A Solid-State NMR, X-ray Diffraction, and ab Initio Computational Study of Hydrogen-Bond Structure and Dynamics of Pyrazole-4-Carboxylic Acid Chains

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Abstract: Using high-resolution solid-state $^{15}$N CMAS NMR, X-ray crystallography, and ab initio calculations, we have studied the structure of solid pyrazole-4-carboxylic acid (I). The crystal structure was determined at 295 and 150 K. Molecules of I are located on a two-fold axis, implying proton disorder of the NH and OH groups; no phase transition was observed between these two temperatures. The compound forms quasi-linear ribbons in which the molecules are linked by cyclic hydrogen bonds between pyrazole and carboxylic acid groups with disordered hydrogen-bonded protons. Crystallography is unable to decide whether the disorder is dynamic or static. NMR shows that this disorder is dynamic, that is, consisting of very fast degenerate double proton transfers between two rapidly interconverting O-HâââN and OâââHâââN hydrogen bridges. However, at low temperature, NMR shows a proton disorder–order transition where the protons are preferentially localized on given nitrogen and oxygen atoms. An amorphous phase exhibiting proton order is observed when the compound is precipitated rapidly. In this case, the defects are annealed by moderate heating. Ab initio calculations performed on oligomers of I show that the O-HâââN hydrogen bridge is about 0.064 Å shorter and less bent (~171°) than the OâââHâââN hydrogen bridge (~150°). For an isolated ribbon, this result leads to structures with localized protons, either to a cycle with about 200 molecules, or to a quasi-linear ribbon involving an undulated structure, or to a combination of both motifs. Only the undulated structure is compatible with the linear ribbon observed by X-ray crystallography, where the fast proton transfer in the high-temperature phase is assisted by the motions of the undulated chain. A disordered structure is assigned to the amorphous phase, which exhibits the combination of the curved and the undulated motifs.

Introduction

Coupled hydrogen-bonded networks with mobile protons are important elements of supramolecular reactivity in chemistry and biology. Unfortunately, these phenomena are very complex and require the study of model systems. In recent years, some of us have demonstrated that solid pyrazoles represent such a class of model systems. Depending on the substituents, these molecules form either linear chains such as the parent compound pyrazole, or cyclic dimers, trimers, or tetramers as depicted in Figure 1. Whereas in the linear chains the protons are ordered and immobile, the cyclic complexes generally form two degenerate states A and B, which interconvert via fast double, triple, or quadruple proton transfers in the millisecond to second time scale, as has been shown using dynamic high-resolution solid-state $^{13}$C and $^{15}$N CP MAS NMR spectroscopy. Accurate rate constants of the proton motions, including the multiple hydrogen/deuterium isotope effects in a wide temperature range, can be obtained using $^{15}$N NMR line shape analysis and magnetization transfer experiments. For the triple proton transfers, such studies revealed a concerted process via a

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hydrogen bond compressed transition state, with strong tunneling contributions at low temperatures.\(^5\)

In contrast to N–H⋯N hydrogen bonds, the related O–H⋯O hydrogen bonds are generally much stronger. Thus, it is not surprising that the double proton transfer dynamics between forms A and B in the related, well-studied carboxylic acid dimers (Figure 1e) are much faster, generally in the microsecond to nanosecond time scale as manifested in the longitudinal \(^1\)H and \(^2\)H NMR relaxation of these molecules.\(^6\) The interest in carboxylic acid also stems from the finding that this group is one of the most important motifs used in organic crystal engineering for self-assembling of organic molecular building blocks.\(^7\) Much less is known about the proton dynamics in such extended networks. As an example, we discuss the case of \(\text{p-terephthalic acid, which consists of linear ribbons of covalently}

\[\text{\begin{align*}
\text{\text{H}} \text{N} & \text{H} \cdots \text{N} \text{H} \cdots \text{N} \\
\text{\text{H}} \text{N} & \text{H} \cdots \text{N} \text{H} \\
\text{\text{H}} & \text{N} \cdots \text{H} \\
\text{\text{H}} & \text{N} \\
\text{\text{H}} & \text{H} \\
\end{align*}}\]

\] linked cyclic carboxylic acid dimers (Figure 1f). Using \(^1\)H NMR spectroscopy and relaxometry, Fischer et al.\(^8\) revealed that the formation of the ribbons does not suppress the proton dynamics. These authors observed a slightly asymmetric double minimum potential for the proton dynamics, exhibiting a free enthalpy difference of 1.8 kJ mol\(^{-1}\), and a time scale of the proton motion in the microsecond- to nanosecond range, which is similar to that of the carboxylic acid dimers.\(^6\) Upon cooling the sample, a proton disorder—order transition was observed at 80 K.

