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Molecular Assemblies from Imidazolyl-Containing Haloalkenes and Haloalkynes: Competition between Halogen and Hydrogen Bonding

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Abstract: The structural characterization of molecular assemblies constructed from imidazolyl-containing haloalkenes and haloalkynes is reported. 1-(3-Iodopropargyl)imidazole (**2**) and 1-(2,3,3-triiodoallyl)imidazole (**5**) were synthesized from 1-propargylimidazole (**1**). In the solid state, these wholly organic modules self-assemble through N···I halogen-bonding interactions, thus giving rise to polymeric chains. The N···I interaction observed in **2** (d(N···I) = 2.717 Å, $\sphericalangle$C(sp)-I···N = 175.8°) is quite strong relative to previously reported data. The N···I interaction in **5** (d(N···I) = 2.901 Å, $\sphericalangle$C(sp^2)-I···N = 173.6°) is weaker, in accordance with the order C(sp)-X←base > C(sp^2)-X←base. Compound **5** was found to give a 1:1 cocrystal **4** with morpholinium iodide (**6**). In the X-ray crystal studies of **4**, N···I halogen-bonding interactions similar to those observed in **5** were shown not to be present, as the arrangement of the molecules is governed by two interwoven hydrogen-bonding networks. The first network involves N-H···O interactions between nearby morpholinium cations, and the second network is based on N-H···N hydrogen bonding between morpholinium cations and imidazolyl groups. Both hydrogen-bonding schemes are charge-assisted. Halogen bonding is not completely wiped out, however, as the triiodoalkene fragment forms a halogen bond with an iodide anion in its vicinity (d(I···I) = 3.470 Å, $\sphericalangle$C(sp^2)-I···I = 170.7°). X-ray crystal studies of **6** show a completely different arrangement from that observed in **4**, namely, N-H···O interactions are not present. In crystalline **6**, morpholinium cations are interconnected through C-H···O bridges (d(H···O) = 2.521 and 2.676 Å), and the NH$_2^+$ groups interact with nearby iodide anions (d(H···I) = 2.633 and 2.698 Å).

Keywords: crystal engineering · donor–acceptor systems · halogen bonding · hydrogen bonds · self-assembly

Introduction and Background

Currently, an intense research effort is being devoted to the construction of wholly organic architectures with controlled topologies by use of noncovalent bonding. This modular approach circumvents the construction of a large number of covalent bonds, thus simplifying the synthetic task and minimizing the chance of side reactions. This activity encompasses several areas of research, such as supramolecular chemistry, crystal engineering, and materials science. One motivation for the synthesis of wholly organic architectures is their topological resemblance to existing inorganic systems; therefore, it is often found that the former exhibit properties similar to those of the latter. For example, wholly organic structures are capable of assembling into 2D[1,2] and 3D[3] networks that resemble structurally and functionally pillared clays and zeolites.

These structures are held together by an appropriate synthon which, very often, relies on hydrogen bonding or charge-assisted hydrogen bonding. Among the most frequently used moieties with hydrogen-bonding capabilities, pyridine, its analogues, and carboxylates occupy the first rank. Another building block that has become quite popular in recent years is imidazole, and the chemistry of this heterocycle is now becoming quite rich and versatile. Indeed, many facets of imidazole chemistry resemble aspects of pyridine chemistry. Just like pyridine, imidazole is capable of assembling through acid–base chemistry with a large number of molecules possessing acidic sites, especially carboxylic acids, and form numerous coordination complexes with many metals.[4,5] Alkylation of imidazoles gives imidazolium

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salts that show many similarities with pyridinium salts, and these salts have proven interesting for a number of reasons: some of them are liquid at, or just above, room temperature or exhibit liquid crystallinity.[6,7] Imidazolium-based ionic liquids are used as media in organic reactions because they are environmentally benign and, in some cases, they perform better than the usually used organic solvents.[8] As a result of their high ionic conductivities,[9] they have considerable potential as electrolytes for batteries and capacitors. Finally, imidazolium salts are useful starting materials for the preparation of metal complexes bearing N-heterocyclic carbene ligands.[10]

In recent years, halogen bonding has become an increasingly important interaction in crystal engineering for the assembly of small organic building blocks.[11] It is a charge-transfer interaction of the $n\rightarrow\sigma^*$ type between an electron-rich atom and a halogen atom bonded to an electron-deficient organic fragment or belonging to a dihalogen molecule.[12] It is a directional interaction that shows many similarities with hydrogen bonding: its strength depends not only on the distance between the bonded atoms but, also, on the D···X-Y angle (D = donor atom; X = halogen; Y = carbon, halogen). Furthermore, it was suggested early on that halogen bonding might be comparable in energy with hydrogen bonding,[13] and recent results from computational studies[14] have confirmed this idea.

Many reports are available concerning halogen bonding in which the donor is a nitrogen-containing group, especially pyridine and its analogues.[12,15–24] Surprisingly, reports are quite scarce concerning the study of halogen-bonded systems in which imidazolyl groups take part. The diiodine basicity of imidazoles has been measured by means of the formation constant of diiodine–imidazole complexes in heptane at 298 K,[25] but the structural characterization of architectures sustained by halogen bonding in which imidazolyl groups are involved has not been reported. C-halogen···N interactions have been observed by X-ray crystal studies of Schiff-base-containing triazoles and 5-bromotetrazole,[26,27] but such interactions are overpowered by hydrogen bonding in the solid-state structures of 3-chloro-1*H*-1,2,4-triazole and 3-bromo-1*H*-1,2,4-triazole.[28]

