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DFT calculations of CH acidity of substituted triazoles and experimental study of their ability to undergo mercuration

Yury S. Halauko [a,*], Vadim E. Matulis [b], Oleg A. Ivashkevich [b], Yury V. Grigoriev [b], Pavel N. Gaponik [b]

[a] Department of General Chemistry of Belarusian State University, 14 Leningradskaya Str., Minsk 220030, Belarus
[b] Research Institute for Physico-Chemical Problems of Belarusian State University, 14 Leningradskaya Str., Minsk 220030, Belarus

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ABSTRACT

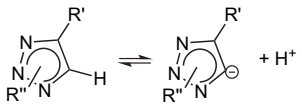
The CH acidity of all possible *N*-methyl substituted nitrotriazoles as well as of some 4-substituted 1,2,3-triazoles and *N*-alkyl-4-nitro-1,2,3-triazoles in the gas phase and in THF and DMSO solution has been calculated with the density functional theory B3LYP method. Electronic effects of substituents on the CH acidity of 4-substituted 1,2,3-triazoles have been examined using linear free energy relationship (LFER) methodology. In order to investigate the relation between the CH acidity of the heterocycles and their ability to undergo electrophilic substitution involving C–H bond cleavage, we have studied the reaction of isomeric *N*-alkyl-4-nitro-1,2,3-triazoles (alkyl=methyl, ethyl, isopropyl and *tert*-butyl) with $HgBr_2$ in alkali solution. It was found that 1-isomers undergo mercuration readily, while mercuration of 2-substituted compounds do not occur under the same conditions, which is in agreement with the results of DFT calculations of the CH acidity of the compounds, showing that 2-isomers have considerably lower CH acidity than 1-isomers.

1. Introduction

This paper continues our previous study[1] on the CH acidity of azoles, and their reactivity in processes involving C–H bond cleavage (mercuration and other electrophilic substitution reactions). Triazole moieties occur in many important compounds, which have wide applications, including components of solid propellants and explosives, and pharmaceutical substances in medicine.[2,3] Nitrotriazoles are also of great interest due to their sufficiently high thermal stability along with considerable energetics and high nitrogen content.[4] So, there is a great necessity in developing effective methods for triazole ring functionalization. The reaction of *C*-nitrotriazoles with electrophilic agents leading to formation of *N*-alkyl-*C*-nitrotriazoles or their salts had been studied by Vereschagin et al.[5] and also had been the object of our previous investigation.[6] Another way of triazole ring functionalization involves C–H bond cleavage followed by carbon–carbon or carbon–element bond formation. Electrophilic substitution reactions involving C–H bond cleavage for 1-alkyltetrazoles were investigated by Gaponik.[7] The influence of the structure of azoles on their ability to undergo electrophilic substitution reactions as well as their possible mechanisms and substitution position were previously discussed.[8] For the development of synthetic methods for triazole ring functionalization through carbon–carbon or carbon–element bond formation, it is important to have data on the CH acidity of triazoles in organic solutions and its dependence on the nature of substituents in the ring.

The thermodynamic parameter associated with the gas-phase acidity is the Gibbs energy of deprotonation of the substance (gas-phase acidity $\Delta_{acid}G$).[9,10]

The acidity of a substance in solution is usually characterized by its pK_a value. For triazoles, in contrast to tetrazoles, two substituents in the ring can influence CH acidity simultaneously (Scheme 1).



$$\Delta_{acid}G = G^0_{298}(R^-) + G^0_{298}(H^+) - G^0_{298}(RH)$$

Scheme 1. Thermodynamic gas phase CH acidity of triazoles.

The short review of papers devoted to experimental and theoretical investigation of CH acidity of azoles is presented in our previous publication.[1]

Most investigations of the electronic effects of substituents in five-membered nitrogen-containing aromatic heterocycles were carried out in 1970–1980s within the framework of linear free

* Corresponding author. Fax: +375 17 2264696; e-mail addresses: hys@tut.by, halauko@bsu.by.

