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Bisquaric Acid: Unusual Solid State NMR, Electronic Structure, and a Predicted Order−Disorder Transition

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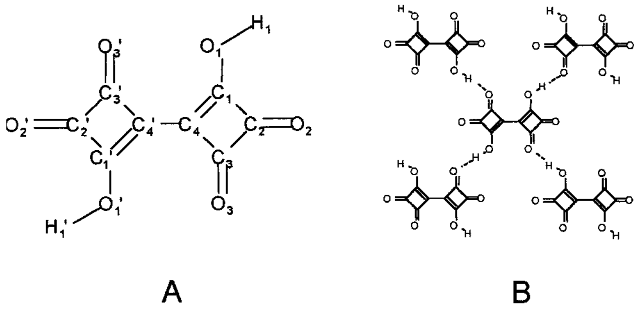
The molecular structure of the recently synthesized compound bisquaric acid was investigated by high-resolution solid state ^{13}C NMR spectroscopy and electronic structure calculations. Variable temperature ^{13}C NMR spectra were found quite unusual compared with the solution phase spectra and not explainable on the basis of the literature data on squaric acid. In particular, the ^{13}C−OH peaks were found to be coincident with the ^{13}C=O peaks. An extensive electronic structure analysis using the density functional theory (B3LYP) was thus performed, including the calculation of the ^{13}C shifts by the GIAO method. Indeed, the calculations indicate that the linker C−C bond has a substantial double-bond character, thereby leading to a strong deshielding of the C−OH carbons. In addition, the theoretical study shows significant differences between bisquaric acid and squaric acid in several molecular properties, such as aromaticity, hydrogen-bonding, dipole moment, and acid−base behavior. Unlike squaric acid, no phase transition was detected for bisquaric acid by ^{13}C NMR. However, the theoretical results suggest the possibility of such a transition at temperatures lower than about 100 °C, but it should be probed by other methods such as specific heat measurements.

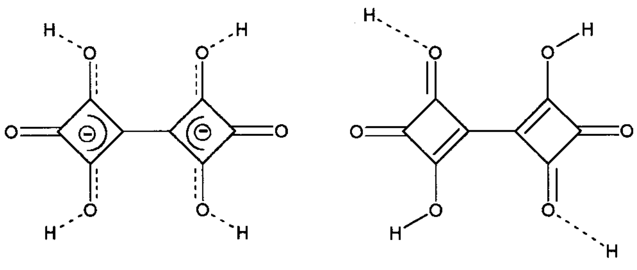
1. Introduction

Over the last several years, various derivatives of cyclobutenedione have been extensively studied in view of their application in different fields such as pharmacology,[1] photography,[2] and polymer science[3] and even in a new generation of the solid-state battery.[4] Recently, Liebeskind and co-workers[5] synthesized for the first time the parent bisquaric acid [4,4′-bis(3-hydroxy-3-cyclobutene-1,2-dione), BSQA] (see Scheme 1A). The authors showed that this compound is an extremely strong Bronsted acid, because it fully ionizes in dimethyl sulfoxide (DMSO).[5] At room temperature, bisquaric acid is a remarkably stable hydrogen-bonded solid.[5] X-ray analysis revealed the structure depicted in Scheme 1B, where the adjoining layers are rotated 90° relative to each another. Although the positions of the hydrogen atoms were not directly determined, all the oxygen atoms other than those collinear with the axes of the bisquarate were found to be involved in hydrogen bonding. In fact, equal lengths of the noncollinear C−O bonds were reported, implying equivalent oxygens participate in identical hydrogen bonds. Additionally, the X-ray data implied a disordered model (Scheme 2A) for the hydrogen atoms, with O$\cdots$O distances of 2.52 Å,[5] virtually identical with that for squaric acid (2.55 Å).[6] This distance is characteristic of hydrogen-bonded compounds that exhibit ferroelectric properties (e.g., spontaneous dipole moment in the unit cell) below a certain temperature, called the Curie point, T_C. Examples are squaric acid ($H_2C_4O_4$) and the family of dihydrogen phosphates (MH_2PO_4, with M = K, Rb, Cs, and NH_4^+). The T_C for squaric acid (SQA) is 100 °C. Below this temperature SQA exhibits an ordered structure with two vicinal and two distal protons in each molecule and clearly localized single and double bonds in the aromatic ring. At 100 °C SQA undergoes a structural transition and the high-temperature structure has a fully disordered C_4O_4 unit and the hydrogens equally distributed on two principal positions in the O$\cdots$O hydrogen bonds.[6] Because of its close structural similarity to SQA and the ferroelectric phosphates, it was of interest to examine BSQA as a parent compound of a new class of ferroelectric materials, with potential for nonlinear optical and dielectric applications.

