Structural Studies of a New Low Molecular Mass Organic Gelator for Organic Liquids Based on Simple Salt

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A series of easy to prepare organic salt based on imidazole derivatives and cyclobutane-1,1-dicarboxylic acid have been studied for their gelation behavior after it was found that imidazolium hydrogen cyclobutane-1,1-dicarboxylate (**1**) can harden few organic liquids. **1** forms remarkably stable gel (remains intact for several months in an open container, gel dissociation temp $T_{Gel} = 66$ °C) with nitrobenzene at a very low concentration of 0.137 wt %, whereas bis-imidazolium cyclobutane-1,1-dicarboxylate (**2**) resulted in a weak and unstable gel with nitrobenzene, indicating the importance of the free COOH group in **1** in gel formation. Molecular packing in the primary assembly unit (fibers) of xerogel of **1**/nitrobenzene is successfully established based on single-crystal X-ray and X-ray powder diffraction data. The morph responsible for gel formation of **1** with nitrobenzene is found to be different from that of its xerogel. Substitution on the imidazole moiety results in nongelators.

Introduction

Low molecular mass organic gelators[1−7] (LMOGs) are viscoelastic materials comprised of an organic gelator and an organic liquid. LMOGs self-assemble into various type of aggregates such as fibers, strands, and tapes, which are formed when a solution containing the gelator molecule is cooled below the gelation temperature (T_g). The aggregates are shown to cross-link among themselves through "junction zones"[8] and form a three-dimensional (3D) network that immobilizes the solvent molecules and thereby results in gels or viscous liquids. Unlike polymeric gels whose 3D network is based on covalent linkage, these physical gels obtained from LMOGs depend on relatively weak nonbonded interactions, for example, hydrogen bonding, $\pi-\pi$ stacking, and van der Waals. Two distinct categories of gelators based on LMOGs, hydrogen-bond-based and non-hydrogen-bond based gelators, are known according to the difference in driving force for the molecular aggregation. While polymeric gels have increasingly found applications in industry such as food, cosmetics, athletic shoes, and chromatography, LMOGs have been found to be used promisingly as agents for oil spill problems,[9] as structure-directing agents (template) for making helical transition metal oxide[10] and silica,[11] in the making of microcelluar materials[5b] and in the CO_2-based coating process,[5b] in the making of dye-sensitized solar cells,[12] and so forth. Therefore, LMOGs have been an active research field in recent years in materials science and supramolecular chemistry. However, to date, only a limited number of LMOGs have been found and many of them are serendipitous. It is also impossible to select a molecule that will definitely gel a selected liquid. Moreover, making most of such gelators involves nontrivial organic synthesis and designing of these fasci-

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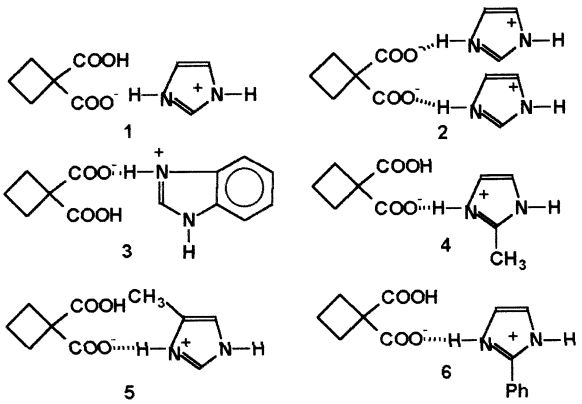
Scheme 1



nating organic materials still remains a major challenge. The major structural issues and other issues important to address are (i) how the molecules pack in the "gel fibers", (ii) how the gel fibers form the junction zones, (iii) what, if any, is the relationship between molecular packing of the bulk crystals of the gelator molecule and gel fiber, and finally (iv) why the metastable gel is formed instead of thermodymically stable crystals. Answering some of these questions will definitely provide valuable information that might decipher the mechanism of gel formation and eventually lead to the successful design of functional gelator molecules.