The electron-poor portion of the charge-transfer complex is generally an electron-deficient organic halide, and so 1,4-diiodotetrafluorobenzene has been used quite extensively.[12,15,16,18,24,29,30] Halogen bonding in which the halide is attached to a double or triple bond is known, but these systems have been the subject of much fewer studies. Polymeric chains result from the interaction between tetraiodoethylene (TIE) and diamines.[16,31] Also, this alkene has been cocrystallized with various diacetylenic molecules in the hope of obtaining host–guest complexes in which the diacetylenic fragments are suitably oriented for topochemical polymerization.[32,33] Halogen bonding involving haloalkynes has been studied in both the solid state and solution. Various complexes between 1-halo-2-phenylacetylenes and halide ions have been prepared, and the structures and stoichiometries of these complexes were found to depend on the nature of the halide ion and type of organic cation.[34–36] Polymers with 1:1 stoichiometries result from the interaction of diiodoacetylene with halide ions,[36–38] and a polymeric network is also obtained by cocrystallization of diiodohexatriyne with triphenylphosphine oxide.[39] In that connection, Goroff and co-workers recently reported some spectacular results: the polymerization of diiododiacetylene was achieved in the solid state despite the explosiveness of this molecule. This "tour de force" was accomplished by forming halogen-bonded complexes between diiododiacetylene and oxalamide-containing hosts terminated with nitrile groups at both ends.[40] In these host–guest complexes, the diacetylenic guest is suitably oriented for topochemical polymerization. Previous attempts to do the same using host molecules with pyridyl groups instead of nitrile groups had been unsuccessful as a result of steric problems.[41]

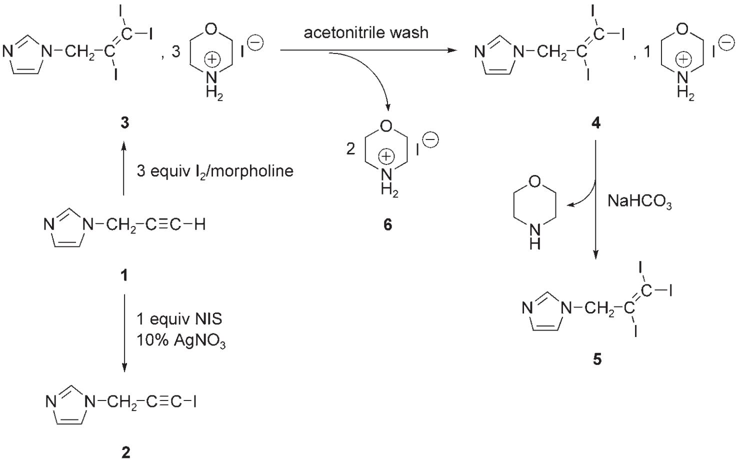
In solution, the strength of the interaction of 1-iodoacetylenes with Lewis bases has been measured by means of vibrational spectroscopy.[42] This technique has proven very useful in the determination of the formation constants of such acid–base complexes.[43] The interactions between $[D_6]$DMSO and diiodohexatriyne and diiodooctatetrayne have been investigated by ^{13}C NMR spectroscopy. The chemical shifts of the carbon atoms bonded to iodine moved from about $\delta = 1$ ppm in $CDCl_3$ to approximately $\delta = 15$ ppm in $[D_6]$DMSO. This effect was attributed to polarization of the iodoalkyne triple bond in a Lewis acid–base complex with the solvent.[39] These results were reproduced computationally.[44] Additional support for this interpretation was obtained from good correlation with various empirical models of solvent basicity, including Gutmann's donor numbers and Taft and Kamlet's β values.[45] Furthermore, poor correlation to Reichardt's E^N_T values and Taft and Kamlet's π^* parameters suggests that solvent polarity does not play a role.[45] Interestingly, the resonance of the I-C(sp^2) moiety of iodoarenes in ^{13}C NMR spectroscopic analysis does not undergo a downfield shift on changing from a noncoordinating to a coordinating solvent, even though complexation occurs.[46] It was proposed that this phenomenon is because the nonrelativistic complexation shifts and the change in the spin-orbit-induced heavy-atom effect of iodine compensate each other.

We describe herein the syntheses of wholly organic architectures in which halogen-bonding interactions between imidazolyl groups and haloalkene and haloalkyne moieties are present. This structural study provides new examples of the utilization of imidazole in the construction of self-assembled networks and improves the current knowledge of halogen bonding with halogenated alkenes and alkynes. The molecules that were selected are 1-(3-iodopropargyl)imidazole (**2**) and 1-(2,3,3-triiodoallyl)imidazole (**5**). Insight into the solid-state organization of these organic modules is of paramount importance to the design of novel functional materials with specific properties (e.g., high microporosity, nonlinear optical response, and liquid crystallinity) and quite valuable in case solid-state reactivity is sought. Also, these compounds are good models for future computational studies. The approach followed herein is similar to that chosen by Czugler,[17] van der Boom,[23] Drabent,[26] and others,[47] namely, the acceptor and donor sites are present in the same molecule. By employing this approach, the chances for disturbance by competing interactions are at a minimum. We also report that these 1D heteroditopic tectons are capable of forming cocrystals with other organic modules with hydrogen-bonding capabilities and that, in this case, halogen bonding is no longer the structure-directing interaction in the solid.

Results and Discussion

Syntheses: 1-Propargylimidazole (**1**) is a known compound that has been prepared by *N*-propargylation of imidazole using different methods.[48] Alternative procedures utilized microwave irradiation in the presence of various types of magnesium oxide catalysts or made use of solid–liquid phase-transfer catalysis.[49,50] In some cases, the reaction is complicated by the formation of substantial amounts of 1-propadienyl-1*H*-imidazole.[50a] We prepared **1** by the reaction between lithiated imidazole and propargyl bromide in anhydrous THF, at −78 °C, in 82 % yield after purification by distillation under reduced pressure.

