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Note

Combined variable-temperature and variable-field ^{15}N cross-polarization magic angle spinning NMR study of ^{15}N,^{14}N residual dipolar coupling in pyrazole derivatives

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ABSTRACT: A study of the residual dipolar ^{15}N, ^{14}N coupling observed in ^{15}N cross-polarization magic angle spinning NMR spectra at variable temperature and variable field in 1-amino- and 1-nitropyrazole is reported. Residual dipolar ^{15}N, ^{14}N coupling is present in high-resolution ^{15}N spectra as an asymmetric (2 : 1) doublet induced by the quadrupolar ^{14}N neighbouring nitrogen on the corresponding ^{15}N signal. The observed spectral splittings were theoretically established by means of a second-order perturbing treatment of the complete Hamiltonian. X-ray diffraction and NQR data and theoretical calculations, in conjunction with several assumptions regarding the quadrupole tensor at each ^{14}N site, were used to obtain successful splitting values. Copyright © 2000 John Wiley & Sons, Ltd.

KEYWORDS: NMR; solid-state ^{15}N NMR; pyrazoles; ^{15}N, ^{14}N residual dipolar coupling

INTRODUCTION

The effects produced by quadrupolar nuclei on the NMR signals of spin-$\frac{1}{2}$ nuclei under high-resolution solid-state NMR conditions are well known and ubiquitous.[1] Many examples of both dipolar and indirect coupling effects have been discovered involving several spin pairs, which are widely distributed across the periodic table. These have been reviewed recently and further cases have been added since the latter review was published.[2–4]

Concerning the quadrupolar spin-1 ^{14}N nucleus, all examples reported in the literature concerning organic compounds show this phenomenon through coupling with the observed ^{13}C nucleus. Here, we describe this effect on the much less common nucleus ^{15}N using ^{15}N-labelled compounds. Only one previous report, by one of us, has been published concerning hydrazine sulfate and a hydrazone.[5] The net effect is the appearance of the signal as a multiplet, which can be asymmetric regarding both the peak heights and their positions.[6] The magnitude of the effect depends on the interplay of the magnetic field strength, the quadrupole interaction and the internuclear distance. It should be noted that the interacting nuclei need not be directly bonded, since the dipolar effect is transmitted through space.[6,7]

It is important to assess the magnitude of these residual effects, since they represent a potential source of uncertainty during spectral assignment and in dynamic NMR studies. Perturbation theory is a very useful aid in calculating the values of the expected line positions when the ratio (χ/ν_S) between the quadrupole coupling constant χ and the resonance frequency ν_S of the quadrupolar nucleus does not exceed 1.[6,7]

In this paper we report the results of variable-field and variable-temperature ^{15}N cross-polarization magic angle spinning (CP/MAS) NMR studies of substituted pyrazoles (Scheme 1). We present both qualitative and quantitative data concerning the ^{14}N, ^{15}N residual dipolar couplings and a second-order perturbation approach which is used to determine the splittings induced on the ^{15}N signals by neighbouring nitrogens.

The splittings produced by quadrupolar nuclei can be calculated, to a good degree of approximation, by perturbation theory.[1,6] The main result of the theory applied to the ^{15}N, ^{14}N residual dipolar couplings is represented by the following equation for the splitting s:

$$s = \nu_2 - \nu_3 = (9D\chi/10\nu_S) \qquad (1)$$

where ν_i are the transition frequencies, D and χ are the dipolar and quadrupolar coupling constants and ν_S is the Zeeman frequency of the quadrupolar nucleus.