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energy relationship (LFER) methodology. The review of these studies was performed by Lopyrev et al.[11] A detailed analysis of the influence of the substituent on acid–base properties for the different series of 1,2,4-triazoles has been carried out previously.[12,13] Authors have found that one-parameter correlation equations have limited applicability for heterocyclic compounds.[12,13] The annelation effect on the acid–base properties of azoles has also been investigated.[14] Previously published data on the influence of the substituent on the triazole ring on the physicochemical properties, including NH acidity of *C*-substituted 1,2,4-triazoles and position of the long-wavelength maximum in the electronic spectra of 1-methyl-4-nitro-1,2,4-triazoles,[13] and chemical shifts of the protons in the NMR spectra of 3(5)-substituted 1,2,4-triazoles,[15] showed poor correlation under traditional Hammett's approach, and two-parameter equations were found as preferable.[13,15] However, Trifonov et al.[16] have found that calculated energies of protonation of 5-substituted tetrazolate anions are in good correlation with the Hammett σ_p constants.

In the present paper, we report on the results of DFT calculations of the CH acidity of some triazole derivatives in the gas phase as well as in THF and DMSO solutions. These two solvents were chosen because of their wide use in CH acidity scales development and synthesis of azoles' derivatives. In order to investigate the influence of the location of a substituent in the cycle on CH acidity, we calculated CH acidity in the gas phase as well as in THF and DMSO solutions for all possible *N*-methyl-*C*-nitrotriazoles. Four alkyl substituents (methyl, ethyl, isopropyl and *tert*-butyl) and different types of electron-donor and electron-acceptor substituents were considered to study the influence of the substituent at the nitrogen or carbon atoms of the triazole ring on CH acidity. In order to investigate the relation between the CH acidity of heterocycles and their ability to undergo electrophilic substitution involving C–H bond cleavage, we studied experimentally a reaction of isomeric *N*-alkyl-4-nitro-1,2,3-triazoles (alkyl=methyl, ethyl, isopropyl and *tert*-butyl) with $HgBr_2$ in alkali solution.

2. Computational details

All calculations were performed using the GAUSSIAN03[17] software package. MO calculations were carried out using the density functional theory B3LYP method.[18] The geometries of all investigated structures were optimized with the 6-31G(d) basis set. In order to perform stationary points characterization, and to calculate zero-point vibrational energies (ZPVE) and thermal corrections to Gibbs free energy, vibrational frequencies were calculated for structures obtained at the B3LYP/6-31G(d) level. To find total energies (E), single point energy calculations were performed with the 6-311+G(d,p) basis set. Gibbs energy in the gas phase (G^0_{298}) was calculated for each species using the following equation:

$$G^0_{298} = E + ZPVE + H_{0\to 298} - TS^0_{298},$$

where $H_{0\to 298}$ is the thermal correction to enthalpy.

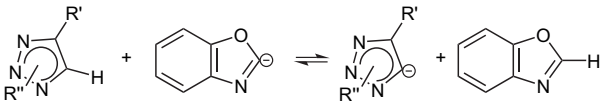
The procedure for calculation of $\Delta_{acid}G$ values, together with grounds on the basis set selection, was described in our previous paper.[1]

The solvent effects for the pK_a calculations were evaluated using the polarized continuum model (PCM)[19] with the default parameters for THF and DMSO. The cavity was built up using the united atom model, and applied on atomic radii of the UFF force field. The PCM energies (E_{PCM}) were calculated at the B3LYP/6-311+G(d,p) level using geometries optimized for isolated structures. The solvation Gibbs energies ($\Delta_{solv}G$) and Gibbs energies in solution (G_s) were calculated for each species by the formulae:

$$\Delta_{solv}G = E_{PCM} - E,$$

$$G_s = G^0_{298} + \Delta_{solv}G.$$

The pK_a values were calculated by the isodesmic reaction method as described in our paper.[1] In the present work, however, we chose benzoxazole (instead of *N*-methylpyrrole) as a reference compound in the isodesmic reactions (Scheme 2):



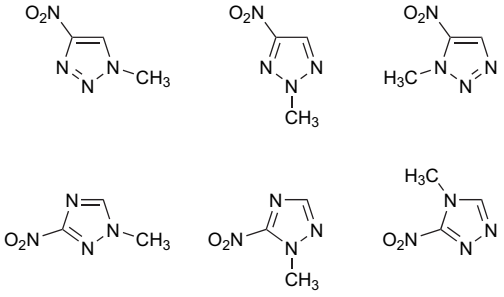
Scheme 2. Isodesmic reactions, considered for calculations of pK_a values of triazoles.

