NMR Properties of the Cyanide Anion, a Quasisymmetric Two-Faced Hydrogen Bonding Acceptor

Ilya G. Shenderovich 1,2,* and Gleb S. Denisov 2

Abstract: The isotopically enriched cyanide anion, (${^{13}\text{C}}\equiv^{15}\text{N})^-$, has a great potential as the NMR probe of non-covalent interactions. However, hydrogen cyanide is highly toxic and can decompose explosively. It is therefore desirable to be able to theoretically estimate any valuable results of certain experiments in advance in order to carry out experimental studies only for the most suitable molecular systems. We report the effect of hydrogen bonding on NMR properties of $^{15}\text{N}={^{13}\text{C}}\equiv\text{X}$ and $^{15}\text{C}=\text{NH}::\text{X}$ hydrogen bonding complexes in solution, where $\text{X} = {^{19}\text{F}}, ^{15}\text{N}$, and $\text{O}={^{31}\text{P}}$, calculated at the uB97XD/def2tzvp and the polarizable continuum model (PCM) approximations. In many cases, the isotropic $^{13}\text{C}$ and $^{15}\text{N}$ chemical shieldings of the cyanide anion are not the most informative NMR properties of such complexes. Instead, the anisotropy of these chemical shieldings and the values of scalar coupling constants, including those across hydrogen bonds, can be used to characterize the geometry of such complexes in solids and solutions. $^{1}(^{15}\text{N}=^{13}\text{C})$ strongly correlates with the length of the $\text{N}=\text{C}$ bond.

Keywords: cyanide; hydrogen bonding; non-covalent interactions; NMR; chemical shift anisotropy; scalar coupling; DFT; GIAO

1. Introduction

Hydrogen cyanide and cyanide salts are ubiquitous compounds. They can be both the starting ingredients of life [1,2] and the reason for its end [3–5]. The most distinctive feature of the cyanide anion is that its two ends are capable of almost equal non-covalent interactions [6]. As a result, its orientation in crystalline cyanide salts is often disordered [7–11]. The same feature is responsible for the polymerization of hydrogen cyanide, resulting in materials with different characteristics and properties [12–15]. Dimers [16–18] and linear clusters [19,20] of hydrogen cyanide, its crystal structure [21], and its aggregates with the cyanide anion [22] and other proton acceptors [23–26] were studied both experimentally and theoretically. The knowledge gained in these studies was used in practical applications [27–32].

A deeper understanding of the properties of non-covalent interactions involving the cyanide anion in condensed matter systems can be obtained using Nuclear Magnetic Resonance (NMR) spectroscopy. Although it can be done using naturally abundant $^{12}\text{C}=^{14}\text{N}^-$ [33,34], $^{13}\text{C}=^{14}\text{N}^-$ [8,35], and $^{12}\text{C}=^{15}\text{N}^-$ [36], more can be learned with isotopically enriched $^{13}\text{C}=^{15}\text{N}^-$ [37–41]. It appears that the isotropic $^{13}\text{C}$ and $^{15}\text{N}$ NMR chemical shifts of the cyanide anion change characteristically when the corresponding atom participates in covalent or non-covalent interactions and can therefore be used to study these interactions [42,43]. In this sense, the properties of these isotropic chemical shifts are similar to the $^{13}\text{C}$ isotopic chemical shift of pyridines [44,45]. However, even for pyridines, non-covalent interactions of different nature can lead to similar changes in the $^{15}\text{N}$ isotopic chemical shift [46]. Direct covalent or non-covalent interactions are not the only factors that can have a measurable effect on the isotopic chemical shift. The vibrational wave function of the molecule [47–49], solvent effects [50,51], molecular exchange [52], and the...
crystal field [53] are important as well. All of these factors are particularly important for the cyanide anion, which has two similar active centers for non-covalent interactions. However, it is this feature that can be used to solve the problem.

Isotropic chemical shifts are not the only NMR parameters that can be useful. In solution, the structure of hydrogen bonded complexes can be elucidated using scalar spin-spin couplings including those across hydrogen bonds [54–59]. For $^{12}$C≡$^{15}$N–H···$^{19}$F dissolved in a CD$_2$F$_5$/CD$_2$Cl$_2$ mixture, three scalar couplings were measured experimentally at 130 K: $J(15^N\equiv1\equiv19^F)$ = 92 Hz, $J(15^N\equiv19^F)$ = 61 Hz, and $J(15^N\equiv1H\equiv19F)$ = 63 Hz [60]. Even when some couplings are not available or averaged to zero by rapid molecular exchange, the $J(13^C\equiv15^N)$ coupling can still provide important information about the qualitative structure of such complexes. In solids, the anisotropy of the chemical shielding is much more sensitive to external influences [61,62] and molecular dynamics [63,64] than the isotropic value. Consequently, ($^{13}$C≡$^{15}$N)$^-$ is an ideal hydrogen bond acceptor for NMR studies both in solutions and in solids, because several independent parameters can be measured for the same sample under the same experimental conditions. However, hydrogen cyanide is highly toxic and can decompose explosively. It is therefore desirable to theoretically estimate any valuable results of certain experiments in advance and to carry out experimental studies only for the most suitable molecular systems.

