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A Dimer of Hydrogen Cyanide Stabilized by A Lewis Acid

Kevin Bläsing,[a] Jonas Bresien,[a] René Labbow,[a] Axel Schulz,*[a,b] and Alexander Villinger[a]

Abstract: A highly labile dimer of hydrogen cyanide, HCN···HCN, was extracted from liquid HCN by adduct formation with the bulky Lewis acid $B(C_6F_5)_3$, affording HCN···HCN-$B(C_6F_5)_3$, which was fully characterized. The influence of the solvent (HCN, CH_2Cl_2, and aromatic hydrocarbons) on the crystallization process was studied, revealing dimer formation when using HCN or CH_2Cl_2 as solvent, whereas aromatic hydrocarbons led to the formation of monomeric Aryl···HCN-$B(C_6F_5)_3$ adducts, additionally stabilized by η^6-coordination of the aromatic ring system similar to well-known half-sandwich complexes.

"L'acide prussique ordinaire recevra le nom d'acide hydrocyanique … ."[1] wrote Gay-Lussac 1815 in his famous article on the chemistry of Prussian blue (ideal formula $Fe^{III}_4[Fe^{II}(CN)_6]_3 \cdot 15H_2O$), hydrogen cyanide (HCN) and the discovery of cyanogen (NC-CN).[2] With this sentence, he coined a new word for the CN radical. On the same page, he also gave an explanation for the origin of the word "*cyanogène*", which he derived from the Greek words κυανός (kyanos, blue) and γεννάω (gennao, I create) in analogy to the German word *Blausäure* ("blue acid" = Prussic acid = hydrogen cyanide) that had been used ever since its discovery by Scheele in 1782 and is still being used in the German language today.[3] However, the actual beginning of cyanide chemistry probably dates back even further, to the year 1706, when Diesbach und Dippel discovered the famous dye Prussian blue.[4,5]

While Scheele obtained HCN from the reaction of $K_4[Fe(CN)_6]$ with H_2SO_4, in industry HCN is nowadays generated by a platinum-catalyzed process from methane and ammonia (BMA process) or in the presence of O_2 (Andrussow process). By the latter two processes, highly toxic hydrogen cyanide (b.p.: 26 °C,[6] m.p.: −13 °C,[6] μ = 2.98 D)[7] is produced on an industrial scale, because it is an important precursor to numerous chemical compounds. Besides, in the past 50 years HCN has attracted attention in the discussion of the primitive earth atmosphere[8–12] and has been found even in the interstellar space.[13,14] Moreover, HCN has been considered as a precursor to amino and nucleic acids on the primitive earth, thus playing an important role in prebiotic synthesis.[8–12,15–17] With respect to the latter, condensation products of HCN are thought to be key intermediates.

Hence, a plethora of theoretical[18–25] and experimental[16,19,20,26–40] studies have been performed on HCN and its clusters (HCN)$_n$ in the gas phase (microwave rotational spectroscopy, IR or matrix IR). These studies indicated that HCN forms linear H-bonded clusters in all its phases. Crystal structure elucidation revealed "infinite" parallel, linear hydrogen-bonded chains,[41] while for the liquid phases, a linear structure with an association state of n = 3 was experimentally derived.[42] Density and heat capacity measurements of HCN gas proved the presence of (HCN)$_n$ oligomers, especially dimeric and trimeric (HCN)$_n$ at 25 °C and 1 atm.[26,43,44] By means of rotational spectroscopy, the HCN dimer and trimer were doubtlessly characterized as H-bonded linear species in the gas phase.[27,45,46]

Much less is known about HCN adducts of which only two were structurally characterized in the solid state (HCN-BF_3, HCN-$NbCl_5$).[47–51] The only experimental study on an HCN···HCN adduct was reported by Leopold *et al.* who investigated HCN···HCN-SO_3 in the gas phase by rotational spectroscopy.[52] Hence, we were intrigued by the idea to stabilize an HCN dimer in the solid state by a strong Lewis acid such as $B(C_6F_5)_3$ and to study the influence of the solvent (HCN, CH_2Cl_2, and aromatic hydrocarbons such as benzene, toluene) on the crystallization process. Hereby, we want to bridge the gap between the gas and condensed phases of HCN cluster chemistry.

