Basicity of Phenyl- and Methyl-Substituted 1,2,4-Oxadiazoles

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Dedicated to Professor *Rolf Huisgen* on the occasion of his 85th birthday

The basicity of a series of 3,5-disubstituted 1,2,4-oxadiazoles in aqueous H_2SO_4 was examined by means of UV and ^{1}H-NMR spectroscopy. The experimental data were analyzed by the modified *Yates – McClelland* method to yield the following pK_{BH^+} values: 3,5-dimethyl-1,2,4-oxadiazole, -1.66 ± 0.06; 3-methyl-5-phenyl-1,2,4-oxadiazole, -2.61 ± 0.02; 3-phenyl-5-methyl-1,2,4-oxadiazole, -2.95 ± 0.01; 3,5-diphenyl-1,2,4-oxadiazole, -3.55 ± 0.06. A pK_{BH^+} value of *ca.* -3.7 was estimated for the parent unsubstituted 1,2,4-oxadiazole based on substituents' additivity increments. Possible protonation sites of the compounds were discussed in terms of both experimental data and theoretical calculations (HF/6-31G**). Generally, protonation is most likely to occur at N(4) of the 1,2,4-oxadiazole ring. However, concurrent formation of both N(4)- and N(2)-protonated species in comparable amounts is possible in the case of 3-phenyl-1,2,4-oxadiazoles.

Introduction. – The 1,2,4-oxadiazole ring [1][2] is a representative of the family of five-membered aromatic heterocycles featuring one O- and two N-atoms. The first 1,2,4-oxadiazoles were described as in early as in the 1880s [3], although the preparation of the unsubstituted parent compound was not reported in the literature until 1962 [4]. 1,2,4-Oxadiazoles exhibit a wide range of biological activity as selective antagonists at the histamine H_3 receptor [5], as potent muscarinic agonists [6], as inhibitors of tyrosine kinases [7], *etc.* These heterocycles have found medicinal use as antitussives [8] and anthelmintics [9], as well as some industrial application [2]. 1,2,4-Oxadiazoles have attracted much interest as bioisosteres for esters and amides [10]. In contrast, the basicity of the 1,2,4-oxadiazole ring, a fundamental property that governs many aspects of its chemical reactivity and is an essential factor influencing practical use of compounds, is still poorly studied. Reports dealing with 1,2,4-oxadiazoles as weak organic bases have been scarce. Thus, the ability of these heterocycles to form azolium ('quaternized') salts was examined and it has been suggested that the 'quaternization' of 5-phenyl-1,2,4-oxadiazoles takes place at N(2) predominantly because of steric reasons [11]. Tautomerism of some functionally substituted 1,2,4-oxadiazoles involving the ring N-atoms in ground and exited states was also reported [12]. An attempt to determine pK_{BH^+} values for 3-methyl- and 3,5-dimethyl-1,2,4-oxadiazoles was undertaken by *Brown* and *Ghosh* [13] back in 1969. However, this effort failed because in both cases protonation of the heterocycle produced too little spectral change. The pK_{BH^+} values of *ca.* -4 (protonation at N(4)) and *ca.* -6 (protonation at N(2)) were estimated for 1,2,4-oxadiazole based on a correlation

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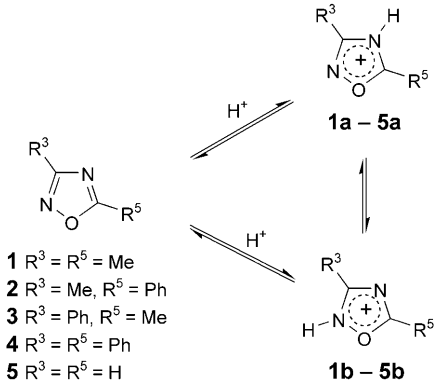
between experimental basicity constants of different azoles and their proton affinity derived from quantum-chemical calculations [14]. Quantitative experimental data on ring basicity of 1,2,4-oxadiazoles both in solutions and in the gas phase seem to be lacking in the literature.