As a consequence of the above considerations, an interesting situation arises if one constructs molecules exhibiting both the acid carboxylic and the basic pyrazole groups. In this case, these

\[\text{\begin{align*}
\text{\text{H}} \text{N} & \text{H} \cdots \text{N} \\
\text{\text{H}} \text{N} & \text{H} \\
\text{\text{H}} & \text{N} \\
\text{\text{H}} & \text{H} \\
\text{\text{H}} & \text{H} \\
\end{align*}}\]

\]...
groups could form either cyclic homodimers with OHO and 
NHN hydrogen bonds or heterodimers with OHN hydrogen 
bonds, where the proton dynamics are intermediate between the 
carboxylic acid and pyrazole dimers. On the other hand, the 
carboxylic acid groups can be expected to act as an acid and 
the pyrazole groups as a base. Evidence for such a situation 
was obtained recently by X-ray diffraction of 2-aminopyrazole-
carboxylic acid, which forms a zwitterionic ribbon in the solid 
state with two OâââH-NN hydrogen bonds,\(^9\) as depicted in Figure 
1g. On the other hand, the acid-base interaction is much weaker 
in 1H-indazole-3-carboxylic acid, which forms a tetrameric 
supercycle with four pyrazole-carboxylic acid links.\(^10\) Finally, 
we would like to mention that Bureiko et al. have reported 
solution studies of the double proton transfer between carboxylic 
acids and N-unsubstituted pyrazoles.\(^11\) These encouraged us to 
look for cocrystals of the two components. We found that 3,5-
dimethylpyrazole is able to form cocrystals with 2,4,6-trimeth-
ylbenzoic acid. However, these do not show any sign of proton 
disorder.\(^12\)

In recent years, in our search for systems in which both 
anchoring groups exhibit a solid-state proton tautomerism we 
have studied one of the simplest compounds of this series, that 
is, pyrazole-4-carboxylic acid \(^1\) (Figure 2). Although \(^1\) was 


colorless crystals of pyrazole-4-carboxylic acid were obtained by slow evaporation of water–ethanol solutions.

**X-ray Diffraction and DSC Measurements.** A transparent colorless crystal with approximate dimensions 0.27 mm × 0.33 mm × 0.40 mm was used to collect X-ray data (〈 1.5418 Å) on a Seifert XRD3000-5 and a Philips PW1100® four circles diffractometer, respectively. Using an Oxford Cryostream device,14 two sets of data were collected, one at 295 K and the other at 150 K. The stated temperatures were measured continuously during data collection. The structure was solved at room temperature by direct methods (SIR97)15 and refined at room- and at low temperature by least-squares procedures on _F_w. The weighting schemes were established16 empirically so as to give no trends in (w_./(F_w.)) vs (_F_w.) or (sin _/(/))2; _w. = _K/(_a_ + _b_ _F_w.) + (0.00005 _F_w.)2. The _a_ and _b_ parameters were adjusted to flatten the initial trends. The scattering factors were taken from the International Tables for X-ray Crystallography.17 Most of the calculations were performed using the Xtal3.6 system10 of programs and PARST.21 The CIF files were deposited with the Cambridge Crystallographic Data Center (CCDC 139857 and 139858). Differential scanning calorimetry experiments of 1 were performed using a Mettler GraphWare instrument.

**Ab Initio Calculations.** All of the calculations have been carried out with the Gaussian-9422 and Gaussian-9823 programs at the B3LYP/ 6-31G* level of theory.24

The two 4-pyrazole-carboxylic acid monomers and the four possible dimers (the total number of different structures is 2^4, where _n_ is the number of monomers for each cluster) have been fully optimized, and frequency calculations have been carried out to confirm the minimum nature of the structures obtained. In all of the cases, they have _C_ symmetry. For the rest of the complexes, this symmetry has been assumed, and no frequency calculations were carried out.

All of the possible trimers (eight) and eight tetramers that correspond to the proton-transfer configurations that can be obtained using AAAAA

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as the initial structure were studied. Finally, two pentamers and two heptamers were considered.

15N Solid-State NMR Spectroscopy of Pyrazole-4-carboxylic Acid. All 15N CPMAS experiments were done on a Bruker CXP-100F fourier NMR spectrometer which was equipped with an Oxford cryomagnet with a field strength of 2.1 T and a Doty MAS probe. The resulting resonance frequencies were 90.02 MHz for 1H and 9.12 MHz for 15N. For the low-temperature measurements, the driving nitrogen gas was cooled with liquid nitrogen with a home-built heat-exchanger. We used a normal cross polarization sequence, which minimizes ringing artifacts, with 3–8 ms cross polarization times, 6–10 µs 1H–90° pulse width, 3–10 s recycle delay. The longitudinal relaxation time was measured using the pulse sequence described by Torchia, without proton decoupling during relaxation period.