$$NaCN + CH_3(CH_2)_{16}COOH \xrightarrow[-Na[OOC(CH_2)_{16}CH_3]]{neat, \Delta} H\text{-}CN \uparrow$$

$$H\text{-}CN + B(C_6F_5)_3 \xrightarrow[0°C \longrightarrow -40°C]{solvent = HCN, CH_2Cl_2} (C_6F_5)_3B \longleftarrow N\equiv C\text{-}H \cdots N\equiv C\text{-}H \quad \mathbf{1}$$
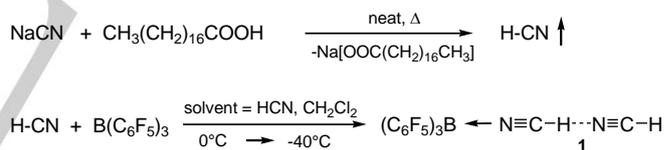
Scheme 1. Synthesis of HCN (H = ^{1}H or ^{2}H (D); **1** = **1H** or **1D**) and trapping of HCN···HCN by adduct formation.

In a first series of experiments, we used an excess of HCN as solvent, which was generated from NaCN and stearic acid (m.p. 69 °C) at 80 - 100 °C under vacuum as depicted in Scheme 1.[53,54] Upon addition of an excess of HCN to neat $B(C_6F_5)_3$ at 0 °C, the borane dissolved at once and almost instantaneously the growth of colourless crystals was observed. X-ray studies revealed unequivocally the presence of the HCN-dimer borane adduct, HCN···HCN-$B(C_6F_5)_3$ (**1H**) as HCN solvate (**1H·0.44HCN**, Figure 1). To study the Raman spectra of HCN in detail (*vide infra*), we also prepared the analogous DCN species **1D** which also crystallized as solvate **1D·0.5DCN**. Interestingly, crystals or HCN (DCN) solutions of **1** were instable with respect to polymerization. At 0° C, decomposition of **1** was observed within 2 h and at −20 °C within 8 h, affording a highly viscous black material.[55,56] Hence, always freshly prepared crystals or solutions were needed for any further studies.

In a second series of experiments, we utilized organic solvents for the reaction of HCN with $B(C_6F_5)_3$. The borane was

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dissolved in CH_2Cl_2 at 0 °C and degassed. After addition of an excess of HCN, the clear solution was cooled down to –40 °C overnight, affording yet again HCN···HCN-B(C_6F_5)$_3$ (**1H**), however, reproducibly as another solvate **1H·2HCN**. Crystals of **1H·2HCN** suspended in CH_2Cl_2 were stable significantly longer (7 days) than pure crystals before signs of decomposition (colour change to yellow) were spotted.

Finally, we used aromatic hydrocarbons (Ar = benzene = benz, toluene = tol and 1,2-dimethylbenzene = xyl) as solvent. In this case, the reaction of HCN and B(C_6F_5)$_3$ always afforded – independently of the utilized stoichiometry – the monoadduct HCN-B(C_6F_5)$_3$ which was stabilized by one η^6-coordinated aryl molecule (**2Ar**) as shown in Figure 2 (Ar = benz; for tol and xyl see Figures S63 - S64). Astonishingly, HCN is sandwiched between B(C_6F_5)$_3$ and the aryl moiety, resulting in thermal stability of these compounds up to over 100 °C. Apparently, the η^6-coordinated aryl molecule prevents the HCN-B(C_6F_5)$_3$ adduct from adding a second HCN molecule. In fact, the coordination of an aryl instead of a second HCN molecule was computationally shown to be thermodynamically favoured (*vide infra*).
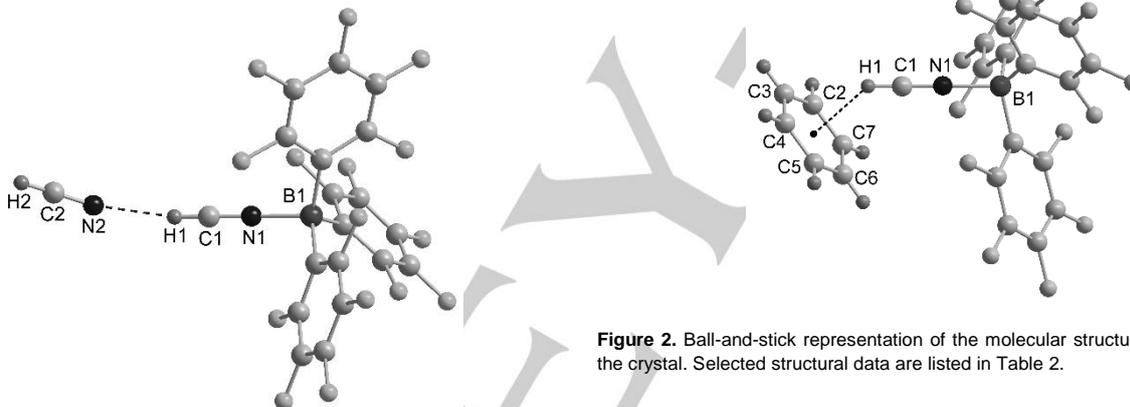
Figure 1. Ball-and-stick representation of the molecular structure of **1H** in the crystal of **1H·0.44**. Disorder of the H2-C2-N2 moiety and solvate HCN (H3-C3-N3) are not shown. Selected structural data are listed in Table 2.