In this work we report on a computational study of a variety of $^{15}$N≡$^{13}$C–H···X and $^{13}$C≡$^{15}$N–H···X hydrogen bonded complexes, where X = $^{19}$F–R, $^{15}$N–R, O=31P–R and cover a wide range of basicity. (Li$^{15}$N$^{13}$C)$_4$···($^1$H$_4$$^{15}$N)$^+$ and (Li$^{13}$C$^{15}$N)$_4$···($^1$H$_4$$^{15}$N)$^+$ hydrogen bonded aggregates have been used to study the effect of competing non-covalent interactions. The objective of this study was to explore the dependence of NMR parameters on the properties of hydrogen bonding. For each of these parameters, we assessed the amplitude of possible changes and the ability to use these changes to differentiate between different interactions.

2. Materials and Methods

Gaussian 09.D.01 program package was used [65]. Geometry optimizations were done in the ωB97XD/def2tzvp approximation [66,67]. The identity of minima was confirmed by the absence of imaginary vibrational frequencies. NMR parameters were calculated using the Gauge-Independent Atomic Orbital GIAO method [68] in the ωB97XD/pcJ-2 approximation [69,70]. All calculations were done using the Polarizable Continuum Model (PCM) with water as a solvent [71–73], unless otherwise noted. The default SCRF=PCM method was used to construct the solute cavity.

The ωB97XD functional and the pcJ-2 basis set are capable of correctly reproducing the experimental values of the chemical shielding and scalar spin-spin coupling [50,53,74]. On the contrary, both the PCM and the solvation model based on density (SMD) approximation [75] underestimate solvent effects on the geometry of hydrogen bonded complexes [51,76]. The resulting deviations can only be neglected in specific cases [77–79]. For polar solvents, a change in the values of the dielectric constant has a negligible effect. There are a number of approaches that can be used to properly simulate solvent effects [80–85]. None of these approaches are universal and effortlessly applicable to an arbitrary molecular system. Consequently, the geometries of the molecular complexes used below do not correspond to either the averaged or the most expected experimental geometries in a polar medium. These geometries are used only for a qualitative assessment of the NMR parameters that can be expected in solution for such complexes.

Chemical shieldings are tensor quantities. For the cyanide anion, the principal components of the $^{13}$C and $^{15}$N shielding tensors, $\sigma_{11} \leq \sigma_{22} \leq \sigma_{33}$, can be easily represented in the molecular coordinate system. One of these components is parallel to the C≡N bond and the other two are normal to this bond and are equal. In this paper the isotropic value of these shielding tensors, $\sigma_{\text{iso}} = (\sigma_{11} + \sigma_{22} + \sigma_{33})/3$, and their span, $\Omega = \sigma_{33} - \sigma_{11}$, will be discussed. More detailed description can be found elsewhere [86–88].
3. Results and Discussion

Figure 1 shows the structures of NCH and CNH complexes with various proton acceptors and their relative energies. For most of these complexes, the NCH···X form is energetically more preferable than the CNH···X form. The opposite situation is observed for complexes with pyridine-4-amine and 1-azabicyclo[2.2.2]octane, Figure 1e,f. This result is associated with the fact that the energy of hydrogen cyanide is 65 kJ/mol lower than the energy of hydrogen isocyanide, Figure 1a. This difference is much smaller in their complexes with proton acceptors. Consequently, one can say that the binding energy of the CNH···X form is much higher [89], and this form may be stable if the carbon atom participates in another covalent or non-covalent interaction [43,90–92]. The analysis of the energetically most favorable structures with the hydrogen bonded cyanide anion at different conditions is beyond the scope of this study. The NMR parameters of both forms are reported below.

![Figure 1](image_url)

3.1. The Effect of Hydrogen Bonding on the NMR Parameters of NCH and CNH

The length of the N≡C bond decreases in the series (N≡C)−, C≡NH, N≡CH, Table 1. However, the NMR parameters of these species are mainly determined by the location of the proton, and not by this contraction. Any of these parameters can be used to distinguish between CNH and NCH. On the contrary, the difference with (NC)−, is large only for the atom carrying the proton. The only exception is $^1$J(15N−13C). The absolute value of this coupling decreases almost linearly with increasing N≡C distance. The difference of $\sigma_{iso}(^{15}N)$ in (NC)− and CNH is similar to that in pyridine and pyridinium [44]. $^2$J(15N−1H) in CNH is the same as in pyridinium [93]. $^2$J(15N−1H) and $^2$J(13C−1H) in NCH and CNH can be measured in the absence of proton exchange.
The N≡C distances, the isotropic chemical shielding, $\sigma_{iso}$, the span, $\Omega$, of the shielding tensors of the $^{15}$N and $^{13}$C nuclei, and scalar coupling constants of NC, NCH, and CNH obtained at the PCM = water approximation.