All spectra are referenced to external polycrystalline 15NH4Cl. To convert these data into the nitromethane scale, we used the relation 26

$$\delta(CH_3NO_2) = \delta^{15NH_4Cl_{(cryo)}} - 338.1 \text{ ppm}$$

(1)

This equation differs from the relation

$$\delta(CH_3NO_2) = \delta^{15NH_4Cl_{(bup)}} - 352.9 \text{ ppm}$$

(2)

where $$\delta^{15NH_4Cl_{(cryo)}}$$ refers to a saturated solution of 15NH4Cl in D2O at 298 K. 26 The difference $$\delta = \delta^{15NH_4Cl_{(cryo)}} - \delta^{15NH_4Cl_{(bup)}} = 17.2$$ ppm arises from different intermolecular interactions.

The 15N CPMAS NMR line shape analysis of pyrazole-4-carboxylic acid was performed using procedures described previously. 27 The proton tautomerism between the two states A and B depicted in Figure 3 modulates the isotropic nitrogen chemical shifts ($\gamma$A and $\gamma$B in Hz). The tautomeration is characterized by the equilibrium constant $K = K_{AB} = \frac{y_A}{y_B}$, where $K_{AB}$ represent the rate constants and y i the mole fractions. Figure 3a shows the line shape contributions of the two individual nitrogen atoms X and Y as a function of an increasing rate constant $K_{AB}$, divided by the chemical shift difference $\Delta \nu = \gamma_A - \gamma_B$. The usual features of a nondegenerate exchange process result. The sum of the two contributions gives the total line shape depicted in Figure 3b. Here, two lines are observed in the slow-exchange regime, which broaden and coalesce into two new lines exhibiting a reduced splitting $\Delta \nu$ in the fast-exchange regime, given by

$$\Delta \nu = (1 - K)/(1 + K)$$

(3)

as stated previously. 27 Figure 3c shows the well-known degenerate case with $K_{AB} = 1$, and Figure 3d shows the case of very fast exchange, where the value of the equilibrium constant $K_{AB}$ varies from a very small value to a value of 1. Here, the two lines continually shift toward each other and can be obtained from the splitting $K_{AB}$ according to eq 3.

Finally, Figure 3e shows the case of a superposition of different sites, all of them exhibiting a fast tautomerism, but characterized by different equilibrium constants. In this graph we assume that the site with $K_{AB} = 1$ that gives rise to the central line and the sites with $K_{AB} \approx 0$ dominate over those with intermediate values. We will show that this kind of line shape is observed for pyrazole-4-carboxylic acid at the proton disorder--order transition temperature.

Results

Crystal Structure of Pyrazole-4-carboxylic Acid (1). The compound, C6H4N2O2, $M_r = 112.088$, presents a tetragonal

the N–H and O–H groups. The main differences between both structures, at 295 and 150 K (Figure 4, a and b), are found in the O7 (z coordinate and U22 and U33 displacement parameters) and N2 atoms (U22 displacement parameter), as tested by normal probability plots.\(^{28}\) The displacement parameters at N2 reflect the differences between the internal angles at the nitrogen atom in the nondisordered compounds as the pyrazole itself,\(^1a\) the C–NH–N angle being greater than the N–N=C angle [113.0(5) vs 103.7(5)° as determined at 108 K].

Hydrogen bonding involving the carboxylic acid and the nitrogen atoms of the pyrazole occurs between molecules related by translation along the c axis, forming O–H⋯N and O⋯H–N hydrogen-bonded chains. The chains pack to form sheets by stacking interactions along the a and b directions as indicated in Figure 4c. The angle between the chains is 14.0(2)°, and the distance from the C4 atom to the pyrazole plane is 3.148(1) Å. The perpendicular sheets are linked by weak C3–H3⋯O7 interactions (Figure 4c).

**NMR Measurements.** When we recorded the first room temperature \(^{15}\)N CPMAS NMR spectrum of 1 (which turned out to be a metastable amorphous form), we observed a line trio centered at 202.7 ppm, as indicated at the top of Figure 5. The trio corresponds to a superposition of at least two nitrogen sites, one characterized by the equilibrium constant of tautomerism \(K_{AB} \approx 0\) and the other by \(K_{AB} \approx 1\). However, a significant line intensity between the lines of the trio indicated additional sites with \(0 < K_{AB} < 1\). When we heated the sample to about 100 °C for about 1 h in the NMR spectrometer and recorded the spectrum at this temperature, a single central line was observed. However, when the sample was measured again at room temperature, the trio had disappeared (Figure 5, second spectrum from the top), and only the central line had survived. This indicated to us that the initial sample corresponded to a metastable amorphous phase. The subsequent studies were then performed on the annealed sample to which we assigned a polycrystalline structure.

