

CROATICA CHEMICA ACTA
CCACAA 76 (2) 177–182 (2003)ISSN-0011-1643
CCA-2869

Original Scientific Paper

A Theoretical and Experimental Study of Dipole Moments of 3-Aminofurazans

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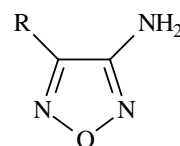
RECEIVED MARCH 4, 2002; REVISED MARCH 14, 2003; ACCEPTED APRIL 14, 2003

Key words
aminofurazans
dipole moment
tautomerism
conformation

Dipole moments of a series of 3-amino-5-R-furazans (R = H, NH₂, OCH₃, CH₃, N₃, COOH, COOCH₃, NO₂) have been determined experimentally and also calculated by means of HF *ab initio* (STO-3G, 3-21G, 4-31G, 6-31G, 6-31G**/4-31G, 6-31G** levels) and semiempirical (MNDO, AM1, PM3) quantum chemical methods. It was shown that semiempirical AM1 and PM3 methods provide generally good agreement with the experimental values of dipole moments. On the other hand, a satisfactory description of this aminofurazan property by *ab initio* method is observed only in the case of calculation levels with the electron correlation and the polarization function included. For these compounds amino-imino tautomeric equilibrium is strongly shifted towards the amino-form. 3-Aminofurazan-4-carboxylic acid and its methyl ester exist in dioxane or benzene solutions at least as a mixture of two different *s-cis*- and *s-trans*-conformers stabilized by conjugation and hydrogen bonding.

INTRODUCTION

Amino derivatives of furazan are widely used as building blocks in fine organic syntheses.^{1–3} On the other hand, according to recent publications, an interest in aminofurazans has arisen from their use as histamine H₂-receptor antagonists instead of urea group.^{4,5} These compounds may also be considered as promising high-energy components in explosive and propellant formulations.^{6,7} Aminofurazans were the objects of different physicochemical investigations. Among others, basicity,^{8–10} prototropic tautomerism,^{10–12} and structure of these compounds were previously studied.^{12–14} However, there is a lack of information on both experimental and theoretical data concerning electric moments of the furazan derivatives.



R = H (1), NH₂ (2), OCH₃ (3), CH₃ (4), N₃ (5), COOH (6), COOCH₃ (7), NO₂ (8)

In the present work we have measured the dipole moments of a series of 3-amino-5-R-furazans **1–8** and have also calculated them by means of *ab initio* (HF at STO-3G, 3-21G, 4-31G, 6-31G, 6-31G**/4-31G, 6-31G** levels) and semiempirical (MNDO, AM1, PM3) quantum chemical methods. Also parent furazan (**9**) was considered as a model compound.

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EXPERIMENTAL

Dipole moments of compounds **2–8** were measured in anhydrous benzene or dioxan at 25 °C by means of a known refractivity method which was described in previous publication.¹⁵

Compounds **2–6** and **8** studied in the present work were obtained by known procedures.^{16–21} Their melting points and spectral characteristics agree with the previously published ones. Previously unknown methyl ester of 3-aminofurazan-4-carboxylic acid (**7**) was synthesized by the similar procedure as ethyl ester of this acid²⁰ and formed colorless crystals, m.p. 113 °C (from water); ¹H NMR (acetone-*d*₆) δ /ppm (Brucker AC 200): 4.01 (s, 3H, Me), 5.90 (s, 2H, NH₂).

Anal. Calcd. for C₄H₅N₃O₃ (*M*_r = 143.03): C 33.57, H 3.52, N 29.36, O 33.54 %; found C 33.53, H 3.58, N 29.21 %.

All calculations were performed using GAMESS program package.²² The stationary points were proved to be minima by frequency calculations carried out at the same computational level.

RESULTS AND DISCUSSION

All resulted dipole moments for compounds **1–9** are given in Table I. It can be seen that the experimental values of dipole moments of aminofurazans **2–8** are notice-

ably larger than that of the parent furazan (**9**) or its alkyl and aryl derivatives.^{23–25} This effect can be ascribed to quite strong polarization of the structure between the electron donating amino-group and the electron-accepting N-O-N fragment of the cycle.²⁶ Among the studied series of compounds, diaminofurazan **2** has a maximum value of dipole moment, whereas the introduction of the electronegative fragments into the cycle decreases this characteristic noticeable. Obviously, the polarization between the different parts of the molecule tends to diminish simultaneously with the increase of the electron-withdrawing effect of substituent. This effect was previously observed for others aromatics.^{27,28} We have studied the quantitative relationships between experimental μ values and the electronic parameters of substituent R. In the Figure 1 it was shown that a good linear regression is observed while Hammett σ_p constants were used. It was precisely this electron constant that related linearly *vs.* a lot of different physico-chemical properties of aromatic heterocycles.^{27,28} However, methoxyfurazan **3** and especially furazancarboxylic acid **6** drop out of the linear relation. The latter may be due to a specificity of the spatial arrangement of these two compounds.