| Compound               | N≡C, Å  | $^{15}$N, ppm | $^{13}$C, ppm | $^{14}$J($^{15}$N,$^{13}$C), Hz | $^{14}$J($^{15}$N,$^{1}$H), Hz | $^{14}$J($^{13}$C,$^{1}$H), Hz |
|------------------------|---------|---------------|---------------|--------------------------------|--------------------------------|---------------------------------|
| $^{15}$N≡$^{13}$C$^-$ | 1.1664  | –46           | 585           | 10                             | 403                           | –7                              |
| $^{15}$N≡$^{13}$C≡H  | 1.1436  | –24           | 548           | 65                             | 302                           | –25                             |
| $^{12}$C≡$^{15}$N≡H  | 1.1855  | 78            | 401           | 13                             | 392                           | –14                             |

NCH is a weak proton donor. The proton transfer only takes place in its complex with F$^-$ anion, (NC)$^-$···H-F, Table 2. The N≡C distance in this complex is shorter than that in free (NC)$^-$, but greater than that in CNH. All other complexes have the NC-H···X structure with the N≡C distance greater than that in free NCH, but shorter than that in free CNH. For the weakest proton acceptor studied here, the O=P group, the N≡C distances in (NC-H)$_2$···O=P, and free NCH are very similar. Note, that in this work we use the (NC-H)$_2$···O=P complex, Figure 1g. The O=P group tends to form two hydrogen bonds at the same time [94–96]. Moreover, the presence of the second bond does not affect the strength of the first one. CNH is a strong proton donor. The structure CN-H···X is present only for pyridine and the P=O group. In these CN-H···X complexes the N≡C distance is very similar to that in (NC)$^-$···H-F, Table 2. It is noteworthy that, for the same proton acceptor, the H···X distance in CN-H···X is shorter than in NC-H···X.

| Base (X) | N≡C, Å  | C···H, Å | H···X, 1 Å | C≡N, Å  | N···H, Å | H···X, 1 Å |
|----------|---------|----------|-----------|---------|----------|-----------|
| F$^-$    | 1.1599  | 1.5754   | 1.0093    | 1.1636  | 1.5202   | 0.9875    |
| H$_3$N   | 1.1461  | 1.1072   | 1.9093    | 1.1646  | 1.6310   | 1.0790    |
| pyridine | 1.1458  | 1.1034   | 1.9051    | 1.1594  | 1.6868   | 1.0570    |
| 4AP      | 1.1463  | 1.1109   | 1.8543    | 1.1650  | 1.7032   | 1.0515    |
| ABCO     | 1.1471  | 1.1282   | 1.7753    | 1.1650  | 1.6868   | 1.0578    |
| P=O      | 1.1448  | 1.087    | 1.90      | 1.1583  | 1.029    | 1.70      |

The distance between the NCH or CNH proton and the proton accepting atom of the base.

$\sigma_{iso}$($^{15}$N) and $\Omega$($^{15}$N) can be used to distinguish between different CN-H···X complexes, Table 3. On the contrary, these parameters are very similar in all (CN)$^-$···H-X and NC-H···X complexes. $\sigma_{iso}$($^{13}$C) and $\Omega$($^{13}$C) are very similar for all NC-H···X complexes. However, these parameters can be used to distinguish between the NC-H···X, (NC)$^-$···H-X, and CNHX complexes.

| Base (X) | $^{15}$N, ppm | $^{13}$C, ppm | $^{15}$N, ppm | $^{13}$C, ppm |
|----------|---------------|---------------|---------------|---------------|
| F$^-$    | –33           | 566           | 5               | 25            | 383          | –17          | 546          | 14            | 397          |
| H$_3$N   | –17           | 538           | 57              | 57            | 335          | –27          | 560          | 13            | 398          |
| pyridine | –20           | 560           | 57              | 57            | 334          | –39          | 461          | 17            | 388          |
| 4AP      | –19           | 541           | 56              | 56            | 336          | –28          | 561          | 11            | 401          |
| ABCO     | –21           | 546           | 55              | 55            | 341          | –24          | 559          | 11            | 403          |
| P=O      | –20           | 544           | 60              | 60            | 331          | 59           | 434          | 17            | 389          |

The geometry of NC-H···X and (NC)$^-$···H-X complexes can be quantitatively characterized using $^4$J($^{13}$C,$^{1}$H), Table 4. The long range $^4$J($^{13}$C,$^h$X) couplings across the hydrogen bond are also large enough to be observed experimentally. The location of the mobile proton in these complexes can be proved using any scalar coupling. This is trivial for
$^1J(^{13}C^1H)$ and $^3J(^1HX)$. However, because the N≡C distances in NC-H···X are shorter than in (NC)$^...$H-X, $^1J(^{15}N^{13}C) \geq 20$ Hz in NC-H···X and about 10 Hz in (NC)$^...$H-X. $^2J(^{13}N^1H)$ can be measured in NC-H···X but not in (NC)$^...$H-X. Surprisingly, $^3J(^{15}N^{13}F)$ in (NC)$^...$H-F is large.