Compounds **2** and **5** have been synthesized before and tested for antibacterial and antifungal activities.[51] Compound **2** was obtained by allowing imidazole to react with 3-iodopropargyl 4-methylbenzenesulfonate in DMF at room temperature. Compound **5** was prepared similarly by using 2,3,3-triiodoallyl 4-methylbenzenesulfonate instead of 3-iodopropargyl 4-methylbenzenesulfonate. Our synthetic approach was different (Scheme 1): iodoalkyne **2** was synthesized by allowing alkyne **1** to react with *N*-iodosuccinimide (NIS) in the presence of 10 mol % $AgNO_3$.[52] Elemental analysis of the resulting pale-yellow solid gave unsatisfactory results. Furthermore, energy-dispersive spectroscopy (EDS) measurements showed that large amounts of silver were present in the solid, presumably coordinated to the imidazole ring of **2**. Several attempts were made to remove the silver by decomplexation with dithizone, KCN, and 1,4,8,11-tetraazacyclotetradecane, but these attempts led to decomposition of the product or met with only limited success. The best method to purify the material consisted of washing the crude solid on a glass frit with hot acetonitrile, decreasing the volume of the filtrate on a rotary evaporator, and allowing the material to crystallize in a freezer.



Scheme 1. Syntheses of compounds **2**–**6**.

Iodination of **1** with three equivalents of the iodine–morpholine complex does not lead to **2**, but solid **3** is obtained instead. ^1H NMR spectroscopic analysis showed that **3** is a mixture of **5** and morpholinium iodide in a 1:3 ratio (Scheme 1). It is noteworthy that **3** was obtained even when an excess of **1** was used. Clearly, under these conditions, addition of iodine across the triple bond of **2** is more facile than iodination of **1**. Washing **3** with acetonitrile yields another solid **4**, whose composition is **5**·1 morpholinium iodide. As will be seen later, the fraction of morpholinium iodide that is not washed away is part of a cocrystal with **5**. Compound **5** is obtained by suspending **4** in a saturated aqueous solution of $NaHCO_3$.

Structure of 2: X-ray quality crystals of **2** were obtained by dissolving a small amount of powder in acetonitrile and allowing the solution to come slowly to dryness. In the solid (Table 1), molecules of **2** form layers that pile up along the *a* axis (Figure 1). Looking at one layer from the top, one can see polymeric chains that run along the *c* axis. These chains resemble undulating wires and are the result of C(sp)-I···N interactions between molecules. These findings explain why **2** is only soluble in coordinating solvents such as dimethyl sulfoxide (DMSO) and acetonitrile: the C(sp)-I···N interactions must be broken for the solid to dissolve. The N···I distance is 2.717 Å and the C(sp)-I···N angle is 175.8°. These values are indicative of strong halogen-bonding interactions.[11] The I···N distance is longer than that found in the PhC≡CI·morpholine complex (2.51 Å)[53] and shorter than the I···N distance in solid IC≡CCN (2.93 Å).[54] These results are consistent with the fact that morpholine is a stronger base than imidazole (pK_b(morpholine) = 5.5; pK_b(imidazole) = 7.01) and the fact that nitrile groups are only weakly basic moieties. There are no I···π interactions such as those observed in the platinum–alkynyl compounds prepared by Adams and Bowen.[55] This difference is because the nitrogen atom at the 3-position of the imidazole ring is more basic than the π cloud of the triple bond. It is also noteworthy that acetonitrile molecules are not present in the structure; there again, these findings agree with the fact that imidazolyl groups are stronger bases than nitrile moieties. Neighbouring imidazole groups in each layer are parallel. The centroid···centroid distance between adjacent rings is 4.377 Å, and the angle between the centroid···centroid vector and the ring normal is 40.9°. These parameters are indicative of weak π···π interactions.[56–58] Yet, given the large number of such interactions in **2**, it is likely that their

Table 1. Crystal data and experimental details of data collection and refinement of **2**, **4**, **5** and **6**.

Compound	**2**	**4**	**5**	**6**
empirical formula	$C_6H_5I_1N_2$	$C_{10}H_{15}I_4N_3O_1$	$C_6H_5I_3N_2$	$C_4H_{10}I_1N_1O_1$
formula weight	232.02	700.87	485.83	215.035
crystal colour	colourless	pale yellow	light brown	pale yellow
crystal size [mm]	0.15×0.20×0.30	0.05×0.05×0.16	0.28×0.30×0.35	0.06×0.10×0.27
crystal system	monoclinic	monoclinic	monoclinic	monoclinic
space group	$P2_1/c$ (no. 14)	$P2_1/c$ (no. 14)	$P2_1/n$ (no. 14)	$P2_1/c$ (no. 14)
a [Å]	8.863(4)	12.4431(6)	4.79500(10)	6.6135(5)
b [Å]	4.377(2)	14.9315(6)	16.5970(3)	10.4064(8)
c [Å]	18.677(1)	9.6060(4)	13.3515(3)	10.1808(8)
α [°]	90	90	90	90
β [°]	95.507(4)	97.002(4)	95.008(4)	98.893(7)
γ [°]	90	90	90	90
V [Å^3]	721.2(5)	1771.43(13)	1058.49(4)	692.25(9)
Z	4	4	4	4
T [K]	173	173	173	173
ρ_{calcd} [g cm^{-3}]	2.137	2.628	3.026	2.063
$F(000)$	432	1264	856	408
μ [mm^{-1}]	4.349	7.031	8.741	4.527
T_{min}, T_{max}	0.49, 0.52	0.70, 0.73	0.07, 0.09	0.37, 0.76
graphite-monochromated $Mo_{K\alpha}$ radiation [Å]	0.71073	0.71073	0.71073	0.71073
θ range [°]	3.027–32.295	3.163–32.304	2.885–32.312	3.118–32.258
index ranges	$-12 \leq h \leq 12$ $-6 \leq k \leq 6$ $-27 \leq l \leq 27$	$-18 \leq h \leq 17$ $-21 \leq k \leq 22$ $-14 \leq l \leq 14$	$-7 \leq h \leq 6$ $-24 \leq k \leq 24$ $-19 \leq l \leq 19$	$-9 \leq h \leq 9$ $-14 \leq k \leq 15$ $-15 \leq l \leq 14$
data collected	12416	27703	20287	12928
unique data, R_{int}	2371, 0.049	5804, 0.067	3493, 0.029	4381, 0.105
observed data ($I_o > 2\sigma(I_o)$)	1518	2238	2710	1518
L.S. parameters, restraints	82, 0	163, 0	100, 0	65, 0
R,[a] R_w[b] (obsd reflns)	0.0501, 0.0355	0.0437, 0.0404	0.0208, 0.0255	0.0344, 0.0201
R,[a] R_w[b] (all reflns)	0.0804, 0.0361	0.1354, 0.0482	0.0310, 0.0257	0.0603, 0.0219
weighting scheme,[c] A_i	13.7, 0.705, 9.65, 6.66, 1.05	8.30, −7.54, 3.87, 1.79, −1.38	12.7, −6.97, 10.7	−34.0, 23.9, −69.7, 22.6, −29.9
max shift/esd	0.000185	0.001276	0.001986	0.000920
goodness-of-fit	1.1126	1.1424	0.9781	1.0155
$\Delta\rho_{min}$, $\Delta\rho_{max}$ [e Å^{-3}]	−1.38, 1.44	−1.25, 1.59	−1.18, 0.99	−1.20, 0.83

