A ^{14}N FT-NQR Investigation on Solid Pyridine and Pyridine-D5*

Roberto Ambrosetti [1], Rocco Angelone [1], and Juan Murgich [2]
[1] Istituto di Chimica Quantistica ed Energetica Molecolare del CNR, via Risorgimento 35, I-56100 Pisa, Italy
[2] Centro de Quìmica, Instituto Venezolano de Investigaciones Cientificas, Apartado 1827, Caracas 1010A, Venezuela

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The FT-NQR spectra of ^{14}N in both pyridine and pyridine-D5 show four sets of resonance lines at − 196 °C, which disappear reversibly at − 191.5 °C and − 187 °C, respectively. This is interpreted as a phase transition, possibly of the order-disorder type. The NQR results can thus be reconciled with X-ray measurements at − 180 °C which suggested a single site for pyridine. The similarity of the NQR spectra of different samples of both compounds, frozen and cooled with widely different procedures, suggests that the high multiplicity of the NQR spectra is not the result of coexistence of different crystal phases. It is shown that previously available data from IR, Raman and NQR spectroscopies can all be put in a non-contradictory scheme.

Introduction

Both pyridine [1] and pyridine-D5 [2] are known to yield four sets of ^{14}N NQR lines at − 196 °C.

This is not in agreement with the only available data on the crystal structure of pyridine, obtained by X-ray on polycristalline samples at − 180 °C [3]. The X-ray data were analyzed assuming crystallization in two crystalline forms, pertaining to the orthorhombic space groups D_{2h}^1 or D_{2h}^2, respectively. The cell dimension and density data show that in both modifications the unit cell contains 8 molecules. The asymmetric unit contains therefore a full molecule.

Pure NQR discriminates among crystallographically unequivalent sites. Based on X-ray data, one expects a single site, hence a single set of lines in ^{14}N NQR of polycristalline samples of pyridine at zero magnetic field. Biswas [3] does not report any findings on a mixture of phases. However, this possibility cannot be ruled out for a physically large sample such as the ones studied in NQR, which can behave quite differently from a sample frozen in a capillary tube. Even in this case only two sets of lines should show up.

A few more data on solid pyridine have been obtained by other techniques. Among them, we quote IR and Raman investigations [4, 5]. The IR spectrum at 77 K exhibits bands whose complexity (up to seven components) is too high [5] in view of the known [3] crystal symmetry. At 77 K two different types of spectra were obtained, depending on the freezing and cooling history. Raman and IR measurements [5] were carried out on oriented thin-film samples of pyridine, of pyridine-D5, and of their mixtures at − 180 °C. After careful freezing and annealing one crystal phase only was obtained at that temperature, either from the liquid or from vapor-deposited samples. A phase transition took place in frozen pyridine-D5 during annealing at − 60 °C. A corresponding transition was not observed in pyridine.

Deuteron NQR on various deuterated pyridines [6] showed unequivalence of the 3 and 5 positions of the ring. However the resolution of the reported spectra is too low to uncover further unequivalence of sites. Finally, we recall the observation by Guibé [7] that ^{14}N NQR lines persisted at liquid hydrogen (− 253 °C) temperature, but could not be observed in solid CO_2 (− 79 °C). His preliminary single-crystal Zeeman measurements also suggested that each component of the NQR spectrum corresponds to more than one crystallographic site.

Further studies concerning pyridine and deuterated pyridines at low temperature, less akin to the main subject of the present paper, are an EPR observation of the pyridinyl radical in ethanol at

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Reprint requests to Dr. R. Ambrosetti, Istituto di Chimica Quantistica ed Energetica Molecolare del CNR, via Risorgimento 35, I-56100 Pisa, Italy.

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− 196 °C [8] and IR/Raman measurements in N_2 matrix at − 253 °C [9]. The latter suggests the existence of molecular pairs of pyridine even in very diluted samples.

Since it is not easy to reconcile the data reported so far, especially those from X-ray and NQR studies, we undertook the present NQR re-investigation on pyridine and pyridine-D5 to gain further insight in the problem.

Experimental

Materials

Commercial pyridine was dried by refluxing over solid KOH, then fractionated through a glass-packed column. A 50 g sample was collected and immediately sealed in a glass vial.

A 10 g sample of pyridine-D5 was obtained from FLUKA (> 99.9% atom deuteration) and studied in the glass vial in which it had been supplied.

