Supplementary Material

Cyclic amidines as precursors for imidazoles

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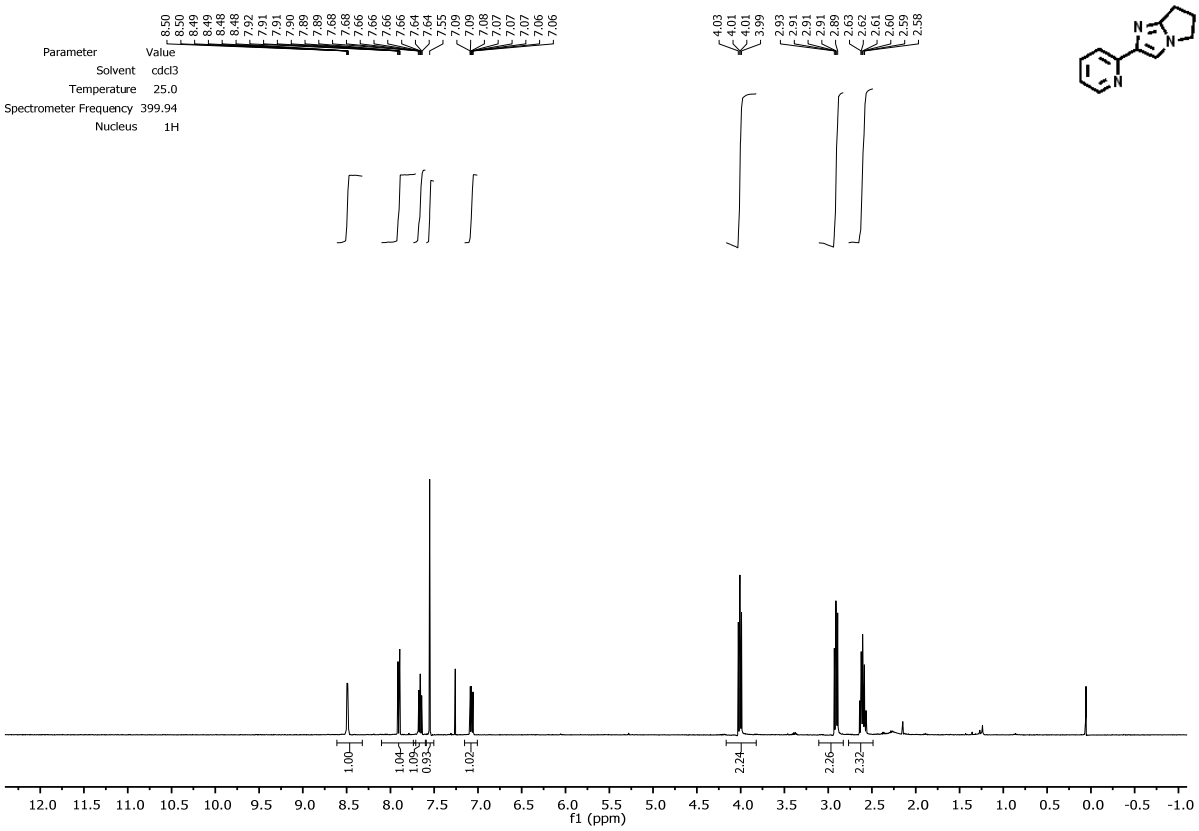
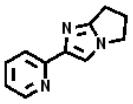
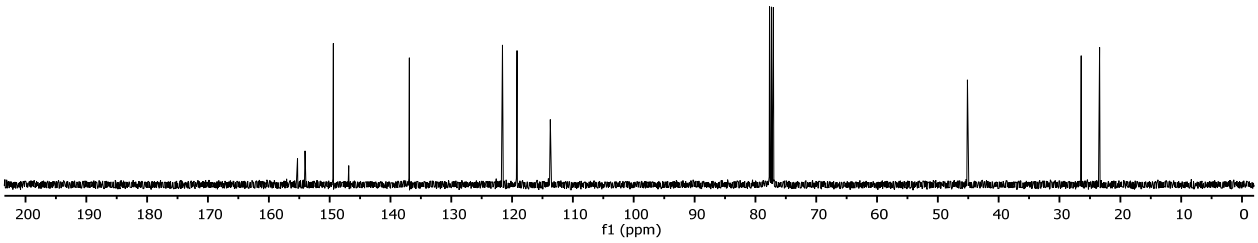
NMR spectra of compound 18

