THE STRUCTURE OF AMINOAZOLES AND ITS RELATIONSHIP WITH AROMATICITY. CRYSTAL AND MOLECULAR STRUCTURE OF TWO POLYMORPHIC FORMS OF 4-AMINOPYRAZOLE

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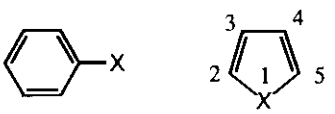
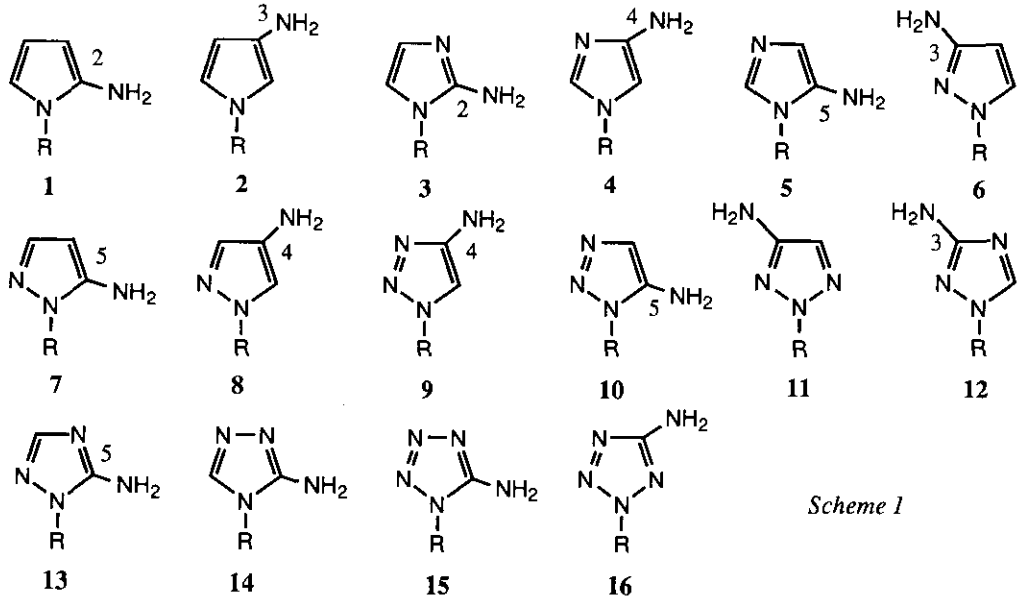
Abstract- Quantum mechanic calculations have been done at MP2 and B3LYP/ 6-31G** levels on six C-aminoazoles (α–aminopyrrole, 3-aminopyrazole, 5-aminopyrazole, 4-aminopyrazole, 5-amino-1,2,4-triazole, and 5-amino-1,2,3,4-tetrazole). These calculations have been used to discuss the molecular structure of these compounds in relation to their aromaticity. The crystal and molecular structure of two polymorphic forms of 4-aminopyrazole has been determined by X-Ray analysis. The main differences, between the two polymorphs, at molecular level lie in the conformation of the amino group and at the packing level in the hydrogen interactions involving the amino group.

Albert,[1] Kauffmann[2] and others[3-5] have proposed a simple qualitative way to classify aromatic heterocycles. According to this principle, azoles are like benzenes substituted with electron releasing groups (X = amino, alkoxy, thioalkoxy): the atom at position 1 (X = NR, O, S) plays the role of the NR_2, OR or SR group in substituted benzenes and for this reason are called π-excedent heterocycles. This is the case for the simplest aromatic five-membered rings, pyrroles, furan and thiophene, but the most common azoles contain other nitrogen atoms in position 2, 3, 4 or 5. The effect of these 'pyridine-like' nitrogen atoms is, according to these authors, comparable to that of a nitro group in benzene derivatives.



