Journal of Molecular Structure 1014 (2012) 63–69

Contents lists available at SciVerse ScienceDirect

Journal of Molecular Structure

journal homepage: www.elsevier.com/locate/molstruc

The interplay of hydrogen bonds in the solid state structure of NH-pyrazoles bearing cyano and amino substituents

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ARTICLE INFO

Article history:
Received 3 October 2011
Received in revised form 18 January 2012
Accepted 19 January 2012
Available online 28 January 2012

Keywords:
Pyrazoles
Crystal structures
Hydrogen bonds

ABSTRACT

The annular tautomeric equilibrium of two 4-cyano-3(5)-aminopyrazoles having hydrogen atom or methyl group in position 5(3) was studied by X-ray crystallography for the solid compounds and by DFT B3LYP/6-31G** and CBS-QB3 calculations for the free molecules. The 3-amino tautomer was found to be the more favorable form for the free molecules and the sole form in the solid state.

1. Introduction

3(5)-Aminopyrazoles are an important group of organic molecules, because many of them exhibit a broad spectrum of biological activity and are useful materials in drug synthesis [1–4]. For example, numerous recent studies dealt with 3(5)-aminopyrazoles as potent and selective p38α inhibitors [5], calcium-sensing receptor antagonists (CaSR) [6], selective Rafkinase inhibitors in melanoma cells [7], or selective adenosine A1 receptor antagonists [8]. 3(5)-Aminopyrazoles have been recognized as valuable synthons for the construction of more complex structures, in particular, of biologically active fused heterocycles (e.g., pyrazolopyrimidines, pyrazolopyridines) [9–13].

Recent studies showed that NH-pyrazoles and pyrazolines are promising synthons in self-assembly. The metal coordination modes of these compounds were described, and it was concluded that the pyrazole ring can be considered as the most flexible ligand group in coordination chemistry [14].

Tautomerism in five-membered heterocyclic systems is an intriguing phenomenon attracting attention for a long time [15–17]. Knowledge of the tautomeric preferences and of the factors affecting the equilibrium is essential for understanding the reactivity of compounds in chemical processes and their influence on biological systems. Due to annular prototropic tautomerism, 3(5)-aminopyrazole *a priori* can exist in two forms, namely, 3-amino-1*H*-pyrazole (**3A**) and 5-amino-1*H*-pyrazole (**5A**). Elguero et al. [18] have found that 5(3)-amino-3(5)-aryl-1*H*-pyrazoles with donor substituents at the aryl ring exist in the solid state as **3A** forms. Surprisingly, crystals of 5(3)-amino-3(5)-aryl-1*H*-pyrazoles with acceptor substituents at the aryl ring appeared to exist as mixtures of **3A** and **5A** tautomeric forms (4-Br) or as **5A** form only (4-NO_2) [18].

N-unsubstituted pyrazoles are very interesting objects from the viewpoint of the N–H···N hydrogen bonding in their crystals. The 1,2-arrangement of N atoms in pyrazoles makes possible formation of at least four kinds of structures: dimers, trimers, tetramers, and catemers [19] (Fig. 1).

However, in case of 3(5)-amino-4-cyanopyrazoles, a number of additional species should be taken into account, because cyano and amino groups can also participate in hydrogen bonding in crystals.

Here we report on a single crystal X-ray diffraction analysis and theoretical studies of NH-pyrazoles bearing cyano and amino groups directly bonded to the pyrazole core, aimed not only to determine the position of the NH ring proton but also to understand its effect on the formation of supramolecular assemblies.

2. Results and discussion

For N-unsubstituted 3(5)-aminopyrazoles, two tautomeric forms are really possible (Scheme 1) [15–17,20]. The predominant tautomeric forms of 3(5)-amino-4-cyanopyrazole **1** and 3(5)-amino-4-cyano-5(3)-methylpyrazole **2** have been examined by X-ray crystallography for the solid state and by DFT B3LYP calculations

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doi:10.1016/j.molstruc.2012.01.026

