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Research Article

Tautomeric Equilibria in Solutions of 2-Phenacylbenzimidazoles

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Detailed NMR spectral analysis of DMSO-d_6 solutions of the series of substituted 2-phenacylbenzimidazoles (ketimine form, **K**) reveals two from three tautomeric forms. Integrals of the ^{1}H NMR signals are used in establishing the molar ratio of tautomers. The experimental analyses are supported by quantum-chemical calculations, which satisfactorily reproduced the experimental trends. Although the reported semiempirical quantum-chemical calculations show that enaminone **E**, i.e., 2-(1,3-dihydro-2*H*-benzo[*d*]imidazol-2-ylidene)-1-phenylethan-1-one, was thermodynamically most stable, the results of MP2 *ab initio* calculations reveal the following order of stability: ketimine > enolimine > enaminone (substituents do not affect this sequence). ^{13}C CPMAS NMR spectral data reveal that in the crystalline state the enolimine tautomer **O** is predominant in the *p*-CH_3 and *p*-NO_2 substituted congeners.

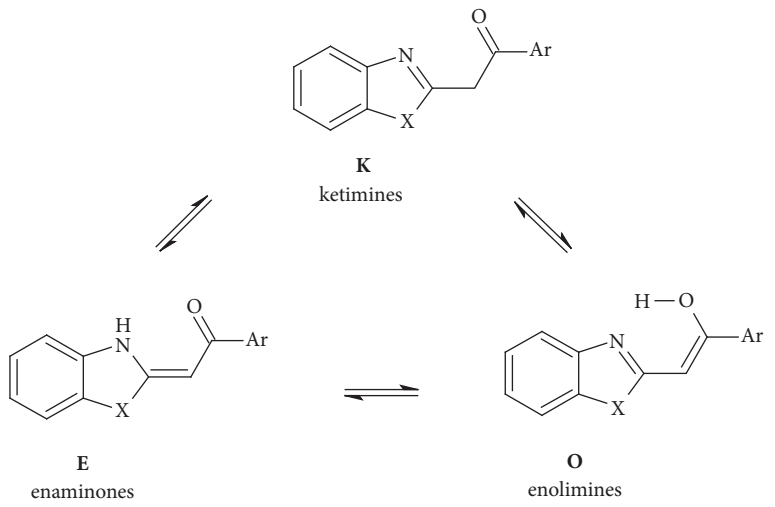
1. Introduction

It was found recently that in chloroform solution 2-phenacylbenzoxazoles (**K** in Scheme 1, X = O) are in equilibrium with (*Z*)-2-(benzo[*d*]oxazol-2-yl)-1-phenylethenols (enolimines, **O**) [1]. Strong electron-donating substituents in the benzene ring were found to stabilize the **K** tautomer. The MP2 *ab initio* calculations supported the energetic preference of the **O** (over **E**) form. ^{13}C CPMAS NMR spectra proved that in the crystalline state the ketimine tautomer **K** is predominant only in the *p*-NMe_2 substituted congener. On the other hand, enolimine forms **O** were detected when the substituent had less electron-donating character or when it had an electron-accepting nature [1].

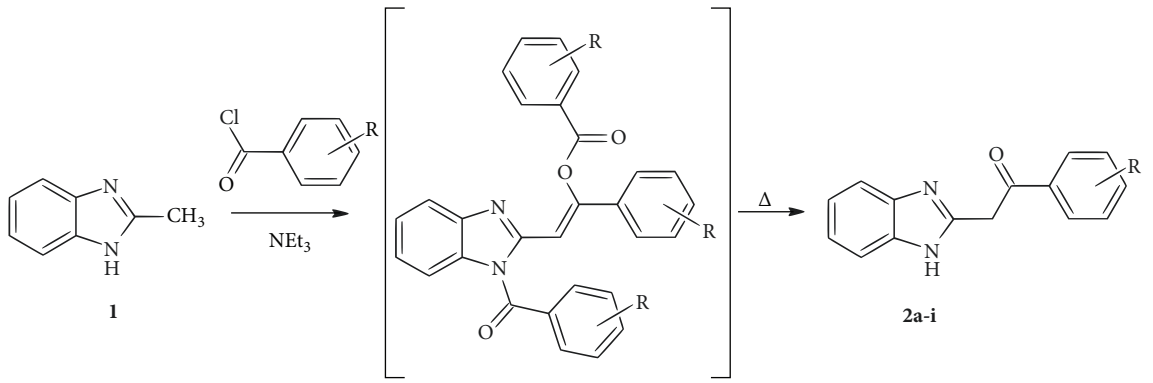
We have previously shown that 1-methyl-2-phenacylbenzimidazoles are similar in chemical properties to 2-phenacylbenzoxazoles [2]. Analysis of NMR spectra and the results of the quantum-chemical calculations showed unequivocally that 1-methyl-2-phenacylbenzimidazoles (**K** - form) are in equilibrium with (*Z*)-2-(1-methyl-1*H*-benzo[*d*]imidazol-2-yl)-1-phenylethen-1-ols (**O** - form).

