

Theoretical Calculations on Pyrazole Derivatives. Part 2.¹ Effect of Cationic C-Substituents (NH_3^+ and N_2^+) on the Basicity and Tautomerism of Pyrazoles

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Semiempirical and *ab initio* calculations have been performed on pyrazoles with 3- or 5-cationic substituents, *e.g.* NH_3^+ and N_2^+ , with the aim of discovering if these substituents were able to shift the tautomeric equilibrium towards one of the tautomers. The ammonium substituent is not amenable to the experiment since 3(5)-aminopyrazoles protonate on the pyrazole ring; however, pyrazole-3(5)-diazonium is stable and has been studied. The conclusion is that these equilibria are strongly shifted towards the 3-substituted tautomer. The azide substituent behaves normally in the sense that both tautomers are of similar stability.

In the preceding paper of this series,¹ we described the behaviour of a large set (156 compounds) of NH and *N*-methylpyrazoles. One of the conclusions of this study and of a preceding one,² is that the difference in energy between tautomers carrying neutral substituents (as different as NO_2 , SO_2CF_3 , OMe , NMe_2 , Bu^t) is quite small: *i.e.* both tautomers exist in comparable amounts.

In a previous paper we described the complex acid-base equilibria of 3(5)-aminopyrazole **1** (see Fig. 1).² This compound exists as a mixture of two tautomers, **1a** and **b**. Monoprotonation can yield three different cations: protonation on the pyrazole ring yields cation **2** which is common to both tautomers. Protonation on the amino group yields cations **3a** and **b**, which, in turn, are in tautomeric equilibrium (the common dication **4** was neither calculated nor measured). All the evidence, experimental as well as theoretical, points to cation **2** as the most stable monoprotonated derivative, both in the gas phase and in solution. For cations **3a** and **b**, only theoretical evidence was gathered (6-31G//6-31G calculations):² owing to a mistake in the graphical representation it appears that cation **3b** was more stable than cation **3a**. Actually (see Fig. 2) cation **3a** is more stable than cation **3b** by 18.33 kcal mol⁻¹ (1 cal = 4.184 J). Cation **2** lies 21.75 kcal mol⁻¹ lower than cation **3a**.

In reference 1, which deals with AM1 calculations, these calculations were repeated, but only for pyrazoles bearing neutral substituents and their common cations, for instance **1a**, **1b** and **2**. We describe here the case of charged substituents NH_3^+ and $\text{N}(\text{CH}_3)_3^+$ including the double charged common cations, such as **4**. For comparative purposes, the case of the azido substituent, $-\text{N}^--\text{N}^+\equiv\text{N}$ was also included. All the results are gathered in Table 1.

Since cations **3a** and **b** cannot be studied experimentally, we decided to explore, both theoretically and experimentally, the related case of pyrazole-3(5)-diazonium **5** (see Fig. 3). Compound **5** has been described by Reimlinger,³ who reports only its UV spectrum. We have prepared this compound as well as its *N*-methyl derivatives **7** and **8** from the corresponding aminopyrazoles.

Results and Discussion

Experimental Study of the Tautomerism of Pyrazole-3(5)-diazonium Hexafluorophosphate.—We have gathered in Table 2 all the spectroscopic information about compounds **5**, **7** and **8**.