#Dedicated to Professor Bernhard Witkop on the occasion of his 80th anniversary

Let us consider, for the sake of simplicity, compounds containing only carbon and nitrogen atoms in the five-membered ring: pyrrole, imidazole, pyrazole, 1,2,3-triazole, 1,2,4-triazole and tetrazole (from now on, azoles, see Scheme 1). According to the above outlines, pyrrole should be like an anisole, imidazole and pyrazole (diazoles) like benzene, and triazoles and tetrazole, like nitrobenzene. We intend to go further on this qualitative principle and try to get some quantitative data. The approach we have tentatively chosen is to use, as a probe of the nature of the azole, the geometry of the C-amino group determined by X-Ray crystallography (already reported or described in this work).



Scheme 1

Simultaneously, we decided to carry out some calculations on the isolated molecules at two different theoretical levels (MP2//6-31G** and B3LYP//6-31G**) in order to avoid some of the shortcomings related to the localization of the hydrogen atoms of the NH_2 group by X-Ray diffraction. The six compounds calculated were 2–aminopyrrole (**1**), 3-aminopyrazole (**6**), 5-aminopyrazole (**7**), 4-aminopyrazole (**8**), 5-amino-1,2,4-triazole (**13**) and 5-amino-1,2,3,4-tetrazole (**15**) (Scheme 1, R = H).

In order to characterize the nature of the hybrid orbital associated with this lone-pair, we shall carry out a Natural Bond Order (NBO) analysis of the compounds under consideration. Very likely, changes in the conjugation of the amino lone-pair with the azole system would be reflected in concomitant changes in the aromaticity of the ring. Recently, Schleyer *et al.*[6] have proposed as a useful aromaticity probe, the so called Nuclear-Independent Chemical Shifts (NICS), defined as the absolute magnetic shielding computed at the ring centers. In this work, we will study whether this index is sensitive enough to account for the differences in aromaticity of the different aminoazoles. The lack of symmetry of the azoles prevents to locate the ring center by symmetry considerations. Hence, we have decided to evaluate the NICS at the (3,+1) ring critical points of the electron density, as defined by Bader.[7] This is an unambiguous choice since at this point, the electron density is a minimum with respect to displacements in the plane of the ring and a maximum with respect to displacements perpendicular to that plane.

RESULTS AND DISCUSSION

Theoretical calculations: comparison between the two methods

Theoretical calculations have been carried out by *ab initio* methods at MP2 and B3LYP/6-31G** levels.[8] The hybridization pattern of the NH_2 group will be reflected in the C-NH_2 bond length, in the HNH bond angle and in the properties of the amino lone pair. There were no data concerning 2-aminopyrrole and 4-aminopyrazole, but since the first one is a liquid it was decided to determine the structure of the second. The results of the calculations together with the experimental results determined by X-Ray crystallography are reported in Table 1. There are some relationships between these values, for instance between CN bond lengths (Å) and HNH angles (°) at the MP2 level (Eq. 1) or between CN distances calculated at the MP2 and B3LYP levels (Eq. 2, Table 1). With the most elaborated method, MP2, d_{CN} decreases in the order **1** > **7** > **8** > **6** > **13** > **15**.

X-Ray structure determination

The molecular structure of the two polymorphic forms of 4-aminopyrazole (**8**) (R = H), **I** and **II**, reported in Table 2 according to the numbering scheme depicted in Figure 1, has been tested by half normal probability plots.[10] The main difference between the two forms lies in the conformation of the NH_2 group, while in **I** the H61 is almost eclipsed to C3, in **II** it is twisted by 87(7)° with respect to the pyrazole ring (Table 2). No significant differences were observed when comparing the bond distances and angles with those of pyrazole itself regardless on whether they are analyzed by X-Ray[11] or by microwave spectroscopy[12] (Table 2) although in the last case the C3-C4 and C5-N1 distances appear to be somewhat lengthened and the angle at N1 enlarged. The H-N-H angle, 119(6)°, is comparable to the values observed in one of the two independent molecules of the aniline [119(4)° and 104(5)°].[14] This N atom lies slightly out of the pyrazole plane by 0.034(5) and 0.090(6) Å for **I** and **II** respectively, versus the 0.113(4) and 0.122(3) Å values found in aniline. In this last compound the conformation of the amino group is similar to that displayed by form **I** [-19(3)/-157(4)° and -29(4)/-156(2)°]. The *ipso* angle at C4 is not affected by the amino substituent[15] contrary to what happens in aniline ($\Delta\alpha$ = - 2.1°).