Equation (1) was derived for the special case of coaxiality between the relevant quadrupolar and dipolar tensors. When this is not the case, a more general equation

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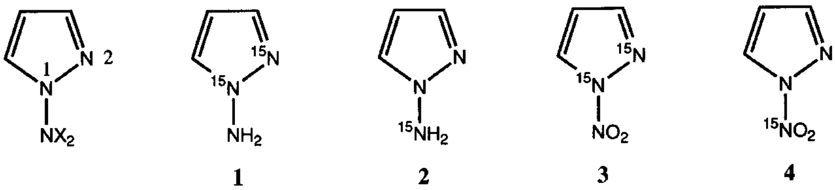

Scheme 1

can be derived:

$$s = (9D\chi/20\nu_S)(3\cos^2\beta^D - 1 + \eta\sin^2\beta^D\cos 2\alpha^D) \quad (2)$$

where β^D and α^D are the polar angles fixing the position of r, the internuclear vector, in the principal axis system of the electric field gradient (EFG) tensor, η being the quadrupole asymmetry.

Equation (2) is applicable to cases where not only the quadrupole coupling constant χ is small compared with the Zeeman frequency ν_S, but also when there are reasons to expect both the indirect coupling J and the anisotropy ΔJ between I and S nuclei to be negligible in comparison with D. This situation is expected to occur on the residual ^{15}N, ^{14}N coupling as well as the ^{13}C, ^{14}N coupling.[1] On the other hand, when coupling to heavy atoms is involved, both J and ΔJ can be significant compared with D.[6] Equation (2) relates the observed ^{15}N CP/MAS NMR splitting for ^{15}N nuclei which are spatially close to ^{14}N nuclei, with a series of structural (r, α^D, β^D) and energetic (χ, ν_S, η) parameters. Knowledge of these parameters allows one to calculate the magnitude of the expected splitting. The value of ν_S is generally known. The values of χ and η are usually available from ^{14}N nuclear quadrupole resonance (NQR) measurements or other spectroscopic techniques. The internuclear distance r may be obtained from the crystal structure determined by diffraction methods or from theoretical calculations. Finally, the geometric factors α^D and β^D depend on the location of the EFG principal axes in the molecular frame. This information can be gathered from spectroscopic techniques such as single-crystal NQR or microwave spectroscopy. It can also be inferred by resorting to Vega's method,[8,9] based on the orbital occupancies of the nitrogen atom. In other cases, the location of EFG axes is simply dictated by symmetry considerations.

EXPERIMENTAL

Synthesis of 1-amino-[$^{15}N_2$]pyrazole (1) and [$^{15}NH_2$]-1-aminopyrazole (2)[10]

In a 50 ml round-bottomed flask were placed a solution of 0.613 g (0.009 mol) of [$^{15}N_2$]pyrazole[11] or pyrazole in 16 ml of aqueous sodium hydroxide (2.4 g, 0.06 mol). The solution was heated to 50 °C and 3 g (0.026 mol) of hydroxylamino-*O*-sulfonic acid or [^{15}N]hydroxylamino-*O*-sulfonic acid[12] were added in small quantities while avoiding a temperature rise above 60 °C (60–90 min). After the addition was completed, the mixture was stirred at room temperature for another 30 min. The resulting solution was extracted with chloroform (3 × 25 ml). The organic layer was washed with water and dried over anhydrous sodium sulfate. The solvent was eliminated under vacuum and the residue was purified by column chromatography over alumina using $CHCl_3$ as eluent (aluminium oxide 90 active, activity I, 70–230 mesh ASTM, $R_f = 0.32$) followed by distillation (bp = 71 °C/15 Torr); yield 0.532–0.609 g (70–80%).