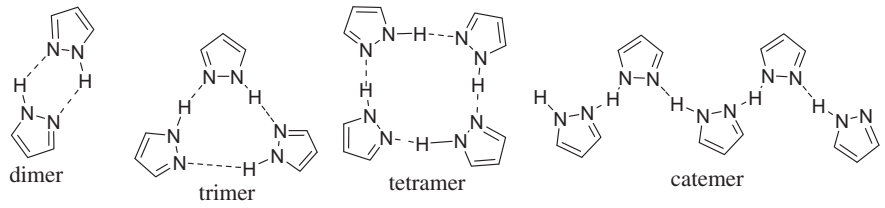
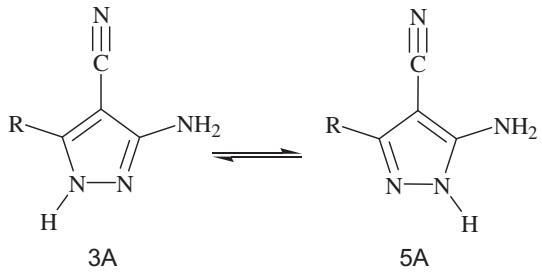


Fig. 1. Traditional hydrogen-bonded structures in crystals of pyrazoles.



Scheme 1. Tautomerism of N-unsubstituted 3(5)-amino-4-cyanopyrazoles.

with 6-31G** basis set and CBS-QB3 calculations for the free molecules.

2.1. Theoretical calculations

The quantum chemical calculations were performed for both tautomeric forms **3A** and **5A** of pyrazoles **1** and **2**. Geometry optimizations were performed with GAMESS-US package [21] using the hybrid exchange–correlation functional B3LYP [22,23] with 6-31G** basis set. Frequency analysis has shown that the optimized structures correspond to the energy minima on the potential surface. The thermodynamic characteristics (free energies, enthalpies at 298.15 K) and dipole moments were computed on the optimized geometries at the same theory level with subsequent CBS-QB3 complete basis set extrapolation [24,25]) full optimization runs using the Gaussian03 package [26]. The results are given in Tables 1 and 2. Since CBS-QB3 ΔE_{tot}, ΔG and ΔH values differ from those obtained by B3LYP/6-31G** by less than 0.7 kcal/mol having the same sign, B3LYP/6-31G** theory level can be considered suitable for the qualitative comparison of the two tautomeric forms of 4-cyanopyrazoles.

According to Table 1, ΔE_{tot} values obtained by B3LYP/6-31G** and CBS-QB3 indicate that the tautomeric form **3A** of a free molecule is more favorable than **5A** for both compounds **1** and **2**. Therefore, the tautomeric form **3A** can be expected to prevail in the solid state. It is significant that dipole moments of tautomeric forms **3A** of compounds **1** and **2** are lower than those of forms **5A**. According to the computational data, the dipole moment vector of the free molecules of **1** and **2** is oriented along the bond between the N atom of the pyrazole ring and the labile proton toward the proton. The orientations of the dipole moment vectors computed by B3LYP/6–31G** and CBS-QB3 methods for each structure under study are essentially the same. See Fig. 2.

Table 1
Total energies (E_{tot}), zero point energies (ZPE), free energies (G), enthalpies (H) (all in hartree), relative energies (ΔE_{tot} and ΔG), enthalpies (ΔH) (all in kcal/mol), and dipole moments (μ, debye) for the tautomeric forms **3A** and **5A** of the free molecules of **1** and **2**, calculated by DFT B3LYP/6-31G** and CBS-QB3 methods.

Compound	E_{tot}	ZPE	G	H	ΔE_{tot}	ΔG	ΔH	μ
*B3LYP/6-31G***								
1–3A	−373.60446	0.08694	−373.54846	−373.50974	−1.17	−1.15	−1.25	4.224
1–5A	−373.60259	0.08700	−373.54663	−373.50775	0	0	0	5.167
2–3A	−412.90091	0.11450	−412.82104	−412.77669	−1.25	−2.34	−1.20	4.309
2–5A	−412.89891	0.11463	−412.81732	−412.77477	0	0	0	4.802
CBS-QB3								
1–3A	−373.22952	0.08588	−373.26047	−373.22171	−1.78	−1.68	−1.83	4.385
1–5A	−373.22669	0.08578	−373.25780	−373.21879	0	0	0	5.296
2–3A	−412.46500	0.11298	−412.49903	−412.45526	−1.65	−2.03	−1.63	4.584
2–5A	−412.46237	0.11286	−412.49579	−412.45266	0	0	0	4.817

Table 2
Selected bond lengths (l, Å) and bond angles (ω, °) for molecules of **1** and **2** obtained by X-ray diffraction analysis of the crystals and by B3LYP/6–31G** and CBS-QB3 calculations for free molecules.