The polymorphs **I** and **II** exhibit different molecular arrangements through N-H···N intermolecular hydrogen bonding (Table 3). In form **I**, the N-H of the ring is involved in a strong hydrogen bond (N1-H1···N6) that induces the formation of infinite chains along [011] direction. These chains are then joined by weaker interactions to give a three-dimensional structure, Figure 2a and b. In **II**, the crystal packing involves two intermolecular hydrogen bonds (N1-H1···N2 and N6-H61···N6) that form sheets parallel to the [101] plane linked through N6-H62···N2 interactions, Figure 2c and d. In both forms, the packing is mainly determined by interactions that involve the N1 atom as donor, interactions which are stronger than those where the amino group participates as acceptor.[16] There are no voids in both structures and the total packing coefficients are 0.70 and 0.65 for the **I** and **II** forms respectively.[17] The difference between these values is also reflected in the density of the two polymorphs (Table 4).

Table 1. HF, MP2/6-31G** and B3LYP/6-31G* calculations and experimental X-Ray values (av means average value of two structures or two independent molecules of the same structure) of the geometry of amino derivatives

	Compound	MP2/6-31G**		B3LYP/6-31G**		Exp.		% s	NICS
		d_{CN} Å	(HNH)°	d_{CN} Å	(HNH)°	d_{CN} Å	(HNH)°		
1	α-Aminopyrrole	1.419	107.1	-----	-----	-----	-----	18.4	-14.7
6	3-aminopyrazole	1.405	109.0	1.398	110.5	1.366(-)	122(-)[a]	17.9	-16.3
7	5-aminopyrazole	1.417	107.3	1.416	107.3	1.377(4)	123(5)[b]	18.5	-14.2
8	4-aminopyrazole	1.410	108.0	1.406	109.0	1.414(7)	119(6)[c]	17.9	-15.1
13	5-amino-1,2,4-triazole[d]	1.394	109.4	-----	-----	1.341(8)	108(6)[e]	17.1	-11.8
15	5-amino-1,2,3,4-tetrazole	1.387	110.0	-----	-----	1.330(2)	119(2)[f]	16.7	-12.2

[a] Refcode: VORNIZ (3-amino-4-acetyl-5-methyl-1*H*-pyrazole); [b] Refcode: MAPARY (1-buten-2'-yl-3-methyl-5-aminopyrazole); [c] This work average values of both polymorphs [polymorph **I**, 1.420(7) Å, 125(5)°, polymorph **II**, 1.408(6) Å, 113(7)°]; [d] 1.371 Å, 112.4° (Hillier: HF/6-31G** calculations).[9] [e] Refcode: AMTRAZ (**13**); [f] Refcode: AMTETZ01 (**15** hydrate).

$$d_{CN}(MP2) = 2.5\pm0.1 - 11\pm1 \times 10^{-3}\ HNH(MP2),\ n = 6,\ r^2 = 0.96 \text{ (worse point: } \mathbf{6}) \quad (1)$$

$$d_{CN}(MP2) = 0.47\pm0.03 + 0.67\pm0.02\ d_{CN}(B3LYP),\ n = 3,\ r^2 = 0.999 \quad (2)$$

Table 2. Geometrical parameters (Å, °) for the two polymorphic form **I** and **II**. **A** and **B** represent the average geometry of pyrazole as obtained by X-Ray[11] and microwave[12] analysis. **C**, **D** and **E** stand for the *ab initio* results for the pyrazole at MP2/6-31G**[13] and for the title compound at MP2 and B3LYP/6-31G** levels respectively.

