, increases ^{1}J(NC) coupling; the compounds **1**, **2**, **6** and **14** are the examples. The explanation of ^{1}J(NC) increasing is not obvious, and cannot be attributed simply to an increase in the CN bond order. It is known from X-ray data, that methylation or protonation occurring at the N6 atom decrease C–N bond order, at least for derivatives of thiatriazole [11,12] **1**. It seems that increasing of ^{1}J(NC) is caused by the effective removal of the electron lone-pair through protonation [40]. The magnitude of ^{1}J(NC) across another bond, N6–R, varies from ca. 0 to 1.2 Hz for the N6–CH_3 and N6–$COCH_3$ bonds, and reach the value of ca. 5 Hz for the N–Ph bond. The protonation at the N6 atom results in an increase of ^{1}J(NC), up to the values from ca. 5 to ca. 14 Hz.

The 1,3,4-thiadiazolium-5-anilide [39] **17** seems to be an exception (Table 2). The ^{1}J(N6–C5) coupling constant of 30.1 Hz exceeds much the values found for mesoionic compounds mentioned so far. In addition, protonation of this compound decrease the magnitude of ^{1}J(NC) coupling. The existence of such an exception, and untypical change of NMR parameter upon protonation, suggests the necessity of further investigation in this field.

3.5. NMR measurements at various temperatures and estimation of activation parameters

^{1}H NMR measurements at various temperatures and the complete band shape analysis were applied for oxatriazoles **5**, **6** and **10**. Satisfactory reproducing of experimental spectra was obtained for oxatriazoles **6** and **10**; no good fit of experimental signals and calculated one have been obtained for oxatriazole **5**. Presumably, the shape of NMR signal reflects two mechanisms, i.e. rotation around C5–N6 and OCH_3 bonds, and two-site exchange model is not adequate. The results are summarized in Table 3 and on Fig. 5, and in the experimental part.

The similar values of $\Delta G^{\#}$, 68 kJ mol^{-1}, were found for 3-phenyl-5-methylimino-1,2,3,4-oxatriazole **6** and 3-phenyl-5-benzylimino-1,2,3,4-oxatriazole **10**. The barrier of A ⟶ B conversion, k, is equal to the barrier of B ⟶ A conversion, k^{-1}, within experimental error; in fact the energy difference between rotamers is very low and does not exceed a value of ca. 0.4 kJ mol^{-1}. One can consider either imine double C=N bond or amide single C–N bond as two extreme models of mesoionic C5–N6 bond. It is believed that E–Z interconversion of imine bond occurs via so called 'lateral shift mechanism', a linear transition state in which the π bond remains intact and the nonbonded electron pair on nitrogen rehybridized to a p orbital [41]. The barrier of E–Z interconversion, attributed to this mechanism, ranges from 84 to 96 kJ mol^{-1}, i.e. it is much greater than

Table 3
E–Z interconversion rates and activation parameters for oxatriazoles **6** and **10**

T (K)[a]	T (K)[b]	**6**		**10**	
		k (s^{-1})	k^{-1} (s^{-1})	k (s^{-1})	k^{-1}(s^{-1})
300.5	299.3	–	–	9.9	9.3
303.0	302.4	14.0	12.1	13.9	13.1
305.5	305.4	20.2	17.4	19.0	17.9
308.0	308.5	29.1	25.2	26.1	24.5
310.5	311.5	39.9	34.2	35.2	33.1
313.0	314.6	54.9	47.1	47.5	44.6
315.5	317.6	72.3	62.1	64.2	60.2
318.0	320.6	103.4	88.9	85.7	80.3
Activation parameters					
r		−0.999	−0.999	−1	−1
$\Delta G^{\#}$ (kJ mol^{-1})		68(2.5)	68(2.5)	67.6(0.5)	67.7(0.5)
$\Delta H^{\#}$ (kJ mol^{-1})		85(1.3)	85(1.3)	79.0(0.3)	78.8(0.3)
$\Delta S^{\#}$ (Jmol^{-1}K^{-1})		57(4)	57(4)	38(1)	37(1)