The main reasons for change were: (1) the pK_a values calculated for benzoxazole are in excellent agreement with the experimental for both solvents (24.3 vs 24.1 in THF[20] and 24.8 vs 24.4 in DMSO[21]), and (2) the pK_a value of benzoxazole lies within the range expected for triazoles.

3. Results and discussion

3.1. CH acidity of *N*-methyl-*C*-nitrotriazoles in the gas phase and in THF and DMSO solutions

Generally, there are several deprotonation sites in azoles, but there is the only one for *N*-methyl-*C*-nitrotriazoles (Scheme 3). The calculated values of gas-phase acidity and pK_a's of nitrotriazoles are given in Table 1.



Scheme 3. Structures of investigated *N*-methyl-*C*-nitrotriazoles.

Table 1
Calculated CH acidity of *N*-methyl-*C*-nitrotriazoles

Compound	$\Delta_{acid}G$[a]	pK_a	
		THF	DMSO
Benzoxazole	361.5	(24.1)[b]	(24.4)
1-Methyl-4-nitro-1,2,3-triazole	343.9 {367.4}[c]	15.5 {27.4}	17.0 {28.0}
2-Methyl-4-nitro-1,2,3-triazole	362.4 {384.4}	24.4 {35.4}	24.8 {34.8}
1-Methyl-5-nitro-1,2,3-triazole	362.2 {386.5}	24.7 {36.0}	25.1 {35.2}
1-Methyl-3-nitro-1,2,4-triazole	351.6 {371.6}	21.0 {28.7}	22.3 {28.8}
1-Methyl-5-nitro-1,2,4-triazole	367.7 {388.1}	28.2 {35.5}	28.5 {34.2}
4-Methyl-3-nitro-1,2,4-triazole	349.3 {371.6}	19.7 {28.3}	21.2 {28.2}

[a] Values are given in kcal mol^{-1}.
[b] Experimental values are given in parentheses.
[c] Data for compounds without nitro group[1] are given in curly brackets.

The values of $\Delta_{acid}G$ calculated for compounds without a nitro group (Table 1) are close to those computed for unsubstituted triazoles using CBS-APNO, G3 and G3B3 composite theoretical

methods.[22] The data of Table 1 show that the gas-phase acidity of triazoles is shifted noticeably with the introduction of a nitro group into the ring. The triazoles can be divided into two groups: (1) more acidic are those that have the C–H bond α to the pyrrole-type nitrogen; (2) less acidic are those in which deprotonation occurs α to the pyridine-type nitrogen. This result is in agreement with our previous investigations supported by NBO analysis,[1] showing that the differences in acidity of hydrogen atoms in the α-positions to the pyrrole- and pyridine-type nitrogens can be explained by a destabilization of the anion formed in the last case, due to repulsion of the two neighbouring lone electron pairs.

The calculated values of gas-phase acidity of *N*-methyl-*C*-nitrotriazoles lie within the range of 343.9 (for deprotonation of 1-methyl-4-nitro-1,2,3-triazole molecule) to 367.7 kcal mol^{-1} (for 1-methyl-5-nitro-1,2,4-triazole). Thereby, the calculated $\Delta_{acid}G$ value of 1-methyl-4-nitro-1,2,3-triazole is close to the $\Delta_{acid}G$ values of rather strong acids in aqueous solution (341.8 kcal mol^{-1} for acetic acid,[23] 339.1 kcal mol^{-1}[14] or 334.8 kcal mol^{-1}[22] for 1-*H*-1,2,3-triazole and 337.0 kcal mol^{-1} for 1-*H*-1,2,4-triazole[17]). This is in agreement with the explanation of the low CH acidity in polar media on the basis of less effective solvation of carbanions comparing to O- or N-centred anions.[10]

CH acidity of triazoles in THF and DMSO solutions rises with the introduction of a nitro group, as found for the gas-phase acidity. The introduction of a nitro group into the triazole ring leads to a decrease in pK_a value by 10–11 units for 1,2,3-triazoles, and by 5–7 units for 1,2,4-triazoles. The calculated pK_a values of isomeric *N*-methyl-*C*-nitrotriazoles in DMSO solution lie in a wide range from 17.0 (for 1-methyl-4-nitro-1,2,3-triazole molecule) to 28.5 (for 1-methyl-5-nitro-1,2,4-triazole). The calculated pK_a values for deprotonation α to the pyrrole-type nitrogen are 7–9 units lower than those for deprotonation α to the pyridine-type nitrogen.