Since the –N=C(–)CH_2CO– moiety also is present in 2-phenacylbenzimidazoles (Scheme 1, X = NH), these compounds and 2-phenacylbenzoxazoles and 1-methyl-2-phenacylbenzimidazoles are expected to behave similarly. However, in drawing such conclusions one has to be very careful: minor modifications in the molecule may affect the tautomeric equilibria significantly [1–3]. Such understanding prompted us to see the effect of substitution of the ring oxygen atom in 2-phenacylbenzoxazoles and NCH_3 group in 1-methyl-2-phenacylbenzimidazoles by the NH group on their susceptibility to proton transfer.

Tautomerism of 2-phenacylbenzimidazoles has been already studied by the NMR methods: 2-phenacylbenzimidazoles (ketimines **K**) in DMSO-d_6 solution were found to equilibrate with 2-(1,3-dihydro-2*H*-benzo[*d*]imidazol-2-ylidene)-1-phenylethan-1-one (enaminones) [4]. Since an unequivocal distinguishing between enolimines **O** and enaminones **E** (any of these two forms can be present in solution), based only on the simple NMR spectra, may be difficult [1–3], *ab initio* calculations were performed in the present paper in order to support or deny the earlier conclusions [4]. The substituent effect on tautomerism of such derivatives is always significant [1–3], so the series of substituted 2-phenacylbenzimidazoles is worth further study.



Scheme 1: Tautomeric equilibria in some selected 2-phenacyl derivatives of benzoxazole, benzimidazole, and 1-methylbenzimidazole.



Scheme 2: Synthesis of 2-phenacylbenzimidazoles.

2. Results and Discussion

2-Phenacylbenzimidazoles can be obtained by a variety of methods [5–13]. The aforementioned syntheses are characterized by low yield; therefore, 2-phenacylbenzimidazoles were prepared by treating methylbenzimidazole **1** with benzoyl chlorides in the presence of triethylamine followed by thermal decomposition of formed (*Z*)-2-(1-benzoyl-1*H*-benzo[d]imidazol-2-yl)-1-phenylvinyl benzoates **2a-i** (Scheme 2) [5, 7, 11].

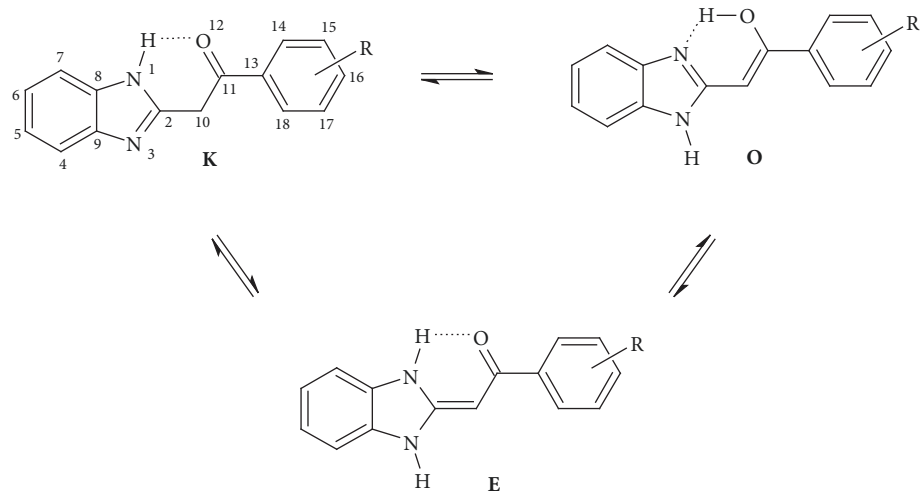
In order to compare 2-phenacylbenzimidazoles with 2-phenacylbenzoxazoles and 1-methyl-2-phenacylbenzimidazoles studied earlier [1, 2], the NMR spectra of the former compounds should be recorded from their deuterated chloroform solutions. Unfortunately, the crystals were sparingly soluble in that solvent, so it was substituted with DMSO-d_6.

There is a single intramolecular hydrogen bond in 2-phenacylbenzimidazoles [2-(1*H*-benzo[*d*]imidazol-2-yl)-1-phenylethan-1-ones] (Scheme 3). In solution, this ketimine **K** is expected to be in equilibrium with the enolimine **O**, or enaminone **E** tautomers.

Due to the presence of the 2,3-dihydro-2-methylene-1*H*-benzo[*d*]imidazole moiety in the molecules, both nitrogen atoms in the enaminone form **E** are equivalent (unless they are differentiated by the intramolecular hydrogen bond).