	I	II	A	B	C	D	E
N1-N2	1.355(6)	1.346(7)	1.341(6)	1.349(10)	1.348	1.344	1.341
N2-C3	1.339(8)	1.330(7)	1.329(10)	1.331(5)	1.347	1.350	1.335
C3-C4	1.397(6)	1.388(7)	1.382(10)	1.416(5)	1.406	1.408	1.408
C4-C5	1.374(7)	1.386(9)	1.376(10)	1.372(5)	1.385	1.390	1.386
C5-N1	1.346(6)	1.354(6)	1.332(11)	1.359(5)	1.360	1.364	1.367
C4-N6	1.420(7)	1.408(6)	-	-	-	1.410	1.406
C5-N1-N2	112.7(4)	112.2(3)	111.8(5)	113.1(3)	113.9	114.0	113.4
N1-N2-C3	104.0(4)	104.7(5)	104.9(5)	104.1(3)	103.4	103.5	104.2
N2-C3-C4	111.6(5)	112.1(4)	111.6(6)	111.9(3)	112.1	112.2	112.1
C3-C4-C5	105.0(4)	104.6(5)	104.4(5)	104.5(3)	104.9	104.7	104.3
C4-C5-N1	106.7(4)	106.4(4)	107.3(7)	106.4(3)	105.7	105.6	106.0
C3-C4-N6	128.1(5)	128.8(4)	-	-	-	127.5	127.2
C5-C4-N6	126.7(4)	126.5(4)	-	-	-	127.6	128.4
C4-N6-H61	109(3)	112(6)	-	-	-	111	112
C4-N6-H62	102(4)	119(4)	-	-	-	112	113
H61-N6-H62	125(5)	113(7)	-	-	-	108	109
$\Sigma\alpha$(N6)	336(4)	344(6)	-	-	-	331	334
N2-C3-C4-N6	-175.3(5)	-177.8(6)	-	-	-	175.6	176.5
C3-C4-N6-H61	-8(4)	87(7)	-	-	-	30	31
C3-C4-N6-H62	-142(4)	-139(6)	-	-	-	151	155

Table 3. Hydrogen bond interactions (Å, °).

Compound	D-H...A	D-H	D...A	H...A	D-H...A
I	N1-H1...N6(1/2-x,y-1/2,z-1/2)	0.88(6)	2.892(6)	2.01(6)	176(5)
	N6-H61...N2(-x,-y,z+1/2)	0.94(6)	3.214(8)	2.33(6)	157(5)
	N6-H62...N2(x,y+1,z)	0.92(7)	3.458(6)	2.72(7)	138(5)
II	N1-H1...N2(1-x,1-y,1/2+z)	1.00(6)	2.949(6)	1.97(6)	164(5)
	N6-H61...N6(3/2-x,y,z+1/2)	0.95(13)	3.069(10)	2.35(12)	132(9)
	N6-H62...N2(x,y-1,z)	0.95(7)	3.173(5)	2.24(7)	169(7)
	C5-H5...CEN1*(1-x,-y,1/2+z)	1.05(7)	3.580(6)	2.68(6)	144(4)

* CEN1 = *pyrazole centroid.*

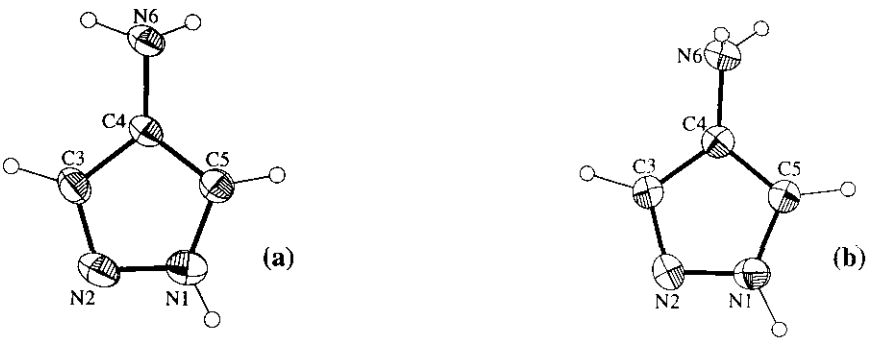


Figure 1. - Perspective view of **I** (**a**) and **II** (**b**) showing the atomic numbering. Displacement ellipsoids are scaled to enclose 30% probability, and the H atoms are denoted as spheres of 0.1Å radii.