The comparison of equilibrium geometries of molecules and their corresponding anions leads to the conclusion that during the deprotonation the most noticeable changes are observed in a region close to reaction centre. The main trend consists of 'ejection' of the deprotonated carbon atom from the heterocycle, accompanied by lengthening of the chemical bonds for deprotonated carbon atom by 0.02–0.06 Å, with a corresponding decreasing of adjacent valence angle (similar to found previously[1]).

3.2. CH acidity of 1-alkyl-4-nitro-1,2,3-triazoles

In order to study the influence of alkyl substituents on CH acidity, we calculated the CH acidity of 1-alkyl-4-nitro-1,2,3-triazoles (alkyl=methyl, ethyl, isopropyl, *tert*-butyl) in the gas phase and in solution (Table 2). CH acidity decreases slightly with increasing electron-donating properties of the substituent (0.4–0.8 kcal mol^{-1} for gas phase and 0.4–0.8 logarithmic units for pK_a's per each alkyl group attached to the α-exocyclic carbon). These results demonstrate that, as expected, CH acidity depends only slightly on the nature of the alkyl substituent attached to the nitrogen atom. However, carbon atoms of the triazole cycle may also have substituents, which can influence CH acidity considerably.

Table 2
Calculated CH acidity of 1-alkyl-4-nitro-1,2,3-triazoles

R	$\Delta_{acid}G$ [a]	pK_a	
		THF	DMSO
Methyl	343.9	15.5	17.0
Ethyl	344.4	16.3	17.8
Isopropyl	345.2	17.1	18.5
tert-Butyl	345.6	17.5	18.8

[a] Values are given in kcal mol^{-1}.

3.3. Electronic effects of substituents on the CH acidity of 4-substituted 1,2,3-triazoles

The Hammett equation is well-known as a useful tool for the prediction of many important physico-chemical characteristics of substances.[24] It was initially proposed for simple aromatic systems, but after some modifications based on the separate consideration of the inductive and resonance effects of substituents, it can be applied to various heterocyclic compounds.

The application of LFER methodology to heterocycles is usually concerned with one of the following aspects:[11] (1) treating the heteroatom as the reaction centre; (2) treating the heteroatom as a substituent in the aromatic ring, with respect to its influence on the properties of the system; (3) consideration of the heterocycle as a single substituent and its influence on the reaction centre; (4) consideration of the heterocycle as a single system in which the substituent and the reaction centre interact.

We concentrated our attention on the last aspect to investigate the influence of substituent nature on the CH acidity. We considered a set of 1-methyl-4-*R*-1,2,3-triazoles with different 'synthetically worthy' electron-donating and electron-withdrawing substituents (Table 3). We also considered the 1-tetrazolyl group, for which we had obtained σ_m, σ_p, *F* and *R* constants earlier,[25] and the 2-tetrazolyl group. The data of Table 3 show that there is a correlation between

Table 3
Calculated CH acidity for 1-methyl-4-*R*-1,2,3-triazoles and substituent constants[24]

R	p$K_{a(THF)}$	p$K_{a(DMSO)}$	$\Delta_{acid}G$[a]	σ_m	σ_p	σ_p^+	σ_p^-	*F*	*R*	R^+	R^-
H	27.4	28.0	367.4	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
F	22.0	22.8	358.5	0.34	0.06	−0.07	−0.03	0.45	−0.39	−0.52	−0.48
CN	18.2	19.8	347.1	0.56	0.66	0.66	1.00	0.51	0.15	0.15	0.49
CH_3	29.4	29.9	369.2	−0.07	−0.17	−0.31	−0.17	0.01	−0.18	−0.32	−0.18
OCH_3	27.2	27.5	366.6	0.12	−0.27	−0.78	−0.26	0.29	−0.56	−1.07	−0.55
CF_3	20.1	21.3	351.2	0.43	0.54	0.61	0.65	0.38	0.16	0.23	0.27
NO_2	15.5	17.0	343.9	0.71	0.78	0.79	1.27	0.65	0.13	0.14	0.62
C_2H_5	29.5	29.9	368.1	−0.07	−0.15	−0.30	−0.19	0.00	−0.15	−0.30	−0.19
C_6H_5	26.7	27.6	359.4	0.06	−0.01	−0.18	0.02	0.12	−0.13	−0.30	−0.10
CHO	21.2	22.1	354.3	0.35	0.42	0.73	1.03	0.33	0.09	0.40	0.70
$CO_2C_2H_5$	23.7	24.3	358.4	0.37	0.45	0.48	0.75	0.34	0.11	0.14	0.41
NH_2	29.2	29.8	368.9	−0.16	−0.66	−1.30	−0.15	0.08	−0.70	−1.38	−0.23
1-Tetrazolyl	19.4	20.9	346.8	0.53[b]	0.50[b]		0.57	0.56[b]	−0.04[b]		0.05
2-Tetrazolyl	20.0	21.2	350.1	0.48[c]	0.46[c]						