Synthesis of 1-nitro-[$^{15}N_2$]pyrazole (3)

This synthesis was carried out according to the procedure described by Klebe and Habraken[13] starting from [$^{15}N_2$]pyrazole.[11]

Synthesis of [$^{15}NO_2$]-1-nitropyrazole (4)

The general procedure for the nitration of aromatic compounds with inorganic salts in trifluoroacetic anhydride described by Crivello[14] was used. In a 50 ml round-bottomed flask equipped with a magnetic stirrer, reflux condenser and drying tube were placed 0.681 g (0.01 mol) of pyrazole, 1.011 g (0.01 mol) of potassium [^{15}N]nitrate and 5 ml (0.035 mol) of trifluoroacetic anhydride. Next, 10 ml of acetonitrile were added, and the reaction was allowed to proceed with stirring at room temperature, until the inorganic salt was dissolved (2 h). The reaction mixture was poured into 50 ml of water and extracted with chloroform (3 × 15 ml). The organic phase was dried over anhydrous sodium sulfate and the solvent removed under vacuum. The residue was purified by column chromatography over silica gel using $CHCl_3$ as eluent ($R_f = 0.43$); yield 0.645 g (60%).

Spectra

The ^{15}N CP/MAS NMR experiments were performed at three different fields, using a Bruker MSL 300 (7.1 T), 300.13 MHz for ^{1}H and 30.41 MHz for ^{15}N and a 5 mm Doty standard highspeed CP/MAS probe, a Bruker AC-200 (4.7 T), 200.13 MHz for ^{1}H and 20.29 MHz for ^{15}N using a 7 mm Bruker DAB 7 probehead, and a Bruker CXP 90 (2.1 T), 90.02 MHz for ^{1}H and 9.12 MHz for ^{15}N equipped with a 7 mm Doty standard probe. On the Bruker MSL 300 and CXP 90 spectrometers a Bruker B-VT-1000 temperature unit was used to control the temperature of the bearing gas stream and a laboratory-built heat exchanger to achieve low temperatures. To avoid problems at low temperatures caused by air moisture, pure nitrogen from evaporating liquid nitrogen was used as bearing and driving gas. All chemical shifts are related to external solid $^{15}NH_4Cl$ and given with an error of 0.3 ppm. CP/MAS spectra were measured using the usual CP pulse sequence with a 6–10 µs ^{1}H 90° pulse width, 3–6 ms contact pulses and a 3–6 s recycle delay. The rotational frequencies were of about 3.5–4.5 kHz. The number of FIDs was as follows: 7.1 T, 32; 4.7 T, 3200; and 2.1 T, 1000. The results obtained in these experiments are reported in Table 1.

RESULTS AND DISCUSSION

Equation (2) requires the prior knowledge of the magnitude of the quadrupolar coupling constants and asymmetry parameters of the EFG tensor at each ^{14}N site present

Table 1. Experimental results: ^{15}N chemical shifts in ppm from external solid $^{15}NH_4Cl$ and linewidths in Hz (NX_2, X = H or O)

			Chemical shift			Linewidth		
Compound	B_0 (T)	T (K)	N1	N2	NX_2	N1	N2	NX_2
1	7.1	297	177.0	265.1	—	39	45	—
1	7.1	201	178.5	266.0	—	327	220	—
1	2.1	281	176.7	264.8	—	32	32	—
1 (Fig. 1)	2.1	173	169.9	265.6	—	146	110	—
			189.4			152		
2	7.1	297	—	—	43.6	—	—	35
2	7.1	193	—	—	44.4	—	—	194
2	2.1	297	—	—	43.7	—	—	39
2 (Fig. 2)	2.1	193	—	—	40.9	—	—	79
					50.5			79
3	7.1	297	234.2	249.6	—	55	55	—
3	4.7	298	234.4	249.8	—	44	42	—
3	2.1	297	234.3	250.0	—	55	61	—
3 (Fig. 3)	2.1	178	234.2	248.0	—	42	46	—
4	7.1	297	—	—	284.3	—	—	84
4	4.7	298	—	—	284.0	—	—	44
					286.8	—	—	55
4 (Fig. 4)	2.1	297	—	—	280.0	—	—	76
					294.8			102

in the molecule under study. NQR studies of several pyrazoles and related compounds have been reported previously,[15–20] but the values for the pyrazoles studied here are not available. However, a comparison between the available data for related compounds reveals that the magnitudes of χ and η are not significantly different for the ^{14}N sites in these molecules. For **1** and **3** the amino ($PhNH_2$) and nitro ($PhNO_2$) benzenes, respectively, were considered.[17,20] Only the N1 values were taken into account for **2** and **4** considering several pyrazole and triazole as models.[16]