In an effort to discuss the geometry and possible tautomerism of aminofurazans **2–8** we have calculated

TABLE I. Experimental and HF-calculated dipole moments (D) of furazans **1–9**

Furazan	Exp.	Form	MNDO	AM1	PM3	STO-3G	3-21G	4-31G	6-31G	6-31G**/ /4-31G ^{f,g}
3-amino- (1)	–	amino	4.63	4.85	4.77	4.27	6.09	6.25	6.22	5.73
		imino ^d	1.26	2.29	2.22	–	–	2.63	1.94	2.12
3,4-diamino- (2)	5.93(d) ^a	diamino	5.74	6.11	6.09	5.35	7.42	6.93	7.52	6.52
		amino-imino ^d	1.69	2.48	2.12	–	–	2.75	–	2.23
		diimino ^d	1.14	1.97	2.94	–	–	2.44	–	2.81
3-amino-4-methoxy- (3)	4.47(b) ^b	3a	3.48	4.50	3.81	3.24	5.78	5.84	5.80	5.60
		3b	5.90	6.26	6.04	5.49	7.96	8.13	8.11	7.45
3-amino-4-methyl- (4)	4.95(b) ^b	amino	4.60	5.09	4.99	4.53	6.43	6.65	6.59	6.08
		imino ^d	1.98	2.40	2.52	–	–	2.56	–	1.81
3-amino-4-azido- (5)	4.27(d) ^a	amino	2.25	2.59	2.12	1.96	4.90	5.25	4.91	4.96
3-amino-4-carboxy- (6)	3.38(d) ^a	6a	2.15	2.85	2.26	3.16	4.62	4.40	4.38	3.83
		6b	–	1.04	–	–	–	1.23	–	0.98
		6c	–	4.80	–	–	–	6.59	–	6.21
		6d	–	4.51	–	–	–	6.36	–	6.06
3-amino-4-methoxycarbonyl- (7)	3.83(b) ^b	7a	2.25	3.05	2.46	3.77	5.08	5.00	4.99	4.37
		7b	–	0.46	–	–	–	1.13	–	1.27
		7c	–	5.30	–	–	–	7.48	–	6.91
		7d	–	6.57	–	–	–	– ^e	–	– ^e
3-amino-4-nitro- (8)	3.53(b) ^b	amino	3.95	3.58	3.52	3.01	3.79	3.93	3.95	3.66
		imino ^d	2.54	2.51	3.20	–	–	2.69	–	–
parent (9)	3.38 ^c	–	3.22	3.26	3.00	2.97	4.55	4.78	1.75	4.16

^a In 1,4-dioxane; ^b In benzene; ^c Published data;³¹ ^d For the most stable *E(Z)*-stereoisomers; ^e According to the frequency calculation using the same basis set this form is not a minimum; ^f For fully optimized HF/6-31G** geometry the values of dipole moments of furazans **1**, **8** (amino form) and **9** are: 5.27, 3.60, 3.81 D, respectively; ^g At MP2/6-31G**//4-31G level the values of dipole moments of furazans **1**, **2**, **3** and **4** (amino form) are: 5.02, 5.74, 4.91, 5.28 D, respectively.

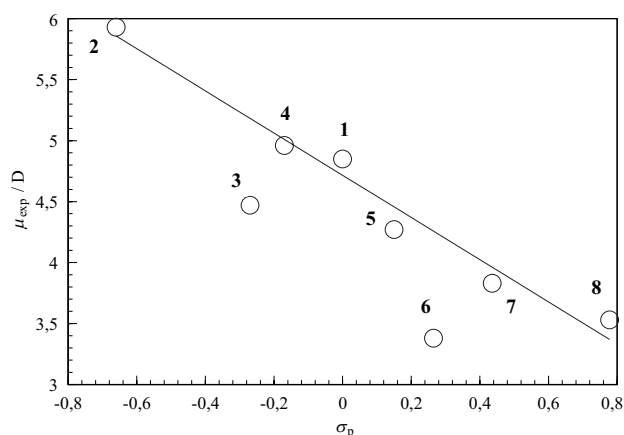
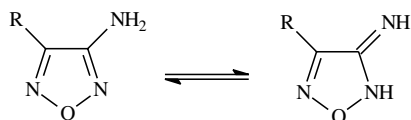