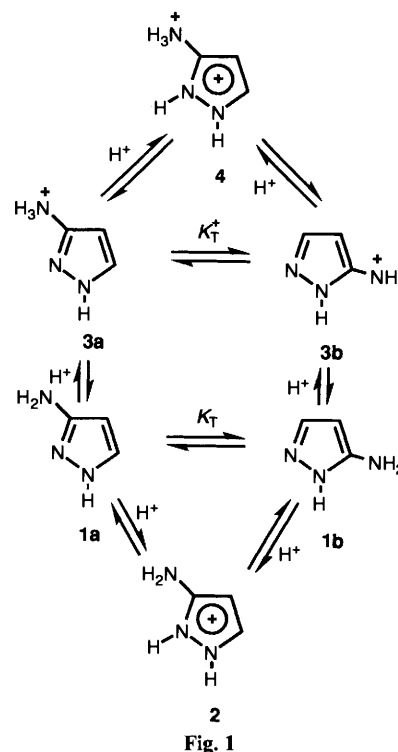


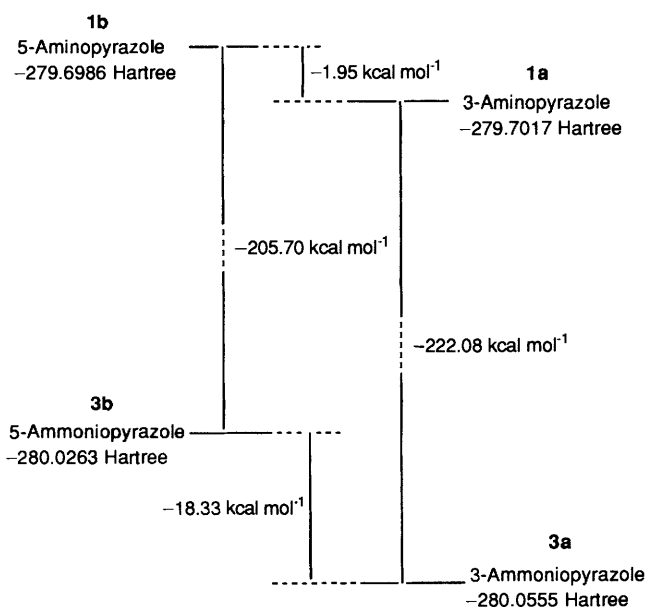
Fig. 1

Compound **7** is a good model of tautomer **5a** but compound **8** is a less convenient model for tautomer **5b** since there is an interaction between the *N*-methyl and the 5-diazonium groups which could affect the spectroscopic properties. Nevertheless, it is clear that compound **5** closely resembles **7** and that it is quite different from **8**. For instance, the UV spectra of **5** and **7** are identical while that of **8** is very different. The same happens if one considers the ¹H chemical shifts, for instance the difference between the signals of protons H₃(H₅)–H₄ is 0.55, 0.57 and 0.07 ppm for **5**, **7** and **8**, respectively. The ³J(¹H–¹H) coupling constants cannot be used for this purpose since the three values are very similar (2.5–2.7 Hz). When the ¹³C NMR spectrum of **7** was recorded in [²H₆]DMSO, the signal of the C₃₍₅₎–H at 134.6 ppm was very broad and that of C₅₍₃₎–N₂⁺ was not observed (that of C₄–H appeared at 115.65 ppm). The addition of a drop of trifluoroacetic acid resulted in a narrowing of all signals which were slightly shifted (between 0.5 and 1 ppm). Again,

Table 1 AM1 Calculations of pyrazoles carrying charged substituents, heat of formation and protonation enthalpies (all values in kcal mol⁻¹)

