

Very High Resolution ^{17}O NMR Evidence for Displacive Behavior in Hydrogen-Bonded Solids: Squaric Acid

N. S. DALAL

Department of Chemistry and Biochemistry and
National High Magnetic Field Laboratory
Florida State University
Tallahassee, FL 32306-4390

K. L. PIERCE*

Department of Chemistry and Biochemistry
Florida State University
Tallahassee, FL 32306-4390

J. PALOMAR

Department of Chemistry and Biochemistry
Florida State University
Tallahassee, FL 32306-4390 and
Departamento de Química Física Aplicada
Universidad Autónoma de Madrid
Spain

R. FU

National High Magnetic Field Laboratory
Florida State University
Tallahassee, FL 32306-4390

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Magic angle sample spinning (MAS) ^{17}O NMR studies of the paraelectric-antiferroelectric phase transition (at $T_C = 373\text{ K}$) of the model hydrogen-bonded compound squaric acid ($\text{H}_2\text{C}_4\text{O}_4$) reveal a significant displacive component in the microscopic mechanism of the transition. The high resolution (400% enhancement over conventional MAS) was obtained by utilizing single crystals. All four oxygens were clearly shown to be chemically different at $T < T_C$. The peak assignment was supported by quantum theoretical calculations of the ^{17}O isotropic chemical shifts using a pentamer model of the crystal structure. There was a clear break in the isotropic part of the chemical shift on lowering the temperature through T_C , implying that the phase transition involves a distortion of the whole $\text{H}_2\text{C}_4\text{O}_4$ framework, and not just the order-disorder rearrangement of the H' 's i.e., future models of the transition should include a displacive component, in addition to an order-disorder part. The observation of the double at $T > T_C$ implies that the

Address correspondence to N. S. Dalal, Department of Chemistry and Biochemistry, Florida State University, Tallahassee, FL 32306-4390, USA. E-mail: dalal@chem.fsu.edu

*Current address: Department of Chemistry, UC Berkeley, Berkeley, CA 94720.

two O—H...O chains retain their difference in the paraelectric phase as well. This is consistent with the one-dimensional Ising chain model, in contrast to the more prevalent, two-dimensional, C₄O₄ square-lattice model.

Keywords NMR; hydrogen bonded solids

1. Introduction

This presentation summarizes our recent, very high resolution NMR measurements of the ¹⁷O isotropic chemical shift of the paraelectric-antiferroelectric phase transition at 373 K [1–4] in the model hydrogen-bonded compound, squaric acid, 3,4-dihydroxy-3-cyclobutene-1,2-dione, H₂C₄O₄, henceforth SQA, whose structure is shown in Fig. 1. The phase transition involves mainly the localization of the H's in the O—H...O bonds which hold the lattice together as essentially a two-dimensional sheet of C₄O₄ squares, held together in three dimensions by weak Van der Waals forces. At T > T_C, SQA has an average C_{4h} symmetry, with the H's occupying positions, on a statistical basis, at the middle of the O—H...O bonds. At T < T_C, the H's are locked close to one or the other O's, the symmetry is thus lowered and the unit cell acquires an antiferroelectric configuration of the electric dipoles on the H₂C₄O₄ units in the lattice. Since the discovery of its phase transition, SQA has been studied extensively, see ref. [9] for a recent review of theoretical effort. Experimentally, one of the important technique, and which is of focus here, has been solid state NMR [10–21]. However, much of the earlier work has focused on the role of the C and H sites; and the role of the O atoms has remained pretty much unexplored.

2. Experimental and Computational Details

Squaric acid was purchased from Sigma and used as received. The ¹⁷O labeling was accomplished by heating the dissolved compound in about 20% ¹⁷O-labeled H₂O, in a closed vessel.