All species were studied by means of ^1H, ^{13}C, ^{14}N and ^{11}B NMR experiments in CD_2Cl_2 (Table 1); however, ^{11}B NMR spectroscopy is particularly well suited to distinguish between free, three-coordinate borane and the four-coordinate boron found in the Lewis acid-base adducts. In the latter case, the ^{11}B resonance (–10.9 **1H**, –7.8 **2benz**, –7.5 **2tol**, and –7.2 **2xyl**) is significantly shifted to lower frequency with respect to free B(C_6F_5)$_3$ by more than 65 ppm (*cf.* B(C_6F_5)$_3$: 59.8 ppm).[57,58] It should be noted that in case of **1H**, all resonances (in the ^1H, ^{13}C, ^{14}N and ^{11}B spectra) are very broad but still detectable at –20 °C indicating a highly dynamic system. For example, even the nitrogen atoms can be observed in the ^{14}N NMR experiment at –128 and –192 ppm with half widths of 960 and 2250 Hz (*cf.* HCN: –125 ppm and $\Delta v_{1/2}$ = 50 Hz). As expected, upon borane adduct formation (Table 1), the resonance of the proton is shifted to lower field by ca. 2 ppm (*cf.* HCN 4.00 vs. 6.42 **1H**) displaying an increase of the acidity. A broad resonance formally assigned to the loosely bound second HCN molecule of **1H** is detected at 4.02 ppm, indicating dynamic exchange between loosely bound and free HCN species. The

Raman data of all considered B(C_6F_5)$_3$ adducts were obtained from the crystals used for the X-ray structure elucidation. As listed in Table 2, sharp bands appear in the expected region between 2090 and 2200 cm^{-1} for the v_{CN} stretching frequencies. Since three different CN groups are present in the crystals of **1**, three different v_{CN} stretching modes are observed (**1H·0.44HCN**: 2131 (-C1N1-B(C_6F_5)$_3$, Figure 1), 2121 (-C2N2-), 2114 (free solvate H3C3N3); **1D·0.5DCN**: 1938, 1924, 1910 cm^{-1}) which could be assigned on the basis of computed frequencies. As previously shown, strong hydrogen bonding and coordination of B(C_6F_5)$_3$ to a NC–R species causes a significant band shift to higher wave numbers (Table 2, Δv_{CN} for CN group attached to B(C_6F_5)$_3$: 34 **1H·0.44HCN**, 43 **1D·0.5DCN**, 84-81 cm^{-1} **2Ar**; *cf.* v_{CN} in solid HCN 2097, 1895 cm^{-1} DCN).[59–61] The shift to higher wave numbers upon adduct formation or stronger hydrogen bonding correlates nicely with a smaller C–N distance (Table 2). The H-C stretching modes appear as weak, broad bands (**1H·0.44HCN**: 3275 and **1D·0.5DCN**: 2575 cm^{-1}) and could not be resolved.[60–62]

Figure 2. Ball-and-stick representation of the molecular structure of **2benz** in the crystal. Selected structural data are listed in Table 2.