SCHEME 1



SCHEME 2



A. Disordered Model B. Ordered model

The present study was thus undertaken with the view of understanding the electronic structure and measuring the hydrogen-bonding dynamics in bisquaric acid (BSQA). Detailed solid-state high-resolution ^{13}C NMR measurements on a powder of BSQA over the range −150 to +250 °C have been carried

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out, in analogy to the earlier studies on squaric acid.[7−9] The studies on SQA include the utilization of single crystals in magic angle spinning studies which reported an order of magnitude enhancement in ^{13}C NMR spectra.[7] The enhanced resolution led to the important conclusion that the mechanism of antiferroelectric transition in squaric acid involves not only the order−disorder motion of the hydrogen atoms but also a displacive component from the ring moiety.[8] In addition, this technique enabled the development of a two-dimensional temperature jump technique[9] in ^{13}C NMR for obtaining information on how the different atomic units correlate to each other when the sample temperature is quickly jumped across the transition temperature. These earlier studies are quite complementary to the present investigation and should be consulted for some experimental details.

The ^{13}C NMR spectra in the solid phase of bisquaric acid were found highly unusual, as compared to those in the solution phase and could not be understood in terms of the X-ray structure, including the possibility of a plausible ferroelectric or antiferroelecteric phase transition. We thus performed electronic structure calculations, employing density functional methods, which have enabled us to explain the unexpected anomalies in the ^{13}C NMR spectra. Additionally, a preliminary theoretical analysis reveals significant differences between BSQA and SQA in terms of their dipole moment, aromaticity, hydrogen-bonding, and acid−base behavior. These new findings might be helpful in tailoring the solid state and related properties of this class of compounds.

2. Experimental and Computational Details

2.1. Computational Details. All the molecular geometries and energies have been calculated by means of the B3LYP[10,11] method in conjunction with a 6-31G** basis set. The theoretical free energies of protonation and deprotonation have been obtained at the same B3LYP/6-31G** computational level, including electronic energies, zero-point energies, enthalpy temperature corrections, and absolute entropies at 298.15 K and 1 atm, together with the entropy term for a free proton in the Sackur−Tetrode equation (7.75 kcal/mol). The isotropic NMR nuclear shieldings (^{13}C σ_{iso}) were calculated at the B3LYP/6-31G** level using the GIAO[12,13] method. The conversion to chemical shifts (^{13}C δ) was done using the experimental−theoretical linear correlation found in ref 14 for related hydrogen-bonded systems. All the calculations have been performed with the Gaussian 98 program.[15]

2.2. NMR Measurements. The NMR spectra were obtained from ^{13}C in natural abundance using the ^{13}C/H double-resonance, cross-polarization (CP) technique,[16] coupled with the magic angle spinning methodology.[17−21] Powdered crystals were employed in the variable temperature MAS measurements. The high-resolution NMR spectra were obtained at a nominal proton Larmor frequency of 360 MHz, using a Chemagnetics CMX-360 system.

The proton-decoupled ^{13}C MAS spectra were obtained after cross-polarization (CP) with the protons using a standard variable amplitude CP pulse sequence, combined with a proton flip-back technique in order to increase the repetition rate. With this procedure, sufficient signal-to-noise was usually achieved with 4−12 accumulations.

