Crystal Engineering of Organic Clay Mimics from 3,5-Pyrazoledicarboxylic Acid and Amines

Alicia M. Beatty,* Krista E. Granger, and Amanda E. Simpson[a]

Abstract: The syntheses and crystal structures of sixteen compounds containing the monoanion of 3,5-pyrazoledicarboxylic acid (H_2PzDCA) and ammonium-based counterions are reported. The cations contain short-chain alkyl, long-chain alkyl, phenyl, and chloro-, methoxy-, and amine-substituted aryl groups. Self-complementary HPzDCA intermolecular hydrogen bonds create nearly planar sheets, to which the cations connect through hydrogen bonds. Twelve of the structures exhibit virtually identical hydrogen-bonded layers, but the distance between layers varies from 9.33 to 14.10 Å (±20%), depending on the cation. The comparison of the sixteen structures leads to the identification of a building block (HPzDCA) that creates remarkably reproducible, lamellar structures despite substantial changes in the counterion.

Keywords: carboxylic acid · clays · crystal engineering · hydrogen bonds · supramolecular chemistry

Introduction

Lamellar materials that mimic the structure and properties of naturally occurring clays[1] are of considerable interest in supramolecular chemistry[2] and crystal engineering.[3] Goals in this research include developing solids that will intercalate or adsorb small molecules and ions for storage,[4] separations[5] and catalysis.[6] Clay mimics may also allow solid-state reactions such as photopolymerizations.[7] As naturally occurring clays are typically composed of metal-oxide layers, inorganic/organic synthetic clay mimics have been constructed from, for example, metal oxide,[8] metal phosphonates,[9] and coordination polymers,[10, 11] where inorganic sheets are interspersed with organic substituents and/or guest molecules. On the other hand, simple organic components have also been used to mimic the structure of clays—hydrogen-bonded[12] ions, such as guanidinium sulfonate[13] and hydrogentrimesate ammonium,[14] hydrogenmalate ammonium,[15] or oxamate ammonium[16] have been used to create organic scaffolds. While these solids are not always as robust as their inorganic counterparts, hydrogen-bonded lamellar materials may be strong enough to remain intact during events such as intercalation.[17]

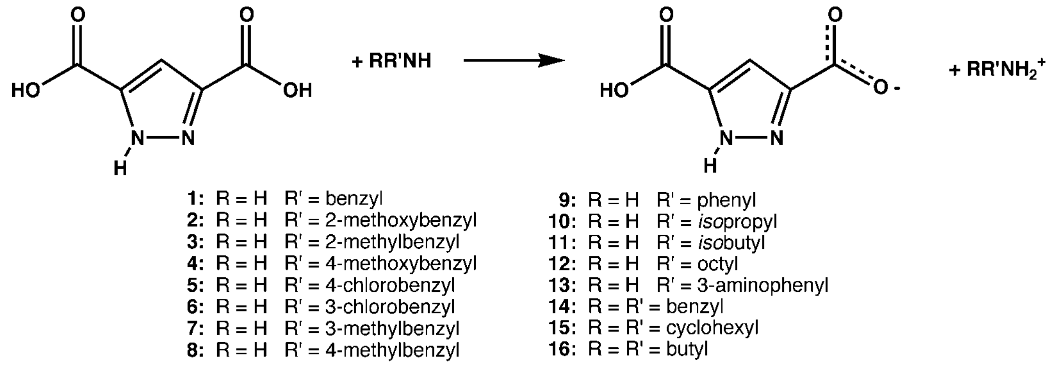
Charge-assisted hydrogen bonds are strong, directional, and reliable,[18] and are therefore useful tools for assembling molecular scaffolding. 3,5-Pyrazoledicarboxylic acid (H_2PzDCA, Scheme 1),[19] which has been used as a ligand in coordination complexes[20] and coordination polymers,[21] is a suitable building block for 2D arrays: the monoanion (HPzDCA) is planar and by itself can interconnect in two dimensions, in one direction through hydrogen-bonded carboxylic acid/carboxylate chains and in a perpendicular direction through hydrogen bonds involving pyrazole ring nitrogen atoms. H_2PzDCA was allowed to react with a number of amines (alkyl and aryl, primary and secondary) to create lamellar solids. The syntheses and X-ray crystallographic studies of sixteen new compounds are reported herein (Scheme 1). The reliability of the system was tested by changing the nature and position of substituents on benzylamine rings (e.g. methyl vs. methoxy vs. chloro) and by changing the length and width of alkyl substituents (e.g. isobutyl vs. *N*-octyl). This allowed an examination of the effect of weaker forces such as π–π, chloro–chloro, and van der Waals interactions on the overall assembly. Our results show that HPzDCA is an extraordinarily reliable tool for building predictable lamellar structures.

