Nitrile Groups as Hydrogen-Bond Acceptors in a Donor-Rich Hydrogen-Bonding Network

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Supplementary Information

Section 1 – Structural Parameters and Diagrams

Table S1 Hydrogen-bonding interactions in $(NH_2)_3C$ cdm from neutron data (c.f. Table 1, main manuscript).

Interaction	D-H (Å)	H···A (Å)	D···A (Å)	D-H···A (°)
N(1)···O(1)#1	1.014(4)	1.882(4)	2.889(2)	171.6(3)
N(1)···N(2)#2	0.993(4)	2.445(5)	3.131(2)	125.8(3)
N(4)···O(1)#3	1.008(5)	1.998(5)	2.877(2)	144.1(4)
N(4)···N(2)	0.998(4)	2.242(5)	3.122(2)	146.2(3)
N(5)···O(1)#3	1.007(4)	1.981(4)	2.881(2)	147.5(3)
N(5)···N(3)#4	1.004(4)	2.291(4)	3.155(2)	143.5(3)
N(6)···N(2)	1.003(4)	2.147(4)	3.054(2)	149.5(3)
N(6)···N(3)#4	1.007(4)	2.021(4)	2.962(2)	154.5(4)

[a] Symmetry equivalents used; #1, -x, -y+1, -z; #2, -x+1, -y+1, -z; #3, 1+x, y-1, z; #4, 1-x, y-3/2, 1/2-z.

Table S2 Hydrogen-bonding interactions in $(NH_2)_3C$ cdm from X-ray data.

Interaction	D-H (Å)	H···A (Å)	D···A (Å)	D-H···A (°)
N(1)···O(1)#1	0.870(16)	2.032(16)	2.8967(13)	172.6(14)
N(1)···N(2)#2	0.878(16)	2.520(16)	3.1243(15)	126.6(13)
N(4)···O(1)#3	0.886(17)	2.101(17)	2.8750(14)	145.5(14)
N(4)···N(2)	0.887(17)	2.334(18)	3.1231(15)	148.2(15)
N(5)···O(1)#3	0.869(18)	2.090(18)	2.8798(15)	150.7(14)
N(5)···N(3)#4	0.896(17)	2.360(17)	3.1526(16)	147.5(14)
N(6)···N(2)	0.899(17)	2.240(17)	3.0603(15)	151.5(15)
N(6)···N(3)#4	0.894(19)	2.124(19)	2.9607(15)	155.6(15)

[a] Symmetry equivalents used as per Table 1

Table S3: Deviations from least-squares mean plane of C5-N4-N5-N6 (the guanidinium cation) in $((NH_2)_3C)$(cdm) from neutron diffraction data.

C5	-0.0155 (0.0013)
N4	0.0052 (0.0004)
N5	0.0051 (0.0004)
N6	0.0052 (0.0004)
H4A	-0.0515 (0.0049)
H4B	-0.0761 (0.0050)
H5A	-0.1541 (0.0048)
H5B	-0.1694 (0.0044)
H6A	-0.0235 (0.0047)
H6B	-0.0816 (0.0049)

Table S4: Deviations from least-squares mean plane of non-hydrogen atoms in the cdm anion from neutron diffraction data.

C1	0.0453 (0.0015)
C2	0.0041 (0.0013)
C3	0.0238 (0.0013)
C4	0.0035 (0.0014)
N1	0.0183 (0.0011)
N2	-0.0359 (0.0010)
N3	-0.0163 (0.0009)
O1	-0.0429 (0.0014)
H1A	0.0226 (0.0040)
H1B	0.1347 (0.0050)