Table 4. Scalar coupling constants in NCH···X obtained at PCM = water.

| Base (X) | $^1J(^{15}N^{13}C)$, Hz | $^2J(^{15}N^1H)$, Hz | $^1J(^{13}C^1H)$, Hz | $^3J(^1HX)$, Hz | $^2J(^{13}CX)$, Hz | $^3J(^{15}NX)$, Hz |
|---------|---------------------|---------------------|---------------------|-----------------|-----------------|-----------------|
| F$^-$   | −10                | −2                  | 31                  | 291$^1$         | 314$^1$         | −22$^1$         |
| H$_3$N  | −22                | −12                 | 258                 | 4$^2$           | 20$^2$          | 1$^2$           |
| pyridine| −22                | −12                 | 259                 | 4$^2$           | −21$^2$         | 1$^2$           |
| 4AP     | −22                | −12                 | 255                 | 4$^2$           | 2$^2$           | 1$^2$           |
| ABCO    | −20                | −12                 | 243                 | 2$^2$           | −23$^2$         | 1$^2$           |
| P=O     | −24                | −12                 | 266                 | −2$^3$          | 7$^3$           | 0$^3$           |

$^1X = ^{19}F, ^2X = ^{15}N, ^3X = ^{31}P.$

A combination of $^1J(^{15}N^1H)$, and $^3hJ(^1HX)$ can be used to quantitatively characterize the geometry of CN-H···X and (CN)$^...$H-X complexes, Table 5. The long range $^3hJ(^{15}NX)$ across the hydrogen bond are large, except $^3hJ(^{15}N^{31}P).$ $^2J(^{13}C^1H)$ can be measured in CN-H···X only. $^1J(^{15}N^{13}C) < 10$ Hz is characteristic for (CN)$^...$H-X. In CN-H···X the value of this coupling is similar to that in (NC)$^...$H-X. $^3J(^{13}C^1F)$ in (CN)$^...$H-F is large enough to be observed experimentally.

Table 5. Scalar coupling constants in CNH···X obtained at PCM = water.

| Base (X) | $^1J(^{15}N^{13}C)$, Hz | $^2J(^{15}N^1H)$, Hz | $^2J(^{13}C^1H)$, Hz | $^1hJ(^1HX)$, Hz | $^3hJ(^{13}CX)$, Hz | $^3J(^{15}NX)$, Hz |
|---------|---------------------|---------------------|---------------------|-----------------|-----------------|-----------------|
| F$^-$   | −10                | −5                  | 3                   | 371$^1$         | $^1hJ(^1HX)$, Hz | $^1hJ(^1HX)$, Hz |
| H$_3$N  | −7                 | 1                   | 1                   | −66$^2$         | −2$^2$          | 12$^2$          |
| pyridine| −13                | −94                 | 22                  | −5$^2$          | −3$^2$          | 16$^2$          |
| 4AP     | −8                 | 3                   | 1                   | −97$^2$         | −2$^2$          | 11$^2$          |
| ABCO    | −8                 | 4                   | 1                   | −73$^2$         | −2$^2$          | 9$^2$           |
| P=O     | −15                | −114                | 25                  | −2$^3$          | 0$^3$           | −3$^3$          |

$^1X = ^{19}F, ^2X = ^{15}N, ^3X = ^{31}P.$

It is worth taking a closer look at the complex of the cyanide anion with hydrogen fluoride. It is obvious that the fluoride anion in solution interacts not only with hydrogen cyanide but also with a cation. The later interaction is simulated here using lithium fluoride. For hydrogen cyanide the structure of this complex is NCH···FLi both at the gas phase and PCM approximations, Table 6. For hydrogen isocyanide the structure of this complex is CNH···FLi at the gas phase approximation and (CN)$^...$HF-Li$^+$ at the PCM approximation. At the gas phase approximation, the H···F distance in CN-H···FLi is much shorter than in NC-H···FLi. The geometry of NC-H···FLi shows that this distance changes much more than other distances when the influence of the solvent is considered.

Table 6. Geometry of NCH···FLi and CNH···FLi hydrogen-bonded complexes obtained at the gas phase and PCM = water approximations.

| PCM | N≡C, Å | C···H, Å | H···F, Å | C≡N, Å | N···H, Å | H···F, Å |
|-----|--------|----------|----------|--------|---------|---------|
| gas | 1.1460 | 1.0980   | 1.6935   | 1.1602 | 1.0438  | 1.5239  |
| water | 1.1484 | 1.1461   | 1.4666   | 1.1605 | 1.2079  | 1.1738  |

The geometric changes cause changes of the chemical shieldings, Table 7. However, these relationships are anything but self-evident. For NC-H···FLi, the use of the PCM approximation leads to large changes in $\sigma_{iso}(^{15}N)$ and $\Omega(^{15}N)$, although the N≡C distance
changes only slightly. CN-H⋯-FLi and (CN)−⋯(H-FLi)+ have similar $\sigma_{\text{iso}}$(13C) and very different $\Omega$(13C). The ambiguity of these changes suggests that correctly interpreting the geometry of hydrogen bonded complexes based on NMR data may require comparing several NMR parameters.