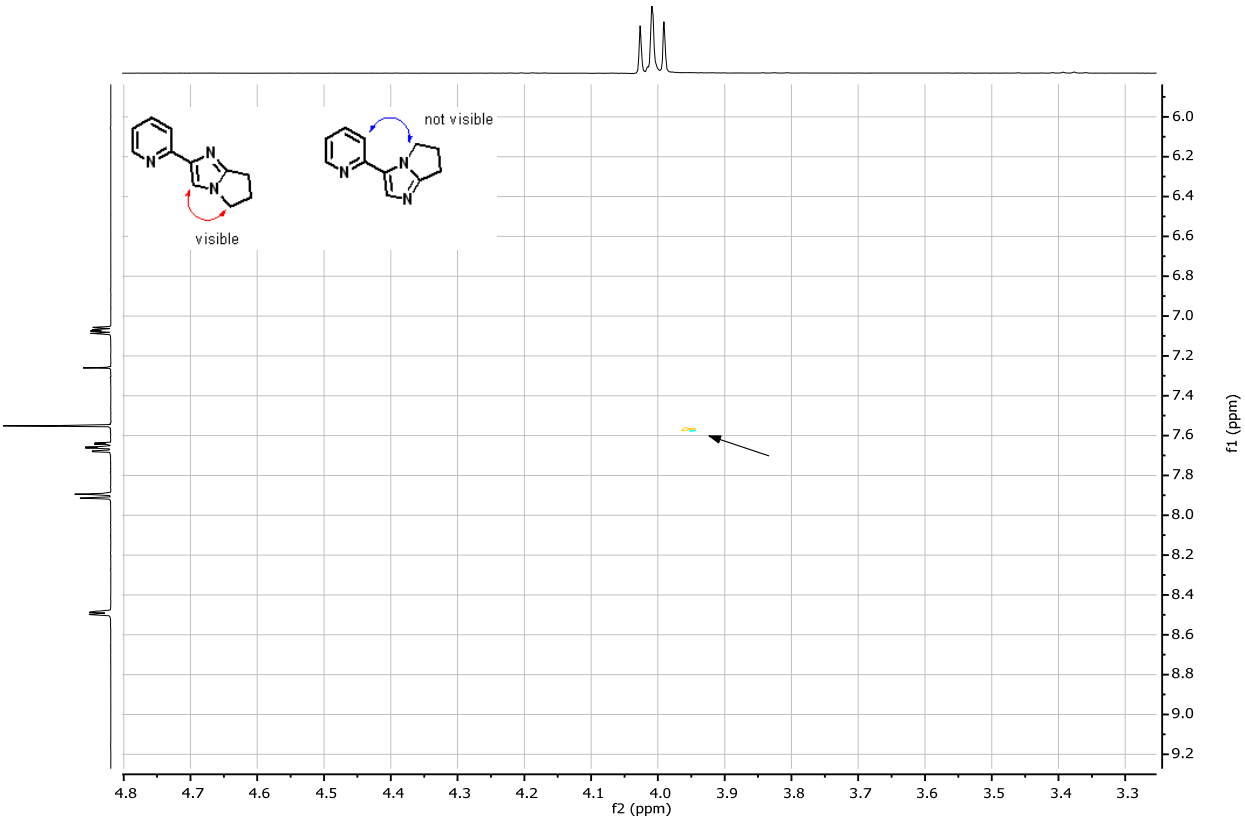


Parameter	Value
Solvent	cdcl3
Temperature	25.0
Spectrometer Frequency	100.58
Nucleus	13C