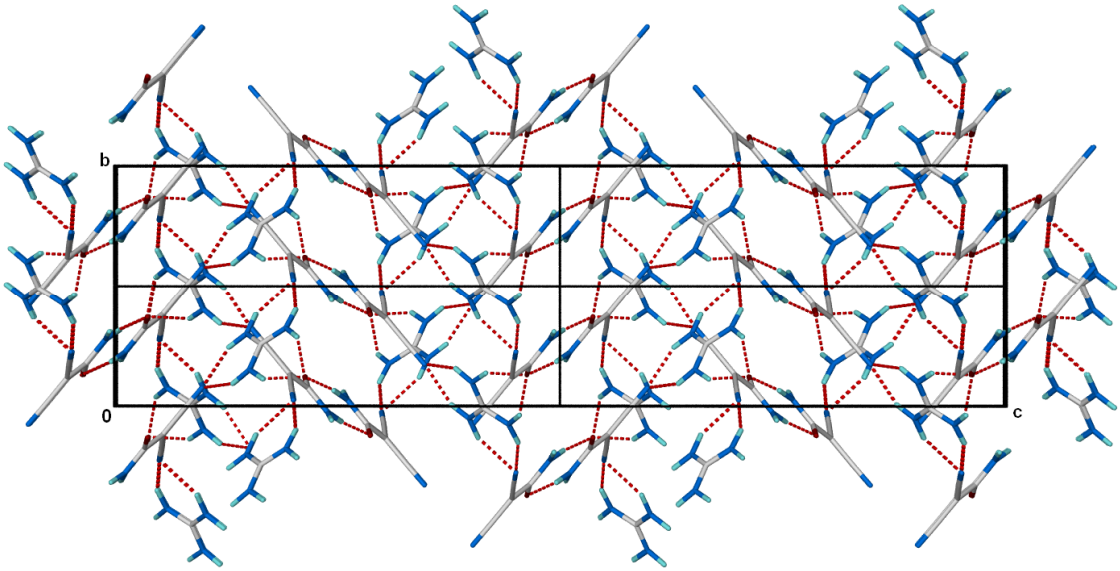

Figure S1: Crystal packing of $((NH_2)_3C)(cdm)$ viewed along the *a*-axis.

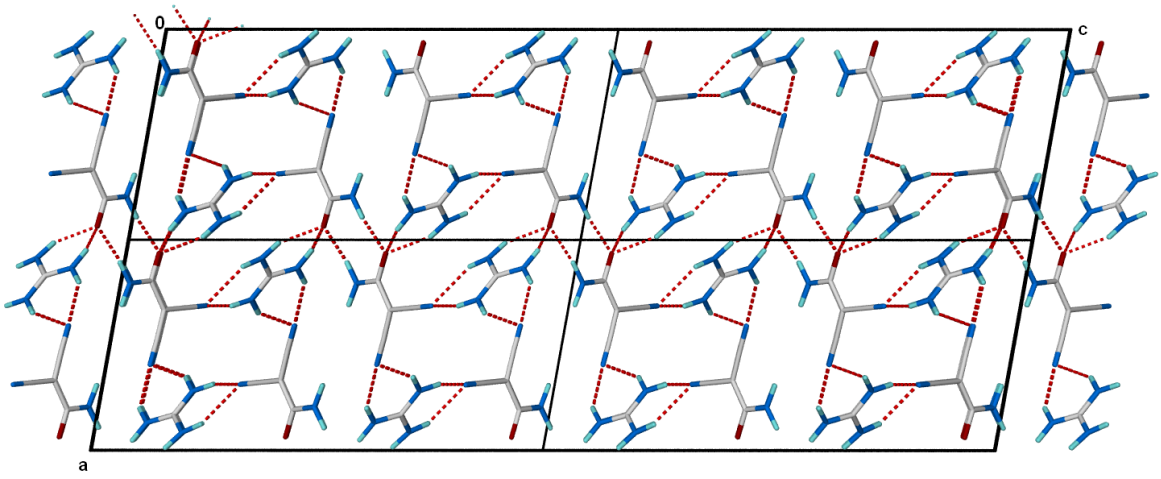

Figure S2: Crystal packing of $((NH_2)_3C)(cdm)$ viewed along the *b*-axis.