The sign of χ and the orientation of the principal directions of the EFG tensor in the molecular frame are also needed to calculate the splitting of the ^{15}N resonance. In the compounds under study, four types of ^{14}N sites are present: —NH_2, —NO_2, —N1$<$ and —N2=. For —NH_2 and —$N_1<$ the principal z_{EFG} axis is expected to lie along the ^{14}N lone pair of electrons, thus $\beta^D = 90°$. The angle α^D is expected to be 90° for an —NH_2 site[21] and 0° or 90° for —N1$<$ (—NH_2 or —NO_2 compound, respectively). In general, χ values of ca 4 MHz have been observed, suggesting that they should be assigned a negative sign.[21]

Quadrupolar parameters at the imino nitrogen, N2, in these heterocyclic compounds are not needed for two reasons. On the one hand, the z_{EFG} axis is coincident with the nitrogen lone electron pair, thus attaining a β^D value of 60°. Since for this value of β^D the term $(3\cos^2\beta^D - 1)$ in Eqn (2) becomes very small, the splittings induced by these imino nitrogens are predicted to be negligible.[21,22] On the other, the effect of this nitrogen is also small since it is far (ca 2.5 Å) from the NH_2 and NO_2 groups. The value of s falls off rapidly with distance due to the factor r_{NN}^{-3} in the coupling constant D. A direct evaluation of these long-range effects shows that they are probably masked by the linewidth of the signals, contributing at most to a broadening. Accordingly, only directly bonded nitrogens were taken into account in the calculation of the splittings. In the latter case, the value of D is approximately 60 Hz. Considering the parameters $\chi = -4$ MHz[18] and $\nu_N = 6.5$ MHz (at 9.12 T), the $9D\chi/20\nu_N$ factor has a value of −20 Hz, which is negligible.

For all compounds values of D were calculated considering the bond lengths obtained by x-ray diffraction.[12,23] Table 2 presents the parameters used for the calculations of the splitting.

In Table 3 the splittings calculated by Eqn (2) are shown at different magnetic fields. Experimental splitting values associated with the nitrogen signals at different temperatures and for each magnetic field are also shown, and will be discussed below.

Aminopyrazoles

The ^{15}N CP/MAS NMR data for **1** are reported in Table 1. No signal splittings of the ^{15}N at high field (7.1 T) are observed for this compound, independently of the temperature at which the spectra were registered. The calculated splitting for N1 is +34 Hz (Table 3), and is probably masked by the signal width. However, at low field (2.1 T) and low temperature, a splitting (+178 Hz) for N1 is observed, with a calculated value of +115 Hz (Fig. 1). The observed difference could be attributed to the difficulties in the selection of the quadrupolar parameters, mainly regarding the asymmetry coefficient.

Table 2. Structural (r, α^D, β^D) and energetic (χ, η) parameters used to calculate the ^{14}N, ^{15}N residual dipolar splittings (s)

Compound	Nitrogen	χ (MHz)	η	r_{N-N} (Å)		β^D (°)	α^D (°)
1	NH_2	-4.0^a	0.300^a	N1–NH_2	1.403^d	90	90
2	N1	-4.3^b	0.383^b		1.403^d	90	0
3	NO_2	-1.2^c	0.461^c	N1–NO_2	1.399^e	0	—[f]
4	N1	-4.3^b	0.383^b		1.399^e	90	90

[a] Ref. 17.

[b] Ref. 16.

[c] Ref. 20.

[d] Ref. 12.

[e] Ref. 23.