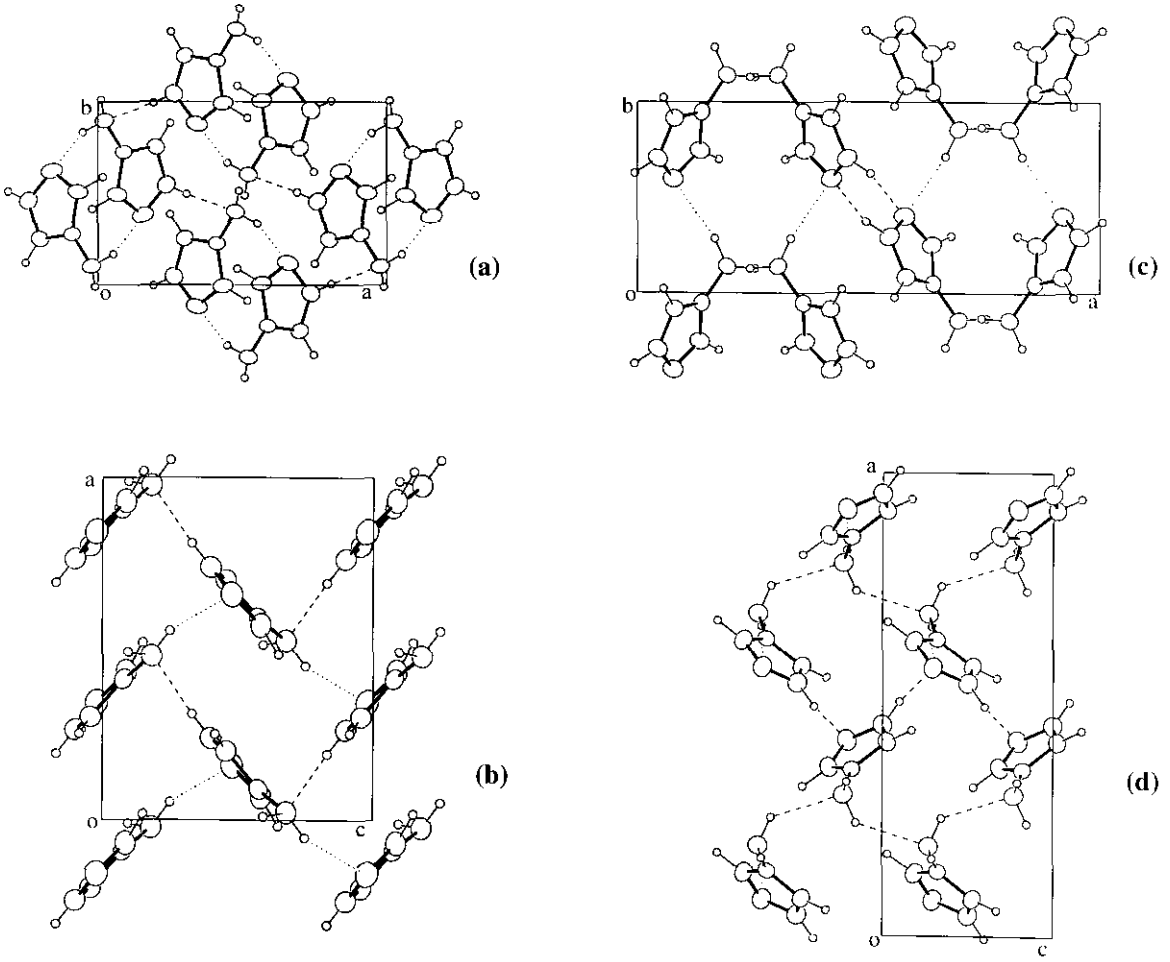


Figure 2. - Crystal packing along the **c** and **b** axes of **I**, [(**a**) and (**b**)]; and **II**, [(**c**) and (**d**)] respectively. Dashed lines show the hydrogen bonds which form the chain in **I** and the sheet in **II** while dotted lines show the interaction joining the chains or sheets in **I** and **II** respectively.