For the substituents studied, presence of the enolimine **O** in DMSO-d_6 solution has never been reported. ^{1}H and ^{13}C as well as ^{1}H,^{13}C HMBC NMR spectra suggest that **K** and **E** forms are present in such solution [4]. There is no doubt about the presence of the former tautomer, but unequivocal distinguishing between enolimines and enaminones cannot be based only on the simple NMR spectra [1–3]. It is why the ^{1}H,^{13}C HMBC technique has been used earlier to prove which of **K** and **E** is present in solution [4]. Using of the IR spectra to identify the form present in the crystalline state **E** [4] also seems unreliable.

The chemical shifts of H10 resonances (Table 1) are comparable to those observed for 2-phenacyl derivatives



Scheme 3: Tautomeric equilibria of 2-phenacylbenzimidazoles.

Table 1: Selected ^{1}H and ^{13}C NMR chemical shifts for 2-phenacylbenzimidazoles [2-(1*H*-benzo[*d*]imidazol-2-yl)-1-phenylethan-1-ones] **K** and (*Z*)-2-(1*H*-benzo[*d*]imidazol-2-yl)-1-phenylethen-1-ol **O** (solutions in DMSO-d_6, regular characters) and ^{13}C CPMAS spectral data (*italics*) [a].

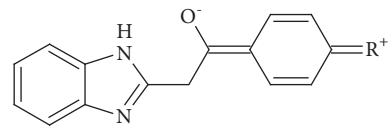
Comp.	Taut.	R =	H10 [b]	H1 and H3	C2	C10	C11	R
2a	**K**	*p*-OCH_3	4.66	12.23	137.44	39.85 [c]	193.89	55.71, 56.06 [d]
2a	**O**	*p*-OCH_3	6.06	12.39	154.34	79.58	169.62	d
2b	**K**	*p*-CH_3	4.64	12.25	137.58	40.03 [c]	195.08	21.41 21.65 [e]
2b	**O**	*p*-CH_3	6.07	12.35	154.21 *154.7*	80.51 *77.5*	168.96 *177.2*	e *22.4*
2c	**K**	*m*-CH_3	4.66	12.33	136.57	40.01 [c]	195.67	21.33, 21.56 [e]
2c	**O**	*m*-CH_3	6.10	12.26	154.14	81.30	169.42	e
2d	**K**	H	4.68	12.34	136.51	40.12 [c]	195.60	-
2d	**O**	H	6.10	12.27	154.11	80.83	169.94	-
2e	**K**	*p*-F	4.67	12.33	135.97	40.09 [c]	194.24	-
2e	**O**	*p*-F	6.00	12.22	153.99	79.12	171.04	-
2f	**K**	*p*-Cl	4.67	12.33	135.20	39.67 [c]	194.06	-
2f	**O**	*p*-Cl	6.03	12.24	153.28	78.89	170.45	-
2g	**K**	*p*-Br	4.67	12.34	135.84	39.80	194.90	-
2g	**O**	*p*-Br	6.03	12.26	153.84	79.38	171.03	
2h	**K**	*m*-F	4.70	12.34	135.64	40.26 [c]	194.66	-
2h	**O**	*m*-F	6.05	12.27	153.81	79.54	170.98	-
2i	**K**	*p*-NO_2	4.78	12.39	f	f	f	-
2i	**O**	*p*-NO_2	6.13	f	153.45	80.33	171.03	
						80.3 [g]	171.1 [g]	-
					152.5	*76.5*	*175.3*	

[a]Literature data collected from DMSO-d_6 solutions. [b]Literature data: 4.6 ppm - 4.8 ppm for **K** and 6.0 ppm - 6.25 ppm for **E** [4–6, 8]. [c]Since this signal is overlapped by the solvent absorptions, DEPT technique was used to determine its position in the spectrum. [d]Due to their comparable intensities, the signals cannot be referred to the definite tautomers ([**K**] ≈ [**O**], see Table 2). [e]The more intense signal was assigned to the **O** tautomer ([**K**] < 50 %, see Table 2). [f]Due to low amount of the **K** tautomer, these signals were not observed. [g]Literature data [4].

Table 2: Content of the **K** form (%) (solutions in DMSO-d_6).

Compound	Substituent R	[K] (%)[a,b]
2a	*p*-OCH_3	49.2 (49.5)[c]; 50 [4]; 52 [5]
2b	*p*-CH_3	32.0 (33.6)[c]
2c	*m*-CH_3	23.1 (24.2)[c]
2d	H	21.9; 20 [4]; 21[5, 7]
2e	*p*-F	21.9
2f	*p*-Cl	13.0; 12 [5]
2g	*p*-Br	15.3
2h	*m*-F	13.0
2i	*p*-NO_2	3.9; 2 [4]; 4 [5]; 0 [8]

[a]Based on integrals of the H10 signals (present paper). [b]Literature data collected from DMSO-d_6 solutions. [c]Values in parentheses are based on integrals of the substituent protons (CH_3, 3.91 ppm for **2a** (form **K**) and 3.87ppm for **2a** (form **O**), 2.51 ppm for **2b** (form **K**) and 2.37 ppm for **2b** (form **O**), 2.51 ppm for **2c** (form **K**) and 2.40 ppm for **2c** (form **O**)).