[a] Values are given in kcal mol^{-1}.
[b] From Ref. 25.
[c] Estimated using equations obtained in present work.

the nature of the substituent (electron-donating/electron-withdrawing) and pK_a change.

It has been expected also, that the Hammett equation in its simple form cannot adequately describe this correlation. The main reasons are as follows:

(1) It was developed for six-membered rings, but not for five-membered heterocycles, where *ortho*-, *meta*-, *para*-positions cannot be found. To avoid steric problems, usually only σ_m and σ_p are considered (although for five-membered rings the steric effect is less due to simple geometry reasons).
(2) The simple Hammett equation usually gives poor correlation when the substituent can interact with the charged reaction centre. The proposed solution consists of defining a new constant σ_p^+ or σ_p^- (the last one is a priori preferable in our case due to carbanion formation) to treat this effect.[24]

Nevertheless, within one-parametric formalism the best equations for calculated CH acidity were obtained when using σ_m constants:

$$pK_a(\mathrm{THF}) = 27.9-16.6\sigma_m (N=13, r^2=0.963, \mathrm{rmse}=0.95)$$

$$pK_a(\mathrm{DMSO}) = 28.4-15.3\sigma_m (N=13, r^2=0.970, \mathrm{rmse}=0.79)$$

$$\Delta_{acid}G = 366.1-31.4\sigma_m (N=13, r^2=0.915, \mathrm{rmse}=2.8)$$

These equations give rather satisfactory correlation (Fig. 1). So, for 1-methyl-4-*R*-1,2,3-triazoles the influence of the substituent on forming a carbanion centre is similar to that for a *meta*-group in a benzene ring.

The electronic effect of a substituent can be split into two main parts: a field/inductive component (F) and a resonance component (R).[26] So, any constant can be expressed as $\sigma_i = F + R_i$. The best equations within the Swain approach are:

$$pK_a(\mathrm{THF}) = 28.8-16.8F-3.6R^- (N=13, r^2=0.955, \mathrm{rmse}=1.1)$$

$$pK_a(\mathrm{DMSO}) = 29.3-15.6F-3.2R^- (N=13, r^2=0.961, \mathrm{rmse}=0.94)$$

$$\Delta_{acid}G = 367.6-30.3F-7.7R^- (N=13, r^2=0.910, \mathrm{rmse}=3.0)$$

The correlation became even less, maybe due to the low importance of the resonance effect.

Jaffe[27] suggested the equation with the constants 'mixed' with different weights: $Property = a_1 + a_2\sigma_m + a_3\sigma_p$ (where a_i—fitted constants), for description of substituent effects in an 'unconventional' five-membered ring. The best equations within the Jaffe method are:

$$pK_a(\mathrm{THF}) = 27.9-17.0\sigma_m+0.2\sigma_p (N=13, r^2=0.963, \mathrm{rmse}=0.99)$$

$$pK_a(\mathrm{DMSO}) = 28.5-16.1\sigma_m+0.5\sigma_p (N=13, r^2=0.970, \mathrm{rmse}=0.82)$$

$$\Delta_{acid}G = 365.4-26.2\sigma_m-3.7\sigma_p (N=13, r^2=0.919, \mathrm{rmse}=2.8)$$

The coefficients in correlation indicate again that the effect of the substituent on the CH acidity of 1-methyl-4-*R*-1,2,3-triazoles is similar to that of a *meta*-group in a benzene ring.