Results

Primary amines: With one exception, **2**, the reaction of H_2PzDCA with one equivalent of a primary amine results in a lamellar motif (Figure 1). The cations reside between the sheets, and the overall motif is an ABA, or bilayer arrangement (A denotes ionic layers and B represents hydrophobic regions between layers). Because the structures are so similar

---

[a] Dr. A. M. Beatty, K. E. Granger, A. E. Simpson
Department of Chemistry and Biochemistry
University of Notre Dame
Notre Dame, IN, 46556-5670 (USA)
Fax: (+1)574-631-6652
E-mail: abeatty@nd.edu



1: R = H R' = benzyl
2: R = H R' = 2-methoxybenzyl
3: R = H R' = 2-methylbenzyl
4: R = H R' = 4-methoxybenzyl
5: R = H R' = 4-chlorobenzyl
6: R = H R' = 3-chlorobenzyl
7: R = H R' = 3-methylbenzyl
8: R = H R' = 4-methylbenzyl
9: R = H R' = phenyl
10: R = H R' = *iso*propyl
11: R = H R' = *iso*butyl
12: R = H R' = octyl
13: R = H R' = 3-aminophenyl
14: R = R' = benzyl
15: R = R' = cyclohexyl
16: R = R' = butyl

Scheme 1.

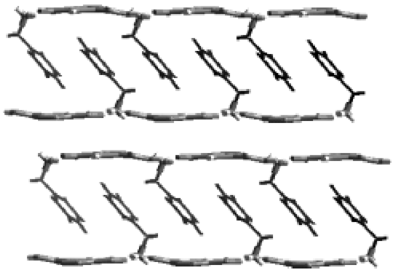


Figure 1. Bilayers in **1**, similar ABA pattern found in **3**–**13**. Benzyl groups separate ionic layers.

they will be discussed collectively in terms of anionic and cationic arrangements.

Inter-anion arrangements: Twelve of the thirteen primary ammonium–HPzDCA structures (**1**, **3**–**13**) exhibit a virtually identical 2D arrangement of the anions: carboxylic acid–carboxylate $O{-}H\cdots O^-$ hydrogen bonds ($r(O\cdots O^-)$ 2.48–2.52 Å) connect the monoanions into linear chains, with all ring nitrogen atoms on the same side of the chain. The chains are parallel and crosslink through $N{-}H\cdots O$ hydrogen bonds ($r(N\cdots O)$ 2.69–2.76 Å) to form near-planar sheets (these sheets coincide with the crystallographic *ab* plane). The ammonium group is attached in a nearly identical fashion in these twelve structures, where two ammonium–carboxylate $N^+{-}H\cdots O^-$ ($r(N^+\cdots O^-)$ 2.77–2.87 Å, and one ammonium–pyrazolate $N^+{-}H\cdots N$ ($r(N^+\cdots N)$ 2.92–2.99 Å) hydrogen bond attach the cation to the anionic layers (Figure 2).

Compound **2** does not display a lamellar structure: while the anions form chains through carboxylic acid–carboxylate $O{-}H\cdots O^-$ hydrogen bonds ($r(O\cdots O^-)$ 2.47 Å), the interchain arrangement is quite different. They are arranged antiparallel and therefore the observed interchain $N{-}H\cdots O$ hydrogen bonds ($r(N\cdots O)$ 2.73 and 2.69 Å), result in a 1D ribbon motif (Figure 3).

Inter-cation arrangements: Of the seven benzylammonium-based layered structures there are two motifs: **1**, **4**, and **8** exhibit an interdigitated arrangement of the benzyl substituents (Figure 4a), and **3** and **5**–**7** are arranged in a non-interdigitated fashion (Figure 4b). The difference is manifested by an angle between the aryl ring and the ionic layer of about 50° for interdigitated and about 25° for noninterdigitated arrangements. The phenyl groups in **9** and **13** and the alkyl groups in **10**–**12** are essentially interdigitated as well (Figure 5). Compound **13**, which is based on 3-aminoaniline and thus contains an additional amine, exhibits $N{-}H\cdots N$ amine–amine hydrogen-bonding interactions ($r(N\cdots N)$ 3.27 Å) between the anionic layers.