No.	Compound	R ₁	R ₃	R ₄	R ₅	Δ _f H	-Δ _p H	μ/D
3a	3-ammonio	H	NH ₃ ⁺	H	H	222.0	93.5	—
3b	5-ammonio	H	H	H	NH ₃ ⁺	232.4	103.9	—
4	common cation	—	—	—	—	495.7	—	—
9a	3-trimethylammonio	H	N(CH ₃) ₃ ⁺	H	H	233.8	105.4	—
9b	5-trimethylammonio	H	H	H	N(CH ₃) ₃	243.1	114.7	—
10	common cation	—	—	—	—	495.6	—	—
5a	3-diazonio	H	N ₂ ⁺	H	H	297.2	81.3	—
5b	5-diazonio	H	H	H	N ₂ ⁺	305.9	90.0	—
6	common cation	—	—	—	—	583.1	—	—
11	4-diazonio	H	H	N ₂ ⁺	H	290.5	94.0	—
12	corresponding cation	—	—	—	—	563.7	—	—
13	3,5-dimethyl-4-diazonio	H	CH ₃	N ₂ ⁺	CH ₃	269.0	104.6	—
14	corresponding cation	—	—	—	—	531.6	—	—
7	1-methyl-3-diazonio	CH ₃	N ₂ ⁺	H	H	299.7	89.2	—
15	corresponding cation	—	—	—	—	577.7	—	—
16	1-methyl-4-diazonio	CH ₃	H	N ₂ ⁺	H	292.4	100.9	—
17	corresponding cation	—	—	—	—	558.7	—	—
8	1-methyl-5-diazonio	CH ₃	H	H	N ₂ ⁺	308.0	96.3	—
18	corresponding cation	—	—	—	—	578.9	—	—
19a	3-azido	H	N ₃	H	H	149.6	205.1	2.93
19b	5-azido	H	H	H	N ₃	151.7	207.2	1.24
20	common cation	—	—	—	—	311.7	—	—
21	3-azido-4-phenyl	H	N ₃	C ₆ H ₅	H	175.0	207.0	2.74
22	corresponding cation	—	—	—	—	335.2	—	—
23	4-azido	H	H	N ₃	H	150.0	200.6	2.84
24	corresponding cation	—	—	—	—	316.6	—	—
25	1-methyl-3-azido	CH ₃	N ₃	H	H	155.2	208.7	3.33
26	corresponding cation	—	—	—	—	313.7	—	—
27	1-methyl-4-azido	CH ₃	H	N ₃	H	155.6	205.4	2.81
28	corresponding cation	—	—	—	—	317.4	—	—
29	1-methyl-5-azido	CH ₃	H	H	N ₃	157.4	210.1	1.52
30	corresponding cation	—	—	—	—	314.5	—	—

^a 1 cal = 4.184 J.

**Fig. 2**

compound **5** is more similar to compound **7** than to compound **8**, both in ¹³C chemical shifts and in ¹H-¹³C coupling constants. The ¹³C CPMAS NMR spectrum of compound **5** does not show any splitting of signals, indicating that only one tautomer is present and the chemical shifts (see Table 2) prove that it is tautomer **5a**.

It is clear that tautomer **5a** predominates in solution and that it is the only one present in the solid state. Nevertheless, the

difference in energy with regard to tautomer **5b** does not seem to be as large as 8.7 kcal mol⁻¹ (see Table 1) since the broadening of signals in DMSO solution points to a slow equilibrium between both tautomers with an appreciable amount of the minor one (the presence of 1% of the minor tautomer corresponds to a difference in energy of less than 2.7 kcal mol⁻¹). The addition of a small amount of trifluoroacetic acid increases the rate of interconversion without shifting the equilibrium.

We carried out a 6-31G//6-31G calculation on compounds **5a** (-332.641 33), **5b** (-332.618 02) and **6** (-332.796 05 Hartree). The difference in energy between both tautomers is 14.63 kcal mol⁻¹, *i.e.*, larger than the AM1 value. Then, we calculated the 6-31G**//6-31G energies of tautomers **5a** and **b** (-332.828 14 and -332.804 25 Hartree) which correspond to a difference in energy of 15.00 kcal mol⁻¹, *i.e.*, a value slightly bigger than the 6-31G//6-31G values.

We now return to the AM1 values of Table 1. Compounds **13** and **21** were studied since they are the only pyrazoles bearing diazonio or azido substituents whose structures have been determined by X-ray crystallography.^{4,5} They can be used to ascertain whether the AM1 optimized geometries are a good approximation to the experimental ones (see supplementary material). Concerning the pyrazole ring, AM1 geometries reproduce the main features of this ring,⁶ but, for compounds **13** and **21**, they overestimate all bond lengths (maximum deviations, C₃-C₄ of compound **13**, Δ*r* = 0.057 Å) except the N₁-N₂ bond which is underestimated (-0.032 and -0.042 Å for compounds **13** and **21**, respectively). Concerning bond angles, deviations up to 3° are observed, these deviations mainly affect the *ipso* carbon atom, *i.e.* C₄ for compound **13** (Δ*θ* = -3.1°) and C₃ for compound **21** (Δ*θ* = -3.2°).

