Tautomerism in Five-membered Nitrogen Heterocycles. A Test of the Reliability of Semiempirical (AM1, PM3, MNDO) Quantum Chemical Methods

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Dedicated to Professor G. Zigeuner on the occasion of his 70th birthday

The reliability of three popular semiempirical quantum chemical methods (AM1, PM3, MNDO) for the treatment of tautomeric equilibria is tested in a series of five-membered nitrogen heterocycles. The known flaw of MNDO to overestimate the stability of compounds with two or more adjacent pyridine-like lone pairs is also present in AM1 and to a somewhat lesser extent in PM3. Tautomeric species differing in the number of adjacent pyridine-like lone pairs, thus, cannot be adequately treated by these semiempirical methods. Both AM1 as well as PM3, however, represent major improvements over MNDO in the case of lactam-lactim tautomerism. The stability of N-oxides as compared to N-hydroxy tautomers seems to be overestimated by the PM3 method. All three semiempirical methods yield quite reliable ionization potentials and dipole moments.

Introduction

Recent calculations of tautomeric equilibria (mainly of the lactam-lactim type) in a variety of heterocyclic molecules [1–8] by the semiempirical AM1 method [9] gave quite reliable results. Thus, the well known deficiencies of the MNDO method (overestimation of the stability of lactim tautomers [10–12]) seem to have been largely corrected in AM1. The tendency of the MNDO method to overestimate the stability of compounds with adjacent pyridine-like lone pairs [13], however, seems also to be present in AM1 [7, 8, 14]. Furthermore, whereas AM1 performs far better than MNDO in six-membered nitrogen heterocycles, the reverse seems to be true in the case of five-membered nitrogen heterocycles [15]. With respect to the tautomerism in azines, the newly developed PM3 method [16] is comparable in accuracy to AM1 [8]. Little, however, seems to be known about the adequacy of this latter method in the treatment of azoles. In continuation of previous work on the application of semiempirical quantum chemical methods to the problem of heterocyclic tautomerism [6–8], in this paper results of such calculations (AM1, PM3, and MNDO) on five-membered nitrogen heterocycles are presented. In the first part tautomerization energies are discussed. Since quantitative gas phase experimental data are scarce (comparisons of the results of quantum chemical calculations with solution data can frequently lead to incorrect conclusions [5]) the reliability of these data will be judged against ab initio calculations. One of the most versatile experimental methods to obtain at least qualitative information about gas phase tautomerism is photoelectron spectroscopy [17–23]. In the second part, thus, calculated ionization potentials (Koopman's theorem, i.e., orbital energies) are compared to experimental IP's and/or ab initio orbital energies. Finally, since dipole moment studies have provided information about tautomerism in solution [24–28], in the third part calculated dipole moments are tabulated.

All calculations were done with the AMPAC program package [9] using the PRECISE option. Geometries were completely optimized without any restrictions, and all structures were characterized as true minima by force constant calculations.

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Results

Tautomerization Energies

Calculated tautomerization energies of the investigated compounds (see Fig. 1 for structures) are listed in Table 1.

Before discussing the reliability of semiempirical tautomerization energies as compared to those obtained by ab initio calculations it should be recalled that the latter ones frequently are quite dependent on