Thereby, among the considered methods, the Jaffe method gives the best equations for CH acidity prediction (e.g., Fig. 2 for pK_a in DMSO). However, one-parametric formalism also gives a rather satisfactory correlation, due to the low importance of resonance effects. The conclusion about the predominance of inductive effects

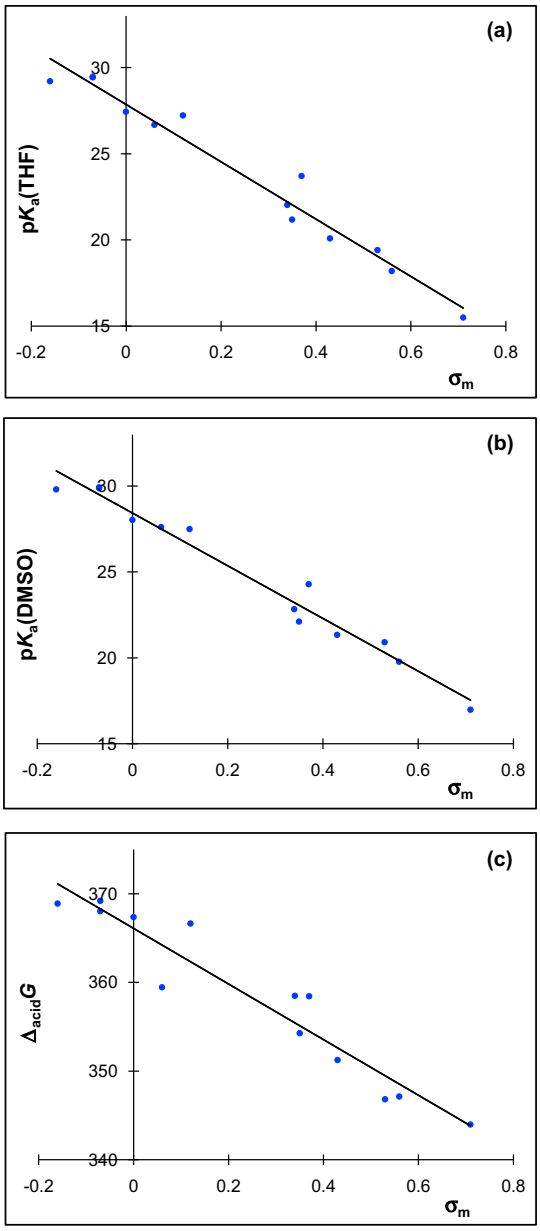


Figure 1. Linear regressions of pK_a (THF) (a) pK_a (DMSO) (b) and $\Delta_{acid}G$ (c) versus σ_m.

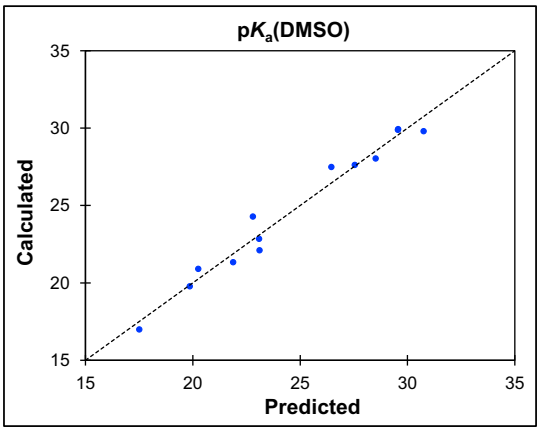


Figure 2. Correlation between calculated and predicted using equations within the Jaffe method pK_a values of triazoles in DMSO solution.

over resonance effects is in agreement with that found for the series of 1,2,4-triazoles.[12]

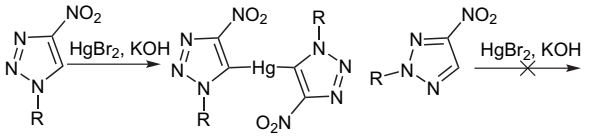
Using the obtained equations we have estimated σ_m and σ_p constants for the 2-tetrazolyl group. The calculated values of substituent constants of the 2-tetrazolyl group are close to those of the 1-tetrazolyl group (Table 3), and show strong electron-withdrawing properties of this substituent.