During the course of our investigation in crystal engineering,[13] we serendipitously discovered that a simple organic salt, namely, imidazolium hydrogen cyclobutane-1,1-dicarboxylic acid (**1**), has the ability to harden few organic liquids. Having been encouraged by this result, we decided to study its gelation behavior and aggregate structure in detail. Thus, a series of salts (Scheme 1) based on cyclobutane-1,1-dicarboxylic acid and imidazole derivatives have been prepared and characterized to gain insight into the structural aspects of the gelation behavior of **1**.

The gelation behavior of **1** and the single-crystal structures of **1** and **3** are presented here. The molecular packing of the primary assembly unit (fibers) in the xerogel of **1** is also established based on X-ray powder diffraction data of bulk crystalline solid of **1**, its xerogel, and single-crystal data. The techniques employed to characterize the compounds and gelation behavior are FT-IR, ^{1}H NMR, X-ray powder diffraction (XRPD), X-ray single-crystal diffraction, optical microscopy, and scanning electron microscopy (SEM).

Experimental Section

Materials and Synthesis. All chemicals are commercially available (Aldrich) and used without further purification. Salts **1** and **3**−**6** were prepared by mixing acid and corresponding base in equimolar amounts in MeOH at room temperature; in salt **2**, the ratio of acid and base was 1:2. In all cases, the yield is nearly quantitative.

Analytical Data. 1: mp 146 °C. ^{1}H NMR 200 MHz (DMSO-d_6): δ 7.88 (1H, s), 7.12 (2H, s), 2.29−2.37 (4H, m), 1.79−1.91 (2H, m). FT-IR (KBr): 3147, 2951, 2847, 2763, 2649, 1945, 1711, 1591, 1427, 1371, 1310, 1208, 1153, 1113, 1055, 975, 893, 842, 781, 691, 631, 516, 483, 432 cm^{-1}.

2: mp 86 °C. ^{1}H NMR 200 MHz (DMSO-d_6): δ 7.88 (2H, s), 7.12 (4H, s), 2.29−2.50 (4H, m), 1.79−1.95 (2H, m). FT-IR (KBr): 3150, 3096, 2954, 2925, 2855, 2728, 2550, 2473, 1990, 1573, 1555, 1463, 1378, 1319, 1221, 1155, 1136, 1085, 1051, 864, 788, 756, 721, 702, 639, 533, 457, 425 cm^{-1}.

3: mp 123 °C. ^{1}H NMR 200 MHz (DMSO-d_6): δ 8.25 (1H, s), 7.57−7.62 (2H, m), 7.17−7.22 (2H, m), 2.33−2.41 (4H, m), 1.77−1.92 (2H, m). FT-IR (KBr): 3143, 3080, 2981, 2937, 2850, 2592, 1920, 1698, 1625, 1598, 1524, 1459, 1436, 1364, 1285, 1243, 1217, 1150, 1128, 1063, 1002, 947, 858, 953, 700, 619, 535, 464, 425 cm^{-1}.

4: mp 149 °C. ^{1}H NMR 200 MHz (DMSO-d_6): δ 7.18 (2H, s), 2.28−2.40 (7H, m), 1.81−1.97 (2H, m). FT-IR (KBr): 3420, 3178, 3122, 2982, 2943, 2852, 2708, 2598, 1891, 1701, 1633, 1573, 1472, 1436, 1358, 1313, 1280, 1214, 1154, 1123, 990, 951, 833, 780, 754, 681, 631, 503, 470, 422 cm^{-1}.

5: mp 87 °C. ^{1}H NMR 200 MHz (DMSO-d_6): δ 8.03 (1H, s), 6.95 (1H, s), 2.29−2.36 (4H, m), 2.17 (3H, s), 1.80−1.96 (2H, m). FT-IR (KBr): 3421, 3176, 3135,3046, 2949, 2866, 2799, 2764, 2694, 2613, 2504, 1919, 1710, 1638, 1561, 1508, 1469, 1384, 1269, 1204, 1150, 1111, 1093, 1053, 1017, 964, 946, 879, 854, 810, 697, 659, 630, 498, 468, 428 cm^{-1}.