In the present work, we experimentally determined pK_{BH^+} values of representative 3,5-disubstituted 1,2,4-oxadiazoles **1**–**4** (*Scheme*) in aqueous H_2SO_4 using ^{1}H-NMR and UV spectroscopy. Using substituent additivity increments, we also estimated the basicity constant for the unsubstituted parent heterocycle **5**. Furthermore, the energies and charge distributions for neutral and all possible protonated forms of compounds **1**–**5** were calculated by *ab initio* method at 6-31G**//6-31G level. The results of the calculations were analyzed *vis-à-vis* experimental data.

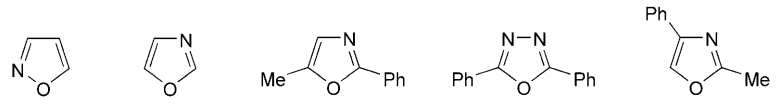
Results and Discussion. – *Protonation Pattern.* The 1,2,4-oxadiazole ring features three potential protonation sites: the O-atom and two pyridine-like N-atoms, N(2) and N(4). Protonation at the O-atom is unfavorable because of the low stability of the resulting OH^+ cation [15–17] and will not be considered further. In contrast, neither of the two non-equivalent ring N-atoms can be *a priori* ruled out as a protonation site. Thus, protonation of neutral 1,2,4-oxadiazoles **1**–**5** could lead to the formation of two isomeric species, azolium cations **1a**–**5a** and **1b**–**5b**, respectively (*Scheme*).

Scheme. *Protonation of 1,2,4-Oxadiazoles*



One can reason that N(2), being proximal to the electronegative O-atom, would be a less-favorable protonation site than the distal N(4). This inference is supported by previously published ^{15}N-NMR data [18] and by the fact that isoxazole (**6**), a model for protonation at N(2), is a substantially weaker base than oxazole (**7**), a model for protonation at N(4). The difference in basicity between these two heterocycles amounts to more than 3.5 units in solution (pK_{BH^+} values of -2.97 [14] and 0.80 [13], respectively) and more than 10 kcal/mol in the gas phase (experimental proton-affinity values of 202.3 [15] and 213.3 kcal/mol [19], respectively).

On the other hand, there is a factor that favors protonation at N(2). The O-atom of the 1,2,4-oxadiazole ring possesses a lone electron pair that repulses the lone pair of the adjacent N(2), and such an interaction is known to destabilize heterocyclic systems



6 **7** **8** **9** **10**

[20]. It is apparent that the destabilizing repulsion would affect the N(4)-protonated 1,2,4-oxadiazole ring but not the N(2)-protonated species. Therefore, while the predominant protonation at N(4) is beyond question, the possibility of formation of 1,2,4-oxadiazol-2-ium cations should not be disregarded.

Spectroscopic Data. The data presented in *Table 1*, *Fig. 1*, and *Fig. 2* show that increase in medium acidity caused notable changes in the spectra of compounds **1**–**4**. As one would expect, protonation resulted in a downfield shift of ^{1}H-NMR signals of both Me groups of compound **1**. The shift is more pronounced for Me–C(5). This suggests predominant formation of the 1,2,4-oxadiazol-4-ium cation **1a**, because otherwise Me–C(3) would display the greater (or, at least, comparable) shift magnitude.

Table 1. *Spectroscopic Characteristics of 1,2,4-Oxadiazoles* **1**–**4** *in Aqueous H_2SO_4 Solutions*

	Neutral form					Protonated form				
	$\delta(^1H)$ [ppm]	λ_{max} [nm]	ε [dm^3 mol^{-1} cm^{-1}]	H_2SO_4 [%]	H_0	$\delta(^1H)$ [ppm]	λ_{max} [nm]	ε [dm^3 mol^{-1} cm^{-1}]	H_2SO_4 [%]	H_0
1	2.49[a]), 2.72[b])	–	–	8.7	– 0.3	2.84[a]), 3.23[b])	–	–	61.6	– 4.7
2	–	251	15350	8.7	– 0.3	–	269	16350	61.6	– 4.7
3	–	237	10700	8.7	– 0.3	–	242	10800	67.3	– 5.5
4	–	246	20500	4.8	– 0.1	–	263	23250	58.8	– 4.4

[a]) Me–C(3). [b]) Me–C(5).