The calculated pK_a values of studied triazoles in THF and DMSO solutions are close to each other (Tables 1–3), which are in agreement with the results of our previous investigations[1] and with the experimental data, shown that in the absence of specific solvation the pK_a values of a substance in THF and DMSO solutions are very close.[10] However, among the investigated triazoles, the strongest CH acids have smaller pK_a values in THF compared with DMSO (Tables 1–3), while the weakest ones have greater pK_a in THF compared with DMSO (Table 1). So, among these two solvents, THF is slightly differentiating for CH acids. It is in agreement with the results of previous investigations, showing a linear correlation between pK_a values of azoles in DMSO and THF solutions with an angular coefficient slightly less than 1.[1,28]

3.4. Mercuration

Mercuration of triazoles (independently from the mechanism of the process) involves C–H bond cleavage and C–Hg bond formation.

So, the thermodynamic possibility of mercuration should depend on the strength of these bonds (of course there are also other factors influencing mercuration). The calculated $\Delta_{acid}G$ and pK_a values of triazoles characterize the heterolytic cleavage of the C–H bond with formation of corresponding triazolate anion (Scheme 1). So, we suppose that more acidic azoles should undergo mercuration easier than less acidic compounds. The results of our previous study show that this is valid for isomeric tetrazoles.[1] The calculated pK_a value in THF solution of 1-methyltetrazole is 7 units lower than that for 2-methyltetrazole,[1] which is in agreement with experimental observations,[29] indicating that mercuration take place easily in the case of 1-alkyltetrazoles but does not occur for 2-substituted derivatives. In the present work we investigated the ability of *N*-alkyl-4-nitro-1,2,3-triazoles (alkyl=methyl, ethyl, isopropyl and *tert*-butyl) to undergo mercuration. It was shown that 1-isomers undergo mercuration readily (giving products **1**–**4**), while mercuration of less acidic 2-substituted compounds does not occur under the same conditions (Scheme 4). So, it seems that five-



Scheme 4. Mercuration of *N*-alkyl-4-nitro-1,2,3-triazoles.

membered nitrogen-containing aromatic heterocycles should have pK_a values for CH acidity in THF or/and DMSO solution less than 23–24 to undergo mercuration with $HgBr_2$ in alkali.

4. Conclusion

The CH acidity in the gas phase and in THF and DMSO solutions of *N*-methyl substituted-*C*-nitrotriazoles, as well as of some *N*-alkyl-4-nitro-1,2,3-triazoles and 1-methyl-4-substituted-1,2,3-triazoles has been calculated. Electronic effects of substituents on the CH acidity of 4-substituted 1,2,3-triazoles have been examined using the linear free energy relationship (LFER) methodology, and equations for CH acidity prediction were obtained. Using these obtained equations, σ_m and σ_p constants for 2-tetrazolyl substituent were estimated. The ability of *N*-alkyl-4-nitro-1,2,3-triazoles (alkyl=methyl, ethyl, isopropyl and *tert*-butyl) to undergo mercuration has been studied experimentally. It was found that 1-isomers undergo mercuration readily, while mercuration of 2-substituted compounds does not occur under the same conditions, which is in agreement with the results of DFT calculations of the CH acidity of these compounds, showing that 2-isomers have considerably lower CH acidity than 1-isomers.

5. Experimental details

5.1. Instruments

The structures of the obtained compounds were verified by using elemental analysis, infrared and nuclear magnetic resonance spectroscopy methods. IR spectra of the powdered samples were obtained on a Bruker Alpha spectrometer in the range of 4000–400 cm^{-1}. ^1H and ^{13}C NMR spectra were recorded on Bruker Avance 500 spectrometer using DMSO-d_6 as a solvent. Thermal analysis was performed on a NETZSCH STA 449 device under nitrogen in the range of 30–600 °C with heating rate of 10 °C min^{-1}.