6: mp 121 °C. ^{1}H NMR 200 MHz (DMSO-d_6): δ 7.91−7.95 (2H, m), 7.31−7.49 (3H, m), 7.18 (2H, s), 2.32−2.40 (4H, m), 1.77−1.93 (2H, m). FT-IR (KBr): 3529, 3399, 3171, 3149, 3114, 2977, 2899, 2765, 2676, 2616, 2465, 2368, 1918, 1845, 1702, 1634, 1570, 1518, 1493, 1471, 1432, 1398, 1338, 1286, 1205, 1151, 1072, 1031, 946, 913, 778, 703, 686, 626, 556, 506, 457, 429 cm^{-1}.

Single-Crystal X-ray Diffraction. X-ray quality single crystal of **1** could be grown by evaporating methanolic solution of **1** under vacuum, whereas good quality crystals of **3** were obtained by slow evaporation of ethanolic solution of **3** at 4 °C.

Data collection (CAD4 diffractometer, Mo Kα, λ = 0.7107 Å), data reduction, structure solution, refinement, and analyses were carried out by using the programs CAD-4 PC,[14] NRCVAX program,[15] SHELX97,[16] and MERCURY,[17] respectively. The structures were solved by direct methods and refined in a routine manner. All non-hydrogen atoms were refined anisotropically and converged. In **1**, hydrogen atoms attached to carbon atoms were fixed at their calculated position (riding model) and refined. The hydrogen atoms attached to imidazole ring nitrogen and carboxylic acid group are located in the difference Fourier map and refined. In **3**, all hydrogen atoms were located on the difference Fourier map and refined.

Single-Crystal Data for 1. Molecular formula = $C_9H_{12}N_2O_4$, FW = 212.21, space group = monoclinic, *Cc*, a = 14.932(3) Å, b = 8.976(3) Å, c = 10.100(4) Å, β = 127.96(3)°, V = 1067.3(6) Å^3, z = 4, calculated crystal density = 1.321 g/cm^3. 932 reflections were collected, of which 859 were observed $I \geq 2\sigma I$, 139 parameters, R = 0.0434, and wR2 = 0.1147.

Single-Crystal Data for 3. Molecular formula = C_{26} H_{28} N_4 O_8, FW = 524.52, space group = monoclinic, $P2_1/a$, a = 19.176(2) Å, b = 5.537(4) Å, c = 25.025(2) Å, β = 108.77(1)°, V = 2515.8(2) Å^3, z = 4, calculated crystal density = 1.385 g/cm^3. 3254 reflections were collected, of which 2459 were observed $I \geq 2\sigma I$, 455 parameters, R = 0.04 and wR2 = 0.0981.

Powder X-ray Diffraction. Powder diffraction patterns of neat gelator, xerogel (nitrobenzene, slowly evaporated), and gel (nitrobenzene) of **1** were recorded on XPERT Philips (Cu Kα radiation).

Optical Microscopy. A gel (nitrobenzene) of **1** was prepared between two glass cover slides and observed under a low-resolution (40×) LEICA optical microscope equipped with crossed polars. A high-resolution (400×) OLYMPUS BX60

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(17) Mercury 1.0 Supplied with Cambridge Structural Database, Copyright CCDC, 2001.

microscope was used to see the fibrous network in detail. The photograph was taken by a digital CCD camera (JVC) interfaced with a computer (software BVMV500 version 1.2.1, Expert Vision Pvt. Ltd., Mumbai, India).

Scanning Electron Microscopy. A drop of 25-μL solution of **1** in nitrobenzene was allowed to form gel on a sample holder of XL 30 ESEM (Philips) and the image was recorded.