Table 1. Selected NMR data of HCN, HCN-B(C_6F_5)$_3$, **1H**, and **2Ar** [δ scale].

compound	^1H	^{11}B	$^{13}C\{^1H\}$	$^{14}N\{^1H\}$
HCN	4.00	-	110.1	−125.0
HCN-B(C_6F_5)$_3$	6.19	−14.7	103.8	−188.8
1H[a] H2C2N2	4.02 [b]	−10.9	106.9	−128.1
H1C1N1	6.42	-	106.9	−192.2
2benz	5.97	−7.8	104.7	−189.5
2tol	5.97	−7.5	104.6	−189.9
2dmp	5.80	−7.2	104.8	−190.8

[a] Very broad signals were observed in all spectra (see Figures S32 - S34). Atom assignment as used in Figure 1. [b] Dynamic exchange with free HCN species.

1H·0.44HCN and **1D·0.5DCN** crystallized in the monoclinic space group *C*2/*c* with eight formula units per cell, but differed in the number of solvate molecules per formula. The solvate HCN (DCN) molecules are localized in voids formed by the B(C_6F_5)$_3$ units and aligned linearly along the *b* axis. Yet, there are no

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interactions between them as they are separated by more than 7 Å (d(HCN···HCN) = 7.01 Å). Likewise, the N···H distances between the solvate molecules and the H-bonded dimer are too large (> 4.9 Å) to be discussed as interaction. However, there are four H···F(borane) contacts (2.68 Å) which lie in the range of the sum of the van der Waals radii (Σr_{vdW}(H···F) = 2.67 Å).[63] It is worthy to note the structural simplicity of the H-bonded dimers in **1**, which reveal themselves as almost linear HCN···HCN-B(C$_6$F$_5$)$_3$ chains, with structural parameters that compare well to those predicted using density functional theory (DFT see ESI, X-ray see Table 2). However, in contrast to the experimental data, the gas phase computations display a perfectly linear chain with C_3 point group symmetry. Hence, the slight bending of the HCN···HCN-B(C$_6$F$_5$)$_3$ chain in the crystal might be attributed to packing effects not allowing C_3 symmetry. In accord with this explanation, the bending potential is extremely flat indicating a highly flexible HCN···HCN-B(C$_6$F$_5$)$_3$ chain (*e.g.* 90° change for ∡N2···C1-N1 within 5 kcal mol^{-1}, Figure S 65). Although crystals of **1H·2HCN** obtained from CH$_2$Cl$_2$ solutions crystalized in the triclinic space group $P\bar{1}$, the structural parameters are very similar to those of **1H·0.44HCN** and **1D·0.5DCN** (Table 2). However, in contrast to **1H·0.44HCN** and **1D·0.5DCN**, centrosymmetric dimers of **1** are observed. Moreover, the structure of **1H·2HCN** contains infinite channel-like voids, which are occupied by approximately two heavily disordered HCN molecules in the crystallographic asymmetric unit. Since no suitable disorder model could be obtained, the solvent molecules were removed from the model and treated as a diffuse contribution to the overall scattering without specific atom positions using the SQUEEZE/PLATON procedure.[64]

Table 2. Selected experimental Raman data (wave numbers in cm^{-1}) and structural data (bond lengths in Å, angles in °).

	1H·0.44HCN	1D·0.5DCN	1H·2HCN	2benz
$\nu_{H/D\text{-}C}$	3275 [a]	2575 [a]	3272 [a]	3200br
$\nu_{1,CN}$[b]	2131	1938	2196 [d]	2181
$\nu_{2,CN}$[b]	2121	1924	2172	-
$\nu_{3,CN}$[b,c]	2114	1910	2116	-
C1-N1[b]	1.126(3)	1.117(4)	1.118(3)	1.125(2)
C2-N2[b]	1.096(7)	1.097(10)	1.066(5)	-
C3-N3[b]	1.062(7)	1.030(9)	- [e]	-
B1-N1	1.606(3)	1.607(4)	1.609(3)	1.611(2)
C1···N2	3.04(3)	3.07(3)	3.038(6)	-
N1-C1-N2	173.3(5)	173.2(6)	178.4(2)	-
C1-N2-C2	153(1)	152(2)	164.6(4)	-

[a] Broad band, the different H/D-C vibrational modes could not be resolved in the Raman experiment, *cf.* IR: HCN···HCN$_{(s,\ Ar\text{-}matrix)}$[23]: 3306 and 3213 cm^{-1}. [b] $\nu_{1,CN}$ corresponds to C1N1 (Figure 1), $\nu_{2,CN}$ corresponds to C2N2, $\nu_{3,CN}$ solvate H/DCN; [c] *cf.* 2097 cm^{-1} pure HCN, 1895 cm^{-1} pure DCN, IR: 2112 and 2093 cm^{-1} in HCN···HCN$_{(s,\ Ar\text{-}matrix)}$[23]. [d] Two further bands at 2202 and 2213 cm^{-1} were observed, which were tentatively assigned to the two HCN molecules in

the voids (see structure discussion). [e] No value can be given due to a non-solved disorder problem.