Secondary amines: Each compound containing a secondary ammonium ion (**14**–**16**) also displays a lamellar structure in the solid state (Figure 6). The dibenzylammonium complex **14**

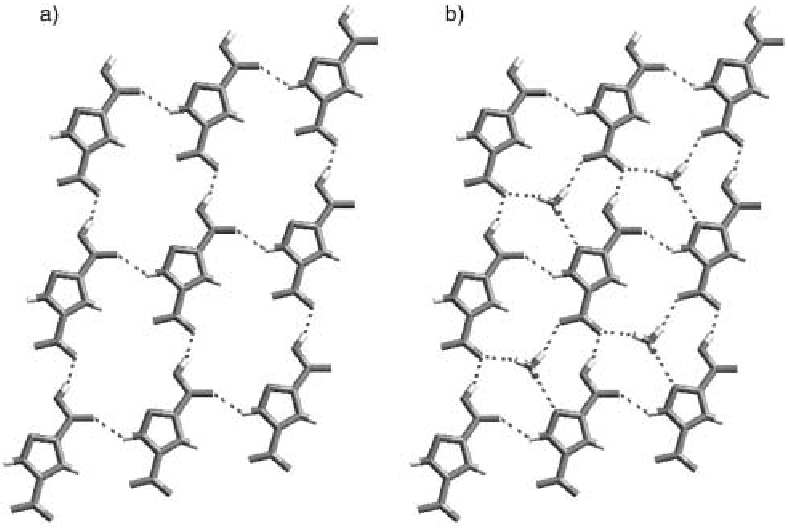


Figure 2. Hydrogen-bonded sheets in **1**. a) HPzDCA sheets from hydrogen-bonded carboxylic acid/carboxylate chains crosslinked by $N{-}H^+\cdots O$ hydrogen bonds. b) Ammonium groups included.

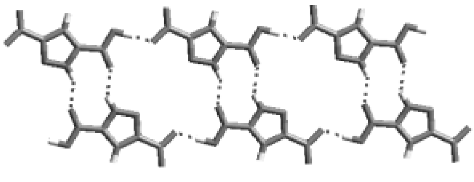


Figure 3. Ribbons in **2**, the sole nonlamellar structure. Antiparallel HPzDCA chains prohibit layer formation.

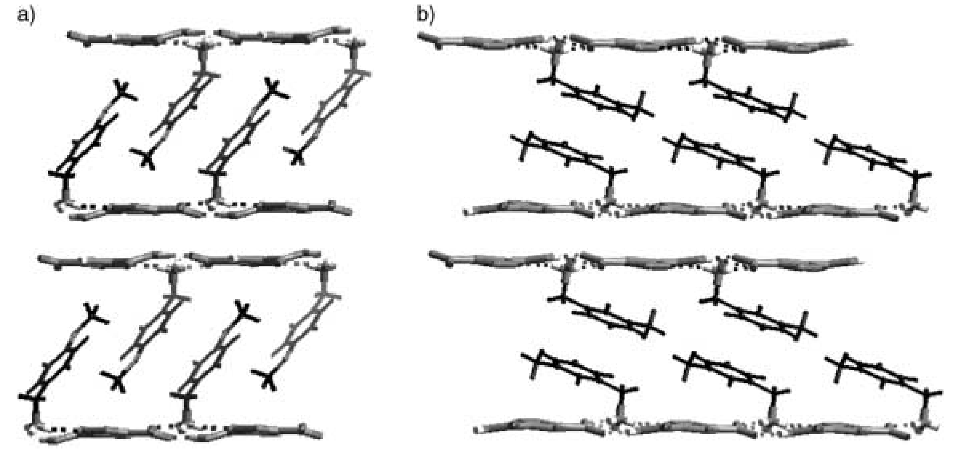


Figure 4. Interdigitation of aryl groups in **4** (a) versus noninterdigitated, parallel arrangement (b) of aryl groups in **7**.

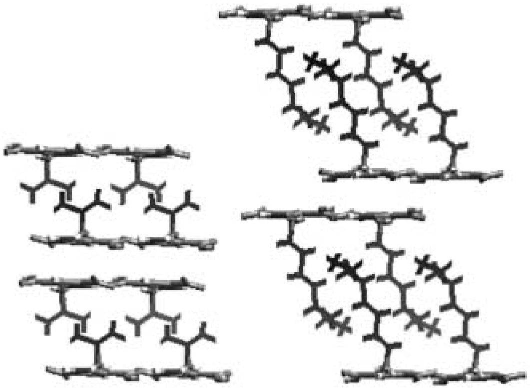


Figure 5. Structures of **10** (left) and **12** with the smallest (9.33 Å, isopropyl) and largest (14.10 Å, octyl) interlayer distances.