Results and Discussion

The gelation behavior of **1** was checked in the following manner. The gelator **1** was suspended in the solvent of choice and a few drops of MeOH were added. The mixture was then heated at ~70 °C until it became a clear solution and left at RT to cool. Due to low solubility of **1** in organic solvent, MeOH was used as a good solvent. Gel was formed within 10 min or few hours depending on the solvent. The role of MeOH seems to be quite significant as another good solvent such as EtOH did not effect gelation with the organic solvents studied here. Salt **1** gave clear solution with aniline, digol, and phenol, precipitate with petrol, plate-shaped crystals with *n*-butanol and *n*-hexane, fibrous crystals with bromobenzene, benzene, ethyl acetate, and acetonitrile, and viscous liquid with methyl salicylate, chloroform, and 1,2-dichlorobenzene. With nitrobenzene (0.137 wt %, at RT), chlorobenzene (1.396 wt %, at RT), and toluene (34.64 wt % at 4 °C) salt **1** did form gel. It is interesting to note that **1** forms the most efficient gel with nitrobenzene. Ten milligrams of compound **1** can gelate 7.28 mL of nitrobenzene, that is, 0.137 wt %, meaning that one gelator molecule can immobilize ~1506 nitrobenzene molecules. Gel of **1** in nitrobenzene was prepared in test tubes and 5-mL beakers (not sealed) and the containers could be inverted and shaken or tapped on a workbench without any deformity of the gel. Nitrobenzene gel of **1** kept at RT is thermoreversible and stable in an open container for several months with a small amount of solvent loss. T_{Gel} of **1** in nitrobenzene was found to be 66 °C and was measured by using the following method: 1.0 wt % gel of **1** in nitrobenzene was prepared in a test tube. A locally made glass ball weighing 0.19 g was placed on the gel surface. The test tube was then heated in an oil bath. The temperature (T_{Gel}) was noted when the ball fell to the bottom of the test tube.

Observation under a low-resolution optical microscope equipped with a cross polar revealed the typical fibrous nature of the gel and the fibers, often radiating from central points, which are optically birefringent, displaying its crystalline nature. More detailed features of these fibers could be seen when a small portion of the gel are viewed under a high-resolution (400×) optical microscope. An optical micrograph (Figure 1) of a small portion of gel of **1** (nitrobenzene) revealed a several hundred micrometers long (often branched) flexible intertwined fibrous network. The diameter of each fiber is ~2.5 μm. A similar type of flexible fiber in an optical micrograph is seen for some other hydrogen-bonded LMOG.[18] It can be assumed that the macroscopic flexible fibers present in the gel (Figure 1) could be comprised of molecular fibers corresponding to the expected hydrogen-bonded 1D molecular fibers (molecular diameter ~2.5 Å) arising from imidazolium hydrogen cyclobutane-1,1-dicarboxalte moiety.

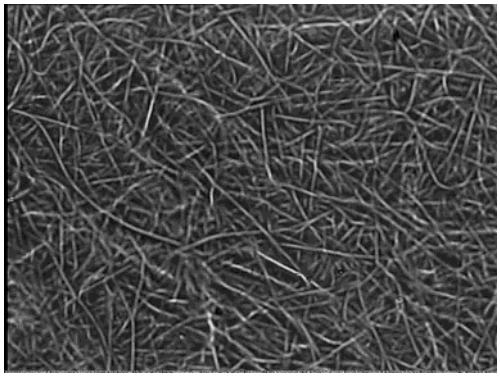

Figure 1. Optical micrograph of the gel **1**/nitrobenzene (400×).

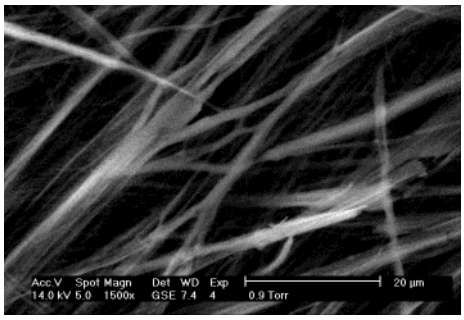

Figure 2. SEM image of the xerogel obtained from **1**/nitrobenzene (1 wt %).

To see further detailed features of the fiber, SEM analyses of a xerogel of **1**/nitrobenzene was performed. Figure 2 depicts the typical 3D network of fibers in the xerogel.

FT-IR spectra of **1** (neat solid) and its nitrobenzene xerogel (obtained by slow evaporation) are found to be identical, meaning that the internal structure of the gelator molecules in a neat solid is identical to its xerogel.