Comparison between calculated and experimental geometries

Concerning 4-aminopyrazole (**8**), this study shows that there are very small differences in the optimized geometries obtained by all methods. As pointed out by Ma *et al.*[18] the B3LYP method affords results that are slightly closer to the experimental values than those obtained by the MP2 method for the first-row atoms (Tables 1 and 2). Thus, in the pyrazole ring (see Figure 1 for the numbering scheme) the N=C double bond (N2-C3) is shortened by 0.015 Å and the angles at N1 and N2 are narrowed and widened by 0.6° and 0.7° respectively. The external angles at C4 (where the amino group is attached), namely C3C4N6 and C5C4N6, calculated by both methods are also different. While the MP2 approach predicts them to be equal, the B3LYP formalism yield values which differ by more than 1 degree. It must be noted however that B3LYP values present the opposite tendency to that shown by the experimental results. The degree of pyramidalization of the N6 atom is found to be analogous to that of the experimental results, this atom deviates by 0.085 Å (MP2), 0.069 Å (B3LYP) from the pyrazole plane. No influence of the amino group on the geometry of the pyrazole has been detected. The perpendicular conformation adopted by the amino (C-C-N-H: ±30/±150°) enables the N atom lone pair to overlap with the π system of the pyrazole. The other two conformations, C-C-N-H: 0/-120° and 90/-150°, have also been computed with similar approaches and both are less stable than the previous one. Apart from the conformation of the amino group in form **II** (see below) there is a good agreement between the theoretical calculation and the experimental results.

The predicted energy difference between 3-amino- (**6**) and 5-aminopyrazole (**7**) is only 1.3 (MP2) or 2.7 kcal mol^{-1} (B3LYP), the 3-amino one (**6**) being the most stable in agreement with the experiment and with other calculations.[19,20] While in the first one, the conformation of the amino group is like in the polymorph **I** of 4-aminopyrazole (N2-C3-N6-H61/H62 = 12/133° and 15/140° for the MP2 and B3LYP geometries) in the second one, the lone pair direction is parallel to the pyrazole plane towards N1, (N1-C5-N6-H61/H62 = 121/-120° and 120/-120° for MP2, B3LYP respectively), with no overlap between it and the pyrazole ring as it was found before for the polymorph **II** of 4-aminopyrazole.

These results show that the energy difference between conformations in which the amino lone pair conjugates with the ring and those where this conjugation is not possible, is only of a few kcal mol^{-1}. Actually, in 5-aminopyrazole, the nitrogen lone pair of the amino group prefers to interact with the positively charged imino hydrogen than to conjugate with the azole. This result is consistent with the fact that this compound presents the longest C-NH_2 bond, the smallest HNH bond angle and the less negative NICS value of the three aminopyrazole isomers. Now, it is possible to compare the calculated and experimental geometries for five out of six compounds of Table 1 [no experimental data for pyrrole (**1**)]. The results (Eqs. 3 and 4) are clearly disappointing.

$$d_{CN}(MP2) = 1.0\pm0.2 + 0.30\pm0.12\ d_{CN}(Exp),\ n = 5,\ r^2 = 0.65 \text{ (worse point: } \mathbf{7}) \quad (3)$$

$$HNH(MP2) = 119\pm11 - 0.09\pm0.09\ HNH(Exp),\ n = 5,\ r^2 = 0.22 \text{ (worse point: } \mathbf{15}) \quad (4)$$

The experimental geometries correspond to compounds containing other substituents than the amino group, only **8** (two polymorphs), **13** and **15** (an hydrate) have identical structures to those that have been calculated. Considering only these compounds, the relationships continue to be very unsatisfactory. Clearly, X-Ray geometries can be reproduced by gas phase calculations only with very moderate success. The use of the X-Ray geometries of amino groups has some shortcomings. The C-N distance is normally known with good precision but the H-N-H angle involves the position of two light hydrogen atoms and is sensitive to hydrogen bonds (both intra and intermolecular), therefore may contain much error.

The structure of aminoazoles in the gas phase and its relationship with aromaticity

Since the experimental approach to the classification of azoles using solid-state geometries has failed it remains that we have a consistent set of calculated geometries at the MP2 level which are as good as experimental geometries in the gas-phase.[13] In Table 1 are reported the geometrical parameters, d_{CN} and HNH angle [but, since they are linearly related, see Eq. (1), we will discuss only the distance], the % of s character of the amino lone-pair (at the same level) and the NICS.