[a] $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. [b] $R_w = [\Sigma(w(F_o^2 - F_c^2)^2)/\Sigma(w(F_o^2)^2)]^{1/2}$. [c] $w = [\text{weight}] \times [1 - (\Delta F/6\sigma(F))^2]^2$; $[\text{weight}] = 1.0/[A_0T_0(x) + A_1T_1(x) + \ldots + A_{n-1}T_{n-1}(x)]$ where A_i are the Chebychev coefficients listed in the Table and $x = F_{calcd}/F_{max}$.

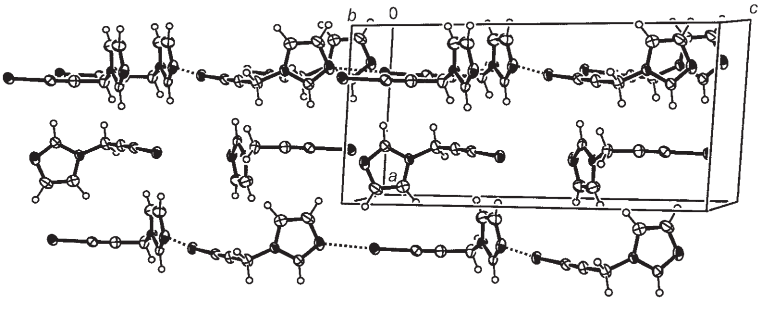


Figure 1. View along the b axis showing the layered structure of **2** and the N···I interactions between molecules in each layer.

contribution to the stabilization of the structure is not zero. There is also a C-H···π contact between the methylene group of one molecule and the imidazole ring of an adjacent molecule in the same layer. The H···Cg distance is 2.70 Å, the C-H···Cg angle is 132.0°, and the angle between the H–Cg axis and H–Hperp vector is 6.6° (Cg: centroid position; Hperp: orthogonal projection of the H position onto the ring). This weak interaction is of type III according to the classification developed by Malone et al.,[59] and the H···Cg distance is the same as that typically found in complexes between alkanes and aromatic species.[60]

Structure of 5: X-ray-quality crystals of **5** were grown from acetonitrile. In the solid state (Table 1), molecules of **5** pile up in stacks along the a axis (Figure 2). The stacks are not isolated but interact with one another: a cut through the stacks along the bc plane shows that alkene **5** self-assembles into polymeric chains that run parallel to the b axis. The molecules are interconnected through halogen bonds, with each halogen bond involving the imidazolyl group of one molecule and the $=CI_2$ fragment of the next molecule. The chains are zigzag-shaped as a result of the crooked form of the organic module. In each molecule, the imidazolyl group and the $CI=CI_2$ fragment lie almost perpendicular to each other. Intermolecular I···N distances are 2.901 Å and the C-(sp^2)-I···N angles are 173.6°, thus indicating that this interaction is reasonably strong; however, it is weaker than that observed in alkyne **2**, in accordance with the order C(sp)-X←base > C(sp^2)-X←base > C(sp^3)-X←base.[11] The I···N distance reported herein is slightly shorter than those observed previously in complexes of TIE with nitrogen bases.[16,32,33] The only exceptions are 1,2-bis(4-pyridyl)ethylene·TIE (2.840 Å)[16] and 1,4-bis(3-quinolyl)-1,3-butadiyne·TIE (2.884 Å).[33] The centroid···centroid distance between two adjacent imidazole rings in one stack is 4.795 Å, and the angle between the centroid···centroid vector and the ring normal is 50.1°. These parameters are indicative of negligible π···π interactions.[56–58] In addition, CH_2···imidazole contacts similar to those observed in solid **2** are not present.