To address the important structural aspect, that is, how do the molecules pack in the elementary fibers, we decided to carry out detailed structural studies using single-crystal and XRPD techniques. Fortunately, a good quality single crystal of **1** could be obtained while evaporating methanolic solution of **1** under vacuum and subjecting it to single-crystal X-ray diffraction. The crystal structure of **1** showed that it is a hydrogen-bonded three-dimensional network involving polymeric 1D hydrogen-bonded chains of imidazolium hydrogen cyclobutane-1,1-dicarboxylate moiety (Figure 3). Such chains in which imidazolium ion is involved in hydrogen bonding with a COO^- anion moiety through N−H···O hydrogen bonding (N···O = 2.647 and 2.920 Å) are arranged in a parallel fashion to generate layer structures. The layers are in turn connected with other layers through COOH···$^-$OOC hydrogen bonding (C···O = 2.582 Å; each moiety coming from two different layers), leading to a hydrogen-bonded 3D network (Figure 3).

To establish whether the molecular packing of **1** as found in its crystal structure is representative of the bulk solid of **1** or not, the XRPD pattern of a neat solid of **1** was recorded and compared with the simulated powder pattern generated from single-crystal data. The

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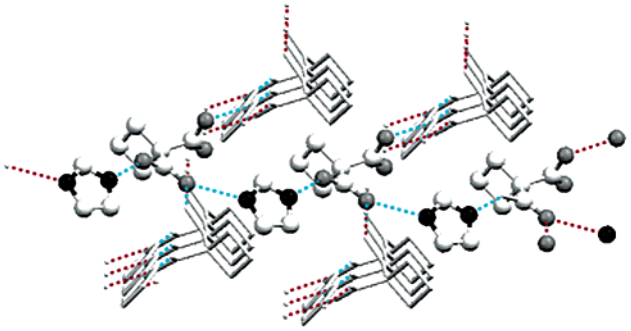

Figure 3. 3D hydrogen-bonded network in a single-crystal structure of **1**. The 1D hydrogen-bonded infinite chain involving imidazolium hydrogen cyclobutane-1,1-dicarboxylate moiety is shown in a ball-and-stick model. In a capped stick model are the same chains oriented approximately orthogonal to the same chains (represented in ball-and-stick) connected via COOH···$^{-}$OOC hydrogen bonding. Hydrogen atoms are not shown for the sake of clarity.

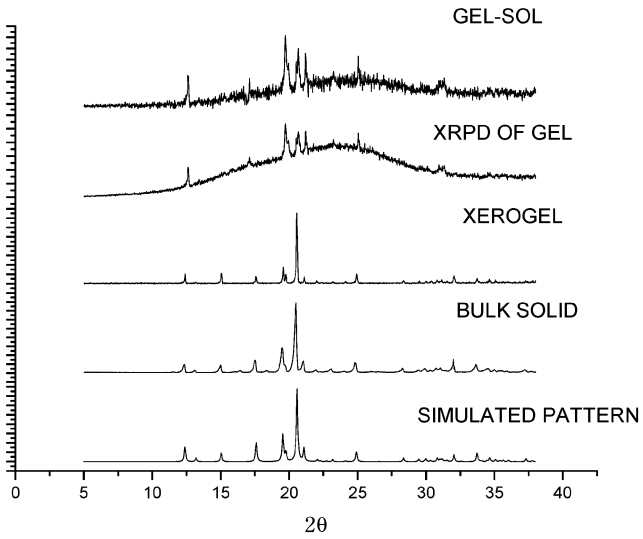

Figure 4. XRPD patterns of **1** under various conditions.

virtually superimposable XRPD patterns (Figure 4) suggest that the single crystal of **1** obtained during evaporation indeed represent the bulk solid of **1** and, therefore, the molecular packing of the crystalline bulk gelator **1** is determined. Interestingly, the powder pattern of nitrobenzene xerogel of **1** was also found to be practically superimposable with the simulated pattern of **1** obtained from its single-crystal structure (Figure 4). Thus, the packing of the molecules within the unit fibers of the xerogel of **1** is unambiguously established.