155.3, 154.1, 149.4, 146.9, 136.9, 121.6, 119.2, 113.7, 45.1, 26.4, 23.4







NOESY NMR interaction showing “straight” structure

Crystallographic Data

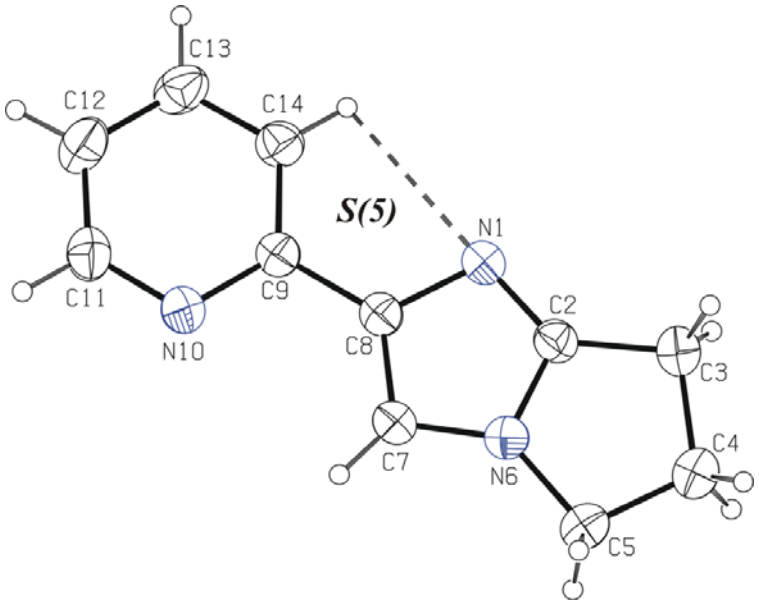


Figure 1 ORTEP representation of the structure of **18** with displacement ellipsoids drawn at the 30% probability level and H atoms shown as small spheres of arbitrary radii. The dashed line depicts the weak C-H···N contact forming an intramolecular pattern. [1,2]

The X-ray analysis of a crystal of **18** showed that this compound crystallizes in the monoclinic $P2_1/n$ space group with four molecules per unit cell, from which one (shown in Figure 2) constitutes a crystallographically independent part. The 6,7-dihydro-5H-pyrrolo[1,2-*a*]imidazole system (Py-Im) of this molecule is essentially planar with the largest deviations from the best least-squares plane being -0.063(0) Å for atom C4. The dihedral angle between the plane of Py-Im system and the pyridine ring plane is only 0.83(3)°. The bond lengths within the pyridine and imidazole rings (Table 1) are in agreement with those given by Allen et al.[3] as typical for pyridine [i.e. 1.380(15) and 1.337(12) Å for C_{ar}-C_{ar} and C_{ar}-N, respectively] and for imidazole [i.e 1.313(11), 1.360(14), 1.376(11), 1.349(18) and 1.370(10) Å for C2=N3, C4=C5, N3-C4, N1-C2 and N1-C5, respectively (according to the atom numbering scheme given by these authors)]. It is noteworthy that the lengths bonds within Py-Im skeleton (Table 1) compare well with the corresponding distances in the compounds, the molecules of which contain also this skeleton[4–7] (Cambridge Structural Database reference codes: YOYJIG, TAHYUX, OSIGIH and FIYWAM, respectively). As Figure 1 shows, there is one weak intramolecular C-H···N contact (Table 2), which links aromatic atom C14, *via* H14, with atom N1 and generates an *S(5)* graph-set motif. [1,2]Analysis of the molecular three-dimensional Hirshfeld surface (Figure 3B) and two-dimensional fingerprint plots (Figures 3C-