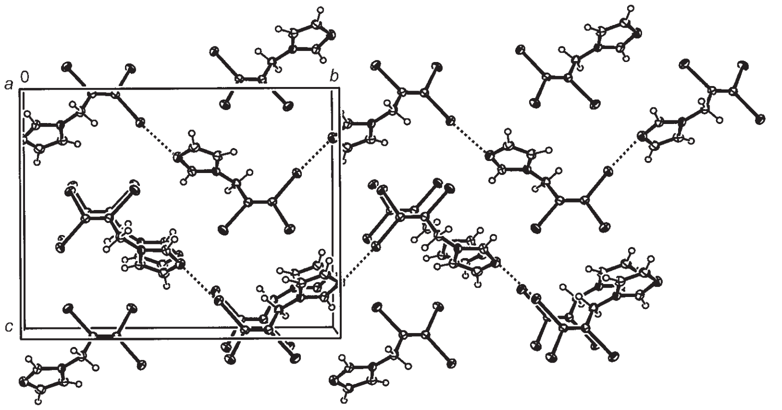


Figure 2. View along the *a* axis showing one layer of **5** and the N···I interactions between molecules in that layer.

Structure of 4: Single crystals of **4** were grown from acetonitrile. A view of the packing is shown in Figure 3 and the corresponding crystallographic data are listed in Table 1. Close inspection of the structure shows that there is no stacking of the molecules as seen in crystalline **2** and **5**. Furthermore, the I···N halogen-bonding interactions observed in **5** are no longer present. There is, however, one halogen bond between the iodide anion and one iodine atom from the =CI_2 fragment. The I···I distance is 3.470 Å and the I···I-C(sp^2) angle is 170.7°. This interaction is appreciably stronger than that found in the [2,2′-bpy(H)]I_3·TIE (bpy = bipyridine) complex, for which I···I interactions between the TIE molecules and the triiodide anions amount to 3.643 and 3.672 Å.[61] The organization of **4** is governed by two hydrogen-bonding networks that are interwoven: the first network involves N-H···O interactions between nearby morpholinium cations, and the second network is based on N-H···N hydrogen bonding between morpholinium cations and imidazolyl groups. Both hydrogen-bonding schemes are charge-assisted. Interactions between the morpholinium cations generate polymeric chains. The $N^+H\cdots O$ distance is 1.983 Å, the N···O distance is 2.843 Å, and the $N^+H\cdots O$ angle is 180.0°. The $N^+H\cdots O$ and N···O distances are comparable to those found in the X-ray crystal structures of morpholinium pentaiodide ($N^+H\cdots O = 2.102$ Å, $N\cdots O = 2.863$ Å)[62] and morpholinium triiodide ($N^+H\cdots O = 2.13$ and 2.18 Å, $N\cdots O = 2.849$ and 2.838 Å).[63] However, the $N^+H\cdots O$ angle observed in crystalline **4** is flat, which suggests that the hydrogen-bonding interaction is stronger ($\sphericalangle N^+H\cdots O = 125.1°$ in morpholinium pentaiodide and 157 and 148° in morpholinium triiodide). The $N^+H\cdots N$ distance is 1.790 Å, the N···N distance is 2.797 Å, and the $N^+H\cdots N$ angle is 179.8°. The only reported structure in which an imidazolyl nitrogen atom interacts with a NH_2^+ fragment is that of 1-hydroxymethyl-4,5,6,7-tetrahydro-1*H*-imidazo(4,5-*c*)pyridine-6-carboxylic acid monohydrate.[64] In this case, the $N^+H\cdots N$ distance is 1.956 Å, the N···N distance is 2.824 Å, and the $N^+H\cdots N$ angle is 171.5°.

The binding of an H^+ species to the morpholine nitrogen atom rather than to the imidazolyl nitrogen atom agrees with the fact that morpholine is a stronger base than imidazole (see the aforementioned pK_b values). However, there exist examples in the literature in which the protonation scheme disagrees with the acidity constants derived from solution. This phenomenon was observed in the X-ray crystal structure of $[NH_2(CH_3)_2]_{12}[H_3TMA][H_2TMA]_3[HTMA]_3[TMA]$ (H_3TMA = trimesic acid).[65] We have obtained confirmation that our assignment is correct by comparing the C–N bond lengths of the imidazole ring and the C–N bond lengths of the morpholinium cation with known data. For the imidazole ring, the C(12)–N(8) bond length is 1.369 Å and C(12)–N(11) is 1.301 Å (Figure 4). These values lie in the same range as those found in **5** (i.e., d(C–N) = 1.344 Å, d(C=N) = 1.318 Å). A search through the Cambridge Structural Database (CSD) indicates that for neutral imidazole moieties the mean C–N bond length is 1.356 Å and the

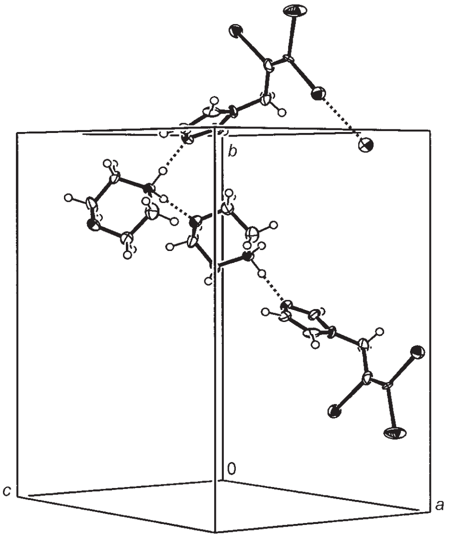


Figure 3. View showing the organization of **4** in the crystalline state.