Bonds	Bond lengths						Bond angles	Angles (X-ray)	
	1			**2**				**1**	**2**
	X-ray	B3LYP/6–31G**	CBS-QB3	X-ray	B3LYP/6–31G**	CBS-QB3			
N1–N2	1.384(1)	1.366	1.363	1.378(2)	1.369	1.367	N1–N2–C3	104.70(8)	103.82(13)
N1–C5	1.331(1)	1.343	1.341	1.332(2)	1.346	1.345	N1–N2–C5	112.66(9)	113.99(13)
N2–C3	1.340(1)	1.330	1.325	1.334(2)	1.328	1.323	N2–C3–C4	110.33(9)	110.82(14)
C3–C4	1.427(1)	1.435	1.434	1.415(2)	1.434	1.434	C3–C4–C5	105.27(9)	105.94(14)
C4–C5	1.388(3)	1.392	1.389	1.390(2)	1.398	1.395	C4–C5–N1	107.04(9)	105.42(14)
C3–N6	1.368(1)	1.379	1.377	1.381(2)	1.380	1.378	C4–C3–N6	127.34(10)	127.50(14)
N1–H1	0.911(16)	1.007	1.006	0.87(2)	1.008	1.007	N2–C3–N6	122.24(9)	121.56(15)

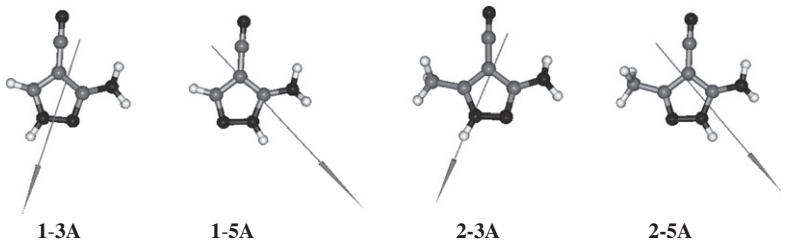
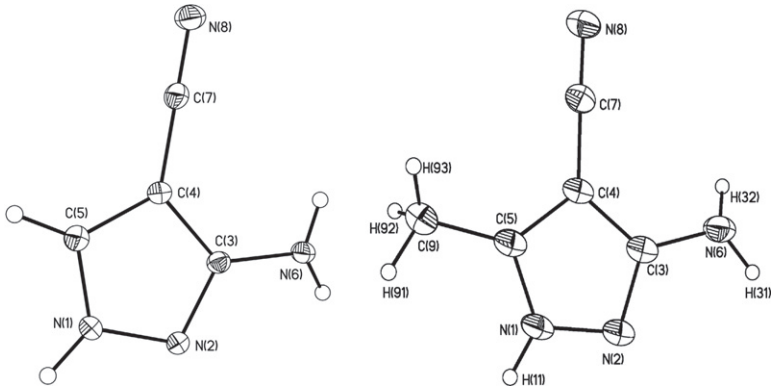


Fig. 2. The B3LYP/6-31G** calculated dipole moment vectors of the free molecules of 1 and 2.



1-3A tautomer **2**-3A tautomer

Fig. 3. A view of the molecules of 1 and 2 with atom numbering. Thermal vibration ellipsoids are drawn at the 50% probability level.

2.2. Crystal structure determination and refinement

The results of single crystal X-ray diffraction studies of pyrazoles **1** and **2** are shown in Figs. 3–5 and Table 4. The X-ray studies showed that these compounds consist of single tautomeric form **3A**, confirming the results of the theoretical calculations. It is interesting that the ^{1}H and ^{13}C NMR spectra of a solution of compound **2** in DMSO-d_6 contain signals of both tautomeric forms **3A** (37%) and **5A** (63%) [20]. It can be assumed that the more polar form **5A** (μ = 4.802 D, B3LYP/6-31G**, Table 1) prevails in the solution of compound **2**, being stabilized more efficiently by stronger solvation with the polar solvent. In addition, it is known that ethyl 5(3)-acetylamino-1*H*-pyrazole-4-carboxylate exists in the solid state as form **3A** [27].

In each molecule, the five-membered pyrazole ring is planar with deviation of the N(1) atom from the least-squares plane by 0.002 Å for **1** and 0.005 Å for **2**.