In accord with the Raman data, three different CN bond lengths (1.03 - 1.26 Å, Table 2) within the range of a CN triple bond (Σr_{cov}(C≡N) = 1.14 Å[65]) were observed for all **1** solvates. The HCN molecule attached to the B(C$_6$F$_5$)$_3$ group in all **1** and **2Ar** species is connected by a strong B–N bond (1.60 - 1.61 Å; *cf.* 1.616(3) Å in CH$_3$CN·B(C$_6$F$_5$)$_3$).[59] The structures of all **2Ar** species consist of separated Ar···HCN-B(C$_6$F$_5$)$_3$ molecules with no significant interactions between them (except from a few F···H van der Waals contacts). The most prominent structural feature is the η^6-coordinated aryl molecule as depicted in Figure 2 for **2benz** (d(Ct···H1) = 2.37(3) Å, *cf.* 2.41[66] in C$_6$H$_6$···HCN$_{(g)}$).[67] In **2benz** and **2tol** the aryl ring is strongly tilted (Ct = centroid, **2benz**: Ct–H1–C1 = 127°, **2tol**: 111° Figure S63), which is in agreement with computed structural data.[68] By contrast, in case of **2xyl** the hydrogen atom H1 points almost directly at the center of the C$_6$ ring (Ct-H-N = 178° Figure S64), although computations favoured the strongly tilted species. Again, the potential for the Ct-H-N angle is very flat so that lattice effects may have a great influence on this structural parameter. Since it is rather difficult to establish correct connectivities (hapticities) of asymmetrically coordinated arenes, we have used the number of contacts with d(H···C$_{aryl}$) < 3.0 Å as criterion (*cf.* Σr_{vdW}(H···C) = 2.90 Å)[63] leading to hapticity values of six for all three species, even though in **2benz** and **2tol** three slightly shorter (2.3 - 2.6 Å) and three longer H···C$_{arene}$ contacts (2.7 - 3.0 Å) were found.[69] The electrostatic potential (ESP) mapped onto the electron density of **2benz** nicely illustrates the electrostatically favourable arrangement of one benzene molecule, allowing strong van der Waals interaction between the H$^{\delta+}$(–CN) center and C$_{benzene}$ centers, while the linear alignment is
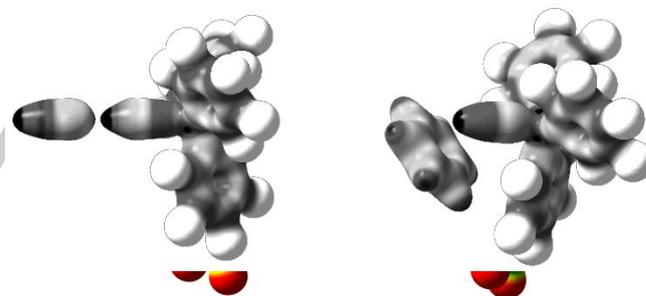
Figure 3. Computed charge density isosurface plot for **1H** and **2benz**. The isosurface has been coloured according to the electrostatic potential ESP (~~red~~white: most negative regions; ~~blue~~black: most positive regions).

Using DFT methods[70] (PBE0-D3BJ/6-31++G(d,p)) with empirical dispersion correction), we investigated the hydrogen bonding and thermodynamics of **1H** and **2Ar**. Energies and structural parameters agree well with available experimental and theoretical data,[18–25,71] *e.g.* d_{exp}(N···C in HCN···HCN$_{(g)}$) = 3.231[29]/3.287[45] vs. 3.242 Å (PBE0-D3BJ) or the enthalpy for HCN dimerization ($\Delta H°_{298}$ = –3.6[29]/–4.45[72] vs. –4.1 kcal·mol^{-1}). Although the dimerization is exothermic at 298 K, it represents a slightly endergonic process with $\Delta G°_{298}$ = 2.21 kcal·mol^{-1} (Table S20). However, upon addition of the strong Lewis acid B(C$_6$F$_5$)$_3$, the dimerization process (HCN + HCN-B(C$_6$F$_5$)$_3$ → **1H**) becomes thermodynamically more favoured with $\Delta H°_{298}$ = –8.9 and $\Delta G°_{298}$