K′

Scheme 4: Resonance structure contributing to the stabilization of the 2-phenacylbenzimidazole tautomer **K** by electron-donating substituents.

of benzoxazoles [1], 1-methy-2-phenacylbenzimidazoles [2], and their enolimine or enaminone tautomers. Thus, the chemical shift values do not reveal whether another tautomer in DMSO-d_6 solution is **O** or **E**. One should keep in mind that signals of the N-*H* protons seen at >12 ppm are comparable to those of the hydroxyl protons in the enolimine tautomers of 2-phenacylbenzoxazoles [1].

On the other hand, the ^{13}C chemical shifts can indicate the tautomer present in solution. C11 signals of other tautomers (**O** or **E**) are located in the range of 161-171 ppm (Table 1). Thus, the 2-phenacylbenzimidazoles **K** are really in equilibrium with the **O** forms ((*Z*)-2-(1*H*-benzo[*d*]imidazole-2yl)-1-phenylethen-1-ols) [14].

The percent content of **K** form based on H10 integrals is given in Table 2. The accuracy of these data was supported by the evaluation based on signal intensities of the substituent protons and the literature data. In many cases, mainly π-electron delocalization was found to be responsible for tautomeric preferences but other effects, such as the strength of the intramolecular hydrogen bond, should be taken into account.

^{13}C CPMAS spectra of **2b** and **2i** show that only one tautomer is present in the solid state. The characteristic chemical shifts of 22.4 ppm ($\mathbf{C}H_3$), 77.5 ppm (C10), and 177.2 ppm (C11) for **2a** and 76.5 ppm (C10) and 175.3 ppm (C11) for **2i**, suggest that it was the enolimine form **O**.

2.1. Substituent Effect on the Tautomeric Equilibrium. As can be seen in Table 2, the tautomeric ratio in solutions of **2a-i** depends strongly on the substituent. Electron-acceptor substituents increase acidic character of the methylene protons in the **K** forms and thus favour this tautomer (Scheme 4). In consequence, their proton transfer to the *aza* atom in these compounds is facile.

The dependence between pK_T for 2-phenacylbenzimidazoles and Hammett substituent constant σ [15] has the linear character ($pK_T = 1.128\sigma - 0.491$, R = 0.977, Figure 1).

2.2. Quantum-Chemical Calculations. The obtained experimental data seemed worthy of comparison with the results of the respective quantum-chemical calculations. Although semiempirical quantum-chemical calculations show that enaminone form **E** of **2d** is thermodynamically more stable than ketimine form **K** of **2d** [4], MP2 procedure is recommended as the most accurate and effective *ab initio* method for studying medium size molecules involving hydrogen bonds [16]. It includes electron correlation so the calculated and experimental data are expected to be comparable [17]. Some optimized bond lengths and dihedral angles in the molecules of 2-phenacylbenzimidazoles and their tautomers are presented in Table 3. Judging from the length of the hydrogen bond, it seems to be stronger in enolimines than in enaminones. Such an interaction is especially weak in ketimines.

The effect of the substituent on conformation of each tautomer is negligible. Twisting of the carbonyl group with respect to the neighbouring benzene ring in the ketimine molecules is equal to 10-15° (Table 3). The six-membered pseudorings, including the intramolecular hydrogen bonds in both enolimines and enaminones, are almost planar. The dihedral angle (Ψ) between the said benzene ring and C10–C11–O12 moiety in these two tautomers is comparable (*ca* 30°).

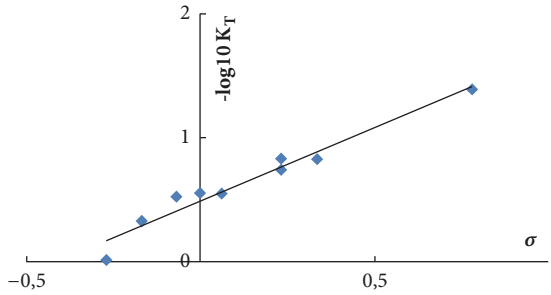


Figure 1: Plot of -log$\mathbf{K_T}$ *vs.* Hammett substituent constants for **2a-i**.

Table 3: Optimized (MP2/6-311+G(d,p)) bond lengths [Å] and dihedral angles [deg] for 2-phenacylbenzimidazoles and their tautomers.