The cyano group lies close to the plane of the pyrazole ring. All formally single bonds C(3)–C(4), C(5)–N(1) and N(1)–N(2) of the pyrazole rings (Table 2) are significantly shortened compared to

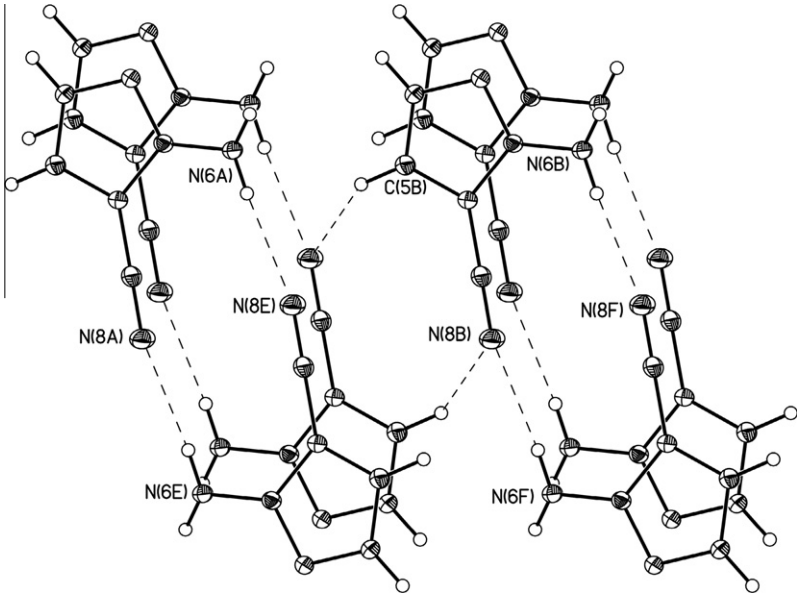


Fig. 4. H-bonded associates in the crystal structure of 1 (dashed lines denote H-bonds).

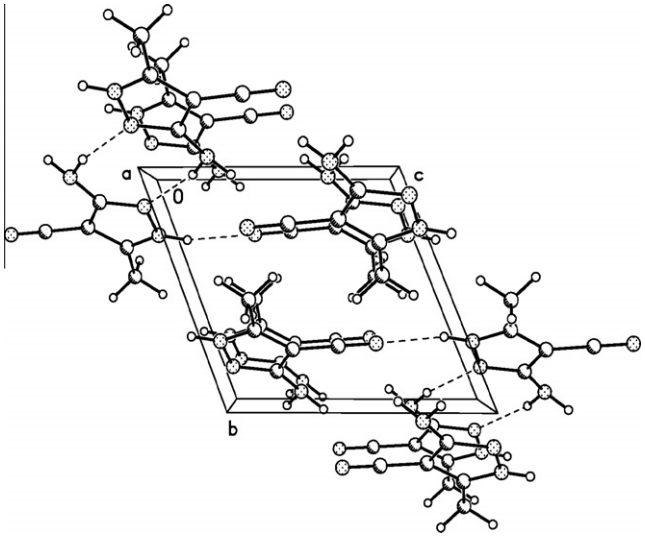


Fig. 5. A fragment of the crystal packing of 2 along the crystallographic plane *bc*.

the typical single bond lengths (1.54, 1.47, and 1.45 Å, respectively [18]), suggesting appreciable π- and *n*-electron delocalization. The calculated bond lengths are in good agreement with the corresponding experimental results (Table 2), with small differences attributable to intermolecular interactions in the crystals. The nitrogen atom of the amino group has a distorted sp^3-hybridization and in both compounds **1** and **2** is out of the pyrazole ring plane: the maximum deviation is 0.054 Å for **1** and 0.083 Å for **2**. The hybridization of the N(6) atom, characterized by the sum of bond angles around it, is 351.0° for compound **1** and 344.2° for compound **2.** The C–NH_2 distance for compound **2 (**1.381 Å) is slightly longer than for **1** (1.368 Å) (Table 2). Apparently, substitution of the C(3) hydrogen with methyl group decreases the conjugation between the amino group and pyrazole ring π system. According to published data [18], in 3-amino-5-phenylpyrazole the sum of the bond angles around N(6) is appreciably smaller (335(6)°), and the C–NH_2 distance is longer (1.393 Å) than those in compounds **1** and **2**. This may be due to the acceptor power of the cyano group.

The crystal structures of compounds **1, 2** are mainly stabilized by intermolecular hydrogen bonds (Table 3) which determine the crystal packing mode (Figs. 4 and 5).