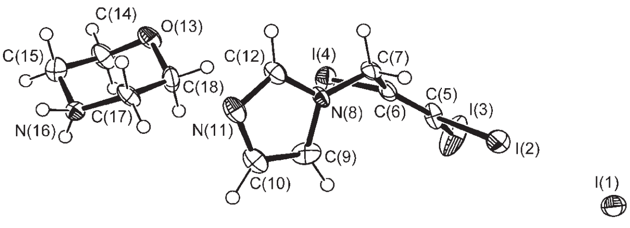


Figure 4. ORTEP diagram of **4** showing ellipsoids at the 50 % probability level and the atom numbering scheme.

mean C=N bond length is 1.313 Å.[66] These bond lengths tend to become almost equal when the imidazole nitrogen atom is protonated or alkylated (mean d(C−N) = 1.326 Å and mean d(C=N) = 1.323 Å).[66] Concerning the morpholinium cation, the C(15)−N(16) bond length is 1.478 Å and C(17)−N(16) is 1.490 Å (Figure 4). These values are similar to those observed in the X-ray crystal structure of morpholinium iodide **6** (discussed below; i.e., d(C−N) = 1.494 and 1.488 Å). In addition, they are much longer than the C−N bond lengths found in the structure of morpholine at 150 K (i.e., 1.466 and 1.469 Å).[67]

Structure of 6: Single crystals of morpholinium iodide (**6**) were obtained by slow concentration of the filtrate recovered from the washing of **3** with acetonitrile. A view of the packing is shown in Figure 5 and the corresponding crystallographic data are listed in Table 1. The structure of **6** differs significantly from that of **4** as it is not sustained by N-H···O interactions. In crystalline **6**, morpholinium cations are interconnected through C-H···O bridges (d(H···O) = 2.521 and 2.676 Å), and the NH_2^+ groups interact with nearby iodide anions (d(H···I) = 2.633 and 2.698 Å). The C-H···O contacts observed herein are close to the mean H···O distance found for complexes in which a CH_2Cl_2 molecule interacts with a C-O-C acceptor (2.50 Å).[68] Furthermore, similar C-H···O bridges were found to govern the organization of morpholine in the solid state (H···O = 2.63 Å).[67] Concerning N-H···I distances, those observed in **6** are much shorter than that found in the X-ray crystal structure of morpholinium pentaiodide (2.788 Å).[62] Also, N-H···I angles are wider (161.6 and 152.6° in **6** versus 148.8° in morpholinium pentaiodide).

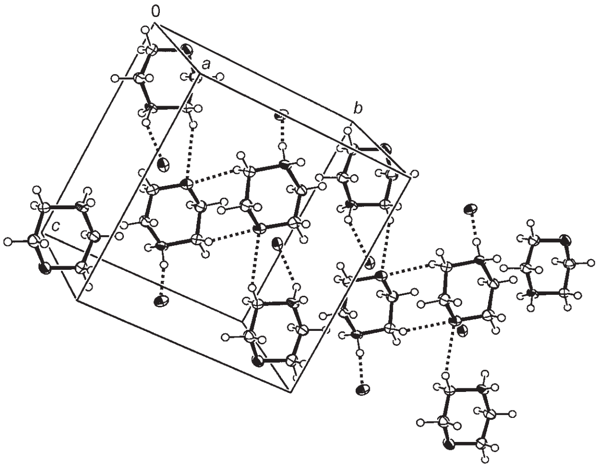


Figure 5. View showing the organization of **6** in the crystalline state.

Conclusion

The study described herein provides new examples of the utilization of imidazole in crystal engineering and improves the current knowledge of halogen bonding with halogenated alkenes and alkynes. 1-(3-Iodopropargyl)imidazole (**2**) and 1-(2,3,3-triiodoallyl)imidazole (**5**) were synthesized and their solid-state organization studied. As anticipated, these wholly organic modules self-assemble through N···I halogen-bonding interactions. The N···I interaction observed in **2** is quite strong relative to data surveyed by Metrangolo et al.[11] The N···I interaction found in **5** is weaker, in accordance with the order C(sp)-X←base > C(sp^2)-X←base.[11] The use of linear modules has made possible the preparation of polymeric chains that run throughout the solid, and the use of organic modules with shapes other than linear should make possible the preparation of 3D networks with open cavities. In addition, this study provides valuable information that can be used to organize suitably diacetylenic molecules for solid-state polymerization, as demonstrated recently by Goroff and co-workers.[40]

We also report that these molecules are capable of forming cocrystals with other organic modules that possess hydrogen-bonding capabilities, as testified by the X-ray crystal structure of **4**. In this case, the N···I halogen-bonding scheme observed in **5** is disrupted because the imidazolyl group, the most basic moiety in the molecule, is part of the hydrogen-bonding network. Nonetheless, halogen bonding is quite persistent as the triiodoalkene fragment is found to participate in a halogen bond with a surrounding anion.

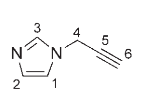
Attempts are currently being made by us to modify the solid-state organization of **2** and **5** to prepare novel functional materials. In particular, complexation of the imidazole nitrogen atom with a metal is being studied. Other types of halogen-bonding schemes are also being investigated, especially through alkylation of the imidazole nitrogen atom with an alkyl halide[69] or using pyridinium perhalometallate salts similar to those utilized by Brammer et al.[70]

Experimental Section

General considerations: The synthesis of **1** was carried out in an inert atmosphere of argon using standard Schlenk-line techniques. THF was distilled over sodium/benzophenone prior to use.

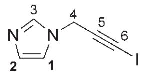
Solution ^1H and ^{13}C NMR spectra were obtained on a Bruker Avance DPX 200 instrument. ^1H NMR chemical shifts were referenced to the protio impurity of the NMR solvent and ^{13}C NMR chemical shifts to the NMR solvent. Infrared spectra were recorded on a Thermo Nicolet Avatar 320 FT-IR spectrometer with a resolution of 4 cm^{-1}. Fast-atom bombardment (FAB) mass spectra were obtained on a Jeol JMS-SX102 A instrument and electrospray ionization (ESI) mass spectra on a Micromass QTOF spectrometer. Melting points were measured on a Büchi B-540 melting point apparatus and are uncorrected. Energy-dispersive spectroscopic (EDS) measurements were carried out using an Oxford X-ray detector mounted on a Cambridge S360 scanning electron microscope. Prior to EDS analysis, the sample was coated with thermally evaporated carbon. Elemental analysis was performed in-house using a Thermo Finnigan FLASH EA 1112 Series analyzer. Determination of the iodine content was carried out at the Service Central de Microanalyse of the Centre National de la Recherche Scientifique (CNRS; Vernaison, France).