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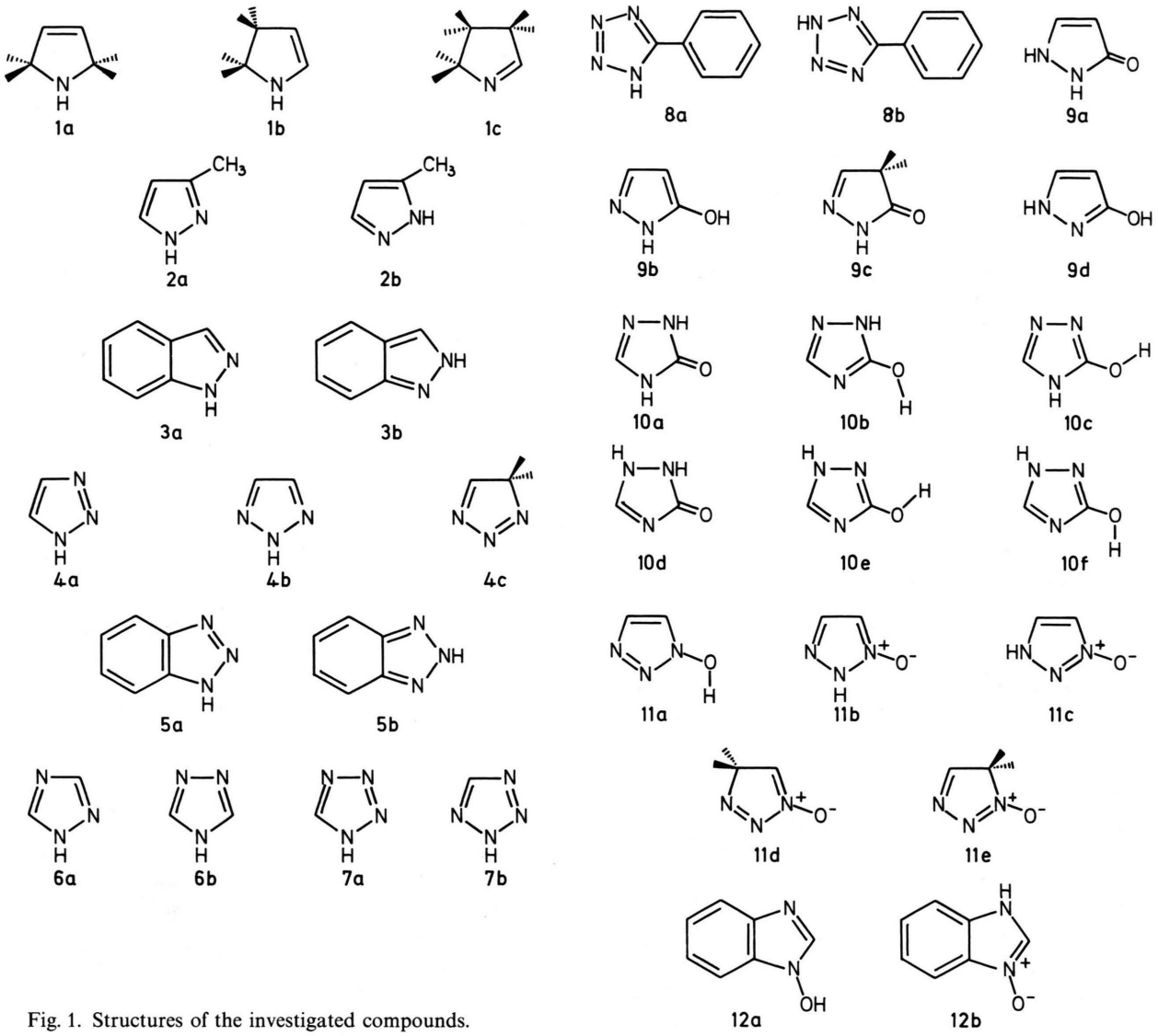

Fig. 1. Structures of the investigated compounds.

the basis set used [30, 37]. In Table 1, thus, the highest level ab initio results available have been listed. In addition, from the known flaws of both MNDO and AM1 mentioned above (i.e. overestimation of the stability of compounds with adjacent pyridine-like lone pairs) major discrepancies between semiempirical and ab initio tautomerization energies might be expected for the tautomeric equilibria **4b**–**4a**, **5b**–**5a**, **6b**–**6a**, and **7b**–**7a**. In compounds lacking this structural feature (e.g. **1b**–**1a**, **1c**–**1a**, **2b**–**2a**, **3b**–**3a**) quite reliable predictions of tautomerization energies should be obtained by the semiempirical methods. The data presented in Table 1 clearly conform to these expectations, one noteable exception being the equilibrium **2b**–**2a**. Here, both AM1 as well as PM3 predict a greater stability for 5-methylpyrazole **2b**, whereas according to MNDO and ab initio results 3-methylpyrazole **2a** should be slightly more stable. Experimentally, from gas phase basicity measurements an energy difference of 0.9 kcal mol^{-1} in favour of **2a** has been estimated [37]. However, as the authors state, this result would correspond to an unreasonably large

Table 1. Comparison of semiempirical (AM1, PM3, MNDO) with ab initio tautomerization energies ([kcal mol^{-1}]) for the investigated compounds [a].