E) obtained for compound **18** shows that the intermolecular H···H contacts make a major contribution in the crystal packing, comprising 53.3% of the total Hirshfeld surface of its molecule. The structure is also dominated by C···H/H···C and H···N/N···H contacts, the proportions of which are smaller but still significant (25.5% and 20.2%, respectively). Moreover, it was found that there are no N···N contacts whatsoever within the crystal, and the contribution of C···C and C···N/N···C interactions is practically negligible (0.5%). The most dominant interactions in the crystal are the shortest H···N/N···H contacts, which are revealed in the molecular Hirshfeld surface in the form of two intense red spots (denoted as *1a* and *1b* in Figure 3B) corresponding to the C-H···N hydrogen bond represented by two antennae in the bottom left-right (donor-acceptor) areas of the fingerprint plot (Figure 3E) at $d_i + d_e \cong 2.6$ Å. As can be seen in Figure 3A, each molecule of **18** is connected to two others by this non-conventional weak hydrogen bond. Atoms C13 at (x, y, z) and (1/2+x,1/2-y,-1/2+z) act as hydrogen-bond donors to atoms N10 belonging to the molecules at (-1/2+x,1/2-y,-1/2+z) and (x, y, z), respectively, so forming a simple one-dimensional chain, which can be described by the graph-set *C(5)*.[1,2] There are no direction-specific interactions between adjacent chains of this type.

Table 1. Bond distances [Å] and angles [°]for symmetry-independent molecule in the crystal structure of **18**.

N1-C2	1.315(2)	C8- N1	1.390(2)
C2-C3	1.486(2)	C8- C9	1.461(2)
C3-C4	1.522(2)	C9-N10	1.340(2)
C4-C5	1.507(2)	N10- C11	1.335(2)
C5-N6	1.457(2)	C11- C12	1.368(2)
N6- C2	1.348(2)	C12- C13	1.369(2)
N6- C7	1.366(2)	C13- C14	1.374(2)
C7- C8	1.373(2)	C14- C9	1.390(2)
C2-N1-C8	104.12(10)	N1-C2-N6	112.52(12)
C11-N10-C9	117.09(12)	N1-C2-C3	136.50(12)
N10-C9-C14	121.90(13)	N6-C2-C3	110.98(12)
N10-C9-C8	117.19(11)	N6-C7-C8	104.99(11)
C14-C9-C8	120.89(12)	C13-C14-C9	119.19(14)
C2-N6-C7	107.80(11)	N10-C11-C12	124.58(14)
C2-N6-C5	113.73(12)	C2-C3-C4	102.82(12)
C7-N6-C5	138.46(12)	C11-C12-C13	117.93(15)
C7-C8-N1	110.57(11)	N6-C5-C4	102.96(12)
C7-C8-C9	128.49(12)	C12-C13-C14	119.30(14)
N1-C8-C9	120.92(11)	C5-C4-C3	109.12(13)

Table 2. Hydrogen-bond geometry [Å, °].

D-H···A	D-H	H···A	D ···A	D-H···A
C14-H14···N1	0.93	2.576(1)	2.889(2)	100(1)
C13-H13···N10$^{(i)}$	0.93	2.636(1)	3.448(2)	146(1)