The UV spectra of phenyloxadiazoles **2**–**4** in acidic media differ noticeably (*Fig. 1*). 3-Phenyl-1,2,4-oxadiazole (**3**) absorbs in a shorter-wavelength region than its 5-phenyl isomer **2**. This dissimilarity could be attributable to a different character of conjugation between the oxadiazole cycle and the Ph substituent at C(3) and C(5), respectively. Such an effect was observed previously for other five-membered aromatic heterocycles [13][21]. Predictably, the UV spectra of the 3,5-diphenyl derivative **4** in both neutral and protonated forms can be viewed as a result of averaging the spectra of monophenyloxadiazoles **2** and **3**. Protonation of compounds **2**–**4** caused a bathochromic shift of the absorption bands ranging from 870 cm^{-1} (**3**) to 2670 cm^{-1} (**2**).

To identify the protonation site(s) of heterocycles **2**–**4**, we compared their protonation-related spectral changes with those of unambiguous model compounds **8**–**10**, respectively. As in the case of 1,2,4-oxadiazoles **2** and **4**, protonation of 2-phenyl-5-methyloxazole (**8**) and 2,5-diphenyl-1,3,4-oxadiazole (**9**) results in the bathochromic shift of the main absorption bands in the UV spectra [22–24]. This similarity offers evidence for the predominant formation of N(4)-protonated cations **2a** and **4a**. In contrast, 2-methyl-4-phenyloxazole (**10**) exhibits a distinct hypsochromic shift upon

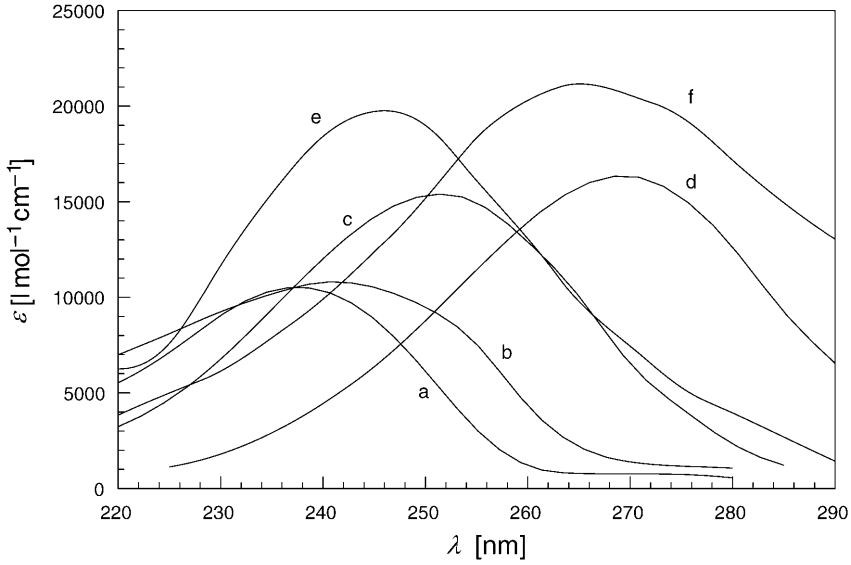


Fig. 1. *UV Spectra of 1,2,4-oxadiazoles* **2**–**4** *in aqueous* H_2SO_4 *solutions* (% H_2SO_4 and *Hammett* acidity function H_0 in parenthesis): *a*) **3** (8.7%, −0.3); *b*) **3** (67.3%, −5.52); *c*) **2** (8.7%, −0.3); *d*) **2** (61.6%, −4.75); *e*) **4** (4.8%, −0.1); *f*) **4** (58.8%, −4.4)