Comp.	Taut.	R =	N1–H1 O12–H12 N3–H3	O12...H1 or N1...H12	H10...H18	Ψ (C14–C13–C11–O12) Ψ (C18–C13–C11–O12)
2a	**K**	*p*-OCH_3	1.01	2.70	2.22,	12.25
			-		3.70[a]	-165.66
			-			
2a	**O**	*p*-OCH_3	-	1.74	2.29	-29.75
			0.99			150.23
			1.01			
2a	**E**	*p*-OCH_3	1.03	1.82	2.25	-28.71
			-			150.53
			1.01			
2d	**K**	H	1.01	2.69	2.25,	-15.81
			-		3.70[a]	162.48
			-			
2d	**O**	H	-	1.74	2.31	-31.42
			0.99			148.46
			1.01			
2d	**E**	H	1.03	1.82	2.28	-30.93
			-			148.00
			1.01			
2i	**K**	*p*-NO_2	1.01	2.82	2.27,	14.17
			-		3.71[a]	-164.73
			-			
2i	**O**	*p*-NO_2	-	1.73	2.26	-28.20
			1.00			151.17
			1.01			
2i	**E**	*p*-NO_2	1.03	1.82	2.26	-29.30
			-			149.28
			1.01			

[a]Distances to H18 from two distinct H10.

Although distances between H18 and methylene protons H10 in 2-phenacylbenzoxazoles were comparable [1], these in 2-phenacylbenzimidazoles (ketimines, **K**) are significantly differentiated (Table 3) because one of these methylene hydrogens experiences steric hindrance by the aryl ring.

The calculated energies of different tautomers (Table 4) prove the **K** form to be the most stable (both electron-donor and electron-acceptor substituents follow this rule).

The enolimine **O** is always less stable than ketimine **K** (the more electron-accepting is the substituent, the

Table 4: MP2(6-311+G(d,p)) calculated relative energies [kJ·mol^{-1}] of different tautomers.

Compound	Tautomer	R =	Energy [kJ·mol^{-1}]
2a	**K**	*p*-OCH_3	0.00 [a]
2a	**O**	*p*-OCH_3	10.06
2a	**E**	*p*-OCH_3	33.94
2d	**K**	H	0.00 [b]
2d	**O**	H	6.29
2d	**E**	H	30.17
2i	**K**	*p*-NO_2	0.00 [c]
2i	**O**	*p*-NO_2	2.10
2i	**E**	*p*-NO_2	23.05

[a]Absolute energy: -875.8329 Hartree.
[b]Absolute energy: -761.5722 Hartree.
[c]Absolute energy: -965.6772 Hartree.

more stable is the enolimine form). As this can be seen in Scheme 3, the six-membered pseudoring including the NH···O=C system in **K** is expected to be less aromatic than the respective pseudorings including the NH···O=C and OH···N moieties in **E** and **O**, respectively. The strong resonance assisted hydrogen bonds (RAHB), such as this present in the molecule of the later tautomer, are well known [18–21]. The least stable tautomer is always **E** (both electron-donor and electron-acceptor substituents follow the rule). It is noteworthy that **O** seems to be really more stable than **E** just because the benzene, pseudo, and imidazole rings are aromatic in the former tautomer, while in the enaminone that is the case for the benzene and pseudorings only (Scheme 3). Thus, from this point of view, 2-phenacylbenzimidazoles resemble 2-phenacylbenzoxazoles [1] and 1-methyl-2-phenylbenzimidazoles [2].

3. Experimental Methods

Melting points were measured on a Boetius table and are uncorrected. Satisfactory elemental analyses (± 0.30 % for C, H and N) were obtained from Perkin Elmer 2400 Series II CHNS/O.

3.1. Syntheses: General Procedure. Benzoyl chloride (0.04 mole) was added in one portion to the stirred solution of 2-methylbenzimidazole **1** (1.46 g, 0.01 mole) and triethylamine (5.6 mL, 4.05 g, 0.04 mole) in diglyme (4 mL). Content of the reaction vessel was heated for 1 h on the boiling water bath. Dropwise addition of water (60 mL) to the stirred cold reaction mixture resulted in precipitation of (*Z*)-2-(1*H*-benzo[*d*]imidazol-2-yl)-1-phenylvinyl benzoates. A solution of the crude material (0.006 mole) and morpholine (1.6 mL, 1,57 g, 0.018 mole) in methanol (9 mL) were heated under reflux with stirring for 10 min. Water (9 mL) was added to the boiling reaction mixture, which cooled to start precipitation. Crystallization of the collected solid from methanol affords pure 2-phenacylbenzimidazoles **2a-i**.