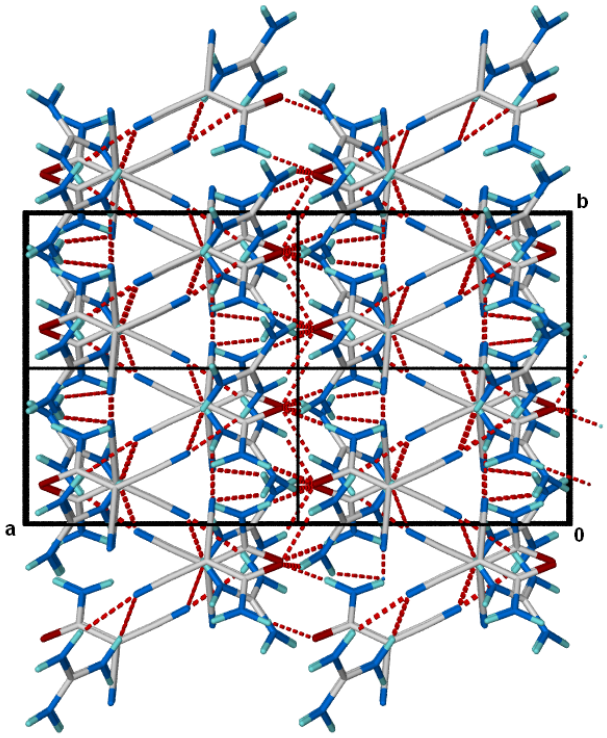

Figure S3: Crystal packing of $((NH_2)_3C)(cdm)$ viewed along the *c*-axis.

Section 2 - Cambridge Structural Database Search Details and Results

Search Details

Searches were carried out using CSD Version 5.33 (November 2011) + 1 update (Feb 2012). In all cases the search parameters required the H···N contacts to be within the sum of the vdW radii (N + H = 2.750 Å). For searches containing 6-membered chelating rings with two NH donor groups it was specified that there must be a non-metal atom between the two nitrogen atoms in order to remove coordinated en/pn from results. Metal-coordinated nitriles (i.e. CN^- ligands) were excluded from all searches. No filters were placed on the bond orders within the chelating donor group.

Results from all searches were limited to those entries that had 3D coordinates determined, R factors <= 0.1 and no disorder or errors. All X-H distances were normalised to neutron distances.

General NH···Nitrile Interactions

An initial search was conducted to examine the spread of distances and geometries of NH···N interactions to organic nitrile groups regardless of what supramolecular motifs they are involved in. Plots shown in Figure S4 show the distribution of NH···N distances that were found for the entire data sample as well as for two sub-categories, SCN groups and acetonitrile molecules. These two sub-classes are very prevalent in the database and were examined briefly to determine whether the type of species that the nitrile group is part of (and therefore the electronic nature of the nitrile group) has any major change on the length of the hydrogen-bonding interaction. The mean NH···N distance for all interactions is 2.211 Å with the mean observed for SCN being slightly shorter (2.116 Å) and that for MeCN being slightly longer (2.223 Å) as would be expected. For the purposes of our intended study (the asymmetry of $R_2^1(6)$ motifs) no distinction will be made between these sub-classes of nitrile acceptor groups.

The NH···Nitrile dataset was also analysed for any relationship between the NH···N distance and the angle of approach, in terms of both the NH···N and C≡N···H angles. These distance vs. angle scatter plots (Figure S5) show a definite preference for both the NH···N and C≡N···H angles to approach linearity from the clustering of points. Whilst this is generally expected for the NH···N interaction it is very interesting to note this trend for the C≡N···H angle which supports the work of Le Questel showing that the minimum electrostatic potential lies at, or near, the lone pair of the *sp* nitrogen atom (see main paper). In addition to this clustering both plots demonstrate a general trend that longer NH···N distances are associated with more acute angles with the trend being more pronounced for NH···N angles than C≡N···H angles.