The geometry of the diazonium group in compound **13** is

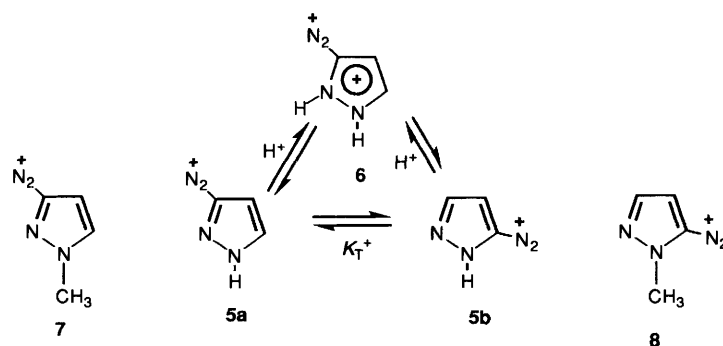


Fig. 3

Table 2 Spectroscopic properties of pyrazole-3(5)-diazoniums **5**, **7** and **8**: UV (λ_{\max} , log ϵ) in CH₃OH and NMR (δ , J) in [2H₆]DMSO solution

Compound	UV	¹ H NMR	¹³ C NMR ^a
5	257 (3.97) ^b	7.75 (H ₄), 8.30 (H ₅), 5.5 (br) (NH) $J_{4,5} = 2.54$	119.95 (C ₃), 114.20 (C ₄), 135.08 (C ₅) C ₃ : ^d C ₄ : ¹ J = 198.6, ² J = 9.1; C ₅ : ¹ J = 202.7, ² J = 6.9
7	257 (3.98)	7.82 (H ₄), 8.39 (H ₅), 4.20 (N-CH ₃) $J_{4,5} = 2.69$	121.76 (C ₃), 116.47 (C ₄), 136.40 (C ₅); ^c 42.03 (N-CH ₃) C ₃ : ² J = 6.3; C ₄ : ¹ J = 198.7, ² J = 10.0; C ₅ : ¹ J = 202.7, ² J = 8.0; ^c CH ₃ : ¹ J = 144.2
8	221 (3.89), 265 (3.94)	8.14 (H ₃), 8.07 (H ₄), 4.31 (N-CH ₃) $J_{3,4} = 2.62$	140.63 (C ₃), 121.03 (C ₄), 113.47 (C ₅), 40.77 (N-CH ₃) C ₃ : ¹ J = 201.1, ² J = 4.0; C ₄ : ¹ J = 197.5, ² J = 11.4; C ₅ : ² J = 7.7; CH ₃ : 145.3

^a In the case of compound **5** a drop of trifluoroacetic acid was added to the [2H₆]DMSO solution. ^b Reimlinger³ reports only a figure from which an approximate value of 255 nm can be read. ^c This carbon atom shows ³J_{Me} 2.7 Hz. ^d The ²J coupling constant cannot be measured.

perfectly described by the AM1 calculation—both bond lengths and angles (see Table 3). The AM1 calculation reproduces correctly the most interesting feature of the 3-azidopyrazoles: ⁵ the azido group is bent towards the N₂ lone pair. The angle C₃-N₃-N₄ is 120.2° (AM1) and 119.2° (X-ray structure of **21**). The main difference between the calculated and the experimental geometry concerns the C₃-N₃-N₄ angle ($\Delta\theta = 6.0^\circ$) and the torsion angles of the 3-azido and the 4-phenyl groups. The experimental geometry has an almost planar phenyl group (torsion 4°) and an out-of-plane azido group (torsion 16°) while the contrary is found in the calculated geometry of **21** (torsions of 38° and 4°, respectively).