It is clear from the single-crystal structure analysis and XRPD data that a strong self-complementary and unidirectional intermolecular hydrogen-bonded 1D self-assembly is present in the primary assembly unit of the xerogel. However, the overall hydrogen-bonded network is a three-dimensional one. According to recent reports by Shinkai et al. and collaborators,[19] a 1D hydrogen-bonded network promotes gelation whereas a 2D and 3D network either produce a weak gel or do not promote gelation at all. Then why does **1** promote gelation? Considering the fact that a solid−solid morphological change of the fibers of the gel (during the transformation from gel to xerogel) can be induced either by solvent removal (while forming xerogel) or by nucleation events initiated by the small amount of gelator that might be present in the solution in the bulk liquid in a gelled state, there is no certainty that the molecular packing in the fiber of a xerogel truly represents that in a gelled state. To see the XRPD pattern of **1** in a gelled state and to see whether it matches with that of xerogel or bulk solid, we adopted a method recently developed by Weiss et al. and collaborators.[20] In this method, the XRPD pattern of the solvent is subtracted from that of the gel. The resulting pattern should represent the gel fibers in the gelled state. Therefore, the pattern of the gel−sol in Figure 4 represents the characteristic pattern for the gel fibers of **1**/nitrobenzene. A comparison of XRPDs of bulk solid and gel−sol revealed that the peak positions and relative intensities of the major peaks in these two patterns do not match because of the following reasons. All seven prominent peaks of bulk solid appear at 2θ = 20.52, 19.52, 17.56, 21.07, 24.90, 12.37, and 15.04° (given in the decreasing order of relative intensities, and the corresponding *d* values are 4.32, 4.54, 5.04, 4.21, 3.57, 7.14, and 5.88 Å), whereas the corresponding values for gel−sol are 2θ = 19.73, 20.69, 21.23, 25.06, 12.66, 17.10, and 31.33° (the corresponding *d* values are 4.49, 4.28, 4.18, 3.54, 6.98, 5.17, and 2.85 Å). It is clear now that the most fundamental parameters of an ordered crystalline sample, that is, *d* values, of these two patterns do not match at all. Therefore, the fiber responsible for gel formation is a different morph and consequently molecular packing of the fibers in the gelled state is definitely not identical to that found in the fibers of the xerogel or bulk solid. It is known that many times the morph responsible for gelation is not the one found by normal crystallization.[20a] It is shown that organo gel fibers are not so "wet" with solvent molecules[21] but the stability of such fibers are solvent-dependent and the solvent molecules are trapped in the inter-unit fiber channels.[22] In accordance with this observation and results obtained by Shinkai et al. and collaborators,[19] it may be reasonable to assume that the fibers responsible for gel formation in the present case could be arising due to the molecular packing rearrangement leading to the formation of a 1D network based on imidazolium hydrogen cyclobutane-1,1-dicarboxylate moiety and the free COOH group of the acid moiety might be playing a role in the entanglement of the fibers, resulting in gel formation.

Although it is not clear what are the factors that induce the formation of crystalline fibers in the gel and the nature of "junction zones", we decided to carry out

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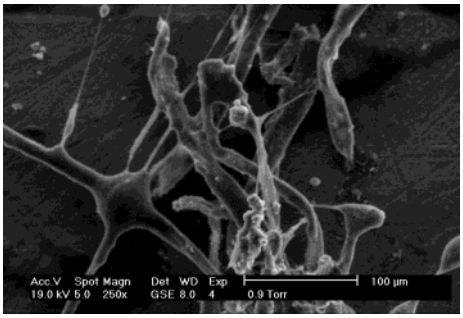

Figure 5. SEM of a xerogel of **2**/nitrobenzene.