The simple Albert-Kauffmann model presented in the introduction,[1,2] implies that the properties of azoles should be related to the number of nitrogen atoms in the five membered ring. The most obvious assumption is that one property of the azoles, in the present case of aminoazoles, the d_{CN} bond length, is related to the number of 'pyridine-like' nitrogen atoms **N** (from pyrrole **N** = 0 to tetrazole **N** = 3), following a Zipf-Mandelbrot relationship (5,6):[21]

$$d_{CN} = 1/(\mathbf{N} + a)^b \qquad (5) \qquad\qquad \log d_{CN} = - b \log (\mathbf{N} + a) \qquad (6)$$

The data of Table 1 for the four azoles that follow Eq. (6) (**1**, **6**, **13**, **15**) were adjusted to the best value of a (less RMS error) which appear to be exactly 2:

$$\log d_{CN} = 0.1596\pm0.0003 - 0.0251\pm0.0005 \log (\mathbf{N}+2),\ n = 4,\ r^2 = 0.999 \qquad (7)$$

Aminopyrazoles (**7**) and (**8**) do not belong to this equation. Fitting their d_{CN} values to Eq. (7), it results in **N** values of 0.12 and 0.58 respectively instead of 1 (as in pyrazole **6**), see Figure 3.

For the three pyrazoles, the **N** values (**6** 1.00, **7** 0.12 and **8** 0.58) are linearly related to the aromaticity as measured by the NICS:

$$\mathbf{N} = -5.2\pm0.3 - 0.38\pm0.02\ \text{NICS},\ n = 3,\ r^2 = 0.997 \qquad (8)$$

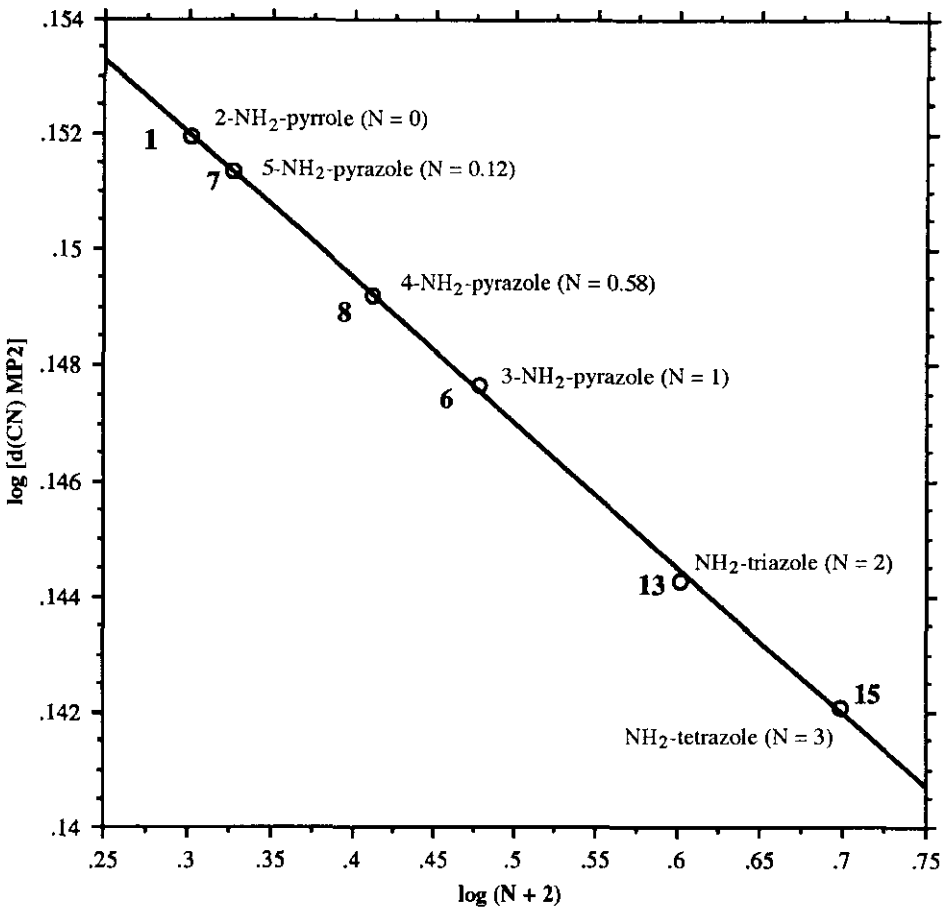


Figure 3. Representation of Eq. (7) using fitting values for aminopyrazoles (**7**) and (**8**)