5.2. General procedure for mercuration

The general procedure for mercuration of 1-alkyl-4-nitro-1,2,3-triazoles was as follows: a solution of 1-*R*-4-nitro-1,2,3-triazole (R=CH_3, C_2H_5, *i*-C_3H_7 and *tert*-C_4H_9) (0.01 mol) and $HgBr_2$ (0.005 mol, 1.8 g) in ethanol (10 mL) was heated at 60 °C. A solution of KOH (0.03 mol, 1.68 g) in ethanol (10 mL) was added dropwise with thorough mixing. The reaction mixture was then mixed without heating for 15 min (for R=*tert*-C_4H_9—60 min), then cold water (20 mL) was added. The obtained residue was filtered, washed with water and methanol and dried under vacuum at room temperature. Bis-(1-*R*-4-nitro-1,2,3-triazol-5-yl)-mercury were obtained as colourless amorphous powders after reprecipitation from DMSO in water.

2-Alkyl-4-nitro-1,2,3-triazoles were found to be inactive under the same conditions.

*5.2.1. Bis-(1-methyl-4-nitro-1,2,3-triazol-5-yl)-mercury (**1**).* Yield: 2.27 g, 99%. Decomposes at 357 °C without melting. IR (ν, cm^{-1}): 1537 (NO_2), 1487 (ring), 1382, 1294, 1257, 1052, 831; ^1H NMR (DMSO-d_6; δ, ppm) 4.29 (6H, s, 2×N–CH_3); ^{13}C NMR (DMSO-d_6; δ, ppm) 38.77 (CH_3), 159.18 (C_5), 159.24 (C_4). Elemental analysis: Calculated for $C_6H_6N_8O_4Hg$ (%): C, 15.85; H, 1.33; N, 24.64; Hg, 44.11. Found (%): C, 15.62; H, 1.15; N, 24.88; Hg, 44.36.

*5.2.2. Bis-(1-ethyl-4-nitro-1,2,3-triazol-5-yl)-mercury (**2**).* Yield: 2.40 g, 99%. Melts at 342–344 °C with decomposition. IR (ν, cm^{-1}): 1537 (NO_2), 1488 (ring), 1384, 1294, 1242, 1052, 838; ^1H NMR (DMSO-d_6; δ, ppm) 1.57 (6H, t, 2×CH_3), 4.67 (4H, q, 2×CH_2); ^{13}C NMR (DMSO-d_6; δ, ppm) 15.94 (CH_3), 47.66 (CH_2), 158.73 (C_5), 159.61 (C_4). Elemental analysis: Calculated for $C_8H_{10}N_8O_4Hg$ (%): C, 19.90; H, 2.09; N, 23.21; Hg, 41.55. Found; C, 19.73; H, 1.95; N, 23.08; Hg, 41.76.

*5.2.3. Bis-(1-isopropyl-4-nitro-1,2,3-triazol-5-yl)-mercury (**3**).* Yield: 2.52 g, 98%. Melts at 340–342 °C with decomposition. IR (ν, cm^{-1}): 1535 (NO_2), 1486 (ring), 1390, 1294, 1263, 1047, 837; ^1H NMR (DMSO-d_6; δ, ppm) 1.66 (12H, d, 4×CH_3), 5.16 (2H, sept, 2×CH); ^{13}C NMR (DMSO-d_6; δ, ppm) 22.86 (CH_3), 55.64 (CH), 157.95 (C_5), 159.60 (C_4). Elemental analysis: Calculated for $C_{10}H_{14}N_8O_4Hg$

(%): C, 23.51; H, 2.76; N, 21.94; Hg, 39.27. Found (%): C, 23.33; H, 2.85; N, 22.06; Hg, 39.23.

*5.2.4. Bis-(1-tert-butyl-4-nitro-1,2,3-triazol-5-yl)-mercury (**4**).* Yield: 2.55 g, 95%. Melts at 306–309 °C with decomposition. IR (ν, cm^{-1}): 1534 (NO_2), 1477 (ring), 1393, 1295, 1244, 1036, 840; ^1H NMR (DMSO-d_6; δ, ppm) 1.84 (18H, s, $2\times C(CH_3)_3$); ^{13}C NMR (DMSO-d_6; δ, ppm) 30.27 (CH_3), 61.93 (C_{quat}), 150.86 (C_5), 160.24 (C_4). Elemental analysis: Calculated for $C_{12}H_{18}N_8O_4Hg$ (%): C, 26.74; H, 3.35; N, 20.80; Hg, 37.23. Found; C, 26.45; H, 3.29; N, 20.92; Hg, 37.31.

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