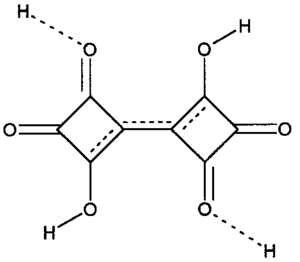
2.3. Synthesis. The bisquaric acid samples used in this work were provided by Dr. Liebeskind of Emory University in Atlanta, who was the first to report the synthesis of this compound.[5] The synthesis details are all described earlier.[5]

TABLE 1: Bond Distances (Å) from X-ray Analysis and from the B3LYP/6-31G Optimized Geometries of the Monomer and Trimer of Bisquaric Acid (Calculated Geometrical Parameters for Bisquarate Dianion Also Tabulated)**

	X-ray[a]	monomer	trimer[e]	dianion
C_1-C_2	1.520 (1.532)[b]	1.505	1.516 (1.505)	1.534
C_2-C_3	1.520	1.567	1.548 (1.567)	1.534
C_3-C_4	1.428 (1.436)[c]	1.507	1.473 (1.507)	1.467
C_1-C_4	1.428	1.382	1.400 (1.383)	1.467
C_4-C_4'	1.435	1.422	1.423	1.425
C_1-O_1	1.244 (1.256)[d]	1.315	1.290 (1.314)	1.234
C_2-O_2	1.198	1.204	1.202 (1.204)	1.228
C_3-O_3	1.244	1.202	1.222 (1.201)	1.234
O_1-H_1		0.973	1.007 (0.973)	
$H_1\cdots O_3'$			1.615	
$O_1\ldots O_3'$	2.523		2.621	

[a] Reference 5. [b] Average value obtained using the B3LYP/6-31G** trimer data: $[d(C_1-C_2) + d(C_2-C_3)]/2$. [c] Average value obtained using the B3LYP/6-31G** trimer data: $[d(C_3-C_4) + d(C_1-C_4)]/2$. [d] Average value obtained using the B3LYP/6-31G** trimer data: $[d(C_1-O_1) + d(C_3-O_3)]/2$. [e] Values in parentheses correspond to the half-unit free of hydrogen-bonds in the trimer.

SCHEME 3



3. Results

3.1. Molecular Geometry. The optimized geometrical parameters of the isolated bisquaric acid (BSQA) molecule, obtained at the B3LYP/6-31G** level, are given in Table 1. The calculated C−C and C−O bonds in this structure have a clear single- or double-bond character. In principle, the BSQA molecule should be less aromatic than the SQA molecule, mainly due to the absence of one of the resonant $O{=}C{-}C{=}C{-}OH$ chains. This is clear from the comparison between the bond distances of BSQA and those of the referenced molecules bicyclobutenediol and bicyclobutandione. We found that the optimized C═C and C═O double bonds are elongated by 0.029 and 0.004 Å in BSQA, as compared to the corresponding values 0.035 and 0.010 Å in SQA.[22]

An interesting observation from this theoretical study was that the linker $C_4'-C_4$ bond in the optimized geometry of BSQA is unusually short (1.422 Å) for a normal single bond. The comparison with the parent compounds shows a similar short $C_4'-C_4$ bond for bicyclobutenediol (1.432 Å), but clearly not for bicyclobutandione (1.529 Å). From the analysis of their electronic structures, we found that these results are due to an electronic displacement from the double $C_1{=}C_4$ bond to the intercyclic $C_4'-C_4$ bond, as drawn in Scheme 3. Therefore, unlike in SQA, the substituent at the C_4 position of the squarate ring of BSQA is an electron acceptor group, and therefore the intercyclic $C_4'-C_4$ link has a substantial double-bond character. This model is supported by the fact that the isolated molecule SQA, even being clearly a more resonant structure than that of BSQA (see Table 1 in ref 23), presents a purer double $C_1{=}C_4$ bond (1.374 Å).[22]

SCHEME 4

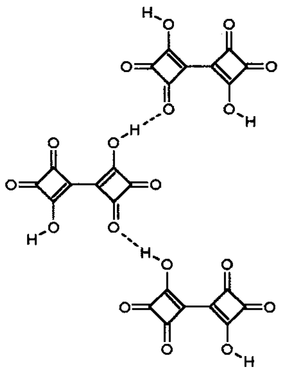


TABLE 2: Theoretical Free Energies (kcal/mol) of Deprotonation (ΔG_{a1} and ΔG_{a2}) and Protonation (ΔG_{b1} and ΔG_{b2}) of Bisquaric Acid and Squaric Acid, Obtained at the B3LYP/6-31G Level**

	bisquaric acid	squaric acid
ΔG_{a1}	298.6	315.6
ΔG_{a2}	696.5	760.6
ΔG_{b1}	−197.7	−191.9
ΔG_{b2}	−311.6	−280.9