	AM1	PM3	MNDO	ab initio
1b–1a	−4.6	−3.3	−2.9	−3.0 [b]
1c–1a	−11.2	−7.8	−9.1	−15.8 [b]
2b–2a	−1.0	−1.0	0.1	0.4 [c]
3b–3a	6.6	4.9	5.2	10.7 [d]
				10.0 [e]
4b–4a	5.9	2.8	6.3 [f]	−4.7 [g]
				−3.5 [h]
4c–4a	11.1	12.4	9.3	–
5b–5a	12.8	7.8	11.1	17.8 [d]
				4.8 [i]
6b–6a	−4.1 [k]	0.1	−3.6 [f]	7.0 [j]
				8.5 (1.4) [k]
				6.7 [l]
7b–7a	3.7	2.2	4.2 [f]	−9.4 (−23.7) [k]
				−1.7 [l, m]
8b–8a	4.3	3.1	4.7	–
9b–9a	−0.6	−0.2	−8.1;	−14.3 [o]
			−11.6 [n];	
			−14.3 [o]	
9c–9a	−12.7	−5.7	−11.1;	−21.0 [o]
			−17.4 [n, o]	
9d–9a	−0.9;	−0.4	−8.8	–
	−11.8 [p]			
10b–10a	8.9 (8.3) [q]	6.6	−2.7	9.4 (17.0) [q]
10c–10a	5.0 (4.4) [q]	7.4	−5.8	17.9 (22.3) [q]
10d–10a	12.0 (22.7) [q]	9.6	9.7	22.1 (24.9) [q]
10e–10a	11.9 (11.3) [q]	8.5	−1.2	12.3 (21.2) [q]
10f–10a	10.9 (10.4) [q]	7.9	−2.2	12.1 (20.8) [q]
11b–11a	16.1	8.2	33.8 (35.4) [r]	–
11c–11a	12.9	0.0	29.2 (28.4) [r]	–
11d–11a	14.9	9.5	31.2	
11e–11a	13.4	11.8	27.4	–
12b–12a	8.6	−1.9	25.9	–

[a] A positive sign indicates greater stability of the tautomeric form **a**. ΔH_f-values are: 24.7 (**1a**), 58.0 (**2a**), 82.3 (**3a**), 86.4 (**4a**), 104.2 (**5a**), 77.0 (**6a**), 109.6 (**7a**), 133.9 (**8a**), 25.9 (**9a**), 28.6 (**10a**), 91.0 (**11a**), 67.8 (**12a**) for AM1; 15.9 (**1a**), 39.6 (**2a**), 65.3 (**3a**), 67.9 (**4a**), 85.4 (**5a**), 51.8 (**6a**), 86.2 (**7a**), 109.6 (**8a**), 4.4 (**9a**), −0.2 (**10a**), 66.6 (**11a**), 45.6 (**12a**) for PM3 and 15.5 (**1a**), 34.5 (**2a**), 58.6 (**3a**), 50.7 (**4a**), 64.9 (**5a**), 44.6 (**6a**), 55.0 (**7a**), 75.0 (**8a**), 3.8 (**9a**), −4.2 (**10a**), 39.8 (**11a**), 37.5 (**12a**) for MNDO.

[b] 4-21G(N*)-basis: Ref. [29]. – [c] 6-31G**//6-31G calculations [30]; STO-3G//STO-3G yields −0.4 kcal mol^{-1}.

[d] Ref. [21]. – [e] 6-31G-basis: Ref. [31]. – [f] Ref. [13].

[g] 6-31G**//6-31G: Ref. [30]; STO-3G//STO-3G yields 2.3 kcal mol^{-1}. – [h] DZ-basis: Ref. [32].