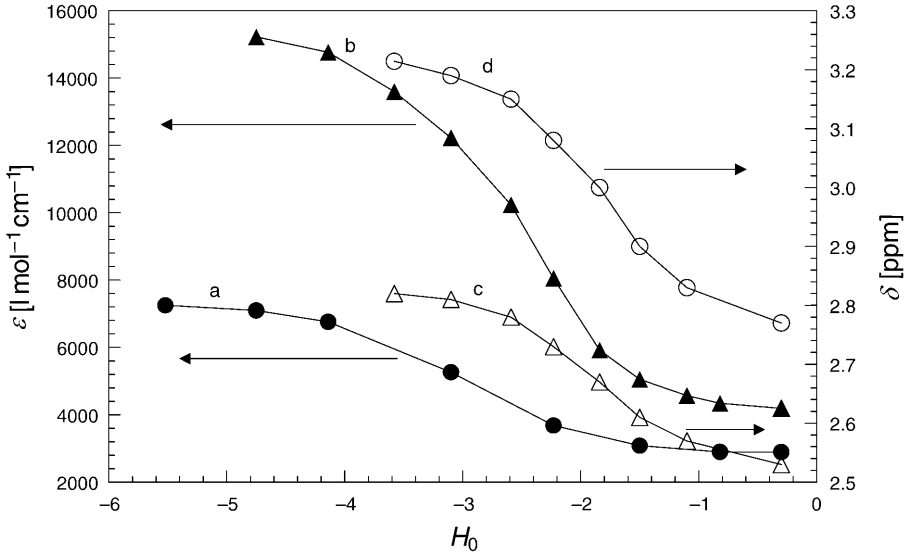


Fig. 2. *Plot of molar absorbance* (ε) *and chemical shift* (δ) vs. *medium acidity* (H_0). *a*) **3** ($\lambda_{analyt.}$ 255 nm); *b*) **2** ($\lambda_{analyt.}$ 275 nm); *c*) **1** (Me–C(3)); *d*) **1** (Me–C(5)).

protonation [22]. Since **10** represents the N(4)-protonation model for **3**, the observed bathochromic effect for the latter could indicate formation of non-negligible amounts of the N(2)-protonated-cation **3b**.

Experimental Basicity Constants. The spectral changes of oxadiazoles **1**–**4** in H_2SO_4 media of different acidity followed a typical sigmoidal curve characteristic for protolytic equilibria (*Fig. 2*). The pK_{BH^+} values were calculated by the modified *Yates–McClelland* method [25][26]:

$$\lg I = -mH_0 + pK'_{BH^+}; \; pK_{BH^+} = pK'_{BH^+}/m, \tag{1}$$

where I is the ionization ratio, H_0 is the *Hammett* acidity function, and m and pK'_{BH^+} are the slope (solvation coefficient) and intercept, respectively, of the linear correlation between $\lg I$ and H_0. The obtained basicity constants, ranging form -1.66 to -3.55 (*Table 2*), position 1,2,4-oxadiazoles **1**–**4** as quite weak organic bases. Their basicity is comparable to that of the isomeric 1,3,4-oxadiazoles [23], and they are more basic than 1,2,5-oxadiazoles (furazanes) [27]. Among the compounds studied, the dimethyl derivative **1** predictably exhibits the highest basicity. Replacing either of the Me groups with a Ph substituent weakens the basic properties of the heterocycle. The observed modest difference in pK_{BH^+} values of the isomeric monophenyl oxadiazoles **2** and **3** could be attributed to the peculiarities of ring conjugation discussed above. Following the trend, introduction of a second Ph substituent leads to a further decrease in basicity, thus making compound **4** the least basic in the series.