In the crystal structure of **1**, two molecules form a dimer via two equal intermolecular N–H···N hydrogen bonds with the N···N distance of 3.080 Å. Each bond is formed by one of the amino hydrogen atoms and the cyano nitrogen atom (Fig. 6, dimer 1.1). It is known that, in crystals of N-substituted 5-aminopyrazoles, molecules are linked to form identical hydrogen-bonded dimers with the N···N distance of 3.147 Å for 5-amino-1-(2-chlorophenyl)pyrazole-4-carbonitrile [28] and 3.10 Å for 5- amino-1-*tert*-butyl-3-(4-methoxyphenyl)pyrazole-4-carbonitrile [29]. Furthermore, hydrogen bonding between the unsubstituted nitrogen atom of the pyrazole ring and NH group of another ring with the N···N distance of 2.934 Å leads to a catemer-like arrangement of molecules of **1** (Fig. 6, catemer 1).

Table 4
Crystal data and structure refinement for 1,2.

	1	**2**
Empirical formula	C4 H4 N4	C5 H6 N4
Formula weight	108.11	122.14
Temperature	100(2) K	120(2) K
Wavelength	0.71073 Å	0.71073 Å
Crystal system	Monoclinic	Triclinic
Space group	P 21/c	P-1
Unit cell dimensions	a = 3.6925(7) Å b = 6.4297(13) Å c = 20.087(4) Å β = 92.14(3)°	a = 6.1435(10) Å b = 7.1154(11) Å c = 7.4732(12) Å α = 67.668(2)° β = 87.601(3)° γ = 76.399(2)°
Volume	476.58(16) $Å^3$	293.29(8) $Å^3$
Z	4	2
Density (calculated)	1.507 Mg/m^3	1.383 Mg/m^3
Absorption coefficient	0.107 mm^{-1}	0.095 mm^{-1}
F(000)	224	128
Crystal size	0.40 × 0.20 × 0.20 mm^3	0.20 × 0.05 × 0.01 mm^3
Theta range for data collection	3.33–28.99°	2.95–29.00°
Index ranges	$-5 \le h \le 4$, $-8 \le k \le 7$, $-13 \le l \le 27$	$-8 \le h \le 8$, $-9 \le k \le 9$, $-10 \le l \le 10$
Reflections collected	2537	3241
Independent reflections	1248 [R(int) = 0.0134]	1552 [R(int) = 0.0292]
Completeness to theta = 28.99°	99.2%	99.4%
Max. and min. transmission	0.9780 and 0.970	0.998 and 0.990
Data/restraints/parameters	1248/0/89	1552/0/106
Goodness-of-fit on F^2	1.004	1.008
Final R indices [for 1145 rflns with $I > 2$sigma(I)]	R1 = 0.0350, wR2 = 0.0751	R1 = 0.0471, wR2 = 0.1040
R indices (all data)	R1 = 0.0380, wR2 = 0.0766	R1 = 0.0752, wR2 = 0.1118
Largest diff. peak and hole	0.326 and −0.220 e $Å^{-3}$	0.288 and −0.270 e $Å^{-3}$

Table 3
Hydrogen bond geometries in crystals of compounds 1 and 2.

Compound		D–H···N	Bond lengths, Å			Bond angles, °
			D–H	H···N	D···N	D–H···N
1	−0.73	N(ring)···H—N(ring)[a]	0.913(17)	2.025(17)	2.934(13)	174.4 (15)
	−0.53	C≡N···H—N(amino)[b]	0.864(16)	2.221(16)	3.080	172.8(14)
	−0.38	N—H(amino)···N(ring)[c]	0.893(17)	2.369(16)	3.258 (15)	174.3(13)
	−0.33	C—H···N≡C	0.965(13)	2.422(14)	3.264(16)	145.7(11)
2	−0.67	C≡N···H—N(ring)[d]	0.87(2)	2.08 (2)	2.927(2)	166 (2)
	−0.55	N(ring)···HN(amino)[e]	0.92(2)	2.20(2)	3.090(2)	165.2(2)
	−0.11	C≡N···HN(amino)	0.89(2)	2.64(2)	3.342	136.8(16)

Symmetry transformations used to generate equivalent atoms.
[a] $-x+1, y-1/2, -z+1/2$.
[b] $-x, -y+2, -z+1$.
[c] $-x, y+1/2, -z+1/2$.
[d] $x, y, z+1$.
[e] $-x+2, -y, -z+2$.