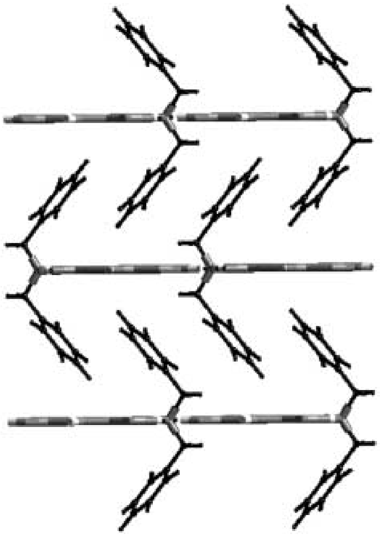


Figure 6. AB layered structure of **14**, with each planar ionic sheet separated by benzyl groups.

exhibits an anionic sheet that is similar to that in compounds **1** and **3**–**13**. However, in this case the anion lies on a crystallographic mirror plane so that the sheets are exactly planar. The secondary ammonium ion in **14** participates in one $N^+{-}H\cdots O^-$ ($r(N^+\cdots O^-)$ 2.95 Å) and one $N{-}H^+\cdots N$ hydrogen bond ($r(N^+\cdots N)$ 2.76 Å; Figure 7). The benzyl groups of each cation lie above and below the anions, resulting in an AB structural pattern (Figure 6).

Compounds **15** and **16**, which crystallize from the reaction of H_2PzDCA with dicyclohexylamine and dibutylamine, respectively, are both ethanol solvates, but their overall motifs are still lamellar. They exhibit the same carboxylic acid–carboxylate chains as those found in **1** and **3**–**14**, but in these structures layer formation is mediated by interchain $N{-}H\cdots O{-}H_{EtOH}\cdots O$ hydrogen bonds instead of by direct $N{-}H\cdots O$ interactions. In **15** the anionic layers are nearly planar, but in **16** the layers are buckled (Figure 8).

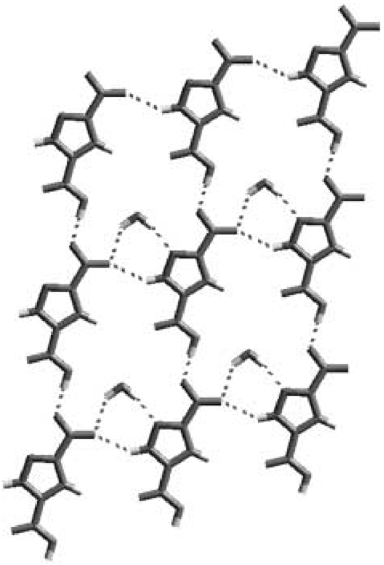


Figure 7. The hydrogen-bonded layer of the secondary ammonium compound **14**. HPzDCA arrangement is virtually identical to that of primary ammonium structures.

Discussion

This structural study demonstrates that HPzDCA is capable of generating lamellar structures in a highly reproducible manner. All sixteen structures have a common structural subunit (HPzDCA chains) based on charge-assisted carboxylic acid–carboxylate hydrogen bonds. In fifteen of these cases, anionic chains are cross-linked into the desired sheets through the additional hydrogen-bond donor of the pyrazole group, which is positioned approximately perpendicular to the direction of chain propagation. The primary ammonium ions are anchored to the sheets through $N{-}H^+\cdots O^-$ or $N{-}H^+\cdots N$ hydrogen bonds, giving rise to an ABA motif exclusively.

The lamellar arrangement of these materials does not change with the nature of the cation, despite potentially