2-(1*H*-benzimidazol-2-yl)-1-(4-methoxyphenyl)ethan-1-one (2a). Yellow solid; yield 0.66 g (57%); mp 205-207°C (lit. 205-207 [22], 208-209°C [4, 5]); ^{1}H NMR (DMSO-d_6 from TMS) δ 3.87 (3H, s, *p*-OCH_3 (**O**)), 3.91 (3H, s, *p*-OCH_3 (**K**)), 4.66 (2H, s, CH_2CO (**K**)), 6.06 (1H, s, C*H*O (**O**)), 7.07 (2H, m (**O**)), 7.15 (2H, m, (**O**)), 7.21 (4H, m, (**K**)), 7.43 (1H, m, (**O**)), 7.58 (3H, m, (**O**)), 7.88 (2H, m, (**K**)), 8.14 (2H, m, (**K**)), 12.24 (1H, s, N*H* (**K**)), 12.39 (1H, s, N*H* (**O**)). ^{13}C NMR δ 39.85, 55.71, 56.06, 79.72, 110.82, 114.21, 114.49, 114.93, 115.32, 121.80, 122.39, 127.63, 129.42, 129.96, 131.36, 132.30, 132.62, 137.44, 149.57, 154.34, 161.06, 163.95, 169,62, 193.89. Anal. Calcd for $C_{16}H_{14}N_2O_2$: C, 72.16; H, 5.30; N, 10.52. Found: C, 72.21; H, 5.15, 10.18.

2-(1*H*-benzimidazol-2-yl)-1-(4-methylphenyl)ethan-1-one (2b). Yellow solid; yield 0.97 g (65%); mp 192-193.5°C (lit. 195-196°C [4]); ^{1}H NMR (DMSO-d_6 from TMS) δ 2.37 (3H, s, *p*-CH_3 (**O**)), 2.51 (3H, s, *p*-CH_3 (**K**)), 4.64 (2H, s, CH_2CO (**K**)), 6.07 (1H, s, C*H*O (**O**)), 7.16 (3H, m (**O**)), 7.27 (2H, d, $^3J_{H,H}$= 7.96 Hz, (**O**)), 7.38 (4H, m (**K**)), 7.50 (1H, m (**O**)), 7.57 (2H, m (**K**)), 7.76 (2H, m (**O**)), 8.00 (2H, m (**K**)), 12.25 (1H, s, N*H* (**K**)), 12.35 1H, s, N*H* (**O**)). ^{13}C NMR δ 21.40, 21.64, 40.03, 80.64, 110.90, 115.13, 122.37, 122.57, 125.96, 129.07, 129.47, 129.83, 130.17, 130.47, 132.30, 134.03, 134.67, 137.58, 139.87, 144.58, 149.42, 154.21, 169.45, 195.08. Anal. Calcd for $C_{16}H_{14}N_2O$: C, 76.78; H, 5.64; N, 11.19. Found: C, 76.81; H, 5.52; N, 11.09.

2-(1H-benzimidazol-2-yl)-1-(3-methylphenyl)ethan-1-one (2c). Yellow solid; yield 1.11 g (70%); mp 166-171°C (lit. 142-143°C [22]); ^{1}H NMR (DMSO-d_6 from TMS) δ 2.40 (3H, s, *m*-CH_3 (**O**)), 2.51 (3H, s, *m*-CH_3 (**K**)), 4.66 (2H, s, CH_2CO (**K**)), 6.66 (1H, s, C*H*O (**O**)), 7.16 (3H, m (**O**)), 7.26 (3H, d $^3J_{H,H}$= 7.48 Hz, (**K**)), 7.35 (3H, t (**K**)), 7.47 (3H, m (**O**)), 7.66 (2H, m (O)), 7.89 (2H, d $^3J_{H,H}$= 7.36 Hz, (**K**)), 12.26 (1H, s, N*H* (**O**)), 12.33 (1H, s, N*H* (**K**)). ^{13}C NMR δ 21.33, 21.56, 40.10, 81.30, 110.99, 115.26, 121.83, 122.53, 123.20, 126.23, 126.50, 126.76, 128.79, 129.15, 129.24, 130.84, 132.36, 134.68, 136.57, 137.40, 138.02, 138.69, 149.37, 154.14, 169.42, 195.67. Anal. Calcd for $C_{16}H_{14}N_2O$: C, 76.78; H, 5.64; N, 11.19. Found: C, 76.58; H, 5.58; N, 10.91.

2-(1H-benzimidazol-2-yl)-1-phenylethan-1-one (2d). Light yellow solid; yield 1.22 g (87%); mp 182-183°C (lit. 176-178 [22], 179 [6], 178-178.5 [7], 178-179°C [4]); ^{1}H NMR (DMSO-d_6 from TMS) δ 4.68 (2H, s, CH_2CO (**K**)), 6.10 (1H, s, C*H*O (**O**)), 7.17 (3H, m (**O**)), 7.42 (1H, m (**O**)), 7.45

(2H, m (**O**)), 7.49 (1H, m (**K**)), 7.57 (5H, m (**K**)), 7.68 (1H, m (**K**)), 7.86 (2H, m (**O**)), 8. 09 (2H, m (**K**)), 12.27 (1H, s, N*H* (**O**)), 12.34 (1H, s, N*H* (**K**)). ^{13}C NMR δ 40.12, 80.83, 110.95, 115.06, 121.86, 122.51, 126.01, 128.88, 128.94, 129.28, 130.17, 132.25, 134.08, 136.51, 137.23, 137.63, 149.31, 154.11, 169.94, 195.60. Anal. Calcd for $C_{15}H_{12}N_2O$: C, 74.22; H, 5.13; N, 10.18. Found: C, 74.35; H, 4.97; N, 10.23.