TABLE 3: Comparisons of Calculated ^{13}C NMR Chemical Shift with the Experimental Data for Squarate Dianion and Bisquaric Acid[a]

	bisquarate		bisquaric acid		
	exp[b]	calcd[c]	exp[d]	trimer[c]	monomer[c]
C_1	193.6 (twice int)	196.8	202.4 (twice int)	203.0 (195.7)[e]	195.8
C_2	205.4	235.2	189.5	192.7 (199.8)[e]	199.7
C_3	193.6	196.8	202.4	201.4 (187.7)[e]	188.3
C_4	164.6	184.6	157.7	159.5 (165.0)[e]	165.3

[a] All values given in ppm relative to TMS. [b] DMSO solution. [c] GIAO method at B3LYP/6-31G** level. [d] Solid state. [e] Values in parentheses correspond to the half-unit free of hydrogen bonds in the trimer.

SCHEME 5

2 x Bisquaric Acid (Monomer) → Bisquaric Acid (Dimer) $\Delta E = E_{HB-1}$ (1)

3 x Bisquaric Acid (Monomer) → Bisquaric Acid (Trimer) $\Delta E'/2 = E_{HB-2}$ (2)

3.2. Hydrogen Bonding. To understand the hydrogen-bonding property of bisquaric acid, we obtained the optimized geometry for the trimer system shown in Scheme 4. This model provides an adequate description of the two hydrogen bonds of the half-unit of bisquaric acid. The model consistency was indicated by the fact that the linker $C_4'{-}C_4$ bond as the geometrical parameter (see Table 1) and the NMR properties (see Table 3 below) for the other half-unit of the double-hydrogen-bonded molecule remain almost unaffected in the trimer. The bond distances for the trimer system optimized at the B3LYP/6-31G** level are summarized in Table 1. As can be seen, the optimized $C_3{=}O_3$, $C_1{-}O_1$, $C_4{=}C_1$, and $C_3{-}C_4$ bonds in the double-hydrogen-bonded structure mainly lose their single- or double-bond character, which clearly indicates a strongly reinforced resonance along the $\cdots O_3{=}C_3{-}C_4{=}C_1{-}O_1{-}H\cdots$ chain in the hydrogen-bonded system. However, we still find an ordered structure with clearly distinguishable hydroxyl and carbonyl oxygens forming the hydrogen bonds.

The calculations also yield the hydrogen-bond energy for bisquaric acid as $\Delta E = E_{HB-1}$ in eq 1 (Scheme 5), according to the widely used theoretical model. The B3LYP/6-31G** calculated value (E_{HB-1} = 10.2 kcal/mol) shows a strong intermolecular hydrogen bond in BSQA, slightly stronger than that in SQA (E_{HB-1} = 9.2 kcal/mol).[23] This result is in line with the slightly shorter O···O distance found in BSQA (2.52 Å) than in SQA (2.55 Å).[5,6] Additionally, the hydrogen-bond energy increases with the number of hydrogen bonds in the system (eq 2; E_{HB-2} = 11.7 kcal/mol).

3.3. Dipole Moment. Another remarkable theoretical result is that the symmetry for the optimized geometry of the BSQA molecule is C_{2h}, and as a result, the dipole moments of the half-units cancel each other, and the global dipole moment is zero (in contrast, SQA possesses a significant dipole moment value, 2.1 D).[24] In addition, since all the hydrogen bonds are identical in BSQA, the C_{2h} symmetry should remain in the crystal. Therefore, unlike SQA, one does not expect BSQA to exhibit ferroelectricity or antiferroelectricity. However, a structural phase transition is a good possibility (vide infra).