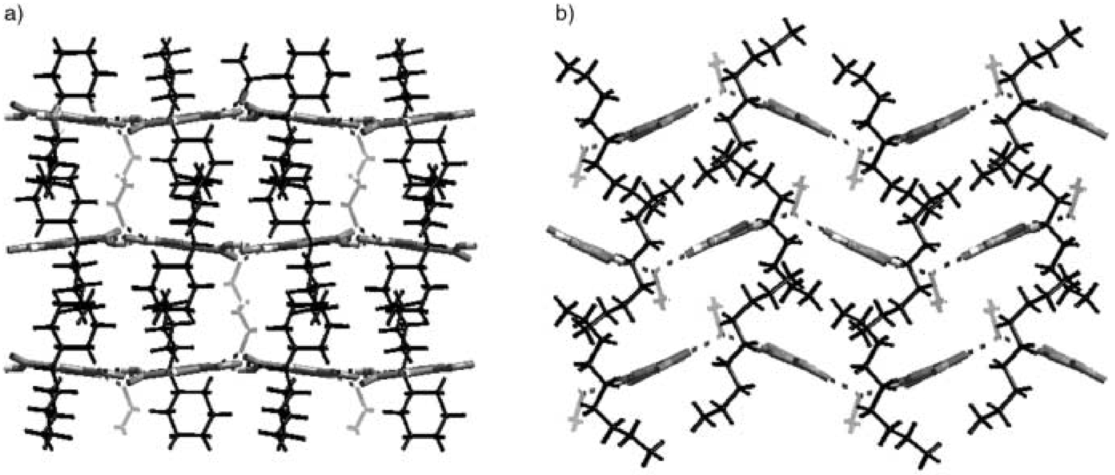


Figure 8. ABA structure in **15** (a; dicyclohexyl) and **16** (b; dibutyl), with near-planar and buckled HPzDCA · EtOH layers, respectively.

interfering π–π and hydrophobic interactions. Not even the NH_2 substituent in **13** disrupts the hydrogen-bonded pyrazolate layer.

The only structural exception, 2-methoxybenzylammonium HPzDCA **2**, can be rationalized by considering the intramolecular hydrogen bond that holds the ammonium group and the methoxy group in the same plane. The steric demands of the methoxy group hinder the interaction of the ammonium moiety with the pyrazolate layer, which prevents layer formation between HPzDCA chains. Lamellar structures in **3** and **4** suggest that substitution in the 2-position alone or the presence of a methoxy group by itself does not interfere with the HPzDCA sheets.

It is surprising that the structures of the primary ammonium compounds exhibit the ABA motif exclusively. In initiating this study, it was expected that either the nature or placement of substituents on the benzylammonium group would influence an AB or ABA arrangement, as has been observed in other hydrogen-bonded lamellar systems.[12, 14, 15] In fact, it is possible that the incorporation of more sterically demanding substituents on primary amines will result in the formation of the AB arrangement. The interdigitation that occurs in some of the benzylammonium structures evidently does not depend exclusively on the nature of the substituent (e.g. chloro versus methyl) or on its location on the ring.

Naturally occurring clays tend to adopt two different structures, either alternating or bilayer arrangements (denoted TO or TOT).[22] Because the addition of primary amines to H_2PzDCA resulted in the consistent formation of the ABA pattern, it was necessary to develop an alternative strategy for synthesizing the AB motif. By using secondary amines, it was possible to mimic this second class of clay structures.

The ABA pattern in the primary ammonium structures can be compared quantitatively to those in naturally occurring smectite clays, which have crystallographic dimensions of $a \approx 5.17$ Å and $b \approx 9.15$ Å, with a variable c parameter.[22] The lamellar primary amine-based structures reported here have the following dimensions:

$a_{av} = 6.63$ Å (variance from 6.54 to 6.71 Å)
$b_{av} = 8.91$ Å (variance from 8.84 to 9.00 Å)
$c_{av} = 11.81$ Å (variance from 9.33 to 14.10 Å)

The a and b dimensions vary by only 1% from structure to structure, but the c dimension varies by ±20%. The similarity in the length of a and b to that of the smectite clays is of course a coincidence, but the fact that the c parameter can vary so dramatically indicates that these materials may intercalate a variety of guests.

Conclusion

The results reported here include all of the crystal structures that were obtained when a primary amine formed a 1:1 salt with H_2PzDCA. With only one exception this system generates reproducible lamellar structures, evidence of extraordinary reliability in a structural building block. We have mimicked the structural aspects of clays—primary ammonium ions lead to the ABA pattern, while secondary ammonium ions generate AB patterns in combination with the same HPzDCA building block. Experiments are currently underway in our laboratory to determine whether these materials can also mimic the physical properties of clays.

Experimental Section

Syntheses: All reagents were obtained from commercial sources and used without further purification. Reactions were carried out in water and ethanol or water and methanol by stirring H_2PzDCA (0.3 mmol) with an equimolar amount of the corresponding amine. Colorless single crystals were obtained by slow evaporation of the solvent at ambient conditions. Details of melting points, crystal habit, and reaction solvent for **1**–**16** are given in Table 1.

X-ray crystallography: Data for compounds **5** and **8** were collected by using a Siemens P4 four-circle diffractometer, **1**–**4**, **6**–**12**, and **14** were collected and integrated by using a Bruker SMART 1000 system, and data for structures **13**, **15**, and **16** were collected and integrated by using a Bruker Apex instrument. In all cases a crystalline sample was placed in inert oil, mounted on a glass pin, and transferred to the cold gas stream of the diffractometer. Data were collected using graphite-monochromated $Mo_{K\alpha}$ ($\lambda = 0.71073$ Å) radiation. The structures were solved by direct methods using SHELXS-97 and refined by using SHELXL-97.[23] Non-hydrogen atoms were found by successive full-matrix least-squares refinement on F^2 and refined with anisotropic thermal parameters. All of

Table 1. Data collection and refinement for **1**–**16**.