Figure 1. Relation of experimentally determined dipole moments of aminofurazans **1–8** vs. σ_p constants of 4-substituent. $\mu_{\text{exp}} = (4.72 \pm 0.07) - (1.73 \pm 0.14) \sigma_p$; r 0.986; s 0.16 (compounds **3** and **6** were not considered, in the case of 3-aminofurazan (**1**) AM1 calculated value was used).

the dipole moment values of these compounds by means of quantum-chemical methods. It is known that in some cases results of theoretical calculation on geometry and electron structure of five-membered aromatic heterocycles do not show the reasonable agreement with experimental data.^{29,30} Therefore, applied to our problem a one to another comparison of as much quantum-chemical approaches as possible has been actual. Here we have used semiempirical MNDO, AM1, and PM3 method, most widely used in the modern organic chemistry, as well as the *ab initio* HF-method with different basis sets. It could be expected that the assembly of methods will be adequate to answer a question: what is the approximation within the limits of HF-method large enough for the satisfactory description of the electron structure of aminofurazans. Results of calculations are also listed in the Table I.

Comparison of the corresponding calculated and experimental data shows that the geometry of the furazan cycle is described in common features by almost all quantum-chemical methods considered in the present work. As this takes place usually,³¹ under the increasing of the basis set, especially while the polarization functions included, the agreement between experimental and calculated data has improved. Effect of substituent on the geometry of the cycle is quite slight what is obviously due to its »rigidity«.

It should be noted that aminofurazans are capable of the amino-imine tautomerism (Scheme 1).



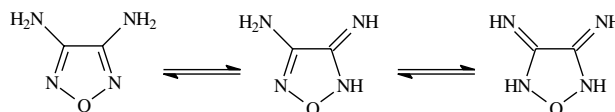
Scheme 1.

TABLE II. Total and relative energies of amino and imino tautomers of furazans **1**, **2**, **4** and **8** calculated at 6-31G**//4-31G computational level^a

Compound	Form	E / a.u.	E_{rel} / kcal mol ⁻¹
1	amino	-315.582770	0
	imino	-315.549528	20.9
2	amino	-370.620051	0
	amino-imino	-370.593820	16.5
	diimino	-370.571787	30.3
4	amino	-354.629452	0
	imino	-354.598973	19.1
8	amino	-519.033204	0
	imino	-518.993618	24.8

^a For the most stable *E/Z*-stereoisomers.

This problem was studied separately. We have calculated full energies of all the possible amino- and imino-tautomeric forms of three aminofurazans **1**, **4** and **8** having the substituents of different nature. In all the cases, true amino forms were the most thermodynamically stable (Table II). In the case of diaminofurazan **2**, three different tautomeric forms can be expected (Scheme 2).

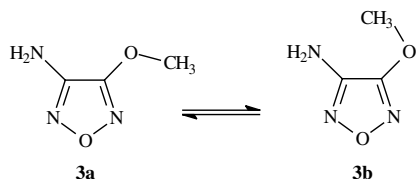


Scheme 2.

However, even in this case, the true diaminoform is much more preferable (Table II). It may be concluded that in non-polar solutions the amount of imino-forms in an equilibrium mixture with amino-ones, is negligible what also agrees with the published data.^{10–12} It should be noted that *E*- and *Z*-stereoisomers of the imino-forms of furazans **1**, **2**, **4** and **8** have close energies (the difference is 1–2 kcal mole⁻¹), whereas their dipole moments noticeably different (Table I). Thus, the possibility of amino-imino tautomerism of compounds **1–8** is not further taken into account.

Now, let us consider a possible spatial isomerism of some aminofurazans. Compounds **3**, **6** and **7** may theoretically exist as different conformers what is governed by a possibility of the molecule fragment rotation around the bond with order more than 1. It may be anticipated that the conformers may possess marketable different dipole moments. The circumstance should be taken into account while the comparison of the experimental and the calculated μ values. On the other hand, it allows us to predict the most preferred isomer in the experimental solutions and ascribes the previously marked effects on relation of μ_{exp} vs. σ_p .

Thus, in the case of aminomethoxyfurazan **3**, two different *s-trans* and *s-cis* conformers **3a** and **3b** differing by a positioning of methyl fragment in relation to C_{ar}-O bond may be awaited (Scheme 3).