The azido substituent, although a neutral one, has a dipolar nature and azidopyrazoles have been the subject of our interest in the past [3(5)-azido- **19** and 3-azido-4-phenyl-pyrazole **21** were among the compounds studied].⁷⁻⁹

Taking into account that the gas phase basicity of pyrazole itself, as calculated by the AM1 method,¹ is $-\Delta_p H = 202.9$ kcal mol⁻¹, the cationic substituents are strongly base-weakening groups. Defining $\delta\Delta_p H = \Delta_p H(\text{pyrazole}) - \Delta_p H(\text{substituted pyrazole})$, these effects are: 3-NH₃⁺ (from **3a**) 109.4; 5-NH₃⁺ (from **3b**) 99.0; 3-NMe₃⁺ (from **9a**) 97.5; 5-NMe₃⁺ (from **9b**) 88.2; 3-N₂⁺ (from **5a**) 121.6; 5-N₂⁺ (from **5b**) 112.9, and 4-N₂⁺ (from **11**) 108.9 kcal mol⁻¹. Thus, the importance of the effect decreases in the order 3 > 5 > 4 and N₂⁺ > NH₃⁺ > N(CH₃)₃⁺.

For the set of 156 pyrazoles,¹ the *N*-methylation effect corresponds to an average increase in the basicity of 5.0 kcal mol⁻¹. This effect is larger for diazonium derivatives (**5a/7**, +7.9, **5b/8**, +6.3, **11/16**, +6.9 kcal mol⁻¹). For the three cationic substituents studied, the tautomeric equilibrium is always significantly shifted towards the 3-substituted tautomer (in parentheses, the AM1 difference in energy): ammonio **3a** (10.4), trimethylammonio **9a** (9.3) and diazonio **5a** (8.7 kcal mol⁻¹).

On the other hand, the azido group behaves like a neutral substituent, the 3-substituted tautomer **19a** is still the most

stable but the difference in energy is much lower (2.1 kcal mol⁻¹). Experimental results,⁸ point out to the predominance of **19a** over **19b**.

Conclusions

In the preceding paper in this series,¹ we analysed the effect of neutral substituents on the basicity of pyrazoles using the Taft-Topsom three parametric model.¹⁰ The σ_x , σ_F and σ_R^+ coefficients are not known for the substituents of the present work (NH₃⁺, NMe₃⁺, N₂⁺ and N₃) but it is evident that the very large $\delta\Delta_p H$ effects observed for the first three substituents cannot be explained in the same way. Probably, the equations established for neutral substituents are not valid for charged ones.

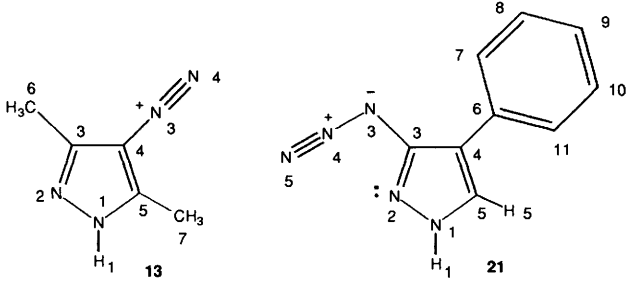
Experimental

Melting points were determined with a Reichert-Jung Thermovar apparatus and are uncorrected. Elemental analyses were obtained from the *Centro Nacional de Química Orgánica*.

General Procedure.—The corresponding aminopyrazole (3-aminopyrazole is commercially available, 3-amino-1-methyl- and 5-amino-1-methyl-pyrazoles have been described previously)¹¹ was added to a mixture of 65% hexafluorophosphoric acid and methanol (to improve the miscibility). The solution was cooled to -20 °C, then isopentyl nitrite was added under stirring. The mixture was left for 1 h at this temperature and then diluted with 15 cm³ of diethyl ether-methanol (5:1). The product, a fine whitish powder, precipitated on cooling at -17 °C.