	1	**2**	**3**	**4**	**5**	**6**
formula	$C_{12}H_{13}N_3O_4$	$C_{13}H_{15}N_3O_5$	$C_{13}H_{15}N_3O_4$	$C_{13}H_{15}N_3O_5$	$C_{12}H_{12}ClN_3O_4$	$C_{12}H_{12}ClN_3O_4$
molecular weight	263.25	293.28	277.28	293.28	297.70	297.70
system	triclinic	triclinic	triclinic	triclinic	triclinic	triclinic
space group	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$	$\mathrm{P}\bar{1}$	$P\bar{1}$
a [Å]	6.572(1)	8.9675(8)	6.6558(7)	6.5981(9)	6.644(1)	6.683(1)
b [Å]	9.001(2)	10.8314(9)	8.901(1)	8.955(1)	8.900(1)	8.839(1)
c [Å]	11.179(2)	15.537(1)	12.114(1)	12.544(2)	12.857(2)	12.059(2)
α [°]	94.211(3)	77.041(2)	95.462(3)	96.588(2)	99.36(1)	90.387(3)
β [°]	102.899(3)	73.803(2)	92.030(2)	92.969(3)	97.64(1)	100.52(3)
γ [°]	110.565(3)	70.223(2)	111.514(2)	111.444(2)	111.51(1)	111.03(3)
V [Å^3]	595.1(2)	1349.5(2)	662.7(1)	681.8(2)	682.3(2)	651.7(2)
Z	2	4	2	2	2	2
ρ [g cm^{-3}]	1.469	1.443	1.390	1.429	1.449	1.517
temperature [K]	173	173	173	173	173	173
θ range [°]	1.90–23.34	1.38–23.33	1.69–23.32	1.64–23.36	1.64–24.99	1.72–27.98
measured reflections	3105	7037	3443	3484	2605	4392
unique reflections	1704	3861	1904	1959	2381	2790
parameters	172	380	181	193	181	181
GOF	1.094	1.087	1.114	1.064	0.998	1.032
$R1$ ($I > 2\sigma I$)	0.0458	0.0556	0.0472	0.0481	0.0727	0.057
$wR2$ (all data)	0.1396	0.1621	0.1406	0.1372	0.2033	0.1431
reaction solvent	water/ethanol	water/ethanol	water/ethanol	water/ethanol	water/methanol	water/ethanol
m. p. [°C]	259–261	250–252	255–256	240–241	277–279	> 260
crystal habit	needle	prism	plate	plate	plate	plate

	7	**8**	**9**	**10**	**11**	**12**
formula	$C_{12}H_{15}N_3O_4$	$C_{13}H_{15}N_3O_4$	$C_{11}H_{11}N_3O_4$	$C_8H_{13}N_3O_4$	$C_9H_{15}N_3O_4$	$C_{13}H_{23}N_3O_4$
molecular weight	277.28	277.28	249.23	215.21	229.24	285.34
system	triclinic	triclinic	triclinic	triclinic	triclinic	triclinic
space group	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$
a [Å]	6.707(7)	6.6065(7)	6.6023(6)	6.693(6)	6.544(1)	6.590(2)
b [Å]	8.883(8)	8.9778(8)	8.8626(7)	8.8396(8)	8.944(1)	8.958(2)
c [Å]	12.14(1)	11.7377(9)	11.2121(9)	9.3274(8)	10.676(2)	14.102(4)
α [°]	89.77(2)	85.525(7)	90.821(2)	80.505(2)	78.881(3)	84.062(5)
β [°]	80.51(2)	87.518(8)	104.272(2)	79.765(2)	75.405(3)	81.021(5)
γ [°]	68.70(2)	68.573(8)	111.057(1)	69.238(2)	69.202(3)	68.502(5)
V [Å^3]	663(1)	646.0(1)	589.50(9)	502.88(8)	561.6(2)	764.1(3)
Z	2	2	2	2	2	2
ρ [g cm^{-3}]	1.388	1.425	1.404	1.421	1.356	1.240
temperature [K]	173	173	173	173	173	173
θ range [°]	1.70–27.44	1.74–25.00	1.89–28.28	2.48–23.26	2.45–28.07	1.46–28.23
measured reflections	3946	2484	4206	2627	3942	5415
unique reflections	2658	2272	2623	1445	2465	3388
parameters	181	248	201	136	145	212
GOF	1.219	1.122	1.057	1.061	1.071	1.071
$R1$ ($I > 2\sigma I$)	0.1269	0.0523	0.0506	0.0379	0.0485	0.0666
$wR2$ (all data)	0.2977	0.1605	0.1545	0.1059	0.1370	0.2109
reaction solvent	water/ethanol	water/ethanol	water/ethanol	water/ethanol	water/ethanol	water/methanol
m. p. [°C]	> 260	> 260	248–250	260–261	256–259	248–250
crystal habit	plate	plate	plate	prism	prism	prism