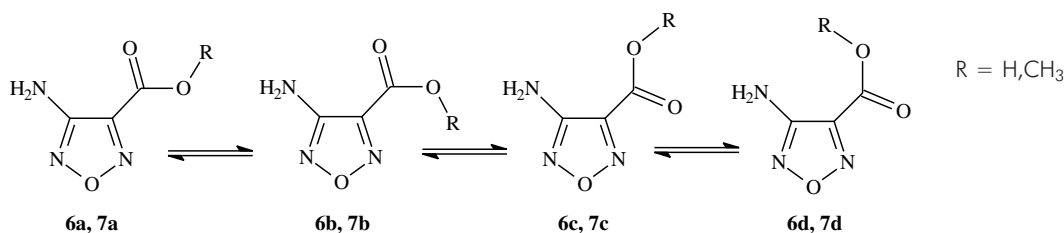
Scheme 3.

Results of calculation show (Table III) that the form **3a** is significantly more thermodynamically stable than **3b** one. It should be noted that in both cases the forms **3a** and **3b** are practically planar, N_{ar}-C_{ar}-O-C dihedral angles are about 0 and 180°, respectively. The calculated dipole moments of conformers of 3-amino-4-methoxyfurazan, **3a** and **3b**, differ by more than 1.5 D from one to another (Table I). Comparison of the experimental and the calculated μ values, similarly to the energy calculations, show that under the condition of experiment furazan **3** exists only as conformer **3a**.

TABLE III. Total and relative energies of *s-cis*- and *s-trans*- stereomers of furazans **3**, **6** and **7** calculated at 6-31G**//4-31G and AM1 computational levels

Com- pound	Form	6-31G**//4-31G		AM1	
		E a.u.	E_{rel} kcal mol ⁻¹	ΔH kcal mol ⁻¹	ΔH_{rel} kcal mol ⁻¹
3	3a	-429.471771	0	48.49	0
	3b	-429.455184	10.41	56.05	7.56
6	6a	-503.204727	0	-3.81	0
	6b	-503.201650	1.93	-0.88	2.93
	6c	-503.199704	3.15	-2.44	1.37
	6d	-503.186392	11.54	3.54	7.35
7	7a	-542.230173	0	2.42	0
	7b	-542.216976	8.28	6.61	4.19
	7c	-542.225234	3.10	3.98	1.56
	7d	- ^a	- ^a	22.83	20.44

^a According to the frequency calculation at the same basis set, this form is not a minimum.



Scheme 4.

A more complicated picture is observed in the case of aminofurazancarboxylic acid **6** and its methyl ester **7** where four different *s-cis* and *s-trans* conformations, obtained by the rotation about C_{ar}-C and C-O_R bonds may be awaited (Scheme 4).

Conformers **6a-6c** and **7a-7c** have quite reliable energies, whereas the forms **6d** and **7d** are thermodynamically unstable what may be due to the steric effects (Table III). In the cases of compounds **6** and **7**, some particular assumptions on prevailing conformers in solutions basing on the calculated dipole moment values may also be proposed (Table I). Taking into account that only two conformations **6a, 6c** and **7a, 7c** are possible for each compound and using a square additivity rule of the dipole moments ($\mu_{exp}^2 = x_a \mu_a^2 + x_c \mu_c^2$, where x_a, x_c – are the percentage and μ_a, μ_c – the AM1 calculated values of dipole moments of the forms **6a, 6c** and **7a, 7c**, respectively),³² following relative assay of forms in the tested solutions may be estimated: **6a** (78 %), **6c** (22 %) and **7a** (71 %), **7c** (29 %). It should be noted that this estimation is quite converted, especially in the case of carboxylic acid **6** where intermolecular interactions may be substantial.

According to the calculated geometry of furazans **3, 6-8** at AM1 and *ab initio* levels, a possibility of intramolecular hydrogen bonding between the oxygen atom of substituent and the amino group may be awaited (Figure 2). This effect should additionally stabilize the conformations **3a, 6a-6c** and **7a-7c**. A possibility of such hydrogen bonding in another amino-heteroaromatics has been proposed earlier.³³

As a whole, the semiempirical methods, especially AM1 and PM3 ones, show best agreement with the experimental data comparing with an *ab initio* one, even in case when high-level basis sets with the included polarization functions were used (Table I). Thus, a difference between the experimental and the calculated dipole moments at 6-31G**//4-31G level for compounds **1-9** reaches 1.13 D (methylfurazan **4**), whereas in the case of semiempirical methods the maximum difference is usually does not exceed 0.2D (excluding azidofurazan **5**). The best description of dipole moments by non-empirical method is observed for nitrofurazan **8** and the worst one for methylfurazan **4**. 3-Amino-4-azidofurazan (**5**) is an exception to the drawback described above. In this case, the *ab initio* method shows the »usual« deviation, while the semiempirical ones lead to principally incorrect results. Almost everywhere the *ab initio* method