3.4. Acid−Base Properties. As noted by Liebeskind et al.,[5] an unusual property of BSQA is its high acidity (pK_2 = 4.49).[5] To understand this, we investigated this behavior for BSQA as well as SQA. The high acidity of SQA acid has been attributed to a greatly resonance stabilized squarate dianion. Zhou et al.[22] showed that the calculated C−C and C−O bonds in the squarate dianion have no clear single- or double-bond character. Similar results have been found for the bisquarate dianion (Table 1). It should be noted, however, that bisquarate dianion contains only one negative charge in each square unit. In Table 2, the calculated free energy of mono- and bis-deprotonation for BSQA, obtained at B3LYP/6-31G** level are collected. Theoretical results indicate the title compound is a stronger acid than SQA, which is also consistent with the available experimental pK_2 values,[5,25] or even sulfuric acid (ΔG_{a1} = 302.5 kcal/mol).[26] In addition, we report (Table 2) results of B3LYP/6-31G** calculations of gas-phase basicity for BSQA and SQA acids. It should be noted that the computed free energies of protonation for the isolated BSQA molecule show bisquaric acid as a remarkably strong base too, more basic than SQA.

3.5. NMR Data. As mentioned in the Introduction, the NMR spectra of solid BSQA were found to be quite unexpected. Typical ^{13}C NMR spectra of BSQA are shown in Figure 1. The spectrum in Figure 1A is that in DMSO, corresponding to the bisquarate dianion. The three peaks labeled 1−3 are at 205.4, 193.6, and 164.6 ppm, in agreement with the data of Liebeskind et al.[5] Since peak 2 at 193.6 ppm is the largest one, it is clearly assigned to the four axial C−O carbons (C_1, C_1', C_3, and C_3'). Peak 1 at 205.4 ppm is then assigned to the equatorial C=O carbons (C_2 and C_2'), while peak 3 at 164.6 ppm corresponds to the two bridge carbons C_4 and C_4'. This assignment is supported by the calculated ^{13}C chemical shifts (Table 3) of the bisquarate dianion, obtained with the GIAO method at the B3LYP/6-31G** level. From the theoretical results, the largest peak (peak 2) clearly results from the overlap of the peaks from four equivalent carbon atoms (C_1, C_1', C_3, and C_3').

Figure 1B shows the CPMAS high-resolution ^{13}C NMR spectrum of powdered BSQA at room temperature. As in Figure 1A, this spectrum also contains three peaks at approximately the same positions (202.4, 189.5, and 157.7 ppm). Surprisingly, however, the signal in the carbonyl region (peak 1) here presents a twice integrated intensity with respect to the other two peaks. This result is not simply understood in terms of the disordered model shown in Scheme 2A. In fact, the ^{13}C NMR spectrum suggests an ordered model for BSQA at room temperature (Scheme 2B). Thus, if peak 1 was a superposition of two overlapped carbonyl resonances, then the hydrogen atoms should be asymmetrically displaced in the O···O bond, making bonded oxygens inequivalent.