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= −1.6 kcal·mol⁻¹, which, in turn, means that the hydrogen bond in **1H** is strengthened by the Lewis acid (Table S20). Interestingly, the reaction of C_6H_6 and HCN-B(C_6F_5)₃ to give **2benz** is even more favoured ($\Delta H°_{298}$ = −11.4 and $\Delta G°_{298}$ = −3.1 kcal·mol⁻¹) nicely explaining why **2benz** is formed rather than **1H** in the presence of aryls. Notably, the formation of the adduct C_6H_6···HCN (without the Lewis acid) is computed to be slightly endergonic ($\Delta G°_{298}$ = +0.6 kcal·mol⁻¹). Moreover, the computed Brønsted acidity of HCN ($pK_{a,H2O}$ = 10.9, $pK_{a,MeCN}$ = 21.4) is significantly increased by ca. 14 pKa units in water as well as in acetonitrile upon addition of the Lewis acid B(C_6F_5)₃ (HCN-B(C_6F_5)₃, $pK_{a,H2O}$ = −3.2, $pK_{a,MeCN}$ = 6.9) ranging now in the area of HCl ($pK_{a,H2O}$ =−3.9, $pK_{a,MeCN}$ = 7.2, see SI), an effect already discussed for water and other weak acids by Beckmann et al.[73] The chemistry of the conjugated base [(CN)B(C_6F_5)₃]⁻[74] as well as the analogous stable water adduct H_2O-B(C_6F_5)₃ was studied by Green et al. The latter was shown to bind up to two additional water molecules via hydrogen bonding.[68,75]

Table 3. Theoretical descriptors for H-bonds: $n \to \sigma^*$ stabilization energies $\Delta E^{(2)}$ (kcal·mol⁻¹, Figure 4), relative weights (w_{II}) for [H-X-H]⁺ Lewis representation, and Q charge transfer (e).

	$\Delta E^{(2)}_{n\to\sigma^*}$	w_{II}	$Q_{X\to H-Y}$	$Q_{HCN\to B}$	$Q_B^{tot[j]}$
(HCN)₂[a]	8.4	0.42	0.02 [d]	-	-
1H[a]	18.9	1.37 [i]	0.04 [d]	0.36	−0.40
HCN-B(C_6F_5)₃	-	-	-	0.38	−0.38
2benz[h]	-	-	0.04 [e]	0.36	−0.40
(HF)₂[b]	11.3	0.51	0.02 [f]	-	-
(H₂O)₂[c]	13.3	0.66	0.02 [g]	-	-

[a] Delocalization of lone pair n(N2)→ σ^*(H1-C1), Figure 4. [b] n(F2)→ σ^*(H1-F1). [c] n(O2) → σ^*(H1-O1). [d] X/Y = CN. [e] X = C_6H_6, Y = CN. [f] X/Y = F. [g] X/Y = O. [h] Identical Q values were computed for **2tol** and **2dmb**.[i] CF₃ instead of C_6F_5. [j] charge transfer onto the entire BR₃ fragment.

lone pair

H——C≡≡≡N: ------ H——C≡≡≡N

$n \longrightarrow \sigma(H\text{-}C)^*$
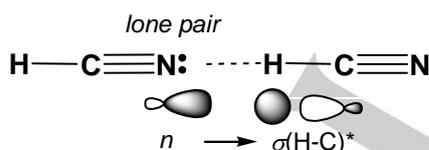
Figure 4. Donor-acceptor $n \to \sigma^*$ stabilization in dimeric HCN species.

Besides these thermodynamic considerations as well as structural evidence from X-ray crystal structures (*vide supra*) and theoretical data, which provide strong support for the characteristically short, near-linear HCN···HCN arrangements in **1H**, there are other representative theoretical descriptors for H-bonding, *e.g.* NBO-based resonance and charge-transfer descriptors (Table 3):[76] the donor-acceptor stabilization energy $\Delta E^{(2)}_{n\to\sigma^*}$, charge-transfer $Q_{D\to A}$ (D = donor, A = acceptor, Figure 4), or the relative weightings w_{II} for Lewis representation II in the resonance: D: H–A (I) ↔ D-H⁺ :A⁻ (II). All these descriptors clearly indicate the increasing strength of the H-bonding in the HCN···HCN dimer upon addition of the Lewis acid B(C_6F_5)₃. For example, the stabilization energy $\Delta E^{(2)}_{n\to\sigma^*}$ provided by n(N2)→