Instrumentation

We used a pulsed Fourier transform ^{14}N NQR instrument, interfaced to a minicomputer for data acquisition and handling [10]. All reported spectra are the modulus of the Fourier transform of the FID signal. The reported frequency and width data were obtained by non-linear least-squares fitting of a Gaussian lineshape to the experimental lines. Although both parameters could be reproduced to about 10 Hz by repeating the same acquisition, sample to sample variations were at least 5 times larger.

The sample temperature was controlled by a cryostat similar to models described elsewhere [11] but modified to allow easier handling and more direct access to the sample. Measurements at − 196 °C were always taken after covering the sample with liquid nitrogen. The temperature was measured using both a Comark model 1623 thermocouple thermometer and a calibrated (at 0 °C, − 80 °C and − 196 °C) Pt resistor. The sensors were mounted on opposite sides of the brass cylinder containing the sample. The resolution of temperature measurements and the resettability of the cryostat were both better than 0.1 °C; however we estimate an overall absolute accuracy of not better than ± 1 °C.

Sample preparation

We measured NQR on different "samples", actually obtained by freezing and cooling in different ways the same pyridine sample (m.p. − 42 °C). The "samples" will be referred to as (i), (ii) and (iii). (i) was obtained by direct, sudden immersion of the whole cryostat in liquid nitrogen, after flushing with dry nitrogen gas. This is of course a dangerous procedure, and in fact a few thin-walled vials were shattered in this way. (ii) was obtained by freezing the supercooled liquid (at − 60 °C) by injecting a drop of liquid nitrogen directly on the glass vial. The solidified sample was annealed for 6 h at − 60 °C, then cooled to − 196 °C at a programmed, constant rate of about 30 °C/h. (iii) was obtained by bringing pre-solidified pyridine somewhat above the melting point until most of it melted again; then the whole sample was frozen at − 50 °C. Thus we obtained slow solidification without supercooling. Annealing and cooling were then carried out as described for sample (ii).

A single "sample" of pyridine-D5 was prepared in a way similar to sample (ii).

Results

In Fig. 1 typical NQR spectra are shown. All samples yielded spurious "piezoelectric" signals. We were forced to truncate the FID by delaying the data acquisition by about 0.7 ms after the end of the rf pulse in order to reduce their relative amplitude (Figure 2). The time-averaged NQR signals remained above noise until about 3 ms (at − 196 °C). However, cutting out the first part of the FID reduced the S/N ratio considerably. The echo was free from spurious signals; however it yielded in practice no sensitivity advantage over the truncated

Table 1. NQR data of pyridine and pyridine-D5 at liquid nitrogen temperature. The data for pyridine-D5 are within parentheses. NQR frequencies in kHz, T_1 in ms. The standard deviation of T_1 is estimated to be about 25% of the corresponding value.

f^+	$T_1(f^+)$	f^-	$T_1(f^-)$
3914.6 (3919.5)	300	2987.3 (2985.5)	3000
3905.2 (3910.3)	500	2956.6 (2953.4)	1000
3894.2 (3899.0)	350	2992.6 (2991.0)	2000
3856.9 (3861.7)	200	3001.4 (2999.6)	250