[f] The value of α^D is not important in this case since $\beta^D = 0$. With the latter β^D value the term $\eta \sin^2\beta^D \cos 2\alpha^D$ is close to zero.[24]

Table 3. Observed and calculated ^{14}N, ^{15}N residual dipolar splittings (*s*)

		Calculated splitting (Hz)			Experimental splitting (Hz)	
Compound	B_0 (T)	N1	NX_2	T (K)	N1	NX_2
1	7.1	+34		297	—	
	7.1			201	—	
	2.1	+115		281	—	
	2.1			173	+178	
2	7.1		+18	293		—
	7.1			193		—
	2.1		+59	297		—
	2.1			193		+88
3	7.1	+18		297	—	
	4.7	+28		298	—	
	2.1	+62		297	—	
	2.1			178	—	
4	7.1		+40	297		—
	4.7		+59	298		+57
	2.1		+133	297		+135

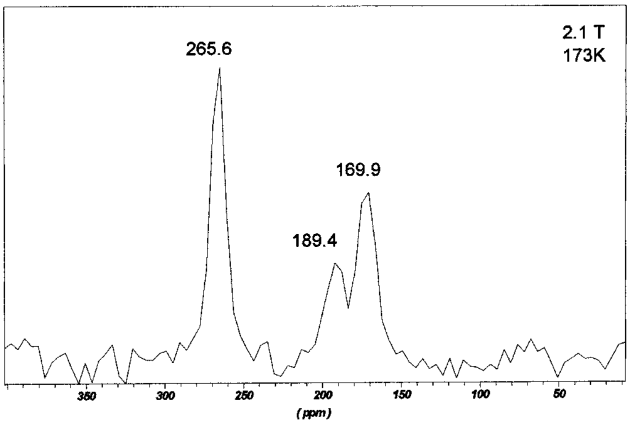

Figure 1. ^{15}N CP/MAS NMR spectra of 1-amino-[$^{15}N_2$]-pyrazole (**1**).

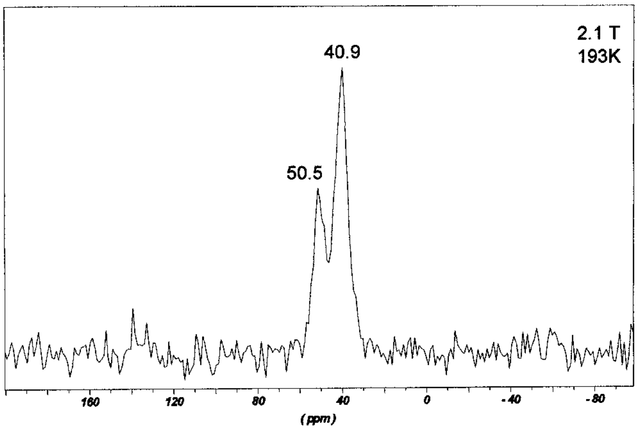

Figure 2. ^{15}N CP/MAS NMR spectra of [$^{15}NH_2$]-1-amino-pyrazole (**2**).

In Table 1 the ^{15}N CP/MAS NMR data for **2** are shown. As in the former case, this compound does not present splittings in the amino group nitrogen signal at high field (7.1 T). The value calculated by Eqn (2) is +18 Hz and thus it is expected that the splitting is masked by the signal width. Nevertheless, at low magnetic field (2.1 T), when the temperature decreases, a splitting of +88 Hz appears (Table 3 and Fig. 2) at 193 K. The calculated splitting at 2.1 T is +59 Hz. Again, the differences between the calculated and the experimental values are probably due to differences between the estimated quadrupolar parameters and their actual values. The values of χ (−4.3 MHz) and η (0.383) correspond to N1 in non-substituted pyrazoles (RNHN=).[18] However, in the case of related heterocyclic compounds (R_2NC—) where the nitrogen is bonded to three carbon residues, the χ values present a small variation ($\chi = -3$ MHz), whereas η is almost zero.[21] The latter value for the asymmetry coefficient reflects the highly symmetric environment for N1 in these compounds. In our case, an intermediate situation is expected since χ for N1 in **2** is larger than that corresponding to the same pyrazole nitrogen. Assuming an η value of 0.2 the splitting is +76 Hz, in agreement with the experimental value (see Table 3).