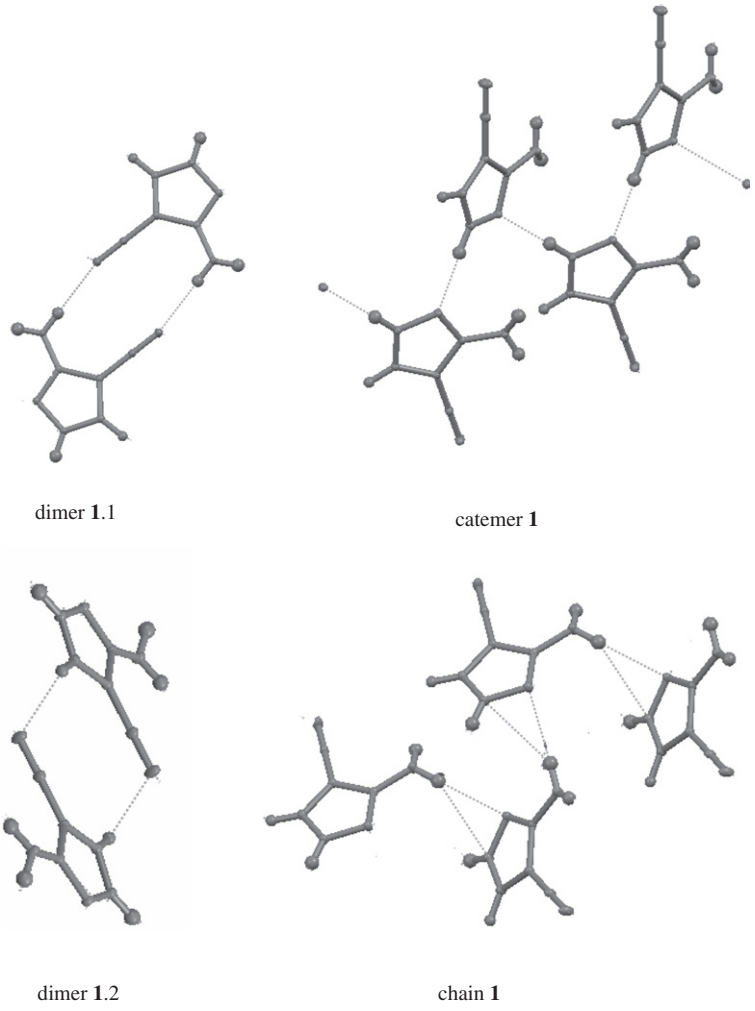


Fig. 6. Motives of hydrogen-bonded structures in crystals of pyrazole 1.

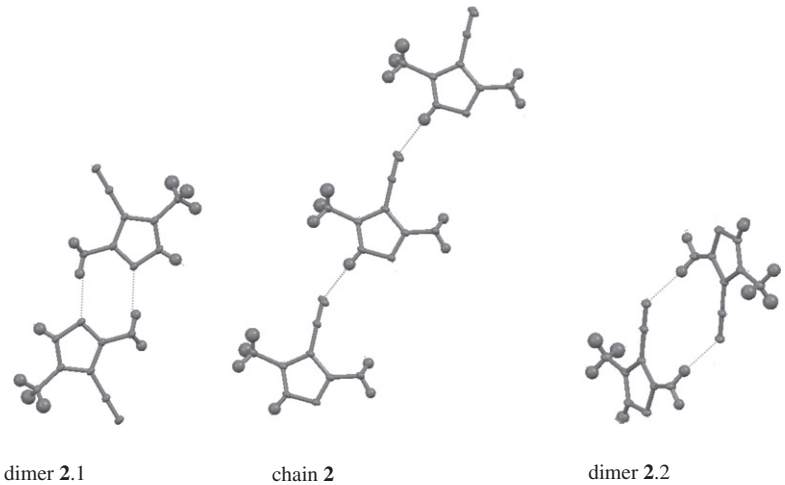


Fig. 7. Motives of hydrogen-bonded structures in crystals of pyrazole 2.

In the solid state, every two neighboring molecules of compound **1** are interconnected through van der Waals contacts between cyano nitrogen atom and C–H hydrogen atom of the ring (bond angles 145.7°) (Fig. 6, dimer 1.2). The amino hydrogen atom is linked with the ring nitrogen atom (Fig. 6, chain 1).