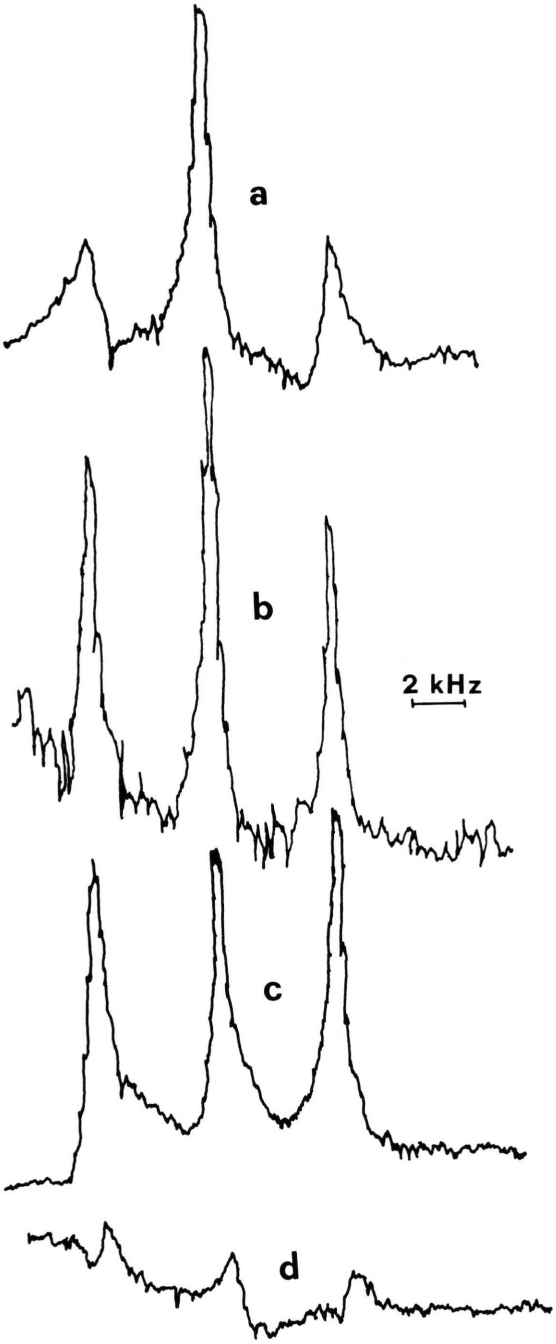

Fig. 1. Some representative FT NQR spectra of ^{14}N in pyridine (modulus presentation). Transmitter frequency 3902.00 kHz, allowing three f^+ lines to be observed together in the available ±20-kHz span. A 5 Hz pulse repetition frequency was used. a) Sample (i) (see text) at −196 °C (2000 FID's time-averaged). Center frequencies are (left to right): 3905.18, 3894.12, 3914.48 kHz. b) Sample (ii) at −196 °C (1000 FID's). Maximum frequency shift with respect to a) is 0.06 kHz. c) Sample (ii) at −193 °C (5000 FID's). d) Sample (ii) at −191.5 °C (10000 FID's). The down-frequency shift of the lines in d) with respect to b) is 0.10 kHz on the average.

FID, requiring instead considerable care in setting up the duration and separation of the pulses. All spectra discussed here were obtained, therefore, by FT of the truncated FID. The piezoelectric signals were especially annoying when we attempted to measure relaxation times. In fact, at high pulse repetition rates the spurious signals became dominant. This, together with the usual problems of non-exponential recovery [12] and pulse imperfection, made accurate T_1 measurements almost impossible.

Table I collects NQR data at − 196 °C. The measured f^+ and f^- resonance frequencies are quite close to the ones observed [1, 2] with cw technique.

We maintain the grouping found by Guibé [1] on the basis of the "difference" lines; however, no attempt at re-observing such lines was successful. They were apparently much weaker than the always present piezoelectric signals. The resulting spurious spectra were not exactly reproducible, making it difficult to recognize genuine NQR lines through the effect of an externally applied Zeeman field.

The relative amplitudes of the lines of samples (i) and (ii) (Fig. 1) are slightly different. The spectra of sample (iii) (not shown here) were essentially identical with those of sample (ii).

The lines of both pyridine and pyridine-D5 first broadened, then disappeared completely upon heating above liquid-nitrogen temperature (Figs. 1 and 3). In fact, we were unable to observe any NQR signal above − 191.5 °C for pyridine and − 187 °C for pyridine-D5. In particular, on sample (ii) we searched unsuccessfully for NQR lines at − 180 °C (range 3790−3915 kHz), at − 150 °C (3825 to 3915 kHz) and at − 60 °C (3700 to 3915 kHz). No hysteresis was observed; the lines reappeared as soon as the samples were cooled below the indicated temperatures.

We checked for residual temperature inhomogeneity over the sample by measuring, in the same cryostat and using the same coil, the width of the f^+ line of a known [11] sample (2,6-dimethylbenzonitrile). It was 350 Hz after slow cooling to − 196 °C followed by overnight immersion in liquid nitrogen.