[i] 6-31G//6-31G: Ref. [33]. – [j] 6-31G*//6-31G*: Ref. [14].

[k] DZ-basis (values in parentheses after CI): Ref. [23].

[l] 6-31G*//6-31G: Ref. [34]. – [m] 6-31G**//6-31G: Ref. [35].

[n] Ref. [18]. – [o] STO-3G basis: Ref. [36]. – [p] Ref. [5].

[q] 6-31G*//3-21G (values in parentheses: 3-21G//3-21G): Ref. [14]. – [r] Ref. [17].

N-methylation effect [37]. Given these experimental uncertainty and the rather large basis set dependence found in the ab initio calculations for this equilibrium [30, 37] no definite conclusion concerning the **2b–2a** tautomerism can at present be drawn. In any case, both compounds appear to be quite close in energy. For indazole **3b–3a** the experimentally estimated tautomerization energy ($\leqq$4.7 kcal mol^{-1} [38]) is in close agreement with either one of the semiempirical results (in fact, even more close than to the ab initio calculations, see Table 1). Experimental results concerning the tautomerism of 1,2,3-triazole are controversial. Early gas phase IR spectra were interpreted in terms of a predominance of the 1H-tautomer **4a** [39]. Based on more recent gas phase experiments [22, 23, 32, 40], however, there seems now consensus that 2H-triazole **4b** is greatly favoured in the gas phase. Especially, from intensity measurements of microwave spectra at room temperature a tautomeric ratio **4a**:**4b** $\approx$ 1:1000, corresponding to $\Delta G \approx$ 4.0 kcal mol^{-1} was estimated [32]. Here all three semiempirical methods clearly lead to incorrect results. Similarly, for 1,2,4-triazole (**6a, b**) and tetrazole (**7a, b**) results obtained by the semiempirical methods (except the PM3 results for **6b–6a**) are at variance with both ab initio calculations (see Table 1) as well as gas phase experiments [22, 23, 42–45]. A unique feature is provided by the tautomerism of benzotriazole (**5a, b**): in this molecule the 1H-tautomer **5a** – despite the presence of destabilizing lone pair interactions – is largely dominant (>99%) in the gas phase [21, 41]. A reasonable rationalization of this fact is provided by the aromatic nature of the 1H-tautomer **5a** vs. the ortho-quinonoid structure of **5b** [33]. For this special molecule, thus, the semiempirical methods yield results in complete agreement with both ab initio calculations as well as experimental findings. In the case of 5-phenyl-tetrazole (**8a, b**) dipole moment studies as well as NMR spectroscopical investigations indicate a shift of the tautomeric equilibrium towards the less polar 2H-form (**8b**) by decreasing the solvent polarity (e.g. DMSO: 86% **8a**, dioxane: 62% **8a**) or by increasing the temperature [25]. Comparison of polarized absorption spectra in polyvinyl alcohol with calculated (CNDO/S) transition moment directions established the 2H-tautomer **8b** as the dominant species in this medium [46].

From the data presented so far it seems clear that neither one of the three semiempirical methods AM1, PM3, and MNDO is suitable to describe annular tautomerism in five-membered nitrogen heterocycles if the various tautomeric species differ in the number of adjacent pyridine-like lone pairs. It is also evident from the data of Table 1 that errors are smallest for the PM3 method.

Table 2. Comparison of semiempirical (AM1, PM3, MNDO) with ab initio orbital energies and experimental ionization potentials (in eV).