the compounds crystallized with one HPzDCA and one cation in the asymmetric unit, except **2** and **13** (two of each) and **14** (one-half of each). Compounds **15** and **16** crystallized with an additional molecule of ethanol in the asymmetric unit. Compound **8** exhibits a twofold disorder of the 4-methylbenzyl group (50%/50%), **9** exhibits a twofold rotational disorder of the phenyl ring (58%/42%), and the four tail carbon atoms of the octyl group in **12** are also twofold disordered (68%/32%). Unit cell parameters and other relevant crystallographic information can be found in Table 1. CCDC-177000–177015 (**1**–**16**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB21EZ, UK; (fax: +44)1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk).

To verify that the crystalline samples were representative of the bulk materials, X-ray powder diffraction patterns were obtained for compounds **1**–**12** and **14** and compared to the simulated pattern from the single-crystal data,[24] and polymorphs or solvates were not found in any of the reaction products. Any impurities were found to be the H_2PzDCA hydrate or in one case a 1:2 acid:base crystalline form was identified by single-crystal X-ray diffraction.[25]

Acknowledgement

We are grateful to Prof. C. B. Aakeröy (Kansas State University) and Prof. A. G. Lappin (University of Notre Dame) for providing laboratory space and equipment. K.E.G. thanks NSF-REU (CHE-9988053) for summer funding.

Table 1. (cont.)

	13	**14**	**15**	**16**
formula	$C_{22}H_{24}N_8O_8$	$C_{19}H_{19}N_3O_4$	$C_{19}H_{33}N_3O_5$	$C_{15}H_{29}N_3O_5$
molecular weight	528.49	353.37	383.48	3331.41
system	triclinic	monoclinic	monoclinic	monoclinic
space group	$P\bar{1}$	$P2(1)/m$	$P2(1)/n$	$P2(1)/c$
a [Å]	8.927(1)	6.8541(6)	10.8200(7)	8.9748(5)
b [Å]	11.365(2)	15.042(1)	14.6271(9)	13.3116(7)
c [Å]	12.763(2)	9.0900(8)	13.5960(8)	15.3147(8)
α [°]	92.960(3)	90	90	90
β [°]	108.204(3)	109.851(2)	93.384(2)	99.800(1)
γ [°]	104.051(3)	90	90	90
V [Å^3]	1181.8(3)	881.5(1)	2148.0(2)	1802.9(2)
Z	4	2	4	4
ρ [g cm^{-3}]	1.485	1.331	1.186	1.221
temperature [K]	100	173	100	100
θ range [°]	1.87–24.70	2.38–23.25	2.05–26.41	2.04–26.38
measured reflections	9722	4575	16177	16849
unique reflections	4025	1324	4397	3689
parameters	343	136	244	324
GOF	1.063	1.043	0.914	1.087
$R1$ ($I > 2\sigma I$)	0.0495	0.0400	0.0544	0.0411
$wR2$ (all data)	0.1399	0.1040	0.0710	0.0907
reaction solvent	water/ethanol	water/ethanol	water/ethanol	water/ethanol
m. p. [°C]	254–256	230–235	210–214	189–194
crystal habit	irregular	prism	prism	needle

[1] K. T. Holman, A. M. Pivovar, J. A. Swift, M. D. Ward, *Acc. Chem. Res.* **2001**, *34*, 107; b) M. J. Zaworotko, *Chem. Commun.* **2001**, 1.

[2] J.-M. Lehn, *Supramolecular Chemistry - Concepts and Perspectives*, VCH, Weinheim, **1995**.

[3] G. R. Desiraju, *Crystal Engineering: The Design of Organic Solids*, Elsevier, New York, **1989**.

[4] a) C. Liu, Y. Y. Fan, M. Liu, H. T. Cong, H. M. Cheng, M. S. Dresselhaus, *Science* **1999**, *286*, 1127; A. Matsumoto, T. Odani, K. Sada, M. Miyata, K. Tashiro, *Nature* **2000**, *405*, 328.