When we cooled this sample to low temperatures, we again observed the appearance of outer lines corresponding to sites with \(K_{AB} \approx 0\), which coexist with sites characterized by intermediate \(K_{AB}\) values, and values with \(K_{AB} \approx 1\). We assign this change to a high-order phase transition of the crystal extending over a large range of temperatures. Now, we found that the temperature-induced line shape changes were reproducible.

Line shape calculations were then performed to extract the distribution of equilibrium constants \(K_{AB}\) of the tautomeric phase transition. For this purpose, we took 20 arbitrarily chosen sites into account. Each site was characterized by a given equilibrium constant between 0 and 1, where each site contributes two Lorentzian nitrogen signals. The probability \(P(K_{AB})\) of finding a certain value of \(K_{AB}\) derived from the spectra of Figure 5 is plotted in Figure 6.

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Results of the ab Initio Calculations. The calculated energies of the various pyrazole-4-carboxylic acid associates are gathered in Table 1. The results indicate that the AB monomer is less stable than the AA monomer, but the energy difference is only 0.15 kcal mol$^{-1}$. A similar situation is observed in the case of the dimers and trimers, where all the structures are within 0.12 and 0.16 kcal mol$^{-1}$, respectively. The same happens in the calculated tetramers, pentamers, and heptamers, where the energy ranges are 0.13, 0.10, and 0.21 kcal mol$^{-1}$, respectively. These small differences indicate the quasi-degeneracy of all the possible structures. In addition, the small energetic differences observed cannot be easily rationalized on the basis of the disposition of smaller cluster or monomers.

In each cluster, a pair of coupled O$\cdots$H$-N$ and O$-H\cdots$N hydrogen bonds are formed. The final geometry of each pair is a compromise to optimize the energy. Thus, while the N$\cdots$H distance (1.776 ± 0.003 Å) is slightly shorter than the O$\cdots$H one (1.840 ± 0.003 Å), the corresponding nitrogen−oxygen distances are almost identical, that is, 2.773 ± 0.003 Å. By contrast, the hydrogen-bond angles are very different, that is, 149.2 ± 0.2° for the O$\cdots$H$-N$ and 171.1 ± 0.0° for the O$-H\cdots$N hydrogen bond. The lack of symmetry in the pyrazole molecules in the direction of the chain produces a small bend in the AAAAA... disposition, while the ABAB... structures are almost linear due to a compensation effect. For the AAAAAA trimmer, this angle is only 178.3°. In larger chains, the cumulative effect is noticeable, as illustrated for the heptamer in Figure 7a. If one composes a larger ribbon from heptamers, a circle of about 200 molecules is obtained, of which one-fourth is illustrated in Figure 7b. However, a perfectly linear ribbon results from heptamers in the ...ABABA...structure, as illustrated in Figure 7, c and d.

Discussion

The structure of pyrazole-4-carboxylic acid in the solid state is an interesting case. We studied it using X-ray crystallography, solid-state NMR and ab initio calculations. The X-ray structure of this molecule (Figure 4) showed a linear ribbon with half-proton densities on the oxygen and nitrogen atoms. Using this method, we observed almost no temperature effects on the sample. When the sample was heated, a similar phase was observed when the sample was cooled to 200 K and below, a complicated disorder−order transition is observed, leading eventually to two types of nitrogen atoms, that is, hydrogen bonds, an O$-H\cdots$N and an O$\cdots$H$-N$ hydrogen bond (see Figure 5). At the transition temperature of about 210 K, both the disordered hydrogen bonds and the two ordered hydrogen bonds are observed in slow exchange. A similar phase was observed when the sample was precipitated rapidly from water.