	AM1	PM3	MNDO	ab initio	Exp.
1a	9.28	9.10	9.71	9.3 [a]	8.6(n) [b]
	10.34	10.23	10.44	10.1(n)	9.7
	12.28(σ)	12.85(σ)	12.79 (σ)		
	13.22(σ)	13.52(σ)	13.51 (σ)		
1b	8.64	8.61	8.97	8.1 [a]	
	11.39	11.18	11.57	12.0(n, π)	
	12.41 (σ)	12.56	12.76 (σ)		
	12.56	13.00 (σ)	13.11		
1c	10.44	10.34 (n)	11.02 [c]	10.5 [a]	9.71 (n) [c]
	10.81 (n)	10.37	11.06 (n)	10.7	10.56
	12.47 (σ)	12.62	12.96 (σ)		12.3
	12.66	13.10 (σ)	13.20		12.7
2a	9.50	9.40	9.61		
	9.66	9.76	11.88 (n)		
	11.53 (n)	11.01 (n)	13.37 (σ)		
	12.85 (σ)	12.97 (σ)	13.79 (σ)		
2b	9.40	9.56	9.52		
	9.84	9.67	9.86		
	11.62 (n)	11.00 (n)	11.93 (n)		
	13.02 (σ)	13.40 (σ)	13.51 (σ)		
3a	8.90	8.95	8.96	9.25 [d]	8.36 [d]
	9.44	9.61	9.40	9.55	9.05
	11.00	10.90	10.82	12.21(n, π)	10.45(n, π)
	11.82 (n)	11.11 (n)	12.01 (n)	12.40(n, π)	11.75 (σ)
3b	8.47	8.63	8.45	7.95 [d]	7.79 [d, e]
	9.47	9.40	9.38	9.72	8.70
	10.82	10.76	10.59	11.25	10.00
	11.34 (n)	11.08 (n)	11.70 (n)	11.60 (n)	10.24
4a	10.18	10.29	10.10	10.21 [f]	
	11.34	10.67 (n)	11.42	11.78 (n)	
	12.07 (n)	10.91	12.17 (n)	11.94	
	12.81 (n)	12.25 (n)	13.11 (n)	13.87 (n)	
4b	10.33	10.25	10.29	10.88 [f]	10.06 [g]
	11.06	10.86	11.10	11.18	10.90
	12.13 (n)	11.36 (n)	12.33 (n)	12.87 (n)	
	12.92 (σ)	12.06 (n)	13.10 (n)	13.74 (n)	12.1
4c	11.72 (n)	10.96 (n)	11.93 (n)		
	11.93	11.49 (n)	11.98		
	12.81 (n)	11.91	12.91 (n)		
	13.18 (n)	13.00 (n)	13.54 (n)		
5a	9.42	9.41	9.33	9.80 [d]	9.08 [d]
	9.80	10.00	9.65	9.99	9.49
	11.78 (n)	10.65 (n)	11.87	11.78 (n)	10.05 (n)
	11.95	11.51	12.02 (n)	12.93	11.44
5b	9.12	9.20	9.10	9.36 [d]	9.30 [d, e]
	9.82	9.81	9.76	10.48	9.63
	11.69	11.41	11.59	12.93	11.72
	11.79 (σ)	11.44 (n)	12.25 (σ)	13.50(σ, n)	12.50
6a	10.27	10.40	10.31	10.73 [f] (10.30) [h]	10.00 [g]
	11.21	10.70	11.27	11.84 (11.19)	10.56
	11.65 (n)	10.71 (n)	11.75 (n)	12.17 (12.01) (n)	11.1 (n)
	13.23 (n)	11.81 (n)	13.34 (n)	13.62 (13.68) (n)	12.15 (n)
6b	10.03	10.21 (n)	10.02	10.78 [f] (10.05) [h]	
	11.61	10.27	11.61 (n)	11.47 (11.55)	

Table 2 (continued)