Table 7. The isotropic chemical shielding, $\sigma_{\text{iso}}$, and the span, $\Omega$, of the shielding tensors of the 15N and 13C nuclei of NCH⋯-FLi and CNH⋯-FLi complexes obtained at the gas phase and PCM = water approximations.

| Complex    | $J^{15N}$, Hz | $J^{13C}$, Hz | $J^{15N}$, Hz | $J^{13C}$, Hz |
|------------|---------------|---------------|---------------|---------------|
| gas        |               |               |               |               |
| NCH⋯-FLi   | −22           | −12           | 256           | −66           |
| CNH⋯-FLi   | −13           | −110          | 24            | −72           |
| water      |               |               |               |               |
| NCH⋯-FLi   | −20           | −12           | 232           | −109          |
| CNH⋯-FLi   | −11           | −57           | 16            | 47            |

In contrast, the values of scalar couplings seem to be only marginally dependent on the use of the PCM approximation, Table 8. For NC-H⋯-FLi the main changes, as expected, are observed for $J^{15N}$, $J^{13C}$, and $J^{15N}$. The change of CN-H⋯-FLi to (CN)−⋯(H-FLi)+ leads to strong changes in $J^{15N}$, $J^{13C}$, and $J^{15N}$. The contractions for the N⋯F distance in (CN)−⋯(H-FLi)+ causes an increase of $J^{13C}$.

Table 8. Scalar coupling constants in NCH⋯-FLi and CNH⋯-FLi obtained at the gas phase and PCM = water approximations.

The complex of hydrogen cyanide with tetrabutylammonium fluoride is the only complex that has so far been characterized in detail experimentally by means of NMR. The experimentally measured $J^{15N}$ value of 92 Hz [60]. Consequently, this complex has the CN-H⋯-F− structure. Other coupling constants are $J^{15N}$, $J^{13C}$, and $J^{15N}$. The values of these three coupling constants are close to those calculated for CN-H⋯-FLi in the gas phase approximation, Table 8. To a first approximation, this result again indicates that the values of these constants depend mainly on the distances and much less on considering the influence of the solvent field. However, the closeness of the experimental and calculated values should not be overestimated. Compare the expected changes in these coupling constants when going from CN-H⋯-FLi to (CN)−⋯(H-FLi)+, Table 8. The experimental value $J^{15N}$ changes from −110 Hz to −57 Hz. The experimental value $J^{13C}$ changes from −72 Hz to 47 Hz. The experimental value $J^{15N}$ changes from −79 Hz to −153 Hz. The experimental value $J^{15N}$ contradicts to the trend. Similar problems were observed for the complex of pyridine with hydroxyl fluoride [50].

3.2. Proton Bound Dimers of Cyanide

Three proton bound dimers of cyanide are possible: [NCHCN]−, [CNHNC]−, and [CNHNC]−. Note that the most energetically favorable structure of HN$_2$C$_2$ is N=C\equiv C=NH$^+$. However, cyanogen does not form spontaneously in hydrogen cyanide solutions [97] and is not discussed here. Proton bound hydrogen cyanide homodimers and more complex clusters [98–100] are also not discussed here.
Table 9. In this centrosymmetric complex, the proton is equally strongly bound to both carbon atoms. The N≡C and C−H distances are very short.

Table 9. The structure of NC−...HCN, NC−...HNC, and −CN...HNC complexes, their relative energies ΔE, the isotropic chemical shielding, \( \sigma_{iso} \), the span, Ω, of the shielding tensors, and scalar coupling constants obtained at PCM = water.

| Parameter | [NC−...H−CN]− | [CN]−...HCN | [CN]−...H-NC |
|-----------|--------------|-------------|-------------|
| ΔE, kJ/mol | 0 | 51 | 64 |
| Base: N≡C, Å | 1.1515 | 1.1655 | 1.1611 |
| Base: X−H, Å | 1.2220 1 | 1.1756 2 | 1.4362 2 |
| Acid: H-Y, Å | 1.2220 3 | 1.2917 3 | 1.0847 4 |
| Acid: N≡C, Å | 1.1515 | 1.1528 | 1.1532 |
| Base: \( \sigma_{iso} \)(15N), ppm | −6 | −17 | −22 |
| Base: Ω(15N), ppm | 525 | 548 | 555 |
| Acid: \( \sigma_{iso} \)(15N), ppm | −6 | −19 | 28 |
| Acid: Ω(15N), ppm | 525 | 544 | 481 |
| Base: \( \sigma_{iso} \)(13C), ppm | 32 | 21 | 16 |
| Base: Ω(13C), ppm | 377 | 385 | 394 |
| Acid: \( \sigma_{iso} \)(13C), ppm | 32 | 32 | 23 |
| Acid: Ω(13C), ppm | 377 | 376 | 382 |
| Base: \( ^1J(15N)_{13C} \), Hz | −13 | −8 | −9 |
| Acid: \( ^1J(15N)_{13C} \), Hz | −13 | −13 | −14 |
| Base: \( ^1J(13C)_{13} \), Hz | 95 | 14 | 5 |
| Acid: \( ^1J(13C)_{13} \), Hz | 95 | 95 | 24 |
| Base: \( ^1J(13N)_{13} \), Hz | −8 | −44 | −9 |
| Acid: \( ^1J(13N)_{13} \), Hz | −8 | −8 | −87 |
| \( ^28J(XHY) \), Hz | 113 5 | −57 6 | 20 7 |

1 X = C. 2 X = N. 3 Y = C. 4 Y = N. 5 \( ^28J(13C)_{15} \), 6 \( ^28J(13C)_{13} \), 7 \( ^28J(15C)_{13} \), 8 \( ^28J(15C)_{13} \), 9 \( ^28J(15N)_{13} \), 10 \( ^28J(15C)_{13} \), 11 \( ^28J(15N)_{13} \).