In both **1** and **2**, the calculated splittings are smaller by about 30–60 Hz than the experimental values (which are only observed at low temperature): compare (Table 3) +115 Hz (calc.) with +178 Hz (exp.) for N1 and +59 Hz (calc.) with +88 Hz (exp.) for NH_2. These differences are attributable to the assumed quadrupolar values being slightly incorrect but probably fairly close to those we have used. We have tried to proceed backwards, for example, for a splitting of +178 Hz observed in **1**, we can deduce using Eqn (2) [$9D\chi/20\nu_{N(2.1\,T)} = 22.2 \times 10^{-6}$, $\beta^D = 90°$ and $\alpha^D = 90°$] a combination of χ and η values in the ranges −4.7/−4.2 MHz and 0.7/0.9 δH respectively. The expected χ value could be in this range, whereas the corresponding η value should be less than 0.7 due to the present asymmetry, but greater than 0.3 (assigned value, Table 2). In the case of **2**, the situation is the reverse one according to the observed splitting (+88 Hz), and using Eqn (2) [$9D\chi/20\nu_{N(2.1)T} = 22.2 \times 10^{-6}$, $\beta^D = 90°$ and $\alpha^D = 0°$] η and χ values are in the ranges 0.0/0.2 and −3.4/−4.9. The η value should be intermediate between the values given in Table 2 and those obtained before.[24] We present in Table 4 a combination of χ and η values that accounts fairly satisfactorily for

Table 4. Calculated ^{14}N, ^{15}N residual dipolar splittings (s) for optimized pairs of χ, η values

Compound	χ	η	B_0 (T)	Calculated splitting (Hz) N1	Calculated splitting (Hz) NX$_2$	Observed splitting (Hz)
1	−4.7	0.5	7.1	+47	—	N.o.[a]
	−4.7	0.5	2.1	+155	—	+178
2	−4.4	0.1	7.1	—	+26	N.o.
	−4.4	0.1	2.1	—	+87	+88
3	−1.1	0.461	7.1	+15	—	N.o.
	−1.1	0.461	4.7	+22	—	N.o.
	−1.1	0.461	2.1	+49	—	N.o.
4	−4.3	0.383	7.1	—	+40	N.o.
	−4.3	0.383	4.7	—	+59	+57
	−4.3	0.383	2.1	—	+133	+135

[a] Not observed.

the observed splittings while remaining within reasonable boundaries.

1-Aminopyrazole forms in the crystal a structure forming a net of hydrogen bonds. The presence of these bonds produces changes in the electronic environment of the nitrogen, hence modifying the energetic (η and χ) and the geometric (α^D and β^D) parameters.

Nitropyrazoles

^{15}N CP/MAS NMR chemical shifts and linewidths for **3** are reported in Table 1, where no splitting is noted for N1 at any temperature and field, even at low fields (2.1 T) and low temperatures (Fig. 3). Calculated values (Table 3) are small and consequently it could be expected that the splitting corresponding to that nitrogen is masked by the signal width.

The ^{15}N CP/MAS NMR data for **4** are reported in Table 1. At 7.1 T no splitting is observed in the signal corresponding to the NO$_2$ nitrogen. However, at both 4.7 and 2.1 T (Fig. 4) +57 and +135 Hz splittings are observed that are highly coincident with the calculated values, namely +59 and +133 Hz (Table 3). It should be pointed out that in **4** the quadrupolar parameters (χ and η) are those for **2.** In Table 4 we have summarized our proposed set of η and χ values that in the case of 1-nitropyrazole **4** are highly satisfactory.