	AM1	PM3	MNDO	ab initio	Exp.
	11.62 (n)	10.88	11.71	12.39 (11.67) (n)	
	12.47 (n)	11.53	12.66 (n)	12.56 (12.94) (n)	
7a	11.41	11.09 (n)	11.43	11.81 [f] (11.49) [h]	
	12.13	11.38	12.26	12.64 (n) (12.32)	
	12.40 (n)	11.59	12.52 (n)	13.08 (12.83) (n)	
	13.03 (n)	11.67 (n)	13.23 (n)	13.32 (12.85) (n)	
7b	11.16	11.08	11.21	11.99 [f] (11.39) [h]	11.3 [g]
	12.29	11.30 (n)	12.37	12.72 (12.21)	12.1
	12.50 (n)	11.80	12.70 (n)	12.88 (12.76) (n)	
	13.22 (n)	12.09 (n)	13.33 (n)	13.54 (13.69) (n)	13.6
8a	9.85	9.89	10.00		
	10.31	10.36	10.05		
	11.63	10.93 (n)	11.15		
	12.02	11.37	12.10		
8b	9.41	9.47	9.56		
	9.88	9.92	9.61		
	11.48	11.18 (n)	11.06		
	11.96 (σ)	11.36	12.30		
9a	9.68	9.51	9.71 [i]		8.78 [i]
	10.83(π, n)	10.73(π, n)	10.88		9.37
	11.59(π, n)	11.35(π, n)	11.61 (n)		10.14 (n)
	13.39	12.73	13.14		11.16
9b	9.39	9.37	9.19 [i]		
	10.10	9.80	10.04		
	11.81 (n)	11.03 (n)	11.94 (n)		
	13.48	13.24	13.74		
9c	9.82	9.88	10.08 [i]		9.08(n_O) [i]
	11.04(n_O)	10.90 (n)	11.27(n_O)		9.76
	12.73(n_N)	12.00 (n)	12.85(n_N)		10.60(n_N)
	13.50	12.80	13.56		
9d	9.27	9.15	9.29		
	9.85	9.91	9.80		
	11.86 (n)	11.32 (n)	12.03 (n)		
	13.76	13.15	13.51		
10a	9.67	9.60	9.92		
	11.42 (n)	10.99 (n)	11.50 (n)		
	12.17	11.29	12.30		
	13.36 (n)	12.34 (n)	13.41		
10b	9.88	9.98	9.96		
	11.23	10.67	11.27		
	11.83 (n)	10.90 (n)	11.91 (n)		
	13.28 (n)	11.84 (n)	13.39 (n)		
10c	9.57	9.76	9.60		
	11.75	10.32 (n)	11.73 (n)		
	11.76 (n)	10.93	11.84		
	12.66 (n)	11.68 (n)	12.83 (n)		
10d	10.32	10.06	10.54		
	11.40 (n)	10.91 (n)	11.46 (n)		
	12.66	11.82	12.73		
	13.01 (n)	12.91	13.09 (n)		

Table 2 (continued)

	AM1	PM3	MNDO	ab initio	Exp.
10e	9.73	9.77	9.81		
	11.22	10.75	11.25		
	11.71 (n)	10.75 (n)	11.80 (n)		
	13.40 (n)	12.04 (n)	13.50 (n)		
10f	9.70	9.77	9.77		
	11.29	10.78	11.32		
	11.78 (n)	10.93 (n)	11.90 (n)		
	13.41 (n)	11.87 (n)	13.50 (n)		
11a	10.33	10.28	10.30 (10.22) [j]		10.1–11.0 [j]
	11.22	10.84 (n)	11.29 (11.19)		(9.7–10.7)
	12.10 (n)	10.94	12.10 (11.82) (n)		12.3 (11.8–12.4)
	13.05 (n)	12.56 (n)	13.24 (12.78) (n)		12.5
11b	9.55	9.80	9.51 (9.24) [j]		(8.65) [j]
	11.08	11.12	11.10 (10.63)		(9.85)
	11.56 (n, π)	11.44 (n, π)	11.62 (11.16) (n, π)		(11.85)
	13.41 (n, π)	12.70 (n)	13.31 (13.29) (n)		(12.3)
11c	9.22	9.44	9.15 (9.02) [j]		(8.35) [j]
	10.80	11.03	10.72 (10.66 (n))		(9.45)
	10.88 (n)	11.36 (n)	10.74 (n) (10.61)		(10.20)
	13.79 (n)	12.63 (n)	13.93 (n) (13.25)		(12.0–12.5)
11d	9.66	10.08	9.60		
	10.99 (n)	10.63 (n)	11.06 (n)		
	13.84	13.20 (n)	13.89 (n)		
	13.88 (n)	13.57	14.06		
11e	9.96	10.40	9.92		
	11.56 (n)	11.19 (n)	11.60 (n)		
	12.55 (n)	12.22 (n)	12.83 (n)		
	13.72	12.92 (n)	13.73		
12a	9.33	9.25	9.14		
	9.44	9.50	9.25		
	11.27 (n)	10.60 (n)	11.33		
	12.38	11.03	11.44 (n)		
12b	8.36	8.49	8.31		
	9.62	9.84	9.55		
	10.37	10.52	10.08		
	10.53 (n)	11.07 (n)	10.27 (n)		