The hetero- and homodimers [CN]−...H-CN and [CN]−...H-NC have similar energies and are asymmetric. The reason why some proton bound homodimers are symmetric and others not was explained in the past [101,102] and recently reviewed [103]. In [CN]−...H-CN, the hydrogen bond is stronger, and the position of the proton is more symmetric. In this complex the N−H distance is shorter than the H-C distance. However, the C≡N distance in the [CN]− unit is similar to that in free [CN]−, while in the H-CN unit this distance is closer to that in free H-CN, Tables 1 and 9. For this reason, we call the former unit in this complex a base, and the latter an acid, regardless of the distance to the proton. The geometry of [CN]−...H-NC is similar to that of proton bound homodimers of pyridine [104] and its derivatives [105]. Some of the NMR parameters of this complex and its derivatives can be found elsewhere [106–108].

In all these complexes \( \sigma_{iso} \)(13C), Ω(13C), \( \sigma_{iso} \)(15N) and Ω(15N) are very similar and can hardly be used to characterize both the complexes and the specific units, except for H-NC in [CN]−...H-NC, Table 9. Scalar couplings are more characteristic. Note how large \( ^28J(13C)_{15} \) and \( ^28J(15C)_{13} \) can be across these hydrogen bonds.

3.3. Solvation by the Cyanide Anions

There are examples of hydrogen bonded aggregates in which several equal units are solvating one center. For example, aggregates (FH)n...F− with n ≤ 6 were extensively investigated both experimentally and theoretically [49,59,109,110]. An increase in n leads to a weakening of each of the hydrogen bonds due to the anticooperativity of their interaction. Here, this effect will be used to determine the amplitude of changes in NMR parameters that are possible for the same type of interaction.

The experimentally observed CN-H−...F− complex was discussed above. The energy of this complex is similar to that of NC-H−...F−, Table 10. For larger (CN-H)n...F− and (NC-H)n...F− aggregates with n = 2−4 (NC-H)n...F− are energetically more favorable
because hydrogen cyanide has lower energy than isocyanide. Here we are interested whether it is possible to recognize aggregates with different \( n \) by NMR. The geometry of these aggregates gradually changes with increasing \( n \). These changes lead to changes in the NMR parameters. How large are the changes in the NMR parameters and are the trends of these changes monotonic?

Table 10. Geometry of \((\text{NCH})_n \cdots \text{F}^-\) and \((\text{CNH})_n \cdots \text{F}^-\) aggregates obtained at PCM = water.

| \( n \) | \( \Delta E \) kJ/mol | \( \text{N} \equiv \text{C}, \text{Å} \) | \( \text{C} \cdots \text{H}, \text{Å} \) | \( \text{H} \cdots \text{F}, \text{Å} \) | \( \text{C} \equiv \text{N}, \text{Å} \) | \( \text{N} \cdots \text{H}, \text{Å} \) | \( \text{H} \cdots \text{F}, \text{Å} \) |
|---|---|---|---|---|---|---|---|
| 1 | 4 | 1.1599 | 1.5754 | 1.0093 | 1.1636 | 1.5202 | 0.9875 |
| 2 | 48 | 1.1485 | 1.1488 | 1.4674 | 1.1590 | 1.1086 | 1.3338 |
| 3 | 93 | 1.1469 | 1.1197 | 1.5819 | 1.1584 | 1.0612 | 1.4651 |
| 4 | 143 | 1.1461 | 1.1062 | 1.6621 | 1.1583 | 1.0412 | 1.5588 |

\(^1\) Relative energies \( \Delta E = E(\text{CNH-form}) - E(\text{NCH-form}) \)

In \((\text{NC-H})_n \cdots \text{F}^-\) with \( n = 2 \sim 4 \) all shielding parameters, \( \sigma_{\text{iso}}^{(13)\text{C}}, \Omega^{(13)\text{C}}, \sigma_{\text{iso}}^{(15)\text{N}} \) and \( \Omega^{(15)\text{N}} \), are similar for all \( n \) and can hardly be used to distinguish between these complexes, Table 11. In contrast, in \((\text{CN-H})_n \cdots \text{F}^-\) only for \( \Omega^{(13)\text{C}} \) the changes are small. The dependence of \( \sigma_{\text{iso}}^{(15)\text{N}} \) and \( \Omega^{(15)\text{N}} \) on the \( \text{N} \cdots \text{H} \) distance is well known. Surprisingly, in this complex, \( \sigma_{\text{iso}}^{(13)\text{C}} \) also strongly depends on this distance. Note that these changes do not correlate with changes in the \( \text{N} \equiv \text{C} \) distance, Table 10.