2-(1*H*-benzimidazol-2-yl)-1-(4-fluorophenyl)ethan-1-one (2e). Brownish solid; yield 0.74 g (59%); mp 196-200˚C (lit. 204-205˚C [22]; ^{1}H NMR (DMSO-d_6 from TMS) δ 4.67 (2H, s, CH_2CO (**K**)), 6.67 (1H, s, C*H*O (**O**)), 7.17 (3H, m (**O**)), 7.28 (2H, m (**O**)), 7.38 (1H, m (**O**)), 7.43 (2H, m (**K**)), 7.55 (4H, m (**K**)), 7.91 (2H, m (**O**)), 8.18 (2H, m (**K**)), 12.22 (1H, s, N*H* (**O**)), 12.33 (1H, s, N*H* (**K**)). ^{13}C NMR δ 40.09, 79.12, 110.82, 114.43, 115.54, 115.76, 116.22, 116.44, 121.91, 122.61, 128.42, 128.51, 131.97, 132.07, 133.23, 133.26, 134.92, 134.95, 135.97, 149.20, 153.99, 162.26, 164.47, 164.71, 166.98, 171.04, 194.24. Anal. Calcd for $C_{15}H_{11}FN_2O$: C, 73.26; H, 4.99; N, 10.05. Found: C, 73.04; H, 5.16; N, 10.02.

2-(1*H*-benzimidazol-2-yl)-1-(4-chlorophenyl)ethan-1-one (2f). Yellow solid; yield 1.05 g (68%); mp 232-234˚C (lit. 226-228˚C [4, 5]; ^{1}H NMR (DMSO-d_6 from TMS) δ 4.67 (2H, s, CH_2CO (**K**)), 6.03 (1H, s, C*H*O (**O**)), 7.14 (3H, m (K)), 7.19 (2H, m (**O**)), 7.48 (4H, m, (O)), 7.63 (3H, d, $^3J_{H,H}$= 8.40 Hz, (**K**)), 7.68 (2H, d, $^3J_{H,H}$= 8.40 Hz, (**O**)), 8.40 (2H, d, $^3J_{H,H}$= 8.40 Hz, (**K**)), 12.24 (1H, s, N*H* (**O**)), 12.33 (1H, s, N*H* (**K**)). ^{13}C NMR δ 39.67, 78.89, 110.33, 113.91, 121.33, 122.12, 127.42, 128.28, 128.84, 130.31, 131.38, 134.16, 134.58, 135.20, 136.78, 138.51, 148.54, 153.28, 170.45, 194.06. Anal. Calcd for $C_{15}H_{11}ClN_2O$: C, 72.41; H, 4.93; N, 9.93. Found: C, 72.46; H, 4.88; N, 9.86.

2-(1*H*-benzimidazol-2-yl)-1-(4-bromophenyl)ethan-1-one (2g). Yellow solid; yield 1.48 g (82%); mp 193-195°C (lit. 238-240 [22], 244-246˚C [4]); ^{1}H NMR (DMSO-d_6 from TMS) δ 4.67 (2H, s, CH_2CO (**K**)), 6.03 (1H, s, C*H*O (**O**)), 7.17 (2H, m (**O**)), 7.37 (3H, s (**K**)), 7.56 (3H, s (**K**)), 7.66 (3H, m (**O**)), 7.80 (3H, m (**O**)), 8.01(2H, m (**K**)), 12.26 (1H, s N*H* (**O**)), 12.34 (1H, s, N*H* (**K**)). ^{13}C NMR δ 39.80,79.38, 110.89, 111.49, 114.45, 121.47, 122.30, 122.54, 122.80, 123.49, 128.23, 130.97, 131.77, 132.37, 133.13, 135.50, 135.84, 137.67, 149.06, 153.84, 171.03, 194.90. Anal. Calcd for $C_{15}H_{11}BrN_2O$: C, 70.19; H, 4.78; N, 9.63. Found: C, 68.99; H, 4.83; N, 9.47.