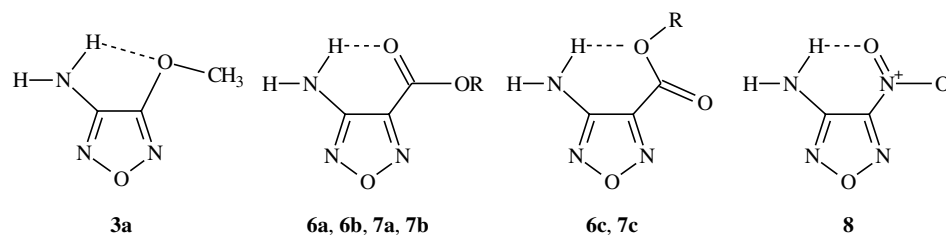


Figure 2. A structure of intramolecular hydrogen bonding in aminofurazans **3**, **6–8**, calculated by AM1 and *ab initio* methods.

noticeably overestimates the dipole moment of furazans **1–9** to experimental data. The difference between the experimental and the calculated μ values does not systematically vary with the enlarging of the basis set. A little better agreement is observed only in the calculations with the polarization functions. Some overestimation of the calculated dipole moments, as compared to the experimental data, by *ab initio* quantum-chemical methods were previously observed on an example of another aromatic nitrogen-containing heterocycles.^{30,34,35} However, in the case of other heterocyclic systems, this overestimation was not so large. It might be awaited that the remarkable effect is inherent in the furazan ring.

Probably, in order to improve a theoretical prediction of dipole moments of such high-polar compounds by means of *ab initio* methods, the electron correlation should be taken into consideration.³⁶ This thesis has been proved here by the calculation of this property of several selected furazans at MP2/6-31G** level. It may be proposed that in the case of semiempirical methods the electron correlation was implicitly accounted during the parametrization procedure. A better agreement between the experimental and the calculated dipole moments may be awaited on the way of using of more flexible (polarizable) basis sets.³⁷

So as the basic tendency in relation between the calculated and the experimental data both for unsubstituted furazan (**9**) and aminofurazans **1–8** is similar, it may be additively concluded that the compounds **1–8** exist predominantly in the true amino-, but not the imino-form.

CONCLUSIONS

A strong polarization of the molecule of aminofurazans **1–8** is observed what leads to abnormally high values of their dipole moments. Semiempirical AM1 and PM3 methods are most preferable for the theoretical prediction of dipole moments of the furazan derivatives. The *ab initio* method gives a good agreement within the experimental data only when the electron correlation is taken into consideration and the basis sets contain polarization functions. In the case of compounds **1–8**, amino-imino equilibrium is strongly shifted towards the true amino forms. 3-Aminofurazan-4-carboxylic acid (**6**) and its methyl ester **7** exist in non-polar solvents in at least two different *s-cis* and *s-trans* conformations, whereas 4-methoxy-3-aminofurazan (**3**) has only one conformation.

Acknowledgment. – This work was supported by Ministry of Education of Russian Federation («Integration» program, Grant I0667).

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SAŽETAK

Teorijsko i eksperimentalno istraživanje dipolnih momenata 3-aminofurazana

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Izmjereni su dipolni momenti za niz 3-amino-5-R-furazana (R = H, NH₂, OCH₃, CH₃, N₃, COOH, COOCH₃, NO₂). Momenti su također izračunani primjenom *ab initio* HF pristupa na STO-3G, 3-21G, 4-31G, 6-31G, 6-31G**/4-31G, 6-31G** razinama te semiempirijskim MNDO, AM1, PM3 kvanto-kemijskim postupcima. Pokazano je da semiempirijske AM1 i PM3 metode dovode općenito do dobrog slaganja s eksperimentalnim vrijednostima dipolnoga momenta. U slučaju aminofurazana dobiveno je zadovoljavajuće slaganje samo na *ab initio* razini i to nakon uključivanja elektronske korelacije i polarizacijskih funkcija. Za ove spojeve je amino-imino tautomerijska ravnoteža jako pomaknuta na stranu amino forme. 3-Aminofurazan-4-karboksilna kiselina i njezin metilni ester postoje u otopini dioksana ili benzena najmanje kao smjesa dvaju različitih *s-cis*- i *s-trans*-konformera, stabiliziranih konjugacijom i vodikovim vezama.