Materials: The following chemicals were obtained from commercial sources and used as supplied: imidazole (Aldrich), 2.5 M solution of *n*-butyllithium in hexanes (Aldrich), 80 weight % solution of propargyl bromide in toluene (Aldrich), *N*-iodosuccinimide (Acrôs Organics), silver nitrate (Fluka), morpholine (Lancaster), and sodium hydrogencarbonate (Prolabo).



1

1-Propargylimidazole (1): Imidazole (8.51 g, 0.125 mol) was introduced in a 250-mL two-necked flask containing a magnetic stirring bar and equipped with a pressure-equalizer dropping funnel. The solid was dissolved in anhydrous THF (100 mL) and the solution cooled to −78 °C. *n*BuLi solution (50 mL, 0.125 mol) was added dropwise. The reaction mixture was kept at −78 °C for 2 h, during which time a white precipitate formed. The suspension was transferred with a cannula into a second flask containing a cold (−78 °C) solution of propargyl bromide (18.58 g, 0.125 mol) in THF (50 mL). The reaction mixture was stirred at −78 °C for 3 h, then at room temperature overnight. A brown solution was obtained. The solvents were removed in vacuo, and the resulting viscous oil was hydrolyzed with deionized water (50 mL). The aqueous solution was washed with dichloromethane (3×150 mL), these organic fractions were combined, and the organic layer was dried over $MgSO_4$. The volatiles were removed and the crude product was purified by vacuum distillation (70 °C, 5 mbar). A yellow oil was obtained (11.13 g, 82 %). The ^1H NMR spectroscopic data were the same as those given in ref. [48d]; ^{13}C NMR (50.3 MHz, $CDCl_3$): $\delta = 36.3$ (C4), 75.1 (C6), 77.1 (C5), 119.1 (C2), 129.6 (C1), 136.9 ppm (C3); IR (CCl_4): $\tilde{\nu} = 3311$ (vs; C(sp)-H), 3117 (w; C(sp^2)-H), 2923 (w; C(sp^3)-H), 2134 (w; C≡C), 1500 cm^{-1} (vs; ring); FAB+ MS (NOBA): *m*/*z* (%): 213 (14) $[2M+H]^+$, 107 (100) $[M+H]^+$, 39 (24) $[CH_2C{\equiv}CH]^+$.

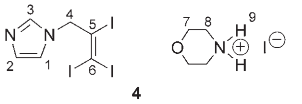


2

1-(3-Iodopropargyl)imidazole (2): *N*-Iodosuccinimide (4.07 g, 18.1 mmol) and silver nitrate (0.31 g, 1.81 mmol) were added successively to a solution of **1** (1.92 g, 18.1 mmol) in acetone (100 mL). The reaction mixture was stirred at room temperature for 3 h and then filtered. The solvent was removed on a rotary evaporator. The residue was washed with water (50 mL) and diethyl ether (50 mL). A beige solid was recovered (2.61 g, 62 %). Elemental analysis of the solid showed large discrepancies between the experimental and the calculated values because of the presence of silver in the sample: elemental analysis calcd (%) for $C_6H_5I_1N_2$ (232.02): C 31.06, H 2.17, N 12.07; found: C 26.56, H 1.86, N 10.08.

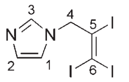
The solid was purified as follows: Crude **2** (0.17 g) was placed on a glass frit, and the solid was washed with hot acetonitrile (25 mL). The volume of the yellow filtrate was reduced on a rotary evaporator, and the concentrated solution was placed in a freezer overnight. A crystalline powder precipitated out which was collected by suction filtration (0.068 g, 40 %). M.p. 227.7–232.4 °C; ^1H NMR (200.1 MHz, $[D_6]$DMSO): $\delta = 5.05$ (s, 2 H; H4), 6.92 (s, 1 H; H1), 7.21 (s, 1 H; H2), 7.67 ppm (s, 1 H; H3); ^{13}C NMR (50.3 MHz, $[D_6]$DMSO): $\delta = 13.1$ (C6), 38.1 (C4), 88.5 (C5), 120.3 (C2), 129.6 (C1), 138.0 ppm (C3); IR (KBr): $\tilde{\nu} = 3110$ (s; C-(sp^2)-H), 2921 (w; C(sp^3)-H), 2174 (m; C≡C), 1503 cm^{-1} (vs; ring); MS (ESI) (CH_3CN): *m*/*z* (%): 232.95 (100) $[M+H]^+$; elemental analysis calcd (%) for $C_6H_5I_1N_2$ (232.02): C 31.06, H 2.17, N 12.07; found: C 32.69, H 2.44, N 14.06.

Cocrystal 1-(2,3,3-triiodoallyl)imidazole·1 morpholinium iodide (4): In an inert atmosphere, morpholine (25 g, 0.287 mol) was added dropwise to a cold (0 °C) solution of iodine (36.47 g, 0.143 mol) in toluene (200 mL). The solution was stirred at room temperature for 2 h. Alkyne **1** (5.08 g, 47.8 mmol) was added, and the reaction mixture was stirred at room temperature overnight. Removal of the toluene in vacuo furnished a brown solid identified as 1-(2,3,3-triiodoallyl)imidazole·3 morpholinium iodide (**3**) by ^1H NMR spectroscopic analysis (52.24 g, 96 %).