2-(1*H*-benzimidazol-2-yl)-1-(3-fluorophenyl)ethan-1-one (2h). Yellow solid; yield 1.32 g (77%); mp 211-213˚C; ^{1}H NMR (DMSO-d_6 from TMS) δ 4.70 (2H, s, CH_2CO (**K**)), 6.05 (1H, s, C*H*O (**O**)), 7.17 (2H, m (**O**)), 7.19 (3H, m (**K**)), 7.28 (1H, m (**O**)), 7.38 (1H, m (**O**)), 7.49 (3H, m (**K**)), 7.51 (1H, m (**O**)), 7.57 (1H, m (**O**)), 7.61 (1H, m (**O**)), 7.64 (2H, m (**K**)), 7.70 (1H, m (**O**)), 12.27 (1H, s, N*H* (**O**)), 12.34 (1H, s, N*H* (**K**)). ^{13}C NMR δ 40.26, 79.54, 110.94, 112.63, 112.85, 114.38, 115.33, 115.55, 116.66, 116.87, 120.89, 121.10, 122.18, 122.72, 125.17, 130.79, 131.49, 131.93, 135.64, 141.34, 149.02, 153.81, 161.63, 164.05, 170.98, 194.66. Anal. Calcd for $C_{15}H_{11}FN_2O$: C, 73.26; H, 4.99; N, 10.05. Found: C, 73.37; H, 5.11; N, 10.22.

2-(1*H*-benzimidazol-2-yl)-1-(4-nitrophenyl)ethan-1-one (2i). Orange solid; yield 1.7 g (95%); mp 159-161 (lit. 165-166 [8], 270-272 [22], 295-297˚C [4, 5]); ^{1}H NMR (DMSO-d_6 from TMS) δ 6.13 (1H, s, C*H*O (**O**)), 7.20 (2H, m (**O**)), 7.41 (1H, s (**O**)), 7.59 (1H, s (**O**)), 8.11 (2H, m (**O**)), 8.30 (2H, m (**O**)), 12.39 (1H, s N*H* (**O**)).^{13}C NMR δ 80.32, 111.06, 114.25, 122.99, 124.07, 131.75, 134.89, 145.06, 148.25, 153.45, 171.03. Anal. Calcd for $C_{15}H_{11}N_3O_3$: C, 71.87; H, 4.90; N, 10.85. Found: C, 71.77; H, 5.10; N, 10.94.

3.2. NMR Spectral Analysis. The ^{1}H and ^{13}C NMR spectra were recorded for diluted DMSO-d_6 solution at 298 K on a Bruker Ascend 400 MHz spectrometer. The chemical shifts are referenced to the signal of internal TMS at δ=0.00 ppm. The ^{1}H, ^{13}C and PFG ^{1}H,^{13}C HMQC and HMBC spectra were recorded on a Bruker Avance DRX 500 spectrometer equipped with an inverse detection probehead and z-gradient accessory working at 500.13 MHz and 125.77 MHz, respectively. The number of data points in PFG ^{1}H,^{13}C HMQC and HMBC measurements were 1024 (f_2) x 256 (f_1). This matrix was zero filled to 2048 x 512 and apodized by a shifted sine bell window function along both axes prior to FT.

The solid state ^{13}C CPMAS NMR spectra were recorded on a Bruker Avance 400 FT NMR spectrometer using the samples packed in 4.0 mm o.d. zirconia rotors. The samples were spun at 10 KHz rate and >1000 transients were accumulated. The FIDs are apodized by 10 Hz exponential window before FT. The shifts are referenced to the C=O signal of glycine standard at δ=176.03 ppm.

3.3. Quantum-Chemical Calculations. Geometries for the isolated molecules (vacuum) of the tautomers were optimized using the second order Möller-Plesset method (MP2) [23, 24]. Computations were carried out utilizing the split-valence triple-zeta basis sets 6-311+G(d,p) [25]. All calculations were realized with use of Gaussian 09 package [26].

4. Conclusions

In DMSO-d_6 solution, 2-phenacylbenzimidazoles (ketimine tautomeric form, **K**) are in equilibrium with (*Z*)-2-(1*H*-benzo[*d*]imidazol-2-yl)-1-phenylethen-1-ol (enolimine form, **O**). 2-(1*H*-benzo[*d*]imidazol-2(3*H*)-ylidene-1-phenylethanones (enaminones **E**) were not detected (our findings are different from those reported earlier by other authors [4]). The molar ratio of different forms in solution (based on the integrals of ^{1}H NMR signals) depends on substituent. Electron-acceptor substituents increase the acidic character of the methylene protons in the ketimine forms **K**. In consequence, the transfer of such a proton to the carbonyl oxygen is very easy in these compounds. The calculated energies of different tautomers prove the ketimine form **K** including the OH···N hydrogen bond to be the most stable (both electron-donor and electron-acceptor substituents follow this rule). The enolimine tautomers **O** are always less stable than ketimines **K**. The most labile tautomer is always enaminone **E**. Enolimine tautomers **O** were detected by solid state ^{13}C CPMAS NMR.

Data Availability

The NMR spectra and computational results data used to support the findings of this study are available from the corresponding author upon request.

Conflicts of Interest

The authors declare that they have no conflicts of interest.

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Supplementary Materials

Supplementary materials in the manuscript include ^{1}H and ^{13}C NMR spectra for all of compounds (2 a-i) and DFT Cartesian coordinates for 2a, 2d, and 2i. *(Supplementary Materials)*

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