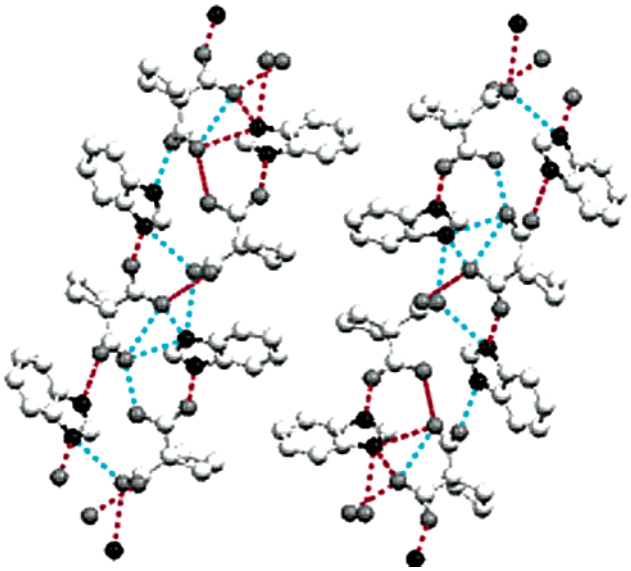

Figure 6. 2D hydrogen-bonded network in a single-crystal structure of **3**. 2D hydrogen-bonded layers are along the *a*−*b* plane and packed along *c* via van der Waals interactions. Hydrogen atoms are not shown for the sake of clarity.

further experiments to see the structural dependence of gel formation in the present system. To see what important role the free COOH of acid moiety might be playing in gel formation, we prepared a 2:1 (imidazole: cyclobutane-1,1-dicarboxylic acid) salt, **2**, in which both the protons of two COOH groups of the acid part are taken away by the imidazole moiety. Interestingly, salt **2** formed a weak gel with nitrobenzene, found to be unstable at RT, losing its solvents slowly over a few hours time. The SEM picture (Figure 5) of xerogel obtained from **2**/nitrobenzene clearly shows that the nature of the fibers is quite different from that found in the xerogel of **1**/nitrobenzene (Figure 2).

It is also important to mention here that 1:1 salts generated from substituted imidazole, salts **3**−**6** (Scheme 1), with cyclobutane-1,1-dicarboxylic acid did not effect gelation with the solvents studied here. Considering that the crystal structures of these salts might throw some light onto the cause of **3**−**6** not forming a gel, we focused our efforts determining the crystal structures. Despite our best efforts, we obtained an X-ray quality single crystal of **3** only. Determination of the single-crystal structure of **3** revealed that there are two hydrogen-bonded ion pairs in the asymmetric unit (unlike in **1** where the asymmetric unit contains a single ion pair) and such assembly propagates parallel to the *a*−*b* plane, leading to a 2D network. The 2D layers are then packed along the *c* axis through van der Waals interactions involving an alicylic ring of acid and aromatic ring of benzimidazole moieties. The packing of the molecules in **3** is displayed in Figure 6. This is in accordance with the finding of Shinkai et al. and collaborators[19] that a 2D network does not promote gelation.

Conclusions

We have successfully demonstrated that an easy to prepare salt, **1**, can harden some organic liquids. The fact that **1** forms a gel with nitrobenzene at such a low concentration of 0.137 wt % is remarkable. A combination of single-crystal X-ray and XRPD data clearly established the molecular packing of the primary assembly unit of **1** in its xerogel. However, the morph responsible for gel formation is different from that of its xerogel. The morph responsible for gel formation might not be the thermodynamically most stable one and, therefore, such phase transformation is quite possible while removing the solvent during xerogel formation. There is no certainty that such a change does occur during xerogel formation, but there is no evidence that it does not. Study of the unit fibers in the gelled state (if possible) is therefore important. Thus, conclusions based on analytical data on xerogel as to the molecular packing of the unit fibers in its gelled state might be misleading, as demonstrated in this example and elsewhere.[20a] The fact that **3** does not form gel and **2** forms only a weak gel with nitrobenzene could be understood to some extent based on the single-crystal structure of **3** and the expected molecular structure and SEM of the xerogel of **2**, respectively. Nongelating behavior of **3**-**6** clearly demonstrates the effect of substitution on imidazole moiety on gel formation. The simplicity of the system in terms of synthesis offers the special advantage of studying the system further without becoming involved with time-consuming nontrivial organic synthesis. Studies on similar systems are underway.

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Supporting Information Available: Photograph of a several month old gel of **1**/nitrobenzene, ORTEP diagram with the atom numbering scheme for **1** and **3**, and their hydrogen-bonding parameters (PDF) and a combined crystallographic information file (CIF). This material is available free of charge via the Internet at http://pubs.acs.org.

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