[5] R. Bishop, *Chem. Soc. Rev.* **1996**, *25*, 311.

[6] J. Y. Ying, C. P. Mehnert, M. S. Wong, *Angew. Chem.* **1999**, *111*, 58; *Angew. Chem. Int. Ed.* **1999**, *38*, 56.

[7] a) A. Matsumoto, T. Odani, M. Chikada, K. Sada, M. Miyata, *J. Am. Chem. Soc.* **1999**, *121*, 11122. b) F. W. Fowler, J. W. Lauher, *J. Phys. Org. Chem.* **2000**, *13*, 850.

[8] D. J. Chesnut, D. Hagrman, P. J. Zapf, R. P. Hammond, R. LaDuca, Jr., R. C. Haushalter, J. Zubieta, *Coord. Chem. Rev.* **1999**, *190–192*, 737.

[9] a) T. E. Mallouk, J. A. Gavin, *Acc. Chem. Res.* **1998**, *31*, 209; b) G. Alberti, E. Brunet, C. Dionigi, O. Juanes, M. J. de la Mata, J. C. Rodríguez-Ubis, R. Vivani, *Angew. Chem.* **1999**, *111*, 3548; *Angew. Chem. Int. Ed.* **1999**, *38*, 3351; c) A. Clearfield, *Prog. Inorg. Chem.* **1998**, *47*, 371.

[10] a) S. R. Batten, R. Robson, *Angew. Chem.* **1998**, *110*, 1558; *Angew. Chem. Int. Ed.* **1998**, *37*, 1460. b) M. Fujita, K. Umemoto, M. Yoshizawa, N. Fujita, T. Kusukawa, K. Biradha, *Chem. Commun.* **2001**, 509.

[11] See, for example: G. K. H. Shimizu, G. D. Enright, C. I. Ratcliffe, J. A. Ripmeester, *Chem. Commun.* **1999**, 461.

[12] G. A. Jeffrey, *An Introduction to Hydrogen Bonding*, Oxford University Press, New York, **1997**.

[13] a) V. A. Russell, M. C. Etter, M. D. Ward, *J. Am. Chem. Soc.* **1994**, *116*, 1941; b) V. A. Russell, M. D. Ward, *J. Mater. Chem.* **1997**, *7*, 1123; c) J. A. Swift, A. M. Reynolds, M. D. Ward, *Chem. Mater.* **1998**, *10*, 4159.

[14] a) C. V. K. Sharma, C. B. Bauer, R. D. Rogers, M. J. Zaworotko, *Chem. Commun.* **1997**, 1559; b) K. Biradha, D. Dennis, V. A. MacKinnon, C. V. K. Sharma, M. J. Zaworotko, *J. Am. Chem. Soc.* **1998**, *120*, 11894.

[15] a) C. B. Aakeröy, M. Nieuwenhuyzen, *J. Am. Chem. Soc.* **1994**, *116*, 10983; b) C. B. Aakeröy, M. Nieuwenhuyzen, *J. Mol. Struct.* **1996**, *374*, 223; c) C. B. Aakeröy, M. Nieuwenhuyzen, *Chem. Mater.* **1996**, *8*, 1229.

[16] a) C. B. Aakeröy, D. P. Hughes, M. Nieuwenhuyzen, *J. Am. Chem. Soc.* **1996**, *118*, 10134.

[17] A hydrogen-bonded organic host–guest network has been shown to withstand significant guest removal: P. Brunet, M. Simard, J. D. Wuest, *J. Am. Chem. Soc.* **1997**, *119*, 2737.

[18] C. B. Aakeröy, *Acta Crystallogr. Sect. B* **1997**, *53*, 569.

[19] The crystal structure of the monohydrate has been reported: N. Ching, L. Pan, X. Y. Huang, J. Li, *Acta Crystallogr.* **2000**, *C56*, 1124.

[20] See, for example: J. C. Bayon, G. Net, P. Esteban, P. G. Rasmussen, D. F. Bergstrom, *Inorg. Chem.* **1991**, *30*, 4771.

[21] See, for example: L. Pan, T. Frydel, M. B. Sander, X. Y. Huang, J. Li, *Inorg. Chem.* **2001**, *40*, 1271.

[22] R. W. McCabe in *Inorganic Materials* (Eds.: D. W. Bruce, D. O'Hare), Wiley, New York, **1992**, 296.

[23] G. M. Sheldrick, University of Göttingen.

[24] Simulated powder patterns were obtained using the Cerius^2 MatSci package, version 4.2.

[25] A. M. Beatty, A. E. Simpson, unpublished results.

Received: January 25, 2002 [F3823]