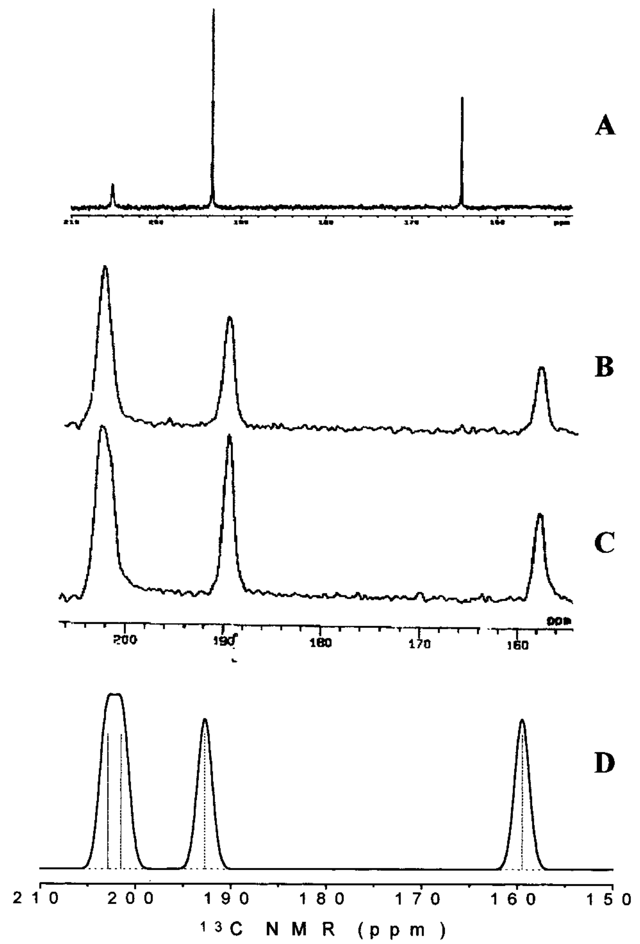


Figure 1. (A) ^{13}C NMR solution spectrum for bisquarate dianion. (B) and (C) solid state ^{13}C CPMAS NMR spectra for bisquaric acid at +18 and −150 °C, respectively. (D) Theoretically calculated ^{13}C NMR spectrum for a bisquaric acid trimer.

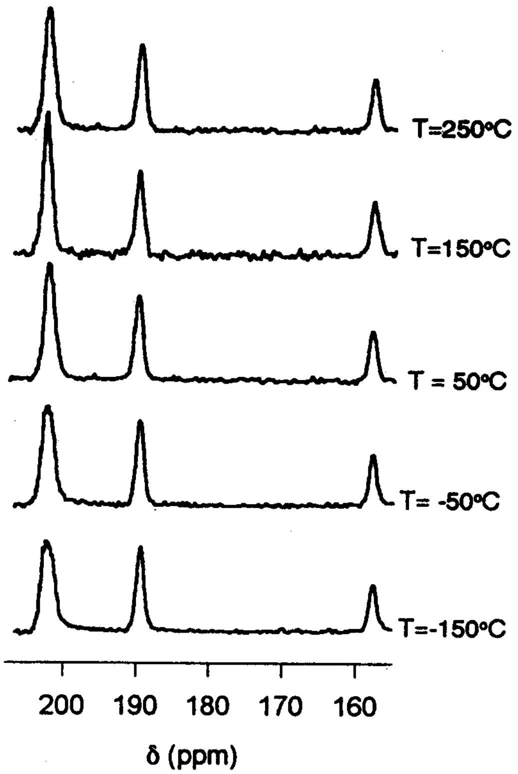


Figure 2. Temperature dependence of the ^{13}C CPMAS NMR spectra for bisquaric acid.

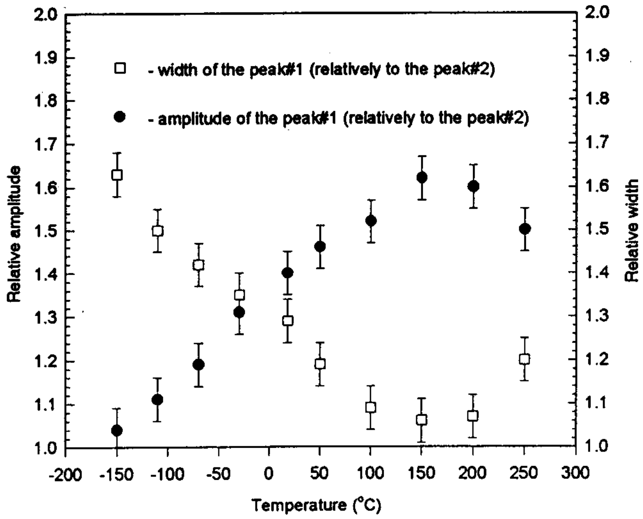


Figure 3. Temperature dependence of intensity (●) and width (□) of the peak 1 in the ^{13}C CPMAS NMR spectra for bisquaric acid. The measurements were done with respect to the peak 2 in the same spectra.

In the case of squaric acid, the NMR signal positions of the carbon atoms adjacent to the O—H···O moiety display a strong temperature dependence.[7] Figure 2 shows some typical ^{13}C CPMAS spectra for BSQA in the −150 to +250 °C temperature range. The spectra show no dramatic splitting, as expected from a structural phase transition, in contrast to the SQA case.[7] However, the shape of this carbonyl peak strongly changes with temperature, showing inverse temperature dependence of its relative height and width values (Figure 3). In fact, the height of peak 1 at −150 °C is close to that of peak 2, while a shoulder appears in the signal (Figure 1C). These results clearly indicate that the carbonyl peak consists of two overlapping resonances, whose chemical shifts have different temperature dependences, but the peak positions are too close for being resolved.