Table 2. *Basicity Constants of 1,2,4-Oxadiazoles* **1**–**4**

	$\lambda_{analyt.}$	Parameters of *Eqn. 1*			Statistic parameters	
	[nm]	pK_{BH^+}	pK'_{BH^+}	m	r	n
1	–[a])	-1.66 ± 0.06	-0.91	0.55	0.98	9
2	275	-2.61 ± 0.02	-2.13	0.82	0.99	11
3	255	-2.95 ± 0.01	-2.27	0.77	1.00	7
4	270	-3.55 ± 0.07	-5.33	1.50	0.99	5

[a]) ^{1}H-NMR Data.

It is pertinent to note that the solvation coefficient m in *Eqn. 1* characterizes the specificity of interaction between the base (in all prototropic forms) and the medium [25][26]. For compounds **1**–**4**, the m values noticeably differ from unity (*Table 2*), suggesting that, unlike typical *Hammett* bases, 1,2,4-oxadiazoles are subject to a specific solvation. Analogous observations were made previously for other O-containing heterocycles [22][23][27].

Estimated Basicity Constant of 1,2,4-Oxadiazole (**5**). The instability of the unsubstituted 1,2,4-oxadiazole (**5**) hampers experimental basicity measurements. Nonetheless, its pK_{BH^+} value can be estimated based on the data of the present work using a substituent additivity increment approach [28]:

$$pK_{BH^+}(\text{unsubstituted}) = pK_{BH^+}(R^3,R^5) - \lg f_{R^3} - \lg f_{R^5}, \tag{2}$$

where $pK_{BH^+}(R^3,R^5)$ is the basicity constant of a 3,5-disubstituted derivative, and $\lg f_{R^3}$ and $\lg f_{R^5}$ are the substituent increments.

As discussed above, there is strong evidence that the protonation of 1,2,4-oxadiazoles **1** and **2** occurs predominantly at N(4) (which, however, may not be the case for their 3-phenyl counterparts **3** and **4**), and compounds of the oxazole series are suitable models for that pattern of protonation. Basicity constants of the unsubstituted oxazole (**7**) and its different Me and Ph derivatives, reported in the literature [13][22], allow for lg *f* values to be calculated using the approach illustrated by *Eqn. 2*. Thus, the pair oxazole-4-methyloxazole yields lg *f* for Me–C(3), the pair oxazole-2-phenyloxazole gives lg *f* for Ph–C(5), *etc.* Obtained lg *f* values and resulting pK_{BH^+} estimates for **5** are given in *Table 3*. The averaged calculated basicity constant for the unsubstituted 1,2,4-oxadiazole (**5**) is *ca.* –3.7. This value is in a notably good agreement with a previous estimation of –4 based on a pK_{BH^+}-proton-affinity correlation [14].

Table 3. *Substituent Additivity Increments and Estimated* pK_{BH^+} *Values for the Unsubstituted 1,2,4-Oxadiazole* (**5**)

	R^3	R^5	lg f_{R^3}	lg f_{R^5}	Σ lg *f*	pK_{BH^+} for **5**
1	Me	Me	–	–	2.11[a])	**–3.77**
1	Me	Me	0.44[a])	1.61[b])	2.05	**–3.71**
2	Me	Ph	0.44[a])	0.47[b])	0.91	**–3.52**

[a]) Derived from data of [13]. [b]) Derived from data of [22].

Ab initio *Calculations.* The results of energy calculations for different prototropic forms of 1,2,4-oxadiazoles **1**–**5** are listed in *Table 4*. Basically, these data corroborate the above-discussed profound influence of Ph substituents on the regioselectivity of protonation. In the case of compounds **1**, **2**, and **5**, the N(4)-protonated forms (**1a**, **2a**, and **5a**) are the thermodynamically most-favorable species. The energy difference between of N(4)- and N(2)-protonated cations for compounds **1**, **2**, and **5** is in the range of 3–4 kcal/mol. However, in the case of 3-Ph derivatives **3** and **4**, thermodynamic stabilities of their N(2)- and N(4)-protonated forms are much closer to each other. Thus, in full agreement with the above discussion, a Ph substituent at C(3) facilitates protonation at N(2) of the 1,2,4-oxadiazole ring. A relative increase in the electron-donating character of N(2) in **3** and **4** as compared to **1** and **2** is also evident in charge distribution (*Table 5*).