The NICS values can only be used within a specific azole, for instance pyrazoles, and in that case the amino substituent seems to modify the aromaticity of the ring which decreases 3-amino (**6**) > 4-amino (**8**) > 5-amino (**7**). The same is reflected in the conjugation of the amino lone pair with the azole π system as measured by its percentage of s character:

$$\log (\%\ s) = 1.301 \pm 0.005 - 0.111 \pm 0.009 \log (N+2),\ n = 6,\ r^2 = 0.97 \qquad (9)$$

EXPERIMENTAL

Materials. 4-Aminopyrazole was obtained by catalytic hydrogenation of 4-nitropyrazole.[3]

X-Ray Crystallography. Two types of crystals slightly different in shape were obtained when crystallizing in chloroform. A summary of data collection and refinement process for the two polimorphic

Table 4. Crystal analysis parameters at room temperature.

	I	II
Crystal data		
Formula	$C_3H_5N_3$	$C_3H_5N_3$
Crystal habit	Colourless prism	Colourless needle
Crystal size (mm)	0.33 x 0.13 x 0.17	0.67 x 0.13 x 0.10
Symmetry	Orthorhombic, $Pna2_1$	Orthorhombic, $Pca2_1$
Unit cell determination:	Least-squares fit from 56 reflexions ($\theta < 45°$)	Least-squares fit from 26 reflexions ($\theta < 43°$)
Unit cell dimensions ($Å^3$,°)	a=9.3259(6)	a=14.3057(16)
	b=5.9212(2)	b=5.9094(4)
	c=7.3649(4)	c=5.2673(3)
	90, 90, 90	90, 90, 90
Packing: V($Å^3$), Z	406.70(3), 4	445.29(5), 4
Dc(g/cm^3), M, F(000)	1.357, 83.09, 176	1.239, 83.09, 176
$\mu(cm^{-1})$	7.79	7.11
Experimental data		
Four circle diffractometer:	Philips PW1100	
	Graphite monochromator. CuKα, ω/2θ scans. Bisecting geometry	
	Detector apertures 1 x 1°.	
$\theta_{max.}$	65.0°	
Scan width	1.5°	
Scan speed	1 min./reflection	
Number of reflexions:		
Independent	373	424
Observed ($2\sigma(I)$ criterion)	312	347
Standard reflexions:	2 reflexions/90 minutes. No variation	
Solution and refinement		
Solution	direct methods, SIR92	
Refinement least-squares on Fo	full matrix	
Secondary extinction (/10)	50(5)	31(4)
Parameters:		
Number of variables	74	74
Degrees of freedom	236	273
Ratio of freedom	4.2	4.7
H atoms	From difference synthesis	
Weighting-scheme	Empirical as to give no trends in $<\omega\Delta^2F>$ vs. $<\|Fobs\|>$ and $<\sin\theta/\lambda>$	
Max. thermal value ($Å^2$)	U11(N(2))=0.083(3)	U11(N(2))=0.072(2)
Final Δρ peaks ($eÅ^{-3}$)	±0.20	±0.23
Final R and Rw	0.041, 0.047	0.046, 0.055

forms (**I** and **II**) is given in Table 4. All non-hydrogen atoms were found by direct methods (SIR92)[22] and the structures were refined with a full matrix least squares procedure on Fobs using anisotropic displacement parameters. All hydrogen atoms were located on the corresponding difference Fourier syntheses and refined isotropically in the last cycles. The atomic scattering factors were taken from the *International Tables for X-Ray Crystallography*.[23] Most calculations were mainly carried out with the XTAL,[24] PESOS,[25] PARST[26] set of programs running on a VAX 6410 computer. The *ab initio* calculations were performed using the GAUSSIAN94 program[8] on a AXP 2100 workstation. Lists of the structure factors, thermal components for the non-hydrogen atoms and hydrogen atom parameters have been deposited at the Cambridge Crystallographic Data Center, Lensfield Rd, Cambridge, U.K. (CCDC).

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