For further confirmation of this interpretation, we calculated ^{13}C NMR data for BSQA using the B3LYP/6-31G** optimized geometries of the isolated molecule and the trimer system. The calculated chemical shifts for BSQA are shown in Table 3. Significantly, the theoretical NMR spectra for the hydrogen-bonded system (trimer model) shows an excellent agreement with the observed NMR solid-state spectra (Figure 1D), supporting the conclusion that peak 1 at 202.4 ppm consists of two overlapping resonances. However, it should be noted that this peak arises from the hydroxyl carbon atom (C_1) and the carbonyl carbon atom (C_3) implicated in the hydrogen bonds, instead of being associated with two carbonyl groups. Consequently, peaks 2 and 3 are associated with the carbon atoms not involved in the hydrogen bonding of BSQA. An important new question from these NMR results is why the ^{13}C—OH peak is at such a high ppm level. As can be seen in Table 3, the unusually high $^{13}C_1$ chemical shift is also found in the isolated molecule. The analysis of the NMR data for BSQA, its parent compounds, and other smaller molecular models show us that the shorter the intercyclic C_4'—C_4 bond the higher the $^{13}C_1$ chemical shift. Therefore, we conclude that the unexpected strong deshielding in atom C_1 is directly related to the electronic migration from C_4=C_1 toward the linker C_4'—C_4 bond.

On the other hand, from the NMR data of the trimer and the isolated molecule (Table 3), we find that the global hydrogen-bonding effect increases the C_1 and C_3 chemical shifts, whereas it shields the C_2 and C_4 components. These results should be interpreted mainly as an increased π-resonance along the

$\cdots O_3{=}C_3{-}C_4{=}C_1{-}O_1{-}H\cdots$ chain. This result is common to other hydrogen-bonded systems connected by π-conjugated double bonds.[27]

The above presented theoretical and experimental results are consistent with an ordered structure in solid bisquaric acid. However, since the signals of the carbons (C_1 and C_3) associated with the hydrogen bonds overlap, it is clear that ^{13}C NMR spectroscopy would fail to detect the presence of a phase transition in BSQA. The published X-ray data at room temperature do not resolve this question either.[5] The reported bond distances and angles could result from a disordered structure due to a structural phase transition, but could as well be a result of the average of the molecules, as shown in Scheme 1B, where the two molecules forming each hydrogen bond are switched.

An indication of a possible phase transition is provided by the temperature dependence of the line shapes of C_1 and C_3 NMR signals. In addition, considering the stronger hydrogen bond and the higher acidity and basicity of BSQA than those of SQA, the former should present a lower energy barrier for the hydrogen movement along the O···O bond. Therefore, a structural phase transition can be expected in bisquaric acid, probably at temperatures lower than 100 °C.

4. Conclusions

The recently synthesized compound bisquaric acid has been investigated by solid state, high-resolution, ^{13}C NMR spectroscopy and density functional calculations. The ^{13}C NMR spectra were found to be unusual, consisting of three peaks, in contrast to four for squaric acid. The highest intensity peak was found to be the most shifted. This peak has been reliablly assigned to the overlapped resonances of the C─OH and C═O carbons participating in the hydrogen bond. The anomalously high chemical shift of the hydroxyl carbon was attributed to electron donation from the alkene group of the squarate unit to the linker C─C bond. Thus, the intercyclic bond behaves as an electron acceptor group. Another significant difference between bisquaric acid and squaric acid arises from the fact that bisquaric acid presents only one resonant O═C─C═C─OH chain. As a consquence, our theoretical study shows noticeably different aromaticity, hydrogen-bonding, and acid−base behavior between these two compounds. In addition, bisquaric acid exhibits no dipole moment in contrast to the strongly polar squaric acid.

No phase transition was detected in bisquaric acid by ^{13}C NMR spectroscopy. This may, however, be due to the accidental overlap of the NMR peaks. The temperature dependence of the ^{13}C NMR spectral line shape and the theoretical results point to a possible structural instability in bisquaric acid. Other techniques such as specific heat measurements should be carried out to verify this hypothesis of the predicted phase transition in bisquaric acid. These studies are currently under progress in our laboratory.

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