σ^*(H1-C1) delocalization (Figures 1 and 4) is expected to be the principal attractive contribution to H-bond formation, which increases by more than 10 kcal·mol⁻¹ from 8.4 for HCN···HCN to 18.9 kcal·mol⁻¹ for **1H**.[21] Also the associated charge transfer HCN→HCN doubles from 0.02 to 0.04 e. These values might be rather small, but even when a little quantity of charge is transferred between HCN monomers (M1,M2) in the M1→M2 sense, monomer M2 acquires a slightly anionic character in the pure HCN···HCN dimer.[21,76] When a Lewis acid is attached to M2, this charge excess on M2 is further shifted to the Lewis acid, increasing the overall charge transfer to the Lewis acid. In this respect, **1H** might be regarded as a push-pull system. Equivalently, the NBO n(N2)→σ^*(H1-C1) charge delocalization can be expressed in resonance language: D: H–A (I) ↔ D-H⁺ :A⁻ (II). The relative weightings of representation II (usually < 1%) were estimated from natural resonance theory (NRT).[21,76] A larger weight of resonance structure II, as it is the case in **1H** (1.03%) compared to HCN···HCN (0.42%), describes a stronger delocalization and thereby a stronger hydrogen bond. It is interesting to note that all descriptors for the naked HCN···HCN dimer are close to those of HF···HF or H_2O···H_2O as illustrated in Table 3. Finally, the charge transfer in **2Ar** (Ar→HCN) is in the same range as found for **1H** (0.04 e).

In summary, highly labile dimeric HCN···HCN was stabilized by adduct formation with the bulky Lewis acid B(C_6F_5)₃ and crystallized from liquid HCN as HCN···HCN-B(C_6F_5)₃·xHCN solvate. Computations indicate stronger H-bonding upon adduct formation. When aromatic hydrocarbons were used as solvents, the crystallization process always led to formation of Aryl···HCN-B(C_6F_5)₃ adducts displaying one η^6-coordinated aryl molecule. Compared to this sandwich complexation of the HCN molecule, HCN dimerization is thermodynamically less favoured. The thermal stability increases along **1H·0.44HCN** / **1D·0.5DCN** < **1H·2HCN** < **2Ar**. Species **1** as well as **2Ar** might be understood as push-pull systems and **2Ar** even as HCN species sandwiched between a frustrated Lewis acid base pair with the aromatic hydrocarbon as weak base.

Experimental Section

Caution! *HCN is highly toxic and can decompose explosively under various conditions! Appropriate safety precautions (HCN detector, gas mask, low temperatures) should be taken.*

Experimental and computational details including all spectra and ORTEP representations of all experimentally studied species are given in the supporting information.

Acknowledgements

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[1] In English "*The ordinary prussic acid should be named hydrogen cyanide*"

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Lewis acid makes it possible.
HCN···HCN-B($C_6F_5)_3$ crystallized from liquid HCN upon addition of B($C_6F_5)_3$ featuring a strongly hydrogen bonded HCN dimer. In the presence of aromatic hydrocarbons such as benzene, Aryl···HCN-B($C_6F_5)_3$ adducts, displaying a η^6-coordinated aryl molecule, are formed.

donor　　　donor

($C_6F_5)_3$**B** ⟵ **N≡C−H**···**N≡C−H**

acceptor　　acceptor

H = ^{1}H, ^{2}H
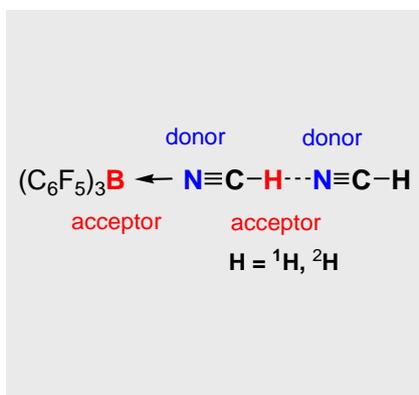
Kevin Bläsing, Jonas Bresien, René Labbow, Axel Schulz,* and Alexander Villinger

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A Dimer of Hydrogen Cyanide Stabilized by A Lewis Acid