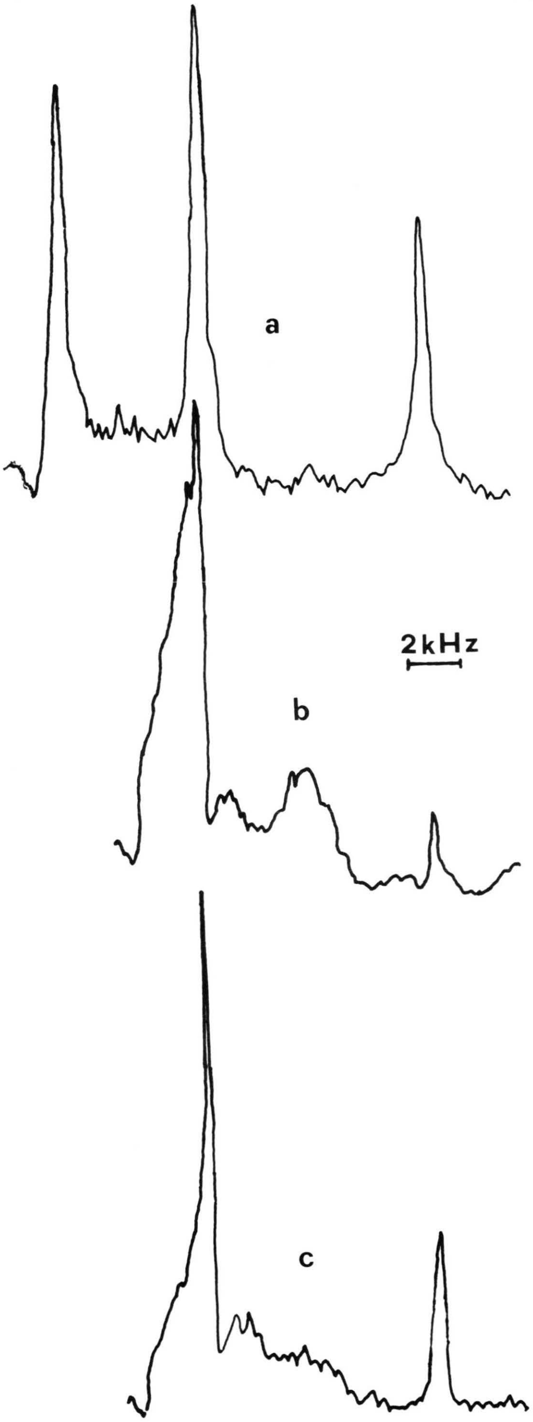

Fig. 2. **a**) Three f^- lines of pyridine-D5 at −196 °C. Transmitter frequency 2983.00 kHz; 40 000 FID's time-averaged; pulse repetition frequency 4 Hz; acquisition delay 0.7 ms. **b**) and **c**): same as a), but recorded with acquisition delay 0.2 ms (the normal value in our instrument) and 0.4 ms, respectively, so as to show the "piezo-electric" spurious signals (see text).

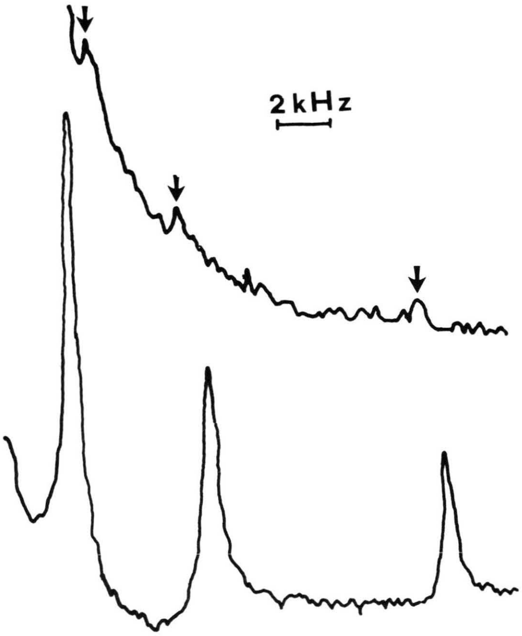

Fig. 3. Spectra of pyridine-D5 (f^+ lines) at −187 °C (above) and −196 °C (below). Resonance frequencies in kHz, left to right: above, 3897.99, 3909.36, 3918.67; below, 3899.00, 3910.28, 3919.48. Transmitter frequency 3902.00 kHz; pulse repetition frequency 3 Hz; 15 000 (above) and 30 000 (below) FID's were time-averaged.

The sample was then heated at − 183 °C. After the first hour the line width had increased to about 450 Hz. This can be read as a rms temperature inhomogeneity of about 0.5 °C, taking into account the temperature coefficient of the NQR lines of 2,6-dimethylbenzonitrile. After three hours at − 183 °C (a typical time for pyridine measurements) the line broadening with respect to − 196 °C was essentially zero. It is also to be noted that the temperature coefficient of the pyridine lines appears to be smaller than that of 2,6-dimethylbenzonitrile (see caption to Figs. 1 and 3), making them less sensitive to temperature gradients.