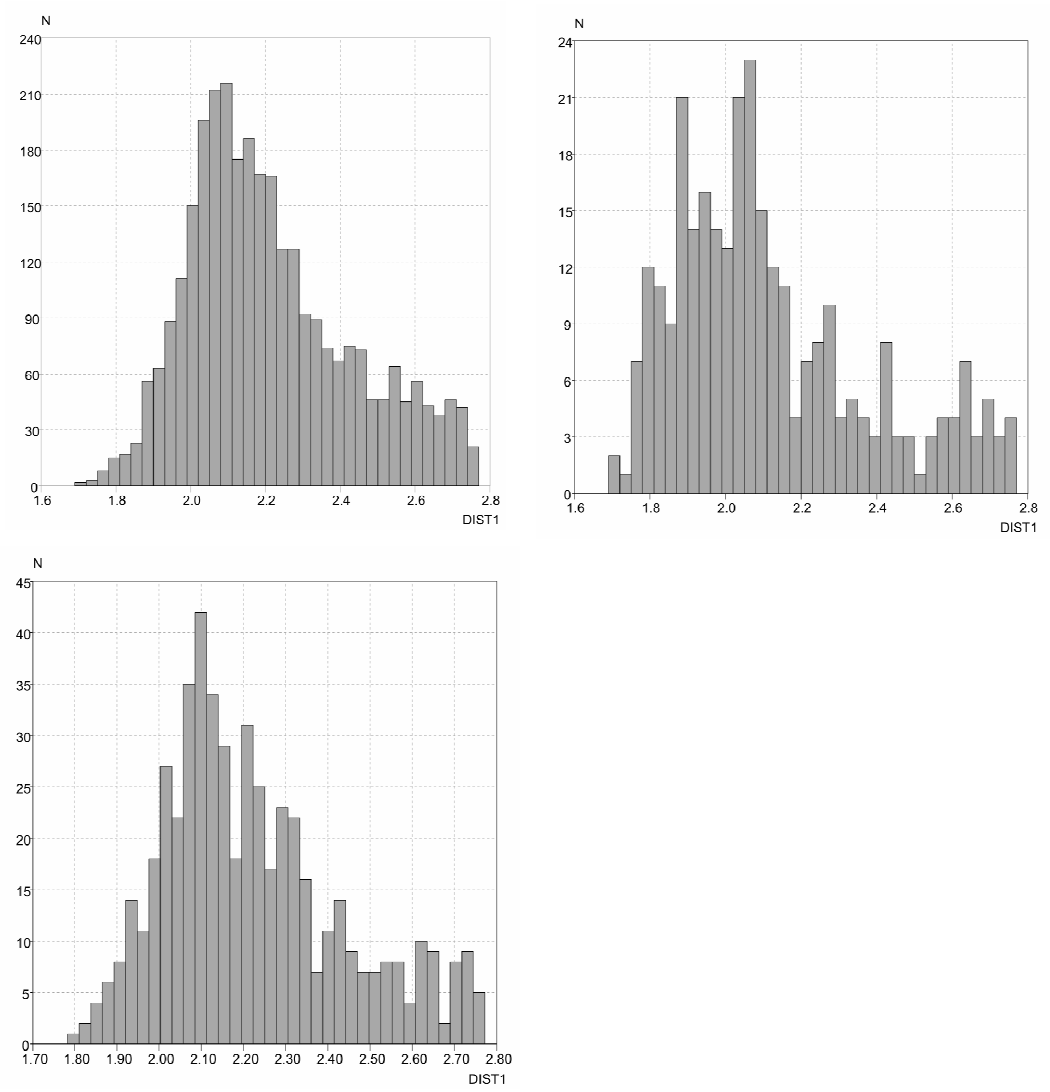

Figure S4: Histograms of NH···N hydrogen bonding distances to organic nitrile groups using normalised N-H distances for all nitrile groups (top left), SCN (top right) and MeCN (bottom left). The data show that there are not vast differences in the distribution depending on the type of nitrile.