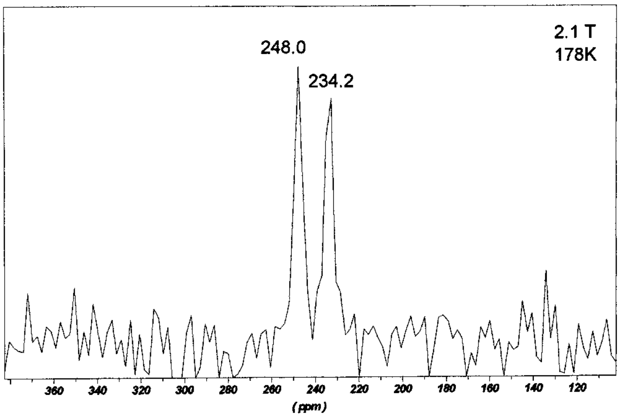

Figure 3. ^{15}N CP/MAS NMR spectra of 1-nitro-[^{15}N$_2$]pyrazole (**3**).

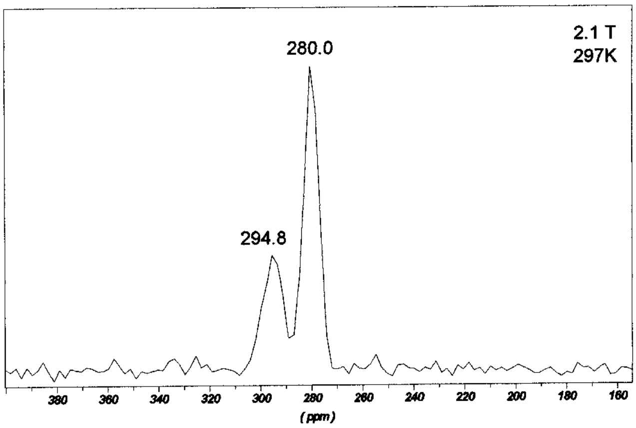

Figure 4. ^{15}N CP/MAS NMR spectra of [^{15}NO$_2$]-1-nitropyrazole (**4**).

The difference observed between amino- and nitropyrazoles is probably related to differences in crystal structure. While 1-nitropyrazole (CSD refcode NIPYAZ)[23,25,26] crystallizes in a very loose structure with individual molecules connected by weak C—H···O interactions, 1-aminopyrazole presents in the crystal a three-dimensional network of hydrogen bonds.[12] Moreover, this compound shows phase transitions between crystal and glass structures, the second one being subject to molecular motions.[12] In general, when motions occur in the crystal, a self-decoupling phenomenon could take place from the residual dipolar coupling, originating a doublet that collapses into a single signal.[6,27] The motions in the kHz regime are effective for relaxation, changing either the size or the direction of the quadrupole interaction. We assume that the splitting is self-decoupled by a dynamic process which leads to fast ^{14}N relaxation. These effects have been reported in other cases,[3,5,22] and are pronounced in 1-aminopyrazole;[12] consequently, only at low temperatures (below 193 K) does a doublet occur (Fig. 1).

CONCLUSIONS

We studied the ^{15}N, ^{14}N residual dipolar coupling in the ^{15}N CP/MAS NMR spectra of four heterocyclic compounds. ^{15}N, ^{14}N residual dipolar coupling makes the interpretation of ^{15}N CP/MAS NMR spectra complex, especially in those recorded at low fields.

Aminopyrazoles **1** and **2** and nitropyrazole **4** present splittings that are observed at low field. In the case of aminopyrazoles, the splittings are observed only when the temperature decreases. The absence of any splitting in the ^{15}N bonded to ^{14}N is due to self-decoupling of the residual dipolar coupling induced by motions in the crystal producing a rapid longitudinal relaxation of the ^{14}N. A first-order perturbative equation was used in order to predict the splitting for each ^{15}N line.

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