Discussion

The measurements on the different "samples" of pyridine were mainly carried out in order to gain information on the possibility of co-existence of phases. If such a possibility is accepted, it is logical to expect quite different amounts of the two phases in samples of different thermal history. In fact, one would expect for a slowly frozen, carefully annealed and cooled sample (such as (iii)) only a set of lines corresponding to a single phase.

Although some differences in the amplitude ratios within the spectra of samples (i) and (ii) exist (Fig. 2), they are small and can be explained during strong radial temperature gradient existing during freezing of sample (i) could yield a different orientation of the crystallites from that in sample (ii) or (iii). Different orientation of the EFG axes with respect to the rf coil could account for the observed differences.

The existence of a mixture of phases is therefore, if not disproved, certainly very unlikely. Since pyridine-D5, gently cooled, also yields a set of four lines of comparable intensity, this conclusion is further strengthened.

Attention is now called to the broadening, fading, and final disappearance of the NQR lines above − 191.5 °C (pyridine) and − 187 °C (pyridine-D5). While this does not rule out the possibility that NQR lines can be found above such temperatures, they are certainly much weaker than at − 196 °C, or their spectral position is displaced considerably. From this we state that a phase transition exists in pyridine just above − 196 °C and no relation between the NQR measurements and either of the phases found by Biswas is to be expected. The simultaneous disappearance of all lines at the phase transition temperature is in agreement with the hypothesis that a single phase is present.

As to the nature of the phase transition, the discussion is speculative. However the broadening of the NQR lines prior to disappearance, not accompanied by a significant frequency shift, seems to point to an "order-disorder" type of phase transition. It is pointed out that time-dependent effects could be detected in the NQR spectra, even at − 196 °C, suggesting some residual degree of motional freedom. For instance, spectrum **b** of Fig. 2 was obtained after 24 h at − 196 °C. 1 h after cooling to that temperature, the relative amplitude of the line at 3894.1 kHz was considerably larger. This is likely related to residual effects of the phase transition. Similarly, spectrum **a** could be taken after about 10 h at − 196 °C. During that time appreciable line narrowing had taken place.

Although caution is needed, we will discuss the T_1 values from a similar point of view. Considering their uncertainties and the moderate span (about 1 order of magnitude) of their values, all of them are in fact quite similar. This may be due to almost equal values of the components of fluctuating magnetic and/or electric fields along all the X and Y EFG axes (such components are responsible for f^+ and f^- NQR transitions). This in turn should stem from essentially isotropic molecular motion. In an anisotropic environment, isotropic molecular motion is hard to believe without some degree of motional freedom.

Unfortunately, the very small temperature range over which the NQR lines were accessible limits the possibility to gain additional information on the relaxation mechanism. Although no measurement was attempted, in setting up the proper pulse repetition rate for pyridine-D5 we realized that the relaxation times of this sample are quite similar to those of the non-deuterated one.

Conclusions

The present NQR investigation points to the existence of a single phase at − 196 °C for both pyridine and pyridine-D5. This implies that four molecules form the asymmetric crystal unit at this temperature. This is the most obvious and direct explanation for the observed NQR spectral multiplicity and it is in contrast to available X-ray results. However we have shown that a phase transition takes place, in both pyridine and pyridine-D5, at a temperature only slightly below that of the X-ray measurements. This makes it possible to reconcile the X-ray and NQR measurements. In fact they should not be compared, as we now know that the measurements were carried out on different physical systems.

The overall behaviour of pyridine in the solid state appears to be quite complex, but a list of non-contradictory results can be compiled. Around −60 °C a phase transition takes place in pyridine-D5 [5], but not in pyridine. At −79 °C [7], and at any temperature below the melting point down to less than −180 °C, NQR cannot be observed, at least with conventional techniques. At −180 °C two phases have been observed by X-ray [3], but only one by IR and Raman spectroscopy when proper cooling procedures were adopted [5]. Below −180 °C we observed a new transition for both compounds, leading to a phase where NQR can be observed easily down to liquid hydrogen temperature [7]. The too high multiplicity of the IR bands at liquid nitrogen temperature [4], previously unexplained, is most probably due to the fact that the measurements were actually carried out on the same phase as seen by NQR, but were tentatively interpreted with reference to the different symmetry of the phase studied by X-ray. Both phases could coexist in some samples (this would be undetectable by NQR), giving rise to the alternative kind of spectra seen by IR.

All this calls for further investigation. The most direct measurements to be taken next would be X-ray on polycristalline or single-crystal samples, and Zeeman NQR on single crystals, both at −196 °C.

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