The ¹⁷O magic angle spinning (MAS) measurements were made using a Bruker 600 MHz wide bore solid state NMR spectrometer. The ¹⁷O resonance frequency was

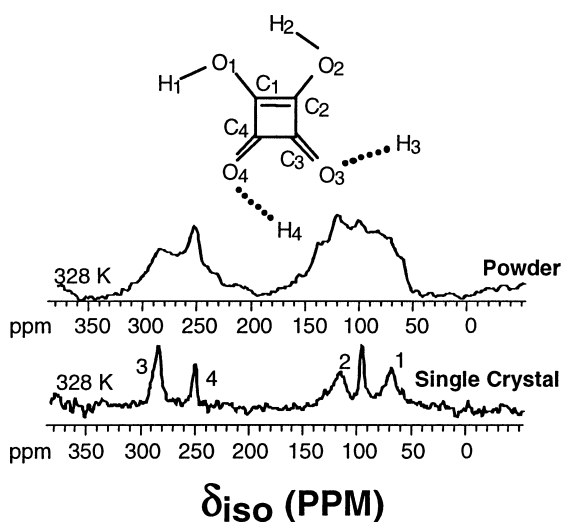


FIGURE 1 ¹⁷O MAS NMR spectra of the central (1/2 → -1/2) transition of a ¹⁷O-labeled SQA in the form of: (a) powder; (b) single crystal.

close to 81 MHz, with the sample spinning at 12.5 kHz. The variable temperatures were achieved by nitrogen gas flow, and controlled to within 0.1 K.

The molecular geometry of the isolated SQA molecule and the pentamer cluster have been obtained using the B3LYP method [23–25] in conjunction with a 6-31G** basis set. In order to avoid the interaction effects between the surrounding SQA units, the two-dimensional pentamer structure was optimized fixing the hydrogen bond angles given by neutron diffraction data at 15 K, but leaving free the rest of coordinates. The details of the geometric optimization and related considerations have been reported recently [9].

3. Results and Discussion

Figure 1 shows some typical ^{17}O NMR spectra from ^{17}O -labeled samples of SQA powder (Fig. 2a) and a single crystal (Fig. 2b) in the low temperature phase ($T < T_C$). It is seen that both the powder and the crystal show four distinct peaks, marked 1, 2, 3 and 4 in light of the numbering in Fig. 1. The remaining peak(s) in Fig. 2 are the spinning side bands, as was verified by the fact that their relative positions change in proportion to the spinning frequency. The observed peaks fall under two distinct sets: the more shifted peaks around 250 ppm can be assigned to the carbonyl ($>\text{C}=\text{O}$) oxygens, while the less shifted doublet (around 100 ppm) can be assigned to the $>\text{C}-\text{O}-\text{H}$ hydroxyl oxygens, in analogy with the earlier reported ^{13}C peaks from SQA [16–20]. Further support for this assignment was provided by our theoretical calculations, as discussed in the following subsection.

Another noteworthy observation from Fig. 1 is that the peaks in 2(b) (single crystal) are narrower by at least a factor of four as compared to those in 2(a) (powder). The mechanism of this effect is not understood at this point. At first it appeared to be related to the reduction of the anisotropic bulk magnetic susceptibility (ABMS) broadening, as described in general by Van der Hart et al. [21]. However, the powder spectra did not exhibit a significantly narrowing on dispersion of the sample in silica, as would be the case if ABMS were the cause. This question thus remains open at this time.

One can also note the much higher sensitivity of the ^{17}O NMR to the effect of the proximity of the H, as compared to that of the ^{13}C , for this type of hydrogen bonded system.

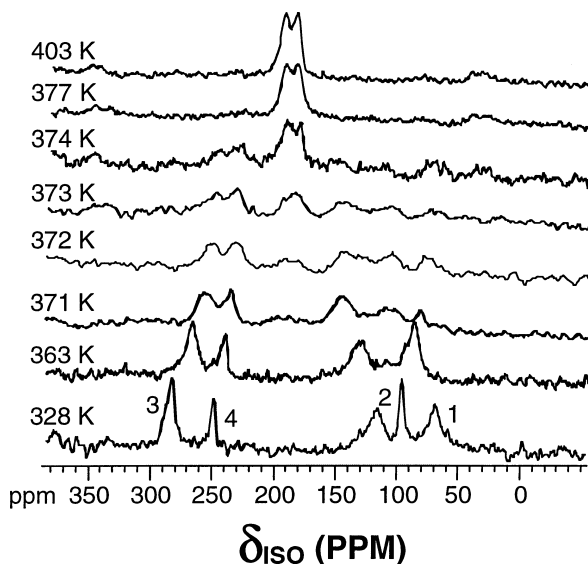


FIGURE 2 Temperature dependence of ^{17}O MAS NMR spectra of single crystal SQA.