E–Z interconversion rates k and k^{-1} have been obtained from ^{1}H NMR data by complete band shape analysis. $\Delta H^{\#}$ and $\Delta S^{\#}$ have been obtained by a least-squares adaptation of the rate constant and corresponding temperatures to a straight line of the form $ln(kT^{-1}) = bT^{-1} + c$, where $\Delta H^{\#} = -8.31$b and $\Delta S^{\#} = 8.31$(c-23.76) [26]. Free energy of activation, $\Delta G^{\#}$, has been calculated by the equation $\Delta G^{\#} = \Delta H^{\#} - T\Delta S^{\#}$ [26]. Standard deviations, given in parentheses have been obtained by a least-squares procedure assuming errors of ±0.2 s^{-1} for k and ±0.2 K for T, with no consideration of systematic error provided by spectrometer.

[a] temperature read from the instrument panel.

[b] corrected temperature with the use of spectrometer calibration curve, based on methanol chemical shift termometer.

the barrier found for mesoionic oxatriazoles. For example, the values of $\Delta G^{\#}$ are 85 and 96 kJ mol^{-1} for $(CH_3)_2$-C=NCH_3 and $(CH_3)_2$C=NPh, respectively [42]. Some heteroatoms attached to imine carbon atom decrease the interconversion barier; for example the $\Delta G^{\#}$ values of 78, 59and 52.4 kJ mol^{-1} were observed for $(CH_3S)_2$C=NCH_3, $(CH_3O)_2$C=NCH_3 and $(CH_3)_2$NCH=NCH_2Ph, respectively [42,43]. Low interconversion barrier in this case has been explained in terms of a mechanism proceeding through

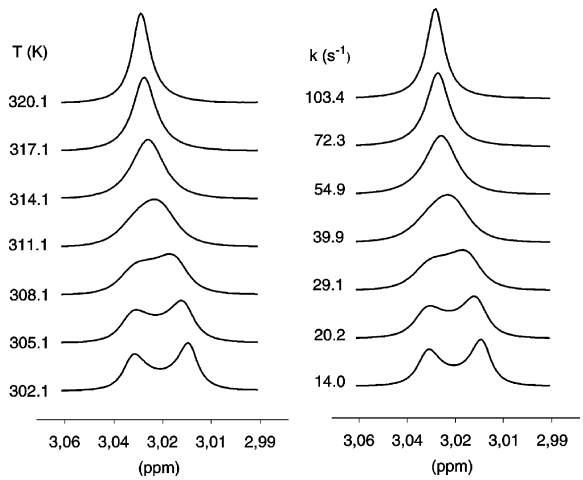


Fig. 5. The signal of oxatriazole **6**(CH_3 group) at various temperatures: experimental spectra (left traces) and calculated spectra (right traces).

a polar transition state in which unsharing of the electrons of the π bond has occurred [44]. The value of $\Delta G^{\#}$ observed for mesoionic oxatriazole are comparable with values found for amides; for example the value of 74 kJ mol^{-1} was observed for $CH_3C(=O)N(CH_3)_2$ [45]. Summarizing this part of work one can conclude that *E*–*Z* interconversion of mesoionic oxatriazolium aminides occurs via rotation around a polar C=N bond, similarly to amides or imines with heteroatoms, and not via linear transition state. It seems that the C=N bond of imines, $(RX)_2C{=}NR$, where X = O, S or NH, are good model of mesoionic C5–N6 bond. This finding agrees with the results of ^{1}J(N6–C5) coupling constant measurements.

4. Conclusions

The ^{14}N, ^{15}N and ^{17}O NMR reveal that mesoionic oxatriazole imines exist in a cyclic, 'mesoionic' form. Protonation of mesoionic oxatriazolium imines occurs at the exocyclic nitrogen atom, N6. Both of the form, free mesoionic bases and its salts exist in a solution as two relatively stable rotamers, *E* and *Z*, depending on the position of exocyclic N$^{\nu}$R group. The value of free activation energy, $\Delta G^{\#}_{298\ K} = 68$ kJ mol^{-1}, is comparable with the values observed for imines containing heteroatoms attached to carbon atom, $(RX)_2C = NR$, where X is an oxygen or nitrogen atom. The measurements of ^{1}J(N6–C5) coupling constant for tetrazole **2** and oxatriazole **6** are in agreement with this founding.

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