For a long time, we had great difficulty finding a scenario to accommodate these findings. It was only when we realized that an O$\cdots$H$-N$ hydrogen bond can be less linear or longer than an O$-H\cdots$N hydrogen bond, as illustrated in Figure 2, that we realized that longer pyrazole-4-carboxylic acid ribbons may also exhibit nonlinear superstructures as illustrated in Figure 2. Accordingly, we applied ab initio calculations of pyrazole-4-carboxylic acid associates to verify this hypothesis. We were surprised to find that the two tautomeric states of each carboxylic acid-pyrazole link exhibit very similar energies, which are affected only slightly by the tautomeric states of the neighboring links (Table 1). On the other hand, the calculated structure of heptamers does indeed exhibit either a curved ribbon structure as in Figures 2b and 7a for the all-anti conformation and an undulated ribbon structure as in Figures 2c and 7c for the all-syn conformation. This result indicates that it is energetically more favorable to have both a quasi-linear O$-H\cdots$N hydrogen bond and a somewhat longer, nonlinear O$\cdots$H$-N$ hydrogen bond with localized protons in each molecular link than two hydrogen bonds exhibiting the same geometry and a degenerate proton motion. However, the calculated energy differences are small.

Table 1. Total and Relative Calculated Energies of the Pyrazole-4-carboxylic Acid Monomers and Associates

<table>
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<tr>
<th>associate</th>
<th>structure</th>
<th>total energy (hartree)</th>
<th>relative energy (kcal mol$^{-1}$)</th>
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<td>—414.773899</td>
<td>0.00</td>
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<td>monomer</td>
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In Figure 8, a and b we compare the average X-ray crystal structure of pyrazole-4-carboxylic acid with the geometries of the seven superposed molecules of the heptamer depicted in Figure 7c. It is clear that the variations of the atomic positions along the undulated ribbon are very small. Hence, the difference between the linear ribbon with a statistical sequence of tautomeric states A and B along the ribbon and the undulated linear ribbon with a strongly alternating sequence ...ABABA... could not be detected by X-ray crystallography. This explains why we did not see different molecular X-ray structures at 295 and 150 K. However, as indicated in Figure 2, a transition between the two phases is accompanied by a localization of the protons, that is the separation of the hydrogen bonds into O–H–N and O–H–N hydrogen bridges. This explains the disorder–order transition from equivalent nitrogen atoms both with a proton density of 0.5 at high temperatures to two kinds of nitrogen atoms, one protonated and the other nonprotonated, at low temperatures, as shown in Figure 5. This transition occurs only at low temperature, as the energy difference between the linear ribbon and the undulated ribbon is very small.

The transition between the two phases is complicated; it starts in a noncorrelated way in different segments of a ribbon. If two ordered segments meet, they may be matched or not-matched; for example, a defect of the type ...ABABABBA- BABA... may be created. On the other hand, if there is a distribution of ribbons of different length in the polycrystalline material, the temperature of the disorder–order transition understandably depends on the chain length, which might explain the NMR finding that both ordered and disordered segments are observed at around 200 K.

We can now also offer an explanation for the observation of a large amount of ordered pyrazole-4-carboxylic acid molecules (Figure 5, top spectrum) when the compound is precipitated rapidly from water. Within the framework of a curved or undulated structure for a ribbon with ordered protons, it is conceivable that ribbons are formed, exhibiting not strongly alternating O–H–N and O–H–N hydrogen bond pairs, as illustrated schematically at the bottom of Figure 9. When the material is annealed, the polycrystalline state exhibiting the linear ribbon structure with disordered protons is reached (center). At low temperatures the undulated ribbon structure eventually forms, again exhibiting ordered protons (top).

Conclusions
We conclude that the case of solid pyrazole-4-carboxylic acid is a very complicated, but interesting, case of a bifunctional...
molecule with two proton donors and two proton acceptors which allows the formation of a molecular linear ribbon in the solid state in which each molecule is involved in four NHO-hydrogen bonds. Moreover, the protons in these hydrogen bonds are mobile and disordered at room temperature, consistent with a degenerate tautomerism and a single type of fast interconverting O–H⋯N and O⋯H–N hydrogen bonds. At low temperatures proton ordering takes place. This process seems to be driven by the tendency of O–H⋯N hydrogen bond to be stronger, shorter, or more linear than the corresponding O⋯H–N hydrogen bond. This phenomenon is associated with a curvature of hydrogen-bonded pyrazole carboxylic acid ribbons in the gas phase or with an undulated linear ribbon structure in the crystal at low temperatures. Thus, the proton-transfer equilibrium detected by $^{15}$N solid-state NMR is a sensitive tool for studying molecular structure that cannot easily be detected by X-ray crystallography. The complicated experimental results were only interpreted with the help of ab initio calculations.

Currently, we are using $^{15}$N- and $^2$H relaxometry to study the dynamics of the proton and the corresponding deuteron motions, which produce interesting kinetic data, including isotope effects. These results will be reported in a future paper, which will also discuss the barrier of the double proton transfer in pyrazole-carboxylic acid links compared to carboxylic acid and pyrazole dimers.

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