[a] 4-21 G(N*)-basis: Ref. [29]. – [b] Ref. [50]. – [c] Ref. [51].
[d] Ref. [21]. – [e] Experimental value for 2-methyl-2 H-indazole.
[f] Ref. [22]. – [g] Ref. [23]. – [h] 6-31 G*//6-31 G: Ref. [34].
[i] Ref. [18]; experimental values are for 1-phenyl-2,3-dimethylpyrazolin-5-one and 1-phenyl-3,4,4-trimethylpyrazolin-5-one, respectively; for clarity ionizations resulting from phenyl π-orbitals are not listed. – [j] Ref. [17]; values in parentheses are for methylated derivatives.

Table 3. Comparison of calculated (AM1, PM3, MNDO) dipole moments (in Debye) with ab initio and experimental results.

	AM1	PM3	MNDO	ab initio	Exp.
1a	1.48	1.36	1.54	1.49 [a]	–
1b	1.23	1.11	1.20	1.25 [a]	–
1c	2.05	2.11	2.01	2.13 [a] (2.43) [b]	–
2a	1.86	2.13	2.11	2.12 (1.87) [c]	–
2b	2.41	2.60	2.09	2.91 (2.56) [c]	–
3a	1.59	1.90	1.85	1.97 (2.09) [d]	1.85 (1.50) [d]
3b	2.36	2.70	2.38	2.57 (3.07) [d]	(3.4) [d]
4a	4.10	4.35	4.03	4.61 (4.13) [c]	4.38 [e]
4b	0.12	0.30	0.24	0.33 (0.06) [c]	0.22 [e]
4c	4.42	4.29	4.24	–	–
5a	3.65	3.75	3.56	4.25 (4.57) [d]; 4.64 [f]	4.15 (3.95) [d, o]
5b	0.13	0.33	0.18	0.55 (1.57) [d]; 0.78 [f]	(0.49) [d, o]
6a	2.73	2.98	2.67 [g]	3.56 [h]; 2.90 [i]	2.72 [j]
6b	5.33	5.69	5.27 [g]	5.99 [i]	
7a	5.13	5.41	5.10 [g]	5.63 [i, k]; 5.17 [h]	5.30 [l]
7b	1.98	2.34	1.90 [g]	2.23 [i, k]; 2.54 [h]	2.19 [l]
8a	5.77	5.84	5.84	–	6.03 [m]
8b	1.78	2.06	1.80	–	2.41 [m]
9a	3.81	3.65	3.55	–	5.03 [n]
9b	1.94	2.40	2.20	–	2.65 [n]
9c	2.23	2.43	2.45	–	2.83 [n]
9d	2.36	2.44	2.20	–	–
10a	3.53	2.95	3.41	–	–
10b	1.65	2.11	1.75	–	–
10c	3.95	4.53	3.98	–	–
10d	4.63	4.66	4.54	–	–
10e	3.56	3.46	3.37	–	–
10f	3.18	3.08	3.13	–	–
11a	3.24	3.18	3.32	–	–
11b	2.35	1.81	2.48	–	–
11c	6.08	6.06	6.09	–	–
11d	4.39	3.92	4.18	–	–
11e	4.98	5.23	5.02	–	–
12a	2.12	2.57	2.11	–	–
12b	4.85	4.57	4.84	–	–