Table 11. The isotropic chemical shielding, \( \sigma_{\text{iso}} \), and the span, \( \Omega \), of the shielding tensors of the \( ^{15}\text{N} \) and \( ^{13}\text{C} \) nuclei of \((\text{NCH})_n \cdots \text{F}^-\) and \((\text{CNH})_n \cdots \text{F}^-\) aggregates obtained at PCM = water.

| \( n \) | \( ^{15}\text{N}, \text{ppm} \) | \( \sigma_{\text{iso}} \) | \( \Omega \) | \( ^{12}\text{C}, \text{ppm} \) | \( \sigma_{\text{iso}} \) | \( \Omega \) | \( ^{15}\text{N}, \text{ppm} \) | \( \sigma_{\text{iso}} \) | \( \Omega \) | \( ^{13}\text{C}, \text{ppm} \) | \( \sigma_{\text{iso}} \) | \( \Omega \) |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 1 | -33 | 566 | 25 | 383 | -17 | 546 | 14 | 397 |
| 2 | -15 | 537 | 51 | 344 | 34 | 470 | 20 | 386 |
| 3 | -16 | 539 | 55 | 339 | 47 | 451 | 29 | 387 |
| 4 | -18 | 540 | 57 | 336 | 55 | 440 | 18 | 389 |

The composition of \((\text{NC-H})_n \cdots \text{F}^-\) can be clearly obtained using \(^1\)J\(^{(13)\text{C}}\)H), \(^1\)J\(^{(15)\text{N}}\)H), and \(^2\)J\(^{(13)\text{C}}\)F), Table 12. For \((\text{CN-H})_n \cdots \text{F}^-\) the same can be done using \(^1\)J\(^{(15)\text{N}}\)H) and \(^2\)J\(^{(15)\text{N}}\)F). The behavior of \(^1\)J\(^{(13)\text{C}}\)F) is not monotonic, Table 12. The reason for this is as follows [59]. \(^1\)J\(^{(13)\text{C}}\)F) is very large and positive at short \( \text{H} \cdots \text{F} \) distances. As this distance increases, \(^1\)J\(^{(13)\text{C}}\)F) decreases, goes through zero, and becomes negative. The absolute value of this coupling increases again, passes through a maximum, and then decreases to zero. In \((\text{NC-H})_n \cdots \text{F}^-\) the \( \text{H} \cdots \text{F} \) distances are larger than in \((\text{CN-H})_n \cdots \text{F}^-\) for the same \( n \) and \(^1\)J\(^{(13)\text{C}}\)F) is close to its negative maximum already at \( n = 2 \), Tables 10 and 12. However, \(^1\)J\(^{(13)\text{C}}\)F) does not depend exclusively on the \( \text{H} \cdots \text{F} \) distance and differs in \((\text{NC-H})_n \cdots \text{F}^-\) and \((\text{CN-H})_n \cdots \text{F}^-\) for the same \( \text{H} \cdots \text{F} \) distance. Note that the same behavior is observed for \(^2\)J\(^{(15)\text{N}}\)F) in \((\text{CN-H})_n \cdots \text{F}^-\) as \( n \) changes from 1 to 3. The long range \(^2\)J\(^{(15)\text{N}}\)H), \(^2\)J\(^{(13)\text{C}}\)H), and \(^3\)J\(^{(15)\text{N}}\)F) are similar for all \( n = 2 \sim 4 \). In contrast, \(^3\)J\(^{(13)\text{C}}\)F) varies greatly with \( n \). \(^1\)J\(^{(15)\text{N}}\)C) cannot be used to distinguish between different \( n = 2 \sim 4 \), but this coupling is characteristic for \((\text{NC-H})_n \cdots \text{F}^-\) and \((\text{CN-H})_n \cdots \text{F}^-\).
Table 12. Scalar coupling constants in (NCH)$_n$...F$^-$ and (CNH)$_n$...F$^-$ aggregates obtained at PCM = water.

| Complex          | $^1$$^1$$^J$($^{15}$N$^{13}$C), Hz | $^1$$^J$($^{15}$N$^1$H), Hz | $^1$$^J$($^{13}$C$^1$H), Hz | $^1h$$^J$($^1$H$^{19}$F), Hz | $^1h$$^J$($^{13}$C$^{19}$F), Hz | $^1h$$^J$($^{15}$N$^{19}$F), Hz |
|------------------|-----------------------------------|----------------------------|----------------------------|----------------------------|----------------------------|----------------------------|
| (NCH)$_3$...F$^-$ | -10                               | -2                        | 31                        | 291                       | 314                       | -22                       |
| (NCH)$_2$...F$^-$ | -20                               | -12                       | 230                       | -108                      | 228                       | -16                       |
| (NCH)$_3$...F$^-$ | -22                               | -12                       | 250                       | -87                       | 171                       | -11                       |
| (NCH)$_4$...F$^-$ | -22                               | -12                       | 257                       | -68                       | 132                       | -8                        |
| (CNH)$_2$...F$^-$ | -8                                | -5                        | 3                         | 371                       | 27                        | -93                       |
| (CNH)$_3$...F$^-$ | -13                               | -87                       | 22                        | -67                       | 29                        | -109                      |
| (CNH)$_4$...F$^-$ | -14                               | -103                      | 25                        | -73                       | 19                        | -80                       |
| (CNH)$_5$...F$^-$ | -15                               | -110                      | 25                        | -61                       | 13                        | -58                       |