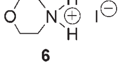
4

Solid **3** was placed on a glass frit, washed with acetonitrile, and the resulting yellow powder was dried in vacuo. The washed solid was identified as 1-(2,3,3-triiodoallyl)imidazole·1 morpholinium iodide (**4**) by ^1H NMR spectroscopic and elemental analyses and by a single-crystal X-ray diffraction study (26.81 g, 80 %). M.p. 132.7–133.9 °C; ^1H NMR (200.1 MHz, $[D_6]$DMSO): $\delta = 3.11$ (t, $J = 4.80$ Hz, 4 H; H8), 3.76 (t, $J = 4.80$ Hz, 4 H; H7), 4.96 (s, 2 H; H4), 7.04 (s, 1 H; H1), 7.16 (s, 1 H; H2), 7.84 (s, 1 H; H3), 8.69 ppm (broad, 2 H; H9); ^{13}C NMR (50.3 MHz, $[D_6]$DMSO): $\delta = 38.1$ (C6), 43.8 (C8), 62.0 (C4), 64.2 (C7), 114.8 (C5), 119.9 (C2), 129.6 (C1), 138.4 ppm (C3); MS (ESI) (CH_3CN): *m*/*z* (%): 972.54 (58) $[2C_3H_3N_2CH_2CI{=}CI_2+H]^+$, 701.77 (31) $[M+H]^+$, 486.74 (100) $[C_3H_3N_2CH_2CI{=}CI_2+H]^+$, 232.97 (55) $[C_3H_3N_2CH_2C{\equiv}CI+H]^+$, 88.07 (18) $[\text{morpholine}+H]^+$; elemental analysis calcd (%) for $C_{10}H_{15}I_4N_3O_1$ (700.87): C 17.14, H 2.16, O 2.28, N 6.00, I 72.43; found: C 17.74, H 2.15, O 3.36, N 6.57, I 71.88.



5

1-(2,3,3-Triiodoallyl)imidazole (5): Compound **4** (5.99 g, 12.3 mmol) was suspended in a saturated aqueous solution of $NaHCO_3$ (100 mL; pH 8) and stirred for 3 h. A yellow solid was obtained after suction filtration (2.54 g, 89 %). M.p. 123.6–127.6 °C; ^1H NMR (200.1 MHz, $[D_6]$DMSO): $\delta = 4.95$ (s, 2 H; H4), 6.98 (s, 1 H; H1), 7.12 (s, 1 H; H2), 7.73 ppm (s, 1 H; H3); ^{13}C NMR (50.3 MHz, $[D_6]$DMSO): $\delta = 36.6$ (C6), 62.0 (C4), 115.1 (C5), 119.8 (C2), 129.9 (C1), 138.5 ppm (C3); MS (ESI) (CH_3CN): *m*/*z* (%): 972.50 (44) $[2M+H]^+$, 486.75 (100) $[M+H]^+$; elemental analysis calcd (%) for $C_6H_5I_3N_2$ (485.83): C 14.83, H 1.04, N 5.77; found: C 14.90, H 0.98, N 5.42.



6

Morpholinium iodide (6): Solid **3** was washed with acetonitrile and the resulting filtrate was concentrated to dryness to yield a brown solid. Recrystallization of the solid from acetonitrile gave a crystalline powder identified as **6** (15.2 g, 70.7 mmol). M.p. 195.2–203.0 °C; ^1H NMR (200.1 MHz, $[D_6]$DMSO): $\delta = 3.12$ (m, 4 H; H2), 3.76 (m, 4 H; H1), 8.69 ppm (broad, 2 H; H3); ^{13}C NMR (50.3 MHz, $[D_6]$DMSO): $\delta = 43.8$ (C2), 64.1 ppm (C1); MS (ESI) (CH_3CN): *m*/*z* (%): 518.05 (6) $[2M+\text{morpholine}+H]^+$, 303.05 (53) $[M+\text{morpholine}+H]^+$, 88.06 (100) $[\text{morpholine}+H]^+$; elemental analysis calcd (%) for $C_4H_{10}I_1N_1O_1$ (215.03): C 22.34, H 4.69, O 7.44, N 6.51; found: C 21.98, H 4.29, O 7.83, N 6.67.

X-ray diffraction: Intensity measurements were carried out at the joint X-ray diffraction facility of the Institut Charles Gerhardt and the Institut Européen des Membranes (Université Montpellier II, France) at 173 K using an Oxford Diffraction Xcalibur-1 CCD diffractometer. The crystal-to-detector distance was 50 mm; other data collection parameters were nearly identical in all four experiments. A total of 678 exposures were taken using ω scans with oscillations of 1°. The counting time per frame varied between 30 and 40 s. The data were corrected for possible intensity decay and absorption using the empirical AbsPack procedure.[71] All four structures were solved by direct methods using SIR2002[72] and refined by least-squares methods on *F* using CRYSTALS.[73] The structure of **6** was initially solved in the noncentrosymmetric space group $P2_1$ as direct methods gave no solution in the centrosymmetric space group $P2_1/c$. Upon close inspection of the solution, an inversion center was added by the Addsym option of the PLATON program.[74] For **2**, **5**, and **6**, the hydrogen atoms were positioned from difference Fourier maps. In the case of **4**, the hydrogen atoms were positioned by taking into account a possible hydrogen-bonding interaction between the morpholine molecule and the imidazole moiety. The nitrogen and oxygen atoms of morpholine were assigned on the basis of observed bond distances (d(C−O) = 1.42 Å and d(C−N) = 1.48 Å). As a consequence of correctly assigning these atoms, temperature factors became "normal". The nitrogen atom at the 3-position of the imidazole ring was assigned by postulating a hydrogen bond with morpholine. There is no interaction between the hydrogen at the 2-position of the imidazole ring and morpholine. Also, there is no interaction between this hydrogen atom and the iodide anion present in the lattice. Final *R* values and the relevant crystallographic data are given in Table 1. CCDC-623 085 (**2**), -623 086 (**4**), -623 088 (**5**), and -623 087 (**6**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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