Table 4. *Total Energies of Neutral and Protonated Forms of 1,2,4-Oxadiazoles* **1**–**5** *and Energy Differences between the Protonated Forms as Calculated Using the* ab initio *Method at 6-31G**//6-31G Level*

	E_{tot} [a.u.]			Δ*E*(N(4) – N(2)-protonated)
	Neutral	N(2)-Protonated	N(4)-Protonated	[kcal/mol]
1	–338.70043	–339.04908	–339.05413	–3.17
2	–529.21986	–529.57732	–529.58251	–3.26
3	–529.21756	–529.57486	–529.57405	0.51
4	–719.73675	–720.10097	–720.10108	–0.07
5	–260.59999	–260.92408	–260.93064	–4.11

Table 5. *Charge Distribution on Ring Heteroatoms and Dipole Moments* (μ) *of Neutral 1,2,4-Oxadiazoles* **1**–**5** *as Calculated Using the* ab initio *Method at 6-31G**//6-31G *Level*

	Charge on heteroatoms [$\bar{e}$]			μ [D]
	N(2)	N(4)	O	
1	– 0.183	– 0.603	– 0.549	2.01
2	– 0.178	– 0.636	– 0.510	2.57
3	– 0.209	– 0.634	– 0.550	2.00
4	– 0.200	– 0.674	– 0.511	2.48
5	– 0.131	– 0.554	– 0.467	1.44

Conclusions. – The experimentally determined basicity constants of a series of 1,2,4-oxadiazoles positioned these compounds as weak organic bases and allowed us to estimate the pK_{BH^+} value of the unsubstituted parent heterocycle **5** (*ca.* – 3.7). In the absence of confounding factors, protonation of the 1,2,4-oxadiazole ring occurs predominantly at N(4). Ring substituents can have a pronounced effect not only on the basicity constant but also on the regioselectivity of protonation. Thus, 3-phenyl-1,2,4-oxadiazoles tend to form both N(4)- and N(2)-protonated cations as evidenced by spectral data and quantum-chemical calculations. Finally, unlike typical *Hammett* bases, 1,2,4-oxadiazoles are subject to a specific solvation in acidic media. This effect could be a manifestation of the ring O-atom's electron-donating properties, although protonation at this atom is thermodynamically unfavorable.

Experimental Part

Compounds **1**–**4** were prepared by known procedures [29]. Their physical and spectral properties were consistent with those reported in the literature.

^{1}H-NMR and UV spectra of **1**–**4** in aq. H_2SO_4 solns. were recorded with *Bruker DPX-300* and *Perkin-Elmer Lambda-40* instruments, respectively. Me_4NBr was used as an internal standard (δ 3.33 ppm) in the NMR studies. The concentrations of H_2SO_4 solns. were established by potentiometric titration.

The pK_{BH^+} values were calculated by *Eqn. 1*. The *I* values were calculated from ^{1}H-NMR data (H_0 dependence of the chemical shift (δ)) for **1** and from the UV data (H_0 dependence of the molar extinction coefficient (ε) at a fixed wavelength (λ_{analyt})) for **2**–**4** as follows:

$$I = (\delta - \delta_B)/(\delta_{BH^+} - \delta);\ I = (\varepsilon - \varepsilon_B)/(\varepsilon_{BH^+} - \varepsilon) \quad (3)$$

The δ_B, δ_{BH^+}, ε_B, and ε_{BH^+} values were assumed as those at ± 1.5 H_0 units from the inflection points of the corresponding sigmoidal curves [26]. The H_0 values of H_2O/H_2SO_4 mixtures were taken from the review on acidity function in [30].

Quantum-chemical calculations were performed using the GAMESS program package [31]. The stationary points were proved to be minimal by frequency calculations carried out at the same computational level.

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