Symmetry code (i) -1/2+x,1/2-y,-1/2+z

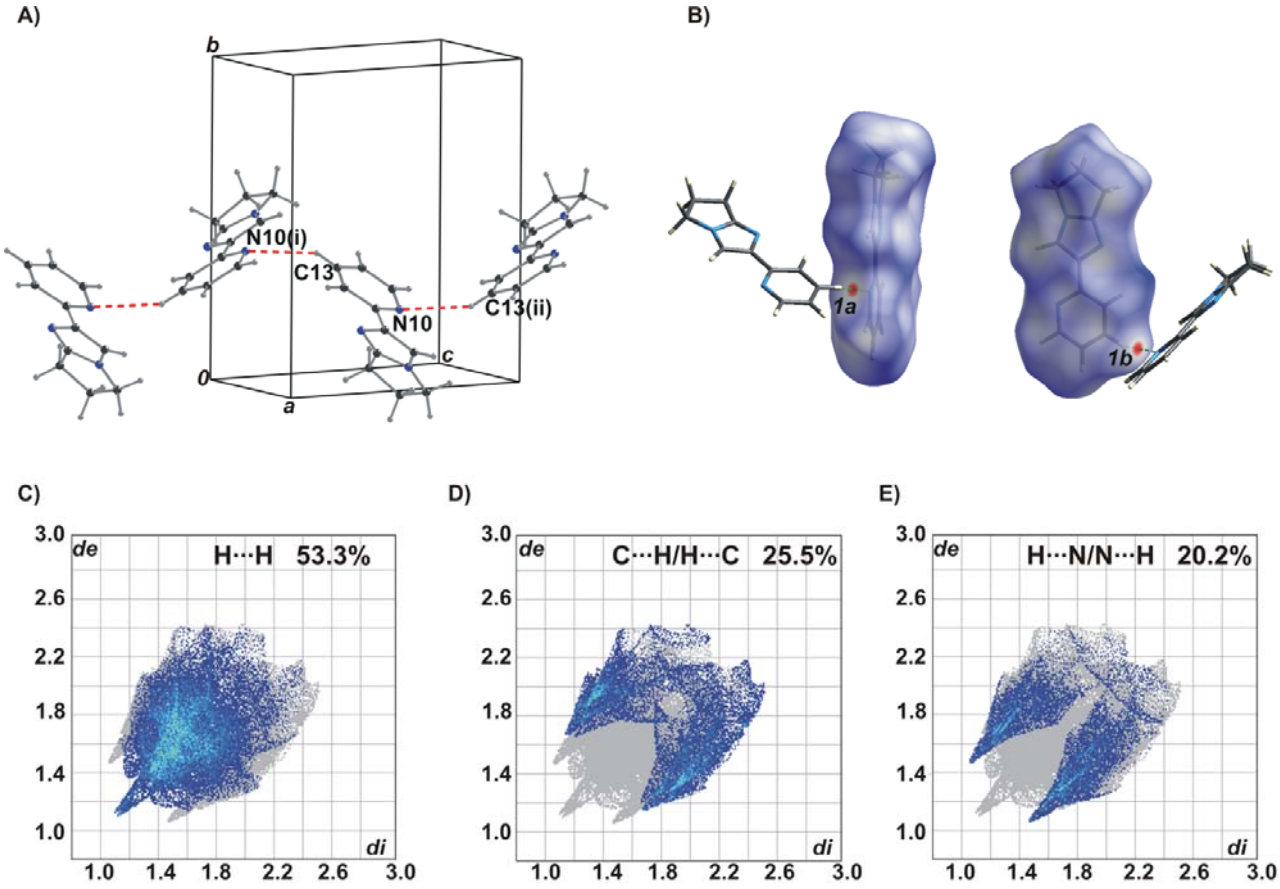
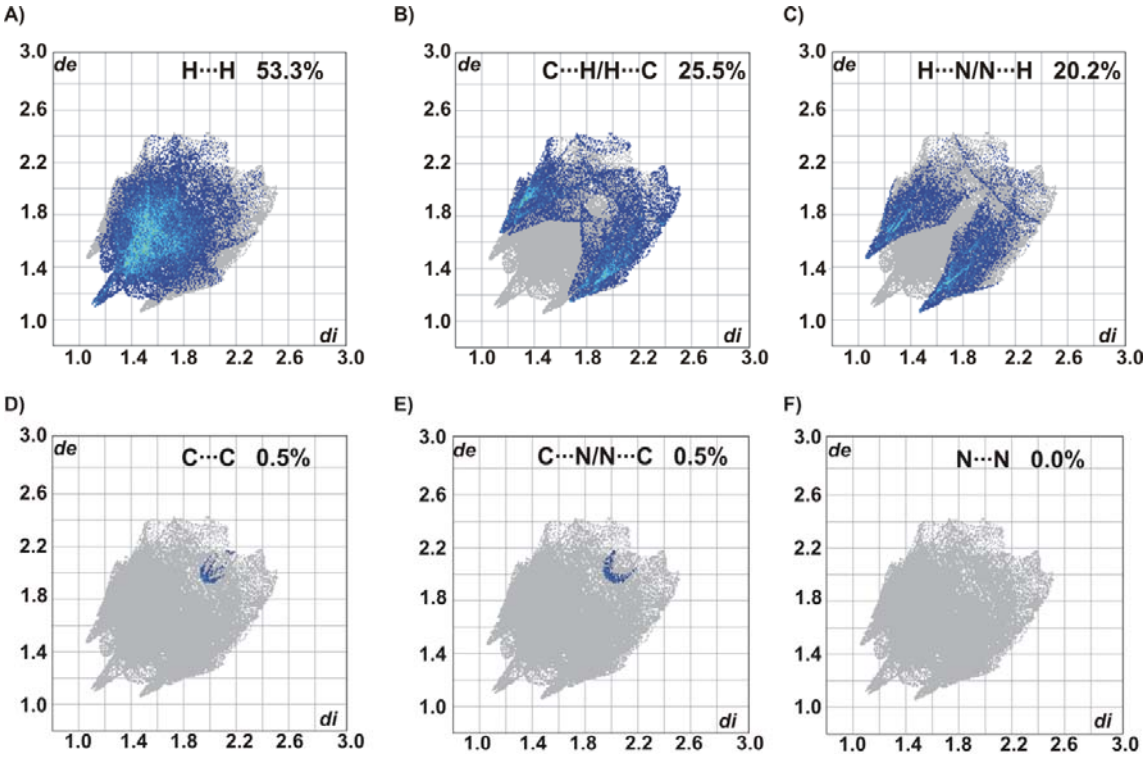