Pyrazole **2** differs from **1** in the composition of units forming the crystal lattice.

The dimers are formed by hydrogen bonds between the nitrogen atom of the pyrazole ring and one of the amino hydrogen atoms (Fig. 7, dimer **2**.1). Hydrogen bonds between the cyano

nitrogen atom and the NH group of the pyrazole ring link molecules of **2** in chains (Fig. 7, chain **2**). Also one can distinguish a dimer formed by weaker H-bonds (angle 136.8°) between the cyano nitrogen and amino hydrogen atoms (Fig 7, dimer **2**.2). It is worth noting that 5-amino-1-*tert*-butyl-3-phenylpyrazole-4-carbonitrile molecules are linked by the same H bonds and form not dimers but chains [28].

Thus, the formation of supramolecular assemblies in the crystals of compounds **1** and **2** is determined by hydrogen bonding with cyano, amino, and ring nitrogen atoms as well as by van der Waals interactions with each of the nitrogen atoms mentioned above.

3. Conclusions

Theoretical study of the free molecules of 3(5)-amino-4-cyanopyrazole and 3(5)-amino-4-cyano-5(3)-methylpyrazole molecules showed that 3-amino tautomers of these compounds are preferable.

Comparison of the total energy, free energy and enthalpy differences between tautomeric forms of the free molecules of 3(5)-amino-4-cyanopyrazole and 3(5)-amino-4-cyano-5(3)-methylpyrazole, calculated by DFT B3LYP/6-31G** and CBS-QB3 methods, showed that both methods can be used for finding the more stable tautomeric form of the free molecules of such 4-cyanopyrazoles.

Single crystal X-ray diffraction analysis showed that 3(5)-amino-4-cyanopyrazoles having hydrogen atom or methyl group in the 5(3)-position exist in the solid state exclusively as 3-amino tautomers.

Nitrogen and hydrogen atoms of the pyrazole ring as well as cyano and amino groups take part in the formation of various supramolecular structures in crystals of N-unsubstituted 3(5)-amino-4-cyanopyrazoles.

4. Experimental

4.1. General procedure

Pyrazoles (**1**, **2**) were prepared by adding ethoxymethylenemalonitrile or methylethoxymethylenemalonitrile to aq. hydrazine hydrate (35%) in ethanol with cooling, which was followed by refluxing for 1 h. After cooling, the resulting solid was collected by filtration and recrystallized from water (**1**) or acetonitrile (**2**) [30].

3(5)-Amino-4-cyanopyrazole **(1)**: mp 175 °C (H_2O), lit. mp 174–175 °C (H_2O) [31].

3(5)-Amino-4-cyano-5(3)-methylpyrazole **(2)**: mp 163 °C (CH_3CN), lit. mp 163 °C (ethanol–H_2O) [30].

4.2. X-ray Crystallography

Single crystals of **1, 2** suitable for X-ray diffraction analysis were grown from ethanol–water mixture (**1**) and acetonitrile (**2**). Diffraction data were collected on a Bruker Smart Apex II CCD (**1**) and Bruker Smart 1000 CCD (**2**) diffractometers [$\lambda(MoK_\alpha)$ = 0.71073 Å] at 100 (**1**) and 120 K (**2**). The substantial redundancy in data allows empirical absorption correction to be performed with SADABS, using multiple measurements of equivalent reflections. The structures were solved by direct methods and refined by the full-matrix least-squares technique against F^2 in the anisotropic-isotropic approximation. The hydrogen atoms were placed in geometrically calculated positions and refined using the rider model. All calculations were performed with the SHELXTL software package [32]. The crystal data and structure refinement parameters are listed in Table 4. The molecular drawings were prepared using ORTEP for Windows [33]. The crystallographic data have been deposited at the Cambridge Crystallographic Data Center, CCDC 836030 and 836031.

4.3. Computational methods

The molecular geometries were first optimized at the HF/6-31G computational level and then reoptimized at the DFT B3LYP/6-31G** computational level within the GAMESS-US package [21]. Frequency calculations at both levels were carried out to confirm that the structures obtained correspond to energy minima. Thermodynamic characteristics were calculated with the B3LYP/6-31G** optimized geometries. CBS-QB3 complete basis set extrapolation runs were done for additional geometry reoptimizations and accurate energy calculations within Gaussian03 package [22].

Acknowledgements

The authors are grateful to the Russian Foundation for Basic Research for the financial support (project no. 10-03-00600-a).

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