TABLE 1 Comparison of Calculated NMR Chemical Shifts from the Theoretical SQA Models with the Experimental Data by High-Resolution Solid-State NMR Spectroscopy

	Isolated ^a	Pentamer ^a	Exp.
O ₁	65	89	70
O ₂	77	95	115
O ₃	324	270	285
O ₄	311	261	250

^aExperimental-theoretical linear correlation: $^{17}\text{O } \delta_{\text{iso}} = 209 - 0.64 \text{ } ^{17}\text{O } \sigma_{\text{iso}}$ (Sd = 25 ppm, R = 0.983).

For SQA, the splitting within a doublet is about 30 ppm for ^{17}O , but only about 1 ppm in the case of ^{13}C [24–28]. This extra dispersion enabled us to follow the phase transition in a much more precise manner (*vide infra*) than was possible with ^{13}C .

As a first step in understanding the chemical shifts of SQA, we calculated the ^{17}O NMR parameters of the isolated (i.e., gas phase) SQA molecule, obtained by GIAO method at B3LYP/6-31G** level. The calculations yield four significantly different ^{17}O chemical shifts for the gas-phase compound (Table 1).

Clearly, this result implies that the electronic environment (bonding) is distinctly different around each oxygen fragment of the asymmetric SQA ring. As expected, the two carbonyl oxygens show much higher ^{17}O chemical shifts than the hydroxyl oxygens.

Figure 2 shows the temperature dependence of the spectra. On increasing the temperature the peaks move toward each other as $T \rightarrow T_C$ from the low-temperature side. At higher temperatures, close to T_C , the peak separation decreases, and within about 2 K of the T_C , they merge to a narrow doublet with about 10 ppm separation.

Figure 3 shows the temperature dependence of δ_{ISO} for all four oxygens in SQA. Even when the broadening of the peaks leads to some dispersion of the data, we can note that the average δ_{ISO} increases steadily as $T \rightarrow T_C$, and exhibits an anomalous increase of about 13 ppm within 2–3 K of the T_C . It is thus seen that the high temperature position of ^{17}O δ_{ISO} is different from that expected from the motional averaging of the four low temperature

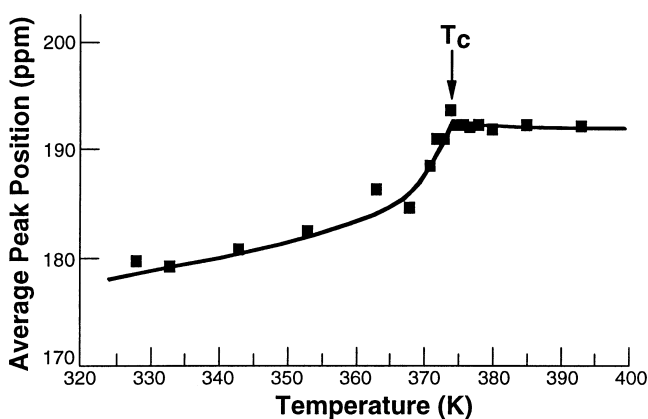


FIGURE 3 Temperature dependence of the average $^{17}\text{O } \delta_{\text{ISO}}$ in the close vicinity of the paraelectric—antiferroelectric phase transition of SQA.

peaks. This result implies that the chemical structure in the paraelectric phase is not just a time-average of the various low symmetry forms, but must include a definitive change in molecular geometry. The transition mechanism must thus involve both an order-disorder and a displacive component.

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