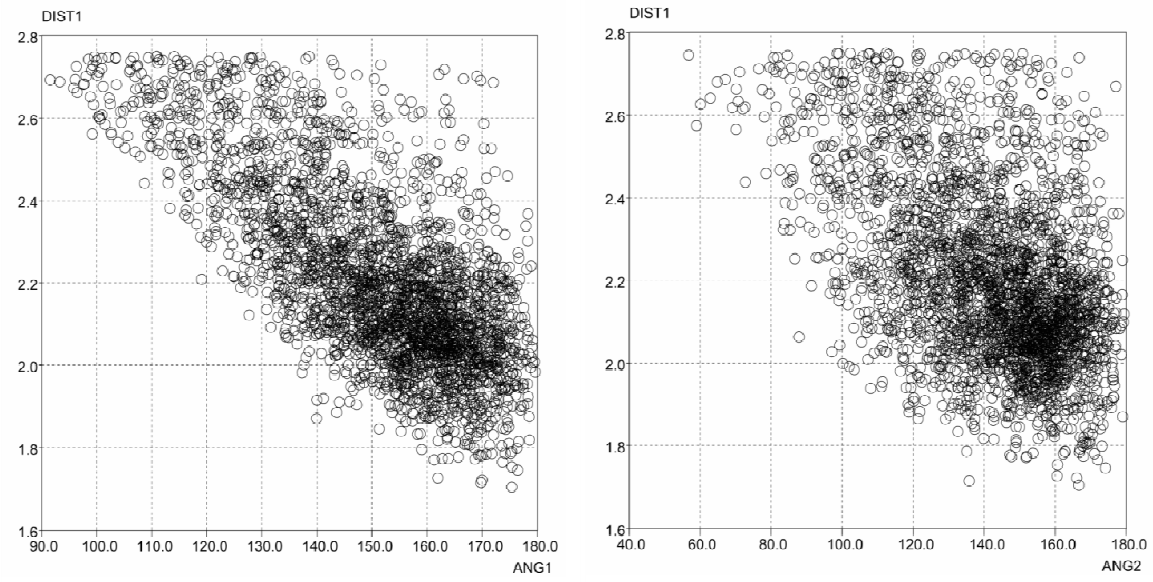

Figure S5: Scatter plots for N···H vs N-H···N (left) and N···H vs H···N≡C (right) for all NH···N interactions to organic nitrile groups.

$R_1^2(6)$ Interactions to Nitrile Groups

A search was conducted using the criteria outlined above to explore the geometrical preferences, if any, associated with $R_2^1(6)$ hydrogen-bonding motifs involving nitrile as the donor group and two N-H units as the donors. The search resulted in 32 hits one of which, CSD code ABGTCU, was excluded due to nonsensical angles around the sp^2 nitrogen donor atoms.

Geometric parameters were extracted from the search results according to Figure S6. These are tabulated in Table S4 with θ_1 set as the largest angle.