The cyanide anion is a quasisymmetric two-faced acceptor of interactions. How strong is the anticooperativity of such interactions? Here we compare ([NC$^-$_]$^2$...[H$_2$N]$^+$, (LiNC)$_4$...[H$_4$N]$^+$, ([CN$^-$_]$^4$...[H$_2$N]$^+$, and (LiCN)$_4$...[H$_2$N]$^+$ aggregates. The hydrogen bonds in ([NC$^-$_]$^4$...[H$_2$N]$^+$ and ([CN$^-$_]$^4$...[H$_2$N]$^+$ are weak. The C...H and N...H distances are large and the N≡C distances are close to that in free [C≡N]$^+$, Tables 1 and 13. The energies of these aggregates are very similar. Although the addition of terminal Li cations weakens these bonds, the effect is small. At the same time, the presence of a new interaction can change the preferred orientation of the cyanide anions, Table 13.

Table 13. Geometry of (NC)$_4$...([H$_4$N]$^+$, (LiNC)$_4$...([H$_4$N]$^+$, (CN)$_4$...([H$_4$N]$^+$, and (LiCN)$_4$...([H$_4$N]$^+$ hydrogen-bonded aggregates obtained at PCM = water.

| B      | $\Delta E$ | $\sigma_{iso}(^{15}$N | $\Omega(^{15}$N) | C$-$H, Å | N$-$H, Å | C$\equiv$N, Å | N$\equiv$H, Å | N$-$H, Å |
|--------|------------|----------------------|------------------|----------|-----------|--------------|-------------|----------|
| No     | -6         | 1.1644               | 2.0233           | 1.0400   | 1.1655    | 1.8751       | 1.0374      |
| Li$^+$ | 10         | 1.1624               | 2.0295           | 1.0382   | 1.1615    | 1.8834       | 1.0359      |

$^1$ Relative energies $\Delta E = E(\text{CNH-form}) - E(\text{NCH-form})$.

Surprisingly, the presence of Li has a great impact on $\sigma_{iso}(^{15}$N) and $\Omega(^{15}$N), regardless of whether it interacts with nitrogen or carbon atoms, Table 14. Its impact on $\sigma_{iso}(^{13}$C) and $\Omega(^{13}$C) can be measurable but is smaller.

Table 14. The isotropic chemical shielding, $\sigma_{iso}$, and the span, $\Omega$, of the shielding tensors of the $^{15}$N and $^{13}$C nuclei of ([NC$^-$_]$^4$...([H$_4$N]$^+$, (LiNC)$_4$...([H$_4$N]$^+$, (CN)$_4$...([H$_4$N]$^+$, and (LiCN)$_4$...([H$_4$N]$^+$ aggregates obtained at PCM = water.

| B      | $\sigma_{iso}(^{15}$N) | $\Omega(^{15}$N) | $\sigma_{iso}(^{13}$C) | $\Omega(^{13}$C) |
|--------|------------------------|------------------|------------------------|------------------|
| No     | -37                    | 572              | 15                     | 398              |
| Li$^+$ | -109                   | 691              | 27                     | 384              |

Scalar couplings in these aggregates are small and are not easy to measure, Table 15. However, the value of $^1$$^J(^{15}$N$^{13}$C) in (Li$^{13}$C$\equiv^{15}$N)$_4$...([H$_4$$^{15}$N]$^+$ is very remarkable. It shows that this coupling increases above 15 Hz when the carbon atom participates in a strong interaction and remains below 15 Hz when such interaction is either weak or directed towards the nitrogen atom, Tables 1 and 15.
4. Conclusions

This work reports on the geometry and NMR parameters of hydrogen cyanide and isocyanide hydrogen bonded to proton acceptors, whose ability to accept protons was distributed over a wide range. The main objective of this study was to find NMR parameters that can be used to unambiguously determine the structure of such complexes. The most important conclusions are as follows.

For weak proton acceptors, the most energetically favorable structure is NC-H⋯X. The NMR parameters of such structures are similar to those of free hydrogen cyanide. The most characteristic parameters of these structures are \(1J(13C\text{H}) > 200 \text{ Hz}\) and \(|1J(15N\text{C})| > 20 \text{ Hz}\).

For strong proton acceptors, the most energetically favorable structure may be C≡N⋯H⋯X. The most characteristic parameters of these structures are the \(15N\) isotropic chemical shift, the span of the \(15N\) chemical shift tensor, and \(1J(15N\text{H})\).

When the cyanide anion interacts with weak acids, both [NC]−⋯H⋯X and [CN]−⋯H⋯X structures are equally possible. The NMR parameters of such structures are similar to those of free cyanide anion. However, if the terminal nitrogen atom in [NC]−⋯H⋯X participates in an additional interaction, its chemical shift can vary greatly.

The most energetically favorable structure of a complex of hydrogen cyanide and the cyanide anion is symmetric, [NC⋯H⋯CN]−, with \(1hJ(13C\text{H})\) about 100 Hz.

The spin-spin coupling across the N≡C bond, \(1J(15N\text{C})\) strongly correlates with the bond length and can be used to identify the structure of hydrogen bonded complexes in cases where other spin-spin couplings are averaged to zero due to proton and molecular exchange, Figure 2. Deviations from this correlation are possible only if both atoms participate in external interactions.

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