[a] 4-21 G(N*)-basis: Ref. [29]. – [b] 4-31 G(N*)-basis: Ref. [53].
[c] 6-31 G**//6-31 G (STO-3 G//STO-3 G results in parentheses): Ref. [30]. – [d] Ref. [21] and references cited therein; values in parentheses are for methyl-derivatives.
[e] Ref. [32]. – [f] 6-31 G//6-31 G: Ref. [33]. – [g] Ref. [13].
[h] Ref. [24]. – [i] 6-31 G*//6-31 G: Ref. [34]. – [j] Ref. [42].
[k] 6-31 G**//6-31 G: Ref. [35]. – [l] Ref. [45].
[m] Experimental values for 1-methyl-5-p-tolyl-1 H-tetrazole and 2-methyl-5-p-tolyl-2 H-tetrazole, respectively: Ref. [25].
[n] Values for fixed derivatives: Ref. [47] and references cited therein. – [o] Ref. [54].

Besides annular tautomerism, in the pyrazolones **9** and triazolones **10** lactam-lactim tautomerism is also possible. For pyrazolones all previous calculations [18, 19, 36, 47] as well as experimental evidence (photoelectron spectroscopy [18, 19]) favour the CH-tautomer **9c**. The present results are completely in line with these findings. The previously mentioned tendency of MNDO [10–12] as well as ab initio STO-3G calculations [48] to overestimate the stability of lactim

tautomers is also evident from the data of Table 1 (i.e. **9b–9a** and **9d–9a**). Similar arguments apply to the tautomerism of the triazolones **10**. Again, MNDO results appear to be unrealistic, whereas both AM1 and PM3 yield results in reasonable agreement with those of ab initio calculations [14]. The two last molecules **11** and **12** provide examples for N-hydroxy-N-oxide tautomerism. By photoelectron spectroscopy up to the decomposition temperature the only detectable tautomer of **11** has been assigned as the 1-hydroxy-1 H-1,2,3-triazole form **11a** [17]. Both MNDO [17] and AM1 calculations are completely in line with this experimental observation. Interestingly, PM3 erroneously yields an equal stability for tautomer **11c**. For compound **12** only solution data seem to be available: by ^{15}N NMR spectroscopy in different solvents the following tautomeric compositions were deduced [49]: 61% **12a** (DMSO), 52% **12a** (MeOH), and 16% **12a** (CF_3CH_2OH). Given this solvent dependency and the results for **11**, a predominance of tautomer **12a** in the gas phase seems reasonable. Indeed, both AM1 and MNDO predict a considerably greater stability for **12a**. In striking contrast, **12b** should be more stable according to the PM3 method (see Table 1). Apparently, thus, this latter method seems to overestimate the stability of compounds with a $HN=X-N^+-O^-$ structural fragment (X=N: **11c**; X=CH: **12b**).

Ionization Potentials

Calculated (AM1, PM3, MNDO) orbital energies are listed in Table 2 and compared to those obtained by ab initio calculations as well as experimental ionization potentials.

Previous studies [1, 7, 8, 52] have indicated a systematic overestimation (ca. 0.5 eV) of ionization potentials for π-type orbitals by both AM1 and MNDO. Considerably larger errors (>1 eV) were reported for MNDO in the case of n-type orbitals [10–12]. In the series of six-membered heterocycles [8] similar deviations were also found for PM3, although this latter method gave somewhat more reliable orbital energies for pyridine-like lone pairs [8]. The data presented in Table 2 largely conform to these previous findings. However, it should be pointed out that orbital energies obtained by either one of the semiempirical methods are at least as reliable as those from ab initio calculations (see Table 2). Presuming the validity of Koopman's theorem (which – although widely used – might be a questionable assumption [23, 34, 35]), thus, orbital energies calculated by the semiempirical methods should be useful for the investigation of gas phase tautomerism by photoelectron spectroscopy.

Dipole Moments

Calculated as well as experimental dipole moments are presented in Table 3.

Generally, the agreement between theoretical (either semiempirical or ab initio) and experimental dipole moments is very satisfactory. Thus, quantum chemical calculations should be a valuable aid in estimating tautomeric equilibria by dipole moment studies.

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