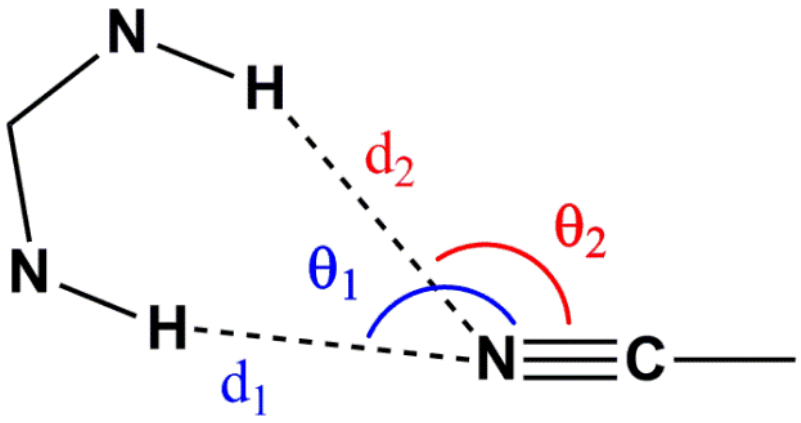

Figure S6: Definition of terms used to describe the geometry of hydrogen-bonding interactions in the $R_2^1(6)$ motif around a nitrile group (*c.f.* Fig. 4, main paper)

Table S4: Geometric parameters for . . . Note that for ($d_2 - d_1$) positive values are instances where the more acute θ angle has a longer associated N···H distance.

CSD RefCode	θ_1	θ_2	d_1	d_2	$\theta_1 - \theta_2$	$d_2 - d_1$
FANXIC	149.391	149.113	2.721	2.084	0.278	-0.637
BAFSOQ	151.324	149.772	2.375	2.367	1.552	-0.008
MAHVAS	154.281	151.504	1.953	2.539	2.777	0.586
CYAMPD03	136.663	124.781	2.198	2.078	11.882	-0.12
WEPFON	150.381	137.158	2.227	1.847	13.223	-0.38
UJETAE	135.148	121.773	2.232	1.965	13.375	-0.267
GAFFAV	154.982	141.359	1.955	2.342	13.623	0.387
YOWDAQ	125.917	112.043	2.169	2.231	13.874	0.062
RENTIN	159.249	144.222	2.082	2.464	15.027	0.382
FOWMEJ	99.804	84.622	2.315	2.437	15.182	0.122
RENTIN01	159.717	144.434	2.082	2.456	15.283	0.374
GAFFAV01	155.957	139.812	1.955	2.365	16.145	0.41
GAFFAV01	157.568	141.13	2.004	2.308	16.438	0.304
GAFFAV	160.285	137.495	2.008	2.299	22.79	0.291
QIXJAJ	152.176	128.175	2.379	2.275	24.001	-0.104
DIDRAJ	163.365	136.927	2.055	2.503	26.438	0.448
GITZUF	166.301	136.312	1.875	2.472	29.989	0.597
REMWOV	134.757	102.009	1.897	1.992	32.748	0.095
HIFZUR	134.598	100.199	1.884	1.998	34.399	0.114
TCAGTU	107.586	70.762	2.124	2.632	36.824	0.508
TCAGTU02	108.37	69.067	2.084	2.618	39.303	0.534
DAWDAH	167.667	127.6	1.948	2.241	40.067	0.293
CEKGOP	126.022	85.749	2.104	2.715	40.273	0.611
ZUZXIB	150.429	109.002	1.977	2.587	41.427	0.61
COFRIY10	158.162	116.678	1.984	2.599	41.484	0.615
EMEMUF	168.536	122.755	1.846	2.205	45.781	0.359
COFROE10	163.635	117.279	2.179	2.694	46.356	0.515
PEFGIR	156.499	109.069	2.119	2.692	47.43	0.573
MAHVAS	154.281	105.891	1.953	2.742	48.39	0.789
HOXVIA	151.806	96.908	2.318	2.464	54.898	0.146
REXZUP	163.005	107.003	2.291	2.056	56.002	-0.235
WUNNUP	142.845	86.148	2.001	2.452	56.697	0.451
TUFDIH	155.38	98.481	2.046	2.413	56.899	0.367
LORLAG	164.431	107.271	1.998	2.253	57.16	0.255

The results in Table S4, in which θ_1 is set as the largest angle, means that if d2-d1 is a positive value then the longer H···N distance is associated with the more acute H···N≡C angle in that $R_1^2(6)$ interaction. Out of the 33 results that are listed only 6 go against this expectations with one of these showing a difference of only 0.008 Å between the two H···N contacts.