1H-Pyrazole-3-diazonium hexafluorophosphate (5). 3(5)-Amino-1H-pyrazole (680 mg, 8.0 mmol), 65% hexafluorophosphoric acid (2 cm³), methanol (0.5 cm³) and of isopentyl nitrite (3.5 cm³), reacting under the conditions given above, yielded 1.20 g (61%) of compound **5**.

Table 3 AM1 Calculated and experimental geometries [bond length/Å, bond angle °, torsion angle °] of 3,5-dimethylpyrazole-4-diazonium chloride **13** (CSD Refcode: DEMCAZ) and 3-azido-4-phenylpyrazole **21** (CSD Refcode: PAZDPY)^a



13		21			
	Calc.	Exp.			
N ₁ -N ₂	1.347	1.379	N ₁ -N ₂	1.331	1.373
N ₂ -C ₃	1.350	1.313	N ₂ -C ₃	1.382	1.360
C ₃ -C ₄	1.480	1.423	C ₃ -C ₄	1.464	1.417
C ₄ -C ₅	1.448	1.404	C ₄ -C ₅	1.408	1.389
N ₁ -C ₅	1.372	1.326	C ₅ -N ₁	1.390	1.359
C ₃ -C ₆	1.472	1.486	C ₃ -N ₃	1.408	1.406
C ₅ -C ₇	1.469	1.475	N ₃ -N ₄	1.266	1.244
C ₄ -N ₃	1.350	1.351	N ₄ -N ₅	1.131	1.140
N ₃ -N ₄	1.115	1.095	C ₄ -C ₆	1.439	1.481
N ₁ -H ₁	1.005	1.079	C _{ar} -C _{ar}	1.397	1.390
C _i -H _i	1.12	1.076	N ₁ -H ₁	0.992	0.967
			C _i -H _i	1.10	1.035
H ₁ N ₁ N ₂	119.0	122.7	H ₁ N ₁ N ₂	119.6	117.9
N ₁ N ₂ C ₃	108.1	106.2	N ₁ N ₂ C ₃	106.3	102.8
N ₂ C ₃ C ₄	107.9	107.9	N ₂ C ₃ C ₄	109.6	112.8
C ₃ C ₄ C ₅	105.4	108.5	C ₃ C ₄ C ₅	104.0	103.9
C ₄ C ₅ N ₁	104.3	102.9	C ₄ C ₅ N ₁	107.0	107.4
C ₅ N ₁ N ₂	114.2	114.4	C ₅ N ₁ N ₂	113.0	113.1
N ₂ C ₃ C ₆	126.5	123.7	N ₂ C ₃ N ₃	127.8	121.5
C ₄ C ₅ C ₇	129.4	131.9	C ₃ N ₃ N ₄	120.2	119.2
C ₃ C ₄ N ₃	126.8	125.4	N ₃ N ₄ N ₅	169.5	171.9
C ₄ N ₃ N ₄	178.7	177.5	C ₃ C ₄ C ₆	129.1	123.6
H _i C _j C _k (Me)	110.0	109.7	C ₄ C ₆ C ₇	121.5	118.0
			H ₅ C ₅ C ₄	130.2	133.4
			C _i C _j C _k (Ar)	120.0	120.0
			H _i C _j C _k	120.0	120.0
C ₃ C ₄ N ₃ N ₄	0.0	0.0	C ₇ C ₆ C ₄ C ₃	39.6	3.8
			C ₁₁ C ₆ C ₄ C ₅	37.9	4.0
			N ₄ N ₃ C ₃ C ₄	175.5	164.5
			N ₅ N ₄ N ₃ C ₃	180.0	173.6

^a CSD: Cambridge Structural Database (F. H. Allen, J. E. Davies, J. J. Galloy, O. Johnson, O. Kennard, C. F. Macrae, E. M. Mitchell, G. F. Mitchell, J. M. Smith and D. G. Watson, *J. Chem. Inf. Comput. Sci.*, 1991, **31**, 187).