Figure 2 (A) Part of the crystal structure of **18** showing the intermolecular C-H···N hydrogen bond (red dashed line) that forms the simple *C(5)* chain [symmetry codes (i) -1/2+x,1/2-y,-1/2+z; (ii) 1/2+x,1/2-y,-1/2+z]. **(B)** Hirshfeld surface for a molecule of this compound, mapped with d_{norm} distance. **(C-E)** Decomposed 2D fingerprint plots of H···H **(C)**, C···H/H···C **(D)** and H···N/N···H **(E)** contacts.



Decomposed 2D fingerprint plots of H···H (A), C···H/H···C (B), H···N/N···H (C), C···C (D), C···N/N···C (E) and N···N (F) contacts in the crystal structure of 18.

Crystallographic data for 18: $C_{11}H_{11}N_3$, M=185.23; monoclinic; $P2_1/n$; a=7.6888(3)Å, b=11.9124(4)Å, c=10.9184(4)Å and β=107.043(4)°; V=956.13(6)Å^3; Z=4 molecules per unit cell; D_c=1.287 g/cm^3; $F(000)$ = 392; crystal size 0.58 x 0.43 x 0.12 mm. Diffraction data were collected at 293(2) K, using an XCALIBUR^{TM}3 CCD diffractometer with graphite-monochromated CuK_α radiation. The structure was solved by direct methods and refined by full-matrix least-squares on F^2 using the SHELX-97 program package.[8] The non-hydrogen atoms were refined anisotropically. The hydrogen atoms were first localized in difference Fourier maps and next treated as riding atoms in geometrically idealized positions, with C–H distances of 0.93 (C_{sp}^2) and 0.97 (C_{sp}^3), and with $Uiso$(H) = 1.2Ueq(C). R=0.0406, wR =0.1152 and S=1.052 for 1525 unique reflections with $I > 2\sigma(I)$ and 128 parameters. Full crystallographic data are contained in CCDC no. **1038693** and can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html or from the Cambridge Crystallographic Data Centre.

Hirshfeld surface analysis for 18

In order to visualize and analyze the intermolecular interactions in the crystal structure of compound **18**, the *CrystalExplorer 3.1* program[9] was used. This enabled us to construct the three-dimensional Hirshfeld surface of a molecule in the crystal,[10] which illustrates the interatomic contacts with distances equal to the sum of the van der Waals radii (represented as white) and with distances shorter (red) and longer (blue) than the values of this sum. This program was also used to obtain the fingerprint plots,[11] which are the two-dimensional (2D)

representations of this surface, and are generated based on the d_e and d_i distances (d_e and d_i are the distances from the Hirshfeld surface to the nearest atom outside and inside the surface, respectively).

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