1-Methyl-1H-pyrazole-3-diazonium hexafluorophosphate (7). 3-Amino-1-methyl-1H-pyrazole (200 mg, 2.0 mmol) 65% hexafluorophosphoric acid (1 cm³), methanol (0.4 cm³), and isopentyl nitrite (0.4 cm³) yielded 0.68 g (95%) of compound **7**.

1-Methyl-1H-pyrazole-5-diazonium hexafluorophosphate (8). 5-Amino-1-methyl-1H-pyrazole (90 mg, 0.9 mmol), 65% hexafluorophosphoric acid (3 cm³), methanol (0.4 cm³) and isopentyl nitrite (0.4 cm³) reacted under the conditions given above, yielding 0.084 g (37%) of compound **8**.

UV Spectroscopy.—The UV spectra were recorded in methanol on a Perkin-Elmer 550 SE spectrophotometer.

NMR Spectroscopy.—The ¹H and ¹³C NMR spectra in solution were recorded on Bruker AM-200 and Varian Gemini instruments working at 200.14 (¹H) and 50 MHz (¹³C).

Table 4 6-31G Optimized geometries of pyrazolediazonium salts

	5a	5b	6
Bond length/Å			
N ₁ -N ₂	1.311	1.322	1.341
N ₂ -C ₃	1.318	1.327	1.347
C ₃ -C ₄	1.410	1.402	1.368
C ₄ -C ₅	1.364	1.376	1.409
C ₅ -N ₁	1.363	1.367	1.322
C ₃ -N ₃	1.385	1.365	1.396
N ₃ -N ₄	1.086	1.091	1.087
N ₁ -H ₁	0.995	0.995	1.006
C ₄ -H ₄	1.064	1.065	1.067
C ₅ -H ₅	1.063	—	1.068
N ₂ -H ₂	—	—	1.004
C ₃ -H ₃	—	1.062	—
Bond angles(°)			
H ₁ -N ₁ -N ₂	118.9	120.0	120.9
N ₁ -N ₂ -C ₃	104.2	107.0	105.8
N ₂ -C ₃ -C ₄	112.7	111.3	111.4
C ₃ -C ₄ -C ₅	103.1	103.1	103.7
C ₄ -C ₅ -N ₁	106.6	108.5	108.1
N ₂ -C ₃ -N ₃	118.3	—	120.8
C ₃ -N ₃ -N ₄	180.0	—	177.3
C ₃ -C ₄ -H ₄	128.4	—	128.7
N ₁ -C ₅ -H ₅	122.5	—	128.0
N ₁ -C ₅ -N ₃	—	122.2	—
C ₅ -N ₃ -N ₄	—	178.4	—
C ₄ -C ₃ -H ₃	—	127.9	—
C ₃ -C ₄ -H ₄	—	128.4	—

Chemical shifts (δ) are given from internal tetramethylsilane with an accuracy of 0.01 (¹H) and 0.1 (¹³C) ppm. Coupling constants (*J*) are accurate to ± 0.2 and ± 0.6 Hz, respectively. The ¹³C solid-state spectra of compound **5** was recorded on a Bruker CXP 400 spectrometer working at 100.63 MHz with CP (cross polarization) and MAS (magic angle spinning). The TOSS sequence was used to suppress side bands.

Calculations.—AM1 calculations¹² were carried out with the MOPAC series of programs.¹³ The 6-31G//6-31G calculations¹⁴ were carried out using the HONDO series of programs.¹⁵

We have collected in Table 4 the 6-31G optimized geometries of compounds **5a**, **5b** and **6** and in Table 3 the calculated (AM1) and experimental geometries of compounds **13** and **21**.

Acknowledgements

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